Particle Technology Laboratory
Prof. Sotiris E. Pratsinis

Sonneggstrasse 3, ML F13, ETH Zentrum

Tel.: +41-44-632 25 10

ETH

Eidgenössische Technische Hochschule Zürich
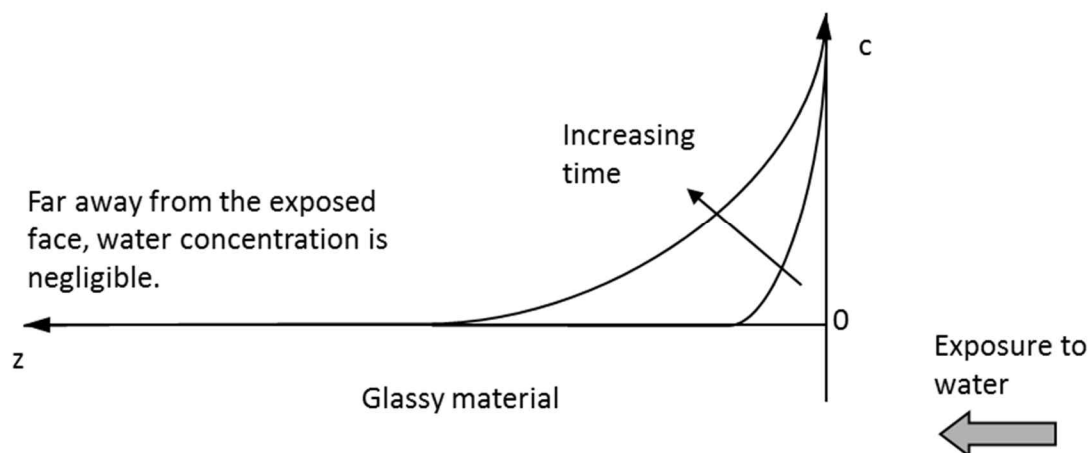Swiss Federal Institute of Technology Zurich

151-0917-00 U Stoffaustausch HS 2017

Exercise 3: Applications Fick's Laws

Chapter 2 Problem 11

We will use the semi-infinite slab equations.

Assumptions: The concentration of water on the surface of the glass (at $z = 0$) remains constant, far away from the surface it is however negligible. Water reacts with glass fast and <u>reversibly</u>, thus for a stoichiometric ratio of 1 to 1 we have:

Water + glass $\leftrightarrow$ glass hydrate
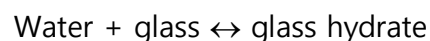
here by water we refer to water molecules that can freely diffuse inside glass, while by glass hydrate we refer to water molecules that have already reacted with glass and can no longer diffuse inside the glass network (they stay immobile). If the reaction constant from left to right ($\rightarrow$) is k_1 and from right to left ($\leftarrow$) is k_2, then:

- Rate of water reaction with glass: $r_1 = k_1 \cdot C_1$ (where C_1 refers to Water)

- Rate of chemical desorption of water from glass: $r_2 = k_2 \cdot C_2$ (where C_2 refers to glass hydrate).

- The net reaction rate for water is: $r = r_1 - r_2$

Now following example 2.3-2 from Cussler (3rd ed.) we have for water and glass hydrate, assuming diffusion in the z-direction only and unsteady state conditions:

Mass balance for water:

$$\frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial z^2} - r \tag{1}$$

Mass balance for glass hydrate:

$$\frac{\partial C_2}{\partial t} = +r \tag{2}$$

By adding the above equations:

$$\frac{\partial(C_1 + C_2)}{\partial t} = \frac{\partial(C_1 + KC_1)}{\partial t} = D \frac{\partial^2 C_1}{\partial z^2} \tag{3}$$

or in other words

$$\frac{\partial C_1}{\partial t} = \frac{D}{1+K} \frac{\partial^2 C_1}{\partial z^2} \tag{4}$$

where K equilibrium constant. For fast reaction of water, K is big, for slow reaction of water, K is small.

So we see that the general equation is virtually the same as in the case of the semi-infinite slab with the only difference being the insertion of the term (1+K). Following the solution procedure in Cussler's book, we obtain for the concentration profile:

$$\frac{C_1 - C_{10}}{C_{1\infty} - C_{10}} = erf \left\{ \frac{z}{\sqrt{\frac{4Dt}{1+K}}} \right\} \tag{5}$$

which can be solved for the concentration C_1:

$$C_1 = C_{10} + (C_{1\infty} - C_{10}) erf \left\{ \frac{z}{\sqrt{\frac{4Dt}{1+K}}} \right\} \tag{6}$$

Inserting this concentration into the flux $j_1 = -D\dfrac{\partial C_1}{\partial z}$ yields (using the definition of the error function, equation 2.3-16 in Cussler):

$$j_1(z) = -D(C_{1\infty} - C_{10})\frac{2}{\sqrt{\pi}}\exp\left\{-\frac{z^2(1+K)}{4Dt}\right\}\frac{1}{\sqrt{\dfrac{4Dt}{1+K}}} \tag{7}$$

For equation 7 remember that:

$$\frac{d}{d\zeta}\operatorname{erf}(\zeta) = \frac{2}{\sqrt{\pi}}e^{-\zeta^2} \tag{8}$$

And with the chain-rule we get:

$$\frac{d}{dz}\operatorname{erf}(f(z)) = \frac{2}{\sqrt{\pi}}e^{-f(z)^2}\cdot\frac{d}{dz}f(z) \tag{9}$$

At z=0, the argument of the exponential function vanishes, giving for the flux:

$$j_1\big|_{z=0} = D\sqrt{\frac{(1+K)}{D\cdot\pi\cdot t}}(C_{10} - C_{1\infty}) = \sqrt{\frac{D(1+K)}{\pi\cdot t}}C_{10} \tag{10}$$

Similarly the total amount of water inside the glass will be:

$$N_1 = \int_0^t j_1\big|_{z=0}\cdot A\,dt = 2A\sqrt{\frac{D(1+K)\cdot t}{\pi}}C_{10} \tag{11}$$

Thus measuring N_1 by ^{15}N nuclear magnetic resonance, the area, A, of the glass accessible to the environment, the diffusivity of water in glass, D, and the equilibrium constant K, we can find the age of the material (solving with respect to t):

$$t = \left(\frac{N_1}{2AC_{10}}\right)^2\frac{\pi}{D(1+K)} \tag{12}$$

where C_{10} is the water concentration on the surface of the glass (which is known by assuming the humidity conditions in the surrounding environment have not changed a lot with time!).

Chapter 2 Problem 16

One of the practical problems an engineer is facing when he is doing extraction is: how long does the process take to extract e.g. sucrose from beets (Zuckerrüben)? This is certainly depending on the diffusion coefficient of the sucrose inside the fruit. But if you do an experiment to determine the coefficient with slices of the fruit you will find an interesting fact: the diffusion coefficient depends on the thickness of the slice. This fact can be explained by the composition of the fruit. The diffusion through vascular channels D_c is fast and dominating the long range transport of sucrose whereas diffusion through cell walls D_w is slow but is dominating the distribution of sucrose in the short range.

The problem can be solved by using the idea of the semi-infinite slab. The sucrose concentration in a semi-infinite slab for this situation is sketched in fig.1.
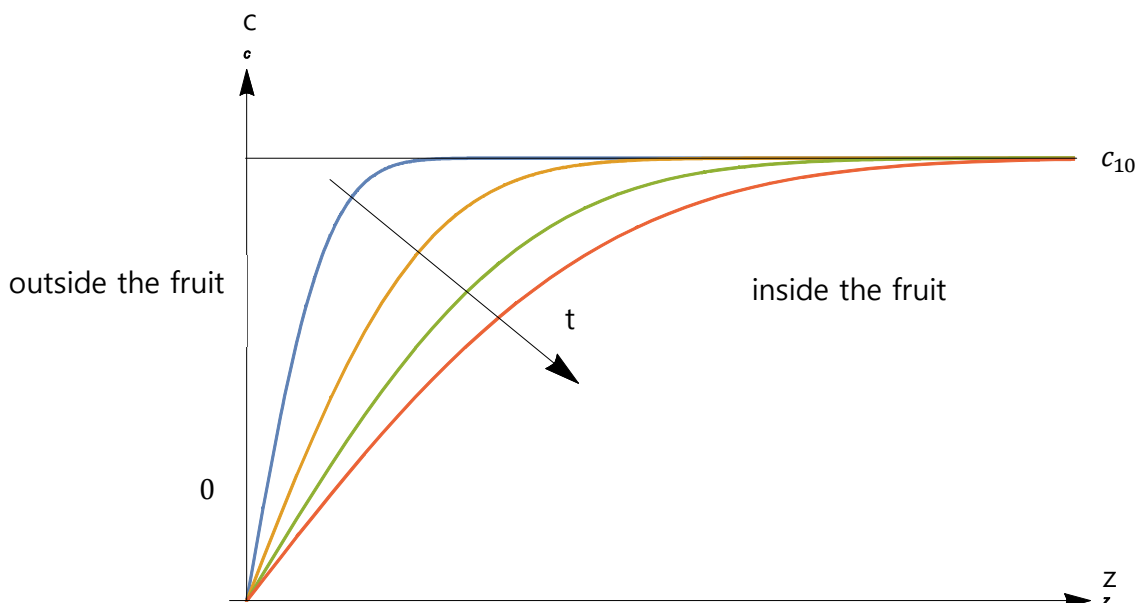

Fig.1

At $z = 0$ (skin of the fruit) the concentration shall be $c_1 = 0$.

At $z = \infty$ (deep inside the fruit) the concentration is $c_1 = c_{10}$.

It may seem a strange assumption that one assumes the inner parts of an obviously finite fruit infinitely away from the skin. But if one takes into account that the ratio of the radius of the fruit compared with the thickness of the diffusion layer is quasi-infinite the assumption appears reasonable.

The task is to develop an average diffusion coefficient combing the two coefficients for the vascular and the cell wall transport. Therefore we need to develop the differential equation for the concentration profile and the flux for this special problem of the semi-infinite slab. In other words we have to use Fick's second and first law plus boundary conditions. The solution is not easy and needs some mathematical tricks. It can be found in Cussler's "Diffusion - mass transfer in fluid systems", 3rd edition, on page 27.

The approach for solving the problem of a semi-infinite slab is using Fick's second law:

$$\frac{\partial c_1}{\partial t} = D \frac{\partial^2 c_1}{\partial z^2} \tag{1}$$

The boundary conditions are as follows:

$$t = 0, \quad all \ z, \quad c_1 = c_{10} \tag{1-1}$$

$$t > 0, \quad z = 0, \quad c_1 = 0 \tag{1-2}$$

$$z = \infty, \quad c_1 = c_{10} \tag{1-3}$$

The first trick is to define a new variable:

$$\zeta = \frac{z}{\sqrt{4Dt}} \tag{2}$$

The differential equation can then be rewritten as

$$\frac{d^2 c_1}{d\zeta^2} + 2\zeta \frac{dc_1}{d\zeta} = 0 \tag{3}$$

Now we have an ordinary differential equation which is much easier to solve.

But we also have to transform the boundary conditions:

$$\zeta = 0, \quad c_1 = 0 \tag{3-1}$$

$$\zeta = \infty, \quad c_1 = c_{10} \tag{3-2}$$

Integration of eq.(3) gives:

5

$$\frac{dc_1}{d\zeta} = ae^{-\zeta^2} \tag{4}$$

where a is an integration constant.

A second integration and use of the boundary condition gives:

$$\frac{c_1 - 0}{c_{10} - 0} = erf\,\zeta \tag{5}$$

$$\text{where } erf\zeta = \frac{2}{\sqrt{\pi}} \int_0^\zeta e^{-s^2}\,ds \tag{6}$$

Now we have determined the concentration profile for our problem.

We get the flux by applying eq. (5) on Fick's first law:

$$j_1 = -D\frac{\partial c_1}{\partial z} = \sqrt{D/\pi t}\; e^{-z^2/4Dt}(0 - c_{10}) \tag{7}$$

The diffusion coefficient D given in the exercise can be derived from eq. (7) as follows:

$$j_1\big|_{z=0} = -\sqrt{D/\pi t}\cdot c_{10} \tag{8}$$

which is the flux at $z = 0$.

The mass per unit area M transported away through the fruit skin after a given time is derived from eq.(8) by integration:

$$M(t) = -\sqrt{D/\pi}\cdot c_{10}\cdot \int_0^t \frac{1}{\sqrt{t*}}dt* = -\sqrt{D/\pi}\cdot c_{10}\cdot\left[2\cdot\sqrt{t*}\right]_0^t = -2\sqrt{D/\pi}\cdot c_{10}\cdot\sqrt{t} \tag{9}$$

Solving for D:

$$D = \frac{\pi}{4t}\left(\frac{M}{c_{10}}\right)^2 \tag{10}$$

This is how the average diffusion coefficient can be measured.

Now we go for the connection between the two diffusivities D_c and D_w already mentioned and the overall diffusivity D.

The fluxes along vascular channels and through cell walls are:

$$j_c = -\sqrt{\frac{D_c}{\pi t}} c_{10} \tag{11}$$

$$j_w = -\sqrt{\frac{D_w}{\pi t}} c_{10} \tag{12}$$

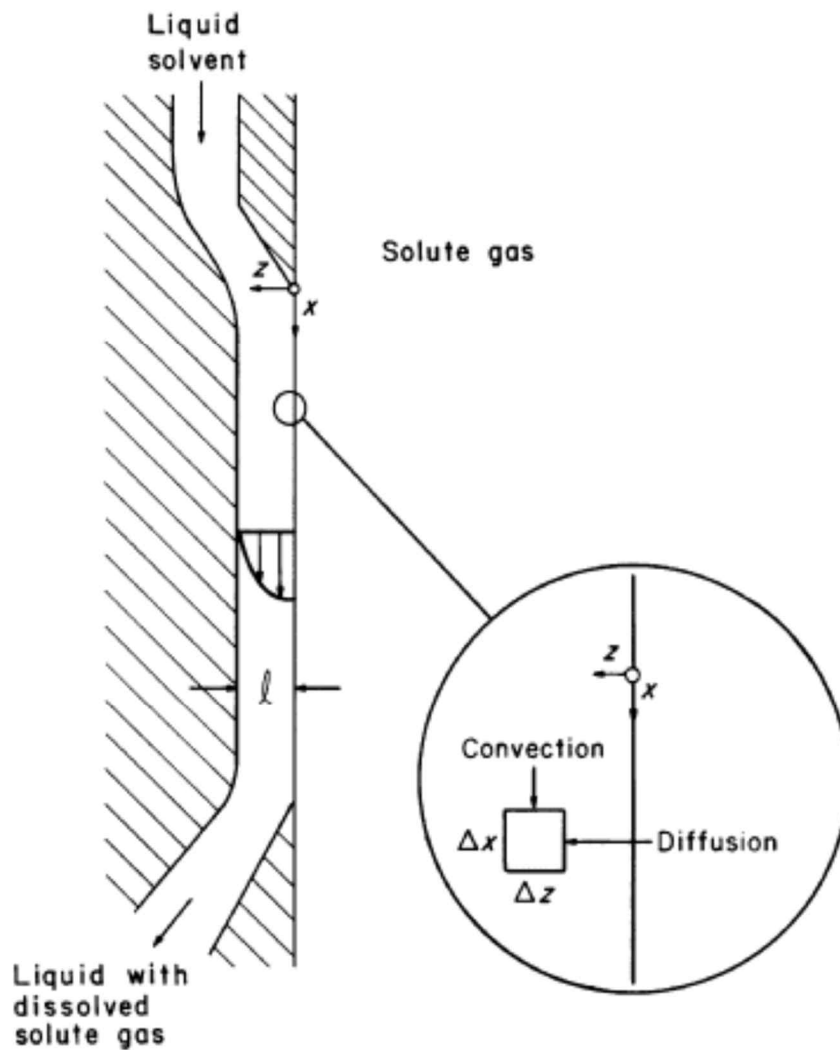The overall flux with the fraction ε of channels:

$$j_1 = (1-\varepsilon) j_w + \varepsilon j_c = -\frac{(1-\varepsilon)\sqrt{D_w} + \varepsilon\sqrt{D_c}}{\sqrt{\pi t}} c_{10} \tag{13}$$

By comparing eq. (8) and (13) we get:

$$\sqrt{D} = (1-\varepsilon)\sqrt{D_w} + \varepsilon\sqrt{D_c} \tag{14}$$

Unsteady diffusion into a falling film

Assumptions:

1.   The solution is dilute

2.   Mass transfer in z-direction and flow (convection) in x-direction

3.   The gas over the film is well mixed (no resistance to diffusion in the gas phase)

4.   Short contact between liquid and gas (for convenience)

Mass balance:

$$\begin{pmatrix} \text{mass accumulation} \\ \text{in w } \Delta x\, \Delta z \end{pmatrix} = \begin{pmatrix} \text{mass diffusing in at z -} \\ \text{mass diffusing out at } z + \Delta z \end{pmatrix} + \begin{pmatrix} \text{mass flowing in at x -} \\ \text{mass flowing out at } x + \Delta x \end{pmatrix} \quad (1)$$

$$\frac{\partial}{\partial t}\left(c_1\, w\,\Delta x\,\Delta z\right)=\left[\left(w\,\Delta x\, j_1\right)_z-\left(w\,\Delta x\, j_1\right)_{z+\Delta z}\right]+\left[\left(w\,\Delta z\, c_1\, v_x\right)_x-\left(w\,\Delta z\, c_1\, v_x\right)_{x+\Delta x}\right] \qquad (2)$$

At steady state and after dividing by the volume (wΔxΔz) and taking the limit as this volume goes to zero:

$$0=-\frac{\partial\, j_1}{\partial\, z}-\frac{\partial}{\partial\, x}c_1\, v_x \qquad (3)$$

We combine this with Fick's law and set $v_x=v_{max}$ (fluid velocity at the interface) as the gas-liquid contact time is short (based on assumption #4)

The implication here is that the solute barely has a chance to cross the interface so slightly diffuses into the fluid.

With that equation (1) becomes:

$$\frac{\partial\, c_1}{\partial\,(x/v_{max})}=D\frac{\partial^2\, c_1}{\partial\, z^2} \qquad (4)$$

Boundary conditions:

$x=0 \qquad \forall z \qquad c_1=0 \qquad\qquad (3)$

$x>0 \qquad z=0 \qquad c_1=c_{10}=0.05c_{1sat} \quad (4)$

$\qquad\qquad z=\ell \qquad c_1=c_{1l}=0 \qquad\quad (5)$

$$c_{1sat}=p_{sat}H=0.14bar\cdot0.18\frac{mol}{kg\cdot atm}\cdot1\frac{atm}{bar}=2.52\times10^{-2}\frac{mol}{kg} \qquad (5)$$

or:

$$c_{1sat}=2.52\times10^{-2}\frac{mol}{kg}\cdot1000\frac{kg}{m^3}=25.2\frac{mol}{m^3} \qquad (6)$$

$$(\rho_{H2O}=1000\frac{kg}{m^3})$$

In this case this problem reduces to that of diffusion in a semi-infinite slab with $t = x/v_{max}$ and the solution is the same:

$$\frac{c_1(z,x) - c_{10}}{c_{1l} - c_{10}} = erf \frac{z}{\sqrt{4 D \dfrac{x}{v_{max}}}}$$

(7)

and the flux at the interface is:

$$j_1\big|_{z=0}(x) = \sqrt{\frac{D}{\pi \left(\dfrac{x}{v_{max}}\right)}} \cdot c_{10}$$

(8)

The total amount of dissolved benzene is obtained by the integration of the total flux $J\big|_{z=0} = A \cdot j_1\big|_{z=0}$ over time (x/v_{max}):

$$
\begin{aligned}
N &= A \cdot \int_0^{t_{max}} j_1\big|_{z=0}\, dt \\
&= A \cdot \int_0^{x/v_{max}} j_1\big|_{z=0}\, d\left(\frac{x}{v_{max}}\right) \\
&= A \cdot c_{10} \cdot \sqrt{\frac{D}{\pi}} \int_0^{x/v_{max}} \frac{1}{\sqrt{\dfrac{x}{v_{max}}}} d\left(\frac{x}{v_{max}}\right) \\
&= 2A \cdot c_{10} \cdot \sqrt{\frac{D}{\pi}} \cdot \sqrt{\frac{x}{v_{max}}}\Bigg|_0^{x/v_{max}} \\
&= 2 \cdot 4\text{m}^4 \cdot 0.05 \cdot 25.2 \frac{\text{mol}}{\text{m}^3} \cdot \sqrt{\frac{1.02 \cdot 10^{-9}\, \dfrac{m^2}{s}}{\pi}} \cdot \sqrt{\frac{5\text{m}}{1\dfrac{m}{s}}} \\
&= 4.06 \times 10^{-4}\, \text{mol}
\end{aligned}
$$

(9)

Additional problem: Chapter 2 Problem 13
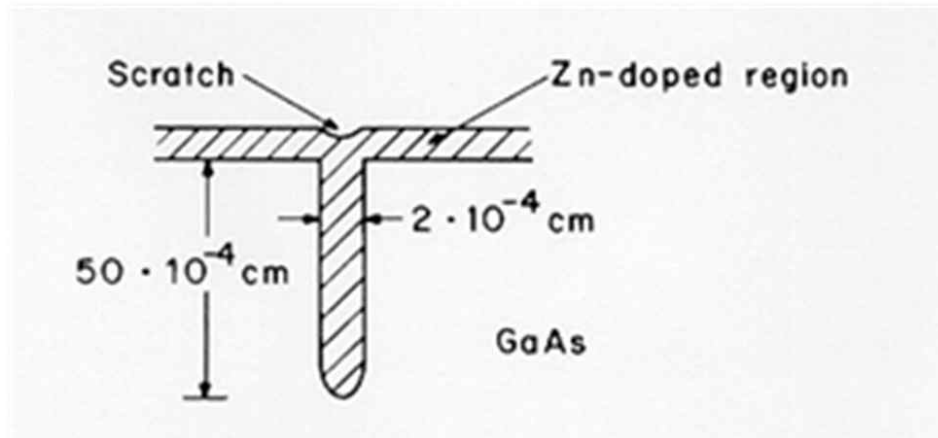
Sketch for Zn diffusion in GaAs, provoked by defects in the crystal which cause an

increase of the diffusion coefficient.

This problem refers the case "Decay of a pulse" in Cussler's book (section 2.4.1). In this exercise the concentration profile as a function of time is needed in order to determine the maximum baking time according to the following condition:

$$\frac{c_1(z = 4 \cdot 10^{-4}, t)}{c_{1,max}} = 0,1$$

Assumptions:

• One-dimensional problem

• Point source, active at $t = 0$ (zinc pulse is applied at the beginning of the baking)

Zinc Balance:

$$\begin{pmatrix} \text{zinc} \\ \text{accumulation} \\ \text{in } A \cdot \Delta z \end{pmatrix} = \begin{pmatrix} \text{zinc} \\ \text{diffusion into} \\ \text{this volume} \end{pmatrix} - \begin{pmatrix} \text{zinc} \\ \text{diffusion out of} \\ \text{this volume} \end{pmatrix} \tag{1}$$

$$\frac{\partial(c_1 \cdot A \cdot \Delta z)}{\partial t} = A \cdot j_1\big|_z - A \cdot j_1\big|_{z+\Delta z} \tag{2}$$

Dividing (2) by the volume of the cell, taking $z \to 0$ and applying Fick`s first law of diffusion results in Fick`s second law:

$$\frac{\partial c_1}{\partial t} = D \cdot \frac{\partial^2 c_1}{\partial z^2} \qquad (3)$$

The boundary conditions for this problem are:

$$t > 0, \qquad z \to \infty, \qquad c_1 = 0 \qquad (4)$$

$$t > 0, \qquad z = 0, \qquad \frac{\partial c_1}{\partial z} = 0 \text{ (symmetry of the pulse)} \qquad (5)$$

with the initial condition

$$t = 0, \qquad c_1 = \frac{M}{A} \delta(z) \qquad (6)$$

The pulse is described by the Dirac-function $\delta(z)$.

A common definition for a pulse function is: (represents the peak width)

$$\int_{-\infty}^{\infty} e^{-\frac{z^2}{\alpha}} \cdot dz = \sqrt{\pi \cdot \alpha} \qquad \Rightarrow \qquad \frac{1}{\sqrt{\pi \cdot \alpha}} \int_{-\infty}^{\infty} e^{-\frac{z^2}{\alpha}} dz = 1 \qquad (7)$$

$$\text{for} \qquad \alpha \to 0 \qquad \frac{1}{\sqrt{\pi \cdot \alpha}} \int_{-\infty}^{\infty} e^{-\frac{z^2}{\alpha}} dz = \int_{-\infty}^{\infty} \delta(z) dz = 1 \qquad (8)$$

A common form for a concentration profile that results from a decay of a pulse is:

$$c_1 = \Omega \frac{1}{\sqrt{\pi a t}} e^{-\frac{z^2}{at}} \qquad (9)$$

In order to prove, that this is a solution of equation (3), we have to check if both the boundary conditions (4) to (6) and equation (3) are satisfied. We can easily see that equation (4) is true.

Taking equation (5), (8) and (9): (with $\alpha = a \cdot t$)

$$t = 0 \qquad \Rightarrow \alpha = 0 \qquad c_1 = \frac{M}{A}\delta(z) = \Omega\frac{1}{\sqrt{\pi a t}}e^{-\frac{z^2}{at}} = \Omega \cdot \delta(z) \tag{10}$$

$$\Rightarrow \quad \Omega = \frac{M}{A} \tag{11}$$

Now we have to check, if Fick`s second law (3) is satisfied:

$$\frac{\partial c_1}{\partial t} = \frac{M}{A}\frac{1}{\sqrt{\pi a t}}\left(\frac{z^2}{at^2} - \frac{1}{2t}\right)e^{-\frac{z^2}{at}} \tag{12}$$

$$\frac{\partial^2 c_1}{\partial z^2} = \frac{M}{A}\frac{1}{\sqrt{\pi a t}}\frac{4}{a}\left(\frac{z^2}{at^2} - \frac{1}{2t}\right)e^{-\frac{z^2}{at}} \tag{13}$$

Therefore a can be determined to:

$$a = 4D \tag{14}$$

The concentration profile is then given by:

$$c_1(z,t) = \frac{M}{A}\frac{1}{\sqrt{4\pi D t}}e^{-\frac{z^2}{4Dt}} \tag{15}$$

The maximum concentration is at z=0 and becomes:

$$c_{1,max} = c_1(z=0) = \frac{M}{A}\frac{1}{\sqrt{4\pi D t}} \tag{16}$$

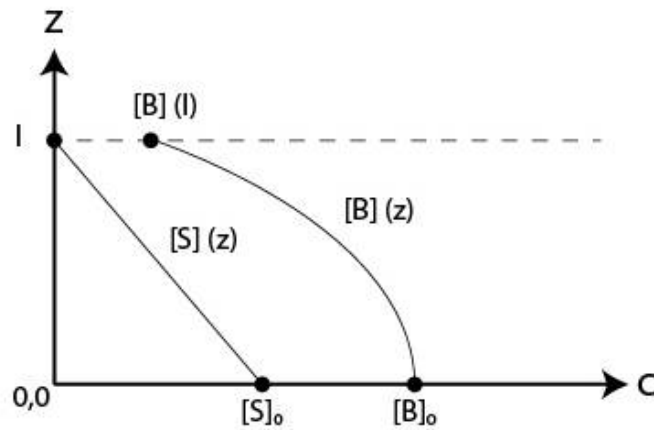We know that the condition for the destruction of the device is:

$$\frac{c_1(4\cdot10^{-4}\,\mathrm{cm}, t_{max})}{c_{1,max}} = 0.1 = e^{-\frac{z^2}{4Dt_{max}}} \tag{17}$$

This can be solved for t_{max}:

$$t_{max} = -\frac{z^2}{4D}\frac{1}{\ln 0.1}$$
(18)

Therefore the maximum baking time can be determined to t_{max} = 1737s = 29 min

Additional problem: Chapter 2 Problem 15

a)

Assuming that the chemical solute is not affected by the bacteria and we are at steady

state, the equation for diffusion across a thin film for the solute S can be applied with the

boundary conditions (given from the description):

$z = 0$, $[S] = [S]_0$

$z = l$, $[S] = 0$

$$j_s = -D \frac{d[S]}{dz}$$

Due to steady state:

$$0 = \frac{dj_s}{dz}$$

With Fick's first law:

$$0 = \frac{d^2[S]}{dz^2}$$

Integration with boundary conditions:

$$[S] = [S]_0 \left(1 - \frac{z}{l}\right)$$

b)

Due to the steady state assumption and the membranes that do not allow the passage of the bacteria, $j_B = 0$ for all z. This results in:

$$0 = -D_0 \frac{d}{dz}[B] + \chi[B]\frac{d}{dz}[S]$$

$$D_0 \frac{d}{dz}[B] = \chi[B]\left(-\frac{[S]_0}{l}\right)$$

Integration gives:

$$\int_{[B]_0}^{[B]_1} \frac{d[B]}{[B]} = -\frac{\chi[S]_0}{D_0 l}\int_0^{z_1} dz$$

$$\ln\frac{[B]_1}{[B]_0} = -\frac{\chi[S]_0 z}{D_0 l}$$

And finally the concentration profile of the bacteria:

$$[B]_1 = [B]_0 e^{-\frac{\chi[S]_0 z}{D_0 l}}$$