Diffusion resistance and non-uniformly active porous solid catalysts
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Consider the case of a porous solid catalyst (heterogeneous catalyst) that may have only a fraction of the porous solid that is active. External mass transfer resistance is specified to be negligible here but internal diffusion resistance may be significant. Specify isothermal conditions, first-order, essentially irreversible reaction, A → B.

Remember the "egg" model of non-uniformly active, spherical catalyst pellets we drew on the board?

The active layer might be (a) the whole egg, (b) the shell, (c) the white, or (d) the yolk. See notes below on the reasons for each type.

k_{local} (m³/mol/s) = constant

$S_{a,local}$ (mol/kg) = constant = local moles of active sites in active zone

where "local" means at a local point in the active part of the catalyst zone and where, for this case, the local values are the same at all points within the active zone.

$k_{local} S_{a,local}$ (m³/kg/s) = constant

You may encounter alternate units, e.g., k_{local} (m/s) and $S_{a,local}$ (m²/kg), where $k_{local}S_{a,local}$ (m³/kg/s), and $S_{a,local}$ is the area of active sites per mass of catalyst in the active zone.

ρ_p (kg/m³) = constant (sub p = pellet, not fluid)

$k_{local} S_{a,local} \rho_p$ (1/s) = constant

D_{eff} (m²/s) = constant

η_b = effectiveness factor from point of view of observer over outer surface of catalyst

θ = fraction of total catalyst mass that is active

$S_{a,local} \theta$ (m²/kg) = active area per total mass of catalyst (active + inactive)

Observed rate per kg of total catalyst mass (active + inactive):

$$-r_{A,obs}\,(\text{mol/kg/s}) = \eta_b\, k_{local}\, S_{a,local}\, \theta\, C_{A,bulk}$$

$$= k_{obs}\, C_{A,bulk}$$

Use the "whole egg" in case with small diffusion resistance and no chemical poisons. Shell in case with very active catalytic sites and strong diffusion resistance. White in case with very active sites and strong diffusion resistance but want some protection against chemical poisons. Yolk in case where not much diffusion resistance but want protection from chemical poisons, or case with reaction with negative-order kinetics for which diffusion resistance lowers reactant concentration inside and, thus, increases the rate.

Consider an isothermal 1D "slab" geometry catalyst layer for convenience. The position variable is r. The catalyst layer has zero-flux boundary condition at the plane at $r = 0$, whether because of symmetry or because that plane is impermeable. The catalyst at the plane at $r = R$ is exposed to reactant A at concentration C_b. The reaction is essentially irreversible with no change in total moles: A$\rightarrow$B .

We will show here the development for a case in which the inner half of the layer is active: $0 <= r <= R/2$, and the outer half of the layer is not active: $R/2 <= r <= R$. **You are responsible for learning how to handle other cases, e.g., outer half active and inner half inactive.**

In this case, the fraction of total catalyst mass that is active is $\theta = (1/2)$. The diffusion constant has the same value in both zones. Let's call C_0 the concentration of reactant A at $r = 0$, and call C_i the concentration of A at $r = R/2$. **We are using "half" as an example and you should be able to handle other fractions, as well as different diffusion coefficients.**

At the internal boundary, the concentrations and fluxes match on each side of the boundary. For this case with the inactive zone "outside" of the active inner zone, the rate of reaction of A in the active zone is equal to the rate of diffusion of A across the inactive zone. Those rates are equal to the rate measured or "observed" over the outside of the catalyst layer:

$$\eta_i\, k_{local}\, S_{a,local}\, C_i\, \rho_P\left(\frac{R}{2}\right) A_X = D_{eff}\frac{(C_b - C_i)}{(R/2)} A_X = \eta_b\, k_{local}\, S_{a,local}\left(\frac{1}{2}\right) C_b\, \rho_P\, R\, A_X$$

$$= k_{obs}\, C_b\, \rho_P\, R\, A_X$$

$$= k_{obs}\, C_b\, W$$

$$= -r_{A,obs}\,(\text{mol/s/kg})\, W\,(\text{kg})$$

The effectiveness factor η_i is from the point of view of an observer at $r = R/2$. The effectiveness factor η_b is from the point of view of an observer at $r = R$ and, if its value is needed, can be expressed in terms of η_i , the diffusivity D_{eff} and other variables. A_x is the geometrical cross-sectional

area of the layer. RA_x is the total volume of the layer. A_x cancels out of the first two lines of the equations, so you only need to know it if you are not given W and need to compute the rate in units of (mol/s).

Since we have a 1st-order reaction in this case, it is simple to express the internal concentration C_i in terms of the other variables. Then that solution can be used to eliminate C_i from the equations.

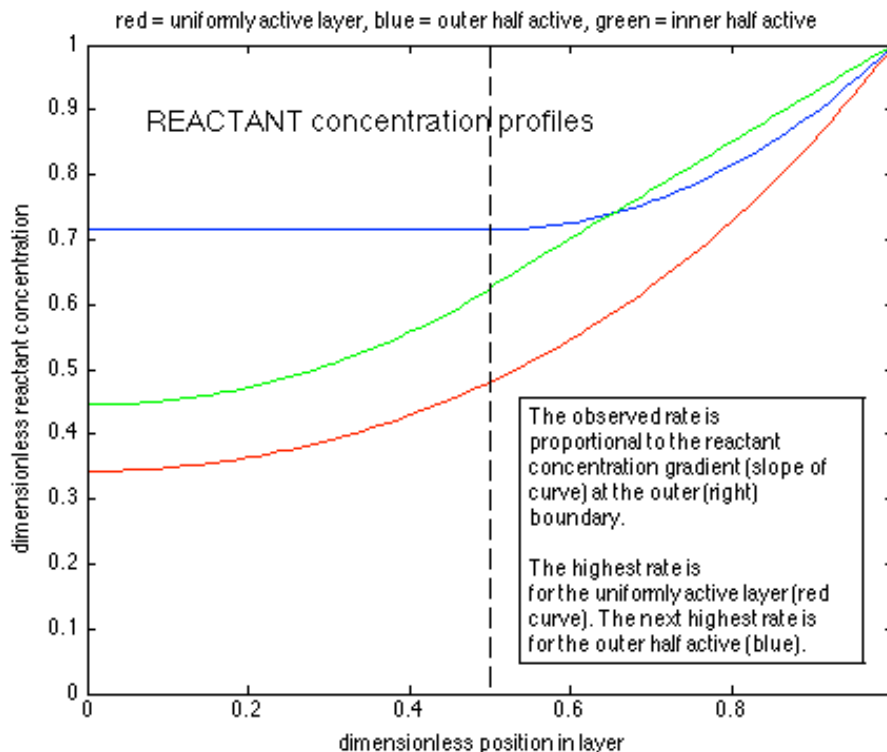For this case of the inner half active and half the original total active sites:

$$C_i = C_b \left[\frac{1}{1 + \eta_i \varphi_i^2} \right] \quad \text{where } \varphi_i \text{ is the Thiele modulus for the active zone}$$
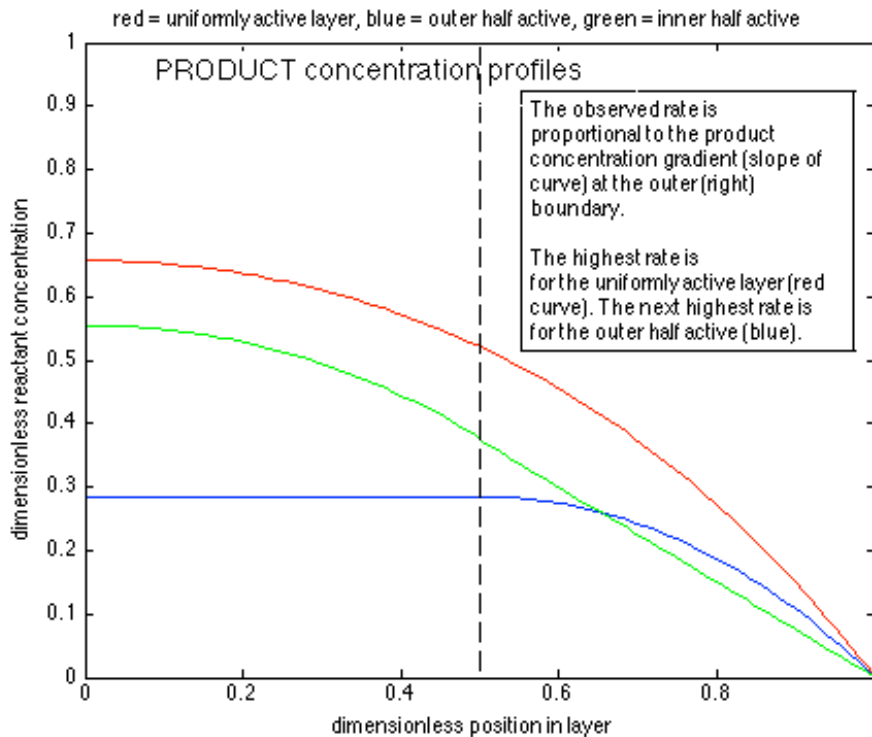
$$\eta_b C_b = \eta_i C_i$$

$$\eta_b = \eta_i \left[\frac{1}{1 + \eta_i \varphi_i^2} \right] \quad \text{where} \quad \eta_i = \frac{\tanh \varphi_i}{\varphi_i}$$

$$k_{obs} = \frac{2 D_{eff}}{\rho R^2} \left[\frac{\eta_i \varphi_i^2}{1 + \eta_i \varphi_i^2} \right] = \eta_b k_{local} S_{a,local} \left(\frac{1}{2} \right)$$

Within the active zone, Thiele's analysis and results for coupled diffusion and reaction over a uniformly active zone apply. See the course notes "Reaction and diffusion in porous catalysts." You should see the similarity between this case and a uniformly active catalyst layer with external mass transfer resistance.

red = uniformly active layer, blue = outer half active, green = inner half active

REACTANT concentration profiles

The observed rate is proportional to the reactant concentration gradient (slope of curve) at the outer (right) boundary.

The highest rate is for the uniformly active layer (red curve). The next highest rate is for the outer half active (blue).

dimensionless reactant concentration

dimensionless position in layer

red = uniformly active layer, blue = outer half active, green = inner half active

PRODUCT concentration profiles

The observed rate is proportional to the product concentration gradient (slope of curve) at the outer (right) boundary.

The highest rate is for the uniformly active layer (red curve). The next highest rate is for the outer half active (blue).

This plot shows the product concentration near zero at the outer (right) boundary. This would be the case with a very high fluid flow rate over the right boundary. These equations for reaction and diffusion in the catalyst layer can be coupled to reactor balance equations to solve for the reactant and product concentration profles in other cases.

Learn how to sketch reactant and product concentration profiles for various cases. Understand the relationship between the slope of a curve at each point, the "gradient" dC/dr, and the material flux across the plane.

The Matlab script for these plots:

```
% profiles in 1D catalyst layer

% first, uniformly active layer

r = linspace(0,1,100); % dimensionless position
R = 1; % (length)
koverD = 3; % (1/length^2)
phi = R*sqrt(koverD) % dimensionless Thiele modulus
eta = tanh(phi)/phi % dimensionless effectiveness factor
c = cosh(phi*r)/cosh(phi); % dimensionless reactant concentration
plot(r,c,'r')
title('red = uniformly active layer, blue = outer half active, green = inner half active')
axis([0 1 0 1])
ylabel('dimensionless reactant concentration')
xlabel('dimensionless position in layer')

% now make inner layer inactive

phi = (R/2)*sqrt(koverD); % Thiele modulus at outer plane for outer layer
c(1:50) = cosh(0)/cosh(phi);
c(51:100) = cosh(phi*(r(51:100)-0.5)/0.5)/cosh(phi);
```

```matlab
hold on
plot(r,c,'b')

% now make outer layer inactive

phi = (R/2)*sqrt(koverD); % Thiele modulus at internal plane for inner layer
eta = tanh(phi)/phi; % eta at internal plane for inner layer
ci = 1/(1+eta*phi^2); % from matching flux at inner plane
c(1:50) = ci * cosh(phi*(r(1:50)/0.5))/cosh(phi)
i = 1:50;
c(51:100) = ci + (1 - ci)*i/50;
plot(r,c,'g')
hold off
```