

# Mass Transfer

## Equations of Change for Multicomponent Systems

Volume element  $\Delta x, \Delta y, \Delta z$  fixed in space through which a binary mixture of A and B is flowing. Within the element, A may be produced by a chemical reaction at a rate of  $r_A$  (M/(L<sup>3</sup>t)).

Rate of change of mass of A in the volume element:  $\frac{\partial \rho_A}{\partial t} \Delta x \Delta y \Delta z$

Input of A across face at x:  $n_{Ax} \big|_x \Delta y \Delta z$

Output of A across face at  $x + \Delta x$ :  $n_{Ax} \big|_{x+\Delta x} \Delta y \Delta z$

Rate of production of A by chemical reaction.  $r_A \Delta x \Delta y \Delta z$

$n_A$  is the mass flux of A:

Considering the input and output terms in the y and z directions, the entire mass balance equation can be written as

$$\frac{\partial \rho_A}{\partial t} + \left( \frac{\partial n_{Ax}}{\partial x} + \frac{\partial n_{Ay}}{\partial y} + \frac{\partial n_{Az}}{\partial z} \right) = r_A \quad \text{Equation of continuity of species A}$$

This represents the change in mass concentration of A w.r.t. time at a fixed point in space, the change resulting from motion of A and chemical reactions producing A

$$\begin{aligned} \frac{\partial \rho_A}{\partial t} + (\nabla \cdot n_A) &= r_A \\ \frac{\partial \rho_B}{\partial t} + (\nabla \cdot n_B) &= r_B \end{aligned} \quad \frac{\partial \rho}{\partial t} + (\nabla \cdot \rho v) = 0$$

In order to obtain the concentration profiles, the fluxes  $n_A$  and  $N_A$  are to be replaced by appropriate expressions involving concentration gradients

$$n_A - w_A (n_A + n_B) = -\rho D_{AB} \nabla w_A \quad \text{Relation involving mass fraction } w_A$$

$$N_A - x_A (N_A + N_B) = -C D_{AB} \nabla x_A \quad \text{Relation involving mole fraction } x_A$$

Substituting in the equation of continuity in the respective cases, the diffusion equation is obtained

$$\frac{\partial \rho_A}{\partial t} + (\nabla \cdot \rho_A v) = (\nabla \cdot \rho D_{AB} \nabla w_A) + r_A \quad w_A (n_A + n_B) = w_A \rho v = \rho_A v$$

$$\frac{\partial \rho_A}{\partial t} + (\nabla \cdot \rho_A v) = (\nabla \cdot \rho D_{AB} \nabla w_A) + r_A$$

Special Case: Constant  $D_{AB}$

$$\frac{\partial \rho_A}{\partial t} + \rho_A (\nabla \cdot v) + v \cdot (\nabla \rho_A) = D_{AB} \nabla^2 \rho_A + r_A$$

$$\frac{\partial \rho_A}{\partial t} + v \cdot (\nabla \rho_A) = D_{AB} \nabla^2 \rho_A + r_A$$

Dividing by  $M_A$

$$\frac{\partial C_A}{\partial t} + v \cdot (\nabla C_A) = D_{AB} \nabla^2 C_A + R_A$$

# Mass Transfer Fundamentals

Fick's Law

$$N_A = x_A (N_A + N_B) - D_{AB} \nabla C_A$$

BSL

Molar Flux      Bulk Flow      Diffusion

$D_{AB} \left( \frac{\partial C_A}{\partial x} + \frac{\partial C_A}{\partial y} + \frac{\partial C_A}{\partial z} \right)$

## Species Balance Equation in Cartesian Coordinate System

$$\left( \frac{\partial C_A}{\partial t} + v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} + v_z \frac{\partial C_A}{\partial z} \right) = D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right] + R_A$$

Transient,      Convection,      Conduction/Diffusion,      Generation

$$\rho \hat{C}_p \left( \frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} + v_z \frac{\partial T}{\partial z} \right) = k \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right] + \mu \phi_v + \dot{Q}$$

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## Observations

$$\left( \frac{\partial C_A}{\partial t} + v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} + v_z \frac{\partial C_A}{\partial z} \right) \\ = D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right] + R_A$$

Homogeneous reaction term appears in the governing equation

Heterogeneous reaction appears as a boundary condition.

Possible boundary conditions

1. Concentration specified at a point e.g. solubility, equilibrium etc.
2. At the catalyst surface, diffusive flux to the surface must be equal to the rate of reaction

$$- D_{AB} \frac{dC_A}{dx} \Big|_{x=\text{cat sur}} = - R_A^{//}$$

// refers to heterogeneous reaction

Boundary conditions contd.

3. Equality of concentration at the interface  $C_{A, s1} = C_{A, s2}$

4. Impervious surface  $dC/dx = 0$  at specified location

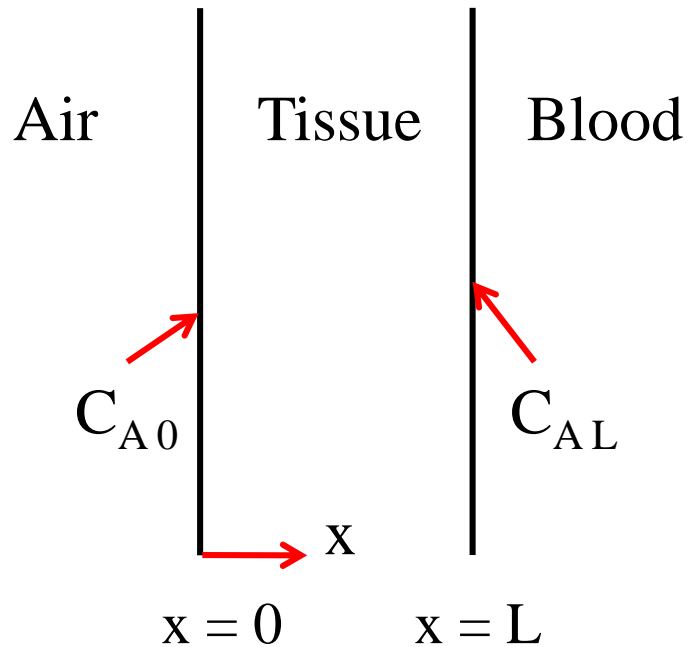
5. Conductive flux to the solid-fluid interface is equal to the convective flux away from the interface,  $-D_{AB} \left. \frac{dC_A}{dx} \right|_{x=L} = h_m (C_{As} - C_{A\infty})$



## Problem

Consider the problem of oxygen transfer from the interior lung cavity, across the lung tissue, to the network of blood vessels on the opposite side. The lung tissue (species B) may be approximated as a plane wall of thickness  $L$ . The inhalation process may be assumed to maintain a constant molar concentration  $C_A(0)$  of oxygen (species A) in the tissue at its inner surface ( $x = 0$ ), and assimilation of oxygen by the blood may be assumed to maintain a constant molar concentration  $C_A(L)$  of oxygen in the tissue at its outer surface ( $x = L$ ). There is oxygen consumption in the tissue due to metabolic processes, and the reaction is zero order, with rate constant equal to  $k_0$ ".

Obtain expressions for the distribution of oxygen concentration in the tissue and for the rate of assimilation of oxygen by the blood per unit tissue surface area.



## Observations

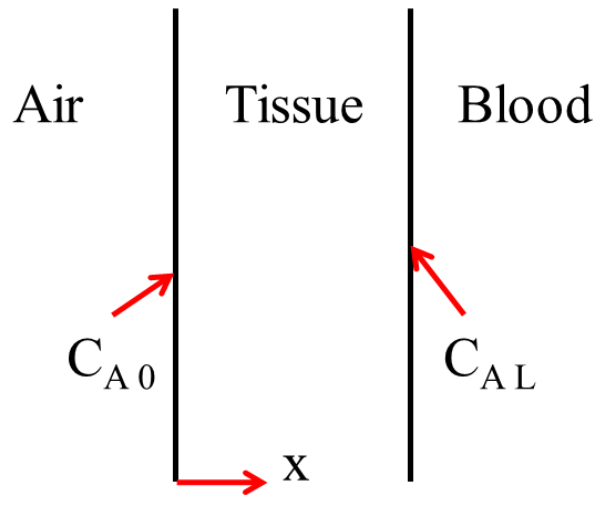
1. Oxygen assimilation in the tissue =  $k_0'''$
2. Homogeneous reaction,  $R_A = -k_0'''$
3. diffusion only reaction, no convection
4. Steady state
5.  $C_A = f(x)$  only


$$\left( \cancel{\frac{\partial C_A}{\partial t}} + v_x \cancel{\frac{\partial C_A}{\partial x}} + v_y \cancel{\frac{\partial C_A}{\partial y}} + v_z \cancel{\frac{\partial C_A}{\partial z}} \right) = D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} + \cancel{\frac{\partial^2 C_A}{\partial y^2}} + \cancel{\frac{\partial^2 C_A}{\partial z^2}} \right] + R_A$$

Obs. 4      3      3      3      5      5      2

Gov. Eqn

$$D_{AB} \frac{d^2 C_A}{dx^2} - k_0''' = 0$$

$$D_{AB} \frac{d^2 C_A}{dx^2} - k_0''' = 0 \quad \text{Air} \quad \text{Tissue} \quad \text{Blood}$$




$$C_A = \frac{k_0'''}{2 D_{AB}} x^2 + C_1 x + C_2$$

Boundary Conditions

$$C_A = C_{A0} \text{ at } x = 0 \quad \longrightarrow \quad C_2 = C_{A0}$$

$$C = C_{AL} \text{ at } x = L \quad \longrightarrow \quad C_1 = \frac{C_{AL} - C_{A0}}{L} - \frac{k_0 L}{2 D_{AB}}$$

Therefore, the concentration distribution of O<sub>2</sub> in the lung tissue is

$$C_A(x) = \frac{k_0'''}{2 D_{AB}} x (x - L) + [C_{AL} - C_{A0}] \frac{x}{L} + C_{A0}$$

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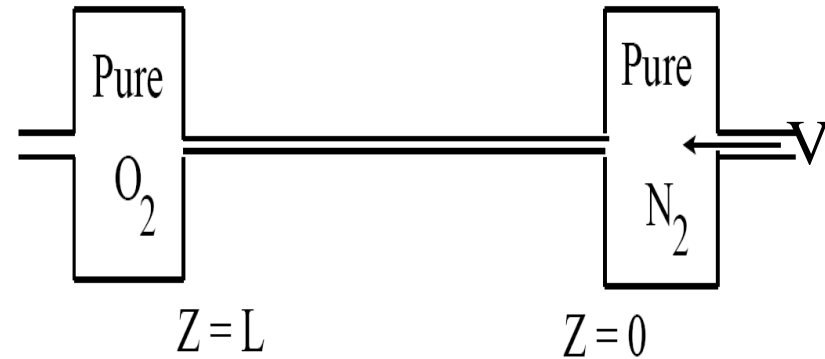
The oxygen assimilation rate per unit area is given by

$$N_A = - D_{AB} \frac{dC_A}{dx} \Big|_{x=L} = - \frac{k_0 L}{2} + \frac{D_{AB}}{L} [C_{A0} - C_{AL}]$$

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## Problem

Two gases ( $\text{O}_2$  and  $\text{N}_2$ ) are separated into two bulbs connected by a narrow diameter capillary. Pure  $\text{N}_2$  flows from right to left (with a velocity  $v$ ), as shown in the figure. To what degree can  $\text{O}_2$  diffuse upstream against the  $\text{N}_2$  flow, i.e., derive the concentration distribution of  $\text{O}_2$  in the tube.



Assume that the system has achieved some steady state and that the volumes at the two ends are so large that each remains nearly pure, even though some exchange takes place (early stage steady state model).

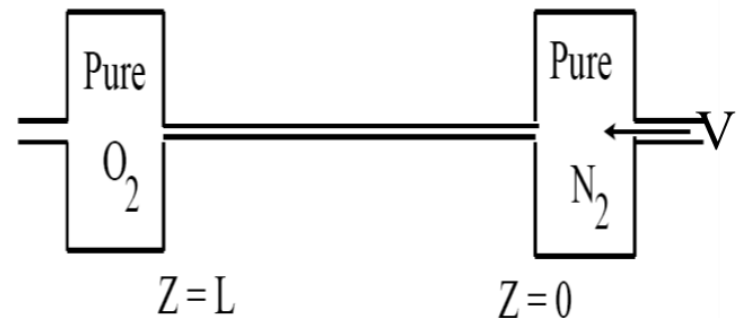
Find the solution for the limiting case of small  $vL/D$ , where  $D$  is the diffusion coefficient.

## Species Balance Equation

$$\left( \frac{\partial C_A}{\partial t} + v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} + v_z \frac{\partial C_A}{\partial z} \right) = D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right] + R_A$$

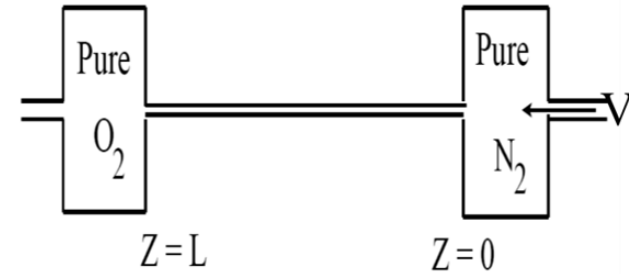
Observations (Component A represents O<sub>2</sub>)

1. No reaction
2. The volumes at the two ends are large such that each remains pure
3. C<sub>A</sub> is a function of z only
4. Steady state
5. v<sub>x</sub> and v<sub>y</sub> are zero, v<sub>z</sub> is nonzero



Therefore, the governing equation becomes

$$v \frac{dC_A}{dz} = D_{AB} \frac{d^2 C}{dz^2}$$



The boundary conditions are

$$C_A = C_{A0} \quad \text{at} \quad Z = L,$$

$$C_A = 0 \quad \text{at} \quad Z = 0$$

$$\text{Let } \frac{dC_A}{dz} = p \quad \Rightarrow \quad \frac{dp}{dz} - \frac{v}{D_{AB}} p = 0$$

$$p = a' e^{vz/D_{AB}} \quad a' \text{ being the integration constant}$$

Therefore,

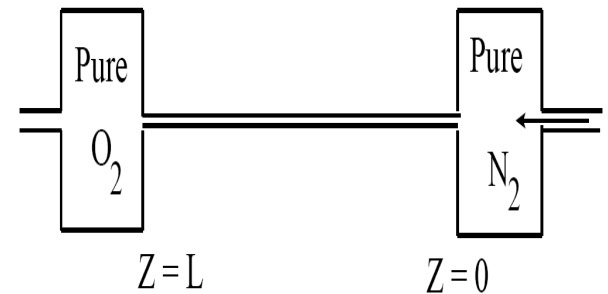
$$C_A = a e^{vz/D_{AB}} + b$$

Using the boundary conditions

$$C_A = C_{A0} \quad \text{at} \quad Z = L, \quad C_A = 0 \quad \text{at} \quad Z = 0$$

a and b can be evaluated and the concentration distribution of  $O_2$  in the tube can be expressed as

$$\frac{C_A}{C_{A0}} = \frac{e^{vZ/D_{AB}} - 1}{e^{vL/D_{AB}} - 1}$$



For very small values of  $(vL)/D_{AB}$ , the above equation becomes

$$\frac{C_A}{C_{A0}} = \frac{vZ/D_{AB}}{vL/D_{AB}} = \frac{Z}{L}$$



## Problem

A model has to be developed for computing the distribution of  $\text{NO}_2$  in the atmosphere. The molar flux of  $\text{NO}_2$  at ground level,  $N''_{A,0}$  (as a result of automobile and other emissions) is known. The concentration of  $\text{NO}_2$  at a distance well above ground level is zero and  $\text{NO}_2$  reacts chemically in the atmosphere with unburned hydrocarbons to produce smog. The reaction is first order with rate expressed as  $N_A = -k_1''' C_A$ .

(i) Assume steady state and a diffusion only process to obtain an expression for the vertical distribution  $C_A(x)$  of the molar concentration of  $\text{NO}_2$  in the atmosphere.

(ii) If an  $\text{NO}_2$  partial pressure of  $p_A = 2 \times 10^{-6}$  bar can cause pulmonary damage, what is the ground level molar flux for which a smog alert is to be issued? Data:  $T = 300\text{K}$ ,  $k_1 = 0.03 \text{ s}^{-1}$ ,  $D_{AB} = 0.15 \times 10^{-4} \text{ m}^2/\text{s}$ ,  $R = 8314 \text{ J/kmol} \cdot \text{K}$

## Species Balance Equation

$$\left( \cancel{\frac{\partial C_A}{\partial t}} + \cancel{v_x} \frac{\partial C_A}{\partial x} + \cancel{v_y} \frac{\partial C_A}{\partial y} + \cancel{v_z} \frac{\partial C_A}{\partial z} \right) = D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} + \cancel{\frac{\partial^2 C_A}{\partial y^2}} + \cancel{\frac{\partial^2 C_A}{\partial z^2}} \right] + \underline{R_A}$$

### Considerations

1. Steady state
2. Stagnant conditions, no convection
3. Homogeneous first order reaction
4.  $C_A$  is a function of  $x$  only
5. Molar flux at the ground level is known
6. Concentration of  $\text{NO}_2$  is zero well above the ground level

Therefore, the governing equation is

$$\frac{d^2 C_A}{dx^2} - k'''_1 C_A = 0 \quad (1)$$

$$C_A = C_1 e^{mx} + C_2 e^{-mx} \quad \text{and} \quad \frac{dC_A}{dx} = mC_1 e^{mx} - mC_2 e^{-mx} \quad (2)$$

$$\text{Where } m = \left( \frac{k'''_1}{D_{AB}} \right)^{1/2}$$

Boundary Conditions

$$C_A(\infty) = 0 \quad (3) \quad \rightarrow \quad C_1 = 0$$

$$\left. \frac{dC_A}{dx} \right|_{x=0} = - \frac{N''_{A0}}{D_{AB}} \quad (4)$$

The molar flux of  $\text{NO}_2$  at ground level,  $N''_{A,0}$  is known.


Known diffusive flux,  $N''_{A0}$  at  $x = 0$

From Eq. (2)  $\frac{dC_A}{dx} \Big|_{x=0} = -mC_2$  (5)

From Eq. (4) and (5) -  $mC_2 = -\frac{N''_{A0}}{D_{AB}}$

Therefore From Eq. (2)

Vertical distribution of  
NO<sub>2</sub> in the atmosphere



$$C_A = \frac{N''_{A0}}{m D_{AB}} e^{-mx}$$

$$m = \left( \frac{k'''_1}{D_{AB}} \right)^{1/2}$$

$$m = \left( \frac{0.03}{0.15 \times 10^{-4}} \right)^{1/2} m^{-1} = 44.7 m^{-1}$$

(ii) At the ground level,  $C_A(0) = \frac{N''_{A0}}{(k'''_1 D_{AB})^{1/2}}$

Partial pressure of NO<sub>2</sub> at the ground level,  $p_A(0)$  is

$$p_A(0) = C_A(0)RT = \frac{RTN''_{A0}}{m D_{AB}} \quad \text{and} \quad C_{A0,Critical} = \frac{p_{A(0)Critical}}{RT}$$

$$C_{A0,Critical} = \frac{2 \times 10^{-6} \times 10^5}{8314 \times 300} = 8 \times 10^{-8} \frac{k \text{ mol}}{m^3}$$

$$R = 8314 \frac{J}{K \text{ mol K}} \quad m = \left( \frac{0.03}{0.15 \times 10^{-4}} \right)^{1/2} m^{-1} = 44.7 m^{-1}$$

$$N''_{A0} = m D_{AB} C_A(0)$$

$$N''_{A0} = 44.7 \times 0.15 \times 10^{-4} \times 8 \times 10^{-8} = 5.37 \times 10^{-11} \frac{k \text{ mol}}{m^2 s}$$

## Problem

A spherical naphthalene ball of initial size of 0.03 m is hanged in a closet. One has to evaluate the time it takes for the naphthalene ball to sublime completely. The following information are known. The concentration of naphthalene in the air is very small, and very low convective mass flux conditions exist inside the closet. Both the air and naphthalene vapor are ideal gases, the temperatures are same everywhere and there are no radiation effects. The molar mass of naphthalene is 128.2 kg/kmol with a density equal to 1100 kg/m<sup>3</sup> and  $D_{AB} = 0.61 \times 10^{-5}$  m<sup>2</sup>/s. The dry air properties at 1 atm and 25° C are  $\rho = 1.184$  kg/m<sup>3</sup>,  $c_p = 1007$  J/Kg.K and  $\alpha = 2.141 \times 10^{-5}$  m<sup>2</sup>/s, the mass fraction of naphthalene on the air side of the surface is  $4.8 \times 10^{-4}$ . You may use the appropriate value of Sherwood number for this case.

Evaluate the time required for the naphthalene ball to sublime completely.

The mass fraction of  $N_2$  in the air is very low and the ball is inside the closet, therefore there will hardly be any natural convection.

For such special cases, it has already been established (by equating the diffusive flux at the interface with the convective flux away from the interface) that the Sherwood number (as well as Nusselt number) has a constant value equal to 2

$$Sh = \frac{h_m D}{D_{AB}} = 2 \quad \rightarrow \quad h_m = \frac{2D_{AB}}{D}$$

The mass of the Naptahalene ball,  $m = \rho_N \frac{1}{6} \pi D^3$

At the solid fluid surface of a sphere in stagnant systems

The diffusive heat (or mass) transfer at the interface denoted by  $-k A \frac{dT}{dr} \Big|_{R=r}$  must be equal to the convective (hypothetical) heat (or mass) transfer away from the interface expressed as  $[h A (T_s - T_\infty)]$  where  $h$  is the convective heat (or mass) transfer coefficient when the velocity approaches zero (stagnant condition).

From Eqn of energy, for a sphere in stagnant condition, at SS with no convection,  $T = f(r)$  only,  $T = T_s$  at  $r = R$  and  $T = T_\infty$  as  $r \rightarrow \infty$

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dT}{dr} \right) = 0$$



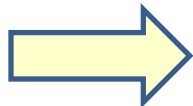
$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dT}{dr} \right) = 0$$

Integrating and using the boundary conditions, the temperature distribution can be written as

$$\frac{T - T_{\infty}}{T_s - T_{\infty}} = \frac{R}{r}$$

$$\frac{dT}{dr} = -\frac{R}{r^2} (T_s - T_{\infty}) \quad \frac{dT}{dr} \Big|_{r=R} = -\frac{1}{R} (T_s - T_{\infty})$$

$$-k \frac{dT}{dr} \Big|_{r=R} = h(T_s - T_{\infty}) = -\frac{k}{R} (T_s - T_{\infty}) \rightarrow \frac{hR}{k} = 1$$



$$\frac{hD}{k} = 2 \rightarrow Nu = 2 \quad \text{and} \quad Sh = 2$$


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The rate of change of the mass of  $N_2$  is equal to the rate of mass transfer from  $N_2$  to air. Therefore, ( $w$  being the mass fraction)

$$\frac{dm}{dt} = -h_m \rho_{Air} A (w_{NS} - w_{N\infty})$$

$$\frac{d}{dt} \left( \frac{1}{6} \rho_N \pi D^3 \right) = - \frac{2 D_{AB}}{D} \rho_{Air} \pi D^2 (w_{NS} - w_{N\infty})$$

$$\frac{\pi}{2} \rho_N D^2 \frac{dD}{dt} = -2 D_{AB} \rho_{Air} \pi D (w_{NS} - w_{N\infty})$$

Integrating from  $D = D_i = 0.03$  m at  $t = 0$  to  $D = 0$  at  $t = t$  (complete sublimation)

$$t = \frac{\rho_N D_i^2}{8 \rho_{Air} D_{AB} (w_{NS} - w_{N\infty})} \quad C_{N\infty} = 0$$

$$t = \frac{1100 \text{ Kg}/m^3 (0.03)^2 m^2}{8 \times 1.184 \text{ Kg}/m^3 \times 0.61 \times 10^{-5} m^2/s \times 4.8 \times 10^{-4}} \text{ s}$$

$$t = 3.57 \times 10^7 \text{ s} = 413 \text{ days}$$


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A timed-release drug is dissolving in the intestine of a person. As a steady state approximation we may assume that the drug is a rod of overall radius  $r_o$  (m) and length  $L$  (m). The timed-release action is accomplished by putting an inert coating on the drug through which the drug diffuses with a diffusivity,  $D_{AB}$ . At the inner edge of the coating ( $r_i$ ) the composition of the drug (mole fraction) is  $x_{ai}$ .

On the outer surface, the digestive juices provide for mass transfer with a mass transfer coefficient of  $k_{ac}$  (m/s) (equivalent to convective heat transfer coefficient). The amount of drug within the intestine can be approximated as  $x_{a\infty} \approx 0$ . Assume that the drug is not released by the two end-caps (circular) of the rod. You may also assume the total concentration of all species within the coating is  $c_t$ , a constant and it is a diffusion only process.

Calculate the rate of drug release (mg/hr) in the intestine. Given:  $r_i = 3\text{mm}$ ,  $r_o = 5\text{ mm}$ ,  $D_{AB} = 10^{-10}\text{ m}^2/\text{s}$ ,  $k_{ac} = 0.1\text{ m/s}$ ,  $L = 5\text{ mm}$ ,  $c_t = 0.4\text{ kg/m}^3$ ,  $x_{ai} = 0.9$ .

Gov. Eqn.

$$\frac{d}{dr} \left( r \frac{dx_A}{dr} \right) = 0$$

B.C.

- i) Known concentration at  $r = r_i$ ;
- ii) Equality of diffusion and convection at  $r = r_o$

The constants of integration can be evaluated

$$x_A = x_{Ai} + \frac{k_{AC} r_o}{D_{AB}} x_{Ao} \ln \frac{r_i}{r}$$

Putting the values

$$x_{Ao} = 3.527 \times 10^{-7}$$

$$\text{Rate of drug release into the intestine} = \text{Area} \times k_{AC} [x_{Ao} - x_{A\infty}] C_t$$

$$= 2 \pi r_o L k_{AC} C_t x_{Ao}$$

$$= 8 \times 10^{-3} \text{ mg/hr}$$

## Heterogeneous Reaction

Nitric Oxide (NO) emissions from auto exhaust can be reduced by a catalytic Converter and the following reaction occurs at the catalyst surface,  $\text{NO} + \text{CO} = 1/2\text{N}_2 + \text{CO}_2$ .

The rate equation is given as.  $r_A'' = -k_1'' C_A$  It may be assumed that NO reaches the catalyst surface by one-dimensional diffusion only process through a thin gas film of thickness L. The exhaust gases are at a temperature of 500 C and pressure of 1.2 bar. The thickness of the film is 1 mm and the reaction rate constant is,  $k_1'' = 0.05 \text{ m/s}$

The catalyst surface area is  $A = 200 \text{ cm}^2$ . The diffusion coefficient  $D_{AB} = 10^{-4} \text{ m}^2/\text{s}$  and the mole fraction of NO in the exhaust gases is  $X_{AL} = 0.15$ .

Evaluate the following

- i) What is the mole fraction of NO at the catalyst surface?
- ii) What is the NO removal rate for a surface area,  $A = 200 \text{ cm}^2$

**Solution:** Governing equation:  $\frac{d}{dz}(N_{AZ}) = 0$

Where  $N_{AZ} = -D_{AB} \frac{dC_A}{dz}$

$$\frac{d^2 C_A}{dz^2} = 0 \quad C \frac{d^2 x_A}{dz^2} = 0 \quad \frac{d^2 x_A}{dz^2} = 0 \quad (x_A \text{ is mole fraction})$$

$$x_A = C_1 z + C_2, \quad C_1 \text{ and } C_2 \text{ are constants.}$$

Boundary condition 1: At  $z = L$ ,  $x_A = x_{AL}$

$$\text{Boundary condition 2:} \quad -D_{AB} C \frac{dx_A}{dz} = -k_1'' C x_{As}$$

(Equality of diffusion rate and reaction rate)

$$-D_{AB} C_1 = -k_1'' x_{As} \quad \rightarrow \quad C_1 = \frac{k_1''}{D_{AB}} x_{As}$$

$$x_A = \frac{k_1''}{D_{AB}} x_{As} z + C_2$$

$$z = L, x_A = x_{AL}$$

$$x_{AL} = \frac{k_1''}{D_{AB}} x_{AS} L + C_2 \quad C_2 = x_{AL} - \frac{k_1''}{D_{AB}} x_{AS} L$$

$$x_A = \frac{k_1''}{D_{AB}} x_{AS} z + x_{AL} - \frac{k_1''}{D_{AB}} x_{AS} L$$

$$x = 0, x_A = x_{AS} \text{ (say)}$$

$$x_{AS} = \frac{x_{AL}}{1 + \frac{k_1'' L}{D_{AB}}} = \frac{0.15}{1 + \frac{0.001 \text{ m} * 0.05 \frac{\text{m}}{\text{s}}}{10^{-4} \frac{\text{m}^2}{\text{s}}}}$$

$$\text{Part (i) } x_{AS} = 0.1$$



$$N_{AS}'' = -k_1'' C_{AS} = -k_1'' C x_{AS} \rightarrow N_{AS}'' = \frac{-k_1'' C x_{AL}}{1 + L \frac{k_1''}{D_{AB}}}$$

$$C = \frac{P}{RT} = \frac{1.2 \text{ bar}}{8.314 * 10^{-2} \frac{\text{m}^3 \cdot \text{bar}}{\text{kmol} \cdot \text{K}} * 773 \text{ K}} = 0.0187 \frac{\text{kmol}}{\text{m}^3}$$

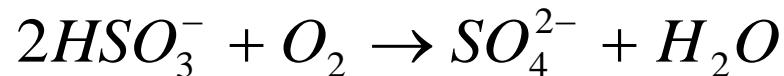
$$N_{AS}'' = -9.35 * 10^{-5} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s}}$$

Molar rate of NO removal for the entire surface

$$N_{AS} = N_{AS}'' \cdot A = -9.35 * 10^{-5} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s}} * 0.02 \text{ m}^2$$

**Part (ii)  $N_{AS} = -1.87 * 10^{-6} \frac{\text{kmol}}{\text{s}}$**

Oxygen diffuses through the wall of drug containers and oxidizes many drugs rendering them inactive. It is the oxygen diffusion/reaction scenario that limits the shelf-life of many pharmaceutical products. To limit the oxidation of drugs, Oxygen scavengers, like sodium bisulfite ( $\text{NaHSO}_3$ ) are often added to the drugs. The reaction to remove oxygen is:



Consider a liquid drug stored in a cylindrical polyethylene container. The container is 15 cm high and has an inner radius of 6 cm. The initial concentration of  $\text{NaHSO}_3$  in the drug formulation is 1 g/lit. Neglect diffusion through the top and bottom of the container and assume that the  $\text{NaHSO}_3$  reacts instantly with the  $\text{O}_2$ . The  $\text{O}_2$  concentration in air is also always 21%; and this may be approximated as the concentration at the outer end of the container. The effective diffusivity of  $\text{O}_2$  through polyethylene is  $9 \times 10^{-13} \text{ m}^2/\text{s}$  and you may assume  $P = 1 \text{ atm}$ ,  $T = 20^\circ\text{C}$ , and the process operates at steady-state. Evaluate the concentration profile of  $\text{O}_2$  in the container material. How thick must the walls of the container be to ensure that 90% of the  $\text{NaHSO}_3$  remains after 1 year?

Steady state diffusion, O<sub>2</sub> conc. in drug = 0, O<sub>2</sub> conc. in air = 21 %  
Mol Wt. of SB = 104

1 D diffusion in cylindrical systems with no reaction

BC

i) known conc. At  $r = r_0$

ii) Zero conc. At  $r = r_i$  (instantaneous reaction)

Thickness 10 mm (approx)

# **Mass Transfer - 2**

# Mass Transfer Fundamentals

Fick's Law

$$N_A = x_A (N_A + N_B) - D_{AB} \nabla C_A$$

BSL

Molar Flux    Bulk Flow    Diffusion

$D_{AB} \left( \frac{\partial C_A}{\partial x} + \frac{\partial C_A}{\partial y} + \frac{\partial C_A}{\partial z} \right)$

## Species Balance Equation in Cartesian Coordinate System

$$\left( \frac{\partial C_A}{\partial t} + v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} + v_z \frac{\partial C_A}{\partial z} \right) = D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right] + R_A$$

Transient,    Convection,    Conduction/Diffusion,    Generation

$$\rho \hat{C}_p \left( \frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} + v_z \frac{\partial T}{\partial z} \right) = k \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right] + \mu \phi_v + \dot{Q}$$

2

## Observations

$$\left( \frac{\partial C_A}{\partial t} + v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} + v_z \frac{\partial C_A}{\partial z} \right) \\ = D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right] + R_A$$

Homogeneous reaction term appears in the governing equation

Heterogeneous reaction appears as a boundary condition.

Possible boundary conditions

1. Concentration specified at a point e.g. solubility, equilibrium etc.
2. At the catalyst surface, diffusive flux to the surface must be equal to the rate of reaction

$$- D_{AB} \frac{dC_A}{dx} \Big|_{x=\text{cat sur}} = - R_A^{//}$$

// refers to heterogeneous reaction

Boundary conditions contd.

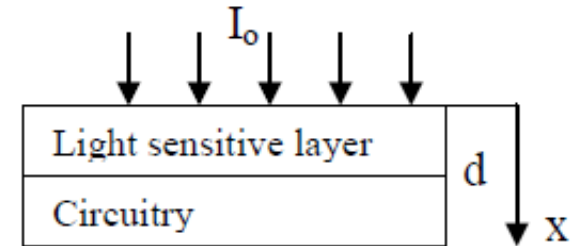
3. Equality of concentration at the interface  $C_{A, s1} = C_{A, s2}$

4. Impervious surface  $dC/dx = 0$  at specified location

5. Conductive flux to the solid-fluid interface is equal to the convective flux away from the interface,  $-D_{AB} \left. \frac{dC_A}{dx} \right|_{x=L} = h_m (C_{As} - C_{A\infty})$

In a photodiode, as shown in the figure (d being the thickness of the sensitive layer), electrons are generated at a rate,  $\dot{M}$  which are directly proportional to the incident light intensity. The intensity varies exponentially with depth as shown below

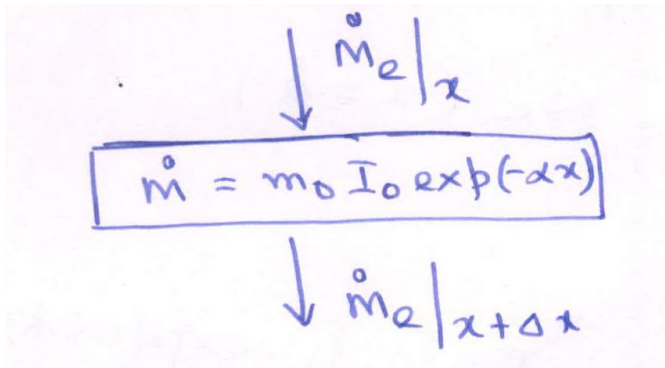
$$I = I_o \exp(-\alpha x) \quad \text{and} \quad \dot{M} \text{ (mol / m}^3 \text{ s)} = m_o I$$



The electrons diffuse toward the circuitry (the generated electrons flow through the interface at  $x=d$ ) and a signal is generated that is proportional to the electron flux at d.

- (a) Evaluate an expression for the concentration profile of electrons,  $C_e$ , in the light sensitive layer. The flow of electrons is governed by a law similar to Fick's law. The diffusivity of electrons is  $D_{es}$ .
- (b) All photodiodes have a dark current,  $I_d$ , due to electrons formed by random thermal means, that is basically noise. The dark current density is proportional to the volume of light sensitive material,  $I_d = I_{no} V$ , where  $V$  is the volume and  $I_{no}$  is a constant. Develop an expression for the signal to noise ratio.





IN – OUT + Generation = Accumulation

$$\dot{M}_e(x) - \dot{M}_e(x + \Delta x) + \dot{M} A_c \Delta x = 0$$

$$-\frac{d\dot{M}_e}{dx} + \dot{M} A_c = 0 \quad (1)$$

Substituting Fick's law for the molar flow rate of electrons

$$\dot{M}_e = A_c N_c = -A_c D_{es} \frac{dc_e}{dx}$$

$$I = I_o \exp(-\alpha x)$$

Therefore Eq. (1) becomes

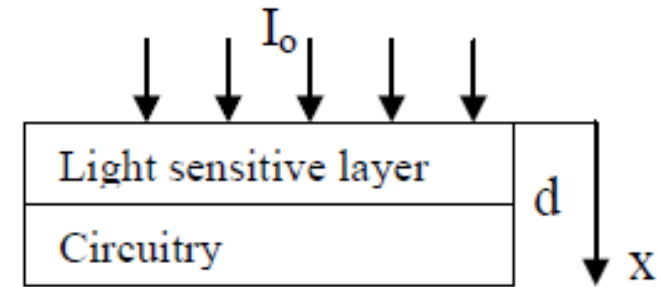
$$\dot{M} \text{ (mol / m}^3 \text{ s)} = m_o I$$

$$D_{es} \frac{d^2 C_e}{dx^2} + m_o I_o \exp(-\alpha x) = 0$$

$$\frac{dC}{dx} = \frac{m_o I_o}{\alpha D_{es}} e^{-\alpha x} + a_1$$

$$C = -\frac{m_o I_o}{\alpha^2 D_{es}} e^{-\alpha x} + a_1 x + a_2$$

## Boundary Conditions



i) No electrons at  $x = 0$

ii) All generated electrons must flow through the interface at  $x = d$

$$x = 0, C_e = 0 \rightarrow a_2 = \frac{m_o I_o}{\alpha^2 D_{es}}$$

$$x = d, M_e = A_c \int_0^d M dx \Rightarrow -D_{es} A_c \left. \frac{dC_A}{dx} \right|_d = A_c \int_0^d m_o I_o e^{-\alpha x} dx$$

$$-D_{es} \left[ \frac{m_o I_o}{\alpha D_{es}} e^{-\alpha x} + a_1 \right]_{x=d} = \left[ \frac{m_o I_o}{\alpha} e^{-\alpha x} \right]_0^d$$

$$\Rightarrow a_1 = -\frac{m_o I_o}{\alpha D_{es}}$$

$$C_e = \frac{m_o I_o}{\alpha^2 D_{es}} [1 - \exp(-\alpha x)] - \frac{m_o I_o}{\alpha D_{es}}$$

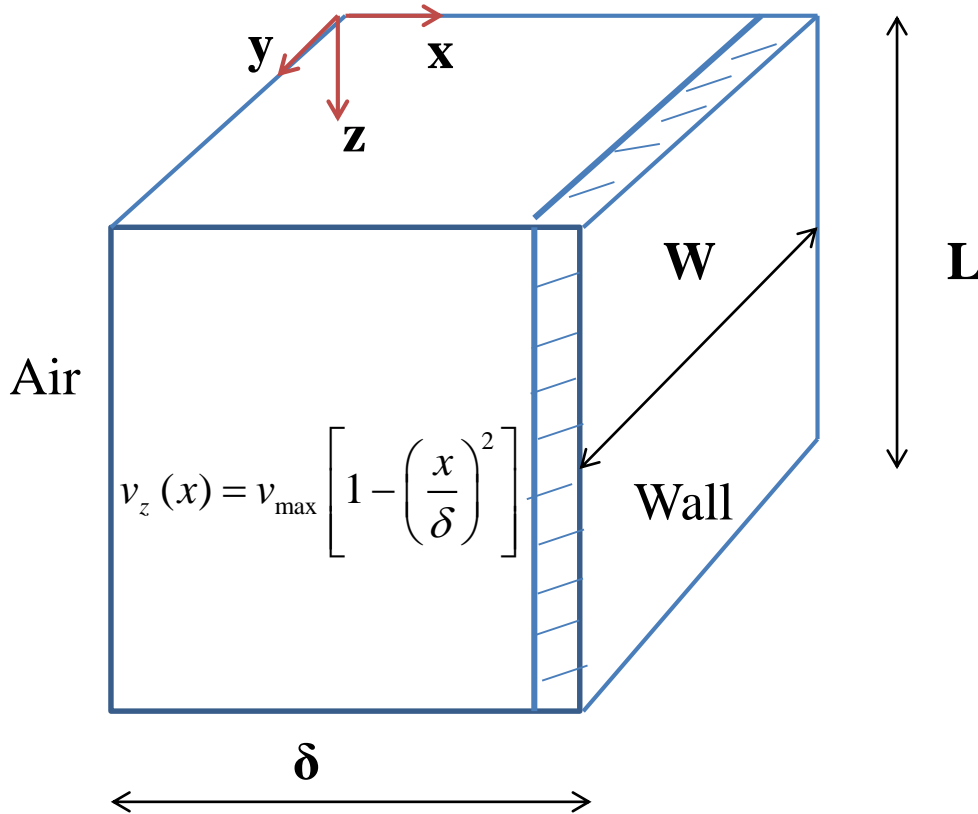
The signal we receive is proportional to the flow of electrons from the active layer.  
The noise is given by the dark current density times the volume of the active layer.

$$Signal = \dot{M}_e(x = d) = A_c N_e(x = d)$$

$$Noise = \dot{I}_{no} A_c d$$

$$\frac{Signal}{Noise} = \frac{N_e(x = d)}{I_{no} d} = \frac{m_o I_o [1 - \exp(-\alpha d)]}{I_{no} d}$$

## Diffusion into a falling Film - Forced Convection Mass Transfer



Absorption of gas A by a laminar falling film of liquid B

- (i) A is only slightly soluble in B
- (ii) Diffusion of A in B takes place very slowly, i.e. A does not penetrate very far into B – penetration distance small compared to the film thickness

$$\left( \cancel{\frac{\partial C_A}{\partial t}} + \cancel{v_x} \frac{\partial C_A}{\partial x} + \cancel{v_y} \frac{\partial C_A}{\partial y} + v_z \frac{\partial C_A}{\partial z} \right) = D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} + \cancel{\frac{\partial^2 C_A}{\partial y^2}} + \cancel{\frac{\partial^2 C_A}{\partial z^2}} \right] + \cancel{R_A}$$

$$\left( v_z \frac{\partial C_A}{\partial z} \right) = D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} \right]$$

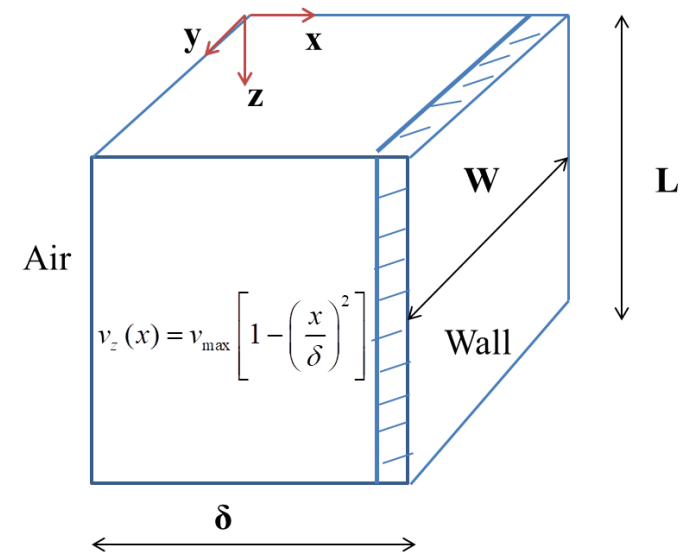
$$v_{\max} \left[ 1 - \left( \frac{x}{\delta} \right)^2 \right] \frac{\partial C_A}{\partial z} = D_{AB} \frac{\partial^2 C_A}{\partial x^2}$$

As the penetration distance of A in B is small (slow diffusion, small length etc.), to the diffusing A molecules the entire liquid film will appear as if travelling with  $v_{\max}$

$$v_{\max} \frac{\partial C_A}{\partial z} = D_{AB} \frac{\partial^2 C_A}{\partial x^2}$$

BC

1. At  $z = 0$ ,  $C_A = 0$
2. At  $x = 0$ ,  $C_A = C_{A0}$
3. At  $x = \delta$ ,  $\partial C_A / \partial x = 0$



BC

$$v_{\max} \frac{\partial C_A}{\partial z} = D_{AB} \frac{\partial^2 C_A}{\partial x^2}$$

1. At  $z = 0$ ,  $C_A = 0$

2. At  $x = 0$ ,  $C_A = C_{AO}$

3. At  $x = \delta$ ,  $\partial C_A / \partial z = 0$

Since the film thickness is large as compared to the penetration distance the 3<sup>rd</sup> BC may be written as

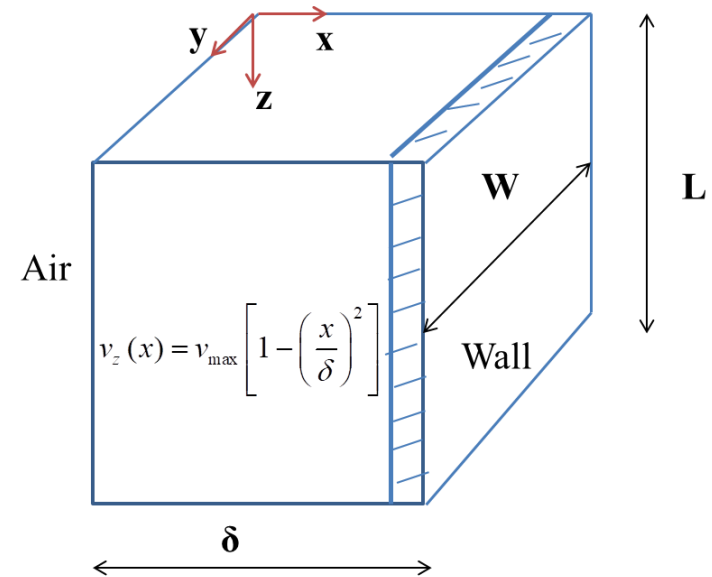
BC

1. At  $z = 0$ ,  $C_A = 0$

2. At  $x = 0$ ,  $C_A = C_{AO}$

**3. At  $x = \infty$ ,  $C_A = 0$**

$$\frac{C_A}{C_{AO}} = 1 - \operatorname{erf} \left( \frac{x}{\sqrt{4D_{AB} z / v_{\max}}} \right)$$

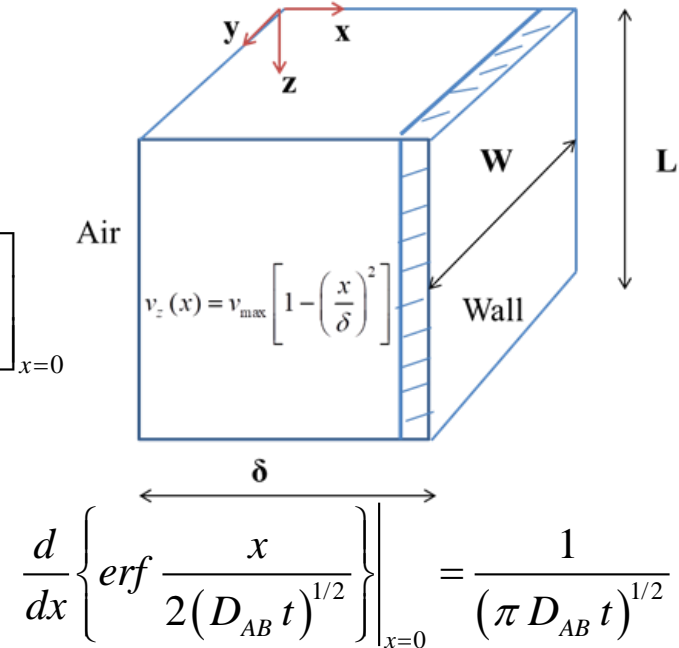


The total mass transfer rate can be calculated by integration of the local mass flux at ( $x = 0$ )

The local mass transfer rate at  $x = 0$

$$N_{Ax}(z)_{x=0} = -D_{AB} \left. \frac{\partial C_A}{\partial x} \right|_{x=0} = C_{Ao} D_{AB} \frac{\partial}{\partial x} \left[ \operatorname{erf} \frac{x}{\sqrt{4D_{AB}z/v_{\max}}} \right]_{x=0}$$

$$N_{Ax}(z)_{x=0} = C_{Ao} \sqrt{\frac{D_{AB} v_{\max}}{\pi z}}$$



$$\frac{d}{dx} \left\{ \operatorname{erf} \frac{x}{2(D_{AB} t)^{1/2}} \right\} \bigg|_{x=0} = \frac{1}{(\pi D_{AB} t)^{1/2}}$$

Total moles of A transferred per unit time from the gas to the film is

$$W_A = \int_0^W \int_0^L N_{Ax_{x=0}} dz dy = W C_{Ao} \int_0^L \sqrt{\frac{D_{AB} v_{\max}}{\pi z}} dz = W L C_{Ao} \sqrt{\frac{4 D_{AB} v_{\max}}{\pi L}}$$

Total moles of A transferred per unit time from the gas to the film is

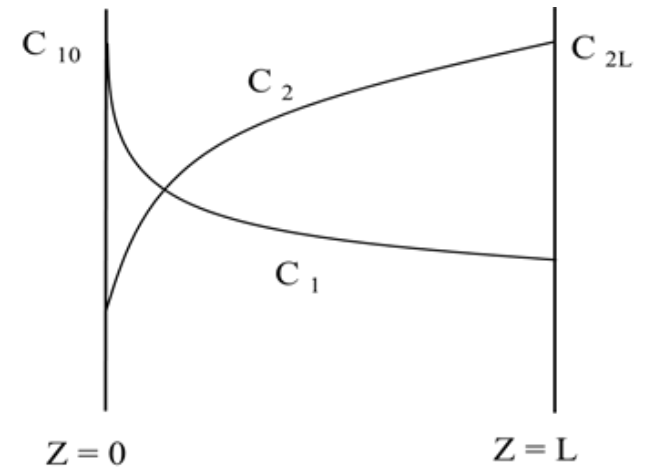
$$W_A = \int_0^W \int_0^L N_{Ax_{x=0}} dz dy = W C_{A0} \int_0^L \sqrt{\frac{D_{AB} v_{\max}}{\pi z}} dz = W L C_{A0} \sqrt{\frac{4 D_{AB} v_{\max}}{\pi L}}$$

The mass transfer rate is

- Directly proportional to the square root of the diffusivity
- Inversely proportional to the square root of the exposure time,  $L/v_{\max}$



Imagine a film of stagnant liquid in which a chemical species of concentration  $C_2$  is dissolved. At the surface  $z = 0$ , in contact with a solid wall, a concentration  $C_{10}$  of another species is maintained. The thickness of the film is  $L$ , over which  $C_1$  changes from a concentration of  $C_{10}$  to 0. and it can be assumed that some external mechanism is present that permits us to maintain  $C_{10}$  at  $z = 0$  and  $C_{2L}$  at  $z = L$ . Species 1 and 2 will diffuse and profiles  $C_1(z)$  and  $C_2(z)$  will be established at steady state

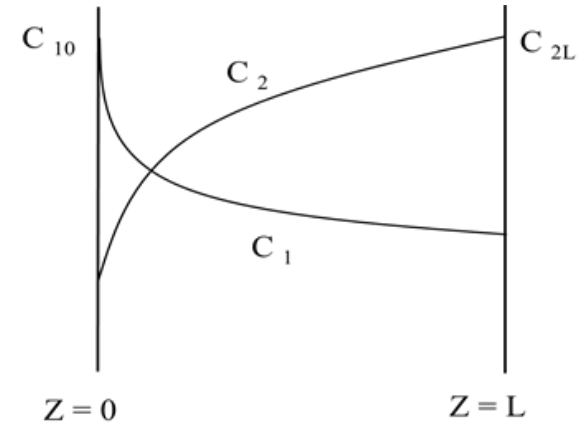


Now further suppose that species 1 and 2 react at a rate  $R_{12} = -k C_1 C_2$  ( $R_{12}$  is the rate of disappearance of 1 and 2). This reaction occurs homogeneously throughout the film. Species 1 and 2 diffuse through the film according to different diffusion coefficients, denoted by  $D_1$  and  $D_2$  respectively. Derive (do not solve) the governing equations (for one-dimensional diffusion only process) for the two species and state clearly the boundary conditions that reflect the physics of the process.

For 1D steady diffusion, the governing equations are -

$$0 = D_1 \frac{d^2 C_1}{d z^2} - k C_1 C_2 \dots \dots \dots (1)$$

$$0 = D_2 \frac{d^2 C_2}{d z^2} - k C_1 C_2 \dots \dots \dots (1)$$



With boundary conditions that reflect the following physical ideas -

### BC at z = 0

At z = 0,  $C_1$  is maintained at  $C_{10}$  and species 2 does not cross the plane at  $z=0$

$$C_1 = C_{10} \quad \text{at } z = 0$$

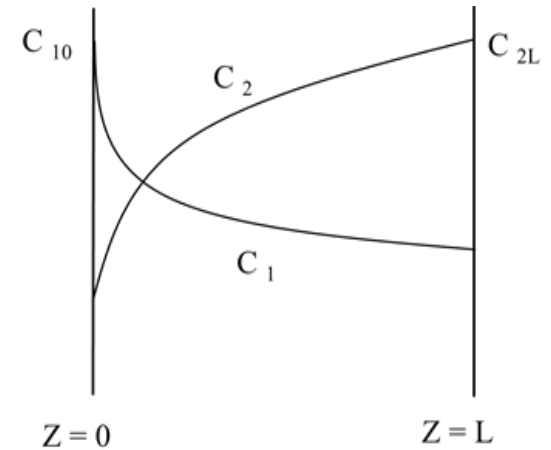
$$\frac{d C_2}{d z} = 0 \quad \text{at } z = 0$$

BC at  $z = L$ ,

At  $z = L$ ,  $C_2$  is maintained at  $C_{2L}$  and species 1 is depleted by reaction before reaching that plane

$$C_2 = C_{2L} \quad at \quad z = L$$

$$C_1 = 0 \quad at \quad z = L$$



Governing equations (1) and (2) are non-linear in the concentration  $C_1$  and  $C_2$ .

**An analytical solution is not possible.**

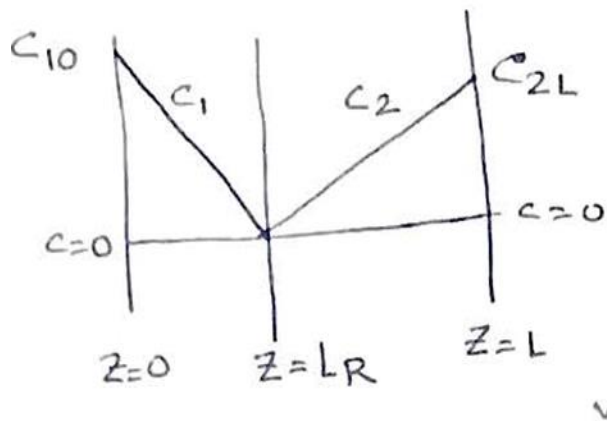
An analytical solution of these coupled nonlinear differential equations is not possible. However, one can make an approximation if it is assumed that the reaction rate is very fast i.e., when the diffusing molecules meet, they react and disappear immediately. Let the plane at which they meet,  $z = L_R$  is called the "reaction front". Derive analytical expressions for the concentration distributions of the two species for this case (in terms of  $L_R$  and other constants) within the respective domains of their existence and sketch the profiles.

Obtain an expression for the location of this "reaction front" i.e. an expression for  $L_R$ .

## If the reaction rate is very fast

When the molecules meet they react and disappear at a plane (  $Z = L_R$  ) - the reaction front

If the reaction is sufficiently fast, the profiles of  $C_1$  and  $C_2$  will appear as follows:



It is assumed that there is no excess of species 2

In the region  $0 \leq Z \leq L_R$  there is no species 2

$$\frac{d^2 C_1}{d z^2} = 0$$

$$\text{with } C_1 = C_{10} \text{ at } z = 0$$

$$\text{and } C_1 = 0 \text{ at } z = L_R$$

By a similar argument, the  $C_2$  profile satisfies

$$\frac{d^2 C_2}{dz^2} = 0$$

$$\text{with } C_2 = C_{2L} \text{ at } z = L$$

$$\text{and } C_2 = 0 \text{ at } z = L_R$$

The solutions are

$$C_1 = a_1 + b_1 z$$

$$C_2 = a_2 + b_2 z$$

$$a_1 = C_{10} ; \quad b_1 = -\frac{C_{10}}{L_R} \quad a_2 = -\frac{C_{2L} L_R}{L - L_R} \quad b_2 = \frac{C_{2L}}{L - L_R}$$

But  $L_R$  is unknown

**Additional physical statement:** Since 1 mole of species 1 reacts with 1 mole of 2, at steady state

$$N_1 = -N_2$$

$$-D_1 \frac{dC_1}{dZ} = D_2 \frac{dC_2}{dZ}$$

$$-D_1 b_1 = D_2 b_2$$

$$\frac{C_{10}D_1}{L_R} = \frac{C_{2L}D_2}{L - L_R} \quad \Rightarrow \quad L_R = \frac{L}{\left(1 + \frac{C_{2L}D_2}{C_{10}D_1}\right)}$$

$$\text{and} \quad N_1 = \frac{C_{10}D_1}{L} \left(1 + \frac{C_{2L}D_2}{C_{10}D_1}\right)$$

The rate of transfer of 1 into the film is enhanced by the reaction, i.e. the chemical reaction may serve to enhance the rate of absorption of a gas by a liquid.

- Design of absorbers
- Biomedical devices

A slab of salt of thickness  $L$  is used to support a deep layer of water. The salt dissolves in the water, maintaining a fixed mass density,  $\rho_{As}$  ( $\text{Kg/m}^3$ ) at the water-salt interface. If the salt density in water is initially zero, how does this density vary with position and time after contact between the solid salt and the water has been made?

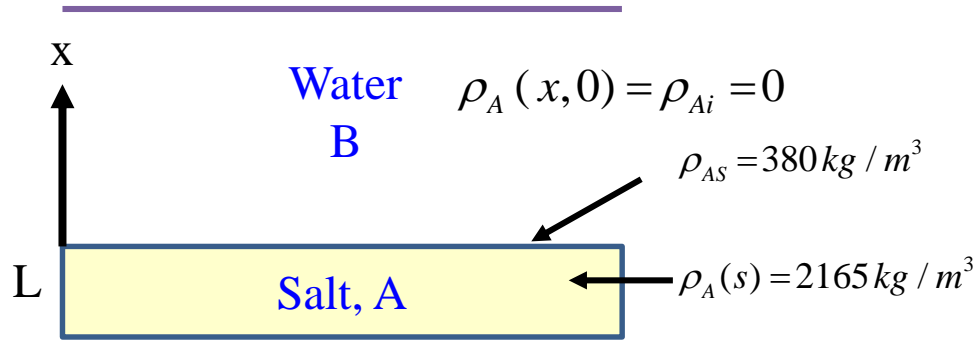
What is the surface recession rate  $dL/dt$  and how does the surface recession vary with time?

If the mass density of the solid salt is  $\rho_A(S) = 2165 \text{ (Kg/m}^3\text{)}$  and the density in the solution at the surface is  $\rho_{As} = 380 \text{ Kg/m}^3$ , by how much the surface recede after 24 h?

The salt-water diffusion coefficient is  $D_{AB} = 1.2 \times 10^{-9} \text{ m}^2/\text{s}$ .



$$\left( \frac{\partial \rho_A}{\partial t} + v_x \frac{\partial \rho_A}{\partial x} + v_y \frac{\partial \rho_A}{\partial y} + v_z \frac{\partial \rho_A}{\partial z} \right) = D_{AB} \left[ \frac{\partial^2 \rho_A}{\partial x^2} + \frac{\partial^2 \rho_A}{\partial y^2} + \frac{\partial^2 \rho_A}{\partial z^2} \right] + r_A$$



$$\frac{\partial \rho_A}{\partial t} = D_{AB} \frac{\partial^2 \rho_A}{\partial x^2}$$

$$IC: \quad \rho_A(x, 0) = \rho_{Ai} = 0$$

$$BC: \quad \rho_A(\infty, t) = 0 \quad \rho_A(0, t) = \rho_{AS}$$

Solution

$$\frac{\rho_A(x, t)}{\rho_{AS}} = 1 - \operatorname{erf} \left[ \frac{x}{2(D_{AB} t)^{1/2}} \right]$$

Performing a mass balance around the slab

$$-\dot{M}_{A,OUT} = \dot{M}_{A,Stored}$$

$$\frac{\rho_A(x,t)}{\rho_{AS}} = 1 - \operatorname{erf} \left[ \frac{x}{2(D_{AB}t)^{1/2}} \right]$$

$$-\dot{M}_{A,OUT} = \dot{M}_{A,Stored}$$

Based on unit surface area

$$-n_{AS}'' A = \frac{d}{dt}(\rho_A(s)L)A$$

$$-n_{AS}'' = \frac{D_{AB} \rho_{AS}}{(\pi D_{AB} t)^{1/2}}$$

$$\frac{D_{AB} \rho_{AS}}{(\pi D_{AB} t)^{1/2}} = \rho_A(s) \frac{dL}{dt}$$

$$\left. \frac{d}{dx} \left\{ \operatorname{erf} \frac{x}{2(D_{AB}t)^{1/2}} \right\} \right|_{x=0} = \frac{1}{(\pi D_{AB}t)^{1/2}}$$

$$\Delta L = -\frac{2\rho_{AS}}{\rho_A(s)} \left( \frac{D_{AB}t}{\pi} \right)^{1/2}$$

$$= -2 \times \frac{380 \text{ kg/m}^3}{2165 \text{ kg/m}^3} \left( \frac{1.2 \times 10^{-9} \text{ m}^2/\text{s} \times 24 \text{ h} \times 3600 \frac{\text{s}}{\text{h}}}{\pi} \right)^{1/2}$$

$$= 2.02 \text{ mm}$$