

# Fundamental of Mass Transfer

by

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## Scope

The importance of the mass-transfer operations in chemical processes is profound. There is scarcely any industrial process that does not require a preliminary purification of raw materials or final separation of products. This is the realm of mass-transfer operations. Frequently, the major part of the cost of a process is that for the separations accomplished in the mass-transfer operations, a good reason for process engineers and designers to master this subject.

Mass transfer plays an important role in many industrial processes. A group of operations for separating the components of mixtures is based on the transfer of material from one homogeneous phase to another. These methods-covered by the term mass-transfer operations- include such techniques as distillation, gas absorption, humidification, liquid extraction, adsorption, membrane separations, and others. The driving force for transfer in these operations is a concentration gradient, much as a temperature gradient provides the driving force for heat transfer.

## Course Objectives

**Lecture 1** Include the following objectives:

- Convert a composition given in mass fraction to mole fraction, and the reverse.
- Transform a material from one measure of concentration to another, including mass/volume and moles/volume.

**Lecture 2** Include the following objectives:

- Define the following terms: mass-average velocity, molar-average velocity, mass (or molar) flux, and diffusion mass (or molar) flux.
- Write down an expression to calculate the mass (or molar) flux relative to a fixed coordinate system in terms of the diffusion mass (or molar) flux and the bulk motion contribution.

**Lecture 3** Include the following objectives:

- Write down Fick's first law for diffusion in a binary, isothermal, isobaric mixture.
- Define the Fick diffusivity and establish the relation between the Fick diffusivity and the Maxwell-Stefan diffusivity for a binary system.

**Lecture 4** Include the following objectives:

- Estimate diffusion coefficients for binary gas systems using the Wilke-Lee equation with tabulated values of the Lennard-Jones parameters.
- Estimate diffusion coefficients for binary gas systems using the Wilke-Lee equation with values of the Lennard-Jones parameters estimated from empirical correlations.

**Lecture 5** Include the following objectives:

- Estimate diffusion coefficients for binary dilute liquid systems using the Wilke and Chang equation.
- Estimate diffusion coefficients for binary dilute liquid systems using the Hayduk and Minhas equation.

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# Chapter 1

## Introduction

Your objectives in studying this section are to be able to:

- 1- Convert a composition given in mass fraction to mole fraction, and the reverse.
- 2- Transform a material from one measure of concentration to another, including mass/volume and moles/volume.

### 1.1 Introduction

When a system contains two or more components whose concentrations vary from point to point, there is a natural tendency for mass to be transferred, minimizing the concentration differences within the system and moving it towards equilibrium. The transport of one component from a region of higher concentration to that of a lower concentration is called mass transfer.

Definition of mass transfer:

Mass transfer is mass in transit as the result of a species concentration difference in a mixture. A species concentration gradient in a mixture provides the driving potential for transport of that species.

What is the meaning of species?

A species is an identifiable molecule, such as carbon dioxide,  $\text{CO}_2$ , that can be transported by diffusion and advection and/or converted to some other form by a chemical reaction. A

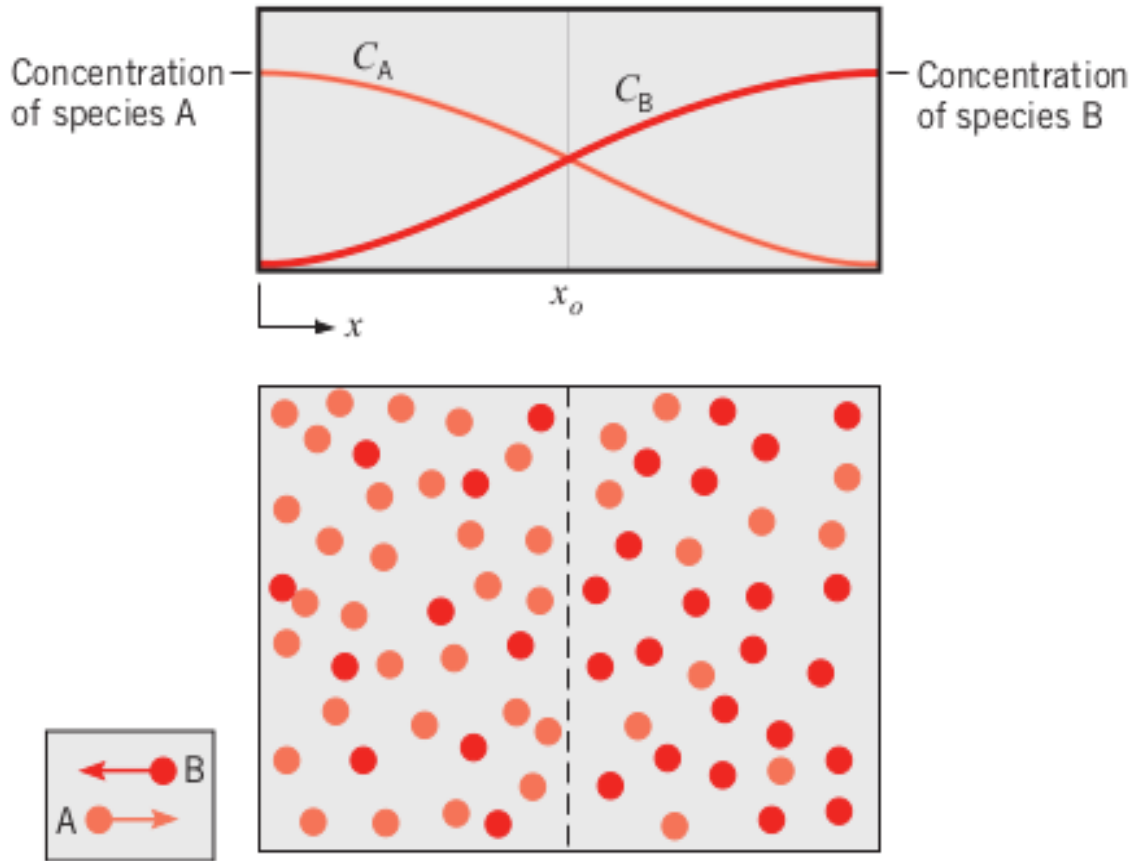


Figure 1.1: Mass transfer by diffusion in a binary gas mixture.

species may be a single atom or a complex poly-atomic molecule. It can also be appropriate to identify a mixture (such as air) as a species.

Mass diffusion occurs in liquids and solids, as well as in gases. However, since mass

transfer is strongly influenced by molecular spacing, diffusion occurs more readily in gases than in liquids and more readily in liquids than in solids.

### Examples of Diffusion:

Examples of diffusion in gases, liquids, and solids, respectively, include nitrous oxide from an automobile exhaust in air, dissolved oxygen in water, and helium in Pyrex.

## 1.2 Mixture Composition

In a multicomponent mixture, the concentration of particular species can be expressed in many ways. A mass concentration for each species, as well as for the mixture, can be defined. For species A, the mass concentration,  $\rho_A$ , is defined as the mass of A per unit volume of the mixture. The total mass concentration, or density,  $\rho$ , is the total mass of the mixture contained in a unit volume; that is,

$$\rho = \sum_{i=1}^n \rho_i \quad (1.1)$$

where  $n$  is the number of species in the mixture.

The mass fraction,  $\omega_A$ , is the mass concentration of species A divided by the total mass density,

$$\omega_A = \frac{\rho_A}{\sum \rho_i} = \frac{\rho_A}{\rho} \quad (1.2)$$

The sum of the mass fractions, by definition, must be 1:

$$\sum_{i=1}^n \omega_i = 1 \quad (1.3)$$

The molar concentration of species A,  $c_A$ , is defined as the number of moles of A present per unit volume of the mixture. By definition, 1 mole of any species contains a mass equivalent to its molecular weight; therefore, the mass concentration and the molar concentration are related by

$$c_A = \frac{\rho_A}{M_A} \quad (1.4)$$

where  $M_A$  is the molecular weight of species A.

When dealing with a gas phase under conditions in which the ideal gas law applies, the molar concentration is given by

$$c_A = \frac{P_A}{RT} \quad (1.5)$$

where  $p_A$  is the partial pressure of the species A in the mixture, T is the absolute temperature, and R is the gas constant.

The total molar concentration,  $c$ , is the total moles of mixture contained in a unit volume; that is,

$$c = \sum c_i \quad (1.6)$$

For a gaseous mixture that obeys the ideal gas law,

$$c = \frac{P}{RT} \quad (1.7)$$

where P is the total pressure.

The mole fraction for liquid or solid mixtures,  $x_A$ , and for gaseous mixtures,  $y_A$ , are the molar concentrations of species A divided by the total molar concentration:

$$x_A = \frac{c_A}{c} \dots \quad \text{for liquid and solids} \quad (1.8)$$

$$y_A = \frac{c_A}{c} \dots \quad \text{for gases} \quad (1.9)$$

Equation 1.9 is an algebraic representation of Dalton's law for gas mixtures. The sum of the mole fractions, by definition, must be 1:

$$\sum_{i=1}^n y_i = \sum_{i=1}^n x_i = 1 \quad (1.10)$$

For a mixture of ideal gases, the mass density and molar concentration of any constituent are related to the partial pressure of the constituent through the ideal gas law. That is,

$$\rho_i = \frac{P_i}{R_i T} \quad (1.11)$$

In terms of molar volume:

$$C_i = \frac{P_i}{RT} \quad (1.12)$$

where  $R_i$  is the gas constant for species  $i$  and  $R$  is the universal gas constant.

Using Dalton's law of partial pressures and above equation:

$$P = \sum_i P_i \quad (1.13)$$

and in similarity:

$$x_i = \frac{C_i}{C} = \frac{P_i}{P} \quad (1.14)$$

### 1.2.1 Properties of binary mixture

If A and B are ideal gases in a mixture, the ideal gas law may be applied to each gas separately to each gas of the mixture:

$$P_A V = n_A RT \quad (1.15)$$

$$P_B V = n_B RT \quad (1.16)$$

$$PV = nRT \quad (1.17)$$

where  $n_A$  and  $n_B$ , are the number of moles of species A and B in the mixture and  $n$  is the total number of moles in a volume  $V$ ,  $P_A$  and  $P_B$  and  $P$  are the respective partial pressures and the total pressure.

$$P_A = \frac{n_A}{V} RT = C_A RT = \frac{m_A}{M_A} RT \quad (1.18)$$

$$P_B = \frac{n_B}{V}RT = C_B RT = \frac{m_B}{M_B}RT \quad (1.19)$$

where  $M_A$  and  $M_B$  are the molecular weight of species A and B

$$P = \frac{n}{V}RT = C_T RT \quad (1.20)$$

From Dalton's law of partial pressures:

$$P = P_A + P_B = RT(C_A + C_B) = RT\left(\frac{m_A}{M_A} + \frac{m_B}{M_B}\right) \quad (1.21)$$

$$C_T = C_A + C_B \quad (1.22)$$

$$1 = x_A + x_B \quad (1.23)$$

### **Problem 1.1**

A gas containing 88% (by volume) CH<sub>4</sub>, 4% C<sub>2</sub>H<sub>6</sub>, 5% *n*-C<sub>3</sub>H<sub>8</sub>, and 3% *n*-C<sub>4</sub>H<sub>10</sub> at 300 K and 500 kPa will be scrubbed by contact with a nonvolatile oil in a gas absorber. The objective of the process is to recover in the liquid effluent as much as possible of the heavier hydrocarbons in the feed (see Figure 1.2). Calculate:

- (a) The total molar concentration in the gas feed.
- (b) The density of the gas feed.
- (c) The composition of the gas feed, expressed in terms of mass fractions.

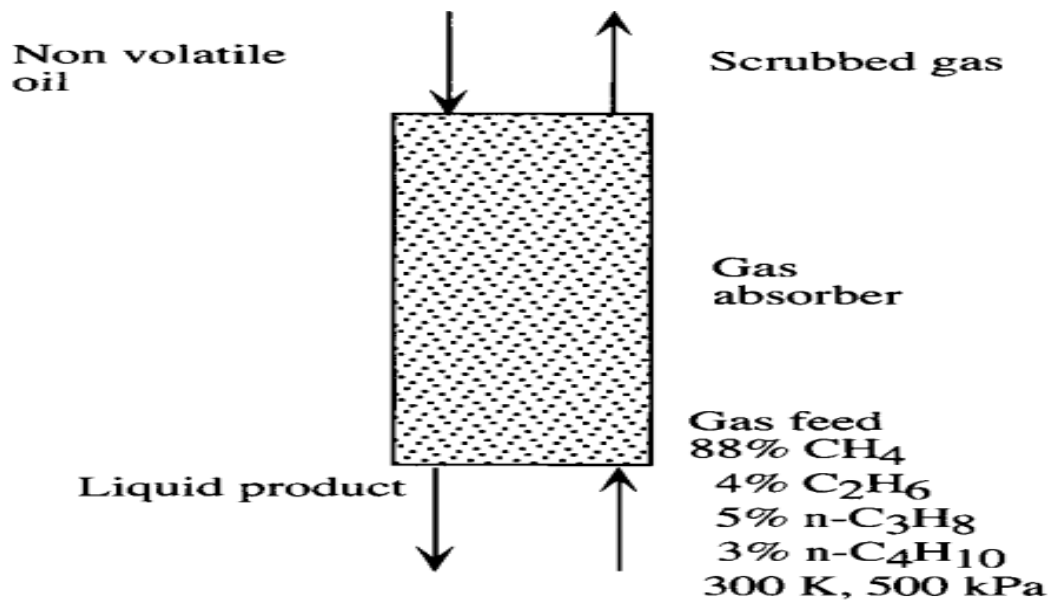


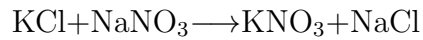
Figure 1.2: Schematic diagram of the gas absorber

Solution:



**Problem 1.2**

In the manufacture of potassium nitrate, potassium chloride reacts with a hot aqueous solution of sodium nitrate according to:



The reaction mixture is cooled down to 293 K and pure  $\text{KNO}_3$  crystallizes. The resulting slurry contains the  $\text{KNO}_3$  crystals and an aqueous solution of both  $\text{KNO}_3$  and  $\text{NaCl}$ . The crystals in the slurry are washed in a multistage process with a saturated  $\text{KNO}_3$  solution to free them of  $\text{NaCl}$  (see Figure 1.3). The equilibrium solubility of  $\text{KNO}_3$  in water at 293 K is 24% (by weight); the density of the saturated solution is  $1162 \text{ kg/m}^3$  (Perry and Chilton, 1973). Calculate:

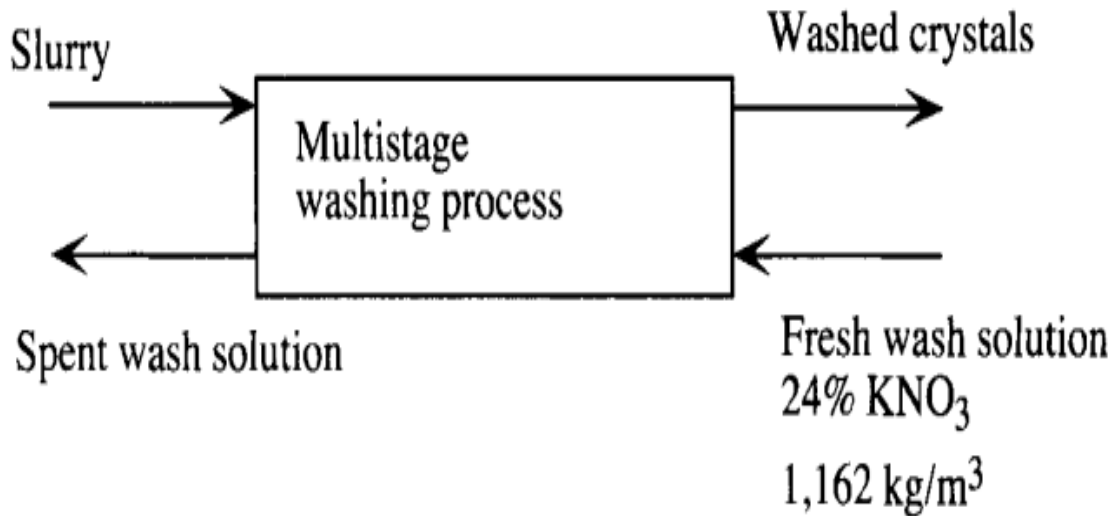


Figure 1.3: Schematic diagram of the washing process

**Solution:**

The next lecture will be about :

## 1.3 Velocities and fluxes

Your objectives in studying this section are to be able to:

- 1 Define the following terms: mass-average velocity, molar-average velocity, mass (or molar) flux, and diffusion mass (or molar) flux.
- 2 Write down an expression to calculate the mass (or molar) flux relative to a fixed coordinate system in terms of the diffusion mass (or molar) flux and the bulk motion contribution.

# Chapter 2

## Mass Transfer Theories

### 2.1 Velocities and Fluxes

Your objectives in studying this section are to be able to:

- 1- Define the following terms: mass-average velocity, molar-average velocity, mass (or molar) flux, and diffusion mass (or molar) flux.
- 2- Write down an expression to calculate the mass (or molar) flux relative to a fixed coordinate system in terms of the diffusion mass (or molar) flux and the bulk motion contribution.

The basic empirical relation to estimate the rate of molecular diffusion, first postulated by Fick (1855) and, accordingly, often referred to as Fick's first law, quantifies the diffusion of component A in an isothermal, isobaric system. According to Fick's law, a species can have a velocity relative to the mass or molar-average velocity (called diffusion velocity) only if gradients in the concentration exist. In a multi-component system the various species will normally move at different velocities; for that reason, an evaluation of a characteristic velocity for the gas mixture requires the averaging of the velocities of each species present.

The mass-average velocity for a multicomponent mixture is defined in terms of the mass densities:

$$v = \frac{\sum_{i=1}^n \rho_i v_i}{\sum_{i=1}^n \rho_i} = \frac{\sum_{i=1}^n \rho_i v_i}{\rho} = \sum_{i=1}^n \omega_i v_i \quad (2.1)$$

where  $v_i$  denotes the absolute velocity of species  $i$  relative to the stationary coordinate axis.

The molar-average velocity for a multicomponent mixture is defined in terms of the molar concentrations of all components by:

$$V = \frac{\sum_{i=1}^n c_i v_i}{\sum_{i=1}^n c_i} = \frac{\sum_{i=1}^n c_i v_i}{c} = \sum_{i=1}^n x_i v_i \quad (2.2)$$

Diffusion rates are most conveniently described in terms of fluxes.

## What is the meaning of mass or molar fluxes?

The mass (or molar) flux of a given species is a vector quantity denoting the amount of the particular species, in either mass or molar units, that passes per given unit time through a unit area normal to the vector. The flux may be defined with reference to coordinates that are fixed in space, coordinates which are moving with the mass-average velocity, or coordinates which are moving with the molar-average velocity.

The *mass flux of species  $i$*  with respect to coordinates that are fixed in space is defined by

$$n_i = \rho_i v_i \quad (2.3)$$

If we sum the component fluxes, we obtain *the total mass flux*,

$$n = \rho v \quad (2.4)$$

The *molar flux of species  $i$*  with respect to coordinates that are fixed in space is given by

$$N_i = c_i v_i \quad (2.5)$$

The *total molar flux* is the sum of these quantities:

$$N = cV \quad (2.6)$$

The *mass diffusion flux* of species i with respect to the mass-average velocity is given by

$$j_i = \rho_i(v_i - v) \quad \text{and} \quad \sum_{i=1}^n j_i = 0 \quad (2.7)$$

The *molar diffusion flux* of species i with respect to the molar-average velocity is given by

$$J_i = c_i(v_i - V) \quad \text{and} \quad \sum_{i=1}^n J_i = 0 \quad (2.8)$$

The *mass flux*  $n_i$  is related to *the mass diffusion flux* as

$$n_i = j_i + \rho_i v = j_i + \omega_i n \quad (2.9)$$

The molar flux  $N_i$  is related to the molar diffusion flux as

$$N_i = J_i + c_i V = J_i + y_i N \quad (2.10)$$

### **Important Note:**

It is important to note that the molar flux,  $N$ , described by equation above is a resultant of two vector quantities:

$J_i$  the molar diffusion flux,  $J$ , resulting from the concentration gradient; this term is referred to as the concentration gradient contribution;

$y_i N = c_i V$  the molar flux resulting as component i is carried in the bulk flow of the fluid; this flux term is designated the bulk motion contribution.

## 2.2 Fick's Law of Diffusion

The general mass diffusion equation for the species A under steady state condition is given by equation 2.11:

$$\frac{\delta^2 C_A}{\delta x^2} + \frac{\delta^2 C_A}{\delta y^2} + \frac{\delta^2 C_A}{\delta z^2} = \frac{1}{D} \frac{\delta C_A}{d\tau} \quad (2.11)$$

The rate equation for mass diffusion is known as Fick's law, and for transfer of species A in a binary mixture of A and B, it may expressed in vector form as:

$$j_A = -\rho D_{AB} \nabla m_A \quad (2.12)$$

The Fick's law can be stated as:

$$N_A = -D_{AB} \frac{dC_a}{dx} \quad (2.13)$$

The quantity  $j_A$  ( $kg/s \cdot m^2$ ) is defined as the diffusive mass flux of species A. It is the amount of A that is transferred by diffusion per unit time and per unit area perpendicular to the direction of transfer, and it is proportional to the mixture mass density,  $\rho = \rho_A + \rho_B$  ( $kg/m^3$ ), and to the gradient in the species mass fraction,  $m_A = \frac{\rho_A}{\rho}$ .

The species flux may also be evaluated on a molar basis, where  $J_A$  ( $kmol/s \cdot m^2$ ) is the diffusive molar flux of species A. It is proportional to the total molar concentration of the mixture,  $C = C_A + C_B$  ( $kmol/m^3$ ), and to the gradient in the species mole fraction,  $x_A = C_A/C$ . The foregoing forms of Fick's law may be simplified when the total mass density  $\rho$  or the total molar concentration  $C$  is a constant.

$$J_A = -CD_{AB} \nabla x_A \quad (2.14)$$

## 2.3 Mass diffusivity

Fick's law defines a second important transport property, namely, the binary diffusion coefficient or mass diffusivity,  $D_{AB}$ . Its fundamental dimensions are obtained from:

$$D_{AB} = \left(\frac{M}{L^2 t}\right) \left(\frac{1}{M/L^3 \cdot 1/L}\right) = \frac{L^2}{t} \quad (2.15)$$

For binary liquid solutions, it is necessary to rely exclusively on experimental measurements. For small concentrations of A (the solute) in B (the solvent),  $D_{AB}$  is known to increase with increasing temperature.

$D_{AB}$  for the binary mixture of two gases, A and B has been given considerable attention for predicting  $D_{AB}$ :

$$D_{AB} \approx \frac{1}{3} \bar{c} \lambda_{mfp} \sim P^{-1} T^{3/2} \quad (2.16)$$

where:

**T**= Absolute temperature in Kelvin

$\bar{c}$ = the mean electron velocity, which increases with increasing the temperature and decreasing molecular weight and therefore the mass diffusivity increases with increasing the temperature and molecular weight.

$\lambda_{mfp}$ = the electron mean free path, which is inversely proportional to gas pressure, so the mass diffusivity decreases with increasing pressure.

Because molecular velocities increase with rise of temperature T, so the diffusivity will increase. For gas, the diffusivity is proportional to  $T^{1.5}$ .

As the pressure P increases, the molecules become closer together and the mean free path is shorter and consequently the diffusivity is reduced. so diffusivity for a gas becoming approximately inversely proportional to the pressure.

$$D_{AB} \propto T^{1.5}/P$$

**$D_{AB} = D_{BA}$**

The value of  $D_{AB}$  for certain combinations of components are available in literature. It can be proved that  $D_{AB} = D_{BA}$ . When one molecule of A moves in the x direction, one molecule of B has to move in the opposite direction. Otherwise a macroscopic density gradient will develop, which is not sustainable, (A is area)

$$N_A/A = -D_{AB} \frac{dC_A}{dx} \quad (2.17)$$

$$N_B/A = -D_{BA} \frac{dC_B}{dx} = -D_{BA} \frac{d(1 - C_A)}{dx} = D_{BA} \frac{dC_A}{dx} \quad (2.18)$$

$$N_A/A = -N_B/A \quad (2.19)$$

$$D_{AB} = D_{BA} \quad (2.20)$$

## 2.4 The stationary medium approximation

When the diffusion of a very small amount of species A occurs within a stagnant species B, the molecular motion associated with the mass transfer will not induce significant bulk motion of the medium. This situation is common when one considers the diffusion of a dilute gas or liquid within a stagnant liquid or a solid host medium, such as when water vapor is transferred through the solid wall of a room. In these cases, the medium can be assumed to be stationary, and advection can be neglected. For situations where this stationary medium approximation is appropriate, the diffusive mass and molar fluxes:

$$n_A = j_A = -\rho D_{AB} \nabla \omega_A \quad (2.21)$$

$$N_A = J_A = -c D_{AB} \nabla x_A \quad (2.22)$$

Furthermore, since the concentration of species A is small, the total density ( $\rho$ ) or concentration ( $C$ ) is approximately that of the host medium, species B.

## 2.5 Conservation of species for a control volume

The rate at which the mass of some species enters a control volume, plus the rate at which the species mass is generated within the control volume, minus the rate at which this species mass leaves the control volume must equal the rate of increase of the species mass stored within the control volume.

For example, any species A may enter and leave the control volume due to both fluid motion and diffusion across the control surface; these processes are surface phenomena represented by  $\hat{M}_{A,in}$  and  $\hat{M}_{A,out}$ . The same species A may also be generated,  $\hat{M}_{A,g}$ , and



accumulated or stored,  $\hat{M}_{A,st}$ , within the control volume. The conservation equation may then be expressed on a rate basis as:

$$\hat{M}_{A,in} + \hat{M}_{A,g} - \hat{M}_{A,out} = \frac{dM_A}{dt} \equiv \hat{M}_{A,st} \quad (2.23)$$

Species generation exists when chemical reactions occur in the system. For example, for a dissociation reaction of the form  $AB \rightarrow A+B$ , there would be net production of species A and B, as well as net reduction of the species AB.

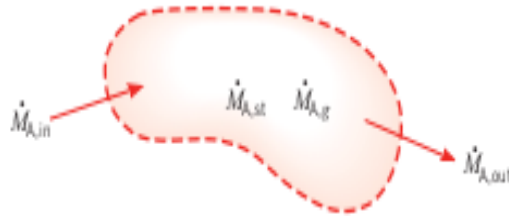


Figure 2.1: Conservation of species for a control volume.

## 2.6 The Mass Diffusion Equation

Allowing for concentration gradients in each of the x, y, and z coordinate directions, we first define a differential control volume,  $dx\ dy\ dz$ , within the medium (Figure 2.2) and consider the processes that influence the distribution of species A. With the concentration gradients, diffusion must result in the transport of species A through the control surfaces. Moreover,

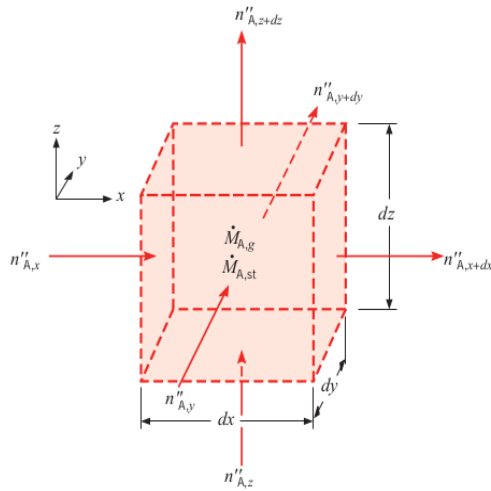


Figure 2.2: Differential control volume,  $dx$ ,  $dy$ ,  $dz$ , for species diffusion analysis in Cartesian coordinates.

relative to stationary coordinates, the species transport rates at opposite surfaces must be related by:

$$n_{a,x+dx}dydz = n_{a,x}dydz + \frac{\partial[n_{a,x}dydz]}{\partial x}dx \quad (2.24)$$

$$n_{a,y+dy}dxdz = n_{a,y}dxdz + \frac{\partial[n_{a,y}dxdz]}{\partial y}dy \quad (2.25)$$

$$n_{a,z+dz}dxdy = n_{a,z}dxdy + \frac{\partial[n_{a,z}dxdy]}{\partial z}dz \quad (2.26)$$

In addition, there may be volumetric (also referred to as homogeneous) chemical reactions occurring throughout the medium, perhaps nonuniformly. The rate at which species A is generated within the control volume due to such reactions may be expressed as

$$\dot{M}_{A,g} = \dot{n}_A dx dy dz \quad (2.27)$$

where  $\dot{n}_A$  is the rate of increase of the mass of species A per unit volume of the mixture ( $kg \cdot s^{-1} \cdot m^{-3}$ ).

Finally, these processes may change the mass of species A stored within the control volume, and the rate of change is

$$\dot{M}_{A,st} = \frac{\partial \rho_A}{\partial t} dx dy dz \quad (2.28)$$

With mass inflow rates determined by  $n_{a,x}$ ,  $n_{A,y}$ , and  $n_{A,z}$  and the outflow rates determined by the equations above, and can be substituted in conservation equation to get the following equation:

$$-\frac{\partial n_A}{\partial x} - \frac{\partial n_A}{\partial y} - \frac{\partial n_A}{\partial z} + \dot{n}_A = \frac{\partial \rho_A}{\partial t} \quad (2.29)$$

Then, substituting the x, y, and z components of Equation, we obtain

$$\frac{\partial}{\partial x}(\rho D_{AB} \frac{\partial \omega_A}{\partial x}) + \frac{\partial}{\partial y}(\rho D_{AB} \frac{\partial \omega_A}{\partial y}) + \frac{\partial}{\partial z}(\rho D_{AB} \frac{\partial \omega_A}{\partial z}) + \dot{n}_A = \frac{\partial \rho_A}{\partial t} \quad (2.30)$$

In terms of the molar concentration, a similar derivation yields

$$\frac{\partial}{\partial x}(C D_{AB} \frac{\partial x_A}{\partial x}) + \frac{\partial}{\partial y}(C D_{AB} \frac{\partial x_A}{\partial y}) + \frac{\partial}{\partial z}(C D_{AB} \frac{\partial x_A}{\partial z}) + \dot{N}_A = \frac{\partial C_A}{\partial t} \quad (2.31)$$

Simplified equation of the foregoing equations can be written as follows if  $D_{AB}$  and  $\rho$  are constant:

$$\frac{\partial^2 \rho_A}{\partial x^2} + \frac{\partial^2 \rho_A}{\partial y^2} + \frac{\partial^2 \rho_A}{\partial z^2} + \frac{\dot{n}_A}{D_{AB}} = \frac{1}{D_{AB}} \frac{\partial \rho_A}{\partial t} \quad (2.32)$$

Similarly, if  $D_{AB}$  and  $c$  are constant, Equations can be simplified as follows:

$$\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2} + \frac{\dot{N}_A}{D_{AB}} = \frac{1}{D_{AB}} \frac{\partial c_A}{\partial t} \quad (2.33)$$

Two boundary conditions must be specified for each coordinate needed to describe the system. Conditions are also needed at an initial time if the problem of interest is transient. Hence it follows that, for analogous boundary and initial conditions, the solution to Equation for  $\rho_A(x, y, z, t)$  or to Equation for  $C_A(x, y, z, t)$ .

### Cylindrical Coordinates

$$\frac{1}{r} \frac{\partial}{\partial r} (cD_{AB}r \frac{\partial x_A}{\partial r}) + \frac{1}{r^2} \frac{\partial}{\partial \phi} (cD_{AB} \frac{\partial x_A}{\partial \phi}) + \frac{\partial}{\partial z} (cD_{AB} \frac{\partial x_A}{\partial z}) + \dot{N}_A = \frac{\partial c_A}{\partial t} \quad (2.34)$$

### Spherical Coordinates

:

$$\frac{1}{r^2} \frac{\partial}{\partial r} (cD_{AB}r^2 \frac{\partial x_A}{\partial r}) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \phi} (cD_{AB} \frac{\partial x_A}{\partial \phi}) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} (cD_{AB} \sin \theta) \frac{\partial x_A}{\partial \theta} + \dot{N}_A = \frac{\partial c_A}{\partial t} \quad (2.35)$$

***Note:***

Simpler forms are, of course, associated with the absence of chemical reactions ( $\dot{n}_A = \dot{N}_A = 0$ ) and with one-dimensional, steady-state conditions.

### Problem:Homework

Beginning with a differential control volume, derive the diffusion equation, on a molar basis, for species A in a three-dimensional (Cartesian coordinates), stationary medium, considering species generation with constant properties.

### **Problem:Homework**

Consider the radial diffusion of a gaseous species (A) through the wall of a plastic tube (B), and allow for chemical reactions that provide for the depletion of A at a rate  $\dot{N}_A$  ( $kmol \cdot s^{-1} \cdot m^{-3}$ ). Derive a differential equation that governs the molar concentration of species A in the plastic.

# Chapter 3

## Stationary Media with Specified Surface Concentrations

### 3.1 Stationary Media with Specified Surface Concentrations

Consider, for example, one-dimensional diffusion of species A through a planar medium of A and B, as shown in Figure ???. For steady-state conditions with no homogeneous chemical reactions, the molar form of the species diffusion equation Equation below:

$$\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2} + \frac{\dot{N}_A}{D_{AB}} = \frac{1}{D_{AB}} \frac{\partial c_A}{\partial t} \quad (3.1)$$

The above equation will be reduced to the following:

**Note:**

- 1- No chemical reaction
- 2- Steady-state
- 3- one dimensional diffusion of species A through a planar medium of A, and B

$$\frac{d}{dx} \left( c D_{AB} \frac{dx_A}{dx} \right) = 0 \quad (3.2)$$

Assuming the total molar concentration and the diffusion coefficient to be constant, Equation 3.2 may be solved and the boundary conditions illustrated in Figure 3.2 below may be applied to yield

$$x_A(x) = (x_{A,s2}) - (x_{A,s1}) \frac{x}{L} + x_{A,s1} \quad (3.3)$$

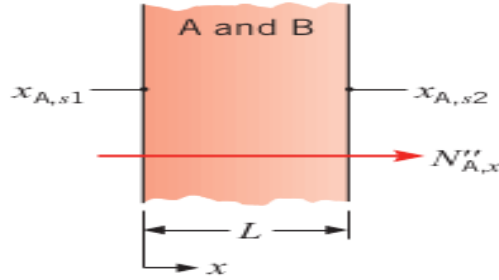


Figure 3.1

Integrate the equation 3.2:

$$N_{A,x} = -cD_{AB} \frac{x_{A,s2} - x_{A,s1}}{L} \dots \quad (3.4)$$

Multiplying by the surface area  $A$  and substituting for  $x_A = C_A/C$ , the molar rate is then:

$$N_{A,x} = -D_{AB}A \frac{c_{A,s2} - c_{A,s1}}{L} \dots \quad (3.5)$$

From this expression we can define a resistance to species transfer by diffusion in a planar medium as

$$R_{m,dif} = \frac{c_{A,s1} - c_{A,s2}}{N_{A,x}} = \frac{L}{D_{AB}} \quad (3.6)$$

The analogy also applies to cylindrical and spherical systems. For one-dimensional, steady diffusion in a cylindrical, nonreacting medium, Equation below:

$$\frac{1}{r} \frac{\partial}{\partial r} (cD_{AB}r \frac{\partial x_A}{\partial r}) + \frac{1}{r^2} \frac{\partial}{\partial \phi} (cD_{AB} \frac{\partial x_A}{\partial \phi}) + \frac{\partial}{\partial z} (cD_{AB} \frac{\partial x_A}{\partial z}) + \dot{N}_A = \frac{\partial c_A}{\partial t} \quad (3.7)$$

The equation will be reduced for the following condition:

1- One -dimensional 2- Steady-state 3- non-reacting medium

$$\frac{d}{dr}(rcD_{AB}\frac{dx_A}{dr}) = 0 \quad (3.8)$$

Similarly, for a spherical medium,

$$\frac{1}{r^2} \frac{\partial}{\partial r}(cD_{AB}r^2 \frac{\partial x_A}{\partial r}) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \phi}(cD_{AB} \frac{\partial x_A}{\partial \phi}) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta}(cD_{AB} \sin \theta) \frac{\partial x_A}{\partial \theta} + \dot{N}_A = \frac{\partial c_A}{\partial t} \quad (3.9)$$

It will be reduced according to the following condition:

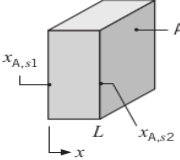
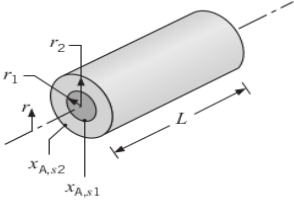
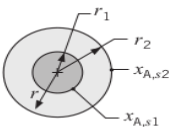
1- one-dimensional

2- steady-state

3-No reaction

$$\frac{d}{dr}(r^2 cD_{AB} \frac{dx_A}{dr}) = 0 \quad (3.10)$$



Geometry	Species Mole Fraction Distribution, $x_A(x)$ or $x_A(r)$	Species Diffusion Resistance, $R_{m,dif}$
	$x_A(x) = (x_{A,s2} - x_{A,s1}) \frac{x}{L} + x_{A,s1}$	$R_{m,dif} = \frac{L}{D_{AB}A}{}^b$
	$x_A(r) = \frac{x_{A,s1} - x_{A,s2}}{\ln(r_1/r_2)} \ln\left(\frac{r}{r_2}\right) + x_{A,s2}$	$R_{m,dif} = \frac{\ln(r_2/r_1)}{2\pi L D_{AB}}{}^c$
	$x_A(r) = \frac{x_{A,s1} - x_{A,s2}}{1/r_1 - 1/r_2} \left(\frac{1}{r} - \frac{1}{r_2}\right) + x_{A,s2}$	$R_{m,dif} = \frac{1}{4\pi D_{AB}} \left(\frac{1}{r_1} - \frac{1}{r_2}\right){}^c$

<sup>a</sup>Assuming  $C$  and  $D_{AB}$  are constant.

<sup>b</sup> $N_{A,x} = (C_{A,s1} - C_{A,s2})/R_{m,dif} = C(x_{A,s1} - x_{A,s2})/R_{m,dif}$ .

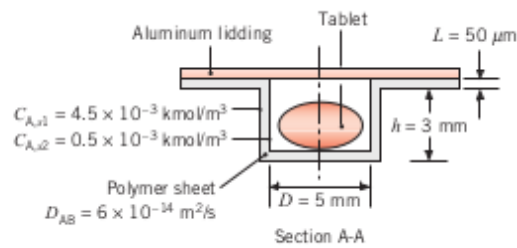
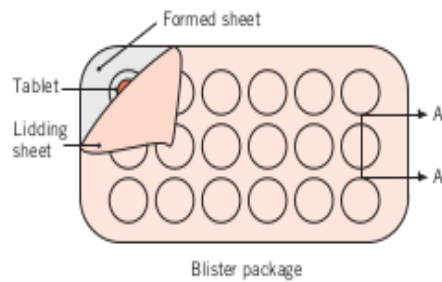
<sup>c</sup> $N_{A,r} = (C_{A,s1} - C_{A,s2})/R_{m,dif} = C(x_{A,s1} - x_{A,s2})/R_{m,dif}$ .

Figure 3.2: Summary of Species Diffusion Solutions for Stationary Media with Specified Surface Concentrations a

### Problem

The efficacy of pharmaceutical products is reduced by prolonged exposure to high temperature, light, and humidity. For water vapor-sensitive consumer products that are in tablet or capsule form, and might be stored in humid environments such as bathroom medicine cabinets, blister packaging is used to limit the direct exposure of the medicine to humid conditions until immediately before its ingestion. Consider tablets that are contained in a blister package composed of a flat lidding sheet and a second, formed sheet that includes troughs to hold each tablet. The formed sheet is  $L=50 \mu\text{m}$  thick and is fabricated of a polymer material. Each trough is of diameter  $D=5 \text{ mm}$  and depth  $h=3 \text{ mm}$ . The lidding sheet is fabricated of aluminum foil. The binary diffusion coefficient for water vapor in the polymer is  $D_{AB}=6 \times 10^{-14} \text{ m}^2/\text{s}$  while the aluminum may be assumed to be impermeable to water vapor. For molar concentrations of water vapor in the polymer at the outer and inner surfaces of  $C_{A,s1}=4.5 \times 10^{-3} \text{ kmol}/\text{m}^3$  and  $C_{A,s2}=0.5 \times 10^{-3} \text{ kmol}/\text{m}^3$ , respectively, determine the rate at which water vapor is transferred through the trough wall to the

tablet.



### Problem:Homework

A thin plastic membrane is used to separate helium from a gas stream. Under steady-state conditions the concentration of helium in the membrane is known to be 0.02 and 0.005  $kmol \cdot m^{-3}$  at the inner and outer surfaces, respectively. If the membrane is 1 mm thick and the binary diffusion coefficient of helium with respect to the plastic is  $10^{-9} m^2 \cdot s^{-1}$ , what is the diffusive flux?

# Chapter 4

## Boundary Conditions and Discontinuous Concentrations at Interfaces

### 4.0.1 Evaporation and Sublimation

A common mass transfer scenario is the transfer of a species A into a gas stream due to evaporation or sublimation from a liquid or solid surface, respectively (Figure 4.19). Conditions within the gas phase are of interest, and the concentration (or partial pressure) of species A in the gas phase at the interface (located at  $x=0$ ) may readily be determined from Raoult's law:

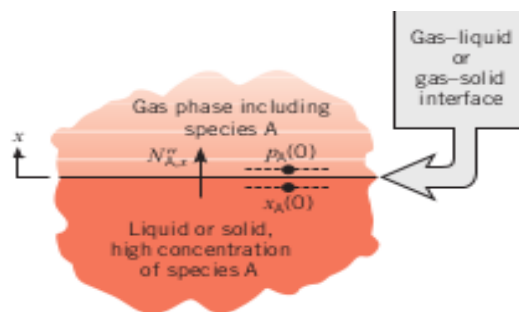


Figure 4.1: Species concentration at a gas-liquid or gas-solid interface. (a) Evaporation or sublimation of species A from a liquid or solid into a gas.

$$p_A(0) = x_A(0)P_{A,sat} \quad (4.1)$$

$P_A$  = The partial pressure of A in the gas phase

$x_A$  = Mole fraction of species A in the liquid or solid

$P_{A,sat.}$  = The saturation pressure of species A at the surface temperature

#### 4.0.2 Solubility of gases in liquids and solids

Another common scenario is mass transfer of species A from a gas phase into a liquid or solid, species B (Figure 4.20). Mass transfer within the liquid or solid phase is of interest, and the concentration of species A at the interface is required as a boundary condition.

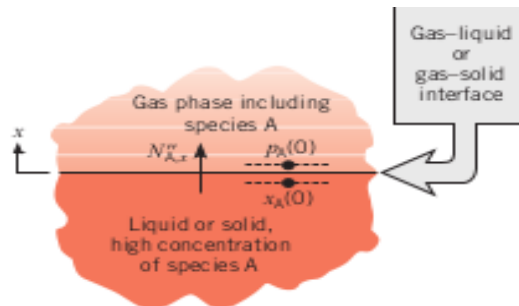


Figure 4.2: Transfer of weakly soluble species A from the gas to a liquid or solid.

If species A is only weakly soluble ( $x_A$  is small) in a liquid, Henry's law may be used to relate the mole fraction of A in the liquid to the partial pressure of A in the gas phase outside the liquid:

$$x_A(0) = \frac{P_A(0)}{H} \quad (4.2)$$

where:

$H$  = Henry's constant

The values for selected aqueous solutions are listed in Tables printed in the Appendix of different sources. Although  $H$  depends in temperature, its pressure dependence may be generally neglected for values of  $P$  up to 5 bar.

Conditions at a gas–solid interface may also be determined if the gas, species A, dissolves in a solid, species B, and a solution is formed. In such cases mass transfer in the solid is independent of the structure of the solid and may be treated as a diffusion process. In contrast, there are many situations for which the porosity of the solid strongly influences gas transport through the solid.

Treating the gas and solid as a solution, we can obtain the concentration of the gas in the solid at the interface through use of a property known as the solubility,  $S$ . It is defined by the expression:

$$C_A(0) = SP_A(0) \tag{4.3}$$

where:

$P_A(0)$  = The partial pressure (bars) of the gas adjoining the interface.

$C_A(0)$  = The molar concentration of A in the solid at the interface,  $C_A(0)$ , is in units of kilomoles of A per cubic meter of solid.

$S$  = Solubility in kilomoles of A per cubic meter of solid per bar (or atm) partial pressure of A.

**Problem(H.W)**

Helium gas is stored at 20°C in a spherical container of fused silica ( $\text{SiO}_2$ ), which has a diameter of 0.20 m and a wall thickness of 2 mm. If the container is charged to an initial pressure of 4 bars, what is the rate at which this pressure decreases with time?

### 4.0.3 Catalytic Surface Reactions

Many mass transfer problems involve specification of the species flux, rather than the species concentration, at a surface. One such problem relates to the process of catalysis, which involves the use of special surfaces to promote heterogeneous chemical reactions. Such a reaction occurs at the surface of a material, can be viewed as a surface phenomenon, and can be treated as a boundary condition. Often a one-dimensional diffusion analysis may be used to approximate the performance of a catalytic reactor.

For example (Figure 4.21), A catalytic surface is placed in a gas stream to promote a heterogeneous chemical reaction involving species A. Assume that the reaction produces species A at a rate  $\dot{N}''_A$ , which is defined as the molar rate of production per unit surface area of the catalyst. Once steady state conditions are reached, the rate of species transfer from the surface,  $N_{A,x}$  must equal the surface reaction rate:

$$N''_{A,x} = \dot{N}''_A \quad (4.4)$$

It is also assumed that species A leaves the surface as a result of one-dimensional transfer

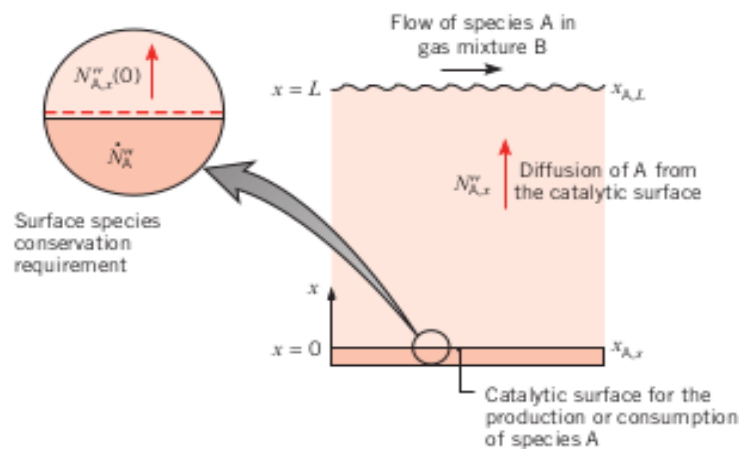


Figure 4.3: One-dimensional diffusion with heterogeneous catalysis.

through a thin film of thickness  $L$  and that no reactions occur within the film itself. The mole fraction of A at  $x=L$ ,  $x_{A,L}$ , corresponds to conditions in the mainstream of the mixture and is presumed to be known. Representing the remaining species of the mixture as a single species B and assuming the medium to be stationary, the Equation reduces to:

$$\frac{d}{dx}(CD_{AB}\frac{dx_A}{dx}) = 0 \quad (4.5)$$

where  $D_{AB}$  is the binary diffusion coefficient for A in B and B may be a multicomponent mixture. Assuming C and  $D_{AB}$  to be constant, Equation 4.163 may be solved subject to the conditions that

$$x_A(L) = x_{A,L}$$

and Equation 4.163 can be written as follows:

$$N''_{A,x}(0) = -CD_{AB}\frac{dx_A}{dx}|_{x=0} = \dot{N}''_A \quad (4.6)$$

For a catalytic surface, the surface reaction rate  $\dot{N}''_A$  generally depends on the surface concentration  $C_A(0)$ . For a first-order reaction that results in species consumption at the surface, the reaction rate is of the form:

$$N''_{A,x} = k_1'' \cdot C_A(0) \quad (4.7)$$

where  $k_1''$  (m/s) is the reaction rate constant. Accordingly, the surface boundary condition, Equation 4.165, reduces to:

$$-D_{AB}\frac{dx_A}{dx}|_{x=0} = -k_1''x_A(0) \quad (4.8)$$

Solving Equation 4.163 subject to the above conditions, it is readily verified that the concentration distribution is linear and of the form:

$$\frac{x_A(x)}{x_{A,L}} = \frac{1 + (xk_1''/D_{AB})}{1 + (Lk_1''/D_{AB})} \quad (4.9)$$

At the catalytic surface this result reduces to:

$$\frac{x_A(0)}{x_{A,L}} = \frac{1}{1 + (Lk_1''/D_{AB})} \quad (4.10)$$

and the molar flux is:

$$N''_A = -CD_{AB}\frac{dx_A}{dx}|_{x=0} = -k_1''Cx_A(0) \quad (4.11)$$



or:

$$N''_A(0) = -\frac{k_1'' C x_{A,L}}{1 + (Lk_1''/D_{AB})} \quad (4.12)$$

The negative sign implies mass transfer to the surface.

Two limiting cases of the foregoing results are of special interest. For the limit  $k_1'' \rightarrow 0$ ,  $(Lk_1''/D_{AB}) \ll 1$  and Equations 4.169 and 4.171 reduce to:

$$\frac{x_{A,s}}{x_{A,L}} \approx 1 \text{ and } N_A''(0) \approx -k_1'' C x_{A,L}$$

In such cases the rate of reaction is controlled by the reaction rate constant, and the limitation due to diffusion is negligible. The process is said to be reaction limited.

Conversely, for the limit  $k_1'' \rightarrow \infty$ ,  $(Lk_1''/D_{AB}) \gg 1$  and Equations 4.169 and 4.171 reduce to:

$$x_{A,s} \approx 0 \text{ and } N_A''(0) \approx -\frac{CD_{AB}x_{A,L}}{L} \quad (4.13)$$

In this case the reaction is controlled by the rate of diffusion to the surface, and the process is said to be diffusion limited.

#### 4.0.4 Mass Diffusion with Homogeneous Chemical Reactions

Just as heat diffusion may be influenced by internal sources of energy, species transfer by diffusion may be influenced by homogeneous chemical reactions. We restrict our attention to stationary media. If we also assume steady, one-dimensional transfer in the x-direction and that  $D_{AB}$  and  $C$  are constant, The equation will be as follows:

$$D_{AB} \frac{d^2 C_A}{dx^2} - k_1 C_A = 0 \quad (4.14)$$

This linear, homogeneous differential equation has the general solution

$$C_A(x) = C_1 e^{mx} + C_2 e^{-mx} \quad (4.15)$$

where  $m = (k_1/D_{AB})^{1/2}$  and the constants  $C_1$  and  $C_2$  depend on the prescribed boundary conditions.

Consider the situation illustrated in Figure 4.22. Gas A is soluble in liquid B, where it is transferred by diffusion and experiences a first-order chemical reaction. The solution is dilute, and the concentration of A in the liquid at the interface is a known constant  $C_{A,0}$ . If the bottom of the container is impermeable to A, the boundary conditions are:

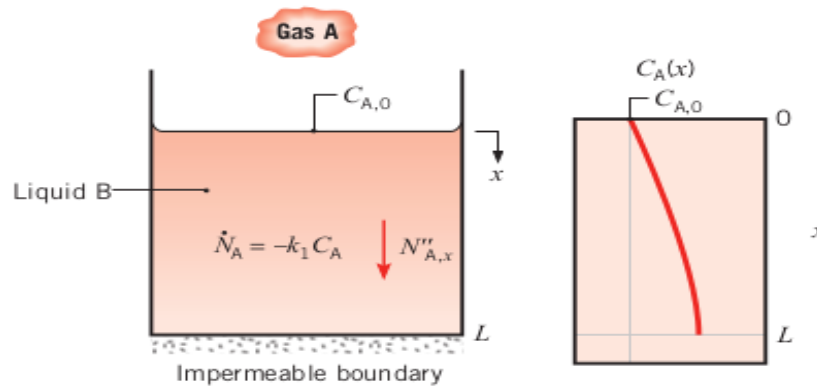


Figure 4.4: Diffusion and homogeneous reaction of gas A in liquid B.

$$C_A(0) = C_{A,0} \text{ and } \left. \frac{dC_A}{dx} \right|_{x=L} = 0 \quad (4.16)$$

These species boundary conditions are analogous to the thermal boundary conditions as follows:

$$C_A(x) = C_{A,0} \frac{\cosh m(L-x)}{\cosh mL} \quad (4.17)$$

Quantities of special interest are the concentration of A at the bottom and the flux of A across the gas-liquid interface. Applying Equation 4.176 at  $x=L$ , we obtain

$$C_A(L) = \frac{C_{A,0}}{\cosh mL} \quad (4.18)$$

Moreover,

$$N''_{A,x}(0) = -D_{AB} \frac{dC_A}{dx} \Big|_{x=0} \quad (4.19)$$

$$N''_{A,x}(0) = D_{AB} C_{A,0} m \frac{\sinh m(L-x)}{\cosh mL} \Big|_{x=0} \quad (4.20)$$

or

$$N''_{A,x}(0) = -D_{AB} C_{A,0} m \tanh mL \quad (4.21)$$

Results for a container with its bottom held at a fixed concentration or an infinitely deep container may be obtained by analogy to the heat transfer cases.

## 4.1 Equimolar Counter Diffusion

The total pressure is constant all through the mixture. Hence the difference in partial pressures will be equal. The Fick's equation when integrated for a larger plane volume of thickness L will give:

For liquids:

$$N_A/A = -D_{ab} \frac{C_{A1} - C_{A2}}{L} \quad (4.22)$$

$$N_B/A = -D_{BA} \frac{C_{B2} - C_{B1}}{L} \quad (4.23)$$

$$N_B/A = -\frac{N_B}{A} \quad (4.24)$$

$$(C_{A1} - C_{A2}) = (C_{B2} - C_{B1}) \quad (4.25)$$

For gases:

$$N_A/A = D/RT \cdot \frac{(P_{A1} - P_{A2})}{x_2 - x_1} \quad (4.26)$$

Where  $P_{A1}$  and  $P_{A2}$  are partial pressures of component A at  $x_1$  and  $x_2$  and  $R$  is the universal gas constant in J/kg mol K.  $T$  is the temperature in absolute units. The distance should be expressed in metre.

The partial pressure variation and diffusion directions are shown in Figure 4.16.

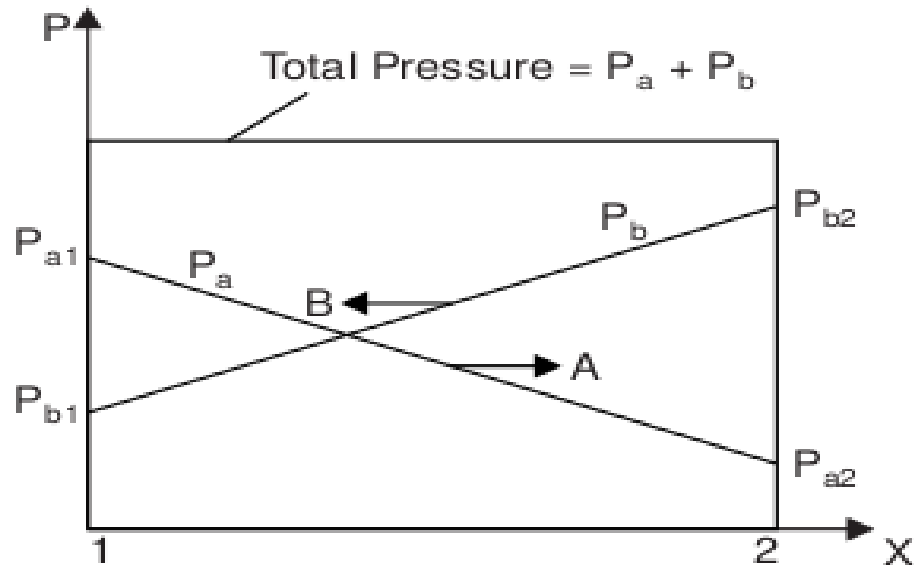


Figure 4.5: Partial Pressure variation of components in equimolar counter diffusion.

### Problem 1

In order to avoid pressure build up ammonia gas at atmospheric pressure in a pipe is vented to atmosphere through a pipe of 3 mm dia and 20 m length. Determine the mass of ammonia diffusing out and mass of air diffusing in per hour. Assume  $D = 0.28 \times 10^{-4} \text{m}^2/\text{s}$ ,  $M = 17 \text{ kg/kg mole}$

Solution: (In the video lecture)

## 4.2 Stationary media with specified surface concentration

In the diffusion of gas from containers, there is diffusion of gas from inside to the outside without the metal molecules diffusing into the gas. In these cases the concentration of gas

at the surfaces should be known. The solubility of the gas in the surface determines the concentration at the surface.

The flow rate can be obtained From equation below:

$$N_A = (C_{A1} - C_{A2})/Resistance \quad (4.27)$$

Where Resistance to diffusion in is different according to the geometry:

1- Case1: Resistance of plane wall:

$$Resistance = L/D_{AB}A \quad (4.28)$$

2-Case2: Resistance of hollow cylindrical configuration

$$Resistance = \frac{\ln (r_2/r_1)}{2\pi D_{AB}L} \quad (4.29)$$

3-Case3: Resistance of hollow sphere configuration

$$Resistance = \frac{1}{4\pi D_{AB}} \left[ \frac{1}{r_1} - \frac{1}{r_2} \right] \quad (4.30)$$

### 4.3 Diffusion of one component into a stationary component or unidirectional diffusion

In this case one of the components diffuses while the other is stationary. For steady conditions the mass diffused should be absorbed continuously at the boundary. In certain cases this is not possible. The popular example is water evaporating into air. In this case, as mentioned earlier, a bulk motion replaces the air tending to accumulate at the interface without being absorbed, causing an increase in the diffusion rate.

$$\frac{N_A}{A} = P/RT \cdot \frac{D}{(x_2 - x_1)} \cdot \ln\left(\frac{P - P_{A2}}{P - P_{A1}}\right) \quad (4.31)$$

In the gas absorption a soluble gas A is transferred to the liquid surface where it dissolves, whereas the insoluble gas B undergoes no net movement with respect to the interface.

The concept of stationary component may envisaged by considering the moving of the box in the opposite of the direction to that in which B is diffusing, at a velocity equal to it's diffusion velocity, so that to the external observer B appears to be stationary. The total velocity at which A is transferred will then be increased to its diffusion velocity plus the velocity of the box.

## 4.4 Convective mass transfer

When a medium deficient in a component flows over a medium having an abundance of the component, then the component will diffuse into the flowing medium. Diffusion in the opposite direction will occur if the mass concentration levels of the component are interchanged. Concentration boundary layer is used to determine convective mass transfer.

The Figure 4.17 shows the flow of a mixture of components A and B with a specified constant concentration over a surface rich in component A. A concentration boundary layer develops. The concentration gradient varies from the surface to the free stream. At the surface the mass transfer is by diffusion. Convective mass transfer coefficient  $h_m$  is defined by the equation, where  $h_m$  has a unit of m/s.

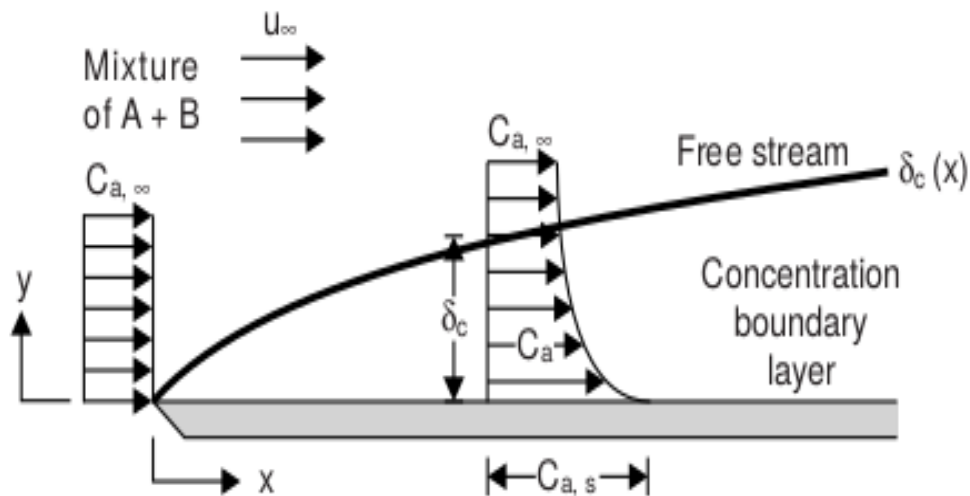


Figure 4.6: Species concentration boundary layer development on a flat plate.

$$Moleflow = h_m(C_{As} - C_{A\infty}) \quad (4.32)$$

The condition for diffusion at the surface is given by:

$$Moleflow = -D_{AB} \frac{\partial C_A}{\partial y} \quad (4.33)$$

The mass flow is to be used to estimate convective mass transfer coefficient  $h_m$ :

$$h_m = \frac{-D_{AB} \cdot \frac{\partial C_A}{\partial y} \Big|_{y=0}}{C_{As} - C_{A\infty}} \quad (4.34)$$

In the above case, if mass flow is to be used then:

$$h_m = \frac{-D_{AB} \cdot \frac{\partial \rho_A}{\partial y} \Big|_{y=0}}{\rho_{As} - \rho_{A\infty}} \quad (4.35)$$

The solutions for boundary layer thickness for convective mass transfer can be obtained according to the following equation:

$$u \frac{\partial C_A}{\partial x} + v \frac{\partial C_A}{\partial y} = D_{AB} \frac{\partial^2 C_A}{\partial y^2} \quad (4.36)$$

Prandtl number Schmidt number defined by:

$$Sc = \nu / D_{AB} \quad (4.37)$$

Nondimensionalising the equation leads to the condition as below:

$$\delta = f(Re, Sc) \quad (4.38)$$

$$Sh = f(Re, Sc) \quad (4.39)$$

where Sherwood number  $Sh$  is defined as:

$$Sh = \frac{h_m x}{D_{AB}} \quad (4.40)$$

In the laminar region flow over plate:

$$\delta_m = \frac{5x}{Re_x} \cdot Sc^{1/3} \quad (4.41)$$

$$Sh_x = \frac{h_m x}{D_{AB}} = 0.332 Re_x^{1/2} Sc^{1/3} \quad (4.42)$$

$$Sh_x = \frac{h_m x}{D_{AB}} = 0.332 Re_x^{1/2} Sc^{1/3} \quad (4.43)$$

$$\overline{Sh}_L = \frac{h_m L}{D_{AB}} = 0.664 Re_L^{1/2} Sc^{1/3} \quad (4.44)$$

In the turbulent region  $Re > 5 \times 10^5$ ,

$$\delta_m = \delta_\nu \quad (4.45)$$

$$Sh_x = \frac{h_m x}{D_{AB}} = 0.0296 Re_x^{0.8} Sc^{1/3} \quad (4.46)$$

$$\overline{Sh}_L = \frac{h_m L}{D_{AB}} = 0.037 Re_L^{1/2} Sc^{1/3} \quad (4.47)$$

**For flow through tubes:**

- **For Laminar Region  $Re < 2000$ :**

- For uniform wall mass concentration:

$$Sh = 3.66 \quad (4.48)$$

- For uniform wall mass flux:

$$Sh = 4.36 \quad (4.49)$$



- **For turbulent region,  $Re > 2000$ :**

$$Sh = 0.023Re^{0.83}Sc^{1/3} \quad (4.50)$$

Check your understanding with Assignment 2 Problem 6,7,8,9,10,11.

## 4.5 Diffusion as a mass flux

**Proposed Question:** (Prove that the diffusional processes does not give rise to equal and opposite mass fluxes)

Ficks law of diffusion is normally expressed in molar units:

$$N_A = -D_{AB} \frac{dC_A}{dy} = -D_{AB} C_T \frac{dx_A}{dy} \quad (4.51)$$

where  $x_A$  is the mole fraction of component A.

If each side of Equation 4.150 is multiplied by the molecular weight of A,  $M_A$  then:

$$J_A = -D_{AB} \frac{dc_A}{dy} = -D_{AB} C_T M_A \frac{dx_A}{dy} \quad (4.52)$$

where  $J_A$  is a flux in mass per unit area and unit time ( $Kg/m^2 \cdot s$ ), and  $c_A$  is a concentration in mass terms ( $kg/m^3$ )

Similarly, for component B:

$$J_B = -D_{BA} \frac{dc_B}{dy} = -D_{BA} C_T M_A \frac{dx_B}{dy} \quad (4.53)$$

The sum of the molar concentrations is constant in an ideal gas at constant pressure, the sum of mass concentration is not constant, and  $(\frac{dc_A}{dy})$  and  $(\frac{dc_B}{dy})$  are not equal and opposite:

Thus,

$$C_A + C_B = C_T = \frac{c_A}{M_A} + \frac{c_B}{M_B} \quad (4.54)$$

Differentiate the above equation:

$$\frac{1}{M_A} \frac{dc_A}{dy} + \frac{1}{M_B} \frac{dc_B}{dy} = 0 \quad (4.55)$$

$$\frac{dc_B}{dy} = -\frac{M_B}{M_A} \frac{dc_A}{dy} \quad (4.56)$$

## 4.6 General case for gas-phase mass transfer in a binary mixture

In the absorption of a soluble gas A from a mixture the bulk velocity must be equal and opposite to the diffusional velocity of B as this latter component undergoes no net transfer .

For any component:

$$\text{Total Transfer} = \text{Transfer by diffusion} + \text{Transfer by bulk flow.}$$

For component A:

$$\text{Total transfer (moles/area time)} = N'_A$$

Diffusional transfer according to Fick's Law:

$$N_A = -D \frac{dC_A}{dy}$$

Transfer by bulk flow:

$$\text{Transfer by bulk flow} = u_F C_A$$

Thus for A:

$$N'_A = N_A + u_F C_A$$

For B:

$$N'_B = N_B + u_F C_B$$

$$\begin{aligned} \text{The bulk flow velocity} &= \frac{\text{Total moles transferred/area time}}{\text{Total molar concentration}} \\ &= \frac{N'_A + N'_B}{C_T} \end{aligned}$$

Substituting:

$$N'_A = N_A + \frac{C_A}{C_T} (N'_A + N'_B)$$

$$N'_A = -D \frac{dC_A}{dy} + x_A(N'_A + N'_B)$$

$$N'_A = -DC_T \frac{dx_A}{dy} + x_A(N'_A + N'_B) \quad (4.57)$$

Similarly for B:

$$N'_B = -DC_T \frac{dx_A}{dy} + (1 - x_A)(N'_A + N'_B)$$

For equimolar counterdiffusion,  $N'_A = -N'_B$ , so Equation 4.156 will be reduced to Fick's Law.

For a system in which B undergoes no net transfer,  $N'_B = 0$  and Equation 4.156 is identical to Stefan's Law.

In a distillation column, the molar latent heat of A is  $f$  times that of B, the condensation of 1 mole of A (Taken as less volatile component) will result in the vaporisation of  $f$  moles of B and the mass transfer rate of B will be  $f$  times that of A in the opposite direction.

For the general case:

$$fN'_A = -N'_B$$

Substituting into Equation 4.156:

$$N'_A = -DC_T \frac{dx_A}{dy} + x_A(N'_A + fN'_A) \quad (4.58)$$

Thus:

$$[1 - x_A(1 - f)]N'_A = -DC_T \frac{dx_A}{dy}$$

If  $x_A$  changes from  $x_{A1}$  to  $x_{A2}$  as  $y$  goes from  $y_1$  to  $y_2$  then:

$$N'_A \int_{y_1}^{y_2} dy = -DC_T \int_{x_{A1}}^{x_{A2}} \frac{dx_A}{1 - x_A(1 - f)}$$

Thus:

$$N'_A(y_2 - y_1) = -DC_T \frac{1}{1-f} \left[ \ln \frac{1}{(1-f)^{-1} - x_A} \right]_{x_{A1}}^{x_{A2}}$$

Or:

$$N'_A(y_2 - y_1) = -DC_T \frac{1}{1-f} \left[ \ln \frac{1}{(1-f)^{-1} - x_A} \right]_{x_{A1}}^{x_{A2}}$$

or:

$$N'_A = \frac{-DC_T}{(y_2 - y_1)} \frac{1}{1-f} \ln \frac{1 - x_{A2}(1-f)}{1 - x_{A1}(1-f)} \quad (4.59)$$

## 4.7 Conservation of species for a control volume

The rate at which the mass of some species enters a control volume, plus the rate at which the species mass is generated within the control volume, minus the rate at which this species mass leaves the control volume must equal the rate of increase of the species mass stored within the control volume.

For example, any species A may enter and leave the control volume due to both fluid motion and diffusion across the control surface; these processes are surface phenomena represented by  $\hat{M}_{A,in}$  and  $\hat{M}_{A,out}$ . The same species A may also be generated,  $\hat{M}_{A,g}$ , and accumulated or stored,  $\hat{M}_{A,st}$ , within the control volume. The conservation equation may then be expressed on a rate basis as:

$$\hat{M}_{A,in} + \hat{M}_{A,g} - \hat{M}_{A,out} = \frac{dM_A}{dt} \equiv \hat{M}_{A,st} \quad (4.60)$$

Species generation exists when chemical reactions occur in the system. For example, for a dissociation reaction of the form  $AB \rightarrow A+B$ , there would be net production of species A and B, as well as net reduction of the species AB.

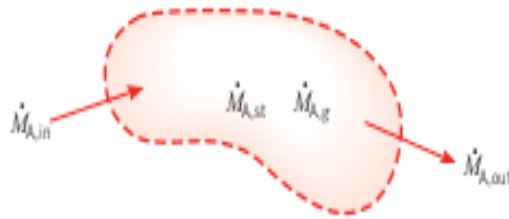


Figure 4.7: Conservation of species for a control volume.

## 4.8 Common mass transfer scenario

### 4.8.1 Evaporation and Sublimation

A common mass transfer scenario is the transfer of a species A into a gas stream due to evaporation or sublimation from a liquid or solid surface, respectively (Figure 4.19).

Conditions within the gas phase are of interest, and the concentration (or partial pressure) of species A in the gas phase at the interface (located at  $x=0$ ) may readily be determined from Raoult's law:

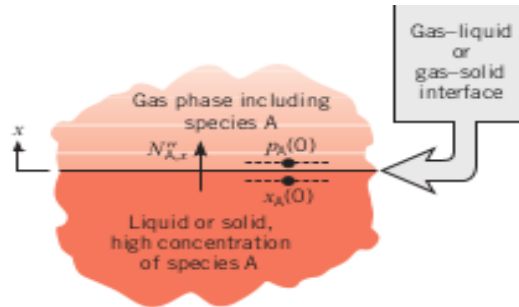


Figure 4.8: Species concentration at a gas–liquid or gas–solid interface. (a) Evaporation or sublimation of species A from a liquid or solid into a gas.

$$p_A(0) = x_A(0)P_{A,sat} \quad (4.61)$$

$P_A$  = The partial pressure of A in the gas phase

$x_A$  = Mole fraction of species A in the liquid or solid

$P_{A,sat.}$  = The saturation pressure of species A at the surface temperature

## 4.8.2 Solubility of gases in liquids and solids

Another common scenario is mass transfer of species A from a gas phase into a liquid or solid, species B (Figure 4.20). Mass transfer within the liquid or solid phase is of interest, and the concentration of species A at the interface is required as a boundary condition.

If species A is only weakly soluble ( $x_A$  is small) in a liquid, Henry's law may be used to relate the mole fraction of A in the liquid to the partial pressure of A in the gas phase outside the liquid:

$$x_A(0) = \frac{P_A(0)}{H} \quad (4.62)$$

where:

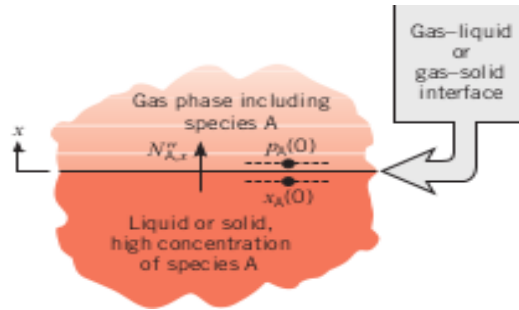


Figure 4.9: Transfer of weakly soluble species A from the gas to a liquid or solid.

$H$  = Henry's constant

The values for selected aqueous solutions are listed in Tables printed in the Appendix of different sources. Although  $H$  depends in temperature, its pressure dependence may be generally neglected for values of  $P$  up to 5 bar.

Conditions at a gas–solid interface may also be determined if the gas, species A, dissolves in a solid, species B, and a solution is formed. In such cases mass transfer in the solid is independent of the structure of the solid and may be treated as a diffusion process. In contrast, there are many situations for which the porosity of the solid strongly influences gas transport through the solid.

Treating the gas and solid as a solution, we can obtain the concentration of the gas in the solid at the interface through use of a property known as the solubility,  $S$ . It is defined by the expression:

$$C_A(0) = SP_A(0) \quad (4.63)$$

where:

$P_A(0)$  = The partial pressure (bars) of the gas adjoining the interface.

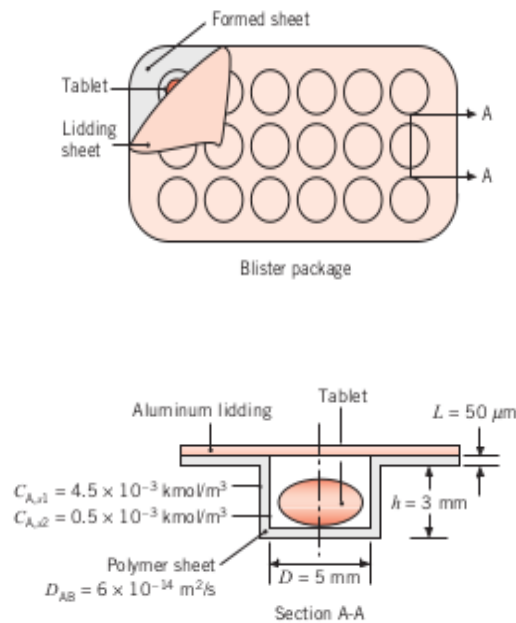
$C_A(0)$  = The molar concentration of A in the solid at the interface,  $C_A(0)$ , is in units of kilomoles of A per cubic meter of solid.

$S$  = Solubility in kilomoles of A per cubic meter of solid per bar (or atm) partial pressure of A.



**Problem**

The efficacy of pharmaceutical products is reduced by prolonged exposure to high temperature, light, and humidity. For water vapor-sensitive consumer products that are in tablet or capsule form, and might be stored in humid environments such as bathroom medicine cabinets, blister packaging is used to limit the direct exposure of the medicine to humid conditions until immediately before its ingestion. Consider tablets that are contained in a blister package composed of a flat lidding sheet and a second, formed sheet that includes troughs to hold each tablet. The formed sheet is  $L=50 \mu\text{m}$  thick and is fabricated of a polymer material. Each trough is of diameter  $D = 5 \text{ mm}$  and depth  $h = 3 \text{ mm}$ . The lidding sheet is fabricated of aluminum foil. The binary diffusion coefficient for water vapor in the polymer is  $D_{AB}=6 \times 10^{-14} \text{ m}^2/\text{s}$  while the aluminum may be assumed to be impermeable to water vapor. For molar concentrations of water vapor in the polymer at the outer and inner surfaces of  $C_{A,s1} = 4.5 \times 10^{-3} \text{ kmol}/\text{m}^3$  and  $C_{A,s2} = 0.5 \times 10^{-3} \text{ kmol}/\text{m}^3$ , respectively, determine the rate at which water vapor is transferred through the trough wall to the tablet.



**Problem(H.W)**

Helium gas is stored at 20°C in a spherical container of fused silica ( $\text{SiO}_2$ ), which has a diameter of 0.20 m and a wall thickness of 2 mm. If the container is charged to an initial pressure of 4 bars, what is the rate at which this pressure decreases with time?

### 4.8.3 Catalytic Surface Reactions

Many mass transfer problems involve specification of the species flux, rather than the species concentration, at a surface. One such problem relates to the process of catalysis, which involves the use of special surfaces to promote heterogeneous chemical reactions. Such a reaction occurs at the surface of a material, can be viewed as a surface phenomenon, and can be treated as a boundary condition. Often a one-dimensional diffusion analysis may be used to approximate the performance of a catalytic reactor.

For example (Figure 4.21), A catalytic surface is placed in a gas stream to promote a heterogeneous chemical reaction involving species A. Assume that the reaction produces species A at a rate  $\dot{N}''_A$ , which is defined as the molar rate of production per unit surface area of the catalyst. Once steady state conditions are reached, the rate of species transfer from the surface,  $N_{A,x}$  must equal the surface reaction rate:

$$N''_{A,x} = \dot{N}''_A \quad (4.64)$$

It is also assumed that species A leaves the surface as a result of one-dimensional transfer

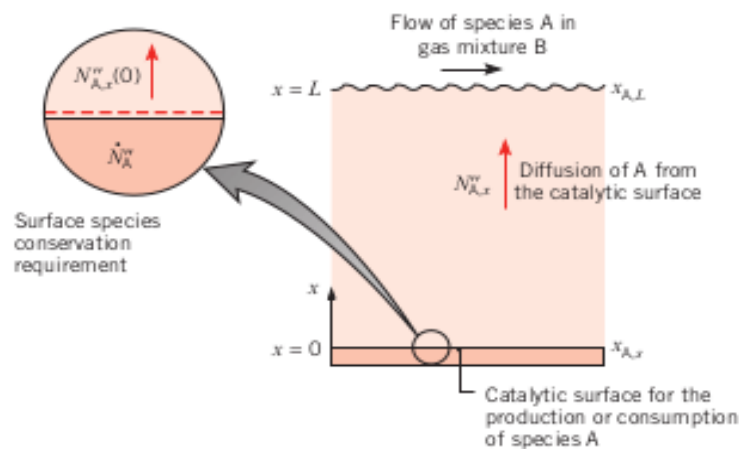


Figure 4.10: One-dimensional diffusion with heterogeneous catalysis.

through a thin film of thickness  $L$  and that no reactions occur within the film itself. The mole fraction of A at  $x=L$ ,  $x_{A,L}$ , corresponds to conditions in the mainstream of the mixture and is presumed to be known. Representing the remaining species of the mixture as a single species B and assuming the medium to be stationary, the Equation reduces to:

$$\frac{d}{dx}(CD_{AB}\frac{dx_A}{dx}) = 0 \quad (4.65)$$

where  $D_{AB}$  is the binary diffusion coefficient for A in B and B may be a multicomponent mixture. Assuming C and  $D_{AB}$  to be constant, Equation 4.163 may be solved subject to the conditions that

$$x_A(L) = x_{A,L}$$

and Equation 4.163 can be written as follows:

$$N''_{A,x}(0) = -CD_{AB}\frac{dx_A}{dx}|_{x=0} = \dot{N}''_A \quad (4.66)$$

For a catalytic surface, the surface reaction rate  $\dot{N}''_A$  generally depends on the surface concentration  $C_A(0)$ . For a first-order reaction that results in species consumption at the surface, the reaction rate is of the form:

$$N''_{A,x} = k_1'' \cdot C_A(0) \quad (4.67)$$

where  $k_1''$  (m/s) is the reaction rate constant. Accordingly, the surface boundary condition, Equation 4.165, reduces to:

$$-D_{AB}\frac{dx_A}{dx}|_{x=0} = -k_1''x_A(0) \quad (4.68)$$

Solving Equation 4.163 subject to the above conditions, it is readily verified that the concentration distribution is linear and of the form:

$$\frac{x_A(x)}{x_{A,L}} = \frac{1 + (xk_1''/D_{AB})}{1 + (Lk_1''/D_{AB})} \quad (4.69)$$

At the catalytic surface this result reduces to:

$$\frac{x_A(0)}{x_{A,L}} = \frac{1}{1 + (Lk_1''/D_{AB})} \quad (4.70)$$

and the molar flux is:

$$N''_A = -CD_{AB}\frac{dx_A}{dx}|_{x=0} = -k_1''Cx_A(0) \quad (4.71)$$

or:

$$N''_A(0) = -\frac{k_1'' C x_{A,L}}{1 + (Lk_1''/D_{AB})} \quad (4.72)$$

The negative sign implies mass transfer to the surface.

Two limiting cases of the foregoing results are of special interest. For the limit  $k_1'' \rightarrow 0$ ,  $(Lk_1''/D_{AB}) \ll 1$  and Equations 4.169 and 4.171 reduce to:

$$\frac{x_{A,s}}{x_{A,L}} \approx 1 \text{ and } N_A''(0) \approx -k_1'' C x_{A,L}$$

In such cases the rate of reaction is controlled by the reaction rate constant, and the limitation due to diffusion is negligible. The process is said to be reaction limited.

Conversely, for the limit  $k_1'' \rightarrow \infty$ ,  $(Lk_1''/D_{AB}) \gg 1$  and Equations 4.169 and 4.171 reduce to:

$$x_{A,s} \approx 0 \text{ and } N_A''(0) \approx -\frac{CD_{AB}x_{A,L}}{L} \quad (4.73)$$

In this case the reaction is controlled by the rate of diffusion to the surface, and the process is said to be diffusion limited.

#### 4.8.4 Mass Diffusion with Homogeneous Chemical Reactions

Just as heat diffusion may be influenced by internal sources of energy, species transfer by diffusion may be influenced by homogeneous chemical reactions. We restrict our attention to stationary media. If we also assume steady, one-dimensional transfer in the x-direction and that  $D_{AB}$  and  $C$  are constant, The equation will be as follows:

$$D_{AB} \frac{d^2 C_A}{dx^2} - k_1 C_A = 0 \quad (4.74)$$

This linear, homogeneous differential equation has the general solution

$$C_A(x) = C_1 e^{mx} + C_2 e^{-mx} \quad (4.75)$$

where  $m = (k_1/D_{AB})^{1/2}$  and the constants  $C_1$  and  $C_2$  depend on the prescribed boundary conditions.

Consider the situation illustrated in Figure 4.22. Gas A is soluble in liquid B, where it is transferred by diffusion and experiences a first-order chemical reaction. The solution is dilute, and the concentration of A in the liquid at the interface is a known constant  $C_{A,0}$ . If the bottom of the container is impermeable to A, the boundary conditions are:

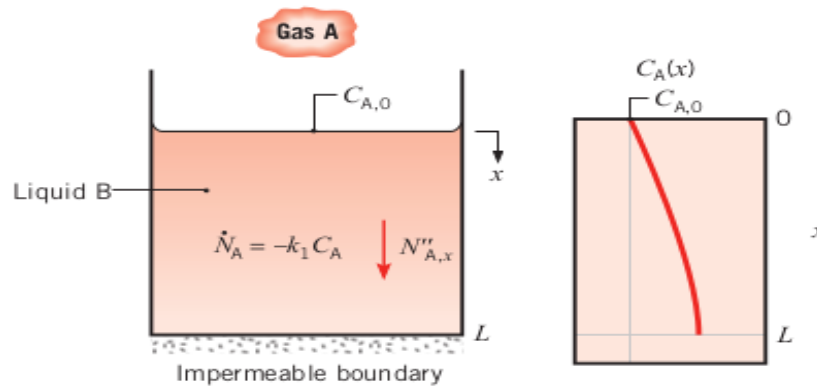


Figure 4.11: Diffusion and homogeneous reaction of gas A in liquid B.

$$C_A(0) = C_{A,0} \text{ and } \frac{dC_A}{dx} \Big|_{x=L} = 0 \quad (4.76)$$

These species boundary conditions are analogous to the thermal boundary conditions as follows:

$$C_A(x) = C_{A,0} \frac{\cosh m(L-x)}{\cosh mL} \quad (4.77)$$

Quantities of special interest are the concentration of A at the bottom and the flux of A across the gas-liquid interface. Applying Equation 4.176 at  $x=L$ , we obtain

$$C_A(L) = \frac{C_{A,0}}{\cosh mL} \quad (4.78)$$

Moreover,

$$N''_{A,x}(0) = -D_{AB} \frac{dC_A}{dx} \Big|_{x=0} \quad (4.79)$$

$$N''_{A,x}(0) = D_{AB} C_{A,0} m \frac{\sinh m(L-x)}{\cosh mL} \Big|_{x=0} \quad (4.80)$$

or

$$N''_{A,x}(0) = -D_{AB} C_{A,0} m \tanh mL \quad (4.81)$$

Results for a container with its bottom held at a fixed concentration or an infinitely deep container may be obtained by analogy to the heat transfer cases.

## Homework

Biofilms, which are colonies of bacteria that can cling to living or inert surfaces, can cause a wide array of human infections. Infections caused by bacteria living within biofilms are often chronic because antibiotics that are applied to the surface of a biofilm have difficulty penetrating through the film thickness. Consider a biofilm that is associated with a skin infection. An antibiotic (species A) is applied to the top layer of a biofilm (species B) so that a fixed concentration of medication,  $C_{A,0} = 4 \times 10^{-3} \text{ kmol/m}^3$ , exists at the upper surface of the biofilm. The diffusion coefficient of the medication within the biofilm is  $D_{AB} = 2 \times 10^{-12} \text{ m}^2/\text{s}$ . The antibiotic is consumed by biochemical reactions within the film, and the consumption rate depends on the local concentration of medication expressed as  $\dot{N}_A = -k_1 C_A$ , where  $k_1 = 0.1 \text{ s}^{-1}$ . To eradicate the bacteria, the antibiotic must be consumed at a rate of at least  $0.2 \times 10^{-3} \text{ kmol/s}\cdot\text{m}^3$  ( $\dot{N}_A \leq 0.2 \times 10^{-3} \text{ kmol/s}\cdot\text{m}^3$ ) since, at smaller absolute consumption rates, the bacteria will be able to grow back faster than it is destroyed. Determine the maximum thickness of a biofilm,  $L$ , that may be treated successfully by the antibiotic.

## Solution

**Known:** Topical antibiotic and biofilm properties, surface concentration of the medication, and required minimum consumption rate of antibiotic.

**Find:** Maximum thickness of a bacteria-laden biofilm,  $L$ , that may be successfully treated.

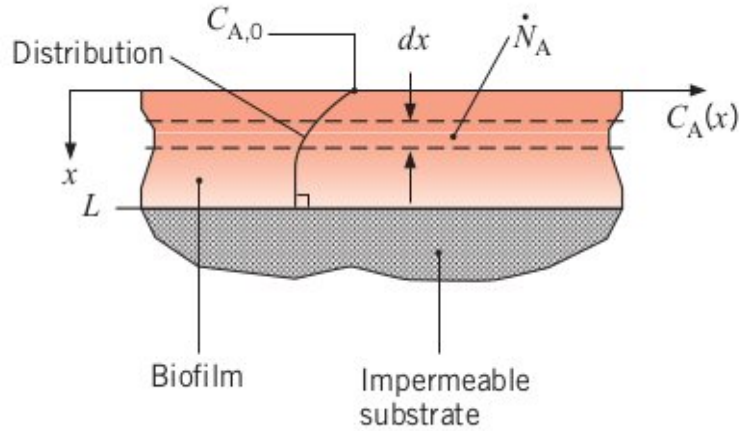
Ans. ( $L = 5.9 \times 10^{-6}$ )

## 4.9 Diffusivity for Gas Mixture

The theory describing diffusion in binary gas mixtures at low to moderate pressures has been well developed. Modern versions of the kinetic theory of gases have attempted to account for the forces of attraction and repulsion between molecules. Hirschfelder et al. (1949), using the Lennard-Jones potential to evaluate the influence of intermolecular forces, presented an equation for the diffusion coefficient for gas pairs of nonpolar, nonreacting molecules:

$$D_{AB} = \frac{0.00266T^{3/2}}{PM_{AB}^{1/2}\sigma_{AB}^2\Omega_D} \quad (4.82)$$





where:

$$M_{AB} = 2 \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{-1}$$

$D_{AB}$  = diffusion coefficient,  $\text{cm}^2/\text{s}$

$M_A, M_B$  = molecular weights of A and B

$T$  = temperature, K

$P$  = pressure, bar

$\sigma_{AB}$  = collision diameter, a Lennard-Jones parameter,  $\text{\AA}$

$\Omega_D$  = diffusion collision integral, dimensionless

The collision integral,  $\Omega_D$ , is a function of the temperature and of the intermolecular potential field for one molecule of A and one molecule of B. It is usually tabulated as a function of  $T^* = kT/\varepsilon_{AB}$ , where  $k$  is the Boltzmann constant ( $1.38 \times 10^{-16} \text{erg/K}$ ), and  $\varepsilon_{AB}$  is the energy of molecular interaction for the binary system A and B - a Lennard-Jones parameter-in erg. A very accurate approximation of  $\Omega_D$ , can be obtained from (Neufield et al., 1972).

$$\Omega_D = \frac{a}{(T^*)^b} + \frac{c}{\exp(dT^*)} + \frac{c}{\exp(dT^*)} + \frac{e}{\exp(fT^*)} + \frac{g}{\exp(hT^*)} \quad (4.83)$$

For a binary system composed of nonpolar molecular pairs, the Lennard-Jones parameters of the pure components may be combined empirically by the following relations:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_b}{2} \quad (4.84)$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B} \quad (4.85)$$

These relations must be modified for polar-polar and polar-nonpolar molecular pairs; the proposed modifications are discussed by Hirschfelder et al. (1954).

The Lennard-Jones parameters for the pure components are usually obtained from viscosity data. In the absence of experimental data, the values of the parameters for pure components may be estimated from the following empirical correlations:

$$\sigma = 1.18V_b^{1/3} \quad (4.86)$$

$$\varepsilon_A/k = 1.15T_b \quad (4.87)$$

where:

$V_b$  = the molar volume of the substance as liquid at its normal boiling point ( $\text{cm}^3/\text{gmol}$ ).

$T_b$  = the normal boiling point temperature

Molar volumes at normal boiling point for some commonly encountered compounds are listed in Table 4.1

One of the most widely used methods, shown to be quite general and reliable, was proposed by **Wilke and Lee** (1955):

$$D_{AB} = \frac{[3.03 - \frac{0.98}{M_{AB}^{1/2}}] \cdot (10^{-3})T^{1.5}}{PM_{AB}^{1/2}\sigma_{AB}^2\Omega_D} \quad (4.88)$$

Table 4.1: Molar Volumes at Normal Boiling Point

Compound	Volume (cm <sup>3</sup> /gmol)	Compound	Volume (cm <sup>3</sup> /mol)
Hydrogen, H <sub>2</sub>	14.3	Nitric oxide, NO	23.6
Oxygen, O <sub>2</sub>	25.6	Nitrous oxide, N <sub>2</sub> O	36.4
Nitrogen, N <sub>2</sub>	31.2	Ammonia, NH <sub>3</sub>	25.8
Air	29.9	Water, H <sub>2</sub> O	18.9
Carbon monoxide, CO	30.7	Hydrogen sulfide, H <sub>2</sub> S	32.9
Carbon dioxide, CO <sub>2</sub>	34	Bromine, Br <sub>2</sub>	53.2
Carbonyl sulfide, COS	51.5	Chlorine, Cl <sub>2</sub>	48.4
Sulfur Dioxide, SO <sub>2</sub>	44.8	Iodine, I <sub>2</sub>	71.5

### **Problem 1.1**

#### **Calculation of Diffusivity by the Wilke-Lee Equation with Known Values of the Lennard-Jones Parameters**

Estimate the diffusivity of carbon disulfide vapor in air at 273 K and 1 bar using the Wilke-Lee equation. Compare this estimate with the experimental value which is 0.894 m<sup>2</sup>Pa/s.

#### **4.9.1 Estimation of diffusivity by using Atomic Volume Contribution of the Elements**

For other compounds not listed in Table 4.1, if a reliable value of the critical volume ( $V_c$ ) is available, the Tyn and Calus (1975) method is recommended:

$$V_b = 0.285V_c^{1.048} \quad (4.89)$$

### **Problem 3.2**

#### **Calculation of Diffusivity by the Wilke-Lee Equation with Estimated Values of the Lennard-Jones Parameters**

Estimate the diffusivity of allyl chloride (C<sub>3</sub>H<sub>5</sub>Cl) in air at 298 K and 1 bar using the Wilke-Lee equation. The experimental value reported by Lugg (1968) is 0.098 cm<sup>2</sup>/s.

Table 4.2: Atomic Volume Contributions of the Elements

Element	Volume (cm <sup>3</sup> /gmol)	Compound	Volume (cm <sup>3</sup> /mol)
Bromine	27	Oxygen, except as noted below	7.4
Carbon	14.8	Oxygen, in methyl esters	9.1
Chlorine	24.6	Oxygen in methyl ethers	9.9
Hydrogen	3.7	Oxygen, in higher ethers, or other esters	11
Iodine	37	Oxygen, in acids	12
Nitrogen	15.6	Sulfur	25.6
Nitrogen in primary amine	10.5		
Nitrogen in 2nd amine	12		
For three-membered ring, such as ethylene oxide, subtract			6
For four-membered ring, such as cyclobutane, subtract			8.5
For five-membered ring, such as furan, subtract			11.5
For pyridine, subtract			15
For benzene ring, subtract			15
For naphthalene ring, subtract			30
For anthracene ring, subtract			47

**Your objectives in studying this section are to be able to:**

1. Estimate diffusion coefficients for binary dilute liquid systems using the Wilke and Chang equation.
2. Estimate diffusion coefficients for binary dilute liquid systems using the Hayduk and Minhas equation.
3. Use a Mathcad routine to implement calculation of diffusion coefficients for binary dilute liquid systems using the Hayduk and Minhas equation.

## 4.10 Diffusion coefficient for dilute liquids

Liquid diffusion coefficients are several orders of magnitude smaller than gas diffusivities, and depend on concentration due to the changes in viscosity with concentration and changes in the degree of ideality of the solution. As the mole fraction of either component in a binary mixture approaches unity, the thermodynamic factor  $\Gamma$  approaches unity and the Fick diffusivity and the MS diffusivity are equal. The diffusion coefficients obtained under these conditions are the infinite dilution diffusion coefficients and are given the symbol  $D^o$ .

The Stokes-Einstein equation is a purely theoretical method of estimating  $D^o$ ,

$$D_{AB}^o = \frac{\kappa T}{6\pi r_A \mu_B} \quad (4.90)$$

where  $r_A$  is the solute particle radius and  $\mu_B$  is the solvent viscosity. This equation has been fairly successful in describing diffusion of colloidal particles or large round molecules through a solvent which behaves as a continuum relative to the diffusing species.

Equation 4.90 has provided a useful starting point for a number of semiempirical correlations arranged into the general form:

$$\frac{D_{AB}^o \mu_B}{\kappa T} = f(V_{bA}) \quad (4.91)$$

In which  $f(V_{bA})$  is a function of the molecular volume of the diffusing solute. Empirical correlations using the general form of equation 4.91 have been developed which attempt to predict the liquid diffusion coefficient in terms of the solute and solvent properties.

Wilke and Chang (1955) have proposed the following still widely used correlation for non-electrolytes in an infinitely dilute solution:

$$\frac{D_{AB}^o \mu_B}{T} = \frac{7.4 \times 10^{-8} (\phi_B M_B)^{1/2}}{V_{bA}^{0.6}} \quad (4.92)$$

where:

$D_{AB}^o$  = diffusivity of A in very dilute solution in solvent B, cm<sup>2</sup>/s

$M_B$  = molecular weight of solvent B

$T$  = temperature, K

$\mu_B$  = viscosity of solvent B, CP

$V_{bA}$  = solute molar volume at its normal boiling point, cm<sup>3</sup>/mol = 75.6 cm<sup>3</sup>/mol for water as solute.

$\phi_B$  = association factor of solvent B, dimensionless

= 2.26 for water as solvent

= 1.9 for methanol as solvent

= 1.5 for ethanol as solvent

= 1.0 for unassociated solvents (e.g., benzene, ether, heptane)

The value of  $V_{bA}$  may be the true value or, if necessary, estimated from equation 4.89, or from the data of Table 4.1, except when water is the diffusing solute, as noted above. The association factor for a solvent can be estimated only when diffusivities in that solvent have been experimentally measured. There is also some doubt about the ability of the Wilke-Chang equation to handle solvents of very high viscosity, say 100 CP or more.

Hayduk and Minhas (1982) considered many correlations for the infinite dilution binary diffusion coefficient. By regression analysis, they proposed several correlations depending on the type of solute-solvent system.

**a.** For solutes in aqueous solutions:

$$D_{AB}^o = 1.25 \times 10^{-8} (V_{bA}^{-0.19} - 0.292) T^{1.52} \mu_B^\varepsilon \quad (4.93)$$

$$\varepsilon = \frac{9.58}{V_{bA}} - 1.12 \quad (4.94)$$

where:

$D_{AB}^o$  = diffusivity of A in very dilute aqueous solution,  $\text{cm}^2/\text{s}$

$T$  = temperature, K

$\mu_B$  = viscosity of water, CP

$V_{bA}$  = solute molar volume at its normal boiling point,  $\text{cm}^3/\text{mol}$

b. For nonaqueous (nonelectrolyte) solutions:

$$D_{AB}^o = 1.55 \times 10^{-8} \frac{V_{bB}^{0.27} T^{1.29} \sigma_b^{0.125}}{V_{bA}^{0.42} \mu_b^{0.92} \sigma_A^{0.105}} \quad (4.95)$$

where  $\sigma$  is surface tension at the normal boiling-point temperature, in  $\text{dyn}/\text{cm}$ . If values of the surface tension are not known, they may be estimated by the Brock and Bird (1955) corresponding states method (limited to nonpolar liquids):

$$\sigma = P_c^{2/3} T_c^{1/3} (0.132\alpha_c - 0.278)(1 - T_{br})^{11/9} \quad (4.96)$$

$$\alpha_c = 0.9076 \left[ 1 + \frac{T_{br} \ln(P_c/1.013)}{1 - T_{br}} \right] \quad (4.97)$$

When using the correlation shown in equation 4.95, there are several restrictions noted by the authors:

1. The method should not be used for diffusion in viscous solvents. Values of  $\mu_B$  above about 20 cP would classify the solvent as viscous.
2. If the solute is water, a dimer value of  $V_{bA}$  should be used ( $V_{bA} = 37.4 \text{ cm}^3/\text{mol}$ ).
3. If the solute is an organic acid and the solvent is other than water, methanol, or butanol, the acid should be considered a dimer with twice the expected value of  $V_{bA}$ .
4. For nonpolar solutes diffusing into monohydroxy alcohols, the values of  $V_{bB}$  should be multiplied by a factor equal to  $8\mu_B$ , where  $\mu_B$  is the solvent viscosity in cP.

### Problem 3.1

#### Calculation of Liquid Diffusivity in Aqueous Solution

Estimate the diffusivity of ethanol ( $\text{C}_2\text{H}_6\text{O}$ ) in a dilute solution in water at 288 K. Compare your estimate with the experimental value reported in the literature. The value was reported to be  $1 \times 10^{-5} \text{ cm}^2/\text{s}$ .

### Problem 3.2

#### Calculation of Liquid Diffusivity in Dilute Nonaqueous Solution

Estimate the diffusivity of acetic acid ( $C_2H_4O_2$ ) in a dilute solution in acetone ( $C_3H_6O$ ) at 313 K. Compare your estimate with the experimental value reported in literature. The following data are available (Reid, et al., 1987):

Parameter	Acetic acid	Acetone
$T_b$ , K	390.4	329.2
$T_c$ , K	594.8	508.0
$P_c$ , bar	57.9	47.0
$V_c$ , $cm^3/mol$	171.0	209.0
$\mu$ , cP	—	0.264
Molecular Weight (M)	60.0	58.0

## 4.11 Diffusion Coefficients for Concentrated Liquids

Most methods for predicting  $D$  in concentrated liquid solutions attempt to combine the infinite dilution coefficients  $(D_{12})^o$  and  $(D_{21})^o$  in a single function of composition. The Vignes formula is recommended by Reid et al. (1987):

$$D_{12} = (D_{12}^o)^{x_2} (D_{21}^o)^{x_1} \quad (4.98)$$

$$D_{12} = D_{12} \times \Gamma \quad (4.99)$$

where  $\Gamma$  is the thermodynamic correction factor

### Problem 3.3

#### Diffusion Coefficients in the System Acetone-Benzene (Taylor and Krishna, 1993)

Estimate the MS and Fick diffusion coefficients for an acetone(1)-benzene(2) mixture of composition  $x_1 = 0.7808$  at 298 K. The infinite dilution diffusivities are:

$$D_{12}^o = 2.75 \times 10^{-9} m^2/s$$



$$D_{21}^o = 4.15 \times 10^{-9} \text{m}^2/\text{s}$$

From the NRTL equation, for this system at the given temperature and concentration, the thermodynamic correction factor  $\Gamma = 0.871$ . The experimental value of  $D_{12}$  at this concentration is  $3.35 \times 10^{-9} \text{m}^2/\text{s}$ .

## 4.12 Common mass transfer scenario

### 4.12.1 Evaporation and Sublimation

A common mass transfer scenario is the transfer of a species A into a gas stream due to evaporation or sublimation from a liquid or solid surface, respectively (Figure 4.19). Conditions within the gas phase are of interest, and the concentration (or partial pressure) of species A in the gas phase at the interface (located at  $x=0$ ) may readily be determined from Raoult's law:

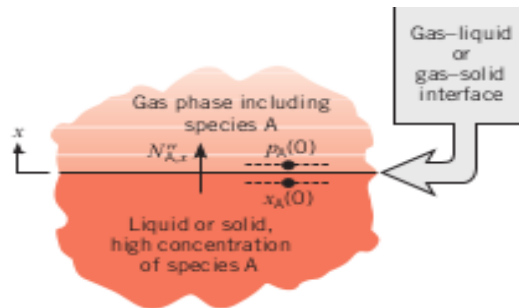


Figure 4.12: Species concentration at a gas–liquid or gas–solid interface. (a) Evaporation or sublimation of species A from a liquid or solid into a gas.

$$p_A(0) = x_A(0)P_{A,sat} \quad (4.100)$$

$P_A$  = The partial pressure of A in the gas phase

$x_A$  = Mole fraction of species A in the liquid or solid

$P_{A,sat}$  = The saturation pressure of species A at the surface temperature

### 4.12.2 Solubility of gases in liquids and solids

Another common scenario is mass transfer of species A from a gas phase into a liquid or solid, species B (Figure 4.20). Mass transfer within the liquid or solid phase is of interest, and the concentration of species A at the interface is required as a boundary condition.

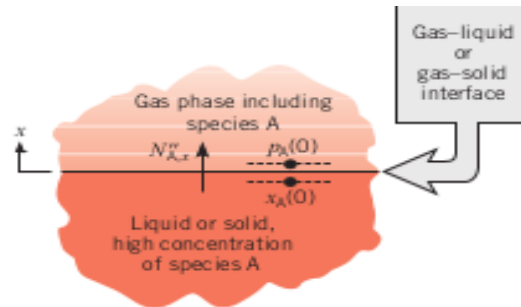


Figure 4.13: Transfer of weakly soluble species A from the gas to a liquid or solid.

If species A is only weakly soluble ( $x_A$  is small) in a liquid, Henry's law may be used to relate the mole fraction of A in the liquid to the partial pressure of A in the gas phase outside the liquid:

$$x_A(0) = \frac{P_A(0)}{H} \quad (4.101)$$

where:

$H$  = Henry's constant

The values for selected aqueous solutions are listed in Tables printed in the Appendix of different sources. Although  $H$  depends in temperature, its pressure dependence may be generally neglected for values of  $P$  up to 5 bar.

Conditions at a gas–solid interface may also be determined if the gas, species A, dissolves in a solid, species B, and a solution is formed. In such cases mass transfer in the solid is independent of the structure of the solid and may be treated as a diffusion process. In contrast, there are many situations for which the porosity of the solid strongly influences gas transport through the solid.

Treating the gas and solid as a solution, we can obtain the concentration of the gas in the solid at the interface through use of a property known as the solubility,  $S$ . It is defined by the expression:

$$C_A(0) = SP_A(0) \quad (4.102)$$

where:

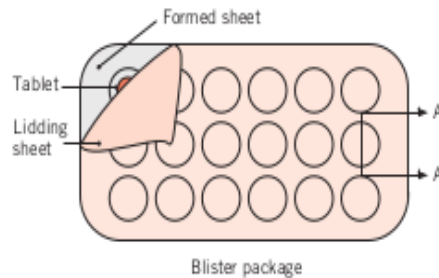
$P_A(0)$  = The partial pressure (bars) of the gas adjoining the interface.

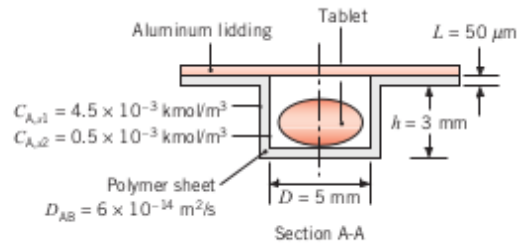
$C_A(0)$  = The molar concentration of A in the solid at the interface,  $C_A(0)$ , is in units of kilomoles of A per cubic meter of solid.

$S$  = Solubility in kilomoles of A per cubic meter of solid per bar (or atm) partial pressure of A.

### Problem

The efficacy of pharmaceutical products is reduced by prolonged exposure to high temperature, light, and humidity. For water vapor-sensitive consumer products that are in tablet or capsule form, and might be stored in humid environments such as bathroom medicine cabinets, blister packaging is used to limit the direct exposure of the medicine to humid conditions until immediately before its ingestion. Consider tablets that are contained in a blister package composed of a flat lidding sheet and a second, formed sheet that includes troughs to hold each tablet. The formed sheet is  $L=50 \mu\text{m}$  thick and is fabricated of a polymer material. Each trough is of diameter  $D = 5 \text{ mm}$  and depth  $h = 3 \text{ mm}$ . The lidding sheet is fabricated of aluminum foil. The binary diffusion coefficient for water vapor in the polymer is  $D_{AB}=6 \times 10^{-14} \text{ m}^2/\text{s}$  while the aluminum may be assumed to be impermeable to water vapor. For molar concentrations of water vapor in the polymer at the outer and inner surfaces of  $C_{A,s1} = 4.5 \times 10^{-3} \text{ kmol/m}^3$  and  $C_{A,s2} = 0.5 \times 10^{-3} \text{ kmol/m}^3$ , respectively, determine the rate at which water vapor is transferred through the trough wall to the tablet.





### Problem(H.W)

Helium gas is stored at  $20^\circ\text{C}$  in a spherical container of fused silica ( $\text{SiO}_2$ ), which has a diameter of 0.20 m and a wall thickness of 2 mm. If the container is charged to an initial pressure of 4 bars, what is the rate at which this pressure decreases with time?

### 4.12.3 Catalytic Surface Reactions

Many mass transfer problems involve specification of the species flux, rather than the species concentration, at a surface. One such problem relates to the process of catalysis, which involves the use of special surfaces to promote heterogeneous chemical reactions. Such a reaction occurs at the surface of a material, can be viewed as a surface phenomenon, and can be treated as a boundary condition. Often a one-dimensional diffusion analysis may be used to approximate the performance of a catalytic reactor.

For example (Figure 4.21), A catalytic surface is placed in a gas stream to promote a heterogeneous chemical reaction involving species A. Assume that the reaction produces species A at a rate  $\dot{N}''_A$ , which is defined as the molar rate of production per unit surface area of the catalyst. Once steady state conditions are reached, the rate of species transfer from the surface,  $N_{A,x}$  must equal the surface reaction rate:

$$N''_{A,x} = \dot{N}''_A \quad (4.103)$$

It is also assumed that species A leaves the surface as a result of one-dimensional transfer

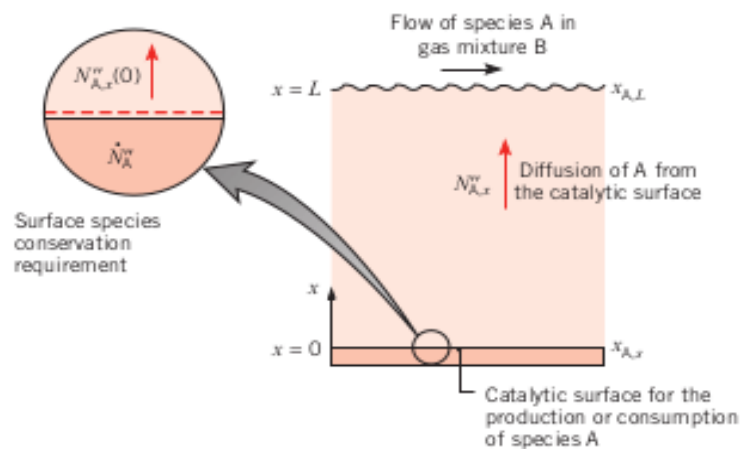


Figure 4.14: One-dimensional diffusion with heterogeneous catalysis.

through a thin film of thickness  $L$  and that no reactions occur within the film itself. The mole fraction of A at  $x=L$ ,  $x_{A,L}$ , corresponds to conditions in the mainstream of the mixture and is presumed to be known. Representing the remaining species of the mixture as a single species B and assuming the medium to be stationary, the Equation reduces to:

$$\frac{d}{dx}(CD_{AB}\frac{dx_A}{dx}) = 0 \quad (4.104)$$

where  $D_{AB}$  is the binary diffusion coefficient for A in B and B may be a multicomponent mixture. Assuming C and  $D_{AB}$  to be constant, Equation 4.163 may be solved subject to the conditions that

$$x_A(L) = x_{A,L}$$

and Equation 4.163 can be written as follows:

$$N''_{A,x}(0) = -CD_{AB}\frac{dx_A}{dx}|_{x=0} = \dot{N}''_A \quad (4.105)$$

For a catalytic surface, the surface reaction rate  $\dot{N}''_A$  generally depends on the surface concentration  $C_A(0)$ . For a first-order reaction that results in species consumption at the surface, the reaction rate is of the form:

$$N''_{A,x} = k_1'' \cdot C_A(0) \quad (4.106)$$

where  $k_1''$  (m/s) is the reaction rate constant. Accordingly, the surface boundary condition, Equation 4.165, reduces to:

$$-D_{AB}\frac{dx_A}{dx}|_{x=0} = -k_1''x_A(0) \quad (4.107)$$

Solving Equation 4.163 subject to the above conditions, it is readily verified that the concentration distribution is linear and of the form:

$$\frac{x_A(x)}{x_{A,L}} = \frac{1 + (xk_1''/D_{AB})}{1 + (Lk_1''/D_{AB})} \quad (4.108)$$

At the catalytic surface this result reduces to:

$$\frac{x_A(0)}{x_{A,L}} = \frac{1}{1 + (Lk_1''/D_{AB})} \quad (4.109)$$

and the molar flux is:

$$N''_A = -CD_{AB}\frac{dx_A}{dx}|_{x=0} = -k_1''Cx_A(0) \quad (4.110)$$

or:

$$N''_A(0) = -\frac{k_1'' C x_{A,L}}{1 + (Lk_1''/D_{AB})} \quad (4.111)$$

The negative sign implies mass transfer to the surface.

Two limiting cases of the foregoing results are of special interest. For the limit  $k_1'' \rightarrow 0$ ,  $(Lk_1''/D_{AB}) \ll 1$  and Equations 4.169 and 4.171 reduce to:

$$\frac{x_{A,s}}{x_{A,L}} \approx 1 \text{ and } N_A''(0) \approx -k_1'' C x_{A,L}$$

In such cases the rate of reaction is controlled by the reaction rate constant, and the limitation due to diffusion is negligible. The process is said to be reaction limited.

Conversely, for the limit  $k_1'' \rightarrow \infty$ ,  $(Lk_1''/D_{AB}) \gg 1$  and Equations 4.169 and 4.171 reduce to:

$$x_{A,s} \approx 0 \text{ and } N_A''(0) \approx -\frac{CD_{AB}x_{A,L}}{L} \quad (4.112)$$

In this case the reaction is controlled by the rate of diffusion to the surface, and the process is said to be diffusion limited.

#### 4.12.4 Mass Diffusion with Homogeneous Chemical Reactions

Just as heat diffusion may be influenced by internal sources of energy, species transfer by diffusion may be influenced by homogeneous chemical reactions. We restrict our attention to stationary media. If we also assume steady, one-dimensional transfer in the x-direction and that  $D_{AB}$  and  $C$  are constant, The equation will be as follows:

$$D_{AB} \frac{d^2 C_A}{dx^2} - k_1 C_A = 0 \quad (4.113)$$

This linear, homogeneous differential equation has the general solution

$$C_A(x) = C_1 e^{mx} + C_2 e^{-mx} \quad (4.114)$$

where  $m = (k_1/D_{AB})^{1/2}$  and the constants  $C_1$  and  $C_2$  depend on the prescribed boundary conditions.

Consider the situation illustrated in Figure 4.22. Gas A is soluble in liquid B, where it is transferred by diffusion and experiences a first-order chemical reaction. The solution is dilute, and the concentration of A in the liquid at the interface is a known constant  $C_{A,0}$ . If the bottom of the container is impermeable to A, the boundary conditions are:

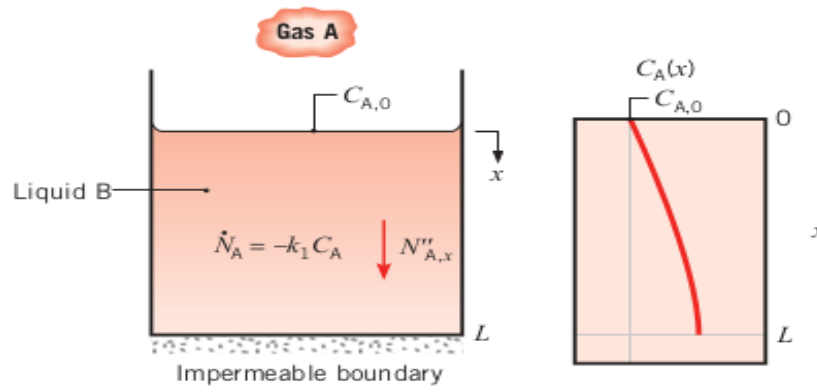


Figure 4.15: Diffusion and homogeneous reaction of gas A in liquid B.

$$C_A(0) = C_{A,0} \text{ and } \left. \frac{dC_A}{dx} \right|_{x=L} = 0 \quad (4.115)$$

These species boundary conditions are analogous to the thermal boundary conditions as follows:

$$C_A(x) = C_{A,0} \frac{\cosh m(L-x)}{\cosh mL} \quad (4.116)$$

Quantities of special interest are the concentration of A at the bottom and the flux of A across the gas-liquid interface. Applying Equation 4.176 at  $x=L$ , we obtain

$$C_A(L) = \frac{C_{A,0}}{\cosh mL} \quad (4.117)$$



Moreover,

$$N''_{A,x}(0) = -D_{AB} \frac{dC_A}{dx} \Big|_{x=0} \quad (4.118)$$

$$N''_{A,x}(0) = D_{AB} C_{A,0} m \frac{\sinh m(L-x)}{\cosh mL} \Big|_{x=0} \quad (4.119)$$

or

$$N''_{A,x}(0) = -D_{AB} C_{A,0} m \tanh mL \quad (4.120)$$

Results for a container with its bottom held at a fixed concentration or an infinitely deep container may be obtained by analogy to the heat transfer cases.

### 4.13 Equimolal Counter Diffusion

The total pressure is constant all through the mixture. Hence the difference in partial pressures will be equal. The Fick's equation when integrated for a larger plane volume of thickness L will give:

For liquids:

$$N_A/A = -D_{ab} \frac{C_{A1} - C_{A2}}{L} \quad (4.121)$$

$$N_B/A = -D_{BA} \frac{C_{B2} - C_{B1}}{L} \quad (4.122)$$

$$N_B/A = -\frac{N_B}{A} \quad (4.123)$$

$$(C_{A1} - C_{A2}) = (C_{B2} - C_{B1}) \quad (4.124)$$

For gases:

$$N_A/A = D/RT \cdot \frac{(P_{A1} - P_{A2})}{x_2 - x_1} \quad (4.125)$$

Where  $P_{A1}$  and  $P_{A2}$  are partial pressures of component A at  $x_1$  and  $x_2$  and  $R$  is the universal gas constant in J/kg mol K.  $T$  is the temperature in absolute units. The distance should be expressed in metre.

The partial pressure variation and diffusion directions are shown in Figure 4.16.

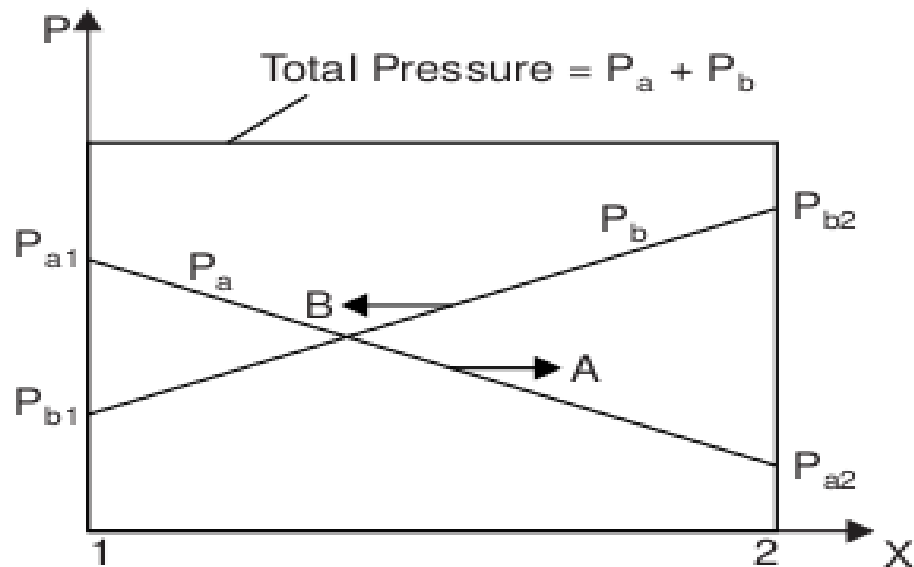


Figure 4.16: Partial Pressure variation of components in equimolar counter diffusion.

### Problem 1

In order to avoid pressure build up ammonia gas at atmospheric pressure in a pipe is vented to atmosphere through a pipe of 3 mm dia and 20 m length. Determine the mass of ammonia diffusing out and mass of air diffusing in per hour. Assume  $D = 0.28 \times 10^{-4} \text{m}^2/\text{s}$ ,  $M = 17 \text{ kg/kg mole}$

Solution: (In the video lecture)

## 4.14 Stationary media with specified surface concentration

In the diffusion of gas from containers, there is diffusion of gas from inside to the outside without the metal molecules diffusing into the gas. In these cases the concentration of gas

at the surfaces should be known. The solubility of the gas in the surface determines the concentration at the surface.

The flow rate can be obtained From equation below:

$$N_A = (C_{A1} - C_{A2})/Resistance \quad (4.126)$$

Where Resistance to diffusion in is different according to the geometry:

1- Case1: Resistance of plane wall:

$$Resistance = L/D_{AB}A \quad (4.127)$$

2-Case2: Resistance of hollow cylindrical configuration

$$Resistance = \frac{\ln (r_2/r_1)}{2\pi D_{AB}L} \quad (4.128)$$

3-Case3: Resistance of hollow sphere configuration

$$Resistance = \frac{1}{4\pi D_{AB}} \left[ \frac{1}{r_1} - \frac{1}{r_2} \right] \quad (4.129)$$

## 4.15 Diffusion of one component into a stationary component or unidirectional diffusion

In this case one of the components diffuses while the other is stationary. For steady conditions the mass diffused should be absorbed continuously at the boundary. In certain cases this is not possible. The popular example is water evaporating into air. In this case, as mentioned earlier, a bulk motion replaces the air tending to accumulate at the interface without being absorbed, causing an increase in the diffusion rate.

$$\frac{N_A}{A} = P/RT \cdot \frac{D}{(x_2 - x_1)} \cdot \ln\left(\frac{P - P_{A2}}{P - P_{A1}}\right) \quad (4.130)$$

In the gas absorption a soluble gas A is transferred to the liquid surface where it dissolves, whereas the insoluble gas B undergoes no net movement with respect to the interface.

The concept of stationary component may envisaged by considering the moving of the box in the opposite of the direction to that in which B is diffusing, at a velocity equal to it's diffusion velocity, so that to the external observer B appears to be stationary. The total velocity at which A is transferred will then be increased to its diffusion velocity plus the velocity of the box.

## 4.16 Convective mass transfer

When a medium deficient in a component flows over a medium having an abundance of the component, then the component will diffuse into the flowing medium. Diffusion in the opposite direction will occur if the mass concentration levels of the component are interchanged. Concentration boundary layer is used to determine convective mass transfer.

The Figure 4.17 shows the flow of a mixture of components A and B with a specified constant concentration over a surface rich in component A. A concentration boundary layer develops. The concentration gradient varies from the surface to the free stream. At the surface the mass transfer is by diffusion. Convective mass transfer coefficient  $h_m$  is defined by the equation, where  $h_m$  has a unit of m/s.

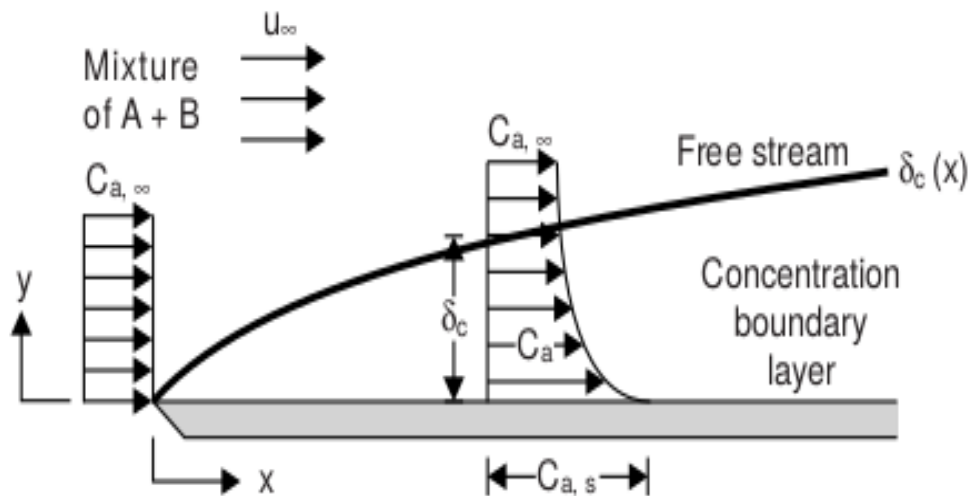


Figure 4.17: Species concentration boundary layer development on a flat plate.

$$Moleflow = h_m(C_{As} - C_{A\infty}) \quad (4.131)$$

The condition for diffusion at the surface is given by:

$$Moleflow = -D_{AB} \frac{\partial C_A}{\partial y} \quad (4.132)$$

The mass flow is to be used to estimate convective mass transfer coefficient  $h_m$ :

$$h_m = \frac{-D_{AB} \cdot \frac{\partial C_A}{\partial y} \Big|_{y=0}}{C_{As} - C_{A\infty}} \quad (4.133)$$

In the above case, if mass flow is to be used then:

$$h_m = \frac{-D_{AB} \cdot \frac{\partial \rho_A}{\partial y} \Big|_{y=0}}{\rho_{As} - \rho_{A\infty}} \quad (4.134)$$

The solutions for boundary layer thickness for convective mass transfer can be obtained according to the following equation:

$$u \frac{\partial C_A}{\partial x} + v \frac{\partial C_A}{\partial y} = D_{AB} \frac{\partial^2 C_A}{\partial y^2} \quad (4.135)$$

Prandtl number Schmidt number defined by:

$$Sc = \nu / D_{AB} \quad (4.136)$$

Nondimensionalising the equation leads to the condition as below:

$$\delta = f(Re, Sc) \quad (4.137)$$

$$Sh = f(Re, Sc) \quad (4.138)$$

where Sherwood number  $Sh$  is defined as:

$$Sh = \frac{h_m x}{D_{AB}} \quad (4.139)$$

In the laminar region flow over plate:

$$\delta_m = \frac{5x}{Re_x} \cdot Sc^{1/3} \quad (4.140)$$

$$Sh_x = \frac{h_m x}{D_{AB}} = 0.332 Re_x^{1/2} Sc^{1/3} \quad (4.141)$$

$$Sh_x = \frac{h_m x}{D_{AB}} = 0.332 Re_x^{1/2} Sc^{1/3} \quad (4.142)$$

$$\overline{Sh}_L = \frac{h_m L}{D_{AB}} = 0.664 Re_L^{1/2} Sc^{1/3} \quad (4.143)$$

In the turbulent region  $Re > 5 \times 10^5$ ,

$$\delta_m = \delta_\nu \quad (4.144)$$

$$Sh_x = \frac{h_m x}{D_{AB}} = 0.0296 Re_x^{0.8} Sc^{1/3} \quad (4.145)$$

$$\overline{Sh}_L = \frac{h_m L}{D_{AB}} = 0.037 Re_L^{1/2} Sc^{1/3} \quad (4.146)$$

**For flow through tubes:**

- **For Laminar Region  $Re < 2000$ :**

- For uniform wall mass concentration:

$$Sh = 3.66 \quad (4.147)$$

- For uniform wall mass flux:

$$Sh = 4.36 \quad (4.148)$$

- **For turbulent region,  $Re > 2000$ :**

$$Sh = 0.023Re^{0.83}Sc^{1/3} \quad (4.149)$$

Check your understanding with Assignment 2 Problem 6,7,8,9,10,11.

## 4.17 Diffusion as a mass flux

**Proposed Question:** (Prove that the diffusional processes does not give rise to equal and opposite mass fluxes)

Ficks law of diffusion is normally expressed in molar units:

$$N_A = -D_{AB} \frac{dC_A}{dy} = -D_{AB} C_T \frac{dx_A}{dy} \quad (4.150)$$

where  $x_A$  is the mole fraction of component A.

If each side of Equation 4.150 is multiplied by the molecular weight of A,  $M_A$  then:

$$J_A = -D_{AB} \frac{dc_A}{dy} = -D_{AB} C_T M_A \frac{dx_A}{dy} \quad (4.151)$$

where  $J_A$  is a flux in mass per unit area and unit time ( $Kg/m^2 \cdot s$ ), and  $c_A$  is a concentration in mass terms ( $kg/m^3$ )

Similarly, for component B:

$$J_B = -D_{BA} \frac{dc_B}{dy} = -D_{BA} C_T M_A \frac{dx_B}{dy} \quad (4.152)$$

The sum of the molar concentrations is constant in an ideal gas at constant pressure, the sum of mass concentration is not constant, and  $(\frac{dc_A}{dy})$  and  $(\frac{dc_B}{dy})$  are not equal and opposite:

Thus,

$$C_A + C_B = C_T = \frac{c_A}{M_A} + \frac{c_B}{M_B} \quad (4.153)$$

Differentiate the above equation:

$$\frac{1}{M_A} \frac{dc_A}{dy} + \frac{1}{M_B} \frac{dc_B}{dy} = 0 \quad (4.154)$$

$$\frac{dc_B}{dy} = -\frac{M_B}{M_A} \frac{dc_A}{dy} \quad (4.155)$$



## 4.18 General case for gas-phase mass transfer in a binary mixture

In the absorption of a soluble gas A from a mixture the bulk velocity must be equal and opposite to the diffusional velocity of B as this latter component undergoes no net transfer .

For any component:

$$\text{Total Transfer} = \text{Transfer by diffusion} + \text{Transfer by bulk flow.}$$

For component A:

$$\text{Total transfer (moles/area time)} = N'_A$$

Diffusional transfer according to Fick's Law:

$$N_A = -D \frac{dC_A}{dy}$$

Transfer by bulk flow:

$$\text{Transfer by bulk flow} = u_F C_A$$

Thus for A:

$$N'_A = N_A + u_F C_A$$

For B:

$$N'_B = N_B + u_F C_B$$

$$\begin{aligned} \text{The bulk flow velocity} &= \frac{\text{Total moles transferred/area time}}{\text{Total molar concentration}} \\ &= \frac{N'_A + N'_B}{C_T} \end{aligned}$$

Substituting:

$$N'_A = N_A + \frac{C_A}{C_T} (N'_A + N'_B)$$

$$N'_A = -D \frac{dC_A}{dy} + x_A(N'_A + N'_B)$$

$$N'_A = -DC_T \frac{dx_A}{dy} + x_A(N'_A + N'_B) \quad (4.156)$$

Similarly for B:

$$N'_B = -DC_T \frac{dx_A}{dy} + (1 - x_A)(N'_A + N'_B)$$

For equimolar counterdiffusion,  $N'_A = -N'_B$ , so Equation 4.156 will be reduced to Fick's Law.

For a system in which B undergoes no net transfer,  $N'_B = 0$  and Equation 4.156 is identical to Stefan's Law.

In a distillation column, the molar latent heat of A is  $f$  times that of B, the condensation of 1 mole of A (Taken as less volatile component) will result in the vaporisation of  $f$  moles of B and the mass transfer rate of B will be  $f$  times that of A in the opposite direction.

For the general case:

$$fN'_A = -N'_B$$

Substituting into Equation 4.156:

$$N'_A = -DC_T \frac{dx_A}{dy} + x_A(N'_A + fN'_A) \quad (4.157)$$

Thus:

$$[1 - x_A(1 - f)]N'_A = -DC_T \frac{dx_A}{dy}$$

If  $x_A$  changes from  $x_{A1}$  to  $x_{A2}$  as  $y$  goes from  $y_1$  to  $y_2$  then:

$$N'_A \int_{y_1}^{y_2} dy = -DC_T \int_{x_{A1}}^{x_{A2}} \frac{dx_A}{1 - x_A(1 - f)}$$

Thus:

$$N'_A(y_2 - y_1) = -DC_T \frac{1}{1-f} \left[ \ln \frac{1}{(1-f)^{-1} - x_A} \right]_{x_{A1}}^{x_{A2}}$$

Or:

$$N'_A(y_2 - y_1) = -DC_T \frac{1}{1-f} \left[ \ln \frac{1}{(1-f)^{-1} - x_A} \right]_{x_{A1}}^{x_{A2}}$$

or:

$$N'_A = \frac{-DC_T}{(y_2 - y_1)} \frac{1}{1-f} \ln \frac{1 - x_{A2}(1-f)}{1 - x_{A1}(1-f)} \quad (4.158)$$

## 4.19 Conservation of species for a control volume

The rate at which the mass of some species enters a control volume, plus the rate at which the species mass is generated within the control volume, minus the rate at which this species mass leaves the control volume must equal the rate of increase of the species mass stored within the control volume.

For example, any species A may enter and leave the control volume due to both fluid motion and diffusion across the control surface; these processes are surface phenomena represented by  $\hat{M}_{A,in}$  and  $\hat{M}_{A,out}$ . The same species A may also be generated,  $\hat{M}_{A,g}$ , and accumulated or stored,  $\hat{M}_{A,st}$ , within the control volume. The conservation equation may then be expressed on a rate basis as:

$$\hat{M}_{A,in} + \hat{M}_{A,g} - \hat{M}_{A,out} = \frac{dM_A}{dt} \equiv \hat{M}_{A,st} \quad (4.159)$$

Species generation exists when chemical reactions occur in the system. For example, for a dissociation reaction of the form  $AB \rightarrow A+B$ , there would be net production of species A and B, as well as net reduction of the species AB.

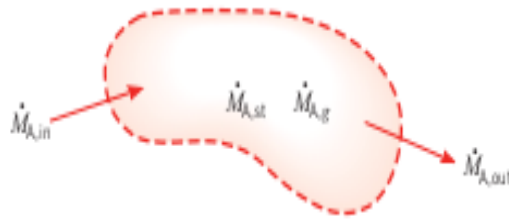


Figure 4.18: Conservation of species for a control volume.

## 4.20 Common mass transfer scenario

### 4.20.1 Evaporation and Sublimation

A common mass transfer scenario is the transfer of a species A into a gas stream due to evaporation or sublimation from a liquid or solid surface, respectively (Figure 4.19).

Conditions within the gas phase are of interest, and the concentration (or partial pressure) of species A in the gas phase at the interface (located at  $x=0$ ) may readily be determined from Raoult's law:

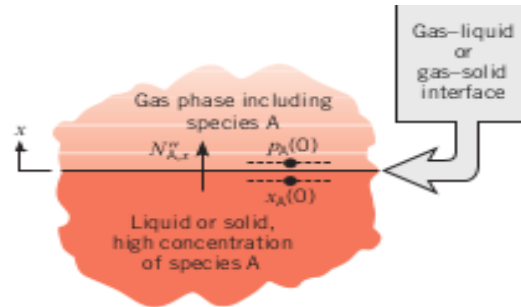


Figure 4.19: Species concentration at a gas–liquid or gas–solid interface. (a) Evaporation or sublimation of species A from a liquid or solid into a gas.

$$p_A(0) = x_A(0)P_{A,sat} \quad (4.160)$$

$P_A$  = The partial pressure of A in the gas phase

$x_A$  = Mole fraction of species A in the liquid or solid

$P_{A,sat.}$  = The saturation pressure of species A at the surface temperature

#### 4.20.2 Solubility of gases in liquids and solids

Another common scenario is mass transfer of species A from a gas phase into a liquid or solid, species B (Figure 4.20). Mass transfer within the liquid or solid phase is of interest, and the concentration of species A at the interface is required as a boundary condition.

If species A is only weakly soluble ( $x_A$  is small) in a liquid, Henry's law may be used to relate the mole fraction of A in the liquid to the partial pressure of A in the gas phase outside the liquid:

$$x_A(0) = \frac{P_A(0)}{H} \quad (4.161)$$

where:

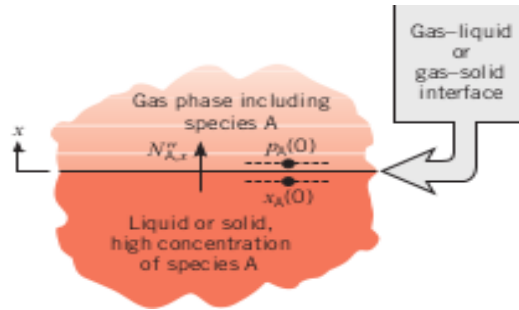


Figure 4.20: Transfer of weakly soluble species A from the gas to a liquid or solid.

$H$  = Henry's constant

The values for selected aqueous solutions are listed in Tables printed in the Appendix of different sources. Although  $H$  depends in temperature, its pressure dependence may be generally neglected for values of  $P$  up to 5 bar.

Conditions at a gas–solid interface may also be determined if the gas, species A, dissolves in a solid, species B, and a solution is formed. In such cases mass transfer in the solid is independent of the structure of the solid and may be treated as a diffusion process. In contrast, there are many situations for which the porosity of the solid strongly influences gas transport through the solid.

Treating the gas and solid as a solution, we can obtain the concentration of the gas in the solid at the interface through use of a property known as the solubility,  $S$ . It is defined by the expression:

$$C_A(0) = SP_A(0) \quad (4.162)$$

where:

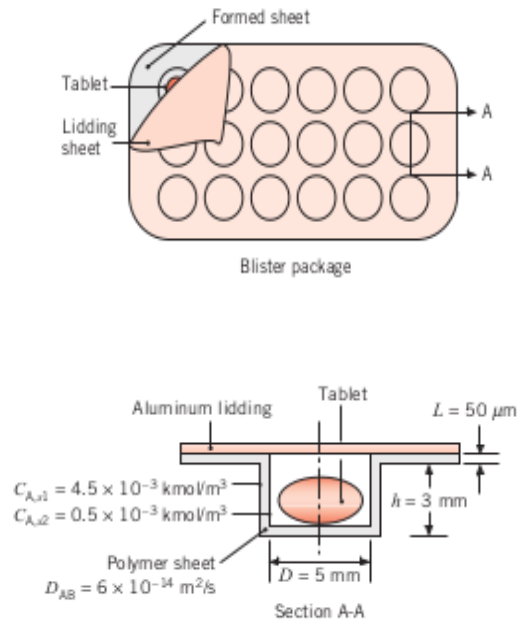
$P_A(0)$  = The partial pressure (bars) of the gas adjoining the interface.

$C_A(0)$  = The molar concentration of A in the solid at the interface,  $C_A(0)$ , is in units of kilomoles of A per cubic meter of solid.

$S$  = Solubility in kilomoles of A per cubic meter of solid per bar (or atm) partial pressure of A.

**Problem**

The efficacy of pharmaceutical products is reduced by prolonged exposure to high temperature, light, and humidity. For water vapor-sensitive consumer products that are in tablet or capsule form, and might be stored in humid environments such as bathroom medicine cabinets, blister packaging is used to limit the direct exposure of the medicine to humid conditions until immediately before its ingestion. Consider tablets that are contained in a blister package composed of a flat lidding sheet and a second, formed sheet that includes troughs to hold each tablet. The formed sheet is  $L=50 \mu\text{m}$  thick and is fabricated of a polymer material. Each trough is of diameter  $D = 5 \text{ mm}$  and depth  $h = 3 \text{ mm}$ . The lidding sheet is fabricated of aluminum foil. The binary diffusion coefficient for water vapor in the polymer is  $D_{AB}=6 \times 10^{-14} \text{ m}^2/\text{s}$  while the aluminum may be assumed to be impermeable to water vapor. For molar concentrations of water vapor in the polymer at the outer and inner surfaces of  $C_{A,s1} = 4.5 \times 10^{-3} \text{ kmol}/\text{m}^3$  and  $C_{A,s2} = 0.5 \times 10^{-3} \text{ kmol}/\text{m}^3$ , respectively, determine the rate at which water vapor is transferred through the trough wall to the tablet.



**Problem(H.W)**

Helium gas is stored at 20°C in a spherical container of fused silica ( $\text{SiO}_2$ ), which has a diameter of 0.20 m and a wall thickness of 2 mm. If the container is charged to an initial pressure of 4 bars, what is the rate at which this pressure decreases with time?



### 4.20.3 Catalytic Surface Reactions

Many mass transfer problems involve specification of the species flux, rather than the species concentration, at a surface. One such problem relates to the process of catalysis, which involves the use of special surfaces to promote heterogeneous chemical reactions. Such a reaction occurs at the surface of a material, can be viewed as a surface phenomenon, and can be treated as a boundary condition. Often a one-dimensional diffusion analysis may be used to approximate the performance of a catalytic reactor.

For example (Figure 4.21), A catalytic surface is placed in a gas stream to promote a heterogeneous chemical reaction involving species A. Assume that the reaction produces species A at a rate  $\dot{N}''_A$ , which is defined as the molar rate of production per unit surface area of the catalyst. Once steady state conditions are reached, the rate of species transfer from the surface,  $N''_{A,x}$  must equal the surface reaction rate:

$$N''_{A,x} = \dot{N}''_A \quad (4.163)$$

It is also assumed that species A leaves the surface as a result of one-dimensional transfer

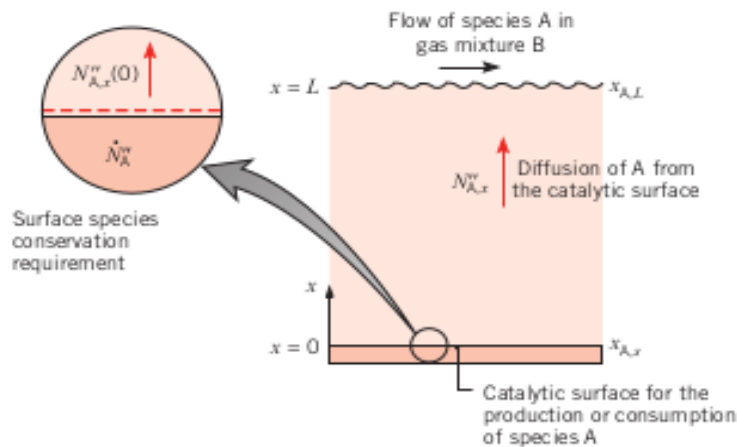


Figure 4.21: One-dimensional diffusion with heterogeneous catalysis.

through a thin film of thickness  $L$  and that no reactions occur within the film itself. The mole fraction of A at  $x=L$ ,  $x_{A,L}$ , corresponds to conditions in the mainstream of the mixture and is presumed to be known. Representing the remaining species of the mixture as a single species B and assuming the medium to be stationary, the Equation reduces to:

$$\frac{d}{dx}(CD_{AB}\frac{dx_A}{dx}) = 0 \quad (4.164)$$

where  $D_{AB}$  is the binary diffusion coefficient for A in B and B may be a multicomponent mixture. Assuming C and  $D_{AB}$  to be constant, Equation 4.163 may be solved subject to the conditions that

$$x_A(L) = x_{A,L}$$

and Equation 4.163 can be written as follows:

$$N''_{A,x}(0) = -CD_{AB}\frac{dx_A}{dx}|_{x=0} = \dot{N}''_A \quad (4.165)$$

For a catalytic surface, the surface reaction rate  $\dot{N}''_A$  generally depends on the surface concentration  $C_A(0)$ . For a first-order reaction that results in species consumption at the surface, the reaction rate is of the form:

$$N''_{A,x} = k_1'' \cdot C_A(0) \quad (4.166)$$

where  $k_1''$  (m/s) is the reaction rate constant. Accordingly, the surface boundary condition, Equation 4.165, reduces to:

$$-D_{AB}\frac{dx_A}{dx}|_{x=0} = -k_1''x_A(0) \quad (4.167)$$

Solving Equation 4.163 subject to the above conditions, it is readily verified that the concentration distribution is linear and of the form:

$$\frac{x_A(x)}{x_{A,L}} = \frac{1 + (xk_1''/D_{AB})}{1 + (Lk_1''/D_{AB})} \quad (4.168)$$

At the catalytic surface this result reduces to:

$$\frac{x_A(0)}{x_{A,L}} = \frac{1}{1 + (Lk_1''/D_{AB})} \quad (4.169)$$

and the molar flux is:

$$N''_A = -CD_{AB}\frac{dx_A}{dx}|_{x=0} = -k_1''Cx_A(0) \quad (4.170)$$

or:

$$N''_A(0) = -\frac{k_1'' C x_{A,L}}{1 + (Lk_1''/D_{AB})} \quad (4.171)$$

The negative sign implies mass transfer to the surface.

Two limiting cases of the foregoing results are of special interest. For the limit  $k_1'' \rightarrow 0$ ,  $(Lk_1''/D_{AB}) \ll 1$  and Equations 4.169 and 4.171 reduce to:

$$\frac{x_{A,s}}{x_{A,L}} \approx 1 \text{ and } N_A''(0) \approx -k_1'' C x_{A,L}$$

In such cases the rate of reaction is controlled by the reaction rate constant, and the limitation due to diffusion is negligible. The process is said to be reaction limited.

Conversely, for the limit  $k_1'' \rightarrow \infty$ ,  $(Lk_1''/D_{AB}) \gg 1$  and Equations 4.169 and 4.171 reduce to:

$$x_{A,s} \approx 0 \text{ and } N_A''(0) \approx -\frac{CD_{AB}x_{A,L}}{L} \quad (4.172)$$

In this case the reaction is controlled by the rate of diffusion to the surface, and the process is said to be diffusion limited.

#### 4.20.4 Mass Diffusion with Homogeneous Chemical Reactions

Just as heat diffusion may be influenced by internal sources of energy, species transfer by diffusion may be influenced by homogeneous chemical reactions. We restrict our attention to stationary media. If we also assume steady, one-dimensional transfer in the x-direction and that  $D_{AB}$  and  $C$  are constant, The equation will be as follows:

$$D_{AB} \frac{d^2 C_A}{dx^2} - k_1 C_A = 0 \quad (4.173)$$

This linear, homogeneous differential equation has the general solution

$$C_A(x) = C_1 e^{mx} + C_2 e^{-mx} \quad (4.174)$$

where  $m = (k_1/D_{AB})^{1/2}$  and the constants  $C_1$  and  $C_2$  depend on the prescribed boundary conditions.

Consider the situation illustrated in Figure 4.22. Gas A is soluble in liquid B, where it is transferred by diffusion and experiences a first-order chemical reaction. The solution is dilute, and the concentration of A in the liquid at the interface is a known constant  $C_{A,0}$ . If the bottom of the container is impermeable to A, the boundary conditions are:

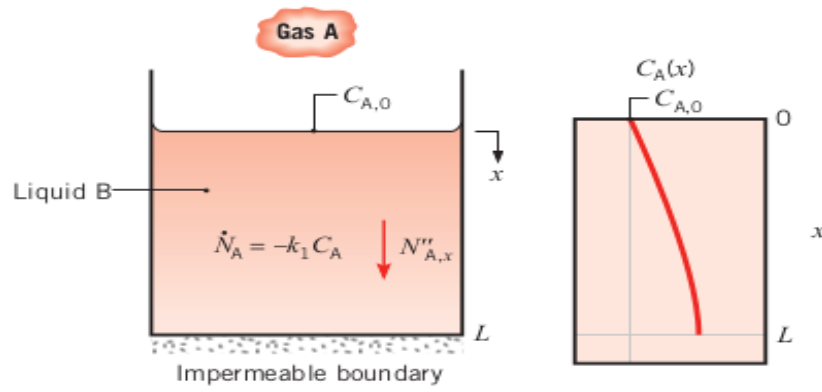


Figure 4.22: Diffusion and homogeneous reaction of gas A in liquid B.

$$C_A(0) = C_{A,0} \text{ and } \frac{dC_A}{dx} \Big|_{x=L} = 0 \quad (4.175)$$

These species boundary conditions are analogous to the thermal boundary conditions as follows:

$$C_A(x) = C_{A,0} \frac{\cosh m(L-x)}{\cosh mL} \quad (4.176)$$

Quantities of special interest are the concentration of A at the bottom and the flux of A across the gas-liquid interface. Applying Equation 4.176 at  $x=L$ , we obtain

$$C_A(L) = \frac{C_{A,0}}{\cosh mL} \quad (4.177)$$

Moreover,

$$N''_{A,x}(0) = -D_{AB} \frac{dC_A}{dx} \Big|_{x=0} \quad (4.178)$$

$$N''_{A,x}(0) = D_{AB} C_{A,0} m \frac{\sinh m(L-x)}{\cosh mL} \Big|_{x=0} \quad (4.179)$$

or

$$N''_{A,x}(0) = -D_{AB} C_{A,0} m \tanh mL \quad (4.180)$$

Results for a container with its bottom held at a fixed concentration or an infinitely deep container may be obtained by analogy to the heat transfer cases.

## Homework

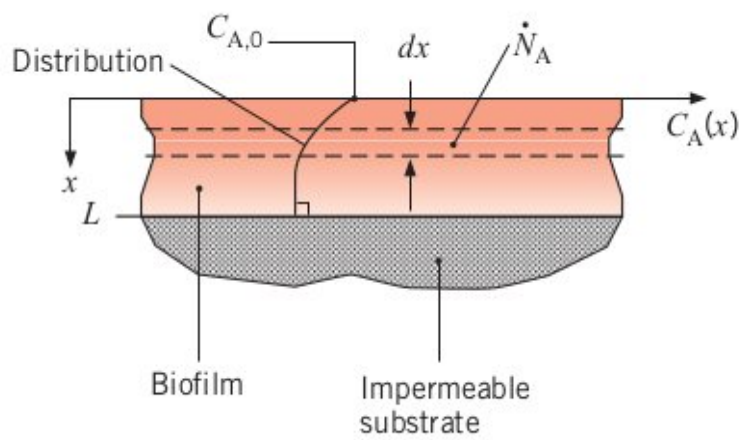
Biofilms, which are colonies of bacteria that can cling to living or inert surfaces, can cause a wide array of human infections. Infections caused by bacteria living within biofilms are often chronic because antibiotics that are applied to the surface of a biofilm have difficulty penetrating through the film thickness. Consider a biofilm that is associated with a skin infection. An antibiotic (species A) is applied to the top layer of a biofilm (species B) so that a fixed concentration of medication,  $C_{A,0} = 4 \times 10^{-3} \text{ kmol/m}^3$ , exists at the upper surface of the biofilm. The diffusion coefficient of the medication within the biofilm is  $D_{AB} = 2 \times 10^{-12} \text{ m}^2/\text{s}$ . The antibiotic is consumed by biochemical reactions within the film, and the consumption rate depends on the local concentration of medication expressed as  $\dot{N}_A = -k_1 C_A$ , where  $k_1 = 0.1 \text{ s}^{-1}$ . To eradicate the bacteria, the antibiotic must be consumed at a rate of at least  $0.2 \times 10^{-3} \text{ kmol/s}\cdot\text{m}^3$  ( $\dot{N}_A \leq 0.2 \times 10^{-3} \text{ kmol/s}\cdot\text{m}^3$ ) since, at smaller absolute consumption rates, the bacteria will be able to grow back faster than it is destroyed. Determine the maximum thickness of a biofilm,  $L$ , that may be treated successfully by the antibiotic.

## Solution

**Known:** Topical antibiotic and biofilm properties, surface concentration of the medication, and required minimum consumption rate of antibiotic.

**Find:** Maximum thickness of a bacteria-laden biofilm,  $L$ , that may be successfully treated.

Ans. ( $L = 5.9 \times 10^{-6}$ )



# Chapter 5

## Maxwell's Law of Diffusion

Your objectives in studying this section are to be able to:

- 1 Define the concepts Fick's Law of diffusion and thermodynamic factor.
- 2 Express the driving force for mass transfer in terms of mole fraction gradients for ideal

### 5.1 Maxwell's law for a binary system

MAXELL postulated that the partial pressure gradient in the direction of diffusion for a constituent of a two-component gaseous mixtures was proportional to:

- 1- the relative velocity of the molecules in the direction of diffusion
- 2- the product of the molar concentrations of the components

Thus:

$$-\frac{dP_A}{dy} = FC_A C_B (u_A - u_B) \quad (5.1)$$

where  $u_A$  and  $u_B$  are the mean molecular velocities of A and B respectively in the direction of mass transfer and F is a coefficient.

Noting that:



$$u_A = \frac{N_A}{C_A} \quad (5.2)$$

$$u_B = \frac{N_B}{C_B} \quad (5.3)$$

$$P_A = C_A RT \quad \text{for an ideal gas} \quad (5.4)$$

The substitution into Equation 5.1:

$$-\frac{dC_A}{dy} = \frac{F}{RT}(N_A C_B - N_B C_A) \quad (5.5)$$

### 5.1.1 Equimolecular counterdiffusion

By definition:

$$N_A = -N_B \quad (5.6)$$

Substituting in Equation 5.7:

$$-\frac{dC_A}{dy} = \frac{FN_A}{RT}(C_A + C_B) \quad (5.7)$$

or:

$$N_A = -\frac{RT}{FC_T} \frac{dC_A}{dy} \quad (5.8)$$

By comparison with Fick's Law:

$$D = \frac{RT}{FC_T} \quad (5.9)$$

$$F = \frac{RT}{DC_T} \quad (5.10)$$

### 5.1.2 Transfer of A through stationary B

By definition:

$$N_B = 0 \quad (5.11)$$

$$-\frac{dC_A}{dy} = \frac{E}{RT} N_A C_B \quad (5.12)$$

$$N_A = -\frac{RT}{FC_T} \frac{C_T}{C_B} \frac{dC_A}{dy} \quad (5.13)$$

Substituting for Equation 5.9 into Equation 5.13:

$$N_A = -D \frac{C_T}{C_B} \frac{dC_A}{dy} \quad (5.14)$$

# Chapter 6

# Chapter 7

# Chapter 8

# Chapter 9



# References



# APPENDICES

# Appendix A

## Assignment-1: Due into one week

### A.1 Mixture Composition

#### Problem 1

Assuming air to be composed exclusively of  $O_2$  and  $N_2$ , with their partial pressures in the ratio 0.21:0.79, what are their mass fractions?

#### Problem 2

Consider an ideal gas mixture of  $n$  species.

a- Derive an equation for determining the mass fraction of species  $i$  from knowledge of the mole fraction and the molecular weight of each of the  $n$  species. Derive an equation for determining the mole fraction of species  $i$  from knowledge of the mass fraction and the molecular weight of each of the  $n$  species.

b- In a mixture containing equal mole fractions of  $O_2$ ,  $N_2$ , and  $CO_2$ , what is the mass fraction of each species? In a mixture containing equal mass fractions of  $O_2$ ,  $N_2$ , and  $CO_2$ , what is the mole fraction of each species?

#### Problem 3

A mixture of  $CO_2$  and  $N_2$  is in a container at  $25^\circ C$ , with each species having a partial pressure of 1 bar. Calculate the molar concentration, the mass density, the mole fraction, and the mass fraction of each species.

#### Problem 4

A He-Xe mixture containing 0.75 mole fraction of helium is used for cooling of electronics in an avionics application. At a temperature of 300 K and atmospheric pressure, calculate the mass fraction of helium and the mass density, molar concentration, and molecular weight of the mixture. If the cooling system capacity is 10 L, what is the mass of the coolant?

**Problem 5**

A mixture of noble gases (helium, argon, krypton, and xenon) is at a total pressure of 150 kPa and a temperature of 500 K. If the mixture has equal mole fractions of each of the gases, determine:

- (a) The composition of the mixture in terms of mass fractions.
- (b) The average molecular weight of the mixture.
- (c) The total molar concentration.
- (d) The mass density

Answer: 2.34 kg/m<sup>3</sup>

**Problem 6**

A solution of carbon tetrachloride and carbon disulfide containing 50% by weight of each is to be continuously distilled at a rate of 5000 kg/h.

- (a) Determine the concentration of the mixture in terms of mole fractions.
- (b) Determine the average molecular weight of the mixture.
- (c) Calculate the feed rate in kmol/h.

Answer: 49.10 kmol/h

# Appendix B

## Assignment-2: Due into 2 weeks

### Problem 1

In order to avoid pressure build up ammonia gas at atmospheric pressure in a pipe is vented to atmosphere through a pipe of 3 mm dia and 20 m length. Determine the mass of ammonia diffusing out and mass of air diffusing in per hour. Assume  $D = 0.28 \times 10^{-4} \text{m}^2/\text{s}$ ,  $M = 17 \text{ kg/kg mole}$

### Problem 2

Hydrogen stored in a vessel diffuses through the steel wall of 20 mm thickness. The molar concentration at the inner surface is  $2 \text{ kg mol/m}^3$ . At the other surface it is zero. Assuming plane wall condition and  $D_{ab} = 0.26 \times 10^{-12} \text{m}^2/\text{s}$ , determine the mass of hydrogen diffused per  $1 \text{ m}^2$ .

### Problem 3

Hydrogen gas is maintained at 4 bar and 1 bar on the opposite sides of a membrane of 0.5 mm thickness. At this temperature the diffusion coefficient is  $8.7 \times 10^{-8} \text{m}^2/\text{s}$ . The solubility of hydrogen in the material which depends on the pressure is  $1.5 \times 10^{-3} \text{ m}^2/\text{s bar}$ . Determine the mass diffusion rate of hydrogen through the membrane.

### Problem 4

Consider the diffusion of hydrogen (species A) in air, liquid water, or iron (species B) at  $T=293 \text{ K}$ . Calculate the species flux on both molar and mass bases if the concentration gradient at a particular location is  $dC_A/dx = 1 \text{ kmol/m}^3 \cdot \text{m}$ . Compare the value of the mass diffusivity to the thermal diffusivity. The mole fraction of the hydrogen,  $x_A$ , is much less than unity.

### **Problem 5**

Derive an expression for the diffusion of one component into a non diffusing (stationary) component.

### **Problem 6**

Air at 25°C and 50% RH flows over water surface measuring 12 m × 6 m at a velocity of 2 m/s. Determine the water loss per day considering flow direction is along the 12 m side.  $D_{AB} = 0.26 \times 10^{-4} \text{ m}^2/\text{s}$ ,  $Sc = 0.60$ ,  $\nu = 15.7 \times 10^{-6} \text{ m}^2/\text{s}$ . The density of water vapour at 25°C at saturated condition, from steam tables = 0.023 kg/m<sup>3</sup>.

### **Problem 7**

Air at 25°C and 20% RH flows through a pipe of 25 mm ID with a velocity of 5.2 m/s. The inside surface is constantly wetted with water and a thin water film is maintained throughout. Determine the water evaporated per  $\text{m}^2$  surface area.

### **Problem 8**

Oxygen diffuses through a layer of 3 mm thickness of a mixture of hydrogen and methane in equal volumes. The total pressure is 1 bar and the temperature is 0°C. The partial pressure of oxygen at the two surfaces are 10000 Pa and 5000 Pa. Determine the rate of diffusion of oxygen. The diffusivity of O<sub>2</sub> into H<sub>2</sub> is  $69.9 \times 10^{-6} \text{ m}^2/\text{s}$  and the diffusivity of oxygen into methane is  $18.6 \times 10^{-6} \text{ m}^2/\text{s}$ .

### **Problem 9**

Ethyl alcohol (C<sub>2</sub>H<sub>6</sub>O) is at the bottom of a glass jar of 30 mm dia at a depth of 80 mm from the top. Air flows at the top and the concentration of alcohol in the air is zero. The total pressure is 1.013 bar and the temperature is 25°C. The partial pressure of alcohol at this temperature is 0.08 bar. Determine the diffusion rate. Diffusion coefficient,  $D = 11.9 \times 10^{-6} \text{ m}^2/\text{s}$ . Molecular weight = 46,  $R_b = 8315/46 = 180.76 \text{ J/kg K}$ .

### **Problem 10**

Dry air at 30°C flows over a plate also at 30°C with the plate surface constantly covered with a water film. The velocity of flow is 6 m/s. The plate is 1 m long. Determine the average convective mass transfer coefficient and also the mass of water evaporated per second.

### **Problem 11**

Pure water at 20°C flows over a slab of salt at a velocity of 1 m/s. At the interface the concentration of salt is 380 kg/m<sup>3</sup>. Determine over a length of 1 m the average convection coefficient for mass transfer and also the rate of diffusion of salt into the water. Assume

turbulent flow from the leading edge.  $D = 1.2 \times 10^{-9} \text{ m}^2/\text{s}$ , density of water =  $1000 \text{ kg/m}^3$ , kinematic viscosity =  $1.006 \times 10^{-6} \text{ m}^2/\text{s}$ ,  $Sc = 1.0006 \times 10^{-6} / 1.2 \times 10^{-9} = 838.33$ .