Transport Processes and Separation Process Principles

(INCLUDES UNIT OPERATIONS)

FOURTH EDITION

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Chapter 7. Principles of Unsteady-State and Convective Mass Transfer

UNSTEADY-STATE DIFFUSION

Derivation of Basic Equation

In Chapter 6 we considered various mass-transfer systems where the concentration or partial pressure at any point and the diffusion flux were constant with time, hence at steady state. Before steady state can be reached, time must elapse after the mass-transfer process is initiated for the unsteady-state conditions to disappear.

In Section 2.3 a general property balance for unsteady-state molecular diffusion was made for the properties momentum, heat, and mass. For no generation present, this was

Equation 2.13-12.

$$\frac{\partial \Gamma}{\partial t} = \delta \frac{\partial^2 \Gamma}{\partial z^2}$$

In Section 5.1 an unsteady-state equation for heat conduction was derived,

Equation 5.1-10.

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$

The derivation of the unsteady-state diffusion equation in one direction for mass transfer is similar to that performed for heat transfer in obtaining Eq. (5.1-10). We refer to Fig. 7.1-1, where mass is diffusing in the x direction in a cube composed of a solid, stagnant gas, or stagnant liquid and having dimensions Δx, Δy, Δz. For diffusion in the x direction we write

Equation 7.1-1.

$$N_{Ax} = -D_{AB} \frac{\partial c_A}{\partial x}$$

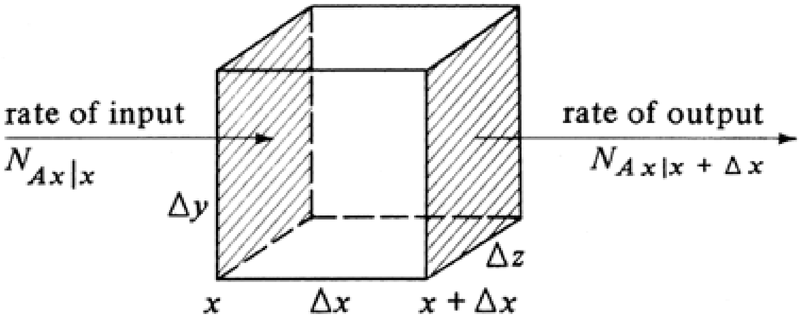


Figure 7.1-1. Unsteady-state diffusion in one direction.

The term $\partial c_A/\partial x$ means the partial of c_A with respect to x or the rate of change of c_A with x when the other variable, time t, is kept constant.

Next we make a mass balance on component A in terms of moles for no generation:

Equation 7.1-2.

$$\text{rate of input} = \text{rate of output} + \text{rate of accumulation}$$

The rate of input and rate of output in kg mol A/s are

Equation 7.1-3.

$$\text{rate of input} = N_{Ax|x} = -D_{AB}\left.\frac{\partial c_A}{\partial x}\right|_x$$

Equation 7.1-4.

$$\text{rate of output} = N_{Ax|x+\Delta x} = -D_{AB}\left.\frac{\partial c_A}{\partial x}\right|_{x+\Delta x}$$

The rate of accumulation is as follows for the volume $\Delta x\,\Delta y\,\Delta z$ m^3:

Equation 7.1-5.

$$\text{rate of accumulation} = (\Delta x\ \Delta y\ \Delta z)\frac{\partial c_A}{\partial t}$$

Substituting Eqs. (7.1-3), (7.1-4), and (7.1-5) into (7.1-2) and dividing by $\Delta x\,\Delta y\,\Delta z$,

Equation 7.1-6.

$$-D_{AB}\frac{\left.\frac{\partial c_A}{\partial x}\right|_x - \left.\frac{\partial c_A}{\partial x}\right|_{x+\Delta x}}{\Delta x} = \frac{\partial c_A}{\partial t}$$

Letting Δx approach zero,

Equation 7.1-7.

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

The above holds for a constant diffusivity D_{AB}. If D_{AB} is a variable,

Equation 7.1-8.

$$\frac{\partial c_A}{\partial t} = \frac{\partial(D_{AB}\,\partial c_A/\partial x)}{\partial x}$$

Equation (7.1-7) relates the concentration c_A with position x and time t. For diffusion in all three directions a similar derivation gives

Equation 7.1-9.

$$\frac{\partial c_A}{\partial t} = D_{AB}\left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2}\right)$$

In the remainder of this section, the solutions of Eqs. (7.1-7) and (7.1-9) will be considered. Note the mathematical similarity between the equation for heat conduction,

Equation 5.1-6.

$$\frac{\partial T}{\partial t} = \alpha\,\frac{\partial^2 T}{\partial x^2}$$

and Eq. (7.1-7) for diffusion. Because of this similarity, the mathematical methods used for solution of the unsteady-state heat-conduction equation can be used for unsteady-state mass transfer. This is discussed more fully in Sections 7.1B, 7.1C, and 7.7.

Diffusion in a Flat Plate with Negligible Surface Resistance

To illustrate an analytical method of solving Eq. (7.1-7), we will derive the solution for unsteady-state diffusion in the x direction for a plate of thickness $2x_1$, as shown in Fig. 7.1-2. For diffusion in one direction,

Equation 7.1-7.

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

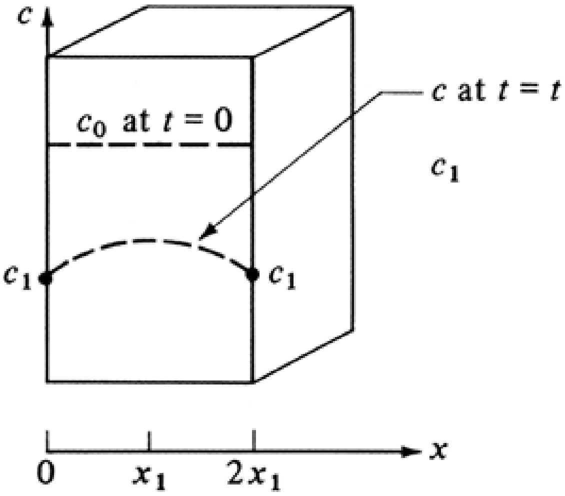


Figure 7.1-2. Unsteady-state diffusion in a flat plate with negligible surface resistance.

Dropping the subscripts *A* and *B* for convenience,

Equation 7.1-10.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

The initial profile of the concentration in the plate at $t = 0$ is uniform at $c = c_0$ for all x values, as shown in Fig. 7.1-2. At time $t = 0$ the concentration of the fluid in the environment outside is suddenly changed to c_1. For a very high mass-transfer coefficient outside the surface resistance will be negligible and the concentration at the surface will be equal to that in the fluid, which is c_1.

The initial and boundary conditions are

Equation 7.1-11.

$$c = c_0, \qquad t = 0, \qquad x = x, \qquad Y = \frac{c_1 - c_0}{c_1 - c_0} = 1$$

$$c = c_1, \qquad t = t, \qquad x = 0, \qquad Y = \frac{c_1 - c_1}{c_1 - c_0} = 0$$

$$c = c_1, \qquad t = t, \qquad x = 2x_1, \qquad Y = \frac{c_1 - c_1}{c_1 - c_0} = 0$$

Redefining the concentration so it goes between 0 and 1,

Equation 7.1-12.

$$Y = \frac{c_1 - c}{c_1 - c_0}$$

Equation 7.1-13.

$$\frac{\partial Y}{\partial t} = D\frac{\partial^2 Y}{\partial x^2}$$

The solution of Eq. (7.1-13) is an infinite Fourier series and is identical to the solution of Eq. (5.1-6) for heat transfer:

Equation 7.1-14.

$$Y = \frac{c_1 - c}{c_1 - c_0} = \frac{4}{\pi}\left[\frac{1}{1}\exp\left(-\frac{1^2\pi^2 X}{4}\right)\sin\frac{1\pi x}{2x_1} + \frac{1}{3}\exp\left(-\frac{3^2\pi^2 X}{4}\right)\sin\frac{3\pi x}{2x_1} + \frac{1}{5}\exp\left(-\frac{5^2\pi^2 X}{4}\right)\sin\frac{5\pi x}{2x_1} + \cdots\right]$$

where

$X = Dt/x_1^2$, dimensionless

c = concentration at point x and time t in slab

Y = $(c_1-c)/(c_1-c_0)$ = fraction of unaccomplished change, dimensionless

1-Y = $(c-c_0)/(c_1-c_0)$ = fraction of change

Solution of equations similar to Eq. (7.1-14) are time-consuming; convenient charts for various geometries are available and will be discussed in the next section.

Unsteady-State Diffusion in Various Geometries

Convection and boundary conditions at the surface

In Fig. 7.1-2 there was no convective resistance at the surface. However, in many cases when a fluid is outside the solid, convective mass transfer is occurring at the surface. A convective mass-transfer coefficient k_c, similar to a convective heat-transfer coefficient, is defined as follows:

Equation 7.1-15.

$$N_A = k_c(c_{L1} - c_{Li})$$

where k_c is a mass-transfer coefficient in m/s, c_{L1} is the bulk fluid concentration in kg mol *A*/m^3, and c_{Li} is the concentration in the fluid just adjacent to the surface of the solid. The coefficient k_c is an empirical coefficient and will be discussed more fully in Section 7.2.

In Fig. 7.1-3a the case where a mass-transfer coefficient is present at the boundary is shown. The concentration drop across the fluid is $c_{L1} - c_{Li}$. The concentration in the solid c_i at the surface is in equilibrium with c_{Li}.

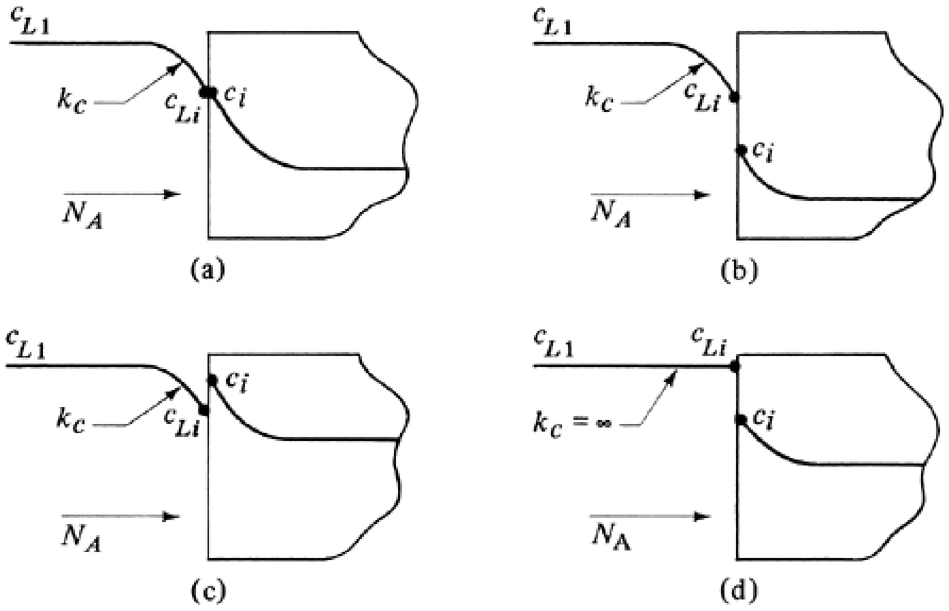


Figure 7.1-3. Interface conditions for convective mass transfer and an equilibrium distribution coefficient $K = c_{Li}/c_i$: (a) $K = 1$. (b) $K > 1$, (c) $K < 1$, (d) $K > 1$ and $k_c = \infty$.

In Fig. 7.1-3a the concentration c_{Li} in the liquid adjacent to the solid and c_i in the solid at the surface are in equilibrium and are equal. However, unlike heat transfer, where the temperatures are equal, the concentrations here are in equilibrium and are related by

Equation 7.1-16.

$$K = \frac{c_{Li}}{c_i}$$

where *K* is the equilibrium distribution coefficient (similar to Henry's law coefficient for a gas and liquid). The value of *K* in Fig. 7.1-3a is 1.0.

In Fig. 7.1-3b the distribution coefficient $K > 1$ and $c_{Li} > c_i$, even though they are in equilibrium. Other cases are shown in Fig. 7.1-3c and d. This was also discussed in Section 6.6B.

Relation between mass- and heat-transfer parameters

In order to use the unsteady-state heat-conduction charts in Chapter 5 for solving unsteady-state diffusion problems, the dimensionless variables or parameters for heat transfer must be related to those for mass transfer. In Table 7.1-1 the relations between these variables are tabulated. For $K \neq 1.0$, whenever k_c appears, it is given as Kk_c, and whenever c_1 appears, it is given as c_1/K.

Table 7.1-1. Relation Between Mass- and Heat-Transfer Parameters for Unsteady-State Diffusion[*]

	Mass Transfer	
Heat Transfer	**$K = c_L/c = 1.0$**	**$K = c_L/c \neq 1.0$**
$Y, \dfrac{T_1 - T}{T_1 - T_0}$	$\dfrac{c_1 - c}{c_1 - c_0}$	$\dfrac{c_1/K - c}{c_1/K - c_0}$
$1 - Y, \dfrac{T - T_0}{T_1 - T_0}$	$\dfrac{c - c_0}{c_1 - c_0}$	$\dfrac{c - c_0}{c_1/K - c_0}$
$X, \dfrac{\alpha t}{x_1^2}$	$\dfrac{D_{AB}t}{x_1^2}$	$\dfrac{D_{AB}t}{x_1^2}$
$\dfrac{x}{2\sqrt{\alpha t}}$	$\dfrac{x}{2\sqrt{D_{AB}t}}$	$\dfrac{x}{2\sqrt{D_{AB}t}}$
$m, \dfrac{k}{hx_1}$	$\dfrac{D_{AB}}{k_c x_1}$	$\dfrac{D_{AB}}{Kk_c x_1}$
$\dfrac{h}{k}\sqrt{\alpha t}$	$\dfrac{k_c}{D_{AB}}\sqrt{D_{AB}t}$	$\dfrac{Kk_c}{D_{AB}}\sqrt{D_{AB}t}$
$n, \dfrac{x}{x_1}$	$\dfrac{x}{x_1}$	$\dfrac{x}{x_1}$

[*] x is the distance from the center of the slab, cylinder, or sphere; for a semi-infinite slab, x is the distance from the surface, c_0 is the original uniform concentration in the solid, c_1 the concentration in the fluid outside the slab, and c the concentration in the solid at position x and time t.

Charts for diffusion in various geometries

The various heat-transfer charts for unsteady-state conduction can be used for unsteady-state diffusion and are as follows:

1. Semi-infinite solid, Fig. 5.3-3.
2. Flat plate, Figs. 5.3-5 and 5.3-6.
3. Long cylinder, Figs. 5.3-7 and 5.3-8.
4. Sphere, Figs. 5.3-9 and 5.3-10.
5. Average concentrations, zero convective resistance, Fig. 5.3-13.

EXAMPLE 7.1-1. Unsteady-State Diffusion in a Slab of Agar Gel

A solid slab of 5.15 wt % agar gel at 278 K is 10.16 mm thick and contains a uniform concentrations of urea of 0.1 kg mol/m^3. Diffusion is only in the x direction through two parallel flat surfaces 10.16 mm apart. The slab is suddenly immersed in pure turbulent water, so the surface resistance can be assumed to be negligible; that is, the convective coefficient k_c is very large. The diffusivity of urea in the agar from Table 6.4-2 is 4.72×10^{-10} m^2/s.

a. Calculate the concentration at the midpoint of the slab (5.08 mm from the surface) and 2.54 mm from the surface after 10 h.

b. If the thickness of the slab is halved, what would be the midpoint concentration in 10 h?

Solution:
For part (a), $c_0 = 0.10$ kg mol/m^3, $c_1 = 0$ for pure water, and c = concentration at distance x from center line and time t s. The equilibrium distribution coefficient K in Eq. (7.1-16) can be assumed to be 1.0, since the water in the aqueous solution in the gel and outside should be very similar in properties. From Table 7.1-1,

$$Y = \frac{c_1/K - c}{c_1/K - c_0} = \frac{0/1.0 - c}{0/1.0 - 0.10}$$

Also, $x_1 = 10.16/(1000 \times 2) = 5.08 \times 10^{-3}$ m (half-slab thickness), $x = 0$ (center), $X = D_{AB}t/x_1^2 = (4.72 \times 10^{-10})(10 \times 3600)/(5.08 \times 10^{-3})^2 = 0.658$. The relative position $n = x/x_1 = 0/5.08 \times 10^{-3} = 0$, and relative resistance $m = D_{AB}/Kk_cx_1 = 0$, since k_c is very large (zero resistance).

From Fig. 5.3-5 for $X = 0.658$, $m = 0$, and $n = 0$,

$$Y = 0.275 = \frac{0 - c}{0 - 0.10}$$

Solving, $c = 0.0275$ kg mol/m^3 for $x = 0$.

For the point 2.54 mm from the surface or 2.54 mm from center, $x = 2.54/1000 = 2.54 \times 10^{-3}$ m, $X = 0.658$, $m = 0$, $n = x/x_1 = 2.54 \times 10^{-3}/5.08 \times 10^{-3} = 0.5$. Then from Fig. 5.3-5, $Y = 0.172$. Solving, $c = 0.0172$ kg mol/m^3.

For part (b) and half the thickness, $X = 0.658/(0.5)^2 = 2.632$, $n = 0$, and $m = 0$. Hence, $Y = 0.0020$ and $c = 2.0 \times 10^{-4}$ kg mol/m^3.

EXAMPLE 7.1-2. Unsteady-State Diffusion in a Semi-infinite Slab

A very thick slab has a uniform concentration of solute A of $c_0 = 1.0 \times 10^{-2}$ kg mol A/m^3. Suddenly, the front face of the slab is exposed to a flowing fluid having a concentration $c_1 = 0.10$ kg mol A/m^3 and a convective coefficient $k_c = 2 \times 10^{-7}$ m/s. The equilibrium distribution coefficient $K = c_L/c_i = 2.0$. Assuming that the slab is a semi-infinite solid, calculate the concentration in the solid at the surface ($x = 0$) and $x = 0.01$ m from the surface after $t = 3 \times 10^4$ s. The diffusivity in the solid is $D_{AB} = 4 \times 10^{-9}$ m^2/s.

Solution: To use Fig. 5.3-3, use Table 7.1-1.

$$\frac{Kk_c}{D_{AB}}\sqrt{D_{AB}t} = \frac{2.0(2 \times 10^{-7})}{4 \times 10^{-9}}\sqrt{(4 \times 10^{-9})(3 \times 10^4)} = 1.095$$

For $x = 0.01$ m from the surface in the solid,

$$\frac{x}{2\sqrt{D_{AB}t}} = \frac{0.01}{2\sqrt{(4 \times 10^{-9})(3 \times 10^4)}} = 0.457$$

From the chart, $1 - Y = 0.26$. Then, substituting into the equation for $(1 - Y)$ from Table 7.1-1 and solving,

$$1 - Y = \frac{c - c_0}{c_1/K - c_0} = \frac{c - 1 \times 10^{-2}}{(10 \times 10^{-2})/2 - (1 \times 10^{-2})} = 0.26$$

$$c = 2.04 \times 10^{-2}\ \text{kg mol/m}^3 \qquad (\text{for } x = 0.01\ \text{m})$$

For $x = 0$ m (i.e., at the surface of the solid),

$$\frac{x}{2\sqrt{D_{AB}t}} = 0$$

From the chart, $1 - Y = 0.62$. Solving, $c = 3.48 \times 10^{-2}$. This value is the same as c_i, as shown in Fig. 7.1-3b. To calculate the concentration c_{Li} in the liquid at the interface,

$$C_{Li} = Kc_i = 2.0(3.48 \times 10^{-2}) = 6.96 \times 10^{-2}\ \text{kg mol/m}^3$$

A plot of these values will be similar to Fig. 7.1-3b.

Unsteady-state diffusion in more than one direction

In Section 5.3F a method was given for unsteady-state heat conduction, in which the one-dimensional solutions were combined to yield solutions for several-dimensional systems. The same method can be used for unsteady-state diffusion in more than one direction. Rewriting Eq. (5.3-11) for diffusion in a rectangular block in the *x, y*, and *z* directions,

Equation 7.1-17.

$$Y_{x,y,z} = (Y_x)(Y_y)(Y_z) = \frac{c_1/K - c_{x,y,z}}{c_1/K - c_0}$$

where $c_{x,y,z}$ is the concentration at the point *x, y, z* from the center of the block. The value of Y_x for the two parallel faces is obtained from Fig. 5.3-5 or 5.3-6 for a flat plate in the *x* direction. The values of Y_y and Y_z are similarly obtained from the same charts. For a short cylinder, an equation similar to Eq. (5.3-12) is used, and for average concentrations, ones similar to Eqs. (5.3-14), (5.3-15), and (5.3-16) are used.

CONVECTIVE MASS-TRANSFER COEFFICIENTS

Introduction to Convective Mass Transfer

In the previous sections of this chapter and in Chapter 6 we have emphasized molecular diffusion in stagnant fluids or fluids in laminar flow. In many cases the rate of diffusion is slow, and more rapid transfer is desired. To do this, the fluid velocity is increased until turbulent mass transfer occurs.

To have a fluid in convective flow usually requires the fluid to be flowing past another immiscible fluid or a solid surface. An example is a fluid flowing in a pipe, where part of the pipe wall is made by a slightly dissolving solid material such as benzoic acid. The benzoic acid dissolves and is transported perpendicular to the main stream from the wall. When a fluid is in turbulent flow and is flowing past a surface, the actual velocity of small particles of fluid cannot be described clearly as in laminar flow. In laminar flow the fluid flows in streamlines and its behavior can usually be described mathematically. However, in turbulent motion there are no streamlines; instead there are large eddies or "chunks" of fluid moving rapidly in seemingly random fashion.

When a solute A is dissolving from a solid surface, there is a high concentration of this solute in the fluid at the surface, and its concentration, in general, decreases as the distance from the wall increases. However, minute samples of fluid adjacent to each other do not always have concentrations close to each other. This occurs because eddies having solute in them move rapidly from one part of the fluid to another, transferring relatively large amounts of solute. This turbulent diffusion or eddy transfer is quite fast in comparison to molecular transfer.

Three regions of mass transfer can be visualized. In the first, which is adjacent to the surface, a thin, viscous sublayer film is present. Most of the mass transfer occurs by molecular diffusion, since few or no eddies are present. A large concentration drop occurs across this film as a result of the slow diffusion rate.

The transition or buffer region is adjacent to the first region. Some eddies are present, and the mass transfer is the sum of turbulent and molecular diffusion. There is a gradual transition in this region from the transfer by mainly molecular diffusion at one end to mainly turbulent at the other end.

In the *turbulent region* adjacent to the buffer region, most of the transfer is by turbulent diffusion, with a small amount by molecular diffusion. The concentration decrease is very small here since the eddies tend to keep the fluid concentration uniform. A more detailed discussion of these three regions is given in Section 3.10G.

A typical plot for the mass transfer of a dissolving solid from a surface to a turbulent fluid in a conduit is given in Fig. 7.2-1. The concentration drop from c_{A1} adjacent to the surface is very abrupt close to the surface and then levels off. This curve is very similar to the shapes found for heat and momentum transfer. The average or mixed concentration $\bar{c}_A$ is shown and is slightly greater than the minimum c_{A2}.

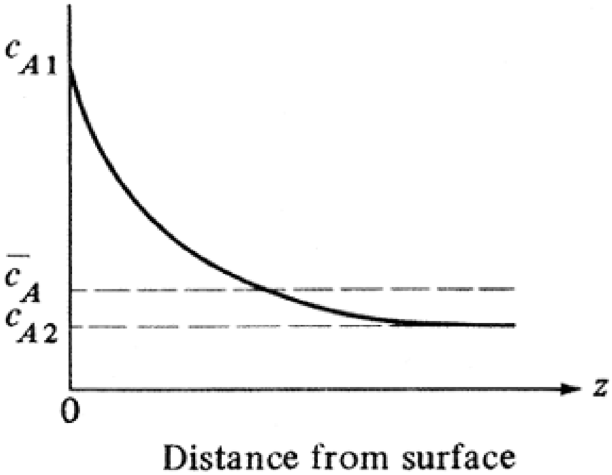


Figure 7.2-1. Concentration profile in turbulent mass transfer from a surface to a fluid.

Types of Mass-Transfer Coefficients

Definition of mass-transfer coefficient

Since our understanding of turbulent flow is incomplete, we attempt to write the equations for turbulent diffusion in a manner similar to that for molecular diffusion. For turbulent mass transfer for constant c, Eq. (6.1-6) is written as

Equation 7.2-1.

$$J_A^* = -(D_{AB} + \varepsilon_M)\frac{dc_A}{dz}$$

where D_{AB} is the molecular diffusivity in m^2/s and ε_M the mass eddy diffusivity in m^2/s. The value of ε_M is variable and is near zero at the interface or surface and increases as the distance from the wall increases. We therefore use an average value $\bar{\varepsilon}_M$ since the variation of ε_M is not generally known. Integrating Eq. (7.2-1) between points 1 and 2,

Equation 7.2-2.

$$J_{A1}^* = \frac{D_{AB} + \bar{\varepsilon}_M}{z_2 - z_1}(c_{A1} - c_{A2})$$

The flux J_{A1}^* is based on the surface area A_1 since the cross-sectional area may vary. The value of $z_2 - z_1$, the distance of the path, is often not known. Hence, Eq. (7.2-2) is simplified and is written using a convective mass-transfer coefficient k_c':

Equation 7.2-3.

$$J_{A1}^* = k_c'(c_{A1} - c_{A2})$$

where J_{A1}^* is the flux of A from the surface A_1 relative to the whole bulk phase, k_c' is $(D_{AB} + \bar{\varepsilon}_M)/(z_2 - z_1)$, an experimental mass-transfer coefficient in kg mol/s · m^2 · (kg mol/m^3) or simplified as m/s, and c_{A2} is the concentration at point 2 in kg mol A/m^3 or, more usually, the average bulk concentration $\bar{c}_{A2}$ This definition of a convective mass-transfer coefficient k_c' is quite similar to the convective heat-transfer coefficient h.

Mass-transfer coefficient for equimolar counterdiffusion

Generally, we are interested in N_A, the flux of A relative to stationary coordinates. We can start with the following equation, which is similar to that for molecular diffusion with the term ε_M added:

Equation 7.2-4.

$$N_A = -c(D_{AB} + \varepsilon_M)\frac{dx_A}{dz} + x_A(N_A + N_B)$$

For the case of equimolar counterdiffusion, where $N_A = -N_B$, and integrating at steady state, calling $k_c' = (D_{AB} + \bar{\varepsilon}_M)/(z_2 - z_1)$,

Equation 7.2-5.

$$N_A = k_c'(c_{A1} - c_{A2})$$

Equation (7.2-5) is the defining equation for the mass-transfer coefficient. Often, however, we define the concentration in terms of mole fraction if a liquid or gas, or in terms of partial pressure if a gas. Hence, we can define the mass-transfer coefficient in several ways. If y_A is mole fraction in a gas phase and x_A in a liquid phase, then Eq. (7.2-5) can be written as follows for equimolar counterdiffusion:

Equation 7.2-6.

$$\text{Gases:} \qquad N_A = k_c'(c_{A1} - c_{A2}) = k_G'(p_{A1} - p_{A2}) = k_y'(y_{A1} - y_{A2})$$

Equation 7.2-7.

$$\text{Liquids:}\quad N_A = k'_c(c_{A1} - c_{A2}) = k'_L(c_{A1} - c_{A2}) = k'_x(x_{A1} - x_{A2})$$

All of these mass-transfer coefficients can be related to each other. For example, using Eq. (7.2-6) and substituting $y_{A1} = c_{A1}/c$ and $y_{A2} = c_{A2}/c$ into the equation,

Equation 7.2-8.

$$N_A = k'_c(c_{A1} - c_{A2}) = k'_y(y_{A1} - y_{A2}) = k'_y\left(\frac{c_{A1}}{c} - \frac{c_{A2}}{c}\right) = \frac{k'_y}{c}(c_{A1} - c_{A2})$$

Hence,

Equation 7.2-9.

$$k'_c = \frac{k'_y}{c}$$

These relations among mass-transfer coefficients, together with the various flux equations, are given in Table 7.2-1.

Table 7.2-1. Flux Equations and Mass-Transfer Coefficients

Flux equations for equimolar counterdiffusion

$$\text{Gases:}\quad N_A = k'_c(c_{A1} - c_{A2}) = k'_G(p_{A1} - p_{A2}) = k'_y(y_{A1} - y_{A2})$$

$$\text{Liquids:}\quad N_A = k'_c(c_{A1} - c_{A2}) = k'_L(c_{A1} - c_{A2}) = k'_x(x_{A1} - x_{A2})$$

Flux equations for A diffusing through stagnant, nondiffusing B

$$\text{(Gases):}\quad N_A = k_c(c_{A1} - c_{A2}) = k_G(p_{A1} - p_{A2}) = k_y(y_{A1} - y_{A2})$$

$$\text{(Liquids):}\quad N_A = k_c(c_{A1} - c_{A2}) = k_L(c_{A1} - c_{A2}) = k_x(x_{A1} - x_{A2})$$

Conversions between mass-transfer coefficients

Gases:

$$k'_c c = k'_c\frac{P}{RT} = k_c\frac{p_{BM}}{RT} = k'_G P = k_G p_{BM} = k_y y_{BM} = k'_y = k_c y_{BM} c = k_G y_{BM} P$$

Liquids:

$$k'_c c = k'_L c = k_L x_{BM} c = k'_L \rho/M = k'_x = k_x x_{BM}$$

(where ρ is density of liquid and *M* is molecular weight)

Units of mass-transfer coefficients

	SI Units	*Cgs Units*	*English Units*
k_c, k_L, k'_c, k'_L	m/s	cm/s	ft/h
k_x, k_y, k'_x, k'_y	$\frac{\text{kg mol}}{\text{s}\cdot\text{m}^2\cdot\text{mol frac}}$	$\frac{\text{g mol}}{\text{s}\cdot\text{cm}^2\cdot\text{mol frac}}$	$\frac{\text{lb mol}}{\text{h}\cdot\text{ft}^2\cdot\text{mol frac}}$
k_G, k'_G	$\frac{\text{kg mol}}{\text{s}\cdot\text{m}^2\cdot\text{Pa}}$ $\frac{\text{kg mol}}{\text{s}\cdot\text{m}^2\cdot\text{atm}}$	$\frac{\text{g mol}}{\text{s}\cdot\text{cm}^2\cdot\text{atm}}$	$\frac{\text{lb mol}}{\text{h}\cdot\text{ft}^2\cdot\text{atm}}$

(preferred)

Mass-transfer coefficient for A diffusing through stagnant, nondiffusing B

For *A* diffusing through stagnant, nondiffusing *B*, where $N_B = 0$, Eq. (7.2-4) gives for steady state

Equation 7.2-10.

$$N_A = \frac{k'_c}{x_{BM}}(c_{A1} - c_{A2}) = k_c(c_{A1} - c_{A2})$$

$$= \frac{k'_x}{x_{BM}}(x_{A1} - x_{A2}) = k_x(x_{A1} - x_{A2})$$

where the x_{BM} and its counterpart y_{BM} are similar to Eq. (6.2-21) and k_c is the mass-transfer coefficient for *A* diffusing through stagnant *B*. Also,

Equation 7.2-11.

$$x_{BM} = \frac{x_{B2} - x_{B1}}{\ln(x_{B2}/x_{B1})} \qquad y_{BM} = \frac{y_{B2} - y_{B1}}{\ln(y_{B2}/y_{B1})}$$

Rewriting Eq. (7.2-10) using other units,

Equation 7.2-12.

$$\text{(Gases):} \qquad N_A = k_c(c_{A1} - c_{A2}) = k_G(p_{A1} - p_{A2}) = k_y(y_{A1} - y_{A2})$$

Equation 7.2-13.

$$\text{(Liquids):} \quad N_A = k_c(c_{A1} - c_{A2}) = k_L(c_{A1} - c_{A2}) = k_x(x_{A1} - x_{A2})$$

Again all the mass-transfer coefficients can be related to each other and are given in Table 7.2-1. For example, setting Eq. (7.2-10) equal to (7.2-13),

Equation 7.2-14.

$$N_A = \frac{k'_c}{x_{BM}}(c_{A1} - c_{A2}) = k_x(x_{A1} - x_{A2}) = k_x\left(\frac{c_{A1}}{c} - \frac{c_{A2}}{c}\right)$$

Hence,

Equation 7.2-15.

$$\frac{k'_c}{x_{BM}} = \frac{k_x}{c}$$

EXAMPLE 7.2-1. Vaporizing A and Convective Mass Transfer

A large volume of pure gas *B* at 2 atm pressure is flowing over a surface from which pure *A* is vaporizing. The liquid *A* completely wets the surface, which is a blotting paper. Hence, the partial pressure of *A* at the surface is the vapor pressure of *A* at 298 K, which is 0.20 atm. The k'_y has been estimated to be 6.78×10^{-5} kg mol/s · m² · mol frac. Calculate N_A, the vaporization rate, and also the value of k_y and k_G.

Solution: This is the case of A diffusing through B, where the flux of B normal to the surface is zero, since B is not soluble in liquid A. p_{A1} = 0.20 atm and p_{A2} = 0 in the pure gas B. Also, $y_{A1} = p_{A1}/P = 0.20/2.0 = 0.10$ and $y_{A2} = 0$. We can use Eq. (7.2-12) with mole fractions:

Equation 7.2-12 .

$$N_A = k_y(y_{A1} - y_{A2})$$

However, we have a value for k'_y which is related to k_y from Table 7.2-1 by

Equation 7.2-16.

$$k_y y_{BM} = k'_y$$

The term y_{BM} is similar to x_{BM} and is, from Eq. (7.2-11),

Equation 7.2-11.

$$y_{BM} = \frac{y_{B2} - y_{B1}}{\ln(y_{B2}/y_{B1})}$$

$$y_{B1} = 1 - y_{A1} = 1 - 0.10 = 0.90 \qquad y_{B2} = 1 - y_{A2} = 1 - 0 = 1.0$$

Substituting into Eq. (7.2-11),

$$y_{BM} = \frac{1.0 - 0.90}{\ln(1.0/0.90)} = 0.95$$

Then, from Eq. (7.2-16),

$$k_y = \frac{k'_y}{y_{BM}} = \frac{6.78 \times 10^{-5}}{0.95} = 7.138 \times 10^{-5}\ \text{kg mol/s} \cdot \text{m}^2 \cdot \text{mol frac}$$

Also, from Table 7.2-1,

Equation 7.2-17.

$$k_G y_{BM} P = k_y y_{BM}$$

Hence, solving for k_G and substituting knowns,

$$k_G = \frac{k_y}{P} = \frac{7.138 \times 10^{-5}}{2 \times 1.01325 \times 10^5\ \text{Pa}} = 3.522 \times 10^{-10}\ \text{kg mol/s} \cdot \text{m}^2 \cdot \text{Pa}$$

$$k_G = \frac{k_y}{P} = \frac{7.138 \times 10^{-5}}{2.0\ \text{atm}} = 3.569 \times 10^{-5}\ \text{kg mol/s} \cdot \text{m}^2 \cdot \text{atm}$$

For the flux, using Eq. (7.2-12),

$$N_A = k_y(y_{A1} - y_{A2}) = 7.138 \times 10^{-5}(0.10 - 0) = 7.138 \times 10^{-6}\ \text{kg mol/s} \cdot \text{m}^2$$

Also,

$$p_{A1} = 0.20\ \text{atm} = 0.20(1.01325 \times 10^5) = 2.026 \times 10^4\ \text{Pa}$$

Using Eq. (7.2-12) again,

$$N_A = k_G(p_{A1} - p_{A2}) = 3.522 \times 10^{-10}(2.026 \times 10^4 - 0)$$

$$= 7.138 \times 10^{-6} \text{ kg mol/s} \cdot \text{m}^2$$

$$N_A = k_G(p_{A1} - p_{A2}) = 3.569 \times 10^{-5}(0.20 - 0)$$

$$= 7.138 \times 10^{-6} \text{ kg mol/s} \cdot \text{m}^2$$

Note that in this case, since the concentrations were dilute, y_{BM} is close to 1.0 and k_y and k'_y differ very little.

Mass Transfer Coefficients for General Case of A and B Diffusing and Convective Flow Using Film Theory

Equation (7.2-4) can be integrated assuming a simplified film theory where the mass transfer is assumed to occur through a thin film next to the wall of thickness δ_f and by molecular diffusion. Then the experimental value of k'_c for dilute solutions is used to determine the film thickness δ_f.

Equation 7.2-18.

$$k'_c = \frac{D_{AB}}{\delta_f}$$

Rewriting Eq. (7.2-4),

Equation 7.2-19.

$$N_A = -c\,\frac{D_{AB}\,dx_A}{dz} + x_A(N_A + N_B)$$

The convective term is $x_A(N_A + N_B)$. Rearranging and integrating,

Equation 7.2-20.

$$\frac{1}{cD_{AB}}\int_{z=0}^{z=\delta_f} dz = -\int_{x_{A1}}^{x_{A2}} \frac{dx_A}{N_A - x_A(N_A + N_B)}$$

Equation 7.2-21.

$$N_A = \frac{N_A}{N_A + N_B}\,k'_c c \ln\left[\frac{N_A/(N_A + N_B) - x_{A2}}{N_A/(N_A + N_B) - x_{A1}}\right]$$

For $N_B = 0$, Eq. (7.2-21) reduces to Eq. (7.2-10).

Mass Transfer Coefficients under High Flux Conditions

The final Eq. (7.2-21) is a result of assuming the film theory where molecular diffusion occurs across the film δ_f. This assumes that this film thickness is unaffected by high fluxes and bulk or convective flow (diffusion-induced convection). As a result, other definitions of the mass-transfer coefficient that include this effect of diffusion-induced convection have been derived. One common method by Bird et al. (B1) and Skelland (S8) is given as follows for the case of *A* diffusing through stagnant, nondiffusing *B* where diffusion-induced convection is present.

Rewriting Eq. (7.2-19) for the flux N_A at the surface $z = 0$ where $x_A = x_{A1}$,

Equation 7.2-22.

$$N_A = -cD_{AB}\left(\frac{dx_A}{dz}\right)_{z=0} + x_{A1}(N_A + 0)$$

Note that the convective term is defined in terms of x_{A1} and not the average value.

Defining a mass-transfer coefficient in terms of the diffusion flux,

Equation 7.2-23.

$$-cD_{AB}\left(\frac{dx_A}{dz}\right)_{z=0} = k_c^0 c(x_{A1} - x_{A2})$$

Substituting Eq. (7.2-23) into (7.2-22) and solving for N_A,

Equation 7.2-24.

$$N_A = \frac{k_c^0 c(x_{A1} - x_{A2})}{1 - x_{A1}}$$

At low concentrations and fluxes, k_c^0 approaches k_c' for no bulk flow, or $N_A = k_c' c(x_{A1} - x_{A2})$

In general, a coefficient k_c may be defined without regard to convective flow:

Equation 7.2-25.

$$N_A = k_c c(x_{A1} - x_{A2})$$

Combining (7.2-24) and (7.2-25),

Equation 7.2-26.

$$k_c^0 = (1 - x_{A1})k_c$$

The relationship between k_c^0 or k_c for high flux and k_c' for low flux will be considered. These corrections or relationships will be derived using the film theory for the transfer of *A* by molecular diffusion and convective flow, with *B* being stagnant and nondiffusing. This has been done previously and is obtained by setting $N_B = 0$ in Eq. (7.2-21) to obtain the following, which is identical to Eq. (7.2-10):

Equation 7.2-27.

$$N_A = \frac{k'_c}{x_{BM}}(c_{A1} - c_{A2}) = k_c(c_{A1} - c_{A2})$$

Hence, for the film theory,

Equation 7.2-28.

$$\frac{k_c}{k'_c} = \frac{1}{x_{BM}} = \frac{k_x}{k'_x}$$

Combining Eqs. (7.2-26) and (7.2-28),

Equation 7.2-29.

$$\frac{k_c^0}{k'_c} = \frac{1 - x_{A1}}{x_{BM}} = \frac{k_x^0}{k'_x}$$

For this film theory, Eqs. (7.2-28) and (7.2-29) are independent of the Schmidt number. These correction factors predicted by the film theory give results that are reasonably close to those using more complex theories—the penetration theory and boundary layer theory— which are discussed later in Section 7.9C. An advantage of this simple film theory is that it is quite useful in solving complex systems.

EXAMPLE 7.2-2. High Flux Correction Factors

Toluene A is evaporating from a wetted porous slab by having inert pure air at 1 atm flowing parallel to the flat surface. At a certain point the mass-transfer coefficient k'_x for very low fluxes has been estimated as 0.20 lb mol/hr · ft^2. The gas composition at the interface at this point is $x_{A1} = 0.65$. Calculate the flux N_A and the ratios k_c/k'_c or k_x/k'_x and k_c^0/k'_c or k_x^0/k'_x to correct for high flux.

***Solution*:** For the flux N_A, using Eq. (7.2-11),

$$x_{BM} = \frac{x_{B2} - x_{B1}}{\ln(x_{B2}/x_{B1})} = \frac{1.00 - 0.35}{\ln(1.00/0.35)} = 0.619$$

Using Eq. (7.2-10) in terms of k'_x where $k'_c c = k'_x$,

$$N_A = \frac{k'_x}{x_{BM}}(x_{A1} - x_{A2}) = \frac{0.20}{0.619}(0.65 - 0) = 0.210 \text{ lb mol/hr} \cdot \text{ft}^2$$

Using Eq. (7.2-28),

$$\frac{k_x}{k'_x} = \frac{k_c}{k'_c} = \frac{1}{x_{BM}} = \frac{1}{0.619} = 1.616$$

Then, $k_x = 1.616\ k'_x = 1.616(0.20) = 0.323$ lb mol/hr · ft^2. Using Eq. (7.2-29),

$$\frac{k_x^0}{k'_x} = \frac{k_c^0}{k'_c} = \frac{1 - x_{A1}}{x_{BM}} = \frac{1 - 0.65}{0.619} = 0.565$$

and k_x^0 = 0.565(0.200) = 0.113 lb mol/hr · ft^2.

Methods for Experimentally Determining Mass-Transfer Coefficients

Many different experimental methods have been employed to obtain mass-transfer coefficients. In determining the mass-transfer coefficient to a sphere, Steele and Geankoplis (S3) used a solid sphere of benzoic acid held rigidly by a rear support in a pipe. Before the run the sphere was weighed. After flow of the fluid for a timed interval, the sphere was removed, dried, and weighed again to give the amount of mass transferred, which was small compared to the weight of the sphere. From the mass transferred and the area of the sphere, the flux N_A was calculated. Then the driving force (c_{AS} − 0) was used to calculate k_L, where c_{AS} is the solubility and the water contained no benzoic acid.

Another method used is to flow gases over various geometries wet with evaporating liquids. For mass transfer from a flat plate, a porous blotter wet with the liquid serves as the plate.

If the solution is quite dilute, then the mass-transfer coefficient measured is $k_c \cong k'_c$ and the dilute low flux coefficient k'_c or k'_x is experimentally obtained.

MASS-TRANSFER COEFFICIENTS FOR VARIOUS GEOMETRIES

Dimensionless Numbers Used to Correlate Data

The experimental data for mass-transfer coefficients obtained using various kinds of fluids, different velocities, and different geometries are correlated using dimensionless numbers similar to those for heat and momentum transfer. Methods of dimensional analysis are discussed in Sections 3.11, 4.14, and 7.8.

The most important dimensionless number is the Reynolds number N_{Re}, which indicates degree of turbulence:

Equation 7.3-1.

$$N_{\text{Re}} = \frac{Lv\rho}{\mu}$$

where L is diameter D_p for a sphere, diameter D for a pipe, or length L for a flat plate. The velocity v is the mass average velocity if in a pipe. In a packed bed the superficial velocity v' in the empty cross section is often used, or sometimes v = v'/ε is used, where v is interstitial velocity and є void fraction of bed.

The *Schmidt number* is

Equation 7.3-2.

$$N_{\text{Sc}} = \frac{\mu}{\rho D_{AB}}$$

The viscosity μ and density ρ used are for the actual flowing mixture of solute *A* and fluid *B*. If the mixture is dilute, properties of the pure fluid *B* can be used. The Prandtl number $c_p\mu/k$ for heat transfer is analogous to the Schmidt number for mass transfer. The Schmidt number is the ratio of the shear component for diffusivity μ/ρ to the diffusivity for mass transfer D_{AB}; it physically relates the relative thickness of the hydrodynamic layer and mass-transfer boundary layer.

The *Sherwood number,* which is dimensionless, is

Equation 7.3-3.

$$N_{\mathrm{Sh}} = k_c' \frac{L}{D_{AB}} = k_c y_{BM} \frac{L}{D_{AB}} = \frac{k_x'}{c} \frac{L}{D_{AB}} = \cdots$$

Other substitutions from Table 7.2-1 can be made for k_c' in Eq. (7.3-3).

The *Stanton number* occurs often and is

Equation 7.3-4.

$$N_{\mathrm{St}} = \frac{k_c'}{v} = \frac{k_y'}{G_M} = \frac{k_G' P}{G_M} = \cdots$$

Again, substitution for k_c' can be made. $G_M = v\rho/M_{\mathrm{av}} = vc$.

Often the mass-transfer coefficient is correlated as a dimensionless J_D factor, which is related to k_c' and N_{Sh} as follows:

Equation 7.3-5.

$$J_D = \frac{k_c'}{v}(N_{\mathrm{Sc}})^{2/3} = \frac{k_G' P}{G_M}(N_{\mathrm{Sc}})^{2/3} = \cdots = N_{\mathrm{Sh}}/(N_{\mathrm{Re}} N_{\mathrm{Sc}}^{1/3})$$

For heat transfer a dimensionless J_H factor is as follows:

Equation 7.3-6.

$$J_H = \frac{h}{c_p G}(N_{\mathrm{Pr}})^{2/3}$$

Analogies Among Mass, Heat, and Momentum Transfer

Introduction

In molecular transport of momentum, heat, or mass there are many similarities, which were pointed out in Chapters 2–6. The molecular diffusion equations of Newton for momentum, Fourier for heat, and Fick for mass are very similar, and we can say that we have analogies among these three molecular transport processes. There are also similarities in turbulent transport, as discussed in Sections 5.7C and 6.1A, where the flux equations were written using the turbulent eddy momentum diffusivity ε_t, the turbulent eddy thermal diffusivity α_t, and the turbulent eddy mass diffusivity ε_M. However, these similarities are not as well defined mathematically or physically and are more difficult to relate to each other.

A great deal of effort has been devoted in the literature to developing analogies among these three transport processes for turbulent transfer so as to allow prediction of one from any of the others. We discuss several next.

Reynolds analogy

Reynolds was the first to note similarities in transport processes and relate turbulent momentum and heat transfer. Since then, mass transfer has also been related to momentum and heat transfer. We derive this analogy from Eqs. (6.1-4)–(6.1-6) for turbulent transport. For fluid flow in a pipe, for heat transfer from the fluid to the wall, Eq. (6.1-5) becomes as follows, where *z* is distance from the wall:

Equation 7.3-7.

$$\frac{q}{A} = -\rho c_p(\alpha + \alpha_t)\frac{dT}{dz}$$

For momentum transfer, Eq. (6.1-4) becomes

Equation 7.3-8.

$$\tau = -\rho\left(\frac{\mu}{\rho} + \varepsilon_t\right)\frac{dv}{dz}$$

Next we assume that α and μ/ρ are negligible and that $\alpha_t = \varepsilon_t$. Then dividing Eq. (7.3-7) by (7.3-8),

Equation 7.3-9.

$$\left(\frac{\tau}{q/A}\right)c_p\, dT = dv$$

If we assume that heat flux q/A in a turbulent system is analogous to momentum flux τ, the ratio $\tau/(q/A)$ must be constant for all radial positions. We now integrate between conditions at the wall where $T = T_i$ and $v = 0$ to some point in the fluid where T is the same as the bulk T, and assume that the velocity at this point is the same as v_{av}, the bulk velocity. Also, q/A is understood to be the flux at the wall, as is the shear at the wall, written as τ_s. Hence,

Equation 7.3-10.

$$\frac{\tau_s}{q/A}c_p(T - T_i) = v_{\text{av}} - 0$$

Also, substituting $q/A = h(T - T_i)$ and $\tau_s = f v_{\text{av}}^2\, \rho/2$ from Eq. (2.10-4) into Eq. (7.3-10),

Equation 7.3-11.

$$\frac{f}{2} = \frac{h}{c_p v_{\text{av}}\rho} = \frac{h}{c_p G}$$

In a similar manner, using Eq. (6.1-6) for J_A^* and $J_A^* = k_c'(c_A - c_{Ai})$, we can relate this to Eq. (7.3-8) for momentum transfer. Then, the complete Reynolds analogy is

Equation 7.3-12.

$$\frac{f}{2} = \frac{h}{c_p G} = \frac{k_c'}{v_{\text{av}}}$$

Experimental data for gas streams agree approximately with Eq. (7.3-12) if the Schmidt and Prandtl numbers are near 1.0 and only skin friction is present in flow past a flat plate or inside a pipe. When liquids are present and/or form drag is present, the analogy is not valid.

Other analogies

The Reynolds analogy assumes that the turbulent diffusivities ε_t, α_t, and ε_M are all equal and that the molecular diffusivities μ/ρ, α, and D_{AB} are negligible compared to the turbulent diffusivities. When the Prandtl number $(\mu/\rho)/\alpha$ is 1.0, then $\mu/\rho = \alpha$; also, for $N_{Sc} = 1.0$, $\mu/\rho = D_{AB}$. Then, $(\mu/\rho + \varepsilon_t) = (\alpha + \alpha_t) = (D_{AB} + \varepsilon_M)$ and the Reynolds analogy can be obtained with the molecular terms present. However, the analogy breaks down when the viscous sublayer becomes important, since the eddy diffusivities diminish to zero and the molecular diffusivities become important.

Prandtl modified the Reynolds analogy by writing the regular molecular diffusion equation for the viscous sublayer and a Reynolds analogy equation for the turbulent core region. Then, since these processes are in series, these equations were combined to produce an overall equation (G1). The results again are poor for fluids where the Prandtl and Schmidt numbers differ from 1.0.

Von Kármán further modified the Prandtl analogy by considering the buffer region in addition to the viscous sublayer and the turbulent core. These three regions are shown in the universal velocity profile in Fig. 3.10-4. Again, an equation is written for molecular diffusion in the viscous sublayer using only the molecular diffusivity and a Reynolds analogy equation for the turbulent core. Both the molecular and eddy diffusivity are used in an equation for the buffer layer, where the velocity in this layer is used to obtain an equation for the eddy diffusivity. These three equations are then combined to give the von Kármán analogy. Since then, numerous other analogies have appeared (P1, S4).

Chilton and Colburn J-factor analogy

The most successful and most widely used analogy is the Chilton and Colburn *J*-factor analogy (C2). This analogy is based on experimental data for gases and liquids in both the laminar and turbulent flow regions and is written as follows:

Equation 7.3-13.

$$\frac{f}{2} = J_H = \frac{h}{c_p G}(N_{\mathrm{Pr}})^{2/3} = J_D = \frac{k'_c}{v_{\mathrm{av}}}(N_{\mathrm{Sc}})^{2/3}$$

Although this is an equation based on experimental data for both laminar and turbulent flow, it can be shown to satisfy the exact solution derived from laminar flow over a flat plate in Sections 3.10 and 5.7.

Equation (7.3-13) has been shown to be quite useful in correlating momentum, heat, and mass-transfer data. It permits the prediction of an unknown transfer coefficient when one of the other coefficients is known. In momentum transfer the friction factor is obtained for the total drag or friction loss, which includes form drag or momentum losses due to blunt objects as well as skin friction. For flow past a flat plate or in a pipe, where no form drag is present, $f/2 = J_H = J_D$. When form drag is present, as in flow in packed beds or past other blunt objects, $f/2$ is greater than J_H or J_D, and $J_H \cong J_D$.

Derivation of Mass-Transfer Coefficients in Laminar Flow

Introduction

When a fluid is flowing in laminar flow and mass transfer by molecular diffusion is occurring, the equations are very similar to those for heat transfer by conduction in laminar flow. The phenomena of heat and mass transfer are not always completely analogous, since in mass transfer several components may be diffusing. Also, the flux of mass perpendicular to the direction of the flow must be small so as not to distort the laminar velocity profile.

In theory it is not necessary to have experimental mass-transfer coefficients for laminar flow, since the equations for momentum transfer and diffusion can be solved. However, in many actual cases it is difficult to describe mathematically the laminar flow for certain geometries, such as flow past a cylinder or in a packed bed. Hence, experimental mass-transfer coefficients are often obtained and correlated. A simplified theoretical derivation will be given for two cases of laminar flow.

Mass transfer in laminar flow in a tube

We consider the case of mass transfer from a tube wall to a fluid inside in laminar flow, where, for example, the wall is made of solid benzoic acid which is dissolving in water. This is similar to heat transfer from a wall to the flowing fluid where natural convection is negligible. For fully developed flow, the parabolic velocity derived as Eqs. (2.6-18) and (2.6-20) is

Equation 7.3-14.

$$v_x = v_{\max}\left[1 - \left(\frac{r}{R}\right)^2\right] = 2v_{\text{av}}\left[1 - \left(\frac{r}{R}\right)^2\right]$$

where v_x is the velocity in the *x* direction at the distance *r* from the center. For steady state diffusion in a cylinder, a mass balance can be made on a differential element where the rate in by convection plus diffusion equals the rate out radially by diffusion to give

Equation 7.3-15.

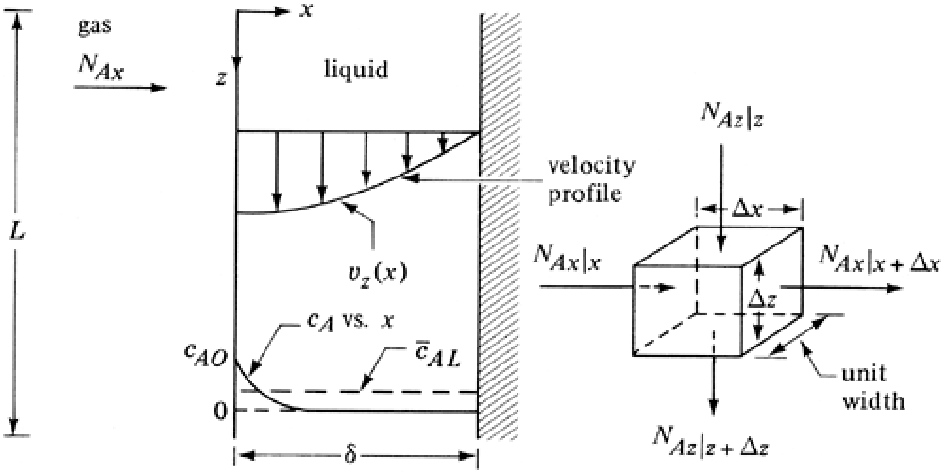
$$v_x \frac{\partial c_A}{\partial x} = D_{AB}\left(\frac{1}{r}\frac{\partial c_A}{\partial r} + \frac{\partial^2 c_A}{\partial r^2} + \frac{\partial^2 c_A}{\partial x^2}\right)$$

Then, $\partial^2 c_A/\partial x^2 = 0$ if the diffusion in the *x* direction is negligible compared to that by convection. Combining Eqs. (7.3-14) and (7.3-15), the final solution (S1) is a complex series similar to the Graetz solution for heat transfer and a parabolic velocity profile.

If it is assumed that the velocity profile is flat, as in rodlike flow, the solution is more easily obtained (S1). A third solution, called the approximate *Leveque solution,* has been obtained, where there is a linear velocity profile near the wall and the solute diffuses only a short distance from the wall into the fluid. This is similar to the parabolic-velocity-profile solution at high flow rates. Experimental design equations are presented in Section 7.3D for this case.

Diffusion in a laminar falling film

In Section 2.9C we derived the equation for the velocity profile in a falling film shown in Fig. 7.3-1a. We will consider mass transfer of solute *A* into a laminar falling film, which is important in wetted-wall columns, in developing theories to explain mass transfer in stagnant pockets of fluids, and in turbulent mass transfer. The solute *A* in the gas is absorbed at the interface and then diffuses a distance into the liquid so that it has not penetrated the whole distance $x = \delta$ at the wall. At steady state the inlet concentration $c_A = 0$. The concentration profile of c_A at a point *z* distance from the inlet is shown in Fig. 7.3-1a.



(a) (b)

Figure 7.3-1. Diffusion of solute A in a laminar falling film: (a) velocity profile and concentration profile, (b) small element for mass balance.

A mass balance will be made on the element shown in Fig. 7.3-1b. For steady state, rate of input = rate of output:

Equation 7.3-16.

$$N_{Ax|x}(1\ \Delta z) + N_{Az|z}(1\ \Delta x) = N_{Ax|x+\Delta x}(1\ \Delta z) + N_{Az|z+\Delta z}(1\ \Delta x)$$

For a dilute solution the diffusion equation for *A* in the *x* direction is

Equation 7.3-17.

$$N_{Ax} = -D_{AB}\frac{\partial c_A}{\partial x} + \text{zero convection}$$

For the *z* direction the diffusion is negligible:

Equation 7.3-18 .

$$N_{Az} = 0 + c_A v_z$$

Dividing Eq. (7.3-16) by $\Delta x\,\Delta z$, letting Δx and Δz approach zero, and substituting Eqs. (7.3-17) and (7.3-18) into the result, we obtain

Equation 7.3-19.

$$v_z\frac{\partial c_A}{\partial z} = D_{AB}\frac{\partial^2 c_A}{\partial x^2}$$

From Eqs. (2.9-24) and (2.9-25), the velocity profile is parabolic and is $v_z = v_{z\max}[1 - (x/\delta^2)]$. Also, $v_{z\,\max} = \frac{3}{2}v_{z\,\text{av}}$. If the solute has penetrated only a short distance into the fluid, that is, short contact times of $t = z/v_{\max}$, then the *A* that has diffused has been carried along at the velocity $v_{z\max}$, or $v_{\max}$ if the subscript *z* is dropped. Then Eq. (7.3-19) becomes

Equation 7.3-20.

$$\frac{\partial c_A}{\partial(z/v_{\max})} = D_{AB}\frac{\partial^2 c_A}{\partial x^2}$$

Using the boundary conditions of $c_A = 0$ at $z = 0$, $c_A = c_{A0}$ at $x = 0$, and $c_A = 0$ at $x = \infty$, we can integrate Eq. (7.3-20) to obtain

Equation 7.3-21.

$$\frac{c_A}{c_{A0}} = \operatorname{erfc}\left(\frac{x}{\sqrt{4D_{AB}z/v_{\max}}}\right)$$

where erf y is the error function and erfc $y = 1 - \operatorname{erf} y$. Values of erf y are standard tabulated functions. To determine the local molar flux at the surface $x = 0$ at position z from the top entrance, we write (B1)

Equation 7.3-22.

$$N_{Ax}(z)|_{x=0} = -D_{AB}\left.\frac{\partial c_A}{\partial x}\right|_{x=0} = c_{A0}\sqrt{\frac{D_{AB}v_{\max}}{\pi z}}$$

The total moles of A transferred per second to the liquid over the entire length $z = 0$ to $z = L$, where the vertical surface is unit width, is

Equation 7.3-23.

$$\begin{aligned} N_A(L\cdot 1) &= (1)\int_0^L (N_{Ax|x=0})\,dz \\ &= (1)\int_0^L c_{A0}\left(\frac{D_{AB}v_{\max}}{\pi}\right)^{1/2}\frac{1}{z^{1/2}}\,dz \\ &= (L\cdot 1)c_{A0}\sqrt{\frac{4D_{AB}v_{\max}}{\pi L}} \end{aligned}$$

The term $L/v_{\max}$ is t_L, time of exposure of the liquid to the solute A in the gas. This means the rate of mass transfer is proportional to $D_{AB}^{0.5}$ and $1/t_L^{0.5}$. This is the basis for the penetration theory in turbulent mass transfer where pockets of liquid are exposed to unsteady-state diffusion (penetration) for short contact times.

Mass Transfer for Flow Inside Pipes

Mass transfer for laminar flow inside pipes

When a liquid or gas is flowing inside a pipe and the Reynolds number $Dv\rho/\mu$ is below 2100, laminar flow occurs. Experimental data obtained for mass transfer from the walls for gases (G2, L1) are plotted in Fig. 7.3-2 for values of $W/D_{AB}\rho L$ less than about 70. The ordinate is $(c_A - c_{A0})/(c_{Ai} - c_{A0})$, where c_A is the exit concentration, c_{A0} inlet concentration, and c_{Ai} concentration at the interface between the wall and the gas. The dimensionless abscissa is $W/D_{AB}\rho L$ or $N_{Re}N_{Sc}(D/L)(\pi/4)$, where W is flow in kg/s and L is length of mass-transfer section in m. Since the experimental data follow the rodlike plot, that line should be used. The velocity profile is assumed fully developed to parabolic form at the entrance.

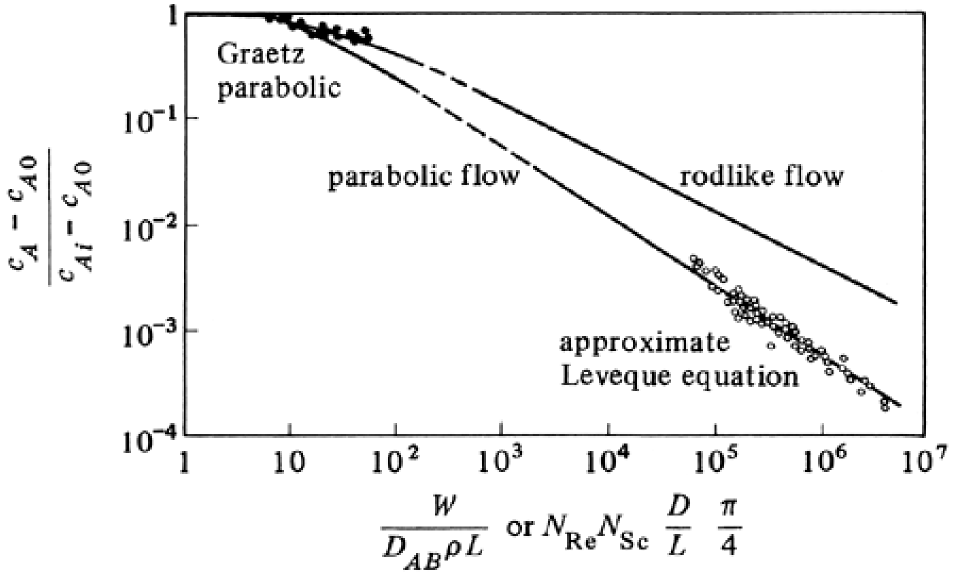


Figure 7.3-2. Data for diffusion in a fluid in streamline flow inside a pipe: filled circles, vaporization data of Gilliland and Sherwood; open circles, dissolving-solids data of Linton and Sherwood. [From W. H. Linton and T. K. Sherwood, Chem. Eng. Progr., ***46,*** *258 (1950). With permission.]*

For liquids that have small values of D_{AB}, data follow the parabolic flow line, which is as follows for $W/D_{AB}\rho L$ over 400:

Equation 7.3-24.

$$\frac{c_A - c_{A0}}{c_{Ai} - c_{A0}} = 5.5\left(\frac{W}{D_{AB}\rho L}\right)^{-2/3}$$

Mass transfer for turbulent flow inside pipes

For turbulent flow when $Dv\rho/\mu > 2100$ for gases or liquids flowing inside a pipe,

Equation 7.3-25.

$$N_{Sh} = k_c' \frac{D}{D_{AB}} = \frac{k_c p_{BM}}{P}\frac{D}{D_{AB}} = 0.023\left(\frac{Dv\rho}{\mu}\right)^{0.83}\left(\frac{\mu}{\rho D_{AB}}\right)^{0.33}$$

The equation holds for N_{Sc} of 0.6 to 3000 (G2, L1). Note that the N_{Sc} for gases is in the range 0.5–3 and for liquids is above 100 in general. Equation (7.3-25) for mass transfer and Eq. (4.5-8) for heat transfer inside a pipe are similar to each other.

Mass transfer for flow inside wetted-wall towers

When a gas is flowing inside the core of a wetted-wall tower, the same correlations that are used for mass transfer of a gas in laminar or turbulent flow in a pipe are applicable. This means that Eqs. (7.3-24) and (7.3-25) can be used to predict mass transfer for the gas. For the mass transfer in the liquid film flowing down the wetted-wall tower, Eqs. (7.3-22) and (7.3-23) can be used for Reynolds numbers of $4\Gamma/\mu$ as defined by Eq. (2.9-29) up to about 1200, and the theoretically predicted values should be multiplied by about 1.5 because of ripples and other factors. These equations hold for short contact times or Reynolds numbers above about 100 (S1).

EXAMPLE 7.3-1. Mass Transfer Inside a Tube

A tube is coated on the inside with naphthalene and has an inside diameter of 20 mm and a length of 1.10 m. Air at 318 K and an average pressure of 101.3 kPa flows through this pipe at a velocity of 0.80 m/s. Assuming that the absolute pressure remains essentially constant, calculate the concentration of naphthalene in the exit air. Use the physical properties given in Example 6.2-4.

Solution: From Example 6.2-4, $D_{AB} = 6.92 \times 10^{-6}$ m²/s and the vapor pressure $p_{Ai} = 74.0$ Pa or $c_{Ai} = p_{A}/RT = 74.0/(8314.3 \times 318) = 2.799 \times 10^{-5}$ kg mol/m³. For air, from Appendix A.3, $\mu = 1.932 \times 10^{-5}$ Pa · s, $\rho = 1.114$ kg/m³. The Schmidt number is

$$N_{Sc} = \frac{\mu}{\rho D_{AB}} = \frac{1.932 \times 10^{-5}}{1.114 \times 6.92 \times 10^{-6}} = 2.506$$

The Reynolds number is

$$N_{Re} = \frac{Dv\rho}{\mu} = \frac{0.020(0.80)(1.114)}{1.932 \times 10^{-5}} = 922.6$$

Hence, the flow is laminar. Then,

$$N_{Re} N_{Sc} \frac{D}{L} \frac{\pi}{4} = 922.6(2.506) \frac{0.020}{1.10} \frac{\pi}{4} = 33.02$$

Using Fig. 7.3-2 and the rodlike flow line, $(c_A - c_{A0})/(c_{Ai} - c_{A0}) = 0.55$. Also, c_{A0}(inlet) = 0. Then, $(c_A - 0)/(2.799 \times 10^{-5} - 0) = 0.55$. Solving c_A (exit concentration) = 1.539×10^{-5} kg mol/m³.

Mass Transfer for Flow Outside Solid Surfaces

Mass transfer in flow parallel to flat plates

The mass transfer and vaporization of liquids from a plate or flat surface to a flowing stream is of interest in the drying of inorganic and biological materials, in the evaporation of solvents from paints, for plates in wind tunnels, and in flow channels in chemical process equipment.

When the fluid flows past a plate in a free stream in an open space the boundary layer is not fully developed. For gases or evaporation of liquids in the gas phase and for the laminar region of $N_{Re,L} = Lv\rho/\mu$ less than 15 000, the data can be represented within ±25% by the equation (S4)

Equation 7.3-26.

$$J_D = 0.664\, N_{Re,L}^{-0.5}$$

Writing Eq. (7.3-26) in terms of the Sherwood number N_{Sh},

Equation 7.3-27.

$$\frac{k_c' L}{D_{AB}} = N_{\text{Sh}} = 0.664\, N_{\text{Re},L}^{0.5} N_{\text{Sc}}^{1/3}$$

where *L* is the length of plate in the direction of flow. Also, $J_D = J_H = f/2$ for this geometry. For gases and $N_{\text{Re},L}$ of 15 000–300 000, the data are represented within ±30% by $J_D = J_H = f/2$ as

Equation 7.3-28.

$$J_D = 0.036\, N_{\text{Re},L}^{-0.2}$$

Experimental data for liquids are correlated within about ±40% by the following for a $N_{\text{Re},L}$ of 600–50 000 (L2):

Equation 7.3-29.

$$J_D = 0.99\, N_{\text{Re},L}^{-0.5}$$

EXAMPLE 7.3-2. Mass Transfer from a Flat Plate

A large volume of pure water at 26.1°C is flowing parallel to a flat plate of solid benzoic acid, where $L = 0.244$ m in the direction of flow. The water velocity is 0.061 m/s. The solubility of benzoic acid in water is 0.02948 kg mol/m^3. The diffusivity of benzoic acid is 1.245×10^{-9} m^2/s. Calculate the mass-transfer coefficient k_L and the flux N_A.

***Solution*:** Since the solution is quite dilute, the physical properties of water at 26.1°C from Appendix A.2 can be used:

$$\mu = 8.71 \times 10^{-4}\ \text{Pa}\cdot\text{s}$$

$$\rho = 996\ \text{kg/m}^3$$

$$D_{AB} = 1.245 \times 10^{-9}\ \text{m}^2/\text{s}$$

The Schmidt number is

$$N_{\text{Sc}} = \frac{8.71 \times 10^{-4}}{996(1.245 \times 10^{-9})} = 702$$

The Reynolds number is

$$N_{\text{Re},L} = \frac{Lv\rho}{\mu} = \frac{0.244(0.0610)(996)}{8.71 \times 10^{-4}} = 1.700 \times 10^4$$

Using Eq. (7.3-29),

$$J_D = 0.99\, N_{\text{Re},L}^{-0.5} = 0.99(1.700 \times 10^4)^{-0.5} = 0.00758$$

The definition of J_D from Eq. (7.3-5) is

Equation 7.3-5.

$$J_D = \frac{k_c'}{v}(N_{\text{Sc}})^{2/3}$$

Solving for $k'_c, k'_c = J_D v (N_{Sc})^{-2/3}$. Substituting known values and solving,

$$k'_c = 0.00758(0.0610)(702)^{-2/3} = 5.85 \times 10^{-6}\ \text{m/s}$$

In this case, diffusion is for *A* through nondiffusing *B*, so k_c in Eq. (7.2-10) should be used:

Equation 7.2-10.

$$N_A = \frac{k'_c}{x_{BM}}(c_{A1} - c_{A2}) = k_c(c_{A1} - c_{A2})$$

Since the solution is very dilute, $x_{BM} \cong 1.0$ and $k'_c \cong k_c$ Also, $c_{A1} = 2.948 \times 10^{-2}$ kg mol/m^3 (solubility) and $c_{A2} = 0$ (large volume of fresh water). Substituting into Eq. (7.2-10),

$$N_A = (5.85 \times 10^{-6})(0.02948 - 0) = 1.726 \times 10^{-7}\ \text{kg mol/s} \cdot \text{m}^2$$

Mass transfer for flow past single spheres

For flow past single spheres and for very low $N_{Re} = D_p v \rho / \mu$, where v is the average velocity in the empty test section before the sphere, the Sherwood number, which is $k'_c D_p / D_{AB}$, should approach a value of 2.0. This can be shown from Eq. (6.2-33), which was derived for a stagnant medium. Rewriting Eq. (6.2-33) as follows, where D_p is the sphere diameter,

Equation 7.3-30.

$$N_A = \frac{2D_{AB}}{D_p}(c_{A1} - c_{A2}) = k_c(c_{A1} - c_{A2})$$

The mass-transfer coefficient k_c, which is k'_c for a dilute solution, is then

Equation 7.3-31.

$$k'_c = \frac{2D_{AB}}{D_p}$$

Rearranging,

Equation 7.3-32.

$$\frac{k'_c D_p}{D_{AB}} = N_{Sh} = 2.0$$

Of course, natural convection effects could increase k'_c.

For gases, for a Schmidt number range of 0.6–2.7 and a Reynolds number range of 1–48 000, a modified equation (G1) can be used:

Equation 7.3-33.

$$N_{Sh} = 2 + 0.552 N_{Re}^{0.53} N_{Sc}^{1/3}$$

This equation also holds for heat transfer, where the Prandtl number replaces the Schmidt number and the Nusselt number hD_p/k replaces the Sherwood number.

For liquids (G3) and a Reynolds number range of 2 to about 2000, the following can be used:

Equation 7.3-34.

$$N_{\text{Sh}} = 2 + 0.95N_{\text{Re}}^{0.50}N_{\text{Sc}}^{1/3}$$

For liquids and a Reynolds number of 2000–17 000, the following can be used (S5):

Equation 7.3-35.

$$N_{\text{Sh}} = 0.347N_{\text{Re}}^{0.62}N_{\text{Sc}}^{1/3}$$

EXAMPLE 7.3-3. Mass Transfer from a Sphere

Calculate the value of the mass-transfer coefficient and the flux for mass transfer from a sphere of naphthalene to air at 45°C and 1 atm abs flowing at a velocity of 0.305 m/s. The diameter of the sphere is 25.4 mm. The diffusivity of naphthalene in air at 45°C is 6.92×10^{-6} m^2/s and the vapor pressure of solid naphthalene is 0.555 mm Hg. Use English and SI units.

Solution: In English units $D_{AB} = 6.92 \times 10^{-6}(3.875 \times 10^4) = 0.2682$ ft^2/h. The diameter $D_p = 0.0254$ m $= 0.0254(3.2808) = 0.0833$ ft. From Appendix A.3 the physical properties of air will be used, since the concentration of naphthalene is low:

$$\mu = 1.93 \times 10^{-5}\ \text{Pa}\cdot\text{s} = 1.93 \times 10^{-5}(2.4191 \times 10^3) = 0.0467\ \text{lb}_\text{m}/\text{ft}\cdot\text{h}$$

$$\rho = 1.113\ \text{kg/m}^3 = \frac{1.113}{16.0185} = 0.0695\ \text{lb}_\text{m}/\text{ft}^3$$

$$v = 0.305\ \text{m/s} = 0.305(3600 \times 3.2808) = 3600\ \text{ft/h}$$

The Schmidt number is

$$N_{\text{Sc}} = \frac{\mu}{\rho D_{AB}} = \frac{0.0467}{0.0695(0.2682)} = 2.505$$

$$N_{\text{Sc}} = \frac{1.93 \times 10^{-5}}{1.113(6.92 \times 10^{-6})} = 2.505$$

The Reynolds number is

$$N_{\text{Re}} = \frac{D_p v \rho}{\mu} = \frac{0.0833(3600)(0.0695)}{0.0467} = 446$$

$$N_{\text{Re}} = \frac{0.0254(0.3048)(1.113)}{1.93 \times 10^{-5}} = 446$$

Equation (7.3-33) for gases will be used:

$$N_{\text{Sh}} = 2 + 0.552(N_{\text{Re}})^{0.53}(N_{\text{Sc}})^{1/3} = 2 + 0.552(446)^{0.53}(2.505)^{1/3} = 21.0$$

From Eq. (7.3-3),

$$N_{\mathrm{Sh}} = k_c' \frac{L}{D_{AB}} = k_c' \frac{D_p}{D_{AB}}$$

Substituting the knowns and solving,

$$21.0 = \frac{k_c'(0.0833)}{0.2682} \qquad k_c' = 67.6 \text{ ft/h}$$

$$21.0 = \frac{k_c'(0.0254)}{6.92 \times 10^{-6}} \qquad k_c' = 5.72 \times 10^{-3} \text{ m/s}$$

From Table 7.2-1,

$$k_c' c = k_c' \frac{P}{RT} = k_G' P$$

Hence, for $T = 45 + 273 = 318$ K = 318(1.8) = 574°R,

$$k_G' = \frac{k_c'}{RT} = \frac{67.6}{(0.730)(573)} = 0.1616 \text{ lb mol/h} \cdot \text{ft}^2 \cdot \text{atm}$$

$$k_G' = \frac{5.72 \times 10^{-3}}{8314(318)} = 2.163 \times 10^{-9} \text{ kg mol/s} \cdot \text{m}^2 \cdot \text{Pa}$$

Since the gas is very dilute, $y_{BM} \cong 1.0$ and $k_G' \cong k_G$. Substituting into Eq. (7.2-12) for A diffusing through stagnant B and noting that $p_{A1} = 0.555/760 = 7.303 \times 10^{-4}$ atm = 74.0 Pa and $p_{A2} = 0$ (pure air),

$$\begin{aligned} N_A &= k_G(p_{A1} - p_{A2}) = 0.1616(7.303 \times 10^{-4} - 0) \\ &= 1.180 \times 10^{-4} \text{ lb mol/h} \cdot \text{ft}^2 \\ &= 2.163 \times 10^{-9}(74.0 - 0) = 1.599 \times 10^{-7} \text{ kg mol/s} \cdot \text{m}^2 \end{aligned}$$

The area of the sphere is

$$\begin{aligned} A &= \pi D_p^2 = \pi(0.0833)^2 = 2.18 \times 10^{-2} \text{ ft}^2 \\ &= (2.18 \times 10^{-2})\left(\frac{1}{3.2808}\right)^2 = 2.025 \times 10^{-3} \text{ m}^2 \end{aligned}$$

Total amount evaporated = $N_A A = (1.18 \times 10^{-4})(2.18 \times 10^{-2}) = 2.572 \times 10^{-6}$ lb mol/h = $(1.599 \times 10^{-7})(2.025 \times 10^{-3}) = 3.238 \times 10^{-10}$ kg mol/s

Mass transfer to packed beds

Mass transfer to and from packed beds occurs often in processing operations, including drying operations, adsorption or desorption of gases or liquids by solid particles such as charcoal, and mass transfer of gases and liquids to catalyst particles. By using a packed bed a large amount of mass-transfer area can be contained in a relatively small volume.

The void fraction in a bed is ε m^3 volume void space divided by the m^3 total volume of void space plus solid. The values range from 0.3 to 0.5 in general. Because of flow channeling, nonuniform packing, and so forth, accurate experimental data are difficult to obtain and data from different investigators can deviate considerably.

For a Reynolds number range of 10–10 000 for gases in a packed bed of spheres (D4), the recommended correlation with an average deviation of about ±20% and a maximum of about ±50% is

Equation 7.3-36.

$$J_D = J_H = \frac{0.4548}{\varepsilon} N_{\mathrm{Re}}^{-0.4069}$$

It has been shown (G4, G5) that J_D and J_H are approximately equal. The Reynolds number is defined as $N_{\mathrm{Re}} = D_p v' \rho/\mu$, where D_p is diameter of the spheres and v' is the superficial mass average velocity in the empty tube without packing. For Eqs. (7.3-36)–(7.3-39) and Eqs. (7.3-5)–(7.3-6), v' is used.

For mass transfer of liquids in packed beds, the correlations of Wilson and Geankoplis (W1) should be used. For a Reynolds number $D_p v' \rho/\mu$ range of 0.0016–55 and a Schmidt number range of 165–70 000, the equation to use is

Equation 7.3-37.

$$J_D = \frac{1.09}{\varepsilon} N_{\mathrm{Re}}^{-2/3}$$

For liquids and a Reynolds number range of 55–1500 and a Schmidt number range of 165–10 690,

Equation 7.3-38.

$$J_D = \frac{0.250}{\varepsilon} N_{\mathrm{Re}}^{-0.31}$$

Or, as an alternate, Eq. (7.3-36) can be used for liquids for a Reynolds number range of 10–1500.

For fluidized beds of spheres, Eq. (7.3-36) can be used for gases and liquids and a Reynolds number range of 10–4000. For liquids in a fluidized bed and a Reynolds number range of 1–10 (D4),

Equation 7.3-39.

$$\varepsilon J_D = 1.1068 N_{\mathrm{Re}}^{-0.72}$$

If packed beds of solids other than spheres are used, approximate correction factors can be used with Eqs. (7.3-36)–(7.3-38) for spheres. This is done, for example, for a given nonspherical particle as follows. The particle diameter to use in the equations for predicting J_D is the diameter of a sphere with the same surface area as the given solid particle. The flux to these particles in the bed is then calculated using the area of the given particles. An alternative approximate procedure is given elsewhere (G6).

Calculation method for packed beds

To calculate the total flux in a packed bed, J_D is first obtained and then k_c in m/s from the J_D. Then, knowing the total volume V_b m^3 of the bed (void plus solids), the total external surface area A m^2 of the solids for mass transfer is calculated using Eqs. (7.3-40) and (7.3-41):

Equation 7.3-40.

$$a = \frac{6(1-\varepsilon)}{D_p}$$

where a is the m^2 surface area/m^3 total volume of bed when the solids are spheres, and

Equation 7.3-41.

$$A = aV_b$$

To calculate the mass-transfer rate, the log mean driving force at the inlet and outlet of the bed should be used:

Equation 7.3-42.

$$N_A A = A k_c \frac{(c_{Ai} - c_{A1}) - (c_{Ai} - c_{A2})}{\ln \dfrac{c_{Ai} - c_{A1}}{c_{Ai} - c_{A2}}}$$

where the final term is the log mean driving force: c_{Ai} is the concentration at the surface of the solid, in kg mol/m^3; c_{A1} is the inlet bulk fluid concentration; and c_{A2} is the outlet. The material-balance equation on the bulk stream is

Equation 7.3-43.

$$N_A A = V(c_{A2} - c_{A1})$$

where V is volumetric flow rate of fluid entering in m^3/s. Equations (7.3-42) and (7.3-43) must both be satisfied. The use of these two equations is similar to the use of the log mean temperature difference and heat balance in heat exchangers. These two equations can also be used for a fluid flowing in a pipe or past a flat plate, where A is the pipe wall area or plate area.

EXAMPLE 7.3-4. Mass Transfer of a Liquid in a Packed Bed

Pure water at 26.1°C flows at the rate of 5.514×10^{-7} m^3/s through a packed bed of benzoic-acid spheres having a diameter of 6.375 mm. The total surface area of the spheres in the bed is 0.01198 m^2 and the void fraction is 0.436. The tower diameter is 0.0667 m. The solubility of benzoic acid in water is 2.948×10^{-2} kg mol/m^3.

a. Predict the mass-transfer coefficient k_c. Compare with the experimental value of 4.665×10^{-6} m/s by Wilson and Geankoplis (W1).
b. Using the experimental value of k_c, predict the outlet concentration of benzoic acid in the water.

Solution: Since the solution is dilute, the physical properties of water will be used at 26.1°C from Appendix A. 2. At 26.1°C, $\mu = 0.8718 \times 10^{-3}$ Pa · s, $\rho = 996.7$ kg/m^3. At 25.0°C, $\mu = 0.8940 \times 10^{-3}$ Pa · s, and from Table 6.3-1, $D_{AB} = 1.21 \times 10^{-9}$ m^2/s. To correct D_{AB} to 26.1°C using Eq. (6.3-9), $D_{AB} \propto T/\mu$. Hence,

$$\begin{aligned} D_{AB}(26.1°\text{C}) &= (1.21 \times 10^{-9})\left(\frac{299.1}{298}\right)\left(\frac{0.8940 \times 10^{-3}}{0.8718 \times 10^{-3}}\right) \\ &= 1.254 \times 10^{-9}\ \text{m}^2/\text{s} \end{aligned}$$

The tower cross-sectional area = $(\pi/4)(0.0667)^2 = 3.494 \times 10^{-3}$ m^2. Then $V' = (5.514 \times 10^{-7})/(3.494 \times 10^{-3}) = 1.578 \times 10^{-4}$ m/s. Then,

$$N_{Sc} = \frac{\mu}{\rho D_{AB}} = \frac{0.8718 \times 10^{-3}}{996.7(1.245 \times 10^{-9})} = 702.6$$

The Reynolds number is

$$N_{\mathrm{Re}} = \frac{Dv'\rho}{\mu} = \frac{0.006375(1.578 \times 10^{-4})(996.7)}{0.8718 \times 10^{-3}} = 1.150$$

Using Eq. (7.3-37) and assuming $k_c = k'_c$ for dilute solutions,

$$J_D = \frac{1.09}{\varepsilon}(N_{\mathrm{Re}})^{-2/3} = \frac{1.09}{0.436}(1.150)^{-2/3} = 2.277$$

Then, using Eq. (7.3-5) and solving,

$$J_D = \frac{k'_c}{v'}(N_{\mathrm{Sc}})^{2/3} \qquad 2.277 = \frac{k'_c}{1.578 \times 10^{-4}}(702.6)^{2/3}$$

The predicted $k'_c = 4.447 \times 10^{-6}$ m/s. This compares with the experimental value of 4.665×10^{-6} m/s.

For part (b), using Eqs. (7.3-42) and (7.3-43),

Equation 7.3-44.

$$Ak_c\frac{(c_{Ai} - c_{A1}) - (c_{Ai} - c_{A2})}{\ln \dfrac{c_{Ai} - c_{A1}}{c_{Ai} - c_{A2}}} = V(c_{A2} - c_{A1})$$

The values to substitute into Eq. (7.3-44) are $c_{Ai} = 2.948 \times 10^{-2}$, $c_{A1} = 0$, $A = 0.01198$, $V = 5.514 \times 10^{-7}$.

$$\frac{0.01198(4.665 \times 10^{-6})(c_{A2} - 0)}{\ln \dfrac{2.948 \times 10^{-2} - 0}{2.948 \times 10^{-2} - c_{A2}}} = (5.514 \times 10^{-7})(c_{A2} - 0)$$

Solving, $c_{A2} = 2.842 \times 10^{-3}$ kg mol/m^3.

Mass transfer for flow past single cylinders

Experimental data have been obtained for mass transfer from single cylinders when the flow is perpendicular to the cylinder. The cylinders are long and mass transfer to the ends of the cylinder is not considered. For the Schmidt number range of 0.6 to 2.6 for gases and 1000 to 3000 for liquids and a Reynolds number range of 50 to 50 000, data from many references (B3, L1, M1, S4, V1) have been plotted, and the correlation to use is as follows:

Equation 7.3-45.

$$J_D = 0.600(N_{\mathrm{Re}})^{-0.487}$$

The data scatter considerably by up to ±30%. This correlation can also be used for heat transfer, with $J_D = J_H$.

Liquid metals mass transfer

In recent years several correlations for mass-transfer coefficients of liquid metals have appeared in the literature. It has been found (G1) that with moderate safety factors, the correlations for nonliquid metals mass transfer may be used for liquid metals mass transfer. Care must be taken to ensure that the solid surface is wetted. Also, if the solid is an alloy, there may exist a resistance to diffusion in the solid phase.

MASS TRANSFER TO SUSPENSIONS OF SMALL PARTICLES

Introduction

Mass transfer from or to small suspended particles in an agitated solution occurs in a number of process applications. In liquid-phase hydrogenation, hydrogen diffuses from gas bubbles, through an organic liquid, and then to small suspended catalyst particles. In fermentation, oxygen diffuses from small gas bubbles, through the aqueous medium, and then to small suspended microorganisms.

For a liquid–solid dispersion, increased agitation over and above that necessary to freely suspend very small particles has very little effect on the mass-transfer coefficient k_L to the particle (B2). When the particles in a mixing vessel are just completely suspended, turbulence forces balance those due to gravity, and the mass-transfer rates are the same as for particles freely moving under gravity. With very small particles of, say, a few μm or so, which is the size of many microorganisms in fermentations and some catalyst particles, their size is smaller than eddies, which are about 100 μm or so in size. Hence, increased agitation will have little effect on mass transfer except at very high agitation.

For a gas–liquid–solid dispersion, such as in fermentation, the same principles hold. However, increased agitation increases the number of gas bubbles and hence the interfacial area. The mass-transfer coefficients from the gas bubble to the liquid and from the liquid to the solid are relatively unaffected.

Equations for Mass Transfer to Small Particles

Mass transfer to small particles <0.6 mm

Equations for predicting mass transfer to small particles in suspension have been developed which cover three size ranges of particles. The equation for particles <0.6 mm (600 μm) is discussed first.

The following equation has been shown to hold for predicting mass-transfer coefficients from small gas bubbles such as oxygen or air to the liquid phase or from the liquid phase to the surface of small catalyst particles, microorganisms, other solids, or liquid drops (B2, C3):

Equation 7.4-1.

$$k'_L = \frac{2D_{AB}}{D_p} + 0.31 N_{\text{Sc}}^{-2/3}\left(\frac{\Delta\rho\,\mu_c g}{\rho_c^2}\right)^{1/3}$$

where D_{AB} is the diffusivity of the solute A in solution in m^2/s, D_p is the diameter of the gas bubble or the solid particle in m, μ_c is the viscosity of the solution in kg/m · s, $g = 9.80665$ m/s^2, $\Delta\rho = (\rho_c - \rho_p)$ or $(\rho_p - \rho_c)$, ρ_c is the density of the continuous phase in kg/m^3, and ρ_p is the density of the gas or solid particle. The value of $\Delta\rho$ is always positive.

The first term on the right in Eq. (7.4-1) is the molecular diffusion term, and the second term is that due to free fall or rise of the sphere due to gravitational forces. This equation has been experimentally checked for dispersions of low-density solids in agitated dispersions and for small gas bubbles in agitated systems.

EXAMPLE 7.4-1. Mass Transfer from Air Bubbles in Fermentation

Calculate the maximum rate of absorption of O_2 in a fermenter from air bubbles at 1 atm abs pressure having diameters of 100 μm at 37°C into water having a zero concentration of dissolved O_2. The solubility of O_2 from air in water at 37°C is 2.26×10^{-7} g mol O_2/cm^3 liquid or 2.26×10^{-4} kg mol O_2/m^3. The diffusivity of O_2 in water at 37°C is 3.25×10^{-9} m^2/s. Agitation is used to produce the air bubbles.

Solution: The mass-transfer resistance inside the gas bubble to the outside interface of the bubble can be neglected since it is negligible (B2). Hence, the mass-transfer coefficient k'_L outside the bubble is needed. The given data are

$$D_p = 100\,\mu\text{m} = 1 \times 10^{-4}\text{ m} \qquad D_{AB} = 3.25 \times 10^{-9}\text{ m}^2/\text{s}$$

At 37°C,

$$\mu_c(\text{water}) = 6.947 \times 10^{-4}\text{ Pa}\cdot\text{s} = 6.947 \times 10^{-4}\text{ kg/m}\cdot\text{s}$$

$$\rho_c(\text{water}) = 994\text{ kg/m}^3 \qquad \rho_p(\text{air}) = 1.13\text{ kg/m}^3$$

$$N_{\text{Sc}} = \frac{\mu_c}{\rho_c D_{AB}} = \frac{6.947 \times 10^{-4}}{(994)(3.25 \times 10^{-9})} = 215$$

$$N_{\text{Sc}}^{2/3} = (215)^{2/3} = 35.9 \qquad \Delta\rho = \rho_c - \rho_p = 994 - 1.13 = 993\text{ kg/m}^3$$

Substituting into Eq. (7.4-1),

$$k'_L = \frac{2D_{AB}}{D_p} + 0.31 N_{\text{Sc}}^{-2/3}\left(\frac{\Delta\rho\,\mu_c g}{\rho_c^2}\right)^{1/3}$$

$$= \frac{2(3.25 \times 10^{-9})}{1 \times 10^{-4}} + \frac{0.31}{35.9}\left[\frac{993 \times 6.947 \times 10^{-4} \times 9.806}{(994)^2}\right]^{1/3}$$

$$= 6.50 \times 10^{-5} + 16.40 \times 10^{-5} = 2.290 \times 10^{-4}\text{ m/s}$$

The flux is as follows, assuming $k_L = k'_L$ for dilute solutions:

$$N_A = k_L(c_{A1} - c_{A2}) = 2.290 \times 10^{-4}(2.26 \times 10^{-4} - 0)$$

$$= 5.18 \times 10^{-8}\text{ kg mol O}_2/\text{s}\cdot\text{m}^2$$

Knowing the total number of bubbles and their area, the maximum possible rate of transfer of O_2 to the fermentation liquid can be calculated.

In Example 7.4-1, k_L was small. For mass transfer of O_2 in a solution to a microorganism with $D_p \cong 1$ μm, the term $2D_{AB}/D_p$ would be 100 times larger. Note that at large diameters the second term in Eq. (7.4-1) becomes small and the mass-transfer coefficient k_L becomes essentially independent of size D_p. In agitated vessels with gas introduced below the agitator in aqueous solutions, or when liquids are aerated with sintered plates, the gas bubbles are often in the size range covered by Eq. (7.4-1) (B2, C3, T1).

In aerated mixing vessels, the mass-transfer coefficients are essentially independent of the power input. However, as the power is increased, the bubble size decreases and the mass transfer coefficient continues to follow Eq. (7.4-1). The dispersions include those in which the solid particles are just completely suspended in mixing vessels. Increase in agitation intensity above the level needed for complete suspension of these small particles results in only a small increase in k_L (C3).

Equation (7.4-1) has also been shown to apply to heat transfer and can be written as follows (B2, C3):

Equation 7.4-2.

$$N_{\mathrm{Nu}} = \frac{hD_p}{k} = 2.0 + 0.31 N_{\mathrm{Pr}}^{1/3} \left(\frac{D_p^3 \rho_c \, \Delta\rho g}{\mu_c^2} \right)^{1/3}$$

Mass transfer to large gas bubbles >2.5 mm

For large gas bubbles or liquid drops >2.5 mm, the mass-transfer coefficient can be predicted by

Equation 7.4-3.

$$k'_L = 0.42 N_{\mathrm{Sc}}^{-0.5} \left(\frac{\Delta\rho \, \mu_c g}{\rho_c^2} \right)^{1/3}$$

Large gas bubbles are produced when pure liquids are aerated in mixing vessels and sieve-plate columns (C1). In this case the mass-transfer coefficient k'_L or k_L is independent of the bubble size and is constant for a given set of physical properties. For the same physical properties the large-bubble Eq. (7.4-3) gives values of k_L about three to four times larger than Eq. (7.4-1) for small particles. Again, Eq. (7.4-3) shows that the k_L is essentially independent of agitation intensity in an agitated vessel and gas velocity in a sieve-tray tower.

Mass transfer to particles in transition region

In mass transfer in the transition region between small and large bubbles in the size range 0.6–2.5 mm, the mass-transfer coefficient can be approximated by assuming that it increases linearly with bubble diameter (B2, C3).

Mass transfer to particles in highly turbulent mixers

In the preceding three regions, the density difference between phases is sufficiently large to cause the force of gravity to primarily determine the mass-transfer coefficient. This also includes solids just completely suspended in mixing vessels. When agitation power is increased beyond that needed for suspension of solid or liquid particles and the turbulence forces become larger than the gravitational forces, Eq. (7.4-1) is not followed, and Eq. (7.4-4) should be used where small increases in are observed (B2, C3):

Equation 7.4-4.

$$k'_L N_{\mathrm{Sc}}^{2/3} = 0.13 \left(\frac{(P/V)\mu_c}{\rho_c^2} \right)^{1/4}$$

where P/V is power input per unit volume as defined in Section 3.4. The data deviate substantially by up to 60% from this correlation. In the case of gas–liquid dispersions it is quite impractical for agitation systems to exceed gravitational forces.

The experimental data are complicated by the fact that very small particles are easily suspended, and if their size is on the order of the smallest eddies, the mass-transfer coefficient will remain constant until a large increase in power input is added above that required for suspension.

MOLECULAR DIFFUSION PLUS CONVECTION AND CHEMICAL REACTION

Different Types of Fluxes and Fick's Law

In Section 6.2B the flux J_A^* was defined as the molar flux of A in kg mol A/s · m^2 relative to the molar average velocity v_M of the whole or bulk stream. Also, N_A was defined as the molar flux of A relative to stationary coordinates. Fluxes and velocities can also be defined in other ways. Table 7.5-1 lists the different types of fluxes and velocities often used in binary systems.

Table 7.5-1. Different Types of Fluxes and Velocities in Binary Systems

	Mass Flux (kg A/s · m²)	**Molar Flux (kg mol A/s · m²)**
Relative to fixed coordinates	$n_A = \rho_A v_A$	$N_A = c_A v_A$
Relative to molar average velocity v_M	$j_A^* = \rho_A(v_A - v_M)$	$J_A^* = c_A(v_A - v_M)$
Relative to mass average velocity v	$j_A = \rho_A(v_A - v)$	$J_A = c_A(v_A - v)$
	Relations Between Fluxes Above	
$N_A + N_B = c v_M$	$N_A = n_A / M_A$	$N_A = J_A + c_A v$
$J_A^* + J_B^* = 0$	$J_A = j_A / M_A$	$n_A + n_B = \rho v$
$j_A + j_B = 0$	$N_A = J_A^* + c_A v_M$	$n_A = j_A + \rho_A v$
	Different Forms of Fick's Law for Diffusion Flux	
$J_A^* = -cD_{AB}\, dx_A/dz$	$j_A = -\rho D_{AB}\, dw_A/dz$	

The velocity v is the mass average velocity of the stream relative to stationary coordinates and can be obtained by actually weighing the flow for a timed increment. It is related to the velocity v_A and v_B by

Equation 7.5-1.

$$v = w_A v_A + w_B v_B = \frac{\rho_A}{\rho} v_A + \frac{\rho_B}{\rho} v_B$$

where w_A is ρ_A/ρ, the weight fraction of A; w_B is the weight fraction of B; and v_A is the velocity of A relative to stationary coordinates in m/s. The molar average velocity v_M in m/s is relative to stationary coordinates:

Equation 7.5-2.

$$v_M = x_A v_A + x_B v_B = \frac{c_A}{c} v_A + \frac{c_B}{c} v_B$$

The molar diffusion flux relative to the molar average velocity v_M defined previously is

Equation 7.5-3.

$$J_A^* = c_A(v_A - v_M)$$

The molar diffusion flux J_A relative to the mass average velocity v is

Equation 7.5-4.

$$J_A = c_A(v_A - v)$$

Fick's law from Table 7.5-1 as given previously is relative to v_M:

Equation 7.5-5.

$$J_A^* = -cD_{AB}\frac{dx_A}{dz}$$

Fick's law can also be defined in terms of a mass flux relative to v as given in Table 7.5-1:

Equation 7.5-6.

$$j_A = -\rho D_{AB}\frac{dw_A}{dz}$$

EXAMPLE 7.5-1. Proof of Mass Flux Equation

Table 7.5-1 gives the following relation:

Equation 7.5-7.

$$j_A + j_B = 0$$

Prove this relationship using the definitions of the fluxes in terms of velocities.

Solution: From Table 7.5-1, substituting $\rho_A(v_A - v)$ for j_A and $\rho_B(v_B - v)$ for j_B, and rearranging,

Equation 7.5-8.

$$\rho_A v_A - \rho_A v + \rho_B v_B - \rho_B v = 0$$

Equation 7.5-9.

$$\rho_A v_A + \rho_B v_B - v(\rho_A + \rho_B) = 0$$

Substituting Eq. (7.5-1) for v and ρ for $\rho_A + \rho_B$, the identity is proved.

Equation of Continuity for a Binary Mixture

A general equation can be derived for a binary mixture of A and B for diffusion and convection that also includes the terms for unsteady-state diffusion and chemical reaction. We shall make a mass balance on component A on an element $\Delta x \Delta y \Delta z$ fixed in space as shown in Fig. 7.5-1. The general mass balance on A is

Equation 7.5-10.

$$\begin{pmatrix}\text{rate of}\\ \text{mass } A \text{ in}\end{pmatrix} - \begin{pmatrix}\text{rate of}\\ \text{mass } A \text{ out}\end{pmatrix} + \begin{pmatrix}\text{rate of}\\ \text{generation of mass } A\end{pmatrix} = \begin{pmatrix}\text{rate of}\\ \text{accumulation}\\ \text{of mass } A\end{pmatrix}$$

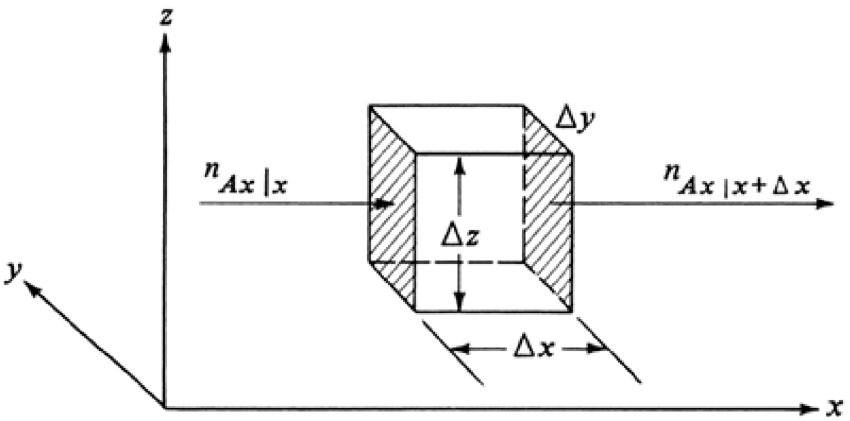


Figure 7.5-1. Mass balance for A in a binary mixture.

The rate of mass A entering in the direction relative to stationary coordinates is $(n_{Ax/x})\Delta y\,\Delta z$ kg A/s and leaving is $(n_{Ax/x+\Delta x})\Delta y\,\Delta z$. Similar terms can be written for the y and z directions. The rate of chemical production of A is r_A kg A generated/s · m^3 volume and the total rate generated is $r_A(\Delta x\,\Delta y\,\Delta z)$ kg A/s. The rate of accumulation of A is $(\partial\rho_A/\partial t)\Delta x\,\Delta y\,\Delta z$. Substituting into Eq. (7.5-10) and letting Δx, Δy, and Δz approach zero,

Equation 7.5-11.

$$\frac{\partial \rho_A}{\partial t} + \left(\frac{\partial n_{Ax}}{\partial x} + \frac{\partial n_{Ay}}{\partial y} + \frac{\partial n_{Az}}{\partial z}\right) = r_A$$

In vector notation,

Equation 7.5-12.

$$\frac{\partial \rho_A}{\partial t} + (\boldsymbol{\nabla}\cdot \boldsymbol{n}_A) = r_A$$

Dividing both sides of Eq. (7.5-11) by M_A,

Equation 7.5-13.

$$\frac{\partial c_A}{\partial t} + \left(\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z}\right) = R_A$$

where R_A is kg mol A generated/s · m^3. Substituting N_A and Fick's law from Table 7.5-1,

Equation 7.5-14.

$$N_A = -cD_{AB}\frac{dx_A}{dz} + c_A v_M$$

and writing the equation for all three directions, Eq. (7.5-13) becomes

Equation 7.5-15.

$$\frac{\partial c_A}{\partial t} + (\boldsymbol{\nabla}\cdot c_A \boldsymbol{v}_M) - (\boldsymbol{\nabla}\cdot cD_{AB}\boldsymbol{\nabla}x_A) = R_A$$

This is the final general equation.

Special Cases of the Equation of Continuity

Equation for constant c and D_{AB}

In diffusion with gases the total pressure P is often constant. Then, since $c = P/RT$, c is constant for constant temperature T. Starting with the general equation (7.5-15) and substituting $\nabla x_A = \nabla c_A/c$, we obtain

Equation 7.5-16.

$$\frac{\partial c_A}{\partial t} + c_A(\nabla \cdot \boldsymbol{v}_M) + (\boldsymbol{v}_M \cdot \nabla c_A) - D_{AB}\nabla^2 c_A = R_A$$

Equimolar counterdiffusion for gases

For the special case of equimolar counterdiffusion of gases at constant pressure and no reaction, c = constant, $v_M = 0$, D_{AB} = constant, $R_A = 0$, and Eq. (7.5-15) becomes

Equation 7.1-9.

$$\frac{\partial c_A}{\partial t} = D_{AB}\left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2}\right)$$

This equation is Eq. (7.1-9), derived previously, which is also used for unsteady-state diffusion of a dilute solute A in a solid or a liquid when D_{AB} is constant.

Equation for constant ρ and D_{AB} (liquids)

In dilute liquid solutions, the mass density ρ and D_{AB} can often be considered constant. Starting with Eq. (7.5-12) we substitute $n_A = -\rho D_{AB}\nabla w_A + \rho_A v$ from Table 7.5-1 into this equation. Then using the fact that for constant ρ, $\nabla w_A = \nabla \rho_A/\rho$ and also that $(\nabla \cdot v) = 0$, substituting these into the resulting equation, and dividing both sides by M_A, we obtain

Equation 7.5-17.

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

Special Cases of the General Diffusion Equation at Steady State

Introduction and physical conditions at the boundaries

The general equation for diffusion and convection of a binary mixture in one direction with no chemical reaction has been given previously:

Equation 6.2-14.

$$N_A = -cD_{AB}\frac{dx_A}{dz} + \frac{c_A}{c}(N_A + N_B)$$

To integrate this equation at steady state, it is necessary to specify the boundary conditions at z_1 and z_2. In many mass-transfer problems the molar ratio N_A/N_B is determined by the physical conditions occurring at the two boundaries.

As an example, one boundary of the diffusion path may be impermeable to species *B* because *B* is insoluble in the phase at this boundary. Diffusion of ammonia (*A*) and nitrogen (*B*) through a gas phase to a water phase at the boundary is such a case, since nitrogen is essentially insoluble in water. Hence, $N_B = 0$, since at steady state N_B must have the same value at all points in the path of $z_2 - z_1$. In some cases, a heat balance in the adjacent phase at the boundary can determine the flux ratios. For example, if component *A* condenses at a boundary and releases its latent heat to component *B*, which vaporizes and diffuses back, the ratios of the latent heats determine the flux ratio.

In another example, the boundary concentration can be fixed by having a large volume of a phase flowing rapidly by with a given concentration x_{A1}. In some cases the concentration x_{A1} may be set by an equilibrium condition, whereby x_{A1} is in equilibrium with some fixed composition at the boundary. Chemical reactions can also influence the rates of diffusion and the boundary conditions.

Equimolar counterdiffusion

For the special case of equimolar counterdiffusion, where $N_A = -N_B$, Eq. (6.2-14) becomes, as shown previously, for steady state and constant *c*,

Equation 7.5-18.

$$N_A = J_A^* = -cD_{AB}\frac{dx_A}{dz} = \frac{D_{AB}(c_{A1} - c_{A2})}{z_2 - z_1}$$

Diffusion of A through stagnant, nondiffusing B

For gas *A* diffusing through stagnant nondiffusing gas *B*, $N_B = 0$, and integration of Eq. (6.2-14) gives Eq. (6.2-22):

Equation 6.2-22.

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

Several other more complicated cases of integration of Eq. (6.2-14) are considered next.

Diffusion and chemical reaction at a boundary

Often in catalytic reactions, where *A* and *B* are diffusing to and from a catalyst surface, the relation between the fluxes N_A and N_B at steady state is controlled by the stoichiometry of a reaction at a boundary. An example is gas *A* diffusing from the bulk gas phase to the catalyst surface, where it reacts instantaneously and irreversibly in a heterogeneous reaction as follows:

Equation 7.5-19.

$$A \rightarrow 2B$$

Gas *B* then diffuses back, as shown in Fig. 7.5-2.

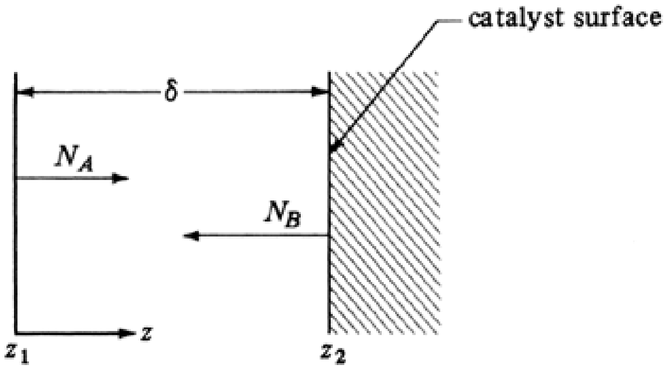


Figure 7.5-2. Diffusion of A and heterogeneous reaction at a surface.

At steady state 1 mol of A diffuses to the catalyst for every 2 mol of B diffusing away, or $N_B = -2N_A$. The negative sign indicates that the fluxes are in opposite directions. Rewriting Eq. (6.2-14) in terms of mole fractions,

Equation 7.5-20.

$$N_A = -cD_{AB}\frac{dx_A}{dz} + x_A(N_A + N_B)$$

Next, substituting $N_B = -2N_A$ into Eq. (7.5-20),

Equation 7.5-21.

$$N_A = -cD_{AB}\frac{dx_A}{dz} + x_A(N_A - 2N_A)$$

Rearranging and integrating with constant c (P = constant), we obtain the following:

Instantaneous surface reaction

Equation 7.5-22.

$$N_A\int_{z_1=0}^{z_2=\delta} dz = -cD_{AB}\int_{x_{A1}}^{x_{A2}} \frac{dx_A}{1 + x_A}$$

Equation 7.5-23.

$$N_A = \frac{cD_{AB}}{\delta}\ln\frac{1 + x_{A1}}{1 + x_{A2}}$$

Since the reaction is instantaneous, $x_{A2} = 0$, because no A can exist next to the catalyst surface. Equation (7.5-23) describes the overall rate of the process of diffusion plus instantaneous chemical reaction.

Slow surface reaction

If the heterogeneous reaction at the surface is not instantaneous but slow for the reaction $A \rightarrow 2B$, and the reaction is first order,

Equation 7.5-24.

$$N_{Az=\delta} = k_1' c_A = k_1' c x_A$$

where k_1' is the first-order heterogeneous reaction velocity constant in m/s. Equation (7.5-23) still holds for this case, but the boundary condition x_{A2} at $z = \delta$ is obtained by solving for x_A in Eq. (7.5-24),

Equation 7.5-25.

$$x_A = x_{A2} = \frac{N_{Az=\delta}}{k_1' c} = \frac{N_A}{k_c'}$$

For steady state, $N_{Az=\delta} = N_A$. Substituting Eq. (7.5-25) into (7.5-23),

Equation 7.5-26.

$$N_A = \frac{cD_{AB}}{\delta} \ln \frac{1 + x_{A1}}{1 + N_A/k_1' c}$$

The rate in Eq. (7.5-26) is less than in Eq. (7.5-23), since the denominator in the latter equation is $1 + x_{A2} = 1 + 0$ and in the former is $1 + N_A/k_1' c$.

EXAMPLE 7.5-2. Diffusion and Chemical Reaction at a Boundary

Pure gas A diffuses from point 1 at a partial pressure of 101.32 kPa to point 2 a distance 2.00 mm away. At point 2 it undergoes a chemical reaction at the catalyst surface and $A \rightarrow 2B$. Component B diffuses back at steady state. The total pressure is $P = 101.32$ kPa. The temperature is 300 K and $D_{AB} = 0.15 \times 10^{-4}$ m^2/s.

a. For instantaneous rate of reaction, calculate x_{A2} and N_A.

b. For a slow reaction where $k_1' = 5.63 \times 10^{-3}$ m/s, calculate x_{A2} and N_A.

Solution: For part (a), $p_{A2} = x_{A2} = 0$ since no A can exist next to the catalyst surface. Since $N_B = -2N_A$, Eq. (7.5-23) will be used as follows: $\delta = 2.00 \times 10^{-3}$m, $T = 300$ K, $c = P/RT = 101.32 \times 10^3/(8314 \times 300) = 4.062 \times 10^{-2}$ kg mol/m^3, $x_{A1} = p_{A1}/P = 101.32 \times 10^3/101.32 \times 10^3 = 1.00$.

$$N_A = \frac{cD_{AB}}{\delta} \ln \frac{1 + x_{A1}}{1 + x_{A2}} = \frac{(4.062 \times 10^{-2})(0.15 \times 10^{-4})}{2.00 \times 10^{-3}} \ln \frac{1 + 1.00}{1 + 0}$$

$$= 2.112 \times 10^{-4} \text{ kg mol } A/\text{s} \cdot \text{m}^2$$

For part (b), from Eq. (7.5-25), $x_{A2} = N_A/k_1' c = N_A/(5.63 \times 10^{-3} \times 4.062 \times 10^{-2})$. Substituting into Eq. (7.5-26),

$$N_A = \frac{(4.062 \times 10^{-2})(0.15 \times 10^{-4})}{2.00 \times 10^{-3}} \ln \frac{1 + 1.00}{1 + N_A/(5.63 \times 10^{-3} \times 4.062 \times 10^{-2})}$$

Solving by trial and error, $N_A = 1.004 \times 10^{-4}$ kg mol A/s · m^2. Then $x_{A2} = (1.004 \times 10^{-4})/(5.63 \times 10^{-3} \times 4.062 \times 10^{-2}) = 0.4390$.

Even though in part (a) of Example 7.5-2 the rate of reaction is instantaneous, the flux N_A is diffusion-controlled. As the reaction rate slows, the flux N_A is decreased also.

Diffusion and homogeneous reaction in a phase

Equation (7.5-23) was derived for the case of chemical reaction of *A* at the boundary on a catalyst surface. In some cases component *A* undergoes an irreversible chemical reaction in the homogeneous phase *B* while diffusing, as follows: $A \rightarrow C$. Assume that component *A* is very dilute in phase *B*, which can be a gas or a liquid. Then at steady state the equation for diffusion of *A* is as follows, where the bulk-flow term is dropped:

Equation 7.5-27.

$$N_{Az} = -D_{AB}\frac{dc_A}{dz} + 0$$

Writing a material balance on *A* shown in Fig. 7.5-3 for the Δz element for steady state,

Equation 7.5-28.

$$\begin{pmatrix}\text{rate of}\\ A\text{ in}\end{pmatrix} + \begin{pmatrix}\text{rate of}\\ \text{generation of } A\end{pmatrix} = \begin{pmatrix}\text{rate of}\\ A\text{ out}\end{pmatrix} + \begin{pmatrix}\text{rate of}\\ \text{accumulation of } A\end{pmatrix}$$

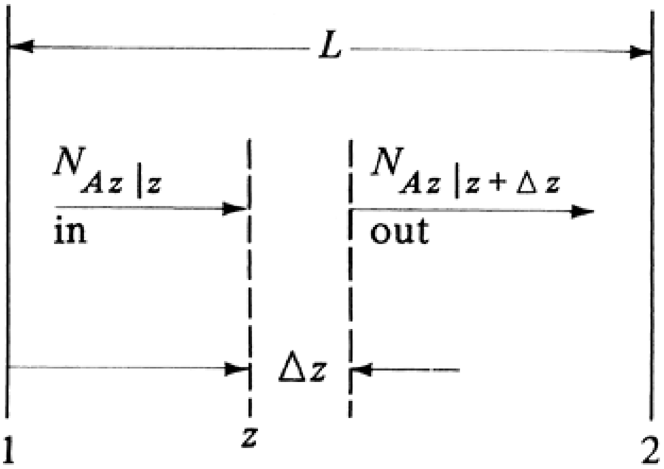


Figure 7.5-3. Homogeneous chemical reaction and diffusion in a fluid.

The first-order reaction rate of *A* per m^3 volume is

Equation 7.5-29.

$$\text{rate of generation} = -k'c_A$$

where k' is the reaction velocity constant in s^{-1}. Substituting into Eq. (7.5-28) for a cross-sectional area of 1 m^2 with the rate of accumulation being 0 at steady state,

Equation 7.5-30.

$$N_{Az|z}(1) - k'c_A(1)(\Delta z) = N_{Az|z+\Delta z}(1) + 0$$

Next we divide through by Δz and let Δz approach zero:

Equation 7.5-31.

$$-\frac{dN_{Az}}{dz} = k'c_A$$

Substituting Eq. (7.5-27) into (7.5-31),

Equation 7.5-32.

$$\frac{d^2c_A}{dz^2} = \frac{k'}{D_{AB}}c_A$$

The boundary conditions are $c_A = c_{A1}$ for $z = 0$ and $c_A = c_{A2}$ for $z = L$. Solving,

Equation 7.5-33.

$$c_A = \frac{c_{A2}\sinh\left(\sqrt{\frac{k'}{D_{AB}}}z\right) + c_{A1}\sinh\left[\sqrt{\frac{k'}{D_{AB}}}(L-z)\right]}{\sinh\left(\sqrt{\frac{k'}{D_{AB}}}L\right)}$$

This equation can be used at steady state to calculate c_A at any z and can be used for reactions in gases, liquids, or even solids, where the solute A is dilute.

As an alternative derivation of Eq. (7.5-32), we can use Eq. (7.5-17) for constant ρ and D_{AB}:

Equation 7.5-17.

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

We set the first term $\partial c_A/\partial t = 0$ for steady state. Since we are assuming dilute solutions and neglecting the bulk flow term, $v = 0$, making the second term in Eq. (7.5-17) zero. For a first-order reaction of A where A disappears, $R_A = -k'c_A$ kg mol A generated/s · m^3. Writing the diffusion term $-D_{AB}\nabla^2 c_A$ for the z direction only, we obtain

Equation 7.5-34.

$$D_{AB}\frac{d^2c_A}{dz^2} = k'c_A$$

which is, of course, identical to Eq. (7.5-32).

Unsteady-State Diffusion and Reaction in a Semi-infinite Medium

Here we consider a case where dilute A is absorbed at the surface of a solid or stagnant fluid phase and then unsteady-state diffusion and reaction occur in the phase. The fluid or solid phase B is considered semi-infinite. At the surface, where $z = 0$, the concentration of c_A is kept constant at c_{A0}. The dilute solute A reacts by a first-order mechanism

Equation 7.5-35.

$$A + B \rightarrow C$$

and the rate of generation is $-k'c_A$. The same diagram as in Fig. 7.5-3 holds. Using Eq. (7.5-30) but substituting $(\partial c_A/\partial t)(\Delta z)(1)$ for the rate of accumulation,

Equation 7.5-36.

$$N_{Az|z}(1) - k'c_A(1)(\Delta z) = N_{Az|z+\Delta z}(1) + \left(\frac{\partial c_A}{\partial t}\right)(\Delta z)(1)$$

This becomes

Equation 7.5-37.

$$\frac{\partial c_A}{\partial t} = D_{AB}\frac{\partial^2 c_A}{\partial z^2} - k' c_A$$

The initial and boundary conditions are

Equation 7.5-38.

$$\begin{aligned} &t = 0, && c_A = 0 && \text{for } z > 0 \\ &z = 0, && c_A = c_{A0} && \text{for } t > 0 \\ &z = \infty, && c_A = 0 && \text{for } t > 0 \end{aligned}$$

The solution by Danckwerts (D1) is

Equation 7.5-39.

$$\begin{aligned} \frac{c_A}{c_{A0}} &= \tfrac{1}{2}\exp(-z\sqrt{k'/D_{AB}})\cdot \operatorname{erfc}\left(\frac{z}{2\sqrt{tD_{AB}}} - \sqrt{k't}\right) \\ &\quad + \tfrac{1}{2}\exp(z\sqrt{k'/D_{AB}})\cdot \operatorname{erfc}\left(\frac{z}{2\sqrt{tD_{AB}}} + \sqrt{k't}\right) \end{aligned}$$

The total amount Q of A absorbed up to time t is

Equation 7.5-40.

$$Q = c_{A0}\sqrt{D_{AB}/k'}\left[(k't + \tfrac{1}{2})\operatorname{erf}\sqrt{k't} + \sqrt{k't/\pi}\,e^{-k't}\right]$$

where Q is kg mol A absorbed/m^2. Many actual cases are approximated by this case. The equation is useful where absorption occurs at the surface of a stagnant fluid or a solid and unsteady-state diffusion and reaction occur in the solid or fluid. The results can be used to measure the diffusivity of a gas in a solution, to determine reaction rate constants k' of dissolved gases, and to determine solubilities of gases in liquids with which they react. Details are given elsewhere (D3).

EXAMPLE 7.5-3. Reaction and Unsteady-State Diffusion

Pure CO_2 gas at 101.32 kPa pressure is absorbed into a dilute alkaline buffer solution containing a catalyst. The dilute, absorbed solute CO_2 undergoes a first-order reaction, with $k' = 35\ \text{s}^{-1}$ and $D_{AB} = 1.5 \times 10^{-9}\ \text{m}^2/\text{s}$. The solubility of CO_2 is 2.961×10^{-7} kg mol/m$^3 \cdot$ Pa (D3). The surface is exposed to the gas for 0.010 s. Calculate the kg mol CO_2 absorbed/m^2 surface.

***Solution*.** For use in Eq. (7.5-40), $k't = 35(0.01) = 0.350$. Also, $c_{A0} = 2.961 \times 10^{-7}$ (kg mol/m$^3 \cdot$ Pa)(101.32×10^3 Pa) $= 3.00 \times 10^{-2}$ kg mol SO_2/m^3.

$$\begin{aligned} Q &= (3.00 \times 10^{-2})\sqrt{1.5 \times 10^{-9}/35}\left[(0.35 + \tfrac{1}{2})\operatorname{erf}\sqrt{0.35} + \sqrt{0.35/\pi}\,e^{-0.35}\right] \\ &= 1.458 \times 10^{-7}\ \text{kg mol } CO_2/\text{m}^2 \end{aligned}$$

Multicomponent Diffusion of Gases

The equations derived in this chapter have been for a binary system of *A* and *B*, which is probably the most important and most useful one. However, multicomponent diffusion sometimes occurs where three or more components *A, B, C*, . . . are present. The simplest case is for diffusion of *A* in a gas through a stagnant, nondiffusing mixture of *B, C, D*, . . . at constant total pressure. Hence, $N_B = 0$, $N_c = 0$, ... The final equation derived using the Stefan–Maxwell method (G1) for steady-state diffusion is

Equation 7.5-41.

$$N_A = \frac{D_{Am} P}{RT(z_2 - z_1) p_{iM}} (p_{A1} - p_{A2})$$

where p_{iM} is the log mean of $p_{i1} = P - p_{A1}$ and $p_{i2} = P - p_{A2}$. Also,

Equation 7.5-42.

$$D_{Am} = \frac{1}{x'_B / D_{AB} + x'_C / D_{AC} + \cdots}$$

where x'_B = mol *B*/mol inerts = $x_B/(1 - x_A)$, $x'_C = x_C/(1 - x_A), \ldots$.

EXAMPLE 7.5-4. Diffusion of A Through Nondiffusing B and C

At 298 K and 1 atm total pressure, methane (*A*) is diffusing at steady state through nondiffusing argon (*B*) and helium (*C*). At $z_1 = 0$, the partial pressures in atm are $p_{A1} = 0.4$, $p_{B1} = 0.4$, and $p_{C1} = 0.2$, and at $z_2 = 0.005$ m, $p_{A2} = 0.1$, $p_{B2} = 0.6$, and $p_{C2} = 0.3$. The binary diffusivities from Table 6.2-1 are $D_{AB} = 2.02 \times 10^{-5}$ m^2/s, $D_{AC} = 6.75 \times 10^{-5}$ m^2/s, and $D_{BC} = 7.29 \times 10^{-5}$ m^2/s. Calculate N_A.

***Solution*:** At point 1, $x'_B = x_B/(1 - x_A) = 0.4/(1 - 0.4) = 0.667$. At point 2, $x'_B = 0.6/(1 - 0.1) = 0.667$. The value of x'_B is constant throughout the path. Also, $x'_C = x_C/(1 - x_A) = 0.2/(1 - 0.4) = 0.333$.

Substituting into Eq. (7.5-42),

$$\begin{aligned} D_{Am} &= \frac{1}{x'_B/D_{AB} + x'_C/D_{AC}} = \frac{1}{0.667/2.02 \times 10^{-5} + 0.333/6.75 \times 10^{-5}} \\ &= 2.635 \times 10^{-5}\ \text{m}^2/\text{s} \end{aligned}$$

For calculating p_{iM}, $p_{i1} = P - p_{A1} = 1.0 - 0.4 = 0.6$ atm, $p_{i2} = P - p_{A2} = 1.0 - 0.1 = 0.90$. Then,

$$p_{iM} = \frac{p_{i2} - p_{i1}}{\ln(p_{i2}/p_{i1})} = \frac{0.90 - 0.60}{\ln(0.90/0.60)} = 0.740\ \text{atm} = 7.496 \times 10^4\ \text{Pa}$$

$$p_{A1} = 0.4(1.01325 \times 10^5) = 4.053 \times 10^4\ \text{Pa}$$

$$p_{A2} = 0.1(1.01325 \times 10^5) = 1.013 \times 10^4\ \text{Pa}$$

Substituting into Eq. (7.5-41),

$$
\begin{aligned}
N_A &= \frac{D_{Am}P}{RT(z_2 - z_1)p_{iM}}(p_{A1} - p_{A2}) \\
&= \frac{(2.635 \times 10^{-5})(1.01325 \times 10^5)(4.053 - 1.013)(10^4)}{(8314)(298)(0.005 - 0)(7.496 \times 10^4)} \\
&= 8.74 \times 10^{-5} \text{ kg mol } A/\text{s} \cdot \text{m}^2
\end{aligned}
$$

Using atm pressure units,

$$
\begin{aligned}
N_A &= \frac{D_{Am}P}{RT(z_2 - z_1)p_{iM}}(p_{A1} - p_{A2}) = \frac{(2.635 \times 10^{-5})(1.0)(0.4 - 0.1)}{(82.06 \times 10^{-3})(298)(0.005 - 0)(0.740)} \\
&= 8.74 \times 10^{-5} \text{ kg mol } A/\text{s} \cdot \text{m}^2
\end{aligned}
$$

A number of analytical solutions have been obtained for other cases, such as for equimolar diffusion of three components, diffusion of components *A* and *B* through stagnant *C*, and the general case of two or more components diffusing in a multicomponent mixture. These are discussed in detail with examples by Geankoplis (G1); the reader is referred there for further details.

DIFFUSION OF GASES IN POROUS SOLIDS AND CAPILLARIES

Introduction

In Section 6.5C diffusion in porous solids that depends on structure was discussed for liquids and gases. For gases it was assumed that the pores were very large and Fickian-type diffusion occurred. However, the pores are often small in diameter and the mechanism of diffusion is basically changed.

Diffusion of gases in small pores frequently occurs in heterogeneous catalysis where gases diffuse through very small pores to react on the surface of the catalyst. In freeze-drying of foods such as turkey meat, gaseous H_2O diffuses through very fine pores of the porous structure.

Since the pores or capillaries of porous solids are often small, the diffusion of gases may depend upon the diameter of the pores. We first define a mean free path λ, which is the average distance a gas molecule travels before it collides with another gas molecule:

Equation 7.6-1.

$$\lambda = \frac{3.2\mu}{P}\sqrt{\frac{RT}{2\pi M}}$$

where λ is in m, μ is viscosity in Pa · s, P is pressure in N/m^2, T is temperature in K, M = molecular weight in kg/kg mol, and $R = 8.3143 \times 10^3$ N · m/kg mol · K. Note that low pressures give large values of λ. For liquids, since λ is so small, diffusion follows Fick's law.

In the next sections we shall consider what happens to the basic mechanisms of diffusion in gases as the relative value of the mean free path compared to the pore diameter varies. The total pressure P in the system will be constant, but partial pressures of *A* and *B* may be different.

Knudsen Diffusion of Gases

In Fig. 7.6-1a a gas molecule *A* at partial pressure p_{A1} at the entrance to a capillary is diffusing through the capillary having a diameter *d* m. The total pressure *P* is constant throughout. The mean free path λ is large compared to the diameter *d*. As a result, the molecule collides with the wall and molecule–wall collisions are important. This type of diffusion is called *Knudsen diffusion.*

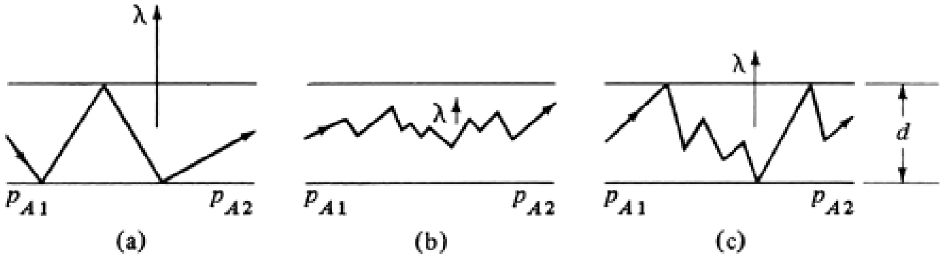


Figure 7.6-1. Types of diffusion of gases in small capillary tubes: (a) Knudsen gas diffusion, (b) molecular or Fick's gas diffusion, (c) transition gas diffusion.

The Knudsen diffusivity is independent of pressure *P* and is calculated from

Equation 7.6-2.

$$D_{KA} = \tfrac{2}{3}\bar{r}\,\bar{v}_A$$

where D_{KA} is diffusivity in m²/s, $\bar{r}$ is average pore radius in m, and $\bar{v}_A$ is the average molecular velocity for component *A* in m/s. Using the kinetic theory of gases to evaluate $\bar{v}_A$ the final equation for D_{KA} is

Equation 7.6-3.

$$D_{KA} = 97.0\bar{r}\left(\frac{T}{M_A}\right)^{1/2}$$

where M_A is molecular weight of *A* in kg/kg mol and *T* is temperature in K.

EXAMPLE 7.6-1. Knudsen Diffusivity of Hydrogen

A $H_2(A)$—$C_2H_6(B)$ gas mixture is diffusing in a pore of a nickel catalyst used for hydrogenation at 1.01325 × 10^5 Pa pressure and 373 K. The pore radius is 60 Å (angstrom). Calculate the Knudsen diffusivity D_{KA} of H_2.

***Solution*:** Substituting into Eq. (7.6-3) for $\bar{r} = 6.0 \times 10^{-9}$ m, $M_A = 2.016$, and $T = 373$ K,

$$D_{KA} = 97.0\bar{r}\left(\frac{T}{M_A}\right)^{1/2} = 97.0(6.0 \times 10^{-9})\left(\frac{373}{2.016}\right)^{1/2}$$

$$= 7.92 \times 10^{-6}\ \text{m}^2/\text{s}$$

The flux equation for Knudsen diffusion in a pore is

Equation 7.6-4.

$$N_A = -D_{KA}\frac{dc_A}{dz} = -\frac{D_{KA}}{RT}\frac{dp_A}{dz}$$

Integrating between $z_1 = 0$, $p_A = p_{A1}$ and $z_2 = L$, $p_A = p_{A2}$,

Equation 7.6-5.

$$N_A = \frac{D_{KA}P}{RTL}(x_{A1} - x_{A2}) = \frac{D_{KA}}{RTL}(p_{A1} - p_{A2})$$

The diffusion of *A* for Knudsen diffusion is completely independent of *B*, since *A* collides with the walls of the pore and not with *B*. A similar equation can be written for component *B*.

When the Knudsen number N_{Kn} defined as

Equation 7.6-6.

$$N_{\text{Kn}} = \frac{\lambda}{2\bar{r}}$$

is ≥10/1, the diffusion is primarily Knudsen, and Eq. (7.6-5) predicts the flux to within about a 10% error. As N_{Kn} gets larger, this error decreases, since the diffusion approaches the Knudsen type.

Molecular Diffusion of Gases

As shown in Fig. 7.6-1b, when the mean free path λ is small compared to the pore diameter *d* or where $N_{\text{Kn}} \leq 1/100$, molecule–molecule collisions predominate and molecule–wall collisions are few. Ordinary molecular or Fickian diffusion holds and Fick's law predicts the diffusion to within about 10%. The error diminishes as N_{Kn} gets smaller since the diffusion approaches more closely the Fickian type.

The equation for molecular diffusion given in previous sections is

Equation 7.6-7.

$$N_A = -\frac{D_{AB}P}{RT}\frac{dx_A}{dz} + x_A(N_A + N_B)$$

A flux ratio factor *α* can be defined as

Equation 7.6-8.

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

Combining Eqs. (7.6-7) and (7.6-8) and integrating for a path length of *L* cm,

Equation 7.6-9.

$$N_A = \frac{D_{AB}P}{\alpha RTL}\ln\frac{1 - \alpha x_{A2}}{1 - \alpha x_{A1}}$$

If the diffusion is equimolar, $N_A = -N_B$ and Eq. (7.6-7) becomes Fick's law. The molecular diffusivity D_{AB} is inversely proportional to the total pressure *P*.

Transition-Region Diffusion of Gases

As shown in Fig. 7.6-1c, when the mean free path λ and pore diameter are intermediate in size between the two limits given for Knudsen and molecular diffusion, transition-type diffusion occurs, where molecule–molecule and molecule–wall collisions are important in diffusion.

The transition-region diffusion equation can be derived by adding the momentum loss due to molecule–wall collisions in Eq. (7.6-4) and that due to molecule–molecule collisions in Eq. (7.6-7) on a slice of capillary. No chemical reactions are occurring. The final differential equation is (G1)

Equation 7.6-10.

$$N_A = -\frac{D_{NA}P}{RT}\frac{dx_A}{dz}$$

where

Equation 7.6-11.

$$D_{NA} = \frac{1}{(1-\alpha x_A)/D_{AB} + 1/D_{KA}}$$

This transition region diffusivity D_{NA} depends slightly on concentration x_A.

Integrating Eq. (7.6-10),

Equation 7.6-12.

$$N_A = \frac{D_{AB}P}{\alpha RTL}\ln\frac{1-\alpha x_{A2} + D_{AB}/D_{KA}}{1-\alpha x_{A1} + D_{AB}/D_{KA}}$$

This equation has been shown experimentally to be valid over the entire transition region (R1). It reduces to the Knudsen equation at low pressures and to the molecular diffusion equation at high pressures. An equation similar to Eq. (7.6-12) can also be written for component *B*.

The term D_{AB}/D_{KA} is proportional to $1/P$. Hence, as the total pressure P increases, the term D_{AB}/D_{KA} becomes very small and N_A in Eq. (7.6-12) becomes independent of total pressure, since $D_{AB}P$ is independent of P. At low total pressures Eq. (7.6-12) becomes the Knudsen diffusion equation (7.6-5), and the flux N_A becomes directly proportional to P for constant x_{A1} and x_{A2}.

This is illustrated, in Fig. 7.6-2, for a fixed capillary diameter where the flux increases as total pressure increases and then levels off at high pressure. The relative position of the curve depends, of course, on the capillary diameter and the molecular and Knudsen diffusivities. Using only a smaller diameter, D_{KA} would be smaller, and the Knudsen flux line would be parallel to the existing line at low pressures. At high pressures the flux line would asymptotically approach the existing horizontal line, since molecular diffusion is independent of capillary diameter.

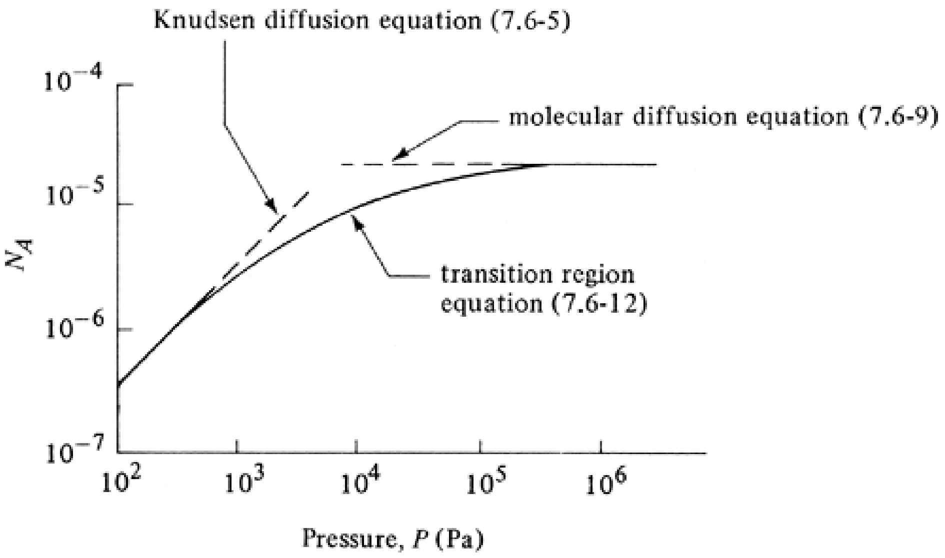


Figure 7.6-2. Effect of total pressure P on the diffusion flux N_A in the transition region.

If A is diffusing in a catalytic pore and reacts at the surface at the end of the pore so that $A \rightarrow B$, then at steady state, equimolar counterdiffusion occurs, or $N_A = -N_B$. Then from Eq. (7.6-8), $\alpha = 1 - 1 = 0$. The effective diffusivity D_{NA} from Eq. (7.6-11) becomes

Equation 7.6-13.

$$D'_{NA} = \frac{1}{1/D_{AB} + 1/D_{KA}}$$

The diffusivity is then independent of concentration and is constant. Integration of (7.6-10) then gives

Equation 7.6-14.

$$N_A = \frac{D'_{NA}P}{RTL}(x_{A1} - x_{A2}) = \frac{D'_{NA}}{RTL}(p_{A1} - p_{A2})$$

This simplified diffusivity D'_{NA} is often used in diffusion in porous catalysts even when equimolar counterdiffusion is not occurring. It greatly simplifies the equations for diffusion and reaction to use this simplified diffusivity.

An alternative simplified diffusivity can be obtained by using an average value of x_A in Eq. (7.6-11), to give

Equation 7.6-15.

$$D''_{NA} = \frac{1}{(1 - \alpha x_{A\,\mathrm{av}})/D_{AB} + 1/D_{KA}}$$

where $x_{A\mathrm{av}} = (x_{A1} + x_{A2})/2$. This diffusivity is more accurate than D'_{NA}. Integration of Eq. (7.6-10) gives

Equation 7.6-16.

$$N_A = \frac{D'_{NA}P}{RTL}(x_{A1} - x_{A2}) = \frac{D'_{NA}}{RTL}(p_{A1} - p_{A2})$$

Flux Ratios for Diffusion of Gases in Capillaries

Diffusion in open system

If diffusion in porous solids or channels with no chemical reaction is occurring where the total pressure P remains constant, then for an open binary counterdiffusing system, the ratio of N_A/N_B is constant in all of the three diffusion regimes and is (G1)

Equation 7.6-17.

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

Hence,

Equation 7.6-18.

$$\alpha = 1 - \sqrt{\frac{M_A}{M_B}}$$

In this case, gas flows past the two open ends of the system. However, when chemical reaction occurs, stoichiometry determines the ratio N_B/N_A, and not Eq. (7.6-17).

Diffusion in closed system

When molecular diffusion is occurring in a closed system, shown in Fig. 6.2-1, at constant total pressure P, equimolar counterdiffusion occurs.

EXAMPLE 7.6-2. Transition-Region Diffusion of He and N_2

A gas mixture at a total pressure of 0.10 atm abs and 298 K is composed of N_2 (A) and He (B). The mixture is diffusing through an open capillary 0.010 m long having a diameter of 5×10^{-6} m. The mole fraction of N_2 at one end is $x_{A1} = 0.8$ and at the other end is $x_{A2} = 0.2$. The molecular diffusivity D_{AB} is 6.98×10^{-5} m²/s at 1 atm, which is an average value determined by several investigators.

a. Calculate the flux N_A at steady state.
b. Use the approximate equations (7.6-14) and (7.6-16) for this case.

***Solution*:** The given values are $T = 273 + 25 = 298$ K, $\bar{r} = 5 \times 10^{-6}/2 = 2.5 \times 10^{-6}$ m, $L = 0.01$ m, $P = 0.1(1.01325 \times 10^5) = 1.013 \times 10^4$ Pa, $x_{A1} = 0.8$, $x_{A2} = 0.2$, $D_{AB} = 6.98 \times 10^{-5}$ m²/s at 1 atm. Other values needed are $M_A = 28.02$ kg/kg mol, $M_B = 4.003$.

The molecular diffusivity at 0.1 atm is $D_{AB} = 6.98 \times 10^{-5}/0.1 = 6.98 \times 10^{-4}$ m²/s. Substituting into Eq. (7.6-3) for the Knudsen diffusivity,

$$D_{KA} = 97.0(2.5 \times 10^{-6})\sqrt{298/28.02} = 7.91 \times 10^{-4}\ \text{m}^2/\text{s}$$

From Eq. (7.6-17),

$$\frac{N_B}{N_A} = -\sqrt{\frac{M_A}{M_B}} = -\sqrt{\frac{28.02}{4.003}} = -2.645$$

From Eq. (7.6-8),

$$\alpha = 1 + \frac{N_B}{N_A} = 1 - 2.645 = -1.645$$

Substituting into Eq. (7.6-12) for part (a),

$$N_A = \frac{(6.98 \times 10^{-4})(1.013 \times 10^4)}{(-1.645)(8314)(298)(0.01)} \ln \frac{1 + 1.645(0.2) + 6.98/7.91}{1 + 1.645(0.8) + 6.98/7.91}$$
$$= 6.40 \times 10^{-5} \text{ kg mol/s} \cdot \text{m}^2$$

For part (b), the approximate equation (7.6-13) is used:

$$D'_{NA} = \frac{1}{1/D_{AB} + 1/D_{KA}} = \frac{1}{1/6.98 \times 10^{-4} + 1/7.91 \times 10^{-4}}$$
$$= 3.708 \times 10^{-4} \text{ m}^2\text{/s}$$

Substituting into Eq. (7.6-14), the approximate flux is

$$N_A = \frac{D'_{NA} P}{RTL}(x_{A1} - x_{A2}) = \frac{(3.708 \times 10^{-4})(1.013 \times 10^4)}{8314(298)(0.01)}(0.8 - 0.2)$$
$$= 9.10 \times 10^{-5} \text{ kg mol/s} \cdot \text{m}^2$$

Hence, the calculated flux is approximately 40% high when using the approximation of equimolar counterdiffusion ($\alpha = 0$).

The more accurate approximate equation (7.6-15) is used next. The average concentration is $x_{A\text{av}} = (x_{A1} + x_{A2})/2 = (0.8 + 0.2)/2 = 0.50$.

$$D''_{NA} = \frac{1}{(1 - \alpha x_{A\,\text{av}})/D_{AB} + 1/D_{KA}}$$
$$= \frac{1}{(1 + 1.645 \times 0.5)/(6.98 \times 10^{-4}) + 1/(7.91 \times 10^{-4})}$$
$$= 2.581 \times 10^{-4} \text{ m}^2\text{/s}$$

Substituting into Eq. (7.6-16),

$$N_A = \frac{D''_{NA}}{RTL}(x_{A1} - x_{A2})$$
$$= \frac{(2.581 \times 10^{-4})(1.013 \times 10^4)}{8314(298)(0.01)}(0.8 - 0.2)$$
$$= 6.33 \times 10^{-5} \text{ kg mol/s} \cdot \text{m}^2$$

In this case the flux is only −1.1% low.

Diffusion of Gases in Porous Solids

In actual diffusion in porous solids, the pores are not straight and cylindrical but irregular. Hence, the equations for diffusion in pores must be modified somewhat for actual porous solids. The problem is further complicated by the fact that the pore diameters vary and the Knudsen diffusivity is a function of pore diameter.

As a result of these complications, investigators often measure effective diffusivities $D_{A\text{ eff}}$ in porous media, where

Equation 7.6-19.

$$N_A = \frac{D_{A\text{ eff}}P}{RTL}(x_{A1} - x_{A2})$$

If a tortuosity factor τ is used to correct the length L in Eq. (7.6-16), and the right-hand side is multiplied by the void fraction ε, Eq. (7.6-16) becomes

Equation 7.6-20.

$$N_A = \frac{\varepsilon D''_{NA}}{\tau}\frac{P}{RTL}(x_{A1} - x_{A2})$$

Comparing Eqs. (7.6-19) and (7.6-20),

Equation 7.6-21.

$$D_{A\text{ eff}} = \frac{\varepsilon D''_{NA}}{\tau}$$

In some cases investigators measure $D_{A\text{ eff}}$ but use D'_{NA} instead of the more accurate D''_{NA} in Eq. (7.6-21).

Experimental data (G4, S2, S6) show that τ varies from about 1.5 to over 10. A reasonable range for many commercial porous solids is about 2–6 (S2). If the porous solid consists of a bidispersed system of micropores and macropores instead of a monodispersed pore system, the above approach should be modified (C4, S6).

Discussions and references for diffusion in porous inorganic-type solids, organic solids, and freeze-dried foods such as meat and fruit are given elsewhere (S2, S6).

Another type of diffusion that may occur is surface diffusion. When a molecular layer of adsorption occurs on the solid, the molecules can migrate on the surface. Details are given elsewhere (S2, S6).

NUMERICAL METHODS FOR UNSTEADY-STATE MOLECULAR DIFFUSION

Introduction

Unsteady-state diffusion often occurs in inorganic, organic, and biological solid materials. If the boundary conditions are constant with time, if they are the same on all sides or surfaces of the solid, and if the initial concentration profile is uniform throughout the solid, the methods described in Section 7.1 can be used. However, these conditions are not always fulfilled, in which case numerical methods must be used.

Unsteady-State Numerical Methods for Diffusion

Derivation for unsteady state for a slab

For unsteady-state diffusion in one direction, Eq. (7.1-9) becomes

Equation 7.7-1.

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

Since this equation is identical mathematically to the unsteady-state heat-conduction Eq. (5.10-10),

Equation 5.10-10.

$$\frac{\partial T}{\partial t} = \alpha\frac{\partial^2 T}{\partial x^2}$$

identical mathematical methods can be used for solving both diffusion and conduction numerically.

Figure 7.7-1 shows a slab of width Δx centered at point n, represented by the shaded area. Making a mole balance of A on this slab at the time t when the rate in − rate out = rate of accumulation in Δts,

Equation 7.7-2.

$$\frac{D_{AB}A}{\Delta x}({}_tc_{n-1} - {}_tc_n) - \frac{D_{AB}A}{\Delta x}({}_tc_n - {}_tc_{n+1}) = \frac{(A\,\Delta x)}{\Delta t}({}_{t+\Delta t}c_n - {}_tc_n)$$

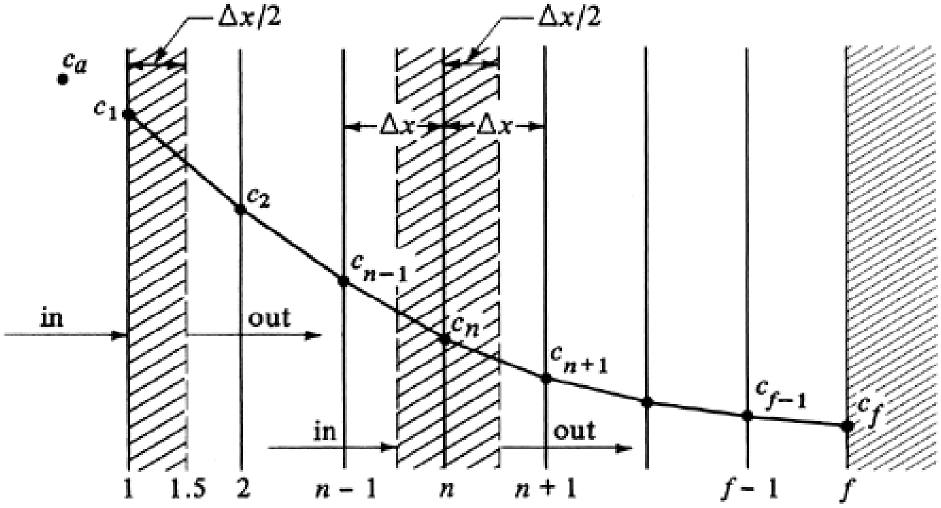


Figure 7.7-1. Unsteady-state diffusion in a slab.

where A is cross-sectional area and ${}_{t+\Delta t}c_n$ is concentration at point n one Δt later. Rearranging,

Equation 7.7-3.

$$_{t+\Delta t}c_n = \frac{1}{M}[{}_tc_{n+1} + (M-2){}_tc_n + {}_tc_{n-1}]$$

where M is a constant.

Equation 7.7-4.

$$M = \frac{(\Delta x)^2}{D_{AB}\Delta t}$$

As in heat conduction, $M \geq 2$.

In using Eq. (7.7-3), the concentration ${}_{t+\Delta t}C_n$ at position n and the new time $t + \Delta t$ is calculated explicitly from the known three points at t. In this calculation method, starting with the known concentrations at $t = 0$, the calculations proceed directly from one time increment to the next until the final time is reached.

Simplified Schmidt method for a slab

If the value of $M = 2$, a simplification of Eq. (7.7-3) occurs, giving the Schmidt method:

Equation 7.7-5.

$$_{t+\Delta t}c_n = \frac{{}_tc_{n-1} + {}_tc_{n+1}}{2}$$

Boundary Conditions for Numerical Methods for a Slab

Convection at a boundary

For the case where convection occurs outside in the fluid and the concentration of the fluid outside is suddenly changed to c_a, we can make a mass balance on the outside half-slab in Fig. 7.7-1. Following the methods used for heat transfer to derive Eq. (5.4-7), we write rate of mass entering by convection − rate of mass leaving by diffusion = rate of mass accumulation in Δt hours:

Equation 7.7-6.

$$k_c A({}_tc_a - {}_tc_1) - \frac{D_{AB}A}{\Delta x}({}_tc_1 - {}_tc_2) = \frac{(A\ \Delta x/2)}{\Delta t}({}_{t+\Delta t}c_{1.25} - {}_tc_{1.25})$$

where ${}_tc_{1.25}$ is the concentration at the midpoint of the 0.5 Δx outside slab. As an approximation, using ${}_tc_1$ for ${}_tc_{1.25}$ and rearranging Eq. (7.7-6),

Equation 7.7-7.

$$_{t+\Delta t}c_1 = \frac{1}{M}[2N{}_tc_a + [M - (2N + 2)]{}_tc_1 + 2{}_tc_2]$$

Equation 7.7-8.

$$N = \frac{k_c\ \Delta x}{D_{AB}}$$

where k_c is the convective mass-transfer coefficient in m/s. Again, note that $M \geq (2N + 2)$.

Insulated boundary condition

For the insulated boundary at f in Fig. 7.7-1, setting $k_c = 0$ ($N = 0$) in Eq. (7.7-7), we obtain

Equation 7.7-9.

$$_{t+\Delta t}c_f = \frac{1}{M}[(M - 2){}_tc_f + 2{}_tc_{f-1}]$$

Alternative convective equation at the boundary

Another form of Eq. (7.7-7) to use if N gets too large can be obtained by neglecting the accumulation in the front half-slab of Eq. (7.7-6) to give

---

Equation 7.7-10.

$$_{t+\Delta t}c_1 = \frac{N}{N+1}\,_{t+\Delta t}c_a + \frac{1}{N+1}\,_{t+\Delta t}c_2$$

The value of M is not restricted by the N value in this equation. When a large number of increments in Δx are used, the amount of mass neglected is small compared to the total.

Procedure for use of initial boundary concentration

For the first time increment, we should use an average value for $_1c_a$ of $(c_a + {}_0c_1)/2$, where $_0c_1$ is the initial concentration at point 1. For succeeding times, the full value of c_a should be used. This special procedure for the value of c_a increases the accuracy of the numerical method, especially after a few time intervals.

In Section 5.4B, concerning numerical methods for heat-transfer, a detailed discussion is given on the best value of M to use in Eq. (7.7-3). The most accurate results are obtained for $M = 4$.

Boundary conditions with distribution coefficient

Equations for boundary conditions in Eqs. (7.7-7) and (7.7-10) were derived for the distribution coefficient K given in Eq. (7.7-7) being 1.0. When K is not 1.0, as in the boundary conditions for steady state, Kk_c should be substituted for k_c in Eq. (7.7-8) to become as follows (see also Sections 6.6B and 7.1C):

Equation 7.7-11.

$$N = \frac{Kk_c\,\Delta x}{D_{AB}}$$

Also, in Eqs. (7.7-7) and (7.7-10), the term c_a/K should be substituted for c_a.

Other cases, such as for diffusion between dissimilar slabs in series, resistance between slabs in series, and so on, are covered in detail elsewhere (G1), with actual numerical examples being given. In reference (G1) the implicit numerical method is discussed.

EXAMPLE 7.7-1. Numerical Solution for Unsteady-State Diffusion with a Distribution Coefficient

A slab of material 0.004 m thick has an initial concentration profile of solute A as follows, where x is distance in m from the exposed surface:

$x(m)$	Concentration (kg mol A/m^3)	Position, n
0	1.0×10^{-3}	1 (exposed)
0.001	1.25×10^{-3}	2
0.002	1.5×10^{-3}	3
0.003	1.75×10^{-3}	4
0.004	2.0×10^{-3}	5 (insulated)

The diffusivity $D_{AB} = 1.0 \times 10^{-9}$ m^2/s. Suddenly, the top surface is exposed to a fluid having a constant concentration $c_a = 6 \times 10^{-3}$ kg mol A/m^3. The distribution coefficient $K = c_a/c_n = 1.50$. The rear surface is insulated, so that unsteady-state diffusion is occurring only in the x direction. Calculate the concentration profile after 2500 s. The convective mass-transfer coefficient k_c can be assumed as infinite. Use $\Delta x = 0.001$ m and $M = 2.0$.

Solution: Figure 7.7-2 shows the initial concentration profile for four slices and $c_a = 6 \times 10^{-3}$. Since $M = 2$, substituting into Eq. (7.7-4) with $\Delta x = 0.001$ m and solving for Δt,

$$M = 2 = \frac{(\Delta x)^2}{D_{AB}\,\Delta t} = \frac{(0.001)^2}{(1 \times 10^{-9})(\Delta t)}$$

$$\Delta t = 500 \text{ s}$$

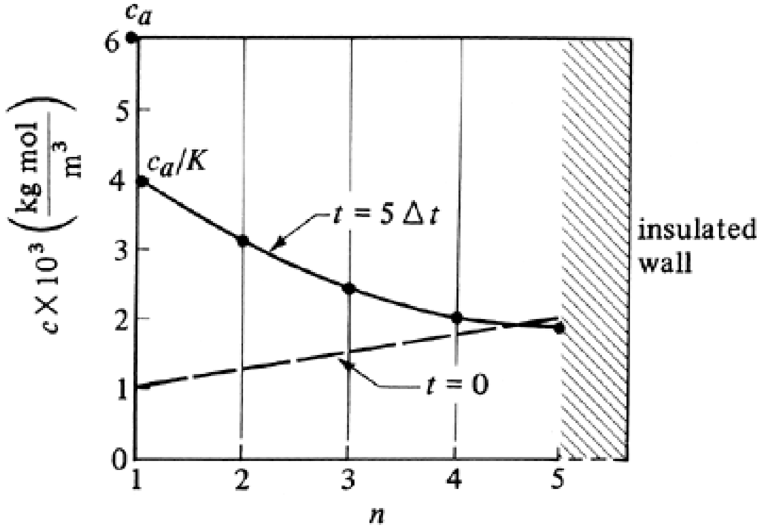


Figure 7.7-2. Concentrations for numerical method for unsteady-state diffusion, Example 7.7-1.

Hence, 2500 s/(500 s/increment) or five time increments are needed.

For the front surface, where $n = 1$, the concentration to use for the first time increment, as stated previously, is

Equation 7.7-12.

$$_1c_a = \frac{c_a/K + {}_0c_1}{2} = {}_1c_1 \qquad (n = 1)$$

where $_0c_1$ is the initial concentration at $n = 1$. For the remaining time increments,

Equation 7.7-13.

$$c_1 = \frac{c_a}{K} \qquad (n = 1)$$

To calculate the concentrations for all time increments for slabs $n = 2, 3, 4$, using Eq. (7.7-5) for $M = 2$,

Equation 7.7-14.

$$_{t+\Delta t}c_n = \frac{{}_tc_{n-1} + {}_tc_{n+1}}{2} \qquad (n = 2, 3, 4)$$

For the insulated end at $n = 5$, substituting $M = 2$ and $f = n = 5$ into Eq. (7.7-9),

Equation 7.7-15.

$$_{t+\Delta t}c_5 = \frac{(2-2)_tc_5 + 2_tc_4}{2} = {}_tc_4 \qquad (n = 5)$$

For 1 Δt or $t + 1\,\Delta t$, the first time increment, calculating the concentration for $n = 1$ by Eq. (7.7-12),

$$_{t+\Delta t}c_1 = \frac{c_a/K + {}_0c_1}{2} = \frac{6 \times 10^{-3}/1.5 + 1 \times 10^{-3}}{2} = 2.5 \times 10^{-3}$$

For *n* = 2, 3, and 4, using Eq. (7.7-14),

$$_{t+\Delta t}c_2 = \frac{_tc_{n-1} + {}_tc_{n+1}}{2} = \frac{_tc_1 + {}_tc_3}{2} = \frac{2.5 \times 10^{-3} + 1.5 \times 10^{-3}}{2} = 2 \times 10^{-3}$$

$$_{t+\Delta t}c_3 = \frac{_tc_2 + {}_tc_4}{2} = \frac{1.25 \times 10^{-3} + 1.75 \times 10^{-3}}{2} = 1.5 \times 10^{-3}$$

$$_{t+\Delta t}c_4 = \frac{_tc_3 + {}_tc_5}{2} = \frac{1.5 \times 10^{-3} + 2 \times 10^{-3}}{2} = 1.75 \times 10^{-3}$$

For *n* = 5, using Eq. (7.7-15),

$$_{t+\Delta t}c_5 = {}_tc_4 = 1.75 \times 10^{-3}$$

For 2 Δ*t*, using Eq. (7.7-13) for *n* = 1, using Eq. (7.7-14) for *n* = 2–4, and using Eq. (7.7-15) for *n* = 5,

$$_{t+2\Delta t}c_1 = \frac{c_a}{K} = \frac{6 \times 10^{-3}}{1.5} = 4.0 \times 10^{-3} \qquad \text{(constant for rest of time)}$$

$$_{t+2\Delta t}c_2 = \frac{_{t+\Delta t}c_1 + {}_{t+\Delta t}c_3}{2} = \frac{4 \times 10^{-3} + 1.5 \times 10^{-3}}{2} = 2.75 \times 10^{-3}$$

$$_{t+2\Delta t}c_3 = \frac{_{t+\Delta t}c_2 + {}_{t+\Delta t}c_4}{2} = \frac{2 \times 10^{-3} + 1.75 \times 10^{-3}}{2} = 1.875 \times 10^{-3}$$

$$_{t+2\Delta t}c_4 = \frac{_{t+\Delta t}c_3 + {}_{t+\Delta t}c_5}{2} = \frac{1.5 \times 10^{-3} + 1.75 \times 10^{-3}}{2} = 1.625 \times 10^{-3}$$

$$_{t+2\Delta t}c_5 = {}_{t+\Delta t}c_4 = 1.75 \times 10^{-3}$$

For 3 Δ*t*,

$$_{t+3\Delta t}c_1 = 4 \times 10^{-3}$$

$$_{t+3\Delta t}c_2 = \frac{4 \times 10^{-3} + 1.875 \times 10^{-3}}{2} = 2.938 \times 10^{-3}$$

$$_{t+3\Delta t}c_3 = \frac{2.75 \times 10^{-3} + 1.625 \times 10^{-3}}{2} = 2.188 \times 10^{-3}$$

$$_{t+3\Delta t}c_4 = \frac{1.875 \times 10^{-3} + 1.75 \times 10^{-3}}{2} = 1.813 \times 10^{-3}$$

$$_{t+3\Delta t}c_5 = 1.625 \times 10^{-3}$$

For 4 Δ*t*,

$$_{t+4\Delta t}c_1 = 4 \times 10^{-3}$$

$$_{t+4\Delta t}c_2 = \frac{4 \times 10^{-3} + 2.188 \times 10^{-3}}{2} = 3.094 \times 10^{-3}$$

$$_{t+4\Delta t}c_3 = \frac{2.938 \times 10^{-3} + 1.813 \times 10^{-3}}{2} = 2.376 \times 10^{-3}$$

$$_{t+4\Delta t}c_4 = \frac{2.188 \times 10^{-3} + 1.625 \times 10^{-3}}{2} = 1.906 \times 10^{-3}$$

$$_{t+4\Delta t}c_5 = 1.813 \times 10^{-3}$$

For 5 Δt,

$$_{t+5\Delta t}c_1 = 4 \times 10^{-3}$$

$$_{t+5\Delta t}c_2 = \frac{4 \times 10^{-3} + 2.376 \times 10^{-3}}{2} = 3.188 \times 10^{-3}$$

$$_{t+5\Delta t}c_3 = \frac{3.094 \times 10^{-3} + 1.906 \times 10^{-3}}{2} = 2.500 \times 10^{-3}$$

$$_{t+5\Delta t}c_4 = \frac{2.376 \times 10^{-3} + 1.813 \times 10^{-3}}{2} = 2.095 \times 10^{-3}$$

$$_{t+5\Delta t}c_5 = 1.906 \times 10^{-3}$$

The final concentration profile is plotted in Fig. 7.7-2. To increase the accuracy, more slab increments and time increments are needed. This type of calculation is suitable for use with a computer spreadsheet.

DIMENSIONAL ANALYSIS IN MASS TRANSFER

Introduction

The use of dimensional analysis enables us to predict the various dimensional groups which are very helpful in correlating experimental mass-transfer data. As we saw for fluid flow and heat transfer, the Reynolds number, Prandtl number, Grashof number, and Nusselt number are often used in correlating experimental data. The Buckingham theorem discussed in Sections 3.11 and 4.14 states that the functional relationship among q quantities or variables whose units may be given in terms of u fundamental units or dimensions may be written as $(q - u)$ dimensionless groups.

Dimensional Analysis for Convective Mass Transfer

We consider a case of convective mass transfer where a fluid is flowing by forced convection in a pipe and mass transfer is occurring from the wall to the fluid. The fluid flows at a velocity v inside a pipe of diameter D, and we wish to relate the mass-transfer coefficient k'_c to the variables D, ρ, μ, v, and D_{AB}. The total number of variables is $q = 6$. The fundamental units or dimensions are $u = 3$ and are mass M, length L, and time t. The units of the variables are

$$k'_c = \frac{L}{t} \qquad \rho = \frac{M}{L^3} \qquad \mu = \frac{M}{Lt} \qquad v = \frac{L}{t} \qquad D_{AB} = \frac{L^2}{t} \qquad D = L$$

The number of dimensionless groups of π's are then 6 − 3, or 3. Then,

Equation 7.8-1.

$$\pi_1 = f(\pi_2, \pi_3)$$

We choose the variables D_{AB}, ρ, and D to be the variables common to all the dimensionless groups, which are

Equation 7.8-2.

$$\pi_1 = D^a_{AB}\rho^b D^c k'_c$$

Equation 7.8-3.

$$\pi_2 = D^d_{AB}\rho^e D^f v$$

Equation 7.8-4.

$$\pi_3 = D^g_{AB}\rho^h D^i \mu$$

For π_1 we substitute the actual dimensions as follows:

Equation 7.8-5.

$$1 = \left(\frac{L^2}{t}\right)^a \left(\frac{M}{L^3}\right)^b (L)^c \left(\frac{L}{t}\right)$$

Summing for each exponent,

Equation 7.8-6.

$$\begin{aligned} &(L) \quad 0 = 2a - 3b + c + 1 \\ &(M) \quad 0 = b \\ &(t) \quad\ \ 0 = a - 1 \end{aligned}$$

Solving these equation simultaneously, $a = -1$, $b = 0$, $c = 1$. Substituting these values into Eq. (7.8-2),

Equation 7.8-7.

$$\pi_1 = \frac{k'_c D}{D_{AB}} = N_{\text{Sh}}$$

Repeating for π_2 and π_3,

Equation 7.8-8.

$$\pi_2 = \frac{vD}{D_{AB}}$$

Equation 7.8-9.

$$\pi_3 = \frac{\mu}{\rho D_{AB}} = N_{\mathrm{Sc}}$$

If we divide π_2 by π_3 we obtain the Reynolds number:

Equation 7.8-10.

$$\frac{\pi_2}{\pi_3} = \frac{vD}{D_{AB}} \bigg/ \left(\frac{\mu}{\rho D_{AB}}\right) = \frac{Dv\rho}{\mu} = N_{\mathrm{Re}}$$

Hence, substituting into Eq. (7.8-1),

Equation 7.8-11.

$$N_{\mathrm{Sh}} = f(N_{\mathrm{Re}}, N_{\mathrm{Sc}})$$

BOUNDARY-LAYER FLOW AND TURBULENCE IN MASS TRANSFER

Laminar Flow and Boundary-Layer Theory in Mass Transfer

In Section 3.10C an exact solution was obtained for the hydrodynamic boundary layer for isothermal laminar flow past a plate, and in Section 5.7A an extension of the Blasius solution was also used to derive an expression for convective heat transfer. In an analogous manner we use the Blasius solution for convective mass transfer for the same geometry and laminar flow. In Fig. 7.9-1 the concentration boundary layer is shown, where the concentration of the fluid approaching the plate is $c_{A\infty}$ and c_{AS} in the fluid adjacent to the surface.

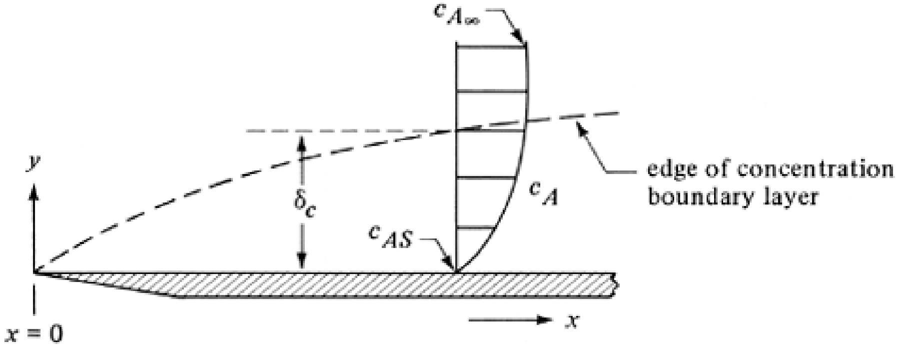


Figure 7.9-1. Laminar flow of fluid past a flat plate and concentration boundary layer.

We start by using the differential mass balance, Eq. (7.5-17), and simplifying it for steady state where $\partial c_A/\partial t = 0$; $R_A = 0$; flow only in the x and y directions, so $v_z = 0$; and neglecting diffusion in the x and z directions to give

Equation 7.9-1.

$$v_x \frac{\partial c_A}{\partial x} + v_y \frac{\partial c_A}{\partial y} = D_{AB} \frac{\partial^2 c_A}{\partial y^2}$$

The momentum boundary-layer equation is very similar:

Equation 3.10-5.

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = \frac{\mu}{\rho} \frac{\partial^2 v_x}{\partial y^2}$$

The thermal boundary-layer equation is also similar:

Equation 5.7-2.

$$v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} = \frac{k}{\rho c_p} \frac{\partial^2 T}{\partial y^2}$$

The continuity equation used previously is

Equation 3.10-3.

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0$$

The dimensionless concentration boundary conditions are

Equation 7.9-2.

$$\frac{v_x}{v_\infty} = \frac{T - T_S}{T_\infty - T_S} = \frac{c_A - c_{AS}}{c_{A\infty} - c_{AS}} = 0 \qquad \text{at } y = 0$$

$$\frac{v_x}{v_\infty} = \frac{T - T_S}{T_\infty - T_S} = \frac{c_A - c_{AS}}{c_{A\infty} - c_{AS}} = 1 \qquad \text{at } y = \infty$$

The similarity among the three differential equations (7.9-1), (3.10-5), and (5.7-2) is obvious, as is the similarity among the three sets of boundary conditions in Eq. (7.9-2). In Section 5.7A the Blasius solution was applied to convective heat transfer when $(\mu/\rho)/\alpha = N_{\text{Pr}} = 1.0$. We use the same type of solution for laminar convective mass transfer when $(\mu/\rho)/D_{AB} = N_{\text{Sc}} = 1.0$.

The velocity gradient at the surface was derived previously:

Equation 5.7-5.

$$\left(\frac{\partial v_x}{\partial y}\right)_{y=0} = 0.332 \frac{v_\infty}{x} N_{\text{Re},x}^{1/2}$$

where $N_{\text{Re},x} = xv_\infty\rho/\mu$. Also, from Eq. (7.9-2),

Equation 7.9-3.

$$\frac{v_x}{v_\infty} = \frac{c_A - c_{AS}}{c_{A\infty} - c_{AS}}$$

Differentiating Eq. (7.9-3) and combining the result with Eq. (5.7-5),

Equation 7.9-4.

$$\left(\frac{\partial c_A}{\partial y}\right)_{y=0} = (c_{A\infty} - c_{AS})\left(\frac{0.332}{x} N_{\mathrm{Re},x}^{1/2}\right)$$

The convective mass-transfer equation can be written as follows and related to Fick's equation for dilute solutions:

Equation 7.9-5.

$$N_{Ay} = k_c'(c_{AS} - c_{A\infty}) = -D_{AB}\left(\frac{\partial c_A}{\partial y}\right)_{y=0}$$

Combining Eqs. (7.9-4) and (7.9-5),

Equation 7.9-6.

$$\frac{k_c' x}{D_{AB}} = N_{\mathrm{Sh},x} = 0.332 N_{\mathrm{Re},x}^{1/2}$$

This relationship is restricted to gases with a $N_{\mathrm{Sc}} = 1.0$.

The relationship between the thickness δ of the hydrodynamic and δ_c of the concentration boundary layers where the Schmidt number is not 1.0 is

Equation 7.9-7.

$$\frac{\delta}{\delta_c} = N_{\mathrm{Sc}}^{1/3}$$

As a result, the equation for the local convective mass-transfer coefficient is

Equation 7.9-8.

$$\frac{k_c' x}{D_{AB}} = N_{\mathrm{Sh},x} = 0.332 N_{\mathrm{Re},x}^{1/2} N_{\mathrm{Sc}}^{1/3}$$

We can obtain the equation for the mean mass-transfer coefficient k_c' from $x = 0$ to $x = L$ for a plate of width b by integrating as follows:

Equation 7.9-9.

$$k_c' = \frac{b}{bL}\int_0^L k_c'\, dx$$

The result is

Equation 7.9-10.

$$\frac{k'_c L}{D_{AB}} = N_{\mathrm{Sh}} = 0.664\, N_{\mathrm{Re},L}^{1/2} N_{\mathrm{Sc}}^{1/3}$$

This is similar to the heat-transfer equation for a flat plate, Eq. (5.7-15), and also agrees with the experimental mass-transfer equation (7.3-27) for a flat plate.

In Section 3.10 an approximate integral analysis was performed for the laminar hydrodynamic and the turbulent hydrodynamic boundary layers. This was also done in Section 5.7 for the thermal boundary layer. An approximate integral analysis can also be done in exactly the same manner for the laminar and turbulent concentration boundary layers.

Prandtl Mixing Length and Turbulent Eddy Mass Diffusivity

In many applications the flow in mass transfer is turbulent and not laminar. The turbulent flow of a fluid is quite complex as the fluid undergoes a series of random eddy movements throughout the turbulent core. When mass transfer is occurring, we refer to this as eddy mass diffusion. In Sections 3.10 and 5.7 we derived equations for turbulent eddy thermal diffusivity and momentum diffusivity using the Prandtl mixing length theory.

In a similar manner we can derive a relation for the turbulent eddy mass diffusivity, ε_M. Eddies are transported a distance *L*, called the Prandtl mixing length, in the *y* direction. At this point *L* the fluid eddy differs in velocity from the adjacent fluid by the velocity v'_x, which is the fluctuating velocity component given in Section 3.10F. The instantaneous rate of mass transfer of *A* at a velocity v'_y for a distance *L* in the *y* direction is

Equation 7.9-11.

$$J^*_{Ay} = c'_A v'_y$$

where c'_A is the instantaneous fluctuating concentration. The instantaneous concentration of the fluid is $c_A = c'_A + \bar{c}_A$, where $\bar{c}_A$ is the mean value and c'_A the deviation from the mean value. The mixing length *L* is small enough that the concentration difference is

Equation 7.9-12.

$$c'_A = L\frac{d\bar{c}_A}{dy}$$

The rate of mass transported per unit area is J^*_{A1}. Combining Eqs. (7.9-11) and (7.9-12),

Equation 7.9-13.

$$J^*_{Ay} = -v'_y L\frac{d\bar{c}_A}{dy}$$

From Eq. (5.7-23),

Equation 7.9-14.

$$v'_y = v'_x = L\left|\frac{d\bar{v}_x}{dy}\right|$$

Substituting Eq. (7.9-14) into (7.9-13),

Equation 7.9-15.

$$J^*_{Ay} = -L^2\left|\frac{d\bar{v}_x}{dy}\right|\frac{d\bar{c}_A}{dy}$$

The term $L^2|d\bar{v}_x/dy|$ is called the turbulent eddy mass diffusivity ε_M. Combining Eq. (7.9-15) with the diffusion equation in terms of D_{AB}, the total flux is

Equation 7.9-16.

$$J^*_{Ay} = -(D_{AB} + \varepsilon_M)\frac{d\bar{c}_A}{dy}$$

The similarities between Eq. (7.9-16) for mass transfer and heat and momentum transfer have been pointed out in detail in Section 6.1A.

Models for Mass-Transfer Coefficients

Introduction

For many years mass-transfer coefficients, which were based primarily on empirical correlations, have been used in the design of process equipment. A better understanding of the mechanisms of turbulence is needed before we can give a theoretical explanation of convective mass-transfer coefficients. Several theories of convective mass transfer, such as the eddy diffusivity theory, have been presented in this chapter. In the following sections we present briefly some of these theories and discuss how they can be used to extend empirical correlations.

Film mass-transfer theory

The film theory, which is the simplest and most elementary theory, assumes the presence of a fictitious laminar film next to the boundary. This film, where only molecular diffusion is assumed to be occurring, has the same resistance to mass transfer as actually exists in the viscous, transition, and turbulent core regions. Then the actual mass-transfer coefficient k'_c is related to this film thickness δ_f by

Equation 7.9-17.

$$J^*_A = k'_c(c_{A1} - c_{A2}) = \frac{D_{AB}}{\delta_f}(c_{A1} - c_{A2})$$

Equation 7.9-18.

$$k'_c = \frac{D_{AB}}{\delta_f}$$

The mass-transfer coefficient is proportional to $D_{AB}^{1.0}$. However, since we have shown that in Eq. (7.3-13) J_D is proportional to $(\mu/\rho D_{AB})^{2/3}$, then $k'_c \propto D_{AB}^{2/3}$. Hence, the film theory is not correct. The great advantage of the film theory is its simplicity where it can be used in complex situations such as simultaneous diffusion and chemical reaction.

Penetration theory

The penetration theory derived by Higbie and modified by Danckwerts (D3) was derived for diffusion or penetration into a laminar falling film for short contact times in Eq. (7.3-23) and is as follows:

Equation 7.9-19.

$$k'_c = \sqrt{\frac{4D_{AB}}{\pi t_L}}$$

where t_L is the time of penetration of the solute in seconds. This was extended by Danckwerts. He modified this for turbulent mass transfer and postulated that a fluid eddy has a uniform concentration in the turbulent core and is swept to the surface and undergoes unsteady-state diffusion. Then the eddy is swept away to the eddy core and other eddies are swept to the surface and stay for a random amount of time. A mean surface renewal factor s in s^{-1} is defined as follows:

Equation 7.9-20.

$$k'_c = \sqrt{D_{AB} s}$$

The mass-transfer coefficient k'_c is proportional to $D_{AB}^{0.5}$. In some systems, such as where liquid flows over packing and semistagnant pockets occur where the surface is being renewed, the results approximately follow Eq. (7.9-20). The value of s must be obtained experimentally. Others (D3, T2) have derived more complex combination film-surface renewal theories predicting a gradual change of the exponent on D_{AB} from 0.5 to 1.0 depending on turbulence and other factors. Penetration theories have been used in cases where diffusion and chemical reaction are occurring (D3).

Boundary-layer theory

The boundary-layer theory has been discussed in detail in Section 7.9 and is useful in predicting and correlating data for fluids flowing past solid surfaces. For laminar flow and turbulent flow the mass-transfer coefficient $k'_c \propto D_{AB}^{2/3}$. This has been experimentally verified for many cases.

PROBLEMS

7.1-1. ***Unsteady-State Diffusion in a Thick Slab.*** Repeat Example 7.1-2 but use a distribution coefficient $K = 0.50$ instead of 2.0. Plot the data.

A1: **Ans.** $c = c_i = 5.75 \times 10^{-2}$ ($x = 0$), $c = 2.78 \times 10^{-2}$ ($x = 0.01$ m), $c_{Li} = 2.87 \times 10^{-2}$ kg mol/m^3

7.1-2. ***Plot of Concentration Profile in Unsteady-State Diffusion.*** Using the same conditions as in Example 7.1-2, calculate the concentration at the points $x = 0$, 0.005, 0.01, 0.015, and 0.02 m from the surface. Also calculate c_{Li} in the liquid at the interface. Plot the concentrations in a manner similar to Fig. 7.1-3b, showing interface concentrations.

7.1-3. ***Unsteady-State Diffusion in Several Directions.*** Use the same conditions as in Example 7.1-1 except that the solid is a rectangular block 10.16 mm thick in the *x* direction, 7.62 mm thick in the *y* direction, and 10.16 mm thick in the *z* direction, and diffusion occurs at all six faces. Calculate the concentration at the midpoint after 10 h.

A3: **Ans.** $c = 6.20 \times 10^{-4}$ kg mol/m^3

7.1-4. ***Drying of Moist Clay.*** A very thick slab of clay has an initial moisture content of c_0 = 14 wt %. Air is passed over the top surface to dry the clay. Assume a relative resistance of the gas at the surface of zero. The equilibrium moisture content at the surface is constant at c_1 = 3.0 wt %. The diffusion of the moisture in the clay can be approximated by a diffusivity of $D_{AB} = 1.29 \times 10^{-8}$ m^2/s. After 1.0 h of drying, calculate the concentration of water at points 0.005, 0.01, and 0.02 m below the surface. Assume that the clay is a semi-infinite solid and that the *Y* value can be represented using concentrations of wt % rather than kg mol/m^3. Plot the values versus *x*.

7.1-5. ***Unsteady-State Diffusion in a Cylinder of Agar Gel.*** A wet cylinder of agar gel at 278 K containing a uniform concentration of urea of 0.1 kg mol/m^3 has a diameter of 30.48 mm and is 38.1 mm long with flat, parallel ends. The diffusivity is 4.72×10^{-10} m^2/s. Calculate the concentration at the midpoint of the cylinder after 100 h for the following cases if the cylinder is suddenly immersed in turbulent pure water:

a. For radial diffusion only.
b. Diffusion occurs radially and axially.

7.1-6. ***Drying of Wood.*** A flat slab of Douglas fir wood 50.8 mm thick containing 30 wt % moisture is being dried from both sides (neglecting ends and edges). The equilibrium moisture content at the surface of the wood due to the drying air blown over it is held at 5 wt % moisture. The drying can be assumed to be represented by a diffusivity of 3.72×10^{-6} m^2/h. Calculate the time for the center to reach 10% moisture.

7.2-1. ***Flux and Conversion of Mass-Transfer Coefficient.*** A value of k_G was experimentally determined to be 1.08 lb mol/h · ft^2 · atm for *A* diffusing through stagnant *B*. For the same flow and concentrations it is desired to predict k'_G and the flux of *A* for equimolar counterdiffusion. The partial pressures are p_{A1} = 0.20 atm, p_{A2} = 0.05 atm, and *P* = 1.0 atm abs total. Use English and SI units.

A7: **Ans.**

$$k'_G = 0.943 \text{ lb mol/h} \cdot \text{ft}^2 \cdot \text{atm}, \; 1.262 \times 10^{-8} \text{ kg mol/s} \cdot \text{m}^2 \cdot \text{Pa},$$
$$N_A = 0.1414 \text{ lb mol } A/\text{h} \cdot \text{ft}^2, \; 1.918 \times 10^{-4} \text{ kg mol/s} \cdot \text{m}^2$$

7.2-2. ***Conversion of Mass-Transfer Coefficients.*** Prove or show the following relationships, starting with the flux equations:

a. Convert k'_c to k_y and k_G.
b. Convert k_L to k_x and k'_x.
c. Convert k_G to k_y and k_c.

7.2-3. ***Absorption of H_2S by Water.*** In a wetted-wall tower an air–H_2S mixture is flowing by a film of water that is flowing as a thin film down a vertical plate. The H_2S is being absorbed from the air to the water at a total pressure of 1.50 atm abs and 30°C. A value for k'_c of 9.567×10^{-4} m/s has been predicted for the gas-phase mass-transfer coefficient. At a given point the mole fraction of H_2S in the liquid at the liquid–gas interface is $2.0(10^{-5})$ and p_A of H_2S in the gas is 0.05 atm. The Henry's law equilibrium relation is p_A (atm) = $609x_A$ (mole fraction in liquid). Calculate the rate of absorption of H_2S. (*Hint:* Call point 1 the interface and point 2 the gas phase. Then calculate p_{A1} from Henry's law and the given x_A. The value of p_{A2} is 0.05 atm.)

A9: **Ans.** $N_A = -1.485 \times 10^{-6}$ kg mol/s · m^2

7.2-4. ***Effect of High Flux on Mass-Transfer Coefficients.*** Using the data from Example 7.2-2, also calculate the flux ratios k_x^0/k'_x for x_{A1} = 0.20 and x_{A1} = 0.01. Tabulate these ratios for the three values of x_{A1} and plot the ratio versus x_{A1}.

7.3-1. ***Mass Transfer from a Flat Plate to a Liquid.*** Using the data and physical properties of Example 7.3-2 calculate the flux for a water velocity of 0.152 m/s and a plate length of L = 0.137 m. Do not assume that x_{BM} = 1.0 but actually calculate its value.

7.3-2. ***Mass Transfer from a Pipe Wall.*** Pure water at 26.1°C is flowing at a velocity of 0.0305 m/s in a tube having an inside diameter of 6.35 mm. The tube is 1.829 m long, with the last 1.22 m having the walls coated with benzoic acid. Assuming that the velocity profile is fully developed, calculate the average concentration of benzoic acid at the outlet. Use the physical property data from Example 7.3-2. [*Hint:* First calculate the Reynolds number $Dv\rho/\mu$. Then calculate $N_{Re}N_{Sc}(D/L)(\pi/4)$, which is the same as $W/D_{AB}\rho L$.]

A12: **Ans.** $(c_A - c_{A0})/(c_{Ai} - c_{A0}) = 0.0744$, $c_A = 2.193 \times 10^{-3}$ kg mol/m^3

7.3-3. ***Mass-Transfer Coefficient for Various Geometries.*** It is desired to estimate the mass-transfer coefficient k_G in kg mol/s · m^2· Pa for water vapor in air at 338.6 K and 101.32 kPa flowing in a large duct past solids of different geometries. The velocity in the duct is 3.66 m/s. The water vapor concentration in the air is small, so the physical properties of air can be used. Water vapor is being transferred to the solids. Do this for the following geometries:

a. A single 25.4-mm-diameter sphere.

b. A packed bed of 25.4-mm spheres with ε = 0.35.

A13: **Ans.** (a) $k_G = 1.984 \times 10^{-8}$ kg mol/s · m^2· Pa (1.482 lb mol/h · ft^2· atm)

7.3-4. ***Mass Transfer to Definite Shapes.*** Estimate the value of the mass-transfer coefficient in a stream of air at 325.6 K flowing in a duct past the following shapes made of solid naphthalene. The velocity of the air is 1.524 m/s at 325.6 K and 202.6 kPa. The D_{AB} of naphthalene in air is 5.16×10^{-6} m^2/s at 273 K and 101.3 kPa.

a. For air flowing parallel to a flat plate 0.152 m in length.

b. For air flowing past a single sphere 12.7 mm in diameter.

7.3-5. ***Mass Transfer to Packed Bed and Driving Force.*** Pure water at 26.1°C is flowing at a rate of 0.0701 ft^3/h through a packed bed of 0.251-in. benzoic-acid spheres having a total surface area of 0.129 ft^2. The solubility of benzoic acid in water is 0.00184 lb mol benzoic acid/ft^3 solution. The outlet concentration c_{A2} is 1.80×10^{-4} lb mol/ft^3. Calculate the mass-transfer coefficient k_c.

7.3-6. ***Mass Transfer in Liquid Metals.*** Mercury at 26.5°C is flowing through a packed bed of lead spheres having a diameter of 2.096 mm with a void fraction of 0.499. The superficial velocity is 0.02198 m/s. The solubility of lead in mercury is 1.721 wt %, the Schmidt number is 124.1, the viscosity of the solution is 1.577×10^{-3} Pa · s, and the density is 13 530 kg/m^3.

a. Predict the value of J_D. Use Eq. (7.3-38) if applicable. Compare with the experimental value of $J_D = 0.076$ (D2).

b. Predict the value of k_c for the case of A diffusing through nondiffusing B.

A16: **Ans.** (a) $J_D = 0.0784$; (b) $k_c = 6.986 \times 10^{-5}$ m/s

7.3-7. ***Mass Transfer from a Pipe and Log Mean Driving Force.*** Use the same physical conditions as in Problem 7.3-2, but the velocity in the pipe is now 3.05 m/s. Do as follows:

a. Predict the mass-transfer coefficient k'_c. (Is this turbulent flow?)

b. Calculate the average benzoic acid concentration at the outlet. [*Note:* In this case, Eqs. (7.3-42) and (7.3-43) must be used with the log mean driving force, where A is the surface area of the pipe.]

c. Calculate the total kg mol of benzoic acid dissolved per second.

7.3-8. ***Derivation of Relation Between J_D and N_{Sh}.*** Equation (7.3-3) defines the Sherwood number and Eq. (7.3-5) defines the J_D factor. Derive the relation between N_{Sh} and J_D in terms of N_{Re} and N_{Sc}.

A18: **Ans.** $N_{\text{Sh}} = J_D N_{\text{Re}} N_{\text{Sc}}^{1/3}$

7.3-9. ***Driving Force to Use in Mass Transfer.*** Derive Eq. (7.3-42) for the log mean driving force to use for a fluid flowing in a packed bed or in a tube. (*Hint:* Start by making a mass balance and a diffusion rate balance over a differential area dA as follows:

$$N_A\,dA = k_c(c_{Ai} - c_A)dA = V\,dc_A$$

where V = m^3/s flow rate. Assume dilute solutions.)

7.4-1. ***Maximum Oxygen Uptake of a Microorganism.*** Calculate the maximum possible rate of oxygen uptake at 37°C of microorganisms having a diameter of $\frac{2}{3}$ μm suspended in an agitated aqueous solution. It is assumed that the surrounding liquid is saturated with O_2 from air at 1 atm abs pressure. It will be assumed that the microorganism can utilize the oxygen much faster than it can diffuse to it. The microorganism has a density very close to that of water.

Use physical-property data from Example 7.4-1. (*Hint:* Since the oxygen is consumed faster than it is supplied, the concentration c_{A2} at the surface is zero. The concentration c_{A1} in the solution is at saturation.)

A20: **Ans.** $k_c = 9.75 \times 10^{-3}$ m/s, $N_A = 2.20 \times 10^{-6}$ kg mol $O_2/s \cdot m^2$

7.4-2. ***Mass Transfer of O_2 in Fermentation Process.*** A total of 5.0 g of wet microorganisms having a density of 1100 kg/m^3 and a diameter of 0.667 μm are added to 0.100 L of aqueous solution at 37°C in a shaker flask for a fermentation. Air can enter through a porous stopper. Use physical property data from Example 7.4-1.

a. Calculate the maximum rate possible for mass transfer of oxygen in kg mol O_2/s to the surface of the microorganisms, assuming that the solution is saturated with air at 101.32 kPa abs pressure.

b. By material balances on other nutrients, the actual utilization of O_2 by the microorganisms is 6.30×10^{-6} kg mol O_2/s. What would be the actual concentration of O_2 in the solution as percent saturation during the fermentation?

A21: **Ans.** (a) $k'_L = 9.82 \times 10^{-3}$ m/s, $N_A A = 9.07 \times 10^{-5}$ kgmol O_2/s; (b) 6.95% saturation

7.5-1. ***Sum of Molar Fluxes.*** Prove the following equation using the definitions in Table 7.5-1:

$$N_A + N_B = c v_M$$

7.5-2. ***Proof of Derived Relation.*** Using the definitions from Table 7.5-1, prove the following:

$$j_A = n_A - w_A(n_A + n_B)$$

7.5-3. ***Different Forms of Fick's Law.*** Using Eq. (1), prove Eq. (2):

Equation 1.

$$j_A = -\rho D_{AB}\frac{dw_A}{dz}$$

Equation 2.

$$j_A = -\frac{c^2}{\rho}M_A M_B D_{AB}\,\frac{dx_A}{dz}$$

(*Hint:* First relate w_A to x_A. Then differentiate this equation to relate dw_A and dx_A. Finally, use $M = x_A M_A + x_B M_B$ to simplify.)

7.5-4. ***Other Form of Fick's Law.*** Show that the following form of Fick's law is valid:

$$c(v_A - v_B) = -\frac{cD_{AB}}{x_A x_B}\,\frac{dx_A}{dz}$$

(*Hint:* Start with $N_A = J_A^* + c_A \boldsymbol{v}_M$. Substitute the expression for J_A^* from Table 7.5-1 and simplify.)

7.5-5. ***Different Form of Equation of Continuity.*** Starting with Eq. (7.5-12),

Equation 7.5-12.

$$\frac{\partial \rho_A}{\partial t} + (\nabla \cdot \boldsymbol{n}_A) = r_A$$

convert this to the following for constant ρ:

Equation 1.

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

[*Hint:* From Table 7.5-1, substitute $n_A = j_A + \rho_A v$ into Eq. (7.5-12). Note that $(\nabla \cdot v) = 0$ for constant ρ. Then substitute Fick's law in terms of j_A.]

7.5-6. ***Diffusion and Reaction at a Surface.*** Gas A is diffusing from a gas stream at point 1 to a catalyst surface at point 2 and reacts instantaneously and irreversibly as follows:

$$2A \rightarrow B$$

Gas B diffuses back to the gas stream. Derive the final equation for N_A at constant pressure P and steady state in terms of partial pressures.

A27: **Ans.**

$$N_A = \frac{2D_{AB}P}{RT(z_2 - z_1)} \ln \frac{1 - p_{A2}/2P}{1 - p_{A1}/2P}$$

7.5-7. ***Unsteady-State Diffusion and Reaction.*** Solute A is diffusing at unsteady state into a semi-infinite medium of pure B and undergoes a first-order reaction with B. Solute A is dilute. Calculate the concentration c_A at points $z = 0$, 4, and 10 mm from the surface for $t = 1 \times 10^5$ s. Physical property data are $D_{AB} = 1 \times 10^{-9}$ m^2/s, $k' = 1 \times 10^{-4}$ s^{-1}, $c_{A0} = 1.0$ kg mol/m^3. Also calculate the kg mol absorbed/m^2.

7.5-8. ***Multicomponent Diffusion.*** At a total pressure of 202.6 kPa and 358 K, ammonia gas (A) is diffusing at steady state through an inert, nondiffusing mixture of nitrogen (B) and hydrogen (C). The mole fractions at $z_1 = 0$ are $x_{A1} = 0.8$, $x_{B1} = 0.15$, and $x_{C1} = 0.05$; and at $z_2 = 4.0$ mm, $x_{A2} = 0.2$, $x_{B2} = 0.6$, and $x_{C2} = 0.2$. The diffusivities at 358 K and 101.3 kPa are $D_{AB} = 3.28 \times 10^{-5}$ m^2/s and $D_{AC} = 1.093 \times 10^{-4}$ m^2/s. Calculate the flux of ammonia.

A29: **Ans.** $N_A = 4.69 \times 10^{-4}$ kg mol A/s · m^2

7.5-9. ***Diffusion in Liquid Metals and Variable Diffusivity.*** The diffusion of tin (A) in liquid lead (B) at 510°C was carried out by using a 10.0-mm-long capillary tube and maintaining the mole fraction of tin at x_{A1} at the left end and x_{A2} at the right end of the tube. In the range of concentrations of $0.2 \le x_A \le 0.4$ the diffusivity of tin in lead has been found to be a linear function of x_A (S7):

$$D_{AB} = A + Bx_A$$

where A and B are constants and D_{AB} is in m^2/s.

a. Assuming the molar density to be constant at $c = c_A + c_B = c_{\text{av}}$, derive the final integrated equation for the flux N_A, assuming steady state and that A diffuses through stagnant B.

b. For this experiment, $A = 4.8 \times 10^{-9}$, $B = -6.5 \times 10^{-9}$, $c_{\text{av}} = 50$ kg mol/m^3, $x_{A1} = 0.4$, $x_{A2} = 0.2$. Calculate N_A.

A30: **Ans.** (b) $N_A = 4.055 \times 10^{-6}$ kg mol A/s · m^2

7.5-10. ***Diffusion and Chemical Reaction of Molten Iron in Process Metallurgy.*** In a steelmaking process using molten pig iron containing carbon, a spray of molten iron particles containing 4.0 wt % carbon falls through a pure-oxygen atmosphere. The carbon diffuses through the molten iron to the surface of the drop, where it is assumed that it reacts instantly at the surface because of the high temperature, as follows, according to a first-order reaction:

$$\mathrm{C} + \tfrac{1}{2}\mathrm{O_2}(g) \rightarrow \mathrm{CO}(g)$$

Calculate the maximum drop size allowable so that the final drop after a 2.0-s fall contains an average of 0.1 wt % carbon. Assume that the mass-transfer rate of gases at the surface is very great, so there is no outside resistance. Assume no internal circulation of the liquid. Hence, the decarburization rate is controlled by the rate of diffusion of carbon to the surface of the droplet. The diffusivity of carbon in iron is 7.5×10^{-9} m^2/s (S7). (*Hint:* Can Fig. 5.3-13 be used for this case?)

A31: **Ans.** radius = 0.217 mm

7.5-11. ***Effect of Slow Reaction Rate on Diffusion.*** Gas A diffuses from point 1 to a catalyst surface at point 2, where it reacts as follows: $2A \rightarrow B$. Gas B diffuses back a distance δ to point 1.

a. Derive the equation for N_A for a very fast reaction using mole fraction units x_{A1}, and so on.

b. For $D_{AB} = 0.2 \times 10^{-4}$ m^2/s, $x_{A1} = 0.97$, $P = 101.32$ kPa, $\delta = 1.30$ mm, and $T = 298$ K, solve for N_A.

c. Do the same as in part (a) but for a slow first-order reaction where k'_1 is the reaction velocity constant.

d. Calculate N_A and x_{A2} for part (c) where $k'_1 = 0.53 \times 10^{-2}$ m/s.

A32: **Ans.** (b) $N_A = 8.35 \times 10^{-4}$ kg mol/s · m^2

7.5-12. ***Diffusion and Heterogeneous Reaction on Surface.*** In a tube of radius R m filled with a liquid, dilute component A is diffusing in the nonflowing liquid phase represented by

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

where z is distance along the tube axis. The inside wall of the tube exerts a catalytic effect and decomposes A so that the heterogeneous rate of decomposition on the wall in kg mol A/s is equal to kc_AA_w, where k is a first-order constant and A_w is the wall area in m^2. Neglect any radial gradients (this means a uniform radial concentration).

Derive the differential equation for unsteady state for diffusion and reaction for this system. [*Hint:* First make a mass balance for A for a Δz length of tube as follows: rate of input (diffusion) + rate of generation (heterogeneous) = rate of output (diffusion) + rate of accumulation.]

A33: **Ans.** $\frac{\partial c_A}{\partial t} = D_{AB}\frac{\partial^2 c_A}{\partial z^2} - \frac{2k}{R}c_A$

7.6-1. ***Knudsen Diffusivities.*** A mixture of He (A) and Ar (B) is diffusing at 1.013×10^5 Pa total pressure and 298 K through a capillary having a radius of 100 Å.

a. Calculate the Knudsen diffusivity of He (A).
b. Calculate the Knudsen diffusivity of Ar (B).
c. Compare with the molecular diffusivity D_{AB}.

A34: **Ans.** (a) $D_{KA} = 8.37 \times 10^{-6}$ m^2/s; (c) $D_{AB} = 7.29 \times 10^{-5}$ m^2/s

7.6-2. ***Transition-Region Diffusion.*** A mixture of He (A) and Ar (B) at 298 K is diffusing through an open capillary 15 mm long with a radius of 1000 Å. The total pressure is 1.013×10^5 Pa. The molecular diffusivity D_{AB} at 1.013×10^5 Pa is 7.29×10^{-5} m^2/s.

a. Calculate the Knudsen diffusivity of He (A).
b. Predict the flux N_A using Eq. (7.6-18) and Eq. (7.6-12) if $x_{A1} = 0.8$ and $x_{A2} = 0.2$. Assume steady state.
c. Predict the flux N_A using the approximate Eqs. (7.6-14) and (7.6-16).

7.6-3. ***Diffusion in a Pore in the Transition Region.*** Pure H_2 gas (A) at one end of a noncatalytic pore of radius 50 Å and length 1.0 mm ($x_{A1} = 1.0$) is diffusing through this pore with pure C_2H_6 gas (B) at the other end at $x_{A2} = 0$. The total pressure is constant at 1013.2 kPa. The predicted molecular diffusivity of H_2–C_2H_6 is 8.60×10^{-5} m^2/s at 101.32 kPa and 373 K. Calculate the Knudsen diffusivity of H_2 and flux N_A of H_2 in the mixture at 373 K and steady state.

A36: **Ans.** $D_{KA} = 6.60 \times 10^{-6}$ m^2/s, $N_A = 1.472 \times 10^{-3}$ kg mol A/s · m^2

7.6-4. ***Transition-Region Diffusion in Capillary.*** A mixture of nitrogen gas (*A*) and helium (*B*) at 298 K is diffusing through a capillary 0.10 m long in an open system with a diameter of 10 μm. The mole fractions are constant at $x_{A1} = 1.0$ and $x_{A2} = 0$. See Example 7.6-2 for physical properties.

a. Calculate the Knudsen diffusivity D_{KA} and D_{KB} at the total pressures of 0.001, 0.1, and 10.0 atm.
b. Calculate the flux N_A at steady state at these pressures.
c. Plot N_A versus P on log–log paper. What are the limiting lines at lower pressures and very high pressures? Calculate and plot these lines.

7.7-1. ***Numerical Method for Unsteady-State Diffusion.*** A solid slab 0.01 m thick has an initial uniform concentration of solute *A* of 1.00 kg mol/m^3. The diffusivity of *A* in the solid is $D_{AB} = 1.0 \times 10^{-10}$ m^2/s. All surfaces of the slab are insulated except the top surface. The surface concentration is suddenly dropped to zero concentration and held there. Unsteady-state diffusion occurs in the one *x* direction with the rear surface insulated. Using a numerical method, determine the concentrations after 12×10^4 s. Use $\Delta x = 0.002$ m and $M = 2.0$. The value of K is 1.0.

A38: **Ans.** $c_1 = 0$ (front surface, $x = 0$ m)

$c_2 = 0.3125$ kg mol/m^3 ($x = 0.002$ m)

$c_3 = 0.5859$ ($x = 0.004$ m)

$c_4 = 0.7813$ ($x = 0.006$ m)

$c_5 = 0.8984$ ($x = 0.008$ m)

$c_6 = 0.9375$ (insulated surface, $x = 0.01$ m)

7.7-2. ***Digital Computer and Unsteady-State Diffusion.*** Using the conditions of Problem 7.7-1, solve that problem by digital computer. Use $\Delta x = 0.0005$ m. Write the spreadsheet program and plot the final concentrations. Use the explicit method, $M = 2$.

7.7-3. ***Numerical Method and Different Boundary Condition.*** Use the same conditions as for Example 7.7-1, but in this case the rear surface is not insulated. At time $t = 0$ the concentration at the rear surface is also suddenly changed to $c_5 = 0$ and held there. Calculate the concentration profile after 2500 s. Plot the initial and final concentration profiles and compare with the final profile of Example 7.7-1.

7.8-1. ***Dimensional Analysis in Mass Transfer.*** A fluid is flowing in a vertical pipe and mass transfer is occurring from the pipe wall to the fluid. Relate the convective mass-transfer coefficient k'_c to the variables D, ρ, μ, v, D_{AB}, g, and $\Delta\rho$, where D is pipe diameter, L is pipe length, and $\Delta\rho$ is the density difference.

A41: **Ans.**

$$\frac{k'_c D}{D_{AB}} = f\left(\frac{gL^3\rho\,\Delta\rho}{\mu^2}, \frac{Dv\rho}{\mu}, \frac{\mu}{\rho D_{AB}}\right)$$

7.9-1. ***Mass Transfer and Turbulence Models.*** Pure water at a velocity of 0.11 m/s is flowing at 26.1°C past a flat plate of solid benzoic acid where L = 0.40 m. Do as follows:

a. Assuming dilute solutions, calculate the mass-transfer coefficient k_c. Use physical-property data from Example 7.3-2.

b. Using the film model, calculate the equivalent film thickness.

c. Using the penetration model, calculate the time of penetration.

d. Calculate the mean surface renewal factor using the modified penetration model.

A42: **Ans.** (b) δ_f = 0.2031 mm; (d) $s = 3.019 \times 10^{-2}$ s^{-1}

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