Heterogeneous catalysis with external mass transfer resistance (no substrate inhibition).

Instructor: Nam Sun Wang

The first equation characterizes mass transfer:

- **mass transfer coefficient:** \( k_L := 1 \) cm/sec
- **bulk substrate concentration:** \( s_b := 1 \) mg/cm\(^3\) = g/liter
- **mass flux:** \( J(s) := k_L (s_b - s) \) mg/cm\(^2\)-sec

The second equation characterizes reaction:

- **rate constants:** \( v_m := 1 \) mg/cm\(^2\)-sec, \( K_m := 1 \) mg/cm\(^3\), \( K_i := 0 \) cm\(^3\)/mg
- **rate of reaction:** \( v(s) := \frac{v_m s}{K_m s + K_i s^2} \)

At steady state, the rate of substrate flux equals the rate of reaction (i.e., the intersection of two curves in the following plot).

\[ s := 0, 0.01 \cdot s_b \ldots s_b \]

The numerical solution is found with an initial guess of \( s := 0 \)

\[ s := \text{root}(J(s) - v(s), s) \]

The substrate concentration at the reaction site (surface) is: \( s = 0.618 \)

**Effectiveness factor:** \( \eta := \frac{\text{actual rate}}{\text{rate without mass transfer resistance}} \)

\[ \eta := \frac{v(s)}{v(s_b)} \]

Thus, mass transfer resistance reduces the rate of reaction by a factor of \( \eta = 0.764 \).
Generate Effectiveness Factor versus Damkohler plot by varying $v_m$.

Vary kinetic rate constant to achieve different Damkohler number.

$$v_m := 0.1, 0.2 \ldots 100$$

Redefine $v$ so that $v_m$ is a parameter that can be varied.

$$v(s, v_m) := \frac{v_m \cdot s}{K_m + s + K_i \cdot s^2}$$

Redefine $J$ so that $s_b$ and $k_L$ are parameters that can be varied.

The substrate concentration at the reaction site (surface) is $s$. A numerical solution is found with an initial guess of $s := 0$

Given

$$J(s, s_b, k_L) := k_L \cdot (s_b - s)$$

Effectiveness factor:

$$\eta(v_m) := \frac{v(s, v_m)}{v(s_b, v_m)}$$

Thus, mass transfer resistance reduces the rate of reaction by a factor of $\eta$.
**Apparent Reaction Rate.** Vary substrate concentration and mass transfer coefficient to see how the observed reaction rate changes.

\[ v_m := 1 \quad s_b := 0, 0.1 \ldots 200 \]

Redefine \( s \) so that \( s_b \) and \( k_L \) are parameters that can be varied, with an initial guess of \( s := 0 \)

Given \( J(s, s_b, k_L) = v(s, v_m) \) \( s(s_b, k_L) := \text{Find}(s) \)

Mass transfer resistance increases the apparent value of \( K_m \) but does not affect the apparent value of \( v_m \). Thus, this is similar to competitive inhibition, where the apparent value of \( K_m \) is affected but the apparent value of \( v_m \) is unaffected.
Approximate mass transfer effect with a Michaelis-Menten form. We often like to express observed (apparent) reaction rate as a Michaelis-Menten-like function of the substrate concentration in the bulk that we can readily measure with a sample grabber. Find the value of $s_b$ when $v$ is half of $v_m$; this gives the apparent value of $K_m$ when $v$ is expressed as a function of $s_b$. Since Michaelis-Menten expression itself is an approximation, this approximation represents a quick engineering short-cut. Reactor calculation is simplified with this model.

$$k_L := 0.2 \quad v_m := 1$$

For clearer notation (to emphasize $s$ being a function of $s_b$ when other parameters are kept constant), redefine $s$ as a function of $s_b$, with an initial guess of $s := 0$

Given $J(s, s_b, k_L) = v(s, v_m)$, $s(s_b) := \text{Find}(s)$

$s_{b, \text{half}} := 1$ ... initial guess

Given $v(s(s_{b, \text{half}}), v_m) = 0.5 v_m$ $s_{b, \text{half}} := \text{Find}(s_{b, \text{half}})$

$s_{b, \text{half}} = 3.5$ $K_{m, \text{app}} := s_{b, \text{half}}$ $v_{m, \text{mm}}(s_b) := \frac{v_m s_b}{K_{m, \text{app}} + s_b}$

If a given problem falls within a given substrate range, we can refine the Michaelis-Menten-like approximation by adjusting the apparent value of $v_m$ as well.

$$v_{m, \text{app}} := 1.1 v_m$$

$v_{m, \text{mm}}(s_b) := \frac{v_{m, \text{app}} s_b}{K_{m, \text{app}} + s_b}$