Solid catalysts are often called "heterogeneous catalysts" meaning that they are in a different phase from fluid reactants and products. The ease of separating solid catalysts from reactants and products gives them an advantage over liquid catalysts in solution with reactants and products ("homogeneous catalysts"). For those of you interested in biochemical reactions, enzymes can be "immobilized" by bonding them to the surfaces of solid supports or entrapping the enzymes or dead cells containing the active enzymes inside porous supports.

Most solid catalysts are porous in order to obtain high active surface area per unit volume and, thus, obtain high activity per unit volume of reactor in order to minimize reactor size. One of the rare exceptions is Pt/Rh wire gauze, which is used to oxidize ammonia in the process of making nitric acid. That catalyst operates at such a high temperature that a porous form wouldn't be able to retain its porosity.

With porous solid catalysts, significant resistance to mass and heat transfer may be present. If you are given a rate equation that applies in the absence of significant resistance to mass and heat transfer ("true", "local", or "intrinsic" rate equation), then you have to realize that the rate obtained in the presence of significant resistance to mass and heat transfer will differ from that given by the rate equation evaluated at the conditions existing in the bulk fluid. The transport resistances will make the species concentrations inside the porous catalyst lower than the concentrations in the bulk fluid, and make the temperature inside the porous catalyst lower (endothermic reaction) or higher (exothermic) than in the bulk fluid. If you measure rates of reaction over a porous catalyst and want to determine a rate equation that applies in the absence of significant resistance to mass and heat transfer, then you have some work to do to account for the transport effects.

Usually, we want to obtain an effectiveness factor that tells us the extent to which transport resistances affect the rate of reaction. In general, the relationship we seek is

$$r_{A,\text{obs}} = \Omega \cdot r_{A,\text{true}}$$

where

- $r_{A,\text{obs}}$ = observed (actual, apparent, overall, average) rate of generation of species A
- $\Omega$ = overall effectiveness factor, a function of bulk fluid composition (except for 1st order rxns) and a function of T
- $r_{A,\text{true}}$ = true (local, intrinsic) rate equation evaluated at bulk (external) conditions

The overall effectiveness factor $\Omega$ is the actual rate with transport resistance divided by the rate that would obtained with all active sites exposed to bulk conditions. Effectiveness factor values less than one can be obtained for reactions which are positive-order in reactant concentration and also for endothermic reactions. Effectiveness factor values greater than one can be obtained for reactions which are negative-order in reactant concentration and also for exothermic reactions. Can you explain to yourself "physically" why these statements are true?

In one type of problem we might face, we would know the equation for $r_{A,\text{true}}$ and, from a knowledge of the geometry of the system and the transport properties, we would have to drive the equation for $\Omega$. A more
difficult problem would be where $\Omega$ $r_{A,\text{true}}$ is unknown and we would have to determine equations for both $r_{A,\text{true}}$ and $\Omega$ from measurements of $r_{A,\text{obs}}$.

When we know the functional forms and parameter values for both $\Omega$ and $r_{A,\text{true}}$, we can design a "heterogeneous" catalytic reactor easily from what we learned about homogeneous reactors. We can write "pseudo-homogeneous" reactor design equations involving bulk fluid composition and $T$ only.

Here, we are going to consider the first type of problem where we know the equation for $r_{A,\text{true}}$ and, from a knowledge of the geometry of the system and the transport properties, we have to drive the equation for $\Omega$. We do this for the case of an essentially irreversible, first-order reaction in an isothermal porous catalyst.

$$A \rightarrow B \quad r_{A,\text{true}} = -k C_A$$

Such a rate equation could be obtained for reaction over a catalyst surface at relatively low reactant concentration such that the denominator in the Langmuir-Hinshelwood rate equation approaches a value of one: $r_{A,\text{true}} = -kC_A/(1+K_AC_A) \approx -kC_A$.

This is the simplest case. The math gets a little more complex for other cases but the procedure is the same. For nonisothermal systems, an energy balance must be written and solved along with the species balance(s).

Our final goal is to get an expression for the "observed" reaction rate $r_{A,\text{obs}}$ in terms of the bulk reactant concentration $C_{A,\text{bulk}}$. With such an expression, we can design a "heterogeneous" catalytic reactor easily from what we learned about homogeneous reactors.

First, we need to find out how the reactant concentration varies inside the porous catalyst in order to find out how the rate of reaction varies inside. We need to write a mole balance on reactant $A$ in a porous catalyst layer, particle, or pellet. We specify steady-state conditions so that the rate of accumulation is zero.

Species balance on species A over differential control volume between $r$ and $r+\Delta r$

$$0 = \left[ -D_{\text{eff}} A_r \frac{dC_A}{dr} \bigg|_r \right] - \left[ -D_{\text{eff}} A_r \frac{dC_A}{dr} \bigg|_{r+\Delta r} \right] - kC_A A_r \Delta r$$

Here, "in" and "out" is by diffusion. The rate of diffusion is given by the Fick's Law expression in the square brackets above since there is no change in moles with reaction (equi-molar counter diffusion) and the pellet is isothermal (no "thermal" diffusion of species resulting from large $T$ gradients).
$D_{\text{eff}}$ is the effective diffusivity of species A in the porous catalyst material. Effective diffusivities are lower than diffusivities in the bulk fluid because the porous solid hinders diffusion. The position coordinate is $r$. $A_r$ is the geometric area across which the diffusive flux is evaluated. For a spherical pellet, $A_r = 4\pi r^2$.

Now we divide the equation through by $\Delta r$ and take the limit as $\Delta r$ approaches zero. Since $A_r$ for a sphere varies with $r$, it is involved in the derivative formed.

$$0 = D_{\text{eff}} \left[ \frac{d^2 C_A}{d r^2} + \frac{2}{r} \frac{d C_A}{d r} \right] - k C_A \quad \text{(sphere)}$$

For a one-dimensional "slab geometry" catalyst layer, $A_r$ does not vary with $r$ and can be divided out of the equation.

$$0 = D_{\text{eff}} \frac{d^2 C_A}{d r^2} - k C_A \quad \text{(slab)}$$

In order to integrate these equations, we want to make them dimensionless:

$$0 = \frac{d^2 \Psi_A}{d \lambda^2} + \frac{2}{\lambda} \frac{d \Psi_A}{d \lambda} - \phi^2 \Psi_A \quad \text{(sphere)}$$

$$0 = \frac{d^2 \Psi_A}{d \lambda^2} - \phi^2 \Psi_A \quad \text{(slab)}$$

where

$$\Psi_A = \frac{C_A(r)}{C_A(R)}$$

$$\lambda = \frac{r}{R}$$

$$\phi^2 = \left( \frac{R^2 k}{D_{\text{eff}}} \right)$$

R is the radius of a spherical pellet or the half-thickness of a slab that has both sides exposed to the bulk fluid.

The dimensionless group $\phi$ is one way of defining the Thiele modulus (or parameter). Thiele solved this problem after developing the McCabe-Thiele diagram for distillation columns in grad school. Russians name the group $\phi$ after Zeldovitch, who solved this problem at about the same time. The square of the Thiele modulus is the ratio of the rate that would be obtained with all active sites exposed to conditions at the external surface of the pellet divided by the diffusion rate in the absence of reaction obtained with the concentration of A held at zero at $r = 0$. Can you re-arrange the equation above to show this relationship?
As an alternative definition, the Thiele modulus also can be defined for an essentially irreversible, first-order reaction in a porous catalyst pellet as:

\[
\phi = \frac{L_c}{\sqrt{\frac{k}{S_a} \frac{S_g}{\rho_p} D_{eff}}}
\]

where \( k \) is the "true" reaction rate constant (synonyms: true, intrinsic, local), \( S_a \) is the total active area inside the porous pellet per gram of pellet (\( S_z \) in Schmidt), and \( \rho_p \) is the pellet density.

\( L_c \) is the "characteristic diffusion distance." For uniformly active pellets, or pellets with an outer active volume surrounding an inert core, \( L_c \) equals the active volume of the pellet divided by the external "geometric" area of the pellet. For a sphere, this external area is \( 4\pi R^2 \).

For uniformly active pellets of the following geometries, \( L_c \) equals:

- Sphere of radius \( R \):
  \[ L_c = \frac{R}{3} \]
- Long Cylinder of radius \( R \):
  \[ L_c = \frac{R}{2} \]
- Large flat plate or "slab":
  \[ L_c = R \]

  - thickness of slab with one face sealed, one fact exposed to fluid
  - half-thickness of slab with both faces exposed to fluid

Taking the species balance for species A in a uniformly active sphere given above, with boundary conditions \( C_A = C_{A,es} \) at \( r = R \) and \( dC_A/dr = 0 \) at \( r = 0 \), and integrating, we get:

\[
C_A \text{ at } r = C_{A,es} \left( \frac{R}{r} \right) \frac{\sinh \left( 3\phi \frac{r}{R} \right)}{\sinh \left( 3\phi \right)} \quad (sphere)
\]

where \( C_{A,es} \) is the concentration of A at the external surface ("es") of the pellet.

For a slab-geometry pellet:

\[
C_A \text{ at } r = C_{A,es} \left( \frac{\cosh \left( \phi \frac{r}{R} \right)}{\cosh \left( \phi \right)} \right) \quad (slab)
\]
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 profiles in other cases.

Now that we have $C_A$ as a function of position inside the pellet, we can get an expression for $(dC_A/dr)$ at the external surface of the pellet so we can use it to get the observed rate. The observed rate is equal to the rate at which $A$ is diffusing into the pellet from its external surface at $r = R$:

$$-\frac{r_A}{A_{obs}} \left( \frac{\text{mol}}{\text{kg s}} \right) = a_{es} \left( \frac{\text{m}^2}{\text{kg}} \right) D_{eff} \left( \frac{\text{m}^2}{\text{s}} \right) \frac{dC_A}{dr} \bigg|_{r = R} \left( \frac{\text{mol} \ 1}{\text{m}^3 \ \text{m}} \right)$$

where $D_{eff}$ is the effective diffusivity of $A$ inside the porous catalyst pellet, and $a_{es}$ is the external "geometric" pellet area per unit mass of pellet (for a sphere, the external area = $4\pi R^2$).

The derivative of $C_A(R)$ with respect to $r$ can be evaluated at the external surface, position $R$, and substituted into our the equation above to give, after some rearranging:

$$-\frac{r_A}{A_{obs}} \left( \frac{\text{mol}}{\text{kg s}} \right) = \eta k \left( \frac{\text{m}}{\text{s}} \right) S_a \left( \frac{\text{m}^2}{\text{kg}} \right) C_{A,es} \left( \frac{\text{mol}}{\text{m}^3} \right)$$

The internal effectiveness factor $\eta$ is the ratio between the observed rate and the rate that would be obtained if all active sites in the pellet were exposed to $A$ at concentration $C_{A,es}$ (i.e., $-r_{A,obs} = k S_a C_{A,es}$).

For a uniformly active spherical pellet:

$$\eta = \frac{1}{\phi} \left( \frac{\phi \ coth (3 \phi)}{3} \right)$$

(sphere)
For a one-dimensional slab pellet, the same rate equation holds, with

\[ \eta = \frac{\tanh \phi}{\phi} \quad (\text{slab}) \]

For all of the pellet geometries mentioned above, \( \eta \) has the following limiting behavior which you should know:

**Negligible diffusion resistance, "kinetic control"**

\[ \frac{D_{\text{eff}}}{L_c^2} \gg k S_a \]

"fast diffusion, slow reaction"

\[ \phi \ll 1, \]

\[ \eta \approx 1 \]

**Significant internal diffusion resistance**

\[ \frac{D_{\text{eff}}}{L_c^2} \ll k S_a \]

"slow diffusion, fast reaction"

\[ \phi \gg 1 \]

\[ \eta \approx \frac{1}{\phi} \]

This looks like a good step along the way to our final goal but \( C_{A,es} \) is not something we can measure, so we need some more work to get rid of it.

The observed rate is ALSO equal to the rate at which reactant "A" is transported from the bulk fluid to the external surface ("es") of the porous catalyst pellet:

\[ -r_{A,\text{obs}} \left( \frac{\text{mol}}{\text{kg s}} \right) = k_m \left( \frac{\text{m}}{\text{s}} \right) a_{es} \left( \frac{\text{m}^2}{\text{kg}} \right) \left( C_{A,\text{bulk}} - C_{A,es} \right) \]

where \( k_m \) is the external mass transfer coefficient. Fogler's \( k_e = k_m, a_e = a_{es} \).

Above, the rates with units (mol kg\(^{-1}\) s\(^{-1}\)) are shown, where the kg is the mass of catalyst pellets. For a given packed bed with a known pellet density and bed void fraction, you can convert to rate in units of (mol m\(^{-3}\) s\(^{-1}\)), where the m\(^3\) is the bed volume.

We want to eliminate \( C_{A,es} \) from the above equations, since \( C_{A,es} \) is not measureable (except possibly with special techniques in a research lab). First, set the two expressions equal to each other and solve for \( C_{A,es} \) in terms of \( C_{A,\text{bulk}} \):

\[ \eta \; k \left( \frac{\text{m}}{\text{s}} \right) S_a \left( \frac{\text{m}^2}{\text{kg}} \right) C_{A,es} \left( \frac{\text{mol}}{\text{m}^3} \right) = k_m \left( \frac{\text{m}}{\text{s}} \right) a_{es} \left( \frac{\text{m}^2}{\text{kg}} \right) \left( C_{A,\text{bulk}} - C_{A,es} \right) \]
\[ C_{A,es} = \left( \frac{k_m a_{es}}{k_m a_{es} + k S_a \eta} \right) C_{A,bulk} \]

Now substitute this expression for \( C_{A,es} \) into either of the above expressions for \( -r_{A,obs} \) (a little quicker with the second one) and rearrange to get OUR FINAL GOAL!

\[ -r_{A,obs} = \Omega k S_a C_{A,bulk} \]

where

\[ \Omega = \left( \frac{\eta k_m a_{es}}{k_m a_{es} + k S_a \eta} \right) \]

and where \( \Omega \), the overall effectiveness factor, is the ratio between the observed rate and the rate that would be obtained if all active sites in the pellet were exposed to \( A \) at concentration \( C_{A,bulk} \).

You should know the following limiting behavior:

**External mass transfer control**

\[ k_m a_{es} << \eta k S_a \]

\[ \Omega \rightarrow \left( \frac{k_m a_{es}}{k S_a} \right) \]

\[ -r_{A,obs} = k_m a_{es} C_{A,bulk} \]

\[ -r_{A,obs} = k_m a_{es} \left( C_{A,bulk} - C_{A,es} \right); \quad C_{A,bulk} >> C_{A,es} \]

**Negligible external mass transfer resistance**

\[ k_m a_{es} >> \eta k S_a \]

\[ \Omega \rightarrow \eta \]

\[ -r_{A,obs} = \eta k S_a C_{A,bulk} \]

With negligible external and internal mass transfer resistance, \( \Omega \rightarrow \eta \rightarrow 1 \), all active sites inside the pellet are exposed to \( C_{A,bulk} \), and we have "kinetic control”:

\[ -r_{A,obs} = k S_a C_{A,bulk} \]

Significant transport resistance can "disguise" kinetic measurements. For example, with mass transfer resistance, the apparent activation energy determined from measurements will be lower than the true activation energy. 

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energy of the reaction. Can you show the relationship between the true and apparent activation energies using the above results for the cases of (a) significant internal diffusion resistance and (b) external mass transfer control?

With significant diffusion resistance, reactions that are not first-order in reactant concentration will have apparent orders determined from measurements that differ from the true orders. For essentially irreversible n-th order reactions,

\[ A \rightarrow B \quad r_{A,\text{true}} = -k C_A^n \]

the Thiele modulus can be defined as:

\[ \phi = L_c \sqrt{\frac{(n+1)}{2}} \frac{k S_a \rho_p C_{A,es}^{(n-1)}}{D_{\text{eff}}} \]

The same limiting behavior for \( \eta \) at small and large \( \phi \) that are given above still hold. For non 1st-order reactions, values of \( \eta \) at intermediate values of \( \phi \) will deviate somewhat from those given by the equations above for 1st-order reactions. What is the apparent order of a 2nd-order reaction in the limit of large internal diffusion resistance? What is the apparent order of a 2nd-order reaction with external mass transfer control?

The derivations above are for "equimolar counter diffusion", i.e., where the change in total moles with reaction is zero or negligible. For the first-order reaction \( A \rightarrow 2B \), how do you think the effectiveness factor will differ from that estimated using the relationships shown above?