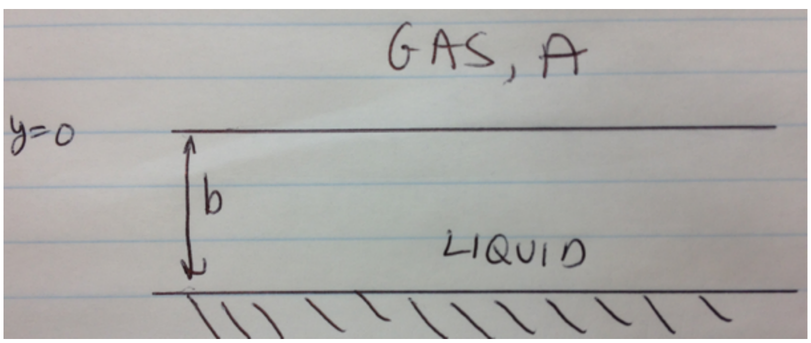
CBE 60544
Spring 2014
Test #1
March 3, 2014

1. Gas absorption into a liquid layer (30 points)

One of the largest volume processes in the chemical industries is gas - liquid contacting. Such processes could be "scrubbing" (removal of a component of a gas so as to purify the rest of the stream), "absorption" (addition of a component of the gas into the for reaction or to make "soda pop") or "stripping" (using the gas to remove a component of the liquid).

As with any process, capital costs are such that the equipment volume needs to be minimized. For a process such as a scrubbing operation, there will be a reduction in total liquid flow if a reaction can be used to increase the effective capacity of the liquid. Further, it is possible that a reaction could also increase the *flux* which would mean a lower contacting area between the liquid and gas (hence less volume for the absorption tower.)



Let's examine this issue using fundamental the transport equations.

Consider the liquid layer into which a gas, "A", will be dissolving (/reacting). The liquid thickness is *b* and the diffusivity of A in the solvent is D_A. The reaction is first order with a rate law, $R_{vi} = - k\, C_A$. You can assume that the concentration of A at y= 0 is C_{A0} and that at y = -b, there is no flux of A through the bottom wall.

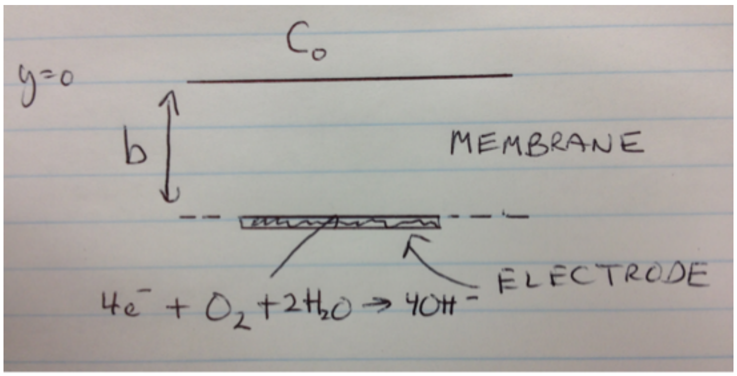
a. Write the requisite transport equation and boundary conditions.
b. Solve the steady-state problem to obtain the concentration profile $C[y]$
c. Do a calculation to demonstrate how the value of the reaction rate constant affects the rate of absorption. Presumably the reaction can be shown to be advantageous.

(You need the flux! Expand and simplify the result to see how the reaction really acts.)

d. Suppose that you have the option of a solvent that is more viscous, and hence has a lower D_A, but has a higher affinity for *A*, hence a higher C_{A0}, explain the how your answer can help decide which is better. (Use the algebraic form to determine this.)

2. Transient diffusion and reaction in a porous membrane (70 points)

The “Clark” electrode, (Clark et el. 1953, *J Appl. Physiol*) has long been a standard tool for measuring oxygen concentrations in gas mixtures or liquids. It works using an electrochemical reaction, that consumes oxygen at a metal cathode surface. To make such probes generally useful, the metal electrode is covered with a porous membrane. The intention of this problem is to examine the operation of a Clark oxygen electrode.



In the diagram, you can consider that you want to measure the oxygen concentration C_o. Oxygen will diffuse through the membrane and react (irreversibly) at the electrode surface. This reaction can actually be considered first order, (rate per area:) $R_{Ai} = - K\, C_i$. The diffusivity, D_i, will be constant.

a. Write down the governing partial differential equation and all relevant boundary and initial conditions. (The reaction is occurring on the surface, not within the membrane. Hence the reaction term is not in the PDE!)

Consider first that the concentration outside the membrane has been constant for a long enough time that all positions in the membrane are at a steady oxygen concentration.

b. Find the oxygen profile and calculate the flux.
c. Explain why the membrane thickness acts as it does in this device. (Does the thickness really affect the flux?)

Now consider the transient reaction-diffusion problem. (All possible partial credit will be given so proceed as far as you can on this problem.)

d. Explain how the PDE can be reduced to solving an ODE in time. Provide this equation and the boundary conditions. (The domain is finite so similarity does not work!)
e. Explain your choice of the set of spatially dependent functions. (One way or the other you need the boundary conditions to be homogenous — or you need to propose a “fix”.) Breaking the solution into a steady state and a transient piece was demonstrated in class!)

For the “make up test”, finish this solution completely for the time dependent concentration.

f. What time scale do you expect will govern the response of the electrode to changes in concentration? If there is some doubt, list all of the relevant time scales and tell the variables that determine each.
g. Why is the effect of membrane thickness different from the steady state?

For these classic devices, the failure mode was the membrane degrading so that liquid would directly contact the electrode. However, when modern lithography techniques are used to make arrays of micro scale devices, two problems can arise that are related to migration of metal atoms from the electrode into the membrane that covers the electrode.
The first is that the membrane diffusivity is reduced and no longer constant.

h. For the steady state problem, if the diffusivity is

$$D(y) = D_{Ao}\left(1-\gamma\left(\frac{y}{b}\right)^3\right) \quad ,$$

what spatially dependent differential equation will govern the flux? (Check this!)

i. If metal ions migrate into the membrane there will be some reaction occurring within the membrane. As a first assumption look at the worst case that the metal is uniformly distributed within the membrane (and electrically connected) so that reaction will be occurring within the membrane. In this case the rate is likely to be slow compared to diffusion but the reaction will now be second order, $R_{vi} = -k\, C_i^2$.

The electrode will still be intact and thus the reaction will still occur at the membrane surface.

Formulate this situation with requisite equations and provide a "correction" to the steady state solution from part b when a slow, second order reaction is occurring everywhere within the membrane.

This is a modification of part b so the diffusivity is constant but the reaction is now second order. You could consider this to be a perturbation problem with the parameter that contains the reaction constant taken to be small. (My answer, with 1 term of correction, worked well up to the parameter value of 0.4)

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + R_{Vi}.$$

$$\mathbf{N}_i = C_i\mathbf{v} + \mathbf{J}_i = C_i\mathbf{v}^{(M)} + \mathbf{J}_i^{(M)}, \qquad \sum_{i=1}^{n} \mathbf{N}_i = C\mathbf{v}^{(M)}, \qquad \sum_{i=1}^{n} \mathbf{J}_i^{(M)} = \mathbf{0} \quad (1.2\text{-}8)$$

Table 1-3

Fick's Law for Binary Mixtures of *A* and *B*

Reference velocity	Mass units	
$\mathbf{v}$	$\mathbf{j}_A = -\rho D_{AB} \nabla \omega_A$	(A)
$\mathbf{v}^{(M)}$	$\mathbf{j}_A^{(M)} = -CM_A D_{AB} \nabla x_A$	(C)

Table 1-2

Flux of Species *i* in Various Reference Frames and Units

Reference velocity	Molar units	Mass units
$\mathbf{0}$	$\mathbf{N}_i$	$\mathbf{n}_i$
$\mathbf{v}$	$\mathbf{J}_i$	$\mathbf{j}_i$
$\mathbf{v}^{(M)}$	$\mathbf{J}_i^{(M)}$	$\mathbf{j}_i^{(M)}$

TABLE 2-2

Continuity Equation in Rectangular, Cylindrical, and Spherical Coordinates

Rectangular (x, y, z, t)

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho v_x) + \frac{\partial}{\partial y}(\rho v_y) + \frac{\partial}{\partial z}(\rho v_z) = 0$$

Cylindrical (r, θ, z, t)

$$\frac{\partial \rho}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(r\rho v_r) + \frac{1}{r}\frac{\partial}{\partial \theta}(\rho v_\theta) + \frac{\partial}{\partial z}(\rho v_z) = 0$$

Spherical (r, θ, ϕ, t)

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\rho v_r) + \frac{1}{r \sin\theta}\frac{\partial}{\partial \theta}(\rho v_\theta \sin\theta) + \frac{1}{r \sin\theta}\frac{\partial}{\partial \phi}(\rho v_\phi) = 0$$

TABLE 2-4

Species Conservation Equations for a Binary or Pseudobinary Mixture in Rectangular, Cylindrical, and Spherical Coordinates[a]

Rectangular (x, y, z, t)

$$\frac{\partial C_i}{\partial t} + v_x \frac{\partial C_i}{\partial x} + v_y \frac{\partial C_i}{\partial y} + v_z \frac{\partial C_i}{\partial z} = D_i \left[\frac{\partial^2 C_i}{\partial x^2} + \frac{\partial^2 C_i}{\partial y^2} + \frac{\partial^2 C_i}{\partial z^2} \right] + R_{Vi}$$

Cylindrical (r, θ, z, t)

$$\frac{\partial C_i}{\partial t} + v_r \frac{\partial C_i}{\partial r} + \frac{v_\theta}{r} \frac{\partial C_i}{\partial \theta} + v_z \frac{\partial C_i}{\partial z} = D_i \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_i}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 C_i}{\partial \theta^2} + \frac{\partial^2 C_i}{\partial z^2} \right] + R_{Vi}$$

Spherical (r, θ, ϕ, t)

$$\frac{\partial C_i}{\partial t} + v_r \frac{\partial C_i}{\partial r} + \frac{v_\theta}{r} \frac{\partial C_i}{\partial \theta} + \frac{v_\phi}{r \sin\theta} \frac{\partial C_i}{\partial \phi} = D_i \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_i}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial C_i}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 C_i}{\partial \phi^2} \right] + R_{Vi}$$

[a]It is assumed that ρ and D_i are constant, where D_i is the binary or pseudobinary diffusivity.

TABLE 2-3

Approximate Forms of the Energy Conservation Equation in Rectangular, Spherical Coordinates (Thermal Effects Only)[a]

Rectangular (x, y, z, t)

$$\frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} + v_z \frac{\partial T}{\partial z} = \alpha \left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right] + \frac{H_V}{\rho \hat{C}_p}$$

Cylindrical (r, θ, z, t)

$$\langle \mathcal{L}_x \Theta, \Phi_n \rangle = \int_a^b \frac{1}{w} \left[\frac{\partial}{\partial x} \left(p \frac{\partial \Theta}{\partial x} \right) + q\Theta \right] \Phi_n w \, dx$$

$$= \int_a^b \frac{\partial}{\partial x} \left(p \frac{\partial \Theta}{\partial x} \right) \Phi_n dx + \int_a^b q \Theta \Phi_n \, dx$$

$$= p \left(\frac{\partial \Theta}{\partial x} \Phi_n - \Theta \frac{d\Phi_n}{dx} \right) \Bigg|_{x=a}^{x=b} + \int_a^b \Theta \left[\frac{d}{dx} \left(p \frac{d\Phi_n}{dx} \right) + q \Phi_n \right] dx \quad (5.4\text{-}1$$

$$= p \left(\frac{\partial \Theta}{\partial x} \Phi_n - \Theta \frac{d\Phi_n}{dx} \right) \Bigg|_{x=a}^{x=b} - \lambda_n^2 \Theta_n.$$

Table 5-1

Original and Subsidiary Problems in a Linear Superposition

Equation	$\Theta(x,t)$	$f(x)$	$\psi(x,t)$
DE	$\frac{\partial \Theta}{\partial t} = \frac{\partial^2 \Theta}{\partial x^2} + 1$	$\frac{d^2 f}{dx^2} = -1$	$\frac{\partial \psi}{\partial t} = \frac{\partial^2 \psi}{\partial x^2}$
BC at $x = 0$	$\Theta(0,t) = 0$	$f(0) = 0$	$\psi(0,t) = 0$
BC at $x = 1$	$\Theta(1,t) = 0$	$f(1) = 0$	$\psi(1,t) = 0$
IC	$\Theta(x,0) = 0$	NA	$\psi(x,0) = -f(x$

Abbreviations: DE, differential equation; BC, boundary condition; IC, initial condition; NA, not applicable.

Orthonormal Functions from Eigenvalue Problems in Cartesian Coordinates[a]

Case	Boundary conditions	Basis functions
I	$\Phi(0) = 0 = \Phi(\ell)$	$\Phi_n(x) = \sqrt{\frac{2}{\ell}} \sin \frac{n\pi x}{\ell}, \quad n = 1, 2, \ldots$
II	$\frac{d\Phi}{dx}(0) = 0 = \Phi(\ell)$	$\Phi_n(x) = \sqrt{\frac{2}{\ell}} \cos\left(n + \frac{1}{2}\right)\frac{\pi x}{\ell}, \quad n = 0, 1, 2, \ldots$
III	$\Phi(0) = 0 = \frac{d\Phi}{dx}(\ell)$	$\Phi_n(x) = \sqrt{\frac{2}{\ell}} \sin\left(n + \frac{1}{2}\right)\frac{\pi x}{\ell}, \quad n = 0, 1, 2, \ldots$
IV	$\frac{d\Phi}{dx}(0) = 0 = \frac{d\Phi}{dx}(\ell)$	$\Phi_n(x) = \sqrt{\frac{2}{\ell}} \cos \frac{n\pi x}{\ell}, \quad n = 1, 2, \ldots$ $\Phi_0(x) = \frac{1}{\sqrt{\ell}}$

[a]All of these functions satisfy $d^2\Phi/dx^2 = -\lambda^2\Phi$ for $0 \le x \le \ell$.

Table 5-3

FFT Problems and Corresponding Eigenvalue Problems

	Geometry	Partial differential equation	Coord.	w	p	Eigenfunctions
1	Rectangular (x,t)	$\frac{\partial \Theta}{\partial t} = \frac{\partial^2 \Theta}{\partial x^2}$	x	1	1	$\sin \lambda x, \cos \lambda x$
2	Rectangular (x,y)	$\frac{\partial^2 \Theta}{\partial x^2} + \frac{\partial^2 \Theta}{\partial y^2} = 0$	x	1	1	$\sin \lambda x, \cos \lambda x$
			y	1	1	$\sin \lambda y, \cos \lambda y$
3	Cylindrical (r,t)	$\frac{\partial \Theta}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \Theta}{\partial r}\right)$	r	r	r	$J_0(\lambda r), Y_0(\lambda r)$
4	Cylindrical (r,z)	$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \Theta}{\partial r}\right) + \frac{\partial^2 \Theta}{\partial z^2} = 0$	r	r	r	$J_0(\lambda r), Y_0(\lambda r)$
			z	1	1	$\sin \lambda z, \cos \lambda z$
5	Cylindrical (r,θ)	$r\frac{\partial}{\partial r}\left(r\frac{\partial \Theta}{\partial r}\right) + \frac{\partial^2 \Theta}{\partial \theta^2} = 0$	θ	1	1	$\sin \lambda\theta, \cos \lambda\theta$
6	Spherical (r,t)	$\frac{\partial \Theta}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \Theta}{\partial r}\right)$	r	r^2	r^2	$\frac{\sin \lambda r}{r}, \frac{\cos \lambda r}{r}$
7	Spherical $(r, \eta = \cos\theta)$	$\frac{\partial}{\partial r}\left(r^2\frac{\partial \Theta}{\partial r}\right) + \frac{\partial}{\partial \eta}\left[(1-\eta^2)\frac{\partial \Theta}{\partial \eta}\right] = 0$	η	1	$1-\eta^2$	$P_n(\eta)$

```
DSolve[{ D[c[y], {y, 2}] - ϕ^2 c[y] == 0}, c[y], y]
```

Out[185]= $\{\{c[y] \to e^{y\phi} C[1] + e^{-y\phi} C[2]\}\}$

```
In[186]:= ExpToTrig[ans]

{{c[y] → C[3] Cosh[y ϕ] + C[4] Sinh[y ϕ]}}
```