Microreactor Engineering

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Solid Catalyzed Reactions

In Affiliation With:

MBI

Microproducts Breakthrough Institute

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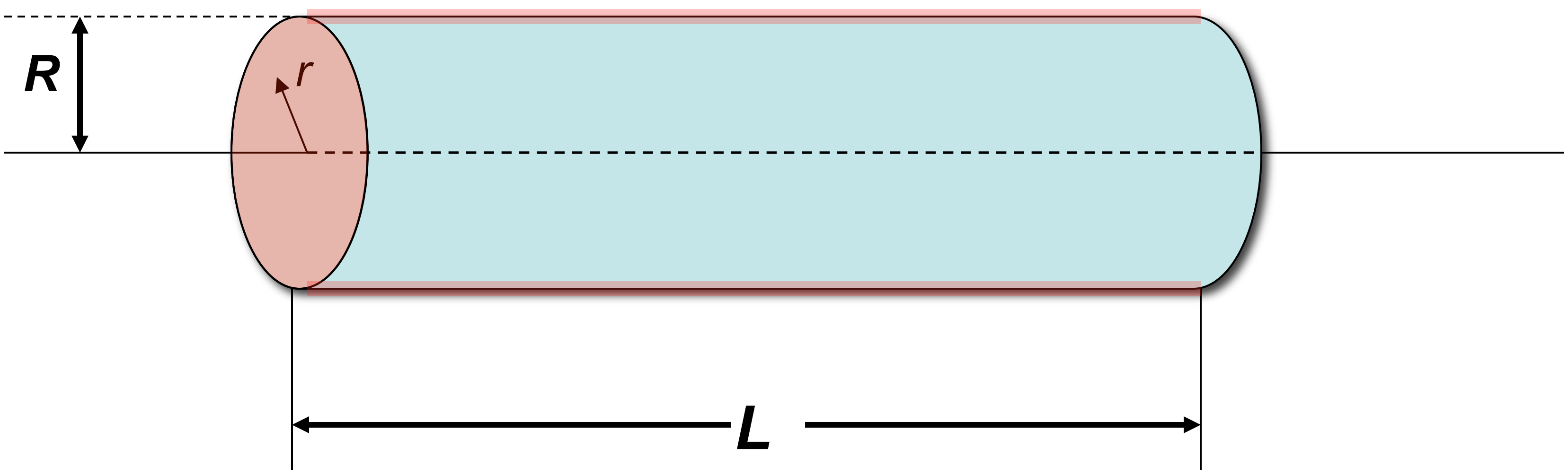
Solid Catalyzed Reactions

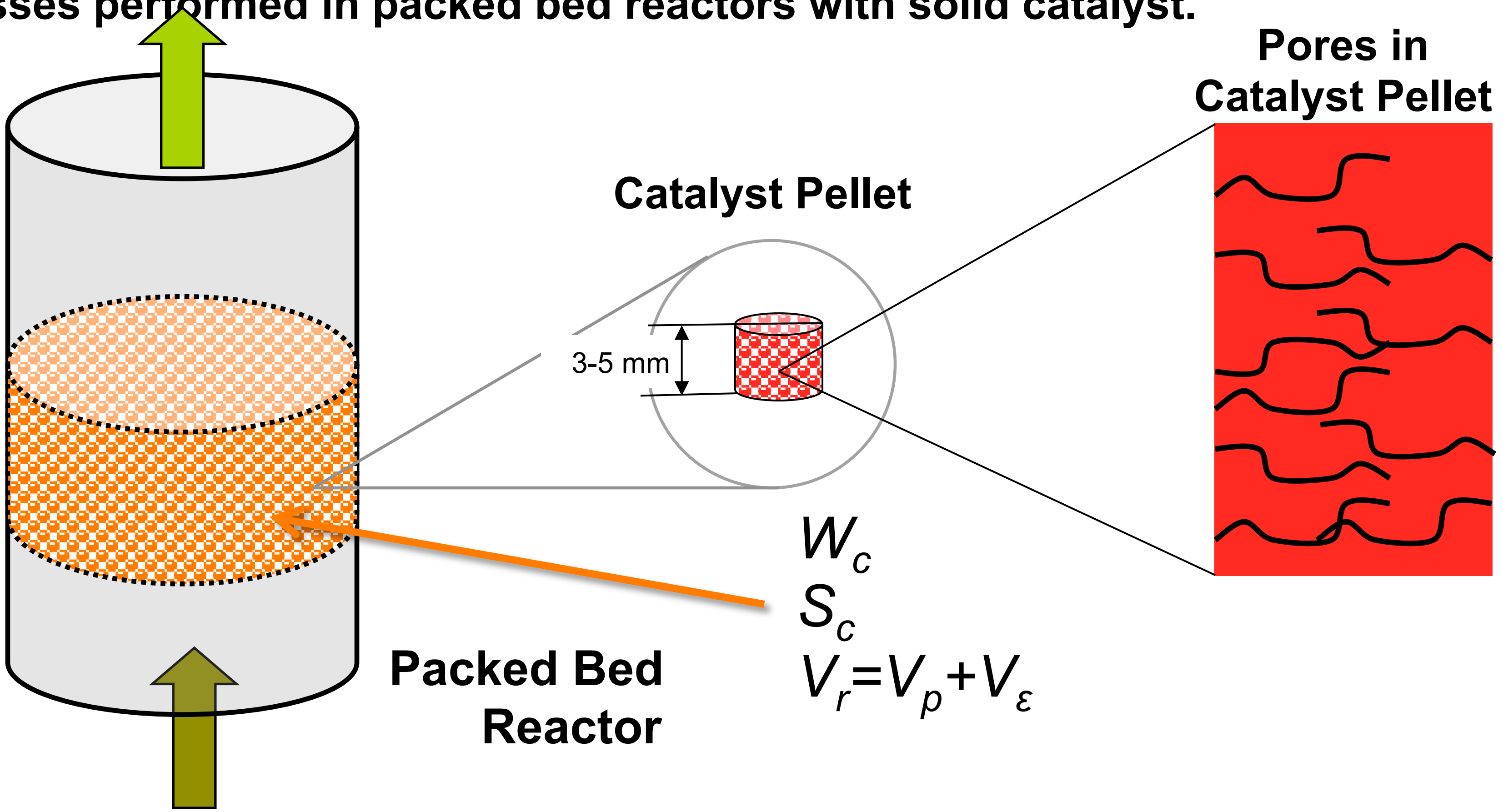
Consider a microchannel vessel with characteristic dimension of approximately ***R* ≈100** μm, and length ***L***; where ***L>>>R***. In addition consider that a solid catalyzed chemical reaction of known kinetics takes place at the walls of the microreactor vessel.



$$\text{Geometric aspect ratio:} \quad \frac{R}{L} <<< 1$$

Catalyst and Definition of Reaction Rates

Most of definitions for the intrinsic chemical reaction kinetics in solid catalyzed chemical reactions evolved form the consideration of a chemical reaction processes performed in packed bed reactors with solid catalyst.



Reaction Rate Definitions

In catalytic systems the rate of reaction can be expressed in one of many equivalent ways (for the first order representation of a heterogeneous catalytic reaction);

$$-r_A = -\frac{1}{V_\varepsilon}\frac{dN_A}{dt} = kC_A\left[\frac{moles\,reacted}{m^3 voids \cdot s}\right]$$

Based on volume of voids in the reactor

$$-r'_A = -\frac{1}{W_c}\frac{dN_A}{dt} = k'C_A\left[\frac{moles\,reacted}{kg\,catalyst \cdot s}\right]$$

Based on weight of catalyst pellets

$$-r''_A = -\frac{1}{S_c}\frac{dN}{dt} = k''C_A\left[\frac{moles\,reacted}{m^2 cat - surface \cdot s}\right]$$

Based on catalyst surface

Reaction Rate Definitions

$$-r_A''' = -\frac{1}{V_p}\frac{dN_A}{dt} = k'''C_A\left[\frac{moles\ reacted}{m^3 solids \cdot s}\right]$$

Based on volume of catalyst pellets

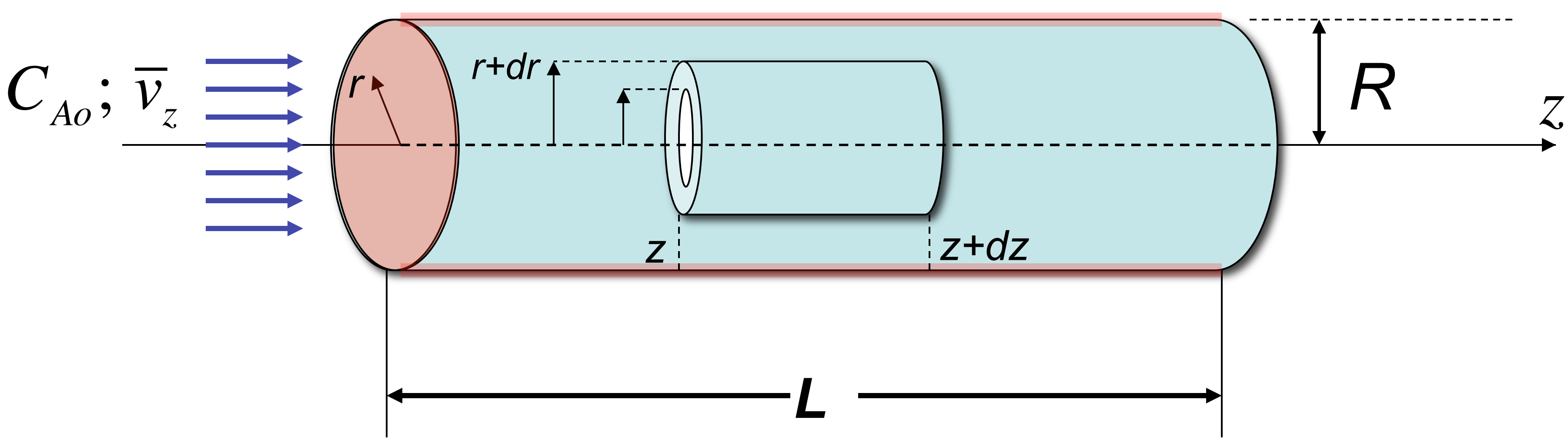
$$-r_A^* = -\frac{1}{V_r}\frac{dN_A}{dt} = k^*C_A\left[\frac{moles\ reacted}{m^3\ reactor \cdot s}\right]$$

Based on total reactor volume

Solid Catalyzed Reactions

Consider a homogenous fluid that enters the microchannel vessel at average velocity $\bar{v}_z$ containing a reactant *A* that undergoes catalytic transformation:

$$A \overset{k''}{\Longrightarrow} B \qquad -r''_A = -\frac{1}{S_c}\frac{dN_A}{dt} = k''C_A \left[\frac{moles\ A\,reacted}{m^2 cat-surface \cdot s}\right]$$



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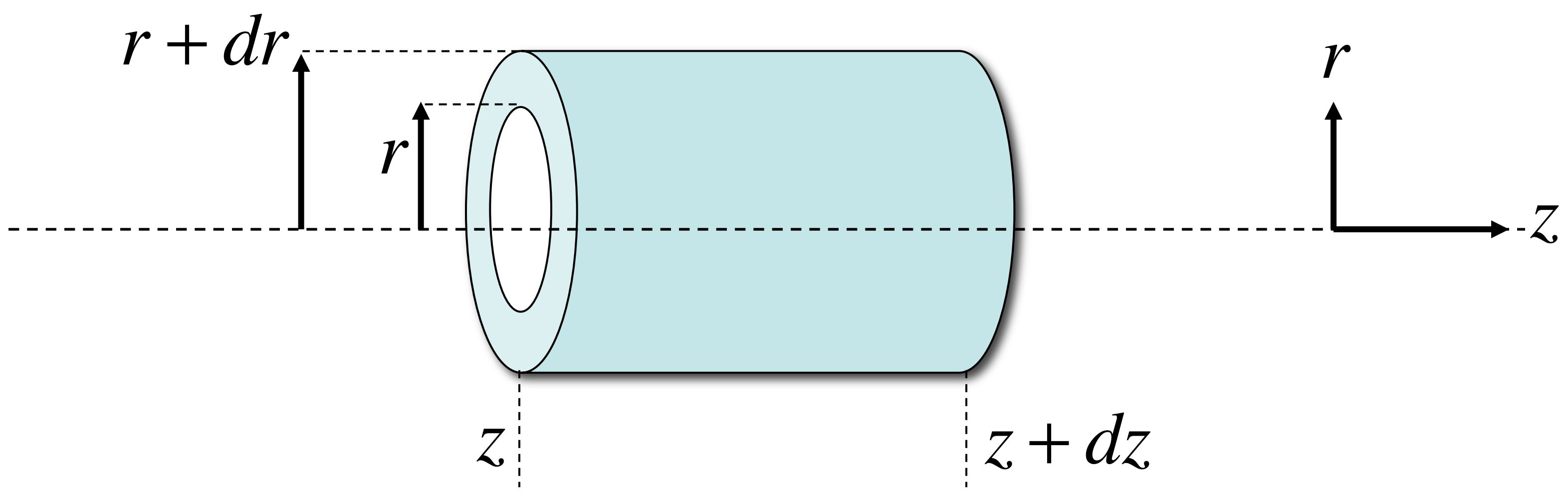
$$-r_A'' = -\frac{1}{S_c}\frac{dN_A}{dt} = k'' C_A \left[\frac{moles\ A\ reacted}{m^2 cat - surface \cdot s} \right]$$



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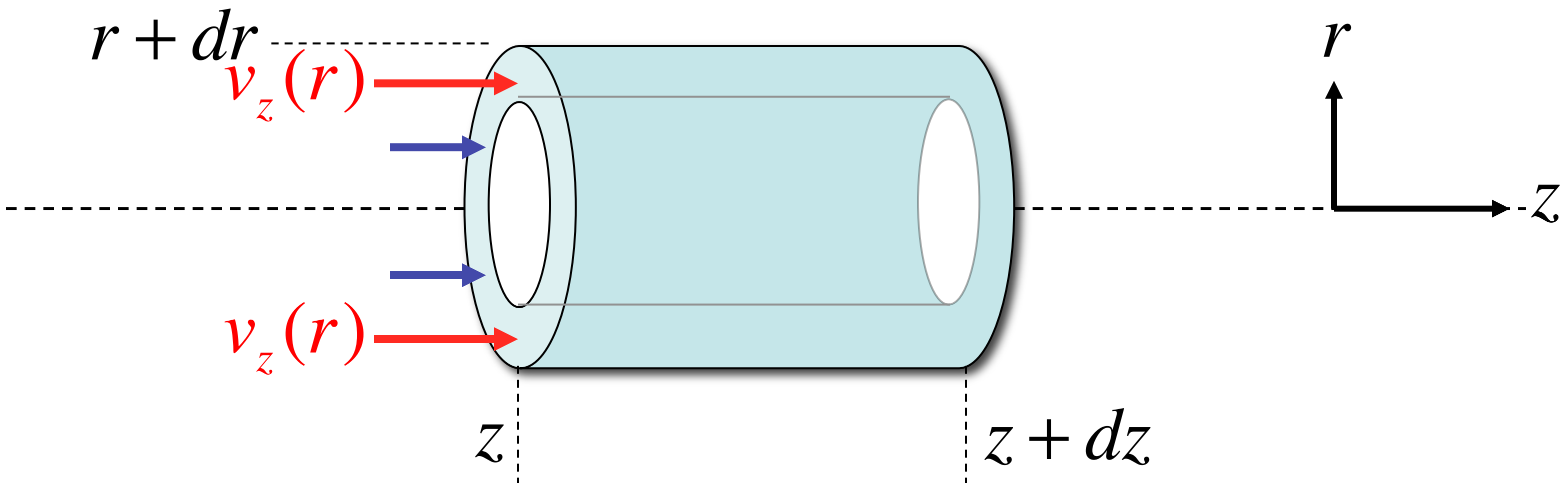


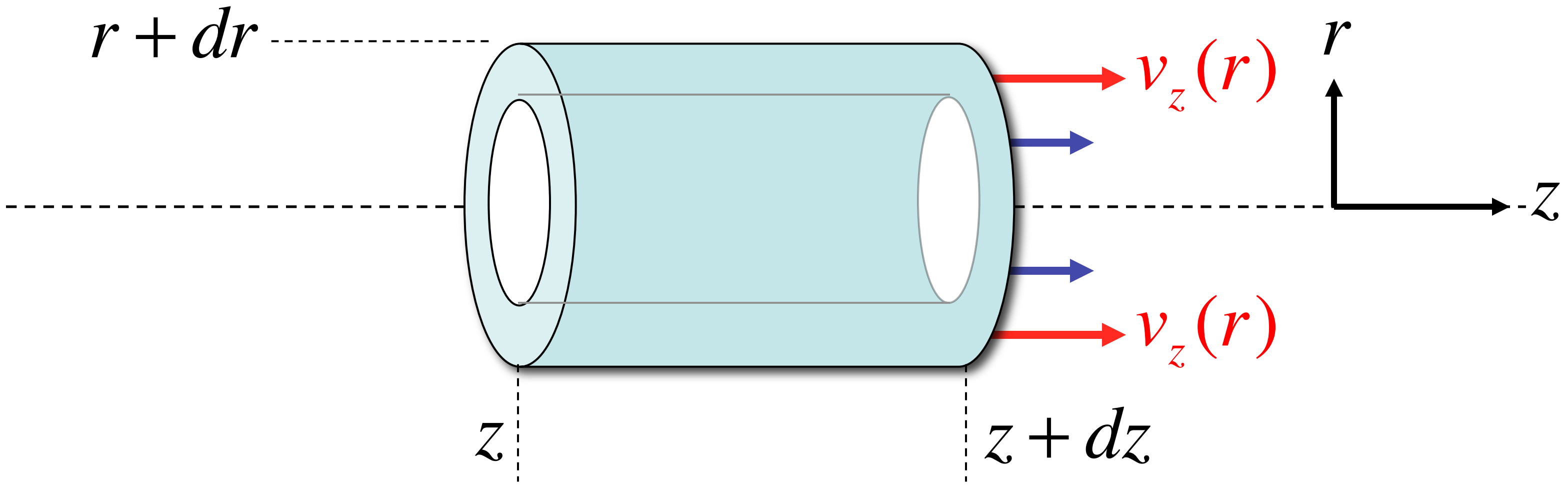
material entering at ***z*** by convection:

$$v_z(r)\cdot 2\pi r\cdot dr\cdot C_A(z,r)\Big|_z\,\Delta t\,[mol]$$

material entering at z by diffusion:

$$-D_A 2\pi r\cdot dr\cdot \frac{\partial C_A(z,r)}{\partial z}\bigg|_z\,\Delta t\,[mol]$$

Similarly, we have convective and diffusive mass transfer at the other end of the differential fluid volume:



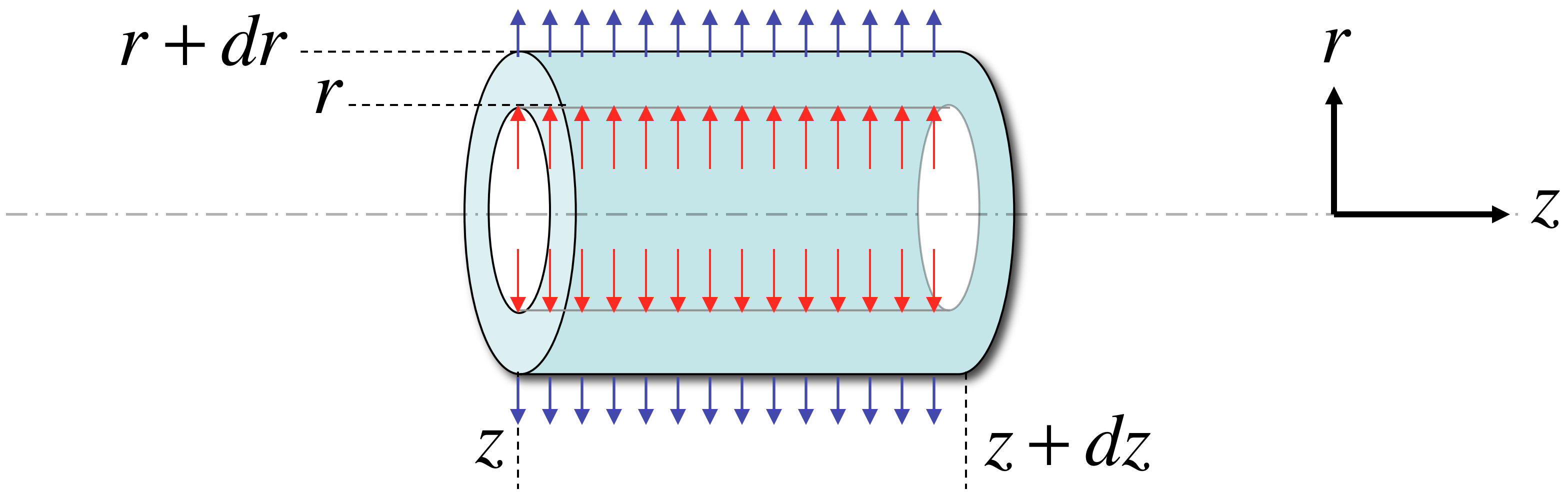
material leaving at ***z+dz*** by convection:

$$v_z(r)\cdot 2\pi r\cdot dr\cdot C_A(z,r)\Big|_{z+dz}\Delta t\,[mol]$$

material leaving at ***z+dz*** by diffusion:

$$-D_A 2\pi r\cdot dr\cdot \frac{\partial C_A(z,r)}{\partial z}\Bigg|_{z+dz}\Delta t\,[mol]$$

There is also diffusive mass transfer in the radial direction IN and OUT of the differential fluid volume (no convective flow in the radial direction):



material entering at (r) by diffusion:

$$-D_A \cdot 2\pi r \cdot dz \cdot \left.\frac{\partial C_A(z,r)}{\partial r}\right|_r \Delta t\,[mol]$$

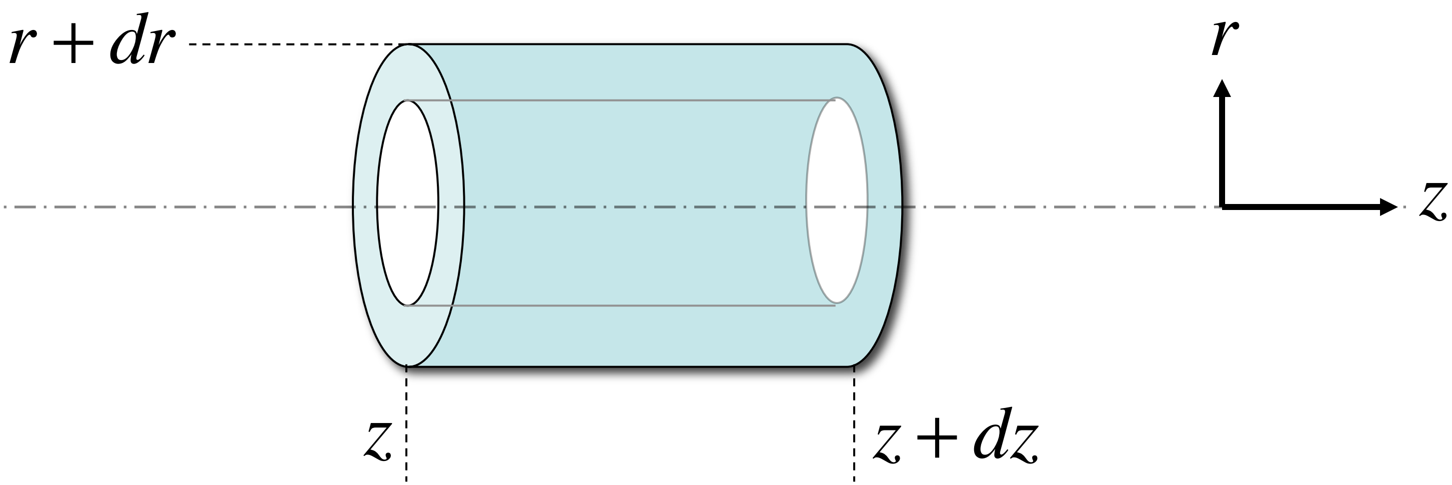
material leaving at ($r+dr$) by diffusion:

$$-D_A(2\pi r) \cdot dz \cdot \left.\frac{\partial C_A(z,r)}{\partial r}\right|_{r+dr} \Delta t\,[mol]$$

Solid Catalyzed Reactions

Finally: Do we have to account for the mass of reactant *A* that disappears by the chemical reaction in the differential volume of fluid?

NO - Reaction takes place in the catalyst layer; which is on the walls of the microchannel; thus, reaction will be part of the boundary condition!



$$A \overset{k}{\Rightarrow} B \qquad \cancel{-\frac{dC_A}{dt} = kC_A \Rightarrow \underbrace{(2\pi r \cdot dr \cdot dz)}_{\textit{differential volume}} \cdot kC_A \cdot \Delta t}\,[mol]$$

Solid Catalyzed Reactions

The overall material balance of the reactant *A* in the differential volume of fluid is given by:

Input - Output = Accumulation

Input ***Output***

$$v_z(r)\cdot 2\pi r\cdot dr\cdot C_A(z,r)\cdot\Delta t\Big|_z - v_z(r)\cdot 2\pi r\cdot dr\cdot C_A(z,r)\cdot\Delta t\Big|_{z+dz}$$

$$-D_A 2\pi r\cdot dr\frac{\partial C_A(z,r)}{\partial z}\cdot\Delta t\Big|_z - \left(-D_A 2\pi r\cdot dr\frac{\partial C_A(z,r)}{\partial z}\cdot\Delta t\Big|_{z+dz}\right)$$

$$-D_A 2\pi r\cdot dz\frac{\partial C_A(z,r)}{\partial r}\cdot\Delta t\Big|_r - \left(-D_A 2\pi r\cdot dz\frac{\partial C_A(z,r)}{\partial r}\cdot\Delta t\Big|_{r+dr}\right)$$

$$\cancel{-\underbrace{2\pi r\cdot dr\cdot dz}_{differential\ volume}\cdot kC_A\cdot\Delta t} = \underbrace{\underbrace{2\pi r\cdot dr\cdot dz}_{differential\ volume}\left(C_A\Big|_{t+\Delta t} - C_A\Big|_t\right)}_{accumulation\ \ term}$$

Solid Catalyzed Reactions

Divide the whole equation by: $\{2\pi \cdot dr \cdot dz \cdot \Delta t\}$

$$v_z(r)\cdot r\,\frac{\left[C_A(z,r)\big|_z - C_A(z,r)\big|_{z+dz}\right]}{dz} + D_A r\,\frac{\left.\dfrac{\partial C_A(z,r)}{\partial z}\right|_{z+dz} - \left.\dfrac{\partial C_A(z,r)}{\partial z}\right|_z}{dz}$$

$$+D_A\,\frac{\left[r\left.\dfrac{\partial C_A(z,r)}{\partial r}\right|_{r+dr} - r\left.\dfrac{\partial C_A(z,r)}{\partial r}\right|_r\right]}{dr} = \frac{r\left(C_A\big|_{t+\Delta t} - C_A\big|_t\right)}{\Delta t}$$

Find a **limes** *of the above equation and let:* $\Delta t \to 0,\ dr \to 0,\ dz \to 0,$

$$\boxed{-v_z(r)\cdot r\,\frac{\partial C_A(z,r)}{\partial z} + D_A r\,\frac{\partial^2 C_A(z,r)}{\partial z^2} + D_A\,\frac{\partial\left(r\,\dfrac{\partial C_A(z,r)}{\partial r}\right)}{\partial r} = r\,\frac{\partial C_A}{\partial t}}$$

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$$\boxed{-v_z(r)\cdot r\frac{\partial C_A(z,r)}{\partial z}+D_A r\frac{\partial^2 C_A(z,r)}{\partial z^2}+D_A\frac{\partial\left(r\frac{\partial C_A(z,r)}{\partial r}\right)}{\partial r}=r\frac{\partial C_A}{\partial t}}$$

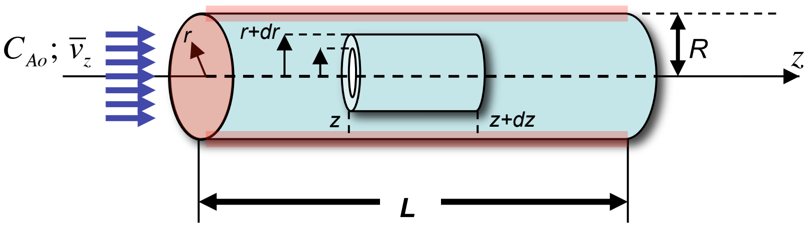
Divide by ***r*** *and obtain:*

$$-v_z(r)\frac{\partial C_A(z,r)}{\partial z}+D_A\frac{\partial^2 C_A(z,r)}{\partial z^2}+\frac{D_A}{r}\frac{\partial\left(r\frac{\partial C_A(z,r)}{\partial r}\right)}{\partial r}=\frac{\partial C_A}{\partial t}$$

And at steady state:

$$\boxed{-v_z(r)\frac{\partial C_A(z,r)}{\partial z}+D_A\frac{\partial^2 C_A(z,r)}{\partial z^2}+\frac{D_A}{r}\frac{\partial\left(r\frac{\partial C_A(z,r)}{\partial r}\right)}{\partial r}=0}$$

Solid Catalyzed Reactions



Finally, the mathematical model takes the form:

$$\boxed{-v_z(r)\frac{\partial C_A(z,r)}{\partial z}+D_A\frac{\partial^2 C_A(z,r)}{\partial z^2}+D_A\frac{\partial^2 C_A(z,r)}{\partial r^2}+\frac{D_A}{r}\frac{\partial C_A(z,r)}{\partial r}=0}$$

With a choice of two axial boundary conditions (in *z* direction):

$$\boxed{at\ z=0\quad \frac{\partial C_A(0,r)}{\partial z}=0}\qquad \boxed{at\ z=0\quad C_A(0,r)=C_{Ao}}$$

$$\boxed{at\ z=L\quad \frac{\partial C_A(L,r)}{\partial z}=0}\qquad \boxed{at\ z=L\quad \bar{C}_A(L)=C_A^*}$$

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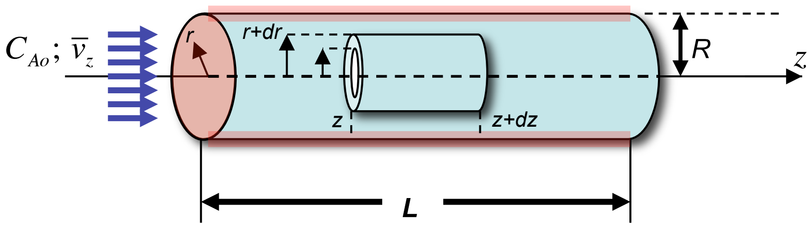
And boundary conditions in ***r*** direction:

$$\boxed{at\ \ r=0 \qquad \frac{\partial C_A(z,0)}{\partial r}=0}$$

$$\boxed{at\ \ r=0 \qquad C_A(z,0)= finite}$$



$$at\ \ r=R$$

$$-\underset{\frac{m^2}{s}}{D}\ \underset{m^2 reactor\ surf.}{2\pi R\cdot dz}\ \left.\frac{\overset{\frac{moles}{m^3 reactor}}{\partial C_A(z,r)}}{\underset{m}{\partial r}}\right|_R = \left.\underset{m^3 reactor}{dV_r}\cdot\underset{\frac{m^2 cat-surface}{m^3 reactor}}{s}\cdot\underset{\frac{moles\ A\ reacted}{m^2 cat-surface\cdot s}}{k''C_A}\right|_R$$

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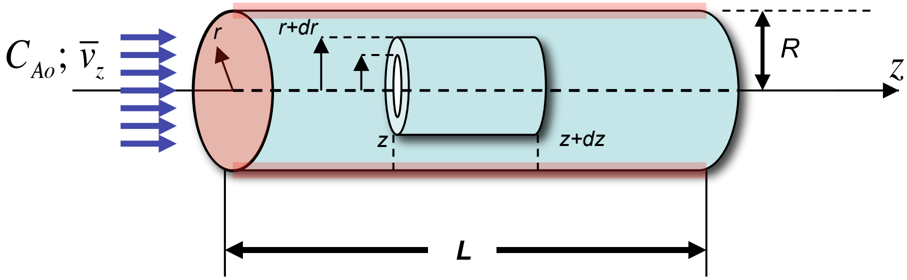
Or alternatively we could define the
*boundary condition at the wall at **r = R***



$$at \ \ r = R$$

$$\left. -\underset{\frac{m^2}{s}}{D}\ \underset{m^2 reactor\ surf.}{2\pi R\cdot dz}\ \overset{\frac{moles}{m^3 reactor}}{\frac{\partial C_A(z,r)}{\underset{m}{\partial r}}}\right|_R = \left. \underset{\substack{m^2 of\ reactor \\ wall\ surface}}{dA} \cdot \underset{\frac{m^2 cat-surface}{m^2\ of\ reactor\ wall\ surface}}{a} \cdot \underset{\frac{moles\ A\ reacted}{m^2 cat-surface\cdot s}}{k'' C_A} \right|_R$$

Solid Catalyzed Reactions – Laminar velocity profile

The differential equation contains functions like : $C_A^* \quad and \quad v_z(r)$

$$C_A^*(L) = \frac{\int_0^R 2\pi r \cdot v_z(r) \cdot C_A(L,r) \cdot dr}{\int_0^R 2\pi r \cdot v_z(r) \cdot dr}$$

The velocity profile is relatively easy to obtain; see handout notes. For the laminar flow in pipe the velocity distribution is:

$$\boxed{v_z(r) = \frac{R^2}{4 \cdot \mu}\left(\frac{\Delta P}{L}\right) \cdot \left[1 - \frac{r^2}{R^2}\right]} \quad at \;\; r = 0 \;\; v_z(r) = \boxed{v_{z\,max} = \frac{R^2}{4 \cdot \mu}\left(\frac{\Delta P}{L}\right)}$$

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Thank you for your attention!