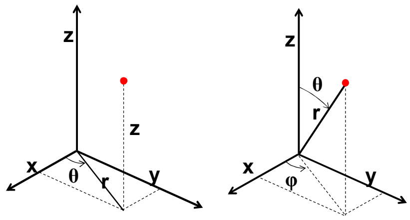
## PDEs in Chemical Engineering

- PDEs in chemical engineering arise problems where we need to know the variation of more than 1 variable.
- Examples:
  - Non-steady 1-dimensional problems
  - 2-dimensional steady problems
  - Non-steady 3-dimensional problems
- We will look at three types of **transport phenomena** in this course
  - Mass transport
  - Heat transport
  - Momentum transport in Fluid mechanics



## Coordinate systems




**Cylindrical coordinates** **Spherical coordinates**

- The <u>**choice**</u> of coordinate system is based on the <u>**geometry**</u> of the problem



## Heat in Cylindrical and Spherical Coordinates

- General Expression: $\frac{DT}{Dt} = \alpha \nabla^2 T + \frac{S}{\rho C_p}$
- Cylindrical coordinates:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \left( u_r \frac{\partial T}{\partial r} + \frac{u_\theta}{r}\frac{\partial T}{\partial \theta} + u_z \frac{\partial T}{\partial z} \right) = k\left( \frac{1}{r}\frac{\partial}{\partial r}\left( r\frac{\partial T}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right) + S$$

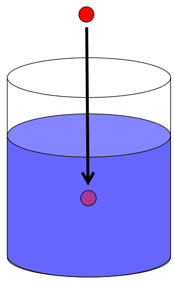
- Spherical coordinates:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \left( u_r \frac{\partial T}{\partial r} + \frac{u_\theta}{r}\frac{\partial T}{\partial \theta} + \frac{u_\phi}{r\sin\theta}\frac{\partial T}{\partial \phi} \right) =$$
$$k\left( \frac{1}{r^2}\frac{\partial}{\partial r}\left( r^2\frac{\partial T}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left( \sin\theta \frac{\partial T}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 T}{\partial \phi^2} \right) + S$$



## Example: Cooling of a Ball Bearing

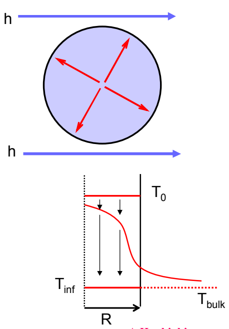
- In the manufacture of ball bearings, the final cooling is done in a water bath
- How long must the ball bearings be in the bath for cooling
- Find the PDE T(position, time)





## What are we Modeling?

- We are wanting to find the temperature distribution <u>***within***</u> the ball bearing
- Don't care about the bulk fluid, other than for the heat transfer coefficient (h)
- h gives us a boundary condition






## Choose Coordinate system

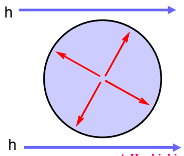
- If we chose Cartesian or cylindrical coordinates, we would have a hard time defining the boundary conditions
- So, we choose spherical

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \left( u_r \frac{\partial T}{\partial r} + \frac{u_\theta}{r}\frac{\partial T}{\partial \theta} + \frac{u_\phi}{r\sin\theta}\frac{\partial T}{\partial \phi} \right) =$$
$$k\left( \frac{1}{r^2}\frac{\partial}{\partial r}\left( r^2\frac{\partial T}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left( \sin\theta \frac{\partial T}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 T}{\partial \phi^2} \right) + S$$

- Equation applies <u>***within***</u> the sphere only (a solid. Therefore, **no** convection

- Temperature is a function of time and position: T(t,r,θ,φ)
- Think about the geometry of the problem
- Heat exiting the sphere in all directions (symmetrically). We are assuming that h is constant across the surface of the sphere
- Therefore, there is no dependence of θ,φ on T.
- T(t,r):

$$\frac{\partial T}{\partial \theta} = \frac{\partial T}{\partial \phi} = 0$$






$$\rho C_p \frac{\partial T}{\partial t} = k\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) + \cancel{\frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial T}{\partial \theta}\right)} + \cancel{\frac{1}{r^2 \sin^2\theta}\frac{\partial^2 T}{\partial \phi^2}}\right) + \cancel{S}$$

$$\rho C_p \frac{\partial T}{\partial t} = k\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right)\right)$$

- This equation is much easier to solve than the original expression.
- We always want to work with the ***simplest*** expression possible



## Fundamental Relationships (Heat)

- Fourier's Law of Heat <u>Diffusion</u>:

$$q = -\frac{k}{\rho c_v}\frac{\partial(\rho c_v T)}{\partial y}$$

- For constant $c_v$ and density:

$$q = -k\frac{\partial T}{\partial y}$$

- Units (Flux of Energy):

$$\frac{\text{W}}{\text{m}^2} = -\frac{\text{W}}{\text{m}\cancel{\text{K}}}\frac{\cancel{\text{K}}}{\text{m}}$$

$$\frac{\text{W}}{\text{m}^2} = \frac{\text{J}}{\text{s}\cdot\text{m}^2}$$



## Fundamental Relationships (Mass)

- Fick's Law of Mass <u>Diffusion</u>:

$$J = -\frac{D}{\rho}\frac{\partial(\rho C)}{\partial y}$$

- For constant density:

$$J = -D\frac{\partial C}{\partial y}$$

- Units (Mass Flux):

$$\frac{\text{mol}}{\text{m}^2\text{s}} = -\frac{\cancel{\text{m}^2}}{\text{s}}\frac{\text{mol}}{\text{m}^3\text{m}}$$



## Fundamental Relationships (Momentum)

- Newton's Law of Viscosity (Momentum Diffusion):

$$\tau_{yx} = -\frac{\mu}{\rho}\frac{\partial \rho u_x}{\partial y}$$

- For constant density:

$$\tau_{yx} = -\mu\frac{\partial u_x}{\partial y}$$

- Units (Momentum Flux):

$$\frac{\text{N}}{\text{m}^2} = -\frac{\text{N}\cdot\text{s}}{\text{m}^2}\frac{\cancel{\text{m}}/\text{s}}{\text{m}}$$

$$\frac{\text{N}}{\text{m}^2} = \frac{\text{kg}\times\text{m}}{\text{s}^2\text{m}^2} = \frac{\text{kg}\times(\text{m/s})}{\text{m}^2\text{s}} = \frac{mV}{At}$$



## Mass Transport Equation with Rxn.

$$Example: A + B \rightarrow C$$

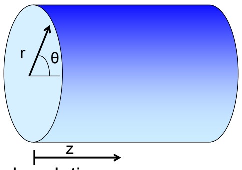
$$\frac{DC_A}{Dt} = D_{AB}\nabla^2 C_A + S$$

- Here, the source is the result of chemical reaction w.r.t. A
- $D_{AB}$ is the diffusion of A in into of B
- Reaction term is $S = -kC_A$ for a 1st order irreversible reaction

## Example: Diffusion in a Tube with Rxn.

- Diffusion of A into B occurs in a tube initially filled with B

$C_A$ = 100mol/m³




$C_A$= 0

- Find the unsteady solution
- Rxn: A+B→C
- The geometry of this problem suggests that we should derive our equations in cylindrical coordinates.



## Diffusion in a Tube

$$\frac{DC_A}{Dt} = D_{AB}\nabla^2 C_A + S$$

$$\frac{\partial C_A}{\partial t} + \nabla C_A = D_{AB}\nabla^2 C_A + -kC_A$$

- Applying cylindrical coordinates

$$\frac{\partial C_A}{\partial t} = -\left(u_r\frac{\partial C_A}{\partial r} + \frac{u_\theta}{r}\frac{\partial C_A}{\partial \theta} + u_z\frac{\partial C_A}{\partial z}\right) + D_{AB}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 C_A}{\partial \theta^2} + \frac{\partial^2 C_A}{\partial z^2}\right) - kC_A$$



$$\frac{\partial C_A}{\partial t} = -\left(u_r\frac{\partial C_A}{\partial r} + \frac{u_\theta}{r}\frac{\partial C_A}{\partial \theta} + u_z\frac{\partial C_A}{\partial z}\right) + D_{AB}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 C_A}{\partial \theta^2} + \frac{\partial^2 C_A}{\partial z^2}\right) - kC_A$$

- Assumptions
  - Velocity is negligible.
  - No dispersion in the theta direction. This makes sense based on the directions of the driving forces.

$$\frac{\partial C_A}{\partial t} = D_{AB}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) + D_{AB}\frac{\partial^2 C_A}{\partial z^2} - kC_A$$



## Boundary Conditions

- The boundaries of a system are those points in space for which something is known
- The number of boundary conditions is determined by the order of the differential
- For time, we normally have 1st order PDE in time.
- This requires an initial condition

$$\frac{\partial C_A}{\partial z} \rightarrow 1\ \text{B.C. for z}$$

$$\frac{\partial^2 C_A}{\partial z^2} \rightarrow 2\ \text{B.C.s for z}$$

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) \rightarrow 2\ \text{B.C.s for r}$$

$$\frac{\partial C_A}{\partial t} \rightarrow 1\ \text{I.C. in time}$$



## Boundary Conditions

- ***Dirichlet Boundary condition:***
  - Exact value of a function is given on a boundary
- ***Neumann Boundary Condition:***
  - The exact value of a function's derivative is given on a boundary
  - Often, seen when the flux of a conserved quantity is given at a boundary. Found when a boundary is insulated or impermeable to fluxes.
- ***Robin or Mixed Boundary Condition:***
  - A linear combination of the value of a function and its derivative is given
  - This commonly occurs when a boundary condition involves convective heat, mass and/or momentum transfer.



## Diffusion in a Tube Boundary Conditions

$$\frac{\partial C_A}{\partial t} = D_{AB}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) + D_{AB}\frac{\partial^2 C_A}{\partial z^2} - kC_A$$

$$C_A(t,z,r)$$

$$C_A(0,z,r) = C_{A0} = 0 \rightarrow \text{IC}$$

$$C_A(t,0,r) = C_{A0} = 100\text{mol/m}^3 \rightarrow \text{BC for z}$$

$$C_A(t,L,r) = C_{AL} = 0 \rightarrow \text{BC for z}$$

$$\left.\frac{\partial C_A}{\partial r}\right|_{(t,z,r=0)} = 0 \rightarrow \text{BC for r}$$

$$\left.\frac{\partial C_A}{\partial r}\right|_{(t,z,r=R)} = 0 \rightarrow \text{BC for r (no penetration of } C_A \text{ into wall)}$$

- 1 IC, two BCs in both r and z

## Diffusion in a Tube (revised)

- Really, it does not make sense that there would be a driving force in the r direction based on the fact that the ends are at constant concentrations everywhere.
- Also the BCs in r are suggesting a trivial solution or a sigmoidal curve (not likely)
- So, we can simplify the equations further



## Diffusion in a Tube Boundary Conditions (revised)

$$\frac{\partial C_A}{\partial t} = D_{AB}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) + D_{AB}\frac{\partial^2 C_A}{\partial z^2} - kC_A$$

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$$C_A(t,L,r) = C_{AL} = 0 \rightarrow \text{BC for z}$$



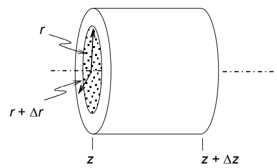
## Diffusion in a Pipe II

- The transport equations for diffusion can be derived utilizing a control volume approach (as in the derivation last Thurs.)
- This technique may be easier than crossing off terms.
- However, we need to understand the problem ***before*** setting up the differential element



## Control Volume

- No variation in the theta direction
- Integrate from 0 to 2π
- Resulting 'tube' is the control volume






## Assumptions

- No velocity in r or theta directions.
  - This can also be stated: Velocity in the z direction dominates
- No diffusion in the theta direction

$$acc = (in - out)_{conv,z} + (in - out)_{diff,z} + (in - out)_{diff,r}$$

$$2\pi r\Delta r\Delta z\frac{\partial C}{\partial t} = u2\pi r\Delta r\left(C|_z - C|_{z+\Delta z}\right) - 2\pi r\Delta rD\left.\frac{\partial C}{\partial z}\right|_z + 2\pi r\Delta rD\left.\frac{\partial C}{\partial z}\right|_{z+\Delta z} + \\ -\left.\left(2\pi r\Delta zD\frac{\partial C}{\partial r}\right)\right|_r + \left.\left(2\pi r\Delta zD\frac{\partial C}{\partial r}\right)\right|_{r+\Delta r}$$



## Simplification

- Divide by constants in front of the accumulation term

$$\frac{\partial C}{\partial t} = u\frac{\left(C|_z - C|_{z+\Delta z}\right)}{\Delta z} - \left(D\left.\frac{\partial C}{\partial z}\right|_z - D\left.\frac{\partial C}{\partial z}\right|_{z+\Delta z}\right)\Big/\Delta z + \\ -\left(\left.\left(rD\frac{\partial C}{\partial r}\right)\right|_r - \left.\left(rD\frac{\partial C}{\partial r}\right)\right|_{r+\Delta r}\right)\Big/r\Delta r$$

- Note that the r in the last two terms of the equation are not equivalent

## Simplification

- Take the limit as the Δr and Δz go to zero
- First 2 terms are easy.
- For last two:

$$-\left(\left(rD\frac{\partial C}{\partial r}\right)\Big|_r-\left(rD\frac{\partial C}{\partial r}\right)\Big|_{r+\Delta r}\right)\Big/ r\Delta r$$

Remember that r is evaluated at two different locations so it doesn't cancel

$$\frac{\partial C}{\partial t}=-u\frac{\partial C}{\partial z}+D\frac{\partial^2 C}{\partial z^2}+\frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)$$



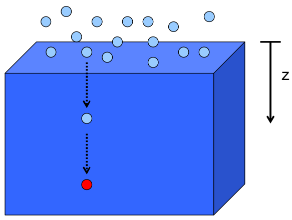
## Diffusion of $O_2$ into a stagnant film

- Oxygen dissolves into and reacts irreversibly with aqueous sodium sulfate solution
- Find the concentration of $O_2$ in the medium
- Gas solubility at the interface is denoted as $C_A$*
- Reaction rate of $O_2$: $r_a=k(C_A)^n$



## Diffusion of $O_2$

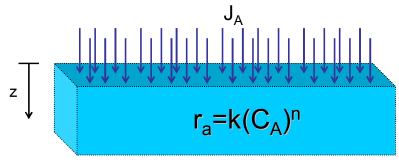
- First part of the path, the oxygen molecule diffuses
- Subsequently, the molecule reacts according to the kinetics
- If the concentration of $O_2$ is the same everywhere on the surface, there will be **no driving force** in the x and y directions






## Diffusion in the z direction

- Choose an area of 1 $m^2$ (shaded area below)
- Perform a mass balance $O_2$ on the differential element






$$acc = in - out + gen$$

$$\frac{\partial}{\partial t}\{\Delta z\cdot 1m^2 C_A\}=\left[-D\cdot 1m^2\frac{\partial C_A}{\partial z}\right]\Bigg|_z+\left[D\cdot 1m^2\frac{\partial C_A}{\partial z}\right]\Bigg|_{z+\Delta z}-\Delta z\cdot 1m^2 kC_A^n$$

$$\frac{\Delta z\cdot 1m^2\frac{\partial}{\partial t}\{C_A\}}{\Delta z\cdot 1m^2}=\frac{1m^2\left[-D\frac{\partial C_A}{\partial z}\right]\Big|_z+\left[D\frac{\partial C_A}{\partial z}\right]\Big|_{z+\Delta z}}{\Delta z\cdot 1m^2}-\frac{\Delta z\cdot 1m^2 kC_A^n}{\Delta z\cdot 1m^2}$$

$$\frac{\partial}{\partial t}\{C_A\}=\frac{\left[D\frac{\partial C_A}{\partial z}\right]\Big|_{z+\Delta z}-\left[D\frac{\partial C_A}{\partial z}\right]\Big|_z}{\Delta z}-kC_A^n$$

$$\lim \Delta z\to 0$$

$$\frac{\partial C_A}{\partial t}=D\frac{\partial^2 C_A}{\partial z^2}-kC_A^n$$



## Boundary conditions

- 1 I.C and 2 B.Cs (in z) required
- 2nd B.C indicates no change in $O_2$ at infinity or that there is **no driving force** to mass transfer

$$\frac{\partial C_A}{\partial t}=D\frac{\partial^2 C_A}{\partial z^2}-kC_A^n$$

$$C_A(t,z)$$

$$IC\rightarrow C_A(0,z)=0$$

$$BC1\rightarrow C_A(t,0)=C_A*(const)$$

$$BC2\rightarrow \frac{\partial C_A}{\partial z}\Bigg|_{t,\infty}=0$$