

# DETERMINING THE BEHAVIOR OF THE ROTATING DISK ELECTRODE SYSTEM

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The *Convection-Diffusion Equation* is a partial differential equation that is used to study the effect of convective and diffusive processes on incompressible fluids. Among other things, it can be used to analyze various types of batteries, including battery setups where the chemical solutions that power the battery are in motion. Between these battery types, one that is commonly used is the *Rotating Disk Electrode (RDE) system*, since its simple geometry makes mathematical analysis of this battery doable. Solutions to the Convection-Diffusion Equation as applied to the RDE system have been presented before, but there are some known issues about them. Therefore, the purpose of this paper is to present additional analysis of the Convection-Diffusion equation as applied to the RDE system and of one of its already published solutions.

## 1. MOTIVATION AND GENERAL BACKGROUND

The main goal behind analyzing the RDE system is to gain new insight into how is a battery's performance affected when it is submitted to non-steady state conditions. This in turn can be useful to develop more efficient batteries. Since understanding the RDE system requires a general understanding of batteries in general, a description of a very basic battery setup known as an *electrochemical cell* has been included. Fig.1 (next page) shows a scheme of the basic electrochemical cell.

**1.1. The Electrochemical Cell.** The basic electrochemical cell works as follows: Two containers are each filled with a *chemical solution*, that is, a homogeneous mixtures of two or more substances (pure elements or molecules). One of the chemical solutions must contain a substance with significantly different *standard redox potentials* (a measure of the relative ability of a chemical substance to give or take electrons from other substances). The higher the standard redox potential of a substance, the more likely that it will accept electrons from other chemicals, and the lower it is, the more likely that it will give up electrons to other chemicals. Optimally, one of the containers will have a chemical solution containing a substance with a high standard redox potential, and the other container will have one with a low standard redox potential, encouraging the transfer of electrons between the two solutions. Since the two substances will eventually react, they are called the *reactants*. This type of reaction is called an *oxidation-reduction (redox) reaction*, recognized by the transfer of electrons between the reactants. Here, the reactant with the lower standard

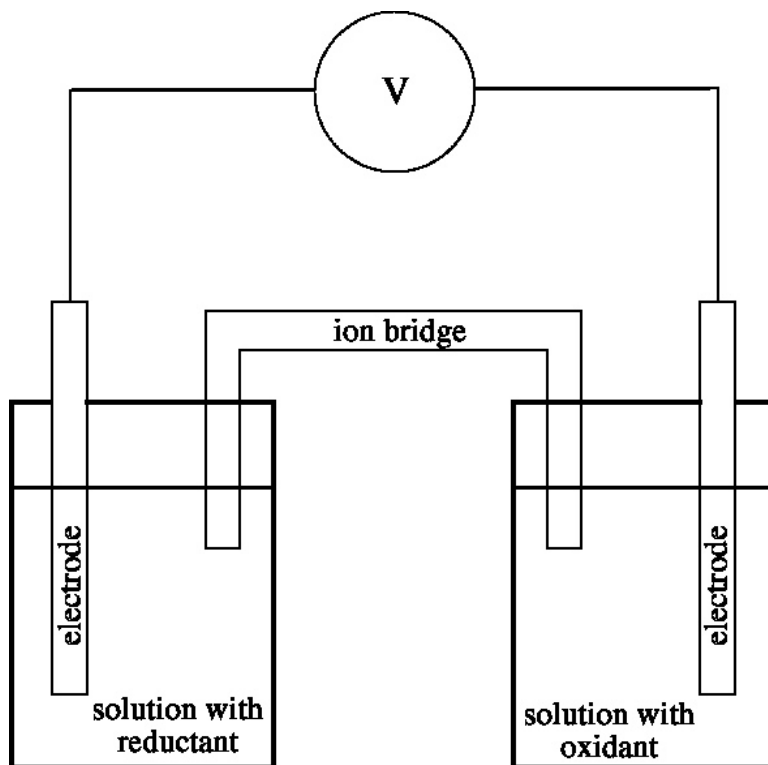


FIGURE 1. The basic setup of an electrochemical cell

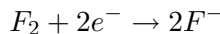
redox potential will donate some of its electrons to the reactant with the higher one.

The chemicals in the solution that do not react are called the *solvents*. Usually, only a small fraction of the chemical solutions will consist of substances that may act as reactants. Therefore, we can think of each chemical solution as composed of a liquid solvent that contains a relatively small number of molecules flowing around it, all of which may react in a redox reaction. The reactant that donates the electrons is called the *reductant*, while the reactant that accepts the electrons is called the *oxidant*.

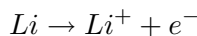
As an illustration, suppose that we want to make an electrochemical cell, using fluoride ( $F_2$ ) and lithium (Li) as the reactants and water ( $H_2O$ ) as the solvent for both of the reactants. To set up the electrochemical cell, we would first have to mix fluoride and water in one of the containers and lithium and water in the other.

Fluoride, being the element with the highest standard redox potential (2.87 [V]), is the strongest oxidant and is therefore very likely to gain electrons from any other reactant. Since each fluorine atom (F) of fluoride ( $F_2$ ) is only one electron away from its most stable

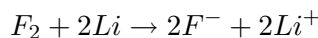
state, each fluorine atom will accept one electron ( $e^-$ ) whenever these are available and each fluoride molecule will undergo the following reaction:



Lithium, on the other hand, is the element with the lowest standard redox potential (-3.04 [V]), and is therefore the strongest reductant. Since lithium becomes more stable by losing one of its electrons, the chemical reaction is:



The larger the difference between the reactants' standard redox potentials, the larger the force driving the transfer of electrons. Not surprisingly, fluoride and lithium will react strongly if in contact. In this case, the chemical formula is:



Note that the solvent (water) doesn't appear in the formula. Since it is already in a stable state, water doesn't need to accept or give up electrons, and is therefore neither an oxidant nor a reductant. The only purpose of water is to allow the fluoride and lithium atoms to flow to a position where these may react.

In order for the reaction to take place, it is not necessary to mix the two solutions. Instead, a circuit connecting the two containers is constructed, allowing electrons to be transmitted between the reactants. This circuit is composed of two *electrodes* (conducting metals that allow the electrons to move from one reactant into the other), each submerged in one of the chemical solutions and connected to each other with a conducting wire. To close the circuit, an *ion bridge* is also placed between the two solutions (an ion bridge conducts ions but not electrons, allowing the newly formed ions, to move between the containers). This conserves charge neutrality between the two solutions, and since the electrons cannot travel through the ion bridge, these are forced to transfer by passing through the electrodes.

The *current* of the circuit is a measure of the amount of charge (electrons) that moves from one reactant to the other per unit of time. This current can be easily measured by incorporating a voltmeter between the electrodes and the wires (see Fig.1). Optionally, the chemical cell can be converted into a battery by replacing the voltmeter by an electronic device, where the electrode in contact with the oxidant becomes the positive terminal of the battery, and the electrode in contact with the reactant becomes the negative terminal of the battery.

**1.2. The RDE system.** The electrochemical cell is one of the simplest battery setups and is therefore relatively easy to analyze. However, in order to study some electrochemical processes, it is necessary to rely on other designs. A tool that has been used for years with this purpose is the RDE system. The arrangement of this battery is very similar to that of an electrochemical cell, the biggest difference being that one of the electrodes is set up to rotate at a constant angular velocity. When analyzing the RDE system, it is enough to

study what happens to the chemical solution where the rotating electrode is placed. Other than determining what the driving force between the reactants will be, what happens to the chemical solution in one container doesn't affect what happens to the chemical solution in the other container. For this reason, when talking about 'the solvent', or 'the reactant', we are referring to the solvent and reactant where the RDE is operating.

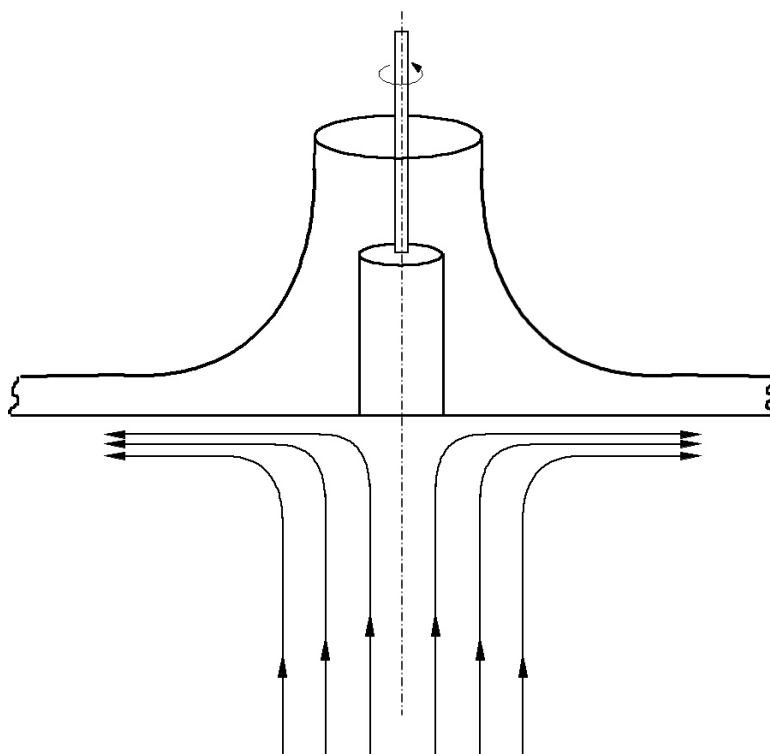


FIGURE 2. The ideal rotating disk electrode

For mathematical convenience, the container and the chemical solution inside are considered to extend infinitely below the RDE's surface and infinitely radially away from its axis of rotation. Since the behavior of the system is essentially the same at distances close to the RDE regardless of the container's volume (provided that the reactant's concentration is the same), and since the behavior of the reactant close to the RDE completely determines what the current throughout the circuit is (since all electrons must pass through the electrode), the assumption doesn't affect the validity of the analysis.

Another assumption necessary for the analysis is that the surface of the rotating disk in contact with the chemical solution must also be infinitely large (which will greatly simplify the analysis). In practice, the assumption is allowable as long as the size of the RDE

is not too small in comparison to the size of the container.

The RDE system is a valuable experimental tool because it allows us to study the effects that *convection* (the transport of the reactants in the solution due to the solvent's flow) and *diffusion* (the transport of the reactants in the solution due to the non-uniform concentration of the reactants as these are used up) have on chemical reactions. This in turn may be helpful in the design of new types of batteries and the understanding of other physical phenomena.

## 2. THE CONVECTION-DIFFUSION EQUATION AND THE RDE SYSTEM

In general, the Convection-Diffusion Equation can be used to describe the transfer of many physical quantities, such as particles or energy, as long as the transfer occurs only due to two processes: convection and diffusion. The most basic form of the Convection-Diffusion Equation is

$$(1) \quad \frac{\partial}{\partial t} c = D \nabla^2 c - \vec{v} \nabla c$$

In the case of the RDE system, the independent variables are the spatial coordinates  $x$ ,  $y$ , and  $z$ , and the time  $t$ . The origin is located at the intersection of the RDE's axis of rotation and the surface of the RDE (see Fig.2). The  $x$  and  $y$  axes extend perpendicularly from the axis of rotation (along the surface of the RDE that is in contact with the fluid). Since the surface of the RDE extends to infinity in all radial directions, the surface of the RDE covers the entire  $xy$  plane. The  $z$  axis extends along the axis of rotation. Since the chemical solution lies only in one side of the  $xy$  plane (below the electrode), this side is considered to be the positive  $z$  axis. The chemical solution also extends to infinity in the positive  $z$  direction, and therefore covers the entire 4 octants where  $z$  is positive. The time  $t$  is equal to zero when the experiment starts, which occurs when the circuit is completed (the RDE is already rotating by then). Therefore, we are only interested in positive values of  $t$ .

The dependent variable  $c = c(x, y, z, t)$  represents the reactant's concentration at a given location and time, which may be given by either the number, mass, or charge of electrons that may be transferred in the redox reaction per unit volume or the number or mass of the reactants containing these electrons per unit volume. The total average concentration can only decrease as time progresses, since once an electron transfers through the RDE, it cannot come back, and no extra reactants are added once the experiment starts. The constant  $D$  is the diffusion coefficient of the chemical solution and  $\vec{v} = \vec{v}(x, y, z, t)$  is the velocity vector of the fluid at any given location and time. Finally,  $\nabla$  and  $\nabla^2$  are the gradient and Laplace operators, respectively.

A derivation of the Convection-Diffusion Equation is included in Appendix 1.

**2.1. Properties of the RDE system.** In order to use the Convection-Diffusion Equation to analyze the RDE system, it is necessary to find an expression for the velocity function  $\vec{v}(x, y, z, t)$  of the fluid. This function, which depends on the properties of the solvent, the geometry of the RDE system, and the angular velocity of the RDE, is what makes the analysis of the RDE system unique. Since the RDE rotates at a constant angular velocity  $\Omega$  throughout the experiment, the fluid flow is stable at all times and  $\vec{v}$  doesn't depend in  $t$ . The properties of the solvent that are necessary for the analysis are the fluid's *viscosity*  $\nu$  (a measure of a fluid's resistance to being deformed) and *diffusivity*  $D$  (proportionality constant between the solvent's flux due to diffusion and the concentration gradient). The geometry of the RDE system has angular symmetry, so the use of cylindrical coordinates is appropriate. As usual,  $r$ ,  $\theta$ , and  $z$  are used, where  $x = r \cos \theta$ ,  $y = r \sin \theta$  and  $z = z$ .

A derivation and analysis of the solvent's velocity function  $\vec{v}(r, \theta, z)$  is included in Appendix 2. The important thing to notice is that the rate at which the fluid reaches the surface depends only on the  $z$  component of the velocity,  $v_z(r, \theta, z)$ . Furthermore, at distances close to the RDE surface,  $v_z$  depends solely on  $z$ . Knowing this, it can be shown that at distances close to the RDE surface, the concentration  $c(r, \theta, z, t) = c(z, t)$ , which significantly reduces the complexity of the problem. From the results of Appendix 2,  $v_z$  is given by

$$(2) \quad v_z = -0.51023\nu^{-1/2}\Omega^{3/2}z^2$$

Substituting Eq.2 into Eq.1, we obtain the Convection-Diffusion Equation as applied to the RDE system (at distances close to the RDE surface):

$$(3) \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} + az^2 \frac{\partial c}{\partial z}$$

where  $a = 0.51023\nu^{-1/2}\Omega^{3/2}$ .

**2.2. Initial and Boundary Conditions.** We can add three boundary conditions to Eq.3. by examining some of the properties of the RDE system.

First, at  $t = 0$ , before the reactants start to react, these are evenly distributed over the fluid (the reactants move along with the fluid as this flows, and since the fluid is incompressible, the reactant remain evenly distributed). Therefore, the initial concentration is constant throughout the fluid. Letting  $c_0$  be the initial concentration,  $c(z, 0) = c_0$ .

Second, at distances far away from the RDE, the effect of the RDE's rotation is minimal and no fluid flow is produced, so the reactants remains still throughout the experiment. Therefore, the concentration remains constant throughout the experiment at a distance far away from the RDE and  $c(\infty, t) = c_0$ .

Finally, since the reactants need to be in contact to the RDE surface in order to transfer electrons, and since once in contact the reaction occurs immediately, any reactants in contact with the RDE after  $t = 0$  (after the circuit is completed) will react immediately and the concentration of reactants at this point will be zero. Then, for  $t > 0$ ,  $c(0, t) = 0$ .

**2.3. Dimensionless version.** To obtain the form of Eq.3 that is generally found in the literature, we introduce the following dimensionless variables

$$(4) \quad C = \frac{c}{c_0}, \quad \tau = (Da^2)^{1/3}t, \quad \zeta = \left(\frac{a}{D}\right)^{1/3}z$$

With this choice of variables, Eq.3 becomes

$$(5) \quad \frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \zeta^2} + \zeta^2 \frac{\partial C}{\partial \zeta}$$

and the initial and boundary conditions become

$$(6) \quad C(\zeta, 0) = 1, \quad C(\infty, \tau) = 1, \quad C(0, \tau) = 0$$

In practice, measuring the concentration  $c$  at different points in the solution is not possible, so the solution to Eq.5 cannot be experimentally tested. Instead, a more useful expression is given by

$$(7) \quad j(\tau) = D \left( \frac{\partial C}{\partial \zeta} \right)_{\zeta=0}$$

which according to Fick's First law, yields the circuit's current  $j$  as a function of time.

### 3. ANALYSIS OF THE RULING EQUATION

We will now concentrate on analyzing Eqs.3 (or 5), with the purpose of understanding what the behavior of Eq.7 is.

**3.1. The Diffusion Equation.** Before fully analyzing Eq.3, it is useful to study how each of the components of Eq.3 contributes to the general behavior of the system.

To analyze the effect the effect that diffusion has on Eq.3 and the overall RDE system, the convection component is eliminated by setting  $v(x, y, z) = 0$ . A zero velocity function can only occur if the RDE's angular velocity  $\Omega = 0$  and there's therefore no fluid flow. The resulting equation, called the Heat Equation, is

$$(8) \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2}$$

We now proceed to solve Eq.8 using the boundary conditions of the RDE system in Eqs.6. In order to do so, we notice that  $z^2 \sim Dt$ , so we can use parabolic scaling to solve the system.

Let  $\varepsilon = \frac{z}{\sqrt{Dt}}$ . We will look for a function  $F$  such that  $F(\varepsilon) = c(z, t)$ . The partial derivatives of  $c = F$  can be rewritten as

$$\frac{\partial F}{\partial t} = -\frac{z}{2\sqrt{Dt^3}} \frac{dF}{d\varepsilon} \quad \text{and} \quad \frac{\partial^2 F}{\partial z^2} = \frac{1}{Dt} \frac{d^2 F}{d\varepsilon^2}$$

Substituting into Eq.8, the Heat Equation becomes

$$(9) \quad F'' + \frac{1}{2}\varepsilon F' = 0$$

Also, the boundary conditions of the RDE system become

$$F(\infty) = c_0 \quad \text{and} \quad F(0) = 0$$

To solve Eq.9, set  $u(\varepsilon) = F'(\varepsilon)$ . The differential equation becomes

$$\nu' + \frac{1}{2}\varepsilon\nu = 0$$

which has a general solution of

$$\nu = C_1 e^{-\varepsilon^2/4}$$

Since  $F'(\varepsilon) = u(\varepsilon)$ , we integrate  $u$  with respect to  $\varepsilon$  and obtain

$$F = C_1 \left( \sqrt{\pi} \text{Erf} \left[ \frac{\varepsilon}{2} \right] \right) + C_2$$

and by using the boundary conditions we obtain

$$F = c_0 \text{Erf} \left[ \frac{\varepsilon}{2} \right]$$

Substituting back the original variables, the solution becomes

$$(10) \quad c(z, t) = c_0 \text{Erf} \left[ \frac{z}{2\sqrt{Dt}} \right]$$

In order to obtain the current, we substitute Eq.10 into Eq.7 (using the corresponding variables) and obtain

$$(11) \quad j(t) = c_0 \sqrt{\frac{D}{\pi}} t^{-1/2}$$

Fig.3 (next page) shows a plot of Eq.11 for  $t < 10$ .

From Eq.11 and Fig.3, we can see that the current  $j(t)$  is very high at the beginning (starts at infinity) but then quickly decreases to a low range of  $j(t)$ . The current decreases more slowly as  $t$  increases and approaches 0 as  $t \rightarrow \infty$ .

The behavior of Eq.11 is similar to what is expected from the RDE system. In the case of the RDE system, the reactants in contact to the surface react immediately after the



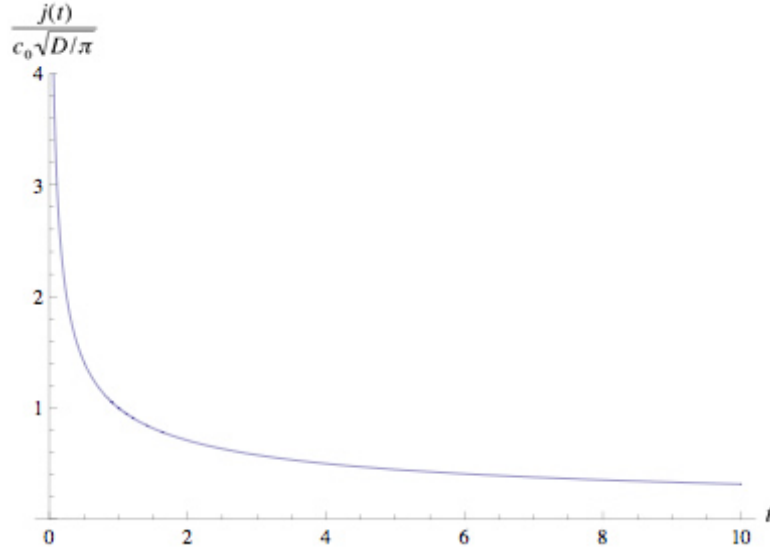


FIGURE 3. Graph of Eq.11

circuit is connected, so the electrons transfer in an infinitesimal amount of time and the current (charge per unit time) becomes infinite. After this, the concentration  $c$  becomes zero at the RDE's surface, and new reactants move to the surface due to the non-uniform concentration (the effect of diffusion). Nonetheless, the current quickly decreases, since all other reactants that reach the surface do it in a finite amount of time. After a small period of time, the current stabilizes and decreases slowly.

What we don't expect from the RDE system is having a current that approaches 0 as  $t \rightarrow \infty$ . Since only diffusion is considered in Eq.11, the reactants only reach the surface due to the uneven concentration, but the rate at which this happens decreases as the distance between the reactants and the electrode increases, so the current goes eventually goes to zero. A solution of Eq.3, on the other hand, will also consider convection. Since the reactants are constantly being taken to the RDE surface by the fluid flow and since the supply is unlimited (infinite volume), the current will not go to zero. Therefore, the effect of the convection component on Eq.3 must be more significant than that of the diffusion component for large values of  $t$ .

**3.2. A Convection Equation.** To analyze the effect of convection on Eq.3, the diffusion component is eliminated by setting by setting  $\partial_z^2 c = 0$  (see Appendix 2). Eq.3 becomes

$$(12) \quad \frac{\partial c}{\partial t} = z^2 \frac{\partial c}{\partial z}$$

We now solve Eq.12 using the boundary conditions of the RDE system. We will look for solutions of the form  $c(z, t) = f(g(z) - t)$ . Let  $\varepsilon = g(z) - t$ . The derivatives of  $f(\varepsilon) = c(z, t)$  are

$$\frac{\partial f}{\partial t} = -\frac{df}{d\varepsilon} \quad \frac{\partial f}{\partial z} = g'(z)\frac{df}{d\varepsilon}$$

Substituting into Eq.12, the differential equation becomes

$$(13) \quad -\frac{df}{d\varepsilon} = z^2 g'(z) \frac{df}{d\varepsilon}$$

which simplifies to  $-1 = z^2 g'(z)$  and has the solution

$$g(z) = \frac{1}{z} + C_1$$

This implies that any function  $f(1/z - t + C_1)$  is a solution to Eq.12. Then, for any function  $f(\varepsilon)$ ,

$$(14) \quad c(z, t) = f\left(\frac{1}{z} - t + C_1\right)$$

Eq.14 shows that at distances close to the RDE, the behavior of  $c(z, t)$  depends mostly on  $z$  (since  $1/z$  dominates  $t$  as  $z \rightarrow 0$ ). Therefore, when only convection is considered, the RDE system behavior doesn't vary much with time at distances close to the RDE, and the current  $j$  given by Eq.7 is independent of time.

The behavior of Eq.14 at small times is not the behavior we expect from the RDE system, since we know that the current changes rapidly at short times. Therefore, we can conclude that at short times, it is diffusion that has the biggest effect on Eq.3.

**3.3. Analyzing the Convection-Diffusion Equation.** We now proceed to study the RDE system when both diffusion and convection are taken into account. For simplicity, we'll analyze the dimensionless Eq.5 and use the Separation of Variables method

Suppose that the solution to Eq.5 is separable, such that  $C(\zeta, \tau) = f(\zeta)g(\tau)$ , where  $f(\zeta)$  and  $g(\tau)$  are unknown. Substituting, Eq.5 becomes

$$(15) \quad \frac{f''(\zeta) + \zeta^2 f'(\zeta)}{f(\zeta)} = \frac{g'(\tau)}{g(\tau)}$$

Since the left side of Eq.15 depends only on  $\zeta$  and the right side depends only on  $\tau$ , these expressions must be constant for all  $\zeta$  and  $\tau$ . Additionally, for reasons that will become clear later on, the constant must be a negative real number. Letting  $\lambda \geq 0$ , we obtain the following two ordinary differential equations

$$(16) \quad \frac{g'(\tau)}{g(\tau)} = -\lambda \quad \text{and} \quad \frac{f''(\zeta) + \zeta^2 f'(\zeta)}{f(\zeta)} = -\lambda$$

Eq.16a can be rewritten as  $g' + \lambda g = 0$ , which has the solution

$$(17) \quad g(\tau) = C_1 e^{-\lambda\tau}$$

for any value of  $\lambda \geq 0$  and where  $C_1$  is unknown. Since  $g(\tau)$  is a decreasing function and  $g(\tau) \rightarrow 0$  as  $\tau \rightarrow \infty$ , the time dependency of  $C(\zeta, \tau)$  is more significant at small times and almost insignificant at large times. Since this is what is expected from the RDE system, our choice of sign for  $\lambda$  is correct (a positive sign would produce the opposite results).

Eq.16b can be rewritten as  $f'' + \zeta^2 f' + \lambda f = 0$ . Eq.16b has non-homogeneous boundary conditions, so the solutions to Eq.16b can't be used to solve Eq.5 using the separation of variables method. Instead, let  $q(\zeta) = f'(\zeta)$ . Eq.16b becomes  $q'(\zeta) + \zeta^2 q(\zeta) = -\lambda f(\zeta)$ . Differentiating with respect to  $\zeta$  we obtain

$$(18) \quad q''(\zeta) + \frac{d}{d\zeta} [\zeta^2 q(\zeta)] = -\lambda q(\zeta)$$

Notice that Eq.18 has homogenous boundary conditions. First, since  $C(\zeta, 0) = 1$  and  $C(0, \tau) = 0$  for  $\tau > 0$  (Eqs.6),  $C(\zeta, \tau)$  becomes a delta function for fix  $\zeta = 0$ , which implies that  $f''(0)=0$  and consequently  $q'(0) = 0$ . Second, since  $C(\infty, \tau) = 1$ , all distance derivatives must go to zero at  $\zeta \rightarrow \infty$ , implying that  $q(\infty) = 0$ .

Now, note that Eq.18 can be rewritten as

$$\frac{d}{d\zeta} \left[ e^{-\zeta^3/3} \frac{d}{d\zeta} \left[ e^{\zeta^3/3} q(\zeta) \right] \right] = -\lambda q(\zeta)$$

and finally by

$$e^{\zeta^3/3} q^* \frac{d}{d\zeta} \left[ e^{-\zeta^3/3} \frac{d}{d\zeta} \left[ e^{\zeta^3/3} q(\zeta) \right] \right] = -\lambda e^{\zeta^3/3} q^* q(\zeta)$$

where  $q^*$  is any function of  $\zeta$ . Integrating both sides of the equation (using integration by parts) we obtain

$$(19) \quad N - \int_0^\infty e^{-\zeta^3/3} \left( \frac{d}{d\zeta} e^{\zeta^3/3} q(\zeta) \right) \left( \frac{d}{d\zeta} e^{\zeta^3/3} q^* \right) d\zeta = -\lambda \int_0^\infty e^{\zeta^3/3} q^* q(\zeta) d\zeta$$

where

$$(20) \quad N = q^* \frac{d}{d\zeta} \left[ e^{\zeta^3/3} q(\zeta) \right] \Big|_0^\infty$$

Since  $q'(0) = 0$  and  $q(\infty) = 0$ , using the Rayleigh-Ritz method, we know that  $N = 0$  or  $N = \infty$ , depending on the value of  $\lambda$  in Eq.18 that produces  $q(\zeta)$ . Since Eq.19 will only have solutions if N is finite, Eq.18 can only be solved for values of  $\lambda$  for which  $N = 0$  (Eq.18 will not have solutions for other values of  $\lambda$ ). By only considering those values of  $\lambda$  that solve Eq.18, and by letting  $q^* = q(\zeta)$ , Eq.19 becomes

$$(21) \quad \lambda = \frac{\int_0^\infty e^{-\zeta^3/3} \left( \frac{d}{d\zeta} e^{\zeta^3/3} q(\zeta) \right)^2 d\zeta}{\int_0^\infty e^{\zeta^3/3} q^2(\zeta) d\zeta}$$

The values of  $\lambda$  that satisfy Eq.21 are called the eigenvalues of the Eq.18, and the corresponding functions  $q(\zeta)$  that solve Eq.18 are called the eigenfunctions of Eq.18. Using the

Rayleigh-Ritz method, it can be shown that Eq.18 has an infinite but countable number of eigenvalues and corresponding eigenfunctions, so we let  $\lambda_0, \lambda_1, \lambda_2, \dots$  be these eigenvalues and  $q_0(\zeta), q_1(\zeta), q_2(\zeta), \dots$  be the corresponding eigenfunctions.

It is easy to show that  $\lambda_0 = 0$  is one of the eigenvalues. To find other eigenvalues, we first note that Eq.19 will only be nonzero if  $\int_0^\infty e^{\zeta^3/3} q^2(\zeta) d\zeta$  is finite and consequently if  $e^{\zeta^3/3} q^2(\zeta) \rightarrow 0$  as  $\zeta \rightarrow \infty$ . The values of these eigenvalues and their corresponding eigenfunctions can be found analytically using advance techniques, but for the purpose of the analysis, numerical methods are appropriate. The first 10 eigenvalues were found using *Mathematica* by first solving Eq.18 for many values of  $\lambda$  and then using the Bisection method to find which of these values satisfy Eq.21. Table 1 contains a list of the first 10 eigenvalues that were found numerically (in addition to  $\lambda_0$ ).

T1: Eigenvalues	
$\lambda_0$	0
$\lambda_1$	3.4694
$\lambda_2$	8.7302
$\lambda_3$	14.998
$\lambda_4$	22.015
$\lambda_5$	29.650
$\lambda_6$	37.832
$\lambda_7$	46.438
$\lambda_8$	55.493
$\lambda_9$	64.938
$\lambda_{10}$	74.719

Fig.4 shows plots of the eigenfunctions  $q(\zeta)$  corresponding to the first four eigenvalues (here we assume that  $q(0) = 1$  to have enough boundary conditions; changing the value of  $q(0)$  affects the eigenfunctions by altering their amplitude, but doesn't change the value of the eigenvalues).

In order to solve for  $C(\zeta, \tau)$ , we would still have to find an expression for the eigenfunctions  $q(\zeta)$  and integrate to get an expression for  $f(\zeta)$ , but since we are only interested in the current  $j(\tau) = Df'(0)g(\tau) = Dq(0)g(\tau)$ , it is not necessary to solve for the eigenfunctions. The full expression for the current  $j(\tau)$  is the linear combination of all solutions, so the current  $j(\tau)$  is given by

$$(22) \quad j(\tau) = D \sum_{i=0}^{\infty} B_i q(0) (C_1 e^{-\lambda_i \tau})$$

where  $B_i$  are unknown constants. At short times, Eq.22 is not too useful, since none of the term in the series can be dropped (since we don't know what the coefficients  $B_i$

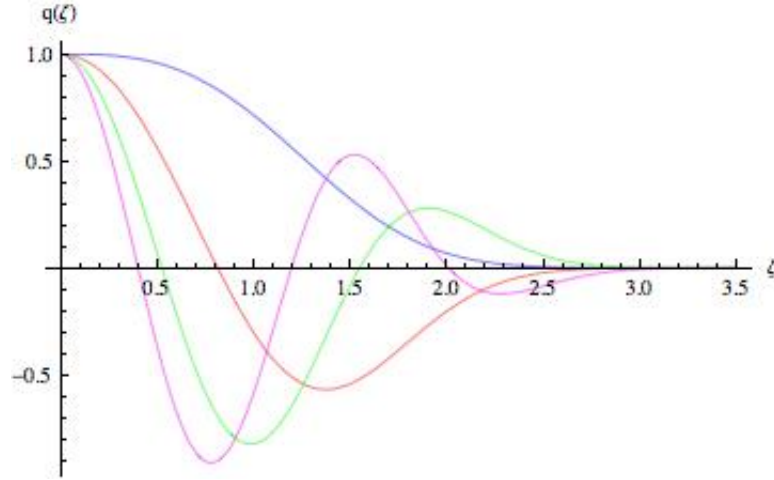


FIGURE 4.  $f(\zeta)$  for eigenvalues  $\lambda_0$  (blue),  $\lambda_1$  (red),  $\lambda_2$  (green), and  $\lambda_3$  (purple)

are). Nevertheless, for long times, the contributions from the terms with large eigenvalues becomes insignificant (as the power of  $e$  becomes more negative), so Eq.22 can be reduced to

$$j(\tau) = Dq(0)C_1 \left( B_0 e^{-\lambda_0 \tau} + B_1 e^{-\lambda_1 \tau} \right)$$

and finally to

$$(23) \quad j(\tau) = k_0 + k_1 e^{-3.4696\tau}$$

where  $k_0$  and  $k_1$  are unknown coefficients.

**3.4. Comparison to the Numerical Solution.** In order to test its accuracy, Eq.23 was compared to a numerical solution obtained using *MatLab*. The coefficients  $k_0$  and  $k_1$  that produce the best correlation between Eq.23 and the numerical solution were determined numerically using the Least Squares method. These values are (for  $D=1$ ):

$$k_0 = 0.9871 \quad k_1 = 1.5687$$

In this case, Eq.23 becomes

$$(24) \quad j(\tau) = 0.9871 + 1.5687 e^{-3.4696\tau}$$

Fig.5 compares Eq.24 to the numerical solution for  $0 < \tau < 1$ . As expected, Eq.24 is not correct at short periods of time ( $\tau < 0.2$ ), but it gains accuracy as  $\tau$  increases.

Fig.6 compares Eq.24 to the numerical solution for  $0.2 < \tau < 1.2$ . At this range, Eq.24 is fairly accurate, so Eq.24 is a good approximation for values of  $\tau > 0.2$ .

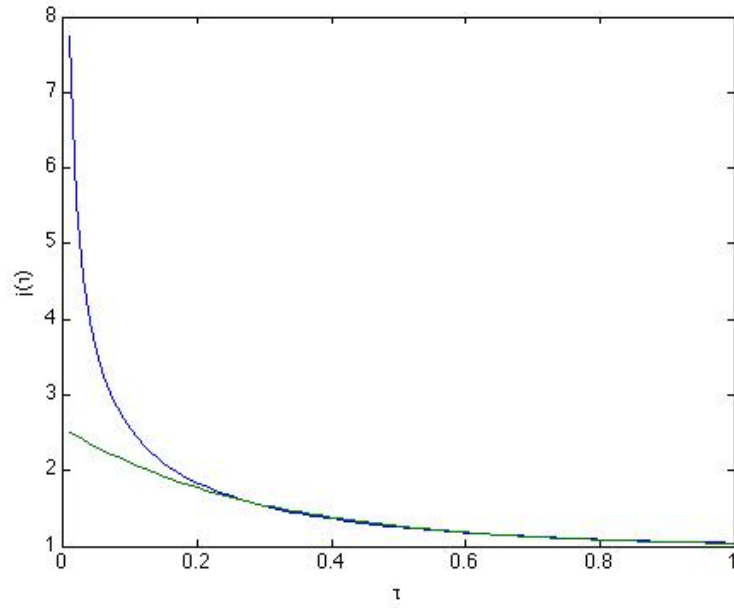


FIGURE 5. Short time comparison: numeric (blue) and Eq.24 (green)

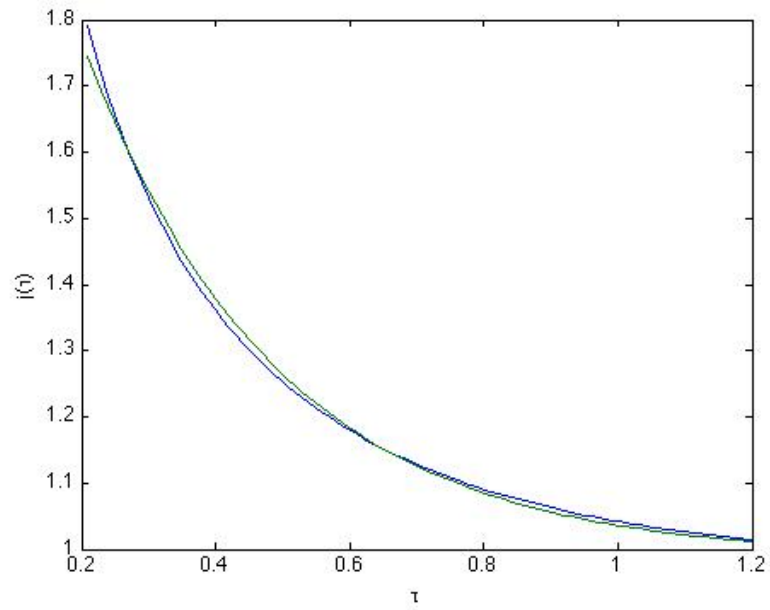


FIGURE 6. Long time comparison: numeric (blue) and Eq.24 (green)

## 4. A SOLUTION TO THE PROBLEM

Since one of our goals is to analyze one of the already published analytical solutions to Eq.3, we will also compare its accuracy to our numerical solution. This solution was published in 1971 by V. S. Krylov and V. N. Babak. The derivation of this solution can be found in Appendix 3. The result, in terms of the current  $j(\tau)$ , is

$$(25) \quad j(\tau) = \frac{c_o(aD^2)^{1/3}}{\sqrt{\pi\tau}} \left( 1 - \pi \sum_{n=1}^{\infty} \theta_n \tau^{3n/2} \right)$$

where the coefficients  $\theta_n$  are given by Eq.58.

The accuracy of Eq.25 depends mainly on two things. First, the techniques used to derive Eq.25 are only suitable for small values of  $\tau$ . Therefore, we expect Eq.25 to be accurate for small values of  $\tau$  and to gradually lose accuracy as  $\tau$  increases. Second, Eq.25 contains an infinite series, so its accuracy will depend on the number of terms used to calculate the current  $j(\tau)$ .

**4.1. Accuracy as a Function of Time.** We will now compare Eq.25 to our numerical solution. For this, we will set  $D = 1$  and  $a = 1$ , and we will use 10 terms in the series to calculate Eq.25 (at small times, the accuracy is practically the same regardless of the number of terms used).

Fig.7 shows both of the solutions for  $0 \leq \tau \leq 0.1$ . The solution is remarkably accurate for this small time domain.

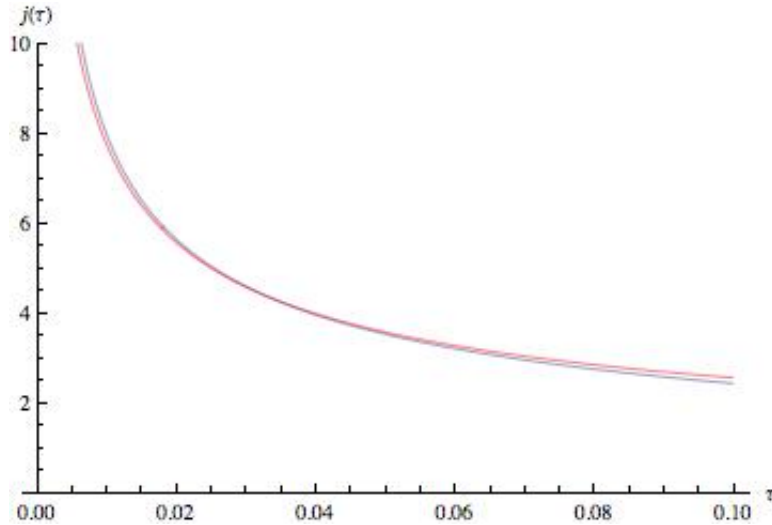


FIGURE 7. Short time comparison: Numeric (red) and Eq.25 (blue)

Since the numeric solution can't start at infinity ( $j(0) = \infty$ ), this solution cannot be completely exact. Therefore, it is impossible to determine the accuracy of Eq.25 by just comparing it to the numerical solution. Nevertheless, by enlarging the initial point in the numerical solution and shortening the spacing between the nodes where the numeric solution is evaluated, the accuracy of the numerical solution increases. Comparing the numerical solution at different accuracies with Eq.25 shows that agreement between the two increases as the numeric solution becomes more accurate, suggesting that Eq.25 is exact at small times.

Fig.8 now shows the two solutions for  $0 \leq \tau \leq 1$ . Not only does the agreement between the numeric solution and Eq.22 diminishes as  $\tau$  increases, but Eq.25 clearly yields incorrect results for the larger times (changing the number of terms used in Eq.25 didn't improve the results).

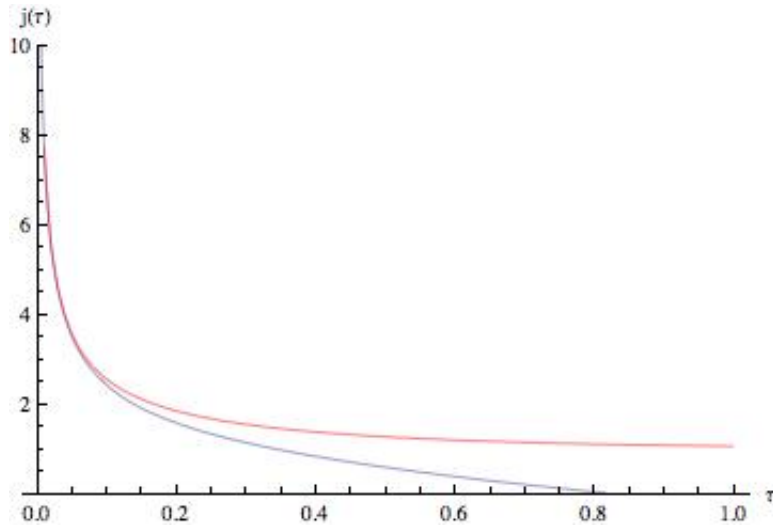


FIGURE 8. Long time comparison: Numeric (red) and Eq.25 (blue)

The accuracy of Eq.25 is lost at about  $\tau = 0.1$ , where the error is 5%. Further comparing Eq.25 to the numerical solution at larger times only suggests that Eq.25 is not correct for large values of  $\tau$ . Since adding more terms to the series in Eq.25 doesn't improve the results, we can conclude that Eq.25 is only accurate for values of  $\tau$  less than 0.1.



**4.2. Accuracy as a Function of the Terms Used.** Generally, we would expect the accuracy and range of applicability of Eq.25 to increase as more terms are used in the series. Nevertheless, Eq.25 instead shows an asymptotic behavior. At small times, the results of Eq.25 are practically the same regardless of the number of terms used (the first term in the series is very dominant at small  $\tau$ ). At large times, on the other hand, the solution produced by Eq.25 is basically the same when a small number of terms is used, but completely blows up if a large number of terms is used.

Fig.9 compares the results of Eq.25 when different number of terms are used.

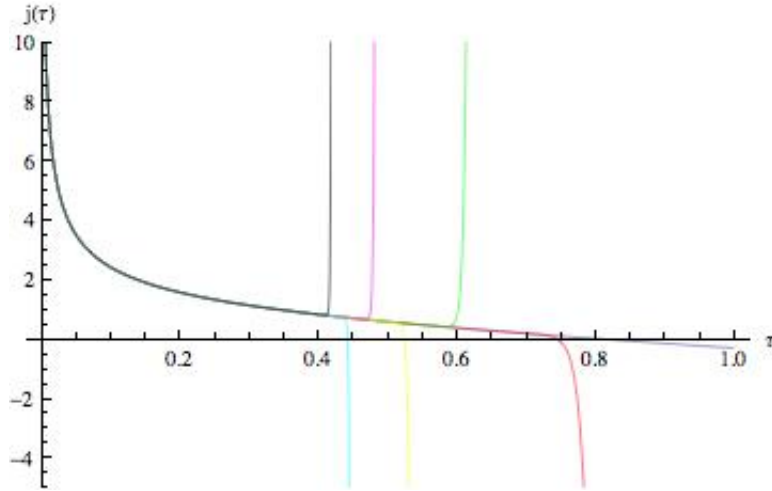


FIGURE 9. 300, 250, 200, 150, 100, 50, and 1 terms, respectively

As Fig.9 shows, the results of Eq.25 at small times are the same, regardless of the number of terms used in the series. But as  $\tau$  increases, the solutions blow up at some point (depending on the number of terms used). Furthermore we can see that the range of applicability of Eq.15 decreases as more terms are added to the series, confirming that Eq.25 has an asymptotic behavior.

A final point to notice is that studying the asymptotic properties of Eq.25 is unnecessary. As shown by Fig.9, Eq.25 blows up after  $\tau = 0.1$ , range at which Eq.25 is not accurate anyways. The range of applicability may be further reduced if more terms are used in the series, but since adding more terms doesn't improve the results of Eq.25, there is no point in calculating more terms.

**4.3. Further Analysis of Eq.22.** Even though Eq.25 is only applicable at a very small range, it is still useful in determining what the behavior of the RDE system at short times

is. As  $\tau \rightarrow 0$ , each of the terms in the series goes to zero (since  $\tau^{3n/2} \rightarrow 0$  as  $\tau \rightarrow 0$  for all  $n = 1, 2, 3, \dots$ ). Therefore, Eq.25 becomes

$$(26) \quad j(\tau) = \frac{c_o(aD^2)^{1/3}}{\sqrt{\pi\tau}}$$

Comparing Eq.26 to Eq.11 (which gives the current  $j(t)$  when only diffusion is considered), we see that these have the same time dependency, namely,  $j(\tau) \sim j(t) \sim t^{-1/2}$ . Therefore, for small  $\tau$ , Eq.26 shows not only that diffusion more dominant than convection, but that the contributions from the later can be neglected.

## 5. CONCLUSION

Even though an analytical solution to Eq.3 that is applicable to the entire time domain was not obtained, the numerical and analytical analysis performed so far tell us much of what we need to know to understand the behavior of the RDE system. The information gained during our analysis definitely constitutes an improvement over just having a numerical solution, since we now know what the time dependency of  $j(\tau)$  is at both short and long times and what causes this behavior.

The only part of Eq.7 that was not studied in detail is the range  $0.1 < \tau < 0.2$ , where  $j(\tau)$  switches from short to long time behavior. Naturally, we could extend the range of applicability of Eq.22 (by using more terms in the series) in order to cover this range of  $\tau$ , but we would still need to determine how Eq.22 and 25 connect. Therefore, future work could concentrate on analyzing the behavior of Eq.7 at this range.

Finally, regarding the analytical solution of Krylov and Babak, our analysis shows this solution is only applicable at small times and that its accuracy at this range is not affected by its asymptotic properties. Therefore, there is no need of further analyzing this solution.

## ACKNOWLEDGEMENTS

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APPENDIX A. DERIVATION OF THE CONVECTION-DIFFUSION EQUATION

**A.1. The Continuity Equation.** To derive Eq.1, we first start by deriving the continuity equation, which simply states that the reactants cannot disappear (conservation of mass) and that these must move continuously throughout space. One simplification that is made is to consider the solvent to be incompressible. This is an allowable simplification, since the volume of the container in the RDE system never changes (not forcing the solvent to compress).

Consider a region shaped as a rectangular box with length  $\Delta x$ , width  $\Delta y$ , and height  $\Delta z$  as shown in Figure 10. This region can be positioned anywhere within the chemical solution. Due to changes in the concentration of reactants (diffusion) and the fluid's flow (convection), the reactants will move in and out of this region. The rate at which the reactants will accumulate inside of the box is the same as the rate at which the reactants enter the box minus the rate at which the reactants leave the box.

Let  $C = C(t)$  be the total number of reactants inside of the box at a given time and  $c(x, y, z, t)$  be the concentration of reactants at a given point. Also, let  $j_x(x)$ ,  $j_y(y)$ , and  $j_z(z)$  represent the flux of reactants into the box in the  $x$ ,  $y$ , and  $z$  faces of the box, respectively, and let  $j_x(x + \Delta x)$ ,  $j_y(y + \Delta y)$ , and  $j_z(z + \Delta z)$  represent the flux of reactants out of the box in the  $x + \Delta x$ ,  $y + \Delta y$ , and  $z + \Delta z$  faces of the box, respectively.

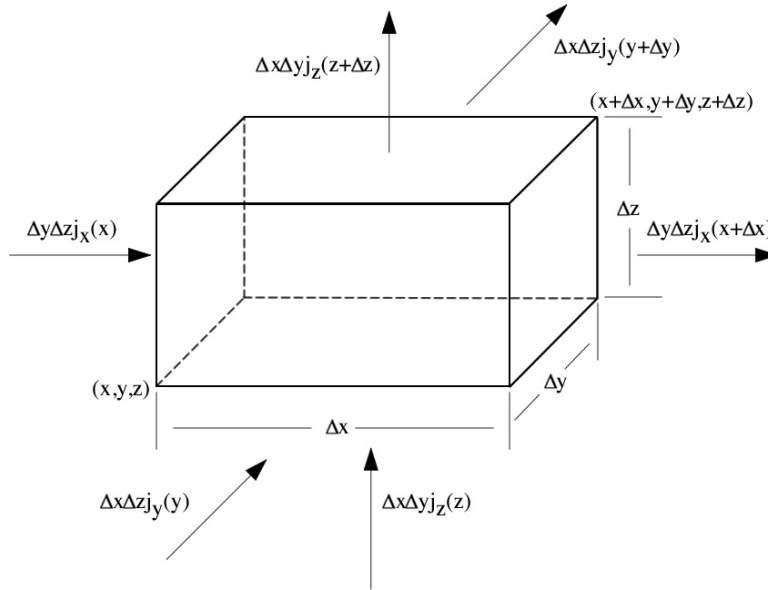


FIGURE 10. Region where the fluid is flowing

At a given time  $t$ , the rate at which the reactants enter the box in a direction  $i = \{x, y, z\}$  is given by  $[j_i(i) - j_i(i + \Delta i)] \times [\text{Area of face perpendicular to } i]$ . Therefore, the total rate at which the reactants enter the box,  $\partial C / \partial t$ , is given by

$$\frac{\partial}{\partial t} C = \Delta y \Delta z [j_x(x) - j_x(x + \Delta x)] + \Delta x \Delta z [j_y(y) - j_y(y + \Delta y)] + \Delta x \Delta y [j_z(z) - j_z(z + \Delta z)]$$

Dividing both sides of the equation by  $\Delta x \Delta y \Delta z$  and letting  $\Delta x \rightarrow 0$ ,  $\Delta y \rightarrow 0$ , and  $\Delta z \rightarrow 0$ , we obtain

$$\frac{\partial}{\partial t} c = -\frac{\partial}{\partial x} j_x - \frac{\partial}{\partial y} j_y - \frac{\partial}{\partial z} j_z$$

Letting  $\vec{j}(x, y, z) = j_x \hat{x} + j_y \hat{y} + j_z \hat{z}$  be the reactant's flux vector, we obtain the Continuity Equation

$$(27) \quad \frac{\partial}{\partial t} c + \nabla \cdot \vec{j} = 0$$

**A.2. The flux due to convection and diffusion.** The Convection-Diffusion Equation only takes into account the reactant's flux due to convection and diffusion. Convection is the movement of molecules within fluids due to the larger scale motion of currents in the fluid. In the RDE system, each of the reactants (which constitute only a small percentage of the overall chemical solution) is carried away by the motion of the solvent. The convective flux at a given point is simply given by the velocity vector  $\vec{v}$  of the fluid carrying the reactants times the reactant's concentration at that point, that is,  $j_c = \vec{v}c$ .

Diffusion is the overall transport of molecules from a region with a higher molecular concentration to a region with a lower molecular concentration due to random molecular motion. In general, the flux due to diffusion at a given point is given by Fick's First Law, which states that the concentration gradient is proportional to the diffusion flux. The constant of proportionality,  $D$ , is called the diffusion constant. Therefore, the diffusion flux is  $j_d = -D\nabla c$ .

Since the total flux is given by the sum of the convection and diffusion fluxes,  $\vec{j}$  is given by

$$(28) \quad \vec{j} = -D\nabla c + \vec{v}c$$

**A.3. Results.** To derive the Convection-Diffusion Equation, substitute Eq.28 into Eq.27

$$\frac{\partial}{\partial t} c + \nabla \cdot (-D\nabla c + \vec{v}c) = 0$$

yielding the general form of the Convective-Diffusion Equation (Eq.1):

$$\frac{\partial}{\partial t} c - D\nabla^2 c + \vec{v}\nabla c = 0$$

## APPENDIX B. DERIVATION OF THE VELOCITY FUNCTION

To obtain an expression for the fluid's velocity function  $\vec{v}(x, y, z, t)$ , the properties of the RDE system are incorporated into the Equations of Continuity and Motion (applicable to any fluid) to get a set of differential equations that can be used to determine  $v$ . In order to do so, the solvent's *dynamic pressure*  $p(x, y, z, t)$  (which measures the pressure of the fluid due to particle collisions at a given point and time) and *density*  $\rho$  (the total mass per total volume of the fluid/solvent) are used.

**B.1. The Equations of Continuity and Motion in Cylindrical Coordinates.** In cylindrical coordinates, the equation of continuity is

$$(29) \quad \frac{1}{r} \frac{\partial}{\partial r}(rv_r) + \frac{1}{r} \frac{\partial}{\partial \theta} v_\theta + \frac{\partial}{\partial z} v_z = 0$$

The  $r$ -component of the equation of motion is

$$(30) \quad \frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta^2}{r} + v_z \frac{\partial v_r}{\partial z} = -\frac{1}{\rho} \frac{\partial p}{\partial r} + \nu \left[ \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r}(rv_r) \right) + \frac{1}{r^2} \frac{\partial^2 v_r}{\partial \theta^2} - \frac{2}{r^2} \frac{\partial v_\theta}{\partial \theta} + \frac{\partial^2 v_r}{\partial z^2} \right]$$

The  $\theta$ -component of the equation of motion is

$$(31) \quad \frac{\partial v_\theta}{\partial t} + v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r v_\theta}{r} + v_z \frac{\partial v_\theta}{\partial z} = -\frac{1}{\rho} \frac{\partial p}{\partial \theta} + \nu \left[ \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r}(rv_\theta) \right) - \frac{1}{r^2} \frac{\partial^2 v_\theta}{\partial \theta^2} + \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} + \frac{\partial^2 v_\theta}{\partial z^2} \right]$$

The  $z$ -component of the equation of motion is

$$(32) \quad \frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_z}{\partial \theta} + v_z \frac{\partial v_z}{\partial z} = -\frac{1}{\rho} \frac{\partial p}{\partial z} + \nu \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_z}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 v_z}{\partial \theta^2} + \frac{\partial^2 v_z}{\partial z^2} \right]$$

**B.2. The Equations of Continuity and Motion and the RDE system.** Eqs. 29 to 32 are simplified when the geometry of the RDE is incorporated. First, since the angular velocity  $\Omega$  of the RDE is constant, the current flow will not change with time, meaning that all derivatives with respect to  $t$  are zero. Similarly, due to the angular symmetry of the RDE system, the velocity components are the same at any angle for a given height and radial distance. Therefore, all derivatives with respect to  $\theta$  are zero.

It can be shown that the solutions to these equations must satisfy the relations

$$(33) \quad v_r = rf(z), \quad v_\theta = rg(z), \quad v_z = h(z), \quad p = p(z)$$

By substituting these equations and letting all derivatives with respect to  $t$  and  $\theta$  equal zero, Eqs. 29 to 32 reduce to

$$(34) \quad \begin{cases} 2f + h' = 0 \\ f^2 - g^2 + hf' = \nu f'' \\ 2fg + hg' = \nu g'' \\ \rho hh' + p' = \rho \nu h'' \end{cases}$$

The boundary conditions of Eq.34 are as follows: At a distance  $z = 0$  from the RDE, the fluid is in contact to the RDE surface and is therefore carried by the RDE at a velocity equal to the angular velocity times the radial distance. Then,  $v_\theta = rg(z) = r\Omega$ , implying that  $g(0) = \Omega$ . For the same reason, the  $r$  or  $z$  velocity components at the surface of the RDE must be zero, and therefore,  $f(0) = 0$  and  $h(0) = 0$ . On the other hand, at a distance far away from the RDE, the RDE's rotation doesn't affect the fluid and the  $\theta$  and  $r$  velocity components are zero. Therefore,  $f(\infty) = 0$  and  $g(\infty) = 0$ .

To eliminate the parameters in Eqs.34, the following dimensionless variables are introduced:

$$(35) \quad Z = z\sqrt{\Omega/\nu}, \quad P = p/(\Omega\rho\nu), \quad G = g/\Omega, \quad F = f/\Omega, \quad H = h/\sqrt{\Omega\nu}$$

Eqs.34 become

$$(36) \quad \begin{cases} 2F + H' = 0 \\ F^2 - G^2 + HF' = F'' \\ 2FG + HG' = G'' \\ HH' + P' = H'' \end{cases}$$

with boundary conditions

$$(37) \quad \begin{cases} F = 0, G = 1, H = 0 & \text{at } Z = 0; \\ F = 0, G = 0 & \text{at } Z = \infty; \end{cases}$$

Approximate solutions to Eqs.36 with boundary conditions Eq.37 at distances close to the RDE surface have been presented before. Since only the  $z$  component of the velocity  $v$  is important in determining the rate at which the reactants approach the surface of the RDE, it is only necessary to determine what  $H$  is (since it is directly proportional to  $v_z$ ). The function  $H$  that satisfies the system, for distances close to the RDE surface, is given by

$$(38) \quad H = -\alpha Z^2 + \frac{1}{3}Z^3 + \frac{\beta}{6}Z^4 + \dots$$

where  $\alpha = 0.51023$  and  $\beta = -0.616$ . When Eq.1 is used to study the RDE system (in the form of Eq.3), only the first term of Eq.38 is conserved, a good approximation for  $Z \ll 1$  (distances close to the RDE's surface). This small range of applicability is all we need to obtain an expression of the current through the RDE, so the simplification is allowable.

Using only the first term in the series and substituting back into the original variables,  $v_z$  becomes

$$(39) \quad v_z = -0.51023\nu^{-1/2}\Omega^{3/2}z^2$$

The most important thing to notice here is that  $v_z$ , the component of the velocity  $\vec{v}$  normal to the RDE surface, only depends on  $z$ , the normal distance from the surface of the disk.

### APPENDIX C. DERIVATION OF THE KRYLOV-BABAK SERIES SOLUTION

The Convection-Diffusion Equation applied to the RDE system (Eq.5) is given by

$$\frac{\partial^2 C}{\partial \zeta^2} + \zeta^2 \frac{\partial C}{\partial \zeta} - \frac{\partial C}{\partial \tau} = 0$$

with boundary conditions (Eqs.6)

$$C(\zeta, 0) = 1, \quad C(\infty, \tau) = 1, \quad C(0, \tau) = 0$$

We'll look for solutions of the form

$$(40) \quad C(\varphi, \tau) = \sum_{n=0}^{\infty} \tau^{\frac{3n}{2}} G_n(\varphi)$$

where  $\varphi \equiv \zeta(2\tau)^{-1/2}$ .

The necessary derivatives of  $C(\varphi, \tau) = C$  are given by

$$\frac{\partial C}{\partial \zeta} = \sum_{n=0}^{\infty} \left( \frac{\sqrt{2}}{2} \tau^{\frac{3n-1}{2}} G'_n(\varphi) \right)$$

$$\frac{\partial^2 C}{\partial \zeta^2} = \sum_{n=0}^{\infty} \left( \frac{1}{2} \tau^{\frac{3n-2}{2}} G''_n(\varphi) \right)$$

$$\frac{\partial C}{\partial \tau} = \sum_{n=0}^{\infty} \left( \frac{3n}{2} \tau^{\frac{3n-2}{2}} G_n(\varphi) - \frac{\varphi}{2} \tau^{\frac{3n-2}{2}} G'_n(\varphi) \right)$$

Substituting these values into Eq.1 and rearranging we obtain

$$\begin{aligned} & \sum_{n=0}^{\infty} \left( \frac{1}{2} \tau^{\frac{3n-2}{2}} G''_n(\varphi) + (2\tau\varphi^2) \frac{\sqrt{2}}{2} \tau^{\frac{3n-1}{2}} G'_n(\varphi) - \frac{3n}{2} \tau^{\frac{3n-2}{2}} G_n(\varphi) + \frac{\varphi}{2} \tau^{\frac{3n-2}{2}} G'_n(\varphi) \right) \\ & = \sum_{n=0}^{\infty} \left( \frac{1}{2} \tau^{\frac{3n-2}{2}} \right) \left( G''_n(\varphi) + 2\sqrt{2}\tau^{3/2}\varphi^2 G'_n(\varphi) - 3nG_n(\varphi) + \varphi G'_n(\varphi) \right) = 0 \end{aligned}$$

By equating the terms with the same power of  $\tau$ , we get the following set of differential equations:

$$(41) \quad \begin{cases} G_0''(\varphi) + \varphi G_0'(\varphi) = 0 \\ G_n''(\varphi) + \varphi G_n'(\varphi) - 3nG_n(\varphi) = -2\sqrt{2}\varphi^2 G_{n-1}'(\varphi) \quad (n = 1, 2, \dots) \end{cases}$$

The boundary conditions for Eq.41 become

$$(42) \quad \begin{cases} G_0(0) = 0 & G_0(\infty) = 1 \\ G_n(0) = 0 & G_n(\infty) = 0 \quad (n = 1, 2, \dots) \end{cases}$$

It is simple to show that the solution to Eq.41a (for  $n = 0$ ) is given by

$$(43) \quad G_0 = erf\left(\frac{\varphi}{\sqrt{2}}\right)$$

To solve Eqs.41b (for  $n = 1, 2, \dots$ ), we will first rewrite them as a set of parabolic cylinder functions. First, we define a function  $P_n(\varphi)$  such that

$$(44) \quad G_n(\varphi) = e^{-\varphi^2/4} P_n(\varphi)$$

The derivatives of  $G_n(\varphi)$  are

$$\begin{aligned} G_n'(\varphi) &= e^{-\varphi^2/4} \left( P_n'(\varphi) - \frac{\varphi}{2} P_n(\varphi) \right) \\ G_n''(\varphi) &= e^{-\varphi^2/4} \left( P_n''(\varphi) - \varphi P_n'(\varphi) + \left( \frac{\varphi^2}{4} - \frac{1}{2} \right) P_n(\varphi) \right) \end{aligned}$$

Substituting these values in Eqs.41b and rearranging we obtain

$$e^{-\varphi^2/4} \left( P_n''(\varphi) + \left( -3n - \frac{1}{2} - \frac{\varphi^2}{4} \right) P_n(\varphi) \right) = f(\varphi)$$

where

$$f(\varphi) = -2\sqrt{2}\varphi^2 e^{-\varphi^2/4} \left( P_{n-1}'(\varphi) - \frac{\varphi}{2} P_{n-1}(\varphi) \right)$$

Finally we let  $\nu = -3n - 1$  and rearrange to obtain

$$(45) \quad P_n''(\varphi) + \left( \nu + \frac{1}{2} - \frac{\varphi^2}{4} \right) P_n(\varphi) = g(\varphi)$$

where  $g(\varphi) = e^{\varphi^2/4} f(\varphi) = -2\sqrt{2}\varphi^2 \left( P_{n-1}'(\varphi) - \frac{\varphi}{2} P_{n-1}(\varphi) \right)$ .

Now, we will solve for the complementary solutions to Eq.45. In order to so, we define a function  $D_\nu(\varphi)$  such that  $D_\nu = D_{-3n-1} = P_n$ . This way, we can rewrite Eqs.45 as a set



of differential equations whose solutions are well known (these are known as the parabolic cylinder functions or Weber-Hermite functions). Eqs.45 become

$$(46) \quad D_\nu''(\varphi) + \left( \nu + \frac{1}{2} - \frac{\varphi^2}{4} \right) D_\nu = 0$$

Due to the properties of all Weber-Hermite functions, Eq.46 has two linearly independent solutions, and if  $D_\nu(\varphi)$  is a solution, then  $D_{-\nu-1}(-i\varphi) = D_{3n}(-i\varphi)$  is also a solution. In that case, we will have the following linearly independent complementary solutions to Eqs.41b

$$(47) \quad g_n^{(1)}(\varphi) = D_{3n}(-i\varphi)e^{-\varphi^2/4} \quad g_n^{(2)}(\varphi) = D_{-3n-1}(\varphi)e^{-\varphi^2/4}$$

Finally, it can be shown that the general solution of Eq.41b will be given by

$$(48) \quad G_n(\varphi) = e^{-\varphi^2/4} \sum_{k^*=-3n-1}^{3n-1} b_k^{(n)} D_k(\varphi)$$

Here,  $b_k^{(n)}$  represent numerical coefficients that can be obtained recursively and the asterisk next to to index  $k$  indicates that we only sum either the even terms when  $n$  is odd, or the odd terms when  $n$  is even.

To obtain the  $b_k^{(n)}$  coefficients, we substitute Eq.48 into Eqs.41b. Using boundary conditions from Eq.42b and equating the terms with the same functional dependence on  $\varphi$ , the following recursive relations are obtained

For  $n = 1$ :

$$(49) \quad b_2^{(1)} = \frac{2}{3\sqrt{\pi}}, \quad b_0^{(1)} = \frac{1}{\sqrt{\pi}}, \quad b_{-2}^{(1)} = 0, \quad b_{-4}^{(1)} = \frac{-1}{\sqrt{\pi}}$$

For  $n > 1$ :

$$(50) \quad \begin{cases} b_{-3n+5 < k < 3n-5}^{(n)} = -\frac{2\sqrt{2}}{3n+k+1} \left[ (k+1)(k+2)b_{k+1}^{(n-1)} + (2k+1)b_{k-1}^{(n-1)} + b_{k-3}^{(n-1)} \right] \\ b_{3n-1}^{(n)} = -\frac{\sqrt{2}}{3n} b_{3n-4}^{(n-1)} \\ b_{3n-3}^{(n)} = -\frac{\sqrt{2}}{3n-1} \left[ b_{3n-6}^{(n-1)} + (6n-5)b_{3n-4}^{(n-1)} \right] \\ b_{-3n+3}^{(n)} = \frac{\sqrt{2}}{2} \left[ (6n-7)b_{-3n+2}^{(n-1)} - (3n-5)(3n-4)b_{-3n+4}^{(n-1)} \right] \\ b_{-3n+1}^{(n)} = -3\sqrt{2}(n-1)(3n-2)b_{-3n+2}^{(n-1)} \\ b_{-3n-1}^{(n)} = -\frac{3n}{2} \Gamma\left(\frac{3n}{2}\right) \sum_{k^*=-3n+1}^{3n-1} \frac{2^{(3n+k+1)/2}}{\Gamma\left(\frac{1-k}{2}\right)} b_k^{(n)} \end{cases}$$

Finally, the solution to Eq.5, given by substituting Eq.43 and Eq.48 into Eq.40, is

$$(51) \quad C(\varphi, \tau) = erf\left(\frac{\varphi}{\sqrt{2}}\right) + \sum_{n=1}^{\infty} \tau^{\frac{3n}{2}} \left( e^{-\varphi^2/4} \sum_{k^*=-3n-1}^{3n-1} b_k^{(n)} D_k(\varphi) \right)$$

To obtain an expression for the current through the RDE (given by Eq.7), we first substitute back into the original variable  $c$ . The current  $j(\tau)$  is given by

$$(52) \quad j(\tau) = D \left( \frac{\partial c}{\partial z} \right)_{z=0} = c_0 (aD^2)^{1/3} (2\tau)^{-1/2} \left( \frac{\partial C}{\partial \varphi} \right)_{\varphi=0}$$

Note that

$$\left( \frac{\partial C}{\partial \varphi} \right)_{\varphi=0} = \left[ \sqrt{\frac{2}{\pi}} e^{-\varphi^2/2} + \sum_{n=0}^{\infty} \tau^{\frac{3n}{2}} \left( -\frac{\varphi}{2} e^{-\varphi^2/4} \sum_{k^*=-3n-1}^{3n-1} b_k^{(n)} D_k(\varphi) + e^{-\varphi^2/4} \sum_{k^*=-3n-1}^{3n-1} b_k^{(n)} D'_k(\varphi) \right) \right]_{\varphi=0}$$

and finally

$$(53) \quad \left( \frac{\partial C}{\partial \varphi} \right)_{\varphi=0} = \sqrt{\frac{2}{\pi}} + \sum_{n=0}^{\infty} \tau^{\frac{3n}{2}} \left( \sum_{k^*=-3n-1}^{3n-1} b_k^{(n)} D'_k(0) \right)$$

To simplify Eq.53, we use the fact that the parabolic cylinder function  $D_k(\varphi)$  can be written as

$$(54) \quad D_k(\varphi) = 2^{k/2} e^{-\varphi^2/4} \left[ \frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{1}{2} - \frac{k}{2})} \Phi(-k/2, 1/2; \varphi^2/2) + \frac{\varphi}{\sqrt{2}} \frac{\Gamma(-\frac{1}{2})}{\Gamma(-\frac{k}{2})} \Phi(1/2 - k/2, 3/2; \varphi^2/2) \right]$$

where  $\Phi(a_\Phi, c_\Phi, x_\Phi)$  is Kummer's series given by

$$(55) \quad \Phi(a_\Phi, c_\Phi, x_\Phi) = 1 + \frac{a_\Phi x_\Phi}{c_\Phi 1!} + \frac{a_\Phi(a_\Phi + 1) x_\Phi^2}{c_\Phi(c_\Phi + 1) 2!} + \dots$$

It is easy to see that

$$\Phi(a_\Phi, c_\Phi, 0) = 1, \quad \text{and} \quad \frac{d}{d\varphi} \Phi(a_\Phi, c_\Phi, \varphi^2/2) = 0$$

These results, along with the fact that  $\Gamma(-1/2) = -2\sqrt{\pi}$ , are now used to calculate  $D'_k(0)$ . The result is

$$(56) \quad D'_k(0) = -\sqrt{2\pi} \frac{2^{k/2}}{\Gamma(-\frac{k}{2})}$$

By substituting Eq.56 into Eq.53 and then into Eq.52 and rearranging, we obtain

$$(57) \quad j(\tau) = \frac{c_0 (aD^2)^{1/3}}{\sqrt{\pi\tau}} \left\{ 1 - \pi \sum_{n=1}^{\infty} \left( \sum_{k^*=-3n-1}^{3n-1} \frac{2^{k/2} b_k^{(n)}}{\Gamma(-\frac{k}{2})} \right) \tau^{3n/2} \right\}$$

\*  $k$  involves values which are only even, for odd  $n$ , or only odd, for even  $n$

For simplicity, we can define the sequence  $\theta_n$  to be given by

$$(58) \quad \theta_n = \sum_{k^*=-3n-1}^{3n-1} \frac{2^{k/2} b_k^{(n)}}{\Gamma(-\frac{k}{2})}$$

Using this notation, Eq.57 becomes

$$j(\tau) = \frac{c_o(aD^2)^{1/3}}{\sqrt{\pi\tau}} \left( 1 - \pi \sum_{n=1}^{\infty} \theta_n \tau^{3n/2} \right)$$

as given by Eq.25.

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