DIFFUSION INTERACTIONS FOR A PAIR OF REACTIVE SPHERES

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Abstract

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In this treatise competition and mutualism interactions are evaluated for two different spheres in an infinite medium with constant Fickian diffusion. Various source and sink reaction types, reaction rates, and size differences are considered. The competition problem is evaluated for the first order surface reactions, and the mutualism problem is modeled with a zeroth order surface source while the sink is either diffusion-limited, first order surface, or a volume distributed reactor. The reaction rate and concentration are evaluated using the bispherical expansion or the Bispherical coordinate system. The bispherical expansion involves one infinite sum, for the mutualism problem and two nested infinite sums for the competition problem. A matrix elimination technique is used to obtain an exact analytical solution from the bispherical expansion. Only one infinite sum is required in the calculation of the reaction rate and concentration for the
bispherical coordinate system. In either case the solution is completely convergent, and often converges rapidly over the full range of parameters. In the competition study three effects were displayed: blocking, competition and a combination of the two. When the two effects were combined and both sinks are diffusion-limited the reaction rate for the larger sink goes through a minimum as the much smaller sink approaches it. The mutualism study, when both the sink and source are impenetrable, produced a surprising maximum in sink reaction as it approaches the larger source when the sink is very reactive and much smaller than the source. The reaction rate of a diffusion-limited sink when exposed to a source with a constant surface concentration is also included; it diverges when the two spheres touch but as the sink and source move further apart it approaches the diffusion-limited single sphere result. Finally, the mutualism problem for a permeable first order sink impermeable zeroth order source is compared with its effective surface reaction counterpart. When the sink is strong there is very good agreement, but when the sink is weak the two solutions diverge. Interestingly, this weak sink diverging region is the most likely physical chemical condition for cellular interaction.
DEDICATION

This is for my daughter, Ayari, my favorite study partner. My grandmother, Ivy Johnson gave me the best mother and aunts anyone could ask for. These women all contributed to my success, they provided for me throughout my life and shaped most of my ideas. I thank my mother, her advice and love sustained my soul and kept me focused. My Aunt Nita took me to school most of my life and insisted that I be vigilant. She taught me to pursue my dreams with immense passion. Smiles, kisses, hugs and home cooked foods from Aunt Joycey were always abundant. My Aunt Sherry and Aunt Pearl always welcomed me home with my favorite dishes. Nicky, life would be boring without our weekend conversations, thanks for your advice and love. Finally, Louise McDonald, my paternal grandmother, gave me nothing but love. From these women I learned that I could do anything because they would allow no one to stand in my way. Thanks to them all I have completed my Ph. D.
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B.2 The rate R₁ equation for sphere 1 in the presence of sphere 2 is generated directly from the integration of the flux in the direction of sphere 1, where the integral is evaluated at the surface of the sphere (Zoia, 1998).
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SYMBOLS

\( a_1 \)  Radius of sphere 1

\( a_2 \)  Radius of sphere 2

\( A_j \)  Coefficient of sphere 1 defined in (3.33)

\( b_n \)  Concentration expansion coefficient defined in (5.21)

\( B_j \)  Coefficient of sphere 1 defined in (3.33)

\( c \)  Reactant concentration

\( c_0 \)  Reactant concentration far away from sphere 1 and 2

\( c_1 \)  Reactant concentration at surface of sphere 1

\( c_2 \)  Reactant concentration at the surface of sphere 2

\( c_{int} \)  Reactant concentration inside sphere 1

\( c_{ext} \)  Reactant concentration outside sphere 1 and 2

\( d \)  Center to center separation distance of sphere 1 and 2

\( d_1 \)  Dimensionless center to center distance for sphere 1 and 2 (2.10)

\( D \)  Fickian diffusion in the bulk phase

\( D_{int} \)  Fickian diffusion inside sphere 1

\( E_j \)  Equation coefficient of sphere 1 defined in (3.35)

\( f \)  Interfocal distance in Bispherical Coordinate System

\( f_{1n} \)  Equation coefficient of sphere 1 defined in (2.14)
\( f_{2n} \)  
Equation coefficient of sphere 2 defined in (2.16)

\( F \)  
Matrix defined in equation (2.19)

\( g_{1n} \)  
Equation coefficient of sphere 1 defined in (5.31)

\( G_a \)  
Equation Coefficient defined in (2.41)

\( G^i_a \)  
Matrix elements for the concentration expansion defined in (2.43) and (2.44)

\( h_{1n} \)  
Coefficient of sphere 1 defined in (2.20)

\( h_\mu \)  
Transform expression from spherical to bispherical coordinates

\( h_\eta \)  
Transform expression from spherical to bispherical coordinates

\( h_\phi \)  
Transform expression from spherical to bispherical coordinates

\( H \)  
Matrix defined in equation (5.28)

\( i_n \)  
Equation coefficient defined in (5.12)

\( i'_n \)  
First derivative of function defined in (5.23)

\( I_{n+\frac{1}{2}} \)  
Modified Bessel Function of the first kind of half integer order (5.12)

\( J \)  
Matrix defined in equation (3.20)

\( k_1 \)  
First order reaction rate constant at the surface of sphere 1

\( k_2 \)  
First order reaction rate constant at the surface of sphere \( s \)

\( k_{seff} \)  
Effective first order surface reaction rate constant for reaction inside sphere 1 (5.48)

\( k_{int} \)  
First order reaction rate constant inside sphere 1

\( K_{nm} \)  
Equation coefficients defined in (2.22)
$K_{nm}^{(i)}$ Matrix elements for the probability expansion defined in (2.26) and (2.27)

$L_{nm}$ Equation Coefficient defined in (3.23)

$L_{nm}^{(i)}$ Matrix elements for the probability expansion defined in (3.26) and (3.27)

$M_n^{(i)}$ Matrix elements defined in (3.28) and (3.29)

$n$ Surface outward normal

$N_{ij}$ Equation coefficient defined by (4.10)

$N_{2j}$ Equation coefficient defined by (4.10)

$p_{1n}$ Equation coefficient of sphere 1 defined in (3.15)

$p_{2n}$ Equation coefficient of sphere 1 defined in (3.17)

$P$ Dimensionless reaction probability of sphere 1 defined in (2.6)

$P_{int}$ Dimensionless reaction probability of internally reactive sphere 1 defined in (5.10)

$P_m$ Dimensionless reaction probability of sphere 1 at infinite dilution defined in (2.45)

$P_n$ Legendre polynomial of the first kind

$Q_n^{(i)}$ Matrix elements defined in (2.28) and (2.29)

$r_1$ Spherical coordinate of sphere 1

$r_2$ Spherical coordinate of sphere 2

$R_l$ Dimensionless reaction rate of sphere 1 in competition with sphere 2 defined in (3.6)
$s$  Modified Bessel function of the first kind argument (5.13)

$S_j$  Quantity defined in (3.36)

$t_{1n}$  Equation coefficient of sphere 1 defined in (5.19)

$t_{2n}$  Equation coefficient of sphere 2 defined in (5.20)

$T_n^{(i)}$  Matrix elements defined in (5.37) and (5.38)

$u$  Dimensionless reactant concentration of the bulk phase in (2.5)

$u_{int}$  Dimensionless reactant concentration inside sphere 1 (5.7a)

$u_{ext}$  Dimensionless reactant concentration of the bulk phase in (5.7b)

$v_{1n}$  Equation coefficient defined in (3.21)

$V_{nm}$  Matrix elements defined in (5.32)

$V_{nm}^{(i)}$  Matrix elements for the probability expansion defined in (5.36) and (5.37)

$W_j$  Equation Coefficient in (4.18)

**Greek Letters**

$\alpha$  Dimensionless source strength (4.5)

$\beta_n$  Equation coefficient defined in (5.30)

$\gamma$  Ratio of sphere 1 radius to sphere 2 radius

$\Gamma_n$  Ratio of two Bessel Functions (5.29)

$\delta_{n0}$  Kroenecker delta

$\varepsilon$  Ratio for external to internal diffusivity constants
η  Bishopspherical coordinate
θ₁  Spherical coordinate of sphere 1
θ₂  Spherical coordinate of sphere 2
κ  Extracellular dimensionless reactant concentration for two competing spheres (3.5)
λ₁  Dimensionless inverse reaction rate coefficient of sphere 1
λ₁eff  Effective surface dimensionless inverse reaction rate coefficient of sphere 1
λ₂  Dimensionless inverse reaction rate coefficient of sphere 2
Λ_kn  Expansion term defined in (2.15) or (3.16)
μ  Bishopspherical coordinate
μ₁  Bishopspherical coordinate value for the surface of sphere 1
μ₂  Bishopspherical coordinate value for the surface of sphere 2
ζ  Coefficient quantity defined in (5.24)
σ₂  Zeroth order rate constant at the surface of sphere 2
τ  Coefficient quantity defined in (5.22)
φ  Spherical and Bishopspherical coordinate
φ₁  Thiele modulus for internally reactive sphere 1 (5.13)
φ₁  Spherical and Bishopspherical coordinate
Ω₁  Dimensionless reaction rate of sphere 1 in bispherical coordinates (3.37)
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CHAPTER 1

HISTORICAL REVIEW OF DIFFUSION AND REACTION IN POROUS MEDIA

1.1 Introduction

The fundamental solution of diffusion to isolated reactive sinks was provided by the monopole solution of Smoluchowski (1916). This well-known theory includes reactions occurring among monodispersed (same size) spherical sinks where the sink volume fraction is so small, interactions between the sinks can be neglected. Diffusion to reactive sinks is significant to biological (Characklis and Marshall, 1990 and Lauffenberger and Linderman, 1993) and non-biological systems (Lifshitz and Pitaevskii, 1981; Voorhees and Schaefer, 1987; Traytak, 1996; and Strieder and Aris, 1973). Physical systems where diffusion reaction is important include: crystal growth and coarsening (Voorhees and Schaefer, 1987), drop coalescence (Lifshitz and Pitaevskii, 1981), combustion of fuel droplets (Traytak, 1996), petroleum cracking catalysts (Strieder and Aris, 1973). Some biological systems are: fermentation in waste water treatment (Coelho and Rodriquez, 1995), drinking water distribution systems (Siebel and Characklis, 1991), microbial remediation of hazardous sites (Characklis and
Marshall, 1990; Converti et al., 1997), production of foods such as tea, coffee, and fruit juices (Geankoplis, 1993), mold fermentations (Shuler and Kargi, 1992) and cellular communication (Lauffenberger and Linderman, 1993). The Smoluchowski (1916) solution only covers the infinitely dilute system where each particle acts as an independent entity and there is no interaction between neighboring spheres (Mattern and Felderhof, 1987). Truly, in most natural and industrial applications this solution is inadequate because neighboring particles are close enough to influence each other.

In the natural, chemical and biological systems mentioned above there is a significant amount of diversity. In biological systems diffusion controls the kinetic rates of many processes from protein-protein encounters (Zhou, 1997 and Northrup and Erickson, 1992), to ligand binding (Lesyng and McCammon, 1993 and Northrup et al., 1984) to signal transmission across synaptic interfaces (Frank et al., 2002 and Zoli and Agnati, 1996). In particular, the biotechnology industry mammalian cells and microorganisms are used to biologically synthesize a wide range of products from polymers to antibiotics to insulin (Converti et al., 1994). This industry has grown to exceed $17 billion (Amundson, 1988). Biosynthesis usually involves many types of microorganisms and each organism may be capable of more than 1,000 different reactions (Bailey and Ollis, 1986) therefore there is significant variation in microorganism type, shape, size, kinetic type and strength of the cells (Wang et al., 1979). One positive implication of diversity is bioremediation where co-metabolism by a consortia, or multiple species working together, allows otherwise persistent pollutants to be degraded to benign
compounds (Siebel and Charcklis, 1991). There are many other instances where these colonies are unwanted, and much effort is taken to discourage their growth (Peyton, 1996 and Melo and Vieira, 1999). It is important to understand how this diversity coupled with environmental parameters will influence the systems’ overall consumption rate.

1.2 Previous Work

1.2.1 The Two Particle System

Two simple systems have been used to gain insight into the effect of interactions between spheres and hence the overall consumption rate. These are Smoluchowski’s (1916) solution for the infinitely dilute (monopole) system and the two sphere system where the solution is generated with either the twin spherical expansion (Ross, 1968 and 1970) or the bispherical coordinates system (Morse and Feshbach, 1953). Since Smoluchowski’s (1916) solution does not deal with interacting particles, it is insufficient for dense interacting systems found throughout engineering; this means solving the two-sphere problem is essential for the second–order correction of the density expansion (Mattern and Felderhof, 1987) for the more realistic systems found throughout engineering and science.

Four studies have focused on diffusion reaction for a pair of monodispersed (same size) particles (Sampson and Deutch, 1977; Zoia and Strieder, 1998; Strieder and Saddawi, 2000; and Tsao, 2001). All of these
problems focused on diffusion to two competing particles where the concentration infinitely far from the two spheres is fixed. Samson and Deutch (1977), Zoia and Strieder, (1998) and Strieder and Saddawi (2000) all use the bispherical coordinate system to resolve the impenetrable sink-sink problem. Samson and Deutch (1977) presented the exact solution for the concentration profiles of two equal sized (monodispersed) spherical sinks with infinitely fast surface reactions (diffusion control). Zoia and Strieder (1998) extended the work of Samson and Deutch (1977) by producing exact, asymptotic solutions of the sink-sink surface reaction problem for two identical sinks with the same first order reaction rate constant at the surface of both spheres. Their work included the development of the reaction rate as an asymptotic expansion in the dimensionless inverse reaction rate for the diffusion to reaction-controlled cases. Strieder and Saddawi (2000) provided an alternate solution for two monodispersed spheres with a first order reaction occurring at the surface of the spheres. These authors used an iterative technique to generate an exact; convergent series expression for the reaction rate of the two spheres.

Tsao (2001) used the method of twin spherical expansion (Ross, 1968 and 1970) to solve the competitive diffusion-reaction problem for diffusion-limited to reaction-limited conditions for two penetrable sinks and two impenetrable sinks. His series expansion solution for the reaction rate for two impenetrable spheres of equal size was compared with the series solution for two permeable spheres of equal size. These rates are expressed in terms of the center-to-center distance. In
the end, Tsao (2001) claimed that the permeable sink can always be well represented by an impermeable sink model.

Keep in mind that it is very unlikely that any two spheres are exactly the same size two key examples are: typical biological cells range is 1 – 100 micrometers (Alberts et al., 1998) and population models of ripening and coarsening where the size of the spheres are always changing (Lifshitz and Pitaevskii, 1981; Voorhees and Schaefer, 1987). Furthermore any insight arising from size difference cannot be illuminated within the context of these four studies.

As seen in diverse cultures of microorganisms, variation in crystal growth rates, and coalescences of particles, size variation is very common. Work for two particles of varying sizes is limited (Voorhees and Schaefer, 1987; Tsao, 2002; Stoy 1989a, 1989b and 1991). Voorhees and Schaefer (1987), used bispherical coordinates (Morse and Feshbach 1953) where the two particles have constant concentrations, differ in size and are far apart, to correlate experimental results for coarsening. Here the authors have neglected to consider the impact proximity may have on the surface concentration of the two spheres, furthermore this method tends to an unphysical infinite reaction rate when the two spheres are in contact. Tsao (2002) obtained a solution for the two impermeable sink problem with first order reactions occurring at the surface of both spheres. Using the bispherical expansions (Ross, 1968 and 1970) he generated a series solution for any combination of diffusion-limited to reaction-limited conditions for the two sinks. Tsao (2002) determined that the interaction is significantly influenced by
the size and reactivity of the interacting particles with diffusive interaction supporting the larger sink even if the smaller sink has a larger reaction rate. His conclusions were based on a few terms, but in order to arrive at a useful approximation of the reaction rate terms above the dipole level must be included. Stoy studied the associated conduction problem (1989a, 1989b, and 1991) and developed an exact solution using recurrent equations in bispherical coordinates (Morse and Feshbach, 1953). No interest was given to the reaction rates in fact his work focused on the potential function, where the concentration contour lines were either parallel or perpendicular to the two spheres. Stoy (1989a, 1989b, and 1991) also included a detailed discussion on the bispherical coordinate system.

1.2.2 The N Particle System

While the two-particle problem is of concern and a useful correction to the N particle problem, the N particle problem is a more realistic system (Torquato, 1991). The diffusion reaction problem for an array of spherical sinks is the topic of many papers (Given et al., 1997; Bonnecaze and Brady, 1991; Doi, 1976; Fradkov et al., 1996, etc.). Rice (1985) and others have solved the $N=2$ sink problem but because the problem is very difficult for $N>2$ most of the work has focused on determining the upper and lower bound of the effective reaction rate for the N sink problem (Reck and Prager, 1965; Reck and Reck, 1968; Rubinstein and Torquato, 1988; and Lu, 1999). Furthermore the system characteristics i.e. whether the sinks are overlapping (Richards, 1986; Strieder, 2000) or non-overlapping (Mattern and Felderhof, 1987; Traytak, 1996, Zheng and Chiew,
1990), permeable (Torquato and Avellaneda, 1991 and Venema and Bedeaux, 1989) or impermeable (Bonnecaze and Brady, 1991; and Rubinstein and Torquato, 1988) further complicates the problem. Some have used variational methods to determine the bounds for the effective rate constant of the N sink diffusion and surface reaction problem (Rice, 1985). This is the preferred method because; the inequalities include the effective reaction rate and the bounds are tightened as more parameters of the microscopic system are available (Torquato and Lado, 1988), often one bound will provide a good estimate of the system even if the other is divergent (Torquato, 1985), and finally a bound can be compared with computer simulations to test their efficacy (Miller and Torquato, 1989).

Because of the complexity of the N sink problem most of the effort to understand the N sink problem has focused on monodispersed systems for the diffusion-limited reaction (Reck and Prager, 1965; Doi, 1976, Rubinstein and Torquato, 1988; Torquato and Avellaneda, 1991; and Tsao et al., 2001). Some work has been done with an interest in sink size distribution (Zheng and Chiew, 1990; Given et al., 1990; Miller and Torquato; 1989 Mandyam et al., 1998). Zheng and Chiew (1990) studied the steady state diffusion-controlled problem for a binary mixture of nonoverlapping traps; they obtained reaction rate constants as a function of the total sink volume. The authors found that the effective reaction rate is directly proportional to the total sink surface area; in fact for small sink size ratio and low sink volume fractions the net rate of the binary dispersion case is a function of the monodispersion case net rate constant.
In the past most efforts to understand the N sink problem focused on the diffusion-limited case. This is an extreme case of the diffusion reaction scheme where the reaction rate is instantaneous and the diffusion rate is finite. Little has been done for the nondiffusion-limited N sink problem even for the simplest case of equisized spheres. Torquato and Avellaneda (1991) studied the permeable N sink problem with first order reaction for both the time dependent and steady state cases. Lu et al., (2002) calculated the steady state rate constant for a cluster of equisized sinks with first order reaction occurring at the surface of the sinks. The author determined that when the reactant concentration is very high the effective reaction rate is less dependent on the volume fraction of sinks in the system. Monte Carlo Simulations were carried out for clusters of monodispersed spheres with internal reactions from diffusion to reaction-limited conditions Riley (1995) determined for the reaction-limited case the overall rate constant is independent of the cellular arrangement (non-overlapping, overlapping and clusters). Weiss (1986), Richards (1986) and Torquato (1991) studied polydispersion for the finite sink case. In all of these papers the work has focused on competitive interaction. Even though in real systems such as remediation there are other relevant types of particle interactions taking place.

Using this approach we have learned that the Smoluchowski (1916) solution cannot be accurately applied to dense N particle systems, the sink-sink interaction is relevant for volume fractions >1%. In these systems the particle interactions become more complex and must be considered (Fradkov et al., 1996 and Mandyam et al., 1998). Recent work by Zoia and Strieder (1998) has shown
that for site volumes fractions $< 10^{-4}$ when the two-sphere problem is explicitly included in the N-sink problem, it could improve the bounds on the effective reaction rate.

### 1.3 Cell-Cell Interaction

Bailey and Ollis (1986) outline a number of different types of cellular interaction with *competition* and *mutualism* described as the two extremes. On the one hand, competition implies that the presence of the second cells results in a negative effect on the growth rate, i.e. the consumption rate, of both cell while mutualism implies that the two cells are mutually beneficial and hence this improves the growth rates of each species. From published experimental results (Cooney and McDonald, 1995; Manz, 1999; Raskin *et al.*, 1996; Rauch, 1999; Stewart *et al.*, 1995 and 1997) it is clear that many if not all of these types of interaction are occurring within a given system. For instance in a biofilm, a highly organized multiphasic system composed of cells, water and metabolic products (Costerton and Stewart, 2001 and De Beer *et al.*, 1994 and 1997), microbial growth is encouraged by the introduction of a substrate (Cao and Alaerts, 1995), this may stimulate competition between like species for say oxygen (Raskin *et al.*, 1996) or mutualism as a consortium of microbes co-metabolizes hazardous waste (Wanner and Gujer, 1986). There have been many attempts to solve the biological N-particle system with numerical simulations while neglecting the importance of cellular interaction (Rodriguez, 1983; Beg and
1.4 Diffusive Interaction in the Two-Particle System

1.4.1 Overview of Two-Particle Model

Consider two non-overlapping reactive spheres of varying sizes with their center to center distance \( d \), where sphere 1 has radius \( a_1 \) and sphere 2 has radius \( a_2 \). The two spheres are surrounded by an inert bulk phase, with reactant and or products diffusing to or from a reactive sphere with the diffusion rate \( D \). Chapters 2-5 all build on this simple system (Figure 1.1). Four versions of this problem with a wide range of radial ratios, center-to-center separation distances, kinetic strengths, kinetic types and interfacial concentrations are studied. Chapter 2 covers the mutualism-like reaction for zeroth order generation of an intermediate product on the surface sphere 2, diffusion away from sphere 2, followed by possible first order consumption of the intermediate product on the surface of sphere 1. The competition problem is studied in Chapter 3 for first order surface consumption by either of the two different spheres of bulk concentration from the surroundings; the calculations include size variations, center-to-center separation distances and kinetic strengths. Chapter 4 uses the bispherical coordinate system to evaluate the mutualism-like reaction for a constant concentration source and diffusion limited sink for a range of intersphere distances and radial ratios. The final chapter, Chapter 5 evaluates the reliability of the surface model given an
internal reaction in sphere 1 and constant flux of an intermediate product from the surface of sphere 2.

The problem considered in the following chapters is the three dimensional, steady-state solution of the partial differential equation called the Laplace equation

\[ DV^2 c = 0 \]  \hspace{1cm} (1.1)

where \( c \) is the concentration of reactant in the inert bulk phase at any point surrounding the two spheres and \( D \) is the Fickian diffusion rate constant for the reactant. In each of the following chapters the concentration profile in the bulk phase is subject to the boundary conditions, these conditions are chosen to simulate different types of surface interactions. Chapter 2, 4 and 5 are variations on the mutualism-like interaction and chapter 3 extends the current knowledge base on the competition problem. Whenever feasible the solutions are as general as possible such that this work is equally applicable to biological and non-biological systems.

### 1.4.2 Solution Methods and Results

There are two approaches to solving the two-sphere problem, using spherical coordinates coupled with the method of bispherical harmonic expansion (Ross, 1968 and 1970) or the bispherical coordinate system (Morse and Feshbach, 1953). Both methods include an infinite sum whose coefficients are acquired
from the set of linear equations. The equations are derived from the application of the boundary equations associated with the problem. The bispherical expansion is used in Chapter 2, 3 and 5 and the bispherical coordinate system is used in Chapter 2 and 4.

In the bispherical expansion the set of linear equations are solved using a matrix elimination method or by iteration. The elimination technique produces a convergent series while the iterative technique is an approximate solution, a convergent-divergent asymptotic solution with an error bound. Hence, Chapter 2, 3 and 5 use the matrix elimination technique developed for the bispherical expansion to solve the two-sphere problem. The matrix elimination method allows for all of the coefficients to be generated using nested, continuous fractions, similar to the nested loop structure of most computer languages. Due to this structure, numerical solutions are easily obtained for both the reaction rate and the concentration profiles. In chapters 2 and 3 a simple summation is used to produce the final results for the concentration and the reaction rates of sphere 1.

Chapter 4 evaluates the constant concentration source and diffusion-controlled sink mutualism-like reaction for the case where the two spheres are not in contact (intersphere distance larger than the sum of the two radii) with the bispherical coordinate system to solve the Laplace equation. This solution is only valid when the two spheres are not in contact. It is a very complex coordinate system that it is very difficult to visualize, however it is a more direct approach than the bispherical harmonic expansion. This approach follows the method outlined by Voorhees and Schaefer (1987). The boundary conditions are applied
directly to the concentration and the reaction rate at the surface of sphere 1 is obtained for any radial ratio, source concentration and intersphere distances greater than the sum of the two radii.

The following four chapters give a unique approach and provide insight into the two-particle problem for different variations on the mutualism and competition interaction. Many phenomena relating to size, reactivity and separation distance are discovered and explained in this treatise. Appendix A is an exact summation of certain infinite series terms used to generate the coefficients in the mutualism-like interactions of Chapter 2 and 5. Finally, a detailed discussion of the bispherical coordinate system including the transformation from spherical to the bispherical coordinates is given in Appendix B.
Figure 1.1: Two spheres of radius $a_1$ and $a_2$ with a center to center distance $d$. 
CHAPTER 2

DIFFUSION REACTION FOR A SPHERICAL SOURCE AND A SPHERICAL SINK

2.1 Introduction

In a very heterogeneous environment mutualism between cells is expected (Stewart et al., 1997). This type of cellular interaction is important in the remediation of contaminated sites (Raskin, et al., 1996 and Siebel and Charackliss, 1991). Mutualism among microorganisms is also significant in the digestion of foods, maintenance of normal bodily functions and oral hygiene (Costerton and Stewart, 2001). Mutualism is described as a relationship between microorganisms where both species profit from each other’s presence (Bailey and Ollis, 1986). In its simplest form the product of one cell becomes the substrate for the second cell.

While there has been some work on competition (Tsao, 2001 and 2002; Zoia and Strieder, 1998, etc.), mutualism is not well understood. An important question is how likely is mutualism between neighboring cells? Embedded within this simple question is a host of others which include: how close do neighboring
cells have to be before they interact, how does cellular size and reactivity influence mutualism and is there an optimum separation distance?

In this chapter the bispherical expansion (Ross, 1968 and 1970) is used to generate the exact analytical solution of the diffusion reaction interaction between a spherical source and spherical sink (mutualism-like). The spherical source and spherical sink are immobile and are immersed in a permeable infinite medium. The two spheres differ in kinetic type with the zeroth order surface generation of the substrate by sphere 2, spherical source. Followed by possible diffusion to the surface of the sink sphere 1 for first order consumption. Zeroth order generation is consistent with the trapping problem, in Monod-type kinetics the cellular consumption rate of a substrate is often zeroth order because the denominator is constant is very small (Bailey and Ollis, 1986) the same is true for receptor mediated endocytosis (Strieder, 2000). Zeroth order generation is also consistent with biological systems because there are many steps to the generation of an extracellular product (Lauffenburger and Linderman, 1993). A cell must trap the substrate in vesicles on its external membrane surface, the vesicles become detached from the membrane and move into the cell they diffuse through the cytosol. Next they are fused with lysosomes for intracellular synthesis, the cell either uses the product or the path is reversed to expel the product (Alberts et al., 1998).
2.2 Mutualism Interaction Between a Spherical Source and Spherical Sink

For any sort of interaction at least two spheres is required, for this mutualism-like interaction, one sphere will consume what the other produces. Therefore the system includes zeroth order generation at the surface of sphere 2, followed by Fickian diffusion of the intermediate product to sphere 1 and first order uptake at the surface of sphere 1. Consider the system of two spheres (Figure 2.1), sphere 1 and 2, with different spherical coordinates originating at the center of each sphere. Sphere 1 has radial vector \( r_1 \) and radius \( a_1 \), the angular vector \( \theta_1 \) is positive in the counter clockwise direction of \( r_1 \). Sphere 2 has a similar set of orienting vectors radial vector \( r_2 \) and radius \( a_2 \), and the angular vector \( \theta_2 \). The two spheres are center to center separation distance \( d \). This three-dimensional steady state problem satisfies the Laplace equation

\[
DV^2 c = 0
\]  
(2.1)

for all points external to the two spheres where \( D \) is the external Fickian diffusion coefficient and the concentration of the intermediate product generated at the surface of the source is \( c \). The concentration far from the two spheres is fixed

\[
c = 0, \quad r_1 \text{ and } r_2 \to \infty.
\]  
(2.2)
The intermediate product is consumed at the surface of sphere 1 the sink as

\[ D \frac{\partial c}{\partial r_1} = k_1 c, \quad r_1 = a_1, \quad (2.3) \]

with first-order kinetic rate constant \( k_1 \) at the surface of sphere 1 and generated at the surface of sphere 2 with

\[ D \frac{\partial c}{\partial r_2} = -\sigma_2, \quad r_2 = a_2 \quad (2.4) \]

with zeroth order rate constant \( \sigma_2 \). It is convenient to define a dimensionless concentration

\[ u = \frac{cD}{a_2 \sigma_2}. \quad (2.5) \]

as a function of the external diffusion coefficient, radius of sphere 2 \( a_2 \), and the generation rate of the intermediate product. The probability \( P \), that a molecule created at the surface of sphere 2 will diffuse to the surface of sphere 1 and be consumed, is defined as
\[
P = \frac{2\pi a_1^2 D c_0}{4\pi a_2 D c_0} \int_0^\pi \left[ \frac{\partial u}{\partial r_1} \right]_r = a_1 \sin \Theta_1 d\Theta_1.
\]  

(2.6)

This \( P \) is the dimensionless steady state consumption rate at sphere 1. By definition \( P \) is always positive. Furthermore, because of the third boundary condition (2.4) the upper bound is unity

\[
0 < P < 1.
\]  

(2.7)

Hence the probability of the product of sphere 2 diffusing to the surface of sphere 1 and becoming trapped depends on the diffusion coefficient, reaction rate at sphere 1, the size of the two particles, and the center-to-center distance of the two spheres. Another useful quantity, the dimensionless inverse sink reaction rate coefficient \( \lambda_1 \), is defined as the ratio of the diffusion coefficient to the product of the reaction rate coefficient and the radius of the sink (sphere 1)

\[
\lambda_1 = \frac{D}{k_1 a_1},
\]  

(2.8)

while the sink to source size ratio is defined as

\[
\gamma = \frac{a_1}{a_2},
\]  

(2.9)
and the dimensionless center-to-center separation distance becomes

\[ d_1 = d / a_1. \]  

(2.10)

2.3 Bispherical Expansion

The dimensionless concentration for all points outside of the spheres, \( u \) (2.5), is determined by solving the Laplace equation (2.1). The solution is called the twin spherical harmonic expansion (Ross, 1970), and it is expressed as a function of the radii \( a_1 \) and \( a_2 \) and the coordinates (Figure 2.1), \( r_1, r_2, \) and Legendre polynomials \( P_n \) in \( \cos(\Theta_1) \) and \( \cos(\Theta_2) \)

\[
    u = \sum_{n=0}^{\infty} \left\{ f_{1n} \left( \frac{a_1}{r_1} \right)^{(n+1)} P_n(\cos\Theta_1) + f_{2n} \left( \frac{a_2}{r_2} \right)^{(n+1)} P_n(\cos\Theta_2) \right\}. \tag{2.11}
\]

The coefficients \( f_{1n} \) and \( f_{2n} \) are determined from the reaction boundary conditions equations (2.3) and (2.4) using the shift equations (Hobson, 1931 and Felderhof, et al., 1982)

\[
    \frac{P_n(\cos\Theta_2)}{r_2^{(n+1)}} = \frac{(-1)^n}{d^{n+1}} \sum_{m=0}^{\infty} \binom{m+n}{m} \left( \frac{r_1}{d} \right)^m P_m(\cos\Theta_1), \quad r_1 < d, \tag{2.12}
\]

and
\[
\frac{P_n(\cos \Theta_1)}{r_1^{(n+1)}} = \frac{1}{d^{n+1}} \sum_{m=0}^{\infty} (-1)^m \binom{m+n}{n} \left(\frac{r_2}{d}\right)^m P_m(\cos \Theta_2), \quad r_2 < d, \quad (2.13)
\]

for any integer \( n \geq 0 \). These two coefficients are expressed as a function of the dimensionless parameters described in equations (2.8) – (2.10) through a series of manipulations. The process begins by initially substituting the first shift formula (2.12) into the dimensionless concentration (2.11) then applying the orthogonality condition of the Legendre polynomials, \( \int_{-1}^{1} P_n(z)P_m(z)dz = \frac{2\delta_{nm}}{1+2n} \), and an identity of the polynomials, \( P_0(\cos \theta) = 1 \), the first coefficient \( f_{1n} \), is the absolutely convergent series

\[
f_{1n} = \Lambda_{1n} \sum_{m=0}^{\infty} f_{2m} (yd_1)^{(m+1)} (-1)^m \binom{m+n}{n}, \quad (2.14)
\]

with

\[
\Lambda_{1n} = \left( \frac{n\lambda_1 - 1}{1 + \lambda_1 + n\lambda_1} \right) \left( \frac{a_1}{d} \right)^n. \quad (2.15)
\]

Similarly, the second coefficient \( f_{2n} \), is obtained by substitution of the second shift formula (2.13) into the dimensionless concentration (2.11) and applying this result to the second boundary condition (2.4). Application of the orthogonality
condition of the Legendre polynomials and the identity, followed by algebraic manipulation yields the completely convergent series

\[ f_{2n} = \delta_{n0} + \left( \frac{-1}{n!d_1} \right)^n \frac{n}{n+1} \sum_{m=0}^{\infty} f_{1m} d_1^{-(m+1)} \binom{n+m}{m}, \quad (2.16) \]

where \( \delta_{n0} \) is the Kronecker delta and equations (2.8) – (2.10) defines the dimensionless parameters.

The trapping probability \( P \), as defined in equation (2.6) can now be evaluated at the surface of sphere 1 by applying the first shift formula (2.12) to the dimensionless concentration (2.11). The shifted dimensionless concentration is differentiated with respect to the first radial coordinate \( r_1 \), and the partial derivative is evaluated at the surface of the sink sphere 1. Substituting \( z = \cos \theta_1 \), in (2.6) and integrating using the orthogonality of the Legendre polynomials and the identity of the Legendre polynomials (both detailed above) the trapping probability is

\[ P = -\gamma f_{10}. \quad (2.17) \]
2.4 Mutualism-like Problem: Analytical Solution

2.4.1 Dimensionless Reaction Probability

It is clear from (2.17), that equations (2.14) and (2.16) must be solved to obtain any valuable information about the reaction probability at sphere 1 $P$, or the concentration outside of the two spheres $u$. Substituting $f_{2m}$, equation (2.16), into $f_{1m}$, equation (2.14), produces an independent linear expression for the first coefficient

$$f_{1m} = \Lambda_{1m} (\gamma d_1)^{-1} \left[ 1 + \sum_{n=0}^{\infty} f_{1n} (d_1)^{(m+1)} F_{nm} \right],$$

(2.18)

where

$$F_{nm} = \sum_{j=0}^{\infty} (\gamma d_1)^{-2j} \binom{j + n}{n} \binom{j + m}{m} \frac{j}{j + 1}.$$  

(2.19)

The matrix $F$ has three distinct properties: it is completely convergent, symmetric and can be expressed in an analytical format for all $n$ and $m$ (see Appendix A for the development of $F$). In order to continue with the trapping probability equation (2.17), the first coefficient $f_{1n}$ is redefined as

$$f_{1n} \equiv \Lambda_{1n} (\gamma d_1)^{-1} h_{1n}$$

(2.20)
with the substitution of (2.20) into (2.18) two simple expressions are obtained,

\[ h_{in} = 1 + \sum_{m=0}^{\infty} K_{nm} h_{1m}, \]  \hspace{1cm} (2.21)

and

\[ K_{nm} = \frac{\Lambda_{1n} F_{nm}}{\gamma d_{1}^{2+n}}. \]  \hspace{1cm} (2.22)

Please note that all \( h_{1n} \) and \( K_{nm} \) are convergent because the initial series for \( f_{1n} \) and \( F \) were absolutely convergent. Applying equations (2.15) and (2.20) to equation (2.17), the probability becomes

\[ P = \frac{h_{10}}{d_{1}(1 + \lambda_{1})}. \]  \hspace{1cm} (2.23)

Equation (2.21) and (2.23) require that all \( h_{1n} \) be known. Though direct matrix inversion can be used to evaluate equations (2.21) it is not recommended because the inversion techniques used in many computer algorithms can produce significant error for a large non-random matrix. An elimination technique is employed to avoid this error. Beginning with equation (2.21) for \( n=0 \)

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\[ h_{10} = \frac{1 + \sum_{m=1}^{\infty} K_{0m} h_{1m}}{1 - K_{00}}, \quad (2.24) \]

This expression is used to eliminate \( h_{10} \) from the remaining equations of (2.21) such that for \( n \geq 1 \)

\[ h_{1n} = 1 + \frac{K_{n0}}{1 - K_{00}} + \sum_{m=1}^{\infty} h_{1m} \left( K_{nm} + \frac{K_{n0} K_{0m}}{1 - K_{00}} \right), \quad n \geq 1. \quad (2.25) \]

Simplifying equation (2.25) becomes

\[ h_{1n} = Q_n^{(1)} + \sum_{m=1}^{\infty} h_{1m} K_{nm}^{(1)}, \quad n \geq 1. \quad (2.26) \]

where

\[ Q_n^{(1)} = Q_n^{(0)} + \frac{Q_0^{(0)} K_{n0}^{(0)}}{1 - K_{00}^{(0)}}, \quad (2.27) \]

\[ Q_n^{(0)} = 1, \quad (2.28) \]

\[ K_{nm}^{(1)} = K_{nm}^{(0)} + \frac{K_{n0}^{(0)} K_{0m}^{(0)}}{1 - K_{00}^{(0)}}, \quad (2.29) \]
and

\[ K_{nm}^{(0)} = K_{nn}, \quad (2.30) \]

Then equation (2.26) is used to explicitly express \( h_{11} \) as a function of all terms where \( m \geq 2 \)

\[ h_{11} = Q_1^{(1)} + \sum_{m=1}^{\infty} h_{1m} K_{1m}^{(1)}, \quad (2.31) \]

or

\[ h_{11} = \frac{Q_1^{(1)} + \sum_{m=2}^{\infty} K_{1m}^{(1)} h_{1m}}{1 - K_{11}^{(1)}}. \quad (2.32) \]

Now that \( h_{11} \) is known it may be eliminated from the remaining expressions.

Substituting equation (2.32) into (2.21) \( h_{1n} \) can be written in a form similar to equation (2.26) for \( n \geq 2 \)

\[ h_{1n} = Q_n^{(1)} + \frac{Q_1^{(1)} K_{n1}^{(1)}}{1 - K_{11}^{(1)}} + \sum_{m=2}^{\infty} h_{1m} \left( K_{nm}^{(1)} + \frac{K_{n1}^{(1)} K_{1m}^{(1)}}{1 - K_{11}^{(1)}} \right), \quad n \geq 2, \quad (2.33) \]

in short
\[ h_{1n} = Q^{(2)}_n + \sum_{m=2}^{\infty} h_{1m} K^{(2)}_{nm}, \quad n \geq 2, \quad (2.34) \]

where

\[ Q^{(2)}_n = Q^{(1)}_n + \frac{Q^{(1)}_1 K^{(1)}_{n1}}{1 - K^{(1)}_{11}}, \quad (2.35) \]

and

\[ K^{(2)}_{nm} = K^{(1)}_{nm} + \frac{K^{(1)}_{n1} K^{(1)}_{1m}}{1 - K^{(1)}_{11}}. \quad (2.36) \]

Then \( h_{12} \) is determined from equation (2.34) for \( n = 2 \) as

\[ h_{12} = \frac{Q^{(2)}_2 + \sum_{m=3}^{\infty} h_{1m} K^{(2)}_{2m}}{1 - K^{(2)}_{22}}. \quad (2.37) \]

Successive eliminations are employed to systematically determine all \( h_{in} \) in terms of \( K_{nm} \). Now suppose \( n \geq i \) then by induction if it is true for \( n \) then it must also be true for \( n + 1 \), hence the \( i^{th} \) modified set of equations becomes
\[ h_{1n} = Q_n^{(i)} + \sum_{m=i}^{\infty} K_{nm}^{(i)} h_{1m} , \quad n \geq i , \quad (2.38) \]

of particular use in future derivations is the case \( n = i \)

\[ h_{ii} = \frac{Q_i^{(i)} + \sum_{m=i+1}^{\infty} K_{im}^{(i)} h_{im}}{1 - K_{ii}^{(i)}}, \quad n = i . \quad (2.39) \]

The forms of the coefficients of equations (2.38) and (2.39) are generalizations of the \( Q_n^{(i)} , K_{nm}^{(i)} \) form (2.27) – (2.30), (2.35) and (2.36) for any integer \( i \)

\[ K_{nm}^{(i+1)} = K_{nm}^{(i)} + \frac{K_{m}^{(i)} K_{nm}^{(i)}}{1 - K_{ii}^{(i)}}, \quad (2.40) \]

\[ K_{nm}^{(0)} = K_{nm}, \quad (2.41) \]

and

\[ Q_n^{(i+1)} = Q_n^{(i)} + \frac{Q_i^{(i)} K_{mi}^{(i)}}{1 - K_{ii}^{(i)}}, \quad (2.42) \]

\[ Q_n^{(0)} = 1. \quad (2.43) \]
They can be calculated exactly for any of the nonnegative integer indices \(i, m,\) and \(n\). Equations (2.40) – (2.43) are similar to continued fractions, and are well suited to nested computer calculations.

In order to calculate the reaction probability \(P\) of equation (2.23) it is necessary by using equations (2.38) and (2.39) to generate an expression for \(h_{10}\).

Using equation (2.38) for \(n = i = 0\)

\[
h_{10} = Q_0^{(0)} + \sum_{m=0}^{\infty} K_{0m}^{(0)} h_{1m}.
\] (2.44)

and applying equation (2.39) for \(i = 0\) to eliminate \(h_{10}\) from the right hand side of equation (2.44)

\[
h_{10} = Q_0^{(0)} + K_{00}^{(0)} \left[ Q_0^{(0)} + \sum_{m=1}^{\infty} K_{m0}^{(0)} h_{1m} \right] + \sum_{m=1}^{\infty} K_{0m}^{(0)} h_{1m}.
\] (2.45)

Rearranging and collecting the coefficients of \(h_{1m}\) with \(Q_0^{(i)}\) from equation (2.27) for \(n = 0\) and \(K_{0m}^{(i)}\) from equation (2.29) for \(n = 0\)

\[
h_{10} = Q_0^{(i)} + \sum_{m=1}^{\infty} K_{0m}^{(i)} h_{1m}.
\] (2.46)
It is important to recognize that equation (2.45) and (2.38) are different. In equation (2.45) \( n = 0 \) and \( i = 1 \) while equation (2.38) requires that \( n \geq i \). Then substituting \( h_{11} \), from equation (2.39) for \( n = i = 1 \), into equation (2.46) and making use of equations (2.40) - (2.43) the first coefficient becomes

\[
\sum_{m=2}^{\infty} \left( K_{0m}^{(1)} + \frac{K_{1m}^{(1)} K_{01}^{(1)}}{1 - K_{11}^{(1)}} \right) h_{1m}.
\]

(2.47)

Using the definitions form (2.35) and (2.36) for \( n = 0 \), we have

\[
Q_0^{(2)} = Q_0^{(1)} + \frac{Q_1^{(1)} K_{01}^{(1)}}{1 - K_{11}^{(1)}}.
\]

(2.48)

and

\[
K_{0m}^{(2)} = K_{0m}^{(1)} + \frac{K_{1m}^{(1)} K_{01}^{(1)}}{1 - K_{11}^{(1)}}
\]

(2.49)

then

\[
h_{10} = Q_0^{(2)} + \sum_{m=2}^{\infty} K_{0m}^{(2)} h_{1m}.
\]

(2.50)
Similarly, the coefficient $h_{12}$ can be eliminated from equation (2.50) by substitution of equation (2.39) for $n = i = 2$

$$h_{10} = Q_0^{(2)} + \frac{Q_2^{(2)} K_{02}^{(2)}}{1 - K_{22}^{(2)}} + \sum_{m=3}^{\infty} K_{0m}^{(2)} \frac{K_{2m}^{(2)} K_{2m}^{(2)}}{1 - K_{22}^{(2)}} h_{1m} . \quad (2.51)$$

As in the previous iteration using (2.40) and (2.42) for $i = 2$ and $n = 0$, we have

$$h_{10} = Q_0^{(3)} + \sum_{m=3}^{\infty} K_{0m}^{(3)} h_{1m} . \quad (2.52)$$

If the first coefficient, $h_{10}$, can be expressed as (2.46), (2.50) and (2.52) then by induction it must be true for all $n$,

$$h_{10} = Q_0^{(n)} + \sum_{m=n}^{\infty} K_{0m}^{(n)} h_{1m} . \quad (2.53)$$

Because the initial series for $f_{1n}$ and $F_{nm}$ were convergent, equation (2.53) is also convergent and for large $n$

$$h_{10} = \lim_{n \to \infty} Q_0^{(n)} , \quad (2.54)$$
So, by eliminating all $h_{im}$ for $m > 0$ and applying equations (2.53) and (2.54) the convergent trapping probability $P$, equation (2.23) becomes

$$P = \frac{1}{d_1(1 + \lambda_1)} \left\{ 1 + \sum_{n=0}^{\infty} \frac{Q_{nn}^{(n)} K_{nn}^{(n)}}{1 - K_{nn}^{(n)}} \right\}.$$  \hspace{1cm} (2.55)

Note equation (2.42) is an iteration in $i$ and the infinite limit of equation (2.54) can be written, using equation (2.42) and (2.43), as the series (2.55). Finally, for all values of dimensionless variables $\gamma, \lambda, \nu$, and $d_1$ the probability of the product of sphere 2 diffusing to the surface of sphere 1 and being consumed by a first order surface reaction is explicitly expressed by equation (2.55). Because the probability only required the generation of $f_{10}, f_{2a}$ was not yet resolved.

### 2.4.2 Dimensionless Concentration

Now that the reaction probability has been expressed the dimensionless concentration is determined in a manner similar to that discussed above. Specifically, the dimensionless concentration $u$, in the neighborhood of the sink is of interest. First the shift formula (2.12), with its limitation is applied to the dimensionless concentration to obtain a unipolar expression for $u$. Then using equation (2.16) $f_{2a}$ is eliminated. At this point the dimensionless concentration $u$ is expressed for the region around sphere 1, $r_1 < d$, in terms of the first family of
coefficients $f_{in}$. Since $h_{1n}$ was actually calculated $f_{1n}$ is replaced with equation (2.20) and the dimensionless concentration becomes

$$u = \frac{1}{(\gamma d_1)} \sum_{n=0}^{\infty} \left\{ \Lambda_{1n} h_{1n} \left[ \frac{a_1}{r_1} \right]^{(n+1)} + \left( \frac{r_i}{a_id_1} \right)^n \right\} \left( 1 + \sum_{m=0}^{\infty} K_{nn} h_{1m} \right) P_n(\cos \Theta_1),$$

(2.56)

$$\frac{r_i}{a_i} < d_1.$$

Applying equation (2.21) to (2.56)

$$u = \frac{1}{(\gamma d_1)} \sum_{n=0}^{\infty} h_{1n} \left\{ \Lambda_{1n} \left[ \frac{a_1}{r_1} \right]^{(n+1)} + \left( \frac{r_i}{a_id_1} \right)^n \right\} P_n(\cos \Theta_1),$$

(2.57)

$$\frac{r_i}{a_i} < d_1,$$

defining a new parameter

$$G_n = \frac{P_n(\cos \Theta_1)}{(\gamma d_1)} \left\{ \Lambda_{1n} \left[ \frac{a_1}{r_1} \right]^{(n+1)} + \left( \frac{r_i}{a_id_1} \right)^n \right\},$$

(2.58)

then
\[ u = \sum_{n=0}^{\infty} h_{in} G_n , \quad \frac{r_1}{a_1} < d_1 . \] (2.59)

Then an elimination technique that is far simpler than the procedure used to derive the probability expression, \( P \) (2.55), (i.e. developed for \( f_{in} \) and \( h_{in} \)) can be used to determine the dimensionless concentration in the neighborhood of sphere 1. Determining the dimensionless concentration around the sink requires successive substitution of all \( h_{in} \). Starting with the substitution of \( h_{i0} \) from equation (2.24) gives

\[ u = \frac{G_{0}^{(0)}}{1 - K_{00}^{(0)}} + \sum_{n=1}^{\infty} h_{in} \left\{ G_{n}^{(0)} + \frac{G_{0}^{(0)} K_{0n}^{(0)}}{1 - K_{00}^{(0)}} \right\} , \] (2.60)

or

\[ u = \frac{G_{0}^{(0)}}{1 - K_{00}^{(0)}} + \sum_{n=1}^{\infty} h_{in} G_{n}^{(1)} , \] (2.61)

where

\[ G_{n}^{(0)} = G_n , \] (2.62)

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\[ G^{(1)}_n = G^{(0)}_n + \frac{G^{(0)}_0 K^{(0)}_{0n}}{1 - K^{(0)}_{00}}, \quad (2.63) \]

and \( K^{(0)}_{0n} \) is defined in equations (2.22) and (2.41). Then substituting equation (2.32) for \( h_{11} \)

\[ u = \frac{G^{(0)}_0 Q^{(0)}_0}{1 - K^{(0)}_{00}} + \frac{G^{(1)}_1 Q^{(1)}_1}{1 - K^{(1)}_{11}} + \sum_{n=2}^{\infty} h_{1n} G^{(2)}_n, \quad (2.64) \]

where

\[ G^{(2)}_n = G^{(1)}_n + \frac{G^{(1)}_1 K^{(1)}_{1n}}{1 - K^{(1)}_{11}}, \quad (2.65) \]

and \( K^{(1)}_{1n} \) is determined by equations (2.22) and (2.29) and \( Q^{(1)}_i \) is defined in equation (2.27). Note equation (2.43) is used in equation (2.64) for \( Q^{(0)}_0 = 1 \).

Extracting the \( n = 2 \) term from the summation and substituting equation (2.37) for \( h_{12} \)

\[ u = \frac{G^{(0)}_0 Q^{(0)}_0}{1 - K^{(0)}_{00}} + \frac{G^{(1)}_1 Q^{(1)}_1}{1 - K^{(1)}_{11}} + \frac{G^{(2)}_2 Q^{(2)}_2}{1 - K^{(2)}_{22}} + \sum_{n=2}^{\infty} h_{1n} \left\{ G^{(2)}_n + \frac{G^{(2)}_2 K^{(2)}_{2n}}{1 - K^{(2)}_{22}} \right\}, \quad (2.66) \]

where
\[ G_n^{(3)} = G_n^{(2)} + \frac{G_2^{(2)} K_{2n}^{(2)}}{1 - K_{22}^{(2)}}, \quad (2.67) \]

with \( Q_2^{(2)} \) defined in equation (2.35) and \( K_{2n}^{(2)} \) by equations (2.22) and (2.36).

Then by induction for all \( n \) the concentration is described by

\[
u = \sum_{n=0}^{\infty} G_n^{(n)} Q_n^{(n)} \left( \frac{r_i}{a_1} < d_1 \right). \quad (2.68)\]

Higher order terms of \( G_n^{(n)} \) are developed similar to \( Q_n^{(n)} \) (2.42) as

\[
G_n^{(i+1)} = G_n^{(i)} + \frac{G_i^{(i)} K_n^{(i)}}{1 - K_i^{(i)}}, \quad i \geq 0 \quad (2.69)
\]

with the initial value, \( G_n^{(0)} \), defined by (2.58). The quantities \( K_n^{(i)} \) and \( Q_n^{(i)} \) for equations (2.68) are determined from equations (2.22) and (2.40) – (2.43).

### 2.5 Results and Discussion

Spherical sink and spherical source mutualism-like interaction model is solved with the bispherical expansion, for first order consumption at the sink surface and a reactant generated at the source surface, with Fickian diffusion in the inert bulk phase. Using the method of elimination outlined above the reaction
probability $P$ (2.55), and the concentration $u$ profile (2.68) in the neighborhood of sphere 1 is completely specified. Both of the equations include a single infinite sum, which converges for all values of the dimensionless parameters $\gamma$, $\lambda_i$ and $d_i$. The infinite sum is calculated as a set of nested continued fractions, equations (2.40) – (2.43), generated from a system of linear equations. Then these types of equations are easily solved as nested loop algorithm on a desktop computer.

The reaction probability $P$, equation (2.55) contains a source term, sink term and a source-sink interaction series. The first factor comes from the monopole reactant concentration arising from the zeroth order reactant generation at the surface of the source. The monopole source concentration at any point $d$ from the center of the source is expressed as

$$c_m = \frac{\sigma z a^2}{dD}. \quad (2.70)$$

If the sink is immersed in the same medium with the uniform concentration $c_m$ at a center to center distance $d$ from the source then the single sphere solution for a finite surface reaction rate is the well-known Smoluchowski diffusion-controlled reaction rate $(4\pi a_i D c_m)$ (Cukier, 1986 and Weiss, 1986) divided by the correction factor $(1 + \lambda_i)$ for the finite surface reaction rate (Reid, 1952). Then for larger sink-source separation distances i.e., the monopole sink reaction rate is
\[ R_m = \frac{4\pi a_i D c_m}{(1 + \lambda_i)}. \]  

(2.71)

Utilizing equation (2.70) and the definition the reaction probability, equation (2.6), the ratio of the sink reaction rate \( R_m \) to the source generation rate \( (4\pi a_i^2 \sigma) \), the monopole sink reaction probability is

\[ P_m = \frac{1}{d_i(1 + \lambda_i)}. \]  

(2.72)

\( P_m \) is the first term in the two body interaction problem (2.55). This implies that the bracketed term must go to unity as the two spheres move farther apart and as the sink and source approach the term must provide the rigorous sink-source interaction multipole correction to all orders.

Figure 2.2 – 2.4 show the probability as a function of dimensionless center-to-center separation distance \( [d/(a_i + a_2) = d_i \gamma/(1 + \gamma)] \) and radius ratio \( \gamma = a_i/a_2 \). In all three graphs the separation distance ranges from unity when the two spheres are in contact to 3, which covers the region of higher order geometric effects. The figures 2.2, 2.3 and 2.4 are plotted for \( \gamma = 10 \) (large sink and small source), \( \gamma = 1 \) (equisized sink and source) and \( \gamma = 0.10 \) (small sink and large source), respectively. These values are selected to simulate typical cell size of 1-10 microns. Each plot also covers a range for the dimensionless inverse reaction rate constant \( \lambda_i = D / k_i a_i \) from a very fast reaction \( \lambda_i = 0.02 \) to a slow reaction.
rate constant $\lambda_i = 50$. The figures 2.2 – 2.4 are produced from the rapidly convergent equation (2.55), they are within 1% of the true value using only the unity and the first 30, 15, and 8 terms from the infinite sum, respectively.

One intuitive statement is well illustrated in these plots i.e., for a large very reactive sink $\gamma \to \infty$, $\lambda_i = 0$ with the two spheres in contact $d/(a_1 + a_2) = 1$, the probability tends to unity, perfect trapping. The converse is also true for $\gamma = 0$, $\lambda_i \to \infty$ with the two spheres at infinite dilution $d/(a_1 + a_2) \to \infty$, the sink is a perfect reflector $(P = 0)$. These two statements require that the probability of any real interactive sink-source pair be bounded below by 0 and above by 1, a tighter lower limit is fixed by $P_m$ which contains the correction factor $(1 + \lambda_i)^{-1}$.

As the center to center distance approaches infinity the equation (2.31) should reduce to equation (2.72) $P_m$. In fact, $P$ and $P_m$ are within 0.1% for figure 2.2 where $\gamma = 10$ for $d/(a_1 + a_2) > 1.01$, Figure 2.3 where $\gamma = 1$ if $d/(a_1 + a_2) > 1.5$, and Figure 2.4 where $\gamma = 0.10$ and $d/(a_1 + a_2) > 1.9$. When the two spheres are within these ranges the multipole correction plays a significant role and must be considered. Outside of this range all three curves are harmonic relations in $d_1$ where $(1 + \lambda_i)^{-1}$ controls the probability such that decreasing $\lambda_i$ (fast reaction, diffusion-controlled) increases the $P$ value.

All of the curves in figure 2.2, 2.3 and the reaction-limited ($\lambda_i \geq 5$) curves in figure 2.4 the maximum occurs at the y-axis where $d/(a_1 + a_2) = 1$ and for all
the slope of the curve is always negative. For the remaining curves in Figure 2.4 for $\gamma = 0.10$ specifically with $\lambda_1 \leq 1$ the maximum occurs to the right of the axis also, as $\lambda_1$ decreases the slope becomes positive and the maximum shifts further away from the axis. As $\lambda_1 \rightarrow 0$ the maximum is near $d/(a_1 + a_2) = 1.17$.

Profiles of the dimensionless concentration contour lines, Figure 2.5 and 2.6, for $\gamma = 0.10$ with finite generation rate at the surface of the source and surface reaction and a diffusion-controlled sink ($\lambda_1 \rightarrow 0$) explain the maximum in Figure 2.4. Though it is not explicitly included in figure 2.4, $\lambda_1 \rightarrow 0$ is selected because the effect is most severe when the sink reaction rate is diffusion-controlled here equation (2.15) reduces to

$$\Lambda_{1n} = -d_1^{-n}. \quad (2.73)$$

These two figures are snapshots of the concentration contours around sphere 1 before and after the maximum, on the right at $[d/(a_1 + a_2) = 1.2]$ for Figure 2.5 and at the left at $[d/(a_1 + a_2) = 1.05]$ for Figure 2.6. As defined by equation (2.42) the dimensionless concentration $u$ and its contours in Figure 2.5 and 2.6 are only valid for $r_1/a_1 < d_1$. This means that the series converge for $r_1/a_1 < 13.2$ in figure 2.5 and for $r_1/a_1 < 11.55$ in Figure 2.6. The reactant flux is in the direction of the sink because the values of the dimensionless concentration contours are zero at the surface of the sink ($r_1 = a_1$) and they increase as $r_1$ increases.
Figure 2.2 – 2.4 shows the monotonic increase as the two sphere move from infinite dilution to closest approach and the concentration and its gradient must also behave this way. The anomalous maxima in Figure 2.4 would imply that this increase in $P$, $u$ and the gradient of $u$ is only true until the extremum is reached. It is most convenient to evaluate the concentration and its gradient at $y_1 = 0$ line where the center to center distance is determined. Here the minimum dimensionless distance between the surface of the sink sphere 1 and the surface of the source sphere 2 is 2.2 and 0.55 for Figure 2.5 and 2.6, respectively. Along this line at $x_i = 1.5$ the dimensionless concentration decreases from 0.2 in Figure 2.6 to 0.19 in Figure 2.5. Similarly the concentration gradient between the source-sink pair along the $y_1 = 0$ is also decreasing form 0.56 to 0.34 in Figure 2.6 and 2.5, respectively.

The contour lines emanating from the surface of the source for Figure 2.5 and 2.6 are markedly different. In figure 2.6 they are nearly perpendicular to the source and are directed toward the sink. This orientation and the distance between the lines represent a very strong flux form the source to the sink. The contours in figure 2.5 do not behave this way. The behavior in Figure 2.6 is indicative of a blocking effect where the source and the very reactive sink are too close for the sink to maximize its consumption potential.

2.6 Summary and Conclusions

This chapter examines the interaction between a spherical sink and spherical source embedded within a permeable medium. The source generates an
intermediate product (growth factor, toxin or nutrient) with zeroth order kinetic rate constant. The intermediate diffuses through a fully permeable medium; such as a biofilm or biological tissue, it may become trapped on the surface of the sink and be consumed with first-order kinetics (nutrient uptake or receptor binding). The bispherical expansion is coupled with a matrix elimination technique to produce a completely convergent series for the dimensionless reaction rate of the sink and the same technique generated the concentration around the sink. Both are completely convergent series with a single infinite sum. The dimensionless reaction rates of the sink is graphically displayed as a function of the sink-source center to center separation distance for a wide range of sink-source size ratio, and sink reactivities from diffusion to reaction-controlled. Concentration contour plots are provided for the infinitely reactive sink in the presence of the source.

The ratio of sink reaction rate to source generation rate displayed in the probability plots are harmonic for dimensionless center to center separation distances larger than 2. The probability approaches the diffusion-controlled limit \( \lambda_i = 0 \) and goes to zero when the sink has no strength \( \lambda_i \to \infty \). When the sink-source size ratio \( \gamma \to \infty \), dimensionless inverse reaction rate \( \lambda_i \to \infty \) and the two spheres are in contact \( d/(a_1 + a_2) = 1 \) the reaction probability goes to unity. Additionally when the source is an order of magnitude larger than the sink and the sink is relatively reactive \( \lambda_i < 1 \) the maximum reactivity does not always occur at closest approach. The concentration profiles illustrate the blocking effect that occurs when the two spheres are too close for the sink to consume much of the product created at the source.
Figure 2.1: Two spheres of radius $a_1$ and $a_2$, spherical coordinates ($r_1, \theta_1$ and $r_2, \theta_2$) separated by center-to-center distance $d$. 
Figure 2.2: Reaction probability $P$ versus the dimensionless center-to-center distance $d(a_1 + a_2)^{-1}$ between the source and sink for a sink to source radius ratio $\gamma(=a_1/a_2)$ of 10. The different curves refer to selected dimensionless, sink surface inverse reaction rate coefficients $\lambda_i(=D(k_{a_i})^{-1})$ of 0.02, 0.1, 0.5, 1, 5, 10 and 50 assigned from the uppermost curve in descending order.
Figure 2.3: Reaction probability $P$ versus the dimensionless center-to-center distance $d/(a_1 + a_2)^{-1}$ between the source and sink for a sink to source radius ratio $\gamma = a_1/a_2$ of 1. The different curves refer to selected dimensionless, sink surface inverse reaction rate coefficients $\lambda_i = D/(k_i a_1)^{-1}$ of 0.02, 0.1, 0.5, 1, 5, 10 and 50 assigned from the uppermost curve in descending order.
Figure 2.4: Reaction probability $P$ versus the dimensionless center-to-center distance $d(a_1 + a_2)^{-1}$ between the source and sink for a sink to source radius ratio $\gamma(=a_1/a_2)$ of 0.10. The different curves refer to selected dimensionless, sink surface inverse reaction rate coefficients $\lambda_i(=D(k_i a_1)^{-1})$ of 0.02, 0.1, 0.5, 1, 5, 10 and 50 assigned from the uppermost curve in descending order.
Figure 2.5: Constant concentration contour curves about the sink are shown labeled for the various dimensionless concentration values $u(=cD/a_1\sigma_1)$. The diffusion-controlled sink ($\lambda_1 \to 0$) is the smaller of the two spheres near the center of the figure, the larger source appears partially at the right. The $x_l, y_l$ grid refers to the coordinates from the center of the sink of radius $a_1 = 1$, and the source has a radius $a_2 = 10$. The center-to-center sink-source separation $d(a_1 + a_2)^{-1} = 1.20$ is taken to be slightly larger than the distance for the maximum reaction probability.
Figure 2.6: Constant concentration contour curves about the sink are shown labeled for the various dimensionless concentration values $u = cD/(a_1\sigma_1)$. The diffusion-controlled sink ($\lambda_1 \to 0$) is the smaller of the two spheres near the center of the figure, the larger source appears partially at the right. The $x_1, y_1$ grid refers to the coordinates from the center of the sink of radius $a_1 = 1$, and the source has radius $a_2 = 10$. The center-to-center sink-source separation $d(a_1 + a_2)^{-1} = 1.05$ is taken to be slightly smaller than the distance for the maximum reaction probability.
CHAPTER 3

COMPETITIVE INTERACTION BETWEEN TWO DIFFERENT SPHERICAL SINKS

3.1 Introduction

Samson and Deutsch (1977) used the bispherical coordinate system \((\mu, \eta, \phi)\) to generate the concentration profile for a monodispersed system in the diffusion control limit, \(k \to \infty\). Since then a lot of work on the monodispersed two-sphere competition problem (Strieder and Sadawwi, 2000; Zoia and Strieder, 1998; Tsao, 2001 etc.) has been done. However little has been done on the polydispersed two-sphere competition problem. From chapter 2 it is clear that there is significant reason to study this problem for possible size, reactivity and spacing effects.

Initially, the overall consumption rate is calculated using the method of bispherical expansion (Ross, 1968 and 1970) for a wide range of sphere ratio, kinetic strength, and intersphere center to center distances. The unexpected results given by the overall consumption rate that was generated by the bispherical expansion (Ross, 1968 and 1970) is validated with bispherical coordinates (Morse and Feshbach, 1953). Bispherical coordinates (Morse and Feshbach, 1953) are used for the limiting case of two infinitely reactive spheres of arbitrary size over a range of center-to-center distances.
Finally, the bispherical coordinate (Morse and Feshbach, 1953) system is used to chart the concentration profile. The theory of competitive interaction is here extended to allow for sink diversity with respect to size, placement, and kinetic strength. The results agree with earlier findings and provide additional information on diverse pairings.

Section 3.2 describes the transport model, boundary conditions, system parameters and the overall consumption rate. Section 3.3 describes the derivation of a concise expression for the consumption rate that is obtained by solving Laplace’s equation using the bispherical expansion (Ross, 1968 and 1970), the shift formulae (Hobson, 1931), and the boundary conditions to derive an infinite set of dependent expressions. The expressions are processed with an elimination method and an independent equation for the overall consumption rate at sphere 1 is displayed in Section 3.4. Section 3.5 revisits the two-sink problem using bispherical coordinates (Morse and Feshbach, 1953) to develop expressions for concentration and overall consumption rate at sphere 1 for two infinitely reactive spheres of varying size and intersphere distances. The results of Sections 3.4 and 3.5, for a range of sink strengths, sink-sink size ratios, and center-to-center separation distance is discussed in Section 3.6. Summary and conclusions are presented in Section 3.7. Appendix B contains a detailed discussion of the bispherical coordinate system.

3.2 Competitive Interaction: Two Sink Problem

The bispherical expansion (Ross, 1968) is used to evaluate two impenetrable competing spheres surrounded by a medium containing a common reactant. The spheres are a center-to-center distance \( d \) apart, with the radii of sphere 1 and 2 defined by
Any point external to the spheres is located using rays of length \( r_1 \) and \( r_2 \), and angle \( \Theta_1 \) and \( \Theta_2 \) respectively. The rays originate at the center of each sphere with the angles positive in the counterclockwise direction (Figure 2.1). The concentration satisfies Laplace equation

\[
D \nabla^2 c = 0 \quad (3.1)
\]

for all points external to the sinks, where \( D \) is the Fickian diffusion coefficient and \( c \) is the concentration of the reactant. The chemical concentration is finite far from either sphere,

\[
c = c_0, \quad r_1 \text{ and } r_2 \to \infty \quad (3.2)
\]

and diminishes in the direction of both spheres. The reactant is supplied by the surroundings for surface reactions at sink 1 or 2 using first-order reactions with kinetic constants \( k_1 \) and \( k_2 \)

\[
D \frac{\partial c}{\partial r_i} = k_i c, \quad r_i = a_i. \quad (3.3)
\]

\[
D \frac{\partial c}{\partial r_2} = k_2 c, \quad r_2 = a_2. \quad (3.4)
\]
Note, boundary conditions (3.2), (3.3) and (3.4) of Laplace’s equation (3.1) show competitive interaction, i.e. first order reactions (consumption) of a common substrate occurring on the surface of each sphere.

There are a few useful dimensionless quantities that allow for a full description of the sink-sink interaction. A dimensionless concentration $u$ is

$$\kappa = \frac{c - c_0}{c_0}, \quad -1 \leq \kappa \leq 0. \quad (3.5)$$

The total reactivity $R_1$, that a reactant molecule will diffuse to sphere 1 rather than 2 become trapped on the surface of the sphere 1 and be consumed, is expressed in spherical coordinates as the integral of the normal derivative of $\kappa$ over the surface of sphere 1,

$$R_1 = \frac{2\pi a_1^2 Dc_0}{4\pi a_1 Dc_0} \int_0^1 \left[ \frac{\partial \kappa}{\partial r_1} \right]_{r=r_i} \sin \Theta_1 d\Theta_1, \quad (3.6)$$

The denominator term in equation (3.6) is Smoluchowski’s (1916) infinitely dilute solution times a correction factor due to the presence of the second sphere, therefore equation (3.6) is the dimensionless steady state sink consumption rate. The ratio $R_1$ is always positive, and due to the boundary condition (3.2), it can never reach unity

$$0 < R_1 < 1. \quad (3.7)$$
The overall reaction rate at sphere 1 $R_1$ will depend on the dimensionless distance between the two spheres $d_i$, the dimensionless inverse sink 1 and 2 reaction rate coefficients $\lambda_1$ and $\lambda_2$, as well as the sink-to-sink radius ratio $\gamma$,

$$d_i = d / a_i,$$
(3.8)

$$\lambda_i = D / (k_i a_i),$$
(3.9)

$$\lambda_2 = D / (k_2 a_2),$$
(3.10)

$$\gamma = a_1 / a_2,$$
(3.11)

Recall, $\lambda$ is the ratio of the diffusion rates (availability) to reaction rate (consumption), a process is diffusion-limited if $\lambda \rightarrow 0$ and is reaction or chemically-limited if $\lambda \rightarrow \infty$.

### 3.3 Bispherical Expansion

Laplace equation (3.1) is solved for $\kappa$, the dimensionless concentration (3.5), as a function of the coordinates of Figure 2.1 as the bispherical harmonic expansion (Ross, 1968 and 1970)

$$\kappa = \sum_{n=0}^{\infty} \left\{ p_{1n} \left( \frac{a_1}{r_1} \right)^{(n+1)} P_n(\cos \Theta_1) + p_{2n} \left( \frac{a_2}{r_2} \right)^{(n+1)} P_n(\cos \Theta_2) \right\},$$
(3.12)
where $P_n$ is the Legendre polynomial of order $n$, and the family of coefficients $p_{1n}$ and $p_{2n}$ are to be determined by the boundary conditions for competitive interaction (3.3) and (3.4). Since equation (3.3) and (3.4) obeys the inequality $r_{1(2)} < d$, it is beneficial to shift $\kappa$ from a two coordinate system to a one coordinate system with the substitution of the shift formulae (Hobson, 1931)

\[
\frac{P_n(\cos \Theta_2)}{r_{2}^{(n+1)}} = \frac{(-1)^n}{d^{n+1}} \sum_{m=0}^{\infty} \binom{m+n}{n} \left( \frac{r_1}{d} \right)^m P_m(\cos \Theta_1), \quad r_1 < d, \quad (3.13)
\]

or

\[
\frac{P_n(\cos \Theta_1)}{r_{1}^{(n+1)}} = \frac{1}{d^{n+1}} \sum_{m=0}^{\infty} (-1)^m \binom{m+n}{n} \left( \frac{r_2}{d} \right)^m P_m(\cos \Theta_2), \quad r_2 < d. \quad (3.14)
\]

After applying the boundary condition (3.3) on sink 1, and substitution of expansions (3.12) and (3.13), applying the orthogonality of the Legendre polynomials,

\[
\int_{-1}^{1} P_n(z) P_m(z) dz = \frac{2 \delta_{nm}}{1 + 2n},
\]

and rearranging the absolutely convergent series, the first set of coefficients are

\[
p_{1n} = A_{1n} \left( \delta_{n0} + \sum_{m=0}^{\infty} (-1)^m \binom{n+m}{n} (\rho d_1)^{m+1} p_{2n} \right) \quad (3.15)
\]
where

\[
\Lambda_{kn} = \left( \frac{a_k}{d} \right)^n \left( \frac{n\lambda_k - 1}{1 + \lambda_k + n\lambda_k} \right), \quad k = 1,2
\]  

(3.16)

and the dimensionless variables are defined in equations (3.8), (3.9), and (3.11). Following the model derived for the expression of the first coefficient \( p_{1n} \); i.e. substituting the second shift formula (3.14) into the bispherical expansion (Ross, 1968 and 1970) \( \kappa \) (3.12), and using the boundary condition of the second sink (3.4), the second coefficient in the dimensionless concentration \( \kappa \) is

\[
p_{2n} = \delta_{n0}\Lambda_{2n} + \Lambda_{2n}(-1)^n \sum_{m=0}^{\infty} \binom{n+m}{m} d_1^{-(m+1)} p_{1m}
\]

(3.17)

where \( \delta_{n0} \) is the Kronecker delta, \( \Lambda_{2n} \) is described in equation (3.16), and equations (3.8) and (3.10) give the dimensionless parameter.

The overall consumption rate of sphere 1 given the presence of sphere 2 is acquired by evaluating equation (3.6). This is achieved by using shift formula (3.13) to eliminate the second set of spherical coordinates in expansion (3.12), differentiating \( \kappa \) with respect to \( r_1 \) and evaluating at the sink surface \( (r_1 = a_i) \). Secondly, substituting \( d(cos\Theta_1) \) for \(-sin\Theta_1d\Theta_1\) the lower and upper bound of the integral become \(-1\) and \(1\) respectively. Next, making use of two properties of Legendre polynomials; orthogonality...
\begin{equation}
\int_{-1}^{1} P_n(z)P_m(z)dz = \frac{2\delta_{nm}}{1+2n} \quad \text{and the identity, } P_0(\cos \Theta) = 1, \text{ the overall reaction at sphere 1 is}
\end{equation}

\begin{equation}
R_1 = -p_{10}.
\end{equation}

Equation (3.18) expresses the reactivity of sphere 1 as the negative of the zeroth term of the first coefficient in the concentration expansion (3.12).

3.4 Competitive Interaction: Analytical Solution

3.4.1 Dimensionless Reaction Rate

While the current form of \( R_1 \) (3.18) is compact, independent solution for \( p_{1n} \) and \( p_{2n} \), equations (3.15) and (3.17) respectively, must be determined. This will allow for a complete solution of the concentration, \( \kappa \), and the overall consumption at sphere 1, \( R_1 \). Substituting the expression for \( p_{2n} \) (3.17) into (3.15) yields a linear equation for the coefficients \( p_{1n} \)

\begin{equation}
p_{1n} = \Lambda_{1n} \left[ \delta_{n0} + (yd_1)^{-1} \Lambda_{20} + (yd_1)^{-1} \sum_{m=0}^{\infty} p_{2m}(d_1)^{-(m+1)} J_{nm} \right],
\end{equation}

where
\[
J_{nm} = \sum_{j=0}^{\infty} (\gamma d_1)^{-j} \Lambda_{2j} \binom{j+n}{m}.
\] (3.20)

The matrix \( J \) is different from equation (2.19) yet like (2.19) it is symmetric in \( n \) and \( m \), and each element converges. To determine the value of \( p_{10} \), equation (3.19) will be processed by the elimination method illustrated in chapter 2, but first the substitution

\[
v_{1n} \equiv \frac{p_{1n}}{\Lambda_{1n} (\delta_{n0} + (\gamma d_1)^{-1} \Lambda_{20})}
\] (3.21)

reduces equations (3.18) - (3.20) to a more manageable expression

\[
v_{1n} = 1 + \sum_{n=0}^{\infty} L_{nm} v_{1n},
\] (3.22)

\[
L_{nm} = \frac{\Lambda_{1n} f_{nm}}{(\gamma d_1^{n+2})} \left( \frac{\Lambda_{20} + \gamma d_1 \delta_{n0}}{\Lambda_{2n} + \gamma d_1 \delta_{n0}} \right).
\] (3.23)

The last term in equation (3.23) shows the effect of the consumption of the second sink on sink 1, it is has similar properties to \( K_{nm} \) in chapter 2. The final form of the consumption rate of sphere 1, \( R_1 \), is determined from equation (3.18), and equation (3.21)

\[
R_1 = -\Lambda_{10} \left( 1 + (\gamma d_1)^{-1} \Lambda_{20} \right) v_{10},
\] (3.24)

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where $\Lambda_{10}$ and $\Lambda_{20}$ are given by equation (3.16).

The first step of the derivation to be used here is similar to the development of equation (2.55) in Section 2.4.1. It suffices to point out that the first equation for $n = 0$, from the linear set of equations for $v_{1n}$ for $n \geq 0$, can be solved for $v_{10}$ in terms of coefficients $v_{1n}$ for $n > 0$, and used to eliminate $v_{10}$ from the rest of the subset for $n \geq 1$ to generate a revised set of linear equations for the coefficients $v_{1n}$ for $n \geq 1$. Subsequently, the first equation $n = 1$ from the first revised set of linear $v_{1n}$ equations provides an expression for $v_{11}$ in terms of $v_{1n}$ for $n > 1$ that can be used to eliminate $v_{11}$ from the $v_{1n}$ revised equations for $n \geq 2$. This second revision gives a set of linear equations for the coefficients $v_{1n}$ for $n \geq 2$. As in Section 2.4.1, if this procedure is repeated one can show by induction that

\[
v_{1n} = M_{n}^{(i)} + \sum_{m=n}^{\infty} L_{nm}^{(i)} v_{1m}, \quad n \geq i, \quad (3.25)
\]

where the nested, sequential expressions for $i \geq 0$

\[
L_{nm}^{(i+1)} = L_{nm}^{(i)} + L_{nm}^{(i)} L_{m}^{(i)} (1 - L_{n}^{(i)})^{-1}, \quad (3.26)
\]

\[
L_{nm}^{(0)} = L_{nm}, \quad (3.27)
\]
\[ M_n^{(i+1)} = M_n^{(i)} + M_i^{(i)} L_m^{(i)} \left(1 - L^{(i)}\right)^{-1}, \]  
(3.28)

\[ M_n^{(0)} = 1, \]  
(3.29)

can be calculated exactly for any of the nonnegative integer indices \( i, m, \) and \( n, \) are similar to continued fractions, and are well suited to nested computer calculations.

Seeking an expression for \( \nu_{1n} \) for any nonnegative integer \( n \) of the same form as equation (3.25), but where \( i \) can be arbitrarily large. Currently in equation (3.25) the index \( i \) cannot exceed \( n. \) The second step is to remove the restriction and to do so the coefficients \( \nu_{1m} \) for \( m > n \) must also be eliminated. From equation (3.25) for the case \( i=n \) it can be shown that

\[ \nu_{1n} = M_n^{(n)} \left(1 - L_n^{(n)}\right)^{-1} + \sum_{m=n+1}^{\infty} L_m^{(n)} \left(1 - L_m^{(n)}\right)^{-1} \nu_{1m}. \]  
(3.30)

With equation (3.26) and (3.28) the \( \nu_{1n} \) coefficients for the equation (3.30) can be reduced to

\[ \nu_{1n} = M_n^{(n+1)} + \sum_{m=n+1}^{\infty} L_m^{(n+1)} \nu_{1m}. \]  
(3.31)
If equation (3.25) is written for \( n+1 \) rather than \( n \) and for the case \( i=n+1 \), then similar to equation (3.30), but for \( v_{1n+1} \),

\[
v_{1n+1} = M_{n+1}^{(n+1)}(1 - L_{n+1}^{(n+1)})^{-1} + \sum_{m=n+2}^{\infty} L_{n+1}^{(n+1)} m (1 - L_{n+1}^{(n+1)})^{-1} v_{1m},
\]

(3.32)

and upon substitution of equation (3.32) into equation (3.31)

\[
v_{1n} = M_{n}^{(n+1)} + L_{n+1}^{(n+1)} \left[ \frac{M_{n+1}^{(n+1)}}{1 + L_{n+1}^{(n+1)}} + \sum_{m=n+2}^{\infty} \frac{L_{n+1}^{(n+1)}}{1 - L_{n+1}^{(n+1)}} v_{1m} \right] + \sum_{m=n+2}^{\infty} L_{n+1}^{(n+1)} v_{1m},
\]

(3.33)

with (3.26) and (3.28) we have

\[
v_{1n} = M_{n}^{(n+2)} + \sum_{m=n+2}^{\infty} L_{n+2}^{(n+2)} v_{1m}.
\]

(3.34)

By induction for any nonnegative integers \( n \) and \( i \), the \( v_{in} \) equation can be written

\[
v_{1n} = M_{n}^{(n+i)} + \sum_{m=n+i}^{\infty} L_{nm}^{(n+i)} v_{1m}.
\]

(3.35)

Because the starting series are convergent in the limit of large \( i \) equation (3.35) yields
\[ v_{1n} = \lim_{i \to \infty} M_n^{(x+i)} = M_n^{(x)} \]  

(3.36)

or alternatively the use of equation (3.28) and (3.29) generates the infinite series expression for the coefficient \( v_{1n} \)

\[ v_{1n} = 1 + \sum_{i=0}^{\infty} M_i^{(i)} L_n^{(i)} (1 - L_n^{(i)})^{-1} \]  

(3.37)

for any nonnegative integer value of \( n \). The dimensionless consumption rate of sphere 1 becomes

\[ R_1 = -\Lambda_n \left(1 + (\gamma d_1)^{-1} \Lambda_{2n}\right) \left[ 1 + \sum_{n=0}^{\infty} M_n^{(n)} L_n^{(n)} (1 - L_n^{(n)})^{-1}\right] \]  

(3.38)

Where \( \Lambda_{kn} \) is defined by equation (3.16), \( M_n^{(n)} \) is defined in equations (3.28) and (3.29) and \( L_n^{(n)} \) is from (3.23), (3.26) and (3.27).

Finally, the dimensionless reaction rate of sink 1, \( R_1 \), is calculated exactly for any of the nonnegative indices \( i, m, \) and \( n \). While direct matrix inversion is possible, the existence of equations (3.26) - (3.29) make it possible to use a continued fraction approach. This technique eliminates the error inherent in computer-generated solutions involving a large non-random matrix, and produces reliable results for any dimensionless center-to-center separation distance \( (d_i) \), radial ratio \( (\gamma) \) and inverse dimensionless reaction rate constant \( (\lambda) \).
3.4.2 Diffusion Limited Concentration and Reaction Rate

Another means of solving the two-sphere problem is Bispherical Coordinates \((\mu, \eta, \phi)\) (Morse and Feshbach, 1953). This provides an alternate method to check the solutions from section 3.4.1, for the important case of \(\lambda_1 \to 0\) and \(\lambda_2 \to 0\). The method is also used in Chapter 4. The coordinates; \(-\infty < \mu < \infty, 0 \leq \eta \leq \pi\) and \(0 \leq \phi \leq 2\pi\) are related to the Cartesian and spherical coordinate system as described in Appendix B. The two spheres are positioned on either side of the vertical axis with their center to center distance \(d\) and an interfocal distance \(f\) (Figure C.1).

The solution extends Voorhees and Schaefer (1987) by evaluating the concentration and reaction rate as the two cells approach. Consider competitive interaction between two sinks with infinitely fast reactions \((\lambda_{i(2)} \to 0)\) with the boundary condition for concentration and the dimensionless concentration set at the interface

\[
c = 0 \Rightarrow \kappa = -1, \quad r_1 = a_1 \Rightarrow \mu = \mu_1, \quad (3.39)
\]

\[
c = 0 \Rightarrow \kappa = -1, \quad r_2 = a_2 \Rightarrow \mu = -\mu_2, \quad (3.40)
\]

here \(\mu_1\) and \(-\mu_2\) represent the radii of the two spheres in bispherical coordinates (Morse and Feshbach, 1953). More detail on the development and calculation of \(\mu_1\) and \(-\mu_2\) are given in Appendix B.

The goal is to obtain the consumption rate of sink 1 for two diffusion–limited sinks i.e., \(\lambda_1 \to 0\) and \(\lambda_2 \to 0\), using bispherical coordinates (Morse and Feshbach,
1953). The reaction rate for this case $\Omega_i$ ($R_i$ for $\lambda_1 \rightarrow 0$ and $\lambda_2 \rightarrow 0$) in spherical coordinates $(r_1, \Theta_1, \phi)$ has the form

$$\Omega_i = 2\pi D c_0 a_i^2 \int_0^{\pi} \left( \partial \kappa / \partial r_1 \right) \sin \Theta_1 \, d\Theta_1, \quad r_1 = a_i, \quad (3.41)$$

where $D$ is the diffusion coefficient, $c_0$ concentration infinitely far from the sphere, $a_i$ is the diameter of sink $1$, $\kappa$ refers to the dimensionless concentration defined by equation (3.5), and spherical coordinate $\Theta_1$, from Figure 2.1.

To express the reaction rate we must first determine the form of the dimensionless concentration in bispherical coordinates (Morse and Feshbach, 1953). Solving the Laplace equation (3.1) the dimensionless concentration is

$$\kappa = \sqrt{\cosh \mu - \cos \eta} \sum_{j=0}^{\infty} \left( A_j e^{\mu (j+\frac{1}{2})} + B_j e^{-\mu (j+\frac{1}{2})} \right) P_j(\cos \eta), \quad (3.42)$$

$P_j$ is the Legendre polynomial of the first kind of order $j$, and $A_j$ and $B_j$ are constants to be determined by the boundary conditions. After applying the boundary conditions (3.39) and (3.40) for infinitely fast reactions ($\lambda \rightarrow 0$) to equation (3.42), the dimensionless concentration in bispherical coordinates becomes,
\[
\kappa = - \sqrt{\cosh \mu - \cos \eta} \sum_{j=0}^{\infty} S_j(\cos \eta) \times \\
\left\{ E_j(\mu_1)\sinh \left[ \mu_1 + \mu_2 \left( j + \frac{1}{2} \right) \right] + E_j(\mu_2)\sinh \left[ \mu_1 - \mu_2 \left( j + \frac{1}{2} \right) \right] \right\}
\]

(3.43)

where

\[
E_j(\mu) = \sqrt{2} \exp \left\{ - \mu \left( j + \frac{1}{2} \right) \right\},
\]

(3.44)

\[
S_j(\eta) = \frac{P_j(\cos \eta)}{\sinh \left[ \mu_1 + \mu_2 \left( j + \frac{1}{2} \right) \right]},
\]

(3.45)

\(P_j\) is the Legendre polynomial of the first kind, \(\mu_1\) and \(\mu_2\) are the absolute values of the interfacial surface of the two spheres in bispherical coordinates (Morse and Feshbach, 1953).

In equation (3.41) the partial derivative of the concentration with respect to \(r_1\) is replaced by the equivalent expression in bispherical coordinates and evaluated at \(\mu = \mu_1\)

\[
\frac{\partial c}{\partial r_1} = - \frac{1}{h_{\mu}} \frac{\partial c}{\partial \mu},
\]

(3.46)

where
\[ h_\mu = \frac{a_i \sinh \mu_i}{\cosh \mu - \cos \eta}, \quad (3.47) \]

With the concentration specified, the total dimensionless consumption rate of sphere 1 is obtained by transforming from spherical to bispherical coordinates (Morse and Feshbach, 1953) using the conversion (Appendix B)

\[ d(\cos \theta) = \frac{\sinh^2 \mu_i}{\cosh \mu_i - \cos \eta} d(\cos \eta). \quad (3.48) \]

Substituting equation (3.48) into equation (3.41), and integrating (3.41) the overall dimensionless reaction rate of sphere 1, \( \Omega_1 \), of two infinitely reactive sinks in bispherical coordinates,

\[ \Omega_1 = \frac{1}{2} \left[ 1 + \sinh \mu_i \sum_{j=0}^{\infty} E_j(\mu_i) \frac{E_j(\mu_1) \cosh \left( (\mu_1 + \mu_2) \left( j + \frac{1}{2} \right) \right) - E_j(\mu_2)}{\sinh \left( (\mu_1 + \mu_2) \left( j + \frac{1}{2} \right) \right)} \right] \quad (3.49) \]

where \( \Omega_i \) is scaled by Smoluchowski’s (1916) infinitely dilute solution for an infinitely reactive sphere 1.
3.5 Results And Discussion

Competitive interaction for two spherical sinks with different radii and reactivity is considered. The sinks are fed by the bulk phase with a fixed reactant concentration far from the pair. The reactant diffuses through the fully permeable medium with constant Fickian diffusion rate. The common reactant is consumed at the surface of both sinks. An exact expression for the dimensionless reaction rate of sphere 1 (3.38) in competition with sphere 2 is presented. Using bispherical expansion the reaction rate $R_1$ (3.38) for two competing sinks with finite dimensionless inverse reaction rate constants is expressed as two nested infinite sums. Here the coefficients are two sets of infinite equations processed through an elimination method. The dimensionless reaction rate $R_1$ (3.38) is dependent upon the matrix elements, $J_{nm}$, $M^{(i)}_n$ and $L^{(i)}_{nm}$. The $J_{nm}$ element is generated from an infinite sum. Element $L^{(0)}_{nm}$ includes the interaction term and $J_{nm}$, and the $i > 0$ elements are acquired through nested calculations. The same is true for $M^{(i)}_n$ where $i > 0$ and $M^{(0)}_n$ is unity. The nested infinite sums generated by the bispherical expansion describes the dimensionless reaction rate $R_1$ (3.38) as a function of the dimensionless center to center separation distance $d/(a_1 + a_2)$, radius ratio $\gamma (= a_1/a_2)$, and the inverse reactivity of sink 1 $\lambda_1 (= D/k_1a_1)$ and sink 2 $\lambda_2 (= D/k_2a_2)$. The exact analytical expression derived from the bispherical expansion $R_1$ (3.38) is summed to within an accuracy of 0.1%, and graphed as shown in Figures 3.1 – 3.9.

The dimensionless reaction rate, $\Omega_1$ (3.49), and the dimensionless concentration, $\kappa$ (3.42), is obtained from bispherical coordinates for two infinitely reactive sinks ($\lambda_1 = 0$ and $\lambda_2 = 0$) where the sink-medium interfacial concentration is zero. The
bispherical coordinate system holds two advantages to the twin spherical expansion, the concentration is valid anywhere in the system and the solution form is simpler because the two sets of coefficients are expressed as concise analytical expressions. Figure (3.10) shows the competitive interaction, equation (3.49), of two infinitely reactive sinks where sink 1 is ten times the size of 2. Equation (3.43) for the dimensionless reactant concentration around the two spheres is displayed using the Cartesian coordinate system in Figure 3.10 and 3.11 to accuracy within 0.1%.

An exact solution for net dimensionless reaction rate of sphere 1 $R_1$ is obtained form the bispherical expansion in equation (3.38) for two spherical sinks with arbitrary size ratio $\gamma(= a_1/a_2)$, with sink 1 reactivity $\lambda_1(= D/k_1 a_1)$ and sink 2 reactivity $\lambda_2(= D/k_2 a_2)$ ranging from diffusion-limited at 0.02 to reaction-limited at 50 for dimensionless center to center separation distance at closest approach $d/(a_1 + a_2) = 1$ to 8. The reaction rate is rendered dimensionless because it is scaled by the single sink diffusion-controlled solution for three reasons: to avoid confusion from overlapping, to maintain the properties of each curve and to force the curves to approach single sink solution. The reaction rate calculation requires 4 parameters: center to center separation distance $d$, sink 1 inverse dimensionless reaction rate $\lambda_1(= D/k_1 a_1)$, sink 2 inverse dimensionless reaction rate $\lambda_2(= D/k_2 a_2)$, and radius ratio $\gamma(= a_1/a_2)$. The figures are generated such that on a single plot a range of sink 1 reactivities may be evaluated as the center to center separation distance varies for a fixed size ratio and sink 2 reactivity.

Fig. 3.1-3.9 show the dimensionless reaction rate of sphere 1, equation (3.38), as a function of dimensionless center to center distance, for inverse dimensionless reaction rates for sink 1 $\lambda_1[= D/k_1 a_1]$ 0.02, 0.1, 0.5, 1, 5, 10 and 50 for all possible combinations
of the size ratio $\gamma = a_1 / a_2 = 0.1, 1, 10$ and inverse dimensionless reaction rate of sink 2 $\lambda_2 = D / k_2 a_2 = 50, 1, 0.02$ (slow to fast reactions). The effect of size and reactivity of sink 2 is determined by comparing the nine figures. In this way three distinct phenomena are observed: pure competition, pure blocking and a combination of the two. In all the figures for a fixed $\lambda_2$ and $\gamma$, the net reaction rate increased as inverse dimensionless reaction rate of sink 1 decreased. In general net consumption rate of sink 1 goes to zero as $\lambda_1 \to \infty$ and at closest approach it goes to a maximum $\lambda_1 \to 0$. The rate is harmonic for larger center to center separation distances $d / (a_1 + a_2)$ increasing to an asymptotic maximum at large separations.

Pure blocking is exhibited in Figure 3.1 ($\lambda_2 = 50$ and $\gamma = 0.1$). Though sink 2 is chemically-limited (slow reaction) its size is ten times that of sphere 1, this advantage allows sink 2 to limit the influence of the smaller more reactive sphere 1. The presence of sink 2 does not affect sphere 1 until they are within a center to center separation distance $d / (a_1 + a_2) \approx 1.5$, for $d / (a_1 + a_2) > 1.5$ the dimensionless reaction rate for the most reactive sink 1 ($\lambda_1 = 0.02$) plateaus at 0.98, and $d / (a_1 + a_2)$ decreases the dimensionless reaction rate for the most reactive sink 1 ($\lambda_1 = 0.02$) decreases rapidly to 0.77 at $d / (a_1 + a_2) = 1$, closest approach. In Figure 3.4 ($\lambda_2 = 50$ and $\gamma = 1$) and ($\lambda_1 = 0.02$) the reaction rate goes from 0.98 at $d / (a_1 + a_2) = 2$ and slowly reaches 0.94 at closest approach. As the inert sphere $a_2$ is smaller than the previous case, the blocking reduction of the reaction on the spherical sink $a_1$ is smaller at closest approach. The maximum blocking effect by spheres of the same size is not large, only about 6%.

Finally, in Figure 3.7 ($\lambda_2 = 50$ and $\gamma = 10$) for a smaller blocking sphere $a_2$ the sink
reaction rate remains virtually unchanged as the smaller inert sphere approaches the sink. The only difference between these three plots is sink-sink size ratio, therefore they are an excellent illustration for the effective center to center separation distance where blocking may have an adverse impact on the reaction rate of sink 1.

In Figure 3.3 when sphere $a_2$ is very reactive and large ($\lambda_2 = 0.02$ and $\gamma = 0.1$) pure competition is exhibited. Unlike the blocking effect which seems limited to a very small center to center separation distance the competition effect is observed for a much larger distance $d/(a_1 + a_2) < 8$. In this figure, when the two sinks are in contact, even a very reactive sink 1 ($\lambda_1 = 0.02$) has a small reaction rate 0.16 and it is even smaller nearly zero for $\lambda_1 = 50$. Here, the effect of size and reactivity of sink 2 is so strong sink $a_1$ reaction rate values are less than 20% of the monopole solution at large separation distances.

Figure 3.2, 3.5 and 3.6 also exhibit pure competition effects and can be compared Figure 3.3. Relative to Figure 3.3 ($\lambda_2 = 0.02$ and $\gamma = 0.1$), for the same sphere 1 ($\lambda_1 = 0.02$) in contact with sphere 2 [$d/(a_1 + a_2) = 1$] the effect of decreasing the size of sink 2 (increasing $\gamma$) increased the reaction rate at sink 1 to 0.69 in Figure 3.6 ($\lambda_2 = 0.02$ and $\gamma = 1$). Decreasing the reactivity of sink 2 increases the reaction rate at sink 1 such that at closest approach [$d/(a_1 + a_2) = 1$] the rate is 0.48 in Figure 3.2 ($\lambda_2 = 1$ and $\gamma = 0.1$). Decreasing both size and reactivity of sink 2 for ($\lambda_2 = 1$ and $\gamma = 10$) in Figure 3.8 the reaction rate goes to 0.97. Similar effects are also shown in Figure 3.5. Pure competitive interaction is best illustrated when sphere 2 is moderately to very reactive and significantly larger than sink 1. These observations imply that for a fixed sink 1 with

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reactivity $\lambda_1$ and radius $a_1$ there are three ways to limit this effect, increase the center to center separation distance, increase the size ratio by decreasing $a_2$, or decrease the reactivity of sink 2.

In Figure 3.8 ($\lambda_2 = 1$ and $\gamma = 10$) and 3.9 ($\lambda_2 = 0.02$ and $\gamma = 10$) a minimum reaction rate for ($\lambda_1 = 0.02$) occurs near center to center separation distance $d/(a_1 + a_2)$ of 1.68 and 1.73, respectively, while in Figure 3.1–3.7 the minimum reaction rate occurs at closest approach [$d/(a_1 + a_2) = 1$]. In these two plots sink 2 is $1/10^{th}$ the size of sink 1, both spheres are moderately to very reactive and several other mild minimum are also present in Fig. 3.8 for $\lambda_1 = 0.1$, 0.02 and in Fig. 3.9 for $\lambda_1 > 1$, with the most severe extremum in Fig. 3.9 for $\lambda_1 = 0.02$. When the two sinks are in contact [$d/(a_1 + a_2) = 1$] the reactant is indiscriminately drawn to the pair, but the much larger surface area of sink 1 allows it to dominate the consumption process effectively minimizing the reaction rate of sink 2. As the pair moves apart the rate at sink 2 dramatically increases such that more reactant is consumed by the second sink, the competition effect (Fig. 3.3). The minimum occurs in the region where pure competition is expected [$d/(a_1 + a_2) > 1.5$], it is small due to the size and reactivity of the second sphere. The minimum becomes more pronounced for ($\gamma = 10$) as both $\lambda_1 \rightarrow 0$ and $\lambda_2 \rightarrow 0$ (Fig. 3.10).

Further insight into the minimum is obtained by evaluating the concentration for the most extreme minimum at $\gamma = 10$ when both sinks are infinitely reactive $\lambda_1 = 0$ and $\lambda_2 = 0$ (Fig. 3.10). Fig. 3.11 display the dimensionless concentration contours around sink 1 near the minimum in the competition zone [$d/(a_1 + a_2) = 1.7$] and Fig. 3.12 in the pure blocking zone [$d/(a_1 + a_2) = 1.01$]. In both plots the center of the two spheres lie
on the $x = 0$ line with the larger sphere sink 1 always above and the smaller sphere sink 2 always below the $z = 0$ line. The dimensionless concentration contours $c/c_0$ is unity far away from the two spheres and diminishes to zero at surface of both sinks. In Fig. 3.11 (competition zone) all contours where $c/c_0 > 0.25$ encompasses both sinks and each sink has its own contour for $c/c_0 \leq 0.2$. This division is around the $x = 0$ line in the neighborhood where the two sinks are closest here dimensionless contour $c/c_0 > 0.25$ has a concave shape because of the strong gradient created by the competitive interaction within this region. In fact, the gradient is so strong the contours for $0.2, 0.15$ around sink 2 and $0.2, 0.15$ and $0.1$ around sink 1 have an eggshell shape, with the maximum distance between the contour and the surface of the corresponding sink along the $x = 0$ line. Additionally, on the $x = 0$ line in this region between the two sinks the gradient for sink 2 is larger ($3.8 \cdot 10^{-2}$) than the gradient around sink 1 ($3.3 \cdot 10^{-2}$).

In contrast the dimensionless concentration contours around the two sinks in Figure 3.12 display the blocking effect at $[d/(a_1 + a_2) = 1.01]$. The figure includes the portion of sphere 1 nearest the smallest sink sphere 2. As in Figure 3.11 the concentration vanishes at the sink-medium interface and is unity when the reactant is very far from the pair. Here the size of sink 1 is effective at diminishing the reaction rate at sink 2 it dictates that true competition will only occur in the region between the two sinks, no matter the reactivity of sphere 2. In the contact region the contours $c/c_0 < 0.01$ hug sphere 2, this is further evidence of successful blocking by sink 1 resulting in localized competition, in between the two sinks. As the two sinks move closer together
less and less of the larger sink 1 is influenced by this interaction, and more of the reactant flows toward the larger sink.

3.6 Summary and Conclusions

The problem of two spheres different in size and reactivity competing for the same reactant is considered. The reactant (ligand, oxygen, or growth factor in a biological system) moves by Fickian diffusion through a medium such as cellular tissue or the extracellular matrix of a biofilm. The cells may consume the reactant (nutrient uptake or receptor ligand binding) with first order kinetic rate constant at the sink-medium interface. Exact analytical solution for the reaction rate and concentration are derived for the interaction as a function of center to center separation distance. The reaction rate expression for two sinks with finite reactivity includes two nested infinite sums derived from the bispherical expansion. The expansion produced a set of linear equations for the coefficients; each coefficient is an infinite sum that is exactly determined form a set of nested, continuous fractions using an elimination method. Reaction rates for sink 1 and concentration for two infinitely reactive sinks for a range of center to center separation distances originate from the Bispherical coordinate system. Unlike twin spherical expansion, which produced nested infinite sums for both net reaction rate and concentration, a single convergent infinite summation is obtained for either quantity in bispherical coordinates. The concentration contours for this competitive interaction are generated for discreet distances and are valid at any point external to the two sinks, no matter the center to center separation distance. Plots were generated over a range of intersphere distances \((d \geq a_1 + a_2)\) i.e., from the two cells in
contact \((d=a_1+a_2)\) to far apart \((d>> a_1+a_2)\), while both sinks experienced variations in size from 1 to 10μm and inverse dimensionless reaction rates for diffusion-controlled \((\lambda_{1,2} \to \infty)\) to kinetic-controlled \((\lambda_{1,2} \to 0)\).

The results show the influence of the size, reactivity and location of a neighboring cell on the efficiency of another with three distinct consequences: pure competition for various reactivities and sink-sink size ratio, pure blocking by a chemically-limited larger or same size sink, and a minimum away from closest approach due to both competition and blocking. The dimensionless net rate (ratio of sink 1 to sink 1 with the correction factor at infinite dilution) is maximized when sink 2 is diffusion limited \((\lambda_2 \to \infty)\), sink 1 is chemically limited \((\lambda_1 \to 0)\) and sink 1 is very large \((\gamma \to \infty)\) for all center-to-center separation distances. The rate increases with decreasing inverse reaction rate constant \(\lambda_1\) and is minimized when sink 1 is chemically-limited no matter the rate of sink 2. The net reaction rate of cell 1 is limited by the blocking (size) of sink 2, as sink-to-sink size ratio increases this effect is diminished. Sink 1 enjoyed the competitive advantage when both size and reactivity were to its advantage, despite closeness of its nearest neighbor. In general sink-to-sink radial ratio \((\gamma =10)\) the net reaction rate of sink 1 tends to a universal minimum away from closest approach, as sink 2 becomes diffusion-limited \((\lambda_2 \to 0)\).

The results indicate that in this limiting case substrate availability in the region nearest the two spheres is the cause for the lowered net reaction rates in both Fig. 3.1, 3.4 and 3.7 and the minimum observed in Fig. 3.8 and 3.9. The minimum is the result blocking effects felt by the very reactive and smaller sink 2 that severely limits the substrate availability in the region where the two sinks are closest. The consequences
arising from possible size and reactivity differences for two sinks for all possible center
to center separation distance has been explained.
Figure 3.1: Dimensionless consumption rate $R_1$ of sphere 1 versus the dimensionless intersphere center-to-center distance $d(a_1 + a_2)^{-1}$ to sphere 2 for sphere 2 inverse dimensionless reactivity $\lambda_2 (= D(k_{2a_2})^{-1}) = 50$, and a sink-to-sink radius ratio $\gamma (= a_1 / a_2)$ of 0.10. The different curves refer to selected dimensionless, surface inverse sphere 1 reaction rate coefficients $\lambda_1 (= D(k_{1a_1})^{-1})$ of 0.02, 0.1, 0.5, 1, 5, 10 and 50 assigned from the uppermost curve in descending order.
Figure 3.2: Dimensionless consumption rate $R_1$ of sphere 1 versus the dimensionless intersphere center-to-center distance $d/(a_1 + a_2)$ to sphere 2 for sphere 2 inverse dimensionless reactivity $\lambda_2 (= D(k_2 a_2)^{-1}) = 1$, and a sink-to-sink radius ratio $\gamma (= a_1 / a_2)$ of 0.10. The different curves refer to selected dimensionless, surface inverse sphere 1 reaction rate coefficients $\lambda_1 (= D(k_1 a_1)^{-1})$ of 0.02, 0.1, 0.5, 1, 5, 10, and 50 assigned from the uppermost curve in descending order.
Figure 3.3: Dimensionless consumption rate $R_1$ of sphere 1 versus the dimensionless intersphere center-to-center distance $d/(a_1 + a_2)$ to sphere 2 for sphere 2 inverse dimensionless reactivity $\lambda_2 = D(k_2a_2)^{-1} = 0.02$, and a sink-to-sink radius ratio $\gamma(a_1/a_2) = 0.1$. The different curves refer to selected dimensionless, surface inverse sphere 1 reaction rate coefficients $\lambda_1 = D(k_1a_1)^{-1}$ of 0.02, 0.1, 0.5, 1, 5, 10 and 50 assigned from the uppermost curve in descending order.
Figure 3.4: Dimensionless consumption rate $R_1$ of sphere 1 versus the dimensionless intersphere center-to-center distance $d(a_1 + a_2)^{-1}$ to sphere 2 for sphere 2 inverse dimensionless reactivity $\lambda_2 (= D(k_2a_2)^{-1}) = 50$, and a sink-to-sink radius ratio $\gamma (= a_1/a_2)$ of 1.0. The different curves refer to selected dimensionless, surface inverse sphere 1 reaction rate coefficients $\lambda_1 (= D(k_1a_1)^{-1})$ of 0.02, 0.1, 0.5, 1, 5, 10 and 50 assigned from the uppermost curve in descending order.
Figure 3.5: Dimensionless consumption rate $R$ of sphere 1 versus the dimensionless intersphere center-to-center distance $d(a_1 + a_2)^{-1}$ to sphere 2 for sphere 2 inverse dimensionless reactivity $\lambda_2 (= D(k_a a_2)^{-1}) = 1$, and a sink-to-sink radius ratio $\gamma (= a_1 / a_2) = 1.0$. The different curves refer to selected dimensionless, surface inverse sphere 1 reaction rate coefficients $\lambda_1 (= D(k_a a_1)^{-1})$ of 0.02, 0.1, 0.5, 1, 5, 10 and 50 assigned from the uppermost curve in descending order.
Figure 3.6: Dimensionless consumption rate $R_i$ of sphere 1 versus the dimensionless intersphere center-to-center distance $d(a_i + a_2)^{-1}$ to sphere 2 for sphere 2 inverse dimensionless reactivity $\lambda_2 (= D(k_2 a_2)^{-1}) = 0.02$, and a sink-to-sink radius ratio $\gamma (= a_1 / a_2)$ of 1.0. The different curves refer to selected dimensionless, surface inverse sphere 1 reaction rate coefficients $\lambda_1 (= D(k_1 a_1)^{-1})$ of 0.02, 0.1, 0.5, 1, 5, 10 and 50 assigned from the uppermost curve in descending order.
Figure 3.7: Dimensionless consumption rate $R$ of sphere 1 versus the dimensionless intersphere center-to-center distance $d(a_1 + a_2)^{-1}$ to sphere 2 for sphere 2 inverse dimensionless reactivity $\lambda_2 (= D(k_a a_2)^{-1}) = 50$, and a sink-to-sink radius ratio $\gamma (= a_1 / a_2)$ of 0.10. The different curves refer to selected dimensionless, surface inverse sphere 1 reaction rate coefficients $\lambda_1 (= D(k_a a_1)^{-1})$ of 0.02, 0.1, 0.5, 1, 5, 10 and 50 assigned from the uppermost curve in descending order.
Figure 3.8: Dimensionless consumption rate $R_1$ of sphere 1 versus the dimensionless intersphere center-to-center distance $d(a_1 + a_2)^{-1}$ to sphere 2 for sphere 2 inverse dimensionless reactivity $\lambda_2\left(= D(k_{1i})^{-1}\right)=1$, and a sink-to-sink radius ratio $\gamma\left(=a_1/a_2\right)$ of 1.0. The different curves refer to selected dimensionless, surface inverse sphere 1 reaction rate coefficients $\lambda_1\left(= D(k_{1i})^{-1}\right)$ of 0.02, 0.1, 0.5, 1, 5, 10 and 50 assigned from the uppermost curve in descending order.
Figure 3.9: Dimensionless consumption rate $R_i$ of sphere 1 versus the dimensionless intersphere center-to-center distance $d/(a_1 + a_2)$ to sphere 2 for sphere 2 inverse dimensionless reactivity $\lambda_2 (=D/k_{i_2}a_2) = 0.02$, and a sink-to-sink radius ratio $\gamma (=a_1/a_2) = 10$. The different curves refer to selected dimensionless, surface inverse sphere 1 reaction rate coefficients $\lambda_1 (=D/k_{i_1}a_1)$ of 0.02, 0.1, 0.5, 1, 5, 10, and 50 assigned from the uppermost curve in descending order.
Figure 3.10: Dimensionless consumption rate $\Omega_1$ of sphere 1 generated from the bispherical coordinate system versus the dimensionless intersphere center-to-center distance $d(a_1 + a_2)^{-1}$ for two infinitely reactive spheres with inverse dimensionless reactivity of sphere 1 $\lambda_1 (= D(k_1a_1)^{-1})$ and sphere 2 $\lambda_2 (= D(k_2a_2)^{-1})$, and a sink-to-sink radius ratio $\gamma (= a_1 / a_2)$ of 10.
Figure 3.11: Constant concentration $c/c_0$ contour curves for two diffusion-controlled sinks. Sphere 2 the smaller sink ($a_2 = 1$) is shown at the center. Only the lower portion of the larger sink ($a_1 = 10$) is shown at the top. The center-to-center separation distance $d/(a_1 + a_2) = 1.7$ is taken near the distance for the minimum reaction for sphere 1 $R_1$. 

$\gamma = a_1/a_2 = 10$
Figure 3.12: Constant concentration $c/c_0$ contour curves for two diffusion-controlled sinks. Sphere 2 the smaller sink ($a_2 = 1$) is shown at the center. Only the lower portion of the larger sink 1 ($a_1 = 10$) is shown at the top. The center-to-center separation distance $d/(a_1+a_2) = 1.01$ is taken near closest approach contact for maximum recovery of $R_1$ from the minimum.
CHAPTER 4

EXACT SOLUTION FOR THE CONSTANT CONCENTRATION SOURCE – REACTIVE SINK PROBLEM

4.1 Introduction

In Chapter 2 the sink source mutualism like interaction was considered where the source had a constant surface generation rate (zeroth order kinetics). The sink in the aforementioned problem was modeled as a first order interfacial reactor. There are many models where the source medium interface exhibits a different behavior. In some catalytic conversion examples the source may require first order or Langmuir Hinshelwood rate constants (Fogler, 1999) while dissolution processes may involve a constant concentration at the source –medium interface (Forsten and Lauffenburger, 1992 and Ham, 1958 and 1959). Primary examples include: crystal growth and coarsening (Voorhees and Schaefer, 1987), drop coalescence (Lifshitz and Pitaevskii, 1981), electric current and heat flow (Stoy, 1989b) and constant oxygen concentration at a source for delivery to microorganisms in the remediation of contaminated soils (Charackliss and Marshall, 1990).
In this chapter the exact steady state solution of the Laplace equation for a spherical source with constant concentration and a diffusion-limited spherical sink is provided. The reactant diffuses by Fick’s law from the source and background through a permeable medium. It is consumed on the surface of the sink at an infinitely fast reaction rate. Expressions for the reactant concentration in the bulk phase and the reaction rate at the sink surface as a single convergent infinite sum form the bispherical coordinate system \((\mu, \eta, \phi)\) (Morse and Feshbach, 1953) are included. The sink reaction rate is plotted for various source surface concentrations and sink size ratios as a function of the dimensionless center to center separation distance. Appendix B is a review of Bispherical coordinate system \((\mu, \eta, \phi)\).

### 4.2 Diffusion-Limited Sink – Constant Source Model

Consider two impenetrable spheres, a sink with radius \(a_1\) and a source with radius \(a_2\), set an arbitrary distance \(d\) apart. The spheres are surrounded by a permeable medium where the concentration of reactant \(c\) is finite far from the sinks \(c_o\) and the reactant diffuses through the inert medium with Fickian diffusion coefficient \(D\). The reactant concentration vanishes at the surface of sphere 1 and is uniform at the surface of sphere 2, \(c_s\). The concentration satisfies the Laplace equation

\[
D \nabla^2 c = 0 \quad (4.1)
\]
for all points external to the sinks, where $D$ is the Fickian diffusion coefficient and $c$ is the concentration of the reacting species. The reactant is consumed on the surface of diffusion limited sink, sphere 1. The source, sphere 2, has a uniform surface concentration. The solution is totally specified by the surface boundary conditions in spherical coordinates $(r, \theta, \phi)$, $c_1$ at $r_1 = a_1$, $c_2$ at $r_2 = a_2$ and far away from the pair $c_0$. Sphere 1 is a sink with

$$c = c_1, \quad r_1 = a_1, \quad (4.2)$$

reactant concentration is uniform at the medium interface for the source

$$c = c_2, \quad r_2 = a_2. \quad (4.3)$$

and the chemical concentration is finite far from either sphere,

$$c = c_0, \quad r_1 \text{ and } r_2 \to \infty. \quad (4.4)$$

There are six distinct inequality combinations for the concentration boundary conditions, $c_0$, $c_1$, and $c_2$. Since sphere 1 is a sink its surface concentration must lie beneath the source sphere ($c_1 < c_2$) restricts the number to three: ($c_0 < c_1 < c_2$), ($c_1 < c_2 < c_0$) and ($c_1 < c_0 < c_2$). The first and second are variations on the competition problem, they can be obtained by adding or
subtracting the last scenario from the results in Chapter 3. Focusing on the third inequality \( c_1 < c_0 < c_2 \) the dimensionless source strength is defined as

\[
\alpha = \frac{c_2}{c_0} - 1, \tag{4.5}
\]

where \( \alpha \) is the nonnegative value. The surroundings contain no reactant for infinite source strength \( (\alpha \to \infty) \), when the source has no strength \( (\alpha = -1) \), and \( \alpha = 0 \) for equivalent source and surroundings concentrations.

The overall dimensionless reaction rate at sphere 1, \( R_1 \), will depend on the dimensionless source strength, the dimensionless distance between the two spheres \( d_1 \)

\[
d_1 = \frac{d}{a_1}, \tag{4.6}
\]

and the sink source radius ratio \( \gamma \)

\[
\gamma = \frac{a_1}{a_2}. \tag{4.7}
\]

The reactivity at sphere 1, \( R_1 \), the possibility that a reactant molecule from the surface of the source or medium will diffuse to sphere 1 become trapped on the surface of the sphere 1 and be consumed, is expressed in spherical coordinates \( (r, \theta, \phi) \) as the integral of the normal derivative of \( c \) over the surface of sphere 1,
\[ R_i = \left(4\pi a_i Dc_0\right)^{-1}\left(2\pi a_i^2 D\right)\int_0^\pi \left[ \frac{\partial c}{\partial r_i} \right] \sin \Theta_i d\Theta_i, \quad r_i = a_i. \quad (4.8) \]

The first term in equation (4.8) is the single sphere solution for an infinitely reactive sphere 1 fed only by the background concentration (no sphere 2 interaction). The ratio \( R_i \) is always positive; since both the source and surroundings feed the sink it may exceed unity

\[ R_i > 0. \quad (4.9) \]

### 4.3 Bispherical Coordinate System: Analytical Solution

#### 4.3.1 Concentration Field

In order to evaluate the reaction rate at the surface of sphere 1, \( R_i \), the Laplace equation (1) must be solved for the concentration. There are two well known solution forms for this two sphere problem, the bispherical expansion (Ross, 1968 and 1970) and the bispherical coordinate system (Morse and Feshbach, 1953). Earlier work by Tsao (2001 and 2002), McDonald and Strieder (2003 and 2004), and others used the method of twin spherical expansion; however Voorhees and Schaefer (1987) developed a solution using Bispherical coordinates \((\mu, \eta, \phi)\) that merits further study. The coordinates are bounded by;
$-\infty < \mu < \infty, \ 0 \leq \eta \leq \pi \ \text{and} \ 0 \leq \phi \leq 2\pi$ \ and are related to the cartesian coordinate \((x,y,z)\) and spherical coordinates \((r,\theta,\phi)\) as described in Appendix B. Then the steady state Laplace equation (4.1) for the two-sphere problem is easily solved with bispherical coordinates \((\mu, \eta, \phi)\) as described by Morse and Feshbach (1953)

\[
\frac{c}{c_0} = 1 + \sqrt{\cosh \mu - \cos \eta} \sum_{j=0}^{\infty} \left( N_{1j} e^{\mu \left(j + \frac{1}{2}\right)} + N_{2j} e^{-\mu \left(j + \frac{1}{2}\right)} \right) P_j(\cos \eta), \quad (4.10)
\]

where \(P_j\) is the Legendre polynomial, and \(N_{1j}\) and \(N_{2j}\) are constants to be determined with the boundary conditions. A detailed discussion on the separation of variables technique used to solve the Laplace equation in Bispherical coordinates is in Appendix B. The sink is above and the source is below the vertical axis, \(z\), with their center-to-center distance fixed at \(d\). Finally, the boundary conditions equations (4.2) and (4.3) in bispherical coordinates \((\mu, \eta, \phi)\) (Morse and Feshbach, 1953)

\[
c = 0, \quad \mu = \mu_1, \quad (4.11)
\]

\[
c = c_2, \quad \mu = -\mu_2. \quad (4.12)
\]

The surface of the sink and source in Bispherical coordinates
\[ \mu_1 = \sinh^{-1}\left( \frac{f}{a_1} \right), \quad \mu = \mu_1, \quad (4.13) \]

and

\[ \mu_2 = \sinh^{-1}\left( \frac{f}{a_2} \right), \quad \mu = -\mu_2. \quad (4.14) \]

where the interfocal distance \( f \) is implicitly determined from

\[ d_1 = \sqrt{1 + \left( \frac{f}{a_1} \right)^2 + \gamma^{-2} + \left( \frac{f}{a_1} \right)^2}. \quad (4.15) \]

The coefficients \( N_{ij} \) and \( N_{2j} \) are determined from the bispherical coordinate boundary conditions (4.11) and (4.12) using the following relation from Morse and Feshbach (1953)

\[ -1 = \sqrt{2} \cos \frac{\mu - \cos \eta}{\sum_{m=0}^{\infty} \exp\left\{-\mu \left( m + \frac{1}{2} \right) \right\} P_m(\cos \eta). \quad (4.16) \]

and the orthogonality condition of the Legendre polynomial

\[ \int_{-1}^{1} P_n(z)P_m(z)dz = \frac{2\delta_{nm}}{1 + 2n}. \] The resultant expressions are solved for coefficients
such that the concentration in the bulk phase as determined by Voorhees and Schaefer (1987) is

\[ c = c_0 - \sqrt{\cosh \mu - \cos \eta} \sum_{j=0}^{\infty} \]

\[ \left\{(c_1 - c_0)W_j(\mu_1)\sinh \left(\mu + \mu_2 \left(j + \frac{1}{2}\right)\right) + \right. \]

\[ \left. (c_2 - c_0)W_j(\mu_2)\sinh \left(\mu_1 - \mu \left(j + \frac{1}{2}\right)\right)\right\} \times \]

\[ \sinh \left(\mu_1 + \mu_2 \left(j + \frac{1}{2}\right)\right)^{-1} P_j(\cos \eta), \]

where

\[ W_j(\mu) = \sqrt{2} \exp \left(\left[-\mu \left(j + \frac{1}{2}\right)\right]\right), \]

and \( P_j \) is the legendre polynomial. Voorhees and Schaefer (1987) derived their equations for deposition during coarsening considering only the case when the spheres are about the same size (\( \gamma \approx 1 \)), and nearly equivalent surface concentrations \( c_1 \approx c_2 \). Furthermore, only the first two terms of the infinite sum \( j = 0 \) and \( j = 1 \) and the case of small \( \exp(-\mu) \) were considered where the spheres are far apart. The concentration boundary equations used by Voorhees and Schaefer (1987) do not apply to the sink-source interaction considered here.
and the small number of infinite sum terms limits the application to large intersphere distances \([d > 4(a_1 + a_2)]\).

### 4.3.2 Dimensionless Reaction Rate

To obtain an analytical solution for the dimensionless reaction rate (4.8) the partial derivative of the concentration with respect to the radial coordinate \(r_{i}\) is transformed from spherical to bispherical coordinates using the transformation (Morse and Feshbach, 1953)

\[
\frac{\partial c}{\partial r_{i}} = -\frac{1}{h_{\mu}} \frac{\partial c}{\partial \mu},
\]

(4.19)

where

\[
h_{\mu} = \frac{a_{i} \sinh \mu_{i}}{\cosh \mu - \cos \eta}.
\]

(4.20)

The transformed expression is then evaluated at the surface of sink 1 where \(\mu = \mu_{i}\) and substituted into the consumption rate of sphere 1, equation (4.8). The total dimensionless consumption rate of sphere 1, \(R_{i}\) in bispherical coordinates can be obtained using the spherical to bispherical coordinate conversion derived from Morse and Feshbach (1953) (Appendix B)
\[
d(\cos \theta) = \frac{\sinh^2 \mu_i}{\cosh \mu_i - \cos \eta} d(\cos \eta).
\] (4.21)

Equation (4.21) with the substitution \( d(\cos \theta_i) = -\sin \theta_i d\theta_i \), is then substituted directly into (4.8). This substitution changes the upper and lower limits of equation (4.8) to -1 and 1 respectively. Integrating the overall dimensionless reaction rate of sphere 1, \( R_1 \), becomes

\[
R_1 = \frac{1}{2} 1 + \sinh \mu_i \sum_{j=0}^{\infty} W_j(\mu_i) \times \left[ \frac{W_j(\mu_i) \cosh \left( \left( \mu_1 + \mu_2 \right) \left( j + \frac{1}{2} \right) \right) + \alpha W_j(\mu_2)}{\sinh \left( \left( \mu_1 + \mu_2 \right) \left( j + \frac{1}{2} \right) \right)} \right],
\] (4.22)

where \( W_j \) is described by equation (4.18). This final expression for the dimensionless reaction rate (4.22) is scaled by Smoluchowski’s (1916) infinitely dilute solution.
4.4 Results and Discussion

Bispherical coordinates are used to obtain an exact analytical expression (4.22) for the dimensionless reaction rate of a diffusion-limited spherical sink in the presence of a generating source sphere with constant surface concentration. The concentration far from the pair is fixed. The solution is an infinite sum described as a function of the dimensionless source strength, sink and source size and intersphere distance $d$. In order to obtain the expression for the reaction rate at the surface of sphere 1 it was necessary to determine the final form of the bulk phase concentration, both are expressed as a single infinite sum as a function of the same parameters. Figures (4.1) – (4.3) show the reaction rate profiles for sink source size ratio ($\gamma$) and dimensionless source strength $\alpha(=c_2/c_0-1)$ as a function of dimensionless center to center separation distance $[d/(a_1 + a_2)]$. The solutions of the dimensionless reaction rate are presented in Figures 4.1 - 4.3 and are accurate to within 0.1%.

Figures (4.1), (4.2) and (4.3) show a wide range of sphere size ratios $\gamma(=a_1/a_2)$ of 0.1, 1, and 10 respectively, in fact the ratios are selected as a general representation of microorganism sizes (Bailey and Ollis, 1986). A second parameter the dimensionless source strength $\alpha(=c_2/c_0-1)$ of 0, 0.2, 0.4, 0.6 and 0.8 generates a family of curves for a given sink source size ratio ($\gamma$). In each of the three figures the minimum reaction is achieved when the concentration at the surface of sphere 2 is nil ($\alpha = -1$) and increases as the dimensionless source strength increase. As the center to center separation distances ($d \rightarrow \infty$) implies
\( \mu_1 \to \infty \) and \( \mu_2 \to \infty \) and all curves approach the Smoluchowski (1916) solution for a single infinitely reactive sink.

As discussed in the previous sections for competition \( \alpha = -1 \), as the source size decreases with constant sink size, effectively increasing (\( \gamma \)), the reaction rate of the sink is dramatically enhanced as shown at \( \frac{d}{(a_1 + a_2)} = 1.1 \) and \( \alpha = -1 \) in Figure (4.1) \( \gamma = 0.1 \) and \( R_1 = 0.22 \), in Figure (4.2) \( \gamma = 1 \) and \( R_1 = 0.71 \) and in Figure (4.3) \( \gamma = 10 \) and \( R_1 = 0.98 \). This effect reverses once \( a_2 \) becomes a strong source as shown at \( \frac{d}{(a_1 + a_2)} = 1.1 \) and \( \alpha = 0.8 \) in Figure 4.1 \( R_1 = 2.12 \), in Figure 4.2 \( R_1 = 2.01 \), and in Figure 4.3 \( R_1 = 1.17 \). By increasing the dimensionless source strength for the same center to center distance \( \frac{d}{(a_1 + a_2)} = 1.1 \) and smallest sink \( \gamma = 0.1 \) the rates increase, \( R_1 = 1.28 \) and \( R_1 = 1.49 \) for \( \alpha = 0 \) and \( \alpha = 0.2 \), respectively.

The sink reaction rate exceeds unity as the spheres approach one another for nonzero source concentrations when the sink is in contact \( \frac{d}{(a_1 + a_2)} = 1 \) the rates become large. When the sink and source move closer together the concentration gradient in the region between the pair will drastically increase regardless of \( \gamma \), sink-source size ratios, because the source concentration \( (c_2 > 0) \) and the diffusion length is zero. This is likely why Voorhees and Schaefer (1987) limited their solution and results to \( d \geq 3.8 \), but their approach is not useful for the mutualism-like source sink interaction because as was determined in Chapter 2 the interaction all but disappears when \( d > 2 \).
4.5 Summary and Conclusions

Exact analytical solution for a constant surface concentration on a spherical source and infinitely reactive spherical sink is developed. A reactant permeable medium with a finite bulk concentration holds both the source and sink. The pair is separated by a center to center distance greater than the sum of the two radii \( d > a_1 + a_2 \). Using bispherical coordinates the bulk phase concentration and the dimensionless sink reaction rate are expressed as a single infinite sum that converges for \( d/(a_1 + a_2) > 1 \).

The results confirm the findings in Chapter 3 for a very reactive spherical sinks. As expected, the solution reduces to the single sphere solution of Smoluchowski (1916) when the two spheres are infinitely far apart for all dimensionless source strength and sink source size ratio. The results approach infinity when the sink and source are in contact.
Figure 4.1: Dimensionless consumption rate of the diffusion-limited sink $R_1$ versus the dimensionless intersphere distance $d/(a_1 + a_2)^{-1}$ between the sink and source for a sink source radius ratio $\gamma = a_1/a_2$ of 0.10. The different curves refer to the dimensionless sphere 2 surface strength $\alpha = (c_2/c_0 - 1)$ of $-1, -0.5, 0, 0.2, 0.4, 0.6, \text{ and } 0.8$ assigned from the lowest curve in ascending order.
Figure 4.2: Dimensionless consumption rate of the diffusion-limited sink $R_1$ versus the dimensionless intersphere distance $d(a_1 + a_2)^{-1}$ between the sink and source for a sink source radius ratio $\gamma (= a_1 / a_2)$ of 1. The different curves refer to the dimensionless sphere 2 surface strength $\alpha (= c_2 / c_0 - 1)$ of -1, -0.5, 0, 0.2, 0.4, 0.6, and 0.8 assigned from the lowest curve in ascending order.
Figure 4.3: Dimensionless consumption rate of the diffusion-limited sink $R_1$ versus the dimensionless intersphere distance $d(a_1 + a_2)^{-1}$ between the sink and source for a sink source radius ratio $\gamma(-a_1/a_2) = 10$. The different curves refer to the dimensionless sphere 2 surface strength $\alpha(-c_2/c_0 - 1)$ of $-1, -0.5, 0, 0.2, 0.4, 0.6, \text{ and } 0.8$ assigned from the lowest curve in ascending order.
CHAPTER 5

DIFFUSION FROM A SPHERICAL SOURCE AND INTERNAL REACTION IN A SPHERICAL SINK

5.1 Introduction

The diffusion interaction between a spherical sink with a reaction distributed within the sink volume and a spherical source with surface generation is considered. Though there are many instances where the sink reaction is internal, usually the surface model with an effective rate is used in its place (Tsao, 2001). Examples of the physical problem include; diffusion into a porous catalyst pellet (Fogler, 1999), diffusion of gas into liquid droplet containing reactant, and reaction in an emulsion with immobilized reactant in the dispersed phase (Bird, Stewart and Lightfoot, 1990). The universal biological type is the importation of a substrate from the bulk medium across the surface of a cell for subsequent intracellular digestion (Alberts et al., 1998). In the biological example the diffusive interaction is called mutualism or commensalism (Bailey and Ollis, 1986) the first requires that both species benefit and the second requires only one
species. Therefore, commensalism is a much more common interaction, where the source will produce a nutrient or growth factor and the sink will consume it.

There are many instances where surface reactions dominate (McDonald and Strieder 2003 and 2004) and Chapter 2 - 4 analyze the two-sphere problem for reactions occurring only on the surface of the spheres. The commensalism or mutualism-like interaction generating the reactant on the surface of sphere 2 at a rate independent of the concentration is consistently used for the source (Forsten and Lauffenburger, 1992 and Lauffenburger and Linderman, 1993). But here, the reactant diffuses into the sink and is consumed inside sphere 1 with first order kinetics (Ochoa et al., 1986; and Wood and Whittaker, 1998). Obviously the presence of an internal reaction introduces more parameters to the problem discussed in Chapter 2, and may have a direct effect on the overall consumption rate of the sink. There is little doubt that external and internal diffusion effects and or the internal reaction rate may add additional barriers to the sink. Consequently this chapter determines whether the surface model is always an accurate description of the two-sphere problem.

Chapter 5 provides an exact solution of the diffusion reaction interaction of two spherical particles immersed in an permeable infinite medium. The two spheres differ in diffusion rates, kinetic type, kinetic strength, and size. The problem and its boundary conditions are described in section 5.2. A number of new parameters, the internal sink concentration and the reaction rate inside the sink are given in Section 5.3. The bispherical expansion (Section 5.4) determines the extracellular reactant concentration for the sink-source pair and provides a
more concise expression for the internal reaction rate. In section 5.5 a matrix elimination method supplied a convergent infinite sum for the internal sink reaction rate. The approximate surface model for internal sink reaction is derived from section 2.5 for all scenarios in Section 5.6. Scenarios where the surface and internal sink reaction model are in disagreement are described in the results and discussion and the conclusion are found in Section 5.7 and 5.8, respectively.

5.2 Penetrable Sink – Impenetrable Source Model

For any sort of interaction at least two spheres is required, for this interaction, one sphere will consume what the other produces. The system includes a spherical source (sphere 2) and spherical sink (sphere 1) embedded in a permeable infinite medium. The source produces a reactant with zeroth order generation at the medium-source interface of sphere 2 (Forsten and Lauffenburger, 1992 and Lauffenburger and Linderman, 1993). The reactant diffuses away from the source and may travel to sphere 1, diffuse across the cellular membrane and is consumed by first order consumption inside the sink (Regalbuto et al., 1989). As illustrated in Figure (2.1) the source-sink pair is separated by a center-to-center distance $d$. Additionally, each sphere has a set of spherical coordinates originating at its center. The spherical source 2 has radius $a_2$, and angle $\Theta_2$; similarly the spherical sink has radius $a_1$, and angle $\Theta_1$ (Figure 2.1). The angles $\Theta_1$ and $\Theta_2$ are positive in the counterclockwise orientation of $r_1$ and $r_2$, respectively (Figure 2.1). The steady state Laplace equation for all points external to the source and sink is
\begin{equation}
D \nabla^2 c_{\text{ext}} = 0
\end{equation}

where \( D \) is the external Fickian diffusion coefficient and the concentration of the reactant is \( c \). The concentration far from the two spheres is fixed as

\begin{equation}
c_{\text{ext}} = 0, \quad \text{for } r_1 \text{ and } r_2 \rightarrow \infty.
\end{equation}

The remaining boundary conditions describe zeroth order generation of a substrate (reactant) occurring at the surface of sphere 2

\begin{equation}
D \frac{\partial c_{\text{ext}}}{\partial r_2} = -\sigma_2, \quad \text{for } r_2 = a_2,
\end{equation}

where it travels away from the source at a rate of \( D \) the substrate either escapes or is trapped and consumed inside sphere 1. The internal diffusion chemical reaction inside the sphere is described by

\begin{equation}
D_{\text{int}} \nabla^2 c_{\text{int}} = k_{\text{int}} c_{\text{int}}, \quad \text{for } r_1 \leq a_1,
\end{equation}

where \( D_{\text{int}} \) is the internal Fickian diffusion rate of the substrate with internal concentration \( c_{\text{int}} \). The reactant is consumed inside sphere 1 by a first-order reaction with kinetic rate constant \( k_{\text{int}} \). The solution of equations (5.1) and (5.4) are both valid at the sink-medium interface because the reactant is transported.
across the interface where the parameters and conditions change. Continuity at the sink-medium interface requires that the concentration obey

$$c_{\text{int}} = c_{\text{ext}}, \quad r_1 = a_1,$$  \hspace{1cm} (5.5)

and its normal derivative must conform to

$$D_{\text{int}} \nabla c_{\text{int}} \cdot \mathbf{n} = D \nabla c_{\text{ext}} \cdot \mathbf{n}, \quad r_1 = a_1.$$  \hspace{1cm} (5.6)

The dimensionless internal sink concentration

$$u_{\text{int}} = \frac{c_{\text{int}} D}{a_2 \sigma_2},$$  \hspace{1cm} (5.7a)

and the bulk phase concentration

$$u_{\text{ext}} = \frac{c_{\text{ext}} D}{a_2 \sigma_2},$$  \hspace{1cm} (5.7b)

are a function of the external diffusion coefficient, radius of sphere 2, $a_2$, and the generation rate, $\sigma_2$, of the reactant. While the sink to source size ratio is

$$\gamma = a_1 / a_2,$$  \hspace{1cm} (5.8)
the dimensionless center-to-center separation distance is

\[ d_1 = d / a_1, \quad (5.9) \]

and the Thiele modulus is

\[ \phi_r = a_1 \sqrt{k_{\text{int}} / D_{\text{int}}}. \quad (5.10) \]

When the modulus is large the rate is limited by the internal diffusion process and a small \( \phi_r \) implies that internal reaction is the rate limiting step (Levenspiel, 1999). The ratio of external to internal diffusion rate is

\[ \varepsilon = D / D_{\text{int}}. \quad (5.11) \]

Since the reaction is volume distributed within the sink, the probability \( P \), that a molecule created at the surface of sphere 2 will diffuse to the surface of sphere 1 and be consumed inside sphere 1, is defined as the volume integral

\[ P_{\text{int}} = 4\pi a_2^2 \sigma_2^{-1} \int_0^{\theta_1} \int_0^{2\pi} k_{\text{int}} c_{\text{int}} r_1^2 \sin \theta_1 d\phi_1 d\theta_1 dr_1. \quad (5.12) \]
This $P_{int}$ is the ratio of the amount of reactant consumed in sphere 1 and the amount produced at sphere 2, hence it is the dimensionless steady state consumption rate of sphere 1. Then the probability $P_{int}$ of the product of sphere 2 diffusing to sphere 1 and reacting inside the sink depends on the internal and external diffusion coefficients, reaction rate inside sphere 1, the size of the two particles, the center-to-center separation distance between the two spheres, and the internal and external concentration. The reaction rate in sphere 1 could also be obtained from the surface integral (equation 2.6) with $c = c_{ext}$. By definition $P_{int}$ is always positive with an upper bound of unity because the sink is fed only by the source as described in boundary condition (5.3),

$$0 < P_{int} < 1.$$  \hspace{1cm} (5.13)

### 5.3 Internal Diffusion Reaction in the Sink

The solution to equation (5.4) the internal diffusion reaction of a spherical sink (catalyst pellet, or microorganism) is

$$u_{int} = \sum_{n=0}^{\infty} b_n i_n(x) P_n(\cos \Theta_1), \hspace{1cm} r_1 \leq a_1.$$  \hspace{1cm} (5.14)

where $b_n$ is the constant to be determined from the boundary equations (5.3), (5.5) and (5.6), $i_n(x) = \sqrt{\pi/2x} I_{n+\frac{1}{2}}(x)$ with $I_{n+\frac{1}{2}}(x)$ is the modified Bessel function
of the first kind of half-integer order with the argument \( x \) and \( P_n \) is the Legendre polynomial of the first kind (Varma and Morbidelli, 1997). The general solution of the dimensionless concentration includes Bessel Functions of the first and second kind and Legendre polynomials of the first and second kind. The second Bessel Function is infinite at \( r = 0 \) (Abramowitz and Stegun, 1972 and Morse and Feshbach, 1953), but the reactant concentration inside the sink must be finite, therefore only the first function remains. Similarly, the second Legendre polynomial has logarithmic singularities at \( \cos \theta = \pm 1 \) (Abramowitz and Stegun, 1972 and Morse and Feshbach, 1953) hence the corresponding coefficients are set to zero. The variable \( x \) is a function of the radial coordinate \( r \), internal diffusion coefficient \( D_{\text{int}} \) and \( k_{\text{int}} \) the internal reaction rate constant

\[
x \equiv r \sqrt{\frac{k_{\text{int}}}{D_{\text{int}}}}, \quad r \leq a_1, \quad (5.15)
\]

At the surface of the sink \( r = a_1 \) equation (5.15) is the Thiele modulus (Varma and Morbidelli, 1997), equation (5.10). When the modulus \( \phi_r \) is large the rate-limiting step is the rate of internal diffusion while small values of \( \phi_r \) implies that the process is limited by the internal reaction.

The probability \( P_{\text{int}} \), as defined in equation (5.12) can now be evaluated over the volume of sphere 1 by direct substitution of the dimensionless internal concentration \( u_{\text{int}} \). The concentration is not a function of \( \phi_1 \), hence the triple
integral is reduced to $2\pi$ times the integration over $r_1$ and $\theta_1$. Substituting $z = \cos \theta_1$, the integration over the angle $\theta_1$, allows the use of orthogonality of the Legendre polynomials $\int_{-1}^{1} P_n(z)P_m(z)dz = \frac{2\delta_{nm}}{1+2n}$ and the identity $P_0(\cos \theta) = 1$.

Finally, substitution of $x = r_1\sqrt{k_{\text{int}}/D_{\text{int}}}$ and integrating with respect to $x$ the probability becomes

$$P_{\text{int}} = \frac{\gamma}{\varepsilon} b_0 \{ \phi_r \cosh \phi_r - \sinh \phi_r \}.$$  \quad (5.16)

where $\gamma$, $\phi_r$ and $\varepsilon$ are defined in equation (5.8), (5.10) and (5.11). The sink internal reaction probability $P_{\text{int}}$ is only a function of the first coefficient generated in the solution for the internal concentration. The solution form for the Laplace equation of the external concentration and the boundary equations: generation at the source surface (5.3), continuity conditions at the sink-medium interface (5.5) and (5.6) are needed to fully specify the internal reaction probability. Equation (5.3) must be used to produce the substrate and the Laplace equation (5.1) must still be used to satisfy the substrate concentration in the bulk phase. Finally, at the interface of the sink and the bulk phase equation must be continuous in both the concentration and its normal first derivative.
5.4 External Concentration

The dimensionless concentration for all points in the bulk phase and on the interface of the bulk and the two spheres, $u_{ext}$, is determined by solving the Laplace equation (5.1). The general solution is called the bispherical harmonic expansion (Ross, 1968 and 1970), and it is expressed as a function of the coordinates (Figure 2.1), $r_1, r_2$, sink radius $a_1$, source radius $a_2$, and Legendre polynomials $P_n$, in $\cos(\Theta_1)$ and $\cos(\Theta_2)$

$$u_{ext} = \sum_{n=0}^{\infty} \left( t_1 \left( \frac{a_1}{r_1} \right)^{n+1} P_n(\cos\Theta_1) + t_2 \left( \frac{a_2}{r_2} \right)^{n+1} P_n(\cos\Theta_2) \right). \quad (5.17)$$

The coefficients $b_n$, $t_{1n}$, and $t_{2n}$ are determined from the reaction boundary condition at the source, equation (5.3), and the continuity equations at the sink surface, equations (5.5) and (5.6). Since the boundary conditions satisfy the inequalities associated with the shift equations (Hobson, 1931 and Felderhof et al., 1982)

$$\frac{P_n(\cos\Theta_2)}{r_2^{n+1}} = \frac{(-1)^n}{d^{n+1}} \sum_{m=0}^{\infty} \left( \begin{array}{c} m+n \\ n \end{array} \right) \left( \frac{r_1}{d} \right)^m P_m(\cos\Theta_1), \quad r_1 < d, \quad (5.18)$$

and
for any non-negative integer \( n \geq 0 \), they are used to create monopole dimensionless external concentration expressions for \( u_{\text{ext}} \).

The source boundary condition is solved applying the second shift formula (5.19) and substituting this shifted equation into (5.3) for \( r_1 = a_1 \). Then the orthogonality condition and identity of the Legendre polynomials (above), provides the second coefficient \( t_{2n} \) as an absolutely convergent series

\[
t_{2n} = \delta_{n0} + \left( \frac{-1}{\gamma d_1} \right)^n \frac{n}{n+1} \sum_{m=0}^{\infty} t_{1m} d_1^{-(m+1)} \binom{n+m}{m}. \tag{5.20}
\]

where \( \delta_{n0} \) is the Kronecker delta, and all other quantities have been defined.

Resolving the continuity expression (5.5) requires substituting the first shift formula (5.18) into equation (5.17) the dimensionless external concentration this monopole expression is equated with the dimensionless internal concentration equation (5.14). Evaluating the expression at the interface of the sink and the bulk phase, \( r_1 = a_1 \), using the previous properties of the Legendre polynomials, the first coefficient of the external concentration is a completely convergent sum

\[
t_{1n} = b_n i_n (\phi_r) - \sum_{m=0}^{\infty} \left[ \frac{t_{2m} (1)^m}{d_1^m (\gamma d_1)^{m+1}} \binom{n+m}{m} \right]. \tag{5.21}
\]
The final set of coefficients $b_n$, are expressed in the third boundary condition (5.6). This equation is satisfied by multiplying the corresponding Fickian diffusion coefficient by the normal derivative of the corresponding dimensionless internal and shifted external concentration, the orthogonality condition of the Legendre polynomials is applied and finally the resulting expression is evaluated at the interface $r_i = a_i$

$$b_n = \tau_n t_{1n} + \zeta_n \sum_{m=0}^{\infty} \left( \frac{t_{2m} (-1)^m}{d_1 (n)} \right)^{m+1} \left( \begin{array}{c} n + m \\ m \end{array} \right).$$

(5.22)

where

$$\tau_n = -\frac{n+1}{\phi_T \phi_T' (\phi_T)} \epsilon,$$

(5.23)

and

$$\zeta_n = \frac{n}{\phi_T \phi_T' (\phi_T)} \epsilon.$$

(5.24)

From the Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables (Abramowitz and Stegun, 1972)
\[ i_1' (\phi_T) = \frac{d}{dx} \left( i_n (x) \right)_{x=\phi_T} = i_{n-1} (\phi_T) - \frac{n+1}{\phi_T} i_n (\phi_T), \quad (5.25) \]

particularly for \( n = 0 \),

\[ i_0' (x) = \frac{d}{dx} \left( \frac{\sinh(x)}{x} \right)_{x=\phi_T} = \left( \frac{\cosh \phi_T}{\phi_T} - \frac{\sinh \phi_T}{\phi_T^2} \right), \quad (5.26) \]

By direct substitution, the expression for the first coefficient of the internal dimensionless concentration \( b_0 \) becomes

\[ b_0 = \tau_0 t_{10} = - \frac{\phi_T \varepsilon}{\phi_T \cosh \phi_T - \sinh \phi_T} t_{10}. \quad (5.27) \]

Applying equation (5.22) to the internal probability expression, (5.16) leads to the elimination of all \( b_n \), and the probability takes the same form as that described in Chapter 2

\[ P_{int} = -\gamma t_{10}. \quad (5.28) \]
5.5 Internal Reaction Probability: Analytical Solution

Simultaneously solving equations (5.20) - (5.22) eliminates all $b_n$ and $t_{2n}$ from $t_{1n}$ and produces a linear independent expression for the first set of coefficients $t_{1n}$. Each $t_{1n}$ equation involves the entire set of expressions and is best solved with the elimination technique outlined in Chapter 2. The completely convergent infinite sum has the form

$$t_{1n} = \frac{\beta_n}{\gamma d_{n+1}} \left[ 1 + \sum_{m=0}^{\infty} \left( \frac{t_{lm}}{d_{n+1}} H_{nm} \right) \right],$$

(5.29)

where

$$H_{nm} = \sum_{j=0}^{\infty} \left( \gamma d_1 \right)^{2j} \left( j + n \right) \left( j + m \right) \left( \frac{j}{j+1} \right).$$

(5.30)

$H_{nm}$ is the symmetric matrix derived in Chapter 2, equation (2.19) and explained in the Appendix A. The contribution from the $2^n$–pole is

$$\beta_n = \frac{\xi_n \gamma_{n+1} (\phi_T)}{1 - \gamma_n \phi_T (\phi_T)} = \frac{\varepsilon (n + 1) + \phi_T \Gamma_n (\phi_T) - n - 1}{\varepsilon (n + 1) + \phi_T \Gamma_n (\phi_T) - n - 1},$$

(5.31)
where \( \varepsilon = D/D_{\text{int}} \), \( \Gamma_n(\phi_T) = I_{n-\frac{1}{2}}(\phi_T)/I_{n+\frac{1}{2}}(\phi_T) \) is the ratio of two modified Bessel function of half order with argument \( \phi_T \), where it is bounded by \(-1 < \beta_n < 1\) for \( n \geq 1 \) and for \( n = 0 \) where \( \beta_0 = (1-\phi_T \coth \phi_T)/(|\varepsilon + \phi_T \coth \phi_T - 1|) \) the bound is \(-1 < \beta_0 < 0\). In order to continue with the elimination method the first coefficient \( t_{1n} \) is redefined as

\[
 t_{1n} = \frac{\beta_n}{\beta d_{11}^{-\frac{1}{n+1}}} g_{1n}, \quad (5.32)
\]

with the substitution of (5.32) into (5.29) two expressions are obtained,

\[
 g_{1n} = 1 + \sum_{m=0}^{\infty} V_{nm} g_{1m}, \quad (5.33)
\]

is a linear expression for all \( g_{1n} \) and

\[
 V_{nm} = \frac{\beta_n H_{nm}}{\gamma d_1^{2(1+\mu)}}, \quad (5.34)
\]

All \( g_{1n} \) and \( V_{nm} \) are convergent because the initial series for \( t_{1n} \) and \( H \) were absolutely convergent.

The probability expression \( P_{\text{int}} \) in terms of these new parameters for \( n = 0 \) becomes
\[ P_{\text{int}} = -\frac{\beta_0}{d_1} g_{10}. \]  

(5.35)

Now equation (5.33) and (5.35), the dimensionless internal probability expression, require that all \( g_{in} \) be known. Section 2.4 detailed an elimination method to solve a system of linear equations. This technique is employed to produce the final expression

\[ g_{10} = 1 + \sum_{n=0}^{\infty} \frac{T_n^{(n)} V_n^{(n)}}{1 - V_{nn}^{(n)}}, \]  

(5.36)

where the matrix elements \( T_n^{(0)}, V_{nm}^{(0)}, T_n^{(i+1)}, V_{nm}^{(i+1)} \) for integer \( n, m \) and \( i > 0 \) are derived in Section 2.4 (see equations (2.40) – (2.43)) for \( Q_n^{(0)}, K_n^{(0)}, Q_n^{(i+1)}, K_n^{(i+1)} \), respectively. The derivation is not repeated; however, the final expressions for \( T_n^{(i+1)} \) and \( V_{nm}^{(i+1)} \) are

\[ V_{nm}^{(i+1)} = V_{nm}^{(i)} + \frac{V_{im}^{(i)} V_{ni}^{(i)}}{1 - V_{ii}^{(i)}}, \]  

(5.37)

\[ V_{nm}^{(0)} = V_{nm}, \]  

(5.38)

and
\[ T^{(i+1)}_n = T^{(i)}_n + \frac{T^{(i)}_i V^{(i)}_m}{1 - V^{(i)}_i}, \]  
\[ T^{(0)}_n = 1. \]  

Finally, for all values of the dimensionless variables \( \varepsilon, \gamma, \phi, \) and \( d \), the probability of an internal reaction in sphere 1 becomes

\[ P_{\text{int}} = -\frac{\beta_0}{d_1} \left\{ 1 + \sum_{n=0}^{\infty} \frac{T^{(n)}_n V^{(n)}_{0n}}{1 - V^{(n)}_{nn}} \right\}. \]  

for the Fickian diffusion of a reactant that was generated at the surface of the spherical source with zeroth order kinetics rate constant \( \sigma_2 \) being consumed by an internal volume distributed first order reaction in the spherical sink is explicitly expressed as the absolutely convergent expression given by equation (5.41). Because the probability only required the generation of \( t_{10}, t_{2n} \) and \( b_n \) were not resolved. If required both sets of coefficients can be exactly determined, from the relationships developed in equations (5.20) - (5.22).

### 5.6 Surface Reaction with an Effective Reaction Rate Constant

The literature includes many examples where the penetrable sink with fast or slow internal reaction is replaced by the impenetrable sink with an effective surface reaction (Imbihl, 2003; Levenspiel, 1999; and Fogler, 1999). The approximation
is accomplished by setting the effective surface reaction rate calculated using the effective surface kinetic constant \( k_{seff} \) equal to the actual volume distributed reaction rate within an isolated sphere,

\[
1 = \frac{2\pi D_{int} \int_{0}^{\infty} \int_{0}^{\pi} \left( \frac{\partial u_{in}}{\partial r_1} \right) r_1^2 \sin \theta \, d\theta \, dr_1}{2\pi a_1^2 \int_{0}^{\pi} k_{seff} u_{ext} \sin \theta \, d\theta_1} . \tag{5.42}
\]

The equation (5.42) serves as the definition of \( k_{seff} \), and this effective surface reaction rate model will give agreement with the volume distributed sink solution when the sink and source are far apart. For the \( k_{seff} \) calculation of equation (5.42) as the sink is isolated, both the surface and volume diffusion-reaction problems are the well known one dimensional radial problem (Aris, 1975), the resultant solution gives

\[
k_{seff} = \frac{D_{int}}{a_1} (\phi_r \coth \phi_r - 1) , \tag{5.43}
\]

for the surface reaction rate constant in the inverse dimensionless reaction rate coefficient, \( \lambda_i = D_i/(k_1 a_i) \). Derived for the surface model in Chapter 2, such that

\[
\lambda_{i,eff} = \frac{\varepsilon}{\phi_r \coth \phi_r - 1} , \tag{5.44}
\]
where \( \varepsilon \) is the ratio of external to internal diffusion rates, and \( \phi_T \) is the Thiele modulus. Using the effective dimensionless inverse reaction rate constant reduces the number of parameters from four in the penetrable sink solution given by equation (5.41) to three in the impenetrable sink probability relation (2.55)

\[
P_{\text{sur}} = \frac{1}{d_1(1 + \lambda_{\text{eff}})} \left\{ 1 + \sum_{n=0}^{\infty} \frac{Q^{(n)}_m K_{mn}^{(n)}}{1 - K_{mm}^{(n)}} \right\}.
\]

(5.45)

where the elements of the matrices, \( K \) and \( Q \) are given by equations (2.22) and (2.40) – (2.43) are

\[
K_{mn}^{(i+1)} = K_{mn}^{(i)} + \frac{K_{mn}^{(i)} K_{mi}^{(i)}}{1 - K_{ii}^{(i)}}, \tag{2.40}
\]

\[
K_{mn}^{(0)} = K_{mn}, \tag{2.41}
\]

\[
Q^{(i+1)}_n = Q_n^{(i)} + \frac{Q_n^{(i)} K_{mn}^{(i)}}{1 - K_{ii}^{(i)}}, \tag{2.42}
\]
\[ Q_n^{(o)} = 1. \] (2.43)

They are all influenced by this change because the elements of the vector \( \Lambda_{in} \) equation (2.15), is altered such that

\[
\Lambda_{in} = \left( \frac{n \lambda_{i\text{eff}} - 1}{1 + \lambda_{i\text{eff}} + n \lambda_{i\text{eff}}} \right) d_i^{-n},
\] (2.15)

The matrix elements \( F_{nm} \) in equation (2.19) is the same as \( H_{nm} \) defined in equation (5.30) therefore it remains unchanged

\[
F_{nm} = \sum_{j=0}^{\infty} (\gamma d_i) ^{j} \binom{j + n}{m} \binom{j + m}{j} \frac{j}{j + 1}.
\] (2.19)

### 5.7 Results and Discussion

The solution for a penetrable spherical sink and impenetrable spherical source is determined. The method of bispherical expansion specified the concentration outside of the two spheres and the concentration inside the sink was determined in spherical coordinates. The source was a zeroth order generator and the sink employed an internal first order reaction scheme with internal Fickian diffusion. The dimensionless concentration inside the penetrable sink \( u_{\text{int}} \)
equation (5.14) and \( u_{\text{ext}} \), the external dimensionless concentration equation (5.17) are used to determine the probability of an internal sink reaction \( P_{\text{int}} \) as a function of external and internal Fickian diffusion rate \( \varepsilon = D / D_{\text{int}} \), sink and source radius ratio \( \gamma = a_1 / a_2 \), sink Thiele modulus \( \phi_r = a_1 \sqrt{k_{\text{int}} / D_{\text{int}}} \), and center to center separation distance \( d / (a_1 + a_2) \). The surface reaction probability from Chapter 2 is fitted with an effective surface reaction rate for direct comparison between the penetrable sink-source interaction and the impenetrable sink-source pair approximation method equation (5.45). Both the approximate and true probability is a completely convergent sum for all parameters.

The effective surface reaction probability \( P_{\text{sur}} \), equation (5.45) with an effective dimensionless inverse reaction rate \( \lambda_{\text{eff}} = D / k_{\text{eff}} a_1 \), sink-source size ratio \( \gamma \) and center to center separation distance \( d \) is compared with the true internal reaction probability \( P_{\text{int}} \) to determine whether the two expressions behave in the same manner for all parameters: Fickian diffusion ratio (equation 5.11), Thiele Modulus \( \phi_r \) (5.10), \( \gamma \) (5.8) and the center to center distance \( d \). Figure 5.1 – 5.9 show the direct relation between the two probabilities for a range of intersphere distances and Thiele modulus values \( \phi_r \) of 0.1, 0.5, 1, 5, 10 and 50 and the corresponding dimensionless inverse effective surface reaction rate constant \( \lambda_{\text{eff}} \) of 30, 1.22, 0.320, 0.025, 0.011, 0.002, for \( \varepsilon = 0.1 \) and \( \gamma = 1 \), 1 and 10, of 300, 12.2, 3.19, 0.25, 0.111 and 0.0204, for \( \varepsilon = 1 \), and 3000, 122, 31.9, 2.50, 1.11 and 0.204 for \( \varepsilon = 10 \) and \( \gamma = 0.1 \), 1 and 10. In this range the approximation is very accurate, whenever the two solutions differ a dashed line
represents $P_{\text{sur}}$ and a solid line represents the exact solution. In all nine figures the probability is largest for the largest $\phi_r$ of 50 and continues to decrease as $\phi_r$ decreases. Figure 5.12 depicts one divergent example for the $P_{\text{int}}$ and $P_{\text{sur}}$ from $d/(a_1 + a_2) = 1$ (two spheres in contact) to $d/(a_1 + a_2) = 1.2$. The figure relates two equisized spheres, $\gamma = 1$, with diffusivity ratio, $\varepsilon = 0.1$, and Thiele modulus $\phi_r = 0.01$. Figure (5.1) – (5.10) are accurate to within 0.1% for the full range of intersphere distances. Some examples of the percent error for deviating $P_{\text{int}}$ and $P_{\text{sur}}$ are provided in Table 5.1 for $\gamma = 1$, $\varepsilon \leq 0.5$ and $\phi_r \leq 0.5$ at closest approach where $d/(a_1 + a_2) = 1$.

Figure (5.1) – (5.9) share a few common observations. In each plot the most reactive sink has Thiele modulus of 50 with the related $\lambda_{\text{eff}}$ listed above. For any $\phi_r$ and $\varepsilon$, increasing the sink source size ratio, $\gamma$, will increase the probability such as from 0.07 in Figure (5.1) to 0.45 in Figure (5.2) to 0.88 in Figure (5.3) at closest approach and $\phi_r = 5$. Additionally, as $\varepsilon \to \infty$ with any $\lambda_{\text{eff}}$ and $\gamma$ the probability will decrease to zero, this is demonstrated for $\gamma = 1$ in Figure (5.2), (5.5) and (5.8) for $\phi_r = 5$ and $d/(a_1 + a_2) = 3$, the probability values are 0.16, 0.13 and 0.05, respectively. This effect is more severe for less reactive sinks and occurs at closest approach for example, in Figure (5.3), (5.6), (5.9) and $\phi_r = 0.5$ the probabilities are, 0.4, 0.07 and 0.01, respectively.

The maximum observed in Figure (2.4) for $\gamma = 0.1$ also occurs in Figure (5.1) where ($\gamma = 0.1$ and $\varepsilon = 0.1$), Figure (5.4) where ($\gamma = 0.1$ and $\varepsilon = 1$) and
Figure (5.7) where \( \gamma = 0.1 \) and \( \varepsilon = 10 \), moreover as the diffusivity ratio increases the number of curves per plot that exhibit the maximum declines from \( \phi_r > 0.5 \) (Figure 5.1) to \( \phi_r > 1 \) (Figure 5.4) to \( \phi_r > 5 \) (Figure 5.7). This is the diffusion ratio effect increasing \( \varepsilon \) means the reactant in the extracellular region is traveling faster than inside the cell, so more reactant can escape to infinity.

In most cases the exact penetrable and fairly accurate impenetrable sink probability solution are interchangeable, the agreement is improved as the Thiele modulus, \( \phi_r \), increases. The curves differ most at closest approach for \( \phi_r < 5 \) and the separation distance \( d \) increases. Because in the penetrable sink solution as \( \phi_r \) increases the reaction moves closer to the sink-medium interface \( (r_i = a_i) \), this is where the reaction occurs in the impenetrable solution.

Tsao (2001) surmised that for a sink-sink interaction (competition) the impenetrable solution with an effective reaction rate is always a good estimate for the corresponding penetrable scenario in addition, this solution requires only three parameters instead of the four needed in the penetrable case. In most of the plots the \( P_{\text{int}} \) and the approximation \( P_{\text{sur}} \) are in agreement, except in the region where both \( \varepsilon \) and \( \phi_r \) are small and the sink-source pair are very close. As the two spheres move closer together the surface reaction with an effective inverse dimensionless reaction rate increases at a faster rate than the true solution, producing a larger probability of interaction making \( P_{\text{sur}} \) always greater at closest approach (figure 5.10). In fact, as the diffusivity ratio and Thiele modulus decrease the error increases in Table (5.1) for \( \varepsilon = 0.5 \) and \( \phi_r = 0.5 \) the percent
difference is $-4.48\%$ and for $\varepsilon = 0.01$ and $\phi_r = 0.01$ the difference is $-8.16\%$.

If a biological cell hopes to survive its limited internal space must be wisely, this would mean that for a first order reaction inside a cellular sink the resultant Thiele modulus must be small and as Weisz (1973) suggests many are below 0.5. The same should be true for two competing cellular sinks (Tsao, 2001), for small diffusivity ratios $\varepsilon \leq 0.5$ and small Thiele modulus $\phi_r \leq 0.5$ the exact penetrable sink solution should be used. So this means the conditions where the two solutions don’t agree, often occur in biological systems and care must be used in applying surface models to microorganisms!

### 5.8 Summary and Conclusions

A comparison between the exact analytical penetrable spherical sink spherical source interaction $P_{\text{int}}$ and the estimated impenetrable – spherical sink spherical source interaction $P_{\text{sur}}$ with an effective dimensionless inverse surface reaction, $\lambda_{\text{eff}}$, was made. The exact penetrable sink required an internal first order reaction in the sink and internal diffusivity and the source was a zeroth order surface generator. Both solutions were determined from the bispherical expansion, using two distinct nested infinite sums. A total of ten plots describing all possible ranges for the effective dimensionless inverse surface reaction rate, and the resulting Thiele modulus, were plotted for combinations of sink source size ratio and diffusivity ratio as a function of the dimensionless center to center separation distance. Percent error for two monodispersed spheres at closest
approach \( \frac{d}{(a_1 + a_2)} = 1 \), small Thiele modulus and small diffusivity ratio is also included.

The reaction rate vanishes as the diffusivity ratio approaches infinity. It increases with increasing Thiele modulus and decreasing effective dimensionless reaction rate constant. It approaches unity as the sink source size ratio increases. Exact and estimated reaction rate probability results show a wide range of agreement between the estimated probability and the exact penetrable sink solution. The two solutions are virtually equal for large Thiele modulus, no matter the intersphere distance, diffusivity ratio or sink source size ratio and the maximum observed and explained in Chapter 2 is also present for the exact analytical penetrable sink zeroth order source solution. In the region of closest approach the two solutions are more likely to differ. In particular when the Thiele modulus is small and the diffusivity ratio is small the exact solution for the penetrable sink source interaction must be used.
Figure 5.1: Reaction probability $P_{\text{int}}$ for a first order penetrable sink and a zeroth order source versus the dimensionless center to center distance $d/(a_1 + a_2)$ between the source and sink, for a sink to source radius ratio $\gamma (= a_1/a_2)$ of 0.1, extracellular to internal sink diffusivity ratio $\epsilon (= D/D_{\text{int}})$ of 0.1 and sink Thiele Modulus $\phi_T (= a_1 \sqrt{k_{\text{int}}/D_{\text{int}}})$ of 0.1, 0.5, 1, 5, 10 and 50. The lower solid lines are the exact reaction probability, equation (5.41), for an internally reactive sink, and the dashed lines refers to the approximate, sink surface reaction probability $P_{\text{sur}}$, equation (5.45), with an effective inverse dimensionless reaction rate coefficient $\lambda_{\text{eff}}^{-1} (= \epsilon / (\phi_T \coth \phi_T - 1))$ of 30, 1.22, 0.320, 0.025, 0.011, and 0.002.
Figure 5.2: Reaction probability $P_{\text{int}}$ for a first order penetrable sink and a zeroth order source versus the dimensionless center to center distance $d/(a_1 + a_2)$ between the source and sink, for a sink to source radius ratio $\gamma = a_1/a_2$ of 1.0, extracellular to internal sink diffusivity ratio $\varepsilon = D/D_{\text{int}}$ of 0.1 and sink Thiele Modulus $\phi_T = a_1 \sqrt{k_{\text{int}}/D_{\text{int}}}$ of 0.1, 0.5, 1, 5, 10 and 5. The lower solid lines are the exact reaction probability, equation (5.41), for an internally reactive sink, and the dashed lines refers to the approximate, sink surface reaction probability $P_{\text{sur}}$, equation (5.45), with the corresponding effective inverse dimensionless reaction rate coefficient $\lambda_{\text{eff}}^{-1} = \varepsilon / (\phi_T \coth \phi_T - 1))$ of 30, 1.22, 0.320, 0.025, 0.011, and 0.002.
Figure 5.3: Reaction probability $P_{\text{int}}$ for a first order penetrable sink and a zeroth order source versus the dimensionless center to center distance $d/(a_1 + a_2)$ between the source and sink, for a sink to source radius ratio $\gamma (= a_1/a_2) = 10$, extracellular to internal sink diffusivity ratio $\varepsilon (= D/D_{\text{int}})$ of 0.1 and sink Thiele Modulus $\phi_T (= a_1 \sqrt{k_{\text{int}}/D_{\text{int}}})$ of 0.1, 0.5, 1, 5, 10 and 50. The lower solid lines are the exact reaction probability, equation (5.41), for an internally reactive sink, and the dashed lines refers to the approximate, sink surface reaction probability $P_{\text{sur}}$, equation (5.45), with an effective inverse dimensionless reaction rate coefficient $\lambda_{\text{eff}}^{-1} (= \varepsilon / (\phi_T \coth \phi_T - 1))$ of 30, 1.22, 0.320, 0.025, 0.011 and 0.002.
Figure 5.4: Reaction probability $P_{\text{int}}$ for a first order penetrable sink and a zeroth order source versus the dimensionless center to center distance $d/(a_1 + a_2)$ between the source and sink, for a sink to source radius ratio $\gamma (=a_1/a_2)$ of 0.10, extracellular to internal sink diffusivity ratio $\varepsilon (=D/D_{\text{int}})$ of 1.0 and sink Thiele Modulus $\phi_r (=a_1 \sqrt{k_{\text{int}}/D_{\text{int}}})$ of 0.5, 1, 5, 10 and 50. The lower solid lines are the exact reaction probability, equation (5.41), for an internally reactive sink, and the dashed lines refers to the approximate, sink surface reaction probability $P_{\text{surr}}$, equation (5.45), with an effective inverse dimensionless reaction rate coefficient $\lambda_{\text{eff}}^{-1} (=\varepsilon/ (\phi_r \coth \phi_r - 1))$ of 12.2, 3.19, 0.25, 0.111 and 0.0204.
Figure 5.5: Reaction probability $P_{\text{int}}$ for a first order penetrable sink and a zeroth order source versus the dimensionless center to center distance $d/(a_1 + a_2)$ between the source and sink, for a sink to source radius ratio $\gamma (= a_1 / a_2)$ of 1, extracellular to internal sink diffusivity ratio $\varepsilon (= D/D_{\text{int}})$ of 1 and sink Thiele Modulus $\phi_T (= a_1 \sqrt{k_{\text{int}} / D_{\text{int}}})$ of 0.5, 1, 5, 10 and 50. The lower solid lines are the exact reaction probability, equation (5.41), for an internally reactive sink, and the dashed lines refers to the approximate, sink surface reaction probability $P_{\text{sur}}$, equation (5.45), with an effective inverse dimensionless reaction rate coefficient $\lambda_{\text{eff}}^{-1} (= \varepsilon / (\phi_T \coth \phi_T - 1))$ of 12.2, 3.19, 0.25, 0.111 and 0.0204.
Figure 5.6: Reaction probability $P_{\text{int}}$ for a first order penetrable sink and a zeroth order source versus the dimensionless center to center distance $d/(a_1 + a_2)$ between the source and sink, for a sink to source radius ratio $\gamma (= a_1/a_2)$ of 10, extracellular to internal sink diffusivity ratio $\varepsilon (= D/D_{\text{int}})$ of 1.0 and sink Thiele Modulus $\phi_T (= a_1 \sqrt{k_{\text{int}} / D_{\text{int}}})$ of 0.5, 1, 5, 10 and 50. The lower solid lines are the exact reaction probability, equation (5.41), for an internally reactive sink, and the dashed lines refers to the approximate, sink surface reaction probability $P_{\text{sur}}$, equation (5.45), with an effective inverse dimensionless reaction rate coefficient $\lambda_{\text{eff}}^{-1} (= \varepsilon / (\phi_T \coth \phi_T - 1))$ of 12.2, 3.19, 0.25, 0.111 and 0.0204.
Figure 5.7: Reaction probability $P_{\text{int}}$ for a first order penetrable sink and a zeroth order source versus the dimensionless center to center distance $d/(a_1 + a_2)$ between the source and sink, for a sink to source radius ratio $\gamma (= a_1/a_2)$ of 0.10, extracellular to internal sink diffusivity ratio $\varepsilon (= D/D_{\text{int}})$ of 10 and sink Thiele Modulus $\phi_T (= a_1 \sqrt{k_{\text{int}}/D_{\text{int}}})$ of 0.5, 1, 5, 10 and 5. The lower solid lines are the exact reaction probability, equation (5.41), for an internally reactive sink, and the dashed lines refers to the approximate, sink surface reaction probability $P_{\text{sur}}$, equation (5.45), with an effective inverse dimensionless reaction rate coefficient $\lambda_{\text{eff}}^{-1} (= \varepsilon / \phi_T \coth \phi_T - 1)$ of 122, 31.9, 2.50, 1.11 and 0.204.
Figure 5.8: Reaction probability $P_{\text{int}}$ for a first order penetrable sink and a zeroth order source versus the dimensionless center to center distance $d/(a_1 + a_2)$ between the source and sink, for a sink to source radius ratio $\gamma(=a_1/a_2)$ of 1.0, extracellular to internal sink diffusivity ratio $\epsilon(=D/D_{\text{int}})$ of 10 and sink Thiele Modulus $\phi_T(=a_1 \sqrt{k_{\text{int}}/D_{\text{int}}})$ of 0.5, 1, 5, 10 and 50. The lower solid lines are the exact reaction probability, equation (5.41), for an internally reactive sink, and the dashed lines refers to the approximate, sink surface reaction probability $P_{\text{sur}}$, equation (5.45), with an effective inverse dimensionless reaction rate coefficient $\lambda_{\text{eff}}^{-1}(=\epsilon/(\phi_T \coth \phi_T - 1))$ of 122, 31.9, 2.50, 1.11 and 0.204.
Figure 5.9: Reaction probability $P_{\text{int}}$ for a first order penetrable sink and a zeroth order source versus the dimensionless center to center distance $d/(a_1 + a_2)$ between the source and sink, for a sink to source radius ratio $\gamma (= a_1 / a_2)$ of 10, extracellular to internal sink diffusivity ratio $\varepsilon (= D/D_{\text{int}})$ of 10 and sink Thiele Modulus $\phi_t (= a_1 \sqrt{k_{\text{int}} / D_{\text{int}}})$ of 0.5, 1, 5, 10 and 50. The lower solid lines are the exact reaction probability, equation (5.41), for an internally reactive sink, and the dashed lines refers to the approximate, sink surface reaction probability $P_{\text{sur}}$, equation (5.45), with an effective inverse dimensionless reaction rate coefficient $\lambda_{\text{eff}}^{-1} (= \varepsilon / (\phi_t \coth \phi_t - 1))$ of 122, 31.9, 2.50, 1.11 and 0.204.
Figure 5.10: Reaction probability $P_{\text{int}}$ for a first order penetrable sink and a zeroth order source versus the dimensionless center to center distance $d/(a_1 + a_2)$ between the source and sink, for a sink to source radius ratio $\gamma(=a_1/a_2)$ of 1.0, extracellular to internal sink diffusivity ratio $\varepsilon(=D/D_{\text{int}})$ of 0.1 and sink Thiele Modulus $\phi_r(=a_1\sqrt{k_{\text{int}}/D_{\text{int}}})$ of 0.01. The lower solid line is the exact reaction probability, equation (5.41), for an internally reactive sink, and the dashed line refers to the approximate, sink surface reaction probability $P_{\text{sur}}$, equation (5.45), with an effective inverse dimensionless reaction rate coefficient $\lambda_{\text{eff}}^{-1}(=\varepsilon / (\phi_r \coth \phi_r - 1))$ of 3000.
TABLE 5.1

PERCENT ERROR FOR THE EXACT AND APPROXIMATE SOLUTION

<table>
<thead>
<tr>
<th>$\phi_T$</th>
<th>$\epsilon = 0.5$</th>
<th>$\epsilon = 0.1$</th>
<th>$\epsilon = 0.05$</th>
<th>$\epsilon = 0.01$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-4.48</td>
<td>-3.98</td>
<td>-2.94</td>
<td>-0.92</td>
</tr>
<tr>
<td>0.3</td>
<td>-5.06</td>
<td>-5.69</td>
<td>-4.92</td>
<td>-2.16</td>
</tr>
<tr>
<td>0.1</td>
<td>-5.39</td>
<td>-7.19</td>
<td>-7.35</td>
<td>-6.22</td>
</tr>
<tr>
<td>0.05</td>
<td>-5.43</td>
<td>-7.38</td>
<td>-7.71</td>
<td>-7.59</td>
</tr>
<tr>
<td>0.01</td>
<td>-5.43</td>
<td>-7.44</td>
<td>-7.83</td>
<td>-8.16</td>
</tr>
</tbody>
</table>

The results show the percent error between the penetrable internally reactive sink exact forms (5.41) and the impenetrable externally reactive sink approximation, equation (5.45) with $\lambda_{1\text{eff}}$ of equation (5.44) for the source-penetrable sink problem. For the cases considered two equisized spheres, $\gamma=1$, are in contact, $d/(a_1+a_2) = 1$, for the Thiele modulus $\phi_T \leq 0.5$ and diffusivity ratios $\epsilon \leq 0.5$.  

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Equation (2.19) is used to determine the reaction probability and the concentration around sphere 1. This equation generates the elements of the symmetric matrix $F_{nm}$ as the sum of an infinite power series. It must be calculated for every $n$, $m$, and $\gamma d_1$, this is a very rigorous process, fortunately, it is possible to develop an analytical expression for $F$ independent of the indices of the sum.

Recall

$$F_{nm} = \sum_{j=0}^{\infty} x^j \binom{j+n}{n} \binom{j+m}{m} \left(\frac{j}{j+1}\right), \quad \text{for } x = (\gamma d_1)^{-2}, \quad (2.17)$$

with the substitution

$$\frac{j}{j+1} = 1 - \frac{1}{j+1}. \quad (A.1)$$

The infinite series is expanded and successive differentiation yields an analytical solution for all $F$ independent of the sums indices.
\[ F_{nm} = \frac{x}{m!} \frac{d}{dx} \left\{ \frac{1}{x} \left[ x^n (1-x)^{(n+1)} \right] \right\} \quad \text{for} \quad x = (\gamma d_1)^{-2}. \quad \text{(A.2)} \]

There are two special cases either \( n \) or \( m \) is zero this yields \( I_{0n} \) and \( I_{n0} \)

\[ F_{n0} = \sum_{j=0}^{\infty} x^j \left( \frac{j+n}{n} \right) \left( \frac{j}{j+1} \right) \quad \text{for} \quad x = (\gamma d_1)^{-2} \quad \text{(A.3)} \]

\[ = \quad (1-x)^{-(n+1)} - \frac{1}{nx} \left[ (1-x)^{-n} - 1 \right] \quad \text{for} \quad x = (\gamma d_1)^{-2}. \quad \text{(A.4)} \]

or both \( n=m=0 \)

\[ F_{00} = \sum_{j=0}^{\infty} x^j \left( \frac{j}{j+1} \right) \quad \text{for} \quad x = (\gamma d_1)^{-2} \quad \text{(A.5)} \]

\[ = \quad (1-x)^{-1} + \frac{1}{x} \ln(1-x) \quad \text{for} \quad x = (\gamma d_1)^{-2}. \quad \text{(A.6)} \]
APPENDIX B

TWO SPHERES IN BISPHERICAL COORDINATES

B.1 Bispherical Coordinates

The bispherical coordinates system \((\mu, \eta, \phi)\) is obtained by rotating bipolar axes about the line between the two poles. From Morse and Feshbach, (1953) the coordinates are related to the rectangular coordinate system \((x,y,z)\) as

\[
\begin{align*}
  z &= \frac{f \sinh \mu}{\cosh \mu - \cos \eta}; \\
  x &= \frac{f \sin \eta \cos \phi}{\cosh \mu - \cos \eta}; \\
  y &= \frac{f \sin \eta \sin \phi}{\cosh \mu - \cos \eta}; \\
  r &= f \sqrt{\frac{\cosh \mu + \cos \eta}{\cosh \mu - \cos \eta}}; \\
  h_\mu = h_\eta &= \frac{f}{\cosh \mu - \cos \eta}; \\
  h_\phi &= \frac{f \sin \eta}{\cosh \mu - \cos \eta};
\end{align*}
\] (B.1)
\[
\n\nabla^2 \psi = \frac{1}{h_\mu^2} \left[ \frac{\partial}{\partial \mu} \left( h_\mu \frac{\partial \psi}{\partial \mu} \right) + \frac{1}{\sin \eta} \frac{\partial}{\partial \eta} \left( h_\mu \sin \eta \frac{\partial \psi}{\partial \eta} \right) + \frac{h_\mu}{\sin^2 \eta} \frac{\partial^2 \psi}{\partial \phi^2} \right] \tag{B.2}
\]

where \( f \) is the interfocal distance and the coordinates \( \mu \) goes from \(-\infty\) to \( \infty \), \( \eta \) goes from 0 to \( \pi \) and \( \phi \) goes from 0 to \( 2\pi \). The surface \( \mu = \mu_i \) is a sphere of radius \( f |\csc h \mu_i| \) with center at \( z_i = f \coth \mu_i, \ x = y = 0 \). The two poles are at \( \mu = \pm \infty \) \( (z = \pm f, x = y = 0) \), and the central plane \( z = 0 \) is the surface \( \mu = 0 \) (Morse and Feshbach, 1953). Therefore, the center to center distance \( d \) between sphere 1 of radius \( a_i \) centered at \( z_1, \ x = y = 0 \) and sphere 2 of radius \( a_2 \) with center at \( -z_2, \ x = y = 0 \) is \( d = (z_1 - z_2) \). The interfocal distance \( f \), is described implicitly through the dimensionless center-to-center separation distance (Zoia, 1998)

\[

\left( \frac{f}{a_i} \right)^2 = 1 + \frac{\sqrt{\frac{(f/a_i)^2}{2}} + \frac{(f/a_i)^2}{\gamma}} + \frac{(f/a_i)^2}{2}, \text{ for } d_i = \frac{d}{a_i} \text{ and } \gamma = \frac{a_i}{a_2}. \tag{B.3}
\]

The surface of \( \eta = \eta_0 \) is a fourth order surface formed by rotating about the \( z \) axis that part of the circle, in the \( x-z \) plane, of radius \( f \csc \eta_0 \) with center at \( z = 0 \), \( x = f \cot \eta_0 \), which is in the positive part of the \( x-z \) plane. All these surfaces, of constant \( \eta \), go through the poles. Those for \( \eta < \pi/2 \) have “dimples” at each pole; those for \( \eta > \pi/2 \) have sharp points there. The surface \( \eta = 0 \) is the \( z \) axis for \( |z| > f \) plus the sphere at infinity, the surface \( \eta = \pi/2 \) is the sphere of radius \( f \)
with center at the origin, and the surface \( \eta = \pi \) is the \( z \) axis for \(|z| < f\) (Morse and Feshbach, 1953) (Figure B.1).

The Laplace equation separates only by setting \( \psi = \sqrt{\cosh \mu - \cos \eta X} \).

The equation \( \nabla^2 \psi = 0 \) then transforms to

\[
\frac{\partial^2 X}{\partial \mu^2} + \frac{1}{\sin \eta} \frac{\partial}{\partial \eta} \left( \sin \eta \frac{\partial X}{\partial \eta} \right) + \frac{1}{\sin^2 \eta} \frac{\partial^2 X}{\partial \phi^2} - \frac{1}{4} \frac{\partial X}{\partial \eta} = 0 \tag{B.4}
\]

which separates into the three equations, \( X = \Phi(\phi)M(\mu)H(\eta) \),

\[
\frac{d^2 \Phi}{d^2 \phi} = -m^2 \Phi, \tag{B.5}
\]

\[
\frac{d^2 M}{d^2 \mu} = \left( n + \frac{1}{2} \right)^2 M, \tag{B.6}
\]

\[
\frac{1}{\sin \eta} \frac{d}{d\eta} \left( \sin \eta \frac{dH}{d\eta} \right) - \frac{m^2 H}{\sin^2 \eta} = -n(n+1)H. \tag{B.7}
\]

In order that \( \Phi \) be continuous as \( \phi \) goes from 0 to \( 2\pi \), \( m \) must be zero or an integer, and in order that \( H \) be finite both at \( \eta = 0 \) and \( \eta = \pi \), \( n \) must be an integer equal to or larger than \( m \). Therefore, typical solutions for the original Laplace equation are
\[
\sqrt{\cosh \mu - \cos \eta} \exp\left[ \pm \mu (n + \frac{1}{2}) \right] P^n_m (\cos \eta) \frac{\cos}{\sin} (m \phi).
\]  
(B.8)

The factor \(\sqrt{\cosh \mu - \cos \eta}\) causes some trouble when the boundary conditions are fixed. In other words it is necessary to compute the expansion of \((\cosh \mu - \cos \eta)^{-1/2}\) in terms of zonal harmonics of \(\cos \eta\). This can be done by taking the expansion of \([1 + \exp(-2 \mu) - 2 \exp(-\mu) \cos \eta]^{-1/2}\), and finally,

\[
\frac{1}{\sqrt{\cosh \mu - \cos \eta}} = \sqrt{2} \sum_{n=0}^{\infty} \exp\left[ - \left( n + \frac{1}{2} \right) \mu \right] P^n_m (\cos \eta).
\]  
(B.9)

**B.2 Concentration Profile**

The exact solution for the concentration in the bulk phase for two fixed spheres of radius \(a_1\) and \(a_2\), and arbitrary center to center distance \(d\) with surface reaction occurring at the sphere bulk phase interface is presented. The explicit problem to be solved is the Laplace equation

\[
D \nabla^2 c(r) = 0 \quad (r \text{ in the inert bulk phase}),
\]  
(B.10)

where \(c(r)\) is the reactant concentration at any point \(r\) outside of either sphere, with the steady state boundary condition that the concentration \(c\) is a constant \(c_0\) at large distances from the reacting pair.
\[ c(r) = c_0 \quad (r \text{ far from either sphere}), \quad (B.11) \]

and the reactant concentration on the external surface of either reactive sphere

\[ c(r) = c_1, \ r = a_1 \quad c(r) = c_2, \ r = a_2 \]

\[ \mu_1 = \sinh^{-1}\left(\frac{f}{a_1}\right), \ 0 < \mu_1, \ r_1 = a_1 \Rightarrow \mu = \mu_1 \]

\[ (B.12) \]

\[ \mu_2 = \sinh^{-1}\left(\frac{f}{a_2}\right), \ 0 < \mu_2, \ r_2 = a_2 \Rightarrow \mu = -\mu_2. \]

After applying the continuity and finiteness condition \((m = 0)\) and rotational symmetry with respect to the \(z\) axis to equation \((B.8)\), the general solution for this problem can be written as

\[ c(r) = c_0 + c_0 \sqrt{\cosh \mu - \cos \eta} \sum_{n=0}^{\infty} \left( A_n e^{(n+1/2)\mu} + B_n e^{-(n+1/2)\mu} \right) P_n(\cos \eta) \quad (B.13) \]

Where \(A_n\) and \(B_n\) are coefficients determined by imposing the boundary conditions \((B.11)\) and \((B.12)\), and by use of \((B.9)\), we have
\[
0 = \frac{c_0 - c_i}{c_0} \sqrt{2} \sum_{n=0}^{\infty} \left( \exp\left[-(n+1/2) |\mu_i|\right] P_n(\cos \eta) + \sum_{n=0}^{\infty} \left( A_n e^{(n+1/2)\mu_i} + B_n e^{-(n+1/2)\mu_i} \right) P_n(\cos \eta) \right),
\]

\[i = 1, 2,\]

where the fixed bispherical coordinate values \( \mu_1 (\mu_1 > 0) \) and \( -\mu_2 (\mu_2 < 0) \) locate, the surfaces of sphere 1 and 2, respectively. Using the orthogonality properties of the Legendre \( P_n \) polynomials \( \int_{-1}^{1} P_n(x) P_j(x) dx = \frac{2 \delta_{nj}}{1 + 2n} \) and after some algebraic manipulations, the concentration is written as

\[
c = c_0 - \sqrt{\cosh \mu - \cos \eta} \sum_{j=0}^{\infty} \left\{ (c_1 - c_0) W_j(\mu_1) \sinh \left[ (\mu + \mu_2) \left( j + \frac{1}{2} \right) \right] + (c_2 - c_0) W_j(\mu_2) \sinh \left[ (\mu_1 - \mu) \left( j + \frac{1}{2} \right) \right] \right\} \times \sinh \left[ (\mu_1 + \mu_2) \left( j + \frac{1}{2} \right) \right] P_j(\cos \eta),
\]

and

\[
W_j(\mu) = \sqrt{2} \exp \left\{ -\mu \left( j + \frac{1}{2} \right) \right\}. \quad (B.16)
\]
B.3 Reaction Rate

The reaction rate for the diffusion-limited sink, sphere 1 with \( c_1 = 0 \), is determined directly from (B.13), (B.15) and (B.16) by obtaining the incoming flux by radial differentiation at the active surface of sphere 1, then integrating the flux across the surface of sphere 1. Consider Equation (B.1) and Figure (B.2), then

\[
w = \frac{f\left(1 - \cos^2 \eta\right)^{1/2}}{\cosh \mu - \cos \eta}, \quad \text{(B.17)}
\]

and

\[
z = \frac{f\left(\cosh^2 \mu - 1\right)^{1/2}}{\cosh \mu - \cos \eta}, \quad \text{(B.18)}
\]

Now consider a first order perturbation to the \( \mu = \mu_0 \) surface in the direction of the radius drawn from the center of the sphere (constant angle \( \theta \)). The point \( (\mu_0, \eta_0) \) or \( (z_0, w_0, \theta) \) on the surface of sphere 1, will move to \( \mu = \mu_0 + \delta \mu_0, \eta = \eta_0 + \delta \eta_0 \). By derivation of \( w \) and \( z \) at constant angle \( \theta \)

\[
dw_\theta = f \frac{\cos \eta \cosh h \mu - 1}{\left(\cosh \mu - \cos \eta\right)^2} \delta \eta_\theta - f \frac{\sin \eta \sinh \mu}{\left(\cosh \mu - \cos \eta\right)^2} \delta \mu_\theta, \quad \text{(B.19)}
\]
and

\[ dz_\theta = f \sin \eta \sinh \mu - 1 \frac{\delta \eta_0}{(\cosh \mu - \cos \eta)^2} \delta \theta - f \frac{1 - \cos \eta \cosh \mu}{(\cosh \mu - \cos \eta)^2} \delta \mu_\theta. \quad \text{(B.20)} \]

Also,

\[ \frac{dw_\theta}{dz_\theta} = \tan \theta_0 = \frac{u_0}{z_0 - z_c} = \frac{\sin \eta_0 \sinh \mu_0}{\cos \eta_0 \cosh \mu_0 - 1}, \quad \text{(B.21)} \]

Where \( z_c \) is the Cartesian coordinate of the center of sphere 1. Equation (B.19) – (B.21) are consistent only if \( \delta \eta_\theta = 0 \), and therefore, if \( \psi = \psi(\mu, \eta) \),

\[ \frac{\partial \psi}{\partial \theta} = \frac{\partial \psi}{\partial \eta_\mu} d\eta_\theta + \frac{\partial \psi}{\partial \mu_\eta} d\mu_\theta = \frac{\partial \psi}{\partial \mu_\eta} d\mu_\theta, \quad \text{(B.22)} \]

where \( d\mu_\theta = dr_\theta \|h_\mu\| \), and \( r \) is the radial coordinate (Figure C.2).

The reaction rate, \( R_1 \), on the surface of sphere 1 in the presence of sphere 2 is generated by integrating the incoming flux to the surface of sphere 1 (Figure C.2).

\[ R_1 = 2\pi a_1^2 D \left[ \frac{\partial c}{\partial r} \right] \sin \theta \ d\theta, \quad r = a_1 \quad \text{(B.23)} \]

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where \( c \) is the concentration of the reactant in the inert matrix. But \( \sin \theta \, d\theta \) can be replaced with \(-d(\cos \theta)\) and recognizing that on the surface of the sphere \( 1 \) where \( \mu = \mu_1 \), the \( z \) expression in equation (B.1) can be transformed to an expression in \( \theta \), \( \mu_1 \) and \( \eta \)

\[
d(\cos \theta) = \frac{\sinh^2 \mu_1}{(\cosh \mu_1 - \cos \eta)^2} d(\cos \eta), \quad (B.24)
\]

and, therefore, by substituting the radial partial derivative for the equivalent partial derivative of \( c \) with respect to \( \mu \), at constant angle \( \theta \), along with (B.24) into (B.23),

\[
R_1 = 2\pi a^2 \int_0^\pi \left[ -\frac{1}{h_\mu} \frac{\partial c}{\partial \mu} \right] \frac{\sinh^2 \mu_1}{(\cosh \mu_1 - \cos \eta)^2} d(\cos \eta), \quad \mu = \mu_1 \quad (B.25)
\]

where
\[
\frac{\partial c}{\partial \mu} = -\frac{1}{2} \sinh \mu_1 (\cosh \mu_1 - \cos \eta)^{-1/2} \sum_{j=0}^{\infty} P_j (\cos \eta) W_j (\mu_1) \\
- (\cosh \mu_1 - \cos \eta)^{1/2} \sum_{j=0}^{\infty} \left( (c_1 - c_0) \left( j + \frac{1}{2} \right) W_j (\mu_1) \times \\
\cosh \left( \mu_1 + \mu_2 \right) \left( j + \frac{1}{2} \right) \right) - (c_2 - c_0) \left( j + \frac{1}{2} \right) W_j (\mu_2) \right), \quad \text{(B.26)} \\
\times \sinh \left( \mu_1 + \mu_2 \right) \left( j + \frac{1}{2} \right)^{-1} P_j (\cos \eta) \\
\mu = \mu_1 .
\]

Substituting equation (B.26) into equation (B.25), and using the expression for 
\((\cosh \mu_1 - \cos \eta)^{-1/2}\) and the Legendre polynomials (equation B.9)

\[
(\cosh \mu - \cos \eta)^{-1/2} = \sqrt{2} \exp \left( -\frac{\mu_1}{2} \right) \sum_{m=0}^{\infty} \exp(-\mu_1 m) P_m (\cos \eta) , \quad \text{(B.9)}
\]

and the relations

\[
(\cosh \mu - \cos \eta)^{-3/2} = \exp \left( -\frac{3\mu_1}{2} \right) 2^{3/2} \sum_{m=0}^{\infty} \exp[-\mu_1 (m - 1)] \frac{dP_m (\cos \eta)}{d(\cos \eta)} , \quad \text{(B.27)}
\]

\[
(1 - \cos^2 \eta) \frac{dP_m}{d \cos \eta} = (m + 1) \cos \eta \ P_m - (m + 1) P_{m+1} , \quad \text{(B.28)}
\]

\[
(2m + 1) \cos \eta \ P_m = (m + 1)P_{m+1} - mP_{m-1} , \quad \text{(B.29)}
\]
Substitution of (B.26) into (B.25) with the relations (B.9) and (B.27)-(B.31) the integrand in reaction rate expression, becomes

\[
\frac{\sinh^2 \mu_1}{a_1} \sqrt{2} \exp(-3\mu_1/2) \sum_{j=0}^\infty P_j(\cos \eta) W_j(\mu_1) \times \\
\left[ \sum_{m=0}^\infty \exp[-\mu_1(m-1)] \sum_{i=0}^{m-2i+1} (2m-4i-1) P_{m-2i-1}(\cos \eta) \right]
\]

\[
+ \quad \frac{\sinh \mu_1}{a_1} \sqrt{2} \exp(-\mu_1/2) \sum_{m=0}^\infty \exp(-\mu_1m) P_m(\cos \eta) \times \\
\left\{ \sum_{j=0}^\infty \left\{ (j+\frac{1}{2}) W_j(\mu_1) \times \cosh \left[ (\mu_1+c_0) \left( j+\frac{1}{2} \right) \right] \right\} \\
- \left( c_2 - c_0 \right) \left( j+\frac{1}{2} \right) W_j(\mu_2), \\
\times \sinh \left[ (\mu_1+c_0) \left( j+\frac{1}{2} \right) \right]^{-1} P_j(\cos \eta) \right\}.
\]

The integration of the products of summations in equation (B.31), by using the orthogonality condition of the Legendre Polynomials
\[
\int_{-1}^{1} P_n(z)P_m(z)dz = \frac{2\delta_{nm}}{1+2n},
\]
\[\text{(B.32)}\]

Integrating the first term is done by considering two separate cases,

- when \( j = 2n+1, \ n = 0,1,2,..., \) is odd and \( m = 2k, \ k = 0,1,2,..., \) is even
  (the \( m \) sum begins at \( j+1 \), or \( 2n+2 \) and the \( i \) sum goes from \( P_{m-1} \) to \( P_1 \)),
- and when \( j = 2n, \ n = 0,1,2,..., \) is even and \( m = 2k+1, \ k = 0,1,2,..., \) is odd
  (the \( m \) sum begins at \( 2n+1 \), and the \( i \) sum goes from \( P_{m-1} \) up to \( P_0 \)).

Finally the last term is directly integrated using the orthogonality condition of Legendre polynomials. After some rearranging the resulting reaction rate of the diffusion-limited sphere 1 (\( c_1 = 0 \)) in the presence of sphere 2 is

\[
R_1 = \frac{1}{2} \left\{ 1 + \sinh \mu_1 \sum_{j=0}^{\infty} W_j(\mu_1) \times \right. \\
\left. \begin{cases} 
W_j(\mu_1) \cosh \left[ (\mu_1 + \mu_2) \left( j + \frac{1}{2} \right) + \frac{c_2 - c_0}{c_0} W_j(\mu_2) \right] \\
\sinh \left[ (\mu_1 + \mu_2) \left( j + \frac{1}{2} \right) \right]
\end{cases} \right\},
\]
\[\text{(B.33)}\]
The rate is scaled by the Smoluchowski diffusion-limited single sphere solution 

\((4\pi a, Dc_0)\).
Figure B.1: The bispherical coordinates ($\mu, \eta, \phi$) and their relationships to the Cartesian coordinates ($x,y,z$) are discussed in Morse and Feshbach (1953). Both sphere centers lie on the $z$-axis with the sphere 1 center on the positive side at $z_1$ and sphere 2 center on the negative side at $z_2$. Lines of constant $\eta$ pass through the focal points, when $\eta < \pi / 2$ the surfaces look like lemons and $\eta > \pi / 2$ are shaped like apples. The fixed bispherical coordinate values $\mu_1 (0 < \mu_1)$ and $-\mu_2 (0 > -\mu_2)$ locate, respectively, the sphere 1 and sphere 2 surfaces (Zoia, 1998).
Figure B.2: The rate $R_1$ equation for sphere 1 in the presence of sphere 2 is generated directly from the integration of the flux in the direction of sphere 1, where the integral is evaluated at the surface of the sphere (Zoia, 1998).
REFERENCES


