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Series Solution to the Transient Convective Diffusion Equation for a Rotating Disk Electrode

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A series solution to the transient convective diffusion equation for the rotating disc electrode system is presented and compared to previously reported solutions. The solution presented here is for the entire time domain and agrees well with both the short and long time solutions presented earlier in the literature.

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The rotating disc electrode (RDE) system is a classical tool that has been used for years in electrochemical engineering.¹ The steady-state solution to the convective diffusion equation for the RDE system was presented many years ago by von Karman.² Analytical and numerical solutions to the nonsteady state convective diffusion equation have been reported.³⁻⁸ Unfortunately, all analytical solutions that have been presented are limited to particular regions of time (*i.e.*, short time or long time). Previous solutions provided by Deslouis *et al.*⁴ terminate with Airy's integrals, which are not invertible back to the time domain. Orazem⁶ discussed the Sturm-Liouville type of solution provided by Nisancioglu and Newman.⁷ Whereas the previous solutions require the evaluation of two separate expressions for short and long times, our solution provides a generalized solution for the problem, that converges over both short and long periods of time.

The Convective Diffusion Equation

The convective diffusion equation can be written as

$$\frac{\partial c}{\partial t} = D \nabla^2 c - \mathbf{v} \cdot \nabla c \quad [1]$$

where c is the concentration of the diffusing species, D , the diffusion coefficient and \mathbf{v} , the velocity of the electrolyte. Following the assumptions made by Orazem,⁶ and considering the region close to the electrode surface, Eq. 1 can be simplified as

$$\frac{\partial c}{\partial t} + \nu_z \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial z^2} \quad [2]$$

where ν_z is the axial component of the velocity and is given by⁶

$$\nu_z = -0.51023\nu^{-(1/2)}\Omega^{(3/2)}z^2 + 0.33333\nu^{-1}\Omega^2z^3 + \dots \quad [3]$$

in which, ν is the kinematic viscosity of the electrolyte, and Ω is the angular velocity of the electrode. Usually, the series in Eq. 3 is approximated with the first term for distances sufficiently close to the electrode surface.⁷ Here we include the first two terms for a better approximation of the velocity profile. Substitution of Eq. 3 into Eq. 2 yields

$$\frac{\partial c}{\partial t} + (-0.51023\nu^{-(1/2)}\Omega^{(3/2)}z^2 + 0.33333\nu^{-1}\Omega^2z^3) \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial z^2} \quad [4]$$

Equation 4 can be written in dimensionless form by defining a dimensionless concentration as follows

$$\theta(\zeta, \tau) = \frac{c_b - c}{(c_b - c)_{\zeta=0}} \quad [5]$$

where⁷

$$\zeta = z \left(\frac{a\nu}{3D} \right)^{1/3} \left(\frac{\Omega}{\nu} \right)^{1/2} \quad [6]$$

According to Eq. 5, the derivative of θ with respect to ζ , evaluated at $\zeta = 0$ is

$$\left(\frac{\partial \theta(\zeta, \tau)}{\partial \zeta} \right)_{\zeta=0} = -1 \quad [7]$$

Equation 7 can be thought of as a step change in the gradient of the concentration at the surface of the disc (*i.e.*, a step change in the flux of the reactant at $\zeta = 0$).

Far away from the electrode surface, the concentration of the reacting species equals its bulk concentration c_b

$$c(\infty, t) = c_b \quad [8]$$

so that

$$\theta(\zeta \rightarrow \infty, \tau) = 0 \quad [9]$$

where

$$\tau = \Omega \left(\frac{D}{\nu} \right)^{1/3} \left(\frac{a}{3} \right)^{2/3} t \quad [10]$$

The initial concentration for all z is given by

$$c(z, 0) = c_b \quad [11]$$

or

$$\theta(\zeta, \tau = 0) = 0 \quad [12]$$

Using the dimensionless variables defined in Eq. 5, 6, and 10, Eq. 4 can be written in nondimensional form as follows

$$\frac{\partial \theta(\zeta, \tau)}{\partial \tau} = (3\zeta^2 - k\zeta^3) \left(\frac{d\theta(\zeta, \tau)}{d\zeta} \right) + \frac{d^2\theta(\zeta, \tau)}{d\zeta^2} \quad [13]$$

where k is a function of the Schmidt number (Sc), as shown in the Notation.

Taking the Laplace Transform of Eq. 13 yields

$$s\theta(\zeta, s) = (3\zeta^2 - k\zeta^3) \left(\frac{d\theta(\zeta, s)}{d\zeta} \right) + \frac{d^2\theta(\zeta, s)}{d\zeta^2} \quad [14]$$

Equations 7 and 9 become, respectively,

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$$\left(\frac{d}{d\zeta}\Theta(\zeta,s)\right)_{\zeta=0} = -\frac{1}{s} \quad [15]$$

and

$$\Theta(\zeta \rightarrow \infty, s) = 0 \quad [16]$$

in the Laplace domain.

Series Solution—the Matrizant

A series solution for Eq. 14-16 can be obtained by using the Matrizant method.⁹ Let

$$\psi(\zeta,s) = \left(\frac{d}{d\zeta}\Theta(\zeta,s)\right) \quad [17]$$

so that the Eq. 14-16 can be written in matrix form

$$\frac{d\mathbf{Y}}{d\zeta} = \mathbf{A}\mathbf{Y} \quad [18]$$

where \mathbf{A} is given by

$$\mathbf{A} = \begin{bmatrix} 0 & 1 \\ s & -3\zeta^2 + k\zeta^3 \end{bmatrix} \quad [19]$$

and \mathbf{Y} is the dependent variable vector

$$\mathbf{Y} = \begin{bmatrix} \Theta(\zeta,s) \\ \psi(\zeta,s) \end{bmatrix} \quad [20]$$

The boundary conditions at $\zeta = 0$ are given by

$$\mathbf{Y}_0 = \begin{bmatrix} Y_{10} \\ -\frac{1}{s} \end{bmatrix} \quad [21]$$

where Y_{10} is the unknown dimensionless concentration, at the surface (*i.e.*, $\Theta(0,s)$).

Equations 18-21 can be solved for $\Theta(\zeta,s)$ using Maple 8 and the technique presented by Subramanian *et al.*⁹ The solution to Eq. 18 can be written as

$$\mathbf{Y} = [\Phi(\mathbf{A})]\mathbf{Y}_0 \quad [22]$$

where $\Phi(\mathbf{A})$ is defined as the matrizant of matrix \mathbf{A} and is given by

$$\Phi(\mathbf{A}) = \mathbf{I} + \int_0^\zeta [\mathbf{A}(\zeta_1)d\zeta_1] + \int_0^\zeta \left[\mathbf{A}(\zeta_1) \int_0^{\zeta_1} [\mathbf{A}(\zeta_2)]d\zeta_2 \right] d\zeta_1 + \int_0^\zeta \left[\mathbf{A}(\zeta_1) \int_0^{\zeta_1} \left[\mathbf{A}(\zeta_2) \int_0^{\zeta_2} [\mathbf{A}(\zeta_3)]d\zeta_3 \right] d\zeta_2 \right] d\zeta_1 + \dots \quad [23]$$

Evaluation of the integrals and substitution of Eq. 23, with two terms included in $\Phi(\mathbf{A})$, into Eq. 22 yields

$$\mathbf{Y} = \begin{bmatrix} \left(1 + \frac{1}{2}s\zeta^2\right)Y_{10} - \frac{\zeta - \frac{1}{4}\zeta^4 + \frac{1}{20}k\zeta^5}{s} \\ \left(s\zeta + \frac{1}{5}ks\zeta^5 - \frac{3}{4}s\zeta^4\right)Y_{10} - \frac{-\zeta^3 + \frac{1}{4}k\zeta^4 + 1 + \frac{1}{32}k^2\zeta^8 - \frac{1}{4}k\zeta^7 + \frac{1}{2}\zeta^6 + \frac{1}{2}s\zeta^2}{s} \end{bmatrix} \quad [24]$$

Next, Y_{10} is determined from the first element of \mathbf{Y} by imposing an approximation to Eq. 16 (*i.e.*, $\Theta(\zeta = 2, s) = 0$) that was obtained from Fig. 2 in Nisancioglu and Newman.⁷ The first element of \mathbf{Y} is (see Eq. 24)

$$\Theta(\zeta,s) = \left(1 + \frac{1}{2}s\zeta^2\right)Y_{10} - \frac{\zeta - \frac{1}{4}\zeta^4 + \frac{1}{20}k\zeta^5}{s} \quad [25]$$

which when set equal to zero with $\zeta = 2$ yields

$$Y_{10} = \frac{8k - 10}{5s(1 + 2s)} \quad [26]$$

Therefore

$$\Theta(\zeta,s) = \frac{\left(1 + \frac{1}{2}s\zeta^2\right)(8k - 10)}{5s(1 + 2s)} - \frac{\zeta - \frac{1}{4}\zeta^4 + \frac{1}{20}k\zeta^5}{s} \quad [27]$$

Equation 27 can be inverted back to the time domain to obtain the transient concentration profile in the time domain, $\theta(\zeta, \tau)$. The expression obtained using Maple is as follows (see Appendix for the Maple Code)

$$\theta(\zeta,\tau) = -\frac{1}{2}e^{-(\tau/2)}\zeta^2 + 2e^{-(\tau/2)} - 2 + \frac{2}{5}ke^{-(\tau/2)}\zeta^2 - \frac{8}{5}ke^{-(\tau/2)} + \frac{8}{5}k - \zeta + \frac{\zeta^4}{4} - k\frac{\zeta^5}{20} \quad [28]$$

Discussion and Conclusion

The solution obtained from the method presented here is useful because it provides an analytical expression for the time-dependent concentration profile of the RDE system for the complete time domain. Figure 1 presents a comparison of our solution to the short and long time solutions presented by others for $\theta_0(\tau)$. Three digit agreement between the short time solution⁷ and our solution (obtained with 11 terms included in $\Phi(\mathbf{A})^a$) was obtained in the range of τ between 0.01 and 0.5. Similar agreement was obtained with the long time series⁷ from $\tau = 0.1$ to 10.

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Appendix

The Matrizant Solution of the Transient Convective Diffusion Equation Using Maple 8

The Matrizant solution presented here includes the first two terms of the series. The number of terms could be increased as required by setting 'terms' to the appropriate value

> restart;

> with (linalg): with (plots): with (intrans): with (DEtools):

The Original Convective Diffusion Equation (after all assumptions and simplifications)

^a Not presented here for brevity; available from Ralph E. White upon request.

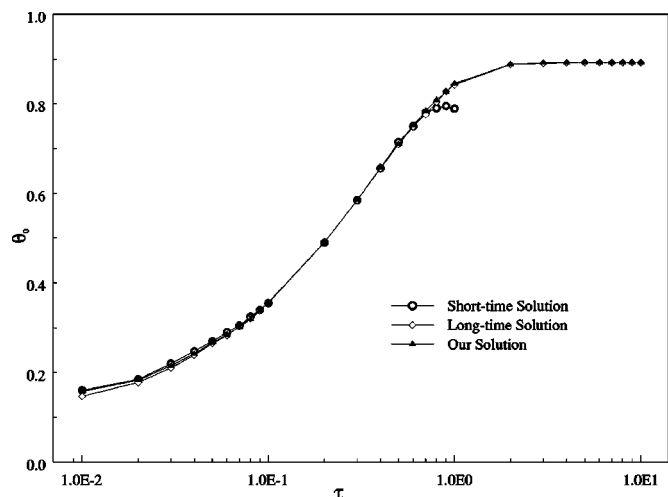


Figure 1. Comparison of our solution with $k = 0.1$ with the short-time solution from Ref. 8 and the long-time solution from Ref. 7.

is

>PDE:=diff(c(z,t),t) + v[z]*diff(c(z,t),z) = Dif*diff(c(z,t),z\$2);

$$PDE := \left(\frac{\partial}{\partial t} c(z,t) \right) + v_z \left(\frac{\partial}{\partial z} c(z,t) \right) = \text{Dif} \left(\frac{\partial^2}{\partial z^2} c(z,t) \right) \quad [A-1]$$

Nondimensional Form

>NPDE:=diff(theta(zeta,tau),zeta\$2) = diff(theta(zeta,tau),tau) + (-3*zeta^2 + k*zeta^3)*diff(theta(zeta,tau),zeta);theta(zeta,0):=0;

$$NPDE := \frac{\partial^2}{\partial \zeta^2} \theta(\zeta, \tau) = \left(\frac{\partial}{\partial \tau} \theta(\zeta, \tau) \right) + (-3\zeta^2 + k\zeta^3) \left(\frac{\partial}{\partial \zeta} \theta(\zeta, \tau) \right) \quad [A-2]$$

$$\theta(\zeta, 0) := 0$$

Boundary conditions

>BC1:=theta(infinity,tau) = 0; BC2:=diff(theta(0,tau),zeta) = -1;

$$BC1 := \theta(\infty, \tau) = 0 \quad [A-3]$$

$$BC2 := \frac{\partial}{\partial \zeta} \theta(0, \tau) = -1 \quad [A-4]$$

Laplace Transformation

>LBC1 :=laplace(BC1,tau,s); LBC2:=laplace(BC2,tau,s);

$$LBC1 := \text{laplace}(\theta(\infty, \tau), \tau, s) = 0 \quad [A-5]$$

$$Y = \begin{bmatrix} \left(1 + \frac{1}{2} s \zeta^2 \right) y_{10} - \frac{\zeta - \frac{1}{4} \zeta^4 + \frac{1}{20} k \zeta^5}{s} \\ \left(s \zeta + \frac{1}{5} k s \zeta^5 - \frac{3}{4} s \zeta^4 \right) y_{10} - \frac{-\zeta^3 + \frac{1}{4} k \zeta^4 + 1 + \frac{1}{32} k^2 \zeta^8 - \frac{1}{4} k \zeta^7 + \frac{1}{2} \zeta^6 + \frac{1}{2} s \zeta^2}{s} \end{bmatrix} \quad [A-15]$$

$$LBC2 := \frac{\partial}{\partial \zeta} \text{laplace}(\theta(0, \tau), \tau, s) = -\frac{1}{s} \quad [A-6]$$

>LBC1 :=subs(diff(laplace(theta(zeta,tau),tau,s),zeta) = eval(D(theta)(zeta),zeta = 1), laplace(theta(zeta,tau),tau,s) = eval(theta(zeta),zeta = 2),LBC1);

$$LBC1 := \theta(2) = 0 \quad [A-7]$$

>LBC2 :=subs(diff(laplace(theta(zeta,tau),tau,s),zeta) = eval(D(theta)(zeta),zeta = 0),laplace(theta(zeta,tau),tau,s) = eval(theta(zeta),zeta = 0),LBC2);

$$LBC2 := D(\theta)(0) = -\frac{1}{s} \quad [A-8]$$

>LDE:=simplify(laplace(NPDE,tau,s));
laplace(theta(zeta,tau),tau,s) :=theta(zeta);
LDE:=eval(LDE);

$$LDE = \frac{d^2}{d\zeta^2} \theta(\zeta) = s\theta(\zeta) - 3 \left(\frac{d}{d\zeta} \theta(\zeta) \right) \zeta^2 + \left(\frac{d}{d\zeta} \theta(\zeta) \right) k\zeta^3 \quad [A-9]$$

The Matrizant Solution

>terms:=2; N:=2;

nvars:=2

N:=2

>A:=matrix([[0,1],[s,-3*zeta^2+k*zeta^3]]);
Y0:=matrix([[y10],[1/s]]);

$$A = \begin{bmatrix} 0 & 1 \\ s & -3\zeta^2 + k\zeta^3 \end{bmatrix} \quad [A-10]$$

$$Y0 := \begin{bmatrix} y_{10} \\ \frac{1}{s} \end{bmatrix} \quad [A-11]$$

>id:=Matrix(N,N,shape = identity);X1:=matrix(N,N):X2:=matrix(N,N):S := matrix(N,N);

$$id := \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad [A-12]$$

>X1:=map(int,subs(zeta = zeta1,evalm(A)),zeta1 = 0..zeta);

$$X1 := \begin{bmatrix} 0 & \zeta \\ s\zeta & -\zeta^3 + \frac{1}{4}k\zeta^4 \end{bmatrix} \quad [A-13]$$

>mat:=evalm(id + X1);

$$mat := \begin{bmatrix} 1 & \zeta \\ s\zeta & -\zeta^3 + \frac{1}{4}k\zeta^4 + 1 \end{bmatrix} \quad [A-14]$$

> for i from 2 to terms do

S:=evalm(subs(zeta = zeta1,evalm(A))&*subs(zeta = zeta1,evalm(X1)));X2

:=map(int,S,zeta1 = 0..zeta):mat:=evalm(mat + X2):X1

:=evalm(X2):od:evalm(mat);

>Y:=evalm(mat&*Y0);

>y:=Y[1,1]; dybdx:=Y[2,1];

$$y := \left(1 + \frac{1}{2} s \zeta^2 \right) y_{10} - \frac{\zeta - \frac{1}{4} \zeta^4 + \frac{1}{20} k \zeta^5}{s} \quad [A-16]$$

>y10:=solve(subs(zeta = 2,y) = 0,y10);

$$y_{10} = \frac{8k-10}{5s(1+2s)} \quad [A-17]$$

>theta(zeta):=eval(y);

$$\theta(\zeta) := \frac{2\left(1 + \frac{s\zeta^2}{2}\right)(-5 + 4k)}{5s(1 + 2s)} - \frac{\zeta - \frac{1}{4}\zeta^4 + \frac{1}{20}k\zeta^5}{s} \quad [\text{A-18}]$$

'tthet' below is the dimensionless concentration in the time domain

>tthet:=invlaplace(theta(zeta), s, tau);

$$\begin{aligned} \text{tthet} := & -\frac{1}{2}e^{-(\tau/2)\zeta^2} + 2e^{-(\tau/2)} - 2 + \frac{2}{5}ke^{-(\tau/2)\zeta^2} - \frac{8}{5}ke^{-(\tau/2)} + \frac{8}{5}k \\ & - \zeta + \frac{\zeta^4}{4} - k\frac{\zeta^5}{20} \end{aligned} \quad [\text{A-19}]$$

List of Symbols

A	the system matrix
a	constant (= 0.51023)
c(z,t)	concentration of the diffusing species (mol/m ³)
c_b	bulk concentration (mol/cm ³)
D	diffusion coefficient (m ² /s)
I	Identity matrix
k	$3.5374 \times \text{Sc}^{-1/3}$
Sc	Schmidt number (ν/D)
s	dimensionless Laplace variable
t	time(s)
v_z	velocity in the z direction (cm/s)

Y	dimensionless vector of unknown $\Theta(\zeta, s)$ and $\psi(\zeta, s)$
Y₀	dimensionless initial condition vector
z	distance (cm) in the axial direction, from the electrode surface
ν	kinematic viscosity (cm ² /s)
Ω	angular velocity of the disc (s ⁻¹)
θ	dimensionless concentration, $\theta(\zeta, \tau) = (c_b - c)/(\partial c/\partial \zeta)_{\zeta=0}$
$\theta_0(\tau)$	dimensionless concentration at the electrode surface ($\zeta = 0$)
$\Theta(\zeta, s)$	dimensionless concentration in the Laplace domain
τ	dimensionless time, $\tau = \Omega(D/\nu)^{1/3}(a/3)^{2/3}t$
ψ	dimensionless concentration flux in the Laplace domain $\psi(\zeta, s) = (d/\Theta(\zeta, s)/d\zeta)$
ζ	dimensionless distance, $\zeta = z(\Omega\nu/3D)^{1/3}\sqrt{\Omega/\nu}$

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