

Steady-State Molecular Diffusion

This part is an application to the general differential equation of mass transfer. The objective is to solve the differential equation of mass transfer under steady state conditions at different conditions (chemical reaction, one dimensional or more etc.).

Two approaches will be used to simplify the differential equations of mass transfer:

1. Fick's equation and the general differential equation for mass transfer can be simplified by eliminating the terms that do not apply to the physical situation.
2. A material balance can be performed on a differential volume element of the control volume for mass transfer.

One dimensional mass transfer independent of chemical reaction

The diffusion coefficient or mass diffusivity for a gas may be experimentally measured in an Arnold diffusion cell. This cell is illustrated schematically in Figure 1. The narrow tube, which is partially filled with pure liquid A, is maintained at a constant temperature and pressure. Gas B, which flows across the open end of the tube, has a negligible solubility in liquid A and is also chemically inert to A. Component A vaporizes and diffuses into the gas phase; the rate of vaporization may be physically measured and may also be mathematically expressed in terms of the molar mass flux.

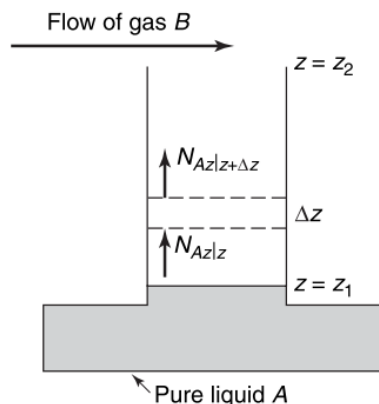


Fig. 1, Arnold diffusion cell

Required: to get the flux and concentration profile for this system.

Assumptions:

1. Steady state conditions
2. Unidirectional mass transfer in z direction
3. No chemical reaction occur

The general differential equation for mass transfer is given by:

$$\nabla \cdot \vec{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0$$

In rectangular coordinates this equation is:

$$\frac{\partial}{\partial x} N_{A,x} + \frac{\partial}{\partial y} N_{A,y} + \frac{\partial}{\partial z} N_{A,z} + \frac{\partial c_A}{\partial t} - R_A = 0$$

Apply the above assumptions to this equation:

$$\therefore \frac{d}{dz} N_{A,z} = 0$$

It means that the molar flux of A is constant over the entire diffusion path from z_1 to z_2 .

The molar flux is defined by the equation:

$$N_A = -cD_{AB} \frac{dy_A}{dz} + y_A(N_A + N_B)$$

According to the conditions of the system (B is insoluble and chemically inert to A)

$$\therefore N_B = 0$$

$$N_A = -cD_{AB} \frac{dy_A}{dz} + y_A N_A$$

$$N_A = -\frac{cD_{AB}}{1 - y_A} \frac{dy_A}{dz}$$

To get the flux N_A the above equation has to be integrated between z_1 and z_2 by using the boundary conditions:

$$\begin{aligned} \text{at } z = z_1 & \quad y_A = y_{A1} \\ \text{at } z = z_2 & \quad y_A = y_{A2} \end{aligned}$$

$$N_A \int_{z_1}^{z_2} dz = cD_{AB} \int_{y_{A1}}^{y_{A2}} -\frac{dy_A}{1-y_A}$$

$$N_A = \frac{cD_{AB}}{z_2 - z_1} \ln \frac{(1 - y_{A2})}{(1 - y_{A1})} \quad (1)$$

The above equation (equation 1) is commonly referred to as equations for steady-state diffusion of one gas through a second non diffusing gas or stagnant gas.

Absorption and humidification are typical operations defined by this two equation.

Some important notes:

Concentration for gas phase:	
Total concentration: $c = \frac{p}{RT}$	Concentration of A: $c_A = \frac{p_A}{RT}$
$y_A = \frac{p_A}{p}$	

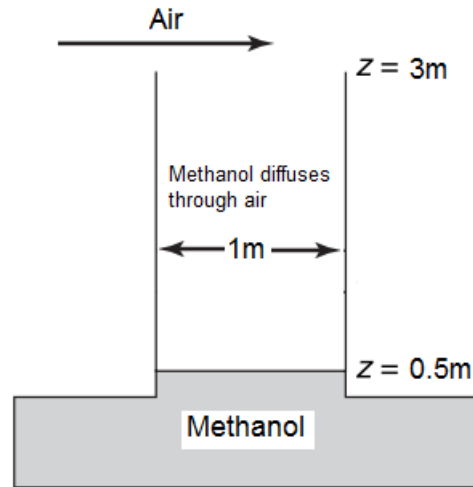
Example 1:

A tank with its top open to the atmosphere contains liquid methanol (CH₃OH, molecular weight 32g/mol) at the bottom of the tank. The tank is maintained at 30 °C. The diameter of the cylindrical tank is 1.0 m, the total height of the tank is 3.0 m, and the liquid level at the bottom of the tank is maintained at 0.5 m. The gas space inside the tank is stagnant and the CH₃OH vapors are immediately dispersed once they exit the tank. At 30 °C, the vapor pressure exerted by liquid CH₃OH is 163 mmHg and at 40 °C the CH₃OH vapor pressure is 265 mmHg. We are concerned that this open tank may be emitting a considerable amount of CH₃OH vapor.

- What is the emission rate of CH₃OH vapor from the tank in units of kg CH₃OH /day when the tank is at a temperature of 30 °C? State all assumptions and boundary conditions.
- If the temperature of the tank is raised to 40 °C, what is the new methanol emission rate? (or calculate the % increase in the rate of emission for 10 °C increasing in temperature)

Solution:

Assume methanol is A and air is B



Basic assumptions:

1. Steady state conditions
2. One dimensional mass transfer in z direction
3. B insoluble in A ($N_B = 0$)
4. No chemical reaction occurs

The mass flow rate = mass flux \times area

$$\text{area} = \frac{\pi}{4} d^2 = 0.785 \text{ m}^2$$

The mass flux = mole flux \times M. wt = $N_A \times \text{M. wt} = N_A \times 32$

$$N_A = -cD_{AB} \frac{dy_A}{dz} + y_A(N_A + N_B)$$

According to the conditions of the system (B is insoluble and chemically inert to A)

$$\therefore N_B = 0$$

$$N_A = -cD_{AB} \frac{dy_A}{dz} + y_A N_A$$

$$N_A = -\frac{cD_{AB}}{1 - y_A} \frac{dy_A}{dz}$$

$$N_A = \frac{cD_{AB}}{z_2 - z_1} \ln \frac{(1 - y_{A2})}{(1 - y_{A1})}$$

$$c = \frac{p}{RT} = \frac{1}{(0.082)(303)} = 4.023 \times 10^{-2} \text{ mol/L} = 40.23 \text{ mol/m}^3$$

Length of the diffusing path: $z_2 - z_1 = 3 - 0.5 = 2.5 \text{ m}$

$$y_{A1} = \frac{p_A}{p} = \frac{163}{760} = 0.2145$$

Since the CH₃OH vapors are immediately dispersed once they exit the tank

$$\therefore y_{A2} = 0$$

The diffusion coefficient D_{AB} is obtained from the Hirschfelder equation:

$$D_{AB} = \frac{0.001858 T^{3/2} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{P \sigma_{AB}^2 \Omega_D}$$

From table (6)

Component	σ	ε/k
Air	3.617	97
methanol	3.538	507

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} = 3.601 \text{ \AA}$$

Ω_D is a function of $\frac{\varepsilon_{AB}}{k}$

$$\frac{\varepsilon_{AB}}{k} = \sqrt{\frac{\varepsilon_A}{k} \frac{\varepsilon_B}{k}}$$

$$\frac{\varepsilon_A}{k} = \sqrt{(97)(507)} = 221.7634 \text{ K}$$

$$\frac{kT}{\varepsilon_{AB}} = \frac{303}{221.7634} = 1.366$$

$$\Omega_D = 1.253 \text{ ergs (from table 7)}$$

Substitute in Hirschfelder equation:

$$\therefore D_{AB} = 1.66 \frac{cm^2}{s} = 1.66 \times 10^{-4} \frac{m^2}{s}$$

$$N_A = \frac{cD_{AB}}{z_2 - z_1} \ln \frac{(1 - y_{A2})}{(1 - y_{A1})} = \frac{40.23 \times 1.66 \times 10^{-4}}{2.5} \ln \left[\frac{1}{(1 - 0.2145)} \right]$$

$$N_A = 6.45 \times 10^{-4} \text{ mol/m}^2 \cdot s$$

$$\text{The mass flux} = 6.45 \times 10^{-4} \times 32 = 2.064 \times 10^{-2} \text{ g/m}^2 \cdot s$$

$$\text{The mass flow rate} = 2.064 \times 10^{-2} \frac{g}{m^2 \cdot s} \times 0.785 \text{ m}^2 = 1.62 \times 10^{-2} \frac{g}{s} = 1.39 \text{ kg/day}$$

For part b:

The same procedure but the diffusion coefficient will be calculated at 313 K

We can use the following equation or Hirschfelder equation

$$D_{AB,T_2,P_2} = D_{AB,T_1,P_1} \left(\frac{P_1}{P_2} \right) \left(\frac{T_2}{T_1} \right)^{3/2} \frac{\Omega_{D,T_1}}{\Omega_{D,T_2}}$$

In part a also we can use this equation and get the value of D_{AB} at 298 K from table 3 and correct it at 313 K.

Answer for part b is 2.6 kg/day

Equimolar Counter diffusion

This type of mass transfer operations is encountered in the distillation of two constituents whose molar latent heats of vaporization are essentially equal.

The flux of one gaseous component is equal to but acting in the opposite direction from the other gaseous component; that is,

$$N_A = -N_B$$

For the case of one dimensional, steady state mass transfer without homogeneous chemical reaction, the general equation:

$$\nabla \cdot \vec{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0$$

is reduced to:

$$\frac{d}{dz} N_{A,z} = 0$$

The above equation specifies that N_A is constant over the diffusion path in the z direction.

Since:

$$N_A = -cD_{AB} \frac{dy_A}{dz} + y_A(N_A + N_B)$$

$$\therefore N_A = -cD_{AB} \frac{dy_A}{dz}$$

For constant temperature and pressure system

$$\therefore N_A = -D_{AB} \frac{dc_A}{dz}$$

The above equation can be integrated using the boundary conditions

$$\text{at } z = z_1 \qquad c_A = c_{A1}$$

$$\text{at } z = z_2 \qquad c_A = c_{A2}$$

$$N_A \int_{z_1}^{z_2} dz = -D_{AB} \int_{c_{A1}}^{c_{A2}} dc_A$$

$$N_A = \frac{D_{AB}}{z_2 - z_1} (c_{A1} - c_{A2}) \quad (2)$$

For ideal gas system, the above equation is written in the following form:

$$N_A = \frac{D_{AB}}{RT(z_2 - z_1)} (p_{A1} - p_{A2}) \quad (3)$$

Equations 2 and 3 are referred as the equations for steady state equimolar counter diffusion without homogenous chemical reaction.

Equation 2 is used for diffusion in liquid and equation 3 is used for diffusion in gas.

The two above equations may be used to describe any process where the bulk contribution term is zero (as equimolar counter diffusion, diffusion of solute through a solid, diffusion through stationary liquid).

Concentration profile

The concentration profile for equimolar counterdiffusion processes may be obtained by substituting equation

$$N_A = -D_{AB} \frac{dc_A}{dz}$$

into the differential equation which describes transfer in the z direction

$$\frac{d}{dz} N_{A,z} = 0$$

$$\therefore \frac{d}{dz} \left(-D_{AB} \frac{dc_A}{dz} \right) = 0$$

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

The above equation may be integrated to yield:

$$c_A = C_1 z + C_2$$

The two constants of integration are evaluated, using the boundary conditions:

$$\text{at } z = z_1$$

$$c_A = c_{A1}$$

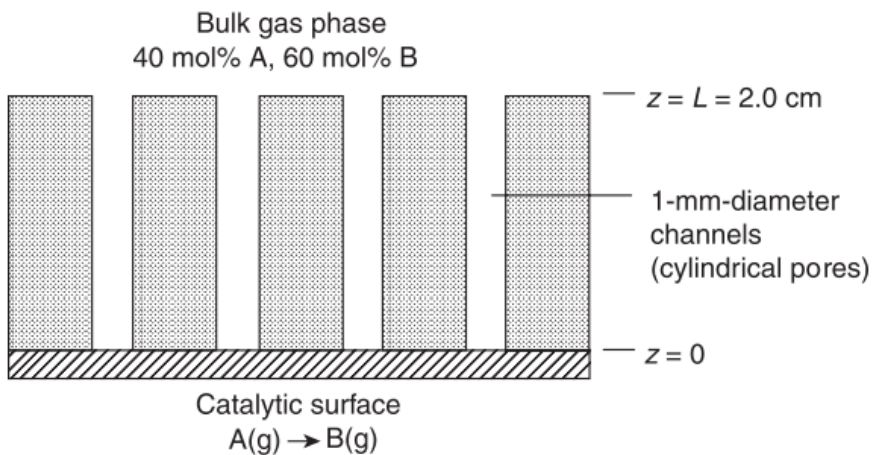
$$\text{at } z = z_2$$

$$c_A = c_{A2}$$

Example 2:

Consider the process shown in the figure below. A slab contains parallel linear channels running through a nonporous slab of thickness 2.0 cm. The gas space over the slab contains a mixture of A and B maintained at a constant composition. Gas phase species A diffuses down a straight, 1.0-mm-diameter channel. At the base of the slab is a catalytic surface that promotes the isomerization reaction $A(g) \rightarrow B(g)$. This reaction occurs very rapidly so that the production of B is diffusion limited. The quiescent gas space in the channel consists of only species A and B. The process is isothermal at 100 °C and isobaric at 2.0 atm total system pressure. The bulk composition over the slab is maintained at 40 mol% A and 60 mol% B. The molecular weight of species A and its isomer B is 58 g/mol.

- Listing all of your assumptions, simplify the general mass transfer equation for species A.
- Develop a final integrated equation for the flux of product B. Be sure to specify your boundary conditions.
- The binary gas-phase molecular diffusion coefficient of species A in species B is $0.1 \text{ cm}^2/\text{s}$ at 25 °C and 1.0 atm. What is a reasonable estimate for the molecular flux of species B in species A under the conditions of the operation?
- If the total production rate is 0.01 mol B/min, what is the required number of 1.0 mm-diameter channels necessary to accomplish this production rate?



Solution:

- a. Listing all of your assumptions, simplify the general mass transfer equation for species A

Assumptions:

1. Steady state conditions
2. One dimensional mass transfer (in z direction)
3. No homogeneous reaction

Therefore the differential equation is simplified to:

$$\frac{d}{dz} N_{A,z} = 0$$

- b. Develop a final integrated equation for the flux of product B. Be sure to specify your boundary conditions.

$$N_A = -cD_{AB} \frac{dy_A}{dz} + y_A(N_A + N_B)$$

According to the stoichiometry of the reaction:

$$N_A = -N_B$$

i.e. equimolar counter diffusion

$$N_A = -cD_{AB} \frac{dy_A}{dz}$$

The above equation can be integrated using the boundary conditions

$$\text{at } z = 0 \quad y_A = 0 \text{ (the reaction occurs very rapidly)}$$

$$\text{at } z = 2 \quad y_A = 0.4$$

$$N_A \int_0^2 dz = -cD_{AB} \int_0^{0.4} dy_A$$

$$N_A = \frac{cD_{AB}}{2} (0 - 0.4)$$

$$N_B = 0.2 c D_{AB}$$

Another method for solution:

Write the equation of Fick in terms of component B

$$N_B = -cD_{AB} \frac{dy_B}{dz} + y_B(N_A + N_B)$$

$$N_B = -cD_{AB} \frac{dy_B}{dz}$$

$$N_B \int_0^2 dz = -cD_{AB} \int_1^{0.6} dy_B$$

$$\therefore N_B = 0.2 c D_{AB}$$

Remember:

For gas phase diffusion $D_{AB} = D_{BA}$

- c. The binary gas-phase molecular diffusion coefficient of species A in species B is $0.1 \text{ cm}^2/\text{s}$ at 25°C and 1.0 atm . What is a reasonable estimate for the molecular flux of species B in species A under the conditions of the operation?

$$c = \frac{p}{RT} = \frac{2}{0.08206 \times 373} = 6.53 \times 10^{-2} \frac{\text{mol}}{\text{L}} = 6.53 \times 10^{-5} \frac{\text{mol}}{\text{cm}^3}$$

$D_{AB} = 0.1 \text{ cm}^2/\text{s}$ at a temperature of 25°C

The diffusion coefficient must be corrected at 100°C by using the equation:

$$D_{AB,T_2,P_2} = D_{AB,T_1,P_1} \left(\frac{P_1}{P_2}\right) \left(\frac{T_2}{T_1}\right)^{3/2} \frac{\Omega_{D,T_1}}{\Omega_{D,T_2}}$$

Neglect the change in the collision integral Ω_D

$$D_{AB} = 0.07 \text{ cm}^2/\text{s}$$

$$\therefore N_A = \frac{(6.53 \times 10^{-5})(0.07)}{2} (0 - 0.4) = -1.829 \times 10^{-6} \text{ mol/cm}^2 \cdot \text{s}$$

$$N_B = -N_A = 1.829 \times 10^{-6} \text{ mol/cm}^2 \cdot s$$

- d. If the total production rate is 0.01 mol B/min., what is the required number of 1.0 mm-diameter channels necessary to accomplish this production rate?

$$\text{Rate of production} = 0.01 \text{ mol/min} = N_B \times \text{total C.S.A}$$

$$\text{Total C.S.A} = \frac{0.01}{(1.829 \times 10^{-6})(60)} = 91.12 \text{ cm}^2$$

$$\text{C.S.A of one channel} = \frac{\pi}{4} d^2 = \frac{\pi}{4} (0.1)^2 = 0.00785$$

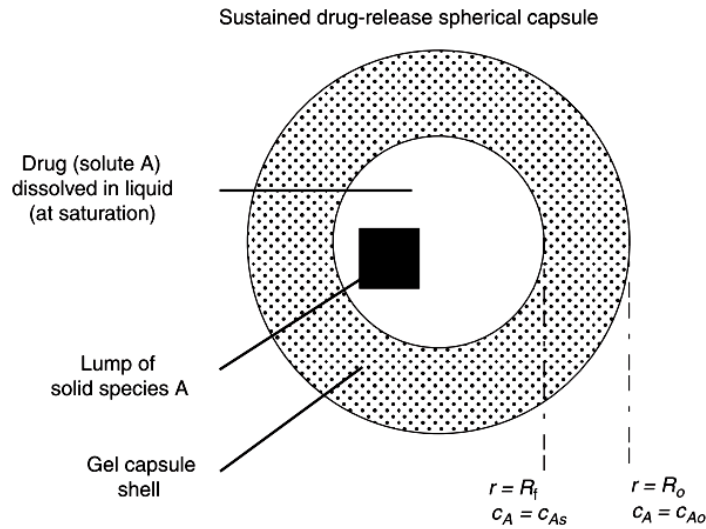
$$\text{Number of channels} = \frac{\text{Total C.S.A}}{\text{C.S.A of one channel}} = \frac{91.12}{0.00785} = 11608$$

Example 3:

The following illustrated spherical capsule is used for long-term, sustained drug release. A saturated liquid solution containing the dissolved drug (solute A) is encapsulated within a rigid gel-like shell. The saturated solution contains a lump of solid A, which keeps the dissolved concentration of A saturated within the liquid core of the capsule. Solute A then diffuses through the gel-like shell (the gel phase) to the surroundings. Eventually, the source for A is depleted, and the amount of solute A within the liquid core goes down with time. However, as long as the lump of solid A exists within the core, the source solution is saturated in A and the concentration c_A is constant. The diffusion coefficient of solute A in the gel phase B is $D_{AB} = 1.5 \times 10^{-5} \text{ cm}^2/s$. The concentrations of solute A in the gel phase at the boundaries of the shell are:

$$\begin{array}{ll} \text{at } r = R_1 = 0.2 \text{ cm} & c_A = c_{As} = c_A = 0.01 \text{ gmol/cm}^3 \\ \text{at } r = R_o = 0.35 \text{ cm} & c_A = c_{Ao} \end{array}$$

where c_{As} is the solubility limit of A in the gel.



- State the differential forms of the flux equation and the differential equation for mass transfer for this diffusion process.
- Develop the final analytical, integrated equation to determine the total rate of drug release from the capsule under the condition where the concentration of A within the liquid core of the capsule remains constant.
- What is the maximum possible rate of drug release from the capsule, in units of gram moles of A per hour?

Solution:

- State the differential forms of the flux equation and the differential equation for mass transfer for this diffusion process.

This system is represented by the differential equation of mass transfer in spherical coordinates.

The general equation is:

$$\nabla \cdot \vec{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0$$

Basic assumptions:

- Steady state
- No homogeneous reaction

3. One dimensional mass transfer (r-direction) 4. Constant T and P

$$\nabla \cdot \vec{N}_A = 0$$

For mass transfer in r-direction (see the general equation in spherical coordinates)

$$\frac{1}{r^2} \frac{d}{dr} (r^2 N_A) = 0$$

$$\therefore \frac{d}{dr} (r^2 N_A) = 0$$

- b. Develop the final analytical, integrated equation to determine the total rate of drug release in mol/s from the capsule under the condition where the concentration of A within the liquid core of the capsule remains constant. (There is no bulk motion).

Assume the total rate of drug release in mol/s is m_A

$$m_A = N_A \times Area$$

$$N_A = -cD_{AB} \frac{dy_A}{dr} + y_A(N_A + N_B)$$

Since there is no bulk motion (rigid gel (solid))

$$N_A = -cD_{AB} \frac{dy_A}{dr} = -D_{AB} \frac{dc_A}{dr}$$

$$Area = 4\pi r^2$$

$$m_A = -4\pi r^2 D_{AB} \frac{dc_A}{dr}$$

$$m_A \int_{0.2}^{0.35} \frac{dr}{r^2} = -4\pi D_{AB} \int_{0.01}^{c_{A0}} dc_A$$

$$m_A = 1.87\pi D_{AB} (0.01 - c_{A0})$$

The above equation is the final analytical, integrated equation to determine the total rate of drug release in mol/s from the capsule under the condition where the concentration of A within the liquid core of the capsule remains constant.

- c. What is the maximum possible rate of drug release from the capsule, in units of gram moles of A per hour?

According to the equation:

$$m_A = 1.87\pi D_{AB}(0.01 - c_{A0})$$

The maximum value of m_A exist when $c_{A0} = 0$

$$m_A \Big|_{max} = 1.87\pi D_{AB} \times 0.01 = 8.807 \times 10^{-7} \frac{mol}{s}$$

$$m_A \Big|_{max} = 8.807 \times 10^{-4} \frac{mol}{h}$$

One-dimensional systems associated with chemical reaction

There are two types of chemical reactions:

1. Homogeneous reaction: the reaction that occurs uniformly throughout a given phase (along the diffusion path as in the case of gas absorption).

This is the one which appears in the general differential equation of mass transfer.

$$\nabla \cdot \vec{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0$$

2. Heterogeneous reaction: the reaction that takes place at a boundary of the phase (as catalytic heterogeneous reactions where the reaction takes place at the catalyst surface and also in the case of combustion of coal).

The rate of disappearance of A by a heterogeneous reaction on a surface or at an interface does not appear in the general differential equation as R_A involves only reactions within the control volume along the diffusion path.

Notes:

1. A heterogeneous reaction enters the analysis as a boundary condition and provides information on the fluxes of the species involved in the reaction. HOW?

For example if there is a heterogeneous reaction occurs at the surface and the reaction is instantaneous (the reaction occurs so rapid). We can say that the concentration of the reacting species at the surface is zero. i.e. at ($z = 0$, $c_A = 0$ or $y_A = 0$)

2. Many industrial processes involve the diffusion of a reactant to a surface where a chemical reaction occurs.

The overall process occurs through two steps, namely;

- I. diffusion step
- II. reaction step

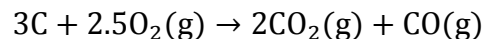
When the reaction rate is instantaneous relative to the rate of diffusion, then the process is said to be diffusion controlled. In contrast, when the reaction rate is slower than mass transfer rate, then the process is said to be reaction controlled or chemically controlled.

Q: Compare between diffusion controlled and reaction controlled processes?

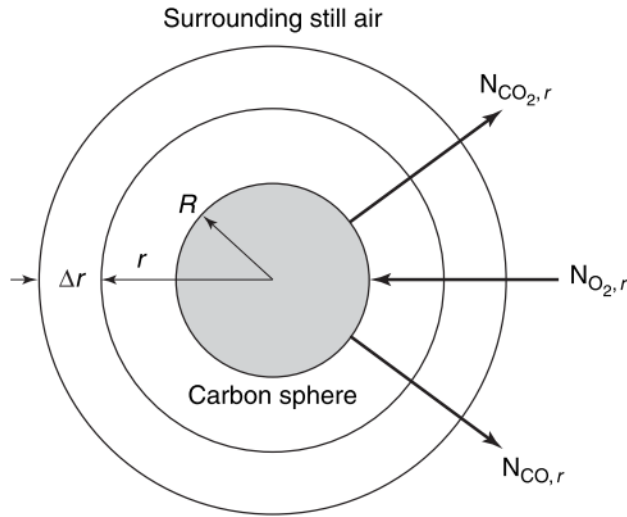
Simultaneous diffusion and heterogeneous, first-order chemical reaction: diffusion with varying area

Example of a simultaneous diffusion and a heterogeneous reaction process is the diffusion controlled combustion of coal in a fluidized bed to produce energy by the heat of combustion. Pulverized coal particles are fluidized within a hot combustion chamber, where oxygen in the air reacts with coal to produce carbon monoxide and/or carbon dioxide gas.

Consider the steady-state, one-dimensional diffusion of oxygen to the surface of a spherical particle of coal along the r coordinate. At the surface of the particle, oxygen gas (O_2) reacts with solid carbon (C) in the coal to form carbon monoxide gas (CO) and carbon dioxide (CO_2) gas according to the heterogeneous reaction equation:



as illustrated in the figure shown below



Diffusion through a spherical film

As the coal particle is oxidized, the particle shrinks with time as the carbon is converted to carbon monoxide and carbon dioxide.

Required:

Derive an expression to predict the moles of oxygen transferred per unit time in terms of the diffusion coefficient and particle radius.

Assumptions:

1. Steady state oxygen diffusion
2. One dimensional mass transfer in r direction
3. No homogenous reaction
4. Instantaneous heterogeneous reaction

Solution:

$$\text{moles of oxygen transferred per unit time} = (\text{mole flux}) \times (\text{area})$$

$$\text{moles of oxygen/time} = N_{O_2} \times 4\pi r^2$$

For N_{O_2} , apply the above assumptions on the general differential equation of mass transfer.

$$\nabla \cdot \vec{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0$$

$$\nabla \cdot \vec{N}_A = 0$$

For diffusion of oxygen in r-direction

$$\frac{1}{r^2} \frac{d}{dr} (r^2 N_{O_2}) = 0$$

$$\therefore \frac{d}{dr} (r^2 N_{O_2}) = 0$$

This equation specifies that $r^2 N_{O_2}$ is constant over the diffusion path in the r direction, so that

$$r^2 N_{O_2} \Big|_r = R^2 N_{O_2} \Big|_R$$

From Fick's equation:

$$N_{O_2} = -cD_{O_2-mix} \frac{dy_{O_2}}{dr} + y_{O_2} (N_{O_2} + N_{CO} + N_{CO_2})$$

Note: Nitrogen is inert $\therefore N_{N_2} = 0$ (non diffusing gas)

From the stoichiometry of the chemical reaction equation:

$$N_{CO} = -\frac{1}{2.5} N_{O_2} \qquad N_{CO_2} = -\frac{1}{1.25} N_{O_2}$$

The negative sign because diffusion of CO_2 and CO is in the opposite direction of O_2

$$N_{O_2} = -cD_{O_2-mix} \frac{dy_{O_2}}{dr} + y_{O_2} \left(N_{O_2} - \frac{1}{2.5} N_{O_2} - \frac{1}{1.25} N_{O_2} \right)$$

$$N_{O_2} = -cD_{O_2-mix} \frac{dy_{O_2}}{dr} - 0.2 y_{O_2} N_{O_2}$$

$$N_{O_2} dr = -cD_{O_2-mix} \frac{dy_{O_2}}{(1 + 0.2 y_{O_2})}$$

$$r^2 N_{O_2} \frac{dr}{r^2} = -\frac{cD_{O_2-mix}}{0.2} \frac{0.2 dy_{O_2}}{(1 + 0.2 y_{O_2})}$$

$$r^2 N_{O_2} \int_R^\infty \frac{dr}{r^2} = -\frac{cD_{O_2-mix}}{0.2} \int_0^{0.21} \frac{0.2 dy_{O_2}}{(1 + 0.2 y_{O_2})}$$

Note: air composition is 0.21 O_2 and 0.79 N_2

$$r^2 N_{O_2} \left(\frac{1}{R} \right) = \frac{c D_{O_2-mix}}{0.2} \ln \left(\frac{1}{1.042} \right)$$

$$r^2 N_{O_2} = R \frac{c D_{O_2-mix}}{0.2} \ln \left(\frac{1}{1.042} \right)$$

$$\text{moles of oxygen/time} = N_{O_2} \times 4\pi r^2$$

$$\therefore \text{moles of oxygen/time} = 4\pi R \frac{c D_{O_2-mix}}{0.2} \ln \left(\frac{1}{1.042} \right)$$

The above equation predicts a negative value for the rate of oxygen being transferred because its direction is opposite to the increasing r direction.

Important note:

What is the benefit of the above heterogeneous reaction in solving the above problem?

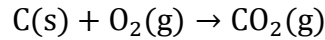
1. The reaction provides important boundary condition *at* $r = R, y_{O_2} = 0$ based on the assumption of instantaneous reaction
2. The reaction also provides a relation between the mole flux of the different components which help in solving the Fick's equation

Q: repeat the above example if the reaction is not instantaneous at the surface and is given by the first order rate equation $-r_A = k_s c_{A_s}$ [k_s is the reaction rate constant m/s]

Example 4:

A fluidized coal reactor has been proposed for a new power plant. If operated at 1145 K, the process will be limited by the diffusion of oxygen countercurrent to the carbon dioxide, CO_2 , formed at the particle surface. Assume that the coal is pure solid carbon with a density of $1.28 \times 10^3 \text{ kg/m}^3$ that the particle is spherical with an initial diameter of $1.5 \times 10^{-4} \text{ m}$ ($150 \mu\text{m}$). Air (21% O_2 and 79% N_2) exists several diameters away from the sphere. Under the conditions of the combustion process, the diffusivity of oxygen in the gas mixture at 1145 K is $1.3 \times 10^{-4} \text{ cm}^2/\text{s}$. If a steady-state process is assumed,

calculate the time necessary to reduce the diameter of the carbon particle to $5 \times 10^{-5} \text{ m}$ ($50 \mu\text{m}$). The surrounding air serves as an infinite source for O_2 transfer, whereas the oxidation of the carbon at the surface of the particle is the sink for O_2 mass transfer. The reaction at the surface is:



At the surface of the coal particle, the reaction is so rapid.

Solution:

The pure carbon particle is the source for the CO_2 flux and the sink for O_2 flux. As the coal particle is oxidized, there will be an output of carbon as stipulated by the stoichiometry of the reaction.

Number of moles of oxygen transferred = number of moles of carbon reacted

Number of moles transferred of oxygen = mole flux \times area

$$\text{Number of moles transferred of oxygen} = N_{\text{O}_2\text{-mix}} \times 4\pi r^2$$

$N_{\text{O}_2\text{-mix}}$ can be obtained by using the general differential equation with the Fick's equation as follows:

By applying the following assumptions on the general differential equation of mass transfer:

$$\nabla \cdot \vec{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0$$

1. Steady state oxygen diffusion
2. One dimensional mass transfer in r direction
3. No homogenous reaction
4. Instantaneous heterogeneous reaction

$$\therefore \nabla \cdot \vec{N}_A = 0$$

For diffusion of oxygen in r-direction

$$\frac{1}{r^2} \frac{d}{dr} (r^2 N_{\text{O}_2}) = 0$$

$$\therefore \frac{d}{dr}(r^2 N_{O_2}) = 0$$

The above equation specifies that $r^2 N_{O_2}$ is constant over the diffusion path in the r direction, so that

$$r^2 N_{O_2} \Big|_r = R^2 N_{O_2} \Big|_R$$

Form Fick's equation:

$$N_{O_2} = -cD_{O_2-mix} \frac{dy_{O_2}}{dr} + y_{O_2}(N_{O_2} + N_{CO_2})$$

But from the stoichiometry of the reaction

$$N_{O_2} = -N_{CO_2}$$

i.e. equimolar counter diffusion

$$\therefore N_{O_2} = -cD_{O_2-mix} \frac{dy_{O_2}}{dr}$$

$$N_{O_2} \int_R^\infty dr = -cD_{O_2-mix} \int_0^{y_{O_2,\infty}} dy_{O_2}$$

$$N_{O_2} r^2 \int_R^\infty \frac{dr}{r^2} = -cD_{O_2-mix} \int_0^{y_{O_2,\infty}} dy_{O_2}$$

$$N_{O_2} r^2 \left(\frac{1}{R} \right) = -cD_{O_2-mix} (y_{O_2,\infty} - 0)$$

$$N_{O_2} r^2 = -RcD_{O_2-mix} y_{O_2,\infty}$$

$$\text{number of moles of oxygen transfered per unit time} = N_{O_2} \times 4\pi r^2$$

$$\text{number of moles of oxygen transfered per unit time} = -4\pi R cD_{O_2-mix} y_{O_2,\infty}$$

The negative sign because the transfer of oxygen is in the opposite direction of r

$$\therefore \text{number of moles of carbon consumed per unit time} = 4\pi R cD_{O_2-mix} y_{O_2,\infty}$$

By applying the law of conservation of mass on the carbon:

Input – output + generation – consumption = accumulation(rate of change)

– consumption = accumulation(rate of change)

$$-4\pi R cD_{O_2-mix} y_{O_2,\infty} = \frac{dN}{dt} = \frac{\rho_c}{M. wt} \frac{dV}{dt}$$

$$V = \frac{4}{3}\pi R^3$$

$$-4\pi R cD_{O_2-mix} y_{O_2,\infty} = \frac{\rho_c}{M. wt} 4\pi R^2 \frac{dR}{dt}$$

$$dt = - \frac{\rho_c}{M. wt} \frac{R dR}{cD_{O_2-mix} y_{O_2,\infty}}$$

by integrating the above equation between the limits:

$$at t = 0 \quad R = R_i = 7.5 \times 10^{-5} m$$

$$at t = t \quad R = R_f = 2.5 \times 10^{-5} m$$

$$\int_0^t dt = - \frac{\rho_c}{M. wt} \frac{1}{cD_{O_2-mix} y_{O_2,\infty}} \int_{R_i}^{R_f} R dR$$

$$t = \frac{\rho_c}{2 M. wt} \frac{(R_i^2 - R_f^2)}{cD_{O_2-mix} y_{O_2,\infty}}$$

$$c = \frac{p}{RT} = 0.0106 kmol/m^3$$

$$y_{O_2,\infty} = 0.21$$

$$\therefore t = 0.92 s$$

Diffusion with a homogeneous, first-order chemical reaction

Example on this process is the absorption of gases where one of a gas mixture is preferentially dissolved in a contacting liquid called a solvent.

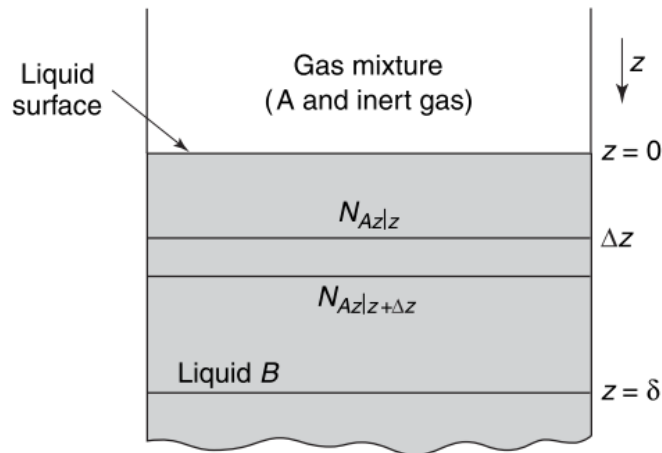
Gas absorption is divided into two types:

1. Physical absorption
2. Chemical absorption (where there is a production or disappearance of the diffusing component)

Mathematical treatment of a system containing homogeneous first order reaction

Consider the a absorption of gas A in a liquid B. The gas A disappeared in the liquid B by a first order chemical reaction defined by:

$$-R_A = k_r c_A$$



Absorption with homogeneous chemical reaction

Referring to the above figure, the composition of A at the liquid surface ($z = 0$) is c_{A_0} , the diffusion path length is δ (beyond this length the concentration of A is always zero). Component A will disappear after penetrating a short distance (δ) into the absorbing medium. Assume the following:

- a) There is very little fluid motion in the film
- b) One dimensional mass transfer

c) The concentration of A in the film is small d) Steady state diffusion of A
By applying these assumptions to the Fick's equation, the molar flux within the diffusion path is given by:

$$N_A = -D_{AB} \frac{dc_A}{dz}$$

and the general differential equation of mass transfer reduces to:

$$\frac{dN_A}{dz} - R_A = 0$$

Substitute the values of N_A and R_A in the above equation:

$$-\frac{d}{dz} \left(D_{AB} \frac{dc_A}{dz} \right) + k_r c_A = 0$$

Solution of the above equation will give the concentration profile.

The required boundary conditions are:

$$\begin{array}{ll} \text{at } z = 0 & c_A = c_{A_0} \\ \text{at } z = \delta & c_A = 0 \end{array}$$

Note:

The presence of homogeneous reaction will affect the shape of the concentration profile (makes it nonlinear).

Supplementary data:

The general differential equation for mass transfer of component A, in rectangular coordinates is

$$\frac{\partial c_A}{\partial t} + \left[\frac{\partial N_{A,x}}{\partial x} + \frac{\partial N_{A,y}}{\partial y} + \frac{\partial N_{A,z}}{\partial z} \right] = R_A$$

in cylindrical coordinates is

$$\frac{\partial c_A}{\partial t} + \left[\frac{1}{r} \frac{\partial}{\partial r} (r N_{A,r}) + \frac{1}{r} \frac{\partial N_{A,\theta}}{\partial \theta} + \frac{\partial N_{A,z}}{\partial z} \right] = R_A$$

and in spherical coordinates is

$$\frac{\partial c_A}{\partial t} + \left[\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 N_{A,r}) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (N_{A,\theta} \sin \theta) + \frac{1}{r \sin \theta} \frac{\partial N_{A,\phi}}{\partial \phi} \right] = R_A$$