Transport Processes and Separation Process Principles

(INCLUDES UNIT OPERATIONS)

FOURTH EDITION

CHRISTIE JOHN GEANKOPLIS

Table of Contents

Chapter 6. Principles of Mass Transfer

INTRODUCTION TO MASS TRANSFER AND DIFFUSION

Similarity of Mass, Heat, and Momentum Transfer Processes

Introduction

In Chapter 1 we noted that the various separation processes have certain basic principles which can be classified into three fundamental transfer (or "transport") processes: momentum transfer, heat transfer, and mass transfer. The fundamental process of *momentum transfer* occurs in such operations as fluid flow, mixing, sedimentation, and filtration. *Heat transfer* occurs in conductive and convective transfer of heat, evaporation, distillation, and drying.

The third fundamental transfer process, *mass transfer,* occurs in distillation, absorption, drying, liquid–liquid extraction, adsorption, ion exchange, crystallization, and membrane processes. When mass is being transferred from one distinct phase to another or through a single phase, the basic mechanisms are the same whether the phase is a gas, liquid, or solid. This was also shown for heat transfer, where the transfer of heat by conduction followed Fourier's law in a gas, solid, or liquid.

General molecular transport equation

All three of the molecular transport processes—momentum, heat, and mass—are characterized by the same general type of equation, given in Section 2.3A:

Equation 2.3-1.

$$\text{rate of a transfer process} = \frac{\text{driving force}}{\text{resistance}}$$

This can be written as follows for molecular diffusion of the property momentum, heat, or mass:

Equation 2.3-2.

$$\psi_z = -\delta \frac{d\Gamma}{dz}$$

Molecular diffusion equations for momentum, heat, and mass transfer

Newton's equation for momentum transfer for constant density can be written as follows in a manner similar to Eq. (2.3-2):

Equation 6.1-1.

$$\tau_{zx} = -\frac{\mu}{\rho}\frac{d(v_x\rho)}{dz}$$

where τ_{zx} is momentum transferred/s · m^2, μ/ρ is kinematic viscosity in m^2/s, z is distance in m, and $v_x \rho$ is momentum/m^3, where the momentum has units of kg · m/s.

Fourier's law for heat conduction can be written as follows for constant ρ and c_p:

Equation 6.1-2.

$$\frac{q_z}{A} = -\alpha \frac{d(\rho c_p T)}{dz}$$

where q_z/A is heat flux in W/m^2, α is the thermal diffusivity in m^2/s, and $\rho c_p T$ is J/m^3.

The equation for molecular diffusion of mass is Fick's law and is also similar to Eq. (2.3-2). It is written as follows for constant total concentration in a fluid:

Equation 6.1-3.

$$J^*_{Az} = -D_{AB} \frac{dc_A}{dz}$$

where J^*_{Az} is the molar flux of component A in the z direction due to molecular diffusion in kg · mol A/s · m^2, D_{AB} the molecular diffusivity of the molecule A in B in m^2/s, c_A the concentration of A in kg · mol/m^3, and z the distance of diffusion in m. In cgs units J^*_{Az} is g mol A/s · cm^2, D_{AB} is cm^2/s, and c_A is g mol A/cm^3. In English units, J^*_{Az} is lb mol/h · ft^2, D_{AB} is ft^2/h, and c_A is lb mol/ft^3.

The similarity of Eqs. (6.1-1), (6.1-2), and (6.1-3) for momentum, heat, and mass transfer should be obvious. All the fluxes on the left-hand side of the three equations have as units transfer of a quantity of momentum, heat, or mass per unit time per unit area. The transport properties μ/ρ, α and D_{AB} all have units of m^2/s, and the concentrations are represented as momentum/m^3, J/m^3, or kg mol/m^3.

Turbulent diffusion equations for momentum, heat, and mass transfer

In Section 5.7C equations were given showing the similarities among momentum, heat, and mass transfer in turbulent transfer. For turbulent momentum transfer and constant density,

Equation 6.1-4.

$$\tau_{zx} = -\left(\frac{\mu}{\rho} + \varepsilon_t\right) \frac{d(v_x \rho)}{dz}$$

For turbulent heat transfer for constant ρ and c_p,

Equation 6.1-5.

$$\frac{q_z}{A} = -(\alpha + \alpha_t) \frac{d(\rho c_p T)}{dz}$$

For turbulent mass transfer for constant c,

Equation 6.1-6.

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

In these equations ε_t is the turbulent or eddy momentum diffusivity in m^2/s, α_t the turbulent or eddy thermal diffusivity in m^2/s, and ε_M the turbulent or eddy mass diffusivity in m^2/s. Again, these equations are quite similar to each other. Many of the theoretical equations and empirical correlations for turbulent transport to various geometries are also quite similar.

Examples of Mass-Transfer Processes

Mass transfer is important in many areas of science and engineering. Mass transfer occurs when a component in a mixture migrates in the same phase or from phase to phase because of a difference in concentration between two points. Many familiar phenomena involve mass transfer. Liquid in an open pail of water evaporates into still air because of the difference in concentration of water vapor at the water surface and the surrounding air. There is a "driving force" from the surface to the air. A piece of sugar added to a cup of coffee eventually dissolves by itself and diffuses to the surrounding solution. When newly cut and moist green timber is exposed to the atmosphere, the wood will dry partially when water in the timber diffuses through the wood to the surface and then to the atmosphere. In a fermentation process nutrients and oxygen dissolved in the solution diffuse to the microorganisms. In a catalytic reaction the reactants diffuse from the surrounding medium to the catalyst surface, where reaction occurs.

Many purification processes involve mass transfer. In uranium processing, a uranium salt in solution is extracted by an organic solvent. Distillation to separate alcohol from water involves mass transfer. Removal of SO_2 from flue gas is done by absorption in a basic liquid solution.

We can treat mass transfer in a manner somewhat similar to that used in heat transfer with Fourier's law of conduction. However, an important difference is that in molecular mass transfer, one or more of the components of the medium is moving. In heat transfer by conduction, the medium is usually stationary and only energy in the form of heat is being transported. This introduces some differences between heat and mass transfer that will be discussed in this chapter.

Fick's Law for Molecular Diffusion

Molecular diffusion or molecular transport can be defined as the transfer or movement of individual molecules through a fluid by means of the random, individual movements of the molecules. We can imagine the molecules traveling only in straight lines and changing direction by bouncing off other molecules after collision. Since the molecules travel in a random path, molecular diffusion is often called a *random-walk process.*

In Fig. 6.1-1 the *molecular diffusion process* is shown schematically. A random path that molecule *A* might take in diffusing through *B* molecules from point (1) to (2) is shown.If there are a greater number of *A* molecules near point (1) than at (2), then, since molecules diffuse randomly in both directions, more *A* molecules will diffuse from (1) to (2) than from (2) to (1). The net diffusion of *A* is from high- to low-concentration regions.

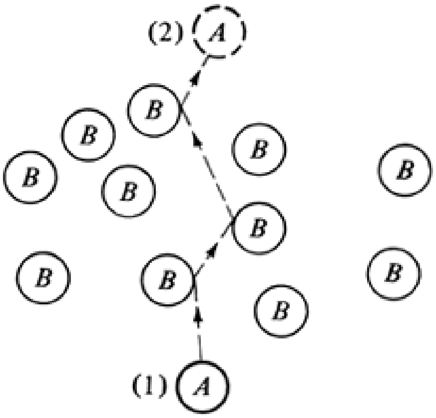


Figure 6.1-1. Schematic diagram of molecular diffusion process.

As another example, a drop of blue liquid dye is added to a cup of water. The dye molecules will diffuse slowly by molecular diffusion to all parts of the water. To increase this rate of mixing of the dye, the liquid can be mechanically agitated by a spoon and *convective mass transfer* will occur. The two modes of heat transfer, conduction and convective heat transfer, are analogous to molecular diffusion and convective mass transfer.

First, we will consider the diffusion of molecules when the whole bulk fluid is not moving but is stationary. Diffusion of the molecules is due to a concentration gradient. The general Fick's law equation can be written as follows for a binary mixture of *A* and *B*:

Equation 6.1-7.

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

where *c* is total concentration of *A* and *B* in kg mol $A + B/\text{m}^3$, and x_A is the mole fraction of *A* in the mixture of *A* and *B*. If *c* is constant, then since $c_A = cx_A$,

Equation 6.1-8.

$$c\,dx_A = d(cx_A) = dc_A$$

Substituting into Eq. (6.1-7) we obtain Eq. (6.1-3) for constant total concentration:

Equation 6.1-3.

$$J_{Az}^{*} = -D_{AB}\frac{dc_A}{dz}$$

This equation is the one more commonly used in many molecular diffusion processes. If *c* varies some, an average value is often used with Eq. (6.1-3).

EXAMPLE 6.1-1. Molecular Diffusion of Helium in Nitrogen

A mixture of He and N_2 gas is contained in a pipe at 298 K and 1 atm total pressure which is constant throughout. At one end of the pipe at point 1 the partial pressure p_{A1} of He is 0.60 atm and at the other end 0.2 m (20 cm) $p_{A2} = 0.20$ atm. Calculate the flux of He at steady state if D_{AB} of the He–N_2 mixture is 0.687×10^{-4} m^2/s (0.687 cm^2/s). Use SI and cgs units.

***Solution*:** Since total pressure *P* is constant, then *c* is constant, where *c* is as follows for a gas according to the perfect gas law:

Equation 6.1-9.

$$PV = nRT$$

Equation 6.1-10.

$$\frac{n}{V} = \frac{P}{RT} = c$$

where *n* is kg · mol *A* plus *B, V* is volume in m^3, *T* is temperature in K, *R* is 8314.3 $\text{m}^3 \cdot \text{Pa/kg} \cdot \text{mol} \cdot \text{K}$ or *R* is 82.057×10^{-3} $\text{m}^3 \cdot \text{atm/kg mol} \cdot \text{K}$, and *c* is kg mol *A* plus B/m^3. In cgs units, *R* is 82.057 $\text{cm}^3 \cdot \text{atm/g mol} \cdot \text{K}$.

For steady state the flux J_{Az}^{*} in Eq. (6.1-3) is constant. Also, D_{AB} for a gas is constant. Rearranging Eq. (6.1-3) and integrating,

Equation 6.1-11.

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

$$J_{AZ}^{*} = \frac{D_{AB}(c_{A1} - c_{A2})}{z_2 - z_1}$$

Also, from the perfect gas law, $p_A V = n_A RT$, and

Equation 6.1-12.

$$c_{A1} = \frac{p_{A1}}{RT} = \frac{n_A}{V}$$

Substituting Eq. (6.1-12) into (6.1-11),

Equation 6.1-13.

$$J^*_{Az} = \frac{D_{AB}(p_{A1} - p_{A2})}{RT(z_2 - z_1)}$$

This is the final equation to use, which is in a form easily used for gases. Partial pressures are p_{A1} = 0.6 atm = 0.6 × 1.01325 × 10^5 = 6.08 × 10^4 Pa and p_{A2} = 0.2 atm = 0.2 × 1.01325 × 10^5 = 2.027 × 10^4 Pa. Then, using SI units,

$$J^*_{Az} = \frac{(0.687 \times 10^{-4})(6.08 \times 10^4 - 2.027 \times 10^4)}{8314(298)(0.20 - 0)}$$
$$= 5.63 \times 10^{-6} \text{ kg mol } A/\text{s} \cdot \text{m}^2$$

If pressures in atm are used with SI units,

$$J^*_{Az} = \frac{(0.687 \times 10^{-4})(0.60 - 0.20)}{(82.06 \times 10^{-3})(298)(0.20 - 0)} = 5.63 \times 10^{-6} \text{ kg mol } A/\text{s} \cdot \text{m}^2$$

For cgs units, substituting into Eq. (6.1-13),

$$J^*_{Az} = \frac{0.687(0.60 - 0.20)}{82.06(298)(20 - 0)} = 5.63 \times 10^{-7} \text{ g mol } A/\text{s} \cdot \text{cm}^2$$

Other driving forces (besides concentration differences) for diffusion also occur because of temperature, pressure, electrical potential, and other gradients. Details are given elsewhere (B3).

Convective Mass-Transfer Coefficient

When a fluid is flowing outside a solid surface in forced convection motion, we can express the rate of convective mass transfer from the surface to the fluid, or vice versa, by the following equation:

Equation 6.1-14.

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

where k_c is a mass-transfer coefficient in m/s, c_{L1} the bulk fluid concentration in kg mol A/m^3, and c_{Li} the concentration in the fluid next to the surface of the solid. This mass-transfer coefficient is very similar to the heat-transfer coefficient h and is a function of the system geometry, fluid properties, and flow velocity. In Chapter 7 we consider convective mass transfer in detail.

MOLECULAR DIFFUSION IN GASES

Equimolar Counterdiffusion in Gases

In Fig. 6.2-1 a diagram is given of two gases *A* and *B* at constant total pressure *P* in two large chambers connected by a tube where molecular diffusion at steady state is occurring. Stirring in each chamber keeps the concentrations in each chamber uniform. The partial pressure $p_{A1} > p_{A2}$ and $p_{B2} > p_{B1}$. Molecules of *A* diffuse to the right and *B* to the left. Since the total pressure *P* is constant throughout, the net moles of *A* diffusing to the right must equal the net moles of *B* to the left. If this is not so, the total pressure would not remain constant. This means that

Equation 6.2-1.

$$J^*_{Az} = -J^*_{Bz}$$

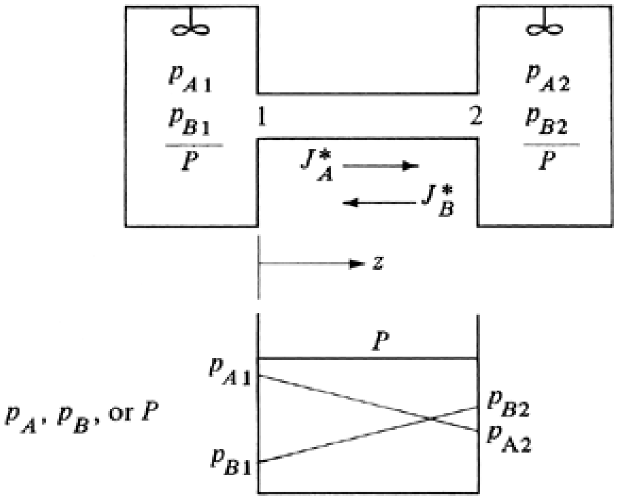


Figure 6.2-1. Equimolar counterdiffusion of gases A and B.

The subscript z is often dropped when the direction is obvious. Writing Fick's law for *B* for constant *c*,

Equation 6.2-2.

$$J^*_B = -D_{BA}\frac{dc_B}{dz}$$

Now since $P = p_A + p_B$ = constant, then

Equation 6.2-3.

$$c = c_A + c_B$$

Differentiating both sides,

Equation 6.2-4.

$$dc_A = -dc_B$$

Equating Eq. (6.1-3) to (6.2-2),

Equation 6.2-5.

$$J_A^* = -D_{AB}\frac{dc_A}{dz} = -J_B^* = -(-)D_{BA}\frac{dc_B}{dz}$$

Substituting Eq. (6.2-4) into (6.2-5) and canceling like terms,

Equation 6.2-6.

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

This shows that for a binary gas mixture of *A* and *B*, the diffusivity coefficient D_{AB} for *A* diffusing into *B* is the same as D_{BA} for *B* diffusing into *A*.

EXAMPLE 6.2-1. Equimolar Counterdiffusion

Ammonia gas (*A*) is diffusing through a uniform tube 0.10 m long containing N_2 gas (*B*) at 1.0132×10^5 Pa pressure and 298 K. The diagram is similar to Fig. 6.2-1. At point 1, $p_{A1} = 1.013 \times 10^4$ Pa and at point 2, $p_{A2} = 0.507 \times 10^4$ Pa. The diffusivity $D_{AB} = 0.230 \times 10^{-4}$ m^2/s.

a. Calculate the flux J_A^* at steady state.

b. Repeat for J_B^*

***Solution*:** Equation (6.1-13) can be used, where $P = 1.0132 \times 10^5$ Pa, $z_2 - z_1 = 0.10$ m, and $T = 298$ K. Substituting into Eq. (6.1-13) for part (a),

$$J_A^* = \frac{D_{AB}(p_{A1} - p_{A2})}{RT(z_2 - z_1)} = \frac{(0.23 \times 10^{-4})(1.013 \times 10^4 - 0.507 \times 10^4)}{8314(298)(0.10 - 0)}$$

$$= 4.70 \times 10^{-7} \text{ kg mol } A/\text{s} \cdot \text{m}^2$$

Rewriting Eq. (6.1-13) for component *B* for part (b) and noting that $p_{B1} = P - p_{A1} = 1.0132 \times 10^5 - 1.013 \times 10^4 = 9.119 \times 10^4$ Pa and $p_{B2} = P - p_{A2} = 1.0132 \times 10^5 - 0.507 \times 10^4 = 9.625 \times 10^4$ Pa,

$$J_B^* = \frac{D_{AB}(p_{B1} - p_{B2})}{RT(z_2 - z_1)} = \frac{(0.23 \times 10^{-4})(9.119 \times 10^4 - 9.625 \times 10^4)}{8314(298)(0.10 - 0)}$$

$$= -4.70 \times 10^{-7} \text{ kg mol } B/\text{s} \cdot \text{m}^2$$

The negative value for J_B^* means the flux goes from point 2 to point 1.

General Case for Diffusion of Gases A and B Plus Convection

Up to now we have considered Fick's law for diffusion in a stationary fluid; that is, there has been no net movement or convective flow of the entire phase of the binary mixture *A* and *B*. The diffusion flux J_A^* occurred because of the concentration gradient. The rate at which moles of *A* passed a fixed point to the right, which will be taken as a positive flux, is J_A^* kg mol *A*/s · m^2. This flux can be converted to a velocity of diffusion of *A* to the right by

Equation 6.2-7.

$$J_A^* (\text{kg mol } A/\text{s} \cdot \text{m}^2) = v_{Ad} c_A \left(\frac{\text{m}}{\text{s}} \frac{\text{kg mol } A}{\text{m}^3}\right)$$

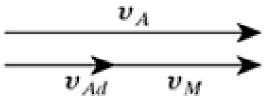
where v_{Ad} is the diffusion velocity of *A* in m/s.

Now let us consider what happens when the whole fluid is moving in bulk or convective flow to the right. The molar average velocity of the whole fluid relative to a stationary point is v_M m/s. Component A is still diffusing to the right, but now its diffusion velocity v_{Ad} is measured relative to the moving fluid. To a stationary observer A is moving faster than the bulk of the phase, since its diffusion velocity v_{Ad} is added to that of the bulk phase v_M. Expressed mathematically, the velocity of A relative to the stationary point is the sum of the diffusion velocity and the average or convective velocity:

Equation 6.2-8.

$$v_A = v_{Ad} + v_M$$

where v_A is the velocity of A relative to a stationary point. Expressed pictorially,



Multiplying Eq. (6.2-8) by c_A,

Equation 6.2-9.

$$c_A v_A = c_A v_{Ad} + c_A v_M$$

Each of the three terms represents a flux. The first term, $c_A v_A$, can be represented by the flux N_A kg mol A/s · m^2. This is the total flux of A relative to the stationary point. The second term is J_A^*, the diffusion flux relative to the moving fluid. The third term is the convective flux of A relative to the stationary point. Hence, Eq. (6.2-9) becomes

Equation 6.2-10.

$$N_A = J_A^* + c_A v_M$$

Let N be the total convective flux of the whole stream relative to the stationary point. Then,

Equation 6.2-11.

$$N = c v_M = N_A + N_B$$

Or, solving for v_M,

Equation 6.2-12.

$$v_M = \frac{N_A + N_B}{c}$$

Substituting Eq. (6.2-12) into (6.2-10),

Equation 6.2-13.

$$N_A = J_A^* + \frac{c_A}{c}(N_A + N_B)$$

Since J_A^* is Fick's law, Eq. (6.1-7),

Equation 6.2-14.

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

Equation (6.2-14) is the final general equation for diffusion plus convection to use when the flux N_A is used, which is relative to a stationary point. A similar equation can be written for N_B.

Equation 6.2-15.

$$N_B = -cD_{BA}\frac{dx_B}{dz} + \frac{c_B}{c}(N_A + N_B)$$

To solve Eq. (6.2-14) or (6.2-15), the relation between the flux N_A and N_B must be known. Equations (6.2-14) and (6.2-15) hold for diffusion in a gas, liquid, or solid.

For equimolar counterdiffusion, $N_A = -N_B$ and the convective term in Eq. (6.2-14) becomes zero. Then, $N_A = J^*_A = -N_B = \times J^*_B$.

Special Case for *A* Diffusing Through Stagnant, Nondiffusing *B*

The case of diffusion of *A* through stagnant or nondiffusing *B* at steady state often occurs. In this case one boundary at the end of the diffusion path is impermeable to component *B*, so it cannot pass through. One example, shown in Fig. 6.2-2a, is in the evaporation of a pure liquid such as benzene (*A*) at the bottom of a narrow tube, where a large amount of inert or nondiffusing air (*B*) is passed over the top. The benzene vapor (*A*) diffuses through the air (*B*) in the tube. The boundary at the liquid surface at point 1 is impermeable to air, since air is insoluble in benzene liquid. Hence, air (*B*) cannot diffuse into or away from the surface. At point 2 the partial pressure $p_{A2} = 0$, since a large volume of air is passing by.

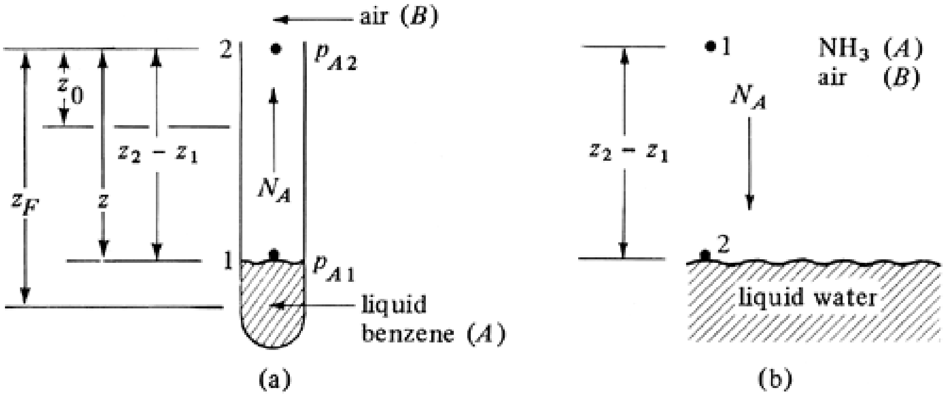


Figure 6.2-2. Diffusion of A through stagnant, nondiffusing B: (a) benzene evaporating into air, (b) ammonia in air being absorbed into water.

Another example, shown in Fig. 6.2-2b, occurs in the absorption of NH_3 (*A*) vapor which is in air (*B*) by water. The water surface is impermeable to the air, since air is only very slightly soluble in water. Thus, since *B* cannot diffuse, $N_B = 0$.

To derive the case for *A* diffusing in stagnant, nondiffusing *B*, $N_B = 0$ is substituted into the general Eq. (6.2-14):

Equation 6.2-16.

$$N_A = -cD_{AB}\frac{dx_A}{dz} + \frac{c_A}{c}(N_A + 0)$$

The convective flux of *A* is $(c_A/c)(N_A + 0)$. Keeping the total pressure *P* constant, substituting $c = P/RT$, $p_A = x_A P$, and $c_A/c = p_A/P$ into Eq. (6.2-16),

Equation 6.2-17.

$$N_A = -\frac{D_{AB}}{RT}\frac{dp_A}{dz} + \frac{p_A}{P}N_A$$

Rearranging and integrating,

Equation 6.2-18.

$$N_A\left(1 - \frac{p_A}{P}\right) = -\frac{D_{AB}}{RT}\frac{dp_A}{dz}$$

Equation 6.2-19.

$$N_A\int_{z_1}^{z_2} dz = -\frac{D_{AB}}{RT}\int_{p_{A1}}^{p_{A2}}\frac{dp_A}{1 - p_A/P}$$

Equation 6.2-20.

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

Equation (6.2-20) is the final equation to be used to calculate the flux of *A*. However, it is often written in another form. A log mean value of the inert *B* is defined as follows. Since $P = p_{A1} + p_{B1} = p_{A2} + p_{B2}$, $p_{B1} = P - p_{A1}$, and $p_{B2} = P - p_{A2}$,

Equation 6.2-21.

$$p_{BM} = \frac{p_{B2} - p_{B1}}{\ln(p_{B2}/p_{B1})} = \frac{p_{A1} - p_{A2}}{\ln[(P - p_{A2})/(P - p_{A1})]}$$

Substituting Eq. (6.2-21) into (6.2-20),

Equation 6.2-22.

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

EXAMPLE 6.2-2. Diffusion of Water Through Stagnant, Nondiffusing Air

Water in the bottom of a narrow metal tube is held at a constant temperature of 293 K. The total pressure of air (assumed dry) is 1.01325×10^5 Pa (1.0 atm) and the temperature is 293 K (20°C). Water evaporates and diffuses through the air in the tube, and the diffusion path $z_2 - z_1$ is 0.1524 m (0.5 ft) long. The diagram is similar to Fig. 6.2-2a. Calculate the rate of evaporation at steady state in lb mol/h · ft^2 and kg mol/s · m^2. The diffusivity of water vapor at 293 K and 1 atm pressure is 0.250×10^{-4} m^2/s. Assume that the system is isothermal. Use SI and English units.

Solution. The diffusivity is converted to ft^2/h by using the conversion factor from Appendix A.1:

$$D_{AB} = 0.250 \times 10^{-4}(3.875 \times 10^4) = 0.969 \text{ ft}^2/\text{h}$$

From Appendix A.2 the vapor pressure of water at 20°C is 17.54 mm, or $p_{A1} = 17.54/760 = 0.0231$ atm = $0.0231(1.01325 \times 10^5) = 2.341 \times 10^3$ Pa, $p_{A2} = 0$ (pure air). Since the temperature is 20°C (68°F), $T = 460 + 68 = 528$°R = 293 K. From Appendix A.1, $R = 0.730$ ft^3 · atm/lb · mol·°R. To calculate the value of p_{BM} from Eq. (6.2-21),

$$p_{B1} = P - p_{A1} = 1.00 - 0.0231 = 0.9769 \text{ atm}$$

$$P_{B2} = P - p_{A2} = 1.00 - 0 = 1.00 \text{ atm}$$

$$p_{BM} = \frac{p_{B2} - p_{B1}}{\ln(p_{B2}/p_{B1})} = \frac{1.00 - 0.9769}{\ln(1.00/0.9769)} = 0.988 \text{ atm} = 1.001 \times 10^5 \text{ Pa}$$

Since p_{B1} is close to p_{B2}, the linear mean $(p_{B1} + p_{B2})/2$ could be used and would be very close to p_{BM}.

Substituting into Eq. (6.2-22) with $z_2 - z_1 = 0.5$ ft (0.1524 m),

$$N_A = \frac{D_{AB}P}{RT(z_2 - z_1)p_{BM}}(p_{A1} - p_{A2}) = \frac{0.969(1.0)(0.0231 - 0)}{0.730(528)(0.5)(0.988)}$$

$$= 1.175 \times 10^{-4} \text{ lb mol/h} \cdot \text{ft}^2$$

$$N_A = \frac{(0.250 \times 10^{-4})(1.01325 \times 10^5)(2.341 \times 10^3 - 0)}{8314(293)(0.1524)(1.001 \times 10^5)}$$

$$= 1.595 \times 10^{-7} \text{ kg mol/s} \cdot \text{m}^2$$

EXAMPLE 6.2-3. Diffusion in a Tube with Change in Path Length

Diffusion of water vapor in a narrow tube is occurring as in Example 6.2-2 under the same conditions. However, as shown in Fig. 6.2-2a, at a given time t, the level is z m from the top. As diffusion proceeds, the level drops slowly. Derive the equation for the time t_F for the level to drop from a starting point of z_0 m at $t = 0$ to z_F at $t = t_F$ s as shown.

***Solution*:** We assume a pseudo-steady-state condition since the level drops very slowly. As time progresses, the path length z increases. At any time t, Eq. (6.2-22) holds; but the path length is z and Eq. (6.2-22) becomes as follows, where N_A and z are now variables:

Equation 6.2-23.

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

Assuming a cross-sectional area of 1 m^2, the level drops dz m in dt s, and $\rho_A(dz \cdot 1)/M_A$ is the kg mol of A that have left and diffused. Then,

Equation 6.2-24.

$$N_A \cdot 1 = \frac{\rho_A(dz \cdot 1)}{M_A\, dt}$$

Equating Eq. (6.2-24) to (6.2-23), rearranging, and integrating between the limits of $z = z_0$ when $t = 0$ and $z = z_F$ when $t = t_F$,

Equation 6.2-25.

$$\frac{\rho_A}{M_A}\int_{z_0}^{z_F} z\, dz = \frac{D_{AB}P(p_{A1} - p_{A2})}{RTp_{BM}}\int_0^{t_F} dt$$

Solving for t_F,

Equation 6.2-26.

$$t_F = \frac{\rho_A(z_F^2 - z_0^2)RTp_{BM}}{2M_AD_{AB}P(p_{A1} - p_{A2})}$$

The method shown in Example 6.2-3 has been used to experimentally determine the diffusivity D_{AB}. In this experiment the starting path length z_0 is measured at $t = 0$ together with the final z_F at t_F. Then Eq. (6.2-26) is used to calculate D_{AB}.

Diffusion Through a Varying Cross-Sectional Area

So far, in the cases at steady state we have considered N_A and J_A^* as constants in the integrations. In these cases the cross-sectional area A m^2 through which the diffusion occurs has been constant with varying distance z. In some situations the area A may vary. Then it is convenient to define N_A as

Equation 6.2-27.

$$N_A = \frac{\overline{N}_A}{4\pi r^2}$$

where $\overline{N}_A$ is kg moles of A diffusing per second or kg mol/s. At steady state, $\overline{N}_A$ will be constant but not A for a varying area.

Diffusion from a sphere

To illustrate the use of Eq. (6.2-27), the important case of diffusion to or from a sphere in a gas will be considered. This situation appears often, in such cases as the evaporation of a drop of liquid, the evaporation of a ball of naphthalene, and the diffusion of nutrients to a sphere-like microorganism in a liquid. In Fig. 6.2-3a is shown a sphere of fixed radius r_1 m in an infinite gas medium. Component (A) at partial pressure p_{A1} at the surface is diffusing into the surrounding stagnant medium (B), where $p_{A2} = 0$ at some large distance away. Steady-state diffusion will be assumed.

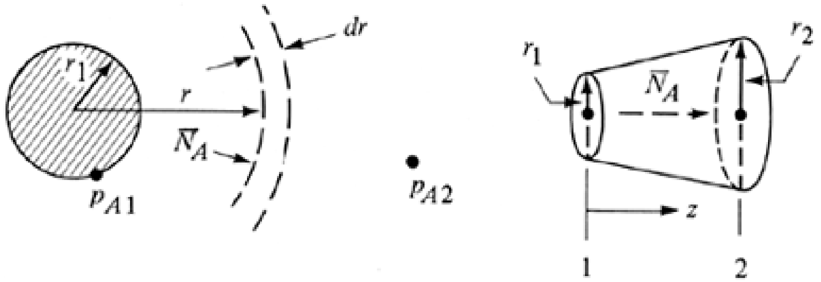


Figure 6.2-3. Diffusion through a varying cross-sectional area: (a) from a sphere to a surrounding medium, (b) through a circular conduit that is tapered uniformally.

The flux N_A can be represented by Eq. (6.2-27), where A is the cross-sectional area $4\pi r^2$ at point r distance from the center of the sphere. Also, $\overline{N}_A$ is a constant at steady state:

Equation 6.2-28.

$$N_A = \frac{\overline{N}_A}{4\pi r^2}$$

Since this is a case of A diffusing through stagnant, nondiffusing B, Eq. (6.2-18) will be used in its differential form and N_A will be equated to Eq. (6.2-28), giving

Equation 6.2-29.

$$N_A = \frac{\overline{N}_A}{4\pi r^2} = -\frac{D_{AB}}{RT}\,\frac{dp_A}{(1 - p_A/P)dr}$$

Note that dr was substituted for dz. Rearranging and integrating between r_1 and some point r_2 a large distance away,

Equation 6.2-30.

$$\frac{\overline{N}_A}{4\pi}\int_{r_1}^{r_2}\frac{dr}{r^2} = -\frac{D_{AB}}{RT}\int_{p_{A1}}^{p_{A2}}\frac{dp_A}{(1 - p_A/P)}$$

Equation 6.2-31.

$$\frac{\overline{N}_A}{4\pi}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) = \frac{D_{AB}P}{RT}\ln\frac{P - p_{A2}}{P - p_{A1}}$$

Since $r_2 \gg r_1$, $1/r_2 \cong 0$. Substituting p_{BM} from Eq. (6.2-21) into Eq. (6.2-31),

Equation 6.2-32.

$$\frac{\overline{N}_A}{4\pi r_1^2} = N_{A1} = \frac{D_{AB}P}{RTr_1}\frac{p_{A1} - p_{A2}}{p_{BM}}$$

This equation can be simplified further. If p_{A1} is small compared to P (a dilute gas phase), $P_{BM} \cong P$. Also, setting $2r_1 = D_1$, diameter, and $c_{A1} = p_{A1}/RT$, we obtain

Equation 6.2-33.

$$N_{A1} = \frac{2D_{AB}}{D_1}(c_{A1} - c_{A2})$$

This equation can also be used for liquids, where D_{AB} is the diffusivity of A in the liquid.

EXAMPLE 6.2-4. Evaporation of a Naphthalene Sphere

A sphere of naphthalene having a radius of 2.0 mm is suspended in a large volume of still air at 318 K and 1.01325×10^5 Pa (1 atm). The surface temperature of the naphthalene can be assumed to be at 318 K and its vapor pressure at 318 K is 0.555 mm Hg. The D_{AB} of naphthalene in air at 318 K is 6.92×10^{-6} m^2/s. Calculate the rate of evaporation of naphthalene from the surface.

***Solution*:** The flow diagram is similar to Fig. 6.2-3a. $D_{AB} = 6.92 \times 10^{-6}$ m^2/s, $p_{A1} = (0.555/760)(1.01325 \times 10^5) = 74.0$ Pa, $p_{A2} = 0$, $r_1 = 2/1000$ m, $R = 8314$ m^3· Pa/kg mol · K, $p_{B1} = P - p_{A1} = 1.01325 \times 10^5 - 74.0 = 1.01251 \times 10^5$ Pa, $p_{B2} = P - p_{A2} = 1.01325 \times 10^5 - 0$. Since the values of p_{B1} and p_{B2} are close to each other,

$$p_{BM} = \frac{p_{B1} + p_{B2}}{2} = \frac{(1.0125 + 1.01325) \times 10^5}{2} = 1.0129 \times 10^5 \text{ Pa}$$

Substituting into Eq. (6.2-32),

$$N_{A1} = \frac{D_{AB}P(p_{A1} - p_{A2})}{RTr_1p_{BM}} = \frac{(6.92 \times 10^{-6})(1.01325 \times 10^5)(74.0 - 0)}{8314(318)(2/1000)(1.0129 \times 10^5)}$$

$$= 9.68 \times 10^{-8} \text{ kg mol } A/\text{s} \cdot \text{m}^2$$

If the sphere in Fig. 6.2-3a is evaporating, the radius r of the sphere decreases slowly with time. The equation for the time it takes for the sphere to evaporate completely can be derived by assuming pseudo-steady state and by equating the diffusion flux equation (6.2-32), where r is now a variable, to the moles of solid A evaporated per dt time and per unit area as calculated from a material balance. (See Problem 6.2-9 for this case.) The material-balance method is similar to Example 6.2-3. The final equation is

Equation 6.2-34.

$$t_F = \frac{\rho_A r_1^2 RT p_{BM}}{2M_A D_{AB} P(p_{A1} - p_{A2})}$$

where r_1 is the original sphere radius, ρ_A the density of the sphere, and M_A the molecular weight.

Diffusion through a conduit of nonuniform cross-sectional area

In Fig. 6.2-3b component A is diffusion at steady state through a circular conduit which is tapered uniformally as shown. At point 1 the radius is r_1 and at point 2 it is r_2. At position z in the conduit, for A diffusing through stagnant, nondiffusing B,

Equation 6.2-35.

$$N_A = \frac{\overline{N}_A}{\pi r^2} = -\frac{D_{AB}}{RT}\frac{dp_A}{(1 - p_A/P)dz}$$

Using the geometry shown, the variable radius r can be related to position z in the path as follows:

Equation 6.2-36.

$$r = \left(\frac{r_2 - r_1}{z_2 - z_1}\right)z + r_1$$

This value of r is then substituted into Eq. (6.2-35) to eliminate r and the equation integrated:

Equation 6.2-37.

$$\frac{\overline{N}_A}{\pi}\int_{z_1}^{z_2} \frac{dz}{\left[\left(\frac{r_2 - r_1}{z_2 - z_1}\right)z + r_1\right]^2} = -\frac{D_{AB}}{RT}\int_{p_{A1}}^{p_{A2}} \frac{dp_A}{1 - p_A/P}$$

A case similar to this is given in Problem 6.2-10.

Diffusion Coefficients for Gases

Experimental determination of diffusion coefficients

A number of different experimental methods have been used to determine the molecular diffusivity for binary gas mixtures. Several of the important methods are as follows. One method is to evaporate a pure liquid in a narrow tube with a gas passed over the top, as shown in Fig. 6.2-2a. The fall in liquid level is measured with time and the diffusivity calculated from Eq. (6.2-26).

In another method, two pure gases having equal pressures are placed in separate sections of a long tube separated by a partition. The partition is slowly removed and diffusion proceeds. After a given time the partition is reinserted and the gas in each section analyzed. The diffusivities of the vapor of solids such as naphthalene, iodine, and benzoic acid in a gas have been obtained by measuring the rate of evaporation of a sphere. Equation (6.2-32) can be used. See Problem 6.2-9 for an example of this.

A method often used is the two-bulb method (N1). The apparatus consists of two glass bulbs with volumes V_1 and V_2 m^3 connected by a capillary of cross-sectional area A m^2 and length L whose volume is small compared to V_1 and V_2, as shown in Fig. 6.2-4. Pure gas A is added to V_1 and pure B to V_2 at the same pressures. The valve is opened, diffusion proceeds for a given time, and then the valve is closed and the mixed contents of each chamber are sampled separately.

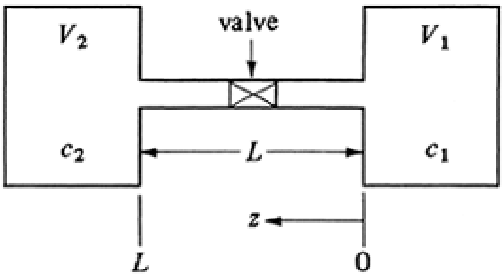


Figure 6.2-4. Diffusivity measurement of gases by the two-bulb method.

The equations can be derived by neglecting the capillary volume and assuming each bulb is always of a uniform concentration. Assuming quasi-steady-state diffusion in the capillary,

Equation 6.2-38.

$$J_A^* = -D_{AB}\frac{dc}{dz} = -\frac{D_{AB}(c_2 - c_1)}{L}$$

where c_2 is the concentration of A in V_2 at time t and c_1 in V_1. The rate of diffusion of A going to V_2 is equal to the rate of accumulation in V_2:

Equation 6.2-39.

$$AJ_A^* = -\frac{D_{AB}(c_2 - c_1)A}{L} = V_2\frac{dc_2}{dt}$$

The average value c_{av} at equilibrium can be calculated by a material balance from the starting compositions c_1^0 and c_2^0 at $t = 0$:

Equation 6.2-40.

$$(V_1 + V_2)c_{av} = V_1c_1^0 + V_2c_2^0$$

A similar balance at time t gives

Equation 6.2-41.

$$(V_1 + V_2)c_{av} = V_1c_1 + V_2c_2$$

Substituting c_1 from Eq. (6.2-41) into (6.2-39), rearranging, and integrating between $t = 0$ and $t = t$, the final equation is

Equation 6.2-42.

$$\frac{c_{\text{av}} - c_2}{c_{\text{av}} - c_2^0} = \exp\left[-\frac{D_{AB}(V_1 + V_2)}{(L/A)(V_2V_1)}t\right]$$

If c_2 is obtained by sampling at t, D_{AB} can be calculated.

Experimental diffusivity data

Some typical data are given in Table 6.2-1. Other data are tabulated in Perry and Green (P1) and Reid et al. (R1). The values range from about 0.05 × 10^{-4} m^2/s, where a large molecule is present, to about 1.0 × 10^{-4} m^2/s, where H_2 is present at room temperatures. The relation between diffusivity in m^2/s and ft^2/h is 1 m^2/s = 3.875 × 10^4 ft^2/h.

Table 6.2-1. Diffusion Coefficients of Gases at 101.32 kPa Pressure

	Temperature			
System	**°C**	**K**	***Diffusivity*** **[*(m^2/s)10^4 or cm^2/s*]**	**Ref.**
Air–NH_3	0	273	0.198	(W1)
Air–H_2O	0	273	0.220	(N2)
	25	298	0.260	(L1)
	42	315	0.288	(M1)
Air–CO_2	3	276	0.142	(H1)
	44	317	0.177	
Air–H_2	0	273	0.611	(N2)
Air–C_2H_5OH	25	298	0.135	(M1)
	42	315	0.145	
Air–CH_3COOH	0	273	0.106	(N2)
Air–*n*-hexane	21	294	0.080	(C1)
Air–benzene	25	298	0.0962	(L1)
Air–toluene	25.9	298.9	0.086	(G1)
Air–*n*-butanol	0	273	0.0703	(N2)
	25.9	298.9	0.087	
H_2–CH_4	25	298	0.726	(C2)
H_2–N_2	25	298	0.784	(B1)
	85	358	1.052	
H_2–benzene	38.1	311.1	0.404	(H2)
H_2–Ar	22.4	295.4	0.83	(W2)
H_2–NH_3	25	298	0.783	(B1)
H_2–SO_2	50	323	0.61	(S1)
H_2–C_2H_5OH	67	340	0.586	(T1)
He–Ar	25	298	0.729	(S2)
He–*n*-butanol	150	423	0.587	(S2)
He–air	44	317	0.765	(H1)
He–CH_4	25	298	0.675	(C2)
He–N_2	25	298	0.687	(S2)
He–O_2	25	298	0.729	(S2)
Ar–CH_4	25	298	0.202	(C2)
CO_2–N_2	25	298	0.167	(W3)
CO_2–O_2	20	293	0.153	(W4)
N_2–*n*-butane	25	298	0.0960	(B2)

System	*Temperature* °C	K	*Diffusivity* [(m^2/s)10^4 *or* cm^2/s]	Ref.
$H_2O–CO_2$	34.3	307.3	0.202	(S3)
$CO–N_2$	100	373	0.318	(A1)
$CH_3Cl–SO_2$	30	303	0.0693	(C3)
$(C_2H_5)_2O–NH_3$	26.5	299.5	0.1078	(S4)

Prediction of diffusivity for gases

The diffusivity of a binary gas mixture in the dilute gas region, that is, at low pressures near atmospheric, can be predicted using the kinetic theory of gases. The gas is assumed to consist of rigid spherical particles that are completely elastic on collision with another molecule, which implies that momentum is conserved.

In a simplified treatment it is assumed that there are no attractive or repulsive forces between the molecules. The derivation uses the mean free path λ, which is the average distance that a molecule has traveled between collisions. The final equation is

Equation 6.2-43.

$$D_{AB} = \tfrac{1}{3}\bar{u}\lambda$$

where $\bar{u}$ is the average velocity of the molecules. The final equation obtained after substituting expressions for $\bar{u}$ and λ into Eq. (6.2-43) is approximately correct, since it correctly predicts D_{AB} proportional to 1/pressure and approximately predicts the temperature effect.

A more accurate and rigorous treatment must consider the intermolecular forces of attraction and repulsion between molecules as well as the different sizes of molecules A and B. Chapman and Enskog (H3) solved the Boltzmann equation, which uses a distribution function instead of the mean free path λ. To solve the equation, a relation between the attractive and repulsive forces between a given pair of molecules must be used. For a pair of nonpolar molecules, a reasonable approximation to the forces is the Lennard–Jones function.

The final relation for predicting the diffusivity of a binary gas pair of A and B molecules is

Equation 6.2-44.

$$D_{AB} = \frac{1.8583 \times 10^{-7} T^{3/2}}{P\sigma_{AB}^2 \Omega_{D,AB}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}$$

where D_{AB} is the diffusivity in m^2/s, T temperature in K, M_A molecular weight of A in kg mass/kg mol, M_B molecular weight of B, and P absolute pressure in atm. The term σ_{AB} is an "average collision diameter" and $\Omega_{D,AB}$ is a collision integral based on the Lennard–Jones potential. Values of σ_A and σ_B as well as $\Omega_{D,AB}$ can be obtained from a number of sources (B3, G2, H3, R1).

The collision integral $\Omega_{D,AB}$ is a ratio giving the deviation of a gas with interactions as compared to a gas of rigid, elastic spheres. This value would be 1.0 for a gas with no interactions. Equation (6.2-44) predicts diffusivities with an average deviation of about 8% up to about 1000 K (R1). For a polar–nonpolar gas mixture, Eq. (6.2-44) can be used if the correct force constant is used for the polar gas (M1, M2). For polar–polar gas pairs, the potential-energy function commonly used is the *Stockmayer potential* (M2).

The effect of concentration of A in B in Eq. (6.2-44) is not included. However, for real gases with interactions, the maximum effect of concentration on diffusivity is about 4% (G2). In most cases the effect is considerably less, and hence it is usually neglected.

Equation (6.2-44) is relatively complicated to use, and often some of the constants such as σ_{AB} are not available or are difficult to estimate. Hence, the semiempirical method of Fuller et al. (F1), which is much more convenient to use is often preferred. The equation was obtained by correlating many recent data and uses atomic volumes from Table 6.2-2, which are summed for each gas molecule. The equation is

Equation 6.2-45.

$$D_{AB} = \frac{1.00 \times 10^{-7} T^{1.75} (1/M_A + 1/M_B)^{1/2}}{P[(\Sigma v_A)^{1/3} + (\Sigma v_B)^{1/3}]^2}$$

Table 6.2-2. Atomic Diffusion Volumes for Use with the Fuller, Schettler, and Giddings Method[*]

Atomic and structural diffusion volume increments, v			
C	16.5	(C1)	19.5
H	1.98	(S)	17.0
O	5.48	Aromatic ring	−20.2
(N)	5.69	Heterocyclic ring	−20.2
Diffusion volumes for simple molecules, E v			
H_2	7.07	CO	18.9
D_2	6.70	CO_2	26.9
He	2.88	N_2O	35.9
N_2	17.9	NH_3	14.9
O_2	16.6	H_2O	12.7
Air	20.1	(CCl_2F_2)	114.8
Ar	16.1	(SF_6)	69.7
Kr	22.8	(Cl_2)	37.7
(Xe)	37.9	(Br_2)	67.2
Ne	5.59	(SO_2)	41.1

***Source:* Reprinted with permission from E. N. Fuller, P. D. Schettler, and J. C. Giddings, *Ind. Eng. Chem.*, 58, 19(1966). Copyright by the American Chemical Society.**

[*] Parentheses indicate that the value listed is based on only a few data points.

where E v_A = sum of structural volume increments, Table 6.2-2, and D_{AB} = m^2/s. This method can be used for mixtures of nonpolar gases or for a polar–nonpolar mixture. Its accuracy is not quite as good as that of Eq. (6.2-44).

The equation shows that D_{AB} is proportional to $1/P$ and to $T^{1.75}$. If an experimental value of D_{AB} is available at a given T and P and it is desired to have a value of D_{AB} at another T and P, one should correct the experimental value to the new T and P by means of the relationship $D_{AB} \propto T^{1.75}/P$.

Schmidt number of gases

The *Schmidt number* of a gas mixture of dilute A in B is dimensionless and is defined as

Equation 6.2-46.

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

where μ is viscosity of the gas mixture, which is viscosity of B for a dilute mixture in Pa · s or kg/m · s, D_{AB} is diffusivity in m^2/s, and ρ is the density of the mixture in kg/m^3. For a gas the Schmidt number can be assumed independent of temperature over moderate ranges and independent of pressure up to about 10 atm or 10×10^5 Pa.

The Schmidt number is the dimensionless ratio of the molecular momentum diffusivity μ/ρ to the molecular mass diffusivity D_{AB}. Values of the Schmidt number for gases range from about 0.5 to 2. For liquids Schmidt numbers range from about 100 to over 10 000 for viscous liquids.

EXAMPLE 6.2-5. Estimation of Diffusivity of a Gas Mixture

Normal butanol (A) is diffusing through air (B) at 1 atm abs. Using the Fuller et al. method, estimate the diffusivity D_{AB} for the following temperatures and compare with the experimental data:

a. For 0°C.

b. For 25.9°C.

c. For 0°C and 2.0 atm abs.

Solution: For part (a), $P = 1.00$ atm, $T = 273 + 0 = 273$ K, M_A (butanol) = 74.1, M_B (air) = 29. From Table 6.2-2,

$$\sum \upsilon_A = 4(16.5) + 10(1.98) + 1(5.48) = 91.28 \text{ (butanol)}$$

$$\sum \upsilon_B = 20.1 \text{ (air)}$$

Substituting into Eq. (6.2-45),

$$D_{AB} = \frac{1.0 \times 10^{-7}(273)^{1.75}(1/74.1 + 1/29)^{1/2}}{1.0[(91.28)^{1/3} + (20.1)^{1/3}]^2}$$

$$= 7.73 \times 10^{-6} \text{ m}^2/\text{s}$$

This value deviates by +10% from the experimental value of 7.03×10^{-6} m^2/s from Table 6.2-1.

For part (b), $T = 273 + 25.9 = 298.9$. Substituting into Eq. (6.2-45), $D_{AB} = 9.05 \times 10^{-6}$ m^2/s. This value deviates by +4% from the experimental value of 8.70×10^{-6} m^2/s.

For part (c), the total pressure $P = 2.0$ atm. Using the value predicted in part (a) and correcting for pressure,

$$D_{AB} = 7.73 \times 10^{-6}(1.0/2.0) = 3.865 \times 10^{-6} \text{ m}^2/\text{s}$$

MOLECULAR DIFFUSION IN LIQUIDS

Introduction

Diffusion of solutes in liquids is very important in many industrial processes, especially in such separation operations as liquid–liquid extraction or solvent extraction, gas absorption, and distillation. Diffusion in liquids also occurs in many situations in nature, such as oxygenation of rivers and lakes by the air and diffusion of salts in blood.

It should be apparent that the rate of molecular diffusion in liquids is considerably slower than in gases. The molecules in a liquid are very close together compared to a gas. Hence, the molecules of the diffusing solute A will collide with molecules of liquid B more often and diffuse more slowly than in gases. In general, the diffusion coefficient in a gas will be on the order of magnitude of about 10^5 times greater than in a liquid. However, the flux in a gas is not that much greater, being only about 100 times faster, since the concentrations in liquids are considerably higher than in gases.

Equations for Diffusion in Liquids

Since the molecules in a liquid are packed together much more closely than in gases, the density and the resistance to diffusion in a liquid are much greater. Also, because of this closer spacing of the molecules, the attractive forces between molecules play an important role in diffusion. Since the kinetic theory of liquids is only partially developed, we write the equations for diffusion in liquids similar to those for gases.

In diffusion in liquids an important difference from diffusion in gases is that the diffusivities are often quite dependent on the concentration of the diffusing components.

Equimolar counterdiffusion

Starting with the general equation (6.2-14), we can obtain for equimolal counterdiffusion, where $N_A = -N_B$, an equation similar to Eq. (6.1-11) for gases at steady state:

Equation 6.3-1.

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

where N_A is the flux of A in kg mol A/s · m^2, D_{AB} the diffusivity of A in B in m^2/s, c_{A1} the concentration of A in kg mol A/m^3 at point 1, x_{A1} the mole fraction of A at point 1, and c_{av} defined by

Equation 6.3-2.

$$c_{av} = \left(\frac{\rho}{M}\right)_{av} = \left(\frac{\rho_1}{M_1} + \frac{\rho_2}{M_2}\right)\Big/2$$

where c_{av} is the average total concentration of $A + B$ in kg mol/m^3, M_1 the average molecular weight of the solution at point 1 in kg mass/kg mol, and ρ_1 the average density of the solution in kg/m^3 at point 1.

Equation (6.3-1) uses the average value of D_{AB}, which may vary some with concentration, and the average value of c, which may also vary with concentration. Usually, the linear average of c is used, as in Eq. (6.3-2). The case of equimolar counterdiffusion in Eq. (6.3-1) only occurs very infrequently in liquids.

Diffusion of A through nondiffusing B

The most important case of diffusion in liquids is that where solute A is diffusing and solvent B is stagnant or nondiffusing. An example is a dilute solution of propionic acid (A) in a water (B) solution being contacted with toluene. Only the propionic acid (A) diffuses through the water phase, to the boundary, and then into the toluene phase. The toluene–water interface is a barrier to diffusion of B and $N_B = 0$. Such cases often occur in industry (T2). If Eq. (6.2-22) is rewritten in terms of concentrations by substituting $c_{av} = P/RT$, $c_{A1} = p_{A1}/RT$, and $x_{BM} = p_{BM}/P$, we obtain the equation for liquids at steady state:

Equation 6.3-3.

$$N_A = \frac{D_{AB}c_{av}}{(z_2 - z_1)x_{BM}}(x_{A1} - x_{A2})$$

where

Equation 6.3-4.

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

Note that $x_{A1} + x_{B1} = x_{A2} + x_{B2} = 1.0$. For dilute solutions x_{BM} is close to 1.0 and c is essentially constant. Then Eq. (6.3-3) simplifies to

Equation 6.3-5.

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

EXAMPLE 6.3-1. Diffusion of Ethanol (A) Through Water (B)

An ethanol (A)–water (B) solution in the form of a stagnant film 2.0 mm thick at 293 K is in contact at one surface with an organic solvent in which ethanol is soluble and water is insoluble. Hence, $N_B = 0$. At point 1 the concentration of ethanol is 16.8 wt % and the solution density is $\rho_1 = 972.8\ \text{kg/m}^3$. At point 2 the concentration of ethanol is 6.8 wt % and $\rho_2 = 988.1\ \text{kg/m}^3$ (P1). The diffusivity of ethanol is $0.740 \times 10^{-9}\ \text{m}^2/\text{s}$ (T2). Calculate the steady-state flux N_A.

Solution. The diffusivity is $D_{AB} = 0.740 \times 10^{-9}\ \text{m}^2/\text{s}$. The molecular weights of A and B are $M_A = 46.05$ and $M_B = 18.02$. For a wt % of 6.8, the mole fraction of ethanol (A) is as follows when using 100 kg of solution:

$$x_{A2} = \frac{6.8/46.05}{6.8/46.05 + 93.2/18.02} = \frac{0.1477}{0.1477 + 5.17} = 0.0277$$

Then $x_{B2} = 1 - 0.0277 = 0.9723$. Calculating x_{A1} in a similar manner, $x_{A1} = 0.0732$ and $x_{B1} = 1 - 0.0732 = 0.9268$. To calculate the molecular weight M_2 at point 2,

$$M_2 = \frac{100\ \text{kg}}{(0.1477 + 5.17)\text{kg mol}} = 18.75\ \text{kg/kg mol}$$

Similarly, $M_1 = 20.07$. From Eq. (6.3-2),

$$c_{\text{av}} = \frac{\rho_1/M_1 + \rho_2/M_2}{2} = \frac{972.8/20.07 + 988.1/18.75}{2} = 50.6\ \text{kg mol/m}^3$$

To calculate x_{BM} from Eq. (6.3-4), we can use the linear mean since x_{B1} and x_{B2} are close to each other:

$$x_{BM} = \frac{x_{B1} + x_{B2}}{2} = \frac{0.9268 + 0.9723}{2} = 0.949$$

Substituting into Eq. (6.3-3) and solving,

$$N_A = \frac{D_{AB}c_{\text{av}}}{(z_2 - z_1)x_{BM}}(x_{A1} - x_{A2}) = \frac{(0.740 \times 10^{-9})(50.6)(0.0732 - 0.0277)}{(2/1000)0.949}$$
$$= 8.99 \times 10^{-7}\ \text{kg mol/s} \cdot \text{m}^2$$

Diffusion Coefficients for Liquids

Experimental determination of diffusivities

Several different methods are used to determine diffusion coefficients experimentally in liquids. In one method, unsteady-state diffusion in a long capillary tube is carried out and the diffusivity determined from the concentration profile. If the solute A is diffusing in B, the diffusion coefficient determined is D_{AB}. Also, the value of diffusivity is often very dependent upon the concentration of the diffusing solute A. For liquids, unlike gases, the diffusivity D_{AB} does not equal D_{BA}.

In a fairly common method a relatively dilute solution and a slightly more concentrated solution are placed in chambers on opposite sides of a porous membrane of sintered glass as shown in Fig. 6.3-1. Molecular diffusion takes place through the narrow passageways of the pores in the sintered glass while the two compartments are stirred. The effective diffusion length is $\tau\delta$, where the tortuosity $\tau > 1$ is a constant and corrects for the fact that the path is actually greater than δ cm. In this method, discussed by Bidstrup and Geankoplis (B4), the effective diffusion length is obtained by calibrating with a solute such as KCl having a known diffusivity.

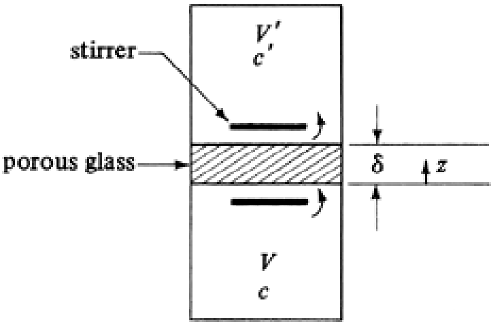


Figure 6.3-1. Diffusion cell for determination of diffusivity in a liquid.

To derive the equation, quasi-steady-state diffusion in the membrane is assumed:

Equation 6.3-6.

$$N_A = \varepsilon D_{AB} = \frac{c - c'}{\tau\delta}$$

where c is the concentration in the lower chamber at a time t, c' is the concentration in the upper chamber, and ε is the fraction of area of the glass open to diffusion. Making a balance on solute A in the upper chamber, where the rate in = rate out + rate of accumulation, making a similar balance on the lower chamber, using volume $V = V'$, and combining and integrating, the final equation is

Equation 6.3-7.

$$\ln \frac{c_0 - c_0'}{c - c'} = \frac{2\varepsilon A}{\tau\delta V} D_{AB} t$$

where $2\varepsilon A/\tau\delta V$ is a cell constant that can be determined using a solute of known diffusivity, such as KCl. The values c_0 and c_0' are initial concentrations and c and c' final concentrations.

Experimental liquid diffusivity data

Experimental diffusivity data for binary mixtures in the liquid phase are given in Table 6.3-1. All the data are for dilute solutions of the diffusing solute in the solvent. In liquids the diffusivities often vary quite markedly with concentration. Hence, the values in Table 6.3-1 should be used with some caution when outside the dilute range. Additional data are given in (P1). Values for biological solutes in solution are given in the next section. As noted in the table, the diffusivity values are quite small and in the range of about 0.5×10^{-9} to 5×10^{-9} m^2/s for relatively nonviscous liquids. Diffusivities in gases are larger by a factor of 10^4–10^5.

Table 6.3-1. Diffusion Coefficients for Dilute Liquid Solutions

		Temperature		*Diffusivity* [$(m^2/s)10^9$ or $(cm^2/s)10^5$]	
Solute	*Solvent*	*°C*	*K*		*Ref.*
NH_3	Water	12	285	1.64	(N2)

		Temperature		*Diffusivity* [$(m^2/s)10^9$ *or* $(cm^2/s)10^5$]	
Solute	***Solvent***	**°*C***	***K***		***Ref.***
		15	288	1.77	
O_2	Water	18	291	1.98	(N2)
		25	298	2.41	(V1)
CO_2	Water	25	298	2.00	(V1)
H_2	Water	25	298	4.8	(V1)
Methyl alcohol	Water	15	288	1.26	(J1)
Ethyl alcohol	Water	10	283	0.84	(J1)
		25	298	1.24	(J1)
n-Propyl alcohol	Water	15	288	0.87	(J1)
Formic acid	Water	25	298	1.52	(B4)
Acetic acid	Water	9.7	282.7	0.769	(B4)
		25	298	1.26	(B4)
Propionic acid	Water	25	298	1.01	(B4)
HCl (9 g mol/liter)	Water	10	283	3.3	(N2)
(2.5 g mol/liter)		10	283	2.5	(N2)
Benzoic acid	Water	25	298	1.21	(C4)
Acetone	Water	25	298	1.28	(A2)
Acetic acid	Benzene	25	298	2.09	(C5)
Urea	Ethanol	12	285	0.54	(N2)
Water	Ethanol	25	298	1.13	(H4)
KCl	Water	25	298	1.870	(P2)
KCl	Ethylene glycol	25	298	0.119	(P2)

Prediction of Diffusivities in Liquids

The equations for predicting diffusivities of dilute solutes in liquids are by necessity semiempirical, since the theory for diffusion in liquids is not well established as yet. The Stokes–Einstein equation, one of the first theories, was derived for a very large spherical molecule (A) diffusing in a liquid solvent (B) of small molecules. Stokes' law was used to describe the drag on the moving solute molecule. Then the equation was modified by assuming that all molecules are alike and arranged in a cubic lattice, and by expressing the molecular radius in terms of the molar volume (W5),

Equation 6.3-8.

$$D_{AB} = \frac{9.96 \times 10^{-16} T}{\mu V_A^{1/3}}$$

where D_{AB} is diffusivity in m^2/s, T is temperature in K, μ is viscosity of solution in Pa · s or kg/m · s, and V_A is the solute molar volume at its normal boiling point in m^3/kg mol. This equation applies very well to very large unhydrated and sphere-like solute molecules of about 1000 molecular weight or greater (R1), or where the V_A is above about 0.500 m^3/kg mol (W5) in aqueous solution.

For smaller solute molar volumes, Eq. (6.3-8) does not hold. Several other theoretical derivations have been attempted, but the equations do not predict diffusivities very accurately. Hence, a number of semitheoretical expressions have been developed (R1). The Wilke–Chang (T3, W5) correlation can be used for most general purposes where the solute (A) is dilute in the solvent (B):

Equation 6.3-9.

$$D_{AB} = 1.173 \times 10^{-16}(\phi M_B)^{1/2}\frac{T}{\mu_B V_A^{0.6}}$$

where M_B is the molecular weight of solvent B, μ_B is the viscosity of B in Pa · s or kg/m · s, V_A is the solute molar volume at the boiling point (L2), which can be obtained from Table 6.3-2, and φ is an "association parameter" of the solvent, where φ is 2.6 for water, 1.9 for methanol, 1.5 for ethanol, 1.0 for benzene, 1.0 for ether, 1.0 for heptane, and 1.0 for other unassociated solvents. When values of V_A are above 0.500 m^3/kg mol (500 cm^3/g mol), Eq. (6.3-8) should be used.

Table 6.3-2. Atomic and Molar Volumes at the Normal Boiling Point

Material		***Atomic Volume(m^3/kg mol) 10^3***	***Material***	***Atomic Volume (m^3/ kg mol) 10^3***
C		14.8	Ring, 3-membered as in ethylene oxide	−6
H		3.7		
O (except as below)		7.4		
Doubly bound as carbonyl		7.4	4-membered	−8.5
			5-membered	−11.5
Coupled to two other elements			6-membered	−15
			Naphthalene ring	−30
	In aldehydes, ketones	7.4	Anthracene ring	−47.5
	In methyl esters	9.1		
	In methyl ethers	9.9		
	In ethyl esters	9.9		
	In ethyl ethers	9.9		*Molecular Volume (m^3/kg mol) 10^3*
	In higher esters	11.0		
	In higher ethers	11.0	Air	29.9
	In acids (−OH)	12.0	O_2	25.6
Joined to S, P, N		8.3	N_2	31.2
N			Br_2	53.2
Doubly bonded		15.6	Cl_2	48.4
In primary amines		10.5	CO	30.7
In secondary amines		12.0	CO_2	34.0
Br	27.0		H_2	14.3
Cl in RCHClR'		24.6	H_2O	18.8
Cl in RCl (terminal)		21.6	H_2S	32.9
F		8.7	NH_3	25.8
I		37.0	NO	23.6
S		25.6	N_2O	36.4
P		27.0	SO_2	44.8

Source: **G. Le Bas, *The Molecular Volumes of Liquid Chemical Compounds*. New York: David McKay Co., Inc., 1915.**

When water is the solute, values from Eq. (6.3-9) should be multiplied by a factor of 1/2.3 (R1). Equation (6.3-9) predicts diffusivities with a mean deviation of 10–15% for aqueous solutions and about 25% in nonaqueous solutions. Outside the range 278–313 K, the equation should be used with caution. For water as the diffusing solute, an equation by Reddy and Doraiswamy is preferred (R2). Skelland (S5) summarizes the correlations available for binary systems. Geankoplis (G2) discusses and gives an equation to predict diffusion in a ternary system, where a dilute solute *A* is diffusing in a mixture of *B* and *C* solvents. This case is often approximated in industrial processes.

EXAMPLE 6.3-2. Prediction of Liquid Diffusivity

Predict the diffusion coefficient of acetone (CH_3COCH_3) in water at 25° and 50°C using the Wilke–Chang equation. The experimental value is 1.28×10^{-9} m²/s at 25°C (298 K).

Solution: From Appendix A.2 the viscosity of water at 25.0°C is $\mu_B = 0.8937 \times 10^{-3}$ Pas and at 50°C, 0.5494×10^{-3}. From Table 6.3-2 for CH_3COCH_3 with 3 carbons + 6 hydrogens + 1 oxygen,

$$V_A = 3(0.0148) + 6(0.0037) + 1(0.0074) = 0.0740 \text{ m}^3\text{kg mol}$$

For water the association parameter $\varphi = 2.6$ and $M_B = 18.02$ kg mass/kg mol. For 25°C, $T = 298$ K. Substituting into Eq. (6.3-9),

$$D_{AB} = (1.173 \times 10^{-16})(\phi M_B)^{1/2} \frac{T}{\mu_B V_A^{0.6}}$$

$$= \frac{(1.173 \times 10^{-16})(2.6 \times 18.02)^{1/2}(298)}{(0.8937 \times 10^{-3})(0.0740)^{0.6}}$$

$$= 1.277 \times 10^{-9} \text{ m}^2/\text{s}$$

For 50°C or $T = 323$ K,

$$D_{AB} = \frac{(1.173 \times 10^{-16})(2.6 \times 18.02)^{1/2}(323)}{(0.5494 \times 10^{-3})(0.0740)^{0.6}}$$

$$= 2.251 \times 10^{-9} \text{ m}^2/\text{s}$$

Prediction of Diffusivities of Electrolytes in Liquids

Electrolytes in aqueous solution such as KCl dissociate into cations and anions. Each ion diffuses at a different rate. If the solution is to remain electrically neutral at each point (assuming the absence of any applied electric-potential field), the cations and anions diffuse effectively as one component, and the ions have the same net motion or flux. Hence, the average diffusivity of the electrolyte KCl is a combination of the diffusion coefficients of the two ions. Its value is in between the diffusivity values for the two ions.

The well-known Nernst–Haskell equation for dilute, single-salt solutions can be used at 25°C to predict the overall diffusivity D_{AB} of the salt *A* in the solvent *B* (R1):

Equation 6.3-10.

$$D^o_{AB} = 8.928 \times 10^{-10} T \frac{(1/n_+ + 1/n_-)}{(1/\lambda_+ + 1/\lambda_-)}$$

where D^o_{AB} is in cm²/s, n_+ is the valence of the cation, n_- is the valence of the anion, and λ_+ and λ_- are the limiting ionic conductances in very dilute solutions in (*A*/cm²)(*V*/cm)(g equiv./cm²). Values of the conductances are given in Table 6.3-3 at 25°C. The value of $T = 298.2$ in Eq. (6.3-10) when using values of λ_+ and λ_- at 25°C.

Table 6.3-3. Limiting Ionic Conductances in Water at 25°C (R4)

Anion	λ_-	*Cation*	λ_+
OH^-	197.6	H^+	349.8
Cl^-	76.3	Li^+	38.7
Br^-	78.3	Na^+	50.1
NO_3^-	71.4	K^+	73.5
$CH_3CO_2^-$	40.9	NH_4^+	73.4
$\frac{1}{2}SO_4^{2-}$	80	$\frac{1}{2}Ca^{2+}$	59.5
CLO_4^-	68.0	$\frac{1}{2}Zn^{2+}$	53
		$\frac{1}{3}La^{3+}$	69.5

Ionic conductances in (*A*/cm^2)(*V*/cm)(g equiv./cm^2)

The diffusion coefficient of an individual ion *i* at 25°C can be calculated from

Equation 6.3-11.

$$D_i = 2.662 \times 10^{-7} \frac{\lambda_i}{n_i}$$

Then Eq. (6.3-10) becomes as follows:

Equation 6.3-12.

$$D^o_{AB} = \frac{n_+ + n_-}{n_-/D_+ + n_+/D_-}$$

To correct D^o_{AB} for temperature, first calculate D^o_{AB} at 25°C from Eq. (6.3-10) using the λ_+ and λ_- values given in Table 6.3-3 at 25°C. Then, multiply this D^o_{AB} at 25°C by $T/(334\,\mu_W)$, where μ_W is the viscosity of water in cp at the new T (R1).

EXAMPLE 6.3-3. Diffusivities of Electrolytes

Predict the diffusion coefficients of dilute electrolytes for the following cases:

a. For KCl at 25°C, predict D^o_{AB} and compare with the value in Table 6.3-1.

b. Predict the value for KCl at 18.5°C. The experimental value is 1.7×10^{-5} cm^2/s (S9).

c. For $CaCl_2$ predict D_{AB} at 25°C. Compare with the experimental value of 1.32×10^{-5} cm^2/s (C10). Also predict D_i of the ion Ca^{2+} and of Cl^- and use Eq. (6.3-12).

Solution: For part (a) from Table 6.3-3, $\lambda_+(K^+) = 73.5$ and $\lambda_-(Cl^-) = 76.3$. Substituting into Eq. (6.3-10),

$$D^o_{AB} = 8.928 \times 10^{-10}(298.2)\frac{(1/1 + 1/1)}{(1/73.5 + 1/76.3)}$$

$$= 1.993 \times 10^{-5} \text{ cm}^2/\text{s}$$

The experimental value in Table 6.3-1 is 1.87×10^{-5} cm^2/s, which is reasonably close considering that this value is not at infinite dilution.

For part (b) the correction factor for temperature is $T/(334\ \mu_w)$. For $T = 273.2 + 18.5 = 291.7$ K from Table A.2-4, $\mu_w = 1.042$ cp. Then $T/(334\ \mu_w) = 291.7/(334 \times 1.042) = 0.8382$. Correcting the value of D^o_{AB} at 25°C to 18.5°C,

$$D^o_{AB(185°C)} = 0.8382 D^o_{AB(25°C)} = 0.8382(1.993 \times 10^{-5})$$
$$= 1.671 \times 10^{-5}\ \text{cm}^2/\text{s}$$

This compares with the experimental value of 1.7×10^{-5} cm^2/s.

For part (c), for $CaCl_2$, from Table 6.3-3, $\lambda_+(Ca^{2+}/2) = 59.5$, $\lambda_-(Cl^-) = 76.3$, $n_+ = 2$, and $n_- = 1$. Again, using Eq. (6.3-10),

$$D^o_{AB} = 8.928 \times 10^{-10}(298.2)\frac{(1/2 + 1/1)}{(1/59.5 + 1/76.3)}$$
$$= 1.335 \times 10^{-5}\ \text{cm}^2/\text{s}$$

This compares well with the experimental value of 1.32×10^{-5} (C10).

To calculate the individual ion diffusivities at 25°C using Eq. (6.3-11),

$$D_{Ca^{2+}} = 2.662 \times 10^{-7}\frac{\lambda_+}{n_+} = 2.662 \times 10^{-7}\frac{(59.5)}{2} = 0.792 \times 10^{-5}\ \text{cm}^2/\text{s}$$

$$D_{Cl^-} = 2.662 \times 10^{-7}\frac{\lambda_-}{n_-} = 2.662 \times 10^{-7}\frac{(76.3)}{1} = 2.031 \times 10^{-5}\ \text{cm}^2/\text{s}$$

Substituting into Eq. (6.3-12) for 25°C,

$$D^o_{AB} = \frac{n_+ + n_-}{n_-/D_+ + n_+/D_-} = \frac{2 + 1}{1/(0.792 \times 10^{-5}) + 2/(2.031 \times 10^{-5})}$$
$$= 1.335 \times 10^{-5}\ \text{cm}^2/\text{s}$$

Hence, one can see that the diffusivity of the salt is in between that of the two ions.

MOLECULAR DIFFUSION IN BIOLOGICAL SOLUTIONS AND GELS

Diffusion of Biological Solutes in Liquids

Introduction

The diffusion of small solute molecules and especially macromolecules (*e.g.,* proteins) in aqueous solutions are important in the processing and storing of biological systems and in the life processes of microorganisms, animals, and plants. Food processing is an important area where diffusion plays an important role. In the drying of liquid solutions of fruit juice, coffee, and tea, water and frequently volatile flavor or aroma constituents are removed. These constituents diffuse through the liquid during evaporation.

In fermentation processes, nutrients, sugars, oxygen, and so on diffuse to the microorganisms, and waste products and at times enzymes diffuse away. In the artificial kidney machine various waste products diffuse through the blood solution to a membrane and then through the membrane to an aqueous solution.

Macromolecules in solution having molecular weights of tens of thousands or more were often called *colloids,* but now we know they generally form true solutions. The diffusion behavior of protein macromolecules in solution is affected by their large sizes and shapes, which can be random coils, rodlike, or globular (spheres or ellipsoids). Also, interactions of the large molecules with the small solvent and/or solute molecules affect the diffusion of the macromolecules as well as the small solute molecules.

Besides the Fickian diffusion to be discussed here, mediated transport often occurs in biological systems where chemical interactions occur. This latter type of transport will not be discussed here.

Interaction and "binding" in diffusion

Protein macromolecules are very large compared to small solute molecules such as urea, KCl, and sodium caprylate, and often have a number of sites for interaction or "binding" of the solute or ligand molecules. An example is the binding of oxygen to hemoglobin in the blood. Human serum albumin protein binds most of the free fatty acids in the blood and increases their apparent solubility. Bovine serum albumin, which is in milk, binds 23 mol sodium caprylate/mol albumin when the albumin concentration is 30 kg/m^3 solution and the sodium caprylate is about 0.05 molar (G6). Hence, Fickian-type diffusion of macromolecules and small solute molecules can be greatly affected by the presence together of both types of molecules even in dilute solutions.

Experimental methods for determining diffusivity

Methods for determining the diffusivity of biological solutes are similar to those discussed previously in Section 6.3 with some modifications. In the diaphragm diffusion cell shown in Fig. 6.3-1, the chamber is made of Lucite® or Teflon® instead of glass, since protein molecules bind to glass. Also, the porous membrane through which the molecular diffusion occurs is composed of cellulose acetate or other polymers (G5, G6, K1).

Experimental data for biological solutes

Most of the experimental data in the literature on protein diffusivities have been extrapolated to zero concentration since the diffusivity is often a function of concentration. A tabulation of diffusivities of a few proteins and also of small solutes often present in biological systems is given in Table 6.4-1.

Table 6.4-1. Diffusion Coefficients for Dilute Biological Solutes in Aqueous Solution

Solute	***Temperature***		***Diffusivity (m^2/s)***	***Molecular Weight***	***Ref.***
	°C	**K**			
Urea	20	293	1.20×10^{-9}	60.1	(N2)
	25	298	1.378×10^{-9}		(G5)
Glycerol	20	293	0.825×10^{-9}	92.1	(G3)
Glycine	25	298	1.055×10^{-9}	75.1	(L3)
Sodium caprylate	25	298	8.78×10^{-10}	166.2	(G6)
Bovine serum albumin	25	298	6.81×10^{-11}	67 500	(C6)
Urease	25	298	4.01×10^{-11}	482 700	(C7)
	20	293	3.46×10^{-11}		(S6)
Soybean protein	20	293	2.91×10^{-11}	361 800	(S6)
Lipoxidase	20	293	5.59×10^{-11}	97 440	(S6)
Fibrinogen, human	20	293	1.98×10^{-11}	339 700	(S6)

Solute	*Temperature*		*Diffusivity* (m^2/s)	*Molecular Weight*	*Ref.*
	°C	*K*			
Human serum albumin	20	293	5.93×10^{-11}	72 300	(S6)
γ-Globulin, human	20	293	4.00×10^{-11}	153 100	(S6)
Creatinine	37	310	1.08×10^{-9}	113.1	(C8)
Sucrose	37	310	0.697×10^{-9}	342.3	(C8)
	20	293	0.460×10^{-9}		(P3)

The diffusion coefficients for the large protein molecules are on the order of magnitude of 5×10^{-11} m^2/s compared to the values of about 1×10^{-9} m^2/s for the small solutes in Table 6.4-1. This means macromolecules diffuse at a rate about 20 times as slow as small solute molecules for the same concentration differences.

When the concentration of macromolecules such as proteins increases, the diffusion coefficient would be expected to decrease, since the diffusivity of small solute molecules decreases with increasing concentration. However, experimental data (G4, C7) show that the diffusivity of macromolecules such as proteins decreases in some cases and increases in others as protein concentration increases. Surface charges on the molecules appear to play a role in these phenomena.

When small solutes such as urea, KCl, and sodium caprylate, which are often present with protein macromolecules in solution, diffuse through these protein solutions, the diffusivity decreases with increasing polymer concentration (C7, G5, G6, N3). Experimental data for the diffusivity of the solute sodium caprylate (A) diffusing through bovine serum albumin (P) solution show that the diffusivity D_{AP} of A through P is markedly reduced as the protein (P) concentration is increased (G5, G6). A large part of the reduction is due to the binding of A to P so that there is less free A to diffuse. The rest is due to blockage by the large molecules.

Prediction of diffusivities for biological solutes

For predicting the diffusivity of small solutes alone in aqueous solution with molecular weights less than about 1000 or solute molar volumes less than about 0.500 m^3/kg mol, Eq. (6.3-9) should be used. For larger solutes the equations to be used are not as accurate. As an approximation the Stokes–Einstein equation (6.3-8) can be used:

Equation 6.3-8.

$$D_{AB} = \frac{9.96 \times 10^{-16} T}{\mu V_A^{1/3}}$$

Probably a better approximate equation to use is the semiempirical equation of Polson (P3), which is recommended for a molecular weight above 1000. A modification of his equation to take into account different temperatures is as follows for dilute aqueous solutions:

Equation 6.4-1.

$$D_{AB} = \frac{9.40 \times 10^{-15} T}{\mu (M_A)^{1/3}}$$

where M_A is the molecular weight of the large molecule A. When the shape of the molecule deviates greatly from a sphere, this equation should be used with caution.

EXAMPLE 6.4-1. Prediction of Diffusivity of Albumin

Predict the diffusivity of bovine serum albumin at 298 K in water as a dilute solution using the modified Polson equation (6.4-1) and compare with the experimental value in Table 6.4-1.

***Solution*:** The molecular weight of bovine serum albumin (A) from Table 6.4-1 is $M_A = 67\,500$ kg/kg mol. The viscosity of water at 25°C is 0.8937×10^{-3} Pa · s and $T = 298$ K. Substituting into Eq. (6.4-1),

$$D_{AB} = \frac{9.40 \times 10^{-15} T}{\mu (M_A)^{1/3}} = \frac{(9.40 \times 10^{-15})298}{(0.8937 \times 10^{-3})(67\,500)^{1/3}}$$

$$= 7.70 \times 10^{-11} \text{ m}^2/\text{s}$$

This value is 11% higher than the experimental value of 6.81×10^{-11} m^2/s.

Prediction of diffusivity of small solutes in protein solution

When a small solute (A) diffuses through a macromolecule (P) protein solution, Eq. (6.3-9) cannot be used for prediction for the small solute because of blockage to diffusion by the large molecules. The data needed to predict these effects are the diffusivity D_{AB} of solute A in water alone, the water of hydration on the protein, and an obstruction factor. A semitheoretical equation that can be used to approximate the diffusivity D_{AP} of A in globular-type protein P solutions is as follows, where only the blockage effect is considered (C8, G5, G6) and no binding is present:

Equation 6.4-2.

$$D_{AP} = D_{AB}(1 - 1.81 \times 10^{-3} c_p)$$

where c_p = kg P/m^3. Then the diffusion equation is

Equation 6.4-3.

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

where c_{A1} is concentration of A in kg mol A/m^3.

Prediction of diffusivity with binding present

When A is in a protein solution P and binds to P, the diffusion flux of A is equal to the flux of unbound solute A in the solution plus the flux of the protein–solute complex. Methods for predicting this flux are available (G5, G6) when binding data have been experimentally obtained. The equation used is

Equation 6.4-4.

$$D_{AP} = \left[D_{AB}(1 - 1.81 \times 10^{-3} c_p)\left(\frac{\%\text{ free A}}{100}\right) + D_P\left(\frac{\%\text{ bound A}}{100}\right)\right]$$

where D_P is the diffusivity of the protein alone in the solution, m^2/s, and free A is that A not bound to the protein, which is determined from the experimental binding coefficient. Then Eq. (6.4-3) is used to calculate the flux, where c_A is the total concentration of A in the solution.

Diffusion in Biological Gels

Gels can be looked upon as semisolid materials which are "porous." They are composed of macromolecules which are usually in dilute aqueous solution with the gel comprising a few wt % of the water solution. The "pores" or open spaces in the gel structure are filled with water. The rates of diffusion of small solutes in the gels are somewhat less than in aqueous solution. The main effect of the gel structure is to increase the path length for diffusion, assuming no electrical-type effects (S7).

Recent studies by electron microscopy (L4) have shown that the macromolecules of the gel agarose (a major constituent of agar) exist as long and relatively straight threads. This suggests a gel structure of loosely interwoven, extensively hydrogen-bonded polysaccharide macromolecules.

Some typical gels are agarose, agar, and gelatin. A number of organic polymers exist as gels in various types of solutions. To measure the diffusivity of solutes in gels, unsteady-state methods are used. In one method the gel is melted and poured into a narrow tube open at one end. After solidification, the tube is placed in an agitated bath containing the solute for diffusion. The solute leaves the solution at the gel boundary and diffuses through the gel itself. After a period of time the amount diffusing in the gel is determined to give the diffusion coefficient of the solute in the gel.

A few typical values of diffusivities of some solutes in various gels are given in Table 6.4-2. In some cases the diffusivity of the solute in pure water is given so that the decrease in diffusivity due to the gel can be seen. For example, from Table 6.4-2, at 278 K urea in water has a diffusivity of 0.880×10^{-9} m^2/s and in 2.9 wt % gelatin, has a value of 0.640×10^{-9} m^2/s, a decrease of 27%.

Table 6.4-2. Typical Diffusivities of Solutes in Dilute Biological Gels in Aqueous Solution

			Temperature			
Solute	***Gel***	***Wt % Gel in Solution***	***K***	***°C***	***Diffusivity (m^2/s)***	***Ref.***
Sucrose	Gelatin	0	278	5	0.285×10^{-9}	(F2)
		3.8	278	5	0.209×10^{-9}	(F2)
		10.35	278	5	0.107×10^{-9}	(F2)
		5.1	293	20	0.252×10^{-9}	(F3)
Urea	Gelatin	0	278	5	0.880×10^{-9}	(F2)
		2.9	278	5	0.644×10^{-9}	(F2)
		5.1	278	5	0.609×10^{-9}	(F3)
		10.0	278	5	0.542×10^{-9}	(F2)
		5.1	293	20	0.859×10^{-9}	(F3)
Methanol	Gelatin	3.8	278	5	0.626×10^{-9}	(F3)
Urea	Agar	1.05	278	5	0.727×10^{-9}	(F3)
		3.16	278	5	0.591×10^{-9}	(F3)
		5.15	278	5	0.472×10^{-9}	(F3)
Glycerin	Agar	2.06	278	5	0.297×10^{-9}	(F3)
		6.02	278	5	0.199×10^{-9}	(F3)
Dextrose	Agar	0.79	278	5	0.327×10^{-9}	(F3)
Sucrose	Agar	0.79	278	5	0.247×10^{-9}	(F3)
Ethanol	Agar	5.15	278	5	0.393×10^{-9}	(F3)
NaCl (0.05 *M*)	Agarose	0	298	25	1.511×10^{-9}	(S7)
		2	298	25	1.398×10^{-9}	(S7)

In both agar and gelatin the diffusivity of a given solute decreases more or less linearly with an increase in wt % gel. However, extrapolation to 0% gel gives a value smaller than that shown for pure water. It should be noted that in different preparations or batches of the same type of gel, the diffusivities can vary by as much as 10 to 20%.

EXAMPLE 6.4-2. Diffusion of Urea in Agar

A tube or bridge of a gel solution of 1.05 wt % agar in water at 278 K is 0.04 m long and connects two agitated solutions of urea in water. The urea concentration in the first solution is 0.2 g mol urea per liter solution and is 0 in the other. Calculate the flux of urea in kg mol/s · m^2 at steady state.

Solution: From Table 6.4-2 for the solute urea at 278 K, $D_{AB} = 0.727 \times 10^{-9}$ m^2/s. For urea diffusing through stagnant water in the gel, Eq. (6.3-3) can be used. However, since the value of x_{A1} is less than about 0.01, the solution is quite dilute and $x_{BM} \cong 1.00$. Hence, Eq. (6.3-5) can be used. The concentrations are $c_{A1} = 0.20/1000 = 0.0002$ g mol/cm^3 = 0.20 kg mol/m^3 and $c_{A2} = 0$. Substituting into Eq. (6.3-5),

$$N_A = \frac{D_{AB}(c_{A1} - c_{A2})}{z_2 - z_1} = \frac{0.727 \times 10^{-9}(0.20 - 0)}{0.04 - 0}$$

$$= 3.63 \times 10^{-9} \text{ kg mol/s} \cdot \text{m}^2$$

MOLECULAR DIFFUSION IN SOLIDS

Introduction and Types of Diffusion in Solids

Even though rates of diffusion of gases, liquids, and solids in solids are generally slower than rates in liquids and gases, mass transfer in solids is quite important in chemical and biological processing. Some examples are leaching of foods, such as soybeans, and of metal ores; drying of timber, salts, and foods; diffusion and catalytic reaction in solid catalysts; separation of fluids by membranes; diffusion of gases through polymer films used in packaging; and treating of metals at high temperatures by gases.

We can broadly classify transport in solids into two types of diffusion: diffusion that can be considered to follow Fick's law and does not depend primarily on the actual structure of the solid, and diffusion in porous solids where the actual structure and void channels are important. These two broad types of diffusion will be considered.

Diffusion in Solids Following Fick's Law

Derivation of equations

This type of diffusion in solids does not depend on the actual structure of the solid. The diffusion occurs when the fluid or solute diffusing is actually dissolved in the solid to form a more or less homogeneous solution—for example, in leaching, where the solid contains a large amount of water and a solute is diffusing through this solution, or in the diffusion of zinc through copper, where solid solutions are present. Also, the diffusion of nitrogen or hydrogen through rubber, or in some cases diffusion of water in foodstuffs, can be classified here, since equations of similar type can be used.

Generally, simplified equations are used. Using the general Eq. (6.2-14) for binary diffusion,

Equation 6.2-14.

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

the bulk-flow term, $(c_A/c)(N_A + N_B)$, even if present, is usually small, since c_A/c or x_A is quite small. Hence, it is neglected. Also, c is assumed constant, giving for diffusion in solids

Equation 6.5-1.

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

where D_{AB} is diffusivity in m^2/s of A through B and is usually assumed constant, independent of pressure for solids. Note that $D_{AB} \neq D_{BA}$ in solids.

Integration of Eq. (6.5-1) for a solid slab at steady state gives

Equation 6.5-2.

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

For the case of diffusion radially through a cylinder wall of inner radius r_1 and outer r_2 and length L,

Equation 6.5-3.

$$\frac{\overline{N}_A}{2\pi r L} = -D_{AB}\frac{dc_A}{dr}$$

Equation 6.5-4.

$$\overline{N}_A = D_{AB}(c_{A1} - c_{A2})\frac{2\pi L}{\ln(r_2/r_1)}$$

This case is similar to conduction heat transfer radially through a hollow cylinder, as shown in Fig. 4.3-2.

The diffusion coefficient D_{AB} in the solid as stated above is not dependent upon the pressure of the gas or liquid on the outside of the solid. For example, if CO_2 gas is outside a slab of rubber and is diffusing through the rubber, D_{AB} would be independent of p_A, the partial pressure of CO_2 at the surface. The solubility of CO_2 in the solid, however, is directly proportional to p_A. This is similar to the case of the solubility of O_2 in water being directly proportional to the partial pressure of O_2 in the air by Henry's law.

The solubility of a solute gas (A) in a solid is usually expressed as S in m^3 solute (at STP of 0°C and 1 atm) per m^3 solid per atm partial pressure of (A). Also, $S = cm^3(STP)/atm \cdot cm^3$ solid in the cgs system. To convert this to c_A concentration in the solid in kg mol A/m^3 using SI units,

Equation 6.5-5.

$$c_A = \frac{S\,\text{m}^3(\text{STP})/\text{m}^3\,\text{solid}\cdot\text{atm}}{22.414\ \text{m}^3(\text{STP})/\text{kg mol}\ A}\,p_A\,\text{atm} = \frac{Sp_A}{22.414}\,\frac{\text{kg mol}\ A}{\text{m}^3\ \text{solid}}$$

Using cgs units,

Equation 6.5-6.

$$c_A = \frac{Sp_A}{22\,414}\,\frac{\text{g mol}\ A}{\text{cm}^3\ \text{solid}}$$

EXAMPLE 6.5-1. Diffusion of H_2 Through Neoprene Membrane

The gas hydrogen at 17°C and 0.010 atm partial pressure is diffusing through a membrane of vulcanized neoprene rubber 0.5 mm thick. The pressure of H_2 on the other side of the neoprene is zero. Calculate the steady-state flux, assuming that the only resistance to diffusion is in the membrane. The solubility S of H_2 gas in neoprene at 17°C is 0.051 m^3 (at STP of 0°C and 1 atm)/m^3 solid · atm and the diffusivity D_{AB} is 1.03×10^{-10} m^2/s at 17°C.

***Solution*.** A sketch showing the concentration is shown in Fig. 6.5-1. The equilibrium concentration c_{A1} at the inside surface of the rubber is, from Eq. (6.5-5),

$$c_{A1} = \frac{S}{22.414}p_{A1} = \frac{0.051(0.010)}{22.414} = 2.28 \times 10^{-5}\ \text{kg mol H}_2/\text{m}^3\ \text{solid}$$

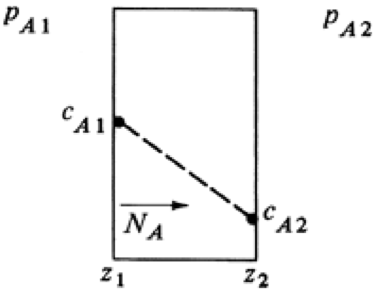


Figure 6.5-1. Concentrations for Example 6.5-1.

Since p_{A2} at the other side is 0, c_{A2} = 0. Substituting into Eq. (6.5-2) and solving,

$$N_A = \frac{D_{AB}(c_{A1} - c_{A2})}{z_2 - z_1} = \frac{(1.03 \times 10^{-10})(2.28 \times 10^{-5} - 0)}{(0.5 - 0)/1000}$$

$$= 4.69 \times 10^{-12} \text{ kg mol H}_2/\text{s} \cdot \text{m}^2$$

Permeability equations for diffusion in solids

In many cases the experimental data for diffusion of gases in solids are not given as diffusivities and solubilities but as permeabilities, P_M, in m^3 of solute gas *A* at STP (0°C and 1 atm press) diffusing per second per m^2 cross-sectional area through a solid 1 m thick under a pressure difference of 1 atm pressure. This can be related to Fick's equation (6.5-2) as follows:

Equation 6.5-2.

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

From Eq. (6.5-5),

Equation 6.5-7.

$$c_{A1} = \frac{Sp_{A1}}{22.414} \qquad c_{A2} = \frac{Sp_{A2}}{22.414}$$

Substituting Eq. (6.5-7) into (6.5-2),

Equation 6.5-8.

$$N_A = \frac{D_{AB}S(p_{A1} - p_{A2})}{22.414(z_2 - z_1)} = \frac{P_M(p_{A1} - p_{A2})}{22.414(z_2 - z_1)} \text{ kg mol/s} \cdot \text{m}^2$$

where the permeability P_M is

Equation 6.5-9.

$$P_M = D_{AB}S \frac{\text{m}^3(\text{STP})}{\text{s} \cdot \text{m}^2\text{C.S.} \cdot \text{atm/m}}$$

Permeability (P_M) is also given in the literature in several other sets of units. For the cgs system, the permeability is given as cm^3(STP)/(s · cm^2C.S. · atm/cm). In some cases in the literature the permeability is given as cm^3(STP)/(s · cm^2C.S. · cm Hg/cm thickness). These are related as follows:

Equation 6.5-10.

$$\frac{1.00\ \text{m}^3(\text{STP})\cdot\text{m}}{\text{s}\cdot\text{m}^2\text{C.S.}\cdot\text{atm}} = \frac{10^4\ \text{cm}^3(\text{STP})\cdot\text{cm}}{\text{s}\cdot\text{cm}^2\cdot\text{atm}}$$

Equation 6.5-11.

$$\frac{1.0\ \text{m}^3(\text{STP})\cdot\text{m}}{\text{s}\cdot\text{m}^2\text{C.S.}\cdot\text{atm}} = \frac{1.316\times 10^2\ \text{cm}^3(\text{STP})\cdot\text{cm}}{\text{s}\cdot\text{cm}^2\text{C.S.}\cdot\text{cmHg}}$$

When there are several solids 1, 2, 3, . . . , in series and L_1, L_2, . . . , represent the thickness of each, then Eq. (6.5-8) becomes

Equation 6.5-12.

$$N_A = \frac{p_{A1} - p_{A2}}{22.414}\,\frac{1}{L_1/P_{M1} + L_2/P_{M2} + \cdots}$$

where $p_{A1} - p_{A2}$ is the overall partial pressure difference.

Experimental diffusivities, solubilities, and permeabilities

Accurate prediction of diffusivities in solids is generally not possible because of the lack of knowledge of the theory of the solid state. Hence, experimental values are needed. Some experimental data for diffusivities, solubilities, and permeabilities are given in Table 6.5-1 for gases diffusing in solids and solids diffusing in solids.

Table 6.5-1. Diffusivities and Permeabilities in Solids

Solute (A)	*Solid (B)*	*T (K)*	*D_{AB}, Diffusion Coefficient [m2/s]*	*Solubility, S* $\left[\frac{m^3\ solute(STP)}{m^3\ solid\cdot atm}\right]$	*Permeability, PM* $\left[\frac{m^3\ solute(STP)}{s\cdot m^2\cdot atm/m}\right]$	*Ref.*
H_2	Vulcanized rubber	298	$0.85(10^{-9})$	0.040	$0.342(10^{-10})$	(B5)
O_2		298	$0.21(10^{-9})$	0.070	$0.152(10^{-10})$	(B5)
N_2		298	$0.15(10^{-9})$	0.035	$0.054(10^{-10})$	(B5)
CO_2		298	$0.11(10^{-9})$	0.90	$1.01(10^{-10})$	(B5)
H_2	Vulcanized neoprene	290	$0.103(10^{-9})$	0.051		(B5)
		300	$0.180(10^{-9})$	0.053		(B5)
H_2	Polyethylene	298			$6.53(10^{-12})$	(R3)
O_2		303			$4.17(10^{-12})$	(R3)
N_2		303			$1.52(10^{-12})$	(R3)
O_2	Nylon	303			$0.029(10^{-12})$	(R3)
N_2		303			$0.0152(10^{-12})$	(R3)
Air	English leather	298			$0.15-0.68\times 10^{-4}$	(B5)
H_2O	Wax	306			$0.16(10^{-10})$	(B5)
H_2O	Cellophane	311			$0.91-1.82(10^{-10})$	(B5)
He	Pyrex glass	293			$4.86(10^{-15})$	(B5)
		373			$20.1(10^{-15})$	(B5)
He	SiO_2	293	$2.4-5.5(10^{-14})$	0.01		(B5)
H_2	Fe	293	$2.59(10^{-13})$			(B5)

Solute (*A*)	Solid (*B*)	*T* (*K*)	D_{AB}, Diffusion Coefficient [*m2/ s*]	Solubility, *S* $\left[\frac{m^3\ solute(STP)}{m^3\ solid \cdot atm}\right]$	Permeability, *PM* $\left[\frac{m^3\ solute(STP)}{s \cdot m^2 \cdot atm/m}\right]$	Ref.
Al	Cu	293	$1.3(10^{-34})$			(B5)

For the simple gases such as He, H_2, O_2, N_2, and CO_2, with gas pressures up to 1 or 2 atm, the solubility in solids such as polymers and glasses generally follows Henry's law and Eq. (6.5-5) holds. Also, for these gases the diffusivity and permeability are independent of concentration, and hence pressure. For the effect of temperature T in K, the ln P_M is approximately a linear function of $1/T$. Also, the diffusion of one gas, say H_2, is approximately independent of the other gases present, such as O_2 and N_2.

For metals such as Ni, Cd, and Pt, where gases such as H_2 and O_2 are diffusing, it has been found experimentally that the flux is approximately proportional to $(\sqrt{p_{A1}} - \sqrt{p_{A2}})$ so Eq. (6.5-8) does not hold (B5). When water is diffusing through polymers, unlike the simple gases, P_M may depend somewhat on the relative pressure difference (C9, B5). Further data are available in monographs by Crank and Park (C9) and Barrer (B5).

EXAMPLE 6.5-2. Diffusion Through a Packaging Film Using Permeability

A polyethylene film 0.00015 m (0.15 mm) thick is being considered for use in packaging a pharmaceutical product at 30°C. If the partial pressure of O_2 outside the package is 0.21 atm and inside it is 0.01 atm, calculate the diffusion flux of O_2 at steady state. Use permeability data from Table 6.5-1. Assume that the resistances to diffusion outside the film and inside are negligible compared to the resistance of the film.

Solution: From Table 6.5-1, $P_M = 4.17(10^{-12})$ m^3 solute(STP)/(s · m^2 · atm/m). Substituting into Eq. (6.5-8),

$$N_A = \frac{P_M(p_{A1} - p_{A2})}{22.414(z_2 - z_1)} = \frac{4.17(10^{-12})(0.21 - 0.01)}{22.414(0.00015 - 0)}$$

$$= 2.480 \times 10^{-10}\ \text{kg mol/s} \cdot \text{m}^2$$

Note that a film made of nylon has a much smaller value of permeability P_M for O_2 and would make a more suitable barrier.

Membrane separation processes

In Chapter 13 a detailed discussion is given of the various membrane separation processes for gas separation by membranes, dialysis, reverse osmosis, ultrafiltration, and microfiltration.

Diffusion in Porous Solids That Depends on Structure

Diffusion of liquids in porous solids

In Section 6.5B we used Fick's law and treated the solid as a uniform homogeneous-like material with an experimental diffusivity D_{AB}. In this section we are concerned with porous solids that have pores or interconnected voids in the solid which affect the diffusion. A cross section of a typical porous solid is shown in Fig. 6.5-2.

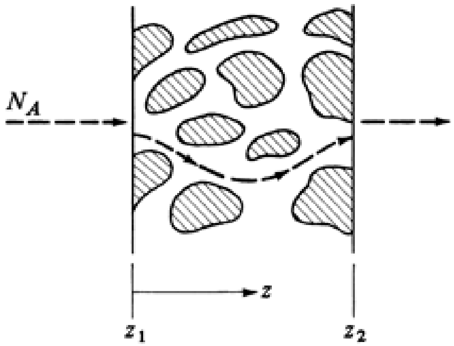


Figure 6.5-2. Sketch of a typical porous solid.

For the situation where the voids are filled completely with liquid water, the concentration of salt in water at boundary 1 is c_{A1} and at point 2 is c_{A2}. The salt, in diffusing through the water in the void volume, takes a tortuous path which is unknown and greater than $(z_2 - z_1)$ by a factor τ, called *tortuosity.* Diffusion does not occur in the inert solid. For a dilute solution using Eq. (6.3-5) for diffusion of salt in water at steady state,

Equation 6.5-13.

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

where ε is the open void fraction, D_{AB} is the diffusivity of salt in water, and τ is a factor which corrects for the path longer than $(z_2 - z_1)$. For inert-type solids τ can vary from about 1.5 to 5. Often the terms are combined into an effective diffusivity:

Equation 6.5-14.

$$D_{A\,\mathrm{eff}} = \frac{\varepsilon}{\tau} D_{AB} \quad \mathrm{m^2/s}$$

EXAMPLE 6.5-3. Diffusion of KCl in Porous Silica

A sintered solid of silica 2.0 mm thick is porous, with a void fraction ε of 0.30 and a tortuosity τ of 4.0. The pores are filled with water at 298 K. At one face the concentration of KCl is held at 0.10 g mol/liter, and fresh water flows rapidly past the other face. Neglecting any other resistance but that in the porous solid, calculate the diffusion of KCl at steady state.

***Solution*.** The diffusivity of KCl in water from Table 6.3-1 is $D_{AB} = 1.87 \times 10^{-9}$ m^2/s. Also, $c_{A1} = 0.10/1000 = 1.0 \times 10^{-4}$ g mol/cm^3 = 0.10 kg mol/m^3, and $c_{A2} = 0$. Substituting into Eq. (6.5-13),

$$N_A = \frac{\varepsilon D_{AB}(c_{A1} - c_{A2})}{\tau(z_2 - z_1)} = \frac{0.30(1.870 \times 10^{-9})(0.10 - 0)}{4.0(0.002 - 0)}$$

$$= 7.01 \times 10^{-9} \text{ kg mol KCl/s} \cdot \text{m}^2$$

Diffusion of gases in porous solids

If the voids shown in Fig. 6.5-2 are filled with gases, then a somewhat similar situation exists. If the pores are very large so that diffusion occurs only by Fickian-type diffusion, then Eq. (6.5-13) becomes, for gases, Equation 6.5-15.

$$N_A = \frac{\varepsilon D_{AB}(c_{A1} - c_{A2})}{\tau(z_2 - z_1)} = \frac{\varepsilon D_{AB}(p_{A1} - p_{A2})}{\tau RT(z_2 - z_1)}$$

Again the value of the tortuosity must be determined experimentally. Diffusion is assumed to occur only through the voids or pores and not through the actual solid particles.

A correlation of tortuosity versus the void fraction of various unconsolidated porous media of beds of glass spheres, sand, salt, talc, and so on (S8) gives the following approximate values of τ for different values of ε: $\varepsilon = 0.2$, $\tau = 2.0$; $\varepsilon = 0.4$, $\tau = 1.75$; $\varepsilon = 0.6$, $\tau = 1.65$.

When the pores are quite small in size and on the order of magnitude of the mean free path of the gas, other types of diffusion occur, which are discussed in Section 7.6.

NUMERICAL METHODS FOR STEADY-STATE MOLECULAR DIFFUSION IN TWO DIMENSIONS

Derivation of Equations for Numerical Methods

Derivation of methods for steady state

In Fig. 6.6-1 a two-dimensional solid shown with unit thickness is divided into squares. The numerical methods for steady-state molecular diffusion are very similar to those for steady-state heat conduction discussed in Section 4.15. Hence, only a brief summary will be given here. The solid inside of a square is imagined to be concentrated at the center of the square at $c_{n,m}$ and is called a "node", which is connected to adjacent nodes by connecting rods through which the mass diffuses.

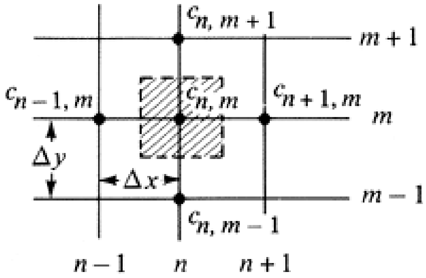


Figure 6.6-1. Concentrations and spacing of nodes for two-dimensional steady-state molecular diffusion.

A total mass balance is made at steady state by stating that the sum of the molecular diffusion to the shaded area for unit thickness must equal zero:

Equation 6.6-1.

$$\frac{D_{AB}\,\Delta y}{\Delta x}(c_{n-1,m} - c_{n,m}) + \frac{D_{AB}\,\Delta y}{\Delta x}(c_{n+1,m} - c_{n,m}) + \frac{D_{AB}\,\Delta x}{\Delta y}(c_{n,m+1} - c_{n,m}) + \frac{D_{AB}\,\Delta x}{\Delta y}(c_{n,m-1} - c_{n,m}) = 0$$

where $c_{n,m}$ is concentration of A at node n,m in kg mol A/m^3. Setting $\Delta x = \Delta y$, and rearranging,

Equation 6.6-2.

$$c_{n,m+1} + c_{n,m-1} + c_{n+1,m} + c_{n-1,m} - 4c_{n,m} = 0$$

Iteration method of numerical solution

In order to solve Eq. (6.6-2), a separate equation is written for each unknown point giving *N* linear algebraic equations for *N* unknown points. For a hand calculation using a modest number of nodes, the iteration method can be used to solve the equations, where the right-hand side of Eq. (6.6-2) is set equal to a residual $\overline{N}_{n,m}$:

Equation 6.6-3.

$$c_{n,m+1} + c_{n,m-1} + c_{n+1,m} + c_{n-1,m} - 4c_{n,m} = \overline{N}_{n,m}$$

Setting the equation equal to zero, $\overline{N}_{n,m} = 0$ for steady state and $c_{n,m}$ is calculated by

Equation 6.6-4.

$$c_{n,m} = \frac{c_{n-1,m} + c_{n+1,m} + c_{n,m+1} + c_{n,m-1}}{4}$$

Equations (6.6-3) and (6.6-4) are the final equations to be used to calculate all the concentrations at steady state.

Example 4.15-1 for steady-state heat conduction illustrates the detailed steps for the iteration method, which are identical to those for steady-state diffusion.

Once the concentrations have been calculated, the flux can be calculated for each element as follows. Referring to Fig. 6.6-1, the flux for the node or element $c_{n,m}$ to $c_{n,m-1}$ is ($\Delta x = \Delta y$)

Equation 6.6-5.

$$N = \frac{AD_{AB}}{\Delta y}(c_{n,m} - c_{n,m-1}) = \frac{[(\Delta x)(1)]D_{AB}}{\Delta y}(c_{n,m} - c_{n,m-1})$$

$$= D_{AB}(c_{n,m} - c_{n,m-1})$$

where the area A is Δx times 1 m deep and N is kg mol A/s. Equations are written for the other appropriate elements and the sum of the fluxes calculated. This numerical method is well suited for use with a computer spreadsheet.

Equations for Special Boundary Conditions for Numerical Method

Equations for boundary conditions

When one of the nodal points $c_{n,m}$ is at a boundary where convective mass transfer is occurring to a constant concentration c_∞ in the bulk fluid shown in Fig. 6.6-2a, a different equation must be derived. Making a mass balance on the node *n, m*, where mass in = mass out at steady state,

Equation 6.6-6.

$$\frac{D_{AB}\,\Delta y}{\Delta x}(c_{n-1,m} - c_{n,m}) + \frac{D_{AB}\,\Delta x}{2\,\Delta y}(c_{n,m+1} - c_{n,m}) + \frac{D_{AB}\,\Delta x}{2\,\Delta y}(c_{n,m-1} - c_{n,m}) = k_c\,\Delta y(c_{n,m} - c_\infty)$$

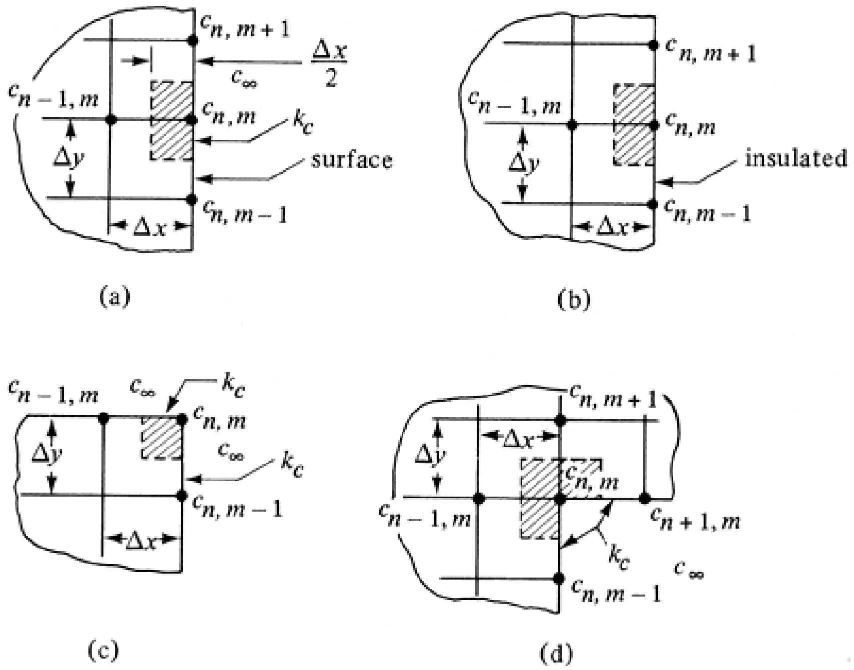


Figure 6.6-2. Different boundary conditions for steady-state diffusion: (a) convection at a boundary, (b) insulated boundary, (c) exterior corner with convective boundary, (d) interior corner with convective boundary.

where k_c is the convective mass-transfer coefficient in m/s defined by Eq. (6.1-14).

Setting $\Delta x = \Delta y$, rearranging, and setting the resultant equation equal to $\overline{N}_{n,m}$, the residual, the following results:

1. For convection at a boundary (Fig. 6.6-2a),

   Equation 6.6-7.

$$\frac{k_c\,\Delta x}{D_{AB}}c_\infty + \tfrac{1}{2}(2c_{n-1,m} + c_{n,m+1} + c_{n,m-1}) - c_{n,m}\left(\frac{k_c\,\Delta x}{D_{AB}} + 2\right) = \overline{N}_{n,m}$$

   This equation is similar to Eq. (4.15-16) for heat conduction and convection, with $k_c\,\Delta x/D_{AB}$ being used in place of $h\,\Delta x/k$. Similarly, Eqs. (6.6-8)–(6.6-10) have been derived for the other boundary conditions shown in Fig. 6.6-2.

2. For an insulated boundary (Fig. 6.6-2b),

   Equation 6.6-8.

$$\tfrac{1}{2}(c_{n,m+1} + c_{n,m-1}) + c_{n-1,m} - 2c_{n,m} = \overline{N}_{n,m}$$

3. For an exterior corner with convection at the boundary (Fig. 6.6-2c),

   Equation 6.6-9.

$$\frac{k_c\,\Delta x}{D_{AB}}c_\infty + \tfrac{1}{2}(c_{n-1,m} + c_{n,m-1}) - \left(\frac{k_c\,\Delta x}{D_{AB}} + 1\right)c_{n,m} = \overline{N}_{n,m}$$

4. For an interior corner with convection at the boundary (Fig. 6.6-2d),

Equation 6.6-10.

$$\frac{k_c\,\Delta x}{D_{AB}}c_\infty + c_{n-1,m} + c_{n,m+1} + \tfrac{1}{2}(c_{n+1,m} + c_{n,m-1}) - \left(3 + \frac{k_c\,\Delta x}{D_{AB}}\right)c_{n,m} = \overline{N}_{n,m}$$

Boundary conditions with distribution coefficient

When Eq. (6.6-7) was derived, the distribution coefficient K between the liquid and the solid at the surface interface was 1.0. The distribution coefficient as shown in Fig. 6.6-3 is defined as

Equation 6.6-11.

$$K = \frac{c_{n,mL}}{c_{n,m}}$$

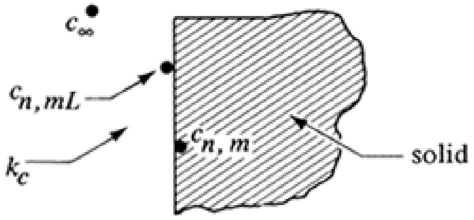


Figure 6.6-3. Interface concentrations for convective mass transfer at a solid surface and an equilibrium distribution coefficient $K = \times c_{n,mL}/c_{n,m}$.

where $c_{n,mL}$ is the concentration in the liquid adjacent to the surface and $c_{n,m}$ is the concentration in the solid adjacent to the surface. Then in deriving Eq. (6.6-6), the right-hand side $k_c\,\Delta y(c_{n,m} - c_\infty)$ becomes

Equation 6.6-12.

$$k_c\,\Delta y(c_{n,mL} - c_\infty)$$

where c_∞ is the concentration in the bulk fluid. Substituting $Kc_{n,m}$ for $c_{n,mL}$ from Eq. (6.6-11) into (6.6-12) and multiplying and dividing by K,

Equation 6.6-13.

$$Kk_c\,\Delta y\left(\frac{Kc_{n,m}}{K} - \frac{c_\infty}{K}\right) = Kk_c\,\Delta y\left(c_{n,m} - \frac{c_\infty}{K}\right)$$

Hence, whenever k_c appears as in Eq. (6.6-7), Kk_c should be substituted, and when c_∞ appears, c_∞/K should be used. Then Eq. (6.6-7) becomes as follows:

1. For convection at a boundary (Fig. 6.6-2a),

   Equation 6.6-14.

   $$\left(\frac{Kk_c\,\Delta x}{D_{AB}}\right)\frac{c_\infty}{K} + \tfrac{1}{2}(2c_{n-1,m} + c_{n,m+1} + c_{n,m-1}) - c_{n,m}\left(\frac{Kk_c\,\Delta x}{D_{AB}} + 2\right) = \overline{N}_{n,m}$$

   Equations (6.6-9) and (6.6-10) can be rewritten in a similar manner as follows:

2. For an exterior corner with convection at the boundary (Fig. 6.6-2c),

Equation 6.6-15.

$$\left(\frac{Kk_c\,\Delta x}{D_{AB}}\right)\frac{c_\infty}{K} + \tfrac{1}{2}(c_{n-1,m} + c_{n,m-1}) - \left(\frac{Kk_c\,\Delta x}{D_{AB}} + 1\right)c_{n,m} = \overline{N}_{n,m}$$

3. For an interior corner with convection at the boundary (Fig. 6.6-2d),

Equation 6.6-16.

$$\left(\frac{Kk_c\,\Delta x}{D_{AB}}\right)\frac{c_\infty}{K} + c_{n-1,m} + c_{n,m+1} + \tfrac{1}{2}(c_{n+1,m} + c_{n,m-1}) - \left(3 + \frac{Kk_c\,\Delta x}{D_{AB}}\right)c_{n,m} = \overline{N}_{n,m}$$

EXAMPLE 6.6-1. Numerical Method for Convection and Steady-State Diffusion

For the two-dimensional hollow solid chamber shown in Fig. 6.6-4, determine the concentrations at the nodes as shown at steady state. At the inside surfaces the concentrations remain constant at 6.00×10^{-3} kg mol/m^3. At the outside surfaces the convection coefficient $k_c = 2 \times 10^{-7}$ m/s and $c_\infty = 2.00 \times 10^{-3}$ kg mol/m^3. The diffusivity in the solid is $D_{AB} = 1.0 \times 10^{-9}$ m^2/s. The grid size is $\Delta x = \Delta y = 0.005$ m. Also, determine the diffusion rates per 1.0 m depth. The distribution coefficient $K = 1.0$.

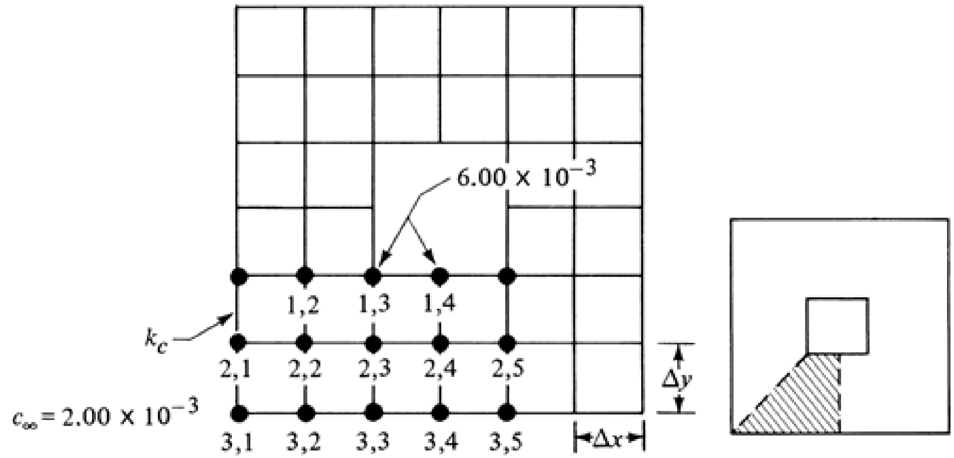


Figure 6.6-4. Concentrations for hollow chamber for Example 6.6-1.

Solution. To simplify the calculations, all the concentrations will be multiplied by 10^3. Since the chamber is symmetrical, we do the calculations on the $\frac{1}{8}$ shaded portion shown. The fixed known values are $c_{1,3} = 6.00$, $c_{1,4} = 6.00$, $c_\infty = 2.00$. Because of symmetry, $c_{1,2} = c_{2,3}$, $c_{2,5} = c_{2,3}$, $c_{2,1} = c_{3,2}$, $c_{3,3} = c_{3,5}$. To speed up the calculations, we will make estimates of the unknown concentrations as follows: $c_{2,2} = 3.80$, $c_{2,3} = 4.20$, $c_{2,4} = 4.40$, $c_{3,1} = 2.50$, $c_{3,2} = 2.70$, $c_{3,3} = 3.00$, $c_{3,4} = 3.20$.

For the interior points $c_{2,2}$, $c_{2,3}$, and $c_{2,4}$ we use Eqs. (6.6-3) and (6.6-4); for the corner convection point $c_{3,1}$, Eq. (6.6-9); for the other convection points $c_{3,2}$, $c_{3,3}$, $c_{3,4}$, Eq. (6.6-7). The term $k_c\Delta x/D_{AB} = (2 \times 10^{-7})(0.005)/(1.0 \times 10^{-9}) = 1.00$.

First approximation. Starting with $c_{2,2}$ we use Eq. (6.6-3) and calculate the residual $\overline{N}_{2,2}$:

$$c_{1,2} + c_{3,2} + c_{2,1} + c_{2,3} - 4c_{2,2} = \overline{N}_{2,2}$$

$$4.20 + 2.70 + 2.70 + 4.20 - 4(3.80) = -1.40$$

Hence, $c_{2,2}$ is not at steady state. Next we set $\overline{N}_{2,2}$ equal to zero and calculate a new value of $c_{2,2}$ from Eq. (6.6-4):

$$c_{2,2} = \frac{c_{1,2} + c_{3,2} + c_{2,1} + c_{2,3}}{4} = \frac{4.20 + 2.70 + 2.70 + 4.20}{4} = 3.45$$

This new value of $c_{2,2}$ replaces the old value.

For $c_{2,3}$,

$$c_{2,2} + c_{2,4} + c_{1,3} + c_{3,3} - 4c_{2,3} = \overline{N}_{2,3}$$

$$3.45 + 4.40 + 6.00 + 3.00 - 4(4.20) = 0.05$$

$$c_{2,3} = \frac{c_{2,2} + c_{2,4} + c_{1,3} + c_{3,3}}{4} = \frac{3.45 + 4.40 + 6.00 + 3.00}{4} = 4.21$$

For $c_{2,4}$,

$$c_{2,3} + c_{2,5} + c_{1,4} + C_{3,4} - 4c_{2,4} = \overline{N}_{2,4}$$

$$4.21 + 4.21 + 6.00 + 3.20 - 4(4.40) = 0.02$$

$$c_{2,4} = \frac{c_{2,3} + c_{2,5} + c_{1,4} + c_{3,4}}{4} = \frac{4.21 + 4.21 + 6.00 + 3.20}{4} = 4.41$$

For $c_{3,1}$, we use Eq. (6.6-9):

$$(1.0)c_\infty + \tfrac{1}{2}(c_{2,1} + c_{3,2}) - (1.0 + 1)c_{3,1} = \overline{N}_{3,1}$$

$$(1.0)2.00 + \tfrac{1}{2}(2.70 + 2.70) - 2.0(2.50) = -0.30$$

Setting Eq. (6.6-9) equal to zero and solving for $c_{3,1}$,

$$(1.0)2.00 + \tfrac{1}{2}(2.70 + 2.70) - (2.0)c_{3,1} = 0 \qquad c_{3,1} = 2.35$$

For $c_{3,2}$, we use Eq. (6.6-7):

$$(1.0)c_\infty + \tfrac{1}{2}(2 \times c_{2,2} + c_{3,1} + c_{3,3}) - (1.0 + 2)c_{3,2} = \overline{N}_{3,2}$$

$$(1.0)2.00 + \tfrac{1}{2}(2 \times 3.45 + 2.35 + 3.00) - (3.0)2.70 = 0.03$$

$$(1.0)2.00 + \tfrac{1}{2}(2 \times 3.45 + 2.35 + 3.00) - (3.0)c_{3,2} = 0 \qquad c_{3,2} = 2.71$$

For $c_{3,3}$,

$$(1.0)c_\infty + \tfrac{1}{2}(2 \times c_{2,3} + c_{3,2} + c_{3,4}) - (3.0)c_{3,3} = \overline{N}_{3,3}$$

$$(1.0)2.00 + \tfrac{1}{2}(2 \times 4.21 + 2.71 + 3.20) - (3.0)3.00 = 0.17$$

$$(1.0)2.00 + \tfrac{1}{2}(2 \times 4.21 + 2.71 + 3.20) - (3.0)c_{3,3} = 0 \qquad c_{3,3} = 3.06$$

For $c_{3,4}$,

$$(1.0)c_\infty + \tfrac{1}{2}(2 \times c_{2,4} + c_{3,3} + c_{3,5}) - (3.0)c_{3,4} = \overline{N}_{3,4}$$

$$(1.0)2.00 + \tfrac{1}{2}(2 \times 4.41 + 3.06 + 3.06) - (3.0)3.20 = -0.13$$

$$(1.0)2.00 + \tfrac{1}{2}(2 \times 4.41 + 3.06 + 3.06) - (3.0)c_{3,4} = 0 \qquad c_{3,4} = 3.16$$

Having completed one sweep across the grid map, we can perform a second approximation using the new values calculated, starting with $c_{2,2}$ or any other node. We continue until all the residuals are as small as desired. The final values after three approximations are $c_{2,2} = 3.47$, $c_{2,3} = 4.24$, $c_{2,4} = 4.41$, $c_{3,1} = 2.36$, $c_{3,2} = 2.72$, $c_{3,3} = 3.06$, $c_{3,4} = 3.16$.

To calculate the diffusion rates we first calculate the total convective diffusion rate, leaving the bottom surface at nodes $c_{3,1}$, $c_{3,2}$, $c_{3,3}$, and $c_{3,4}$ for 1.0 m depth:

$$\begin{aligned} N &= k_c(\Delta x \cdot 1)\left[\frac{c_{3,1} - c_\infty}{2} + (c_{3,2} - c_\infty) + (c_{3,3} - c_\infty) + \frac{c_{3,4} - c_\infty}{2}\right] \\ &= (2 \times 10^{-7})(0.005 \times 1)\left[\frac{2.36 - 2.00}{2} + (2.72 - 2.00)\right. \\ &\qquad\qquad \left. + (3.06 - 2.00) + \frac{3.16 - 2.00}{2}\right] \times 10^{-3} \\ &= 2.540 \times 10^{-12} \text{ kg mol/s} \end{aligned}$$

Note that the first and fourth paths include only one-half of a surface. Next we calculate the total diffusion rate in the solid entering the top surface inside, using an equation similar to Eq. (6.6-5):

$$\begin{aligned} N &= \frac{D_{AB}(\Delta x \cdot 1)}{\Delta y}\left[(c_{1,3} - c_{2,3}) + \frac{c_{1,4} - c_{2,4}}{2}\right] \\ &= \frac{(1.0 \times 10^{-9})(0.005 \times 1)}{0.005}\left[(6.00 - 4.24) + \frac{6.00 - 4.41}{2}\right] \times 10^{-3} \\ &= 2.555 \times 10^{-12} \text{ kg mol/s} \end{aligned}$$

At steady state the diffusion rate leaving by convection should equal that entering by diffusion. These results indicate a reasonable check. Using smaller grids would give even more accuracy. Note that the results for the diffusion rate should be multiplied by 8.0 for the whole chamber.

PROBLEMS

6.1-1. ***Diffusion of Methane Through Helium.*** A gas of CH_4 and He is contained in a tube at 101.32 kPa pressure and 298 K. At one point the partial pressure of methane is $p_{A1} = 60.79$ kPa, and at a point 0.02 m distance away, $p_{A2} = 20.26$ kPa. If the total pressure is constant throughout the tube, calculate the flux of CH_4 (methane) at steady state for equimolar counterdiffusion.

A1: **Ans.**

$$J^*_{Az} = 5.52 \times 10^{-5} \text{ kg mol } A/\text{s} \cdot \text{m}^2 \ (5.52 \times 10^{-6} \text{ g mol } A/\text{s} \cdot \text{cm}^2)$$

6.1-2. ***Diffusion of CO_2 in a Binary Gas Mixture.*** The gas CO_2 is diffusing at steady state through a tube 0.20 m long having a diameter of 0.01 m and containing N_2 at 298 K. The total pressure is constant at 101.32 kPa. The partial pressure of CO_2 is 456 mm Hg at one end and 76 mm Hg at the other end. The diffusivity D_{AB} is 1.67×10^{-5} m^2/s at 298 K. Calculate the flux of CO_2 in cgs and SI units for equimolar counterdiffusion.

6.2-1. ***Equimolar Counterdiffusion of a Binary Gas Mixture.*** Helium and nitrogen gas are contained in a conduit 5 mm in diameter and 0.1 m long at 298 K and a uniform constant pressure of 1.0 atm abs. The partial pressure of He at one end of the tube is 0.060 atm and at the other end is 0.020 atm. The diffusivity can be obtained from Table 6.2-1. Calculate the following for steady-state equimolar counterdiffusion:

a. Flux of He in kg mol/s · m^2 and g mol/s · cm^2.

b. Flux of N_2.

c. Partial pressure of He at a point 0.05 m from either end.

6.2-2. ***Equimolar Counterdiffusion of NH_3 and N_2 at Steady State.*** Ammonia gas (*A*) and nitrogen gas (*B*) are diffusing in counterdiffusion through a straight glass tube 2.0 ft (0.610 m) long with an inside diameter of 0.080 ft (24.4 mm) at 298 K and 101.32 kPa. Both ends of the tube are connected to large mixed chambers at 101.32 kPa. The partial pressure of NH_3 is constant at 20.0 kPa in one chamber and 6.666 kPa in the other. The diffusivity at 298 K and 101.32 kPa is 2.30×10^{-5} m^2/s.

a. Calculate the diffusion of NH_3 in lb mol/h and kg mol/s.

b. Calculate the diffusion of N_2.

c. Calculate the partial pressures at a point 1.0 ft (0.305 m) in the tube and plot ρ_A, ρ_B, and P versus distance z.

A4: **Ans.** (a) Diffusion of $NH_3 = 7.52 \times 10^{-7}$ lb mol *A*/h, 9.48×10^{-11} kg mol *A*/s; (c) $\rho_A = 1.333 \times 10^4$ Pa

6.2-3. ***Diffusion of A Through Stagnant B and Effect of Type of Boundary on Flux.*** Ammonia gas is diffusing through N_2 under steady-state conditions with N_2 nondiffusing since it is insoluble in one boundary. The total pressure is 1.013×10^5 Pa and the temperature is 298 K. The partial pressure of NH_3 at one point is 1.333×10^4 Pa, and at the other point 20 mm away it is 6.666×10^3 Pa. The D_{AB} for the mixture at 1.013×10^5 Pa and 298 K is 2.30×10^{-5} m^2/s.

a. Calculate the flux of NH_3 in kg mol/s · m^2.

b. Do the same as (a) but assume that N_2 also diffuses; that is, both boundaries are permeable to both gases and the flux is equimolar counterdiffusion. In which case is the flux greater?

A5: **Ans.** (a) $N_A = 3.44 \times 10^{-6}$ kg mol/s · m^2

6.2-4. ***Diffusion of Methane Through Nondiffusing Helium.*** Methane gas is diffusing in a straight tube 0.1 m long containing helium at 298 K and a total pressure of 1.01325×10^5 Pa. The partial pressure of CH_4 is 1.400×10^4 Pa at one end and 1.333×10^3 Pa at the other end. Helium is insoluble in one boundary, and hence is nondiffusing or stagnant. The diffusivity is given in Table 6.2-1. Calculate the flux of methane in kg mol/sm^2 at steady state.

6.2-5. ***Mass Transfer from a Naphthalene Sphere to Air.*** Mass transfer is occurring from a sphere of naphthalene having a radius of 10 mm. The sphere is in a large volume of still air at 52.6°C and 1 atm abs pressure. The vapor pressure of naphthalene at 52.6°C is 1.0 mm Hg. The diffusivity of naphthalene in air at 0°C is 5.16×10^{-6} m^2/s.

Calculate the rate of evaporation of naphthalene from the surface in kg mol/s · m^2. [*Note:* The diffusivity can be corrected for temperature using the temperature-correction factor from the Fuller et al. equation (6.2-45).]

6.2-6. ***Estimation of Diffusivity of a Binary Gas.*** For a mixture of ethanol (CH_3CH_2OH) vapor and methane (CH_4), predict the diffusivity using the method of Fuller et al.

a. At 1.0132×10^5 Pa and 298 and 373 K.
b. At 2.0265×10^5 Pa and 298 K.

A8: **Ans.** (a) $D_{AB} = 1.43 \times 10^{-5}$ m^2/s (298 K)

6.2-7. ***Diffusion Flux and Effect of Temperature and Pressure.*** Equimolar counterdiffusion is occurring at steady state in a tube 0.11 m long containing N_2 and CO gases at a total pressure of 1.0 atm abs. The partial pressure of N_2 is 80 mm Hg at one end and 10 mm at the other end. Predict the D_{AB} by the method of Fuller et al.

a. Calculate the flux in kg mol/s · m^2 at 298 K for N_2.
b. Repeat at 473 K. Does the flux increase?
c. Repeat at 298 K but for a total pressure of 3.0 atm abs. The partial pressure of N_2 remains at 80 and 10 mm Hg, as in part (a). Does the flux change?

A9: **Ans.** (a) $D_{AB} = 2.05 \times 10^{-5}$ m^2/s, $N_A = 7.02 \times 10^{-7}$ kg mol/s · m^2; (b) $N_A = 9.92 \times 10^{-7}$ kg mol/s · m^2; (c) $N_A = 2.34 \times 10^{-7}$ kg mol/s · m^2

6.2-8. ***Evaporation Losses of Water in Irrigation Ditch.*** Water at 25°C is flowing in a covered irrigation ditch below ground. Every 100 ft there is a vent line 1.0 in. inside diameter and 1.0 ft long to the outside atmosphere at 25°C. There are 10 vents in the 1000-ft ditch. The outside air can be assumed to be dry. Calculate the total evaporation loss of water in lb$_m$/d. Assume that the partial pressure of water vapor at the surface of the water is the vapor pressure, 23.76 mm Hg at 25°C. Use the diffusivity from Table 6.2-1.

6.2-9. ***Time to Completely Evaporate a Sphere.*** A drop of liquid toluene is kept at a uniform temperature of 25.9°C and is suspended in air by a fine wire. The initial radius $r_1 = 2.00$ mm. The vapor pressure of toluene at 25.9°C is $P_{A1} = 3.84$ kPa and the density of liquid toluene is 866 kg/m^3.

a. Derive Eq. (6.2-34) to predict the time t_F for the drop to evaporate completely in a large volume of still air. Show all steps.
b. Calculate the time in seconds for complete evaporation.

A11: **Ans.** (b) $t_F = 1388$ s

6.2-10. ***Diffusion in a Nonuniform Cross-Sectional Area.*** The gas ammonia (A) is diffusing at steady state through N_2 (B) by equimolar counterdiffusion in a conduit 1.22 m long at 25°C and a total pressure of 101.32 kPa abs. The partial pressure of ammonia at the left end is 25.33 kPa and at the other end 5.066 kPa. The cross section of the conduit is in the shape of an equilateral triangle, the length of each side of the triangle being 0.0610 m at the left end and tapering uniformly to 0.0305 m at the right end. Calculate the molar flux of ammonia. The diffusivity is $D_{AB} = 0.230 \times 10^{-4}$ m^2/s.

6.3-1. ***Diffusion of A Through Stagnant B in a Liquid.*** The solute HCl (*A*) is diffusing through a thin film of water (*B*) 2.0 mm thick at 283 K. The concentration of HCl at point 1 at one boundary of the film is 12.0 wt % HCl (density ρ_1 = 1060.7 kg/m^3), and at the other boundary at point 2 it is 6.0 wt % HCl (ρ_2 = 1030.3 kg/m^3). The diffusion coefficient of HCl in water is 2.5 × 10^{-9} m^2/s. Assuming steady state and one boundary impermeable to water, calculate the flux of HCl in kg mol/s · m^2.

A13: **Ans.** $N_A = 2.372 \times 10^{-6}$ kg mol/s · m^2

6.3-2. ***Diffusion of Ammonia in an Aqueous Solution.*** An ammonia (*A*)–water (*B*) solution at 278 K and 4.0 mm thick is in contact at one surface with an organic liquid at this interface. The concentration of ammonia in the organic phase is held constant and is such that the equilibrium concentration of ammonia in the water at this surface is 2.0 wt % ammonia (density of aqueous solution 991.7 kg/m^3) and the concentration of ammonia in water at the other end of the film 4.0 mm away is 10 wt % (density 961.7 kg/m^3). Water and the organic are insoluble in each other. The diffusion coefficient of NH_3 in water is 1.24 × 10^{-9} m^2/s.

a. At steady state, calculate the flux N_A in kg mol/s·m^2.

b. Calculate the flux N_B. Explain.

6.3-3. ***Estimation of Liquid Diffusivity.*** It is desired to predict the diffusion coefficient of dilute acetic acid (CH_3COOH) in water at 282.9 K and at 298 K using the Wilke–Chang method. Compare the predicted values with the experimental values in Table 6.3-1.

A15: **Ans.** $D_{AB} = 0.897 \times 10^{-9}$ m^2/s (282.9 K), $D_{AB} = 1.396 \times 10^{-9}$ m^2/s (288 K)

6.3-4. ***Estimation of Diffusivity of Methanol in H_2O.*** The diffusivity of dilute methanol in water has been determined experimentally to be 1.26 × 10^{-9} m^2/s at 288 K.

a. Estimate the diffusivity at 293 K using the Wilke–Chang equation.

b. Estimate the diffusivity at 293 K by correcting the experimental value at 288 K to 293 K. (*Hint:* Do this by using the relationship $D_{AB} \propto T/\mu_B$.)

6.3-5. ***Estimation of Diffusivity of Electrolyte NaOH.*** Dilute NaOH is diffusing in an aqueous solution. Do as follows:

a. Estimate the diffusivity of NaOH at 25°C. Also, calculate the diffusivity of the individual ions Na^+ and OH^-.

b. Estimate the diffusivity of NaOH at 15°C.

A17: **Ans.**

(a) $D^o_{AB} = 2.128 \times 10^{-5}$ cm^2/s; (b) $D^o_{AB} = 1.609 \times 10^{-5}$ cm^2/s

6.3.6. ***Estimation of Diffusivity of $LaCl_3$ and Temperature Effect.*** Estimate the diffusion coefficient of the salt $LaCl_3$ in dilute aqueous solution at 25°C and at 35°C. Also, calculate the diffusion coefficient for the ions La^{3+} and Cl^- at 25°C. What percent increase in rate of diffusion will occur in going from 25 to 35°C if the same dilute concentration difference is present at both temperatures?

A18: **Ans.** $D^{o}_{AB}\ (35°\text{C}) = 1.649 \times 10^{-5}\ \text{cm}^2/\text{s}$

6.4-1. ***Prediction of Diffusivity of Enzyme Urease in Solution.*** Predict the diffusivity of the enzyme urease in a dilute solution in water at 298 K using the modified Polson equation and compare the result with the experimental value in Table 6.4-1.

A19: **Ans.** Predicted $D_{AB} = 3.995 \times 10^{-11}$ m^2/s

6.4-2. ***Diffusion of Sucrose in Gelatin.*** A layer of gelatin in water 5 mm thick containing 5.1 wt % gelatin at 293 K separates two solutions of sucrose. The concentration of sucrose in the solution at one surface of the gelatin is constant at 2.0 g sucrose/100 mL solution, and 0.2 g/100 mL at the other surface. Calculate the flux of sucrose in kg sucrose/s·m^2 through the gel at steady state.

6.4-3. ***Diffusivity of Oxygen in Protein Solution.*** Oxygen is diffusing through a solution of bovine serum albumin (BSA) at 298 K. Oxygen has been shown not to bind to BSA. Predict the diffusivity D_{AP} of oxygen in a protein solution containing 11 g protein/100 mL solution. (*Note:* See Table 6.3-1 for the diffusivity of O_2 in water.)

A21: **Ans.** $D_{AP} = 1.930 \times 10^{-9}$ m^2/s

6.4-4. ***Diffusion of Uric Acid in Protein Solution and Binding.*** Uric acid (A) at 37°C is diffusing in an aqueous solution of proteins (P) containing 8.2 g protein/100 mL solution. Uric acid binds to the proteins, and over the range of concentrations present, 1.0 g mol of acid binds to the proteins for every 3.0 g mol of total acid present in the solution. The diffusivity D_{AB} of uric acid in water is 1.21×10^{-5} cm^2/s and $D_P = 0.091 \times 10^{-5}$ cm^2/s.

a. Assuming no binding, predict the ratio D_{AP}/D_{AB} due only to blockage effects.

b. Assuming blockage plus binding effects, predict the ratio D_{AP}/D_{AB}. Compare this with the experimental value for D_{AP}/D_{AB} of 0.616 (C8).

c. Predict the flux in g uric acid/s.·.cm^2 for a concentration of acid of 0.05 g/L at point (1) and 0 g/L at point (2) a distance 1.5 μm away.

A22: **Ans.** (c) $N_A = 2.392 \times 10^{-6}$ g/s · cm^2

6.5-1. ***Diffusion of CO_2 Through Rubber.*** A flat plug 30 mm thick having an area of 4.0×10^{-4} m^2 and made of vulcanized rubber is used for closing an opening in a container. The gas CO_2 at 25°C and 2.0 atm pressure is inside the container. Calculate the total leakage or diffusion of CO_2 through the plug to the outside in kg mol CO_2/s at steady state. Assume that the partial pressure of CO_2 outside is zero. From Barrer (B5) the solubility of the CO_2 gas is 0.90 m^3 gas (at STP of 0°C and 1 atm) per m^3 rubber per atm pressure of CO_2. The diffusivity is 0.11×10^{-9} m^2/s.

A23: **Ans.** 1.178×10^{-13} kg mol CO_2/s

6.5-2. ***Leakage of Hydrogen Through Neoprene Rubber.*** Pure hydrogen gas at 2.0 atm abs pressure and 27°C is flowing past a vulcanized neoprene rubber slab 5 mm thick. Using the data from Table 6.5-1, calculate the diffusion flux in kg mol/s · m^2 at steady state. Assume no resistance to diffusion outside the slab and zero partial pressure of H_2 on the outside.

6.5-3. ***Relation Between Diffusivity and Permeability.*** The gas hydrogen is diffusing through a sheet of vulcanized rubber 20 mm thick at 25°C. The partial pressure of H_2 is 1.5 atm inside and 0 outside. Using the data from Table 6.5-1, calculate the following:

a. The diffusivity D_{AB} from the permeability P_M and solubility S, and compare with the value in Table 6.5-1.

b. The flux N_A of H_2 at steady state.

A25: **Ans.** (b) $N_A = 1.144 \times 10^{-10}$ kg mol/s · m^2

6.5-4. ***Loss from a Tube of Neoprene.*** Hydrogen gas at 2.0 atm and 27°C is flowing in a neoprene tube 3.0 mm inside diameter and 11 mm outside diameter. Calculate the leakage of H_2 through a tube 1.0 m long in kg mol H_2/s at steady state.

6.5-5. ***Diffusion Through Membranes in Series.*** Nitrogen gas at 2.0 atm and 30°C is diffusing through a membrane of nylon 1.0 mm thick and polyethylene 8.0 mm thick in series. The partial pressure at the other side of the two films is 0 atm. Assuming no other resistances, calculate the flux N_A at steady state.

6.5-6. ***Diffusion of CO_2 in a Packed Bed of Sand.*** It is desired to calculate the rate of diffusion of CO_2 gas in air at steady state through a loosely packed bed of sand at 276 K and a total pressure of 1.013×10^5 Pa. The bed depth is 1.25 m and the void fraction ε is 0.30. The partial pressure of CO_2 is 2.026×10^3 Pa at the top of the bed and 0 Pa at the bottom. Use a τ of 1.87.

A28: **Ans.** $N_A = 1.609 \times 10^{-9}$ kg mol CO_2/s · m^2

6.5-7. ***Packaging to Keep Food Moist.*** Cellophane is being used to keep food moist at 38°C. Calculate the loss of water vapor in g/d at steady state for a wrapping 0.10 mm thick and an area of 0.200 m^2 when the vapor pressure of water vapor inside is 10 mm Hg and the air outside contains water vapor at a pressure of 5 mm Hg. Use the larger permeability in Table 6.5-1.

A29: **Ans.** 0.1663 g H_2O/day.

6.5-8. ***Loss of Helium and Permeability.*** A window of SiO_2 2.0 mm thick and 1.0×10^{-4} m^2 in area is used to view the contents in a metal vessel at 20°C. Helium gas at 202.6 kPa is contained in the vessel. To be conservative use $D_{AB} = 5.5 \times 10^{-14}$ m^2/s from Table 6.5-1.

a. Calculate the loss of He in kg mol/h at steady state.

b. Calculate the permeability P_M.

A30: **Ans.** (a) Loss = 8.833×10^{-15} kg mol He/h

6.6-1. ***Numerical Method for Steady-State Diffusion.*** Using the results from Example 6.6-1, calculate the total diffusion rate in the solid using the bottom nodes and paths of $c_{2,2}$ to $c_{3,2}$, $c_{2,3}$ to $c_{3,3}$, and so on. Compare with the other diffusion rates in Example 6.6-1.

A31: **Ans.** $N = 2.555 \times 10^{-12}$ kg mol/s

6.6-2. ***Numerical Method for Steady-State Diffusion with Distribution Coefficient.*** Use the conditions given in Example 6.6-1 except that the distribution coefficient defined by Eq. (6.6-11) between the concentration in the liquid adjacent to the external surface and the concentration in the solid adjacent to the external surface is $K = 1.2$. Calculate the steady-state concentrations and the diffusion rates.

6.6-3. ***Spreadsheet Solution for Steady-State Diffusion.*** Use the conditions given in Example 6.6-1 but instead of using $\Delta x = 0.005$ m, use $\Delta x = \Delta y = 0.001$ m. The overall dimensions of the hollow chamber remain as in Example 6.6-1; the only difference is that more nodes will be used. Write the spreadsheet program and solve for the steady-state concentrations using the numerical method. Also, calculate the diffusion rates and compare with Example 6.6-1.

6.6-4. ***Numerical Method with Fixed Surface Concentrations.*** Steady-state diffusion is occurring in a two-dimensional solid as shown in Fig. 6.6-4. The grid $\Delta x = \Delta y = 0.010$ m. The diffusivity $D_{AB} = 2.00 \times 10^{-9}$ m^2/s. At the inside of the chamber the surface concentration is held constant at 2.00×10^{-3} kg mol/m^3. At the outside surfaces, the concentration is constant at 8.00×10^{-3}. Calculate the steady-state concentrations and the diffusion rates per m of depth.

REFERENCES

Bibliography

[ch06biblio01entry01] (A1) I., Amdur, and L. M. Shuler, *J. Chem. Phys.*, **38**, 188 (1963).

[ch06biblio01entry02] (A2) D. K., Anderson, Hall. J. R., and A. L. Babb, *J. Phys. Chem.*, **62**, 404 (1958).

[ch06biblio01entry03] (B1) R. E. Bunde, *Univ. Wisconsin Naval Res. Lab. Rept. No. CM-850*, August 1955.

[ch06biblio01entry04] (B2) C. A., Boyd, N., Stein, V., Steingrimisson, and W. F. Rumpel, *J. Chem. Phys.*, **19**, 548 (1951).

[ch06biblio01entry05] (B3) R. B., Bird, W. E., Stewart, and E. N. Lightfoot, *Transport Phenomena*. New York: John Wiley & Sons, Inc., 1960.

[ch06biblio01entry06] (B4) D. E., Bidstrup, and C. J. Geankoplis, *J. Chem. Eng. Data*, **8**, 170 (1963).

[ch06biblio01entry07] (B5) R. M. Barrer, *Diffusion in and Through Solids*. London: Cambridge University Press, 1941.

[ch06biblio01entry08] (C1) L. T., Carmichael, B. H., Sage, and W. N. Lacey, *A.I.Ch.E. J.*, **1**, 385 (1955).

[ch06biblio01entry09] (C2) A. J., Carswell, and J. C. Stryland, *Can. J. Phys.*, **41**, 708 (1963).

[ch06biblio01entry10] (C3) P. K., Chakraborti, and P. Gray, *Trans. Faraday Soc.*, **62**, 3331 (1961).

[ch06biblio01entry11] (C4) S. Y. M. S. Chang, thesis, Massachusetts Institute of Technology, 1959.

[ch06biblio01entry12] (C5) Pin, Chang, and C. R. Wilke, *J. Phys. Chem.*, **59**, 592 (1955).

[ch06biblio01entry13] (C6) P. A. Charlwood, *J. Phys. Chem.*, **57**, 125 (1953).

[ch06biblio01entry14] (C7) J. R. Cameron, M.S. thesis, Ohio State University, 1973.

[ch06biblio01entry15] (C8) C. K., Colton, K. A., Smith, E. W., Merrill, and J. M. Reece, *Chem. Eng. Progr. Symp.*, **66**(99), 85 (1970).

[ch06biblio01entry16] (C9) J., Crank, and G. S. Park, *Diffusion in Polymers*. New York: Academic Press, Inc., 1968.

[ch06biblio01entry17] (C10) E. L. Cussler, *Diffusion Mass Transfer in Fluid Systems*, 2nd ed. New York: Cambridge University Press, 1997.

[ch06biblio01entry18] (F1) E. N., Fuller, P. D., Schettler, and J. C. Giddings, *Ind. Eng. Chem.*, **58**, 19 (1966).

[ch06biblio01entry19] (F2) L., Friedman, and E. O. Kramer, *J. Am. Chem. Soc.*, **52**, 1298 (1930).

[ch06biblio01entry20] (F3) L. Friedman, *J. Am. Chem. Soc.*, **52**, 1305, 1311 (1930).

[ch06biblio01entry21] (G1) E. R. Gilliland, *Ind. Eng. Chem.*, **26**, 681 (1934).

[ch06biblio01entry22] (G2) C. J. Geankoplis, *Mass Transport Phenomena*. Columbus, Ohio: Ohio State University Bookstores, 1972.

[ch06biblio01entry23] (G3) G. H., Garner, and P. J.M. Marchant, *Trans. Inst. Chem. Eng. (London)*, **39**, 397 (1961).

[ch06biblio01entry24] (G4) L. S. Gosting, *Advances in Protein Chemistry*, Vol. 1. New York: Academic Press, Inc., 1956.

[ch06biblio01entry25] (G5) C. J., Geankoplis, M. R., Okos, and E. A. Grulke, *J. Chem. Eng. Data*, **23**, 40 (1978).

[ch06biblio01entry26] (G6) C. J., Geankoplis, E. A., Grulke, and M. R. Okos, *Ind. Eng. Chem. Fund.*, **18**, 233 (1979).

[ch06biblio01entry27] (H1) J. N., Holsen, and M. R. Strunk, *Ind. Eng. Chem. Fund.*, **3**, 143 (1964).

[ch06biblio01entry28] (H2) G. H., Hudson, J. C., McCoubrey, and A. R. Ubbelohde, *Trans. Faraday Soc.*, **56**, 1144 (1960).

[ch06biblio01entry29] (H3) J. O., Hirschfelder, C. F., Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*. New York: John Wiley & Sons, Inc., 1954.

[ch06biblio01entry30] (H4) B. R., Hammond, and R. H. Stokes, *Trans. Faraday Soc.*, **49**, 890 (1953).

[ch06biblio01entry31] (J1) P. A., Johnson, and A. L. Babb, *Chem. Revs.*, **56**, 387 (1956).

[ch06biblio01entry32] (K1) K. H., Keller, and S. K. Friedlander, *J. Gen. Physiol.*, **49**, 68 (1966).

[ch06biblio01entry33] (L1) C. Y., Lee, and C. R. Wilke, *Ind. Eng. Chem.*, **46**, 2381 (1954).

[ch06biblio01entry34] (L2) G. Le Bas, *The Molecular Volumes of Liquid Chemical Compounds*. New York: David McKay Co., Inc., 1915.

[ch06biblio01entry35] (L3) L. G. Longsworth, *J. Phys. Chem.*, **58**, 770 (1954).

[ch06biblio01entry36] (L4) A. G., Langdon, and H. C. Thomas, *J. Phys. Chem.*, **75**, 1821 (1971).

[ch06biblio01entry37] (M1) E. A., Mason, and L. Monchick, *J. Chem. Phys.*, **36**, 2746 (1962).

[ch06biblio01entry38] (M2) L., Monchick, and E. A. Mason, *J. Chem. Phys.*, **35**, 1676 (1961).

[ch06biblio01entry39] (N1) E. P., Ney, and F. C. Armistead, *Phys. Rev.*, **71**, 14 (1947).

[ch06biblio01entry40] (N2) National Research Council, *International Critical Tables*, Vol. V. New York: McGraw-Hill Book Company, 1929.

[ch06biblio01entry41] (N3) R. M., Narvari, J. L., Gainer, and K. R. Hall, *A.I.Ch.E. J.*, **17**, 1028 (1971).

[ch06biblio01entry42] (P1) R. H., Perry, and D. Green, *Perry's Chemical Engineers' Handbook*, 6th ed. New York: McGraw-Hill Book Company, 1984.

[ch06biblio01entry43] (P2) L. R., Perkins, and C. J. Geankoplis, *Chem. Eng. Sci.*, **24**, 1035 (1969).

[ch06biblio01entry44] (P3) A. Polson, *J. Phys. Colloid Chem.*, **54**, 649 (1950).

[ch06biblio01entry45] (R1) R. C., Reid, J. M., Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed. New York: McGraw-Hill Book Company, 1977.

[ch06biblio01entry46] (R2) K. A., Reddy, and L. K. Doraiswamy, *Ind. Eng. Chem. Fund.*, **6**, 77 (1967).

[ch06biblio01entry47] (R3) C. E. Rogers, *Engineering Design for Plastics*. New York: Reinhold Publishing Co., Inc., 1964.

[ch06biblio01entry48] (R4) R. A., Robinson, and R. H. Stokes, *Electrolytic Solutions*, 2nd ed. New York: Academic Press, 1959.

[ch06biblio01entry49] (S1) K. L. Schafer, *Z. Elecktrochem.*, **63**, 111 (1959).

[ch06biblio01entry50] (S2) S. L., Seager, L. R., Geertson, and J. C. Giddings, *J. Chem. Eng. Data*, **8**, 168 (1963).

[ch06biblio01entry51] (S3) F. A., Schwertz, and J. E. Brow, *J. Chem. Phys.*, **19**, 640 (1951).

[ch06biblio01entry52] (S4) B. N., Srivastava, and I. B. Srivastava, *J. Chem. Phys.*, **38**, 1183 (1963).

[ch06biblio01entry53] (S5) A. H.P. Skelland, *Diffusional Mass Transfer*. New York: McGraw-Hill Book Company, 1974.

[ch06biblio01entry54] (S6) H. A. Sorber, *Handbook of Biochemistry, Selected Data for Molecular Biology*. Cleveland: Chemical Rubber Co., Inc., 1968.

[ch06biblio01entry55] (S7) G. E. Spalding, *J. Phys. Chem.*, **73**, 3380 (1969).

[ch06biblio01entry56] (S8) C. N. Satterfield, *Mass Transfer in Heterogeneous Catalysis*. Cambridge, Mass.: The MIT Press, 1978.

[ch06biblio01entry57] (S9) J. D., Seader, and E. J. Henley, *Separation Process Principles*. New York: John Wiley & Sons, 1998.

[ch06biblio01entry58] (T1) M., Trautz, and Muller, *W. Ann. Physik*, **22**, 333 (1935).

[ch06biblio01entry59] (T2) R. E. Treybal, *Liquid Extraction*, 2nd ed. New York: McGraw-Hill Book Company, 1963.

[ch06biblio01entry60] (T3) R. E. Treybal, *Mass Transfer Operations*, 3rd ed. New York: McGraw-Hill Book Company, 1980.

[ch06biblio01entry61] (V1) J. E., Vivian, and C. J. King, *A.I.Ch.E. J.*, **10**, 220 (1964).

[ch06biblio01entry62] (W1) V. E. Wintergerst, *Ann. Physik*, **4**, 323 (1930).

[ch06biblio01entry63] (W2) A. A., Westenberg, and G. Frazier, *J. Chem. Phys.*, **36**, 3499 (1962).

[ch06biblio01entry64] (W3) R. E., Walker, and A. A. Westenberg, *J. Chem. Phys.*, **29**, 1139 (1958).

[ch06biblio01entry65] (W4) R. E., Walker, and A. A. Westenberg, *J. Chem. Phys.*, **32**, 436 (1960).

[ch06biblio01entry66] (W5) C. R., Wilke, and Pin. Chang, *A.I.Ch.E. J.*, **1**, 264 (1955).