1

Fundamentals of Mass Transfer

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 toward equilibrium. The transport of one component from a region of higher concentration to that of a lower concentration is called *mass transfer*.

Many of our daily experiences involve mass-transfer phenomena. The invigorating aroma of a cup of freshly brewed coffee and the sensuous scent of a delicate perfume both reach our nostrils from the source by diffusion through air. A lump of sugar added to the cup of coffee eventually dissolves and then diffuses uniformly throughout the beverage. Laundry hanging under the sun during a breezy day dries fast because the moisture evaporates and diffuses easily into the relatively dry moving air.

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.

Distillation separates, by partial vaporization, a liquid mixture of miscible and volatile substances into individual components or, in some cases, into groups of components. The separation of a mixture of methanol and water into its components; of liquid air into oxygen, nitrogen, and argon; and of crude petroleum into gasoline, kerosene, fuel oil, and lubricating stock are examples of distillation.

Principles and Modern Applications of Mass-Transfer Operations, Third Edition, Jaime Benitez.

In *gas absorption*, a soluble vapor is absorbed by means of a liquid in which the solute gas is more or less soluble, from its mixture with an inert gas. The washing of ammonia from a mixture of ammonia and air by means of liquid water is a typical example. The solute is subsequently recovered from the liquid by distillation, and the absorbing liquid can be either discarded or reused. When a solute is transferred from the solvent liquid to the gas phase, the operation is known as *desorption or stripping*.

In *humidification* or *dehumidification* (depending upon the direction of transfer), the liquid phase is a pure liquid containing but one component while the gas phase contains two or more substances. Usually the inert or carrier gas is virtually insoluble in the liquid. Removal of water vapor from air by condensation on a cold surface and the condensation of an organic vapor, such as carbon tetrachloride out of a stream of nitrogen, are examples of dehumidification. In humidification operations, the direction of transfer is from the liquid to the gas phase.

The *adsorption* operations exploit the ability of certain solids preferentially to concentrate specific substances from solution onto their surfaces. In this manner, the components of either gaseous or liquid solutions can be separated from each other. A few examples will illustrate the great variety of practical applications of adsorption. It is used to dehumidify air and other gases, to remove objectionable odors and impurities from industrial gases, to recover valuable solvent vapors from dilute mixtures with air and other gases, to remove objectionable taste and odor from drinking water, and many other applications.

Liquid extraction is the separation of the constituents of a liquid solution by contact with another insoluble liquid. If the substances constituting the original solution distribute themselves differently between the two liquid phases, a certain degree of separation will result. The solution which is to be extracted is called the *feed*, and the liquid with which the feed is contacted is called the *solvent*. The solvent-rich product of the operation is called the *extract*, and the residual liquid from which the solute has been removed is called the *raffinate*.

Membrane separations are rapidly increasing in importance. In general, the membranes serve to prevent intermingling of two miscible phases. They also prevent ordinary hydrodynamic flow, and movement of substances through them is by diffusion. Separation of the components of the original solution takes place by selectively controlling their passage from one side of the membrane to the other. An example of a membrane-mediated, liquid–liquid separation process is *dialysis*. In this process, a colloid is removed from a liquid solution by contacting the solution with a solvent through an intervening membrane which is permeable to the solution, but not to the larger colloidal particles. For example, aqueous beet-sugar solutions containing undesired colloidal material are freed of the latter by contact with water through a semipermeable membrane. Sugar and water diffuse through the membrane, but not the colloid.

Returning to the lump of sugar added to the cup of coffee, it is evident that the time required for the sugar to distribute uniformly depends upon whether the liquid is quiescent, or whether it is mechanically agitated by a spoon. In general, the mechanism of mass transfer depends upon the dynamics of the system in which it occurs. Mass can be transferred by random molecular motion in quiescent fluids, or it can be transferred from a surface into a moving fluid, aided by the dynamic characteristics of the flow. These two distinct modes of transport, *molecular mass transfer* and *convective mass transfer*, are analogous to conduction heat transfer and convective heat transfer. Each of these modes of mass transfer will be described and analyzed. The two mechanisms often act simultaneously. Frequently, when this happens, one mechanism can dominate quantitatively so that approximate solutions involving only the dominant mode can be used.

1.2 MOLECULAR MASS TRANSFER

As early as 1815, it was observed qualitatively that whenever a gas mixture contains two or more molecular species, whose relative concentrations vary from point to point, an apparently natural process results which tends to diminish any inequalities in composition. This macroscopic transport of mass, independent of any convection effects within the system, is defined as *molecular diffusion*.

In the specific case of a gaseous mixtures, a logical explanation of this transport phenomenon can be deduced from the kinetic theory of gases. At any temperature above absolute zero, individual molecules are in a state of continual yet random motion. Within dilute gas mixtures, each solute molecule behaves independently of the other solute molecules, since it seldom encounters them. Collisions between the solute and the solvent molecules are continually occurring. As a result of the collisions, the solute molecules move along a zigzag path, sometimes toward a region of higher concentration, sometimes toward a region of lower concentration.

Consider a hypothetical section passing normal to the concentration gradient within an isothermal, isobaric gaseous mixture containing solute and solvent molecules. The two thin, equal elements of volume above and below the section will contain the same number of molecules, as stipulated by Avogadro's law (Welty et al., 1984).

Although it is not possible to state which way any particular molecule will travel in a given interval of time, a definite number of the molecules in the lower element of volume will cross the hypothetical section from below, and the same number of molecules will leave the upper element and cross the section from above. With the existence of a concentration gradient, there are more solute molecules in one of the elements of volume than in the other; accordingly, an overall net transfer from a region of higher concentration to one of lower concentration will result. The net flow of each molecular species occurs in the direction of a negative concentration gradient.

The laws of mass transfer show the relation between the flux of the diffusing substance and the concentration gradient responsible for this mass transfer. Since diffusion occurs only in mixtures, its evaluation must involve an examination of the effect of each component. For example, it is often desired to know the diffusion rate of a specific component relative to the velocity of the mixture in which it is moving. Since each component may possess a different mobility, the mixture velocity must be evaluated by averaging the velocities of all the components present.

In order to establish a common basis for future discussions, definitions and relations which are often used to explain the role of components within a mixture are considered next.

1.2.1 Concentrations

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.

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*, ρ_A, is defined as the mass of A per unit volume of the mixture. The total mass concentration, or *density*, ρ, is the total mass of the mixture contained in a unit volume; that is,

$$\rho = \sum_{i=1}^{n} \rho_i \tag{1-1}$$

where n is the number of species in the mixture. The *mass fraction*, ω_A, is the mass concentration of species A divided by the total mass density,

$$\omega_A = \frac{\rho_A}{\sum_{i=1}^{n} \rho_i} = \frac{\rho_A}{\rho} \tag{1-2}$$

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

$$\sum_{i=1}^{n} \omega_i = 1 \tag{1-3}$$

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, one mol of any species contains a mass equivalent to its molecular weight; therefore, the mass concentration and the molar concentration are related by

$$c_A = \frac{\rho_A}{M_A} \tag{1-4}$$

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

$$c_A = \frac{p_A}{RT} \tag{1-5}$$

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,

$$c = \sum_{i=1}^{n} c_i \tag{1-6}$$

For a gaseous mixture that obeys the ideal gas law,

$$c = \frac{P}{RT} \tag{1-7}$$

where P is the total pressure. The *mol 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:

$$\begin{aligned} x_A &= \frac{c_A}{c} \quad \text{(liquids and solids)} \\ y_A &= \frac{c_A}{c} \quad \text{(gases)} \end{aligned} \tag{1-8}$$

For a gaseous mixture that obeys the ideal gas law, the mol fraction, y_A, can be written in terms of pressures:

$$y_A = \frac{c_A}{c} = \frac{p_A}{P} \tag{1-9}$$

Equation (1-9) is an algebraic representation of Dalton's law for gas mixtures. The sum of the mol fractions, by definition, must be 1.

$$\sum_{i=1}^{n} y_i = \sum_{i=1}^{n} x_i = 1.0 \tag{1-10}$$

Example 1.1 Concentration of Feed to a Gas Absorber

A gas containing 88% (by volume) CH_4, 4% C_2H_6, 5% n-C_3H_8, and 3% n-C_4H_{10} 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 1.1). Calculate:

(a) Total molar concentration in the gas feed.

(b) Density of the gas feed.

(c) Composition of the gas feed, expressed in terms of mass fractions.

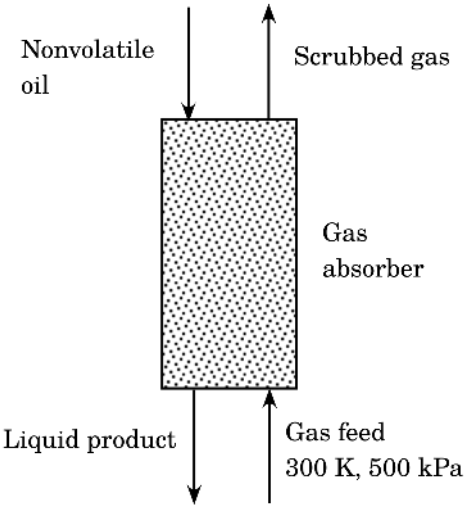


Figure 1.1 Schematic diagram of gas absorber of Example 1.1.

Solution

(a) Use Equation (1-7) to calculate the total molar concentration:

$$c = \frac{P}{RT} = \frac{500}{8.314 \times 300} = 0.20 \ \frac{\text{kmol}}{\text{m}^3}$$

(b) Calculate the gas average molecular weight, M_{av}:

Basis: 100 kmol of gas mixture

Component	kmol	Molecular weight	Mass, kg
CH_4	88	16.04	1411.52
C_2H_6	4	30.07	120.28
n-C_3H_8	5	44.09	220.45
n-C_4H_{10}	3	58.12	174.36
Total	100		1926.61

$$M_{av} = \frac{1926.61}{100} = 19.26 \ \frac{\text{kg}}{\text{kmol}}$$

To calculate the mixture mass density:

$$\rho = cM_{av} = 0.20 \times 19.26 = 3.85 \ \frac{\text{kg}}{\text{m}^3}$$

(c) Calculate the mass fraction of each component in the gas mixture from the intermediate results of part (b):

Component	Mass, kg	Mass fraction
CH_4	1411.52	(1411.52/1926.61) = 0.733
C_2H_6	120.28	0.062
n-C_3H_8	220.45	0.114
n-C_4H_{10}	174.36	0.091
Total	1926.61	1.000

Example 1.2 Concentration of Potassium Nitrate Wash Solution

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

$$KCl + NaNO_3 \rightarrow KNO_3 + NaCl$$

The reaction mixture is cooled down to 293 K and pure KNO_3 crystallizes. The resulting slurry contains the KNO_3 crystals and an aqueous solution of both KNO_3 and NaCl. The crystals in the slurry are washed in a multistage process with a saturated KNO_3 solution to free them of NaCl (see Figure 1.2). The equilibrium solubility of KNO_3 in water at 293 K is 24% (by weight); the density of the saturated solution is 1162 kg/m^3 (Perry and Chilton, 1973). Calculate:

(a) Total molar density of the fresh wash solution.

(b) Composition of the fresh wash solution, expressed in terms of molar fractions.

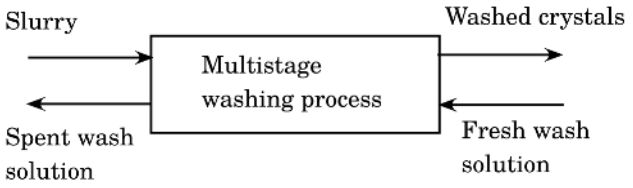


Figure 1.2 Schematic diagram of the washing process in Example 1.2.

Solution

(a) Calculate the average molecular weight, M_{av}, of the wash solution, and then its total molar density.

Basis: 100 kg of fresh wash solution

Component	Mass, kg	Molecular weight	kmol
KNO_3	24	101.10	0.237
H_2O	76	18.02	4.218
Total	100		4.455

Therefore,

$$M_{av} = \frac{100}{4.455} = 22.45 \ \frac{\text{kg}}{\text{kmol}}$$

$$c = \frac{\rho}{M_{av}} = \frac{1162}{22.45} = 51.77 \ \frac{\text{kmol}}{\text{m}^3}$$

(b) Calculate the mol fractions from intermediate results in part (a):

Component	kmol	Mol fraction
KNO_3	0.237	(0.237/4.455) = 0.053
H_2O	4.218	0.947
Total	4.455	1.000

Example 1.3 Material Balances on a Bio-Artificial Kidney (Montgomery et al., 1998)

The primary functions of the kidneys are to remove waste products (such as urea, uric acid, and creatinine), and to maintain the fluid and salt balance in the blood. Blood consists of two parts: blood cells, mostly red (45% by volume), and plasma (55% by volume). Urea, uric acid, creatinine, and water are all found in the plasma. If the kidneys fail, wastes start to accumulate and the body becomes overloaded with fluid. Fortunately, patients with renal failure can use an external dialysis machine, also known as an artificial kidney, to clean the blood. The cleaning of the blood in the artificial kidney is due to the difference in toxin concentrations between the blood and the dialysis fluid. Semi-permeable membranes in the machine selectively allow toxins to pass from the blood to the dialysis fluid.

During a dialysis procedure, a patient was connected to the machine for 4 hours. The blood was pumped through the artificial kidney at the rate of 1200 mL/min. The partially cleansed blood was returned to the patient's body, and the wastes removed were collected in the used dialysis fluid. During the procedure, the patient's kidneys were completely inactive. A total of 1540 g of urine was collected with an urea concentration of 1.3% by weight. A sample of the blood plasma was analyzed before the dialysis and found to contain 155.3 mg/dL of urea. The specific gravity of the plasma was measured at 1.0245. Calculate:

(a) The urea removal efficiency by the artificial kidney.

(b) The urea concentration in the plasma of the cleansed blood, in mg/dL.

Solution

(a) Write a material balance for urea on the artificial kidney.

Basis: 4 hours

Assuming that the rate of formation and decomposition of urea during the procedure is negligible, and that no urea is removed by the patient's kidneys:

urea in "clean" blood = urea in "dirty" blood – urea in urine

The mass of urea in the urine is simply 1540 × 0.013 = 20.0 g. Calculate the mass of urea in the "dirty" blood by the following procedure:

• Calculate the total volume of plasma that flows through the artificial kidney in 4 hours:

$$\frac{1200\ \text{mL of blood}}{\text{min}}\left|\frac{60\,\text{min}}{\text{h}}\right|\frac{0.55\,\text{mL of plasma}}{\text{mL of blood}}\left|\frac{1\ \text{dL}}{100\ \text{mL}}\right|\frac{4\ \text{h}}{} = 1584\ \text{dL}$$

• Calculate the urea in the "dirty" blood from the given plasma concentration:

$$\frac{155.3 \text{ mg of urea}}{\text{dL of plasma}}\left|\frac{1.0 \text{ g}}{1000 \text{ mg}}\right|\frac{1584 \text{ dL of plasma}}{} = 246 \text{ g of urea}$$

The urea removal efficiency is then (20/246) × 100 = 8.1%.

(b) Substituting in the material balance, the mass of urea in the clean blood is found to be 246 – 20 = 226 g. To calculate the corresponding concentration, the volume of plasma remaining after dialysis must be calculated. Assuming that no cells are removed by the machine during the procedure, the mass of plasma remaining is the difference between the mass of plasma entering the artificial kidney and the mass of urine removed. The mass of plasma entering is given by

$$\frac{1.0245 \text{ g of plasma}}{\text{mL of plasma}}\left|\frac{100 \text{ mL}}{1.0 \text{ dL}}\right|\frac{1584 \text{ dL of plasma}}{} = 162{,}280 \text{ g of plasma}$$

The mass of plasma remaining is 162,280 – 1540 = 160,740 g. The volume of plasma remaining is (160,740/(1.0245 × 100) = 1569 dL of plasma. Therefore, the urea concentration in the remaining plasma is (226 × 1000)/1569 = 144 mg/dL.

Notice that in the artificial kidney the removal efficiency of all the wastes must be kept relatively low because of the need to maintain homeostasis in the patient's body at all times. If too many wastes are removed at one time, death may occur.

1.2.2 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 multicomponent system, the various species will normally move at dif-

ferent 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

$$\mathbf{v} = \frac{\sum_{i=1}^{n} \rho_i \mathbf{v}_i}{\sum_{i=1}^{n} \rho_i} = \frac{\sum_{i=1}^{n} \rho_i \mathbf{v}_i}{\rho} = \sum_{i=1}^{n} \omega_i \mathbf{v}_i \tag{1-11}$$

where $\mathbf{v}_i$ denotes the absolute velocity of species i relative to stationary coordinate axis. The mass-average velocity is the velocity that would be measured by a pitot tube. On the other hand, the *molar-average velocity* for a multicomponent mixture is defined in terms of the molar concentrations of all components by

$$\mathbf{V} = \frac{\sum_{i=1}^{n} c_i \mathbf{v}_i}{\sum_{i=1}^{n} c_i} = \frac{\sum_{i=1}^{n} c_i \mathbf{v}_i}{c} = \sum_{i=1}^{n} x_i \mathbf{v}_i \tag{1-12}$$

Diffusion rates are most conveniently described in terms of 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

$$\mathbf{n}_i = \rho_i \mathbf{v}_i \tag{1-13}$$

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

$$\mathbf{n} = \rho \mathbf{v} \tag{1-14}$$

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

$$\mathbf{N}_i = c_i \mathbf{v}_i \tag{1-15}$$

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

$$\mathbf{N} = c\mathbf{V} \tag{1-16}$$

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

$$\mathbf{j}_i = \rho_i \left(\mathbf{v}_i - \mathbf{v} \right) \quad \text{and} \quad \sum_{i=1}^{n} \mathbf{j}_i = 0 \tag{1-17}$$

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

$$\mathbf{J}_i = c_i \left(\mathbf{v}_i - \mathbf{V} \right) \quad \text{and} \quad \sum_{i=1}^{n} \mathbf{J}_i = 0 \tag{1-18}$$

The mass flux $\mathbf{n}_i$ is related to the mass diffusion flux as

$$\mathbf{n}_i = \mathbf{j}_i + \rho_i \mathbf{v} = \mathbf{j}_i + \omega_i \mathbf{n} \tag{1-19}$$

The molar flux $\mathbf{N}_i$ is related to the molar diffusion flux as

$$\mathbf{N}_i = \mathbf{J}_i + c_i \mathbf{V} = \mathbf{J}_i + y_i \mathbf{N} \tag{1-20}$$

It is important to note that the molar flux, $\mathbf{N}_i$, described by equation (1-20) is a resultant of the two vector quantities:

$\mathbf{J}_i$ — the molar diffusion flux, $\mathbf{J}_i$, resulting from the concentration gradient; this term is referred to as the *concentration gradient contribution*;

and

$y_i \mathbf{N} = c_i \mathbf{V}$ — 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*.

Either or both quantities can be a significant part of the total molar flux, $\mathbf{N}_i$. Whenever equation (1-20) is applied to describe molar diffusion, the vector nature of the individual fluxes, $\mathbf{N}_i$, must be considered. The same applies for the mass fluxes in equation (1-19).

Example 1.4 Oxygen Transport in the Human Body

Oxygen is important for living organisms, since metabolic processes in the body involve oxygen. The transport of oxygen in the body is therefore crucial to life. The blood in the human circulatory system transports oxygen from the lungs to every single cell in the body. In the larger blood vessels, most of the oxygen transport is due to the bulk motion contribution, while the concentration gradient contribution is more important in smaller blood vessels and capillaries. In the larger vessels, blood flow is rapid and unimpeded, and the oxygen concentration in the fluid

remains relatively constant. On the other hand, in smaller vessels oxygen diffuses out of the veins into the surrounding tissue, resulting in decreasing concentrations in the blood.

When referring to the oxygen concentration in the blood, both oxygen bound to hemoglobin and aqueous oxygen dissolved in the plasma are included. Each molecule of hemoglobin, a protein in red blood cells, can bind four oxygen molecules. The vast majority of the blood oxygen is coupled to hemoglobin. In the larger blood vessels, any dissolved oxygen lost to the surrounding tissues by diffusion is replaced by oxygen dissociating from the hemoglobin into the plasma to maintain its constant concentration.

1.2.3 The Maxwell–Stefan Relations

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

1. Write down the Maxwell–Stefan (MS) equations for a binary system, and for multicomponent systems.
2. Define the concepts MS diffusivity, and thermodynamic factor.
3. Express the driving force for mass transfer in terms of mole fraction gradients for ideal and nonideal systems.

Consider a binary mixture of ideal gases 1 and 2 at constant temperature and pressure. From a momentum balance describing collisions between molecules of species 1 and molecules of species 2, we obtain (Taylor and Krishna, 1993)

$$\nabla p_1 = -f_{12} y_1 y_2 \left(\mathbf{v}_1 - \mathbf{v}_2 \right) \tag{1-21}$$

where f_{12} is an empirical parameter analogous to a friction factor or a drag coefficient. For convenience, we define an inverse drag coefficient $D_{12} = P/f_{12}$ and rewrite equation (1-21) as

$$\mathbf{d}_1 = \frac{\nabla p_1}{P} = -\frac{y_1 y_2 \left(\mathbf{v}_1 - \mathbf{v}_2 \right)}{D_{12}} \tag{1-22}$$

where $\mathbf{d}_1$ is the driving force for diffusion of species 1 in an ideal gas mixture at constant temperature and pressure.

Equation (1-22) is the MS equation for the diffusion of species 1 in a binary ideal gas mixture. The symbol D_{12} is the MS diffusivity. From a similar analysis for species 2,

$$\mathbf{d}_2 = \frac{\nabla p_2}{P} = -\frac{y_1 y_2 \left(\mathbf{v}_2 - \mathbf{v}_1\right)}{D_{21}} \tag{1-23}$$

For all the applications considered in this book the system pressure is constant across the diffusion path. Then, equations (1-22) and (1-23) simplify to

$$\begin{aligned} \frac{\nabla y_1}{P} &= -\frac{y_1 y_2 \left(\mathbf{v}_1 - \mathbf{v}_2\right)}{D_{12}} \\ \frac{\nabla y_2}{P} &= -\frac{y_1 y_2 \left(\mathbf{v}_2 - \mathbf{v}_1\right)}{D_{21}} \end{aligned} \tag{1-24}$$

Example 1.5 Diffusivities in Binary Mixtures

Show that, for a binary mixture, $D_{12} = D_{21}$.

Solution

Since for a binary mixture $(y_1 + y_2) = 1.0$,

$$\nabla y_1 = -\nabla y_2$$

Then, from equation (1-24)

$$-\frac{y_1 y_2 \left(\mathbf{v}_1 - \mathbf{v}_2\right)}{D_{12}} = \frac{y_1 y_2 \left(\mathbf{v}_2 - \mathbf{v}_1\right)}{D_{21}}$$

which can be true only if $D_{12} = D_{21}$.

For multicomponent mixtures, equation (1-22) can be generalized to (Taylor and Krishna, 1993)

$$\mathbf{d}_i = -\sum_{j=1}^{n} \frac{y_i y_j \left(\mathbf{v}_i - \mathbf{v}_j\right)}{D_{ij}} \qquad i = 1, 2, \ldots, n-1 \tag{1-25}$$

Equations (1-25) can be written in terms of the molar fluxes $\mathbf{N}_i = c_i \mathbf{v}_i$ to get

$$\mathbf{d}_i = -\sum_{j=1}^{n} \frac{y_i \mathbf{N}_j - y_j \mathbf{N}_i}{cD_{ij}} \qquad i = 1,2,\ldots,n-1 \tag{1-26}$$

or, in terms of the diffusion fluxes, $\mathbf{J}_i$

$$\mathbf{d}_i = -\sum_{j=1}^{n} \frac{y_i \mathbf{J}_j - y_j \mathbf{J}_i}{cD_{ij}} \qquad i = 1,2,\ldots,n-1 \tag{1-27}$$

These are the MS diffusion equations for multicomponent systems. They are named after the Scottish physicist James Clerk Maxwell and the Austrian scientist Josef Stefan who were primarily responsible for their development around 1870. It is important to point out that only $(n - 1)$ of the MS equations are independent because the $\mathbf{d}_i$ must sum to zero. Also, for a multicomponent ideal gas mixture, a more elaborate analysis than that of Example 1.5 is needed to show that (Taylor and Krishna, 1993)

$$D_{ij} = D_{ji} \tag{1-28}$$

It is easy to show, for a binary mixture of ideal gases where the driving force for diffusion is the mol fraction gradient, equation (1-27) reduces to

$$\mathbf{J}_1 = -cD_{12}\mathbf{d}_1 = -cD_{12}\nabla y_1 \tag{1-29}$$

For nonideal fluids the driving force for diffusion must be defined in terms of chemical potential gradients as

$$\mathbf{d}_i = \frac{x_i}{RT}\nabla_{T,P}\boldsymbol{\mu}_i \tag{1-30}$$

The subscripts *T,P* are to emphasize that the gradient is to be calculated under constant temperature and pressure conditions. We may express equation (1-30) in terms of activity coefficients, γ_i, and mol fraction gradients as

$$\mathbf{d}_i = \sum_{j=1}^{n-1} \boldsymbol{\Gamma}_{ij} \nabla x_j = \boldsymbol{\Gamma} \nabla x_i \tag{1-31}$$

where the *thermodynamic factor matrix* Γ is given by

$$\boldsymbol{\Gamma}_{ij} = \delta_{ij} + \left.\frac{\partial \ln \gamma_i}{\partial x_j}\right|_{T,P,\Sigma} \tag{1-32}$$

where δ_{ij} is the *Kronecker delta* defined as

$$\delta_{ij} = \begin{cases} 1 \text{ if } i = j \\ 0 \text{ if } i \neq j \end{cases} \tag{1-33}$$

The symbol Σ is used in equation (1-32) to indicate that the differentiation with respect to mol fraction is to be carried out in such a manner that the mol fractions always add up to 1.0. Combining equations (1-26), (1-27), and (1-31) we obtain

$$\Gamma \nabla x_i = \sum_{j=1}^{n} \frac{x_i \mathbf{J}_j - x_j \mathbf{J}_i}{cD_{ij}} = \sum_{j=1}^{n} \frac{x_i \mathbf{N}_j - x_j \mathbf{N}_i}{cD_{ij}} \qquad i = 1, 2, \ldots, n-1 \tag{1-34}$$

For a multicomponent mixture of ideal gases, equation (1-34) becomes

$$\nabla y_i = \sum_{j=1}^{n} \frac{y_i \mathbf{J}_j - y_j \mathbf{J}_i}{cD_{ij}} = \sum_{j=1}^{n} \frac{y_i \mathbf{N}_j - y_j \mathbf{N}_i}{cD_{ij}} \qquad i = 1, 2, \ldots, n-1 \tag{1-35}$$

For a binary mixture, equation (1-34) reduces to

$$\mathbf{J}_1 = -cD_{12} \Gamma \nabla x_1 \tag{1-36}$$

where the *thermodynamic factor* Γ is given by

$$\Gamma = 1 + x_1 \frac{\partial \ln \gamma_1}{\partial x_1} \tag{1-37}$$

The thermodynamic factor is evaluated for liquid mixtures from activity coefficient models. For a *regular solution*, for example,

$$\ln \gamma_1 = A\left(1 - x_1\right)^2 \tag{1-38}$$

therefore, equation (1-37) yields

$$\Gamma = 1 - 2A x_1 x_2 \tag{1-39}$$

1.2.4 Fick's First Law for Binary Mixtures

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

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

At about the same time that Maxwell and Stefan were developing their ideas of diffusion in multicomponent mixtures, Adolf Fick and others were attempting to uncover the basic diffusion equations through experimental studies involving binary mixtures (Fick, 1855). The result of Fick's work was the "law" that bears his name. The Fick equation for a binary mixture in an isothermal, isobaric system is

$$\mathbf{J}_1 = -c\mathrm{D}_{12}\nabla x_1 \tag{1-40}$$

where D_{12} is the *Fick diffusivity or diffusion coefficient*. Comparing equations (1-36) and (1-40) we see that, for a binary system, the Fick diffusivity D and the MS diffusivity D are related by

$$\mathrm{D}_{12} = D_{12}\Gamma \tag{1-41}$$

For ideal systems, Γ is unity and the diffusivities are identical.

$$\mathrm{D}_{12} = D_{12} \quad \text{for ideal systems} \tag{1-42}$$

The correlation and prediction of Fick and MS diffusion coefficients are discussed in the section that follows. The Fick diffusivity incorporates two aspects: (1) the significance of an inverse drag coefficient (D), and (2) thermodynamic nonideality (Γ). Consequently, the physical interpretation of the Fick diffusion coefficient is less transparent than for the MS diffusivity.

1.3 THE DIFFUSION COEFFICIENT

Fick's law proportionality factor, D_{12}, is known as the diffusion coefficient or diffusivity. Its fundamental dimensions, which are obtained from equation (1-40),

$$\mathrm{D}_{12} = -\frac{\mathbf{J}_1}{c\nabla x_1} = \left(\frac{\mathrm{M}}{\mathrm{L}^2\mathrm{t}}\right)\left(\frac{1}{\mathrm{M}/\mathrm{L}^3 \times 1/\mathrm{L}}\right) = \frac{\mathrm{L}^2}{\mathrm{t}}$$

are identical to the fundamental dimensions of the other transport properties: kinematic viscosity, ν, and thermal diffusivity, α. The mass diffusivity is usually reported in units of cm^2/s; the SI units are m^2/s, which is a factor 10^{-4} smaller.

The diffusion coefficient depends upon the pressure, temperature, and composition of the system. Experimental values for the diffusivities of gases, liquids, and solids are tabulated in Appendix A. As one might expect from consideration of the mobility of the molecules, the diffusivities are generally higher for gases (in the range of 0.5×10^{-5} to 1.0×10^{-5} m^2/s) than for liquids (in the range of 10^{-10} to 10^{-9} m^2/s) which are higher than the values reported for solids (in the range of 10^{-14} to 10^{-10} m^2/s). In the absence of experimental data, semitheoretical expressions have been developed which give approximations, sometimes as valid as experimental values due to the difficulties encountered in their measurement.

1.3.1 Diffusion Coefficients for Binary Ideal Gas Systems

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

1. Estimate diffusion coefficients for binary gas systems using the Wilke–Lee equation with tabulated values of the Lennard–Jones parameters.
2. Estimate diffusion coefficients for binary gas systems using the Wilke–Lee equation with values of the Lennard–Jones parameters estimated from empirical correlations.
3. Use a Mathcad® routine to implement calculation of diffusion coefficients for binary gas systems using the Wilke–Lee equation.

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 the following equation to estimate the diffusion coefficient for gas pairs of nonpolar, nonreacting molecules:

$$D_{AB} = \frac{0.00266T^{1.5}}{PM_{AB}^{0.5}\sigma_{AB}^{2}\Omega_{D}} \tag{1-43}$$

where

$$M_{AB} = \frac{2M_A M_B}{M_A + M_B}$$

D_{AB} = diffusion coefficient, cm^2/s
M_A, M_B = molecular weights of A and B
T = temperature, K
P = pressure, bar
σ_{AB} = "collision diameter," a Lennard–Jones parameter, Å
Ω_D = diffusion collision integral, dimensionless

The collision integral, Ω_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 $T^* = \kappa T/\varepsilon AB$, where κ is the Boltzmann constant (1.38×10^{-16} erg/K) and ε_{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 Ω_D can be obtained from (Neufield et al., 1972)

(1-44)

where $T^* = kT/\varepsilon_{AB}$, $a = 1.06036$ $b = 0.15610$
$c = 0.19300$ $d = 0.47635$ $e1 = 1.03587$
$f = 1.52996$ $g = 1.76474$ $h = 3.89411$

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:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \qquad \varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B} \tag{1-45}$$

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. Appendix B tabulates some of the data available. In the absence of experimental data, the values of the parameters for pure components may be estimated from the following empirical correlations:

$$\sigma = 1.18V_b^{1/3} \tag{1-46}$$

$$\varepsilon / \kappa = 1.15T_b \tag{1-47}$$

where V_b is the molar volume of the substance as liquid at its normal boiling point, in cm^3/gmol, and T_b is the normal boiling point temperature. Molar volumes at normal boiling point for some commonly encountered compounds are listed in Table 1.1. For other compounds not listed in Table 1.1, if a reliable value of the critical volume (V_c) is available, the Tyn and Calus (1975) method is recommended:

$$V_b = 0.285V_c^{1.048} \tag{1-48}$$

Otherwise, the atomic volume of each element present are added together as per the molecular formula of the compound. Table 1.2 lists the contributions for each of the constituent atoms.

Several proposed methods for estimating D_{AB} in low-pressure binary gas systems retain the general form of equation (1-43), with empirical constants based on experimental data. One of the most widely used methods, shown to be quite general and reliable, was proposed by Wilke and Lee (1955):

$$D_{AB} = \frac{\left[3.03 - \left(\frac{0.98}{M_{AB}^{0.5}}\right)\right]\left(10^{-3}\right)T^{1.5}}{PM_{AB}^{0.5}\sigma_{AB}^2\Omega_D} \tag{1-49}$$

where all the symbols are as defined under equation (1-43). The use of the Wilke–Lee equation is illustrated in the following examples.

Table 1.1 Molar Volumes at Normal Boiling Point

Compound	Volume (cm^3/gmol)	Compound	Volume (cm^3/gmol)
Hydrogen, H_2	14.3	Nitric oxide, NO	23.6
Oxygen, O_2	25.6	Nitrous oxide, N_2O	36.4
Nitrogen, N_2	31.2	Ammonia, NH_3	25.8
Air	29.9	Water, H_2O	18.9
Carbon monoxide, CO	30.7	Hydrogen sulfide, H_2S	32.9
Carbon dioxide, CO_2	34.0	Bromine, Br_2	53.2
Carbonyl sulfide, COS	51.5	Chlorine, Cl_2	48.4
Sulfur dioxide, SO_2	44.8	Iodine, I_2	71.5

Source: Data from Welty et al. (1984).

Table 1.2 Atomic Volume Contributions of the Elements

Element	Volume (cm^3/gmol)	Element	Volume (cm^3/gmol)
Bromine	27.0	Oxygen, except as	
Carbon	14.8	noted below	7.4
Chlorine	24.6	Oxygen, in methyl	
Hydrogen	3.7	esters	9.1
Iodine	37.0	Oxygen, in methyl	
Nitrogen	15.6	ethers	9.9
Nitrogen, in		Oxygen, in higher	
primary amines	10.5	ethers and other esters	11.0
Nitrogen, in		Oxygen, in acids	12.0
secondary amines	12.0	Sulfur	25.6

For three-membered ring, such as ethylene oxide, subtract	6.0
For four-membered ring, such as cyclobutane, subtract	8.5
For five-membered ring, such as furan, subtract	11.5
For pyridine, subtract	15.0
For benzene ring, subtract	15.0
For naphthalene ring, subtract	30.0
For anthracene ring, subtract	47.5

Source: Data from Welty et al. (1984).

Example 1.6 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 (1-49). Compare this estimate with the experimental value reported in Appendix A.

Solution

Values of the Lennard–Jones parameters (σ and ε/κ) are obtained from Appendix B:

	σ, in Å	ε/κ, in K	M, g/mol
CS_2	4.483	467	76
Air	3.620	97	29

Evaluate the various parameters of equation (1-49) as follows:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} = 4.052 \text{ Å}$$

$$\frac{\varepsilon_{AB}}{\kappa} = \sqrt{\frac{\varepsilon_A}{\kappa} \times \frac{\varepsilon_B}{\kappa}} = \sqrt{467 \times 97} = 212.8 \text{ K}$$

$$\frac{\kappa T}{\varepsilon_{AB}} = \frac{273.0}{212.8} = 1.283 \qquad \Omega_D = 1.282 \quad \left[\text{from equation (1-44)}\right]$$

$$M_{AB} = 2\left[\frac{M_A M_B}{M_A + M_B}\right] = \frac{2 \times 76 \times 29}{76 + 29} = 41.981$$

Substituting these values into the Wilke-Lee equation yields

$$D_{AB} = \frac{0.001\left(3.03 - \dfrac{0.98}{\sqrt{41.981}}\right)(273)^{1.5}}{(1.0)(4.052)^2(1.282)\sqrt{41.981}} = 0.0952 \ \frac{\text{cm}^2}{\text{s}}$$

$$D_{AB} = 9.52 \times 10^{-6} \ \frac{\text{m}^2}{\text{s}}$$

As evidenced by this example, estimation of binary diffusivities can be quite tedious. Most mass-transfer problems involve the calculation of one or more values of diffusivities. Convenience therefore suggests the use of a computer software package for technical calculations, such as Mathcad, for that purpose. Figure 1.3 shows a Mathcad routine to estimate the gas phase binary diffusivity using the Wilke-Lee equation and the conditions for this example. For any other set of conditions, only the two lines of the program following the "Enter Data" expression must be modified accordingly. The experimental value for this example is obtained from Appendix A:

$$D_{AB}P = 0.894 \ \frac{m^2 \times Pa}{s}$$

$$D_{AB} = 0.894 \ \frac{m^2 \times Pa \times 1bar}{s \times 1bar \times 10^5 Pa}$$

$$D_{AB} = 8.94 \times 10^{-6} \ \frac{m^2}{s}$$

The error of the estimate, compared to the experimental value, is 6.5%.

Example 1.7 Calculation of Diffusivity by the Wilke–Lee Equation with Estimated Values of the Lennard–Jones Parameters

Estimate the diffusivity of allyl chloride (C_3H_5Cl) in air at 298 K and 1 bar using the Wilke-Lee equation (1-49). The experimental value reported by Lugg (1968) is 0.098 cm^2/s.

Solution

Values of the Lennard-Jones parameters for allyl chloride (A) are not available in Appendix B. Therefore, they must be estimated from equations (1-46) and (1-47). From Table 1.2,

$$V_b = (3)(14.8) + (5)(3.7) + 24.6 = 87.5 \text{ cm}^3/\text{mol}$$

An alternate method to estimate V_b for allyl chloride is using equation (1-48) with a value of V_c = 234 cm^3/mol (Reid et al., 1987).

$$V_b = (0.285)(234)1.048 = 86.7 \text{ cm}^3/\text{mol}$$

The two estimates are virtually identical. From equation (1-46), σ_A = 5.24 Å. The normal boiling point temperature for allyl chloride is T_b = 318.3 K (Reid et al., 1987). From equation (1-47), ε_A/κ = 366 K. The molecular weight of allyl chloride is 76.5 g/mol. The corresponding values for air are σ_B = 3.62 Å, ε_B/κ = 97 K, and M_B = 29 g/mol. Substituting these values into the Mathcad routine of Figure 1.3 yields

$$D_{AB} = 0.0992 \text{ cm}^2/\text{s}$$

The error of this estimate, compared to the experimental value, is 1.2%.

It must be emphasized that, for low-pressure binary gas systems, the diffusivity does not depend on the composition of the mixture. Either component can be chosen as component A or component B. As the next section will show, the estimation of diffusivities in liquid mixtures is much more complex.

In the Wilke-Lee equation, T is temperature in K, P is absolute pressure in bar, M is molecular weight in g/mol, the Lennard-Jones parameters are from Appendix B with the units specified there. The data presented here are from Example 1.6.

Enter Data: $T := 273$ $P := 1.0$ $M_A := 76$ $M_B := 29$

$\sigma_A := 4.483$ $\sigma_B := 3.620$ $\varepsilon_{Ak} := 467$ $\varepsilon_{Bk} := 97$

$$\sigma_{AB} := \frac{(\sigma_A + \sigma_B)}{2} = 4.052$$

$$\varepsilon_{ABk} := \sqrt{\varepsilon_{Ak} \cdot \varepsilon_{Bk}} = 212.836 \qquad x := \frac{T}{\varepsilon_{ABk}} = 1.283$$

$a := 1.06026$ $b := 0.15610$ $c := 0.19300$
$d := 0.47635$ $e1 := 1.03587$ $f := 1.52996$
$g := 1.76474$ $h := 3.89411$

$$M_{AB} := 2 \cdot \left\{ \frac{1}{M_A} + \frac{1}{M_B} \right\}^{-1} = 41.981$$

$$\Omega := \frac{a}{x^b} + \frac{c}{e^{d \cdot x}} + \frac{e1}{e^{f \cdot x}} + \frac{g}{e^{h \cdot x}} = 1.282$$

$$D_{AB} := \frac{0.001 \cdot \left(3.03 - \frac{0.98}{\sqrt{M_{AB}}} \right) \cdot T^{1.5}}{P \cdot {\sigma_{AB}}^2 \cdot \Omega \cdot \sqrt{M_{AB}}} \cdot \frac{\text{cm}^2}{\text{s}} = 0.0952 \ \frac{\text{cm}^2}{\text{s}}$$

Figure 1.3 Mathcad routine to estimate gas-phase mass diffusivities using the Wilke-Lee equation.

1.3.2 Diffusion Coefficients for Dilute Liquids

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 correlations.
3. Use a Mathcad routine to implement calculation of diffusion coefficients for binary dilute liquid systems using the Hayduk and Minhas equation.

In contrast to the case for gases, where an advanced kinetic theory to explain molecular motion is available, theories of the structure of liquids and their transport characteristics are still inadequate to allow a rigorous treatment. 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 mol fraction of either component in a binary mixture approaches unity, the thermodynamic factor Γ 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^0.

The Stokes–Einstein equation is a theoretical method of estimating D^0,

$$D^0_{AB} = \frac{\kappa T}{6\pi r_A \mu_B} \tag{1-50}$$

where r_A is the solute particle radius, and μ_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 (1-50) has provided a useful starting point for a number of semiempirical correlations arranged into the general form

$$\frac{D^0_{AB}\mu_B}{\kappa T} = f\left(V_{bA}\right) \tag{1-51}$$

in which $f(V_{bA})$ is a function of the molecular volume of the diffusing solute. Empirical correlations using the general form of equation (1-51) 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 nonelectrolytes in an infinitely dilute solution:

$$\frac{D_{AB}^{0}\mu_B}{T} = \frac{7.4\times10^{-8}\left(\Phi_B M_B\right)^{0.5}}{V_{bA}^{0.6}} \tag{1-52}$$

where

D_{AB}^{0} = diffusivity of A in very dilute solution in solvent B, cm^2/s
M_B = molecular weight of solvent B
T = temperature, K
μB = viscosity of solvent B, cP
V_{bA} = solute molar volume at its normal boiling point, cm^3/mol
= 75.6 cm^3/mol for water as solute
Φ_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 (1-48), or from the data of Table 1.2, 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*:

$$D_{AB}^{0} = 1.25\times10^{-8}\left(V_{bA}^{-0.19} - 0.292\right)T^{1.52}\mu_B^{\varepsilon}$$
$$\varepsilon = \frac{9.58}{V_{bA}} - 1.12 \tag{1-53}$$

where

D_{AB}^{0} = diffusivity of A in very dilute aqueous solution , cm^2/s
T = temperature, K
μ_B = viscosity of water, cP
V_{bA} = solute molar volume at its normal boiling point, cm3/mol

(b) For *nonaqueous (nonelectrolyte) solutions*:

$$D_{AB}^{0} = 1.55\times10^{-8}\frac{V_{bB}^{0.27}T^{1.29}\sigma_B^{1.25}}{V_{bA}^{0.42}\mu_B^{0.92}\sigma_A^{0.105}} \tag{1-54}$$

where σ is surface tension at the normal boiling point temperature, in dyn/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):

$$\sigma\left(T_b\right) = P_c^{2/3} T_c^{1/3} \left(0.132\alpha_c - 0.278\right)\left(1 - T_{br}\right) \tag{1-55}$$

$$T_{br} = \frac{T_b}{T_c}$$

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

where

$\sigma(T_b)$ = surface tension at the normal boiling point temperature, dyn/cm
P_c = critical pressure, bar
T_c = critical temperature, K

When using the correlation shown in equation (1-54), the authors note several restrictions:

1. The method should not be used for diffusion in viscous solvents. Values of μ_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 cm^3/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 μ_B is the solvent viscosity in cP.

Example 1.8 Calculation of Liquid Diffusivity in Aqueous Solution

Estimate the diffusivity of ethanol (C_2H_6O) in a dilute solution in water at 288 K. Compare your estimate with the experimental value reported in Appendix A.

Solution

(a) Use the Wilke–Chang correlation, equation (1-52). Calculate the molar volume of ethanol using equation (1-48) with V_c = 167.1 cm^3/mol (Reid et al., 1987):

$$V_{bA} = 0.285\left(167.1\right)^{1.048} = 60.9 \ \frac{\text{cm}^3}{\text{mol}}$$

The viscosity of liquid water at 288 K is μ_B = 1.153 cP (Reid et al., 1987). Substituting in equation (1-52) gives

$$D_{AB}^{0} = \frac{\left(7.4\times10^{-8}\right)\left(288\right)\left[\left(2.26\right)\left(18\right)\right]^{1/2}}{\left(1.153\right)\left(60.9\right)^{0.6}} = 1.002\times10^{-5}\ \frac{\text{cm}^2}{\text{s}}$$

The experimental value reported in Appendix A is 1.0×10^{-5} cm^2/s. Therefore, the error of the estimate is only 0.2%. (This is not typical!)

(b) Using the Hayduk and Minhas correlation for aqueous solutions:

$$\varepsilon = \frac{9.58}{60.9} - 1.12 = -0.963$$

$$D_{AB}^{0} = 1.25\times10^{-8}\left[60.9^{-0.19} - 0.292\right]\left(288\right)^{1.52}\left(1.153\right)^{-0.693}$$

$$= 0.991\times10^{-5}\ \frac{\text{cm}^2}{\text{s}}$$

The error of the estimate in this case is –0.9%.

Example 1.9 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 Appendix A. 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, bars	57.9	47.0
V_c, cm^3/mol	171	209
μ, cP	---	0.264
M	60	58

Solution

(a) Use the Wilke–Chang correlation, equation (1-52). Calculate the molar volume of acetic acid using equation (1-48) with V_c = 171 cm^3/mol: V_{bA} = 62.4 cm^3/mol. The association factor for acetone is Φ = 1.0. From equation (1-52),

$$D_{AB}^{0} = \frac{\left(7.4\times10^{-8}\right)\left(313\right)\left[\left(1\right)\left(58\right)\right]^{1/2}}{\left(0.264\right)\left(62.4\right)^{0.6}} = 5.595\times10^{-5}\ \frac{\text{cm}^2}{\text{s}}$$

From Appendix A, the experimental value is 4.04×10^{-5} cm^2/s. Therefore, the error of the estimate is 38.5%.

(b) Use the Hayduk and Minhas correlation for nonaqueous solutions. According to restriction 3 mentioned above, the molar volume of the acetic acid to be used in equation (1-54) should be $V_{bA} = 2 \times 62.4 = 124.8$ cm^3/mol. The molar volume of acetone is calculated from equation (1-48): $V_{bB} = 77.0$ cm^3/mol. Estimates of the surface tension at the normal boiling point of each component are calculated from equation (1-55) as follows:

For acetone (B):

$$T_{br} = \frac{329.2}{508} = 0.648$$
$$\alpha_c = 7.319$$
$$\sigma_B = 20.0 \text{ dyn/cm}$$

For acetic acid (A):

$$T_{br} = \frac{390.4}{594.8} = 0.656$$
$$\alpha_c = 7.910$$
$$\sigma_B = 26.2 \text{ dyn/cm}$$

Substituting numerical values in equation (1-54):

$$D^0_{AB} = 1.55 \times 10^{-8} \frac{(77)^{0.27}(313)^{1.29}(20)^{0.125}}{(124.8)^{0.42}(0.264)^{0.92}(26.2)^{0.105}}$$
$$D^0_{AB} = 3.84 \times 10^{-5} \frac{\text{cm}^2}{\text{s}}$$

From Appendix A, the experimental value is 4.04×10^{-5} cm^2/s. Therefore, the error of the estimate is –5.0%.

Figure 1.4 shows a Mathcad routine to estimate liquid-phase binary diffusivities for nonaqueous solutions using the Hayduk and Minhas equation and the conditions for this example. For any other set of conditions, only the four lines of the program following the "Enter Data" expression must be modified accordingly.

In this equation, temperatures are in K, pressures in bar, molar volumes in cc/mol, and viscosity of the solvent in cP.

Enter Data:

$T_{bA} := 390.4$ $T_{cA} := 594.8$ $T := 313$

$P_{cA} := 57.9$ $V_{bA} := 124.8$ $\mu_B := 0.264$

$T_{bB} := 329.2$ $T_{cB} := 508.0$

$P_{cB} := 47.0$ $V_{bB} := 77.0$

$$T_{brA} := \frac{T_{bA}}{T_{cA}} = 0.656 \qquad T_{brB} := \frac{T_{bB}}{T_{cB}} = 0.648$$

$$\alpha_{cA} := 0.9076 \cdot \left[1 + \frac{T_{brA} \cdot \ln\left(\frac{P_{cA}}{1.013}\right)}{1 - T_{brA}}\right] = 7.921$$

$$\alpha_{cB} := 0.9076 \cdot \left[1 + \frac{T_{brB} \cdot \ln\left(\frac{P_{cB}}{1.013}\right)}{1 - T_{brB}}\right] = 7.32$$

$$\sigma_A := P_{cA}^{\frac{2}{3}} \cdot T_{cA}^{\frac{1}{3}} \cdot \left[0.132 \cdot \alpha_{cA} - 0.278\right] \cdot \left[1 - T_{brA}\right]^{\frac{11}{9}} = 26.185$$

$$\sigma_B := P_{cB}^{\frac{2}{3}} \cdot T_{cB}^{\frac{1}{3}} \cdot \left[0.132 \cdot \alpha_{cB} - 0.278\right] \cdot \left[1 - T_{brB}\right]^{\frac{11}{9}} = 19.959$$

$$D_{L0} := \frac{1.55 \cdot 10^{-8} \cdot V_{bB}^{0.27} \cdot T^{1.29} \cdot \sigma_B^{0.125}}{V_{bA}^{0.42} \cdot \mu_B^{0.92} \cdot \sigma_A^{0.105}} \cdot \frac{\text{cm}^2}{\text{s}} = \left(3.839 \cdot 10^{-5}\right) \frac{\text{cm}^2}{\text{s}}$$

Figure 1.4 Mathcad routine to estimate liquid-phase mass diffusivities in dilute nonaqueous solutions using the Hayduk and Minhas equation.

1.3.3 Diffusion Coefficients for Concentrated Liquids

Most methods for predicting D in concentrated liquid solutions attempt to combine the infinite dilution diffusion coefficients $(D_{12})^0$ and $(D_{21})^0$ in a single function of composition. The Vignes formula is recommended by Reid et al. (1987):

$$D_{12} = \left(D_{12}^0\right)^{x_2} \left(D_{21}^0\right)^{x_1} \qquad \text{(1-56)}$$
$$\mathrm{D}_{12} = D_{12}\Gamma$$

Example 1.10 Diffusion Coefficients for 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:

$$D_{12}^0 = 2.75 \times 10^{-9} \ \frac{\mathrm{m}^2}{\mathrm{s}}$$
$$D_{21}^0 = 4.15 \times 10^{-9} \ \frac{\mathrm{m}^2}{\mathrm{s}}$$

From the non–random–two–liquid (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 3.35×10^{-9} m^2/s.

Solution

Substituting in equation (1-56):

$$D_{12} = \left(2.75 \times 10^{-9}\right)^{0.2192} \times \left(4.155 \times 10^{-9}\right)^{0.7808}$$
$$D_{12} = 3.792 \times 10^{-9} \ \frac{\mathrm{m}^2}{\mathrm{s}}$$
$$\mathrm{D}_{12} = 3.792 \times 10^{-9} \times 0.871$$
$$\mathrm{D}_{12} = 3.30 \times 10^{-9} \ \frac{\mathrm{m}^2}{\mathrm{s}}$$

The predicted value of the Fick diffusivity is in excellent agreement with the experimental result.

1.3.4 Effective Diffusivities in Multicomponent Mixtures

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

1. Estimate the effective diffusivity of a component in a multicomponent mixture of gases from its binary diffusion coefficients with each of the other constituents of the mixture.
2. Estimate the effective diffusivity of a dilute solute in a homogeneous solution of mixed solvents from its infinite dilution binary diffusion coefficients into each of the individual solvents.

The MS equations for diffusion in multicomponent systems can become very complicated, and they are sometimes handled by using an *effective diffusivity or pseudobinary approach*. The effective diffusivity is defined by assuming that the rate of diffusion of component i depends only on its own composition gradient; that is,

$$\mathbf{J}_i = -c\mathrm{D}_{i,eff}\nabla x_i \qquad i = 1, 2, \ldots, n \tag{1-57}$$

where $\mathrm{D}_{i,eff}$ is some characteristic diffusion coefficient of species i in the mixture which must be synthesized from the binary MS diffusivities.

In gases, the binary MS diffusivities are normally assumed independent of composition. With this approximation, the effective diffusivity of component i in a multicomponent gas mixture can be derived from the MS equation to give (Treybal, 1980)

$$\mathrm{D}_{i,eff} = \frac{\mathbf{N}_i - y_i \sum_{j=1}^{n} \mathbf{N}_j}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{1}{D_{ij}} \left(y_j \mathbf{N}_i - y_i \mathbf{N}_j \right)} \tag{1-58}$$

In order to use this equation, the relation between the values of the **N**'s must be known. This relation, called a *bootstrap condition* (Taylor and Krishna, 1993), is usually fixed by other considerations, such as reaction stoichiometry or energy balances. Consider, for instance, the general chemical reaction, written as

$$\sum_i \nu_i A_i = 0$$

where the ν_i are called stoichiometric numbers and A_i stands for a chemical formula. The sign convention for ν_i is positive (+) for products and negative (–) for reactants (Smith et al., 1996). For diffusion with heterogeneous chemical reaction, the relations between the fluxes are specified by the stoichiometry of the reaction as described by the following equations:

$$\frac{\mathbf{N}_1}{\nu_1} = \frac{\mathbf{N}_2}{\nu_2} = \frac{\mathbf{N}_3}{\nu_3} = \cdots = \frac{\mathbf{N}_i}{\nu_i} \tag{1-59}$$

For example, if ammonia is being cracked on a solid catalyst according to

$$NH_3 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2$$

under circumstances such that NH_3 (1) diffuses to the catalyst surface, and N_2 (2) and H_2 (3) diffuse back, applying equation (1-59) gives

$$N_2 = -\tfrac{1}{2}N_1$$
$$N_3 = -\tfrac{3}{2}N_1$$

Equation (1-58) suggests that the effective diffusivity may vary considerably along the diffusion path, but a linear variation with distance can usually be assumed (Bird et al., 1960). Therefore, if $D_{i,eff}$ changes significantly from one end of the diffusion path to the other, the arithmetic average of the two values should be used.

A common situation in multicomponent diffusion is when all the **N**'s except $\mathbf{N}_1$ are zero (i.e., all but component 1 is stagnant). Equation (1-58) then becomes

$$D_{1,eff} = \frac{1 - y_1}{\sum_{i=2}^{n} \frac{y_i}{D_{1,i}}} = \frac{1}{\sum_{i=2}^{n} \frac{y_i'}{D_{1,i}}} \tag{1-60}$$

where y_i' is the mole fraction of component i on a component 1-free base, that is

$$y_i' = \frac{y_i}{1 - y_i} \qquad i = 2,3,\ldots,n \tag{1-61}$$

Example 1.11 Calculation of Effective Diffusivity in a Multicomponent Gas Mixture

Ammonia is being cracked on a solid catalyst according to the reaction

$$NH_3 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2$$

At one place in the apparatus where the pressure is 1 bar and the temperature 300 K, the analysis of the gas is 40% NH_3 (1), 20% N_2 (2), and 40% H_2 (3) by volume. Estimate the effective diffusivity of ammonia in the gaseous mixture.

Solution

Calculate the binary diffusivities of ammonia in nitrogen (D_{12}) and ammonia in hydrogen (D_{13}) using the Mathcad routine developed in Example 1.6 to implement the Wilke-Lee equation. Values of the Lennard-Jones parameters (σ and ε/κ) are obtained from Appendix B. The data needed are:

	σ, in Å	ε/κ, in K	M, g/mol
NH_3	2.900	558.3	17
N_2	3.798	71.4	28
H_2	2.827	59.7	2

Therefore, the following results were obtained:

$D_{12} = 0.237$ cm^2/s
$D_{13} = 0.728$ cm^2/s

Figure 1.5 shows the flux of ammonia (1) toward the catalyst surface where it is consumed by chemical reaction, and the fluxes of nitrogen (2) and hydrogen (3) produced by the reaction migrating away from the same surface.

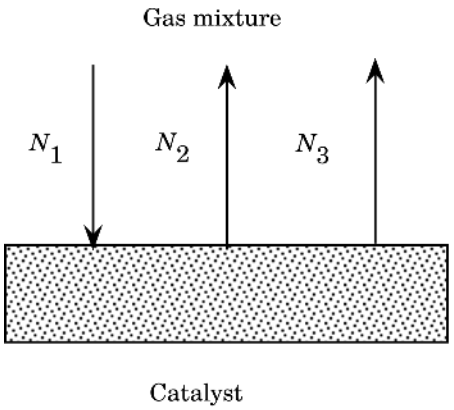


Figure 1.5 Catalytic cracking of ammonia (1) into N_2 (2) and H_2 (3).

As was shown before, the stoichiometry of the reaction fixes the relationship between the individual fluxes, which, in this particular case, becomes $N_2 = -(1/2)N_1$, $N_3 = -(3/2)N_1$; $N_1 + N_2 + N_3 = -N_1$. Substituting in equation (1-58), we obtain

$$D_{1,eff} = \frac{N_1\left(1+y_1\right)}{\frac{y_2 N_1 + \frac{1}{2}y_1 N_1}{D_{12}} + \frac{y_3 N_1 + \frac{3}{2}y_1 N_1}{D_{13}}}$$

$$= \frac{\left(1+y_1\right)}{\frac{y_2 + \frac{1}{2}y_1}{D_{12}} + \frac{y_3 + \frac{3}{2}y_1}{D_{13}}}$$

$$= \frac{1.4}{\frac{0.2+0.5\times 0.4}{0.237} + \frac{0.4+1.5\times 0.4}{0.728}}$$

$$= 0.457 \ \frac{\text{cm}^2}{\text{s}}$$

Example 1.12 Calculation of Effective Diffusivity in a Multicomponent Stagnant Gas Mixture

Ammonia is being absorbed from a stagnant mixture of nitrogen and hydrogen by contact with a 2 *N* sulfuric acid solution. At one place in the apparatus where the pressure is 1 bar and the temperature 300 K, the analysis of the gas is 40% NH_3 (1), 20% N_2 (2), and 40% H_2 (3) by volume. Estimate the effective diffusivity of ammonia in the gaseous mixture.

Solution

The binary diffusivities are the same as for the previous example. However, in this case, only the ammonia diffuses toward the liquid interphase since neither nitrogen nor hydrogen is soluble in the sulfuric acid solution. Therefore, (1-60) applies. Calculate the mole fractions of nitrogen (2) and hydrogen (3) on an ammonia (1)-free base from equation (1-61):

$$y_2' = \frac{y_2}{1-y_1} = \frac{0.2}{1-0.4} = 0.333$$

$$y_3' = \frac{y_3}{1-y_1} = \frac{0.4}{1-0.4} = 0.667$$

Substituting in equation (1-60) gives us

$$D_{1,eff} = \frac{1}{\frac{y_2'}{D_{12}} + \frac{y_3'}{D_{13}}}$$

$$= \frac{1}{\frac{0.333}{0.237} + \frac{0.667}{0.728}}$$

$$= 0.431 \ \frac{\text{cm}^2}{\text{s}}$$

For multicomponent liquid mixtures, it is usually very difficult to obtain numerical values of the diffusion coefficients relating fluxes to concentration gradients. One important case of multicomponent diffusion for which simplified empirical correlations have been proposed is when a dilute solute diffuses through a homogeneous solution of mixed solvents. Perkins and Geankoplis (1969) evaluated several methods and suggested

$$D^0_{1,eff}\mu_M^{0.8} = \sum_{j=2}^{n} x_j D^0_{1,j}\mu_j^{0.8} \qquad (1\text{-}62)$$

where

$D^0_{1,eff}$ = effective diffusivity for a dilute solute A into the mixture, cm^2/s

$D^0_{1,j}$ = infinite dilution binary diffusivity of solute a into solvent j, cm^2/s

x_j = mol fraction of component j

μ_M = mixture viscosity, cP

μ_j = pure component viscosity, cP

When tested with data for eight ternary systems, errors were normally less than 20%, except for cases where CO_2 was the solute. For CO_2 as a dilute solute diffusing into mixed solvents, Takahashi et al. (1982) recommend

$$D^0_{CO_2,eff}\left(\frac{\mu_M}{V_M}\right)^{1/3} = \sum_{\substack{j=1 \\ j\neq CO_2}}^{n} x_j D^0_{CO_2,j}\left(\frac{\mu_j}{V_j}\right)^{1/3} \qquad (1\text{-}63)$$

where

V_M = molar volume of the mixture at T, cm^3/mol

V_j = molar volume of the pure component j at T, cm^3/mol

Tests with a number of ternary systems involving CO_2 led to deviations from experimental values usually less than 4%. (Reid et al., 1987).

Example 1.13 Calculation of Effective Diffusivity of a Dilute Solute in a Homogeneous Mixture of Solvents

Estimate the diffusion coefficient of acetic acid at very low concentrations diffusing into a mixed solvent containing 40.0 wt% ethyl alcohol in water at a temperature of 298 K.

Solution

Let 1 = acetic acid, 2 = water, and 3 = ethyl alcohol. Estimate the infinite dilution diffusion coefficient of acetic acid in water at 298 K using equation (1-53). The required data are (Reid, et al., 1987): (1) at 298 K, $\mu_B = 0.894$ cP; (2) $V_{cA} = 171.0$ cm^3/mol. From equation (1-48), $V_{bA} = 62.4$ cm^3/mol. Substituting in equation (1-53),

$$D_{12}^0 = 1.32 \times 10^{-5} \text{ cm}^2/\text{s}$$

Estimate the infinite dilution diffusion coefficient of acetic acid in ethanol at 298 K. The following data are available (Reid, et al., 1987):

Parameter	Acetic acid	Ethanol
T_b, K	390.4	351.4
T_c, K	594.8	513.9
P_c, bar	57.9	61.4
V_c, cm^3/mol	171	167
μ @ 298 K, cP	---	1.043

Use the Hayduk and Minhas correlation for nonaqueous solutions. According to restriction 3 mentioned above, the molar volume of the acetic acid to be used in equation (1-54) should be $V_{bA} = 2 \times 62.4 = 124.8$ cm^3/mol. The molar volume of ethanol is calculated from equation (1-48): $V_{bB} = 60.9$ cm^3/mol. Using the Mathcad routine developed in Example 1.9, we have

$$D_{13}^0 = 1.0 \times 10^{-5} \text{ cm}^2/\text{s}$$

The viscosity of a 40 wt% aqueous ethanol solution at 298 K is $\mu_M = 2.35$ cP (Perkins and Geankoplis, 1969). Before substituting in equation (1-62), the solution composition must be changed from mass to molar fractions following a procedure similar to that illustrated in Example 1.2. Accordingly, a 40 wt% aqueous ethanol solution converts to 20.7 mol%. Substituting in equation (1-62) yields

$$D^0_{1,eff} = \frac{10^{-5}}{(2.35)^{0.8}}\left[(0.207)(1.0)(1.043)^{0.8} + (0.793)(1.32)(0.894)^{0.8}\right]$$
$$= 0.591 \times 10^{-5} \text{ cm}^2/\text{s}$$

The experimental value reported by Perkins and Geankoplis (1969) is 0.571×10^{-5} cm^2/s. Therefore, the error of the estimate is 3.5%.

1.4 STEADY-STATE MOLECULAR DIFFUSION IN FLUIDS

1.4.1 Molar Flux and the Equation of Continuity

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

1. State the equation of continuity for a system of variable composition.
2. Simplify the equation of continuity for steady-state diffusion in one direction in rectangular coordinates and without chemical reaction.

The *equation of continuity* for component A in a mixture describes the change of concentration of A with respect to time at a fixed point in space resulting from mass transfer of A and chemical reactions producing A. In vector symbolism, the resulting equation is (Bird et al., 1960)

$$\nabla \cdot \mathbf{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0 \tag{1-64}$$

The first term in equation (1-64), the divergence of the molar flux vector, represents the net rate of molar efflux per unit volume. In rectangular coordinates, this term can be expanded as

$$\nabla \cdot \mathbf{N}_A = \frac{\partial N_{A,x}}{\partial x} + \frac{\partial N_{A,y}}{\partial y} + \frac{\partial N_{A,z}}{\partial z} \tag{1-65}$$

The second term in equation (1-64) represents the molar rate of accumulation of A per unit volume. The term R_A represents the volumetric rate of formation of A by chemical reaction (mol of A formed/volume-time). An expression similar to equation (1-64) can be written for each component of the mixture:

$$\nabla \cdot \mathbf{N}_i + \frac{\partial c_i}{\partial t} - R_i = 0 \qquad i = 1,2,\ldots,n \tag{1-66}$$

Consider, now, steady-state diffusion (no accumulation) without chemical reaction. In that case, equation (1-66) reduces to

$$\nabla \cdot \mathbf{N}_i = 0 \qquad i = 1,2,\ldots,n \tag{1-67}$$

In rectangular coordinates, with diffusion only in the z direction, equation (1-67) simplifies to

$$\frac{dN_{i,z}}{dz} = 0 \qquad i = 1,2,\ldots,n \tag{1-68}$$

This relation stipulates a constant molar flux of each component in the mixture, and a constant total molar flux. Therefore, for steady-state, one-dimensional diffusion without chemical reaction:

$$\begin{aligned} N_i &= N_{i,z} = \text{ constant}_i \qquad i = 1,2,\ldots,n \\ \sum_{i=1}^{n} N_i &= \text{ constant} \end{aligned} \tag{1-69}$$

1.4.2 Steady-State Molecular Diffusion in Gases

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

1. Calculate molar fluxes during steady-state molecular, one-dimensional diffusion in gases.
2. Calculate molar fluxes for steady-state gaseous diffusion of A through stagnant B, and for equimolar counterdiffusion.

Consider steady-state diffusion only in the z direction without chemical reaction in a binary gaseous mixture. For the case of one-dimensional diffusion, equation (1-20) becomes

$$N_A = -c\mathrm{D}_{AB}\frac{dy_A}{dz} + y_A N_A = -c\mathrm{D}_{AB}\frac{dy_A}{dz} + y_A\left(N_A + N_B\right) \tag{1-70}$$

For a gaseous mixture, if the temperature and pressure are constant, c and D_{AB} are constant, independent of position and composition. According to equation (1-69), all the molar fluxes are also constant. Equation (1-70) may then be integrated between the two boundary conditions:

$$\text{at } z = z_1 \qquad y_A = y_{A1}$$
$$\text{at } z = z_2 \qquad y_A = y_{A2}$$

where 1 indicates the beginning of the diffusion path (y_A high) and 2 the end of the diffusion path (y_A low).

However, before equation (1-70) can be integrated, the bootstrap relation between the molar flux of component A and the total molar flux (N) must be established a priori based on stoichiometric or energy balance considerations as mentioned before. The next example will illustrate the simplest case: that when the total molar flux vanishes and there is no bulk motion contribution to the flux of either component.

Example 1.14 Steady-State Equimolar Counterdiffusion

This is a situation frequently encountered in binary distillation operations when the molar latent heat of vaporization of both components is similar. In this case, $N_B = -N_A = \text{const.}, \Sigma N_i = N = 0$. For an ideal gas mixture, equation (1-70) simplifies to

$$N_A = -c\mathrm{D}_{AB}\frac{dy_A}{dz} = -\frac{\mathrm{D}_{AB}P}{RT}\frac{dy_A}{dz} \tag{1-71}$$

Separating variables and integrating with constant N_A, we have

$$\begin{aligned} N_A &= \frac{\mathrm{D}_{AB}P}{RT\delta}\left(y_{A1} - y_{A2}\right) \\ &= \frac{\mathrm{D}_{AB}}{RT\delta}\left(p_{A1} - p_{A2}\right) \end{aligned} \tag{1-72}$$

where we let $z_2 - z_1 = \delta$. Notice that in equation (1-72), derived for equimolar counterdiffusion, the driving force for mass transfer is linear, that is, the flux of component A is directly proportional to the difference in concentrations or partial pressures between the extremes of the diffusion path. This result is a direct consequence of the fact that the process described is of a purely diffusional nature, with no bulk motion contribution. A plot of y_A versus position would be a straight line.

Consider the following numerical example. A binary gaseous mixture of components A and B at a pressure of 1 bar and temperature of 300 K undergoes steady-state equimolar counterdiffusion along a 1-mm-thick diffusion path. At one end of

the path the mole fraction of component A is 70%, while at the other end it is 20%. Under these conditions, $D_{AB} = 0.1$ cm^2/s. Calculate the molar flux of component A.

Solution

Direct substitution into equation (1-72) yields

$$N_A = \frac{\left(10^{-5}\,\mathrm{m^2/s}\right)\left(10^5\,\mathrm{Pa}\right)\left(0.7-0.2\right)}{\left(8.314\,\frac{\mathrm{m^3\cdot Pa}}{\mathrm{mol\cdot K}}\right)\left(300\,\mathrm{K}\right)\left(10^{-3}\,\mathrm{m}\right)}$$
$$= 0.20\ \mathrm{mol/m^2\cdot s}$$

In the general case, the bulk motion contribution to the flux must be included, as shown by equation (1-70). Separating the variables in equation (1-70):

$$\frac{-dy_A}{N_A - y_A\left(N_A + N_B\right)} = \frac{dz}{c\mathrm{D}_{AB}} \tag{1-73}$$

Equation (1-73) may then be integrated between the two boundary conditions:

$$\frac{1}{N_A + N_B}\ln\left[\frac{N_A - y_{A2}\left(N_A + N_B\right)}{N_A - y_{A1}\left(N_A + N_B\right)}\right] = \frac{\delta}{c\mathrm{D}_{AB}} \tag{1-74}$$

Multiplying both sides of equation (1-74) by N_A and rearranging:

$$N_A = \frac{N_A}{N_A + N_B}\frac{c\mathrm{D}_{AB}}{\delta}\ln\left[\frac{\frac{N_A}{N_A + N_B} - y_{A2}}{\frac{N_A}{N_A + N_B} - y_{A1}}\right] \tag{1-75}$$

Define the molar flux fraction, Ψ_A:

$$\Psi_A = \frac{N_A}{N_A + N_B} \tag{1-76}$$

In this expression, N_A gives the positive direction of z. Any flux in the opposite direction will carry a negative sign. Notice that the molar flux fraction Ψ_A depends exclusively on the bootstrap relation between N_A and the other fluxes, a relation that is known *a priori* based on other considerations, as was shown before. Therefore, equation (1-75) becomes

$$N_A = \Psi_A \frac{cD_{AB}}{\delta} \ln\left[\frac{\Psi_A - y_{A2}}{\Psi_A - y_{A1}}\right] \tag{1-77}$$

Equation (1-77) is one of the most fundamental relations in the analysis of mass-transfer phenomena. It was derived by integration assuming that all the molar fluxes were constant, independent of position. Integration under conditions where the fluxes are not constant is also possible. Consider steady-state radial diffusion from the surface of a solid sphere into a fluid. Equation (1-70) can be applied, but the fluxes are now a function of position owing to the geometry. Most practical problems which deal with such matters, however, are concerned with diffusion under turbulent conditions, and the transfer coefficients which are then used are based upon a flux expressed in terms of some arbitrarily chosen area, such as the surface of the sphere. These matters are discussed in detail in Chapter 2.

Most practical problems of mass transfer in the gas phase are at conditions such that the mixture behaves as an ideal gas. Then, combining equations (1-7) and (1-77):

$$N_A = \Psi_A \frac{D_{AB}P}{RT\delta} \ln\left[\frac{\Psi_A - y_{A2}}{\Psi_A - y_{A1}}\right] \tag{1-78}$$

Example 1.15 Steady-State Diffusion of A Through Stagnant B

Consider steady-state, one-dimensional diffusion of A through nondiffusing B. This might occur, for example, if ammonia (A) is absorbed from air (B) into water. In the gas phase, since air does not dissolve appreciably in water, and neglecting the evaporation of water, only the ammonia diffuses. Thus, $N_B = 0$, N_A = constant, and

$$\Psi_A = \frac{N_A}{N_A + N_B} = 1$$

Equation (1-78) then becomes

$$N_A = \frac{D_{AB}P}{RT\delta} \ln\left[\frac{1 - y_{A2}}{1 - y_{A1}}\right] \tag{1-79}$$

Substituting equation (1-9) into equation (1-79), the driving force for mass transfer is expressed in terms of partial pressures:

$$N_A = \frac{D_{AB}P}{RT\delta}\ln\left[\frac{P - p_{A2}}{P - p_{A1}}\right] \tag{1-80}$$

Notice that in equation (1-80), as in all the relations derived so far to calculate the molar flux when the bulk motion contribution is significant, the driving force is of a logarithmic nature. The resulting concentration profiles for components A and B are no longer linear. The concentration profile of component A can be derived integrating equation (1-73) from point 1 to any arbitrary position z, substituting the expression for N_A obtained in equation (1-79), and rearranging,

$$\begin{aligned} y_A(z) &= 1 - (1 - y_{A1})\left[\frac{1 - y_{A2}}{1 - y_{A1}}\right]^{\frac{z}{\delta}} \\ y_B(z) &= 1 - y_A(z) \end{aligned} \tag{1-81}$$

Figure 1.6 shows schematically the concentration profiles for diffusion of A through stagnant B. Substance A diffuses by virtue of its concentration gradient, $-dy_A/dz$. Substance B is also diffusing relative to the average molar velocity at a flux J_B which depends upon $-dy_B/dz$, but like a fish which swims upstream at the same velocity as the water flows downstream, $N_B = 0$ relative to a fixed place in space.

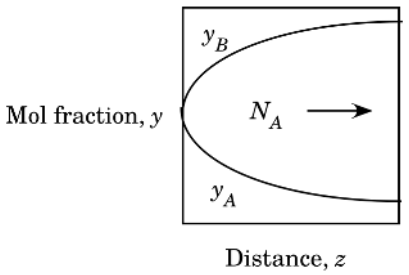


Figure 1.6 Diffusion of A through stagnant B.

It will be shown in Chapter 2 that, for diffusion under turbulent conditions, the flux is usually calculated as the product between an empirical mass-transfer coefficient and a linear driving force. For comparison purposes, we will now manipulate equation (1-80) to rewrite it in terms of a linear driving force. Since

$$P - p_{A2} = p_{B2} \qquad P - p_{A1} = p_{B1}$$
$$p_{B2} - p_{B1} = p_{A1} - p_{A2}$$

then

$$N_A = \frac{D_{AB}P}{RT\delta}\left[\frac{p_{A1} - p_{A2}}{p_{B2} - p_{B1}}\right]\ln\left[\frac{p_{B2}}{p_{B1}}\right] \tag{1-82}$$

Define the logarithmic mean partial pressure of B, $p_{B,M}$:

$$p_{B,M} = \frac{p_{B2} - p_{B1}}{\ln\left[\frac{p_{B2}}{p_{B1}}\right]} \tag{1-83}$$

then

$$N_A = \frac{D_{AB}P}{RT\delta p_{B,M}}\left(p_{A1} - p_{A2}\right) \tag{1-84}$$

Comparing equations (1-72) and (1-84), when all other conditions are equal, the ratio of the molar flux of component A under conditions of stagnant B ($N_B = 0$) to the corresponding value under conditions of equimolar counterdiffusion ($N_B = -N_A$) is given by $P/p_{B,M}$. For very dilute mixtures of component A in B, this ratio approaches a unit value. However, for concentrated mixtures, this ratio can be significantly higher than 1.0.

For illustration purposes, calculate the molar flux of component A for the conditions of Example 1.14, but for diffusion of A through stagnant B.

Solution

Calculate the partial pressures of component B at the ends of the diffusion path: p_{B2} = 0.8 bar, p_{B1} = 0.3 bar. Substituting in equation (1-83), $p_{B,M}$ = 0.51 bar. Therefore, using the result of Example 1.14,

$$N_A = 0.2 \text{ mol/m}^2 \cdot \text{s} \times \frac{1.0 \text{ bar}}{0.51 \text{ bar}} = 0.39 \text{ mol/m}^2 \cdot \text{s}$$

Example 1.16 Production of Nickel Carbonyl: Steady-State, One-Dimensional Binary Flux Calculation

Nickel carbonyl (A) is produced by passing carbon monoxide (B) at 323 K and 1 atm over a nickel slab. The following reaction takes place at the solid surface:

$$\mathrm{Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(g)}$$

The reaction is very rapid, so that the partial pressure of CO at the metal surface is essentially zero. The gases diffuse through a film 0.625 mm thick. At steady-state, estimate the rate of production of nickel carbonyl, in mol/m^2 of solid surface per second. The composition of the bulk gas phase is 50 mol% CO. The binary gas diffusivity under these conditions is D_{AB} = 20.0 mm^2/s.

Solution

Figure 1.7 is a schematic diagram of the diffusion process. The stoichiometry of the reaction determines the relation between the fluxes: from equation (1-59), $N_B = -4N_A$, $N_A + N_B = -3N_A$. Calculate the molar flux fraction, Ψ_A. From equation (1-76):

$$\Psi_A = \frac{N_A}{N_A + N_B} = \frac{N_A}{-3N_A} = -\frac{1}{3}$$

Combining this result with equation (1-78)

$$N_A = -\frac{D_{AB}P}{3RT\delta}\ln\left[\frac{-\frac{1}{3} - y_{A2}}{-\frac{1}{3} - y_{A1}}\right] = \frac{D_{AB}P}{3RT\delta}\ln\left[\frac{\frac{1}{3} + y_{A1}}{\frac{1}{3} + y_{A2}}\right]$$

Substituting numerical values:

$$N_A = \frac{\left(2.0\times10^{-5}\right)\left(1.013\times10^{5}\right)}{3\times\left(8.314\right)\left(323\right)\left(0.625\times10^{-3}\right)}\ln\left[\frac{\frac{1}{3}+1.0}{\frac{1}{3}+0.5}\right] = 0.189\ \mathrm{mol/m^2\cdot s}$$

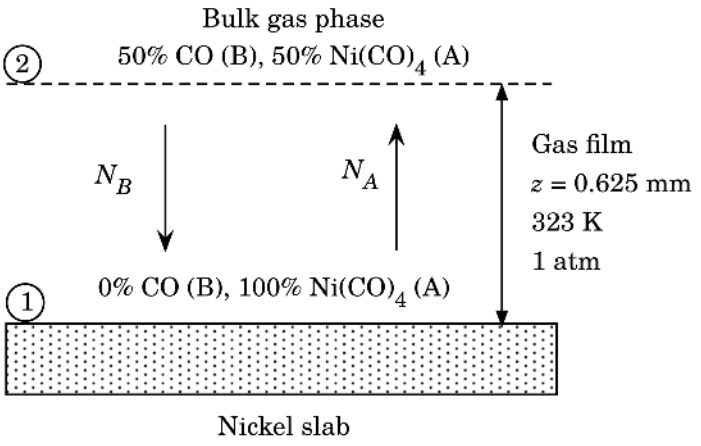


Figure 1.7 Schematic diagram for Example 1.16.

Example 1.17 Multicomponent, Steady-State, Gaseous Diffusion in a Stefan Tube (Taylor and Krishna, 1993)

The Stefan tube, depicted schematically in Figure 1.8, is a simple device sometimes used for measuring diffusion coefficients in binary vapor mixtures. In the bottom of the tube is a pool of quiescent liquid. The vapor that evaporates from this pool diffuses to the top of the tube. A stream of gas across the top of the tube keeps the mole fraction of the diffusing vapors there to essentially zero. The composition of the vapor at the vapor–liquid interface is its equilibrium value. Carty and Schrodt (1975) evaporated a binary liquid mixture of acetone (1) and methanol (2) in a Stefan tube. Air (3) was used as the carrier gas. In one of their experiments the composition of the vapor at the liquid interface was $y_1 = 0.319$, $y_2 = 0.528$, and $y_3 = 0.153$. The pressure and temperature in the gas phase were 99.4 kPa and 328.5 K, respectively. The length of the diffusion path was 0.238 m. The MS diffusion coefficients of the three binary pairs are:

$$D_{12} = 8.48 \text{ mm}^2/\text{s}$$
$$D_{13} = 13.72 \text{ mm}^2/\text{s}$$
$$D_{23} = 19.91 \text{ mm}^2/\text{s}$$

Calculate the molar fluxes of acetone and methanol, and the composition profiles predicted by the MS equations. Compare your results with the experimental data.

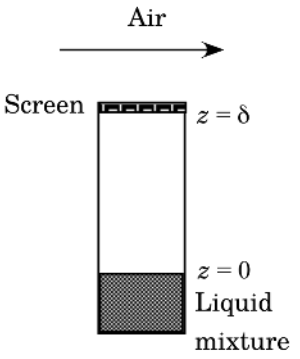


Figure 1.8 Schematic diagram of a Stefan tube.

Solution

For a multicomponent mixture of ideal gases such as this, the MS equations (1-35) must be solved simultaneously for the fluxes and the composition profiles. At constant temperature and pressure the total molar density c and the binary diffusion coefficients are constant. Furthermore, diffusion in the Stefan tube takes place in only one direction, up the tube. Therefore, the continuity equation simplifies to equation (1-69). Air (3) diffuses down the tube as the evaporating mixture diffuses up, but because air does not dissolve in the liquid its flux N_3 is zero (i.e., the diffusion flux J_3 of the gas down the tube is exactly balanced by the diffusion-induced bulk flux $y_3 \times N$ up the tube).

With the above assumptions, the MS relations given by equation (1-35) reduce to a system of two first-order differential equations

$$\begin{aligned} \frac{dy_1}{dz} &= \frac{y_1 N_2 - y_2 N_1}{cD_{12}} + \frac{y_1 N_3 - \left(1 - y_1 - y_2\right) N_1}{cD_{13}} \\ \frac{dy_2}{dz} &= \frac{y_2 N_1 - y_1 N_2}{cD_{12}} + \frac{y_2 N_3 - \left(1 - y_1 - y_2\right) N_2}{cD_{23}} \end{aligned} \tag{1-85}$$

subject to the boundary conditions

$$z = 0, \quad y_i = y_{i0} \qquad z = \delta, \quad y_i = y_{i\delta} \qquad i = 1, 2 \tag{1-86}$$

Define:

$$\eta = \frac{z}{\delta} \qquad F_{12} = \frac{cD_{12}}{\delta} \qquad F_{13} = \frac{cD_{13}}{\delta} \qquad F_{23} = \frac{cD_{23}}{\delta}$$

The MS relations then become

$$\frac{dy_1}{d\eta} = \frac{y_1 N_2 - y_2 N_1}{F_{12}} + \frac{y_1 N_3 - \left(1 - y_1 - y_2\right) N_1}{F_{13}}$$
$$\frac{dy_2}{d\eta} = \frac{y_2 N_1 - y_1 N_2}{F_{12}} + \frac{y_2 N_3 - \left(1 - y_1 - y_2\right) N_2}{F_{23}} \tag{1-87}$$

Equation (1-87) involves not only two variable concentrations (y_1 and y_2), but also three unknown fluxes (N_1, N_2, and N_3). From equation (1-68) we obtain three additional constraints:

$$\frac{dN_1}{d\eta} = 0 \qquad \frac{dN_2}{d\eta} = 0 \qquad \frac{dN_3}{d\eta} = 0 \tag{1-88}$$

Equations (1-87) and (1-88) with boundary conditions given by equation (1-86) constitute a *boundary-value problem*. Notice that there are five first-order ordinary differential equations (ODEs) and only four boundary conditions specified. Therefore, an additional piece of information, the bootstrap condition, must be specified *a priori* to completely define the problem. Before attempting to solve this set of equations, we will reformulate them in dimensionless form. Define a vector of dimensionless dependent variables, **u**, such that

$$u_1 \equiv y_1 \quad u_2 \equiv y_2 \quad u_3 \equiv \frac{N_1}{F_{12}} \quad u_4 \equiv \frac{N_2}{F_{12}} \quad u_5 \equiv \frac{N_3}{F_{12}} \tag{1-89}$$

Equations (1-87) and (1-88) can be written in terms of the components of vector **u** as

$$\frac{du_1}{d\eta} = u_1 u_4 + \frac{u_1 u_5 - \left(1 - u_1 - u_2\right) u_3}{r_1}$$
$$\frac{du_2}{d\eta} = u_2 u_3 + \frac{u_2 u_5 - \left(1 - u_1 - u_2\right) u_4}{r_2} \tag{1-90}$$
$$\frac{du_3}{d\eta} = 0, \quad \frac{du_4}{d\eta} = 0, \quad \frac{du_5}{d\eta} = 0$$

where $r_1 = F_{13}/F_{12}$ and $r_2 = F_{23}/F_{12}$.

An analytical solution of these equations for Stefan diffusion ($N_3 = 0$) in a ternary mixture is available (Carty and Schrodt, 1975). However—with the objective of presenting a general method of solution that can be used for any number of components, and any relation between the fluxes—we solved these equations

numerically using the shooting method (Fausett, 2002). This method reduces the solution of a boundary-value problem to the iterative solution of an *initial-value problem*. The usual approach involves a trial-and-error procedure. That boundary point having the most known conditions is selected as the initial point. Any other missing initial conditions are assumed, and the initial-value problem is solved using a step-by-step procedure, such as the *fourth-order Runge–Kutta method* (Fausett, 2002). Unless the computed solution agrees with the known boundary conditions (unlikely on the first try!), the assumed initial conditions are adjusted and the problem is solved again. The process is repeated until the assumed initial conditions yield, within specified tolerances, a solution that agrees with the known boundary conditions.

An initial-value problem, consisting of a system of first-order ODEs and the corresponding set of initial conditions, can be expressed compactly in vector notation as

$$\mathbf{u}' = \mathbf{f}\left(x, \mathbf{u}\right) \qquad \mathbf{u}\left(a\right) = \mathbf{u}^{(0)} \qquad a \le x \le b \tag{1-91}$$

The fourth-order Runge–Kutta method approximates the solution $\mathbf{u}(x)$ of the system of ODEs using n steps of size $h = (b - a)/n$ and grid points located at $x_i = a + h \times i$ according to the following algorithm (Fausett, 2002):

$$\begin{aligned}
\mathbf{k}1 &= h\mathbf{f}\left[x_i, \mathbf{u}^{(i)}\right] \\
\mathbf{k}2 &= h\mathbf{f}\left[x_i + \frac{h}{2}, \mathbf{u}^{(i)} + \frac{\mathbf{k}1}{2}\right] \\
\mathbf{k}3 &= h\mathbf{f}\left[x_i + \frac{h}{2}, \mathbf{u}^{(i)} + \frac{\mathbf{k}2}{2}\right] \\
\mathbf{k}4 &= h\mathbf{f}\left[x_i + h, \mathbf{u}^{(i)} + \mathbf{k}3\right] \\
\mathbf{u}^{(i+1)} &= \mathbf{u}^{(i)} + \frac{\mathbf{k}1}{6} + \frac{\mathbf{k}2}{3} + \frac{\mathbf{k}3}{3} + \frac{\mathbf{k}4}{6}
\end{aligned} \tag{1-92}$$

The Mathcad intrinsic function *rkfixed* provides the basic approach for solving numerically a system of first-order ODEs implementing the fourth-order Runge–Kutta algorithm. The call to this function has the form

$$rkfixed\left(\mathbf{u}^{(0)}, a, b, n, \mathbf{D}\right)$$

where $\mathbf{D}$ is a vector containing the first derivatives of the dependent variables (the right-hand side of the system of ODEs, $\mathbf{u}' = \mathbf{f}(x,\mathbf{u})$). The function *rkfixed* returns the solution in the form of a matrix with $(n + 1)$ rows and $(j + 1)$ columns, where j

is the number of dependent variables. The first column contains the values of the independent variable at which the solution is given; the remaining columns contain the corresponding solution values for the dependent variables.

To implement the shooting method in Mathcad, define a function explicitly in terms of the solution matrix returned by the function *rkfixed* and the missing initial conditions (in this case, $u_3^{(0)}$, $u_4^{(0)}$, and $u_5^{(0)}$). After specifying the bootstrap condition (in this case, $u_5^{(0)} = 0$), use the "solve block" feature of Mathcad to solve for the values of the missing initial conditions that yield a solution in agreement with the known boundary conditions at the end of the diffusion path. Once convergence is achieved by the "solve block," calculate the fluxes from the corresponding initial conditions. Remember that, according to the equation of continuity (equation 1-69), the fluxes are constant, independent of position; therefore,

$$\begin{aligned} u_3 &= u_3^{(0)} \qquad N_1 = u_3^{(0)} F_{12} \\ u_4 &= u_4^{(0)} \qquad N_2 = u_4^{(0)} F_{12} \\ u_5 &= u_5^{(0)} \qquad N_3 = u_5^{(0)} F_{12} \end{aligned} \tag{1-93}$$

The concentration profiles are obtained directly from the converged solution.

Figure 1.9 shows the Mathcad implementation of the shooting method for Stefan flow, and compares the results predicted by solving the MS equations to the experimental values obtained by Carty and Schrodt (1975). The predicted fluxes and concentration profiles are in excellent agreement with the observed experimental results.

Example 1.18 Multicomponent, Steady-State, Gaseous Diffusion with Chemical Reaction

Consider the vapor phase dehydrogenation of ethanol (1) to produce acetaldehyde (2) and hydrogen (3):

$$C_2H_6O(g) \rightarrow C_2H_4O(g) + H_2(g)$$

carried out at a temperature of 548 K and 101.3 kPa (Taylor and Krishna, 1993). The reaction takes place at a catalyst surface with a reaction rate that is first order in the ethanol mole fraction, with a rate constant k_r = 10 mol/(m^2·s·mol fraction). Reactant and products diffuse through a gas film 1 mm thick. The bulk gas–phase composition is 60 mol% ethanol (1), 20% acetaldehyde (2), and 20% hydrogen (3).

Enter data:

$ORIGIN := 1 \qquad P := 0.994\ \text{bar} \qquad T := 328.5\ \text{K} \qquad \delta := 0.238\ \text{m} \qquad num := 100$

$R := 8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}} \qquad D12 := 8.48\ \frac{\text{mm}^2}{\text{s}} \qquad D13 := 13.72\ \frac{\text{mm}^2}{\text{s}} \qquad D23 := 19.91\ \frac{\text{mm}^2}{\text{s}}$

Preliminary calculations:

$c := \frac{P}{R\cdot T} = 36.395\ \frac{\text{mol}}{\text{m}^3} \qquad F12 := \frac{c\cdot D12}{\delta} = 0.0013\ \frac{\text{mol}}{\text{m}^2\cdot\text{s}}$

$F13 := \frac{c\cdot D13}{\delta} = 0.0021\ \frac{\text{mol}}{\text{m}^2\cdot\text{s}} \qquad r_1 := \frac{F13}{F12} = 1.618$

$F23 := \frac{c\cdot D23}{\delta} = 0.00304\ \frac{\text{mol}}{\text{m}^2\cdot\text{s}} \qquad r_2 := \frac{F23}{F12} = 2.348$

Define dimensionless dependent variables:

$u_1 = y_1 \qquad u_2 = y_2 \qquad u_3 = \frac{N1}{F12} \qquad u_4 = \frac{N2}{F12} \qquad u_5 = \frac{N3}{F12}$

Fourth-order Runge--Kutta:

$$D(\eta, u) := \begin{bmatrix} \frac{u_1\cdot u_4 - u_2\cdot u_3}{1} + \frac{u_1\cdot u_5 - \left(1 - u_1 - u_2\right)\cdot u_3}{r_1} \\ \frac{u_2\cdot u_3 - u_1\cdot u_4}{1} + \frac{u_2\cdot u_5 - \left(1 - u_1 - u_2\right)\cdot u_4}{r_2} \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

Matrix of first derivatives

$$S1(u30, u40, u50) := \text{rkfixed}\left(\begin{bmatrix} 0.319 \\ 0.528 \\ u30 \\ u40 \\ u50 \end{bmatrix}, 0, 1, num, D\right)$$

Function in terms of unknown initial values and Runge--Kutta solution

$u1(u30, u40, u50) := S1(u30, u40, u50)^{\langle 2 \rangle}$

$u2(u30, u40, u50) := S1(u30, u40, u50)^{\langle 3 \rangle}$

The solutions u1 and u2 are the second and third columns of S1 and depend on the guess values of u30, u40, and u50.

Figure 1.9 Mathcad solution of Example 1.17.

Shooting method:

$u50 := 0$ Bootstrap condition for Stefan flow: $N_3 = 0$

Guess Values

$u30 := 1$

$u40 := 1$

Constraints

$u1(u30, u40, u50)_{num+1} = 0$

$u2(u30, u40, u50)_{num+1} = 0$

Known boundary conditions

Solver

$\begin{bmatrix} u30 \\ u40 \end{bmatrix} := \mathbf{Find}(u30, u40) = \begin{bmatrix} 1.375 \\ 2.412 \end{bmatrix}$

Computational results:

$N_1 := u30 \cdot F12 = (1.783 \cdot 10^{-3}) \ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$

$N_2 := u40 \cdot F12 = (3.128 \cdot 10^{-3}) \ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$

Calculated fluxes

$y_1 := u1(u30, u40, u50)$ $y_2 := u2(u30, u40, u50)$ Calculated concentration profiles

$y_3 := 1 - y_1 - y_2$ $z := \delta \cdot S1(u30, u40, u50)^{\langle 1 \rangle}$

Experimental results (Carty and Schrodt, 1975)

$N_{1ex} := (1.779 \cdot 10^{-3}) \ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$ $N_{2ex} := (3.121 \cdot 10^{-3}) \ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$ Measured Fluxes

$$zex := \begin{bmatrix} 4.45 \\ 7 \\ 9.45 \\ 11.9 \\ 14.4 \\ 17 \\ 19.4 \end{bmatrix} \cdot \text{cm} \quad y1ex := \begin{bmatrix} 0.263 \\ 0.251 \\ 0.232 \\ 0.217 \\ 0.185 \\ 0.153 \\ 0.113 \end{bmatrix} \quad y2ex := \begin{bmatrix} 0.457 \\ 0.460 \\ 0.421 \\ 0.379 \\ 0.307 \\ 0.243 \\ 0.168 \end{bmatrix} \quad y3ex := \overrightarrow{1 - y1ex - y2ex}$$

Measured concentration profiles

Comparison of results (% error):

$Err1 := \frac{N_1 - N_{1ex}}{N_{1ex}} \cdot 100 = 0.2307$ $Err2 := \frac{N_2 - N_{2ex}}{N_{2ex}} \cdot 100 = 0.2296$

Figure 1.9 Mathcad solution of Example 1.17 (continuation).

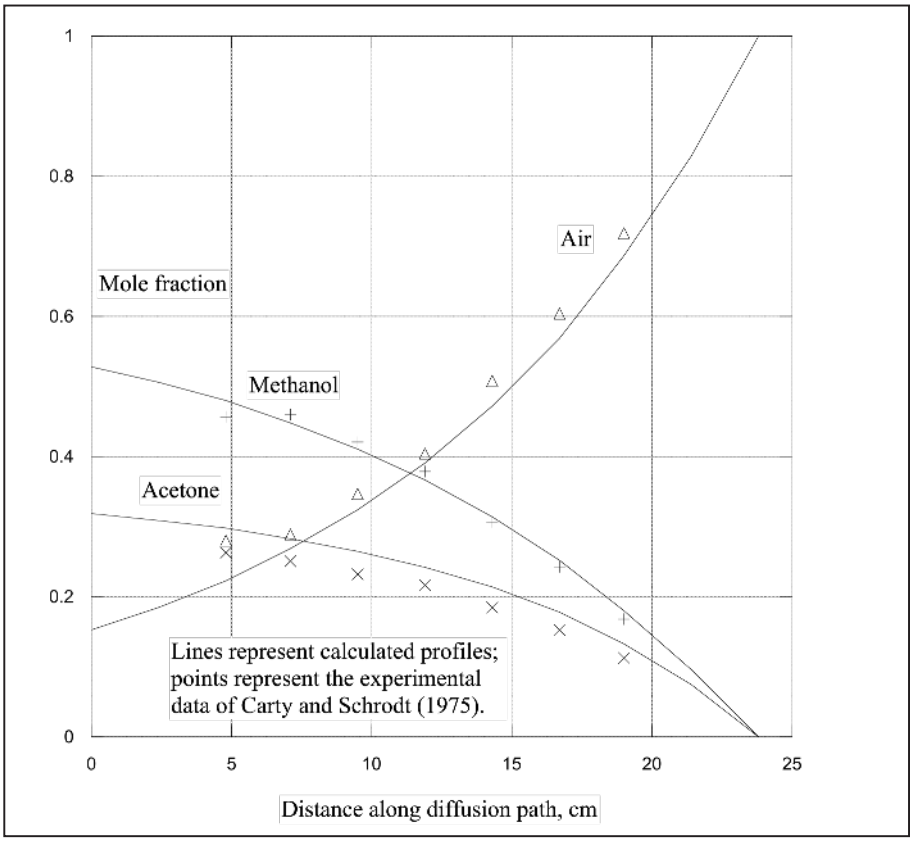


Figure 1.9 Mathcad solution of Example 1.17 (continuation).

Estimate the overall rate of reaction at steady state. The MS diffusion coefficients are

$$D_{12} = 72 \text{ mm}^2/\text{s} \qquad D_{13} = 230 \text{ mm}^2/\text{s} \qquad D_{23} = 230 \text{ mm}^2/\text{s}$$

Solution

Equations (1-85) also apply to this problem; however, there are three additional unknown quantities: N_3, $y_{1\delta}$, and $y_{2\delta}$. The mol fractions at the interface ($z = \delta$) cannot be specified arbitrarily, but are fixed by the reaction stoichiometry. Thus, the interface mol fractions must be determined simultaneously with the molar fluxes. The flux of ethanol is determined by the rate of chemical reaction at the catalyst

surface. Furthermore, for every mol of ethanol that diffuses to the catalyst surface, one mol of acetaldehyde and one mol of hydrogen diffuse in the opposite direction. That is, the boundary condition and bootstrap relations are, respectively:

$$\begin{aligned} N_1 &= k_r y_{1\delta} \\ N_2 &= N_3 = -N_1 \end{aligned} \tag{1-94}$$

Equations (1-94) can be expressed in terms of the components of the dimensionless vector of dependent variables **u**—defined in equation (1-89)—as

$$\begin{aligned} u_3^{(0)} &= \kappa u_{1\delta} \\ u_1^{(0)} &= u_5^{(0)} = -u_3^{(0)} \end{aligned} \tag{1-95}$$

where $\kappa = k_r/F_{12}$. The shooting method is again implemented using Mathcad to solve the boundary-value problem consisting of equations (1-90) and (1-95). The converged solution predicts an overall rate of reaction $N_1 = 0.888$ mol of ethanol/m^2 surface area·s, and an interface composition of 8.8 mol % ethanol, 58.3% acetaldehyde, and 32.9% hydrogen. More details of the solution, including the complete concentration profiles, are provided in Appendix C.

1.4.3 Steady-State Molecular Diffusion in Liquids

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

1. Calculate molar fluxes during steady-state molecular, one-dimensional diffusion in liquids.
2. Calculate molar fluxes for steady-state diffusion of A through stagnant B, and for equimolar counterdiffusion, both in the liquid phase.

The integration of equation (1-70), to put it in the form of equation (1-77), requires the assumption that D_{AB} and c are constant. This is satisfactory for gas mixtures but not in the case of liquids, where both may vary considerably with concentration. Nevertheless, it is customary to use equation (1-77) to predict molecular diffusion in liquids with an average c and the best average value of D_{AB} available. Equation (1-77) is conveniently written for dilute solutions as

$$N_A = \Psi_A \frac{D_{AB}^0}{\delta} \left(\frac{\rho}{M}\right)_{av} \ln\left[\frac{\Psi_A - x_{A2}}{\Psi_A - x_{A1}}\right] \tag{1-96}$$

where ρ and M are the solution density and molecular weight, respectively. As for

gases, the value of Ψ_A must be established by the prevailing circumstances. For the most commonly occurring cases, we have, as for gases:

1. Steady-state diffusion of A through stagnant B

For this case, N_A = const, $N_B = 0$, $\Psi_A = 1$, then equation (1-96) becomes

$$N_A = \frac{D^0_{AB}}{\delta x_{B,M}} \left(\frac{\rho}{M}\right)_{av} \left(x_{A1} - x_{A2}\right) \tag{1-97}$$

where

$$x_{B,M} = \frac{x_{B2} - x_{B1}}{\ln\left(x_{B2} / x_{B1}\right)} \tag{1-98}$$

2. Steady-state equimolar counterdiffusion

For this case, $N_A = -N_B$ and

$$N_A = \frac{D^0_{AB}}{\delta} \left(\frac{\rho}{M}\right)_{av} \left(x_{A1} - x_{A2}\right) \tag{1-99}$$

Example 1.19 Steady-State Molecular Diffusion in Liquids

A crystal of chalcanthite ($CuSO_4 \cdot 5H_2O$) dissolves in a large tank of pure water at 273 K. Estimate the rate at which the crystal dissolves by calculating the flux of $CuSO_4$ from the crystal surface to the bulk solution. Assume that molecular diffusion occurs through a liquid film uniformly 0.01 mm thick surrounding the crystal. At the inner side of the film—adjacent to the crystal surface—the solution is saturated with $CuSO_4$, while at the outer side of the film the solution is virtually pure water. The solubility of chalcanthite in water at 273 K is 24.3 g of crystal/100 g of water and the density of the corresponding saturated solution is 1140 kg/m^3 (Perry and Chilton, 1973). The diffusivity of $CuSO_4$ in dilute aqueous solution at 273 K can be estimated as 3.6×10^{-10} m^2/s (see Problem 1.20). The density of pure liquid water at 273 K is 999.8 kg/m^3.

Solution

The crystal dissolution process may be represented by the equation

$$CuSO_4 \cdot 5H_2O(s) \rightarrow CuSO_4(aq) + 5H_2O(l)$$

Accordingly, for each mol of chalcanthite (molecular weight 249.71) that dissolves, one mol of $CuSO_4$ (molecular weight 159.63) and five moles of hydration water diffuse through the liquid film from the surface of the crystal to the bulk of the liquid phase. This is shown schematically in Figure 1.10 (substance A is $CuSO_4$ and substance B is water). Notice that both fluxes are in the same direction; therefore,

they are both positive and the bootstrap relation is $N_B = 5N_A$. From equation (1-76), $\Psi_A = 1/6 = 0.167$.

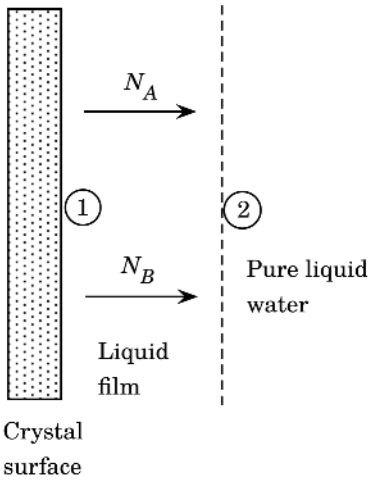


Figure 1.10 Schematic diagram for the crystal dissolution process of Example 1.19.

Next, we calculate the mol fraction of component A at the inner side of the film (x_{A1}), a saturated solution of chalcanthite in water at 273 K. The solubility of the salt under these conditions is 24.3 g/100 g H_2O:

Basis: 100 g of H_2O (24.3 g of $CuSO_4 \bullet 5H_2O$)

The mass of $CuSO_4$ in 24.3 g of the crystal is (24.3)(159.63)/(249.71) = 15.53 g. The mass of hydration water in the crystal is 24.3 – 15.53 = 8.77 g. Then, the total mass of water is 100 + 8.77 = 108.77 g. Therefore,

$$x_{A1} = \frac{\dfrac{15.53}{159.63}}{\dfrac{15.53}{159.63} + \dfrac{108.77}{18}} = 0.0158$$

The other end of the film is virtually pure water; therefore,

$$x_{A2} \approx 0$$

Next, we calculate the film average molar density. At point 1, the average molecular weight is $M_1 = (0.0158)(159.63) + (1 - 0.0158)(18) = 20.24$ kg/kmol. The corresponding molar density is $\rho_1/M_1 = 1140/20.24 = 56.32$ kmol/m^3. At point 2, the

molar density is $\rho_2/M_2 = 999.8/18 = 55.54$ kmol/m^3. Then

$$\left(\frac{\rho}{M}\right)_{av} = \frac{56.32 + 55.54}{2} = 55.93 \text{ kmol/m}^3$$

Substituting in equation (1-96):

$$N_A = \frac{0.167 \times 3.6 \times 10^{-10} \times 55.93 \times \ln\left[\dfrac{0.167 - 0}{0.167 - 0.0158}\right]}{0.01 \times 10^{-3}}$$

$$= 3.342 \times 10^{-5} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s}}$$

The rate of dissolution of the crystal is $(3.342 \times 10^{-5})(249.71)(3600) = 30$ kg/m^2 of crystal surface area per hour.

1.5 STEADY-STATE DIFFUSION IN SOLIDS

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

1. Describe the mechanisms of diffusion through polymeric, crystalline, and porous solids.
2. Calculate the mean free path for gases, and the Knudsen number for gas flow through porous solids.
3. Calculate effective molecular and Knudsen diffusion coefficients in porous solids.
4. Calculate fluxes through porous solids when both molecular and Knudsen diffusion are important.
5. Calculate the hydrodynamic flow of gases through porous solids under a total pressure gradient.
6. Use the "dusty gas" model to calculate multicomponent fluxes in porous solids.

Some of the mass-transfer operations, such as adsorption and membrane separations, involve contact of fluids with solids. In these cases, some of the diffusion occurs in the solid phase and may proceed according to any of several mechanisms. The structure of the solid and its interaction with the diffusing substance determine how diffusion occurs and the rate of mass transport. The solids may be *polymeric*, *crystalline*, or *porous*.

Thin, dense, nonporous polymeric membranes are widely used to separate gas and liquid mixtures. Diffusion of solutes through certain types of polymeric solids is more like diffusion through liquid solutions than any of the other solid-diffusion

phenomena, at least for the permanent gases as solutes. Consider, for example, two portions of a gas at different pressures separated by a polymeric membrane. The gas dissolves in the solid at the faces exposed to the gas to an extent usually directly proportional to the pressure. The dissolved gas then diffuses from the high- to the low-pressure side in a manner describable by Fick's first law.

Diffusion through nonporous crystalline solids depends markedly on the crystal lattice structure and the diffusing entity. The mechanisms of diffusion in crystalline solids include (Seader and Henley, 2006):

1. Direct exchange of lattice position by two atoms or ions.
2. Migration of small solutes through interlattice spaces called *interstitial sites*.
3. Migration to a vacant site in the lattice.
4. Migration along lattice imperfections or grain boundaries.

Diffusion coefficients associated with the first three mechanisms can vary widely and are almost always at least one order of magnitude smaller than diffusion coefficients in low-viscosity liquids. As might be expected, diffusion by the fourth mechanism can be much faster than by the other three mechanisms.

When solids are porous, it is possible to predict the diffusivity of gaseous and liquid solute species in the pores. In this case, any of the following mass-transfer mechanisms or combinations thereof may take place (Seader and Henley, 2006):

1. Ordinary molecular diffusion through pores, which present tortuous paths and hinder the movement of large molecules when their diameter is more than 10% of the pore diameter.
2. Knudsen diffusion, which involves collisions of diffusing gaseous molecules with the pore walls when the pore diameter and gas pressure are such that the molecular mean free path is large compared to the pore diameter.
3. Surface diffusion involving the jumping of molecules adsorbed on the pore walls from one adsorption site to another based on surface concentration-driving force.
4. Hydrodynamic flow through or into the pores driven by a total pressure gradient.

The vast majority of the solids used for mass-transfer operations are porous. Porous solids are also frequently used in catalytic chemical reactors. Because of their importance, the following sections explore with greater detail the four mass-transfer mechanisms in porous solids mentioned above.

1.5.1 Steady-State Binary Molecular Diffusion in Porous Solids

When treating diffusion of solutes in porous materials where diffusion is considered to occur only in the fluid inside the pores, it is common to refer to an effective diffusivity, $D_{AB,eff}$, which is based on (1) the total cross-sectional area of the

porous solid rather than the cross-sectional area of the pore and (2) on a straight path, rather than the pore actual path, which is usually quite tortuous. In a binary system, if pore diffusion occurs only by ordinary molecular diffusion, Fick's law can be used with an effective diffusivity that can be expressed in terms of the ordinary diffusion coefficient, D_{AB}, as

$$D_{AB,eff} = \frac{\varepsilon D_{AB}}{\tau} \tag{1-100}$$

where ε is the fractional porosity (typically 0.5) of the solid and τ is the pore-path tortuosity (typically 2 to 4). The *tortuosity* is defined as the ratio of the pore actual length to the length if the pore were straight in the direction of diffusion.

For binary mixtures diffusing inside porous solids, the applicability of equation (1-100) depends upon the value of a dimensionless ratio called the *Knudsen number*, Kn, defined as

$$\mathrm{Kn} = \frac{\lambda}{d} \tag{1-101}$$

where d is the pore diameter and λ is the mean free path of the diffusing molecules. Equation (1-100) applies when Kn is less than about 0.05 for all the diffusing species (Treybal, 1980).

For liquids, the mean free path is commonly a few angstroms, so the Knudsen number is almost always very small and diffusion inside the pores is usually only by ordinary molecular diffusion. In gases, the mean free path can be estimated from the following (Cussler, 1997):

$$\lambda = \frac{\kappa T}{\sqrt{2}\pi\sigma_{AB}^2 P} \tag{1-102}$$

where κ is Boltzmann constant and σ_{AB} is the collision diameter of the diffusing species.

Example 1.20 Steady-State Molecular Diffusion in Porous Solid

Estimate the effective diffusivity of hydrogen in ethane in a porous solid with an average pore size of 4000 Å, 40% porosity, and tortuosity of 2.5. The gas mixture is at a pressure of 10 atm and temperature of 373 K. For this system, the ordinary diffusion coefficient is given by $D_{AB} = 0.86/P$ in cm^2/s with total pressure P in atm (Seader and Henley, 2006).

Solution

Calculate the mean free path from equation (1-102). Using data from Appendix B for hydrogen and ethane, and equation (1-45), $\sigma_{AB} = 3.635$ Å. Then, from equation

(1-102), λ = 86.54 Å. From equation (1-101), Kn = 0.022 < 0.05. Therefore, diffusion inside the pores occurs only by ordinary molecular diffusion. At a total pressure of 10 atm, D_{AB} = 0.086 cm^2/s. Substituting the given values of porosity and tortuosity in equation (1-100), $D_{AB,eff}$ = 0.014 cm^2/s.

1.5.2 Knudsen Diffusion in Porous Solids

When the Knudsen number is large (Kn > 5.0), the molecular mean free path is much larger than the diameter of the channel in which the diffusing molecules reside. When this happens, the molecules bounce from wall to wall rather than colliding with other molecules. Since molecular collisions are unimportant under these conditions, each gas diffuses independently. This mode of transport is known as *Knudsen diffusion*. From the kinetic theory of gases, in a straight cylindrical pore of diameter d and length l, the Knudsen diffusivity, $D_{K,i}$, is given by (Treybal, 1980)

$$D_{K,i} = \frac{d}{3}\left(\frac{8RT}{\pi M_i}\right)^{0.5} \tag{1-103}$$

and the Knudsen flux is given by

$$N_i = \frac{D_{K,i}\left(p_{i1} - p_{i2}\right)}{RTl} \tag{1-104}$$

For Knudsen diffusion at constant total pressure, it can be shown that there is a bootstrap condition given by (Do, 1998)

$$\sum_{j=1}^{n} N_j \sqrt{M_j} = 0 \tag{1-105}$$

This is known as *Graham's law of effusion* for Knudsen diffusion of a multicomponent system at constant total pressure. For binary gas mixtures, equation (1-105) simplifies to

$$\frac{N_B}{N_A} = -\sqrt{\frac{M_A}{M_B}} \tag{1-106}$$

For Knudsen diffusion in porous solids of porosity ε and tortuosity τ,

$$D_{K,i,eff} = \frac{\varepsilon D_{K,i}}{\tau} \tag{1-107}$$

and

$$N_i = \frac{D_{K,i,eff}\left(p_{i1} - p_{i2}\right)}{RTl} \tag{1-108}$$

Example 1.21 Knudsen Diffusion in Porous Solid

A mixture of O_2 (A) and N_2 (B) diffuses through the pores of a 2-mm-thick piece of unglazed porcelain at a total pressure of 0.1 atm and a temperature of 293 K. The average pore diameter is 0.1 μm, the porosity is 30.5%, and the tortuosity is 4.39. Estimate the diffusion fluxes of both components when the mole fractions of O_2 are 80 and 20% on either side of the porcelain.

Solution

Calculate the mean free path from equation (1-102). Using data from Appendix B for oxygen and nitrogen, and equation (1-45), σ_{AB} = 3.632 Å. Then, from equation (1-102), λ = 6807 Å. From equation (1-101), Kn = 6.807 > 5.0. Therefore, transport inside the pores is mainly by Knudsen diffusion. From equation (1-103), $D_{K,A}$ = 0.147 cm^2/s. From equation (1-107), $D_{K,A,eff}$ = 0.0102 cm^2/s; from equation (1-108), $N_A = 1.27 \times 10^{-3}$ $mol/m^2 \cdot s$. From equation (1-106), $N_B = -NA \times (32/28)^{0.5} = -1.07N_A = -1.36 \times 10^{-3}$ $mol/m^2 \cdot s$.

In the range of Kn from roughly 0.02 to 5.0, a transition range, both molecular and Knudsen diffusion have influence, and the flux for binary mixtures is given by (Treybal, 1980)

$$N_A = \Psi_A \frac{PD_{AB,eff}}{RTl} \ln\left[\frac{\Psi_A\left(1 + \frac{D_{AB,eff}}{D_{K,A,eff}}\right) - y_{A2}}{\Psi_A\left(1 + \frac{D_{AB,eff}}{D_{K,A,eff}}\right) - y_{A1}}\right] \tag{1-109}$$

Further, for open-ended pores, the bootstrap relation given by equation (1-106) for constant total pressure applies throughout the transition range for solids whose pore diameters are of the order of 10 μm or less (Treybal, 1980).

Example 1.22 Combined Molecular and Knudsen Diffusion in Porous Solid

Repeat Example 1.21 for an average pore diameter of 0.3 μm, while the porosity

and tortuosity remain unchanged. At the temperature of 293 K and pressure of 0.1 atm, D_{AB} = 2.01 cm^2/s.

Solution

For a pore diameter of 0.3 μm, Kn = 2.27, which means that both molecular and Knudsen diffusion are important and equation (1-109) must be used to calculate N_A. Since the pore diameter is less than 10 μm, the bootstrap relation of equation (1-106) applies:

$$\Psi_A = \frac{N_A}{N_A + N_B} = \frac{1}{1 + N_B / N_A} = \frac{1}{1 - 1.069} = -14.49$$

From equation (1-100),

$$D_{AB,eff} = \frac{2.01 \times 0.305}{4.39} = 0.14 \ \frac{\text{cm}^2}{\text{s}}$$

From equation (1-103), $D_{K,A}$ = 0.440 cm^2/s; from equation (1-107), $D_{K,A,eff}$ = 0.031 cm^2/s. Then, $D_{AB,eff}/D_{K,A,eff}$ = 0.14/0.031 = 4.57. From equation (1-109):

$$N_A = \frac{-14.49\left(1.4 \times 10^{-5}\right)\left(10{,}130\right)}{8.314\left(293\right)\left(0.002\right)} \ln\left[\frac{-14.49\left(1 + 4.57\right) - 0.2}{-14.49\left(1 + 4.57\right) - 0.8}\right]$$

$$= 3.11 \times 10^{-3} \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$$

$$N_B = -1.069 N_A = -3.32 \times 10^{-3} \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$$

Knudsen diffusion is not known for liquids, but important reductions in diffusion rates occur when the molecular size of the diffusing solute, d_m, becomes significant relative to the pore size of the solid. In that case, the effective diffusivity is given by (Seader and Henley, 2006)

$$D_{AB,eff} = \frac{\varepsilon D_{AB}}{\tau} K_r \qquad (1\text{-}110)$$

where K_r is a restrictive factor that accounts for interfering collisions of the diffusing solute with the pore wall, and is given by

$$K_r = \left[1 - \frac{d_m}{d}\right]^4 \qquad \frac{d_m}{d} \le 1.0 \tag{1-111}$$

Example 1.23 Dextrin Diffusion in a Porous Membrane

Beck and Schultz (1972) measured the effective diffusivity of several sugars in aqueous solutions through microporous membranes of mica. One of the sugars studied was β-dextrin. Dextrins are a group of low-molecular-weight carbohydrates produced by the hydrolysis of starch. They have the same general formula as carbohydrates but are of shorter chain length. Dextrins find widespread use in industry, due to their non-toxicity and low price. They are used as water-soluble glues, as thickening agents in food processing, and as binding agent in pharmaceuticals. The membrane used by Beck and Schultz (1972) had an average pore diameter of 88.8 Å, tortuosity of 1.1, and a porosity of 2.33%. The molecular diameter of β-dextrin is 17.96 Å, and its diffusivity in dilute aqueous solution at 298 K is 3.22×10^{-6} cm^2/s. Estimate the effective diffusivity of β-dextrin through this membrane at 298 K.

Solution

Calculate the restrictive factor and effective diffusivity from equations (1-111) and (1-110), respectively:

$$K_r = \left[1 - \frac{17.96}{88.8}\right]^4 = 0.405$$

$$D_{AB,eff} = \frac{0.0233\left(3.22 \times 10^{-6}\right)\left(0.405\right)}{1.1} = 2.78 \times 10^{-8} \text{ cm}^2/\text{s}$$

1.5.3 Hydrodynamic Flow of Gases in Porous Solids

If there is a difference in total pressure across a porous solid, a hydrodynamic flow of gas through the solid will occur. Consider a solid consisting of uniform straight capillary tubes of diameter d and length l reaching from the high- to low-pressure side. In most practical applications, the flow inside the capillaries will be laminar. For a single gas, this can be described by Poiseuille's law for compressible fluids obeying the ideal gas law:

$$N_A = \frac{d^2 P_{av}\left(P_1 - P_2\right)}{32\mu RTl} \tag{1-112}$$

where $P_{av} = (P_1 + P_2)/2$. This assumes that the entire pressure difference is the result of friction in the pores and ignores entrance and exit losses and kinetic-energy effects, which is satisfactory for present purposes. Since usually the pores are neither straight nor of constant diameter, it is best to base N_A on the gross external cross-sectional area of the solid and write equation (1-112) as

$$N_A = \frac{B_0 P_{av}\left(P_1 - P_2\right)}{\mu R T l} \tag{1-113}$$

where B_0 is an empirical factor characterizing the porous solid called the *viscous flow parameter* (Do, 1998).

When the gas is a mixture, the hydrodynamic flux given by equations (1-112) or (1-113) is the flux of the mixture, that is, the mixture moves as a whole under the total pressure gradient. All species move at the same speed (that is, no separation is achieved) and the individual flux of each component is the product of its mol fraction times the total flux. In that case, the viscosity in equations (1-112) and (1-113) is the viscosity of the mixture. If the gas is a mixture with different concentrations and different total pressure on either side of the porous solid, the flow may be a combination of hydrodynamic, Knudsen, and diffusive.

Example 1.24 Hydrodynamic Flow in a Porous Diaphragm

A porous carbon diaphragm 25.4 mm thick of average pore diameter 0.01 cm allowed the flow of nitrogen at the rate of 0.05 m^3 (measured at 300 K and 1 atm)/m^2·s with a pressure difference across the diaphragm of 500 Pa. The temperature was 300 K and the downstream pressure 0.1 atm. The viscosity of nitrogen at 300 K is 180 μP.

(a) Estimate the value of the viscous flow parameter, B_0, for this solid.

(b) Calculate the nitrogen flow to be expected at 400 K with the same pressure difference. At 400 K, the viscosity of nitrogen is 220 μP.

Solution

(a) From the information given, P_2 = 10,130 Pa, P_1 = 10,630 Pa, P_{av} = 10,380 Pa. At the average pressure and the temperature of 300 K, the mean free path for nitrogen is estimated from equation (1-102) to be λ = 0.622 μm. For a pore diameter of 0.01 cm, this corresponds to a Knudsen number, Kn = 6.22×10^{-3}. Therefore, Knudsen diffusion will not occur and all the flow observed is of a hydrodynamic nature.

From the ideal gas law, the nitrogen flux corresponding to the volumetric flow rate of 0.05 m^3/m^2·s at 300 K and 1 atm is 2.031 mol/m^2·s. Equation (1-113) is solved for B_0 and numerical values are substituted:

$$B_0 = \frac{1.8\times10^{-5}\left(8.314\right)\left(300\right)\left(2.031\left(0.0254\right)\right)}{\left(10,380\right)\left(500\right)}$$
$$= 4.462\times10^{-10}\ \text{m}^2$$

(b) At 393 K, the viscosity of nitrogen is 220 μP. Substituting in equation (1-113) the new values of temperature and viscosity and the value of B_0 obtained in part (a), while maintaining the pressure conditions unchanged, N_A = 1.269 mol/m^2·s. This corresponds to a volumetric flow rate of 0.041 m^3 (measured at 300 K and 1 atm)/m^2·s.

1.5.4 "Dusty Gas" Model for Multicomponent Diffusion

Modeling multicomponent gaseous diffusion in porous media depends upon the value of the Knudsen number. For very large pores, corresponding to very small values of Kn, the MS equations (1-34) can be used with effective binary diffusivities given by

$$D_{ij,eff} = \frac{\varepsilon D_{ij}}{\tau} \tag{1-114}$$

For very small pores, corresponding to very large values of Kn, Knudsen diffusion prevails and the flux of each individual component is calculated using equations (1-103) to (1-108). In either case, if there is a significant difference in total pressure across the solid, the hydrodynamic flow contribution must be added.

Modeling multicomponent diffusion in porous media is complicated when the mean free path of the molecules is of the order of magnitude of the pore diameter. The difficulties posed by this intermediate case may be circumvented by a method originally proposed by Maxwell in 1866. He suggested that the porous material be described as a supplementary "dust" species consisting of very large molecules that are kept motionless by some unspecified external force. The Chapman–Enskog kinetic theory is then applied to the new pseudo gas mixture, whereby the interaction between the dust and gas molecules simulates the interaction between the solid matrix and the gas species. In this way, one is no longer faced with the problem of flux and composition variations across a pore and problems related to the solid geometry.

The price paid for this simplification is that certain physical features of the porous medium are "lost." One of the more important issues is that the model is no longer dealing with channels of finite size corresponding to the pores in the real medium. Thus, there is no introduction of the hydrodynamic fluxes in the formal development of the equations. These have to be added empirically. The working form of the "dusty ideal gas" model equations is (Higler et al., 2000):

$$\frac{P}{RT}\nabla y_i + \frac{y_i}{RT}\left(1 + \frac{B_0 P}{\mu D_{K,i,eff}}\right)\nabla P = \sum_{j=1}^{n} \frac{y_i N_j - y_j N_i}{D_{ij,eff}} - \frac{N_i}{D_{K,i,eff}} \quad i = 1,\ldots,n \quad \text{(1-115)}$$

Notice that equation (1-115) can be written for all the n components, unlike the original MS equations which are valid for only $(n - 1)$ components. However, another variable, the total pressure, has been added. Therefore, a bootstrap relation between the fluxes is still needed to complete the problem formulation.

An explicit expression for the total pressure gradient can be obtained from equation (1-115) by summing with respect to all components:

$$\frac{\nabla P}{RT} = -\frac{\sum_{i=1}^{n} \frac{N_i}{D_{K,i,eff}}}{1 + \frac{B_0 P}{\mu} \sum_{i=1}^{n} \frac{1}{D_{K,i,eff}}} \quad \text{(1-116)}$$

Equation (1-116) can be substituted into (1-115), written for $(n - 1)$ components, to eliminate the total pressure gradient from those equations. The resulting $(n - 1)$ equations are then augmented with equation (1-116) and the bootstrap condition to solve for the n fluxes and the total pressure gradient. The resulting boundary-value problem can be solved by modifying the Mathcad program developed in Examples 1.17 and 1.18.

1.6 DIFFUSION WITH HOMOGENEOUS CHEMICAL REACTION

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

1. Define the concept of homogeneous chemical reaction and learn to incorporate it into the continuity equation.
2. Define the Damkohler number for first-order chemical reaction and ascertain its effect on mass-transfer rates.
3. Derive the Krogh model for oxygen transport in skeletal muscle with Michaelis–Menten chemical reaction kinetics.

In many processes, diffusion rates are altered by homogeneous chemical reactions. A homogeneous reaction is one that takes place in solution. In that case, the R_A term in equation (1-64), representing the volumetric rate of formation of component A by chemical reaction, is different from zero. The following examples illustrate some of the effects of homogeneous chemical reactions on mass-transfer rates.

Example 1.25 Mass Transfer with First-Order Chemical Reaction

A liquid is in contact with a well-mixed gas containing substance A to be absorbed. Near the surface of the liquid there is a film of thickness δ across which A diffuses steadily while being consumed by a first-order homogeneous chemical reaction with a rate constant k_1. At the gas–liquid interface, the liquid solution is in equilibrium with the gas and its concentration is c_{Ai}; at the other side of the film, its concentration is virtually zero. Assuming dilute solutions, derive an expression for the ratio of the absorption flux with chemical reaction to the corresponding flux without chemical reaction.

Solution

Let us first determine the one-dimensional steady-state absorption flux of component A (that is, at the gas–liquid interface, $z = 0$) without chemical reaction. From the equation of continuity, assuming that the bulk-motion contribution to the flux is negligible for dilute solutions:

$$\frac{d^2c_A}{dz^2} = 0 \qquad c_A(z) = c_{Ai}\left(1 - \frac{z}{\delta}\right)$$

$$N_A\Big|_{z=0} = N_A = -D_{AB}\frac{dc_A}{dz} = \frac{c_{Ai}D_{AB}}{\delta}$$

For one-dimensional steady-state diffusion including a first-order homogeneous reaction, neglecting the bulk-motion contribution, the equation of continuity becomes

$$\frac{dN_A^1}{dz} = -k_1c_A \qquad N_A^1 = -D_{AB}\frac{dc_A}{dz}$$

$$\frac{d^2c_A}{dz^2} - \frac{k_1}{D_{AB}}c_A = 0$$

where $N_A{}^1$ is the flux in the presence of a first-order reaction. The second-order differential equation describing the concentration profile is easily solved substituting in it the trial solution e^{mz}, solving the resulting characteristic equation for the values of m, and applying the boundary conditions (Perry and Chilton, 1973). The complete solution is

$$c_A(z) = c_{Ai}\frac{\sinh\left(\sqrt{\frac{k_1}{D_{AB}}}(\delta - z)\right)}{\sinh\left(\sqrt{\frac{k_1}{D_{AB}}}\delta\right)}$$

Evaluate $N_A{}^1$ from the expression for the concentration profile:

$$N_A^1 = -D_{AB}\frac{dc_A}{dz} = c_{Ai}\sqrt{k_1 D_{AB}}\,\frac{\cosh\left[\sqrt{k_1/D_{AB}}(\delta - z)\right]}{\sinh\left(\sqrt{k_1/D_{AB}}\delta\right)}$$

The absorption flux at the gas–liquid interface ($z = 0$) is, then

$$N_A^1\Big|_{z=0} = c_{Ai}\sqrt{k_1 D_{AB}}\coth\left[\sqrt{k_1/D_{AB}}\delta\right]$$

Therefore, the ratio of absorption flux with chemical reaction to absorption flux without reaction is given by

$$\frac{N_A^1\Big|_{z=0}}{N_A\Big|_{z=0}} = \frac{c_{Ai}\sqrt{k_1 D_{AB}}\coth\left[\sqrt{k_1/D_{AB}}\delta\right]}{c_{Ai}D_{AB}/\delta} = \sqrt{\frac{k_1\delta^2}{D_{AB}}}\coth\left(\sqrt{\frac{k_1\delta^2}{D_{AB}}}\right)$$

Define the *Damkohler number for first-order reaction*, $\mathrm{Da} = k_1\delta^2/D_{AB}$. Then,

$$\frac{N_A^1\Big|_{z=0}}{N_A\Big|_{z=0}} = \sqrt{\mathrm{Da}}\coth\left[\sqrt{\mathrm{Da}}\right]$$

This is the desired result. Two limits are instructive. First, when the reaction is slow, Da is small and the series expansion for coth (x) can be truncated to include only the first two terms, giving

$$\frac{N_A^1\Big|_{z=0}}{N_A\Big|_{z=0}} = \sqrt{\mathrm{Da}}\left[\frac{1}{\sqrt{\mathrm{Da}}} + \frac{\sqrt{\mathrm{Da}}}{3} - \frac{\left(\sqrt{\mathrm{Da}}\right)^3}{45} + \cdots\right] \approx 1 + \frac{\mathrm{Da}}{3}$$

Second, when the chemical reaction is very fast, Da is large and, since coth (x) approaches 1.0 for large values of x,

$$\frac{N_A^1\Big|_{z=0}}{N_A\Big|_{z=0}} = \sqrt{\mathrm{Da}}$$

Example 1.26 Oxygen Transport in Skeletal Muscle: Krogh Model

In 1922, August Krogh proposed that oxygen was transported from capillaries to surrounding tissue by passive diffusion. He formulated a simple geometric model to describe this phenomenon. The Krogh model is a simplification of a capillary bed; a group of parallel identical units, each containing a central capillary and a surrounding cylinder of tissue, as shown in Figure 1.11. The goal of the Krogh model is to predict the concentration of oxygen as a function of position within the tissue cylinder. Each tissue cylinder is assumed to be supplied with oxygen exclusively by the capillary within it. Oxygen diffusion in the axial direction is neglected, as evidenced by the fact that the oxygen concentration gradient is much steeper in the radial direction than in the axial direction.

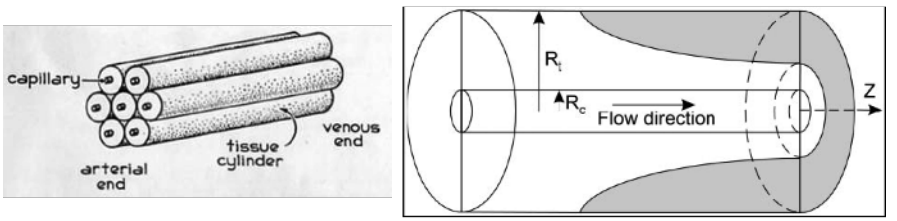


Figure 1.11 Geometry of the Krogh cylinder-type model. Inner cylinder represents the capillary. Outer cylinder corresponds to tissue cylinder. Shaded area: example of hypoxic region under conditions of high demand. R_t, tissue cylinder radius; R_c, capillary radius; z, distance along the capillary. (McGuire and Secomb, 2001. Reproduced with permission of the American Physiological Society.)

Applying Fick's law of diffusion in the radial direction ($R_c \le r \le R_t$) and conservation of mass lead to the following equation for oxygen diffusion in muscle tissue (McGuire and Secomb, 2001.):

$$D_{AB,eff}\left[\frac{1}{r}\frac{d}{dr}\left(r\frac{dc_A}{dr}\right)\right] = R_A\left(c_A\right) \tag{1-117}$$

where c_A is the oxygen concentration in tissue. In studies of oxygen transport, it is customary to express the concentration in tissue in terms of an equivalent oxygen partial pressure, $p_A = Hc_A$, where H is a modified form of Henry's law constant. Then, equation (1-117) can be written in terms of the oxygen partial pressure in tissue as

$$K\left[\frac{1}{r}\frac{d}{dr}\left(r\frac{dp_A}{dr}\right)\right] = M(p_A) \qquad R_c \le r \le R_t \tag{1-118}$$

where K (known as the *Krogh diffusion coefficient*) = $D_{AB,eff}/H$, and $M(p_A)$ is the oxygen consumption rate per unit volume of the tissue cylinder. Oxygen consumption in skeletal muscle is usually assumed to follow *Michaelis–Menten kinetics*, a model that describes the kinetics of many enzymatic reactions, given by

$$M\left(p_A\right) = \frac{M_0 p_A}{p_0 + p_A} \tag{1-119}$$

where M_0 is the oxygen demand (i.e., the consumption when the oxygen supply is not limiting) and p_0 is the partial pressure of oxygen when consumption is half of the demand. The Michaelis–Menten equation reduces to first-order kinetics for values of p_A much smaller than p_0, and to zero-order kinetics for values of p_A much larger than p_0. For the purpose of this example, we will assume zero-order kinetics; therefore, $M(p_A) = M_0$.

The two boundary conditions needed to solve equation (1-118) are:

1. Neglecting the oxygen-diffusion resistance of the capillary wall, at the capillary–tissue interface, the oxygen partial pressure in the tissue is approximately equal to the average partial pressure of oxygen within the blood, $p_{A,b}$; that is, $p_A(R_c) = p_{A,b}$.
2. It is assumed that no oxygen is exchanged across the outer boundary of the tissue cylinder, so that

$$\left.\frac{dp_A}{dr}\right|_{R_t} = 0$$

The complete solution for zero-order kinetics is

$$p_A(r) = p_{A,b} + \frac{M_0}{4K}\left(r^2 - R_c^2\right) - \frac{M_0 R_t^2}{2K}\ln\left(\frac{r}{R_c}\right) \qquad R_c \le r \le R_t \quad \text{(1-120)}$$

Equation (1-120) can be used to predict whether, under a given set of parameters, there are *hypoxic regions*—where the partial pressure of oxygen is less than 1 torr—in the tissue cylinder. Table 1.3 summarizes parameter values used in the Krogh model.

To illustrate the use of equation (1-120), we use the parameters of Table 1.3, with an oxygen consumption of 0.4 cm^3 O^2/cm^3·min, and estimate that the lowest oxygen partial pressure in the tissue surrounding the capillary entrance is 49.9 torr at $r = R_t$. Therefore, all the tissue at this position is exposed to a healthy oxygen concentration with no hypoxic regions. Moreover, since p_A is everywhere much higher than p_0, the assumption of zero-order kinetics is validated.

However, as blood flows along the capillary, oxygen is extracted by the tissue and the oxygen partial pressure in the blood declines rapidly. The oxygen partial pressure in the tissue also declines rapidly and a point is reached where zero-order kinetics no longer applies. The complete form of the Michaelis–Menten equation must be used, requiring a numerical solution of equation (1-118). McGuire and Secomb (2001) showed numerically that, under the set of conditions considered in this example, as much as 37% of the tissue was hypoxic.

Table 1.3 Parameter Values in Krogh Model

Parameter	Value
Partial pressure of oxygen within the blood at capillary entrance, $p_{A,b}$	100 torr
Krogh diffusion constant in tissue, K	9.4×10^{-10} $cm^2/s{\cdot}torr$
Oxygen demand, M_0	0–0.80 cm^3 $O_2/cm^3{\cdot}min$
Half-maximal oxygen consumption pressure, p_0	1 torr
Capillary radius, R_c	2.5 μm
Tissue cylinder radius, R_t	26 μm
Capillary length, L	500 μm

Source: Data from McGuire and Secomb (2001).

1.7 ANALOGIES AMONG MOLECULAR TRANSFER PHENOMENA

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

1. Identify the analogies among molecular momentum, heat, and mass transfer for the simple case of fluid flow past a flat plate.
2. Define and interpret the following dimensionless numbers: Schmidt, Prandtl, and Lewis.

In the flow of a fluid past a phase boundary, there will be a velocity gradient within the fluid which results in a transfer of momentum through it. In some cases, there is also a transfer of heat by virtue of a temperature gradient. The processes of momentum, heat, and mass transfer under these conditions are intimately related, and it is useful to consider at this point the analogies among them.

Consider the velocity profile for the case of a fluid flowing past a stationary flat plate. Since the velocity at the solid surface is zero, there must necessarily be a sublayer adjacent to the surface where the flow is predominantly laminar. Within this region, the shearing stress t required to maintain the velocity gradient is given by

$$\tau = -\mu \frac{du}{dz} \tag{1-121}$$

where u is the fluid velocity parallel to the surface, and z is measured as increasing toward the surface. This can be written as

$$\tau = -\frac{\mu}{\rho} \frac{d(u\rho)}{dz} = -\nu \frac{d(u\rho)}{dz} \tag{1-122}$$

where ν is the *kinematic viscosity*, μ/ρ, also known as the *momentum diffusivity*.

The kinematic viscosity has the same dimensions as the mass diffusivity, length^2/time, while the quantity $u\rho$ can be interpreted as a volumetric momentum concentration. The shearing stress τ may also be interpreted as a viscous momentum flux towards the solid surface. Equation (1-122) is, therefore, a rate equation analogous to Fick's first law, equation (1-40). The *Schmidt number* is defined as the dimensionless ratio of the momentum and mass diffusivities:

$$\mathrm{Sc} = \frac{\mu}{\rho D_{AB}} \tag{1-123}$$

When a temperature gradient exists between the fluid and the plate, the rate of heat transfer in the laminar region is

$$q = -k\frac{dT}{dz} \tag{1-124}$$

where k is the thermal conductivity of the fluid. This can also be written as

$$q = -\frac{k}{\rho C_p}\frac{d\left(\rho C_p T\right)}{dz} = -\alpha\frac{d\left(\rho C_p T\right)}{dz} \tag{1-125}$$

where C_p is the specific heat at constant pressure. The quantity $TC_p\rho$ may be looked upon as a volumetric thermal concentration, and $\alpha = k/C_p\rho$ is the thermal diffusivity, which, like the momentum and mass diffusivities, has dimensions of length^2/time. Equation (1-125) is therefore a rate equation analogous to the corresponding equations for momentum and mass transfer.

The *Prandtl number* is defined as the dimensionless ratio of the momentum and thermal diffusivities:

$$\mathrm{Pr} = \frac{\nu}{\alpha} = \frac{C_p\mu}{k} \tag{1-126}$$

A third dimensionless group, the *Lewis number*, is formed by dividing the thermal by the mass diffusivity:

$$\mathrm{Le} = \frac{\alpha}{D_{AB}} = \frac{\mathrm{Sc}}{\mathrm{Pr}} \tag{1-127}$$

The Lewis number plays an important role in problems of simultaneous heat and mass transfer, such as humidification operations.

An elementary consideration of the processes of momentum, heat, and mass transfer leads to the conclusion that in certain simplified situations there is a direct analogy between them. In general, however, modification of the simple analogy is necessary when mass and momentum transfer occur simultaneously. Nevertheless, even the limited analogies which exist are put to important practical use, as will be seen in Chapter 2.

PROBLEMS

The problems at the end of each chapter have been grouped into four classes (designated by a superscript after the problem number).

Class a: Illustrates direct numerical application of the formulas in the text.
Class b: Requires elementary analysis of physical situations, based on the subject material in the chapter.
Class c: Requires somewhat more mature analysis.
Class d: Requires computer solution.

1.1[a]. Concentration of a gas mixture

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^3

1.2[a]. Concentration of liquid solution fed to a distillation column

A solution of carbon tetrachloride and carbon disulfide containing 50% by weight of each is to be continuously distilled at the 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

1.3[a]. Concentration of liquefied natural gas

A sample of liquefied natural gas, LNG, from Alaska has the following molar

composition: 93.5% CH_4, 4.6% C_2H_6, 1.2% C_3H_8, and 0.7% CO_2. Calculate:

(a) Average molecular weight of the LNG mixture.

(b) Weight fraction of CH_4 in the mixture.

Answer: 87.11%

(c) The LNG is heated to 320 K and 140 kPa, and vaporizes completely. Estimate the density of the gas mixture under these conditions.

Answer: 0.904 kg/m^3

1.4[b]. Concentration of a flue gas

A flue gas consists of carbon dioxide, oxygen, water vapor, and nitrogen. The *molar* fractions of CO_2 and O_2 in a sample of the gas are 12% and 6%, respectively. The *weight* fraction of H_2O in the gas is 6.17%. Estimate the density of this gas at 500 K and 110 kPa.

Answer: 0.772 kg/m^3

1.5[b]. Material balances around an ammonia gas absorber

A gas stream flows at the rate of 10.0 m^3/s at 300 K and 102 kPa. It consists of an equimolar mixture of ammonia and air. The gas enters through the bottom of a packed-bed gas absorber, where it flows countercurrent to a stream of pure liquid water that absorbs 95% of all of the ammonia, and virtually no air. The absorber vessel is cylindrical with an internal diameter of 2.2 m.

(a) Neglecting the evaporation of water, calculate the ammonia mol fraction in the gas leaving the absorber.

(b) Calculate the outlet gas mass velocity (defined as mass flow rate per unit empty tube cross-sectional area).

Answer: 1.61 kg/m^2·s

1.6[b]. Velocities and fluxes in a gas mixture

A gas mixture at a total pressure of 150 kPa and 295 K contains 20% H_2, 40% O_2, and 40% H_2O by volume. The absolute velocities of each species are –10 m/s, –2 m/s, and 12 m/s, respectively, all in the direction of the z-axis.

(a) Determine the mass average velocity, **v**, and the molar average velocity, **V**, for

the mixture.

(b) Evaluate the four fluxes: $\boldsymbol{j}_{O_2}$, $\boldsymbol{n}_{O_2}$, $\boldsymbol{J}_{O_2}$, $\boldsymbol{N}_{O_2}$.

Answer: $\boldsymbol{j}_{O_2} = -3.74$ kg/m^2·s

1.7[b]. Properties of air saturated with water vapor

Air, stored in a 30-m^3 container at 340 K and 150 kPa, is saturated with water vapor. Determine the following properties of the gas mixture:

(a) Mol fraction of water vapor.

(b) Average molecular weight of the mixture.

(c) Total mass contained in the tank.

(d) Mass of water vapor in the tank

Answer: 5.22 kg

1.8[c]. Water balance around an industrial cooling tower

The cooling water flow rate to the condensers of a big coal-fired power plant is 8970 kg/s. The water enters the condensers at 29 °C and leaves at 45 °C. From the condensers, the water flows to a cooling tower, where it is cooled down back to 29 °C by countercurrent contact with air (see Figure 1.12). The air enters the cooling tower at the rate of 6500 kg/s of dry air, at a dry-bulb temperature of 30 °C, pressure of 1 atm, and a humidity of 0.016 kg of water/kg of dry air. It leaves the cooling tower saturated with water vapor at 38 °C.

(a) Calculate the water losses by evaporation in the cooling tower.

(b) To account for water losses in the cooling tower, part of the effluent from a nearby municipal wastewater treatment plant will be used as makeup water. This makeup water contains 500 mg/L of dissolved solids. To avoid fouling of the condenser heat-transfer surfaces, the circulating water is to contain no more than 2000 mg/L of dissolved solids. Therefore, a small amount of the circulating water must be deliberately discarded (blowdown). Windage losses from the tower are estimated at 0.2% of the recirculation rate. Estimate the makeup-water requirement.

Answer: 238 kg/s

1.9[b]. Water balance around a soap dryer

It is desired to dry 10 kg/min of soap continuously from 20% moisture by weight to 4% moisture in a countercurrent stream of hot air. The air enters the

dryer at the rate of 30.0 m^3/min at 350 K, 101.3 kPa, and initial water-vapor partial pressure of 2 kPa. The dryer operates at constant temperature and pressure.

(a) Calculate the moisture content of the entering air, in kg of water/kg of dry air.

(b) Calculate the flow rate of dry air, in kg/min.

(c) Calculate the water-vapor partial pressure and relative humidity in the air leaving the dryer.

Answer: 24.7% relative humidity

1.10[b]. Activated carbon adsorption; material balances

A waste gas contains 0.5% toluene in air and occupies a volume of 2500 m^3 at 298 K and 101.3 kPa. In an effort to reduce the toluene content of this gas, it is exposed to 100 kg of activated carbon, initially free of toluene. The system is allowed to reach equilibrium at constant temperature and pressure.

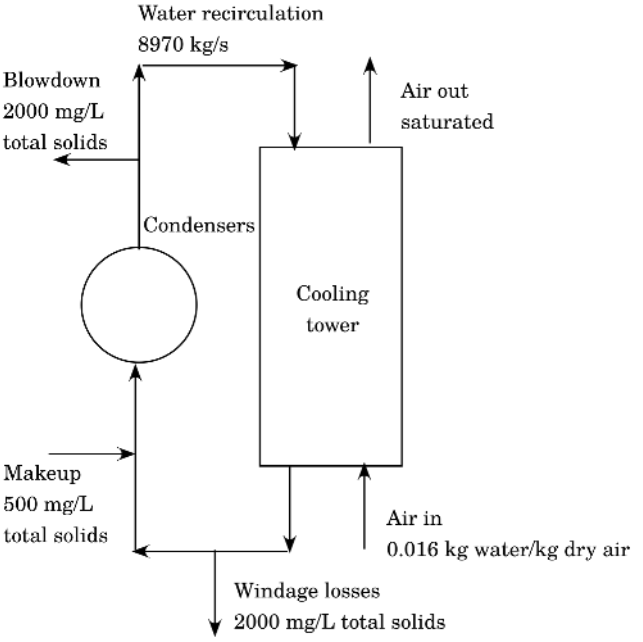


Figure 1.12 Flowsheet for Problem 1.8.

Assuming that the air does not adsorb on the carbon, calculate the equilibrium concentration of toluene in the gaseous phase, and the amount of toluene adsorbed by the carbon. The adsorption equilibrium for this system is given by the Freundlich isotherm (USEPA, 1987):

$$W = 0.208\left(p^*\right)^{0.11}$$

where W is the carbon equilibrium adsorptivity, in kg of toluene/kg of carbon, and p^* is the equilibrium toluene partial pressure, in Pa, and must be between 0.7 and 345 Pa.

1.11[b]. Activated carbon adsorption; material balances

It is desired to adsorb 99.8% of the toluene originally present in the waste gas of Problem 1.10. Estimate how much activated carbon should be used if the system is allowed to reach equilibrium at constant temperature and pressure.

Answer: 225 kg

1.12[a, d]. Estimation of gas diffusivity by the Wilke–Lee equation

Larson (1964) measured the diffusivity of chloroform in air at 298 K and a pressure of 1 atm and reported its value as 0.093 cm^2/s. Estimate the diffusion coefficient by the Wilke–Lee equation and compare it with the experimental value.

1.13[a, d]. Estimation of gas diffusivity by the Wilke–Lee equation

(a) Estimate the diffusivity of naphthalene ($C_{10}H_8$) in air at 303 K and 1 bar. Compare it with the experimental value of 0.087 cm^2/s reported in Appendix A. The normal boiling point of naphthalene is 491.1 K, and its critical volume is 413 cm^3/mol.

Answer: Error = –20.1%

(b) Estimate the diffusivity of pyridine (C_5H_5N) in hydrogen at 318 K and 1 atm. Compare it with the experimental value of 0.437 cm^2/s reported in Appendix A. The normal boiling point of pyridine is 388.4 K, and its critical volume is 254 cm^3/mol.

Answer: Error = –9.9%

(c) Estimate the diffusivity of aniline (C_6H_7N) in air at 273 K and 1 atm. Compare it with the experimental value of 0.061 cm^2/s (Guilliland, 1934). The normal boiling point of aniline is 457.6 K, and its critical volume is 274 cm^3/mol.

Answer: Error = 15.1%

1.14[d]. Diffusivity of polar gases

If one or both components of a binary gas mixture are polar, a modified Lennard–Jones relation is often used. Brokaw (1969) has suggested an alternative method for this case. Equation (1-49) is used, but the collision integral is now given by

$$\Omega_D = \Omega_D\left[\text{Eq.}(1-44)\right] + \frac{0.19\delta_{AB}^2}{T^*} \tag{1-128}$$

where

$$\delta = \frac{1.94\times10^{-3}\mu_p^2}{V_b T_b} \tag{1-129}$$

μ_p = dipole moment, debye [1 debye = 3.162×10^{-25} $(J\cdot m^3)^{1/2}$]

$$\frac{\varepsilon}{\kappa} = 1.18\left(1+1.3\delta^2\right)T_b \tag{1-130}$$

$$\sigma = \left[\frac{1.585V_b}{1+1.3\delta^2}\right]^{1/3} \tag{1-131}$$

$$\delta_{AB} = \sqrt{\delta_A\delta_B} \qquad \sigma_{AB} = \sqrt{\sigma_A\sigma_B} \qquad \frac{\varepsilon_{AB}}{\kappa} = \sqrt{\frac{\varepsilon_A}{\kappa}\frac{\varepsilon_B}{\kappa}} \tag{1-132}$$

(a) Modify the Mathcad routine of Figure 1.3 to implement Brokaw's method.

(b) Estimate the diffusion coefficient for a mixture of methyl chloride and sulfur dioxide at 1 bar and 323 K, and compare it to the experimental value of 0.078 cm^2/s. The data required to use Brokaw's relation are shown below (Reid et al., 1987):

Parameter	Methyl chloride	Sulfur dioxide
T_b , K	249.1	263.2
V_b , cm^3/mol	50.6	43.8
μ_p, debyes	1.9	1.6
M	50.5	64.1

Answer: Error = 7.8%

1.15[d]. Diffusivity of polar gases

Evaluate the diffusion coefficient of hydrogen chloride in water at 420 K and 1.2 bar. The data required to use Brokaw's relation (see Problem 1.14) are shown below (Reid et al., 1987):

Parameter	Hydrogen chloride	Water
T_b , K	188.1	373.2
V_b , cm^3/mol	30.6	18.9
μ_p, debyes	1.1	1.8
M	36.5	18.0

Answer: 0.283 cm^2/s

1.16[d]. Diffusivity of polar gases

Evaluate the diffusion coefficient of hydrogen sulfide in sulfur dioxide at a temperature of 298 K and a pressure of 1.5 bar. The data required to use Brokaw's relation (see Problem 1.14) are shown below (Reid et al., 1987):

Parameter	Hydrogen sulfide	Sulfur dioxide
T_b , K	189.6	263.2
V_b , cm^3/mol	35.03	43.8
μ_p, debyes	0.9	1.6
M	34.08	64.06

Answer: 0.065 cm^2/s

1.17[a,d]. Effective diffusivity in a multicomponent stagnant gas mixture

Calculate the effective diffusivity of nitrogen through a stagnant gas mixture at 400 K and 1.5 bar. The mixture composition is:

O_2	15 mol %
CO	30%
CO_2	35%
N_2	20%

Answer: 0.216 cm^2/s

1.18[a,d]. Mercury removal from flue gases by sorbent injection

Mercury is considered for possible regulation in the electric power industry under Title III of the 1990 Clean Air Act Amendments. One promising approach for removing mercury from fossil-fired flue gas involves the direct injection of activated carbon into the gas. Meserole et al. (1999) describe a theoretical model for estimating mercury removal by the sorbent injection process. An important parameter of the model is the effective diffusivity of mercuric chloride vapor traces in the flue gas. If the flue gas is at 1.013 bar and 408 K, and its composition (on a mercuric chloride-free basis) is 6% O_2, 12% CO_2, 7% H_2O, and 75% N_2, estimate the effective diffusivity of mercuric chloride in the flue gas. Assume that only the $HgCl_2$ is adsorbed by the activated carbon. Meserole et al. reported an effective diffusivity value of 0.22 cm^2/s.

Answer: 0.156 cm^2/s

1.19[b]. Diffusion in electrolyte solutions

When a salt dissociates in solution, ions rather than molecules diffuse. In the absence of an electric potential, the diffusion of a single salt may be treated as molecular diffusion. For dilute solutions of a *single salt*, the diffusion coefficient is given by the Nernst–Haskell equation (Harned and Owen, 1950):

$$D_{AB}^{0} = \frac{RT\left[\left(1/n_{+}\right)+\left(1/n_{-}\right)\right]}{\mathrm{F}^{2}\left[\left(1/\lambda_{+}^{0}\right)+\left(1/\lambda_{-}^{0}\right)\right]} \tag{1-133}$$

where

D_{AB}^{0} = diffusivity at infinite dilute solution, based on molecular concentration, cm^2/s

R = gas constant, 8.314 J/mol·K

T = temperature, K

$\lambda_{+}^{0}, \lambda_{-}^{0}$ = limiting (zero concentration) ionic conductances, $(A/cm^2)(V/cm)(g\text{-}equiv/cm^3)$

n_+, n_- = valences of cation and anion, respectively

F = Faraday's constant = 96,500 C/g-equiv

Values of limiting ionic conductances for some ionic species at 298 K are included in Table 1.4. If conductance values at other temperatures are needed, an approximate correction factor is $T/(334\mu_W)$, where μ_W is the viscosity of water at T, in cP.

(a) Estimate the diffusion coefficient at 298 K for a very dilute solution of HCl in water.

Answer: 3.33×10^{-5} cm^2/s

(b) Estimate the diffusion coefficient at 273 K for a very dilute solution of $CuSO_4$ in water. The viscosity of liquid water at 273 K is 1.79 cP.

Answer: 3.59×10^{-6} cm^2/s

Table 1.4 Limiting Ionic Conductances in Water at 298

Anion	λ_-^0	Cation	λ_+^0
OH^-	197.6	H^+	349.8
Cl^-	76.3	Li^+	38.7
Br^-	78.3	Na^+	50.1
NO_3^-	71.4	NH_4^+	73.4
HCO_3^-	44.5	Mg^{2+}	53.1
$CH_3CO_2^-$	40.9	Ca^{2+}	59.5
SO_4^{2-}	80.0	Cu^{2+}	54.0
$C_2O_4^{2-}$	74.2	Zn^{2+}	53.0

Units: (A × cm^2)/(V × g-equiv).

Source: Data from Harned and Owen (1950).

1.20[a]. Oxygen diffusion in water: Hayduk and Minhas correlation

Estimate the diffusion coefficient of oxygen in liquid water at 298 K. Use the Hayduk and Minhas correlation for solutes in aqueous solutions. At this temperature, the viscosity of water is 0.9 cP. The critical volume of oxygen is 73.4 cm^3/mol. The experimental value of this diffusivity was reported as 2.1×10^{-5} cm^2/s (Cussler, 1997).

Answer: Error = –8.1%

1.21[a, d]. Liquid diffusivity: Hayduk and Minhas correlation

Estimate the diffusivity of carbon tetrachloride in a dilute solution in *n*-hexane at 298 K using the Hayduk and Minhas correlation for nonaqueous solutions. Compare the estimate to the reported value of 3.7×10^{-5} cm^2/s. The following data are available (Reid et al., 1987):

Parameter	Carbon tetrachloride	*n*-Hexane
T_b, K	349.9	341.9
T_c, K	556.4	507.5
P_c, bar	45.6	30.1
V_c, cm^3/mol	275.9	370
μ, cP	—	0.3
M	153.8	86.2

Answer: Error = 8.4%

1.22[b]. Estimating molar volumes from liquid diffusion data

The diffusivity of allyl alcohol (C_3H_6O) in dilute aqueous solution at 288 K is 0.9×10^{-5} cm^2/s (Reid, et al., 1987). Based on this result, and the Hayduk and Minhas correlation for aqueous solutions, estimate the molar volume of allyl alcohol at its normal boiling point. Compare to the result obtained using Table 1.2. The viscosity of water at 288 K is 1.15 cP.

1.23[b, d]. Concentration dependence of binary liquid diffusivities

(a) Estimate the diffusivity of ethanol in water at 298 K when the mol fraction of ethanol in solution is 40%. Under these conditions (Hammond and Stokes, 1953),

$$\left[1 + \frac{\partial \ln \gamma_A}{\partial \ln x_A}\right]_{T,P} = 0.355$$

The experimental value reported by Hammond and Stokes (1953) is 0.42×10^{-5} cm^2/s. The critical volume of ethanol is 167.1 cm^3/mol; the viscosity of water at 298 K is 0.91 cP.

Answer: Error = 8.3%

(b) Estimate the diffusivity of acetone in water at 298 K when the mol fraction of acetone in solution is 65%. For this system at 298 K, the activity coefficient for acetone is given by the Wilson equation (Smith et al., 1996):

$$\ln \gamma_A = -\ln\left(x_A + x_B\Lambda_{AB}\right) + x_B\left[\frac{\Lambda_{AB}}{x_A + x_B\Lambda_{AB}} - \frac{\Lambda_{BA}}{x_B + x_A\Lambda_{BA}}\right]$$

$$\Lambda_{AB} = 0.149 \qquad \Lambda_{BA} = 0.355 \qquad @298\ \text{K}$$

The critical volume for acetone is 209 cm^3/mol.

Answer: 0.73×10^{-5} cm^2/s

1.24[b, d]. Steady-state, multicomponent, gas-phase flux calculation

A flat plate of solid carbon is being burned in the presence of pure oxygen according to the reaction

$$2C(s) + \tfrac{3}{2}O_2(g) \rightarrow CO(g) + CO_2(g)$$

Molecular diffusion of gaseous reactant and products takes place through a gas film adjacent to the carbon surface; the thickness of this film is 1.0 mm. On the outside of the film, the gas concentration is 40% CO, 20% O_2, and 40% CO_2. The reaction at the surface may be assumed to be instantaneous; therefore, next to the carbon surface, there is virtually no oxygen.The temperature of the gas film is 600 K, and the pressure is 1 bar. Estimate the rate of combustion of the carbon, in $kg/m^2 \cdot min$, and the interface concentration.

Answer: 0.241 $kg/m^2 \cdot min$

1.25[b]. Steady-state, one-dimensional, liquid-phase flux calculation

A crystal of Glauber's salt ($Na_2SO_4 \bullet 10H_2O$) dissolves in a large tank of pure water at 288 K. Estimate the rate at which the crystal dissolves by calculating the flux of Na_2SO_4 from the crystal surface to the bulk solution. Assume that molecular diffusion occurs through a liquid film 0.085 mm thick surrounding the crystal. At the inner side of the film—adjacent to the crystal surface—the solution

is saturated with Na_2SO_4, while at the outer side of the film the solution is virtually pure water. The solubility of Glauber's salt in water at 288 K is 36 g of crystal/100 g of water and the density of the corresponding saturated solution is 1240 kg/m^3 (Perry and Chilton, 1973). The diffusivity of Na_2SO_4 in dilute aqueous solution at 288 K can be estimated as suggested in Problem 1.19. The density of pure liquid water at 288 K is 999.8 kg/m^3; the viscosity is 1.153 cP.

Answer: 12.9 kg of crystal/m^2·h

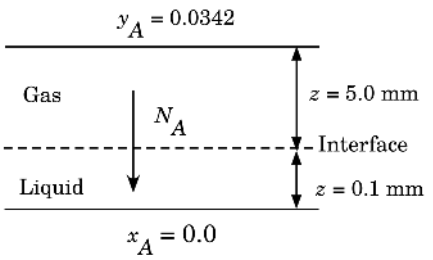
1.26[c, d]. Molecular diffusion through a gas–liquid interface

Ammonia, NH_3, is being selectively removed from an air–NH_3 mixture by absorption into water. In this steady-state process, ammonia is transferred by molecular diffusion through a stagnant gas layer 5 mm thick and then through a stagnant water layer 0.1 mm thick. The concentration of ammonia at the outer boundary of the gas layer is 3.42 mol% and the concentration at the lower boundary of the water layer is essentially zero.

The temperature of the system is 288 K and the total pressure is 1 atm. The diffusivity of ammonia in air under these conditions is 0.215 cm^2/s and in liquid water is 1.77×10^{-5} cm^2/s. Neglecting water evaporation, determine the rate of diffusion of ammonia, in kg/m^2·h. Assume that the gas and liquid are in equilibrium at the interface.

The equilibrium data for ammonia over very dilute aqueous solution at 288 K and 1 atm can be represented by (Welty et al., 1984)

$$y_A = 0.121 + 0.013 \ln x_A$$



Hint: At steady state, the ammonia rate of diffusion through the gas layer must equal the rate of diffusion through the liquid layer.

Answer: 0.053 kg/m^2·h

1.27[c]. Steady-state molecular diffusion in gases

A mixture of ethanol and water vapor is being rectified in an adiabatic distillation column. The alcohol is vaporized and transferred from the liquid to the vapor phase. Water vapor condenses—enough to supply the latent heat of vaporization needed by the alcohol being evaporated—and is transferred from the vapor to the liquid phase. Both components diffuse through a gas film 0.1 mm thick. The temperature is 368 K and the pressure is 1 atm. The mol fraction of ethanol is 0.8 on one side of the film and 0.2 on the other side of the film. Calculate the rate of diffusion of ethanol and of water, in kg/m^2·s. The latent heat of vaporization of the alcohol and water at 368 K can be estimated by the Pitzer acentric factor correlation (Reid et al., 1987)

$$\frac{\Delta H_v}{RT_c} = 7.08\left(1 - T_r\right)^{0.354} + 10.95\omega\left(1 - T_r\right)^{0.456}$$

$$0.5 \le \left(T_r = T / T_c\right) \le 1.0$$

where ω is the acentric factor.

Answer: 0.17 kg ethanol/m^2·s

1.28[a, d]. Analogy between molecular heat and mass transfer

It has been observed that for the system air-water vapor at near-ambient conditions, Le = 1.0 (Treybal, 1980). This observation, called the *Lewis relation*, has profound implications in humidification operations, as will be seen later. Based on the Lewis relation, estimate the diffusivity of water vapor in air at 300 K and 1 atm. Compare your result with the value predicted by the Wilke–Lee equation. For air at 300 K and 1 atm: C_p = 1.01 kJ/kg·K, k = 0.0262 W/m·K, $\mu = 1.846 \times 10^{-5}$ kg/m·s, and ρ = 1.18 kg/m^3.

1.29[b, d]. Steady-state molecular diffusion in gases

Water evaporating from a pond at 298 K does so by molecular diffusion across an air film 1.5 mm thick. If the relative humidity of the air at the outer edge of the film is 20%, and the total pressure is 1 bar, estimate the drop in the water level per day, assuming that conditions in the film remain constant. The vapor pressure of water as a function of temperature can be accurately estimated from the Wagner equation (Reid et al., 1987)

$$\ln\left(\frac{P_W}{P_c}\right) = \frac{-7.7645\tau + 1.4584\tau^{1.5} - 2.7758\tau^3 - 1.2330\tau^6}{T_r}$$

$$\tau = 1 - T_r$$

$$T_r = \frac{T}{T_c}$$

P_W = water vapor pressure

Answer: 2.81 cm

1.30[b, d]. Steady-state molecular diffusion in a ternary gas system

Calculate the fluxes and concentration profiles for the ternary system hydrogen (1), nitrogen (2), and carbon dioxide (3) under the following conditions. The temperature is 308 K and the pressure is 1 atm. The diffusion path length is 86 mm. At one end of the diffusion path, the concentration is 20 mol% H_2, 40% N_2, 40% CO_2; at the other end, the concentration is 50% H_2, 20% N_2, 30% CO_2. The total molar flux is zero, $N = 0$. The MS diffusion coefficients are $D_{12} = 83.8$ mm^2/s, $D_{13} = 68.0$ mm^2/s, $D_{23} = 16.8$ mm^2/s.

Answer: $N_1 = -0.0104$ mol/m^2·s

1.31[b]. Membrane area required for dialysis

One of the oldest membrane materials used for dialysis is porous cellophane, a thin transparent sheet made of regenerated cellulose. Typical values of parameters for commercial cellophane membranes are as follows: thickness = 80 μm, porosity = 0.45, tortuosity = 5.0, and pore diameter = 40 Å (Seader and Henley, 2006).

(a) Estimate the effective diffusivity of urea through this membrane at 298 K. The diffusivity of urea in dilute aqueous solution at this temperature is 1.38×10^{-5} cm^2/s. The molecular diameter of urea is 5.28 Å.

(b) The artificial kidney of Example 1.3 uses a cellophane membrane. If the urea concentration difference across the membrane is 25 mg/dL, estimate the membrane area required.

Answer: 6.3 m^2

1.32[a]. Knudsen diffusion in a porous solid

Porous silica gel is used to adsorb propane from helium at 373 K and 1 atm. Typical values of parameters for porous silica gel are as follows: porosity = 0.486, tortuosity = 3.35, and pore diameter = 22 Å.

(a) Calculate the Knudsen number for diffusion inside the pores.

(b) Calculate the effective diffusivity of propane under these conditions.

Answer: 0.045 mm^2/s

1.33[b]. Combined molecular and Knudsen diffusion in a porous solid

It is desired to increase by 50% the oxygen flux in the process described in Example 1.22 by changing the pore size while maintaining all the other conditions unchanged. Calculate the required pore size. Remember to calculate the new value of the Knudsen number to corroborate that you have used the correct set of equations to relate flux to pore size.

1.34[b]. Flow of pure gases through a porous porcelain plate

An unglazed porcelain plate 5 mm thick has an average pore diameter of 0.2 μm. Pure oxygen gas at an absolute pressure of 20 mm Hg, 400 K, on one side of the plate passed through at a rate of 0.10 cm^3 (at 20 mm Hg, 400 K)/$cm^2 \cdot s$ when the pressure on the downstream side was so low as to be considered negligible.

(a) Calculate the Knudsen number for flow inside the pores.

(b) Estimate the rate of passage of hydrogen gas through the plate at 300 K and an absolute pressure of 10 mm Hg, with negligible downstream pressure.

Answer: 1.85×10^{-3} $mol/m^2 \cdot s$

1.35[b]. Hydrodynamic flow through a porous diaphragm

Consider the hydrodynamic flow of nitrogen at 400 K through the porous diaphragm described in Example 1.24. It is desired to achieve a superficial gas velocity through the diaphragm of 0.28 kg of $N_2/m^2 \cdot s$ by increasing the upstream pressure while maintaining the downstream pressure constant at 0.1 atm. Calculate the upstream pressure required.

Answer: 13.64 kPa

1.36[b] Mass transfer with first-order chemical reaction

Oxygen uptake by the blood is faster than oxygen uptake by water because of the reaction of oxygen with hemoglobin. Many chemists have dreamed of inventing a new compound capable of fast, selective reaction with oxygen. Aqueous solutions of this compound could then be used as the basis of a process for oxygen separation from air. Such a compound would complex with oxygen at low temperatures but would give up the oxygen at high temperatures. In an experiment with one potential compound, a researcher observed that the oxygen absorption flux in dilute aqueous solution of this compound at 298 K was 2.5 higher than the absorption flux with pure water at the same temperature, for a film thickness of 0.5 mm.

(a) Calculate the corresponding value of the Damkohler number.

(b) Estimate the reaction rate constant, assuming first-order kinetics.

Answer: 3.06 min^{-1}

1.37[b]. Krogh model of oxygen transport in muscles

Consider the Krogh cylinder model for oxygen transport in skeletal muscles described in Example 1.26.

(a) At what radial position in the tissue surrounding the capillary entrance is the oxygen partial pressure down to 60.0 torr?

(b) At a position along the capillary where the oxygen partial pressure in the blood is 25 torr, the lowest oxygen partial pressure in the surrounding tissue is 10.0 torr. Estimate the corresponding value of the oxygen demand, M_0.

(c) For the conditions described in part (b), estimate the oxygen flux leaving the capillary wall.

Answer: 0.109 cm^3 $O_2/cm^2 \cdot h$

1.38[d]. Krogh model of oxygen transport using Michaelis–Menten kinetics

As discussed in Example 1.26, zero-order kinetics is a good approximation to the Michaelis–Menten model as long as p_A is much larger than p_0. However, when p_A and p_0 are of the same order of magnitude, the complete Michaelis–Menten equation must be used to describe the reaction kinetics. In that case, equation (1-118) must be solved numerically.

(a) Show that equations (1-118) and (1-119) can be written in dimensionless form as

$$\frac{d^2u_1}{d\eta^2} + \frac{1}{\eta}\frac{du_1}{d\eta} = \frac{u_1 \mathrm{Da}}{\theta + u_1} \tag{1-134}$$

where

$u_1 = p_A/p_{A,b}$ $\eta = r/R_t$

$\theta = p_0/p_{A,b}$ $\mathrm{Da} = M_0 R_t^2/Kp_{A,b}$

with boundary conditions

(1) $\eta = R_c/R_t$ $u_1 = 1.0$

(2) $\eta = 1.0$ $du_1/d\eta = 0$

(b) Transform the second-order differential equation (1-134) into a system of two simultaneous first-order equations by defining $u_2 = du_1/d\eta$. The resulting boundary-value problem can be solved numerically by the shooting method using the *rkfixed* intrinsic function of Mathcad as illustrated in Example 1.17.

(c) For the conditions of Example 1.26, McGuire and Secomb (2001) showed that at the venous end of the capillary the oxygen partial pressure in blood had dropped to 25 torr. Solve equation (1-34) numerically and show that for these conditions, hypoxic conditions prevail all the way from a radial position of 20 μm to the end of the tissue cylinder at 26 μm.

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