The flux of protein at the surface $z = 0$ is

$$N_{iz}(z = 0) = \sqrt{\frac{D_{ij}}{\pi t}}C_0. \tag{6.8.27}$$

If the process is diffusion limited, then the rate of adsorption equals the flux at the surface:

$$\frac{dC_{ads}}{dt} = N_{iz}(z = 0). \tag{6.8.28}$$

The adsorbed concentration C_{ads} is in units of mass per unit area. Substituting Equation (6.8.27) into Equation (6.8.28) and integrating gives the surface concentration as a function of time for diffusion-limited adsorption:

$$C_{ads} = 2C_0\sqrt{\frac{D_{ij}t}{\pi}}. \tag{6.8.29}$$

The amount adsorbed thus increases with the square root of the product of the diffusion coefficient and time.

Equation (6.8.29) has been used to identify the major proteins in blood that adsorb to surfaces. According to that equation, the larger $C_0\sqrt{D_{ij}}$ is, the more the protein adsorbs to a surface. Values of $C_0\sqrt{D_{ij}}$ are tabulated in Table 6.7. The data indicate that diffusion-limited kinetics favor albumin adsorption.

The kinetics of protein adsorption are diffusion limited only during the first few minutes of adsorption. At later times, adsorption is dominated by the affinity of a particular molecule for the surface. For all concentrations, the first minute or two are dominated by diffusion-limited kinetics. At low plasma dilutions (0.25%), the amount of fibrinogen adsorbed increases monotonically, suggesting that the surface is incompletely covered and that a number of different molecules can adsorb. As the plasma concentration increases, however, proteins cover the surface completely. As a result, a weakly adsorbing protein such as fibrinogen is displaced by a protein with a higher affinity. This effect is more pronounced with less dilute plasma concentrations.

TABLE 6.7

Major Plasma Proteins Involved in Diffusion-Limited Adsorption (from [21])

Protein	Concentration C_0, mg ml^{-1}	Molecular weight	$D_{ij} \times 10^7$ cm^2 s^{-1}	$C_0\sqrt{D_{ij}} \times 10^7$, M cm s$^{-\frac{1}{2}}$
Albumin	40	66,000	6.1	4.73
IgG	8–17	150,000	4.0	0.38–0.72
LDL	4	2,000,000	2.0	0.0089
HDL	3	170,000	4.6	0.12
α-macro-globulin	2.7	725,000	2.4	0.018
Fibrinogen	2–3	340,000	2.0	0.026–0.039
Transferrin	2.3	77,000	5.0	0.21
α-antitrypsin	2	54,000	5.2	0.27
Haptoglobins	2	100,000	4.7	0.14
C3	1.6	180,000	4.5	0.060
IgA	1–4	150,000	4.0	0.042–0.17

6.8.2 One-Dimensional Unsteady Diffusion in a Finite Medium

Diffusion in a semi-infinite medium leads to an analytical solution that is valid for values of time that are less than or equal to those listed in Equation (6.8.24). However, we seek a result that describes diffusion in a finite medium and is valid until a steady state is reached. Three cases are considered in this section: unsteady diffusion in rectangular coordinates, spherical coordinates, and unsteady diffusion from a point source.

Unsteady Diffusion in Rectangular Coordinates. In this case, a rectangular slab of thickness $2L$ contains a diffusing material at a concentration C_0. At time zero, the surfaces at $y = L$ and $y = -L$ are raised to a concentration C_1. We want to find the concentration within the slab as a function of time and position. Reaction and convection do not occur.

The conservation of mass for one-dimensional unsteady diffusion is

$$\frac{\partial C_i}{\partial t} = D_{ij}\frac{\partial^2 C_i}{\partial y^2}. \tag{6.8.30}$$

The boundary conditions are as follows:

$$-L \le y \le L \quad t \le 0 \quad C_i = C_0, \tag{6.8.31a}$$

$$y = 0 \quad t \ge 0 \quad \frac{\partial C_i}{\partial y} = 0, \tag{6.8.31b}$$

$$y = \pm L \quad t \ge 0 \quad C_i = C_1. \tag{6.8.31c}$$

Note that the boundary condition at the center of the slab, $y = 0$, is a symmetry condition because both sides of the domain are identical. Thus, it is necessary to solve the problem over only one-half of the domain, $0 \le y \le L$. The solution to this problem can be generalized by casting the problem in a dimensionless form. The following dimensionless variables are used:

$$\eta = \frac{y}{L} \quad \theta = \frac{C_i - C_0}{C_1 - C_0} \quad \tau = \frac{tD_{ij}}{L^2}.$$

The dimensionless concentration θ is defined such that it varies from zero in the center to unity at the surface $y = L$. Recalling that we need to solve the problem over only half of the region, we can restate Equation (6.8.30) and the associated boundary conditions as

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial \eta^2}, \tag{6.8.32}$$

$$0 \le \eta \le 1 \qquad \tau \le 0 \qquad \theta = 0, \tag{6.8.33a}$$

$$\eta = 0 \qquad \tau \ge 0 \qquad \frac{\partial \theta}{\partial \eta} = 0, \tag{6.8.33b}$$

and

$$\eta = 1 \qquad \tau \ge 0 \qquad \theta = 1. \tag{6.8.33c}$$

To apply separation of variables, both boundary conditions need to be homogeneous. They can be made so with the following transformation:

$$\theta'(\eta, \tau) = 1 - \theta(\eta, \tau). \tag{6.8.34}$$

-Equations (6.8.32) and (6.8.33) now become

$$\frac{\partial \theta'}{\partial \tau} = \frac{\partial^2 \theta'}{\partial \eta^2}. \tag{6.8.35}$$

The boundary conditions are

$$0 \le \eta \le 1 \qquad \tau \le 0 \qquad \theta' = 1, \tag{6.8.36a}$$

$$\eta = 0 \qquad \tau \ge 0 \qquad \frac{\partial \theta'}{\partial \eta} = 0, \tag{6.8.36b}$$

and

$$\eta = 1 \qquad \tau \ge 0 \qquad \theta' = 0. \tag{6.8.36c}$$

Equation (6.8.35) and the associated initial and boundary conditions can now be solved by the method of separation of variables. (See Section A.2 of the Appendix.) Assume a solution of the form $\theta'(\eta, \tau) = X(\eta)T(\tau)$. Substituting this solution into Equation (6.8.35) and rearranging terms yields

$$\frac{1}{T}\frac{dT}{d\tau} = \frac{1}{X}\frac{d^2X}{d\eta^2}. \tag{6.8.37}$$

The left-hand side of Equation (6.8.37) is a function of τ only, and the right-hand side is a function of η only. This can be true if and only if each side equals a constant $\pm\lambda^2$. To ensure that a characteristic-value problem results, the sign of λ^2 is chosen such that

$$\frac{d^2X}{d\eta^2} = -\lambda^2 X \qquad \frac{dT}{d\tau} = -\lambda^2 T. \tag{6.8.38a,b}$$

The negative sign ensures that T decreases with time. If the sign were positive, the concentration would increase without limit. The solutions of these two equations are

$$\theta' = XT = (A\sin(\lambda\eta) + B\cos(\lambda\eta))\exp(-\lambda^2\tau). \tag{6.8.39}$$

Applying the boundary condition at zero yields

$$\left.\frac{\partial \theta'}{\partial \eta}\right|_{\eta=0} = 0 = \lambda(A\cos(\lambda\eta) - B\sin(\lambda\eta))\exp(-\lambda^2\tau)\Big|_{\eta=0}. \tag{6.8.40}$$

For $\eta = 0$, the sine term is zero, but the cosine term is unity. Therefore, A must equal zero to satisfy this boundary condition. Equation (6.8.40) reduces to

$$\theta' = B\cos(\lambda\eta)\exp(-\lambda^2\tau). \tag{6.8.41}$$

At $\eta = 1$, $\theta' = 0$. If B were to equal zero, then the result would be trivial: the concentration would not change. We know that this is not the case. Alternatively, the cosine term is zero when λ is $\pi/2$, $3\pi/2$, $5\pi/2$, and so on. This condition can be written as

$$\lambda = (n + 1/2)\pi \qquad n = 0, 1, 2, 3 \ldots. \tag{6.8.42}$$

Substituting Equation (6.8.42) into the expression for θ [Equation (6.8.41)] and summing over all values of n yields

$$\theta' = \sum_{n=0}^{\infty} B_n \cos[(n + 1/2)\pi\eta]\exp(-(n + 1/2)^2\pi^2\tau). \tag{6.8.43}$$

The terms B_n are evaluated from the initial condition and the orthogonality relations for the cosine function over the domain [0, 1]. At time $\tau = 0$,

$$1 = \sum_{n=0}^{\infty} B_n \cos[(n + 1/2)\pi\eta]. \tag{6.8.44}$$

The orthogonality condition is obtained by multiplying both sides by $\cos[(m + 1/2)\pi\eta]$ and integrating from $\eta = 0$ to $\eta = 1$.

The result is

$$\int_0^1 \cos[(m + 1/2)\pi\eta]\,d\eta = \sum_{n=0}^{\infty} B_n \int_0^1 \cos[(m + 1/2)\pi\eta]\cos[(m + 1/2)\pi\eta]\,d\eta. \tag{6.8.45}$$

The right-hand side of Equation (6.8.45) is nonzero only when $m = n$. Performing the integrations leads to the following values for B_n:

$$B_n = \frac{2(-1)^n}{(n + 1/2)\pi}. \tag{6.8.46}$$

The final result for θ is

$$\theta = 1 - \theta' = 1 - 2\sum_{n=0}^{\infty} \frac{(-1)^n}{(n + 1/2)\pi}\cos[(n + 1/2)\pi\eta]\exp(-(n + 1/2)^2\pi^2\tau). \tag{6.8.47}$$

The most convenient way to present this result is in graphical form. Shown in Figure 6.19 is the solution for rectangular coordinates. Note that the time for the concentration at $y = 0$ to reach 99% of the final concentration is approximately $2L^2/D_{ij}$, which justifies the use of this quantity as the characteristic diffusion time.