Heterogeneous catalysis with external mass transfer resistance (Damkohler Effectiveness Plot)
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The first equation characterizes mass transfer:

mass flux: $J(s, k_l, s_b) := k_l \cdot (s_b - s)$

The second equation characterizes reaction:

rate constants: $K_i := 0$

rate of reaction: $v(s, v_m, K_m) := \dfrac{v_m \cdot s}{K_m + s + K_i \cdot s^2}$

At, steady state, the rate of substrate flux equals the rate of reaction. (Utilize |Math|Smartmath| to find a closed analytical solution. With K_i, the highest order term equivalent to the cubic term, equal to a non-zero value, MathCAD fails to find an analytical solution.)

Given $J(s, k_l, s_b) = v(s, v_m, K_m)$

$$\text{Find}(s) \rightarrow \left[\frac{-1}{(2 \cdot k_l)} \cdot \left(-k_l \cdot s_b + k_l \cdot K_m + v_m + \sqrt{k_l^2 \cdot s_b^2 + 2 \cdot k_l^2 \cdot s_b \cdot K_m - 2 \cdot k_l \cdot s_b \cdot v_m + k_l^2 \cdot K_m^2 + 2 \cdot k_l \cdot K_m \cdot v_m + v_m^2} \right) \right.$$

The substrate concentration, which is a function of various kinetic and transport parameters, is formulated by copying the above formula (only one of them, the 2nd solution, is valid) and split among two lines.

$$s(s_b, k_l, v_m, K_m) := \frac{-1}{(2 \cdot k_l)} \cdot \left(-k_l \cdot s_b + k_l \cdot K_m + v_m \cdots \atop + -\sqrt{k_l^2 \cdot s_b^2 + 2 \cdot k_l^2 \cdot s_b \cdot K_m - 2 \cdot k_l \cdot s_b \cdot v_m + k_l^2 \cdot K_m^2 + 2 \cdot k_l \cdot K_m \cdot v_m + v_m^2} \right)$$

After further manual simplifying,

$$s(s_b, k_l, v_m, K_m) := \frac{s_b}{2} \cdot \left[1 - \frac{K_m}{s_b} - \frac{v_m}{k_l \cdot s_b} + \sqrt{\left(1 + \frac{K_m}{s_b} - \frac{v_m}{k_l \cdot s_b}\right)^2 + 4 \cdot \frac{K_m \cdot v_m}{k_l \cdot s_b^2}} \right]$$

Effectiveness factor:

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

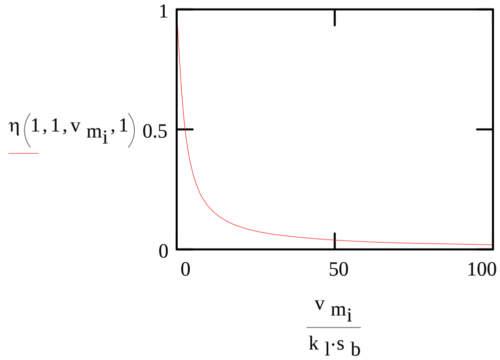
An example: $s_b := 1$ $k_l := 1$ $v_m := 1$ $K_m := 1$

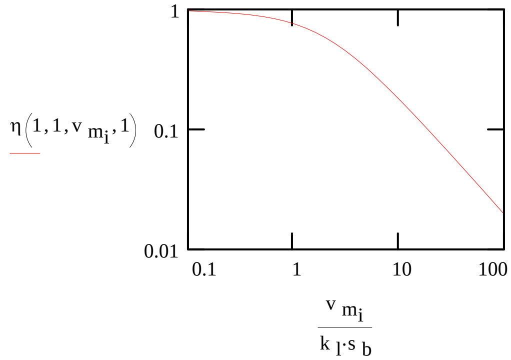
The substrate concentration at the reaction site (surface) is: $s(s_b, k_l, v_m, K_m) = 0.618$

Mass transfer resistance reduces the rate of reaction by a factor of $\eta(s_b, k_l, v_m, K_m) = 0.764$

Vary kinetic rate constant to achieve different Damkohler number.

$i := 1 .. 1000 \qquad v_{m_i} := 0.1 \cdot i$





Derive analytically the dependence of reaction rate on s_b and k_l.

Start with the flux and reaction balance equation.

$$k_l\cdot\left(s_b - s\right) = \frac{v_m\cdot s}{K_m + s}$$

Mark s above and choose |Symbolic|Solve for Variable| yields:

$$\begin{bmatrix} \dfrac{-1}{\left(2\cdot k_l\right)}\cdot\left(-k_l\cdot s_b + k_l\cdot K_m + v_m + \sqrt{k_l^2\cdot s_b^2 + 2\cdot k_l^2\cdot s_b\cdot K_m - 2\cdot k_l\cdot s_b\cdot v_m + k_l^2\cdot K_m^2 + 2\cdot k_l\cdot K_m\cdot v_m + v_m^2}\right) \\ \dfrac{-1}{\left(2\cdot k_l\right)}\cdot\left(-k_l\cdot s_b + k_l\cdot K_m + v_m - \sqrt{k_l^2\cdot s_b^2 + 2\cdot k_l^2\cdot s_b\cdot K_m - 2\cdot k_l\cdot s_b\cdot v_m + k_l^2\cdot K_m^2 + 2\cdot k_l\cdot K_m\cdot v_m + v_m^2}\right) \end{bmatrix}$$

Find rate v as a function of the substrate concentration in the bulk phase s_b. We substitute the expression for s into the rate equation.

$$v = \frac{v_m\cdot s}{K_m + s}$$

Copying the expression for s (which is the second element above), marking s in the last equation and choose |Symbolic|Substitute for Variable| yields:

$$v = \frac{-1}{2}\cdot\frac{v_m}{k_l}\cdot\frac{-k_l\cdot s_b + k_l\cdot K_m + v_m - \sqrt{k_l^2\cdot s_b^2 + 2\cdot k_l^2\cdot s_b\cdot K_m - 2\cdot k_l\cdot s_b\cdot v_m + k_l^2\cdot K_m^2 + 2\cdot k_l\cdot K_m\cdot v_m + v_m^2}}{K_m - \frac{1}{\left(2\cdot k_l\right)}\cdot\left(-k_l\cdot s_b + k_l\cdot K_m + v_m - \sqrt{k_l^2\cdot s_b^2 + 2\cdot k_l^2\cdot s_b\cdot K_m - 2\cdot k_l\cdot s_b\cdot v_m + k_l^2\cdot K_m^2 + 2\cdot k_l\cdot K_m\cdot v_m +}\right.}$$

Choose |Symbolic|Simplify| yields:

$$v = v_m\cdot\frac{k_l\cdot s_b - k_l\cdot K_m - v_m + \sqrt{k_l^2\cdot s_b^2 + 2\cdot k_l^2\cdot s_b\cdot K_m - 2\cdot k_l\cdot s_b\cdot v_m + k_l^2\cdot K_m^2 + 2\cdot k_l\cdot K_m\cdot v_m + v_m^2}}{k_l\cdot K_m + k_l\cdot s_b - v_m + \sqrt{k_l^2\cdot s_b^2 + 2\cdot k_l^2\cdot s_b\cdot K_m - 2\cdot k_l\cdot s_b\cdot v_m + k_l^2\cdot K_m^2 + 2\cdot k_l\cdot K_m\cdot v_m + v_m^2}}$$

Further manual simplifying yields,

$$v = v_m\cdot\frac{k_l\cdot s_b - k_l\cdot K_m - v_m + \alpha}{k_l\cdot s_b + k_l\cdot K_m - v_m + \alpha} \qquad \text{where} \qquad \alpha^2 = \left(k_l\cdot s_b + k_l\cdot K_m - v_m\right)^2 + 4\cdot k_l\cdot K_m\cdot v_m$$

Since the above equation remains fairly complicated, let us substitute s into the **mass flux equation**. Both approach should yield the same answer.

$$v = k_l \cdot (s_b - s)$$

Copying the expression for s, marking s in the last equation and choose |Symbolic|Substitute for Variable| yields:

$$v = k_l \cdot \left[s_b + \frac{1}{(2 \cdot k_l)} \cdot \left(-k_l \cdot s_b + k_l \cdot K_m + v_m - \sqrt{k_l^2 \cdot s_b^2 + 2 \cdot k_l^2 \cdot s_b \cdot K_m - 2 \cdot k_l \cdot s_b \cdot v_m + k_l^2 \cdot K_m^2 + 2 \cdot k_l \cdot K_m \cdot v_m + v_m^2} \right. \right.$$

Choose |Symbolic|Simplify| yields:

$$v = \frac{1}{2} \cdot \left(k_l \cdot s_b + k_l \cdot K_m + v_m - \sqrt{k_l^2 \cdot s_b^2 + 2 \cdot k_l^2 \cdot s_b \cdot K_m - 2 \cdot k_l \cdot s_b \cdot v_m + k_l^2 \cdot K_m^2 + 2 \cdot k_l \cdot K_m \cdot v_m + v_m^2} \right)$$

Further manual simplifying yields,

$$v = \frac{1}{2} \cdot \left(k_l \cdot s_b + k_l \cdot K_m + v_m - \alpha \right)$$

Find the apparent value of v_m.

As $s_b \rightarrow \infty$, we have:

$$\lim_{s_b \to \infty} v_m \cdot \frac{k_l \cdot s_b - k_l \cdot K_m - v_m + \sqrt{(k_l \cdot s_b + k_l \cdot K_m - v_m)^2 + 4 \cdot k_l \cdot K_m \cdot v_m}}{k_l \cdot s_b + k_l \cdot K_m - v_m + \sqrt{(k_l \cdot s_b + k_l \cdot K_m - v_m)^2 + 4 \cdot k_l \cdot K_m \cdot v_m}}$$

Choose |Symbolic|Evaluate|Evaluate Symbolically| or |Symbolic|Simplify| yields:

$$\lim_{s_b \to \infty} v = v_m$$

With the second equation, we have:

$$\lim_{s_b \to \infty} \frac{1}{2} \cdot \left[(k_l \cdot s_b + k_l \cdot K_m + v_m) - \sqrt{(k_l \cdot s_b + k_l \cdot K_m - v_m)^2 + 4 \cdot k_l \cdot K_m \cdot v_m} \right]$$

$$\lim_{s_b \to \infty} v = v_m$$

Find the apparent Michaelis-Menten constant K_{mapp} when $v=v_m/2$.

$$\frac{v_m}{2} = \frac{1}{2} \cdot \left[k_l \cdot s_b + k_l \cdot K_m + v_m - \sqrt{(k_l \cdot s_b + k_l \cdot K_m - v_m)^2 + 4 \cdot k_l \cdot K_m \cdot v_m} \right]$$

Mark s_b, and choose |Symbolic|Solve for Variable| yields the value of s_b at $v_m/2$:

$$K_{mapp} = \frac{1}{2} \cdot \frac{(v_m + 2 \cdot k_l \cdot K_m)}{k_l} = \frac{v_m}{2 \cdot k_l} + K_m$$ ← K_m increases as k_l decreases.

In summary, since v_m is unchanged and K_m increases, the effect is **similar to competitive inhibition**.

Plot reaction rate as a function of the substrate concentration in the bulk solution for the following rate parameters.

$$v_m := 1 \qquad K_m := 1$$

Based on v_m as $s \rightarrow \infty$ and based on the value of s at $v_m/2$, the Michaelis-Menten approximation to the rate expression in the presence of mass transfer resistance is:

$$K_{mapp}(k_l) := \frac{v_m}{2 \cdot k_l} + K_m \qquad v_{mm}(s_b, k_l) := \frac{v_m \cdot s_b}{K_{mapp}(k_l) + s_b}$$

Rate from the reaction equation gives:

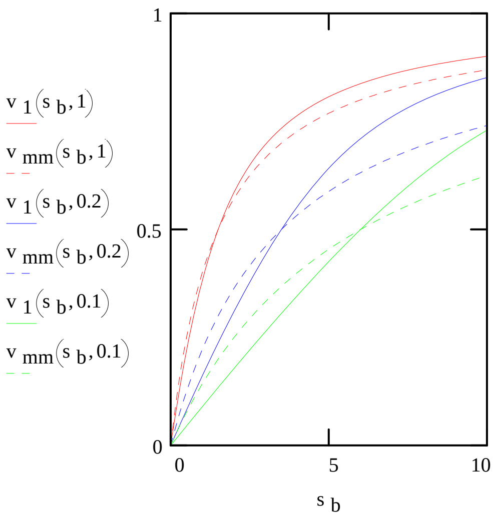
$$\alpha(s_b, k_l) := \sqrt{(k_l \cdot s_b + k_l \cdot K_m - v_m)^2 + 4 \cdot k_l \cdot K_m \cdot v_m}$$

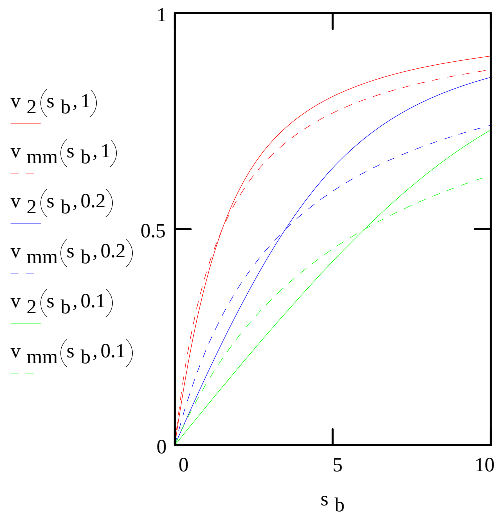
$$v_1(s_b, k_l) := v_m \cdot \frac{k_l \cdot s_b - k_l \cdot K_m - v_m + \alpha(s_b, k_l)}{k_l \cdot s_b + k_l \cdot K_m - v_m + \alpha(s_b, k_l)}$$

Rate from the mass transfer equation gives:

$$v_2(s_b, k_l) := \frac{1}{2} \cdot (k_l \cdot s_b + k_l \cdot K_m + v_m - \alpha(s_b, k_l))$$

Plot reaction rate versus s_b over $s_b := 0, 0.1 .. 10$





Solid Line: Rate /w mass transfer resistance.
Dotted Line: Michaelis-Menten approximation.

Effectiveness factor

$$\eta = \frac{v(s)}{v(s_b)} = \frac{v_m \cdot \frac{k_l \cdot s_b - k_l \cdot K_m - v_m + \sqrt{(k_l \cdot s_b + k_l \cdot K_m - v_m)^2 + 4 \cdot k_l \cdot K_m \cdot v_m}}{k_l \cdot s_b + k_l \cdot K_m - v_m + \sqrt{(k_l \cdot s_b + k_l \cdot K_m - v_m)^2 + 4 \cdot k_l \cdot K_m \cdot v_m}}}{\frac{v_m \cdot s_b}{K_m + s_b}}$$

Simplifying yields,

$$\eta = \frac{K_m + s_b}{s_b} \cdot \frac{k_l \cdot s_b - k_l \cdot K_m - v_m + \alpha}{k_l \cdot s_b + k_l \cdot K_m - v_m + \alpha}$$

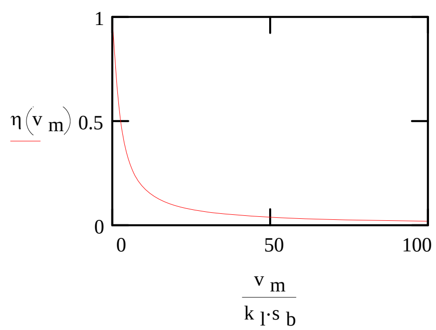
where

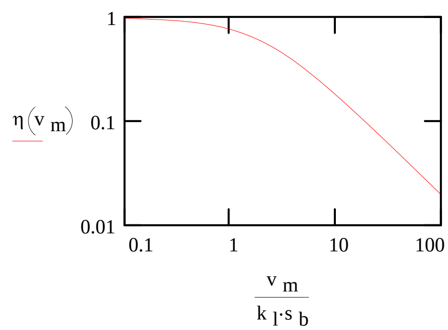
$$\alpha^2 = (k_l \cdot s_b + k_l \cdot K_m - v_m)^2 + 4 \cdot k_l \cdot K_m \cdot v_m$$

Damkohler Plot: $s_b := 1$ $k_l := 1$ $K_m := 1$ $v_m := 0.1, 0.2 .. 100$

$$\alpha(v_m) := \sqrt{(k_l \cdot s_b + k_l \cdot K_m - v_m)^2 + 4 \cdot k_l \cdot K_m \cdot v_m}$$

$$\eta(v_m) := \frac{K_m + s_b}{s_b} \cdot \frac{k_l \cdot s_b - k_l \cdot K_m - v_m + \alpha(v_m)}{k_l \cdot s_b + k_l \cdot K_m - v_m + \alpha(v_m)}$$





Express effectiveness factor in dimensionless groups.

$S = \frac{s}{s_b}$ $\quad V = \frac{v}{v_m}$ $\quad \beta := \frac{K_m}{s_b}$

Dimensional — Nondimensional

$\alpha = \sqrt{\left(k_l \cdot s_b + k_l \cdot K_m - v_m\right)^2 + 4 \cdot k_l \cdot K_m \cdot v_m}$ $\qquad \alpha(\beta, Da) := \sqrt{(1 + \beta - Da)^2 + 4 \cdot \beta \cdot Da}$

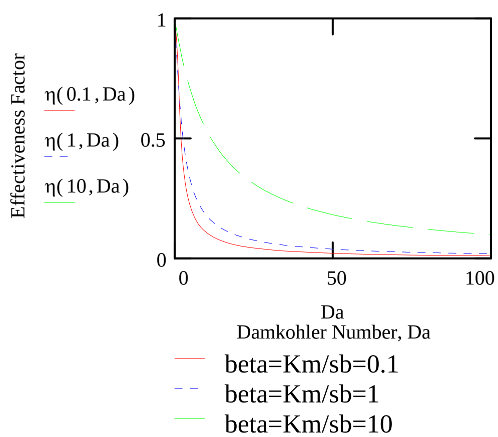
Substrate at surface: $s = \frac{1}{2} \cdot \left(s_b - K_m - \frac{v_m}{k_l} + \frac{\alpha}{k_l}\right)$ $\qquad S = \frac{1}{2} \cdot (1 - \beta - Da + \alpha)$

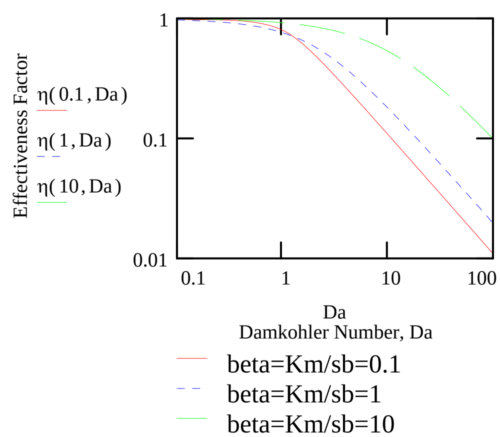
Reaction rate: $v = v_m \cdot \frac{k_l \cdot s_b - k_l \cdot K_m - v_m + \alpha}{k_l \cdot s_b + k_l \cdot K_m - v_m + \alpha}$ $\qquad V = \frac{1 - \beta - Da + \alpha}{1 + \beta - Da + \alpha}$

Flux rate: $v = \frac{1}{2} \cdot \left(k_l \cdot s_b + k_l \cdot K_m + v_m - \alpha\right)$ $\qquad V = \frac{1}{2} \cdot \left(\frac{1}{Da} + \frac{\beta}{Da} + 1 - \frac{\alpha}{Da}\right)$

Effectiveness factor: $\eta = \frac{K_m + s_b}{s_b} \cdot \frac{k_l \cdot s_b - k_l \cdot K_m - v_m + \alpha}{k_l \cdot s_b + k_l \cdot K_m - v_m + \alpha}$ $\qquad \eta(\beta, Da) := (\beta + 1) \cdot \frac{1 - \beta - Da + \alpha(\beta, Da)}{1 + \beta - Da + \alpha(\beta, Da)}$

$Da := 0.1, 0.2 .. 100$





$$\frac{-1}{(2\cdot k_l)}\cdot\left(-k_l\cdot s_b+k_l\cdot K_m+v_m-\sqrt{k_l^2\cdot s_b^2+2\cdot k_l^2\cdot s_b\cdot K_m-2\cdot k_l\cdot s_b\cdot v_m+k_l^2\cdot K_m^2+2\cdot k_l\cdot K_m\cdot v_m+v_m^2}\right)\bigg]$$