# *Preface to the Third Edition*

Like its earlier editions, this book has two purposes. First, it presents a clear description of diffusion, the mixing process caused by molecular motion. Second, it explains mass transfer, which controls the cost of processes like chemical purification and environmental control. The first of these purposes is scientific, explaining how nature works. The second purpose is more practical, basic to the engineering of chemical processes.

While diffusion was well explained in earlier editions, this edition extends and clarifies this material. For example, the Maxwell–Stefan alternative to Fick's equation is now treated in more depth. Brownian motion and its relation to diffusion are explicitly described. Diffusion in composites, an active area of research, is reviewed. These topics are an evolution of and an improvement over the material in earlier editions.

Mass transfer is much better explained here than it was earlier. I believe that mass transfer is often poorly presented because it is described only as an analogue of heat transfer. While this analogue is true mathematically, its overemphasis can obscure the simpler physical meaning of mass transfer. In particular, this edition continues to emphasize dilute mass transfer. It gives a more complete description of differential distillation than is available in other introductory sources. This description is important because differential distillation is now more common than staged distillation, normally the only form covered. This edition gives a much better description of adsorption than has been available. It provides an introduction to mass transfer applied in biology and medicine.

The result is an engineering book which is much more readable and understandable than other books covering these subjects. It provides much more physical insight than conventional books on unit operations. It explores the interactions between mass transfer and chemical reaction, which are omitted by many books on transport phenomena. The earlier editions are good, but this one is better.

The book works well as a text either for undergraduates or graduate students. For a one-semester undergraduate chemical engineering course of perhaps 45 lectures plus recitations, I cover Chapter 2, Sections 3.1 to 3.2 and 5.1 to 5.2, Chapters 8 to 10, 12 to 15, and 21. If there is time, I add Sections 16.1 to 16.3 and Sections 17.1 to 17.3. If this course aims at describing separation processes, I cover crystallization before discussing membrane separations. We have successfully taught such a course here at Minnesota for the last 10 years.

For a one semester graduate course for students from chemistry, chemical engineering, pharmacy, and food science, I plan for 45 lectures without recitations. This course covers Chapters 2 to 9 and Chapters 16 to 19. It has been a mainstay at many universities for almost 30 years.

This description of academic courses should not restrict the book's overall goal. Diffusion and mass transfer are often interesting because they are slow. Their rate controls many processes, from the separation of air to the spread of pollutants to the size of a human sperm. The study of diffusion is thus important, but it is also fun. I hope that this book catalyzes that fun for you.

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# *Preface to Second Edition*

The purpose of this second edition is again a clear description of diffusion useful to engineers, chemists, and life scientists. Diffusion is a fascinating subject, as central to our daily lives as it is to the chemical industry. Diffusion equations describe the transport in living cells, the efficiency of distillation, and the dispersal of pollutants. Diffusion is responsible for gas absorption, for the fog formed by rain on snow, and for the dyeing of wool. Problems like these are easy to identify and fun to study.

Diffusion has the reputation of being a difficult subject, much harder than, say, fluid mechanics or solution thermodynamics. In fact, it is relatively simple. To prove this to yourself, try to explain a diffusion flux, a shear stress, and chemical potential to some friends who have little scientific training. I can easily explain a diffusion flux: It is how much diffuses per area per time. I have more trouble with a shear stress. Whether I say it is a momentum flux or the force in one direction caused by motion in a second direction, my friends look blank. I have never clearly explained chemical potentials to anyone.

However, past books on diffusion have enhanced its reputation as a difficult subject. These books fall into two distinct groups that are hard to read for different reasons. The first group is the traditional engineering text. Such texts are characterized by elaborate algebra, very complex examples, and turgid writing. Students cheerfully hate these books; moreover, they remember what they have learned as scattered topics, not an organized subject.

The second group of books consists of texts on transport processes. These books present diffusion by analogy with fluid flow and heat transfer. They are much more readable than the traditional texts, especially for the mathematically adroit. They do have two significant disadvantages. First, topics important to diffusion but not to fluid flow tend to be omitted or deemphasized. Such cases include simultaneous diffusion and chemical reaction. Second, these books usually present diffusion last, so that fluid mechanics and heat transfer must be at least superficially understood before diffusion can be learned. This approach effectively excludes students outside of engineering who have little interest in these other phenomena. Students in engineering find difficult problems emphasized because the simple ones have already been covered for heat transfer. Whether they are engineers or not, all conclude that diffusion must be difficult.

In the first edition, I tried to describe diffusion clearly and simply. I emphasized physical insight, sometimes at the loss of mathematical rigor. I discussed basic concepts in detail, without assuming prior knowledge of other phenomena. I aimed at the scope of the traditional texts and at the clarity of books on transport processes. This second edition is evidence that I was partly successful. Had I been completely successful, no second edition would be needed. Had I been unsuccessful, no second edition would be wanted.

In this second edition, I've kept the emphasis on physical insight and basic concepts, but I've expanded the book's scope. Chapters 1–7 on diffusion are largely unchanged, though some description of diffusion coefficients is abridged. Chapter 8 on mass transfer is expanded to even more detail, for I found many readers need more help. Chapters 9–12, a description of traditional chemical processes are new. The remaining seven chapters, a spectrum of topics, are either new or significantly revised. The result is still useful broadly, but deeper on engineering topics.

I have successfully used the book as a text for both undergraduate and graduate courses, of which most are in chemical engineering. For an undergraduate course on unit operations, I first review the mass transfer coefficients in Chapter 8, for I find that students' memory of these ideas is motley. I then cover the material in Chapters 9–12 in detail, for this is the core of the subject. I conclude with simultaneous heat and mass transfer, as discussed in Chapters 19–20. The resulting course of 50 classes is typical of many offered on this subject. On their own, undergraduates have used Chapters 2–3 and 8–9 for courses on heat and mass transfer, but this book's scope seems too narrow to be a good text for that class.

For graduate students, I give two courses in alternate years. Neither requires the other as a prerequisite. In the first graduate course, on diffusion, I cover Chapters 1–7, plus Chapter 17 (on membranes). In the second graduate course, on mass transfer, I cover Chapters 8–9, Chapters 13–16, and Chapter 20. These courses, which typically have about 35 lectures, are an enormous success, year after year. For nonengineering graduate students and for various short courses, I've usually used Chapters 2, 8, 15–16, and any other chapters specific to a given discipline. For example, for those in the drug industry, I might cover Chapters 11 and 18.

I am indebted to many who have encouraged me in this effort. My overwhelming debt is to my colleagues at the University of Minnesota. When I become disheartened, I need simply to visit another institution to be reminded of the advantages of frank discussion without infighting. My students have helped, especially Sameer Desai and Diane Clifton, who each read large parts of the final manuscript. Mistakes that remain are my fault. Teresa Bredahl typed most of the book, and Clover Galt provided valuable editorial help. Finally, my wife Betsy gives me a wonderful rich life.

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## CHAPTER 1

# *Models for Diffusion*

If a few crystals of a colored material like copper sulfate are placed at the bottom of a tall bottle filled with water, the color will slowly spread through the bottle. At first the color will be concentrated in the bottom of the bottle. After a day it will penetrate upward a few centimeters. After several years the solution will appear homogeneous.

The process responsible for the movement of the colored material is diffusion, the subject of this book. Diffusion is caused by random molecular motion that leads to complete mixing. It can be a slow process. In gases, diffusion progresses at a rate of about 5 cm/min; in liquids, its rate is about 0.05 cm/min; in solids, its rate may be only about 0.00001 cm/min. In general, it varies less with temperature than do many other phenomena.

This slow rate of diffusion is responsible for its importance. In many cases, diffusion occurs sequentially with other phenomena. When it is the slowest step in the sequence, it limits the overall rate of the process. For example, diffusion often limits the efficiency of commercial distillations and the rate of industrial reactions using porous catalysts. It limits the speed with which acid and base react and the speed with which the human intestine absorbs nutrients. It controls the growth of microorganisms producing penicillin, the rate of the corrosion of steel, and the release of flavor from food.

In gases and liquids, the rates of these diffusion processes can often be accelerated by agitation. For example, the copper sulfate in the tall bottle can be completely mixed in a few minutes if the solution is stirred. This accelerated mixing is not due to diffusion alone, but to the combination of diffusion and stirring. Diffusion still depends on random molecular motions that take place over smaller distances. The agitation or stirring is not a molecular process, but a macroscopic process that moves portions of the fluid over much larger distances. After this macroscopic motion, diffusion mixes newly adjacent portions of the fluid. In other cases, such as the dispersal of pollutants, the agitation of wind or water produces effects qualitatively similar to diffusion; these effects, called dispersion, will be treated separately.

The description of diffusion involves a mathematical model based on a fundamental hypothesis or “law.” Interestingly, there are two common choices for such a law. The more fundamental, Fick’s law of diffusion, uses a diffusion coefficient. This is the law that is commonly cited in descriptions of diffusion. The second, which has no formal name, involves a mass transfer coefficient, a type of reversible rate constant.

Choosing between these two models is the subject of this chapter. Choosing Fick’s law leads to descriptions common to physics, physical chemistry, and biology. These descriptions are explored and extended in Chapters 2–7. Choosing mass transfer coefficients produces correlations developed explicitly in chemical engineering and used implicitly in chemical kinetics and in medicine. These correlations are described in Chapters 8–15. Both approaches are used in Chapters 16–21.

We discuss the differences between the two models in Section 1.1 of this chapter. In Section 1.2 we show how the choice of the most appropriate model is determined.

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In Section 1.3 we conclude with additional examples to illustrate how the choice between the models is made.

## 1.1 The Two Basic Models

In this section we want to illustrate the two basic ways in which diffusion can be described. To do this, we first imagine two large bulbs connected by a long thin capillary (Fig. 1.1-1). The bulbs are at constant temperature and pressure and are of equal volumes. However, one bulb contains carbon dioxide, and the other is filled with nitrogen.

To find how fast these two gases will mix, we measure the concentration of carbon dioxide in the bulb that initially contains nitrogen. We make these measurements when only a trace of carbon dioxide has been transferred, and we find that the concentration of carbon dioxide varies linearly with time. From this, we know the amount transferred per unit time.

We want to analyze this amount transferred to determine physical properties that will be applicable not only to this experiment but also in other experiments. To do this, we first define the flux:

$$(\text{carbon dioxide flux}) = \left(\frac{\text{amount of gas removed}}{\text{time (area capillary)}}\right) \tag{1.1-1}$$

In other words, if we double the cross-sectional area, we expect the amount transported to double. Defining the flux in this way is a first step in removing the influences of our particular apparatus and making our results more general. We next assume that the flux is proportional to the gas concentration:

$$(\text{carbon dioxide flux}) = k\begin{pmatrix}\text{carbon dioxide}\\ \text{concentration}\\ \text{difference}\end{pmatrix} \tag{1.1-2}$$

The proportionality constant $k$ is called a mass transfer coefficient. Its introduction signals one of the two basic models of diffusion. Alternatively, we can recognize

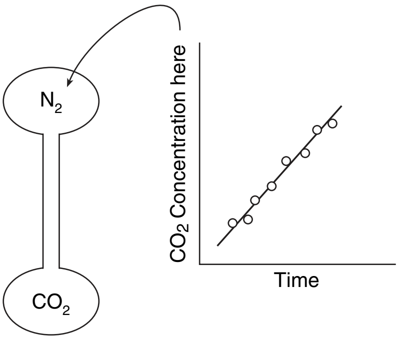

Fig. 1.1-1. A simple diffusion experiment. Two bulbs initially containing different gases are connected with a long thin capillary. The change of concentration in each bulb is a measure of diffusion and can be analyzed in two different ways.

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that increasing the capillary's length will decrease the flux, and we can then assume that

$$(\text{carbon dioxide flux}) = D\left(\frac{\text{carbon dioxide concentration difference}}{\text{capillary length}}\right) \tag{1.1-3}$$

The new proportionality constant $D$ is the diffusion coefficient. Its introduction implies the other model for diffusion, the model often called Fick's law.

These assumptions may seem arbitrary, but they are similar to those made in many other branches of science. For example, they are similar to those used in developing Ohm's law, which states that

$$\begin{pmatrix}\text{current, or}\\ \text{area times flux}\\ \text{of electrons}\end{pmatrix} = \left(\frac{1}{\text{resistance}}\right)\begin{pmatrix}\text{voltage, or}\\ \text{potential}\\ \text{difference}\end{pmatrix} \tag{1.1-4}$$

Thus, the mass transfer coefficient $k$ is analogous to the reciprocal of the resistance. An alternative form of Ohm's law is

$$\begin{pmatrix}\text{current density}\\ \text{or flux of}\\ \text{electrons}\end{pmatrix} = \left(\frac{1}{\text{resistivity}}\right)\left(\frac{\begin{matrix}\text{potential}\\ \text{difference}\end{matrix}}{\text{length}}\right) \tag{1.1-5}$$

The diffusion coefficient $D$ is analogous to the reciprocal of the resistivity.

Neither the equation using the mass transfer coefficient $k$ nor that using the diffusion coefficient $D$ is always successful. This is because of the assumptions made in their development. For example, the flux may not be proportional to the concentration difference if the capillary is very thin or if the two gases react. In the same way, Ohm's law is not always valid at very high voltages. But these cases are exceptions; both diffusion equations work well in most practical situations, just as Ohm's law does.

The parallels with Ohm's law also provide a clue about how the choice between diffusion models is made. The mass transfer coefficient in Eq. 1.1-2 and the resistance in Eq. 1.1-4 are simpler, best used for practical situations and rough measurements. The diffusion coefficient in Eq. 1.1-3 and the resistivity in Eq. 1.1-5 are more fundamental, involving physical properties like those found in handbooks. How these differences guide the choice between the two models is the subject of the next section.

## 1.2 Choosing Between the Two Models

The choice between the two models outlined in Section 1.1 represents a compromise between ambition and experimental resources. Obviously, we would like to express our results in the most general and fundamental ways possible. This suggests working with diffusion coefficients. However, in many cases, our experimental measurements will dictate a more approximate and phenomenological approach. Such approximations often imply mass transfer coefficients, but they usually still permit us to reach our research goals.

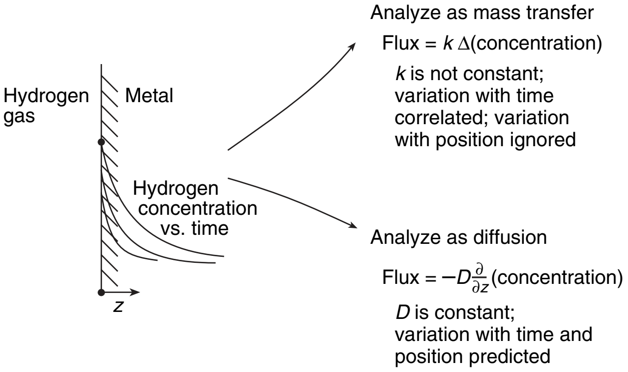

Fig. 1.2-1. Hydrogen diffusion into a metal. This process can be described with either a mass transfer coefficient $k$ or a diffusion coefficient $D$. The description with a diffusion coefficient correctly predicts the variation of concentration with position and time, and so is superior.

This choice and the resulting approximations are best illustrated by two examples. In the first, we consider hydrogen diffusion in metals. This diffusion substantially reduces a metal's ductility, so much so that parts made from the embrittled metal frequently fracture. To study this embrittlement, we might expose the metal to hydrogen under a variety of conditions and measure the degree of embrittlement versus these conditions. Such empiricism would be a reasonable first approximation, but it would quickly flood us with uncorrelated information that would be difficult to use effectively.

As an improvement, we can undertake two sets of experiments. First, we can saturate metal samples with hydrogen and determine their degrees of embrittlement. Thus we know metal properties versus hydrogen concentration. Second, we can measure hydrogen uptake versus time, as suggested in Fig. 1.2-1, and correlate our measurements as mass transfer coefficients. Thus we know average hydrogen concentration versus time.

To our dismay, the mass transfer coefficients in this case will be difficult to interpret. They are anything but constant. At zero time, they approach infinity; at large time, they approach zero. At all times, they vary with the hydrogen concentration in the gas surrounding the metal. They are an inconvenient way to summarize our results. Moreover, the mass transfer coefficients give only the *average* hydrogen concentration in the metal. They ignore the fact that the hydrogen concentration very near the metal's surface will reach saturation but the concentration deep within the metal will remain zero. As a result, the metal near the surface may be very brittle but that within may be essentially unchanged.

We can include these details in the diffusion model described in the previous section. This model assumed that

$$\begin{pmatrix}\text{hydrogen}\\ \text{flux}\end{pmatrix} = D\,\frac{\begin{pmatrix}\text{hydrogen}\\ \text{concentration at } z=0\end{pmatrix} - \begin{pmatrix}\text{hydrogen}\\ \text{concentration at } z=l\end{pmatrix}}{(\text{thickness at } z=l) - (\text{thickness at } z=0)} \tag{1.2-1}$$

or, symbolically,

$$j_1 = D\frac{c_1|_{z=0} - c_1|_{z=l}}{l-0} \tag{1.2-2}$$

where the subscript 1 symbolizes the diffusing species. In these equations, the distance $l$ is that over which diffusion occurs. In the previous section, the length of the capillary was appropriately this distance; but in this case, it seems uncertain what the distance should be. If we assume that it is very small,

$$j_1 = D\lim_{l\to 0}\frac{c_1|_{z=z} - c_1|_{z=z+l}}{z|_{z+l} - z|_z} = -D\frac{\mathrm{d}c_1}{\mathrm{d}z} \tag{1.2-3}$$

We can use this relation and the techniques developed later in this book to correlate our experiments with only one parameter, the diffusion coefficient $D$. We then can correctly predict the hydrogen uptake versus time and the hydrogen concentration in the gas. As a dividend, we get the hydrogen concentration at all positions and times within the metal.

Thus the model based on the diffusion coefficient gives results of more fundamental value than the model based on mass transfer coefficients. In mathematical terms, the diffusion model is said to have distributed parameters, for the dependent variable (the concentration) is allowed to vary with all independent variables (like position and time). In contrast, the mass transfer model is said to have lumped parameters (like the average hydrogen concentration in the metal).

These results would appear to imply that the diffusion model is superior to the mass transfer model and so should always be used. However, in many interesting cases the models are equivalent. To illustrate this, imagine that we are studying the dissolution of a solid drug suspended in water, as schematically suggested by Fig. 1.2-2. The dissolution of this drug is known to be controlled by the diffusion of the dissolved drug away from the solid surface of the undissolved material. We measure the drug concentration versus time as shown, and we want to correlate these results in terms of as few parameters as possible.

One way to correlate the dissolution results is to use a mass transfer coefficient. To do this, we write a mass balance on the solution:

$$\begin{pmatrix}\text{accumulation}\\ \text{of drug in}\\ \text{solution}\end{pmatrix} = \begin{pmatrix}\text{total rate of}\\ \text{dissolution}\end{pmatrix}$$

$$\begin{aligned} V\frac{\mathrm{d}c_1}{\mathrm{d}t} &= Aj_1 \\ &= Ak[c_1(\text{sat}) - c_1] \end{aligned} \tag{1.2-4}$$

where $V$ is the volume of solution, $A$ is the total area of the drug particles, $c_1(\text{sat})$ is the drug concentration at saturation and at the solid's surface, and $c_1$ is the concentration in the bulk solution. Integrating this equation allows quantitatively fitting our results with one parameter, the mass transfer coefficient $k$. This quantity is independent of drug solubility, drug area, and solution volume, but it does vary with physical properties like stirring rate and solution viscosity. Correlating the effects of these properties turns out to be straightforward.

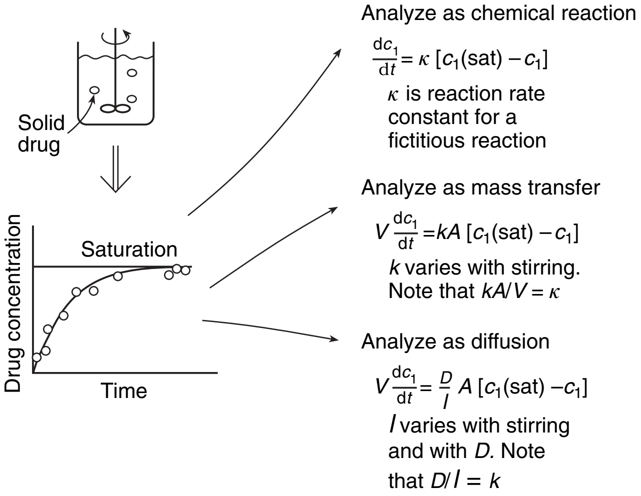

Fig. 1.2-2. Rates of drug dissolution. In this case, describing the system with a mass transfer coefficient $k$ is best because it easily correlates the solution's concentration versus time. Describing the system with a diffusion coefficient $D$ gives a similar correlation but introduces an unnecessary parameter, the film thickness $l$. Describing the system with a reaction rate constant $k$ also works, but this rate constant is a function not of chemistry but of physics.

The alternative to mass transfer is diffusion theory, for which the mass balance is

$$V\frac{dc_1}{dt} = A\left(\frac{D}{l}\right)[c_1(\text{sat}) - c_1] \tag{1.2-5}$$

in which $l$ is an unknown parameter, equal to the average distance across which diffusion occurs. This unknown, called a film or unstirred layer thickness, is a function not only of flow and viscosity but also of the diffusion coefficient itself.

Equations 1.2-4 and 1.2-5 are equivalent, and they share the same successes and shortcomings. In the former, we must determine the mass transfer coefficient experimentally; in the latter, we determine instead the thickness $l$. Those who like a scientific veneer prefer to measure $l$, for it genuflects toward Fick's law of diffusion. Those who are more pragmatic prefer explicitly recognizing the empirical nature of the mass transfer coefficient.

The choice between the mass transfer and diffusion models is thus often a question of taste rather than precision. The diffusion model is more fundamental and is appropriate when concentrations are measured or needed versus both position and time. The mass transfer model is simpler and more approximate and is especially useful when only average concentrations are involved. The additional examples in section 1.3 should help us decide which model is appropriate for our purposes.

Before going on to the next section, we should mention a third way to correlate the results other than the two diffusion models. This third way is to assume that the dissolution shown in Fig. 1.2-2 is a first-order, reversible chemical reaction. Such a reaction might be described by

$$\frac{dc_1}{dt} = \kappa c_1(\text{sat}) - \kappa c_1 \tag{1.2-6}$$

In this equation, the quantity $\kappa c_1(\text{sat})$ represents the rate of dissolution, $\kappa c_1$ stands for the rate of precipitation, and $\kappa$ is a rate constant for this process. This equation is mathematically identical with Eqs. 1.2-4 and 1.2-5 and so is equally successful. However, the idea of treating dissolution as a chemical reaction is flawed. Because the reaction is hypothetical, the rate constant is a composite of physical factors rather than chemical factors. We do better to consider the physical process in terms of a diffusion or mass transfer model.

## 1.3 Examples

In this section, we give examples that illustrate the choice between diffusion coefficients and mass transfer coefficients. This choice is often difficult, a juncture where many have trouble. I often do. I think my trouble comes from evolving research goals, from the fact that as I understand the problem better, the questions that I am trying to answer tend to change. I notice the same evolution in my peers, who routinely start work with one model and switch to the other model before the end of their research.

We shall not solve the following examples. Instead, we want only to discuss which diffusion model we would initially use for their solution. The examples given certainly do not cover all types of diffusion problems, but they are among those about which I have been asked in the last year.

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**Example 1.3-1: Ammonia scrubbing** Ammonia, the major material for fertilizer, is made by reacting nitrogen and hydrogen under pressure. The product gas can be washed with water to dissolve the ammonia and separate it from other unreacted gases. How can you correlate the dissolution rate of ammonia during washing?

***Solution*** The easiest way is to use mass transfer coefficients. If you use diffusion coefficients, you must somehow specify the distance across which diffusion occurs. This distance is unknown unless the detailed flows of gases and the water are known; they rarely are (see Chapters 8 and 9).

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**Example 1.3-2: Reactions in porous catalysts** Many industrial reactions use catalysts containing small amounts of noble metals dispersed in a porous inert material like silica. The reactions on such a catalyst are sometimes slower in large pellets than in small ones. This is because the reagents take longer to diffuse into the pellet than they do to react. How should you model this effect?

***Solution*** You should use diffusion coefficients to describe the simultaneous diffusion and reaction in the pores in the catalyst. You should not use mass transfer coefficients because you cannot easily include the effect of reaction (see Sections 16.1 and 17.1).

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**Example 1.3-3: Corrosion of marble** Industrial pollutants in urban areas like Venice cause significant corrosion of marble statues. You want to study how these pollutants penetrate marble. Which diffusion model should you use?

***Solution*** The model using diffusion coefficients is the only one that will allow you to predict pollutant concentration versus position in the marble. The model using