

Chapter 2

Chemicals in the Environment, Diffusive Transport

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Glossary

Convection	Mass transfer effected by flow due to applied forces like pressure (forced convection) or to density differences (free convection).
Diffusion	Mixing caused by molecular motion.
Diffusion coefficient	The negative of the flux per concentration gradient.
Diffusivity	Another name for the diffusion coefficient.
Dispersion	Mixing caused by diffusion and simultaneous flow.
Flux	Mass or moles transferred per area per time.
Mass transfer	Diffusion and dispersion, especially across interfaces.
Mass transfer coefficient	The flux per concentration difference, especially near an interface.
Overall mass transfer coefficient	The flux per virtual concentration difference from one phase across an interface into a second phase.

This chapter was originally published as part of the Encyclopedia of Sustainability Science and Technology edited by Robert A. Meyers. DOI:[10.1007/978-1-4419-0851-3](https://doi.org/10.1007/978-1-4419-0851-3)

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Definition of the Subject

Diffusion is mixing without stirring. It is mixing caused by Brownian motion, that is, by thermally induced random motion of molecules or small particles. Because diffusion is often slow, it frequently limits the overall rate of the process. Diffusion has the reputation of being a difficult subject, which it can be; however, the difficulty most often comes from complicated units, from interfaces, or from the combination of diffusion and convection. By itself, diffusion is not hard. It is easier than viscous flow and much easier than ideas like entropy or chemical potential.

Two other phenomena, closely related to diffusion, are also reviewed in this entry. Dispersion is mixing caused by the interaction of flow and diffusion. Often, it is described using mathematics similar to those which describe diffusion. In environmental problems, these two phenomena are sometimes treated without distinction and without penalty. Mass transfer, an alternative description of diffusion, assumes that all concentration changes occur near interfaces. While it is used largely to describe chemical processing, it has considerable value in environmental problems.

Introduction

This entry is organized as four sections. The first section gives the mathematical description of diffusion itself. The second reviews dispersion, a different phenomenon that is mathematically similar to diffusion but which is caused by different physical effects. The third [section, “Diffusion Coefficients,”](#) reviews values of the diffusion coefficients themselves; and the fourth [section “Diffusion Across Interfaces,”](#) explains mass transfer across interfaces, especially air–water interfaces. Finally, the [section “Important Special Cases”](#) reports some common situations which have important features.

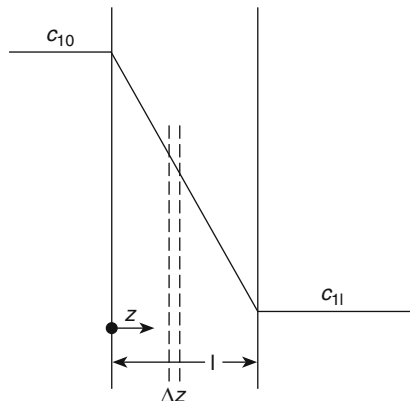
Basic Diffusion

The basic mathematical description of diffusion is Fick’s Law, suggested by Adolph Fick (1829–1910) when he was just 26 years old. For a dilute solution, Fick’s Law is:

$$j_1 = -D \frac{dc_1}{dz} \quad (2.1)$$

where j_i is the flux of a solute “1,” and dc_1/dz is the concentration gradient, that is, the change of the solute concentration with position. The diffusion coefficient D is a proportionality constant which is nearly constant in almost all situations. The flux is the amount of solute moving per cross-sectional area per time and so has the

Fig. 2.1 Concentration profile across a thin film



dimensions of mass (M) per area (length squared L^2) per time (t). The concentration gradient has dimensions of concentration (M/L^3) per distance (L). Thus the diffusion coefficient has dimensions of (L^2/t).

The form of Fick's Law in Eq. 2.1 has some hidden implications. First, it is a one-dimensional equation of what is actually a more general vector relation. Because at least four out of five diffusion problems are one-dimensional, this is often not a major issue. Second, the concentration can be expressed in different units. If it were expressed in moles per volume, then the flux would be in moles per area per time. If it were expressed as a mole fraction or a mass fraction or a partial pressure, then unit conversions would be necessary and annoying, but not difficult. Third, the minus sign in Eq. 2.1 is arbitrary, stuck in to make the diffusion coefficient positive. The only difficult implication of Eq. 2.1 is the restriction to dilute solutions, explored in more detail at the end of this section. The restriction is rarely important because solutions in the environment are so often dilute. For example, liquid water contains 55 mol/l, so almost every aqueous solution is dilute.

The most important case of Fick's law is diffusion across a thin film, described next. Other important cases and concentrated solutions are reviewed later.

Diffusion Across a Thin Film

The simplest case, steady diffusion across a film, is also the most important. Imagine a thin film separating two well-stirred solutions, as shown in Fig. 2.1. On the left, the solution has a concentration c_{10} ; on the right, the concentration is c_{1l} . The key parts of this case are the variation of concentration across the film $c_1(z)$ and the flux j_1 . Finding these requires a mass balance on a differential volume Δz thick and located at an arbitrary position z within the film:

$$(\text{mass accumulation}) = (\text{mass diffusing in} - \text{out})$$

$$\frac{\partial}{\partial t}(c_1 A \Delta z) = (j_1 A)_z - (j_1 A)_{z+\Delta z} \quad (2.2)$$

where A is the constant cross-sectional area of the film. Because diffusion is steady, the concentration does not change with time, the left-hand side of Eq. 2.2 is zero, and

$$0 = \frac{j_1|_z - j_1|_{z+\Delta z}}{(z + \Delta z) - z}$$

$$0 = -\frac{dj_1}{dz} \quad (2.3)$$

This restates the assumption of steady-state diffusion, independent of time. Combining this relation with Fick's Law (Eq. 2.1) yields:

$$0 = D \frac{d^2 c_1}{dz^2} \quad (2.4)$$

This is subject to two boundary conditions:

$$z = 0 \quad c_1 = c_{10} \quad (2.5)$$

$$z = \ell \quad c_1 = c_{1\ell} \quad (2.6)$$

This is enough to solve this important problem.

Equation 2.4 may be integrated once to find:

$$\frac{dc_1}{dz} = A \quad (2.7)$$

where A is an integration constant. Integrating a second time gives:

$$c_1 = Az + B \quad (2.8)$$

where B is a second integration constant. Evaluating A and B from Eqs. 2.5 and 2.6 gives:

$$\frac{c_1 - c_{10}}{c_{1\ell} - c_{10}} = \frac{z}{\ell} \quad (2.9)$$

The flux can now be found by combining this result with Fick's Law:

$$j_1 = -D \frac{dc_1}{dz}$$

$$= \frac{D}{\ell} (c_{10} - c_{1\ell}) \quad (2.10)$$

If the concentration difference across the film is doubled, the flux doubles. If the diffusion coefficient is twice as big, the flux will be twice as big, too. If the film thickness increases two times, the flux will be cut in half.

This important example is so simple mathematically that many novices tend to skip over it. This is a mistake. Its nuances are explored by the following questions:

1. *How does the flux change if the film is chemically different than the adjacent solutions?*

In this case, the boundary conditions in Eqs. 2.5 and 2.6 change to:

$$z = 0 \quad c_1 = Hc_{10} \quad (2.11)$$

$$z = \ell \quad c_1 = Hc_{1\ell} \quad (2.12)$$

where H is a partition coefficient, the ratio at equilibrium of the concentration inside the film to that in the adjacent solution. Paralleling the arguments above,

$$j_1 = \frac{(DH)}{\ell} (c_{10} - c_{1\ell}) \quad (2.13)$$

The diffusion coefficient D in Eq. 2.10 is replaced with the product (DH) , which is called the permeability. (The term (DH/ℓ) is called the permeance.) As will be shown later, diffusion coefficients in gases and liquids do not vary much, but partition coefficients vary a lot. Thus partition is often the key to permeability.

2. *How is the flux changed by a fast reversible reaction giving an immobile product?*

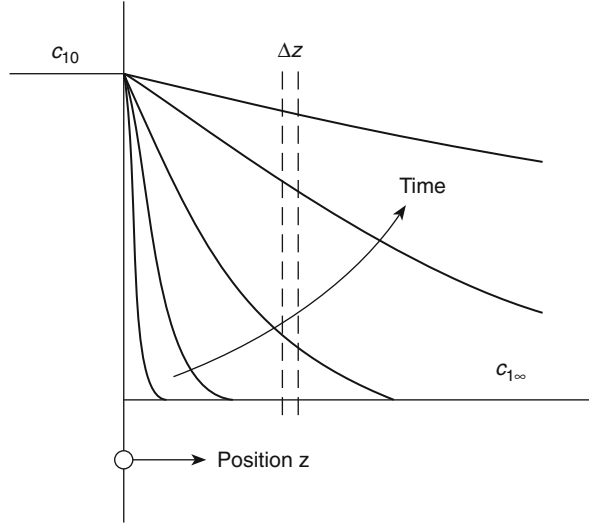
This case occurs surprisingly frequently in, for example, adsorption in soil or dyeing of wool. The answer is that at steady state, the flux does not change. Every point crossing the film has a different concentration which is in equilibrium with a different absorbed amount. Still, at steady state, the reaction is at local equilibrium and does not affect the flux. This is not the case for unsteady state, for irreversible reactions, or for mobile reaction products.

Other Important Cases

Many diffusion problems are not thin films. Surprisingly, many do behave as if they were thin films. For example, for a sphere of radius R slowly dissolving in a stagnant fluid with a concentration of $c_{1\infty}$, the flux is:

$$j_1 = \frac{D}{R} (c_{10} - c_{1\infty}) \quad (2.14)$$

Fig. 2.2 Concentration profile into a semi-infinite slab



where c_{10} is the concentration in solution at the surface of the sphere. For diffusion from a solution of c_{10} through a very thin, impermeable film with a cylindrical orifice of radius R , and into a solution at $c_{1\infty}$, the flux is:

$$j_1 = \frac{D}{\frac{\pi}{2}R} (c_{10} - c_{1\infty}) \quad (2.15)$$

The fluxes in these cases are strong mathematical parallels to that in Eq. 2.10. The mathematics in these cases is different, but the final result is remarkably similar. The thin film limit is a good guide about 80% of the time.

For unsteady state diffusion, this is not true. Fluxes and concentration profiles for a wide variety of unsteady cases have been calculated and are tabulated in a few clear texts. One of these cases, useful in perhaps 10% of all cases, is unsteady diffusion into a semi-infinite slab, shown in Fig. 2.2. In this case, a mass balance gives:

$$\frac{\partial c_1}{\partial t} = D \frac{\partial^2 c_1}{\partial z^2} \quad (2.16)$$

where t is the time. For this semi-infinite slab, the initial and boundary conditions are:

$$t = 0 \quad \text{all } z \quad c_1 = c_{1\infty} \quad (2.17)$$

$$t = 0 \quad z = 0 \quad c_1 = c_{10} \quad (2.18)$$

$$t = 0 \quad z = \infty \quad c_1 = c_{1\infty} \quad (2.19)$$

Table 2.1 Flux across a film or into a slab. These two cases are important because they bracket almost all diffusion problems. In this table, K is the equilibrium constant of the rapid chemical reaction

	Thin film	Semi-infinite slab
Concentration difference	Δc_1	Δc_1
Diffusion coefficient	D	\sqrt{D}
Thickness	ℓ^{-1}	—
Time	—	t^{-1}
Flux without reaction	$j_1 = \frac{D}{\ell} \Delta c_1$	$j_1 = \sqrt{\frac{D}{\pi t}} \Delta c_1$
Flux with fast reversible reaction	$j_1 = \frac{D}{\ell} \Delta c_1$	$j_1 = \sqrt{\frac{D(1+K)}{\pi t}} \Delta c_1$

The concentration profile in this case is:

$$\frac{c_1 - c_{1\infty}}{c_{10} - c_{1\infty}} = 1 - \operatorname{erf} \frac{z}{\sqrt{4Dt}} \quad (2.20)$$

where erf is the error function. The flux at the edge of the slab, that is, at $z = 0$, is:

$$j_1 = \left(\sqrt{\frac{D}{\pi t}} \right) (c_1 - c_{1\infty}) \quad (2.21)$$

This is the key result for this case.

The cases of a thin film and a semi-infinite slab are especially important because they bracket observed behavior. More specifically, the result in [Eq. 2.21](#) for a semi-infinite slab is compared with the flux across a thin film in [Table 2.1](#). In both cases, the flux will double if the concentration difference doubles. If the diffusion coefficient doubles, the flux across a thin film doubles, but the flux into the semi-infinite slab increases $\sqrt{2}$ times. If the film's thickness doubles, the flux drops two times for the film, but is unchanged for the slab. If diffusion occurs for twice as long, the flux for the thin film keeps its steady value, but that for the slab drops by a factor of $1/\sqrt{2}$. These limits will usually bracket all diffusion behavior because all shapes will be between the film and the slab. These two cases are key to understanding the mathematics of diffusion.

A third special case is especially important for environmental engineering. This is the decay of a pulse. In this case, a large amount of solute is released at a particular plane at $z = 0$. Solute diffuses away from this position in only one dimension. The solute concentration as a function of position z and time t gives the details of any environmental impact.

The mathematics follows the same route as the slab: a mass balance is subject to initial and boundary conditions, which are combined with Fick's Law and solved to give the concentration profile. The mass balance is:

$$\frac{\partial c_1}{\partial t} = D \frac{\partial^2 c_1}{\partial z^2} \quad (2.22)$$

This mass balance, identical with the mass balance for the slab (Eq. 2.16), occurs so frequently that some just call it “the diffusion equation.” The initial and boundary conditions are different from Eqs. 2.17–2.19 for the slab:

$$t = 0 \quad \text{all } z \quad c_1 = \frac{M}{A} \delta(z) \quad (2.23)$$

$$t = 0 \quad z = 0 \quad \frac{dc_1}{dz} = 0 \quad (2.24)$$

$$z = \infty \quad c_1 = 0 \quad (2.25)$$

In these conditions, M is the total solute injected, A is the cross-sectional area, and $\delta(z)$ is the Dirac function, equal to zero everywhere except at $z = 0$, where it is infinity. While the mathematical solution of Eqs. 2.22–2.25 is tricky, the answer is simple:

$$c_1 = \left[\frac{M/A}{\sqrt{4\pi Dt}} \right] e^{-\frac{z^2}{4Dt}} \quad (2.26)$$

In this Gaussian concentration profile, the quantity in square brackets is the maximum concentration, which drops as time grows. The mathematical form of this important result is also observed for other environmental problems which do not depend only on diffusion, as described in the section “Dispersion.”

Concentrated Diffusion

One reason that diffusion has the reputation of being difficult comes from the major complexities of concentrated solutions. These complexities are rarely important in environmental engineering and so should be ignored unless there are good experimental reasons not to do so. These complexities are mentioned here only to illustrate when they are important.

To explore this, imagine putting a pot of room temperature water of 25°C on a stove that is turned off. The flux of any evaporating water will be given by Eq. 2.10. If the air above the stove were dry, $c_{1\ell}$ would be zero. Because the water at 25°C has a vapor pressure of about 25 mmHg, c_{10} is about:

$$\begin{aligned}
 c_{10} &= \left[\frac{25 \text{ mm Hg}}{750 \text{ mm Hg}} \right] \frac{1 \text{ mol}}{22.4 \times 10^{-3} \text{ m}^3} \\
 &= 1.5 \frac{\text{mol}}{\text{m}^3}
 \end{aligned}
 \tag{2.27}$$

If the liquid water in the pot is 0.1 m below the rim and the diffusion coefficient of water vapor in air is about $2.8 \times 10^{-5} \text{ m}^2/\text{s}$, the flux is:

$$\begin{aligned}
 j_1 &= \frac{D}{\ell} (c_{10} - c_{1\ell}) \\
 &= \frac{2.8 \times 10^{-5} \text{ m}^2/\text{s}}{0.1 \text{ m}} \left(1.5 \frac{\text{mol}}{\text{m}^3} - 0 \right) \\
 &= 4 \times 10^{-4} \frac{\text{mol}}{\text{m}^2 \text{s}}
 \end{aligned}
 \tag{2.28}$$

Now imagine heating the liquid water in the pot to boiling. If the heat flux q is 20 kJ/m² s, then the molar flux caused by boiling is:

$$\begin{aligned}
 n_1 &= \frac{q}{\Delta \tilde{H}_{\text{vap}}} \\
 &= \frac{20 \text{ kJ /m}^2 \text{s}}{48 \text{ kJ/mol}} \\
 &= 0.4 \frac{\text{mol}}{\text{m}^2 \text{s}}
 \end{aligned}
 \tag{2.29}$$

The boiling flux n_1 is 1,000 times greater than the diffusion flux at room temperature, but it is not a function of D . Thus slow dilute evaporation is a function of the diffusion coefficient; but boiling depends not on diffusion but on heating rate.

But what about intermediate cases? For example, how fast will evaporation take place at 50°C?

Answering this question requires a more complete form of Fick's Law. Unfortunately, there is no single way to do this. One choice is the following:

$$\begin{aligned}
 [\text{Total flux}] &= [\text{Diffusion flux}] + [\text{Convective flux}] \\
 n_1 &= c_1(v_1 - v) + c_1 v = j_1 + c_1 v \\
 &= -D \frac{dc_1}{dz} + c_1 v
 \end{aligned}
 \tag{2.30}$$

where v is most often a volume average velocity. The most common alternative form of Fick's law, strongly advocated by a few zealots, may be approximated as:

$$\nabla c_1 = \frac{c_1 c_2}{cD} (v_2 - v_1)
 \tag{2.31}$$

where c_2 and v_2 are the concentration and velocity of the solvent. This form avoids choosing a convective velocity, but it can cloud the physical significance of the problem.

Fortunately, the result for a problem like the water evaporation given above is the same for both forms of Fick's Law given in Eqs. 2.30 and 2.31. If water at 50°C is evaporating from the pot above into dry stagnant air, the total flux is:

$$\begin{aligned}
 n_1 &= -\frac{Dc}{\ell} \ln\left(1 - \frac{c_{10}}{c}\right) \\
 &= \frac{-2.8 \times 10^{-5} \text{ m}^2/\text{s} \left(\frac{1 \text{ mol}}{22.4 \times 10^{-3} \text{ m}^3}\right)}{0.1 \text{ m}} \ln\left(1 - \frac{92.5}{760}\right) \\
 &= 1.62 \times 10^{-3} \text{ mol/m}^2\text{s}
 \end{aligned} \tag{2.32}$$

This is about 7% greater than the result would be if calculated from Eq. 2.10 for a dilute solution at 50°C. The moral is clear: the effects of concentrated diffusion will only rarely be important in the atmospheric and aquatic environments.

This completes our basic description of the three cases key to understanding diffusion. These are the thin film (80% of the cases), the semi-infinite slab (10% of the cases), and the decay of a pulse (5% of the cases). Other cases with different boundary conditions do occur, and solutions for these are tabulated in the literature. However, these other cases are not as common in practice. Similarly, diffusion in concentrated solutions is complicated but infrequently important. The simple form of Fick's Law in these three cases is the best way to get started.

Dispersion

We now turn to an environmentally important problem mathematically similar to diffusion but with a different physical origin. To make this problem specific, imagine dealing with the spill of a single toxin on the ground. Imagine the concentration of the toxin spreads in one dimension with time and groundwater flow, producing a roughly Gaussian concentration profile. We want to know how the spread of this toxin varies with the diffusion coefficient of the toxin.

The answer is surprising: if the diffusion coefficient increases, the spread of the toxin may be bigger, smaller, or unchanged. The toxin's concentration profile is:

$$c_1 = \frac{M/A}{\sqrt{4\pi Et}} e^{-\frac{(z-vt)^2}{4Et}} \tag{2.33}$$

where M is the total amount of toxin, A is the cross-sectional area across which the dispersion occurs, and v is the velocity of any flow through the soil. The dispersion coefficient E has the same units as the diffusion coefficient but will often be much larger. This result, a complete analogue to Eq. 2.26, can be derived from parallels to

Eqs. 2.22–2.25 by replacing the diffusion coefficient D with the dispersion coefficient E . However, while this mathematical parallel is complete, it does not explain the physics responsible for dispersion.

To explore the physics involved, imagine the toxin is injected as a pulse into a small tube of diameter d . The toxin's dispersion will be a strong function of how much flow is in the tube. If there is absolutely no flow, then the dispersion coefficient equals the diffusion coefficient:

$$E = D \quad (2.34)$$

Increasing diffusion increases dispersion. If there is a small, laminar flow of velocity v , then:

$$E = \frac{v^2 d^2}{192D} \quad (2.35)$$

Increasing diffusion decreases dispersion. The velocity where Eq. 2.35 becomes dominant is when:

$$\frac{v^2 d^2}{192D^2} \gg 1 \quad (2.36)$$

For non-absorbing soil with the equivalent of 500 μm particles and diffusion in water liquid, D is about $10^{-9} \text{ m}^2/\text{s}$, so v must be much greater than 30 $\mu\text{m}/\text{s}$ or 2 m/day for Eq. 2.35 to swamp Eq. 2.34. If there is a large, turbulent flow ($dv/v > 2,000$), then:

$$E = \frac{dv}{2} \quad (2.37)$$

Dispersion, now independent of diffusion, is due to the coupled turbulent fluctuations of concentration and velocity. The physical basis of Eqs. 2.33–2.37 is associated with G.I. Taylor.

Those with a more practical bent may correctly be skeptical of modeling flow through a soil as occurring in a straight tube. Others sharing this skepticism have extended this analysis to flow in packed beds. The key results involve two new quantities:

$$\bar{t} = t(1 + k') \quad (2.38)$$

$$k' = \left[\frac{\text{Soil concentration}}{\text{Solution concentration}} \right] \left(\frac{1 - \varepsilon}{\varepsilon} \right) \quad (2.39)$$

where ε is the void fraction available for flow. In physical terms, \bar{t} is the time corrected for any absorption by the soil, including material that diffuses into the soil's pores. The quantity k' is a type of equilibrium constant between the soil and the solution, lumping together adsorption and absorption. In this case, a pulse of toxin may still be dispersed to give the Gaussian concentration profile in Eq. 2.24, but with time t replaced by \bar{t} . The dispersion coefficient E is now given by:

$$E = D(1 + k') + \frac{d^2 v^2}{192D} \left(\frac{1 + 6k' + 11(k')^2}{1 + k'} \right) + \frac{\delta^2 v^2}{3D'} \left(\frac{k'}{1 + k'} \right) \quad (2.40)$$

where δ is an equivalent thickness of an absorbent and D' is the diffusion coefficient in the absorbent, not in the solution. The first term on the right-hand side of Eq. 2.40, the parallel of Eq. 2.34, is due to diffusion in the direction of flow. The second term, the analogue of Eq. 2.37, comes from Taylor dispersion and is often the most important. The third term is new, the result of the rate of absorption.

This overview of dispersion is intended as a caution and a starting point. The caution is that many Gaussian concentration profiles are due to diffusion coupled with other phenomena. The starting point in understanding these profiles is recognizing that their spread can depend inversely on diffusion. In other words, slow diffusion may result in wide dispersion.

Diffusion Coefficients

Diffusion is an important process because it is slow, and diffusion coefficients thus often control the overall rate of processes involving diffusion, flow, and chemical reaction. Typical values of diffusion coefficients, shown in Table 2.2, are chosen from the wide number of references in the literature but corrected to a temperature of 25°C. This wide literature is much less extensive than studies of other physical properties like viscosity or Young's modulus, because diffusion coefficients are relatively difficult to measure.

The values in Table 2.2 show diffusion in gases is about 10,000 times faster than diffusion in liquids, which is in turn over a billion times faster than diffusion in solids. Diffusion coefficients in gases fall around $10^{-5} \text{ m}^2/\text{s}$. Diffusion coefficients in liquids fall around $10^{-9} \text{ m}^2/\text{s}$. Diffusion coefficients in solids are much more variable, but are so slow that most of the mass transport occurs in fluid-filled gaps and pores within the solid. For example, in a bed of sand, most transport occurs in the spaces between sand grains and relatively little within the bulk of the grains themselves. In environmental problems, diffusion in gases and liquids is more important.

Table 2.2 Diffusion coefficients. Values given are in m^2/s and at 298 K and 1 atm

Gases	
Gas pair	Diffusion coefficient
Air-H ₂ O	2.6×10^{-5}
CO ₂ -O ₂	1.6×10^{-5}
H ₂ -N ₂	7.8×10^{-5}
H ₂ -O ₂	8.9×10^{-5}
N ₂ -O ₂	2.2×10^{-5}
N ₂ -H ₂ O	2.9×10^{-5}
O ₂ -H ₂ O	2.8×10^{-5}
O ₂ -octane	0.7×10^{-5}
Solids	
	Diffusion coefficient
C in Fe (BCC)	6×10^{-25}
Fe in Fe (BCC)	3×10^{-52}
B in Si	7×10^{-33}
He in SiO ₂	4×10^{-14}
Na ⁺ in NaCl	1×10^{-36}
Ag ⁺ in AgCl	1×10^{-19}
Liquids	
Solute-solvent	Diffusion coefficient
O ₂ -H ₂ O	2.10×10^{-9}
CO ₂ -H ₂ O	1.92×10^{-9}
H ₂ S-H ₂ O	1.41×10^{-9}
HCl-H ₂ O	3.33×10^{-9}
NaCl-H ₂ O	1.61×10^{-9}
CaCl-H ₂ O	1.33×10^{-9}
NH ₃ -H ₂ O	1.64×10^{-9}
Urea-H ₂ O	1.38×10^{-9}
Sucrose-H ₂ O	0.52×10^{-9}
Albumin-H ₂ O	0.08×10^{-9}
H ₂ O-C ₂ H ₅ OH	1.24×10^{-9}
Benzene-butanol	0.99×10^{-9}
Hexane-heptane	4.21×10^{-9}

The diffusion coefficients, given in Table 2.2 for 1 atm and 25°C, do change with process variables, as outlined in Table 2.3. The variation with temperature in gases and liquids is small. For example, the temperature must be increased from 25°C (= 298° K) to 200°C (= 473° K) to double the diffusion coefficient in gases. Because the viscosity of a liquid drops as the temperature rises, the diffusion coefficient in a liquid changes faster with temperature, but the change is still modest. In contrast, diffusion coefficients in solids usually change more rapidly with temperature, doubling every 10°C or so.

Other process variables also have relatively small effects. The diffusion coefficient in gases does vary inversely with pressure; but the gas concentration varies

Table 2.3 Variations of diffusion coefficients

	Gases	Liquids	Solids
Typical value, m ² /s	10 ⁻⁵	10 ⁻⁹	Much smaller
vs. T	$T^{3/2}$	T	Large
vs. p	p^{-1}	—	—
vs. solute diameter	size ⁻²	size ⁻¹	size ²
vs. viscosity μ	μ^1	μ^{-1}	—

directly with pressure; so the flux, related to the diffusion coefficient times the concentration, may remain more constant. The diffusion coefficient does vary inversely with the size of the diffusing species. While these effects are usually modest for gases and liquids, they can be much larger for solids. These generalizations are justified by the approximate physical arguments given next.

Gases. The diffusion coefficients in gases can be predicted with reasonable accuracy from kinetic theory. This theory assumes that a gas contains individual molecules moving with thermal motion and colliding with each other only as pairs. Under these cases, the diffusion coefficient is given by:

$$D = \frac{1}{3} \lambda v \quad (2.41)$$

where λ is the distance between collisions and v is the molecular velocity. For a monatomic gas, this velocity is kinetic, related to the thermal energy:

$$\frac{1}{2} m v^2 = k_B T \quad (2.42)$$

where m is the molecular mass and k_B is Boltzmann's constant. Keep in mind that here v is a molecular velocity. It is the sonic velocity; it is much greater than the average velocity \bar{v} used in Eqs. 2.30 and 2.31.

We must now estimate the distance between collisions λ . There are two cases. First, for the bulk gas, λ is found from the volume occupied by one molecule:

$$\begin{aligned} & [\text{Volume of one molecule}] = \\ & [\text{Distance between collisions}] \times \\ & [\text{Area swept out between collisions}] \end{aligned}$$

$$\frac{k_B T}{p} = \lambda \left[\frac{\pi}{4} \sigma^2 \right] \quad (2.43)$$

where σ is the molecular diameter. Equations 2.41–2.43 can be combined to find:

$$D = \left(\frac{4\sqrt{2}}{3\pi} \right) \frac{(k_B T)^{\frac{3}{2}}}{p \sigma^2 \sqrt{m}} \quad (2.44)$$

This approximate relation is close to that found from more complex theories: D does vary inversely with p , σ^2 , and \sqrt{m} ; it does vary with T to a power greater than one and less than two.

The second important limit of Eq. 2.41 occurs only for a gas diffusing in small pores of diameter d . In this case, the diffusing species is much more likely to collide with the pore walls than with other molecules. Thus the combination of Eqs. 2.41 and 2.34 becomes:

$$D = \frac{\sqrt{2}}{3} d \sqrt{\frac{k_B T}{m}} \quad (2.45)$$

This case, called Knudsen diffusion, has a diffusion coefficient which depends on the pore diameter d , but not on the molecular diameter σ . Now, the diffusion coefficient is independent of pressure, though it does vary inversely with the square root of solute mass. Under ambient temperature and pressure, Knudsen diffusion is important when the pores are much less than 0.1 μm .

Liquids. Diffusion in liquids is normally not described by a kinetic theory but as the motion of a rigid, spherical solute diffusing in a continuum of solvent. Despite the major approximations obviously made by this simple model, it gives remarkably good results. It is the standard against which new predictions are always judged.

The model begins by describing the friction on a solute sphere:

$$\text{Force} = [\text{Coefficient of friction } f] \times \text{Velocity } v_1 \quad (2.46)$$

The velocity v_1 now is the average and not the sonic value v used for gases. The coefficient of friction f is given by Stokes Law:

$$f = 6\pi\mu R \quad (2.47)$$

where μ is the solvent viscosity and R is the solute radius. The force was suggested by Einstein to be the negative of the gradient of the chemical potential μ_1 . Thus:

$$\begin{aligned} -\frac{d\mu_1}{dz} &= [6\pi\mu R]v_1 \\ &= -\nabla(k_B T \ln c_1) = -\frac{k_B T}{c_1} \frac{dc_1}{dz} \end{aligned} \quad (2.48)$$

Rearranging:

$$-c_1 v_1 = \left(\frac{k_B T}{6\pi\mu R} \right) \frac{dc_1}{dz} \quad (2.49)$$

But $(c_1 v_1)$ is the total flux n_1 , equal in dilute solution to the diffusion flux j_1 . Comparing this with Eq. 2.33 gives:

$$D = \frac{k_{\text{B}}T}{6\pi\mu R} \quad (2.50)$$

The diffusion coefficient in liquids varies inversely with solute size and with solvent velocity. This simple relation is called the Stokes–Einstein equation.

Equation 2.50 often gives good estimates of diffusion in liquids. Its simplicity is an invitation to attempt improvements. These include assuming the sphere is not solid but gas, replacing the sphere with an ellipsoid, allowing the sphere to spin, and putting it in a small pore. Other attempts at improvement allow for nonideal solutions, assigning different friction coefficients to solute and solvent, and considering changes close to the spinoidal. While none of these efforts is definitive, each can clarify the perspective of a particular chemical system. Still, the simple Stokes–Einstein equation is the best place to start for understanding diffusion in liquids.

Solids. As explained above, the diffusion in solids is so slow that most transport usually occurs in any fluid-filled flows and voids within the solid. Some solid processes are certainly dramatically affected by diffusion – metallic welds and doped semiconductors are two good examples – but the diffusion of chemicals in the environment is usually through fluids.

The relative unimportance of diffusion in solids is fortunate, because diffusion coefficients in solids scatter. These coefficients do not cluster around a single value, and they depend strongly on crystal structures. For example, the diffusion of carbon in body-centered cubic iron is 10^{10} times faster than the diffusion of carbon in face-centered cubic iron. Sometimes, an anomalously high coefficient reflects different types of vacancies in the solid crystals. For example, silver ion diffuses 10^{17} times faster in AgCl than sodium ion diffuses in NaCl.

Estimates of diffusion in solids, which normally begin with a face-centered cubic lattice, assume a coefficient given by:

$$D = R^2 N \omega \quad (2.51)$$

where R is now the distance between atoms or ions in the crystal; N is the dimensionless fraction of vacant sites; and ω is the jump frequency, the number of atomic or ionic movements per time. The size of R is estimated from crystal structure, and the fraction N from the free energy of mixing. The jump frequency ω is often felt to have an Arrhenius temperature dependence. Arguments like this are not predictions but are rationales to organize data.

Diffusion Across Interfaces

Diffusion from one phase to another is an important and complex limit, a source of confusion for many. In this case, there are two limits that are close parallels to the

cases of a thin film and a semi-infinite slab discussed above in the [sections “Diffusion Across a Thin Film”](#) and [“Other Important Cases.”](#) One case is exemplified by the so-called infinite couple, when two alloy bars of different but homogeneous composition are closely joined together. In this case, each atomic species can diffuse between the two bars, giving concentration profiles that are known. This limit is rarely important in environmental science and engineering.

The second, much more important limit occurs when solutes diffuse from one relatively well-mixed phase across a phase boundary to a second relatively well-mixed phase. This limit approximates what happens when sulfur dioxide in the air diffuses into a lake. In this case, bulk air is often well-mixed, and the bulk water in the lake is, too. However, this good mixing does not extend all the way to the air–water interface. About the last one millimeter of air and about the last one-tenth millimeter of the water are not well-mixed. Diffusion across these two films, one in air and the other in the water, is what governs the rate of sulfur dioxide dissolution in the lake.

We develop these ideas below. [“The Mathematics of Mass Transfer”](#) derives the mathematical framework. [“Concentration Units”](#) details transport across interfaces. [“The Meaning of \$c_1^*\$ ”](#) uses this framework to calculate the mass transfer in several environmentally relevant situations.

The Mathematics of Mass Transfer

To begin our study of mass transfer, imagine a small volume of air containing hydrogen sulfide at concentration c_{10} that is suddenly contacted with a large volume of water. The sulfide dissolves in the water so that its concentration c_1 drops with time. Predicting this concentration change with the diffusion equations given above is possible, but difficult. Often, an easier prediction is to use an alternative tool, a mass transfer analysis, which is more suitable for engineering applications.

This mass transfer analysis begins by writing a mass balance on the H_2S in the air:

$$\begin{aligned} &[\text{Accumulation in the air}] = \\ &[\text{Amount dissolved in water}] \\ &V \frac{dc_1}{dt} = -AK(c_1 - c_1^*) \end{aligned} \quad (2.52)$$

where V is the air volume, A is the interfacial area between air and water, and c_1^* is proportional to the concentration of the H_2S in the water. When there is a lot of pure, well-mixed water present, this concentration is zero. The rate constant K in [Eq. 2.52](#) is an overall mass transfer coefficient, a function of H_2S diffusion in both

the water and the air. It has the units of velocity, that is, of length L per time t . This mass balance is subject to the initial condition:

$$t = 0 \quad c_1 = c_{10} \quad (2.53)$$

Integrating, [Eq. 2.52](#) becomes:

$$\frac{c_1}{c_{10}} = e^{-K(\frac{L}{v})t} \quad (2.54)$$

The H_2S concentration in the air decays exponentially with time, as if it were undergoing a first-order chemical reaction. The rate constant of this reaction (KA/V) has units of reciprocal time. However, the concentration in air is not dropping because of a chemical reaction but because of diffusion of H_2S from the air into the water.

As a second example, imagine absorbing carbon dioxide from flue gas. The flue gas is steadily flowing upward in a small absorption tower. Excess strong base is steadily flowing downward through the tower. A mass balance on the carbon dioxide in a small differential volume dV in the tower results in:

$$\begin{aligned} [\text{Accumulation in } dV] &= [\text{CO}_2 \text{ Flow in} - \text{out}] \\ &\quad + [\text{CO}_2 \text{ Absorbed by base}] \\ 0 &= Q \frac{dc_1}{dV} - Ka(c_1 - c_1^*) \end{aligned} \quad (2.55)$$

where Q is the volumetric flow rate of flue gas, a is the interfacial area per volume in the tower, and c_1^* is about zero because the base is strong and there is a lot of it. As before, K is an overall mass transfer coefficient describing the rate of reaction. This mass balance is subject to a boundary condition:

$$V = 0 \quad c_1 = c_{10} \quad (2.56)$$

Integration gives:

$$\frac{c_1}{c_{10}} = e^{-Ka(\frac{V}{Q})} \quad (2.57)$$

The CO_2 concentration exiting the absorption column decreases exponentially as the column volume V is increased or as the column flow Q is decreased. Note that [Eqs. 2.54](#) and [2.57](#) are complete mathematical parallels, even though the former describes unsteady dissolution without flow, and the latter describes steady absorption with flow.

Interfacial mass transfer is not hard. It is just an alternative description of diffusion which complements that given by Fick's Law. The three features do

make interfacial mass transfer complicated. These three complications are the units of concentration, the detailed meaning of c_1^* , and the values of the mass transfer coefficient K . Details of these features follow.

Concentration Units

The first issue, concentration units, results because the units used for clearly explaining the ideas are not always those easiest to use in practice. The concentration units implied in this essay are of the amount per volume, for example, moles per liter or grams per cubic meter. The concentration units used in practice are different. In gases, the units are sometimes partial pressures; in liquids, the units are often mole fractions.

Expressing concentrations as partial pressures or mole fractions leads to different definitions of mass transfer coefficients. In particular, the total flux across the interface N_1 from one dilute gaseous solution into another dilute liquid solution may be defined as:

$$\begin{aligned} N_1 &= n_1|_{\text{interface}} = j_1|_{\text{interface}} \\ &= K(c_1 - c_1^*) \end{aligned} \quad (2.58)$$

where c_1 is the concentration of species “1” in the gas. The restriction to dilute solution is not a major constraint. Alternatively, the interfacial flux can be defined as:

$$N_1 = K_p(p_1 - p_1^*) \quad (2.59)$$

where p_1 is the partial pressure of solute “1” in the gas, and K_p is a new, different overall mass transfer coefficient. But from the ideal gas law:

$$p_1 = \frac{n_1 RT}{V} = c_1 RT \quad (2.60)$$

Comparing the two equations shows:

$$K_p = \frac{K}{RT} \quad (2.61)$$

If K has units of meters per second, then K_p may have units of moles per square meter per second per pascal.

Similarly, for mass transfer from a liquid into a gas, an alternative definition is:

$$N_1 = K(c_1 - c_1^*) \quad (2.62)$$

where c_1 is now the concentration of species “1” in the liquid, and K is an overall mass transfer coefficient different from that in Eq. 2.58. Alternatively,

$$N_1 = K_x(x_1 - x_1^*) \quad (2.63)$$

where x_1 is the mole fraction of species “1” in the liquid, and K_x is still another overall mass transfer coefficient. Because

$$c_1 = cx_1 \quad (2.64)$$

where c is the total concentration in the liquid, the two overall coefficients are related:

$$K_x = cK \quad (2.65)$$

For example, if K is in meters per second, and c is in moles per meter cubed, then K_x will have units of moles per square meters per second. Other definitions of coefficients are also possible, but are no harder.

*The Meaning of c_1^**

The meaning of the concentration c_1^* appearing in Eqs. 2.52, 2.55, 2.58, 2.59, and 2.62 is the hardest step in this description. These flux equations all assert that the flux is proportional to a concentration difference. The flux will be zero when the concentration is zero. Thus, c_1^* must be the hypothetical gaseous concentration of species “1” that is in equilibrium with species “1” dissolved in the liquid. This is harder than interfacial heat transfer: there, the heat flux is proportional to the temperature on one side of the interface minus that on the other side. Here, the mass flux is proportional to a concentration difference which equals to one real concentration that does exist minus a second one which is hypothetical.

To be more specific, imagine the case in Eq. 2.58, where c_1 is the actual concentration of species “1” in the well-mixed, bulk gas on one side of the interface. The concentration c_1^* is equal to the concentration in the well-mixed, bulk liquid times some type of Henry’s Law constant, which describes equilibrium between gas and liquid. Sometimes, those studying this point for the first time can be helped by silently chanting

▼ c_1^* is the concentration that would be in the gas if it were in equilibrium with the liquid (which it isn’t).

Remembering this chant may help mastering this difficult point.

To try to make this point clearer, imagine in calculating the flux of oxygen in air into wastewater with a concentration of 1×10^{-4} mol/ℓ. At equilibrium,

$$c_1(\text{gas}) = 30c_1(\text{liquid}) \quad (2.66)$$

Thus,

$$c_1^*(\text{gas}) = 30 \times 10^{-4} \text{ mol/}\ell \quad (2.67)$$

As a result,

$$\begin{aligned} c_1 - c_1^* &= \frac{0.21 \text{ mol}}{22.4\ell} - 30 \times 10^{-4} \frac{\text{mol}}{\ell} \\ &= 64 \times 10^{-4} \text{ mol/}\ell \end{aligned} \quad (2.68)$$

Understanding problems like these is often helped by always checking what happens when the system is at equilibrium.

Values of Mass Transfer Coefficients

We now turn to the variations of the overall mass transfer coefficient with quantities like the diffusion coefficient in the adjacent phases. The most common case is that of transfer from a gas into a liquid. The concentration in the gas is expressed as a partial pressure, and the concentration in the liquid is expressed as a mole fraction. The flux N_1 across the interface is then:

$$\begin{aligned} N_1 &= K_p(p_1 - p_1^*) \\ &= k_p(p_1 - p_{1i}) \\ &= k_x(x_{1i} - x_1) \end{aligned} \quad (2.69)$$

where p_1 and x_1 are the average concentrations in the gas and liquid, respectively; and p_{1i} and x_{1i} are the corresponding but unknown gas and liquid concentrations at the interface. The mass transfer coefficients k_p and k_x describe transport in the gas and in the liquid. Sensibly, the individual mass transfer coefficient k_p is a function of diffusion in the gas, but not of diffusion in the liquid; and the individual mass transfer coefficient k_x is the reverse.

The concentrations across the interface will normally be in equilibrium, so that:

$$p_{1i} = Hx_{1i} \quad (2.70)$$

where H is a Henry's Law constant. Combining this constraint with Eq. 2.69 gives:

$$N_1 = \left[\frac{1}{\frac{1}{k_p} + \frac{H}{k_x}} \right] (p_1 - Hx_1) \quad (2.71)$$

By comparing this with the overall mass transfer coefficient K_p yields:

$$K_p = \frac{1}{\frac{1}{k_p} + \frac{H}{k_x}} \quad (2.72)$$

$$p_1^* = Hx_1 \quad (2.73)$$

These are the results sought. Obviously, similar equations are possible for other concentrations and other equilibria analogous to Henry's Law.

The way in which k_p and k_x vary with the diffusion coefficients can be estimated either from experiments or from theories. The experiments are summarized as correlations, most often in terms of dimensionless numbers. For example, for mass transfer into a liquid flowing through a packed tower with packing of size d , the most widely accepted correlation is:

$$k_x = k(\text{liquid})c(\text{liquid}) \quad (2.74)$$

$$k(\text{liquid}) \left(\frac{1}{vg} \right)^{\frac{1}{3}} = 0.0051 \left(\frac{v}{av} \right)^{0.67} \left(\frac{D}{v} \right)^{0.50} (ad)^{0.4} \quad (2.75)$$

where v is the kinematic viscosity of the liquid, g is the acceleration due to gravity, v is the superficial liquid velocity, a is the surface area per volume of the packing, and D is the diffusion coefficient in the liquid. The quantity (v/av) is one form of the dimensionless Reynolds number; the quotient (v/D) is the dimensionless Schmidt number. Correlations like this, which are based on extensive experiments, should be used for estimates whenever possible.

In many cases, however, appropriate correlations may not be reliable, or may not be available at all. In these cases, estimates for liquids can be made by assuming that:

$$k(\text{liquid}) = \frac{D}{\ell} = \frac{D}{10^{-4}\text{m}} \quad (2.76)$$

where D is the diffusion coefficient in the liquid and ℓ is often called the film thickness or the boundary layer. This casual description can be confusing, because these terms are more specifically defined in theories of mass transfer. A corresponding estimate for gases is:

$$k(\text{gas}) = \frac{D}{\ell} = \frac{D}{10^{-3}\text{m}} \quad (2.77)$$

where D is now the diffusion coefficient in gases, typically 10^4 times larger than that in liquids. [Equations 2.76](#) and [2.77](#) are major approximations to be used only in desperation.

Important Special Cases

The sections above describe the mathematics of diffusion and dispersion. They have summarized characteristics of diffusion coefficients and listed some typical values. They have discussed mass transfer coefficients as an alternative description of interfacial diffusion frequently valuable in environmental engineering. None of the ideas presented are especially difficult to understand.

However, actually putting these ideas into practice can be complicated, largely because of difficult units and subtle definitions. This final section considers specific chemical examples that illustrate the ideas involved. These examples are approximate but can serve as a warning of where trouble can occur.

Overall Mass Transfer Coefficient of Oxygen (Case #1)

Imagine wanting to estimate the mass transfer coefficient K_p of oxygen from air into water. From Table 2.2 and Eq. 2.77,

$$k(\text{gas}) = \frac{D}{\ell} = \frac{2 \times 10^{-4} \text{ m}^2/\text{s}}{10^{-3} \text{ m}} = 0.02 \text{ m/s} \quad (2.78)$$

The coefficient k_p is found from this by a unit conversion:

$$k_p = \frac{k(\text{gas})}{RT} = \frac{0.02 \text{ m/s}}{\left(8.2 \times 10^{-6} \frac{\text{m}^2 \text{ atm}}{\text{mol}^\circ\text{K}}\right) 298^\circ\text{K}} = 8 \frac{\text{mol}}{\text{m}^2 \text{ s atm}} \quad (2.79)$$

Similarly, from Table 2.3 and Eq. 2.76,

$$k(\text{liquid}) = \frac{2 \times 10^{-9} \text{ m}^2/\text{s}}{10^{-4} \text{ m}} = 2 \times 10^{-5} \text{ m/s} \quad (2.80)$$

The coefficient k_x has a different conversion:

$$\begin{aligned} k_x &= k(\text{liquid})c = (2 \times 10^{-5} \text{ m/s}) \left(\frac{1 \text{ mol}}{18 \times 10^{-6} \text{ m}^3} \right) \\ &= 1.1 \frac{\text{mol}}{\text{m}^2 \text{ s}} \end{aligned} \quad (2.81)$$

Henry's Law for this system is (cf. Eq. 2.70):

$$p_1 = (4.3 \times 10^4 \text{ atm})x_1 \quad (2.82)$$

Thus from Eq. 2.72,

$$\begin{aligned}
 K_p &= \frac{1}{\frac{\text{m}^2\text{s atm}}{8 \text{ mol}} + \frac{4.3 \times 10^4 \text{ atm m}^2\text{s}}{1.1 \text{ mol}}} \\
 &= 2.6 \times 10^{-5} \frac{\text{mol}}{\text{m}^2\text{s atm}}
 \end{aligned} \tag{2.83}$$

This coefficient describes oxygen transport between air and water when the concentration difference is expressed as partial pressures of oxygen.

Overall Mass Transfer Coefficient of Oxygen (Case #2)

The example above is straightforward because it matches the detailed equations given earlier. The same problem can be solved in different units. Thus, the flux N_I is:

$$N_I = K_c(c_1^* - c_1) \tag{2.84}$$

where c_I is the actual oxygen concentration in water, c_I^* is the oxygen concentration in water that is in equilibrium with air, K_c is a different overall mass transfer coefficient given by:

$$K_c = \frac{1}{\frac{m}{k(\text{gas})} + \frac{1}{k(\text{liquid})}} \tag{2.85}$$

and m is a different form of Henry's Law constant, defined by the equilibrium:

$$c_1(\text{liquid}) = mc_1(\text{gas}) \tag{2.86}$$

Comparing Eqs. 2.81 and 2.82 gives:

$$\begin{aligned}
 m &= \frac{c(\text{liquid})RT}{H} \\
 &= \left(\frac{\text{mol}}{18 \times 10^{-6} \text{m}^3} \right) \left(8.2 \times 10^{-6} \frac{\text{m}^3 \text{ atm}}{\text{mol} \circ \text{K}} \right) \\
 &\quad \left(\frac{298^\circ \text{K}}{4.3 \times 10^{-4} \text{atm}} \right) \\
 &= 0.03
 \end{aligned} \tag{2.87}$$

The numerical value of Henry's Law constant is completely different. The combination of Eqs. 2.78, 2.80, 2.85, and 2.87 gives:

$$K_c = \frac{-1}{\frac{0.03}{0.02 \text{ m/s}} + \frac{3}{2 \times 10^{-5} \text{ m/s}}} \quad (2.88)$$

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

In both this formulation and that in [Eq. 2.83](#), diffusion in the liquid dominates the mass transfer. This is often taken as a consequence of the slower diffusion in the liquid. This is not completely true, as the next example shows.

Overall Mass Transfer Coefficient of Ammonia from Air into Water

This example illustrates how the rate at which ammonia is dissolved in water can be estimated. The individual mass transfer coefficients of ammonia are easily found:

$$k(\text{gas}) = \frac{D(\text{gas})}{\ell} = \frac{2.3 \times 10^{-5} \text{ m}^2/\text{s}}{10^{-3} \text{ m}} = 0.023 \text{ m/s} \quad (2.89)$$

and

$$k(\text{liquid}) = \frac{D(\text{liquid})}{\ell} = \frac{1.6 \times 10^{-9} \text{ m}^2/\text{s}}{10^{-4} \text{ m}} \quad (2.90)$$

$$= 1.6 \times 10^{-4} \text{ m/s}$$

One Henry's Law constant for dilute acid is given in the literature as:

$$p_1(\text{atm}) = \left(7000 \frac{\text{atm } \ell}{\text{mol}} \right) c_1(\text{liquid, molar}) \quad (2.91)$$

Converting the pressure into a molar concentration:

$$c_1(\text{gas, molar}) = \left(7000 \frac{\text{atm } \ell}{\text{mol}} \right) \left(\frac{\text{mol} \circ \text{K}}{0.082 \text{ atm } \ell} \right) \quad (2.92)$$

$$\left[\frac{c_1(\text{liquid, molar})}{298^\circ \text{K}} \right]$$

$$= 290 c_1(\text{liquid, molar})$$

Combining these results with [Eq. 2.85](#) gives:

$$K_c = \frac{1}{\frac{290}{0.023 \text{ m/s}} + \frac{1}{1.6 \times 10^{-5} \text{ m/s}}} \quad (2.93)$$

$$= 1.3 \times 10^{-4} \text{ m/s}$$

The much higher solubility of ammonia in dilute acid means the mass transfer is now more affected by diffusion in air.

Toxin Diffusion in a Biofilm

The final example imagines a dilute toxin dissolved in water and metabolized irreversibly by microorganisms immobilized in a biofilm. This example, which is not as chemically specific as the first three, also assumes that the concentration of dissolved oxygen is much greater than the concentration of the toxin. Thus, the rate per biofilm area N_1 is given by the overall rate of diffusion of the toxin to the biofilm, followed by the diffusion and reaction of the toxin within the biofilm.

This overall rate is mathematically equivalent to mass transfer across an interface, where the solute diffused through the gas to reach the interface, quickly crossed the interface, and then diffused into the liquid. In fact, the biofilm case is often easier because most biofilms are largely water and hence their partition coefficient m is one. Thus,

$$N_1 = \frac{c_1}{\frac{1}{k(\text{liquid})} + \frac{1}{k(\text{biofilm})}} \quad (2.94)$$

The coefficient k (liquid) can often be found from mass transfer correlations; [Equation 2.76](#) provides a first guess. The value in the biofilm depends on the details of the reaction. However, delightfully, most theories give the same result:

$$k(\text{biofilm}) = \left[\frac{D(\text{biofilm})}{\tau} \right]^{\frac{1}{2}} \quad (2.95)$$

where τ is the half-life of the reaction. While beyond the scope of this entry, this result is carefully derived in most books on diffusion and reaction. This result underscores the value of the simple ideas of diffusion and reaction presented here.

Future Directions

After 150 years of concentrated effort, diffusion is an established subject. Active research does continue on, for example, semiconductors and polymer membranes, but this does not have major environmental application.

Diffusion is an important tool for describing environmentally significant mass transfer. In many cases, this transfer can be described in terms of diffusion coefficients. In many air pollution problems, mass transfer can be described in

terms of dispersion, which is mathematically similar to diffusion but due to coupled diffusion and flow.

The underused description of mass transfer, especially across interfaces, is in terms of mass transfer coefficients. These are functions of diffusion coefficients and of other parameters, like velocity and viscosity. Exploiting this topic offers potential gain for environmental engineering.

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