When the system is strongly mass-transfer limited, $[S_s] \approx 0$, since the reaction is rapid compared to mass transfer, and

$$v \approx k_L[S_b], \qquad (\text{for Da} >> 1) \tag{3.54}$$

and the system behaves as pseudo first order.

When the system is reaction limited (Da << 1), the reaction rate is often expressed as

$$v = \frac{V'_m [S_b]}{K_{m,\text{app}} + [S_b]} \tag{3.55a}$$

where, with appropriate assumptions,

$$K_{m,\text{app}} = K_m \left\{ 1 + \frac{V'_m}{k_L([S_b] + K_m)} \right\} \tag{3.55b}$$

Under these circumstances, the apparent Michaelis–Menten "constant" is a function of stirring speed. Usually, $K_{m,\text{app}}$ is estimated experimentally as the value of $[S_b]$, giving one-half of the maximal reaction rate.

Example 3.4

Consider a system where a flat sheet of polymer coated with enzyme is placed in a stirred beaker. The intrinsic maximum reaction rate (V_m) of the enzyme is 6×10^{-6} mol/s-mg enzyme. The amount of enzyme bound to the surface has been determined to be 1×10^{-4} mg enzyme/cm^2 of support. In solution, the value of K_m has been determined to be 2×10^{-3} mol/l. The mass-transfer coefficient can be estimated from standard correlations for stirred vessels. We assume in this case a very poorly mixed system where $k_L = 4.3 \times 10^{-5}$ cm/s. What is the reaction rate when (a) the bulk concentration of the substrate is 7×10^{-3} mol/l? (b) $S_b = 1 \times 10^{-2}$ mol/l?

Solution The solution is given in Fig. 3.18. The key is to note that the mass-transfer rate equals the reaction rate at steady state, and as a consequence the right side of eq. 3.53 must equal the left side. In case (a), this occurs at a substrate surface concentration of about 0.0015 mol/l with a reaction rate of 2.3×10^{-10} mol/s-cm^2. By increasing the bulk substrate concentration to 0.01 mol/l, the value of $[S_s]$ increases to 0.0024 mol/l with a reaction rate about 3.3×10^{-10} mol/s-cm^2.

3.4.2.2. Diffusion effects in enzymes immobilized in a porous matrix. When enzymes are immobilized on internal pore surfaces of a porous matrix, substrate diffuses through the tortuous pathway among pores and reacts with enzyme immobilized on pore surfaces. Diffusion and reaction are simultaneous in this case, as depicted in Fig. 3.19.

Assume that enzyme is uniformly distributed in a spherical support particle; the reaction kinetics are expressed by Michaelis–Menten kinetics, and there is no partitioning of the substrate between the exterior and interior of the support. Then we write the following equation, stating that diffusion rate is equal to reaction rate at steady state: