Fundamentals of Mass Transfer

Diffusion is the process by which molecules, ions, or other small particles spontaneously mix, moving from regions of relatively high concentration into regions of lower concentration. This process can be analyzed in two ways. First, it can be described with Fick's law and a diffusion coefficient, a fundamental and scientific description used in the first two parts of this book. Second, it can be explained in terms of a mass transfer coefficient, an approximate engineering idea that often gives a simpler description. It is this simpler idea that is emphasized in this part of this book.

Analyzing diffusion with mass transfer coefficients requires assuming that changes in concentration are limited to that small part of the system's volume near its boundaries. For example, in the absorption of one gas into a liquid, we assume that all gases and liquids are well mixed, except near the gas–liquid interface. In the leaching of metal by pouring acid over ore, we assume that the acid is homogeneous, except in a thin layer next to the solid ore particles. In studies of digestion, we assume that the contents of the small intestine are well mixed, except near the villi at the intestine's wall. Such an analysis is sometimes called a "lumped-parameter model" to distinguish it from the "distributed-parameter model" using diffusion coefficients. Both models are much simpler for dilute solutions.

If you are beginning a study of diffusion, you may have trouble deciding whether to organize your results as mass transfer coefficients or as diffusion coefficients. I have this trouble too. The cliché is that you should use the mass transfer coefficient approach if the diffusion occurs across an interface, but this cliché has many exceptions. Instead of depending on the cliché, I believe you should always try both approaches to see which is better for your own needs. In my own work, I have found that I often switch from one to the other as the work proceeds and my objectives evolve.

This chapter discusses mass transfer coefficients for dilute solutions; extensions to concentrated solutions are deferred to Section 13.5. In Section 8.1, we give a basic definition for a mass transfer coefficient and show how this coefficient can be used experimentally. In Section 8.2, we present other common definitions that represent a thicket of prickly alternatives rivaled only by standard states for chemical potentials. These various definitions are why mass transfer often has a reputation with students of being a difficult subject. In Section 8.3, we list existing correlations of mass transfer coefficients; and in Section 8.4, we explain how these correlations can be developed with dimensional analysis. Finally, in Section 8.5, we discuss processes involving diffusion across interfaces, a topic that leads to overall mass transfer coefficients found as averages of more local processes. This last idea is commonly called mass transfer resistances in series.

8.1 A Definition of Mass Transfer Coefficients

The definition of mass transfer is based on empirical arguments like those used in developing Fick's law in Chapter 2. Imagine we are interested in the transfer of mass

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from some interface into a well-mixed solution. We expect that the amount transferred is proportional to the concentration difference and the interfacial area:

$$\begin{pmatrix} \text{rate of mass} \\ \text{transferred} \end{pmatrix} = k \begin{pmatrix} \text{interfacial} \\ \text{area} \end{pmatrix} \begin{pmatrix} \text{concentration} \\ \text{difference} \end{pmatrix} \qquad (8.1\text{-}1)$$

where the proportionality is summarized by k, called a mass transfer coefficient. If we divide both sides of this equation by the area, we can write the equation in more familiar symbols:

$$N_1 = k(c_{1i} - c_1) \qquad (8.1\text{-}2)$$

where N_1 is the flux at the interface and c_{1i} and c_1 are the concentrations at the interface and in the bulk solution, respectively. The flux N_1 includes both diffusion and convection; it is like the total flux n_1 except that it is located at the interface. The concentration c_{1i} is at the interface but in the same fluid as the bulk concentration c_1. It is often in equilibrium with the concentration across the interface in a second, adjacent fluid phase; we will defer discussion of transport across this interface until section 8.5.

The flux equation in Eq. 8.1-2 makes practical sense. It says that if the concentration difference is doubled, the flux will double. It also suggests that if the area is doubled, the total amount of mass transferred will double but the flux per area will not change. In other words, this definition suggests an easy way of organizing our thinking around a simple constant, the mass transfer coefficient k.

Unfortunately, this simple scheme conceals a variety of approximations and ambiguities. Before introducing these complexities, we shall go over some easy examples. These examples are important. Study them carefully before you go on to the harder material that follows.

Example 8.1-1: Humidification   Imagine that water is evaporating into initially dry air in the closed vessel shown schematically in Fig. 8.1-1(a). The vessel is isothermal at 25°C, so the water's vapor pressure is 23.8 mm Hg. This vessel has 0.8 liter of water with 150 cm^2 of surface area in a total volume of 19.2 liters. After 3 minutes, the air is five percent saturated. What is the mass transfer coefficient? How long will it take to reach ninety percent saturation?

Solution   The flux at 3 minutes can be found directly from the values given:

$$N_1 = \frac{\begin{pmatrix} \text{vapor} \\ \text{concentration} \end{pmatrix} \begin{pmatrix} \text{air} \\ \text{volume} \end{pmatrix}}{\begin{pmatrix} \text{liquid} \\ \text{area} \end{pmatrix} (\text{time})}$$

$$= \frac{0.05 \left(\dfrac{23.8}{760} \right) \left(\dfrac{1 \text{ mol}}{22.4 \text{ liters}} \right) \left(\dfrac{273}{298} \right) (18.4 \text{ liters})}{(150 \text{ cm}^2)(180 \text{ sec})}$$

$$= 4.4 \cdot 10^{-8} \text{ mol/cm}^2\text{-sec}$$

The concentration difference is that at the water's surface minus that in the bulk solution. That at the water's surface is the value at saturation; that in bulk at short times is essentially

(a) Humidification

(b) Packed Bed

(c) Liquid Drops
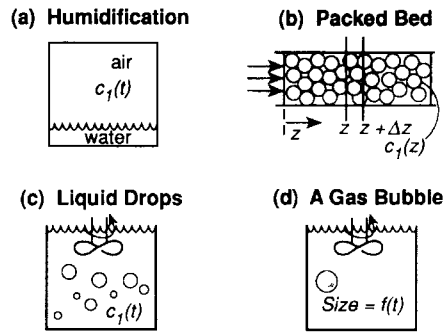
(d) A Gas Bubble

Fig. 8.1-1. Four easy examples. We analyze each of the physical situations shown in terms of mass transfer coefficients. In (a), we assume that the air is at constant humidity, except near the air–water interface. In (b), we assume that water flowing through the packed bed is well mixed, except very close to the solid spheres. In (c) and (d), we assume that the liquid solution, which is the continuous phase, is at constant composition, except near the droplet or bubble surfaces.

zero. Thus, from Eq. 8.1-2, we have

$$4.4 \cdot 10^{-8} \text{ mol/cm}^2\text{-sec} = k \left(\frac{23.8}{760} \frac{1 \text{ mol}}{22.4 \cdot 10^3 \text{ cm}^3} \frac{273}{298} - 0 \right)$$

$$k = 3.4 \cdot 10^{-2} \text{ cm/sec}$$

This value is lower than that commonly found for transfer in gases.

The time required for ninety percent saturation can be found from a mass balance:

$$\begin{pmatrix} \text{accumulation} \\ \text{in gas phase} \end{pmatrix} = \begin{pmatrix} \text{evaporation} \\ \text{rate} \end{pmatrix}$$

$$\frac{d}{dt} V c_1 = A N_1$$

$$= A k [c_1(\text{sat}) - c_1]$$

The air is initially dry, so

$$t = 0, \quad c_1 = 0$$

We use this condition to integrate the mass balance:

$$\frac{c_1}{c_1(\text{sat})} = 1 - e^{-(kA/V)t}$$

Rearranging the equation and inserting the values given, we find

$$t = -\frac{V}{kA} \ln \left(1 - \frac{c_1}{c_1(\text{sat})} \right)$$

$$= -\frac{18.4 \cdot 10^3 \text{ cm}^3}{(3.4 \cdot 10^{-2} \text{ cm/sec}) \cdot (150 \text{ cm}^2)} \ln(1 - 0.9)$$

$$= 8.3 \cdot 10^3 \text{ sec} = 2.3 \text{ hr}$$

It takes over 2 hours to saturate the air this much.

Example 8.1-2: Mass transfer in a packed bed   Imagine that 0.2 centimeter-diameter spheres of benzoic acid are packed into a bed like that shown schematically in Fig. 8.1-1(b). The spheres have 23 cm^2 surface per 1 cm^3 of bed. Pure water flowing at a superficial velocity of 5 cm/sec into the bed is sixty-two percent saturated with benzoic acid after it has passed through 100 centimeters of bed. What is the mass transfer coefficient?

Solution   The answer to this problem depends on the concentration difference used in the definition of the mass transfer coefficient. In every definition, we choose this difference as the value at the sphere's surface minus that in the solution. However, we can define different mass transfer coefficients by choosing the concentration difference at various positions in the bed. For example, we can choose the concentration difference at the bed's entrance and so obtain

$$N_1 = k[c_1(\text{sat}) - 0]$$

$$\frac{0.62 c_1(\text{sat})(5 \text{ cm/sec})A}{(23 \text{ cm}^2/\text{cm}^3)(100 \text{ cm})A} = k c_1(\text{sat})$$

where A is the bed's cross section. Thus

$$k = 1.3 \cdot 10^{-3} \text{cm/sec}$$

This definition for the mass transfer coefficient is infrequently used.

Alternatively, we can choose as our concentration difference that at a position z in the bed and write a mass balance on a differential volume $A\Delta z$ at this position:

$$(\text{accumulation}) = \left(\begin{array}{c} \text{flow in} \\ \text{minus flow out} \end{array} \right) + \left(\begin{array}{c} \text{amount of} \\ \text{dissolution} \end{array} \right)$$

$$0 = A \left(c_1 v^0 \Big|_z - c_1 v^0 \Big|_{z+\Delta z} \right) + (A\Delta z) a N_1$$

where a is the sphere surface area per bed volume. Substituting for N_1 from Eq. 8.1-2, dividing by $A\Delta z$, and taking the limit as Δz goes to zero, we find

$$\frac{dc_1}{dz} = \frac{ka}{v^0}[c_1(\text{sat}) - c_1]$$

This is subject to the initial condition that

$$z = 0, \quad c_1 = 0$$

Integrating, we obtain an exponential of the same form as in the first example:

$$\frac{c_1}{c_1(\text{sat})} = 1 - e^{-(ka/v^0)z}$$

Rearranging the equation and inserting the values given, we find

$$k = \left(\frac{v^0}{az} \right) \ln \left(1 - \frac{c_1}{c_1(\text{sat})} \right)$$

$$= -\frac{5 \text{ cm/sec}}{(23 \text{ cm}^2/\text{cm}^3)(100 \text{ cm})} \ln(1 - 0.62)$$

$$= 2.1 \cdot 10^{-3} \text{ cm/sec}$$

This value is typical of those found in liquids. This type of mass transfer coefficient definition is preferable to that used first, a point explored further in Section 8.2.

A tangential point worth discussing is the specific chemical system of benzoic acid dissolving in water. This system is academically ubiquitous, showing up again and again in problems of mass transfer. Indeed, if you read the literature, you can get the impression that it is the only system where mass transfer is important, which is not true. Why is it used so much?

Benzoic acid is studied thoroughly for three distinct reasons. First, its concentration is relatively easily measured, for the amount present can be determined by titration with base, by UV spectrophotometry of the benzene ring, or by radioactively tagging either the carbon or the hydrogen. Second, the dissolution of benzoic acid is accurately described by one mass transfer coefficient. This is not true of all dissolutions. For example, the dissolution of aspirin is essentially independent of events in solution (see Section 15.3). Third, and most subtle, benzoic acid is solid, so mass transfer takes place across a solid–fluid interface. Such interfaces are an exception in mass transfer problems; fluid–fluid interfaces are much more common. However, solid–fluid interfaces are the rule for heat transfer, the intellectual precursor of mass transfer. Experiments with benzoic acid dissolving in water can be compared directly with heat transfer experiments. These three reasons make this chemical system popular.

Example 8.1-3: Mass transfer in an emulsion   Bromine is being rapidly dissolved in water, as shown schematically in Fig. 8.1-1(c). Its concentration is about half saturated in 3 minutes. What is the mass transfer coefficient?

Solution   Again, we begin with a mass balance:

$$\frac{d}{dt} V c_1 = A N_1 = A k[c_1(\text{sat}) - c_1]$$

$$\frac{dc_1}{dt} = ka[c_1(\text{sat}) - c_1]$$

where $a (= A/V)$ is the surface area of the bromine droplets divided by the volume of aqueous solution. If the water initially contains no bromine,

$$t = 0, \quad c_1 = 0$$

Using this in our integration, we find

$$\frac{c_1}{c_1(\text{sat})} = 1 - e^{-kat}$$

Rearranging,

$$ka = -\frac{1}{t} \ln\left(1 - \frac{c_1}{c_1(\text{sat})}\right)$$

$$= -\frac{1}{3 \text{ min}} \ln(1 - 0.5)$$

$$= 3.9 \cdot 10^{-3} \text{ sec}^{-1}$$

This is as far as we can go; we cannot find the mass transfer coefficient, only its product with a.

Such a product occurs often and is a fixture of many mass transfer correlations. The quantity ka is very similar to the rate constant of a first-order reversible reaction with an equilibrium constant equal to unity. This particular problem is similar to the calculation of a half-life for radioactive decay. Such a parallel is worth thinking through and will become a very useful concept in Chapter 15.

Example 8.1-4: Mass transfer from an oxygen bubble   A bubble of oxygen originally 0.1 centimeter in diameter is injected into excess stirred water, as shown schematically in Fig. 8.1-1(d). After 7 minutes, the bubble is 0.054 centimeter in diameter. What is the mass transfer coefficient?

Solution   This time, we write a mass balance not on the surrounding solution but on the bubble itself:

$$\frac{d}{dt}\left(c_1\frac{4}{3}\pi r^3\right) = AN_1$$

$$= -4\pi r^2 k[c_1(\text{sat}) - 0]$$

This equation is tricky; c_1 refers to the oxygen concentration in the bubble, 1 mol/22.4 liters at standard conditions, but $c_1(\text{sat})$ refers to the oxygen concentration at saturation in water, about $1.5 \cdot 10^{-3}$ moles per liter under similar conditions. Thus

$$\frac{dr}{dt} = -k\frac{c_1(\text{sat})}{c_1}$$

$$= -0.034k$$

This is subject to the condition

$$t = 0, \quad r = 0.05 \text{ cm}$$

so integration gives

$$r = 0.05 \text{ cm} - 0.034kt$$

Inserting the numerical values given, we find

$$0.027 \text{ cm} = 0.05 \text{ cm} - 0.034k(420 \text{ sec})$$

$$k = 1.6 \cdot 10^{-3} \text{ cm/sec}$$

Remember that this coefficient is defined in terms of the concentration in the liquid; it would be numerically different if it were defined in terms of the gas-phase concentration.

Table 8.2-1. *Mass transfer coefficient compared with other rate coefficients*

Effect	Basic equation	Rate	Force	Coefficient
Mass transfer	$N_1 = k\Delta c_1$	Flux per area relative to an interface	Difference of concentration	The mass transfer coefficient $k ([=]L/t)$ is a function of flow
Diffusion	$-\mathbf{j}_i = D\nabla c_1$	Flux per area relative to the volume average velocity	Gradient of concentration	The diffusion coefficient $D ([=]L^2/t)$ is a physical property independent of flow
Dispersion	$-\overline{c_1'\mathbf{v}_1'} = E\nabla\bar{c}_1$	Flux per area relative to the mass average velocity	Gradient of time average concentration	The dispersion coefficient $E([=]L^2/t)$ depends on the flow
Homogeneous chemical reaction	$r_1 = \kappa_1 c_1$	Rate per volume	Concentration	The rate constant $\kappa_1 ([=]1/t)$ is a physical property independent of flow
Heterogeneous chemical reaction	$r_1 = \kappa_1 c_1$	Flux per interfacial area	Concentration	The rate constant $\kappa_1([=]L/t)$ is a surface property often defined in terms of a bulk concentration

8.2 Other Definitions of Mass Transfer Coefficients

We now want to return to some of the problems we glossed over in the simple definition of a mass transfer coefficient given in the previous section. We introduced this definition with the implication that it provides a simple way of analyzing complex problems. We implied that the mass transfer coefficient will be like the density or the viscosity, a physical quantity that is well defined for a specific situation.

In fact, the mass transfer coefficient is often an ambiguous concept, reflecting nuances of its basic definition. To begin our discussion of these nuances, we first compare the mass transfer coefficient with the other rate constants given in Table 8.2-1. The mass transfer coefficient seems a curious contrast, a combination of diffusion and dispersion. Because it involves a concentration difference, it has different dimensions than the diffusion and dispersion coefficients. It is a rate constant for an interfacial physical reaction, most similar to the rate constant of an interfacial chemical reaction.

Unfortunately, the definition of the mass transfer coefficient in Table 8.2-1 is not so well accepted that the coefficient's dimensions are always the same. This is not true for the other processes in this table. For example, the dimensions of the diffusion coefficient are always taken as L^2/t. If the concentration is expressed in terms of mole fraction or partial pressure, then appropriate unit conversions are made to ensure that the diffusion coefficient keeps the same dimensions.

This is not the case for mass transfer coefficients, where a variety of definitions are accepted. Four of the more common of these are shown in Table 8.2-2. This variety is

Table 8.2-2. *Common definitions of mass transfer coefficients*[a]

Basic equation	Typical units of k^b	Remarks
$N_1 = k\Delta c_1$	cm/sec	Common in the older literature; used here because of its simple physical significance (Treybal, 1980)
$N_1 = k_p\Delta p_1$	mol/cm²-sec-atm	Common for a gas absorption; equivalent forms occur in biological problems (McCabe Smith, and Harriot, 1985; Sherwood, Pigford, and Wilke, 1975)
$N_1 = k_x\Delta x_1$	mol/cm²-sec	Preferred for practical calculations, especially in gases (Bennett and Myers, 1974)
$N_1 = k\Delta c_1 + c_1 v^0$	cm/sec	Used in an effort to include diffusion-induced convection (cf. k in Eq. 13.5-2 et seq.) (Bird, Stewart, and Lightfoot, 1960)

Notes: [a] In this table, N_1 is defined as moles per $L^2 t$, and c_1 as moles per L^3. Parallel definitions where N_1 is in terms of $M/L^2 t$ and c_1 is $M/L^3 t$ are easily developed. Definitions mixing moles and mass are infrequently used.
[b] For a gas of constant molar concentration c, $k = RT k_p = k_y/c$. For a dilute liquid solution $k = (\tilde{M}_2/\rho)k_x$, where $\tilde{M}_2$ is the molecular weight of the solvent, and ρ is the solution density.

largely an experimental artifact, arising because the concentration can be measured in so many different units, including partial pressure, mole and mass fractions, and molarity.

In this book, we will most frequently use the first definition in Table 8.2-2, implying that mass transfer coefficients have dimensions of length per time. If the flux is expressed in moles per area per time we will usually express the concentration in moles per volume. If the flux is expressed in mass per area per time, we will give the concentration in mass per volume. This choice is the simplest for correlations of mass transfer coefficients reviewed in this chapter and for predictions of these coefficients given in Chapters 13–14. Expressing the mass transfer coefficient in dimensions of velocity is also simplest in the cases of chemical reaction and simultaneous heat and mass transfer described in Chapters 15, 16, and 20.

However, in some other cases, alternative forms of the mass transfer coefficients lead to simpler final equations. This is especially true in the design of equipment for gas adsorption, distillation, and extraction described in Chapters 9–11. There, we will frequently use k_x, the third form in Table 8.2.2, which expresses concentrations in mole fractions. In some cases of gas adsorption, we will find it convenient to respect seventy years of tradition and use k_p, with concentrations expressed as partial pressures. In the membrane separations in Chapter 17, we will mention forms like k_x but will carry out our discussion in terms of forms equivalent to k.

The mass transfer coefficients defined in Table 8.2-2 are also complicated by the choice of a concentration difference, by the interfacial area for mass transfer, and by the treatment of convection. The basic definitions given in Eq. 8.1-2 or Table 8.2-1 are ambiguous, for the concentration difference involved is incompletely defined. To explore the ambiguity more carefully, consider the packed tower shown schematically in Fig. 8.2-1. This tower is basically a piece of pipe standing on its end and filled with crushed inert material like broken glass. Air containing ammonia flows upward through the column. Water trickles down through the column and absorbs the ammonia: Ammonia is scrubbed out of the gas
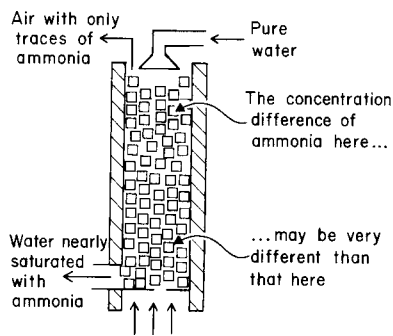
Fig. 8.2-1. Ammonia scrubbing. In this example, ammonia is separated by washing a gas mixture with water. As explained in the text, the example illustrates ambiguities in the definition of mass transfer coefficients. The ambiguities occur because the concentration difference causing the mass transfer changes and because the interfacial area between gas and liquid is unknown.

mixture with water. The flux of ammonia into the water is proportional to the ammonia concentration at the air–water interface minus the ammonia concentration in the bulk water. The proportionality constant is the mass transfer coefficient. The concentration difference between interface and bulk is not constant but can vary along the height of the column. Which value of concentration difference should we use?

In this book, we always choose to use the local concentration difference at a particular position in the column. Such a choice implies a "local mass transfer coefficient" to distinguish it from an "average mass transfer coefficient." Use of a local coefficient means that we often must make a few extra mathematical calculations. However, the local coefficient is more nearly constant, a smooth function of changes in other process variables. This definition was implicitly used in Examples 8.1-1, 8.1-3, and 8.1-4 in the previous section. It was used in parallel with a type of average coefficient in Example 8.1-2.

Another potential source of ambiguity in the definition of the mass transfer coefficient is the interfacial area. As an example, we again consider the packed tower in Fig. 8.2-1. The surface area between water and gas is usually experimentally unknown, so that the flux per area is unknown as well. Thus the mass transfer coefficient cannot be easily found. This problem is dodged by lumping the area into the mass transfer coefficient and experimentally determining the product of the two. We just measure the flux per column volume. This may seem like cheating, but it works like a charm.

Finally, mass transfer coefficients can be complicated by diffusion-induced convection normal to the interface. This complication does not exist in dilute solution, just as it does not exist for the dilute diffusion described in Chapter 2. For concentrated solutions, there may be a larger convective flux normal to the interface that disrupts the concentration profiles near the interface. The consequence of this flux, which is like the concentrated diffusion problems in Section 3.3, is that the flux will not double when the concentration difference is doubled. This diffusion-induced convection is responsible for the last definition in Table 8.2-2, where the interfacial velocity is explicitly included. Fortunately, most solutions are dilute, so we can successfully defer discussing this problem until Section 13.5.

I find these points difficult, hard to understand without careful thought. To spur this thought, try solving the examples that follow.

Example 8.2-1: The mass transfer coefficient in a blood oxygenator   Blood oxygenators are used to replace the human lungs during open-heart surgery. To improve oxygenator design, you are studying mass transfer of oxygen into water in one specific blood oxygenator. From published correlations of mass transfer coefficients, you expect that the mass transfer coefficient based on the oxygen concentration difference in the water is $3.3 \cdot 10^{-3}$ centimeters per second. You want to use this coefficient in an equation given by the oxygenator manufacturer

$$N_1 = k_p(p_{O_2} - p_{O_2}^*)$$

where p_{O_2} is the actual oxygen partial pressure in the gas, and $p_{O_2}^*$ is the hypothetical oxygen partial pressure (the "oxygen tension") that would be in equilibrium with water under the experimental conditions. The manufacturer expressed both pressures in millimeters of O_2. You also know the Henry's law constant of oxygen in water at your experimental conditions:

$$p_{O_2} = 44,000 \text{ atm } x_{O_2}$$

where x_{O_2} is the mole fraction of the total oxygen in the water.
   Find the mass transfer coefficient k_p.

   Solution   Because the correlations are based on the concentrations in the liquid, the flux equation must be

$$N_1 = 3.3 \cdot 10^{-3} \text{ cm/sec } (c_{O_2,i} - c_{O_2})$$

where $c_{O_2,i}$ and c_{O_2} refer to concentrations at the interface and the bulk solution, respectively. We can convert these concentrations to the oxygen tensions as follows:

$$c_{O_2} = cx_{O_2} = \left(\frac{\rho}{\tilde{M}} \frac{p_{O_2}}{H}\right)$$

where c is the total concentration in the liquid water, ρ is the liquid's density, and $\tilde{M}$ is its average molecular weight. Because the solution is dilute,

$$c_{O_2} = \left[\frac{1 \text{ g/cm}^3}{18 \text{ g/mol}} \frac{1}{4.4 \cdot 10^4 \text{ atm}} \frac{\text{atm}}{760 \text{ mm Hg}}\right] p_{O_2}$$

Combining with the earlier definition, we see

$$N_1 = 3.3 \cdot 10^{-3} \frac{\text{cm}}{\text{sec}} \left[\frac{1.67 \cdot 10^{-9} \text{mol}}{\text{cm}^3 \text{ mm Hg}}\right] (p_{O_2,i} - p_{O_2})$$

$$= 5.5 \cdot 10^{-12} \frac{\text{mol}}{\text{cm}^2 \text{ sec mm Hg}} (p_{O_2,i} - p_{O_2})$$

The new coefficient k_p equals $5.5 \cdot 10^{-12}$ in the units given.

Example 8.2-2: Converting units of ammonia mass transfer coefficients   A packed tower is being used to study ammonia scrubbing with 25°C water. The mass transfer coefficients reported for this tower are 1.18 lb-mol NH_3/hr-ft^2 for the liquid and 1.09 lb-mol NH_3/hr-ft^2-atm for the gas. What are these coefficients in centimeters per second?

Solution   From Table 8.2-2, we see that the units of the liquid-phase coefficient correspond to k_x. Thus

$$k = \frac{\tilde{M}_2}{\rho} k_x$$

$$= \left(\frac{18 \text{ lb/mol}}{62.4 \text{ lb/ft}^3} \right) \left(\frac{1.18 \text{ lb-mol NH}_3}{\text{ft}^2\text{-hr}} \right) \left(\frac{30.5 \text{ cm}}{\text{ft}} \right) \left(\frac{\text{hr}}{3,600 \text{ sec}} \right)$$

$$= 2.9 \cdot 10^{-3} \text{ cm/sec}$$

For the gas phase, we see from Table 8.2-2 that the coefficient has the units of k_p. Thus

$$k = RT k_p$$

$$= \left(\frac{1.314 \text{ atm-ft}^3}{\text{lb-mol-}^\circ\text{K}} \right) \left(\frac{1.09 \text{ lb-mol}}{\text{hr-ft}^2\text{-atm}} \right) \left(\frac{30.5 \text{ cm}}{\text{ft}} \right) \left(\frac{\text{hr}}{3,600 \text{ sec}} \right) (298^\circ\text{K})$$

$$= 3.6 \text{ cm/sec}$$

These conversions take time and thought, but are not difficult.

Example 8.2-3: Averaging a mass transfer coefficient   Imagine two porous solids whose pores contain different concentrations of a particular dilute solution. If these solids are placed together, the flux N_1 from one to the other will be (see Section 2.3)

$$N_1 = \sqrt{D/\pi t} \, \Delta c_1$$

By comparison with Eq. 8.1-2, we see that the local mass transfer coefficient is

$$k = \sqrt{D/\pi t}$$

Note that this coefficient is initially infinite.

We want to correlate our results not in terms of this local value but in terms of a total experimental time t_0. This implies an average coefficient, $\bar{k}$, defined by

$$\bar{N}_1 = \bar{k} \Delta c_1$$

where $\bar{N}_1$ is the total solute transferred per area divided by t_0. How is $\bar{k}$ related to k?

Solution   From the problem statement, we see that

$$\bar{N}_1 = \frac{\int_0^{t_0} N_1 dt}{\int_0^{t_0} dt} = \frac{\int_0^{t_0} \sqrt{D/\pi t} \, \Delta c_1 dt}{t_0} = 2\sqrt{D/\pi t_0} \, \Delta c_1$$

Thus

$$\bar{k} = 2\sqrt{D/\pi t_0}$$

which is twice the value of k evaluated at t_0. Note that "local" refers here to a particular time rather than a particular position.

Example 8.2-4: Log mean mass transfer coefficients   Consider again the packed bed of benzoic acid spheres shown in Fig. 8.1-1(b) that was basic to Example 8.1-2. Mass transfer coefficients in a bed like this are sometimes reported in terms of a log mean driving force:

$$\bar{N}_1 = k_{\log} \left(\frac{\Delta c_{1,\text{inlet}} - \Delta c_{1,\text{outlet}}}{\ln \left(\dfrac{\Delta c_{1,\text{inlet}}}{\Delta c_{1,\text{outlet}}} \right)} \right)$$

For this specific case, $\bar{N}_1$ is the total benzoic acid leaving the bed divided by the total surface area in the bed. The bed is fed with pure water, and the benzoic acid concentration at the sphere surfaces is at saturation; that is, it equals $c_1(\text{sat})$. Thus

$$\bar{N}_1 = k_{\log} \frac{[c_1(\text{sat}) - 0] - [c_1(\text{sat}) - c_1(\text{out})]}{\ln \left(\dfrac{c_1(\text{sat}) - 0}{c_1(\text{sat}) - c_1(\text{out})} \right)}$$

Show how $k_{\log}$ is related to the local coefficient k used in the earlier problem.

Solution   By integrating a mass balance on a differential length of bed, we showed in Example 8.1-2 that for a bed of length L,

$$\frac{c_1(\text{out})}{c_1(\text{sat})} = 1 - e^{-(ka/v^0)L}$$

Rearranging, we find

$$\frac{c_1(\text{sat}) - c_1(\text{out})}{c_1(\text{sat}) - 0} = e^{-(ka/v^0)L}$$

Taking the logarithm of both sides and rearranging,

$$v^0 = \frac{kaL}{\ln \left(\dfrac{c_1(\text{sat}) - 0}{c_1(\text{sat}) - c_1(\text{out})} \right)}$$

Multiplying both sides by $c_1(\text{out})$,

$$c_1(\text{out})v^0 = kaL \left(\frac{[c_1(\text{sat}) - 0] - [c_1(\text{sat}) - c_1(\text{out})]}{\ln \left(\dfrac{c_1(\text{sat}) - 0}{c_1(\text{sat}) - c_1(\text{out})} \right)} \right)$$

By definition,

$$\overline{N}_1 = \frac{c_1(\text{out})v^0 A}{a(AL)}$$

where A is the bed's cross section and AL is its volume. Thus

$$\overline{N}_1 = k \left(\frac{[c_1(\text{sat}) - 0] - [c_1(\text{sat}) - c_1(\text{out})]}{\ln \left(\dfrac{c_1(\text{sat}) - 0}{c_1(\text{sat}) - c_1(\text{out})} \right)} \right)$$

and

$$k_{\log} = k$$

The coefficients are identical.

Many argue that the log mean mass transfer coefficient is superior to the local value used mostly in this book. Their reasons are that the coefficients are the same or (at worst) closely related and that $k_{\log}$ is macroscopic and hence easier to measure. After all, these critics assert, you implicitly repeat this derivation every time you make a mass balance. Why bother? Why not use $k_{\log}$ and be done with it?

This argument has merit, but it makes me uneasy. I find that I need to think through the approximations of mass transfer coefficients every time I use them and that this review is easily accomplished by making a mass balance and integrating. I find that most students share this need. My advice is to avoid log mean coefficients until your calculations are routine.

8.3 Correlations of Mass Transfer Coefficients

In the previous two sections we have presented definitions of mass transfer coefficients and have shown how these coefficients can be found from experiment. Thus we have a method for analyzing the results of mass transfer experiments. This method can be more convenient than diffusion when the experiments involve mass transfer across interfaces. Experiments of this sort include liquid–liquid extraction, gas absorption, and distillation.

However, we often want to predict how one of these complex situations will behave. We do not want to correlate experiments; we want to avoid experiments as much as possible. This avoidance is like that in our studies of diffusion, where we often looked up diffusion coefficients so that we could calculate a flux or a concentration profile. We wanted to use someone else's measurements rather than painfully make our own.

8.3.1 Dimensionless Numbers

In the same way, we want to look up mass transfer coefficients whenever possible. These coefficients are rarely reported as individual values, but as correlations of dimensionless numbers. These numbers are often named, and they are major weapons that engineers use to confuse scientists. These weapons are effective because the names sound so scientific, like close relatives of nineteenth-century organic chemists.

The characteristics of the common dimensionless groups frequently used in mass transfer correlations are given in Table 8.3-1. Sherwood and Stanton numbers involve the mass transfer coefficient itself. The Schmidt, Lewis, and Prandtl numbers involve different kinds of diffusion, and the Reynolds, Grashof, and Peclet numbers describe flow. The second Damkohler number, which certainly is the most imposing name, is one of many groups used for diffusion with chemical reaction.

A key point about each of these groups is that its exact definition implies a specific physical system. For example, the characteristic length l in the Sherwood number kl/D will be the membrane thickness for membrane transport, but the sphere diameter for a dissolving sphere. A good analogy is the dimensionless group "efficiency." An efficiency of thirty percent has very different implications for a turbine and for a running deer. In

Table 8.3-1. *Significance of common dimensionless groups*

Group[a]	Physical meaning	Used in
Sherwood number $\dfrac{kl}{D}$	$\dfrac{\text{mass transfer velocity}}{\text{diffusion velocity}}$	Usual dependent variable
Stanton number $\dfrac{k}{v^0}$	$\dfrac{\text{mass transfer velocity}}{\text{flow velocity}}$	Occasional dependent variable
Schmidt number $\dfrac{v}{D}$	$\dfrac{\text{diffusivity of momentum}}{\text{diffusivity of mass}}$	Correlations of gas or liquid data
Lewis number $\dfrac{\alpha}{D}$	$\dfrac{\text{diffusivity of energy}}{\text{diffusivity of mass}}$	Simultaneous heat and mass transfer
Prandtl number $\dfrac{v}{\alpha}$	$\dfrac{\text{diffusivity of momentum}}{\text{diffusivity of energy}}$	Heat transfer; included here for completeness
Reynolds number $\dfrac{lv^0}{v}$	$\dfrac{\text{inertial forces}}{\text{viscous forces}}$ or $\dfrac{\text{flow velocity}}{\text{"momentum velocity"}}$	Forced convection
Grashöf number $\dfrac{l^3 g \Delta \rho / \rho}{v^2}$	$\dfrac{\text{buoyancy forces}}{\text{viscous forces}}$	Free convection
Péclet number $\dfrac{v^0 l}{D}$	$\dfrac{\text{flow velocity}}{\text{diffusion velocity}}$	Correlations of gas or liquid data
Second Damköhler number or (Thiele modulus)^2 $\dfrac{\kappa l^2}{D}$	$\dfrac{\text{reaction velocity}}{\text{diffusion velocity}}$	Correlations involving reactions (see Chapters 15–16)

Note: [a] The symbols and their dimensions are as follows:
D diffusion coefficient (L^2/t)
g acceleration due to gravity (L/t^2)
k mass transfer coefficient (L/t)
l characteristic length (L)
v^0 fluid velocity (L/t)
α thermal diffusivity (L^2/t)
κ first-order reaction rate constant (t^{-1})
v kinematic viscosity (L^2/t)
$\Delta \rho / \rho$ fractional density change

the same way, a Sherwood number of 2 means different things for a membrane and for a dissolving sphere. This flexibility is central to the correlations that follow.

8.3.2 Frequently Used Correlations

Correlations of mass transfer coefficients are conveniently divided into those for fluid–fluid interfaces and those for fluid–solid interfaces. The correlations for fluid–fluid interfaces are by far the more important, for they are basic to gas adsorption, liquid–liquid extraction, and nonideal distillation. Correlations of these mass transfer coefficients are also important for aeration and water cooling. These correlations usually have no known parallel correlations in heat transfer, where fluid–fluid interfaces are not common.

Some of the more useful correlations for fluid–fluid interfaces are given in Table 8.3-2. The accuracy of these correlations is typically of the order of thirty percent, but larger errors are not uncommon. Raw data can look more like the result of a shotgun blast than any sort of coherent experiment because the data include wide ranges of chemical and physical properties. For example, the Reynolds number, that characteristic parameter of forced convection, can vary 10,000 times. The Schmidt number, the ratio (ν/D), is about 1 for gases but about 1000 for liquids. Over a more moderate range, experimental data can be reliable. Still, while the correlations are useful for the preliminary design of small pilot plants, they should not be used for the design of full-scale equipment without experimental checks on the specific chemical systems involved.

Many of the correlations in Table 8.3-2 have the same general form. They typically involve a Sherwood number, which contains the mass transfer coefficient, the quantity of interest. This Sherwood number varies with Schmidt number, a characteristic of diffusion. The variation of Sherwood number with flow is more complex because the flow has two different physical origins. In most cases, the flow is caused by external stirring or pumping. For example, the liquids used in extraction are rapidly stirred; the gas in ammonia scrubbing is pumped through the packed tower; the blood in the artificial kidney is pumped by the heart through the dialysis unit. This type of externally driven flow is called "forced convection." In other cases, the fluid velocity is a result of the mass transfer itself. The mass transfer causes density gradients in the surrounding solution; these in turn cause flow. This type of internally generated flow is called "free convection." For example, the dispersal of pollutants and the dissolution of drugs are often accelerated by free convection.

The dimensionless form of the correlations for fluid–fluid interfaces may disguise the very real quantitative similarities between them. To explore these similarities, we consider the variations of the mass transfer coefficient with fluid velocity and with diffusion coefficient. These variations are surprisingly uniform. The mass transfer coefficient varies with the 0.7 power of the fluid velocity in four of the five correlations for packed towers in Table 8.3-2. It varies with the diffusion coefficient to the 0.5 to 0.7 power in every one of the correlations. Thus any theory that we derive for mass transfer across fluid–fluid interfaces should imply variations with velocity and diffusion coefficient like those shown here.

Some frequently quoted correlations for fluid–solid interfaces are given in Table 8.3-3. These correlations are rarely important in common separation processes like absorption and extractions. They are important in leaching, in membrane separations, and in electrochemistry. However, the real reason that these correlations are quoted in undergraduate and graduate courses is that they are close analogues to heat transfer. Heat transfer is an older subject, with a strong theoretical basis and more familiar nuances. This analogy gets lazy lecturers merely mumble, "Mass transfer is just like heat transfer" and quickly compare the correlations in Table 8.3-2 with the heat transfer parallels.

The correlations for solid–fluid interfaces in Table 8.3-3 are much like their heat transfer equivalents. More significantly, these less important, fluid–solid correlations are analogous but more accurate than the important fluid–fluid correlations in Table 8.3-2. Accuracies for solid–fluid interfaces are typically average ±10%; for some correlations like laminar flow in a single tube, accuracies can be ±1%. Such precision, which is truly rare for mass transfer measurements, reflects the simpler geometry and stable flows in these cases. Laminar flow of one fluid in a tube is much better understood than turbulent flow of gas and liquid in a packed tower.

The correlations for fluid–solid interfaces often show mathematical forms like those for fluid–fluid interfaces. The mass transfer coefficient is most often written as a Sherwood

Table 8.3-2 Selected mass transfer correlations for fluid–fluid interfaces[a]

Physical situation	Basic equation[b]	Key variables	Remarks
Liquid in a packed tower	$k\left(\dfrac{1}{\nu g}\right)^{1/3} = 0.0051\left(\dfrac{\nu^0}{a\nu}\right)^{0.67}\left(\dfrac{D}{\nu}\right)^{0.50}(ad)^{0.4}$	a = packing area per bed volume d = nominal packing size	Probably the best available correlation for liquids; tends to give lower values than other correlations.
	$\dfrac{kd}{D} = 25\left(\dfrac{d\nu^0}{\nu}\right)^{0.45}\left(\dfrac{\nu}{D}\right)^{0.5}$	d = nominal packing size	The classical result, widely quoted; probably less successful than above.
	$\dfrac{k}{\nu^0} = \alpha\left(\dfrac{d\nu^0}{\nu}\right)^{-0.3}\left(\dfrac{D}{\nu}\right)^{0.5}$	d = nominal packing size	Based on older measurements of height of transfer units (HTU's); α is of order one.
Gas in a packed tower	$\dfrac{k}{aD} = 3.6\left(\dfrac{\nu^0}{a\nu}\right)^{0.70}\left(\dfrac{\nu}{D}\right)^{1/3}(ad)^{-2.0}$	a = packing area per bed volume d = nominal packing size	Probably the best available correlation for gases.
	$\dfrac{kd}{D} = 1.2(1-\epsilon)^{0.36}\left(\dfrac{d\nu^0}{\nu}\right)^{0.64}\left(\dfrac{\nu}{D}\right)^{1/3}$	d = nominal packing size ϵ = bed void fraction	Again, the most widely quoted classical result.
Pure gas bubbles in a stirred tank	$\dfrac{kd}{D} = 0.13\left(\dfrac{(P/V)d^4}{\rho\nu^3}\right)^{1/4}\left(\dfrac{\nu}{D}\right)^{1/3}$	d = bubble diameter P/V = stirrer power per volume	Note that k does not depend on bubble size.
Pure gas bubbles in an unstirred liquid	$\dfrac{kd}{D} = 0.31\left(\dfrac{d^3 g\Delta\rho/\rho}{\nu^2}\right)^{1/3}\left(\dfrac{\nu}{D}\right)^{1/3}$	d = bubble diameter $\Delta\rho$ = density difference between gas and liquid	For small swarms of bubbles rising in a liquid.
Large liquid drops rising in unstirred solution	$\dfrac{kd}{D} = 0.42\left(\dfrac{d^3\Delta\rho g}{\rho\nu^2}\right)^{1/3}\left(\dfrac{\nu}{D}\right)^{0.5}$	d = bubble diameter $\Delta\rho$ = density difference between bubbles and surrounding fluid	Drops 0.3-cm diameter or larger.
Small liquid drops rising in unstirred solution	$\dfrac{kd}{D} = 1.13\left(\dfrac{d\nu^0}{D}\right)^{0.8}$	d = drop diameter ν^0 = drop velocity	These small drops behave like rigid spheres.
Falling films	$\dfrac{kz}{D} = 0.69\left(\dfrac{z\nu^0}{D}\right)^{0.5}$	z = position along film ν^0 = average film velocity	Frequently embroidered and embellished.

Notes: [a] The symbols used include the following: D is the diffusion coefficient; g is the acceleration due to gravity; k is the local mass transfer coefficient; ν^0 is the superficial fluid velocity; and ν is the kinematic viscosity. Dimensionless groups are as follows: $d\nu/\nu$ and $\nu/a\nu$ are Reynolds numbers; ν/D is the Schmidt number; $d^3 g(\Delta\rho/\rho)/\nu^2$ is the Grashoff number, kd/D is the Sherwood number; and $k/(\nu g)^{1/3}$ is an unusual form of Stanton number.
[b] Dimensionless groups are as follows: $d\nu/\nu$ and $\nu/a\nu$ are Reynolds numbers; ν/D is the Schmidt number; $d^3 g(\Delta\rho/\rho)/\nu^2$ is the Grashoff number, kd/D is the Sherwood number; and $k/(\nu g)^{1/3}$ is an unusual form of Stanton number.

Table 8.3-3 *Selected mass transfer correlations for fluid–solid interfaces*[a]

Physical situation	Basic equation[b]	Key variables	Remarks
Membrane	$\dfrac{kl}{D} = 1$	l = membrane thickness	Often applied even where membrane is hypothetical.
Laminar flow along flat plate[c]	$\dfrac{kL}{D} = 0.646\left(\dfrac{Lv^0}{\nu}\right)^{1/2}\left(\dfrac{\nu}{D}\right)^{1/3}$	L = plate length; v^0 = bulk velocity	Solid theoretical foundation, which is unusual.
Turbulent flow through horizontal slit	$\dfrac{kd}{D} = 0.026\left(\dfrac{dv^0}{\nu}\right)^{0.8}\left(\dfrac{\nu}{D}\right)^{1/3}$	v^0 = average velocity in slit; $d = [2/\pi]$ (slit width)	Mass transfer here is identical with that in a pipe of equal wetted perimeter.
Turbulent flow through circular tube	$\dfrac{kd}{D} = 0.026\left(\dfrac{dv^0}{\nu}\right)^{0.8}\left(\dfrac{\nu}{D}\right)^{1/3}$	v^0 = average velocity in tube; d = pipe diameter	Same as slit, because only wall regime is involved.
Laminar flow through circular tube	$\dfrac{kd}{D} = 1.62\left(\dfrac{d^2 v^0}{LD}\right)^{1/3}$	d = pipe diameter; L = pipe length; v^0 = average velocity in tube	Very strong theory and experiment
Flow outside and parallel to a capillary bed	$\dfrac{kd}{D} = 1.25\left(\dfrac{d_e^2 v^0}{\nu l}\right)^{0.93}\left(\dfrac{\nu}{D}\right)^{1/3}$	d_e = 4 area/wetted perimeter; v^0 = superficial velocity	Not reliable because of channeling in bed.
Flow outside and perpendicular to a capillary bed	$\dfrac{kd}{D} = 0.80\left(\dfrac{dv^0}{\nu}\right)^{0.47}\left(\dfrac{\nu}{D}\right)^{1/3}$	d = capillary diameter; v^0 = velocity approaching bed	Reliable if capillaries evenly spaced.
Forced convection around a solid sphere	$\dfrac{kd}{D} = 2.0 + 0.6\left(\dfrac{dv^0}{\nu}\right)^{1/2}\left(\dfrac{\nu}{D}\right)^{1/3}$	d = sphere diameter; v^0 = velocity of sphere	Very difficult to reach $(kd/D) = 2$ experimentally; no sudden laminar-turbulent transition.
Free convection around a solid sphere	$\dfrac{kd}{D} = 2.0 + 0.6\left(\dfrac{d^3\Delta\rho g}{\rho\nu^2}\right)^{1/4}\left(\dfrac{\nu}{D}\right)^{1/3}$	d = sphere diameter; g = gravitational acceleration	For a 1-cm sphere in water, free convection is important when $\Delta\rho = 10^{-9}$ g/cm³.
Packed beds	$\dfrac{k}{v^0} = 1.17\left(\dfrac{dv^0}{\nu}\right)^{-0.42}\left(\dfrac{D}{\nu}\right)^{2/3}$	d = particle diameter; v^0 = superficial velocity	The superficial velocity is that which would exist without packing.
Spinning disc	$\dfrac{kd}{D} = 0.62\left(\dfrac{d^2\omega}{\nu}\right)^{1/2}\left(\dfrac{\nu}{D}\right)^{1/3}$	d = disc diameter; ω = disc rotation (radians/time)	Valid for Reynolds numbers between 100 and 20,000.

number, though occasionally as a Stanton number. The effect of diffusion coefficient is most often expressed as a Schmidt number. The effect of flow is most often expressed as a Reynolds number for forced convection, and as a Grashöf number for free convection.

These fluid–solid dimensionless correlations can conceal how the mass transfer coefficient varies with fluid flow v and diffusion coefficient D, just as those for fluid–fluid interfaces obscured these variations. Basically, k often varies with the square root of v. The variation is lower for some laminar flows and higher for turbulent flows. It usually varies with $D^{2/3}$, though this variation is rarely checked carefully by those who develop the correlations. Variation of k with $D^{2/3}$ does have some theoretical basis, a point explored further in Chapter 13.

Example 8.3-1: Dissolution rate of a spinning disc   A solid disc of benzoic acid 2.5 centimeters in diameter is spinning at 20 rpm and 25°C. How fast will it dissolve in a large volume of water? How fast will it dissolve in a large volume of air? The diffusion coefficients are $1.00 \cdot 10^{-5}$ cm^2/sec in water and 0.233 cm^2/sec in air. The solubility of benzoic acid in water is 0.003 g/cm^3; its equilibrium vapor pressure is 0.30 mm Hg.

Solution   Before starting this problem, try to guess the answer. Will the mass transfer be higher in water or in air?

In each case, the dissolution rate is

$$N_1 = kc_1(\text{sat})$$

where $c_1(\text{sat})$ is the concentration at equilibrium. We can find k from Table 8.3-2:

$$k = 0.62 D \left(\frac{\omega}{v}\right)^{1/2} \left(\frac{v}{D}\right)^{1/3}$$

For water, the mass transfer coefficient is

$$k = 0.62(1.00 \cdot 10^{-5} \text{ cm}^2/\text{sec}) \left(\frac{(20/60)(2\pi/\text{sec})}{0.01 \text{ cm}^2/\text{sec}}\right)^{1/2} \left(\frac{0.01 \text{ cm}^2/\text{sec}}{1.00 \cdot 10^{-5} \text{ cm}^2/\text{sec}}\right)^{1/3}$$

$$= 0.90 \cdot 10^{-3} \text{ cm/sec}$$

Thus the flux is

$$N_1 = (0.90 \cdot 10^{-3} \text{ cm/sec})(0.003 \text{ g/cm}^3)$$

$$= 2.7 \cdot 10^{-6} \text{ g/cm}^2\text{-sec}$$

For air, the values are very different:

$$k = 0.62(0.233 \text{ cm}^2/\text{sec}) \left(\frac{(20/60)(2\pi/\text{sec})}{0.15 \text{ cm}^2/\text{sec}}\right)^{1/2} \left(\frac{0.15 \text{ cm}^2/\text{sec}}{0.233 \text{ cm}^2/\text{sec}}\right)^{1/3}$$
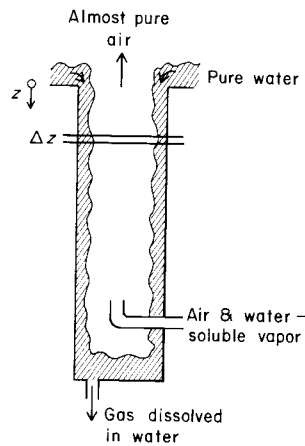
$$= 0.47 \text{ cm/sec}$$

Fig. 8.3-1. Gas scrubbing in a wetted-wall column. A water-soluble gas is being dissolved in a falling film of water. The problem is to calculate the length of the column necessary to reach a liquid concentration equal to ten percent saturation.

which is much larger than before. However, the flux is

$$N_1 = (0.47 \text{ cm/sec}) \left[\left(\frac{0.3 \text{ mm Hg}}{760 \text{ mm Hg}} \right) \left(\frac{1 \text{ mol}}{22.4 \cdot 10^3 \text{ cm}^3} \right) \left(\frac{273}{298} \right) \left(\frac{122 \text{ g}}{\text{mol}} \right) \right]$$

$$= 0.9 \cdot 10^{-6} \text{g/cm}^2 \text{ sec}$$

The flux in air is about one-third of that in water, even though the mass transfer coefficient in air is about 500 times larger than that in water. Did you guess this?

Example 8.3-2: Gas scrubbing with a wetted-wall column   Air containing a water-soluble vapor is flowing up and water is flowing down in the experimental column shown in Fig. 8.3-1. The water flow in the 0.07-centimeter-thick film is 3 centimeters per second, the column diameter is 10 centimeters, and the air is essentially well mixed right up to the interface. The diffusion coefficient in water of the absorbed vapor is $1.8 \cdot 10^{-5}$ cm^2/sec. How long a column is needed to reach a gas concentration in water that is ten percent of saturation?

Solution   The first step is to write a mass balance on the water in a differential column height Δz :

$$(\text{accumulation}) = (\text{flow in minus flow out}) + (\text{absorption})$$

$$0 = [\pi d l v^0 c_1]_z - [\pi d l v^0 c_1]_{z+\Delta z} + \pi d \Delta z k [c_1(\text{sat}) - c_1]$$

in which d is the column diameter, l is the film thickness, v is the flow, and c_1 is the vapor concentration in the water. This balance leads to

$$0 = -l v^0 \frac{dc_1}{dz} + k [c_1(\text{sat}) - c_1]$$

From Table 8.3-2, we have

$$k = 0.69 \left(\frac{D v^0}{z} \right)^{1/2}$$

We also know that the entering water is pure; that is, when

$$z = 0, \quad c_1 = 0$$

Combining these results and integrating, we find

$$\frac{c_1}{c_1(\text{sat})} = 1 - e^{-1.38(Dz/l^2 v^0)^{1/2}}$$

Inserting the numerical values given,

$$z = \left(\frac{l^2 v}{1.90 D} \right) \left[\ln \left(1 - \frac{c_1}{c_1(\text{sat})} \right) \right]^2$$

$$= \left(\frac{(0.07 \text{ cm})^2 (3 \text{ cm/sec})}{(1.90) 1.8 \cdot 10^{-5} \text{ cm}^2/\text{sec}} \right) [\ln(1 - 0.1)]^2$$

$$= 4.8 \text{ cm}$$

This approximate calculation has been improved elaborately, even though its practical value is small.

Example 8.3-3: Measuring stomach flow   Imagine we want to estimate the average flow in the stomach by measuring the dissolution rate of a nonabsorbing solute present as a large spherical pill. From in vitro experiments, we know that this pill's dissolution is accurately described with a mass transfer coefficient. How can we do this?

   Solution   We first calculate the concentration c_1 of the dissolving solute in the stomach and then show how this is related to the flow. From a mass balance,

$$V \frac{dc_1}{dt} = \pi d^2 k [c_1(\text{sat}) - c_1]$$

where V is the stomach's volume, πd^2 is the pill's area, k is the mass transfer coefficient, and $c_1(\text{sat})$ is the solute's solubility. Because no solute is initially present,

$$c_1 = 0 \quad \text{when} \quad t = 0$$

Integrating,

$$k = \frac{V}{\pi d^2 t} \ln \left(\frac{c_1(\text{sat})}{c_1(\text{sat}) - c_1} \right)$$

If we assume that stomach flow is essentially forced convection, we find, from Table 8.3-3,

$$\frac{kd}{D} = 2 + 0.6 \left(\frac{dv}{\nu} \right)^{1/2} \left(\frac{\nu}{D} \right)^{1/3}$$

where d is the pill diameter, D is the diffusion coefficient, and v is the unknown stomach flow. Combining and rearranging,

$$v = \frac{25}{9}\left(\frac{v^{1/3}D^{2/3}}{d}\right)\left[\frac{V}{\pi dt D}\ln\left(\frac{c_1(\text{sat})}{c_1(\text{sat})-c_1}\right)-2\right]^2$$

which is the desired result. Note the assumptions in this problem: The flow is due to forced convection, the pill diameter is constant, and flow in and out of the stomach is negligible.

Example 8.3-4: Glucose uptake by red blood cells   The uptake of glucose across the red blood cell membrane has a maximum rate ranging from 0.1 to 5 μmol/cm^2-hr. Apparently, these differences result from differences in experimental conditions. Using the correlation for liquid drops in Table 8.3-2, estimate the effect of mass transfer in the bulk to see when it could have affected these uptake rates. To make the estimation more quantitative, assume that a typical experiment is made in a beaker containing 100 cm^3 of red blood cells suspended in 1 liter of plasma. The beaker is stirred with a 1/50-hp motor. The cells originally contain little glucose. At time zero, radioactively tagged glucose is added and its uptake measured. The diffusion coefficient of glucose is about $6 \cdot 10^{-6}$ cm^2/sec, and the plasma viscosity is approximately that of water.

   Solution   We are interested in the case in which glucose uptake is dominated by mass transfer. In this case, glucose will diffuse to the membrane and then almost instantaneously be taken into the cell. Thus

$$N_1 = kc_1$$

where c_1 is the bulk concentration. If we can calculate k, then we can estimate N_1, the desired quantity. We see from Table 8.3-2 that for a suspension of liquid drops,

$$k = 0.13\left(\frac{P}{V}\right)^{1/4}\rho^{-1/4}v^{-5/12}D^{2/3}$$

$$= 0.13\left(\frac{1/50\text{ hp}}{1,000\text{ cm}^3}\frac{7.45\cdot 10^9\text{ g-cm}^2}{\text{hp-sec}^3}\right)^{1/4}\left(\frac{1\text{g}}{\text{cm}^3}\right)^{-1/4}$$

$$\cdot\left(\frac{0.01\text{ cm}^2}{\text{sec}}\right)^{-5/12}\left(6\cdot 10^{-6}\frac{\text{cm}^2}{\text{sec}}\right)^{2/3}$$

$$= 5.7\cdot 10^{-3}\text{ cm/sec} = 21\text{ cm/hr}$$

The flux is

$$N_1 = (21\text{ cm/hr})c_1$$

Whether or not diffusion outside the cells is significant depends on c_1, the amount of glucose used. The flux equals 5 μmol/cm^2-hr when c_1 is about 0.3 mmol/liter. If c_1 far exceeds 0.3 mmol/liter, then the flux due to diffusion will be much faster than that due to the cell membrane. The measurements will then truly represent membrane properties. However, if the glucose concentration is less than 0.3 mmol/liter, then the measurements will be

functions both of the membrane and of mass transfer in plasma. Such restrictions can compromise measurements in biological systems.

8.4 Dimensional Analysis: The route to Correlations

The correlations in the previous section provide a useful and compact way of presenting experimental information. Use of these correlations quickly gives reasonable estimates of mass transfer coefficients. However, when we find the correlations inadequate, we will be forced to make our own experiments and develop our own correlations. How can we do this?

The basic form of mass transfer correlations is easily developed using a method called dimensional analysis (Bridgeman, 1922; Becker, 1976). This method is easily learned via the two specific examples that follow. Before embarking on this description, I want to emphasize that most people go through three mental states concerning this method. At first they believe it is a route to all knowledge, a simple technique by which any set of experimental data can be greatly simplified. Next they become disillusioned when they have difficulties in the use of the technique. These difficulties commonly result from efforts to be too complete. Finally, they learn to use the method with skill and caution, benefiting both from their past successes and from their frequent failures. I mention these three stages because I am afraid many may give up at the second stage and miss the real benefits involved. We now turn to the examples.

8.4.1 Aeration

Aeration is a common industrial process and yet one in which there is often serious disagreement about correlations. This is especially true for deep-bed fermentors and for sewage treatment, where the rising bubbles can be the chief means of stirring. We want to study this process using the equipment shown schematically in Fig. 8.4-1. We plan to inject oxygen into a variety of aqueous solutions and measure the oxygen concentration in the bulk with oxygen selective electrodes. We expect to vary the average bubble velocity v, the solution's density ρ and viscosity μ, the entering bubble diameter d, and the depth of the bed L.

We measure the steady-state oxygen concentration as a function of position in the bed. These data can be summarized as a mass transfer coefficient in the following way. From a mass balance, we see that

$$0 = -v\frac{dc_1}{dz} + ka[c_1(\text{sat}) - c_1]$$

(8.4-1)

where a is the total bubble area per column volume. This equation, a close parallel to the many mass balances in Section 8.1, is subject to the initial condition

$$z = 0, \quad c_1 = 0$$

(8.4-2)

Thus

$$ka = \frac{v}{z} \ln\left(\frac{c_1(\text{sat})}{c_1(\text{sat}) - c_1(z)}\right)$$

(8.4-3)
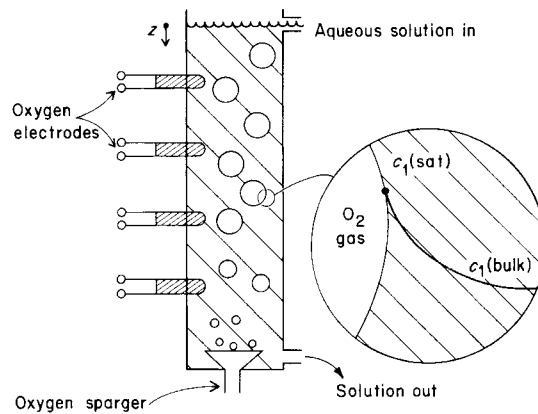
Fig. 8.4-1. An experimental apparatus for the study of aeration. Oxygen bubbles from the sparger at the bottom of the tower partially dissolve in the aqueous solution. The concentration in this solution is measured with electrodes that are specific for dissolved oxygen. The concentrations found in this way are interpreted in terms of mass transfer coefficients; this interpretation assumes that the solution is well mixed, except very near the bubble walls.

Ideally, we would like to measure k and a independently, separating the effects of mass transfer and geometry. This would be difficult here, so we report only the product ka.

Our experimental results now consist of the following:

$$ka = ka(v, \rho, \mu, d, z) \tag{8.4-4}$$

We assume that this function has the form

$$ka = [\text{constant}]v^\alpha \rho^\beta \mu^\gamma d^\delta z^\epsilon \tag{8.4-5}$$

where both the constant in the square brackets and the exponents are dimensionless. Now the dimensions or units on the left-hand side of this equation must equal the dimensions or units on the right-hand side. We cannot have centimeters per second on the left-hand side equal to grams on the right. Because ka has dimensions of the reciprocal of time $(1/t)$, v has dimensions of length/time (L/t), ρ has dimensions of mass per length cubed (M/L^3), and so forth, we find

$$\frac{1}{t} [=] \left(\frac{L}{t}\right)^\alpha \left(\frac{M}{L^3}\right)^\beta \left(\frac{M}{Lt}\right)^\gamma (L)^\delta (L)^\epsilon \tag{8.4-6}$$

The only way this equation can be dimensionally consistent is if the exponent on time on the left-hand side of the equation equals the sum of the exponents on time on the right-hand side:

$$-1 = -\alpha - \gamma \tag{8.4-7}$$

Similar equations hold for the mass:

$$0 = \beta + \gamma \tag{8.4-8}$$

and for the length:

$$0 = \alpha - 3\beta - \gamma + \delta + \epsilon \tag{8.4-9}$$

Equations 8.4-7 to 8.4-9 give three equations for the five unknown exponents.

We can solve these equations in terms of the two key exponents and thus simplify Eq. 8.4-5. We choose the two key exponents arbitrarily. For example, if we choose the exponent on the viscosity γ and that on column height ϵ, we obtain

$$\alpha = 1 - \gamma \tag{8.4-10}$$

$$\beta = -\gamma \tag{8.4-11}$$

$$\gamma = \gamma \tag{8.4-12}$$

$$\delta = -\gamma - \epsilon - 1 \tag{8.4-13}$$

$$\epsilon = \epsilon \tag{8.4-14}$$

Inserting these results into Eq. 8.4-5 and rearranging, we find

$$\left(\frac{kad}{v}\right) = [\text{constant}] \left(\frac{dv\rho}{\mu}\right)^{-\gamma} \left(\frac{z}{d}\right)^{\epsilon} \tag{8.4-15}$$

The left-hand side of this equation is a type of Stanton number. The first term in parentheses on the right-hand side is the Reynolds number, and the second such term is a measure of the tank's depth.

This analysis suggests how we should plan our experiments. We expect to plot our measurements of Stanton number versus two independent variables: Reynolds number and z/d. We want to cover the widest possible range of independent variables. Our resulting correlation will be a convenient and compact way of presenting our results, and everyone will live happily ever after.

Unfortunately, it is not always that simple for a variety of reasons. First, we had to assume that the bulk liquid was well mixed, and it may not be. If it is not, we shall be averaging our values in some unknown fashion, and we may find that our correlation extrapolates unreliably. Second, we may find that our data do not fit an exponential form like Eq. 8.4-5. This can happen if the oxygen transferred is consumed in some sort of chemical reaction, which is true in aeration. Third, we do not know which independent variables are important. We might suspect that ka varies with tank diameter, or sparger shape, or surface tension, or the phases of the moon. Such variations can be included in our analysis, but they make it complex.

Still, this strategy has produced a simple method of correlating our results. The foregoing objections are important only if they are shown to be so by experiment. Until then, we should use this easy strategy.

8.4.2 The Artificial Kidney

The second example to be discussed in this section is the mass transfer out of the tube shown schematically in Fig. 8.4-2. Such tubes are basic to the artificial kidney. There, blood flowing in a tubular membrane is dialyzed against well-stirred saline solution. Toxins in the blood diffuse across the membrane into the saline, thus purifying the blood. This dialysis is often slow; it can take more than 40 hours per week. Increasing the mass transfer in this system would greatly improve its clinical value.

The first step in increasing this rate is to stir the surrounding saline rapidly. This mixing increases the rate of mass transfer on the saline side of the membrane, so that only a small part of the concentration difference is there, as shown in Fig. 8.4-2. In other words, we have decreased the resistance to mass transfer on the saline side. The second step in increasing
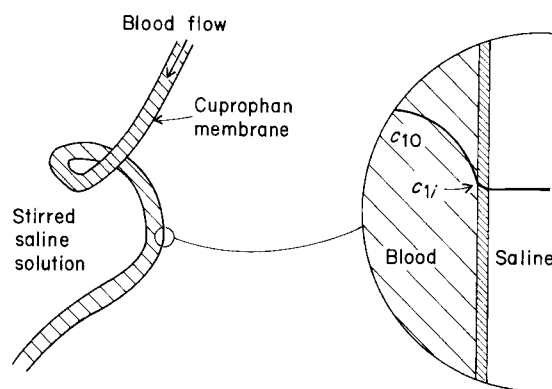
Fig. 8.4-2. Mass transfer in an artificial kidney. Arterial blood flows through a dialysis tube that is immersed in saline. Toxins in the blood diffuse across the tube wall and into the saline. If the saline is well stirred and if the tube wall is thin, then the rate of toxin removal depends on the concentration gradient in the blood. Experiments in this situation are easily correlated using dimensional analysis.

the rate is to make the membrane as thin as possible. Although too thin a membrane would rupture, existing membranes are already so thin that the membrane thickness has only a minor effect. The result is that the concentration difference across the membrane is not the largest part of the overall concentration difference, again as shown in Fig. 8.4-2.

The rate of toxin removal now depends only on what happens in the blood. We want to correlate our measurements of toxin removal as a function of blood flow, tube size, and so forth. To do this, we find the flux for each case:

$$\text{flux } N_1 = \frac{\text{amount transferred}}{(\text{area}) (\text{time})} \tag{8.4-16}$$

By definition,

$$N_1 = k(c_1 - c_{1i})$$
$$\doteq kc_1 \tag{8.4-17}$$

Because we know N_1 and c_1, we can find the mass transfer coefficient k.

As before, we recognize that the mass transfer coefficient of a particular toxin varies with the system's properties:

$$k = k(v, \rho, \mu, D, d) \tag{8.4-18}$$

where v, ρ, and μ are the velocity, density, and viscosity of the blood, D is the diffusion coefficient of the toxin in blood, and d is the diameter of the tube. We assume that this relation has the form

$$k = [\text{constant}]v^\alpha \rho^\beta \mu^\gamma D^\delta d^\epsilon \tag{8.4-19}$$

where the constant is dimensionless. The dimensions or units on the left-hand side of this equation must equal the dimensions or units on the right-hand side; so

$$\frac{L}{t} [=] \left(\frac{L}{t}\right)^\alpha \left(\frac{M}{L^3}\right)^\beta \left(\frac{M}{Lt}\right)^\gamma \left(\frac{L^2}{t}\right)^\delta L^\epsilon \tag{8.4-20}$$

This equation will be dimensionally consistent only if the exponent on the length on the left-hand side of the equation equals the sum of the exponents on the right-hand side:

$$1 = \alpha - 3\beta - \gamma + 2\delta + \epsilon \tag{8.4-21}$$

Similar equations must hold for mass:

$$0 = \beta + \gamma \tag{8.4-22}$$

and for time:

$$-1 = -\alpha - \gamma - \delta \tag{8.4-23}$$

We solve these equations in terms of the exponents α and δ:

$$\alpha = \alpha \tag{8.4-24}$$
$$\beta = \alpha + \delta - 1 \tag{8.4-25}$$
$$\gamma = 1 - \alpha - \delta \tag{8.4-26}$$
$$\delta = \delta \tag{8.4-27}$$
$$\epsilon = \alpha - 1 \tag{8.4-28}$$

We combine these results with Eq. 8.4-19 and collect terms:

$$\frac{kd\rho}{\mu} = [\text{constant}] \left(\frac{dv\rho}{\mu}\right)^{\alpha} \left(\frac{\mu}{\rho D}\right)^{-\delta} \tag{8.4-29}$$

By convention, we multiply both sides of this equation by the dimensionless quantity $\mu/\rho D$ to obtain

$$\frac{kd}{D} = [\text{constant}] \left(\frac{dv\rho}{\mu}\right)^{\alpha} \left(\frac{\mu}{\rho D}\right)^{1-\delta} \tag{8.4-30}$$

This equation is the desired correlation. As in the first example, a key step in the analysis is the arbitrary choice of the two exponents α and δ. Any other pair of exponents could have been chosen and would have given a completely equivalent correlation. However, the particular manipulations here are made so that the dimensionless groups found are consistent with traditional patterns. Such traditional patterns sometimes reflect experience and sometimes merely mirror convention. Multiplying both sides of Eq. 8.4-29 $\mu/\rho D$ involves these factors.

The trouble with this analysis is that it is not the whole story. From experiments at low flow, we would find that the mass transfer coefficient k does vary with the cube root of the velocity v and with the two thirds power of the diffusion coefficient D. This suggests that Eq. 8.4-30 can be rewritten

$$\frac{kd}{D} = [\text{constant}] \left(\frac{dv}{D}\right)^{1/3} \tag{8.4-31}$$

that is, that $\alpha = (1 - \delta) = 1/3$. However, if we then measured k as a function of the tube diameter d, we would find it proportional to $d^{-1/3}$, not $d^{-2/3}$ as suggested by Eq. 8.4-31. After a good start, our dimensional analysis is failing.

The reason for this failure is that we did not choose all the relevant variables at the very beginning, in Eq. 8.4-18. We should have included the tube length L; we could have omitted the density ρ and viscosity μ. Had we done so, we would have obtained:

$$\frac{kd}{D} = [\text{constant}] \left(\frac{d^2 v}{DL}\right)^{1/3} \tag{8.4-32}$$

which is the result quoted in Table 8.3-3. However, from dimensional analysis alone, we have no reason to be critical of our original result in Eq. 8.4-30. We can only be critical and make improvements as our experimental experience grows and as our physical insight sharpens.

8.5 Mass Transfer Across Interfaces

In the previous sections, we used mass transfer coefficients as an easy way of describing diffusion occurring from an interface into a relatively homogeneous solution. These coefficients involved many approximations and sparked the explosion of definitions exemplified by Table 8.2-2. Still, they are a very easy way to correlate experimental results or to make estimates using the published relations summarized in Tables 8.3-2 and 8.3-3.

In this section, we extend these definitions to transfer across an interface, from one well-mixed bulk phase into another different one. This case occurs much more frequently than does transfer from an interface into one bulk phase; indeed, I had trouble dreaming up examples earlier in this chapter. Transfer across an interface again sparks potentially major problems of unit conversion, but these problems are often simplified in special cases.

8.5.1 The Basic Flux Equation

Presumably, we can describe mass transfer across an interface in terms of the same type of flux equation as before:

$$N_1 = K \Delta c_1 \tag{8.5-1}$$

where N_1 is the solute flux relative to the interface, K is called an "overall mass transfer coefficient," and Δc_1 is some appropriate concentration difference. But what is Δc_1?

Choosing an appropriate value of Δc_1 turns out to be difficult. To illustrate this, consider the two situations shown in Fig. 8.5-1. In the first term, hot benzene is placed on top of cold benzene. The benzene cools and the water warms until they reach the same temperature. This temperature is the criterion for equilibrium, and the amount of energy transferred is not proportional to the temperature difference between the liquids. Everything seems secure.

As a second example, shown in Fig. 8.5-1(b), imagine that a benzene solution of bromine is placed on top of water containing the same concentration of bromine. After a while, we find that the initially equal concentrations have changed, that the bromine concentration in the benzene is much higher than that in water. This is because the bromine is more soluble in benzene, so that its concentration in the final solution is higher.

This result suggests which concentration difference we can use in Eq. 8.5-1. We should not use the concentration in benzene minus the concentration in water; that is initially zero, and yet there is a flux. Instead, we can use the concentration actually in benzene minus the

(a) Heat transfer
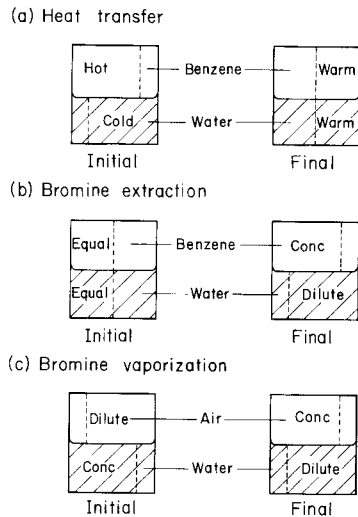
(b) Bromine extraction

(c) Bromine vaporization

Fig. 8.5-1. Driving forces across interfaces. In heat transfer, the amount of heat transferred depends on the temperature difference between the two liquids, as shown in (a). In mass transfer, the amount of solute that diffuses depends on the solute's "solubility" or, more exactly, on its chemical potential. Two cases are shown. In (b), bromine diffuses from water into benzene because it is much more soluble in benzene; in (c), bromine evaporates until its chemical potentials in the solutions are equal. This behavior complicates analysis of mass transfer.

concentration that would be in benzene that was in equilibrium with the actual concentration in water. Symbolically,

$$N_1 = K[c_1(\text{in benzene}) - Hc_1(\text{in water})] \tag{8.5-2}$$

where H is a partition coefficient, the ratio at equilibrium of the concentration in benzene to that in water. Note that this does predict a zero flux at equilibrium.

A better understanding of this phenomenon may come from the third case, shown in Fig. 8.5-1(c). Here, bromine is vaporized from water into air. Initially, the bromine's concentration in water is higher than that in air; afterward, it is lower. Of course, this reversal of the concentration in the liquid might be expressed in moles per liter and that in gas as a partial pressure in atmospheres, so it is not surprising that strange things happen.

As you think about this more carefully, you will realize that the units of pressure or concentration cloud a deeper truth: Mass transfer can be described in terms of more fundamental chemical potentials. If this were done, the peculiar concentration differences would disappear. However, chemical potentials turn out to be very difficult to use in practice, and so the concentration differences for mass transfer across interfaces will remain complicated by units.

8.5.2 The Overall Mass Transfer Coefficient

We want to include these qualitative observations in more exact equations. To do this, we consider the example of the gas–liquid interface in Fig. 8.5-2. In this case, gas on
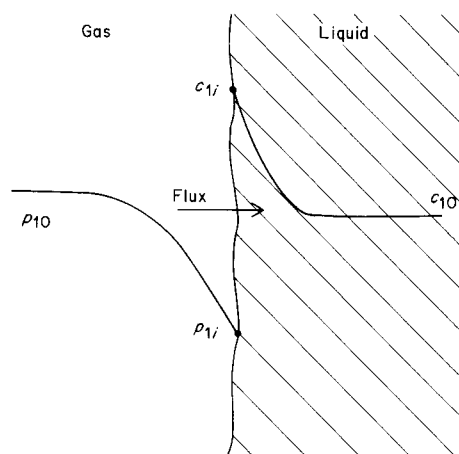
Fig. 8.5-2. Mass transfer across a gas–liquid interface. In this example, a solute vapor is diffusing from the gas on the left into the liquid on the right. Because the solute concentration changes both in the gas and in the liquid, the solute's flux must depend on a mass transfer coefficient in each phase. These coefficients are combined into an overall flux equation in the text.

the left is being transferred into the liquid on the right. The flux in the gas is

$$N_1 = k_p(p_{10} - p_{1i}) \tag{8.5-3}$$

where k_p is the gas-phase mass transfer coefficient (typically in mol/cm²-sec-atm), p_{10} is the bulk pressure, and p_{1i} is the interfacial pressure. Because the interfacial region is thin, the flux across it will be in steady state, and the flux in the gas will equal that in the liquid. Thus,

$$N_1 = k_L(c_{1i} - c_{10}) \tag{8.5-4}$$

where the liquid-phase mass transfer coefficient k_L is typically in centimeters per second and c_{1i} and c_{10} are the interfacial and bulk concentrations, respectively.

We now need to eliminate the unknown interfacial concentrations from these equations. In almost all cases, equilibrium exists across the interface:

$$p_{1i} = Hc_{1i} \tag{8.5-5}$$

where H is a type of Henry's law or partition constant (here in cm³-atm/mol). Combining Eqs. 8.5-3 through 8.5-5, we can find the interfacial concentrations

$$c_{1i} = \frac{p_{1i}}{H} = \frac{k_p p_{10} + k_L c_{10}}{k_p H + k_L} \tag{8.5-6}$$

and the flux

$$N_1 = \frac{1}{1/k_p + H/k_L}(p_{10} - Hc_{10}) \tag{8.5-7}$$

You should check the derivations of these results.

Before proceeding further, we make a quick analogy. This result is often compared to an electric circuit containing two resistances in series. The flux corresponds to the current,

and the concentration difference $p_{10} - Hc_{10}$ corresponds to the voltage. The resistance is then $1/k_p + H/k_L$, which is roughly a sum of two resistances in series. This is a good way of thinking about these effects. You must remember, however, that the resistances $1/k_p$ and $1/k_L$ are not directly added, but always weighted by partition coefficients like H.

We now want to write Eq. 8.5-7 in the form of Eq. 8.5-1. We can do this in two ways. First, we can write

$$N_1 = K_L(c_1^* - c_{10}) \tag{8.5-8}$$

where

$$K_L = \frac{1}{1/k_L + 1/k_p H} \tag{8.5-9}$$

and

$$c_1^* = \frac{p_{10}}{H} \tag{8.5-10}$$

K_L is called an "overall liquid-side mass transfer coefficient," and c_1^* is the hypothetical liquid concentration that would be in equilibrium with the bulk gas. Alternatively,

$$N_1 = K_p(p_{10} - p_1^*) \tag{8.5-11}$$

where

$$K_p = \frac{1}{1/k_p + H/k_L} \tag{8.5-12}$$

and

$$p_1^* = Hc_{10} \tag{8.5-13}$$

K_p is an "overall gas-side mass transfer coefficient," and p_1^* is the hypothetical gas-phase concentration that would be in equilibrium with the bulk liquid.

We now turn to a variety of examples illustrating mass transfer across an interface. These examples have the annoying characteristic that they are initially difficult to do, but they are trivial after you understand them. Remember that most of the difficulty comes from that ancient but common curse: unit conversion.

Example 8.5-1: Oxygen mass transfer   Estimate the overall liquid-side mass transfer coefficient at 25°C for oxygen from water into air. In this estimate, assume that each individual mass transfer coefficient is

$$k = \frac{D}{0.01 \text{ cm}}$$

This relation is justified in Section 13.1.

   Solution   For oxygen in air, the diffusion coefficient is $0.23 \text{ cm}^2/\text{sec}$; for oxygen in water, the diffusion coefficient is $2.1 \cdot 10^{-5} \text{ cm}^2/\text{sec}$. The Henry's law constant in this case is $4.4 \cdot 10^4$ atmospheres. We need only calculate k_L and k_p and plug these values into

Eq. 8.5-9. Finding k_L is easy:

$$k_L = \frac{D_L}{0.01 \text{ cm}} = \frac{2.1 \cdot 10^{-5} \text{ cm}^2/\text{sec}}{0.01 \text{ cm}}$$

$$= 2.1 \cdot 10^{-3} \text{ cm/sec}$$

Finding k_p and H is harder because of unit conversions. From Eq. 8.5-3 and Table 8.2-2

$$k_p = \frac{k_G}{RT} = \frac{D_G}{(0.01 \text{ cm})(RT)}$$

$$= \frac{0.23 \text{ cm}^2/\text{sec}}{(0.01 \text{ cm})(82 \text{ cm}^3\text{-atm/g-mol-}^\circ\text{K})(298^\circ\text{K})}$$

$$= 9.4 \cdot 10^{-4} \text{ g-mol/cm}^2\text{-sec-atm}$$

From the units of the Henry's law constant, we see that the value given implies

$$p_{1i} = H'x_{1i}$$

By comparison with Eq. 8.5-5,

$$p_{1i} = Hc_{1i} = (Hc)x_{1i}$$

Thus

$$H = \left(\frac{H'}{c}\right) = \frac{4.4 \cdot 10^4 \text{ atm}}{1 \text{ g-mol/18 cm}^3} = 7.9 \cdot 10^5 \text{ atm-cm}^3/\text{g-mol}$$

Inserting these results into Eq. 8.5-9, we find

$$K_L = \frac{1}{1/k_L + 1/k_p H}$$

$$= \frac{1}{\dfrac{1}{2.1 \cdot 10^{-3} \text{ cm/sec}} + \dfrac{1}{(9.4 \cdot 10^{-4} \text{ g-mol/cm}^2\text{-sec-atm})(7.9 \cdot 10^5 \text{ cm}^3\text{-atm/g-mol})}}$$

$$= 2.1 \cdot 10^{-3} \text{ cm/sec}$$

The mass transfer is dominated by the liquid-side resistance. This would also be true if we calculated the overall gas-side mass transfer coefficient, a consequence of the slow diffusion in the liquid state. It is the usual case for problems of this sort.

Example 8.5-2: Perfume extraction Jasmone ($C_{11}H_{16}O$) is a valuable material in the perfume industry, used in many soaps and cosmetics. Suppose we are recovering this material from a water suspension of jasmine flowers by an extraction with benzene. The aqueous phase is continuous; the mass transfer coefficient in the benzene drops is $3.0 \cdot 10^{-4}$ centimeters per second; the mass transfer coefficient in the aqueous phase is $2.4 \cdot 10^{-3}$ centimeters per second. Jasmone is about 170 times more soluble in benzene than in the suspension. What is the overall mass transfer coefficient?

Solution For convenience, we designate all concentrations in the benzene phase with a prime and all those in the water without a prime. The flux is

$$N_1 = k(c_{10} - c_{1i}) = k'(c'_{1i} - c'_{10})$$

The interfacial concentrations are in equilibrium:

$$c'_{1i} = Hc_{1i}$$

Eliminating these interfacial concentrations, we find

$$N_1 = \left[\frac{1}{1/k' + H/k} \right] (Hc_{10} - c'_{10})$$

The quantity in square brackets is the overall coefficient K' that we seek. This coefficient is based on a driving force in benzene. Inserting the values,

$$K' = \frac{1}{\dfrac{1}{3.0 \cdot 10^{-4} \text{ cm/sec}} + \dfrac{170}{2.4 \cdot 10^{-3} \text{ cm/sec}}}$$

$$= 1.3 \cdot 10^{-5} \text{ cm/sec}$$

Similar results for the overall coefficient based on a driving force in water are easily found.

Two points about this problem deserve mention. First, the result is a complete parallel to Eq. 8.5-12, but for a liquid–liquid interface instead of a gas–liquid interface. Second, mass transfer in the water dominates the process even though the mass transfer coefficient in water is larger because jasmone is so much more soluble in benzene.

Example 8.5-3: Overall mass transfer coefficients in a packed tower   We are studying gas absorption into water at 2.2 atmospheres total pressure in a packed tower containing Berl saddles. From earlier experiments with ammonia and methane, we believe that for both gases the mass transfer coefficient times the packing area per tower volume is 18 lb-mol/hr-ft^3 for the gas side and 530 lb-mol/hr-ft^3 for the liquid side. The values for these two gases may be similar because methane, and ammonia have similar molecular weights. However, their Henry's law constants are different: 9.6 atmospheres for ammonia and 41,000 atmospheres for methane. What is the overall gas-side mass transfer coefficient for each gas?

Solution   This is essentially a problem in unit conversion. Although you can extract the appropriate equations from the text, I always feel more confident if I repeat parts of the derivation.

The quantity we seek, the overall gas-side transfer coefficient K_y, is defined by

$$N_1 a = K_y a(y_{10} - y_1^*)$$

$$= k_y a(y_{10} - y_{1i})$$

$$= k_x a(x_{1i} - x_{10})$$

where y_1 and x_1 are the gas and liquid mole fractions.

The interfacial concentrations are related by Henry's law:

$$p_{1i} = py_{1i} = Hx_{1i}$$

When these interfacial concentrations are eliminated, we find that

$$\frac{1}{K_y a} = \frac{1}{k_y a} + \frac{H/p}{k_x a}$$

In passing, we recognize that y_1^* must equal Hx_{10}/p.

We can now find the overall coefficient for each gas. For ammonia,

$$\frac{1}{K_y a} = \frac{1}{18 \text{ lb-mol/hr-ft}^3} + \frac{9.6 \text{ atm/2.2 atm}}{530 \text{ lb-mol/hr-ft}^3}$$

$$K_y a = 16 \text{ lb-mol/hr-ft}^3$$

The gas-side resistance controls the rate. For methane,

$$\frac{1}{K_y a} = \frac{1}{18 \text{ lb-mol/hr-ft}^3} + \frac{41,000 \text{ atm/2.2 atm}}{530 \text{ lb-mol/hr-ft}^3}$$

$$K_y a = 0.03 \text{ lb-mol/hr-ft}^3$$

The coefficient for methane is smaller and is dominated by the liquid-side mass transfer coefficient.

8.6 Conclusions

This chapter presents an alternative model for diffusion, one using mass transfer coefficients rather than diffusion coefficients. The model is most useful for diffusion across phase boundaries. It assumes that large changes in the concentration occur only very near these boundaries and that the solutions far from the boundaries are well mixed. Such a description is called a lumped-parameter model.

In this chapter, we have shown how experimental results can be converted into mass transfer coefficients. We have also shown how these coefficients can be efficiently organized as dimensionless correlations, and we have cataloged published correlations that are commonly useful. These correlations are compromised by problems with units that come out of a plethora of closely related definitions.

Mass transfer coefficients provide especially useful descriptions of diffusion in complex multiphase systems. They are basic to the analysis and design of industrial processes like absorption, extraction, and distillation. They should find major applications in the study of physiologic processes like membrane diffusion, blood perfusion, and digestion; physiologists and physicians do not often use these models but would benefit from doing so.

Mass transfer coefficients are not useful in chemistry when the focus is on chemical kinetics or chemical change. They are not useful in studies of the solid state, where concentrations vary with both position and time, and lumped-parameter models do not help much. However, mass transfer coefficients are used in analyzing etching processes, like those used in making silicon chips.

All in all, the material in this chapter is a solid alternative for analyzing diffusion near interfaces. It is basic stuff for chemical engineers, but it is an unexplored method for many others. It repays careful study.