Numerical Solution to Problems of Mass Transfer in One Dimension

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NUMERICAL SOLUTIONS TO PROBEMS OF MASS TRANSFER

1. Consider a porous solid rod with one end in contact with a liquid, the other in contact with a gas, and the sides are surrounded by non-porous solid material.

At the base of the rod, the conc. is @ it equil. (with the liquid) value of $C_A = 10\ \text{mol.dm}^{-3}$. The gas at the top exhibits a conc. of $5\ \text{mol.dm}^{-3}$. (High pressure). We are interested in the steady state concentration profile.

By discretization of the governing equations, develop the relevant equation that can be used to find the concentration profile through the tube length. State any assumptions used. (The rod has a length of 1 m)

2. Consider the same problem as described in question 1, for the unsteady state case. Assume this time that the tube initially contained none of comp-A, and that the gas phase concentration was not fixed. The only data available is that, at the base, the concentration of ~~the~~ A will be the equilibrium value, whereas at the top, there is no gradient in concentrat

For both questions, the f/g. approximation will prove useful:

$$\frac{\partial^2 y}{\partial x^2} = \frac{y|_{x+\Delta x} - 2\, y|_x + y|_{x-\Delta x}}{(\Delta x)^2}$$

3. Develop the variation in conc. profile in the radial direction for a cylinder of radius 20 cm if the surface concentration is 10 mol.m^{-3} $= C_S$,

surface mass transfer coefficient is $k_S = 5 \cdot 10^{-5}$ m.s^{-1}

diffusivity $D_{AB} = 1 \cdot 10^{-7}$ m^2.s^{-1}

for both the steady and unsteady state given the following sets of boundary conditions:

3.1 fixed boundary points: $C_A(r=0) = C_c = C_S/2$

$C_A(r=R) = C_S$

3.2 surface conc. fixed, symmetry cond^n @ centre:

$$C_A(r=R) = C_S$$

$$\left.\frac{dC_A}{dr}\right|_{r=0} = 0$$

3.3 mass transfer limitation in external film, concentration symmetry @ centre:

$$D_{AB} \left.\frac{dC_A}{dr}\right|_{r=R} = k_c (C_A - C_{AS})$$

$$\left.\frac{dC_A}{dr}\right|_{r=0} = 0$$

Develop the relevant equations from 1st principles

The ffg. approximations are useful: $\frac{dy}{dx} = \frac{y_{i+1} - y_i}{x_{i+1} - x_i}$

$$\frac{d^2y}{dx^2} = \frac{y_{i+1} - 2y_i + y_{i-1}}{(\Delta x)^2}$$

4. Perform the same operation as 3. for a sphere.

SOLUTIONS

1. Steady state, 1-D $\rightarrow \dfrac{\partial^2 C_A}{\partial x^2} = 0$

numerical approx $\rightarrow C_{A_{i-1}} - 2C_{A_i} + C_{A_{i+1}} = 0$

have also two end points given:

$C_{A_1} = C_s/2, \quad C_{A_N} = C_s$ (boundary cond^{n}s.)

choose $N=5$

$\therefore i=1 \rightarrow C_{A_1} = C_s/2$

$i=2 \rightarrow C_{A_1} - 2C_{A_2} + C_{A_3} = 0$

$i=3 \rightarrow C_{A_2} - 2C_{A_3} + C_{A_4} = 0$

$i=4 \rightarrow C_{A_3} - 2C_{A_4} + C_{A_5} = 0$

$i=5 \rightarrow C_{A_5} = C_s$

Which may be put in vector-matrix form:

$$\underline{\underline{A}} \times \underline{c} = \underline{b} \qquad (1)$$

where

$$\underline{\underline{A}} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 1 & -2 & 1 & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 \\ 0 & 0 & 1 & -2 & 1 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad \underline{c} = \begin{bmatrix} C_{A_1} \\ C_{A_2} \\ C_{A_3} \\ C_{A_4} \\ C_{A_5} \end{bmatrix}, \quad \underline{b} = \begin{bmatrix} C_s/2 \\ 0 \\ 0 \\ 0 \\ C_s \end{bmatrix}$$

$\therefore$ can simply invert $\underline{\underline{A}}$ to get $\underline{c}$ as follows:

$$\underline{c} = inv(\underline{\underline{A}}) \times \underline{b} \rightarrow$$

This problem is really trivial, since $\dfrac{\partial^2 C_A}{\partial x^2} = 0$ can be twice integrated to give $C_A = k_1 x + k_2 \rightarrow$ straight line

2. Unsteady state, 1-D $\rightarrow \dfrac{dC_A}{dt} = D_{AB}\dfrac{\partial^2 C_A}{\partial x^2}$

Discretize $\rightarrow \dfrac{C_{i,j+1} - C_{i,j}}{\Delta t} = D_{AB}\dfrac{C_{i+1,j} - 2C_{i,j} + C_{i-1,j}}{(\Delta x)^2}$ — ①

where index i refers to argument x and index j refers to argument t. ✓

Rearrange ① to get:

$$C_{i,j+1} = C_{i,j} + \frac{D_{AB}\Delta t}{(\Delta x)^2}\left(C_{i-1,j} - 2C_{i,j} + C_{i+1,j}\right) \quad -③$$

we recognize that a similar system of eqns @ we had in Q.1 will arise. We expect a general form that looks like

$$\underline{C}_{j+1} = \underline{C}_j + \frac{D_{AB}\Delta t}{(\Delta x)^2}\underline{\underline{A}}\,\underline{C}_j \quad -②$$

How about boundary conditions?

if we have i) 2 fixed points: $C_{1,j} = \tilde{C}_1$ and $C_{N,j} = \tilde{C}_2$

ii) surface fixed and symmetry at centre:

$$C_{N,j} = C_S$$

and $\left.\dfrac{dC_A}{dx}\right|_{x=L} = 0 \rightarrow C_{1,j} = C_{2,j}$

iii) (a) mass transfer limitation in ext. film + (b) symmetry @ centre

(a) $D_{AB}\left.\dfrac{dC_A}{dx}\right|_{x=L} = k_c\left(C_S - C_A|_{x=L}\right)$

$\rightarrow \dfrac{C_{AN,j} - C_{AN-1,j}}{\Delta x} = \dfrac{k_c}{D_{AB}}\left(C_S - C_{AN,j}\right)$

$\therefore C_{AN,j}\left(\dfrac{1}{\Delta x} + \dfrac{k_c}{D_{AB}}\right) + C_{AN-1,j}\left(-\dfrac{1}{\Delta x}\right) = \dfrac{k_c C_S}{D_{AB}}$

(b) $C_{A1,j} = C_{A2,j}$

The question actually specifies that at the base, the concentration is the equil. value → one fixed point, whereas at the top, no gradient.
∴ B.C. set ii) applies.

How to solve it numerically? Suggest using ③ to get $\underline{c}_j$ and force B.C.'s in @ end points:

$$c_{1,j} = C_S$$
$$c_{N,j} = c_{N-1,j}$$

Initial condition:
$C_{A_0}(x>0)=0,\ C_{A_0}(x=0)=C_{A_e}$
$\rightarrow \underline{C}_{A_{j=1}} = [C_{A_e}\ 0\ 0 \cdots 0]^T$

<u>Q.3 Solution:</u> For cylinder governing PDE is

$$\frac{dC_A}{dt} = D_{AB}\left(\frac{\partial^2 C_A}{\partial r^2} + \frac{1}{r}\frac{\partial C_A}{\partial r}\right)$$

$$\therefore \frac{C_{i,j+1} - C_{i,j}}{\Delta t} = D_{AB}\left(\frac{C_{Ai+1,j} - 2C_{Ai,j} + C_{Ai-1,j}}{(\Delta r)^2} + \frac{1}{r}\frac{C_{Ai+1} - C_{Ai-1}}{2\Delta r}\right) \quad (4)$$

This time, recognise that we have an extra $\frac{1}{r}$ factor (see last term) - equations not so simple.
However, if Δr is const. for each interval, then we realize that $r = (i-1)\Delta r$
∴ (4) becomes

$$C_{i,j+1} = C_{i,j} + \frac{D_{AB}\Delta t}{(\Delta r)^2}\left[C_{i+1,j}\left(1+\frac{1}{2(i-1)}\right) - 2C_{i,j} + C_{i-1,j}\left(1-\frac{1}{2(i-1)}\right)\right]$$

Which again suggests using the form:

$$\underline{c}_{j+1} = \underline{c}_j + \left(\frac{D_{AB}\Delta t}{(\Delta r)^2}\right) \underline{\underline{A}} \times \underline{c}_j$$

Where

$$\underline{\underline{A}} = \begin{bmatrix} \ddots & \ddots & & & 0 \\ \ddots & \ddots & \ddots & & \\ & \left(1-\frac{1}{2(i-1)}\right) & (-2) & \left(1+\frac{1}{2(i-1)}\right) & \\ & & \ddots & \ddots & \ddots \\ 0 & & & \ddots & \ddots \end{bmatrix}$$

How about boundary conditions?

3.1. a. $C_A(r=0) = C_s \rightarrow C_{1,j} = C_s/2$

b. $C_A(r=R) = C_s \rightarrow C_{N,j} = C_s$

I.C.: $\underline{C}_0 = \left[\frac{C_s}{2} \;\; 0 \;\; 0 \ldots 0 \;\; C_s\right]^T$

3.2 a. $C_A(r=R) = C_s \rightarrow C_{N,j} = C_s$

b. $\left.\frac{dC_A}{dr}\right|_{r=0} = 0 \rightarrow \frac{C_{A_{2,j}} - C_{A_{1,j}}}{\Delta r} = 0 \rightarrow C_{A_{1,j}} - C_{A_{2,j}} = 0$

I.C.: $\underline{C}_0 = [0 \;\; 0 \cdots 0 \;\; C_s]^T$

3.3 a. $D_{AB} \left.\frac{dC_A}{dr}\right|_{r=R} = k_c \left(C_s - C_A\right)\Big|_{r=R}$

$\rightarrow D_{AB} \frac{C_{A_{N,j}} - C_{A_{N-1,j}}}{\Delta r} = k_c \left(C_s - C_{A_{N,j}}\right)$

$\rightarrow C_{A_{N,j}} \left(\frac{D_{AB}}{\Delta r} + k_c\right) + C_{A_{N-1,j}} \left(-\frac{D_{AB}}{\Delta r}\right) = k_c C_s$

b. $\left.\frac{dC_A}{dr}\right|_{r=0} = 0 \rightarrow C_{A_{1,j}} - C_{A_{2,j}} = 0$

I.C.: $\underline{C}_0 = [0 \;\; 0 \;\; 0 \ldots 0]^T$

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% R Rawatlal, School of Chemical Engineering, University of KwaZulu-Natal,
% October 2004
% Numerical solution to the diffusion equation in 1-D

close all; clear all;clc
r1 = 0; r2 = .02; N = 20; r = linspace(r1,r2,N); Dr = r(2)-r(1);
t1 = 0; t2 = 3e3; M = 1000; t = linspace(t1,t2,M); Dt = t(2)-t(1);

BC = 3  ; % 1 - fixed end points, 2 - centre has symmetry condition, 3 - free end points with fixed conc in fluid phase

Cs = 10;  % Surface concentration or bulk fluid concentration
Cc = 5;   % Centre concentration
DAB = 1e-7; % Diffusivity
ks = 5e-5;  % Surface/external film mass transfer coefficient
% ================================================

for i = 2:(N-1)
   A(i,i-1) = 1 + 1/2/(i-1);
   A(i,i)   = -2;
   A(i,i+1) = 1 - 1/2/(i-1);
end;
b = zeros(N,1);

c0 = zeros(N,1);

if (BC == 1)
   A(1,1) = 1; A(1,2) = -1; c0(1) = Cc;
   A(N,N) = 1; A(N,N-1) = -1; c0(N) = Cs;
elseif (BC == 2)
   A(1,1) = -1; A(1,2) = 1;
   A(N,N) = 1;              c(N) = Cs;
elseif (BC == 3)
   A(1,1) = -1; A(1,2) = 1; b(1) = 0;
   A(N,N-1) = DAB/Dr;  A(N,N) = -DAB/Dr+ks;  b(N) = ks*Cs;
end;

c(1,:) = c0';
for j = 2:M
   c(j,:) = c(j-1,:) + Dt*DAB/(Dr^2)*(A*c(j-1,:)')';
   if (BC == 1)
      c(j,1) = Cc;
      c(j,N) = Cs;
   elseif (BC == 2)
      c(j,1) = c(j,2);
      c(j,N) = Cs;
   elseif (BC == 3)
      c(j,1) = c(j,2);
      c(j,N) = (ks*Cs + c(j,N-1)*DAB/Dr)/(DAB/Dr+ks);
   end;
end;
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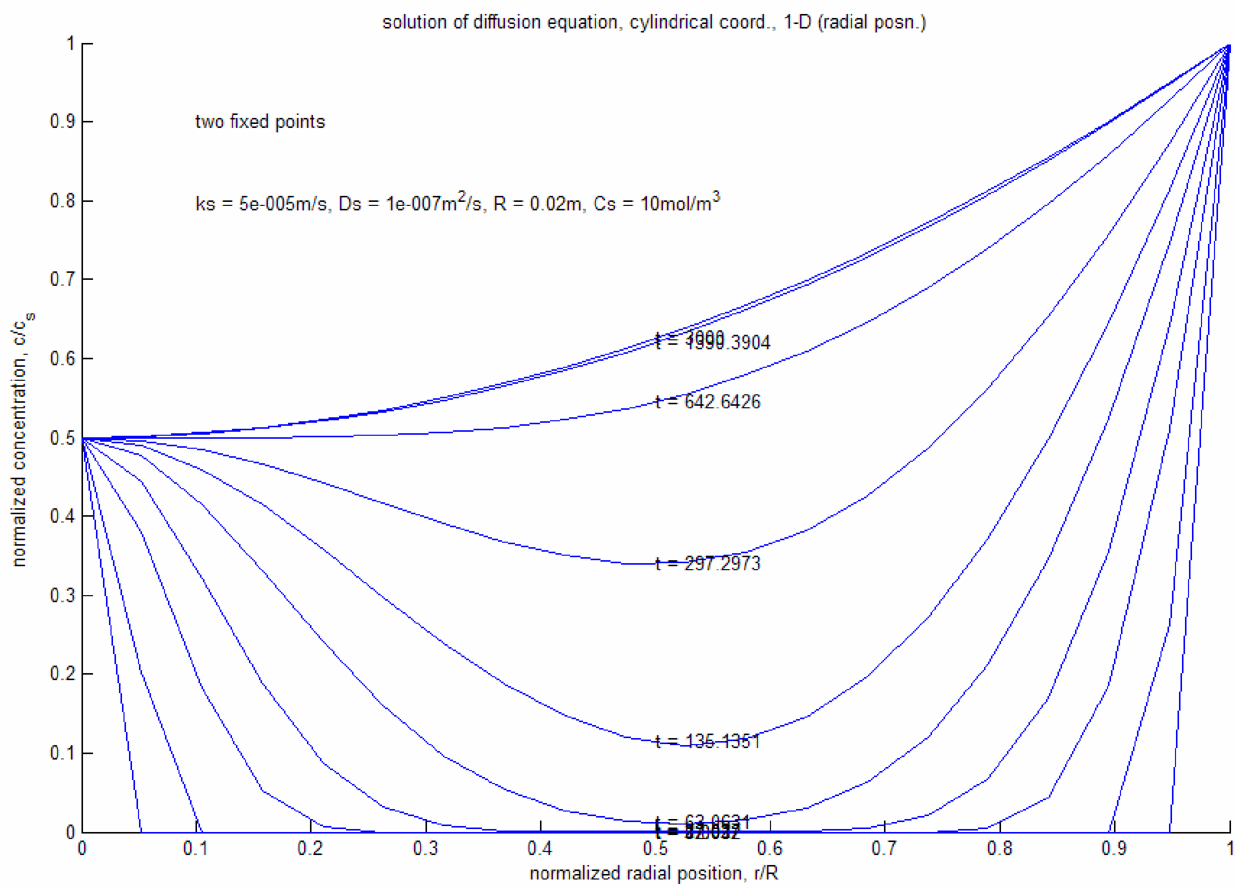
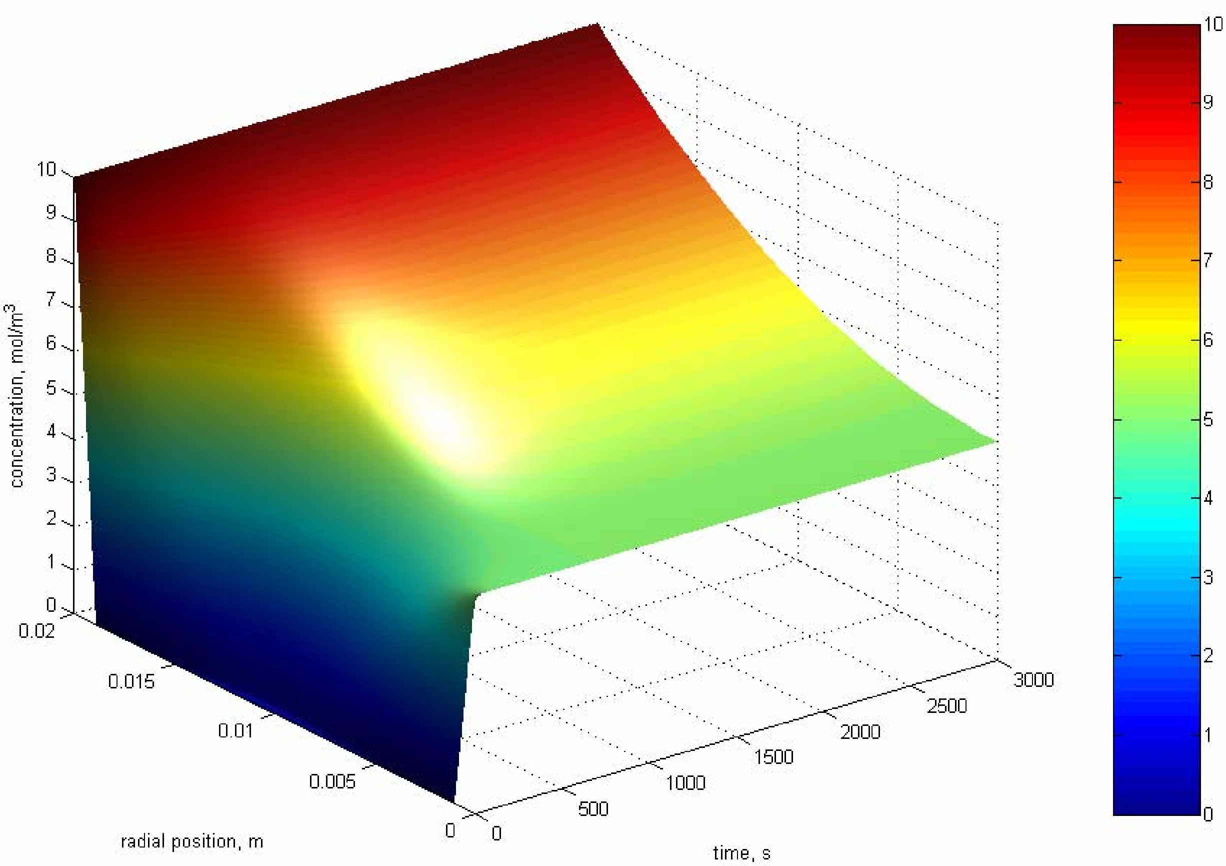
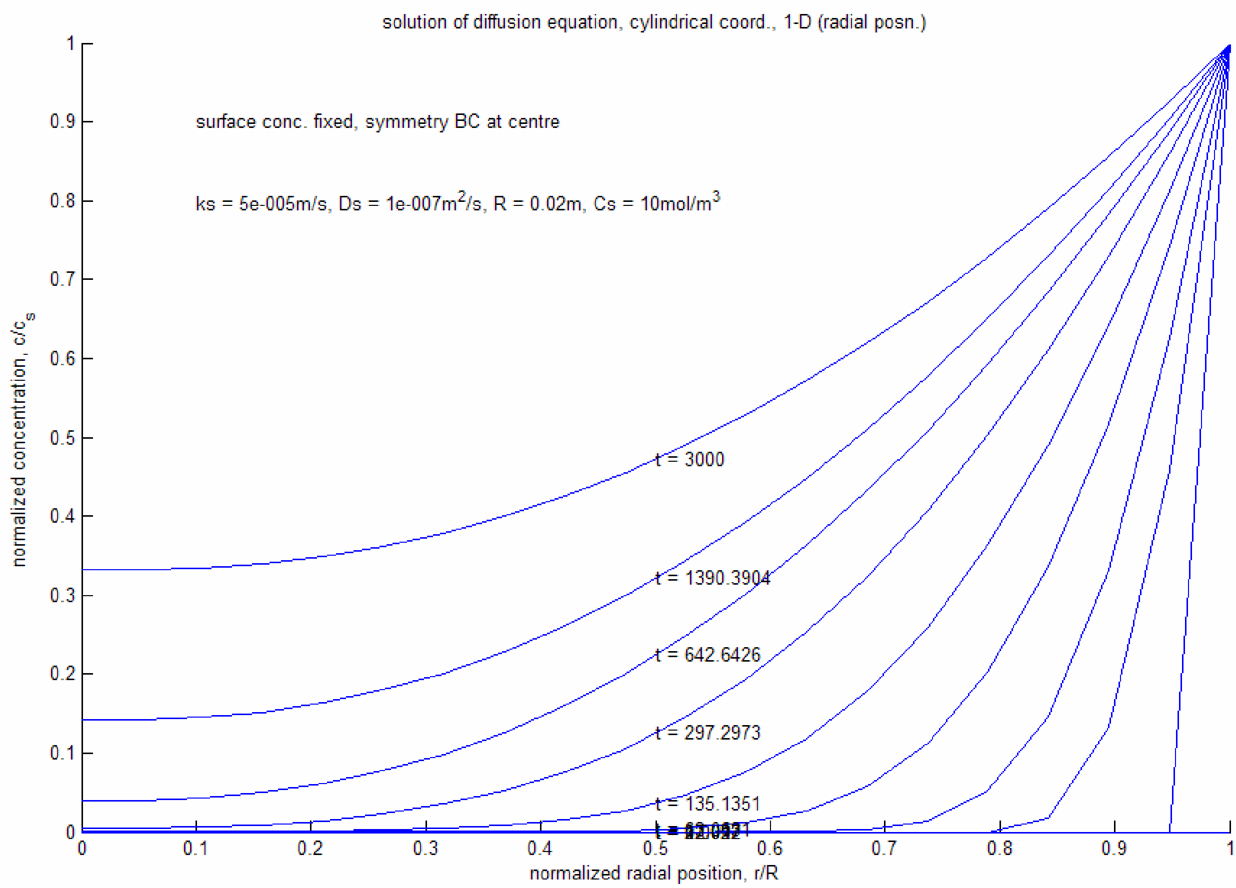
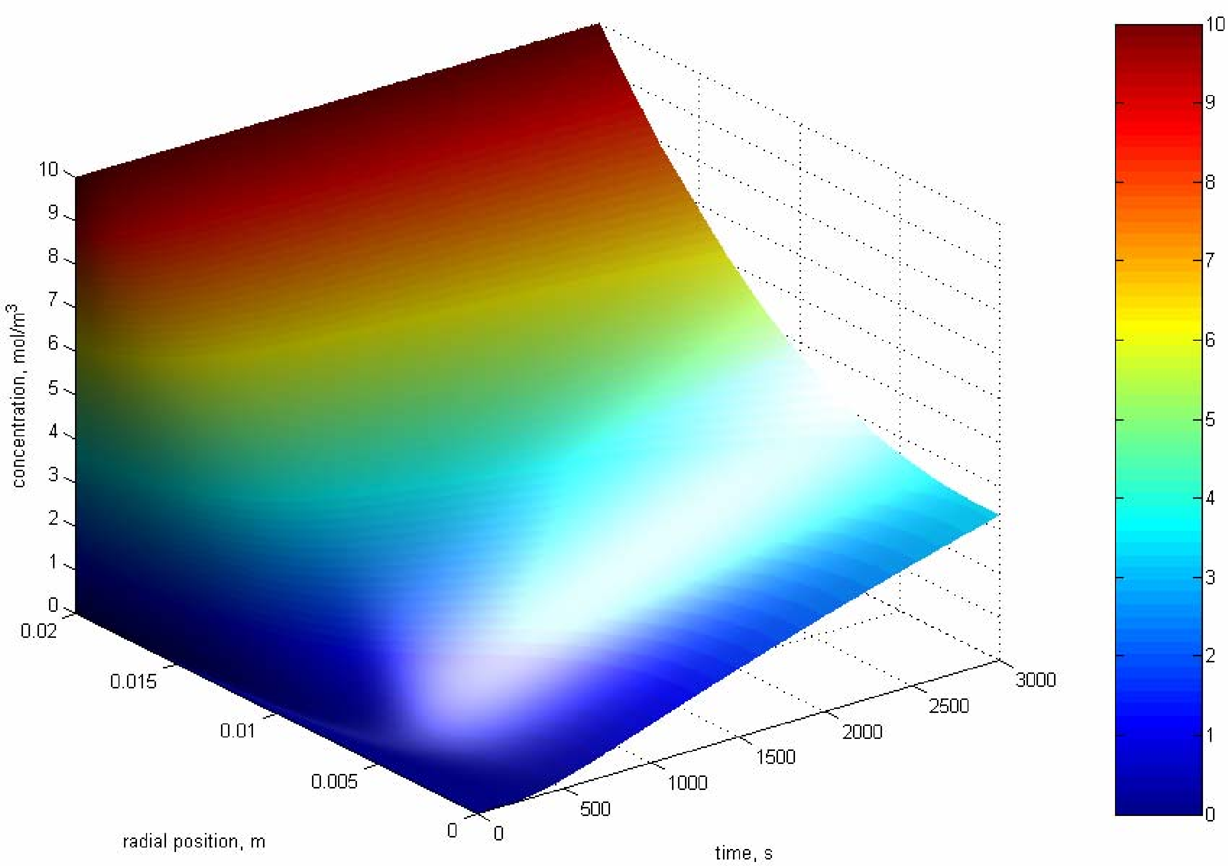


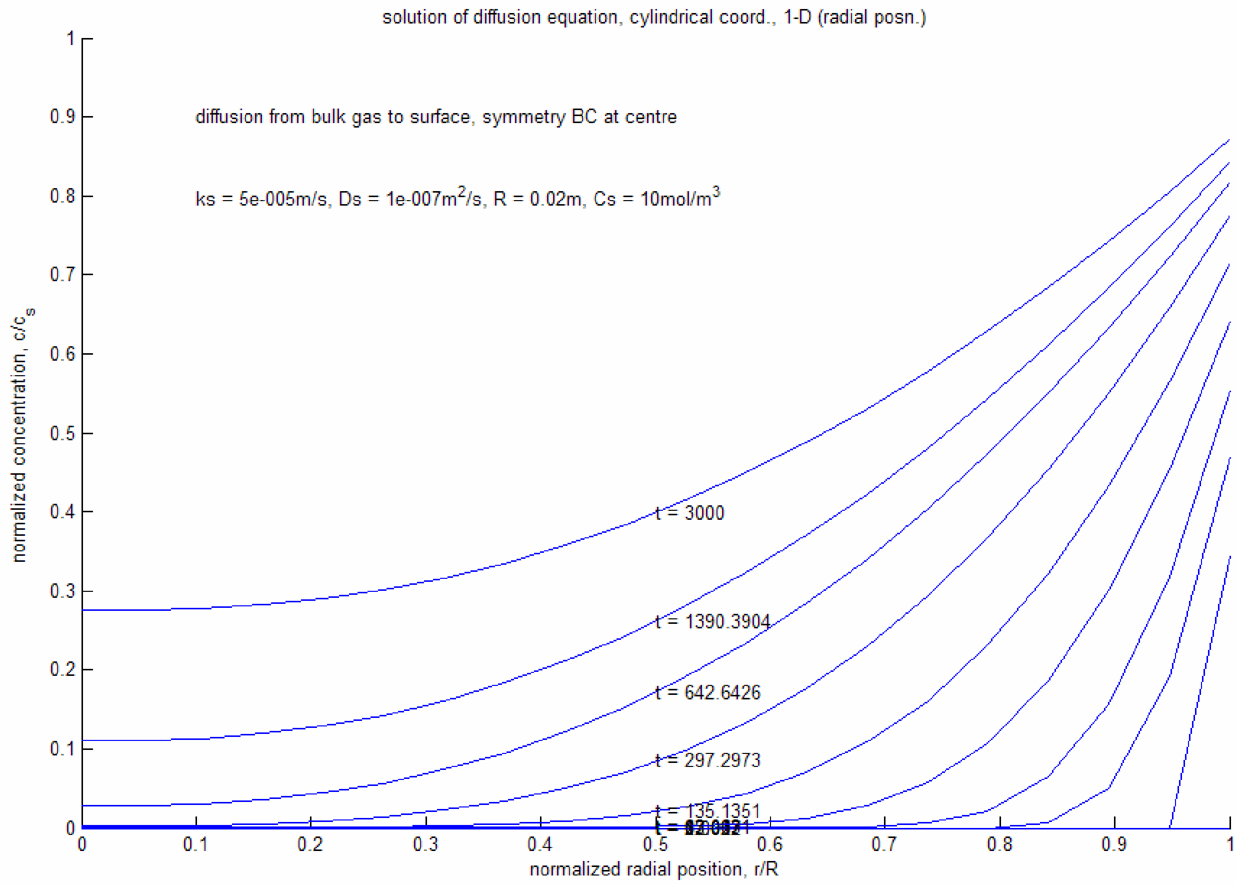
solution of diffusion equation, cylindrical coord., 1-D (radial posn.)
two fixed points
ks = 5e-005m/s, Ds = 1e-007m^2/s, R = 0.02m, Cs = 10mol/m^3
t = 1990.3904
t = 642.6426
t = 297.2973
t = 135.1351
normalized concentration, c/c$_s$
normalized radial position, r/R



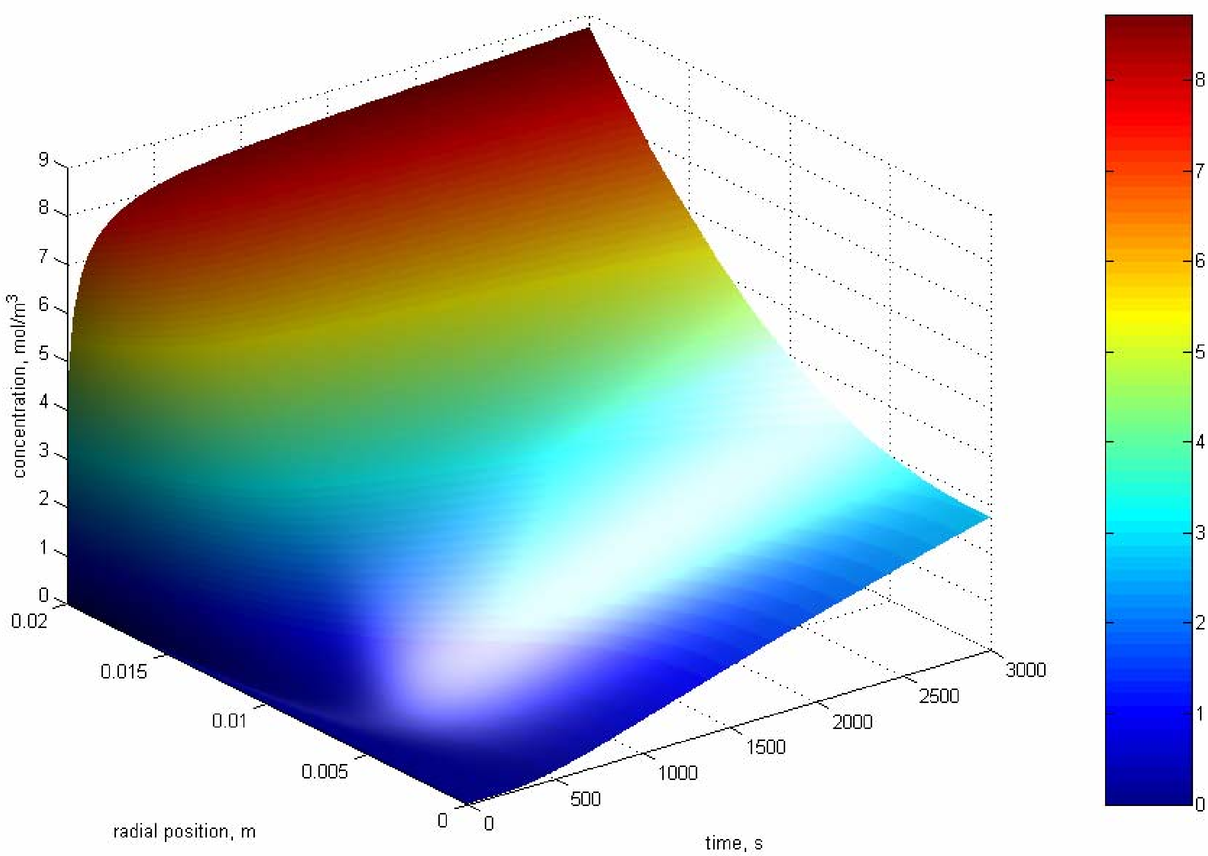
concentration, mol/m^3
radial position, m
time, s


solution of diffusion equation, cylindrical coord., 1-D (radial posn.)
surface conc. fixed, symmetry BC at centre
ks = 5e-005m/s, Ds = 1e-007m²/s, R = 0.02m, Cs = 10mol/m³
t = 3000
t = 1390.3904
t = 642.6426
t = 297.2973
t = 135.1351
normalized concentration, c/c_s
normalized radial position, r/R
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1


concentration, mol/m³
radial position, m
time, s
0.02
0.015
0.01
0.005
0
500
1000
1500
2000
2500
3000
10



solution of diffusion equation, cylindrical coord., 1-D (radial posn.)
diffusion from bulk gas to surface, symmetry BC at centre
ks = 5e-005m/s, Ds = 1e-007m²/s, R = 0.02m, Cs = 10mol/m³
t = 3000
t = 1390.3904
t = 642.6426
t = 297.2973
t = 135.1351
normalized concentration, c/c_s
normalized radial position, r/R



concentration, mol/m³
radial position, m
time, s