To this point we have restricted our attention to heat transfer problems that did not involve any mass transfer. However, many significant heat transfer problems encountered in practice involve mass transfer. For example, about one-third of the heat loss from a resting person is due to evaporation. It turns out that mass transfer is analogous to heat transfer in many respects, and there is close resemblance between heat and mass transfer relations. In this chapter we discuss the mass transfer mechanisms and develop relations for the mass transfer rate for some situations commonly encountered in practice.

Distinction should be made between mass transfer and the bulk fluid motion (or fluid flow) that occurs on a macroscopic level as a fluid is transported from one location to another. Mass transfer requires the presence of two regions at different chemical compositions, and mass transfer refers to the movement of a chemical species from a high concentration region toward a lower concentration one relative to the other chemical species present in the medium. The primary driving force for fluid flow is the pressure difference, whereas for mass transfer it is the concentration difference. Therefore, we do not speak of mass transfer in a homogeneous medium.

We begin this chapter by pointing out numerous analogies between heat and mass transfer and draw several parallels between them. We then discuss boundary conditions associated with mass transfer and one-dimensional steady and transient mass diffusion. Following is a discussion of mass transfer in a moving medium. Finally, we consider convection mass transfer and simultaneous heat and mass transfer.
14–1 · INTRODUCTION

It is a common observation that whenever there is an imbalance of a commodity in a medium, nature tends to redistribute it until a “balance” or “equality” is established. This tendency is often referred to as the driving force, which is the mechanism behind many naturally occurring transport phenomena.

If we define the amount of a commodity per unit volume as the concentration of that commodity, we can say that the flow of a commodity is always in the direction of decreasing concentration; that is, from the region of high concentration to the region of low concentration (Fig. 14–1). The commodity simply creeps away during redistribution, and thus the flow is a diffusion process. The rate of flow of the commodity is proportional to the concentration gradient \( \frac{dC}{dx} \), which is the change in the concentration \( C \) per unit length in the flow direction \( x \), and the area \( A \) normal to flow direction and is expressed as

\[
\text{Flow rate} \propto (\text{Normal area})(\text{Concentration gradient})
\]

or

\[
\dot{Q} = -k_{\text{diff}}A \frac{dC}{dx} \quad (14-1)
\]

Here the proportionality constant \( k_{\text{diff}} \) is the diffusion coefficient of the medium, which is a measure of how fast a commodity diffuses in the medium, and the negative sign is to make the flow in the positive direction a positive quantity (note that \( \frac{dC}{dx} \) is a negative quantity since concentration decreases in the flow direction). You may recall that Fourier’s law of heat conduction, Ohm’s law of electrical conduction, and Newton’s law of viscosity are all in the form of Equation 14–1.

To understand the diffusion process better, consider a tank that is divided into two equal parts by a partition. Initially, the left half of the tank contains nitrogen \( N_2 \) gas while the right half contains air (about 21 percent \( O_2 \) and 79 percent \( N_2 \)) at the same temperature and pressure. The \( O_2 \) and \( N_2 \) molecules are indicated by dark and light circles, respectively. When the partition is removed, we know that the \( N_2 \) molecules will start diffusing into the air while the \( O_2 \) molecules diffuse into the \( N_2 \), as shown in Figure 14–2. If we wait long enough, we will have a homogeneous mixture of \( N_2 \) and \( O_2 \) in the tank. This mass diffusion process can be explained by considering an imaginary plane indicated by the dashed line in the figure as: Gas molecules move randomly, and thus the probability of a molecule moving to the right or to the left is the same. Consequently, half of the molecules on one side of the dashed line at any given moment will move to the other side. Since the concentration of \( N_2 \) is greater on the left side than it is on the right side, more \( N_2 \) molecules will move toward the right than toward the left, resulting in a net flow of \( N_2 \) toward the right. As a result, \( N_2 \) is said to be transferred to the right. A similar argument can be given for \( O_2 \) being transferred to the left. The process continues until uniform concentrations of \( N_2 \) and \( O_2 \) are established throughout the tank so that the number of \( N_2 \) (or \( O_2 \)) molecules moving to the right equals

\[
\dot{Q} = -k_{\text{diff}}A \frac{dC}{dx}
\]
the number moving to the left, resulting in zero net transfer of $\text{N}_2$ or $\text{O}_2$ across an imaginary plane.

The molecules in a gas mixture continually collide with each other, and the diffusion process is strongly influenced by this collision process. The collision of like molecules is of little consequence since both molecules are identical and it makes no difference which molecule crosses a certain plane. The collisions of unlike molecules, however, influence the rate of diffusion since unlike molecules may have different masses and thus different momentums, and thus the diffusion process will be dominated by the heavier molecules. The diffusion coefficients and thus diffusion rates of gases depend strongly on temperature since the temperature is a measure of the average velocity of gas molecules. Therefore, the diffusion rates will be higher at higher temperatures.

Mass transfer can also occur in liquids and solids as well as in gases. For example, a cup of water left in a room will eventually evaporate as a result of water molecules diffusing into the air (liquid-to-gas mass transfer). A piece of solid CO$_2$ (dry ice) will also get smaller and smaller in time as the CO$_2$ molecules diffuse into the air (solid-to-gas mass transfer). A spoon of sugar in a cup of coffee will eventually move up and sweeten the coffee although the sugar molecules are much heavier than the water molecules, and the molecules of a colored pencil inserted into a glass of water will diffuse into the water as evidenced by the gradual spread of color in the water (solid-to-liquid mass transfer). Of course, mass transfer can also occur from a gas to a liquid or solid if the concentration of the species is higher in the gas phase. For example, a small fraction of O$_2$ in the air diffuses into the water and meets the oxygen needs of marine animals. The diffusion of carbon into iron during case-hardening, doping of semiconductors for transistors, and the migration of doped molecules in semiconductors at high temperature are examples of solid-to-solid diffusion processes (Fig. 14–3).

Another factor that influences the diffusion process is the molecular spacing. The larger the spacing, in general, the higher the diffusion rate. Therefore, the diffusion rates are typically much higher in gases than they are in liquids and much higher in liquids than in solids. Diffusion coefficients in gas mixtures are a few orders of magnitude larger than these of liquid or solid solutions.

**14–2 ANALOGY BETWEEN HEAT AND MASS TRANSFER**

We have spent a considerable amount of time studying heat transfer, and we could spend just as much time (perhaps more) studying mass transfer. However, the mechanisms of heat and mass transfer are analogous to each other, and thus we can develop an understanding of mass transfer in a short time with little effort by simply drawing parallels between heat and mass transfer. Establishing those “bridges” between the two seemingly unrelated areas will make it possible to use our heat transfer knowledge to solve mass transfer problems. Alternately, gaining a working knowledge of mass transfer will help us to better understand the heat transfer processes by thinking of heat as a massless substance as they did in the nineteenth century. The short-lived caloric theory of heat is the origin of most heat transfer terminology used
today and served its purpose well until it was replaced by the kinetic theory. Mass is, in essence, energy since mass and energy can be converted to each other according to Einstein’s formula \( E = mc^2 \), where \( c \) is the speed of light. Therefore, we can look at mass and heat as two different forms of energy and exploit this to advantage without going overboard.

**Temperature**

The driving force for heat transfer is the *temperature difference*. In contrast, the driving force for mass transfer is the *concentration difference*. We can view temperature as a measure of “heat concentration,” and thus a high temperature region as one that has a high heat concentration (Fig. 14–4). Therefore, both heat and mass are transferred from the more concentrated regions to the less concentrated ones. If there is no temperature difference between two regions, then there is no heat transfer. Likewise, if there is no difference between the concentrations of a species at different parts of a medium, there will be no mass transfer.

**Conduction**

You will recall that heat is transferred by conduction, convection, and radiation. Mass, however, is transferred by conduction (called diffusion) and convection only, and there is no such thing as “mass radiation” (unless there is something Scotty knows that we don’t when he “beams” people to anywhere in space at the speed of light) (Fig. 14–5). The rate of heat conduction in a direction \( x \) is proportional to the temperature gradient \( \frac{dT}{dx} \) in that direction and is expressed by *Fourier’s law of heat conduction* as

\[
\dot{Q}_{\text{cond}} = -kA \frac{dT}{dx}
\]  

(14-2)

where \( k \) is the thermal conductivity of the medium and \( A \) is the area normal to the direction of heat transfer. Likewise, the rate of mass diffusion \( \dot{m}_{\text{diff}} \) of a chemical species \( A \) in a stationary medium in the direction \( x \) is proportional to the concentration gradient \( \frac{dC_A}{dx} \) in that direction and is expressed by *Fick’s law of diffusion* by (Fig. 14–6)

\[
\dot{m}_{\text{diff}} = -D_{AB} A \frac{dC_A}{dx}
\]  

(14-3)

where \( D_{AB} \) is the diffusion coefficient (or mass diffusivity) of the species in the mixture and \( C_A \) is the concentration of the species in the mixture at that location.

It can be shown that the differential equations for both heat conduction and mass diffusion are of the same form. Therefore, the solutions of mass diffusion equations can be obtained from the solutions of corresponding heat conduction equations for the same type of boundary conditions by simply switching the corresponding coefficients and variables.

**Heat Generation**

Heat generation refers to the conversion of some form of energy such as electrical, chemical, or nuclear energy into *sensible heat* energy in the medium.
Heat generation occurs throughout the medium and exhibits itself as a rise in temperature. Similarly, some mass transfer problems involve chemical reactions that occur within the medium and result in the generation of a species throughout. Therefore, species generation is a volumetric phenomenon, and the rate of generation may vary from point to point in the medium. Such reactions that occur within the medium are called homogeneous reactions and are analogous to internal heat generation. In contrast, some chemical reactions result in the generation of a species at the surface as a result of chemical reactions occurring at the surface due to contact between the medium and the surroundings. This is a surface phenomenon, and as such it needs to be treated as a boundary condition. In mass transfer studies, such reactions are called heterogeneous reactions and are analogous to specified surface heat flux.

Convection
You will recall that heat convection is the heat transfer mechanism that involves both heat conduction (molecular diffusion) and bulk fluid motion. Fluid motion enhances heat transfer considerably by removing the heated fluid near the surface and replacing it by the cooler fluid further away. In the limiting case of no bulk fluid motion, convection reduces to conduction. Likewise, mass convection (or convective mass transfer) is the mass transfer mechanism between a surface and a moving fluid that involves both mass diffusion and bulk fluid motion. Fluid motion also enhances mass transfer considerably by removing the high concentration fluid near the surface and replacing it by the lower concentration fluid further away. In mass convection, we define a concentration boundary layer in an analogous manner to the thermal boundary layer and define new dimensionless numbers that are counterparts of the Nusselt and Prandtl numbers.

The rate of heat convection for external flow was expressed conveniently by Newton’s law of cooling as

$$\dot{Q}_{\text{conv}} = h_{\text{conv}} A_s (T_s - T_c)$$  \hspace{1cm} (14-4)

where $h_{\text{conv}}$ is the heat transfer coefficient, $A_s$ is the surface area, and $T_s - T_c$ is the temperature difference across the thermal boundary layer. Likewise, the rate of mass convection can be expressed as (Fig. 14–7)

$$\dot{m}_\text{conv} = h_{\text{mass}} A_s (C_s - C_c)$$  \hspace{1cm} (14-5)

where $h_{\text{mass}}$ is the mass transfer coefficient, $A_s$ is the surface area, and $C_s - C_c$ is a suitable concentration difference across the concentration boundary layer.

Various aspects of the analogy between heat and mass convection are explored in Section 14–9. The analogy is valid for low mass transfer rate cases in which the flow rate of species undergoing mass flow is low (under 10 percent) relative to the total flow rate of the liquid or gas mixture.

14–3 • MASS DIFFUSION
Fick’s law of diffusion, proposed in 1855, states that the rate of diffusion of a chemical species at a location in a gas mixture (or liquid or solid solution) is proportional to the concentration gradient of that species at that location.

FIGURE 14–7
Analogy between convection heat transfer and convection mass transfer.
Although a higher concentration for a species means more molecules of that species per unit volume, the concentration of a species can be expressed in several ways. Next we describe two common ways.

1 Mass Basis

On a mass basis, concentration is expressed in terms of density (or mass concentration), which is mass per unit volume. Considering a small volume $V$ at a location within the mixture, the densities of a species (subscript $i$) and of the mixture (no subscript) at that location are given by (Fig. 14–8)

Partial density of species $i$: $\rho_i = m_i / V$  
Total density of mixture: $\rho = m / V = \sum m_i / V = \sum \rho_i$

Therefore, the density of a mixture at a location is equal to the sum of the densities of its constituents at that location. Mass concentration can also be expressed in dimensionless form in terms of mass fraction $w$ as

$$ w_i = \frac{m_i}{m} = \frac{m_i / V}{m / V} = \frac{\rho_i}{\rho} \quad (14-6) $$

Note that the mass fraction of a species ranges between 0 and 1, and the conservation of mass requires that the sum of the mass fractions of the constituents of a mixture be equal to 1. That is, $\sum w_i = 1$. Also note that the density and mass fraction of a constituent in a mixture, in general, vary with location unless the concentration gradients are zero.

2 Mole Basis

On a mole basis, concentration is expressed in terms of molar concentration (or molar density), which is the amount of matter in kmol per unit volume. Again considering a small volume $V$ at a location within the mixture, the molar concentrations of a species (subscript $i$) and of the mixture (no subscript) at that location are given by

Partial molar concentration of species $i$: $C_i = N_i / V$  
Total molar concentration of mixture: $C = N / V = \sum N_i / V = \sum C_i$

Therefore, the molar concentration of a mixture at a location is equal to the sum of the molar concentrations of its constituents at that location. Molar concentration can also be expressed in dimensionless form in terms of mole fraction $y$ as

$$ y_i = \frac{N_i}{N} = \frac{N_i / V}{N / V} = \frac{C_i}{C} \quad (14-7) $$

Again the mole fraction of a species ranges between 0 and 1, and the sum of the mole fractions of the constituents of a mixture is unity, $\sum y_i = 1$.

The mass $m$ and molar number $N$ of a substance are related to each other by $m = NM$ (or, for a unit volume, $\rho = CM$) where $M$ is the molar mass (also called the molecular weight) of the substance. This is expected since the mass of 1 kmol of the substance is $M$ kg, and thus the mass of $N$ kmol is $NM$ kg. Therefore, the mass and molar concentrations are related to each other by
\[ C_i = \frac{p_i}{M_i} \quad \text{(for species } i \text{)} \quad \text{and} \quad C = \frac{p}{M} \quad \text{(for the mixture)} \quad (14-8) \]

where \( M \) is the molar mass of the mixture which can be determined from
\[ M = \frac{m}{N} = \frac{\sum N_i M_i}{N} = \frac{\sum N_i}{N} M_i = \sum y_i M_i \quad (14-9) \]

The mass and mole fractions of species \( i \) of a mixture are related to each other by
\[ w_i = \frac{\rho_i}{\rho} = \frac{C_i M_i}{CM} = \frac{y_i M_i}{M} \quad (14-10) \]

Two different approaches are presented above for the description of concentration at a location, and you may be wondering which approach is better to use. Well, the answer depends on the situation on hand. Both approaches are equivalent, and the better approach for a given problem is the one that yields the desired solution more easily.

**Special Case: Ideal Gas Mixtures**

At low pressures, a gas or gas mixture can conveniently be approximated as an ideal gas with negligible error. For example, a mixture of dry air and water vapor at atmospheric conditions can be treated as an ideal gas with an error much less than 1 percent. The total pressure of a gas mixture \( P \) is equal to the sum of the partial pressures \( P_i \) of the individual gases in the mixture and is expressed as \( P = \sum P_i \). Here \( P_i \) is called the partial pressure of species \( i \), which is the pressure species \( i \) would exert if it existed alone at the mixture temperature and volume. This is known as Dalton’s law of additive pressures. Then using the ideal gas relation \( PV = NRT \) where \( R \) is the universal gas constant for both the species \( i \) and the mixture, the pressure fraction of species \( i \) can be expressed as (Fig. 14–9)
\[ \frac{P_i}{P} = \frac{N_i R T}{N R T} = \frac{N_i}{N} = y_i \quad (14-11) \]

Therefore, the pressure fraction of species \( i \) of an ideal gas mixture is equivalent to the mole fraction of that species and can be used in place of it in mass transfer analysis.

**Fick’s Law of Diffusion:**

**Stationary Medium Consisting of Two Species**

We mentioned earlier that the rate of mass diffusion of a chemical species in a stagnant medium in a specified direction is proportional to the local concentration gradient in that direction. This linear relationship between the rate of diffusion and the concentration gradient proposed by Fick in 1855 is known as Fick’s law of diffusion and can be expressed as

\[ \text{Mass flux} = \text{Constant of proportionality} \times \text{Concentration gradient} \]
Mass basis:

\[ j_{\text{diff,}A} = \frac{\dot{m}_{\text{diff,}A}}{A} = -\rho D_{AB} \frac{d(p_A/p)}{dx} = -\rho D_{AB} \frac{dw_{A}}{dx} \quad \text{(kg/s \cdot m}^2\text{)} \]

Mole basis:

\[ \dot{N}_{\text{diff,}A} = CAD_{AB} \frac{d\bar{C}_A}{dx} = -CD_{AB} \frac{d(C_A/C)}{dx} = -CD_{AB} \frac{d\bar{C}_A}{dx} \quad \text{(mol/s \cdot m}^2\text{)} \quad (14-12) \]

Here \( j_{\text{diff,}A} \) is the (diffusive) mass flux of species A (mass transfer by diffusion per unit time and per unit area normal to the direction of mass transfer, in kg/s \cdot m\(^2\)) and \( \dot{N}_{\text{diff,}A} \) is the (diffusive) molar flux (in kmol/s \cdot m\(^2\)). The mass flux of a species at a location is proportional to the density of the mixture at that location. Note that \( \rho = \rho_A + \rho_B \) is the density and \( C = C_A + C_B \) is the molar concentration of the binary mixture, and in general, they may vary throughout the mixture. Therefore, \( \rho d(p_A/p) \neq d\rho_A \) or \( C d(C_A/C) \neq dC_A \). But in the special case of constant mixture density \( \rho \) or constant molar concentration \( C \), the relations above simplify to

Mass basis (\( \rho \) = constant): \( j_{\text{diff,}A} = -D_{AB} \frac{dp_A}{dx} \quad \text{(kg/s \cdot m}^2\text{)} \)

Mole basis (\( C \) = constant): \( \dot{N}_{\text{diff,}A} = -D_{AB} \frac{dC_A}{dx} \quad \text{(mol/s \cdot m}^2\text{)} \quad (14-13) \)

The constant density or constant molar concentration assumption is usually appropriate for solid and dilute liquid solutions, but often this is not the case for gas mixtures or concentrated liquid solutions. Therefore, Eq. 14–12 should be used in the latter case. In this introductory treatment we will limit our consideration to one-dimensional mass diffusion. For two- or three-dimensional cases, Fick’s law can conveniently be expressed in vector form by simply replacing the derivatives in the above relations by the corresponding gradients (such as \( \mathbf{j}_A = -\rho D_{AB} \nabla w_A \)).

Remember that the constant of proportionality in Fourier’s law was defined as the transport property thermal conductivity. Similarly, the constant of proportionality in Fick’s law is defined as another transport property called the binary diffusion coefficient or mass diffusivity, \( D_{AB} \). The unit of mass diffusivity is m\(^2\)/s, which is the same as the units of thermal diffusivity or momentum diffusivity (also called kinematic viscosity) (Fig. 14–11).

Because of the complex nature of mass diffusion, the diffusion coefficients are usually determined experimentally. The kinetic theory of gases indicates that the diffusion coefficient for dilute gases at ordinary pressures is essentially independent of mixture composition and tends to increase with temperature while decreasing with pressure as

\[ D_{AB} \approx \frac{T^{3/2}}{P} \quad \text{or} \quad \frac{D_{AB,1}}{D_{AB,2}} = \frac{P_2}{P_1} \left( \frac{T_1}{T_2} \right)^{3/2} \quad (14-14) \]
This relation is useful in determining the diffusion coefficient for gases at different temperatures and pressures from a knowledge of the diffusion coefficient at a specified temperature and pressure. More general but complicated relations that account for the effects of molecular collisions are also available. The diffusion coefficients of some gases in air at 1 atm pressure are given in Table 14–1 at various temperatures.

The diffusion coefficients of solids and liquids also tend to increase with temperature while exhibiting a strong dependence on the composition. The diffusion process in solids and liquids is a great deal more complicated than that in gases, and the diffusion coefficients in this case are almost exclusively determined experimentally.

The binary diffusion coefficient for several binary gas mixtures and solid and liquid solutions are given in Tables 14–2 and 14–3. We make these two observations from these tables:

1. The diffusion coefficients, in general, are highest in gases and lowest in solids. The diffusion coefficients of gases are several orders of magnitude greater than those of liquids.
2. Diffusion coefficients increase with temperature. The diffusion coefficient (and thus the mass diffusion rate) of carbon through iron during a hardening process, for example, increases by 6000 times as the temperature is raised from 500°C to 1000°C.

Due to its practical importance, the diffusion of water vapor in air has been the topic of several studies, and some empirical formulas have been developed for the diffusion coefficient $D_{H_2O \text{-air}}$. Marrero and Mason proposed this popular formula (Table 14–4):

\[ D_{H_2O \text{-air}} = \frac{2.5 \times 10^{-5}}{T} \times 10^{12} \]

\*Multiply by 10.76 to convert to ft²/s.

### Table 14–1

| Binary Diffusion Coefficient, \( m^2/s \times 10^6 \) |
|---|---|---|---|---|
| \( T, K \) | \( O_2 \) | \( CO_2 \) | \( H_2 \) | \( NO \) |
| 200 | 0.95 | 0.74 | 3.75 | 0.88 |
| 300 | 1.88 | 1.57 | 7.77 | 1.80 |
| 400 | 5.25 | 2.63 | 12.5 | 3.03 |
| 500 | 4.75 | 3.85 | 17.1 | 4.43 |
| 600 | 6.46 | 5.37 | 24.4 | 6.03 |
| 700 | 8.38 | 6.84 | 31.7 | 7.82 |
| 800 | 10.5 | 8.57 | 39.3 | 9.78 |
| 900 | 12.6 | 10.5 | 47.7 | 11.8 |
| 1000 | 15.2 | 12.4 | 56.9 | 14.1 |
| 1200 | 20.6 | 16.9 | 77.7 | 19.2 |
| 1400 | 26.6 | 21.7 | 99.0 | 24.5 |
| 1600 | 33.2 | 27.5 | 125 | 30.4 |
| 1800 | 40.3 | 32.8 | 152 | 37.0 |
| 2000 | 48.0 | 39.4 | 180 | 44.8 |

*Multiply by 10.76 to convert to ft²/s.

### Table 14–2

<table>
<thead>
<tr>
<th>Substance A</th>
<th>Substance B</th>
<th>( T, K )</th>
<th>( D_{AB} \text{ or } D_{BA} \text{ in m}^2/\text{s} )</th>
<th>Substance A</th>
<th>Substance B</th>
<th>( T, K )</th>
<th>( D_{AB} \text{ or } D_{BA} \text{ in m}^2/\text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>Acetone</td>
<td>273</td>
<td>1.1 x 10^{-5}</td>
<td>Argon, Ar</td>
<td>Nitrogen, N₂</td>
<td>293</td>
<td>1.9 x 10^{-5}</td>
</tr>
<tr>
<td>Air</td>
<td>Ammonia, NH₃</td>
<td>298</td>
<td>2.6 x 10^{-5}</td>
<td>Carbon dioxide, CO₂</td>
<td>Benzene</td>
<td>318</td>
<td>0.72 x 10^{-5}</td>
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<tr>
<td>Air</td>
<td>Benzene</td>
<td>298</td>
<td>0.88 x 10^{-5}</td>
<td>Carbon dioxide, CO₂</td>
<td>Hydrogen, H₂</td>
<td>273</td>
<td>5.5 x 10^{-5}</td>
</tr>
<tr>
<td>Air</td>
<td>Carbon dioxide</td>
<td>298</td>
<td>1.6 x 10^{-5}</td>
<td>Carbon dioxide, CO₂</td>
<td>Nitrogen, N₂</td>
<td>293</td>
<td>1.6 x 10^{-5}</td>
</tr>
<tr>
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<td>273</td>
<td>1.2 x 10^{-5}</td>
<td>Carbon dioxide, CO₂</td>
<td>Oxygen, O₂</td>
<td>273</td>
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<td>Water vapor</td>
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<td>1.6 x 10^{-5}</td>
</tr>
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<td>7.0 x 10^{-5}</td>
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<td>Water vapor</td>
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<td>Water vapor</td>
<td>Nitrogen, N₂</td>
<td>298</td>
<td>2.5 x 10^{-5}</td>
</tr>
</tbody>
</table>

Note: The effect of pressure and temperature on $D_{AB}$ can be accounted for through $D_{AB} = T^{1/2} \cdot P$. Also, multiply $D_{AB}$ values by 10.76 to convert them to ft²/s.
TABLE 14–3  
Binary diffusion coefficients of dilute liquid solutions and solid solutions at 1 atm
(from Barrer, Ref. 2; Reid et al., Ref. 15; Thomas, Ref. 19; and van Black, Ref. 20)

<table>
<thead>
<tr>
<th>Substance (Solute)</th>
<th>Substance (Solvent)</th>
<th>T, K</th>
<th>$D_{AB}$, m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>Water</td>
<td>285</td>
<td>$1.6 \times 10^{-9}$</td>
</tr>
<tr>
<td>Benzene</td>
<td>Water</td>
<td>293</td>
<td>$1.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>Water</td>
<td>298</td>
<td>$2.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Water</td>
<td>285</td>
<td>$1.4 \times 10^{-9}$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Water</td>
<td>283</td>
<td>$0.84 \times 10^{-9}$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Water</td>
<td>288</td>
<td>$1.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Water</td>
<td>298</td>
<td>$1.2 \times 10^{-9}$</td>
</tr>
<tr>
<td>Glucose</td>
<td>Water</td>
<td>298</td>
<td>$0.69 \times 10^{-9}$</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Water</td>
<td>298</td>
<td>$6.3 \times 10^{-9}$</td>
</tr>
<tr>
<td>Methane</td>
<td>Water</td>
<td>275</td>
<td>$0.85 \times 10^{-9}$</td>
</tr>
<tr>
<td>Methane</td>
<td>Water</td>
<td>293</td>
<td>$1.5 \times 10^{-9}$</td>
</tr>
<tr>
<td>Methane</td>
<td>Water</td>
<td>333</td>
<td>$3.6 \times 10^{-9}$</td>
</tr>
<tr>
<td>Methanol</td>
<td>Water</td>
<td>288</td>
<td>$1.3 \times 10^{-9}$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Water</td>
<td>298</td>
<td>$2.6 \times 10^{-9}$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Water</td>
<td>298</td>
<td>$2.4 \times 10^{-9}$</td>
</tr>
<tr>
<td>Water</td>
<td>Ethanol</td>
<td>298</td>
<td>$1.2 \times 10^{-9}$</td>
</tr>
<tr>
<td>Water</td>
<td>Ethylene glycol</td>
<td>298</td>
<td>$0.18 \times 10^{-9}$</td>
</tr>
<tr>
<td>Water</td>
<td>Methanol</td>
<td>298</td>
<td>$1.8 \times 10^{-9}$</td>
</tr>
<tr>
<td>Chloroform</td>
<td>Methanol</td>
<td>288</td>
<td>$2.1 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance (Solute B)</th>
<th>Substance (Solvent)</th>
<th>T, K</th>
<th>$D_{AB}$, m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>Natural rubber</td>
<td>298</td>
<td>$1.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Natural rubber</td>
<td>298</td>
<td>$1.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Natural rubber</td>
<td>298</td>
<td>$2.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>Helium</td>
<td>Pyrex</td>
<td>773</td>
<td>$2.0 \times 10^{-12}$</td>
</tr>
<tr>
<td>Helium</td>
<td>Pyrex</td>
<td>293</td>
<td>$4.5 \times 10^{-15}$</td>
</tr>
<tr>
<td>Helium</td>
<td>Silicon dioxide</td>
<td>298</td>
<td>$4.0 \times 10^{-14}$</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Iron</td>
<td>298</td>
<td>$2.6 \times 10^{-13}$</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Nickel</td>
<td>358</td>
<td>$1.2 \times 10^{-12}$</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Nickel</td>
<td>438</td>
<td>$1.0 \times 10^{-11}$</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Copper</td>
<td>293</td>
<td>$2.7 \times 10^{-19}$</td>
</tr>
<tr>
<td>Zinc</td>
<td>Copper</td>
<td>773</td>
<td>$4.0 \times 10^{-18}$</td>
</tr>
<tr>
<td>Zinc</td>
<td>Copper</td>
<td>1273</td>
<td>$5.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>Antimony</td>
<td>Silver</td>
<td>293</td>
<td>$3.5 \times 10^{-25}$</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Lead</td>
<td>293</td>
<td>$1.1 \times 10^{-20}$</td>
</tr>
<tr>
<td>Mercury</td>
<td>Lead</td>
<td>293</td>
<td>$2.5 \times 10^{-19}$</td>
</tr>
<tr>
<td>Copper</td>
<td>Aluminum</td>
<td>773</td>
<td>$4.0 \times 10^{-14}$</td>
</tr>
<tr>
<td>Copper</td>
<td>Aluminum</td>
<td>1273</td>
<td>$1.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>Carbon</td>
<td>Iron (fcc)</td>
<td>773</td>
<td>$5.0 \times 10^{-15}$</td>
</tr>
<tr>
<td>Carbon</td>
<td>Iron (fcc)</td>
<td>1273</td>
<td>$3.0 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

$D_{H,O} = 1.87 \times 10^{-10} \frac{T^{2.072}}{P}$ (m²/s), 280 K < T < 450 K  (14-15)

In a binary ideal gas mixture of species $A$ and $B$, the diffusion coefficient of $A$ in $B$ is equal to the diffusion coefficient of $B$ in $A$, and both increase with temperature.

$D_{H,O,AB} = D_{H,O} = D_{H,O,BA}$  (m²/s)

$T$, °C  $D_{H,O,AB}$ or $D_{H,O,BA}$ (at 1 atm, in m²/s)  (from Eq. 14–15)

<table>
<thead>
<tr>
<th>T, °C</th>
<th>$D_{H,O,AB}$ or $D_{H,O,BA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$2.09 \times 10^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>$2.17 \times 10^{-5}$</td>
</tr>
<tr>
<td>10</td>
<td>$2.25 \times 10^{-5}$</td>
</tr>
<tr>
<td>15</td>
<td>$2.33 \times 10^{-5}$</td>
</tr>
<tr>
<td>20</td>
<td>$2.42 \times 10^{-5}$</td>
</tr>
<tr>
<td>25</td>
<td>$2.50 \times 10^{-5}$</td>
</tr>
<tr>
<td>30</td>
<td>$2.59 \times 10^{-5}$</td>
</tr>
<tr>
<td>35</td>
<td>$2.68 \times 10^{-5}$</td>
</tr>
<tr>
<td>40</td>
<td>$2.77 \times 10^{-5}$</td>
</tr>
<tr>
<td>50</td>
<td>$2.96 \times 10^{-5}$</td>
</tr>
<tr>
<td>100</td>
<td>$3.99 \times 10^{-5}$</td>
</tr>
<tr>
<td>150</td>
<td>$5.18 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

where $P$ is total pressure in atm and $T$ is the temperature in K.

The primary driving mechanism of mass diffusion is the concentration gradient, and mass diffusion due to a concentration gradient is known as the **ordinary diffusion**. However, diffusion may also be caused by other effects. Temperature gradients in a medium can cause **thermal diffusion** (also called the **soret effect**), and pressure gradients may result in **pressure diffusion**. Both of these effects are usually negligible, however, unless the gradients are very large. In centrifuges, the pressure gradient generated by the centrifugal effect is used to separate liquid solutions and gaseous isotopes. An external force field such as an electric or magnetic field applied on a mixture or solution can be used successfully to separate electrically charged or magnetized molecules (as in an electrolyte or ionized gas) from the mixture. This is called **forced diffusion**. Also, when the pores of a porous solid such as silica-gel are smaller than the mean free path of the gas molecules, the molecular collisions may be negligible and a free molecule flow may be initiated. This is known as **Knudsen diffusion**. When the size of the gas molecules is comparable to the pore size, adsorbed molecules move along the pore walls. This is known as **surface diffusion**. Finally, particles whose diameter is under 0.1 μm such as mist and soot particles act like large molecules, and the diffusion process of such particles due to the concentration gradient is called **Brownian motion**. Large particles (those whose diameter is greater than 1 μm) are not affected.
by diffusion as the motion of such particles is governed by Newton’s laws. In our elementary treatment of mass diffusion, we will assume these additional effects to be nonexistent or negligible, as is usually the case, and refer the interested reader to advanced books on these topics.

**EXAMPLE 14–1** Determining Mass Fractions from Mole Fractions

The composition of dry standard atmosphere is given on a molar basis to be 78.1 percent N₂, 20.9 percent O₂, and 1.0 percent Ar and other constituents (Fig. 14–12). Treating other constituents as Ar, determine the mass fractions of the constituents of air.

**SOLUTION** The molar fractions of the constituents of air are given. The mass fractions are to be determined.

**Assumptions** The small amounts of other gases in air are treated as argon.

**Properties** The molar masses of N₂, O₂, and Ar are 28.0, 32.0, and 39.9 kg/kmol, respectively (Table A–1).

**Analysis** The molar mass of air is determined to be

\[ M = \sum y_i M_i = 0.781 \times 28.0 + 0.209 \times 32.0 + 0.01 \times 39.9 = 29.0 \text{ kg/kmol} \]

Then the mass fractions of constituent gases are determined from Eq. 14–10 to be

\[ \begin{align*}
\text{N}_2: & \quad w_{\text{N}_2} = \frac{y_{\text{N}_2}}{M} \frac{M_{\text{N}_2}}{M} = (0.781) \frac{28.0}{29.0} = 0.754 \\
\text{O}_2: & \quad w_{\text{O}_2} = \frac{y_{\text{O}_2}}{M} \frac{M_{\text{O}_2}}{M} = (0.209) \frac{32.0}{29.0} = 0.231 \\
\text{Ar:} & \quad w_{\text{Ar}} = \frac{y_{\text{Ar}}}{M} \frac{M_{\text{Ar}}}{M} = (0.01) \frac{39.9}{29.0} = 0.014
\end{align*} \]

Therefore, the mass fractions of N₂, O₂, and Ar in dry standard atmosphere are 75.4 percent, 23.1 percent, and 1.4 percent, respectively.

### 14–4 BOUNDARY CONDITIONS

We mentioned earlier that the mass diffusion equation is analogous to the heat diffusion (conduction) equation, and thus we need comparable boundary conditions to determine the species concentration distribution in a medium. Two common types of boundary conditions are the (1) specified species concentration, which corresponds to specified temperature, and (2) specified species flux, which corresponds to specified heat flux.

Despite their apparent similarity, an important difference exists between temperature and concentration: temperature is necessarily a continuous function, but concentration, in general, is not. The wall and air temperatures at a wall surface, for example, are always the same. The concentrations of air on the two sides of a water–air interface, however, are obviously very different (in fact, the concentration of air in water is close to zero). Likewise, the concentrations of water on the two sides of a water–air interface are also different even when air is saturated (Fig. 14–13). Therefore, when specifying a
boundary condition, specifying the location is not enough. We also need to specify the side of the boundary. To do this, we consider two imaginary surfaces on the two sides of the interface that are infinitesimally close to the interface. Whenever there is a doubt, we indicate the desired side of the interface by specifying its phase as a subscript. For example, the water (liquid or vapor) concentration at the liquid and gas sides of a water–air interface at $x = 0$ can be expressed on a molar basis is

\[ y_{\text{H}_2\text{O, liquid side (0)}} = y_1 \quad \text{and} \quad y_{\text{H}_2\text{O, gas side (0)}} = y_2 \]  

(14-16)

Using Fick’s law, the constant species flux boundary condition for a diffusing species $A$ at a boundary at $x = 0$ is expressed, in the absence of any blowing or suction, as

\[ -CD_{\text{AB}} \frac{dy_A}{dx} \bigg|_{x=0} = j_{A,0} \quad \text{or} \quad -\rho D_{\text{AB}} \frac{dw_A}{dx} \bigg|_{x=0} = j_{A,0} \]  

(14-17)

where $\bar{j}_{A,0}$ and $j_{A,0}$ are the specified mole and mass fluxes of species $A$ at the boundary, respectively. The special case of zero mass flux ($\bar{j}_{A,0} = j_{A,0} = 0$) corresponds to an impermeable surface for which $dy_A(0)/dx = dw_A(0)/dx = 0$ (Fig. 14–14).

To apply the specified concentration boundary condition, we must know the concentration of a species at the boundary. This information is usually obtained from the requirement that thermodynamic equilibrium must exist at the interface of two phases of a species. In the case of air–water interface, the concentration values of water vapor in the air are easily determined from saturation data, as shown in Example 14–2.

**EXAMPLE 14–2**  
**Mole Fraction of Water Vapor at the Surface of a Lake**

Determine the mole fraction of the water vapor at the surface of a lake whose temperature is $15^\circ\text{C}$ and compare it to the mole fraction of water in the lake (Fig. 14–15). Take the atmospheric pressure at lake level to be 92 kPa.

**SOLUTION**  
The mole fraction of the water vapor at the surface of a lake and the mole fraction of water in the lake are to be determined and compared.

**Assumptions**  
1 Both the air and water vapor are ideal gases. 2 The mole fraction of dissolved air in water is negligible.

**Properties**  
The saturation pressure of water at $15^\circ\text{C}$ is 1.705 kPa (Table A–9).

**Analysis**  
The air at the water surface will be saturated. Therefore, the partial pressure of water vapor in the air at the lake surface will simply be the saturation pressure of water at $15^\circ\text{C}$,

\[ P_{\text{vapor}} = P_{\text{sat at } 15^\circ\text{C}} = 1.705 \text{ kPa} \]

Assuming both the air and vapor to be ideal gases, the mole fraction of water vapor in the air at the surface of the lake is determined from Eq. 14–11 to be

\[ y_{\text{vapor}} = \frac{P_{\text{vapor}}}{P} = \frac{1.705 \text{ kPa}}{92 \text{ kPa}} = 0.0185 \]  

(or 1.85 percent)
The situation is similar at solid–liquid interfaces. Again, at a given temperature, only a certain amount of solid can be dissolved in a liquid, and the solubility of the solid in the liquid is determined from the requirement that thermodynamic equilibrium exists between the solid and the solution at the interface. The solubility represents the maximum amount of solid that can be dissolved in a liquid at a specified temperature and is widely available in chemistry handbooks. In Table 14–5 we present sample solubility data for sodium chloride (NaCl) and calcium bicarbonate [Ca(HCO₃)₂] at various temperatures. For example, the solubility of salt (NaCl) in water at 310 K is 36.5 kg per 100 kg of water. Therefore, the mass fraction of salt in the brine at the interface is simply

$$w_{\text{salt, liquid side}} = \frac{m_{\text{salt}}}{m} = \frac{36.5 \text{ kg}}{100 + 36.5 \text{ kg}} = 0.267$$

(or 26.7 percent)

whereas the mass fraction of salt in the pure solid salt is $w = 1.0$. Note that water becomes saturated with salt when 36.5 kg of salt are dissolved in 100 kg of water at 310 K.

Many processes involve the absorption of a gas into a liquid. Most gases are weakly soluble in liquids (such as air in water), and for such dilute solutions the mole fractions of a species $i$ in the gas and liquid phases at the interface are observed to be proportional to each other. That is, $y_i, \text{gas side} \propto y_i, \text{liquid side}$ or $P_i, \text{gas side} \propto P y_i, \text{liquid side}$ since $y_i, \text{gas side} = P_i, \text{gas side}/P$ for ideal gas mixtures. This is known as Henry’s law and is expressed as

$$y_i, \text{liquid side} = \frac{P_i, \text{gas side}}{H} \quad \text{(at interface)}$$

where $H$ is Henry’s constant, which is the product of the total pressure of the gas mixture and the proportionality constant. For a given species, it is a function of temperature only and is practically independent of pressure for pressures under about 5 atm. Values of Henry’s constant for a number of aqueous solutions are given in Table 14–6 for various temperatures. From this table and the equation above we make the following observations:

1. The concentration of a gas dissolved in a liquid is inversely proportional to Henry’s constant. Therefore, the larger Henry’s constant, the smaller the concentration of dissolved gases in the liquid.
2. Henry's constant increases (and thus the fraction of a dissolved gas in the liquid decreases) with increasing temperature. Therefore, the dissolved gases in a liquid can be driven off by heating the liquid (Fig. 14–16).

3. The concentration of a gas dissolved in a liquid is proportional to the partial pressure of the gas. Therefore, the amount of gas dissolved in a liquid can be increased by increasing the pressure of the gas. This can be used to advantage in the carbonation of soft drinks with CO₂ gas.

Strictly speaking, the result obtained from Eq. 14–18 for the mole fraction of dissolved gas is valid for the liquid layer just beneath the interface and not necessarily the entire liquid. The latter will be the case only when thermodynamic phase equilibrium is established throughout the entire liquid body.

### TABLE 14–6

Henry's constant $H$ (in bars) for selected gases in water at low to moderate pressures for gas $i$, $H = \frac{P_{i, \text{gas side}}}{y_{i, \text{water side}}}$

(from Mills, Ref. 13, Table A.21, p. 874)

<table>
<thead>
<tr>
<th>Solute</th>
<th>290 K</th>
<th>300 K</th>
<th>310 K</th>
<th>320 K</th>
<th>330 K</th>
<th>340 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>440</td>
<td>560</td>
<td>700</td>
<td>830</td>
<td>980</td>
<td>1140</td>
</tr>
<tr>
<td>CO₂</td>
<td>1280</td>
<td>1710</td>
<td>2170</td>
<td>2720</td>
<td>3220</td>
<td>—</td>
</tr>
<tr>
<td>O₂</td>
<td>38,000</td>
<td>45,000</td>
<td>52,000</td>
<td>57,000</td>
<td>61,000</td>
<td>65,000</td>
</tr>
<tr>
<td>H₂</td>
<td>67,000</td>
<td>72,000</td>
<td>75,000</td>
<td>76,000</td>
<td>77,000</td>
<td>76,000</td>
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<tr>
<td>CO</td>
<td>51,000</td>
<td>60,000</td>
<td>67,000</td>
<td>74,000</td>
<td>80,000</td>
<td>84,000</td>
</tr>
<tr>
<td>Air</td>
<td>62,000</td>
<td>74,000</td>
<td>84,000</td>
<td>92,000</td>
<td>99,000</td>
<td>104,000</td>
</tr>
<tr>
<td>N₂</td>
<td>76,000</td>
<td>89,000</td>
<td>101,000</td>
<td>110,000</td>
<td>118,000</td>
<td>124,000</td>
</tr>
</tbody>
</table>

### EXAMPLE 14–3  Mole Fraction of Dissolved Air in Water

Determine the mole fraction of air dissolved in water at the surface of a lake whose temperature is 17°C (Fig. 14–17). Take the atmospheric pressure at lake level to be 92 kPa.

**SOLUTION**

The mole fraction of air dissolved in water at the surface of a lake is to be determined.

**Assumptions** 1 Both the air and water vapor are ideal gases. 2 Air is weakly soluble in water so that Henry’s law is applicable.

**Properties** The saturation pressure of water at 17°C is 1.92 kPa (Table A–9). Henry's constant for air dissolved in water at 290 K is $H = 62,000$ bar (Table 14–6).

**Analysis** This example is similar to the previous example. Again the air at the water surface will be saturated, and thus the partial pressure of water vapor in the air at the lake surface will be the saturation pressure of water at 17°C,

\[ P_{\text{vapor}} = P_{\text{sat @ 17°C}} = 1.92 \text{ kPa} \]

Assuming both the air and vapor to be ideal gases, the partial pressure of dry air is determined to be

\[ P_{\text{dry air}} = P - P_{\text{vapor}} = 92 - 1.92 = 90.08 \text{ kPa} = 0.9008 \text{ bar} \]
We mentioned earlier that the use of Henry's law is limited to dilute gas–liquid solutions; that is, a liquid with a small amount of gas dissolved in it. Then the question that arises naturally is, what do we do when the gas is highly soluble in the liquid (or solid), such as ammonia in water? In this case the linear relationship of Henry's law does not apply, and the mole fraction of a gas dissolved in the liquid (or solid) is usually expressed as a function of the partial pressure of the gas in the gas phase and the temperature. An approximate relation in this case for the mole fractions of a species on the liquid and gas sides of the interface is given by Raoult's law as

\[ \frac{P_{i, \text{gas side}}}{P_{i, \text{sat}(T)}} = \frac{y_{i, \text{gas side}}}{y_{i, \text{liquid side}}} \]  

where \( P_{i, \text{sat}(T)} \) is the saturation pressure of the species \( i \) at the interface temperature and \( P \) is the total pressure on the gas phase side. Tabular data are available in chemical handbooks for common solutions such as the ammonia–water solution that is widely used in absorption-refrigeration systems.

Gases may also dissolve in solids, but the diffusion process in this case can be very complicated. The dissolution of a gas may be independent of the structure of the solid, or it may depend strongly on its porosity. Some dissolution processes (such as the dissolution of hydrogen in titanium, similar to the dissolution of CO\(_2\) in water) are reversible, and thus maintaining the gas content in the solid requires constant contact of the solid with a reservoir of that gas. Some other dissolution processes are irreversible. For example, oxygen gas dissolving in titanium forms TiO\(_2\) on the surface, and the process does not reverse itself.

The concentration of the gas species \( i \) in the solid at the interface \( C_{i, \text{solid side}} \) is proportional to the partial pressure of the species \( i \) in the gas \( P_{i, \text{gas side}} \) on the gas side of the interface and is expressed as

\[ C_{i, \text{solid side}} = \mathcal{S} \times P_{i, \text{gas side}} \quad \text{(kmol/m}\text{)}^3 \]  

where \( \mathcal{S} \) is the solubility. Expressing the pressure in bars and noting that the unit of molar concentration is kmol per m\(^3\), the unit of solubility is kmol/m\(^3\) · bar. Solubility data for selected gas–solid combinations are given in Table 14–7. The product of the solubility of a gas and the diffusion coefficient of the gas in a solid is referred to as the permeability \( P \), which is a measure of the ability of the gas to penetrate a solid. That is, \( P = \mathcal{S} D_{AB} \) where \( D_{AB} \) is

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Gas} & \text{Solid} & T, \text{K} & \mathcal{S} \text{ kmol/m}^3 \cdot \text{bar} \\
\hline
\text{O}_2 & \text{Rubber} & 298 & 0.00312 \\
\text{N}_2 & \text{Rubber} & 298 & 0.00156 \\
\text{CO}_2 & \text{Rubber} & 298 & 0.04015 \\
\text{He} & \text{SiO}_2 & 293 & 0.00045 \\
\text{H}_2 & \text{Ni} & 358 & 0.00901 \\
\hline
\end{array}
\]
the diffusivity of the gas in the solid. Permeability is inversely proportional to thickness and has the unit kmol/s · bar.

Finally, if a process involves the *sublimation* of a pure solid (such as ice or solid CO₂) or the *evaporation* of a pure liquid (such as water) in a different medium such as air, the mole (or mass) fraction of the substance in the liquid or solid phase is simply taken to be 1.0, and the partial pressure and thus the mole fraction of the substance in the gas phase can readily be determined from the saturation data of the substance at the specified temperature. Also, the assumption of thermodynamic equilibrium at the interface is very reasonable for pure solids, pure liquids, and solutions, except when chemical reactions are occurring at the interface.

**EXAMPLE 14–4 Diffusion of Hydrogen Gas into a Nickel Plate**

Consider a nickel plate that is in contact with hydrogen gas at 358 K and 300 kPa. Determine the molar and mass density of hydrogen in the nickel at the interface (Fig. 14–18).

**SOLUTION** A nickel plate is exposed to hydrogen. The molar and mass density of hydrogen in the nickel at the interface is to be determined.

**Assumptions** Nickel and hydrogen are in thermodynamic equilibrium at the interface.

**Properties** The molar mass of hydrogen is \( M = \frac{1}{2} \) kg/kmol (Table A–1). The solubility of hydrogen in nickel at 358 K is 0.00901 kmol/m³ · bar (Table 14–7).

**Analysis** Noting that 300 kPa = 3 bar, the molar density of hydrogen in the nickel at the interface is determined from Eq. 14–20 to be

\[
C_{H_2, \text{solid side}} = \mathcal{J} \times P_{H_2, \text{gas side}} = (0.00901 \text{ kmol/m}^3 \cdot \text{bar})(3 \text{ bar}) = 0.027 \text{ kmol/m}^3
\]

It corresponds to a mass density of

\[
\rho_{H_2, \text{solid side}} = C_{H_2, \text{solid side}} M_{H_2} = (0.027 \text{ kmol/m}^3)(2) = 0.054 \text{ kg/m}^3
\]

That is, there will be 0.027 kmol (or 0.054 kg) of H₂ gas in each m³ volume of nickel adjacent to the interface.

**14–5 STEADY MASS DIFFUSION THROUGH A WALL**

Many practical mass transfer problems involve the diffusion of a species through a plane-parallel medium that does not involve any homogeneous chemical reactions under one-dimensional steady conditions. Such mass transfer problems are analogous to the steady one-dimensional heat conduction problems in a plane wall with no heat generation and can be analyzed similarly. In fact, many of the relations developed in Chapter 3 can be used for mass transfer by replacing temperature by mass (or molar) fraction, thermal conductivity by \( \rho D_{AB} \) (or \( CD_{AB} \)), and heat flux by mass (or molar) flux (Table 14–8).
Consider a solid plane wall (medium B) of area A, thickness L, and density ρ. The wall is subjected on both sides to different concentrations of a species A to which it is permeable. The boundary surfaces at x = 0 and x = L are located within the solid adjacent to the interfaces, and the mass fractions of A at those surfaces are maintained at \( w_{A,1} \) and \( w_{A,2} \), respectively, at all times (Fig. 14–19). The mass fraction of species A in the wall will vary in the \( x \)-direction only and can be expressed as \( w_A(x) \). Therefore, mass transfer through the wall in this case can be modeled as steady and one-dimensional. Here we determine the rate of mass diffusion of species A through the wall using a similar approach to that used in Chapter 3 for heat conduction.

The concentration of species A at any point will not change with time since operation is steady, and there will be no production or destruction of species A since no chemical reactions are occurring in the medium. Then the conservation of mass principle for species A can be expressed as the mass flow rate of species A through the wall at any cross section is the same. That is

\[
m_{\text{diff},A} = j_A A = \text{constant} \quad \text{(kg/s)}
\]

Then Fick’s law of diffusion becomes

\[
j_A = \frac{m_{\text{diff},A}}{A} = -\rho D_{AB} \frac{dw_A}{dx} \quad \text{constant}
\]

Separating the variables in this equation and integrating across the wall from \( x = 0 \), where \( w(0) = w_{A,1} \), to \( x = L \), where \( w(L) = w_{A,2} \), we get

\[
m_{\text{diff},A} \int_0^L dx = -\int_{w_{A,1}}^{w_{A,2}} \rho D_{AB} dw_A
\]

where the mass transfer rate \( m_{\text{diff},A} \) and the wall area \( A \) are taken out of the integral sign since both are constants. If the density \( \rho \) and the mass diffusion coefficient \( D_{AB} \) vary little along the wall, they can be assumed to be constant.

The integration can be performed in that case to yield

\[
m_{\text{diff},A, \text{wall}} = \rho D_{AB} A \frac{w_{A,1} - w_{A,2}}{L} = D_{AB} A \frac{\rho_{A,1} - \rho_{A,2}}{L} \quad \text{(kg/s)} (14-22)
\]

This relation can be rearranged as

\[
m_{\text{diff},A, \text{wall}} = \frac{w_{A,1} - w_{A,2}}{L/d_{AB} A} = \frac{R_{\text{diff, wall}}}{\rho \rho_{A,1} - \rho_{A,2}} \quad \text{(kg/s)} (14-23)
\]

where

\[
R_{\text{diff, wall}} = \frac{L}{\rho D_{AB} A}
\]

is the diffusion resistance of the wall, in s/kg, which is analogous to the electrical or conduction resistance of a plane wall of thickness \( L \) and area \( A \) (Fig. 14–20). Thus, we conclude that the rate of mass diffusion through a plane wall is proportional to the average density, the wall area, and the concentration difference across the wall, but is inversely proportional to the wall thickness. Also, once the rate of mass diffusion is determined, the mass fraction \( w_A(x) \) at any location \( x \) can be determined by replacing \( w_A(x) \) in Eq. 14–22 by \( w_A(x) \) and \( L \) by \( x \).
The preceding analysis can be repeated on a molar basis with this result,

$$\dot{N}_{\text{diff, A, wall}} = CD_{AB} A \frac{y_{A,1} - y_{A,2}}{L} = D_{AB} A \frac{C_{A,1} - C_{A,2}}{L} = \frac{y_{A,1} - y_{A,2}}{R_{\text{diff, wall}}}$$ (14-24)

where $R_{\text{diff, wall}} = L/C_{D_{AB}}$ is the molar diffusion resistance of the wall in s/kmol. Note that molar fractions are accompanied by molar concentrations and mass fractions are accompanied by density. Either relation can be used to determine the diffusion rate of species $A$ across the wall, depending on whether the mass or molar fractions of species $A$ are known at the boundaries. Also, the concentration gradients on both sides of an interface are different, and thus diffusion resistance networks cannot be constructed in an analogous manner to thermal resistance networks.

In developing these relations, we assumed the density and the diffusion coefficient of the wall to be nearly constant. This assumption is reasonable when a small amount of species $A$ diffuses through the wall and thus the concentration of $A$ is small. The species $A$ can be a gas, a liquid, or a solid. Also, the wall can be a plane layer of a liquid or gas provided that it is stationary.

The analogy between heat and mass transfer also applies to cylindrical and spherical geometries. Repeating the approach outlined in Chapter 3 for heat conduction, we obtain the following analogous relations for steady one-dimensional mass transfer through nonreacting cylindrical and spherical layers (Fig. 14–21)

$$\dot{m}_{\text{diff, A, cyl}} = 2\pi L p_{DAB} \frac{w_{A,1} - w_{A,2}}{\ln(r_2/r_1)} = 2\pi L D_{AB} \frac{\rho_{A,1} - \rho_{A,2}}{\ln(r_2/r_1)}$$ (14-25)

$$\dot{m}_{\text{diff, A, sph}} = 4\pi r_1 r_2 p_{DAB} \frac{w_{A,1} - w_{A,2}}{r_2 - r_1} = 4\pi r_1 r_2 D_{AB} \frac{\rho_{A,1} - \rho_{A,2}}{r_2 - r_1}$$ (14-26)

or, on a molar basis,

$$\dot{N}_{\text{diff, A, cyl}} = 2\pi L C_{DAB} \frac{y_{A,1} - y_{A,2}}{\ln(r_2/r_1)} = 2\pi L D_{AB} \frac{C_{A,1} - C_{A,2}}{\ln(r_2/r_1)}$$ (14-27)

$$\dot{N}_{\text{diff, A, sph}} = 4\pi r_1 r_2 C_{DAB} \frac{y_{A,1} - y_{A,2}}{r_2 - r_1} = 4\pi r_1 r_2 D_{AB} \frac{C_{A,1} - C_{A,2}}{r_2 - r_1}$$ (14-28)

Here, $L$ is the length of the cylinder, $r_1$ is the inner radius, and $r_2$ is the outer radius for the cylinder or the sphere. Again, the boundary surfaces at $r = r_1$ and $r = r_2$ are located within the solid adjacent to the interfaces, and the mass fractions of $A$ at those surfaces are maintained at $w_{A,1}$ and $w_{A,2}$, respectively, at all times. (We could make similar statements for the density, molar concentration, and mole fraction of species $A$ at the boundaries.)

We mentioned earlier that the concentration of the gas species in a solid at the interface is proportional to the partial pressure of the adjacent gas and was expressed as $C_A, \text{solid side} = \mathcal{S}_{AB} P_A, \text{gas side}$, where $\mathcal{S}_{AB}$ is the solubility (in kmol/m$^3$ bar) of the gas $A$ in the solid $B$. We also mentioned that the product of solubility and the diffusion coefficient is called the permeability, $\mathcal{P}_{AB} = \mathcal{S}_{AB} D_{AB}$ (in kmol/m · s · bar). Then the molar flow rate of a gas through a solid under steady one-dimensional conditions can be expressed in terms of the partial pressures of the adjacent gas on the two sides of the solid by replacing $C_A$ in these relations by $\mathcal{S}_{AB} P_A$ or $\mathcal{P}_{AB} P_A / D_{AB}$. In the case of a plane wall, for example, it gives (Fig. 14–22)
\[ \dot{N}_{\text{diff},A, \text{wall}} = D_{AB} f_{AB} A \frac{P_{A,1} - P_{A,2}}{L} = \varphi_{AB} A \frac{P_{A,1} - P_{A,2}}{L} \text{ (kmol/s)} \quad (14-29) \]

where \( P_{A,1} \) and \( P_{A,2} \) are the partial pressures of gas A on the two sides of the wall. Similar relations can be obtained for cylindrical and spherical walls by following the same procedure. Also, if the permeability is given on a mass basis (in kg/m \( \cdot \) s \( \cdot \) bar), then Eq. 14–29 will give the diffusion mass flow rate.

Noting that 1 kmol of an ideal gas at the standard conditions of \( 0^\circ \text{C} \) and 1 atm occupies a volume of 22.414 m\(^3\), the volume flow rate of the gas through the wall by diffusion can be determined from

\[ V_{\text{diff},A} = 22.414 \dot{N}_{\text{diff},A} \text{ (standard m}^3\text{/s, at } 0^\circ\text{C and 1 atm)} \]

The volume flow rate at other conditions can be determined from the ideal gas relation \( P_{A} V = \dot{N}_{A} R_{A} T \).

**EXAMPLE 14–5** Diffusion of Hydrogen through a Spherical Container

Pressurized hydrogen gas is stored at 358 K in a 4.8-m-outerdiameter spherical container made of nickel (Fig. 14–23). The shell of the container is 6 cm thick. The molar concentration of hydrogen in the nickel at the inner surface is determined to be 0.087 kmol/m\(^3\). The concentration of hydrogen in the nickel at the outer surface is negligible. Determine the mass flow rate of hydrogen by diffusion through the nickel container.

**SOLUTION** Pressurized hydrogen gas is stored in a spherical container. The diffusion rate of hydrogen through the container is to be determined.

**Assumptions** 1 Mass diffusion is steady and one-dimensional since the hydrogen concentration in the tank and thus at the inner surface of the container is practically constant, and the hydrogen concentration in the atmosphere and thus at the outer surface is practically zero. Also, there is thermal symmetry about the center. 2 There are no chemical reactions in the nickel shell that result in the generation or depletion of hydrogen.

**Properties** The binary diffusion coefficient for hydrogen in the nickel at the specified temperature is \( 1.2 \times 10^{-12} \text{ m}^2/\text{s} \) (Table 14–3b).

**Analysis** We can consider the total molar concentration to be constant (\( C = C_{A,1} + C_{B} \equiv C_{B} = \text{constant} \) ), and the container to be a stationary medium since there is no diffusion of nickel molecules (\( \dot{N}_{B} = 0 \) ) and the concentration of the hydrogen in the container is extremely low (\( C_{A} \ll 1 \)). Then the molar flow rate of hydrogen through this spherical shell by diffusion can readily be determined from Eq. 14–28 to be

\[ \dot{N}_{\text{diff}} = 4\pi r_{1} r_{2} D_{AB} \frac{C_{A,1} - C_{A,2}}{r_{2} - r_{1}} = 4\pi (2.34 \text{ m})(2.40 \text{ m})(1.2 \times 10^{-12} \text{ m}^2/\text{s}) \frac{(0.087 - 0) \text{ kmol/m}^3}{2.40 - 2.34} \]

\[ = 1.228 \times 10^{-10} \text{ kmol/s} \]

Moisture greatly influences the performance and durability of building materials, and thus moisture transmission is an important consideration in the construction and maintenance of buildings.

The dimensions of wood and other hygroscopic substances change with moisture content. For example, a variation of 4.5 percent in moisture content causes the volume of white oak wood to change by 2.5 percent. Such cyclic changes of dimensions weaken the joints and can jeopardize the structural integrity of building components, causing "squeaking" at the minimum. Excess moisture can also cause changes in the appearance and physical properties of materials: corrosion and rusting in metals, rotting in woods, and peeling of paint on the interior and exterior wall surfaces. Soaked wood with a water content of 24 to 31 percent is observed to decay rapidly at temperatures 10 to 38°C. Also, molds grow on wood surfaces at relative humidities above 85 percent. The expansion of water during freezing may damage the cell structure of porous materials.

Moisture content also affects the effective conductivity of porous mediums such as soils, building materials, and insulations, and thus heat transfer through them. Several studies have indicated that heat transfer increases almost linearly with moisture content, at a rate of 3 to 5 percent for each percent increase in moisture content by volume. Insulation with 5 percent moisture content by volume, for example, increases heat transfer by 15 to 25 percent relative to dry insulation (ASHRAE Handbook of Fundamentals, Ref. 1, Chap. 20) (Fig. 14–24). Moisture migration may also serve as a transfer mechanism for latent heat by alternate evaporation and condensation. During a hot and humid day, for example, water vapor may migrate through a wall and condense on the inner side, releasing the heat of vaporization, with the process reversing during a cool night. Moisture content also affects the specific heat and thus the heat storage characteristics of building materials.

Moisture migration in the walls, floors, or ceilings of buildings and in other applications is controlled by either vapor barriers or vapor retarders. Vapor barriers are materials that are impermeable to moisture, such as sheet metals,
heavy metal foils, and thick plastic layers, and they effectively bar the vapor from migrating. *Vapor retarders*, on the other hand, *retard or slow down* the flow of moisture through the structures but do not totally eliminate it. Vapor retarders are available as solid, flexible, or coating materials, but they usually consist of a thin sheet or coating. Common forms of vapor retarders are *reinforced plastics or metals, thin foils, plastic films, treated papers, coated felts, and polymeric or asphaltic paint coatings*. In applications such as the building of walls where vapor penetration is unavoidable because of numerous openings such as electrical boxes, telephone lines, and plumbing passages, vapor retarders are used instead of vapor barriers to allow the vapor that somehow leaks in to exit to the outside instead of trapping it in. Vapor retarders with a permeance of $57.4 \times 10^{-9}$ kg/s · m² are commonly used in residential buildings.

The insulation on *chilled water lines* and other impermeable surfaces that are always cold must be wrapped with a *vapor barrier jacket*, or such cold surfaces must be insulated with a material that is impermeable to moisture. This is because moisture that migrates through the insulation to the cold surface will condense and remain there indefinitely with no possibility of vaporizing and moving back to the outside. The accumulation of moisture in such cases may render the insulation useless, resulting in excessive energy consumption.

Atmospheric air can be viewed as a mixture of dry air and water vapor, and the atmospheric pressure is the sum of the pressure of dry air and the pressure of water vapor, which is called the *vapor pressure* $P_v$. Air can hold a certain amount of moisture only, and the ratio of the actual amount of moisture in the air at a given temperature to the maximum amount air can hold at that temperature is called the *relative humidity* $\phi$. The relative humidity ranges from 0 for dry air to 100 percent for *saturated* air (air that cannot hold any more moisture). The partial pressure of water vapor in saturated air is called the *saturation pressure* $P_{\text{sat}}$. Table 14–9 lists the saturation pressure at various temperatures.

The amount of moisture in the air is completely specified by the temperature and the relative humidity, and the vapor pressure is related to relative humidity $\phi$ by

$$P_v = \phi P_{\text{sat}} \tag{14-30}$$

where $P_{\text{sat}}$ is the saturation (or boiling) pressure of water at the specified temperature. Then the mass flow rate of moisture through a plain layer of thickness $L$ and normal area $A$ can be expressed as

$$m_v = \Phi A \frac{P_{v,1} - P_{v,2}}{L} = \Phi A \frac{\phi_1 P_{\text{sat},1} - \phi_2 P_{\text{sat},2}}{L} \tag{14-31}$$

where $\Phi$ is the vapor permeability of the material, which is usually expressed on a mass basis in the unit kg/s · m · Pa, where kg = $10^{-12}$ kg and 1 Pa = $10^{-5}$ bar. Note that vapor migrates or diffuses from a region of higher vapor pressure toward a region of lower vapor pressure.

**TABLE 14–9**

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Saturation Pressure, Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>−40</td>
<td>13</td>
</tr>
<tr>
<td>−36</td>
<td>20</td>
</tr>
<tr>
<td>−32</td>
<td>31</td>
</tr>
<tr>
<td>−28</td>
<td>47</td>
</tr>
<tr>
<td>−24</td>
<td>70</td>
</tr>
<tr>
<td>−20</td>
<td>104</td>
</tr>
<tr>
<td>−16</td>
<td>151</td>
</tr>
<tr>
<td>−12</td>
<td>218</td>
</tr>
<tr>
<td>−8</td>
<td>310</td>
</tr>
<tr>
<td>−4</td>
<td>438</td>
</tr>
<tr>
<td>0</td>
<td>611</td>
</tr>
<tr>
<td>5</td>
<td>872</td>
</tr>
<tr>
<td>10</td>
<td>1,228</td>
</tr>
<tr>
<td>15</td>
<td>1,705</td>
</tr>
<tr>
<td>20</td>
<td>2,339</td>
</tr>
<tr>
<td>25</td>
<td>3,169</td>
</tr>
<tr>
<td>30</td>
<td>4,246</td>
</tr>
<tr>
<td>35</td>
<td>5,628</td>
</tr>
<tr>
<td>40</td>
<td>7,384</td>
</tr>
<tr>
<td>50</td>
<td>12,349</td>
</tr>
<tr>
<td>100</td>
<td>101,330</td>
</tr>
<tr>
<td>200</td>
<td>$1.55 \times 10^6$</td>
</tr>
<tr>
<td>300</td>
<td>$8.58 \times 10^6$</td>
</tr>
</tbody>
</table>
The permeability of most construction materials is usually expressed for a given thickness instead of per unit thickness. It is called the permeance \( \mathcal{M} \), which is the ratio of the permeability of the material to its thickness. That is,

\[
\mathcal{M} = \frac{\varphi}{L} \quad \text{(kg/s \cdot m\(^2\) \cdot Pa)} \quad (14-32)
\]

The reciprocal of permeance is called (unit) vapor resistance and is expressed as

\[
R_v = \frac{1}{\mathcal{M}} = \frac{L}{\varphi} \quad \text{(s \cdot m\(^2\) \cdot Pa/kg)} \quad (14-33)
\]

Note that vapor resistance represents the resistance of a material to water vapor transmission.

It should be pointed out that the amount of moisture that enters or leaves a building by diffusion is usually negligible compared to the amount that enters with infiltrating air or leaves with exfiltrating air. The primary cause of interest in the moisture diffusion is its impact on the performance and longevity of building materials.

The overall vapor resistance of a composite building structure that consists of several layers in series is the sum of the resistances of the individual layers and is expressed as

\[
R_{v,\text{total}} = R_{v,1} + R_{v,2} + \cdots + R_{v,n} = \sum R_{v,i} \quad (14-34)
\]

Then the rate of vapor transmission through a composite structure can be determined in an analogous manner to heat transfer from

\[
m_v = A \left( \frac{\Delta P_v}{R_{v,\text{total}}} \right) \quad \text{(kg/s)} \quad (14-35)
\]

Vapor permeance of common building materials is given in Table 14–10.

### Table 14–10

<table>
<thead>
<tr>
<th>Materials and Its Thickness</th>
<th>Permeance ng/s \cdot m(^2) \cdot Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete (1:2:4 mix, 1 m)</td>
<td>4.7</td>
</tr>
<tr>
<td>Brick, masonry, 100 mm</td>
<td>46</td>
</tr>
<tr>
<td>Plaster on metal lath, 19 mm</td>
<td>860</td>
</tr>
<tr>
<td>Plaster on wood lath, 19mm</td>
<td>630</td>
</tr>
<tr>
<td>Gypsum wall board, 9.5 mm</td>
<td>2860</td>
</tr>
<tr>
<td>Plywood, 6.4 mm</td>
<td>40–109</td>
</tr>
<tr>
<td>Still air, 1 m</td>
<td>174</td>
</tr>
<tr>
<td>Mineral wool insulation (unprotected), 1 m</td>
<td>245</td>
</tr>
<tr>
<td>Expanded polyurethane insulation board, 1 m</td>
<td>0.58–2.3</td>
</tr>
<tr>
<td>Aluminum foil, 0.025 mm</td>
<td>0.0</td>
</tr>
<tr>
<td>Aluminum foil, 0.009 mm</td>
<td>2.9</td>
</tr>
<tr>
<td>Polyethylene, 0.051 mm</td>
<td>9.1</td>
</tr>
<tr>
<td>Polyethylene, 0.2 mm</td>
<td>2.3</td>
</tr>
<tr>
<td>Polyester, 0.19 mm</td>
<td>4.6</td>
</tr>
<tr>
<td>Vapor retarder latex paint, 0.070 mm</td>
<td>26</td>
</tr>
<tr>
<td>Exterior acrylic house and trim paint, 0.040 mm</td>
<td>313</td>
</tr>
<tr>
<td>Building paper, unit mass of 0.16–0.68 kg/m(^2)</td>
<td>0.1–2400</td>
</tr>
</tbody>
</table>

*Data vary greatly. Consult manufacturer for more accurate data. Multiply by 1.41 \( \times 10^{-6} \) to convert to lbm/s \cdot ft\(^2\) \cdot psi. Also, 1 ng = 10\(^{-12}\) kg.
The indoor conditions are 20°C and 60 percent relative humidity while the outside conditions are −16°C and 70 percent relative humidity. Determine if condensation or freezing of moisture will occur in the insulation.

**SOLUTION** The thermal and vapor resistances of different layers of a wall are given. The possibility of condensation or freezing of moisture in the wall is to be investigated.

**Assumptions** 1 Steady operating conditions exist. 2 Heat transfer through the wall is one-dimensional. 3 Thermal and vapor resistances of different layers of the wall and the heat transfer coefficients are constant.

**Properties** The thermal and vapor resistances are as given in the problem statement. The saturation pressures of water at 20°C and −16°C are 2339 Pa and 151 Pa, respectively (Table 14–9).

**Analysis** The schematic of the wall as well as the different elements used in its construction are shown in Figure 14–25. Condensation is most likely to occur at the coldest part of insulation, which is the part adjacent to the exterior sheathing. Noting that the total thermal resistance of the wall is 3.05 m²·°C/W, the rate of heat transfer through a unit area of the wall is

\[
Q_{\text{wall}} = A \frac{T_i - T_o}{R_{\text{total}}} = (1 \text{ m}^2) \frac{20 - (-16)\degree\text{C}}{3.05 \text{ m}^2 \cdot °\text{C/W}} = 11.8 \text{ W}
\]

The thermal resistance of the exterior part of the wall beyond the insulation is 0.03 + 0.14 + 0.23 = 0.40 m²·°C/W. Then the temperature of the insulation–outer sheathing interface is

\[
T_i = T_o + \frac{Q_{\text{wall}}R_{\text{ext}}}{3.05 \text{ m}^2 \cdot °\text{C/W}} = -16\degree\text{C} + (11.8 \text{ W})(0.40\text{m}^2\cdot°\text{C/W}) = -11.3\degree\text{C}
\]

The saturation pressure of water at −11.3°C is 234 Pa, as shown in Table 14–9, and if there is condensation or freezing, the vapor pressure at the insulation–outer sheathing interface will have to be this value. The vapor pressure at the indoors and the outdoors is

\[
P_{v,1} = \phi_1 P_{\text{sat},1} = 0.60 \times (2340 \text{ Pa}) = 1404 \text{ Pa}
\]

\[
P_{v,2} = \phi_2 P_{\text{sat},2} = 0.70 \times (151 \text{ Pa}) = 106 \text{ Pa}
\]

Then the rate of moisture flow through the interior and exterior parts of the wall becomes
14–7 TRANSIENT MASS DIFFUSION

The steady analysis discussed earlier is useful when determining the leakage rate of a species through a stationary layer. But sometimes we are interested in the diffusion of a species into a body during a limited time before steady operating conditions are established. Such problems are studied using transient analysis.

For example, the surface of a mild steel component is commonly hardened by packing the component in a carbonaceous material in a furnace at high temperature. During the short time period in the furnace, the carbon molecules diffuse through the surface of the steel component, but they penetrate to a depth of only a few millimeters. The carbon concentration decreases exponentially from the surface to the inner parts, and the result is a steel component with a very hard surface and a relatively soft core region (Fig. 14–26).

The same process is used in the gem industry to color clear stones. For example, a clear sapphire is given a brilliant blue color by packing it in titanium and iron oxide powders and baking it in an oven at about 2000 °C for about a month. The titanium and iron molecules penetrate less than 0.5 mm in the sapphire during this process. Diffusion in solids is usually done at high temperatures to take advantage of the high diffusion coefficients at high temperatures and thus to keep the diffusion time at a reasonable level. Such diffusion or “doping” is also commonly practiced in the production of n- or p-type semiconductor materials used in the manufacture of electronic components. Drying processes such as the drying of coal, timber, food, and textiles constitute another major application area of transient mass diffusion.

\[
\dot{m}_{v, \text{interior}} = A \frac{\Delta P}{R_v} = A \frac{P_{v,1} - P_{v,l}}{R_v, \text{interior}} = \frac{(1404 - 234) \text{ Pa}}{(0.012 + 0.0004) \text{ Pa m}^2 \cdot \text{s}/\text{ng}} = 94,355 \text{ ng/s} = 94.4 \text{ µg/s}
\]

\[
\dot{m}_{v, \text{exterior}} = A \frac{\Delta P}{R_v} = A \frac{P_{v,1} - P_{v,l}}{R_v, \text{exterior}} = \frac{(234 - 106) \text{ Pa}}{(0.019 + 0.0138) \text{ Pa m}^2 \cdot \text{s}/\text{ng}} = 3902 \text{ ng/s} = 3.9 \text{ µg/s}
\]

That is, moisture is flowing toward the interface at a rate of 94.4 µg/s but flowing from the interface to the outdoors at a rate of only 3.9 µg/s. Noting that the interface pressure cannot exceed 234 Pa, these results indicate that moisture is freezing in the insulation at a rate of

\[
\dot{m}_{v, \text{freezing}} = \dot{m}_{v, \text{interior}} - \dot{m}_{v, \text{exterior}} = 94.4 - 3.9 = 90.5 \text{ µg/s}
\]

This corresponds to 7.82 g during a 24-h period, which can be absorbed by the insulation or sheathing, and then flows out when the conditions improve. However, excessive condensation (or frosting at temperatures below 0 °C) of moisture in the walls during long cold spells can cause serious problems. This problem can be avoided or minimized by installing vapor barriers on the interior side of the wall, which will limit the moisture flow rate to 3.9 µg/s. Note that if there were no condensation or freezing, the flow rate of moisture through a 1 m² section of the wall would be 28.7 µg/s (can you verify this?).

14–7 TRANSIENT MASS DIFFUSION

The steady analysis discussed earlier is useful when determining the leakage rate of a species through a stationary layer. But sometimes we are interested in the diffusion of a species into a body during a limited time before steady operating conditions are established. Such problems are studied using transient analysis. For example, the surface of a mild steel component is commonly hardened by packing the component in a carbonaceous material in a furnace at high temperature. During the short time period in the furnace, the carbon molecules diffuse through the surface of the steel component, but they penetrate to a depth of only a few millimeters. The carbon concentration decreases exponentially from the surface to the inner parts, and the result is a steel component with a very hard surface and a relatively soft core region (Fig. 14–26).

The same process is used in the gem industry to color clear stones. For example, a clear sapphire is given a brilliant blue color by packing it in titanium and iron oxide powders and baking it in an oven at about 2000 °C for about a month. The titanium and iron molecules penetrate less than 0.5 mm in the sapphire during this process. Diffusion in solids is usually done at high temperatures to take advantage of the high diffusion coefficients at high temperatures and thus to keep the diffusion time at a reasonable level. Such diffusion or “doping” is also commonly practiced in the production of n- or p-type semiconductor materials used in the manufacture of electronic components. Drying processes such as the drying of coal, timber, food, and textiles constitute another major application area of transient mass diffusion.
Transient mass diffusion in a stationary medium is analogous to transient heat transfer provided that the solution is dilute and thus the density of the medium \( \rho \) is constant. In Chapter 4 we presented analytical and graphical solutions for one-dimensional transient heat conduction problems in solids with constant properties, no heat generation, and uniform initial temperature. The analogous one-dimensional transient mass diffusion problems satisfy these requirements:

1. The diffusion coefficient is constant. This is valid for an isothermal medium since \( D_{AB} \) varies with temperature (corresponds to constant thermal diffusivity).
2. There are no homogeneous reactions in the medium that generate or deplete the diffusing species \( A \) (corresponds to no heat generation).
3. Initially \( (t = 0) \) the concentration of species \( A \) is constant throughout the medium (corresponds to uniform initial temperature).

Then the solution of a mass diffusion problem can be obtained directly from the analytical or graphical solution of the corresponding heat conduction problem given in Chapter 4. The analogous quantities between heat and mass transfer are summarized in Table 14–11 for easy reference. For the case of a semi-infinite medium with constant surface concentration, for example, the solution can be expressed in an analogous manner to Eq. 4-24 as

\[
\frac{C_A(x, t) - C_{A,i}}{C_{A,i} - C_{A}} = \text{erfc} \left( \frac{x}{2\sqrt{D_{AB}t}} \right)
\]

(14-36)

where \( C_{A,i} \) is the initial concentration of species \( A \) at time \( t = 0 \) and \( C_{A} \) is the concentration at the inner side of the exposed surface of the medium. By using the definitions of molar fraction, mass fraction, and density, it can be shown that for dilute solutions,

\[
\frac{C_A(x, t) - C_{A,i}}{C_{A,i} - C_{A}} = \frac{\rho(x, t) - \rho_{A,i}}{\rho_{A,i} - \rho_{A}} = \frac{w_A(x, t) - w_{A,i}}{w_{A,i} - w_{A}} = \frac{\gamma_A(x, t) - \gamma_{A,i}}{\gamma_{A,i} - \gamma_{A}}
\]

(14-37)

since the total density or total molar concentration of dilute solutions is usually constant (\( \rho = \) constant or \( C = \) constant). Therefore, other measures of concentration can be used in Eq. 14–36.

A quantity of interest in mass diffusion processes is the depth of diffusion at a given time. This is usually characterized by the penetration depth defined as the location \( x \) where the tangent to the concentration profile at the surface \( (x = 0) \) intercepts the \( C_A = C_{A,i} \) line, as shown in Figure 14–27. Obtaining the concentration gradient at \( x = 0 \) by differentiating Eq. 14–36, the penetration depth is determined to be

\[
\delta_{\text{diff}} = \frac{C_{A,i} - C_{A}}{(dC_A/dx)_{x=0}} = \frac{C_{A,i} - C_{A}}{(C_{A,i} - C_{A})/\sqrt{\pi D_{AB}t}} = \sqrt{\pi D_{AB}t}
\]

(14-38)

Therefore, the penetration depth is proportional to the square root of both the diffusion coefficient and time. The diffusion coefficient of zinc in copper at 1000°C, for example, is \( 5.0 \times 10^{-12} \) m²/s. Then the penetration depth of zinc in copper in 10 h is

\[
\delta_{\text{diff}} = \sqrt{\pi D_{AB}t} = \sqrt{\pi \times 5.0 \times 10^{-12} \times 10^2} = 100 \text{ m}
\]

FIGURE 14–27

The concentration profile of species \( A \) in a semi-infinite medium during transient mass diffusion and the penetration depth.
That is, zinc will penetrate to a depth of about 0.38 mm in an appreciable amount in 10 h, and there will hardly be any zinc in the copper block beyond a depth of 0.38 mm.

The diffusion coefficients in solids are typically very low (on the order of $10^{-9}$ to $10^{-15}$ m²/s), and thus the diffusion process usually affects a thin layer at the surface. A solid can conveniently be treated as a semi-infinite medium during transient mass diffusion regardless of its size and shape when the penetration depth is small relative to the thickness of the solid. When this is not the case, solutions for one-dimensional transient mass diffusion through a plane wall, cylinder, and sphere can be obtained from the solutions of analogous heat conduction problems using the Heisler charts or one-term solutions presented in Chapter 4.

\[
\delta_{\text{diff}} = \sqrt{\pi D_{\text{AB}t}} = \sqrt{\pi (5.0 \times 10^{-12} \text{ m}^2/\text{s})(10 \times 3600 \text{ s})} = 0.00038 \text{ m} = 0.38 \text{ mm}
\]
14–8 DIFFUSION IN A MOVING MEDIUM

To this point we have limited our consideration to mass diffusion in a stationary medium, and thus the only motion involved was the creeping motion of molecules in the direction of decreasing concentration, and there was no motion of the mixture as a whole. Many practical problems, such as the evaporation of water from a lake under the influence of the wind or the mixing of two fluids as they flow in a pipe, involve diffusion in a moving medium where the bulk motion is caused by an external force. Mass diffusion in such cases is complicated by the fact that chemical species are transported both by diffusion and by the bulk motion of the medium (i.e., convection). The velocities and mass flow rates of species in a moving medium consist of two components: one due to molecular diffusion and one due to convection (Fig. 14–29).

Diffusion in a moving medium, in general, is difficult to analyze since various species can move at different velocities in different directions. Turbulence will complicate the things even more. To gain a firm understanding of the physical mechanism while keeping the mathematical complexities to a minimum, we limit our consideration to systems that involve only two components (species A and B) in one-dimensional flow (velocity and other properties change in one direction only, say the x-direction). We also assume the total density (or molar concentration) of the medium remains constant. That is, \( \rho = \rho_A + \rho_B = \text{constant} \) (or \( C = C_A + C_B = \text{constant} \)) but the densities of species A and B may vary in the x-direction.

Several possibilities are summarized in Figure 14–30. In the trivial case (case a) of a stationary homogeneous mixture, there will be no mass transfer by molecular diffusion or convection since there is no concentration gradient or bulk motion. The next case (case b) corresponds to the flow of a well-mixed fluid mixture through a pipe. Note that there is no concentration gradients and thus molecular diffusion in this case, and all species move at the bulk flow velocity of \( \dot{V} \). The mixture in the third case (case c) is stationary (\( \dot{V} = 0 \)) and thus it corresponds to ordinary molecular diffusion in stationary mediums, which we discussed before. Note that the velocity of a species at a location in

\[
\frac{x}{2\sqrt{D_{AB}t}} = 0.17
\]

Then solving for the time \( t \) gives

\[
t = \frac{x^2}{4D_{AB}(0.17)^2} = \frac{(0.0005 \text{ m})^2}{4 \times (4.8 \times 10^{-10} \text{ m}^2/\text{s})(0.17)^2} = 4505 \text{ s} = 1 \text{ h 15 min}
\]

Discussion The steel component in this case must be held in the furnace for 1 h and 15 min to achieve the desired level of hardening. The diffusion coefficient of carbon in steel increases exponentially with temperature, and thus this process is commonly done at high temperatures to keep the diffusion time at a reasonable level.
this case is simply the diffusion velocity, which is the average velocity of a group of molecules at that location moving under the influence of concentration gradient. Finally, the last case (case d) involves both molecular diffusion and convection, and the velocity of a species in this case is equal to the sum of the bulk flow velocity and the diffusion velocity. Note that the flow and the diffusion velocities can be in the same or opposite directions, depending on the direction of the concentration gradient. The diffusion velocity of a species is negative when the bulk flow is in the positive x-direction and the concentration gradient is positive (i.e., the concentration of the species increases in the x-direction).

Noting that the mass flow rate at any flow section is expressed as \( \dot{m} = \rho \dot{V} A \) where \( \rho \) is the density, \( \dot{V} \) is the velocity, and \( A \) is the cross sectional area, the conservation of mass relation for the flow of a mixture that involves two species \( A \) and \( B \) can be expressed as

\[ \dot{m} = \dot{m}_A + \dot{m}_B \]

or

\[ \rho \dot{V} A = \rho_A \dot{V}_A A + \rho_B \dot{V}_B A \]

Canceling \( A \) and solving for \( \dot{V} \) gives
\[ \dot{V} = \frac{\rho_A \dot{V}_A + \rho_B \dot{V}_B}{\rho} = \frac{\rho_A}{\rho} \dot{V}_A + \frac{\rho_B}{\rho} \dot{V}_B = \dot{w}_A \dot{V}_A + \dot{w}_B \dot{V}_B \]  

(14-39)

where \( \dot{V} \) is called the **mass-average velocity** of the flow, which is the velocity that would be measured by a velocity sensor such as a pitot tube, a turbine device, or a hot wire anemometer inserted into the flow.

The special case \( \dot{V} = 0 \) corresponds to a **stationary medium**, which can now be defined more precisely as a medium whose mass-average velocity is zero. Therefore, mass transport in a stationary medium is by diffusion only, and zero mass-average velocity indicates that there is no bulk fluid motion.

When there is no **concentration gradient** (and thus no molecular mass diffusion) in the fluid, the velocity of all species will be equal to the mass-average velocity of the flow. That is, \( \dot{V} = \dot{V}_A = \dot{V}_B \). But when there is a concentration gradient, there will also be a simultaneous flow of species in the direction of decreasing concentration at a diffusion velocity of \( \dot{V}_{\text{diff}} \). Then the average velocity of the species \( A \) and \( B \) can be determined by superimposing the average flow velocity and the diffusion velocity as (Fig. 14–31)

\[ \dot{V}_A = \dot{V} + \dot{V}_{\text{diff}, A} \]

\[ \dot{V}_B = \dot{V} + \dot{V}_{\text{diff}, B} \]  

(14-40)

Similarly, we apply the superposition principle to the species mass flow rates to get

\[ \dot{m}_A = \rho_A \dot{V}_A = \rho_A (\dot{V} + \dot{V}_{\text{diff}, A}) = \rho_A \dot{V} + \rho_A \dot{V}_{\text{diff}, A} = \dot{m}_{\text{conv}, A} + \dot{m}_{\text{diff}, A} \]

\[ \dot{m}_B = \rho_B \dot{V}_B = \rho_B (\dot{V} + \dot{V}_{\text{diff}, B}) = \rho_B \dot{V} + \rho_B \dot{V}_{\text{diff}, B} = \dot{m}_{\text{conv}, B} + \dot{m}_{\text{diff}, B} \]  

(14-41)

Using Fick’s law of diffusion, the total mass fluxes \( j = \dot{m}/A \) can be expressed as

\[ j_A = \rho_A \dot{V} + \rho_A \dot{V}_{\text{diff}, A} = \frac{\rho_A}{\rho} \rho \dot{V} - \rho D_{AB} \frac{dw_A}{dx} = w_A (j_A + j_B) - \rho D_{AB} \frac{dw_A}{dx} \]

\[ j_B = \rho_B \dot{V} + \rho_B \dot{V}_{\text{diff}, B} = \frac{\rho_B}{\rho} \rho \dot{V} - \rho D_{BA} \frac{dw_B}{dx} = w_B (j_A + j_B) - \rho D_{BA} \frac{dw_B}{dx} \]  

(14-42)

Note that the diffusion velocity of a species is negative when the molecular diffusion occurs in the negative \( x \)-direction (opposite to flow direction). The mass diffusion rates of the species \( A \) and \( B \) at a specified location \( x \) can be expressed as

\[ \dot{m}_{\text{diff}, A} = \rho_A \dot{V}_{\text{diff}, A} = \rho_A (\dot{V}_A - \dot{V})A \]

\[ \dot{m}_{\text{diff}, B} = \rho_B \dot{V}_{\text{diff}, B} = \rho_B (\dot{V}_B - \dot{V})A \]  

(14-43)

By substituting the \( \dot{V} \) relation from Eq. 14–39 into Eq. 11–43, it can be shown that at any cross section

\[ \dot{m}_{\text{diff}, A} + \dot{m}_{\text{diff}, B} = 0 \rightarrow \dot{m}_{\text{diff}, A} = -\dot{m}_{\text{diff}, B} \rightarrow -\rho A D_{AB} \frac{dw_A}{dx} = \rho A D_{BA} \frac{dw_B}{dx} \]  

(14-44)

which indicates that the rates of diffusion of species \( A \) and \( B \) must be equal in magnitude but opposite in sign. This is a consequence of the assumption
\[ w = w_A + w_B = 1 \]

In a binary mixture of species A and B with \( \rho = \rho_A + \rho_B \) constant, the rates of mass diffusion of species A and B are equal magnitude and opposite in direction.

\[ \frac{dw_A}{dx} = - \frac{dw_B}{dx} \]

\[ \dot{m}_{\text{diff}, A} = - \dot{m}_{\text{diff}, B} \]

\[ D_{AB} = D_{BA} \]

Figure 14–32

In a binary mixture of species A and B with \( \rho = \rho_A + \rho_B \) constant, and it indicates that anytime the species A diffuses in one direction, an equal amount of species B must diffuse in the opposite direction to maintain the density (or the molar concentration) constant. This behavior is closely approximated by dilute gas mixtures and dilute liquid or solid solutions. For example, when a small amount of gas diffuses into a liquid, it is reasonable to assume the density of the liquid to remain constant.

Thus we conclude from Eq. 14–44 that (Fig. 14–32)

\[ D_{AB} = D_{BA} \]  

That is, in the case of constant total concentration, the diffusion coefficient of species A into B is equal to the diffusion coefficient of species B into A.

We now repeat the analysis presented above with molar concentration \( C \) and the molar flow rate \( \dot{N} \). The conservation of matter in this case is expressed as

\[ \dot{N} = \dot{N}_A + \dot{N}_B \]

or

\[ \rho \overline{V}_A = \rho_A \overline{V}_A + \rho_B \overline{V}_B A \]  

(14-47)

Canceling A and solving for \( \overline{V} \) gives

\[ \overline{V} = \frac{C_A \overline{V}_A + C_B \overline{V}_B}{C} = \frac{C_A}{C} \overline{V}_A + \frac{C_B}{C} \overline{V}_B = y_A \overline{V}_A + y_B \overline{V}_B \]

(14-48)

where \( \overline{V} \) is called the molar-average velocity of the flow. Note that \( \overline{V} \neq \overline{v} \) unless the mass and molar fractions are the same. The molar flow rates of species are determined similarly to be

\[ \dot{N}_A = C_A \overline{V}_A + C_A \overline{V}_{\text{diff}, A} = \frac{C_A}{C} C \overline{V} - CD_{AB} \frac{dy_A}{dx} = y_A (\dot{j}_A + \dot{j}_B) - CD_{AB} \frac{dy_A}{dx} \]

\[ \dot{N}_B = C_B \overline{V}_B + C_B \overline{V}_{\text{diff}, B} = \frac{C_B}{C} C \overline{V} - CD_{BA} \frac{dy_B}{dx} = y_B (\dot{j}_A + \dot{j}_B) - CD_{BA} \frac{dy_B}{dx} \]

(14-49)

Using Fick’s law of diffusion, the total molar fluxes \( \dot{j} = \dot{N}/A \) and diffusion molar flow rates \( \dot{N}_{\text{diff}} \) can be expressed as

\[ \dot{j}_A = C_A \overline{V} + C_A \overline{V}_{\text{diff}, A} = C_A C \overline{V} - CD_{AB} \frac{dy_A}{dx} = y_A (\dot{j}_A + \dot{j}_B) - CD_{AB} \frac{dy_A}{dx} \]

\[ \dot{j}_B = C_B \overline{V} + C_B \overline{V}_{\text{diff}, B} = C_B C \overline{V} - CD_{BA} \frac{dy_B}{dx} = y_B (\dot{j}_A + \dot{j}_B) - CD_{BA} \frac{dy_B}{dx} \]

(14-50)

and

\[ \dot{N}_{\text{diff}, A} = C_A \overline{V}_{\text{diff}, A} = C_A (\overline{V}_A - \overline{V}) A \]

\[ \dot{N}_{\text{diff}, B} = C_B \overline{V}_{\text{diff}, B} A = C_B (\overline{V}_B - \overline{V}) A \]

(14-51)
By substituting the $\bar{V}$ relation from Eq. 14–48 into these two equations, it can be shown that

$$
\dot{N}_{\text{diff},A} + \dot{N}_{\text{diff},B} = 0 \quad \rightarrow \quad \dot{N}_{\text{diff},A} = -\dot{N}_{\text{diff},B} \quad (14-52)
$$

which again indicates that the rates of diffusion of species $A$ and $B$ must be equal in magnitude but opposite in sign.

It is important to note that when working with molar units, a medium is said to be stationary when the molar-average velocity is zero. The average velocity of the molecules will be zero in this case, but the apparent velocity of the mixture as measured by a velocimeter placed in the flow will not necessarily be zero because of the different masses of different molecules. In a mass-based stationary medium, for each unit mass of species $A$ moving in one direction, a unit mass of species $B$ moves in the opposite direction. In a mole-based stationary medium, however, for each mole of species $A$ moving in one direction, one mole of species $B$ moves in the opposite direction. But this may result in a net mass flow rate in one direction that can be measured by a velocimeter since the masses of different molecules are different.

You may be wondering whether to use the mass analysis or molar analysis in a problem. The two approaches are equivalent, and either approach can be used in mass transfer analysis. But sometimes it may be easier to use one of the approaches, depending on what is given. When mass-average velocity is known or can easily be obtained, obviously it is more convenient to use the mass-based formulation. When the total pressure and temperature of a mixture are constant, however, it is more convenient to use the molar formulation, as explained next.

**Special Case: Gas Mixtures at Constant Pressure and Temperature**

Consider a gas mixture whose total pressure and temperature are constant throughout. When the mixture is homogeneous, the mass density $\rho$, the molar density (or concentration) $C$, the gas constant $R$, and the molar mass $M$ of the mixture are the same throughout the mixture. But when the concentration of one or more gases in the mixture is not constant, setting the stage for mass diffusion, then the mole fractions $y_i$ of the species will vary throughout the mixture. As a result, the gas constant $R$, the molar mass $M$, and the mass density $\rho$ of the mixture will also vary since, assuming ideal gas behavior,

$$
M = \sum y_i M_i, \quad R = \frac{R_u}{M}, \quad \text{and} \quad \rho = \frac{P}{RT}
$$

where $R_u = 8.314 \text{ kJ/kmol} \cdot \text{K}$ is the universal gas constant. Therefore, the assumption of constant mixture density ($\rho = \text{constant}$) in such cases will not be accurate unless the gas or gases with variable concentrations constitute a very small fraction of the mixture. However, the molar density $C$ of a mixture remains constant when the mixture pressure $P$ and temperature $T$ are constant since

$$
P = \rho RT = \frac{R}{M} C_T = CR_u T \quad (14-53)\)
The condition $C = \text{constant}$ offers considerable simplification in mass transfer analysis, and thus it is more convenient to use the molar formulation when dealing with gas mixtures at constant total pressure and temperature (Fig. 14–33).

**Diffusion of Vapor through a Stationary Gas: Stefan Flow**

Many engineering applications such as heat pipes, cooling ponds, and the familiar perspiration involve condensation, evaporation, and transpiration in the presence of a noncondensable gas, and thus the *diffusion* of a vapor through a stationary (or stagnant) gas. To understand and analyze such processes, consider a liquid layer of species $A$ in a tank surrounded by a gas of species $B$, such as a layer of liquid water in a tank open to the atmospheric air (Fig. 14–34), at constant pressure $P$ and temperature $T$. Equilibrium exists between the liquid and vapor phases at the interface ($x = 0$), and thus the vapor pressure at the interface must equal the saturation pressure of species $A$ at the specified temperature. We assume the gas to be insoluble in the liquid, and both the gas and the vapor to behave as ideal gases.

If the surrounding gas at the top of the tank ($x = L$) is not saturated, the vapor pressure at the interface will be greater than the vapor pressure at the top of the tank ($P_{A,0} > P_{A,L}$) and thus $y_{A,0} > y_{A,L}$ since $y_A = P_A/P$, and this pressure (or concentration) difference will drive the vapor upward from the air–water interface into the stagnant gas. The upward flow of vapor will be sustained by the evaporation of water at the interface. Under steady conditions, the molar (or mass) flow rate of vapor throughout the stagnant gas column remains constant. That is,

$$
\bar{J}_A = \bar{N}_A/A = \text{constant} \quad \text{or} \quad \bar{m}_A/A = \text{constant}
$$

The pressure and temperature of the gas–vapor mixture are said to be constant, and thus the molar density of the mixture must be constant throughout the mixture, as shown earlier. That is, $C = C_A + C_B = \text{constant}$, and it is more convenient to work with mole fractions or molar concentrations in this case instead of mass fractions or densities since $\rho = \text{constant}$.

Noting that $y_A + y_B = 1$ and that $y_{A,0} > y_{A,L}$, we must have $y_{B,0} < y_{B,L}$. That is, the mole fraction of the gas must be decreasing downward by the same amount that the mole fraction of the vapor is increasing. Therefore, gas must be diffusing from the top of the column toward the liquid interface. However, the gas is said to be *insoluble* in the liquid, and thus there can be no net mass flow of the gas downward. Then under steady conditions, there must be an *upward bulk fluid motion* with an average velocity $\bar{v}$ that is just large enough to balance the diffusion of air downward so that the net molar (or mass) flow rate of the gas at any point is zero. In other words, the upward bulk motion offsets the downward diffusion, and for each air molecule that moves downward, there is another air molecule that moves upward. As a result, the air appears to be *stagnant* (it does not move). That is,

$$
\bar{J}_B = \bar{N}_B/A = 0 \quad \text{or} \quad \bar{m}_B/A = 0
$$

The diffusion medium is no longer stationary because of the bulk motion. The implication of the bulk motion of the gas is that it transports vapor as well as
the gas upward with a velocity of \( \dot{V} \), which results in additional mass flow of vapor upward. Therefore, the molar flux of the vapor can be expressed as

\[
\bar{j}_A = \dot{N}_A = \bar{j}_{A,\text{con}} + \bar{j}_{A,\text{diff}} = y_A (\bar{j}_A + \bar{j}_B) - CD_{AB} \frac{dy_A}{dx} \tag{14-54}
\]

Noting that \( \bar{j}_B = 0 \), it simplifies to

\[
\bar{j}_A = y_A \bar{j}_A - CD_{AB} \frac{dy_A}{dx} \tag{14-55}
\]

Solving for \( \bar{j}_A \) gives

\[
\bar{j}_A = - CD_{AB} \frac{dy_A}{1 - y_A} \rightarrow - \frac{1}{1 - y_A} \frac{dy_A}{dx} = \frac{\bar{j}_A}{CD_{AB}} = \text{constant} \tag{14-56}
\]

since \( \bar{j}_A = \text{constant} \), \( C = \text{constant} \), and \( D_{AB} = \text{constant} \). Separating the variables and integrating from \( x = 0 \), where \( y_A(0) = y_{A,0} \), to \( x = L \), where \( y_A(L) = y_{A,L} \) gives

\[
- \int_{y_{A,0}}^{y_{A,L}} \frac{dy_A}{1 - y_A} = \int_0^L \frac{\bar{j}_A}{CD_{AB}} dx \tag{14-57}
\]

Performing the integrations,

\[
\ln \left( \frac{1 - y_{A,L}}{1 - y_{A,0}} \right) = \frac{\bar{j}_A}{CD_{AB}} L \tag{14-58}
\]

Then the molar flux of vapor \( A \), which is the evaporation rate of species \( A \) per unit interface area, becomes

\[
\bar{j}_A = \dot{N}_A = \frac{CD_{AB}}{L} \ln \left( \frac{1 - y_{A,L}}{1 - y_{A,0}} \right) \text{ (kmol/s · m²)} \tag{14-59}
\]

This relation is known as Stefan’s law, and the induced convective flow described that enhances mass diffusion is called the Stefan flow.

An expression for the variation of the mole fraction of \( A \) with \( x \) can be determined by performing the integration in Eq. 14–57 to the upper limit of \( x \) where \( y_A(x) = y_A \) (instead of to \( L \) where \( y_A(L) = y_{A,L} \)). It yields

\[
\ln \left( \frac{1 - y_A}{1 - y_{A,0}} \right) = \frac{\bar{j}_A}{CD_{AB}} x \tag{14-60}
\]

Substituting the \( \bar{j}_A \) expression from Eq. 14–59 into this relation and rearranging gives

\[
\frac{1 - y_A}{1 - y_{A,0}} = \left( \frac{1 - y_{A,L}}{1 - y_{A,0}} \right)^{\frac{x}{L}} \quad \text{and} \quad \frac{y_B}{y_{B,0}} = \left( \frac{y_{B,L}}{y_{B,0}} \right)^{\frac{x}{L}} \tag{14-61}
\]

The second relation for the variation of the mole fraction of the stationary gas \( B \) is obtained from the first one by substituting \( 1 - y_A = y_B \) since \( y_A + y_B = 1 \).
To maintain isothermal conditions in the tank during evaporation, heat must be supplied to the tank at a rate of
\[
\dot{Q} = m_A h_{fg,A} = j_A A h_{fg,A} = (\bar{j}_A M_A)A h_{fg,A} \quad \text{(kJ/s) } (14-62)
\]
where \(A \) is the surface area of the liquid–vapor interface, \(h_{fg,A} \) is the latent heat of vaporization, and \(M_A \) is the molar mass of species \(A \).

**Equimolar Counterdiffusion**

Consider two large reservoirs connected by a channel of length \(L \), as shown in Figure 14–35. The entire system contains a binary mixture of gases \(A \) and \(B \) at a uniform temperature \(T \) and pressure \(P \) throughout. The concentrations of species are maintained constant in each of the reservoirs such that \(y_{A,0} > y_{A,L} \) and \(y_{B,0} < y_{B,L} \). The resulting concentration gradients will cause the species \(A \) to diffuse in the positive \(x\)-direction and the species \(B \) in the opposite direction. Assuming the gases to behave as ideal gases and thus \(P \) and \(T \) are constant, the total molar concentration of the mixture \(C \) will remain constant throughout the mixture since \(P \) and \(T \) are constant. That is,
\[
C = C_A + C_B = \text{constant} \quad \text{(kmol/m}^3\text{)}
\]
This requires that for each molecule of \(A \) that moves to the right, a molecule of \(B \) moves to the left, and thus the molar flow rates of species \(A \) and \(B \) must be equal in magnitude and opposite in sign. That is,
\[
\dot{N}_A = -\dot{N}_B \; \text{or} \; \dot{N}_A + \dot{N}_B = 0 \quad \text{(kmol/s)}
\]
This process is called **equimolar counterdiffusion** for obvious reasons. The net molar flow rate of the mixture for such a process, and thus the molar-average velocity, is zero since
\[
\dot{N} = \dot{N}_A + \dot{N}_B = 0 \quad \rightarrow \quad C\bar{V} = 0 \quad \rightarrow \quad \bar{V} = 0
\]
Therefore, the mixture is stationary on a molar basis and thus mass transfer is by diffusion only (there is no mass transfer by convection) so that
\[
\bar{j}_A = \frac{\dot{N}_A}{A} = -CD_{AB} \frac{dy_A}{dx} \quad \text{and} \quad \bar{j}_B = \frac{\dot{N}_B}{A} = -CD_{BA} \frac{dy_B}{dx} \quad (14-63)
\]
Under steady conditions, the molar flow rates of species \(A \) and \(B \) can be determined directly from Eq. 14–24 developed earlier for one-dimensional steady diffusion in a stationary medium, noting that \(P = CR_t T \) and thus \(C = P/IR_t T \) for each constituent gas and the mixture. For one-dimensional flow through a channel of uniform cross sectional area \(A \) with no homogeneous chemical reactions, they are expressed as
\[
\begin{align*}
\dot{N}_{\text{diff},A} &= CD_{AB} A \frac{y_{A,1} - y_{A,2}}{L} = D_{AB} A \frac{C_{A,1} - C_{A,2}}{L} = D_{AB} \frac{P_{A,0} - P_{A,L}}{R_t T} \frac{A}{L} \\
\dot{N}_{\text{diff},B} &= CD_{BA} A \frac{y_{B,1} - y_{B,2}}{L} = D_{BA} A \frac{C_{B,1} - C_{B,2}}{L} = D_{BA} \frac{P_{B,0} - P_{B,L}}{R_t T} \frac{A}{L} \quad (14-64)
\end{align*}
\]
These relations imply that the mole fraction, molar concentration, and the partial pressure of either gas vary linearly during equimolar counterdiffusion. It is interesting to note that the mixture is stationary on a molar basis, but it is not stationary on a mass basis unless the molar masses of A and B are equal. Although the net molar flow rate through the channel is zero, the net mass flow rate of the mixture through the channel is not zero and can be determined from

$$m = \dot{m}_A + \dot{m}_B = \dot{N}_A M_A + \dot{N}_B M_B = \dot{N}_A (M_A - M_B) \quad (14-65)$$

since $\dot{N}_B = -\dot{N}_A$. Note that the direction of net mass flow rate is the flow direction of the gas with the larger molar mass. A velocity measurement device such as an anemometer placed in the channel will indicate a velocity of $\dot{V} = \dot{m}/\rho A$ where $\rho$ is the total density of the mixture at the site of measurement.

**EXAMPLE 14–8 Venting of Helium into the Atmosphere by Diffusion**

The pressure in a pipeline that transports helium gas at a rate of 2 kg/s is maintained at 1 atm by venting helium to the atmosphere through a 5-mm-internal-diameter tube that extends 15 m into the air, as shown in Figure 14–36. Assuming both the helium and the atmospheric air to be at 25°C, determine (a) the mass flow rate of helium lost to the atmosphere through an individual tube, (b) the mass flow rate of air that infiltrates into the pipeline, and (c) the flow velocity at the bottom of the tube where it is attached to the pipeline that will be measured by an anemometer in steady operation.

**SOLUTION**  The pressure in a helium pipeline is maintained constant by venting to the atmosphere through a long tube. The mass flow rates of helium and air through the tube and the net flow velocity at the bottom are to be determined.

**Assumptions** 1 Steady operating conditions exist. 2 Helium and atmospheric air are ideal gases. 3 No chemical reactions occur in the tube. 4 Air concentration in the pipeline and helium concentration in the atmosphere are negligible so that the mole fraction of the helium is 1 in the pipeline and 0 in the atmosphere (we will check this assumption later).

**Properties**  The diffusion coefficient of helium in air (or air in helium) at normal atmospheric conditions is $D_{AB} = 7.20 \times 10^{-5}$ m²/s (Table 14–2). The molar masses of air and helium are 29 and 4 kg/kmol, respectively (Table A–1).

**Analysis**  This is a typical equimolar counterdiffusion process since the problem involves two large reservoirs of ideal gas mixtures connected to each other by a channel, and the concentrations of species in each reservoir (the pipeline and the atmosphere) remain constant.

(a) The flow area, which is the cross sectional area of the tube, is

$$A = \pi D^2/4 = \pi(0.005 \text{ m})^2/4 = 1.963 \times 10^{-5} \text{ m}^2$$

Noting that the pressure of helium is 1 atm at the bottom of the tube ($x = 0$) and 0 at the top ($x = L$), its molar flow rate is determined from Eq. 14–64 to be
\[ \dot{N}_{\text{helium}} = \dot{N}_{\text{diff, A}} = \frac{D_{AB} A P_{A,0} - P_{A, L}}{R_i T L} \]
\[ = (7.20 \times 10^{-5} \text{ m}^2/\text{s})(1.963 \times 10^{-5} \text{ m}^2) \left( \frac{1 \text{ atm} - 0}{15 \text{ m}} \right) \left( \frac{101.3 \text{ kPa}}{1 \text{ atm}} \right) \]
\[ = 3.85 \times 10^{-12} \text{ kmol/s} \]

Therefore,
\[ m_{\text{helium}} = (\dot{N} M)_{\text{helium}} = (3.85 \times 10^{-12} \text{ kmol/s})(4 \text{ kg/kmol}) = 1.54 \times 10^{-11} \text{ kg/s} \]
which corresponds to about 0.5 g per year.

(b) Noting that \( \dot{N}_B = -\dot{N}_A \) during an equimolar counterdiffusion process, the molar flow rate of air into the helium pipeline is equal to the molar flow rate of helium. The mass flow rate of air into the pipeline is
\[ \dot{m}_{\text{air}} = (\dot{N} M)_{\text{air}} = (-3.85 \times 10^{-12} \text{ kmol/s})(29 \text{ kg/kmol}) = -112 \times 10^{-12} \text{ kg/s} \]
The mass fraction of air in the helium pipeline is
\[ w_{\text{air}} = \frac{\dot{m}_{\text{air}}}{\dot{m}_{\text{total}}} = \frac{112 \times 10^{-12} \text{ kg/s}}{(2 + 112 \times 10^{-12} - 1.54 \times 10^{-11}) \text{ kg/s}} = 5.6 \times 10^{-11} = 0 \]
which validates our original assumption of negligible air in the pipeline.

(c) The net mass flow rate through the tube is
\[ \dot{m}_{\text{net}} = \dot{m}_{\text{helium}} + \dot{m}_{\text{air}} = 1.54 \times 10^{-11} - 112 \times 10^{-12} = -9.66 \times 10^{-11} \text{ kg/s} \]
The mass fraction of air at the bottom of the tube is very small, as shown above, and thus the density of the mixture at \( x = 0 \) can simply be taken to be the density of helium, which is
\[ \rho \equiv \rho_{\text{helium}} = \frac{P}{RT} = \frac{101.325 \text{ kPa}}{(2.0769 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(298 \text{ K})} = 0.1637 \text{ kg/m}^3 \]
Then the average flow velocity at the bottom part of the tube becomes
\[ \dot{V} = \frac{\dot{m}}{\rho A} = \frac{-9.66 \times 10^{-11} \text{ kg/s}}{(0.01637 \text{ kg/m}^3)(1.963 \times 10^{-5} \text{ m}^2)} = -3.02 \times 10^{-5} \text{ m/s} \]
which is difficult to measure by even the most sensitive velocity measurement devices. The negative sign indicates flow in the negative \( x \)-direction (toward the pipeline).

**EXAMPLE 14–9  Measuring Diffusion Coefficient by the Stefan Tube**

A 3-cm-diameter Stefan tube is used to measure the binary diffusion coefficient of water vapor in air at 20°C at an elevation of 1600 m where the atmospheric
pressure is 83.5 kPa. The tube is partially filled with water, and the distance from the water surface to the open end of the tube is 40 cm (Fig. 14–37). Dry air is blown over the open end of the tube so that water vapor rising to the top is removed immediately and the concentration of vapor at the top of the tube is zero. In 15 days of continuous operation at constant pressure and temperature, the amount of water that has evaporated is measured to be 1.23 g. Determine the diffusion coefficient of water vapor in air at 20°C and 83.5 kPa.

**SOLUTION** The amount of water that evaporates from a Stefan tube at a specified temperature and pressure over a specified time period is measured. The diffusion coefficient of water vapor in air is to be determined.

**Assumptions**

1. Water vapor and atmospheric air are ideal gases.
2. The amount of air dissolved in liquid water is negligible.
3. Heat is transferred to the water from the surroundings to make up for the latent heat of vaporization so that the temperature of water remains constant at 20°C.

**Properties** The saturation pressure of water at 20°C is 2.34 kPa (Table A–9).

**Analysis** The vapor pressure at the air–water interface is the saturation pressure of water at 20°C, and the mole fraction of water vapor (species A) at the interface is determined from

\[ y_{vapor,0} = y_{A,0} = \frac{P_{vapor,0}}{P} = \frac{2.34 \text{ kPa}}{83.5 \text{ kPa}} = 0.0280 \]

Dry air is blown on top of the tube and, thus, \( y_{vapor,L} = y_{A,L} = 0 \). Also, the total molar density throughout the tube remains constant because of the constant temperature and pressure conditions and is determined to be

\[ C = \frac{P}{R_T \cdot T} = \frac{83.5 \text{ kPa}}{(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(293 \text{ K})} = 0.0343 \text{ kmol/m}^3 \]

The cross-sectional area of the tube is

\[ A = \pi D^2/4 = \pi(0.03 \text{ m})^2/4 = 7.069 \times 10^{-4} \text{ m}^2 \]

The evaporation rate is given to be 1.23 g per 15 days. Then the molar flow rate of vapor is determined to be

\[ \dot{N}_A = \dot{N}_{vapor} = \frac{\dot{m}_{vapor}}{M_{vapor}} = \frac{1.23 \times 10^{-3} \text{ kg}}{(15 \times 24 \times 3600 \text{ s})(18 \text{ kg/kmol})} = 5.27 \times 10^{-11} \text{ kmol/s} \]

Finally, substituting the information above into Eq. 14–59 we get

\[ \frac{5.27 \times 10^{-11} \text{ kmol/s}}{7.069 \times 10^{-4} \text{ m}^2} = \frac{(0.0343 \text{ kmol/m}^3)D_{AB}}{0.4 \text{ m}} \ln \frac{1 - 0}{1 - 0.028} \]

which gives

\[ D_{AB} = 3.06 \times 10^{-5} \text{ m}^2/\text{s} \]

for the binary diffusion coefficient of water vapor in air at 20°C and 83.5 kPa.
14–9  •  MASS CONVECTION

So far we have considered mass diffusion, which is the transfer of mass due to a concentration gradient. Now we consider mass convection (or convective mass transfer), which is the transfer of mass between a surface and a moving fluid due to both mass diffusion and bulk fluid motion. We mentioned earlier that fluid motion enhances heat transfer considerably by removing the heated fluid near the surface and replacing it by the cooler fluid further away. Likewise, fluid motion enhances mass transfer considerably by removing the high-concentration fluid near the surface and replacing it by the lower-concentration fluid further away. In the limiting case of no bulk fluid motion, mass convection reduces to mass diffusion, just as convection reduces to conduction. The analogy between heat and mass convection holds for both forced and natural convection, laminar and turbulent flow, and internal and external flow.

Like heat convection, mass convection is also complicated because of the complications associated with fluid flow such as the surface geometry, flow regime, flow velocity, and the variation of the fluid properties and composition. Therefore, we will have to rely on experimental relations to determine mass transfer. Also, mass convection is usually analyzed on a mass basis rather than on a molar basis. Therefore, we will present formulations in terms of mass concentration (density $\rho$ or mass fraction $\omega$) instead of molar concentration (molar density $C$ or mole fraction $y$). But the formulations on a molar basis can be obtained using the relation $C = \rho/M$ where $M$ is the molar mass. Also, for simplicity, we will restrict our attention to convection in fluids that are (or can be treated as) binary mixtures.

Consider the flow of air over the free surface of a water body such as a lake under isothermal conditions. If the air is not saturated, the concentration of water vapor will vary from a maximum at the water surface where the air is always saturated to the free steam value far from the surface. In heat convection, we defined the region in which temperature gradients exist as the thermal boundary layer. Similarly, in mass convection, we define the region of the fluid in which concentration gradients exist as the concentration boundary layer, as shown in Figure 14–38. In external flow, the thickness of the concentration boundary layer $\delta_c$ for a species $A$ at a specified location on the surface is defined as the normal distance $y$ from the surface at which

$$\frac{\rho_{A,s} - \rho_A}{\rho_{A,s} - \rho_{A,x}} = 0.99$$

where $\rho_{A,s}$ and $\rho_{A,x}$ are the densities of species $A$ at the surface (on the fluid side) and the free stream, respectively.

In internal flow, we have a concentration entrance region where the concentration profile develops, in addition to the hydrodynamic and thermal entry regions (Fig. 14–39). The concentration boundary layer continues to develop in the flow direction until its thickness reaches the tube center and the boundary layers merge. The distance from the tube inlet to the location where this merging occurs is called the concentration entry length $L_{c,e}$ and the region beyond that point is called the fully developed region, which is characterized by
\[
\frac{\partial}{\partial x} \left( \frac{p_{A,s} - p_A}{p_{A,b} - p_{A,b}} \right) = 0
\]  
(14-66)

where \( p_{A,b} \) is the bulk mean density of species \( A \) defined as

\[
p_{A,b} = \frac{1}{A_v V_{ave}} \int_A p_A V dA
\]  
(14-67)

Therefore, the nondimensionalized concentration difference profile as well as the mass transfer coefficient remain constant in the fully developed region. This is analogous to the friction and heat transfer coefficients remaining constant in the fully developed region.

In heat convection, the relative magnitudes of momentum and heat diffusion in the velocity and thermal boundary layers are expressed by the dimensionless \textit{Prandtl number}, defined as (Fig. 14–40)

\[
\text{Prandtl number: } \text{Pr} = \frac{\nu}{\alpha} = \frac{\text{Momentum diffusivity}}{\text{Thermal diffusivity}}
\]  
(14-68)

The corresponding quantity in mass convection is the dimensionless \textit{Schmidt number}, defined as

\[
\text{Schmidt number: } \text{Sc} = \frac{\nu}{D_{AB}} = \frac{\text{Momentum diffusivity}}{\text{Mass diffusivity}}
\]  
(14-69)

which represents the relative magnitudes of molecular momentum and mass diffusion in the velocity and concentration boundary layers, respectively.

The relative growth of the velocity and thermal boundary layers in laminar flow is governed by the Prandtl number, whereas the relative growth of the velocity and concentration boundary layers is governed by the Schmidt number. A Prandtl number of near unity (\( \text{Pr} \approx 1 \)) indicates that momentum and heat transfer by diffusion are comparable, and velocity and thermal boundary layers almost coincide with each other. A Schmidt number of near unity (\( \text{Sc} \approx 1 \)) indicates that momentum and mass transfer by diffusion are comparable, and velocity and concentration boundary layers almost coincide with each other.

It seems like we need one more dimensionless number to represent the relative magnitudes of heat and mass diffusion in the thermal and concentration boundary layers. That is the \textit{Lewis number}, defined as (Fig. 14–41)

\[
\text{Lewis number: } \text{Le} = \frac{\text{Sc}}{\text{Pr}} = \frac{\alpha}{D_{AB}} = \frac{\text{Thermal diffusivity}}{\text{Mass diffusivity}}
\]  
(14-70)

The relative thicknesses of velocity, thermal, and concentration boundary layers in laminar flow are expressed as

\[
\frac{\delta_{\text{velocity}}}{\delta_{\text{thermal}}} = \text{Pr}^n, \quad \frac{\delta_{\text{velocity}}}{\delta_{\text{concentration}}} = \text{Sc}^n, \quad \text{and} \quad \frac{\delta_{\text{thermal}}}{\delta_{\text{concentration}}} = \text{Le}^n
\]  
(14-71)

where \( n = \frac{1}{4} \) for most applications in all three relations. These relations, in general, are not applicable to turbulent boundary layers since turbulent mixing in this case may dominate the diffusion processes.
Note that species transfer at the surface \((y = 0)\) is by diffusion only because of the no-slip boundary condition, and mass flux of species \(A\) at the surface can be expressed by Fick’s law as (Fig. 14–42)

\[
j_A = \dot{m}_A / A = -\rho D_{AB} \frac{\partial w_A}{\partial y} \bigg|_{y=0} \quad \text{(kg/s m²)} \tag{14-72}
\]

This is analogous to heat transfer at the surface being by conduction only and expressing it by Fourier’s law.

The rate of heat convection for external flow was expressed conveniently by Newton’s law of cooling as

\[
\dot{Q}_{\text{conv}} = h_{\text{conv}} A (T_i - T_w)
\]

where \(h_{\text{conv}}\) is the average heat transfer coefficient, \(A\) is the surface area, and \(T_i - T_w\) is the temperature difference across the thermal boundary layer. Likewise, the rate of mass convection can be expressed as

\[
\dot{m}_{\text{conv}} = h_{\text{mass}} A (\rho_{A,i} - \rho_{A,w}) = h_{\text{mass}} \rho A (w_{A,i} - w_{A,w}) \quad \text{(kg/s)} \tag{14-73}
\]

where \(h_{\text{mass}}\) is the average mass transfer coefficient, in m/s; \(A\) is the surface area; \(\rho_{A,i} - \rho_{A,w}\) is the mass concentration difference of species \(A\) across the concentration boundary layer; and \(\rho\) is the average density of the fluid in the boundary layer. The product \(h_{\text{mass}} \rho\), whose unit is kg/m² s, is called the mass transfer conductance. If the local mass transfer coefficient varies in the flow direction, the average mass transfer coefficient can be determined from

\[
h_{\text{mass, ave}} = \frac{1}{A} \int_A h_{\text{mass}} dA \tag{14-74}
\]

In heat convection analysis, it is often convenient to express the heat transfer coefficient in a nondimensionalized form in terms of the dimensionless Nusselt number, defined as

\[
\text{Nusselt number:} \quad Nu = \frac{h_{\text{conv}} L}{k} \tag{14-75}
\]

where \(L\) is the characteristic length of \(k\) is the thermal conductivity of the fluid. The corresponding quantity in mass convection is the dimensionless Sherwood number, defined as (Fig. 14–43)

\[
\text{Sherwood number:} \quad Sh = \frac{h_{\text{mass}} L}{D_{AB}} \tag{14-76}
\]

where \(h_{\text{mass}}\) is the mass transfer coefficient and \(D_{AB}\) is the mass diffusivity. The Nusselt and Sherwood numbers represent the effectiveness of heat and mass convection at the surface, respectively.

Sometimes it is more convenient to express the heat and mass transfer coefficients in terms of the dimensionless Stanton number as

\[
\text{Heat transfer Stanton number:} \quad St = \frac{h_{\text{conv}}}{\rho \bar{v} C_p} = Nu \frac{1}{Re Pr} \tag{14-77}
\]
and

$$\text{Mass transfer Stanton number: } St_{\text{mass}} = \frac{h_{\text{mass}}}{V} = Sh \frac{1}{Re \cdot Sc} \quad (14-78)$$

where $V$ is the free steam velocity in external flow and the bulk mean fluid velocity in internal flow.

For a given geometry, the average Nusselt number in forced convection depends on the Reynolds and Prandtl numbers, whereas the average Sherwood number depends on the Reynolds and Schmidt numbers. That is,

$$\text{Nusselt number: } Nu = f(Re, Pr)$$
$$\text{Sherwood number: } Sh = f(Re, Sc)$$

where the functional form of $f$ is the same for both the Nusselt and Sherwood numbers in a given geometry, provided that the thermal and concentration boundary conditions are of the same type. Therefore, the Sherwood number can be obtained from the Nusselt number expression by simply replacing the Prandtl number by the Schmidt number. This shows what a powerful tool analogy can be in the study of natural phenomena (Table 14–12).

In natural convection mass transfer, the analogy between the Nusselt and Sherwood numbers still holds, and thus $Sh = f(Gr, Sc)$. But the Grashof number in this case should be determined directly from

$$\text{Gr} = \frac{g(p_a - p)}{\rho v^2} L_c^3 = \frac{g(\Delta p/\rho) L_c^3}{v^2} \quad (14-79)$$

which is applicable to both temperature- and/or concentration-driven natural convection flows. Note that in homogeneous fluids (i.e., fluids with no concentration gradients), density differences are due to temperature differences only, and thus we can replace $\Delta p/\rho$ by $\beta \Delta T$ for convenience, as we did in natural convection heat transfer. However, in nonhomogeneous fluids, density differences are due to the combined effects of temperature and concentration differences, and $\Delta p/\rho$ cannot be replaced by $\beta \Delta T$ in such cases even when all we care about is heat transfer and we have no interest in mass transfer. For example, hot water at the bottom of a pond rises to the top. But when salt is placed at the bottom, as it is done in solar ponds, the salty water (brine) at the bottom will not rise because it is now heavier than the fresh water at the top (Fig. 14-44).

Concentration-driven natural convection flows are based on the densities of different species in a mixture being different. Therefore, at isothermal conditions, there will be no natural convection in a gas mixture that is composed of gases with identical molar masses. Also, the case of a hot surface facing up corresponds to diffusing fluid having a lower density than the mixture (and thus rising under the influence of buoyancy), and the case of a hot surface facing down corresponds to the diffusing fluid having a higher density. For example, the evaporation of water into air corresponds to a hot surface facing up since water vapor is lighter than the air and it will tend to rise. But this will not be the case for gasoline unless the temperature of the gasoline–air mixture at the gasoline surface is so high that thermal expansion overwhelms the density differential due to higher gasoline concentration near the surface.

<table>
<thead>
<tr>
<th>TABLE 14–12</th>
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<tbody>
<tr>
<td>Analogy between the quantities that appear in the formulation and solution of heat convection and mass convection</td>
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<table>
<thead>
<tr>
<th>Heat Convection</th>
<th>Mass Convection</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>$C$, $y$, $p$, or $w$</td>
</tr>
<tr>
<td>$h_{\text{conv}}$</td>
<td>$h_{\text{mass}}$</td>
</tr>
<tr>
<td>$\delta_{\text{thermal}}$</td>
<td>$\delta_{\text{concentration}}$</td>
</tr>
<tr>
<td>$Re = \frac{\nu L_c}{v}$</td>
<td>$Re = \frac{\nu L_c}{v}$</td>
</tr>
<tr>
<td>$Gr = \frac{g(\beta(T_a - T_c) L_c^3)}{\nu^2}$</td>
<td>$Gr = \frac{g(p_a - p_c) L_c^3}{\rho v^2}$</td>
</tr>
<tr>
<td>$Pr = \frac{\nu}{\alpha}$</td>
<td>$Sc = \frac{\nu}{D_{AB}}$</td>
</tr>
<tr>
<td>$St = \frac{h_{\text{conv}}}{\rho v C_p}$</td>
<td>$St_{\text{mass}} = \frac{h_{\text{mass}}}{V}$</td>
</tr>
<tr>
<td>$Nu = \frac{h_{\text{conv}} L_c}{k}$</td>
<td>$Sh = \frac{h_{\text{mass}} L_c}{D_{AB}}$</td>
</tr>
<tr>
<td>$Nu = f(Re, Pr)$</td>
<td>$Sh = f(Re, Sc)$</td>
</tr>
<tr>
<td>$Nu = f(Gr, Pr)$</td>
<td>$Sh = f(Gr, Sc)$</td>
</tr>
</tbody>
</table>

20°C | Fresh water |
| No convection currents | SOLAR POND |
| 70°C | Brine |
| $\rho_{\text{brine}} > \rho_{\text{water}}$ | Salt |

**FIGURE 14-44**
A hot fluid at the bottom will rise and initiate natural convection currents only if its density is lower.
Analogy between Friction, Heat Transfer, and Mass Transfer Coefficients

Consider the flow of a fluid over a flat plate of length $L$ with free stream conditions of $T_{\infty}$, $V_{\infty}$, and $w_{A,\infty}$ (Fig. 14–45). Noting that convection at the surface ($y = 0$) is equal to diffusion because of the no-slip condition, the friction, heat transfer, and mass transfer conditions at the surface can be expressed as

**Wall friction:**
$$
\tau_y = \mu \left. \frac{\partial V_y}{\partial y} \right|_{y=0} = \frac{f}{2} \rho V_\infty^2
$$

**Heat transfer:**
$$
\dot{q}_s = -k \left. \frac{\partial T}{\partial y} \right|_{y=0} = h_{\text{heat}}(T_s - T_\infty)
$$

**Mass transfer:**
$$
\dot{j}_{A,s} = -D_{AB} \left. \frac{\partial w_A}{\partial y} \right|_{y=0} = h_{\text{mass}}(w_{A,s} - w_{A,\infty})
$$

These relations can be rewritten for internal flow by using *bulk mean properties* instead of free stream properties. After some simple mathematical manipulations, the three relations above can be rearranged as

**Wall friction:**
$$
\frac{d(V/V_\infty)}{d(y/L)} \bigg|_{y=0} = \frac{f}{2} \frac{\rho V_\infty L}{\mu} = \frac{f}{2} \text{Re}
$$

**Heat transfer:**
$$
\frac{d[(T - T_\infty)/(T_s - T_\infty)]}{d(y/L)} \bigg|_{y=0} = \frac{h_{\text{heat}} L}{k} = \text{Nu}
$$

**Mass transfer:**
$$
\frac{d[(w_A - w_{A,\infty})/(w_{A,s} - w_{A,\infty})]}{d(y/L)} \bigg|_{y=0} = \frac{h_{\text{mass}} L}{D_{AB}} = \text{Sh}
$$

The left sides of these three relations are the slopes of the normalized velocity, temperature, and concentration profiles at the surface, and the right sides are the dimensionless numbers discussed earlier.

**Special Case: Pr ≈ Sc ≈ 1 (Reynolds Analogy)**

Now consider the hypothetical case in which the molecular diffusivities of momentum, heat, and mass are identical. That is, $\nu = \alpha = D_{AB}$ and thus $Pr = Sc = Le = 1$. In this case the normalized velocity, temperature, and concentration profiles will coincide, and thus the slope of these three curves at the surface (the left sides of Eqs. 14–83 through 14–85) will be identical (Fig. 14–46). Then we can set the right sides of those three equations equal to each other and obtain

$$
\frac{f}{2} \text{Re} = \text{Nu} = \text{Sh} \quad \text{or} \quad \frac{f \rho V_\infty L}{\mu} = \frac{h_{\text{heat}} L}{k} = \frac{h_{\text{mass}} L}{D_{AB}}
$$

Noting that $Pr = Sc = 1$, we can also write this equation as

$$
\frac{f}{2} = \frac{\text{Nu}}{\text{Re Pr}} = \frac{\text{Sh}}{\text{Re Sc}} \quad \text{or} \quad \frac{f}{2} = \text{St} = \text{St}_{\text{mass}}
$$

This relation is known as the *Reynolds analogy*, and it enables us to determine the seemingly unrelated friction, heat transfer, and mass transfer coefficients when only one of them is known or measured. (Actually the original
Reynolds analogy proposed by O. Reynolds in 1874 is \( St = f/2 \), which is then extended to include mass transfer. However, it should always be remembered that the analogy is restricted to situations for which \( Pr \approx Sc = 1 \). Of course the first part of the analogy between friction and heat transfer coefficients can always be used for gases since their Prandtl number is close to unity.

**General Case: \( Pr \neq Sc \neq 1 \) (Chilton–Colburn Analogy)**

The Reynolds analogy is a very useful relation, and it is certainly desirable to extend it to a wider range of \( Pr \) and \( Sc \) numbers. Several attempts have been made in this regard, but the simplest and the best known is the one suggested by Chilton and Colburn in 1934 as

\[
\frac{f}{2} = St \frac{Pr^{2/3}}{St_{mass}Sc^{2/3}}
\]

for \( 0.6 < Pr < 60 \) and \( 0.6 < Sc < 3000 \). This equation is known as the **Chilton–Colburn analogy**. Using the definition of heat and mass Stanton numbers, the analogy between heat and mass transfer can be expressed more conveniently as (Fig. 14-47)

\[
\frac{St}{St_{mass}} = \left( \frac{Sc}{Pr} \right)^{2/3}
\]

or

\[
\frac{h_{heat}}{h_{mass}} = \rho C_p \left( \frac{Sc}{Pr} \right)^{2/3} = \rho C_p \left( \frac{\alpha}{D_{AB}} \right)^{2/3} = \rho C_p \cdot \text{Le}^{2/3}
\]

For air–water vapor mixtures at 298 K, the mass and thermal diffusivities are \( D_{AB} = 2.5 \times 10^{-5} \text{ m}^2/\text{s} \) and \( \alpha = 2.18 \times 10^{-5} \text{ m}^2/\text{s} \) and thus the Lewis number is \( \text{Le} = \alpha/D_{AB} = 0.872 \). (We simply use the \( \alpha \) value of dry air instead of the moist air since the fraction of vapor in the air at atmospheric conditions is low.) Then \( (\alpha/D_{AB})^{2/3} = 0.872^{2/3} = 0.913 \), which is close to unity. Also, the Lewis number is relatively insensitive to variations in temperature. Therefore, for air–water vapor mixtures, the relation between heat and mass transfer coefficients can be expressed with a good accuracy as

\[
\frac{h_{heat}}{h_{mass}} = \frac{\rho C_p}{\rho C_p} = 1
\]

(14-90)

where \( \rho \) and \( C_p \) are the density and specific heat of air at mean conditions (or \( \rho C_p \) is the specific heat of air per unit volume). Equation 14–90 is known as the **Lewis relation** and is commonly used in air-conditioning applications. Another important consequence of \( \text{Le} \approx 1 \) is that the *wet-bulb* and *adiabatic saturation temperatures* of moist air are nearly identical. In turbulent flow, the Lewis relation can be used even when the Lewis number is not 1 since eddy mixing in turbulent flow overwheels any molecular diffusion, and heat and mass are transported at the same rate.

The Chilton–Colburn analogy has been observed to hold quite well in laminar or turbulent flow over plane surfaces. But this is not always the case for internal flow and flow over irregular geometries, and in such cases specific relations developed should be used. When dealing with flow over blunt bodies, it is important to note that \( f \) in these relations is the *skin friction coefficient*, not the total drag coefficient, which also includes the pressure drag.
Limitation on the Heat–Mass Convection Analogy

Caution should be exercised when using the analogy in Eq. 14–88 since there are a few factors that put some shadow on the accuracy of that relation. For one thing, the Nusselt numbers are usually evaluated for smooth surfaces, but many mass transfer problems involve wavy or roughened surfaces. Also, many Nusselt relations are obtained for constant surface temperature situations, but the concentration may not be constant over the entire surface because of the possible surface dryout. The blowing or suction at the surface during mass transfer may also cause some deviation, especially during high speed blowing or suction.

Finally, the heat–mass convection analogy is valid for low mass flux cases in which the flow rate of species undergoing mass flow is low relative to the total flow rate of the liquid or gas mixture so that the mass transfer between the fluid and the surface does not affect the flow velocity. (Note that convection relations are based on zero fluid velocity at the surface, which is true only when there is no net mass transfer at the surface.) Therefore, the heat–mass convection analogy is not applicable when the rate of mass transfer of a species is high relative to the flow rate of that species.

Consider, for example, the evaporation and transfer of water vapor into air in an air washer, an evaporative cooler, a wet cooling tower, or just at the free surface of a lake or river (Fig. 14–48). Even at a temperature of 40°C, the vapor pressure at the water surface is the saturation pressure of 7.4 kPa, which corresponds to a mole fraction of 0.074 or a mass fraction of \( w_A \) for the vapor. Then the mass fraction difference across the boundary layer will be, at most, \( \Delta w = w_{A,s} - w_{A,\infty} = 0.047 - 0 = 0.047 \). For the evaporation of water into air, the error involved in the low mass flux approximation is roughly \( \Delta w/2 \), which is 2.5 percent in the worst case considered above. Therefore, in processes that involve the evaporation of water into air, we can use the heat–mass convection analogy with confidence. However, the mass fraction of vapor approaches 1 as the water temperature approaches the saturation temperature, and thus the low mass flux approximation is not applicable to mass transfer in boilers, condensers, and the evaporation of fuel droplets in combustion chambers. In this chapter we limit our consideration to low mass flux applications.

Mass Convection Relations

Under low mass flux conditions, the mass convection coefficients can be determined by either (1) determining the friction or heat transfer coefficient and then using the Chilton–Colburn analogy or (2) picking the appropriate Nusselt number relation for the given geometry and analogous boundary conditions, replacing the Nusselt number by the Sherwood number and the Prandtl number by the Schmidt number, as shown in Table 14–13 for some representative cases. The first approach is obviously more convenient when the friction or heat transfer coefficient is already known. Otherwise, the second approach should be preferred since it is generally more accurate, and the Chilton–Colburn analogy offers no significant advantage in this case. Relations for convection mass transfer in other geometries can be written similarly using the corresponding heat transfer relation in Chapters 6 and 7.
### TABLE 14–13

Sherwood number relations in mass convection for specified concentration at the surface corresponding to the Nusselt number relations in heat convection for specified surface temperature

<table>
<thead>
<tr>
<th>Convective Heat Transfer</th>
<th>Convective Mass Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Forced Convection over a Flat Plate</td>
<td></td>
</tr>
<tr>
<td>(a) Laminar flow (Re &lt; 5 × 10^5)</td>
<td></td>
</tr>
<tr>
<td>Nu = 0.664 Re^{0.5} Pr^{1/3}, Pr &gt; 0.6</td>
<td></td>
</tr>
<tr>
<td>Sh = 0.664 Re^{0.5} Sc^{1/3}, Sc &gt; 0.5</td>
<td></td>
</tr>
<tr>
<td>(b) Turbulent flow (5 × 10^5 &lt; Re &lt; 10^7)</td>
<td></td>
</tr>
<tr>
<td>Nu = 0.037 Re^{0.8} Pr^{1/3}, Pr &gt; 0.6</td>
<td></td>
</tr>
<tr>
<td>Sh = 0.037 Re^{0.8} Sc^{1/3}, Sc &gt; 0.5</td>
<td></td>
</tr>
<tr>
<td>2. Fully Developed Flow in Smooth Circular Pipes</td>
<td></td>
</tr>
<tr>
<td>(a) Laminar flow (Re &lt; 2300)</td>
<td></td>
</tr>
<tr>
<td>Nu = 3.66</td>
<td></td>
</tr>
<tr>
<td>Sh = 3.66</td>
<td></td>
</tr>
<tr>
<td>(b) Turbulent flow (Re &gt; 10,000)</td>
<td></td>
</tr>
<tr>
<td>Nu = 0.023 Re^{0.8} Pr^{0.4}, 0.7 &lt; Pr &lt; 160</td>
<td></td>
</tr>
<tr>
<td>Sh = 0.023 Re^{0.8} Sc^{0.4}, 0.7 &lt; Sc &lt; 160</td>
<td></td>
</tr>
<tr>
<td>3. Natural Convection over Surfaces</td>
<td></td>
</tr>
<tr>
<td>(a) Vertical plate</td>
<td></td>
</tr>
<tr>
<td>Nu = 0.59(Gr Pr)^{1/4}, 10^5 &lt; Gr Pr &lt; 10^9</td>
<td></td>
</tr>
<tr>
<td>Nu = 0.1(Gr Pr)^{1/3}, 10^6 &lt; Gr Pr &lt; 10^{11}</td>
<td></td>
</tr>
<tr>
<td>Sh = 0.59(Gr Sc)^{1/4}, 10^5 &lt; Gr Sc &lt; 10^9</td>
<td></td>
</tr>
<tr>
<td>Sh = 0.1(Gr Sc)^{1/3}, 10^6 &lt; Gr Sc &lt; 10^{11}</td>
<td></td>
</tr>
<tr>
<td>(b) Upper surface of a horizontal plate</td>
<td></td>
</tr>
<tr>
<td>Surface is hot (T_s &gt; T_c)</td>
<td></td>
</tr>
<tr>
<td>Nu = 0.54(Gr Pr)^{1/4}, 10^4 &lt; Gr Pr &lt; 10^7</td>
<td></td>
</tr>
<tr>
<td>Nu = 0.15(Gr Pr)^{1/3}, 10^7 &lt; Gr Pr &lt; 10^{11}</td>
<td></td>
</tr>
<tr>
<td>Sh = 0.54(Gr Sc)^{1/4}, 10^4 &lt; Gr Sc &lt; 10^7</td>
<td></td>
</tr>
<tr>
<td>Sh = 0.15(Gr Sc)^{1/3}, 10^7 &lt; Gr Sc &lt; 10^{11}</td>
<td></td>
</tr>
<tr>
<td>(c) Lower surface of a horizontal plate</td>
<td></td>
</tr>
<tr>
<td>Surface is hot (T_s &gt; T_c)</td>
<td></td>
</tr>
<tr>
<td>Nu = 0.27(Gr Pr)^{1/4}, 10^5 &lt; Gr Pr &lt; 10^11</td>
<td></td>
</tr>
<tr>
<td>Fluid near the surface is light (p_s &lt; p_a)</td>
<td></td>
</tr>
<tr>
<td>Sh = 0.27(Gr Sc)^{1/4}, 10^5 &lt; Gr Sc &lt; 10^{11}</td>
<td></td>
</tr>
</tbody>
</table>

**EXAMPLE 14–10 Mass Convection inside a Circular Pipe**

Consider a circular pipe of inner diameter \( D = 0.015 \) m whose inner surface is covered with a layer of liquid water as a result of condensation (Fig. 14–49). In order to dry the pipe, air at 300 K and 1 atm is forced to flow through it with an average velocity of 1.2 m/s. Using the analogy between heat and mass transfer, determine the mass transfer coefficient inside the pipe for fully developed flow.

**SOLUTION** The liquid layer on the inner surface of a circular pipe is dried by blowing air through it. The mass transfer coefficient is to be determined.

**Assumptions** 1 The low mass flux model and thus the analogy between heat and mass transfer is applicable since the mass fraction of vapor in the air is low (about 2 percent for saturated air at 300 K). 2 The flow is fully developed.

**Properties** Because of low mass flux conditions, we can use dry air properties for the mixture at the specified temperature of 300 K and 1 atm, for which \( \nu = 1.58 \times 10^{-5} \) m^2/s (Table A–15). The mass diffusivity of water vapor in the air at 300 K is determined from Eq. 14–15 to be

\[
D_{AB} = D_{H_2O-air} = 1.87 \times 10^{-10} \frac{T^{2.072}}{P} = 1.87 \times 10^{-10} \frac{300^{2.072}}{1} = 2.54 \times 10^{-5} \text{ m}^2/\text{s}
\]
The Reynolds number for this internal flow is

\[ \text{Re} = \frac{\nu D}{v} = \frac{(1.2 \text{ m/s})(0.015 \text{ m})}{1.58 \times 10^{-5} \text{ m}^2/\text{s}} = 1139 \]

which is less than 2300 and thus the flow is laminar. Therefore, based on the analogy between heat and mass transfer, the Nusselt and the Sherwood numbers in this case are

\[ \text{Nu} = 3.66 \]

Using the definition of Sherwood number, the mass transfer coefficient is determined to be

\[ h_{\text{mass}} = \frac{ShD_{\text{AB}}}{D} = \frac{(3.66)(2.54 \times 10^{-5} \text{ m}^2/\text{s})}{0.015 \text{ m}} = 0.00620 \text{ m/s} \]

The mass transfer rate (or the evaporation rate) in this case can be determined by defining the logarithmic mean concentration difference in an analogous manner to the logarithmic mean temperature difference.

EXAMPLE 14–11 Analogy between Heat and Mass Transfer

Heat transfer coefficients in complex geometries with complicated boundary conditions can be determined by mass transfer measurements on similar geometries under similar flow conditions using volatile solids such as naphthalene and dichlorobenzene and utilizing the Chilton–Colburn analogy between heat and mass transfer at low mass flux conditions. The amount of mass transfer during a specified time period is determined by weighing the model or measuring the surface recession.

During a certain experiment involving the flow of dry air at 25°C and 1 atm at a free stream velocity of 2 m/s over a body covered with a layer of naphthalene, it is observed that 12 g of naphthalene has sublimated in 15 min (Fig. 14–50). The surface area of the body is 0.3 m². Both the body and the air were kept at 25°C during the study. The vapor pressure of naphthalene at 25°C is 11 Pa and the mass diffusivity of naphthalene in air at 25°C is \( D_{\text{AB}} = 0.61 \times 10^{-5} \text{ m}^2/\text{s} \). Determine the heat transfer coefficient under the same flow conditions over the same geometry.

SOLUTION Air is blown over a body covered with a layer of naphthalene, and the rate of sublimation is measured. The heat transfer coefficient under the same flow conditions over the same geometry is to be determined.

Assumptions 1 The low mass flux conditions exist so that the Chilton–Colburn analogy between heat and mass transfer is applicable (will be verified). 2 Both air and naphthalene vapor are ideal gases.

Properties The molar mass of naphthalene is 128.2 kg/kmol. Because of low mass flux conditions, we can use dry air properties for the mixture at the specified temperature of 25°C and 1 atm, at which \( \rho = 1.184 \text{ kg/m}^3 \), \( C_p = 1007 \text{ J/kg} \cdot \text{K} \), and \( \alpha = 2.141 \times 10^{-5} \text{ m}^2/\text{s} \) (Table A–15).

Analysis The incoming air is free of naphthalene, and thus the mass fraction of naphthalene at free stream conditions is zero, \( w_{\text{A,v}} = 0 \). Noting that the vapor pressure of naphthalene at the surface is 11 Pa, its mass fraction at the surface is determined to be...
Many mass transfer processes encountered in practice occur isothermally, and thus they do not involve any heat transfer. But some engineering applications involve the vaporization of a liquid and the diffusion of this vapor into the surrounding gas. Such processes require the transfer of the latent heat of vaporization to the liquid in order to vaporize it, and thus such problems involve simultaneous heat and mass transfer. To generalize, any mass transfer problem involving phase change (evaporation, sublimation, condensation, melting, etc.) must also involve heat transfer, and the solution of such problems needs to be analyzed by considering simultaneous heat and mass transfer.

Examples of simultaneous heat and mass problems are drying, evaporative cooling, transpiration (or sweat) cooling, cooling by dry ice, combustion of fuel droplets, and ablation cooling of space vehicles during reentry, and even ordinary events like rain, snow, and hail. In warmer locations, for example, the snow melts and the rain evaporates before reaching the ground (Fig. 14–51).

To understand the mechanism of simultaneous heat and mass transfer, consider the evaporation of water from a swimming pool into air. Let us assume that the water and the air are initially at the same temperature. If the air is saturated (a relative humidity of \( \phi = 100 \) percent), there will be no heat or mass transfer as long as the isothermal conditions remain. But if the air is not

![Diagram of heat and mass transfer](image-url)
saturated (φ < 100 percent), there will be a difference between the concentration of water vapor at the water–air interface (which is always saturated) and some distance above the interface (the concentration boundary layer). Concentration difference is the driving force for mass transfer, and thus this concentration difference will drive the water into the air. But the water must vaporize first, and it must absorb the latent heat of vaporization in order to vaporize. Initially, the entire heat of vaporization will come from the water near the interface since there is no temperature difference between the water and the surroundings and thus there cannot be any heat transfer. The temperature of water near the surface must drop as a result of the sensible heat loss, which also drops the saturation pressure and thus vapor concentration at the interface. This temperature drop creates temperature differences within the water at the top as well as between the water and the surrounding air. These temperature differences drive heat transfer toward the water surface from both the air and the deeper parts of the water, as shown in Figure 14–52. If the evaporation rate is high and thus the demand for the heat of vaporization is higher than the amount of heat that can be supplied from the lower parts of the water body and the surroundings, the deficit will be made up from the sensible heat of the water at the surface, and thus the temperature of water at the surface will drop further. The process will continue until the latent heat of vaporization is equal to the rate of heat transfer to the water at the surface. Once the steady operation conditions are reached and the interface temperature stabilizes, the energy balance on a thin layer of liquid at the surface can be expressed as

\[ \dot{Q}_{\text{sensible, transferred}} = \dot{Q}_{\text{latent, absorbed}} \quad \text{or} \quad \dot{Q} = \dot{m}_v h_{fg} \quad (14-91) \]

where \( \dot{m}_v \) is the rate of evaporation and \( h_{fg} \) is the latent heat of vaporization of water at the surface temperature. Various expressions for \( \dot{m}_v \) under various approximations are given in Table 14–14. The mixture properties such as the specific heat \( C_p \) and molar mass \( M \) should normally be evaluated at the mean film composition and mean film temperature. However, when dealing with air–water vapor mixtures at atmospheric conditions or other low mass flux situations, we can simply use the properties of the gas with reasonable accuracy.

### Table 14–14

Various expressions for evaporation rate of a liquid into a gas through an interface area \( A_t \) under various approximations (subscript \( v \) stands for vapor, \( s \) for liquid–gas interface, and \( \infty \) away from surface)

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Evaporation Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>General</td>
<td>( \dot{m}<em>v = h</em>{\text{mass}} A_v \left( \rho_{v,s} - \rho_{v,\infty} \right) )</td>
</tr>
<tr>
<td>Assuming vapor to be an ideal gas, ( P_v = \rho_v R_v T )</td>
<td>( \dot{m}<em>v = \frac{h</em>{\text{mass}} A_v}{R_v} \left( \frac{P_{v,s}}{T_s} - \frac{P_{v,\infty}}{T_{\infty}} \right) )</td>
</tr>
<tr>
<td>Using Chilton–Colburn analogy, ( h_{\text{heat}} = \rho C_p h_{\text{mass}} L e^{2/3} )</td>
<td>( \dot{m}<em>v = \frac{h</em>{\text{mass}} A_v}{\rho C_p L e^{2/3} R_v} \left( \frac{P_{v,s}}{T_s} - \frac{P_{v,\infty}}{T_{\infty}} \right) )</td>
</tr>
<tr>
<td>Using ( \frac{1}{T_s} - \frac{1}{T_{\infty}} = \frac{1}{T} ), where ( T = \frac{T_s + T_{\infty}}{2} ) and ( P = \rho RT = \rho (R_v/M) T )</td>
<td>( \dot{m}<em>v = \frac{h</em>{\text{mass}} A_v}{\rho C_p L e^{2/3} M \rho_{v,s}} \left( \frac{P_{v,s}}{T_s} - \frac{P_{v,\infty}}{T_{\infty}} \right) )</td>
</tr>
</tbody>
</table>
The $\dot{Q}$ in Eq. 14–91 represents all forms of heat from all sources transferred to the surface, including convection and radiation from the surroundings and conduction from the deeper parts of the water due to the sensible energy of the water itself or due to heating the water body by a resistance heater, heating coil, or even chemical reactions in the water. If heat transfer from the water body to the surface as well as radiation from the surroundings is negligible, which is often the case, then the heat loss by evaporation must equal heat gain by convection. That is,

$$\dot{Q}_{\text{conv}} = m_v h_f$$

or

$$h_{\text{conv}} A_s (T_v - T_s) = \frac{h_{\text{conv}} A_s h_f M_p P_{v, w} - P_{v, w}}{C_p L_e^{2/3} \frac{M_p}{P}}$$

Canceling $h_{\text{conv}} A_s$ from both sides of the second equation gives

$$T_s = T_v - \frac{h_{\text{fg}} w}{C_p L_e^{2/3} \frac{M_p}{P}}$$

which is a relation for the temperature difference between the liquid and the surrounding gas under steady conditions.

**EXAMPLE 14–12 Evaporative Cooling of a Canned Drink**

During a hot summer day, a canned drink is to be cooled by wrapping it in a cloth that is kept wet continually, and blowing air to it with a fan (Fig. 14–53). If the environment conditions are 1 atm, 30°C, and 40 percent relative humidity, determine the temperature of the drink when steady conditions are reached.

**SOLUTION** Air is blown over a canned drink wrapped in a wet cloth to cool it by simultaneous heat and mass transfer. The temperature of the drink when steady conditions are reached is to be determined.

**Assumptions** 1 The low mass flux conditions exist so that the Chilton–Colburn analogy between heat and mass transfer is applicable since the mass fraction of vapor in the air is low (about 2 percent for saturated air at 300 K). 2 Both air and water vapor at specified conditions are ideal gases (the error involved in this assumption is less than 1 percent). 3 Radiation effects are negligible.

**Properties** Because of low mass flux conditions, we can use dry air properties for the mixture at the average temperature of $(T_v + T_s)/2$ which cannot be determined at this point because of the unknown surface temperature $T_s$. We know that $T_s < T_v$ and, for the purpose of property evaluation, we take $T_s$ to be 20°C. Then the properties of water at 20°C and the properties of dry air at the average temperature of 25°C and 1 atm are (Tables A–9 and A–15)

Water: $h_{fg} = 2454 \text{ kJ/kg}, P_v = 2.34 \text{ kPa};$ also, $P_v = 4.25 \text{ kPa}$ at 30°C

Dry air: $C_p = 1.007 \text{ kJ/kg \cdot °C}, \alpha = 2.141 \times 10^{-5} \text{ m}^2/\text{s}$

The molar masses of water and air are 18 and 29 kg/kmol, respectively (Table A–1). Also, the mass diffusivity of water vapor in air at 25°C is $D_{v, w-air} = 2.50 \times 10^{-5} \text{ m}^2/\text{s}$ (Table 14–4).

**Analysis** Utilizing the Chilton–Colburn analogy, the surface temperature of the drink can be determined from Eq. 14–92.
HEAT TRANSFER

\[ T_s = T_w - \frac{h_{fg} M_e (P_{v,w} - P_{v,x})}{C_p Le^{2/3} M} \]

where the Lewis number is

\[ Le = \frac{\alpha}{D_{ab}} = \frac{2.141 \times 10^{-5} \text{ m}^2/\text{s}}{2.5 \times 10^{-5} \text{ m}^2/\text{s}} = 0.856 \]

Note that we could take the Lewis number to be 1 for simplicity, but we chose to incorporate it for better accuracy.

The air at the surface is saturated, and thus the vapor pressure at the surface is simply the saturation pressure of water at the surface temperature (2.34 kPa). The vapor pressure of air far from the surface is determined from

\[ P_{v,x} = \phi P_{\text{sat}, x} \]

Noting that the atmospheric pressure is 1 atm = 101.3 kPa, substituting gives

\[ T_s = 30^\circ C - \frac{2454 \text{ kJ/kg}}{(1.007 \text{ kJ/kg} \cdot ^\circ C)(0.872)^{2/3}} \frac{18 \text{ kg/kmol}}{29 \text{ kg/kmol}} \frac{2.34 - 1.70 \text{ kPa}}{101.3 \text{ kPa}} = 19.4^\circ C \]

Therefore, the temperature of the drink can be lowered to 19.4°C by this process.

EXAMPLE 14–13 Heat Loss from Uncovered Hot Water Baths

Hot water baths with open tops are commonly used in manufacturing facilities for various reasons. In a plant that manufactures spray paints, the pressurized paint cans are temperature tested by submerging them in hot water at 50°C in a 40-cm-deep rectangular bath and keeping them there until the cans are heated to 50°C to ensure that the cans can withstand temperatures up to 50°C during transportation and storage (Fig. 14–54). The water bath is 1 m wide and 3.5 m long, and its top surface is open to ambient air to facilitate easy observation for the workers. If the average conditions in the plant are 92 kPa, 25°C, and 52 percent relative humidity, determine the rate of heat loss from the top surface of the water bath by (a) radiation, (b) natural convection, and (c) evaporation. Assume the water is well agitated and maintained at a uniform temperature of 50°C at all times by a heater, and take the average temperature of the surrounding surfaces to be 20°C.

SOLUTION Spray paint cans are temperature tested by submerging them in an uncovered hot water bath. The rates of heat loss from the top surface of the bath by radiation, natural convection, and evaporation are to be determined.

Assumptions 1 The low mass flux conditions exist so that the Chilton–Colburn analogy between heat and mass transfer is applicable since the mass fraction of vapor in the air is low (about 2 percent for saturated air at 300 K). 2 Both air and water vapor at specified conditions are ideal gases (the error involved in this assumption is less than 1 percent). 3 Water is maintained at a uniform temperature of 50°C.
Properties Relevant properties for each mode of heat transfer are determined below in respective sections.

Analysis (a) The emissivity of liquid water is given in Table A–18 to be 0.95. Then the radiation heat loss from the water to the surrounding surfaces becomes

\[
\dot{Q}_{\text{rad}} = eA_\text{s}\sigma(T_\text{s}^4 - T_{\text{surr}}^4)
\]

\[
= (0.95)(3.5 \text{ m}^2)(5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4)((323 \text{ K})^4 - (293 \text{ K})^4)
\]

\[= 663 \text{ W}\]

(b) The air–water vapor mixture is dilute and thus we can use dry air properties for the mixture at the average temperature of \((T_\text{s} + T_\text{a})/2 = (25 + 50)/2 = 37.5 \text{°C}\). Noting that the total atmospheric pressure is 92/101.3 = 0.9080 atm, the properties of dry air at 37.5\°C and 0.908 atm are

\[k = 0.02644 \text{ W/m \cdot °C}, \quad \text{Pr} = 0.7261 \text{ (independent of pressure)}\]

\[\alpha = (2.311 \times 10^{-5} \text{ m}^2/\text{s})/0.9080 = 2.545 \times 10^{-5} \text{ m}^2/\text{s}\]

\[\nu = (1.678 \times 10^{-5} \text{ m}^2/\text{s})/0.9080 = 1.848 \times 10^{-5} \text{ m}^2/\text{s}\]

The properties of water at 50\°C are

\[h_{fg} = 2383 \text{ kJ/kg} \quad \text{and} \quad P_\text{v} = 12.35 \text{ kPa}\]

The air at the surface is saturated, and thus the vapor pressure at the surface is simply the saturation pressure of water at the surface temperature (12.35 kPa). The vapor pressure of air far from the water surface is determined from

\[P_{\text{v, s}} = \phi P_{\text{sat} @ 25\°C} = (0.52)(3.17 \text{ kPa}) = 1.65 \text{ kPa}\]

Treating the water vapor and the air as ideal gases and noting that the total atmospheric pressure is the sum of the vapor and dry air pressures, the densities of the water vapor, dry air, and their mixture at the water–air interface and far from the surface are determined to be

At the surface:

\[\rho_{\text{v, s}} = \frac{P_{\text{v, s}}}{R_{\text{T}_\text{s}}} = \frac{12.35 \text{ kPa}}{(0.4615 \text{ kPa \cdot m}^3/\text{kg \cdot K})(323 \text{ K})} = 0.0828 \text{ kg/m}^3\]

\[\rho_{\text{a, s}} = \frac{P_{\text{a, s}}}{R_{\text{T}_\text{s}}} = \frac{92 - 12.35 \text{ kPa}}{(0.287 \text{ kPa \cdot m}^3/\text{kg \cdot K})(323 \text{ K})} = 0.8592 \text{ kg/m}^3\]

\[\rho_3 = \rho_{\text{v, s}} + \rho_{\text{a, s}} = 0.0828 + 0.8592 = 0.9420 \text{ kg/m}^3\]

and

Away from the surface:

\[\rho_{\text{v, s}} = \frac{P_{\text{v, s}}}{R_{\text{T}_\text{s}}} = \frac{1.65 \text{ kPa}}{(0.4615 \text{ kPa \cdot m}^3/\text{kg \cdot K})(298 \text{ K})} = 0.0120 \text{ kg/m}^3\]

\[\rho_{\text{a, s}} = \frac{P_{\text{a, s}}}{R_{\text{T}_\text{s}}} = \frac{92 - 1.65 \text{ kPa}}{(0.287 \text{ kPa \cdot m}^3/\text{kg \cdot K})(298 \text{ K})} = 1.0564 \text{ kg/m}^3\]

\[\rho_3 = \rho_{\text{v, s}} + \rho_{\text{a, s}} = 0.0120 + 1.0564 = 1.0684 \text{ kg/m}^3\]

The area of the top surface of the water bath is \(A_s = (3.5 \text{ m})(1 \text{ m}) = 3.5 \text{ m}^2\) and its perimeter is \(p = 2(3.5 + 1) = 9 \text{ m}\). Therefore, the characteristic length is
\[ L_c = \frac{A_s}{P} = \frac{3.5 \text{ m}^2}{9 \text{ m}} = 0.3889 \text{ m} \]

Then using densities (instead of temperatures) since the mixture is not homogeneous, the Grashof number is determined to be

\[
Gr = \frac{g(\rho_\alpha - \rho_\beta)L_c^3}{\nu^2} = \frac{(9.81 \text{ m/s}^2)(1.0684 - 0.9420 \text{ kg/m}^3)(0.3889 \text{ m})^3}{[(0.9420 + 1.0684)/2 \text{ kg/m}^3](1.848 \times 10^{-5} \text{ m}^2/\text{s})^2} = 2.125 \times 10^8
\]

Recognizing that this is a natural convection problem with hot horizontal surface facing up, the Nusselt number and the convection heat transfer coefficients are determined to be

\[
Nu = 0.15(Gr Pr)^{1/3} = 0.15(2.125 \times 10^8 \times 0.7261)^{1/3} = 80.45
\]

and

\[
h_{\text{conv}} = \frac{Nu k}{L_c} = \frac{(80.45)(0.02644 \text{ W/m} \cdot \text{°C})}{0.3889 \text{ m}} = 5.47 \text{ W/m}^2 \cdot \text{°C}
\]

Then the natural convection heat transfer rate becomes

\[ \dot{Q}_{\text{conv}} = h_{\text{conv}} A_s (T_s - T_c) = (5.47 \text{ W/m}^2 \cdot \text{°C})(3.5 \text{ m}^2)(50 - 25)\text{°C} = 479 \text{ W} \]

Note that the magnitude of natural convection heat transfer is comparable to that of radiation, as expected.

(c) Utilizing the analogy between heat and mass convection, the mass transfer coefficient is determined the same way by replacing Pr by Sc. The mass diffusivity of water vapor in air at the average temperature of 310.5 K is determined from Eq. 14–15 to be

\[
D_{AB} = D_{H_2O - \text{air}} = 1.87 \times 10^{-10} \frac{T^{2.072}}{P} = 1.87 \times 10^{-10} \frac{310.5^{2.072}}{0.908} = 3.00 \times 10^{-5} \text{ m}^2/\text{s}
\]

The Schmidt number is determined from its definition to be

\[
Sc = \frac{v}{D_{AB}} = \frac{1.848 \times 10^{-5} \text{ m}^2/\text{s}}{3.00 \times 10^{-5} \text{ m}^2/\text{s}} = 0.616
\]

The Sherwood number and the mass transfer coefficients are determined to be

\[
Sh = 0.15(Gr Sc)^{1/3} = 0.15(2.125 \times 10^8 \times 0.616)^{1/3} = 76.2
\]

and

\[
h_{\text{mass}} = \frac{Sh D_{AB}}{L_c} = \frac{(76.2)(3.00 \times 10^{-5} \text{ m}^2/\text{s})}{0.3889 \text{ m}} = 0.00588 \text{ m/s}
\]
Then the evaporation rate and the rate of heat transfer by evaporation become

\[
m_e = h_{\text{mass}} A (\rho_i - \rho_g) = (0.00588 \text{ m/s})(3.5 \text{ m}^2)(0.0828 - 0.0120) \text{ kg/m}^3 = 0.00146 \text{ kg/s} = 5.25 \text{ kg/h}
\]

and

\[
\dot{Q}_{\text{evap}} = m_e h_f = (0.00146 \text{ kg/s})(2383 \text{ kJ/kg}) = 3.479 \text{ kW} = 3479 \text{ W}
\]

which is more than seven times the rate of heat transfer by natural convection.

Finally, noting that the direction of heat transfer is always from high to low temperature, all forms of heat transfer determined above are in the same direction, and the total rate of heat loss from the water to the surrounding air and surfaces is

\[
\dot{Q}_{\text{total}} = \dot{Q}_{\text{rad}} + \dot{Q}_{\text{conv}} + \dot{Q}_{\text{evap}} = 663 + 479 + 3479 = 4621 \text{ W}
\]

Discussion

Note that if the water bath is heated electrically, a 4.6 kW resistance heater will be needed just to make up for the heat loss from the top surface. The total heater size will have to be larger to account for the heat losses from the side and bottom surfaces of the bath as well as the heat absorbed by the spray paint cans as they are heated to 50°C. Also note that water needs to be supplied to the bath at a rate of 5.25 kg/h to make up for the water loss by evaporation. Also, in reality, the surface temperature will probably be a little lower than the bulk water temperature, and thus the heat transfer rates will be somewhat lower than indicated here.

SUMMARY

Mass transfer is the movement of a chemical species from a high concentration region toward a lower concentration one relative to the other chemical species present in the medium. Heat and mass transfer are analogous to each other, and several parallels can be drawn between them. The driving forces are the temperature difference in heat transfer and the concentration difference in mass transfer. Fick’s law of mass diffusion is of the same form as Fourier’s law of heat conduction. The species generation in a medium due to homogeneous reactions is analogous to heat generation. Also, mass convection due to bulk fluid motion is analogous to heat convection. Constant surface temperature corresponds to constant concentration at the surface, and an adiabatic wall corresponds to an impermeable wall. However, concentration is usually not a continuous function at a phase interface.

The concentration of a species A can be expressed in terms of density \( \rho_A \) or molar concentration \( C_A \). It can also be expressed in dimensionless form in terms of mass or molar fraction as

Mass fraction of species A: \( w_A = \frac{m_A}{m} = \frac{m_A/V}{m/V} = \frac{\rho_A}{\rho} \)

Mole fraction of species A: \( y_A = \frac{N_A}{N} = \frac{N_A/N}{V/V} = \frac{C_A}{C} \)

In the case of an ideal gas mixture, the mole fraction of a gas is equal to its pressure fraction. Fick’s law for the diffusion of a species A in a stationary binary mixture of species A and B in a specified direction x is expressed as

Mass basis: \( j_{\text{diff}, A} = \frac{\dot{m}_{\text{diff}, A}}{A} = -\rho D_{AB} \frac{d\rho_A/\rho}{dx} \)

Mole basis: \( \dot{j}_{\text{diff}, A} = \frac{\dot{N}_{\text{diff}, A}}{A} = -C D_{AB} \frac{d(C_A/C)}{dx} \)
where $D_{AB}$ is the diffusion coefficient (or mass diffusivity) of the species in the mixture, $j_{\text{diff}, A}$ is the diffusive mass flux of species A, and $f_{\text{diff}, A}$ is the molar flux.

The mole fractions of a species $i$ in the gas and liquid phases at the interface of a dilute mixture are proportional to each other and are expressed by Henry’s law as

$$y_i, \text{ liquid side} = \frac{P_i, \text{ gas side}}{H}$$

where $H$ is Henry’s constant. When the mixture is not dilute, an approximate relation for the mole fractions of a species on the liquid and gas sides of the interface are expressed approximately by Raoult’s law as

$$P_{i, \text{ sat}(T)} = y_i, \text{ gas side} \cdot P = y_i, \text{ liquid side} \cdot P_{i, \text{ gas side}(T)}$$

where $P_{i, \text{ sat}(T)}$ is the saturation pressure of the species $i$ at the interface temperature and $P$ is the total pressure on the gas phase side.

The concentration of the gas species $i$ in the solid at the interface $C_i, \text{ solid side}$ is proportional to the partial pressure of the species $i$ in the gas $P_{i, \text{ gas side}}$ on the gas side of the interface and is expressed as

$$C_i, \text{ solid side} = \mathcal{S} \times P_{i, \text{ gas side}}$$

where $\mathcal{S}$ is the solubility. The product of the solubility of a gas and the diffusion coefficient of the gas in a solid is referred to as the permeability $\mathcal{P}$, which is a measure of the ability of the gas to penetrate a solid.

In the absence of any chemical reactions, the mass transfer rates $\dot{m}_{\text{diff}, A}$ through a plane wall of area $A$ and thickness $L$ and cylindrical and spherical shells of inner and outer radii $r_1$ and $r_2$ under one-dimensional steady conditions are expressed as

$$\dot{m}_{\text{diff}, A, \text{ wall}} = \rho D_{AB} A \frac{w_{A, 1} - w_{A, 2}}{L} = D_{AB} A \frac{P_{A, 1} - P_{A, 2}}{L}$$

$$\dot{m}_{\text{diff}, A, \text{ cyl}} = 2\pi L p D_{AB} \frac{w_{A, 1} - w_{A, 2}}{\ln(r_2/r_1)} = 2\pi L \alpha D_{AB} \frac{P_{A, 1} - P_{A, 2}}{\ln(r_2/r_1)}$$

$$\dot{m}_{\text{diff}, A, \text{ sph}} = 4\pi r_1 r_2 p D_{AB} \frac{w_{A, 1} - w_{A, 2}}{r_2 - r_1} = 4\pi r_1 r_2 D_{AB} \frac{P_{A, 1} - P_{A, 2}}{r_2 - r_1}$$

The mass flow rate of a gas through a solid plane wall under steady one-dimensional conditions can also be expressed in terms of the partial pressures of the adjacent gas on the two sides of the solid as

$$\dot{m}_{\text{diff}, A, \text{ wall}} = D_{AB} \mathcal{S}_{AB} A \frac{P_{A, 1} - P_{A, 2}}{L} = \mathcal{S}_{AB} A \frac{P_{A, 1} - P_{A, 2}}{L}$$

where $P_{A, 1}$ and $P_{A, 2}$ are the partial pressures of gas $A$ on the two sides of the wall.

During mass transfer in a moving medium, chemical species are transported both by molecular diffusion and by the bulk fluid motion, and the velocities of the species are expressed as

$$\dot{V}_A = \dot{V} + \dot{V}_{\text{diff}, A}$$

$$\dot{V}_B = \dot{V} + \dot{V}_{\text{diff}, B}$$

where $\dot{V}$ is the mass-average velocity of the flow. It is the velocity that would be measured by a velocity sensor and is expressed as

$$\dot{V} = w_A \dot{V}_A + w_B \dot{V}_B$$

The special case $\dot{V} = 0$ corresponds to a stationary medium. Using Fick’s law of diffusion, the total mass fluxes $\dot{j} = \dot{m} / A$ in a moving medium are expressed as

$$\dot{j}_A = \rho_A \dot{V} + \rho_A \dot{V}_{\text{diff}, A} = w_A (\dot{j}_A + \dot{j}_B) - \rho D_{AB} \frac{\partial w_A}{\partial x}$$

$$\dot{j}_B = \rho_B \dot{V} + \rho_B \dot{V}_{\text{diff}, B} = w_B (\dot{j}_A + \dot{j}_B) - \rho D_{BA} \frac{\partial w_B}{\partial x}$$

The rate of mass convection of species $A$ in a binary mixture is expressed in an analogous manner to Newton’s law of cooling as

$$\dot{m}_{\text{conv}, A} = h_{\text{mass}, A} (\rho_{A, 1} - \rho_{A, 2}) = h_{\text{mass}, A} (w_{A, 1} - w_{A, 2})$$

where $h_{\text{mass}}$ is the average mass transfer coefficient, in $\text{m/s}$.

The counterparts of the Prandtl and Nusselt numbers in mass convection are the Schmidt number $\text{Sc}$ and the Sherwood number $\text{Sh}$, defined as

$$\text{Sc} = \frac{\dot{V}}{D_{AB}} = \frac{\text{Momentum diffusivity}}{\text{Mass diffusivity}}$$

$$\text{Sh} = \frac{h_{\text{mass}}}{D_{AB}} = \frac{\text{Mass diffusivity}}{\text{Mass diffusivity}}$$

The relative magnitudes of heat and mass diffusion in the thermal and concentration boundary layers are represented by the Lewis number, defined as

$$\text{Le} = \frac{\text{Sc}}{\text{Pr}} = \frac{\text{Thermal diffusivity}}{\text{Mass diffusivity}}$$

Heat and mass transfer coefficients are sometimes expressed in terms of the dimensionless Stanton number, defined as

$$\text{St}_{\text{heat}} = \frac{h_{\text{conv}}}{\dot{V} \rho C_P} = \frac{1}{\text{Nu}} \frac{1}{\text{Re Pr}}$$

and

$$\text{St}_{\text{mass}} = \frac{\dot{m}_{\text{conv}}}{\dot{V}} = \text{Sh} \frac{1}{\text{Re Sc}}$$

where $\dot{V}$ is the free-stream velocity in external flow and the bulk mean fluid velocity in internal flow. For a given geometry and boundary conditions, the Sherwood number in natural or
forced convection can be determined from the corresponding Nusselt number expression by simply replacing the Prandtl number by the Schmidt number. But in natural convection, the Grashof number should be expressed in terms of density difference instead of temperature difference.

When the molecular diffusivities of momentum, heat, and mass are identical, we have \( v = \alpha = D_{AB} \), and thus \( \text{Pr} = \text{Sc} = \text{Le} = 1 \). The similarity between momentum, heat, and mass transfer in this case is given by the Reynolds analogy, expressed as

\[
\frac{f}{2\text{Re}} = \frac{\text{Nu}}{\text{Sh}} \quad \text{or} \quad \frac{f}{2\sqrt{Le}} = \frac{h_{\text{heat}}L}{k} = \frac{h_{\text{mass}}L}{D_{AB}} \quad \text{or} \quad \frac{f}{2} = \frac{\text{St}}{\text{St}_{\text{mass}}}
\]

For the general case of \( \text{Pr} \neq \text{Sc} \neq 1 \), it is modified as

\[
\frac{f}{2} = \text{St Pr}^{2/3} = \text{St}_{\text{mass}} \text{Sc}^{2/3}
\]

which is known as the Chilton–Colburn analogy. The analogy between heat and mass transfer is expressed more conveniently as

\[
h_{\text{heat}} = \rho C_p \text{Le}^{2/3} h_{\text{mass}} = \rho C_p (\alpha D_{AB})^{2/3} h_{\text{mass}}
\]

For air–water vapor mixtures, \( \text{Le} \approx 1 \), and thus this relation simplifies further. The heat–mass convection analogy is limited to low mass flux cases in which the flow rate of species undergoing mass flow is low relative to the total flow rate of the liquid or gas mixture. The mass transfer problems that involve phase change (evaporation, sublimation, condensation, melting, etc.) also involve heat transfer, and such problems are analyzed by considering heat and mass transfer simultaneously.

**REFERENCES AND SUGGESTED READING**

**PROBLEMS*\(^*\)**

**Analogy between Heat and Mass Transfer**

14–1C How does mass transfer differ from bulk fluid flow? Can mass transfer occur in a homogeneous medium?

14–2C How is the concentration of a commodity defined? How is the concentration gradient defined? How is the diffusion rate of a commodity related to the concentration gradient?

14–3C Give examples for (a) liquid-to-gas, (b) solid-to-liquid, (c) solid-to-gas, and (d) gas-to-liquid mass transfer.

14–4C Someone suggests that thermal (or heat) radiation can also be viewed as mass radiation since, according to Einstein’s formula, an energy transfer in the amount of \( E \) corresponds to a mass transfer in the amount of \( m = E/c^2 \). What do you think?

14–5C What is the driving force for (a) heat transfer, (b) electric current flow, (c) fluid flow, and (d) mass transfer?

14–6C What do (a) homogeneous reactions and (b) heterogeneous reactions represent in mass transfer? To what do they correspond in heat transfer?

**Mass Diffusion**

14–7C Both Fourier’s law of heat conduction and Fick’s law of mass diffusion can be expressed as \( Q = -kA(dT/dx) \). What do the quantities \( Q \), \( k \), \( A \), and \( T \) represent in (a) heat conduction and (b) mass diffusion?

14–8C Mark these statements as being True or False for a binary mixture of substances \( A \) and \( B \).

___(a) The density of a mixture is always equal to the sum of the densities of its constituents.

___(b) The ratio of the density of component \( A \) to the density of component \( B \) is equal to the mass fraction of component \( A \).

___(c) If the mass fraction of component \( A \) is greater than 0.5, then at least half of the mass of the mixture is component \( A \).

___(d) If both \( A \) and \( B \) are ideal gases, then the pressure fraction of \( A \) is equal to its mole fraction.

___(e) If the mole fractions of \( A \) and \( B \) are both 0.5, then the molar mass of the mixture is simply the arithmetic average of the molar masses of \( A \) and \( B \).

14–9C Mark these statements as being True or False for a binary mixture of substances \( A \) and \( B \).

___(a) The molar concentration of a mixture is always equal to the sum of the molar concentrations of its constituents.

___(b) The ratio of the molar concentration of \( A \) to the molar concentration of \( B \) is equal to the mole fraction of component \( A \).

___(c) If the mole fraction of component \( A \) is greater than 0.5, then at least half of the mass of the mixture is component \( A \).

___(d) If both \( A \) and \( B \) are ideal gases, then the pressure fraction of \( A \) is equal to its mole fraction.

___(e) If the mole fractions of \( A \) and \( B \) are both 0.5, then the molar mass of the mixture is simply the arithmetic average of the molar masses of \( A \) and \( B \).

14–10C Fick’s law of diffusion is expressed on the mass and mole basis as \( m_{\text{diff}, A} = -pA_{\text{diff}}(dw_A/dx) \) and \( N_{\text{diff}, A} = -CAD_{\text{diff}}(dn_A/dx) \), respectively. Are the diffusion coefficients \( D_{\text{diff}} \) in the two relations the same or different?

14–11C How does the mass diffusivity of a gas mixture change with (a) temperature and (b) pressure?

14–12C At a given temperature and pressure, do you think the mass diffusivity of air in water vapor will be equal to the mass diffusivity of water vapor in air? Explain.

14–13C At a given temperature and pressure, do you think the mass diffusivity of copper in aluminum will be equal to the mass diffusivity of aluminum in copper? Explain.

14–14C In a mass production facility, steel components are to be hardened by carbon diffusion. Would you carry out the hardening process at room temperature or in a furnace at a high temperature, say 900°C? Why?

14–15C Someone claims that the mass and the mole fractions for a mixture of \( \text{CO}_2 \) and \( \text{N}_2 \) gases are identical. Do you agree? Explain.

14–16 The composition of moist air is given on a molar basis to be 78 percent \( \text{N}_2 \), 20 percent \( \text{O}_2 \), and 2 percent water vapor. Determine the mass fractions of the constituents of air. Answers: 76.4 percent \( \text{N}_2 \), 22.4 percent \( \text{O}_2 \), 1.2 percent \( \text{H}_2\text{O} \)

14–17E A gas mixture consists of 5 lbm of \( \text{O}_2 \), 8 lbm of \( \text{N}_2 \), and 10 lbm of \( \text{CO}_2 \). Determine (a) the mass fraction of each component, (b) the mole fraction of each component, and (c) the average molar mass of the mixture.

14–18 A gas mixture consists of 8 kmol of \( \text{H}_2 \) and 2 kmol of \( \text{N}_2 \). Determine the mass of each gas and the apparent gas constant of the mixture.

*Problems designated by a “C” are concept questions, and students are encouraged to answer them all. Problems designated by an “E” are in English units, and the SI users can ignore them. Problems with an EES-CD icon \( \text{\textbullet} \) are solved using EES, and complete solutions together with parametric studies are included on the enclosed CD. Problems with a computer-EES icon \( \text{\textbullet} \) are comprehensive in nature, and are intended to be solved with a computer, preferably using the EES software that accompanies this text.
**14–19** The molar analysis of a gas mixture at 290 K and 250 kPa is 65 percent N₂, 20 percent O₂, and 15 percent CO₂. Determine the mass fraction and partial pressure of each gas.

**14–20** Determine the binary diffusion coefficient of CO₂ in air at (a) 200 K and 1 atm, (b) 400 K and 0.8 atm, and (c) 600 K and 3 atm.

**14–21** Repeat Problem 14–20 for O₂ in N₂.

**14–22E** The relative humidity of air at 80°F and 14.7 psia is increased from 30 percent to 90 percent during a humidification process at constant temperature and pressure. Determine the percent error involved in assuming the density of air to have remained constant.  
*Answer: 2.1 percent*

**14–23** The diffusion coefficient of hydrogen in steel is given as a function of temperature as

\[ D_{AB} = 1.65 \times 10^{-6} \exp(-4630/T) \text{ (m}^2\text{/s)} \]

where \( T \) is in K. Determine the diffusion coefficients from 200 K to 1200 K in 200 K increments and plot the results.

**14–24** Reconsider Problem 14–23. Using EES (or other) software, plot the diffusion coefficient as a function of the temperature in the range of 200 K to 1200 K.

**Boundary Conditions**

**14–25C** Write three boundary conditions for mass transfer (on a mass basis) for species A at \( x = 0 \) that correspond to specified temperature, specified heat flux, and convection boundary conditions in heat transfer.

**14–26C** What is an impermeable surface in mass transfer? How is it expressed mathematically (on a mass basis)? To what does it correspond in heat transfer?

**14–27C** Consider the free surface of a lake exposed to the atmosphere. If the air at the lake surface is saturated, will the mole fraction of water vapor in air at the lake surface be the same as the mole fraction of water in the lake (which is nearly 1)?

**14–28C** When prescribing a boundary condition for mass transfer at a solid–gas interface, why do we need to specify the side of the surface (whether the solid or the gas side)? Why did we not do it in heat transfer?

**14–29C** Using properties of saturated water, explain how you would determine the mole fraction of water vapor at the surface of a lake when the temperature of the lake surface and the atmospheric pressure are specified.

**14–30C** Using solubility data of a solid in a specified liquid, explain how you would determine the mass fraction of the solid in the liquid at a specified temperature.

**14–31C** Using solubility data of a gas in a solid, explain how you would determine the molar concentration of the gas in the solid at the solid–gas interface at a specified temperature.

**14–32C** Using Henry’s constant data for a gas dissolved in a liquid, explain how you would determine the mole fraction of the gas dissolved in the liquid at the interface at a specified temperature.

**14–33C** What is permeability? How is the permeability of a gas in a solid related to the solubility of the gas in that solid?

**14–34E** Determine the mole fraction of the water vapor at the surface of a lake whose temperature at the surface is 60°F, and compare it to the mole fraction of water in the lake. Take the atmospheric pressure at lake level to be 13.8 psia.

**14–35** Determine the mole fraction of dry air at the surface of a lake whose temperature is 15°C. Take the atmospheric pressure at lake level to be 100 kPa.  
*Answer: 98.3 percent*

**14–36** Reconsider Problem 14–35. Using EES (or other) software, plot the mole fraction of dry air at the surface of the lake as a function of the lake temperature as the temperature varies from 5°C to 25°C, and discuss the results.

**14–37** Consider a rubber plate that is in contact with nitrogen gas at 298 K and 250 kPa. Determine the molar and mass densities of nitrogen in the rubber at the interface.

*Answers: 0.0039 kmol/m³, 0.1092 kg/m³*
14–38 A wall made of natural rubber separates O₂ and N₂ gases at 25°C and 500 kPa. Determine the molar concentrations of O₂ and N₂ in the wall.

14–39 Consider a glass of water in a room at 20°C and 97 kPa. If the relative humidity in the room is 100 percent and the water and the air are in thermal and phase equilibrium, determine (a) the mole fraction of the water vapor in the air and (b) the mole fraction of air in the water.

14–40E Water is sprayed into air at 80°F and 14.3 psia, and the falling water droplets are collected in a container on the floor. Determine the mass and mole fractions of air dissolved in the water.

14–41 Consider a carbonated drink in a bottle at 27°C and 130 kPa. Assuming the gas space above the liquid consists of a saturated mixture of CO₂ and water vapor and treating the drink as water, determine (a) the mole fraction of the water vapor in the CO₂ gas and (b) the mass of dissolved CO₂ in a 200-ml drink. Answers: (a) 2.77 percent, (b) 0.36 g

14–42C Write down the relations for steady one-dimensional heat conduction and mass diffusion through a plane wall, and identify the quantities in the two equations that correspond to each other.

14–43C Consider steady one-dimensional mass diffusion through a wall. Mark these statements as being True or False.

(a) Other things being equal, the higher the density of the wall, the higher the rate of mass transfer. True

(b) Other things being equal, doubling the thickness of the wall will double the rate of mass transfer. True

(c) Other things being equal, the higher the temperature, the higher the rate of mass transfer. True

(d) Other things being equal, doubling the mass fraction of the diffusing species at the high concentration side will double the rate of mass transfer. True

14–44C Consider one-dimensional mass diffusion of species A through a plane wall of thickness L. Under what conditions will the concentration profile of species A in the wall be a straight line?

14–45C Consider one-dimensional mass diffusion of species A through a plane wall. Does the species A content of the wall change during steady mass diffusion? How about during transient mass diffusion?

14–46 Helium gas is stored at 293 K in a 3-m-outer-diameter spherical container made of 5-cm-thick Pyrex. The molar concentration of helium in the Pyrex is 0.00073 kmol/m³ at the inner surface and negligible at the outer surface. Determine the mass flow rate of helium by diffusion through the Pyrex container. Answer: 7.2 × 10⁻¹⁵ kg/s

14–47 A thin plastic membrane separates hydrogen from air. The molar concentrations of hydrogen in the membrane at the inner and outer surfaces are determined to be 0.065 and 0.003 kmol/m³, respectively. The binary diffusion coefficient of hydrogen in plastic at the operation temperature is 5.3 × 10⁻¹⁰ m²/s. Determine the mass flow rate of hydrogen by diffusion through the membrane under steady conditions if the thickness of the membrane is (a) 2 mm and (b) 0.5 mm.

14–48 The solubility of hydrogen gas in steel in terms of its mass fraction is given as \( w_H = 2.09 \times 10^{-4} \exp(-3950/T)P_{0.5} \) where \( P_{0.5} \) is the partial pressure of hydrogen in bars and \( T \) is the temperature in K. If natural gas is transported in a 1-cm-thick, 3-m-internal-diameter steel pipe at 500 kPa pressure and the mole fraction of hydrogen in the natural gas is 8 percent, determine the highest rate of hydrogen loss through a 100-m-long section of the pipe at steady conditions at a temperature of 293 K if the pipe is exposed to air. Take the diffusivity of hydrogen in steel to be 2.9 × 10⁻¹³ m²/s. Answer: 3.98 × 10⁻¹⁴ kg/s
Reconsider Problem 14–48. Using EES (or other) software, plot the highest rate of hydrogen loss as a function of the mole fraction of hydrogen in natural gas as the mole fraction varies from 5 to 15 percent, and discuss the results.

Helium gas is stored at 293 K and 500 kPa in a 1-cm-thick, 2-m-inner-diameter spherical tank made of fused silica (SiO₂). The area where the container is located is well ventilated. Determine (a) the mass flow rate of helium by diffusion through the tank and (b) the pressure drop in the tank in one week as a result of the loss of helium gas.

You probably have noticed that balloons inflated with helium gas rise in the air the first day during a party but then fall down the next day and act like ordinary balloons filled with air. This is because the helium in the balloon slowly leaks out through the wall while air leaks in by diffusion.

Consider a balloon that is made of 0.1-mm-thick soft rubber and has a diameter of 15 cm when inflated. The pressure and temperature inside the balloon are initially 110 kPa and 25°C. The permeability of rubber to helium, oxygen, and nitrogen at 25°C are $9.4 \times 10^{-13}$, $7.05 \times 10^{-13}$, and $2.6 \times 10^{-13}$ kmol/m·s·bar, respectively. Determine the initial rates of diffusion of helium, oxygen, and nitrogen through the balloon wall and the mass fraction of helium that escapes the balloon during the first 5 h assuming the helium pressure inside the balloon remains nearly constant. Assume air to be 21 percent oxygen and 79 percent nitrogen by mole numbers and take the room conditions to be 100 kPa and 25°C.

Assuming the volume to remain constant and disregarding the diffusion of air into the balloon, obtain a relation for the variation of pressure in the balloon with time. Using the results obtained and the numerical values given in the problem, determine how long it will take for the pressure inside the balloon to drop to 100 kPa.

Pure N₂ gas at 1 atm and 25°C is flowing through a 10-m-long, 3-cm-inner diameter pipe made of 1-mm-thick rubber. Determine the rate at which N₂ leaks out of the pipe if the medium surrounding the pipe is (a) a vacuum and (b) atmospheric air at 1 atm and 25°C with 21 percent O₂ and 79 percent N₂.

Answers: (a) $4.48 \times 10^{-10}$ kmol/s, (b) $9.4 \times 10^{-11}$ kmol/s

Consider a tank that contains moist air at 3 atm and whose walls are permeable to water vapor. The surrounding air at 1 atm pressure also contains some moisture. Is it possible for the water vapor to flow into the tank from surroundings? Explain.

Express the mass flow rate of water vapor through a wall of thickness $L$ in terms of the partial pressure of water vapor on both sides of the wall and the permeability of the wall to the water vapor.

How does the condensation or freezing of water vapor in the wall affect the effectiveness of the insulation in the wall? How does the moisture content affect the effective thermal conductivity of soil?

Moisture migration in the walls, floors, and ceilings of buildings is controlled by vapor barriers or vapor retarders. Explain the difference between the two, and discuss which is more suitable for use in the walls of residential buildings.

What are the adverse effects of excess moisture on the wood and metal components of a house and the paint on the walls?

Why are the insulations on the chilled water lines always wrapped with vapor barrier jackets?

Explain how vapor pressure of the ambient air is determined when the temperature, total pressure, and relative humidity of the air are given.

The diffusion of water vapor through plaster boards and its condensation in the wall insulation in cold weather are of concern since they reduce the effectiveness of insulation. Consider a house that is maintained at 20°C and 60 percent

Water Vapor Migration in Buildings

Consider a balloon that is made of 0.1-mm-thick soft rubber and has a diameter of 15 cm when inflated. The pressure and temperature inside the balloon are initially 110 kPa and 25°C. The permeability of rubber to helium, oxygen, and nitrogen at 25°C are $9.4 \times 10^{-13}$, $7.05 \times 10^{-13}$, and $2.6 \times 10^{-13}$ kmol/m·s·bar, respectively. Determine the initial rates of diffusion of helium, oxygen, and nitrogen through the balloon wall and the mass fraction of helium that escapes the balloon during the first 5 h assuming the helium pressure inside the balloon remains nearly constant. Assume air to be 21 percent oxygen and 79 percent nitrogen by mole numbers and take the room conditions to be 100 kPa and 25°C.

Assuming the volume to remain constant and disregarding the diffusion of air into the balloon, obtain a relation for the variation of pressure in the balloon with time. Using the results obtained and the numerical values given in the problem, determine how long it will take for the pressure inside the balloon to drop to 100 kPa.

Pure N₂ gas at 1 atm and 25°C is flowing through a 10-m-long, 3-cm-inner diameter pipe made of 1-mm-thick rubber. Determine the rate at which N₂ leaks out of the pipe if the medium surrounding the pipe is (a) a vacuum and (b) atmospheric air at 1 atm and 25°C with 21 percent O₂ and 79 percent N₂.

Answers: (a) $4.48 \times 10^{-10}$ kmol/s, (b) $9.4 \times 10^{-11}$ kmol/s

Consider a tank that contains moist air at 3 atm and whose walls are permeable to water vapor. The surrounding air at 1 atm pressure also contains some moisture. Is it possible for the water vapor to flow into the tank from surroundings? Explain.

Express the mass flow rate of water vapor through a wall of thickness $L$ in terms of the partial pressure of water vapor on both sides of the wall and the permeability of the wall to the water vapor.

How does the condensation or freezing of water vapor in the wall affect the effectiveness of the insulation in the wall? How does the moisture content affect the effective thermal conductivity of soil?

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Explain how vapor pressure of the ambient air is determined when the temperature, total pressure, and relative humidity of the air are given.

The diffusion of water vapor through plaster boards and its condensation in the wall insulation in cold weather are of concern since they reduce the effectiveness of insulation. Consider a house that is maintained at 20°C and 60 percent
relative humidity at a location where the atmospheric pressure is 97 kPa. The inside of the walls is finished with 9.5-mm-thick gypsum wallboard. Taking the vapor pressure at the outer side of the wallboard to be zero, determine the maximum amount of water vapor that will diffuse through a 3-m × 8-m section of a wall during a 24-h period. The permeance of the 9.5-mm-thick gypsum wallboard to water vapor is \(2.86 \times 10^{-9} \text{ kg/s} \cdot \text{m}^2 \cdot \text{Pa}\).

**14–62** Reconsider Problem 14–61. In order to reduce the migration of water vapor through the wall, it is proposed to use a 0.2-mm-thick polyethylene film with a permeance of \(2.3 \times 10^{-12} \text{ kg/s} \cdot \text{m}^2 \cdot \text{Pa}\). Determine the amount of water vapor that will diffuse through the wall in this case during a 24-h period.

**Answer:** 6.7 g

**14–63** The roof of a house is 15 m × 8 m and is made of a 20-cm-thick concrete layer. The interior of the house is maintained at 25°C and 50 percent relative humidity and the local atmospheric pressure is 100 kPa. Determine the amount of water vapor that will migrate through the roof in 24 h if the average outside conditions during that period are 3°C and 30 percent relative humidity. The permeability of concrete to water vapor is \(24.7 \times 10^{-12} \text{ kg/s} \cdot \text{m} \cdot \text{Pa}\).

**14–64** Reconsider Problem 14–63. Using EES (or other) software, investigate the effects of temperature and relative humidity of air inside the house on the amount of water vapor that will migrate through the roof. Let the temperature vary from 15°C to 30°C and the relative humidity from 30 to 70 percent. Plot the amount of water vapor that will migrate as functions of the temperature and the relative humidity, and discuss the results.

**14–65** Reconsider Problem 14–63. In order to reduce the migration of water vapor, the inner surface of the wall is painted with vapor retarder latex paint whose permeance is \(26 \times 10^{-12} \text{ kg/s} \cdot \text{m}^2 \cdot \text{Pa}\). Determine the amount of water vapor that will diffuse through the roof in this case during a 24-h period.

**14–66** A glass of milk left on top of a counter in the kitchen at 25°C, 88 kPa, and 50 percent relative humidity is tightly sealed by a sheet of 0.009-mm-thick aluminum foil whose permeance is \(2.9 \times 10^{-12} \text{ kg/s} \cdot \text{m}^2 \cdot \text{Pa}\). The inner diameter of the glass is 12 cm. Assuming the air in the glass to be saturated at all times, determine how much the level of the milk in the glass will recede in 12 h. **Answer:** 0.00079 mm

**Transient Mass Diffusion**

**14–67C** In transient mass diffusion analysis, can we treat the diffusion of a solid into another solid of finite thickness (such as the diffusion of carbon into an ordinary steel component) as a diffusion process in a semi-infinite medium? Explain.

**14–68C** Define the penetration depth for mass transfer, and explain how it can be determined at a specified time when the diffusion coefficient is known.

**14–69C** When the density of a species \(A\) in a semi-infinite medium is known at the beginning and at the surface, explain how you would determine the concentration of the species \(A\) at a specified location and time.

**14–70** A steel part whose initial carbon content is 0.12 percent by mass is to be case-hardened in a furnace at 1150 K by exposing it to a carburizing gas. The diffusion coefficient of carbon in steel is strongly temperature dependent, and at the furnace temperature it is given to be \(D_{AB} = 7.2 \times 10^{-12} \text{ m}^2/\text{s}\).
Also, the mass fraction of carbon at the exposed surface of the steel part is maintained at 0.011 by the carbon-rich environment in the furnace. If the hardening process is to continue until the mass fraction of carbon at a depth of 0.7 mm is raised to 0.32 percent, determine how long the part should be held in the furnace. \( \text{Answer: 9 \, h} \)

14–71 \( \text{Repeat Problem 14–70 for a furnace temperature of 500 K at which the diffusion coefficient of carbon in steel is } D_{AB} = 2.1 \times 10^{-20} \, \text{m}^2/\text{s}. \)

14–72 \( \text{A pond with an initial oxygen content of zero is to be oxygenated by forming a tent over the water surface and filling the tent with oxygen gas at } 25^\circ \text{C and 130 kPa. Determine the mole fraction of oxygen at a depth of 2 cm from the surface after 12 h.} \)

14–73 \( \text{A long nickel bar with a diameter of 5 cm has been stored in a hydrogen-rich environment at 358 K and 300 kPa for a long time, and thus it contains hydrogen gas throughout uniformly. Now the bar is taken into a well-ventilated area so that the hydrogen concentration at the outer surface remains at almost zero at all times. Determine how long it will take for the hydrogen concentration at the center of the bar to drop by half. The diffusion coefficient of hydrogen in the nickel bar at the room temperature of 298 K can be taken to be } D_{AB} = 1.2 \times 10^{-12} \, \text{m}^2/\text{s}. \) \( \text{Answer: 3.3 years} \)

### Diffusion in a Moving Medium

14–74C \( \text{Define the following terms: mass-average velocity, diffusion velocity, stationary medium, and moving medium.} \)

14–75C \( \text{What is diffusion velocity? How does it affect the mass-average velocity? Can the velocity of a species in a moving medium relative to a fixed reference point be zero in a moving medium? Explain.} \)

14–76C \( \text{What is the difference between mass-average velocity and mole-average velocity during mass transfer in a moving medium? If one of these velocities is zero, will the other also necessarily be zero? Under what conditions will these two velocities be the same for a binary mixture?} \)

14–77C \( \text{Consider one-dimensional mass transfer in a moving medium that consists of species } A \text{ and } B \text{ with } p = \rho_A + \rho_B = \text{constant. Mark these statements as being True or False.} \)

\( \text{(a) The rates of mass diffusion of species } A \text{ and } B \text{ are equal in magnitude and opposite in direction.} \)

\( \text{(b) } D_{AB} = D_{BA}. \)

\( \text{(c) During equimolar counterdiffusion through a tube, equal numbers of moles of } A \text{ and } B \text{ move in opposite directions, and thus a velocity measurement device placed in the tube will read zero.} \)

\( \text{(d) The lid of a tank containing propane gas (which is heavier than air) is left open. If the surrounding air and the propane in the tank are at the same temperature and pressure, no propane will escape the tank and no air will enter.} \)

14–78C \( \text{What is Stefan flow? Write the expression for Stefan’s law and indicate what each variable represents.} \)

14–79E \( \text{The pressure in a pipeline that transports helium gas at a rate of 5 lbm/s is maintained at 14.5 psia by venting helium to the atmosphere through a } \frac{1}{4} \text{-in. internal diameter tube that extends 30 ft into the air. Assuming both the helium and the atmospheric air to be at } 80^\circ \text{F, determine (a) the mass flow rate of helium lost to the atmosphere through an individual tube, (b) the mass flow rate of air that infiltrates into the pipeline, and (c) the flow velocity at the bottom of the tube where it is attached to the pipeline that will be measured by an anemometer in steady operation.} \)

14–80E \( \text{Repeat Problem 14–79E for a pipeline that transports carbon dioxide instead of helium.} \)

14–81 \( \text{A tank with a 2-cm thick shell contains hydrogen gas at the atmospheric conditions of } 25^\circ \text{C and 90 kPa. The charging valve of the tank has an internal diameter of 3 cm and extends 8 cm above the tank. If the lid of the tank is left open so that hydrogen and air can undergo equimolar counterdiffusion through the 10-cm-long passageway, determine the mass flow rate of hydrogen lost to the atmosphere through the valve at the initial stages of the process.} \) \( \text{Answer: } 4.20 \times 10^{-8} \, \text{kg/s} \)
Reconsider Problem 14–81. Using EES (or other) software, plot the mass flow rate of hydrogen lost as a function of the diameter of the charging valve as the diameter varies from 1 cm to 5 cm, and discuss the results.

A 1-in.-diameter Stefan tube is used to measure the binary diffusion coefficient of water vapor in air at 70°F and 13.8 psia. The tube is partially filled with water with a distance from the water surface to the open end of the tube of 10 in. Dry air is blown over the open end of the tube so that water vapor rising to the top is removed immediately and the concentration of vapor at the top of the tube is zero. During 10 days of continuous operation at constant pressure and temperature, the amount of water that has evaporated is measured to be 0.0015 lbm. Determine the diffusion coefficient of water vapor in air at 70°F and 13.8 psia.

A 8-cm-internal-diameter, 30-cm-high pitcher half filled with water is left in a dry room at 15°C and 87 kPa with its top open. If the water is maintained at 15°C at all times also, determine how long it will take for the water to evaporate completely. Answer: 1125 days

What is a concentration boundary layer? How is it defined for flow over a plate?

What is the physical significance of the Schmidt number? How is it defined? To what dimensionless number does it correspond in heat transfer? What does a Schmidt number of 1 indicate?

What is the physical significance of the Sherwood number? How is it defined? To what dimensionless number does it correspond in heat transfer? What does a Sherwood number of 1 indicate for a plain fluid layer?

What is the physical significance of the Lewis number? How is it defined? What does a Lewis number of 1 indicate?

In natural convection mass transfer, the Grashof number is evaluated using density difference instead of temperature difference. Can the Grashof number evaluated this way be used in heat transfer calculations also?

Using the analogy between heat and mass transfer, explain how the mass transfer coefficient can be determined from the relations for the heat transfer coefficient.

It is well known that warm air in a cooler environment rises. Now consider a warm mixture of air and gasoline (C₈H₁₈) on top of an open gasoline can. Do you think this gas mixture will rise in a cooler environment?

Consider two identical cups of coffee, one with no sugar and the other with plenty of sugar at the bottom. Initially, both cups are at the same temperature. If left unattended, which cup of coffee will cool faster?

Under what conditions will the normalized velocity, thermal, and concentration boundary layers coincide during flow over a flat plate?

What is the relation \( \frac{f}{2} \) \( Re \) \( Nu \) \( Sh \) known as? Under what conditions is it valid? What is the practical importance of it?

What is the name of the relation \( \frac{f}{2} = St \) \( Pr^{2/3} \) \( St_{\text{max}} Sc^{2/3} \) and what are the names of the variables in it? Under what conditions is it valid? What is the importance of it in engineering?

What is the relation \( h_{\text{heat}} = \rho C_p h_{\text{mass}} \) known as? For what kind of mixtures is it valid? What is the practical importance of it?

What is the low mass flux approximation in mass transfer analysis? Can the evaporation of water from a lake be treated as a low mass flux process?

Consider a circular pipe of inner diameter \( D = 0.5 \) in. whose inner surface is covered with a thin layer of liquid water as a result of condensation. In order to dry the pipe, air at 540 R and 1 atm is forced to flow through it with an average velocity of 4 ft/s. Using the analogy between heat and
mass transfer, determine the mass transfer coefficient inside the pipe for fully developed flow. Answer: 0.024 ft/s

14–101 The average heat transfer coefficient for air flow over an odd-shaped body is to be determined by mass transfer measurements and using the Chilton–Colburn analogy between heat and mass transfer. The experiment is conducted by blowing dry air at 1 atm at a free stream velocity of 2 m/s over a body covered with a layer of naphthalene. The surface area of the body is 0.75 m², and it is observed that 100 g of naphthalene has sublimated in 45 min. During the experiment, both the body and the air were kept at 25°C, at which the vapor pressure and mass diffusivity of naphthalene are 11 Pa and \( D_{AB} = 0.61 \times 10^{-5} \) m²/s, respectively. Determine the heat transfer coefficient under the same flow conditions over the same geometry.

14–102 Consider a 15-cm-internal-diameter, 10-m-long circular duct whose interior surface is wet. The duct is to be dried by forcing dry air at 1 atm and 15°C through it at an average velocity of 3 m/s. The duct passes through a chilled room, and it remains at an average temperature of 15°C at all times. Determine the mass transfer coefficient in the duct.

14–103 Reconsider Problem 14–102. Using EES (or other) software, plot the mass transfer coefficient as a function of the air velocity as the velocity varies from 1 m/s to 8 m/s, and discuss the results.

14–104 Dry air at 15°C and 92 kPa flows over a 2-m-long wet surface with a free stream velocity of 4 m/s. Determine the average mass transfer coefficient. Answer: 0.00514 m/s

14–105 Consider a 5-m \( \times \) 5-m wet concrete patio with an average water film thickness of 0.3 mm. Now wind at 50 km/h is blowing over the surface. If the air is at 1 atm, 15°C, and 35 percent relative humidity, determine how long it will take for the patio to dry completely. Answer: 18.6 min

14–106E A 2-in.-diameter spherical naphthalene ball is suspended in a room at 1 atm and 80°F. Determine the average mass transfer coefficient between the naphthalene and the air if air is forced to flow over naphthalene with a free stream velocity of 15 ft/s. The Schmidt number of naphthalene in air at room temperature is 2.35. Answer: 0.0525 ft/s

14–107 Consider a 3-mm-diameter raindrop that is falling freely in atmospheric air at 25°C. Taking the temperature of the raindrop to be 9°C, determine the terminal velocity of the raindrop at which the drag force equals the weight of the drop and the average mass transfer coefficient at that time.

14–108 In a manufacturing facility, wet brass plates coming out of a water bath are to be dried by passing them through a section where dry air at 1 atm and 25°C is blown parallel to their surfaces. If the plates are at 20°C and there are no dry spots, determine the rate of evaporation from both sides of a plate.

Simultaneous Heat and Mass Transfer

14–111C Does a mass transfer process have to involve heat transfer? Describe a process that involves both heat and mass transfer.

14–112C Consider a shallow body of water. Is it possible for this water to freeze during a cold and dry night even when the ambient air and surrounding surface temperatures never drop to 0°C? Explain.
HEAT TRANSFER

14–113C During evaporation from a water body to air, under what conditions will the latent heat of vaporization be equal to convection heat transfer from the air?

14–114 Jugs made of porous clay were commonly used to cool water in the past. A small amount of water that leaks out keeps the outer surface of the jug wet at all times, and hot and relatively dry air flowing over the jug causes this water to evaporate. Part of the latent heat of evaporation comes from the water in the jug, and the water is cooled as a result. If the environment conditions are 1 atm, 30°C, and 35 percent relative humidity, determine the temperature of the water when steady conditions are reached.

![Image](image1.png)

**FIGURE P14–114**

14–115 Reconsider Problem 14–114. Using EES (or other) software, plot the water temperature as a function of the relative humidity of air as the relative humidity varies from 10 to 100 percent, and discuss the results.

14–116E During a hot summer day, a 2-L bottle drink is to be cooled by wrapping it in a cloth kept wet continually and blowing air to it with a fan. If the environment conditions are 1 atm, 80°F, and 30 percent relative humidity, determine the temperature of the drink when steady conditions are reached.

14–117 A glass bottle washing facility uses a well-agitated hot water bath at 55°C with an open top that is placed on the ground. The bathtub is 1 m high, 2 m wide, and 4 m long and is made of sheet metal so that the outer side surfaces are also at about 55°C. The bottles enter at a rate of 800 per minute at ambient temperature and leave at the water temperature. Each bottle has a mass of 150 g and removes 0.6 g of water as it leaves the bath wet. Makeup water is supplied at 15°C. If the average conditions in the plant are 1 atm, 25°C, and 50 percent relative humidity, and the average temperature of the surrounding surfaces is 15°C, determine (a) the amount of heat and water removed by the bottles themselves per second; (b) the rate of heat loss from the top surface of the water bath by radiation, natural convection, and evaporation; (c) the rate of heat loss from the side surfaces by natural convection and radiation; and (d) the rate at which heat and water must be supplied to maintain steady operating conditions. Disregard heat loss through the bottom surface of the bath and take the emissivities of sheet metal and water to be 0.61 and 0.95, respectively.

Answers: (a) 61,337 W, (b) 1480 W, (c) 3773 W, (d) 79,960 W, 44.9 kg/h

14–118 Repeat Problem 14–117 for a water bath temperature of 50°C.

14–119 One way of increasing heat transfer from the head on a hot summer day is to wet it. This is especially effective in windy weather, as you may have noticed. Approximating the head as a 30-cm-diameter sphere at 30°C with an emissivity of 0.95, determine the total rate of heat loss from the head at ambient air conditions of 1 atm, 25°C, 40 percent relative humidity, and 25 km/h winds if the head is (a) dry and (b) wet. Take the surrounding temperature to be 25°C.

Answers: (a) 40.6 W, (b) 352 W

14–120 A 2-m-deep 20-m \times 20-m heated swimming pool is maintained at a constant temperature of 30°C at a location where the atmospheric pressure is 1 atm. If the ambient air is at 20°C and 60 percent relative humidity and the effective sky temperature is 0°C, determine the rate of heat loss from the top surface of the pool by (a) radiation, (b) natural convection, and (c) evaporation. (d) Assuming the heat losses to the ground to be negligible, determine the size of the heater.

14–121 Repeat Problem 14–120 for a pool temperature of 25°C.

**Review Problems**

14–122C Mark these statements as being True or False.

(a) The units of mass diffusivity, heat diffusivity, and momentum diffusivity are all the same.

(b) If the molar concentration (or molar density) $C$ of a mixture is constant, then its density $\rho$ must also be constant.

(c) If the mass-average velocity of a binary mixture is zero, then the mole-average velocity of the mixture must also be zero.

(d) If the mole fractions of $A$ and $B$ of a mixture are both 0.5, then the molar mass of the mixture is simply the arithmetic average of the molar masses of $A$ and $B$.

14–123 Using Henry’s law, show that the dissolved gases in a liquid can be driven off by heating the liquid.
14–124 Show that for an ideal gas mixture maintained at a constant temperature and pressure, the molar concentration $C$ of the mixture remains constant but this is not necessarily the case for the density $\rho$ of the mixture.

14–125E A gas mixture in a tank at 600 R and 20 psia consists of 1 lbm of CO$_2$ and 3 lbm of CH$_4$. Determine the volume of the tank and the partial pressure of each gas.

14–126 Dry air whose molar analysis is 78.1 percent N$_2$, 20.9 percent O$_2$, and 1 percent Ar flows over a water body until it is saturated. If the pressure and temperature of air remain constant at 1 atm and 25°C during the process, determine (a) the molar analysis of the saturated air and (b) the density of air before and after the process. What do you conclude from your results?

14–127 Consider a glass of water in a room at 25°C and 100 kPa. If the relative humidity in the room is 70 percent and the water and the air are at the same temperature, determine (a) the mole fraction of the water vapor in the room air, (b) the mole fraction of the water vapor in the air adjacent to the water surface, and (c) the mole fraction of air in the water near the surface.

*Answers: (a) 2.22 percent, (b) 3.17 percent, (c) $1.34 \times 10^{-5}$ percent*

14–128 The diffusion coefficient of carbon in steel is given as

$$D_{AB} = 2.67 \times 10^{-5} \exp(-17,400/T) \text{ m}^2/\text{s}$$

where $T$ is in K. Determine the diffusion coefficient from 300 K to 1500 K in 100 K increments and plot the results.

14–129 A carbonated drink is fully charged with CO$_2$ gas at 17°C and 600 kPa such that the entire bulk of the drink is in thermodynamic equilibrium with the CO$_2$–water vapor mixture. Now consider a 2-L soda bottle. If the CO$_2$ gas in that bottle were to be released and stored in a container at 25°C and 100 kPa, determine the volume of the container.

*Answer: 12.7 L*

14–130 Consider a brick house that is maintained at 20°C and 60 percent relative humidity at a location where the atmospheric pressure is 85 kPa. The walls of the house are made of 20-cm thick brick whose permeance is $23 \times 10^{-9}$ kg/s · m$^2$ · Pa. Taking the vapor pressure at the outer side of the wallboard to be zero, determine the maximum amount of water vapor that will diffuse through a 4-m × 7-m section of a wall during a 24-h period.

14–131E Consider a masonry cavity wall that is built around 6-in.-thick concrete blocks. The outside is finished with 4-in. face brick with ½-in. cement mortar between the bricks and concrete blocks. The inside finish consists of ½-in. gypsum wallboard separated from the concrete block by ½-in.-thick air space. The thermal and vapor resistances of various components for a unit wall area are as follows:
The indoor conditions are 70°F and 65 percent relative humidity while the outdoor conditions are 32°F and 40 percent relative humidity. Determine the rates of heat and water vapor transfer through a 9-ft × 25-ft section of the wall.

Answers: 1436 Btu/h, 4.03 lbm/h

14–132 The oxygen needs of fish in aquariums are usually met by forcing air to the bottom of the aquarium by a compressor. The air bubbles provide a large contact area between the water and the air, and as the bubbles rise, oxygen and nitrogen gases in the air dissolve in water while some water evaporates into the bubbles. Consider an aquarium that is maintained at room temperature of 25°C at all times. The air bubbles are observed to rise to the free surface of water in 2 s. If the air entering the aquarium is completely dry and the diameter of the air bubbles is 4 mm, determine the mole fraction of water vapor at the center of the bubble when it leaves the aquarium. Assume no fluid motion in the bubble so that water vapor propagates in the bubble by diffusion only.

Answer: 3.13 percent

14–133 Oxygen gas is forced into an aquarium at 1 atm and 25°C, and the oxygen bubbles are observed to rise to the free surface in 2 s. Determine the penetration depth of oxygen into water from a bubble during this time period.

14–134 Consider a 30-cm-diameter pan filled with water at 15°C in a room at 20°C, 1 atm, and 30 percent relative humidity. Determine (a) the rate of heat transfer by convection, (b) the rate of evaporation of water, and (c) the rate of heat transfer to the water needed to maintain its temperature at 15°C. Disregard any radiation effects.

14–135 Repeat Problem 14–134 assuming a fan blows air over the water surface at a velocity of 3 m/s. Take the radius of the pan to be the characteristic length.

14–136 Naphthalene is commonly used as a repellent against moths to protect clothing during storage. Consider a 1-cm-diameter spherical naphthalene ball hanging in a closet at 25°C and 1 atm. Considering the variation of diameter with time, determine how long it will take for the naphthalene to sublimate completely. The density and vapor pressure of naphthalene at 25°C are 0.11 Pa and 1100 kg/m³ and 11 Pa, respectively, and the mass diffusivity of naphthalene in air at 25°C is $D_{AB} = 0.61 \times 10^{-5}$ m²/s.

Answer: 45.7 days

14–137E A swimmer extends his wet arms into the windy air outside at 1 atm, 40°F, 50 percent relative humidity, and 20 mph. If the average skin temperature is 80°F, determine the rate at which water evaporates from both arms and the corresponding rate of heat transfer by evaporation. The arm can be modeled as a 2-ft-long and 3-in.-diameter cylinder with adiabatic ends.

14–138 A thick part made of nickel is put into a room filled with hydrogen at 3 atm and 85°C. Determine the hydrogen concentration at a depth of 2-mm from the surface after 24 h.

Answer: $4.1 \times 10^{-7}$ kmol/m³

14–139 A membrane made of 0.1-mm-thick soft rubber separates pure O₂ at 1 atm and 25°C from air at 1.2 atm pressure. Determine the mass flow rate of O₂ through the membrane per unit area and the direction of flow.

14–140E The top section of an 8-ft-deep 100-ft × 100-ft heated solar pond is maintained at a constant temperature of 80°F at a location where the atmospheric pressure is 1 atm. If the ambient air is at 70°F and 100 percent relative humidity

<table>
<thead>
<tr>
<th>Construction</th>
<th>$R$-Value, $h \cdot \text{ft}^2 \cdot ^\circ\text{F}/\text{Btu}$</th>
<th>$R_p$-Value, $s \cdot \text{ft}^2 \cdot \text{psi}/\text{lbm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Outside surface,</td>
<td>0.17</td>
<td>—</td>
</tr>
<tr>
<td>15 mph wind</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Face brick, 4 in.</td>
<td>0.43</td>
<td>15,000</td>
</tr>
<tr>
<td>3. Cement mortar,</td>
<td>0.10</td>
<td>1930</td>
</tr>
<tr>
<td>0.5 in.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Concrete block, 6-in.</td>
<td>4.20</td>
<td>23,000</td>
</tr>
<tr>
<td>5. Air space, 1/2-in.</td>
<td>1.02</td>
<td>77.6</td>
</tr>
<tr>
<td>6. Gypsum wallboard, 0.5 in.</td>
<td>0.45</td>
<td>332</td>
</tr>
<tr>
<td>7. Inside surface, still air</td>
<td>0.68</td>
<td>—</td>
</tr>
</tbody>
</table>

FIGURE P14–132

FIGURE P14–136

FIGURE P14–136

FIGURE P14–136
and wind is blowing at an average velocity of 40 mph, determine the rate of heat loss from the top surface of the pond by (a) forced convection, (b) radiation, and (c) evaporation. Take the average temperature of the surrounding surfaces to be 60°F.

14–141E Repeat Problem 14–140E for a solar pond surface temperature of 90°F.

Answers: (a) 299,400 Btu/h, (b) 1,057,000 Btu/h, (c) 3,396,000 Btu/h

Computer, Design, and Essay Problems

14–142 Write an essay on diffusion caused by effects other than the concentration gradient such as thermal diffusion, pressure diffusion, forced diffusion, knudsen diffusion, and surface diffusion.

14–143 Write a computer program that will convert the mole fractions of a gas mixture to mass fractions when the molar masses of the components of the mixture are specified.

14–144 One way of generating electricity from solar energy involves the collection and storage of solar energy in large artificial lakes of a few meters deep, called solar ponds. Solar energy is stored at the bottom part of the pond at temperatures close to boiling, and the rise of hot water to the top is prevented by planting salt to the bottom of the pond. Write an essay on the operation of solar pond power plants, and find out how much salt is used per year per m². If the cost is not a factor, can sugar be used instead of salt to maintain the concentration gradient? Explain.

14–145 The condensation and even freezing of moisture in building walls without effective vapor retarders is a real concern in cold climates as it undermines the effectiveness of the insulation. Investigate how the builders in your area are coping with this problem, whether they are using vapor retarders or vapor barriers in the walls, and where they are located in the walls. Prepare a report on your findings and explain the reasoning for the current practice.

14–146 You are asked to design a heating system for a swimming pool that is 2 m deep, 25 m long, and 25 m wide. Your client desires that the heating system be large enough to raise the water temperature from 20°C to 30°C in 3 h. The heater must also be able to maintain the pool at 30°C at the outdoor design conditions of 15°C, 1 atm, 35 percent relative humidity, 40 mph winds, and effective sky temperature of 10°C. Heat losses to the ground are expected to be small and can be disregarded. The heater considered is a natural gas furnace whose efficiency is 80 percent. What heater size (in Btu/h input) would you recommend that your client buy?