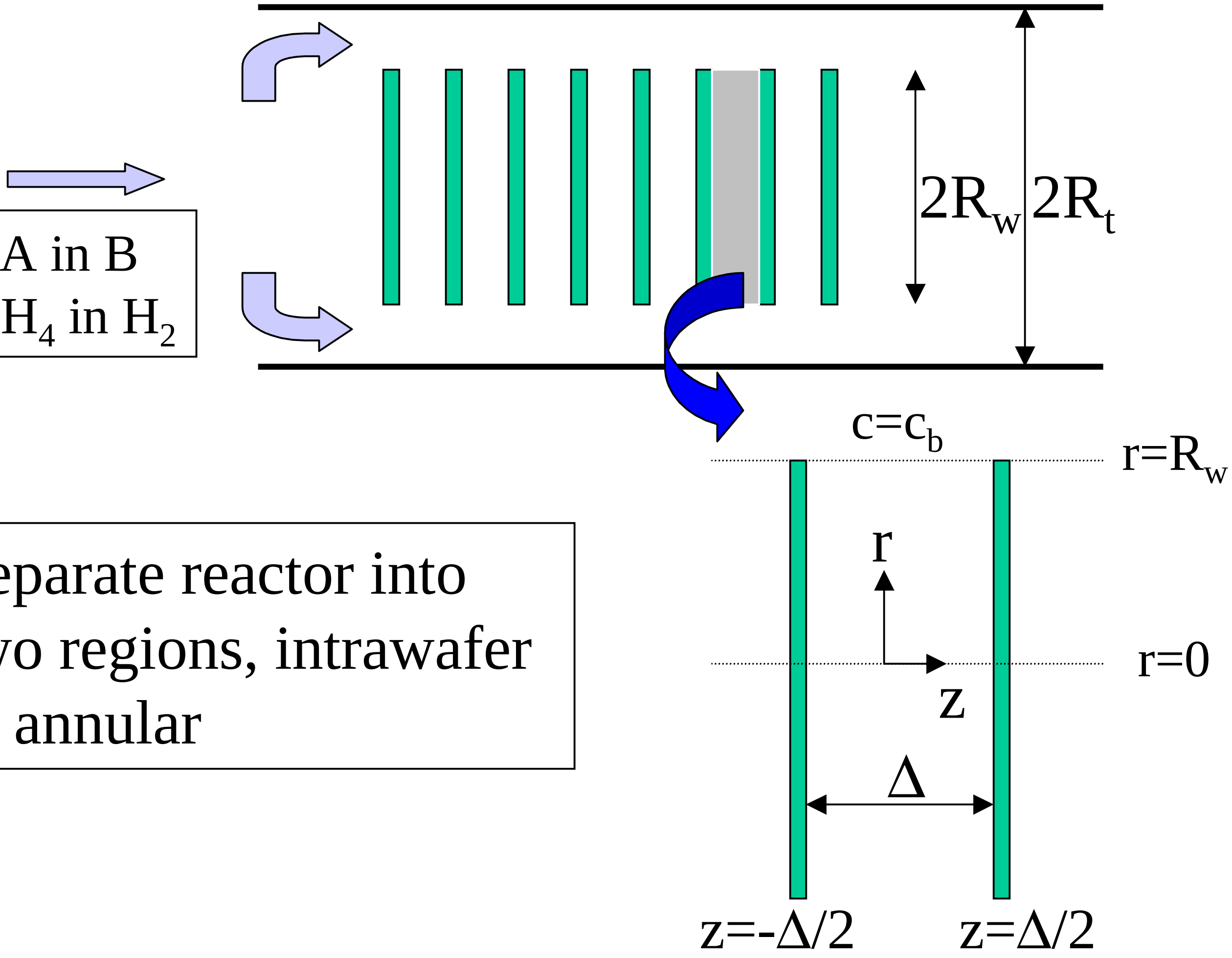
Coupled Mass Transport and Reaction in LPCVD Reactors



Dilute A in B
e.g., SiH_4 in H_2

Separate reactor into two regions, intrawafer & annular

Continuity Eqn: Convection-Diffusion-Reaction Eqns

Assumptions

- Dilute species i in major carrier gas (e.g., H_2) i=SiH_4
- Isothermal
- Constant D_i and density

No rxn in the gas

$$D_i \nabla^2 c_i - \cancel{\vec{u} \cdot \nabla c_i} + \cancel{R_i} = \cancel{\frac{\partial c_i}{\partial t}}$$

~ 0

Assume stagnant in
the intrawafer
region

Steady state

Equations and Boundary Conditions for the intrawafer region

$$\boxed{\frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} = 0}$$

$$\boxed{\begin{aligned}
&\frac{\partial c}{\partial r} = 0 \quad @ \quad r = 0 \\
&c = c_b \quad @ \quad r = R_w \\
&D\frac{\partial c}{\partial z} = r_s \quad @ \quad z = -\Delta / 2 \\
&D\frac{\partial c}{\partial z} = -r_s \quad @ \quad z = \Delta / 2
\end{aligned}}$$

r_s = surface reaction rate (net loss rate of SiH_4); related to the deposition rate

- If r_s is linear in c then there is an analytic solution
- If r_s is nonlinear we have to seek numerical solution

Approximate solution – "Fin Approximation"

- Take $r_s = kc$ & average over z direction
- Averaging over the small dimension (z) is called the "fin approximation": an approximation which is very good for 2-D regions with high aspect ratio (R/Δ)

$$\int_{-\Delta/2}^{\Delta/2} \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial c}{\partial r}\, dz + \int_{-\Delta/2}^{\Delta/2} \frac{\partial^2 c}{\partial z^2}\, dz = 0$$

$$\Delta \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial C}{\partial r} + \left.\frac{\partial C}{\partial z}\right|_{z=\Delta/2} - \left.\frac{\partial C}{\partial z}\right|_{z=-\Delta/2} = 0$$

$$\Delta \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial C}{\partial r} + \left(-\frac{kC}{D} - \frac{kC}{D} \right) = 0$$

$$D \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial C}{\partial r} - \frac{2}{\Delta} kC = 0$$

$$let \quad C(r) = \frac{\int_{-\Delta/2}^{\Delta/2} c(r,z)\, dz}{\int_{-\Delta/2}^{\Delta/2} dz} = \frac{1}{\Delta} \int_{-\Delta/2}^{\Delta/2} c(r,z)\, dz$$

$$\frac{2}{\Delta} = \frac{2\pi R_w^2}{\Delta \pi R_w^2} = \frac{surface\ area}{volume}$$

note

Nondimensionalization & Solution

$$\xi = \frac{r}{R_w} \qquad \theta = \frac{C}{c_b}$$

$$\frac{1}{\xi}\frac{\partial}{\partial \xi}\xi\frac{\partial \theta}{\partial \xi} = \frac{2kR_w^2}{D\Delta}$$

$$\Phi^2 = \frac{2kR_w^2}{D\Delta}$$

$$\frac{\partial^2 \theta}{\partial \xi^2} + \frac{1}{\xi}\frac{\partial \theta}{\partial \xi} - \Phi^2 \theta = 0$$

Bessel's equation (Mickley Sherwood & Reid, Applied Math in ChE p. 174)

Φ is the Thiele Modulus

$$= \frac{reaction\ rate}{diffusion\ rate} = \frac{diffusion\ \ time\ \ scale}{reaction\ \ time\ \ scale}$$

$$\theta = AI_o(\Phi\xi) + BK_o(\Phi\xi)$$

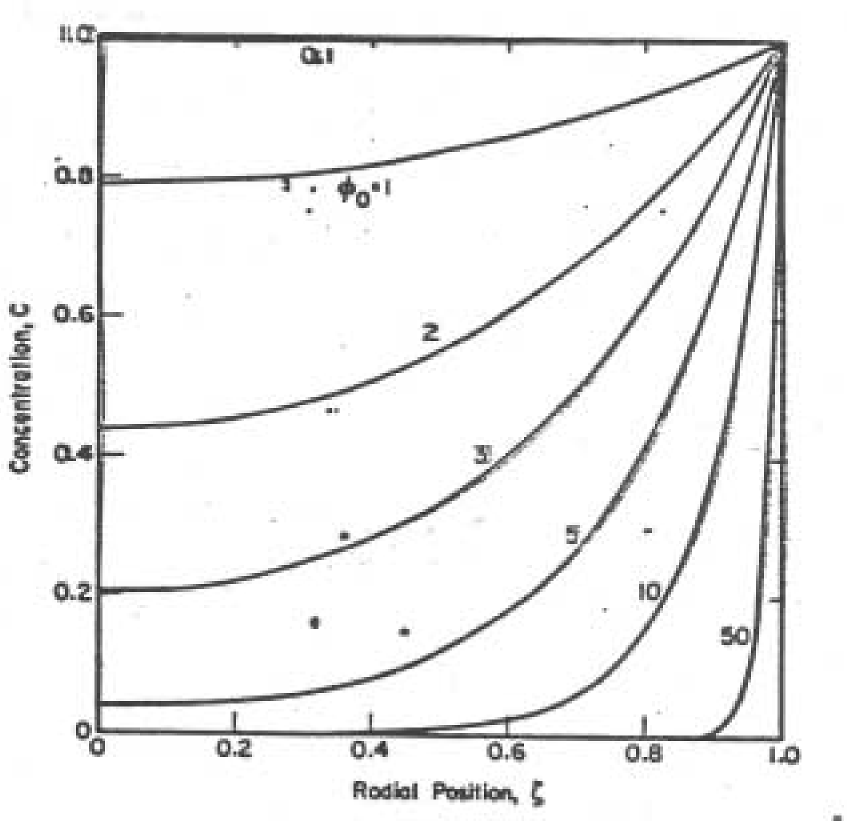
Zero order Bessel functions of the 2nd kind

Concentration profile in the intrawafer region

K_o has logarithmic singularity at $\xi=0 \Rightarrow B = 0$

Using $\theta=1$ at $\xi=1 \Rightarrow 1 = AI_o(\Phi)$

$$\boxed{\theta = \frac{I_o(\Phi\xi)}{I_o(\Phi)}}$$

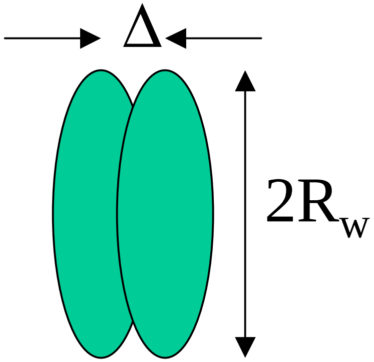


- as $\Phi \rightarrow 0$ uniformity gets better and C increases; reaction limited; diffusion faster than rxn
- as $\Phi >>1$ uniformity degrades and C decreases; diffusion limited; rxn faster than diffusion

$$\Phi = \frac{reaction\ rate}{diffusion\ rate}$$

Quantifying Uniformity

$$\eta = \text{“Uniformity Index”} = \frac{\textit{actual deposition rate}}{\textit{deposition rate if } c = c_b \textit{ throughout}}$$



$$\boxed{\eta = \frac{2\pi R_w \Delta \quad D \left.\dfrac{dC}{dr}\right|_{r=R_w}}{2k_s c_b \pi R_w^2}}$$

$$\boxed{\left.\frac{dC}{dr}\right|_{r=R_w} = \frac{C_b}{R_w}\left.\frac{d\theta}{d\xi}\right|_{\xi=1} = \frac{C_b\Phi}{R_w}\frac{I_1(\Phi\xi)\big|_{\xi=1}}{I_o(\Phi)} = \frac{C_b\Phi}{R_w}\frac{I_1(\Phi)}{I_o(\Phi)}}$$

$$\boxed{\eta = \frac{2\pi R_w \Delta\, D c_b \Phi I_1(\Phi)}{2k_s c_b \pi R_w^3 I_o(\Phi)}}$$

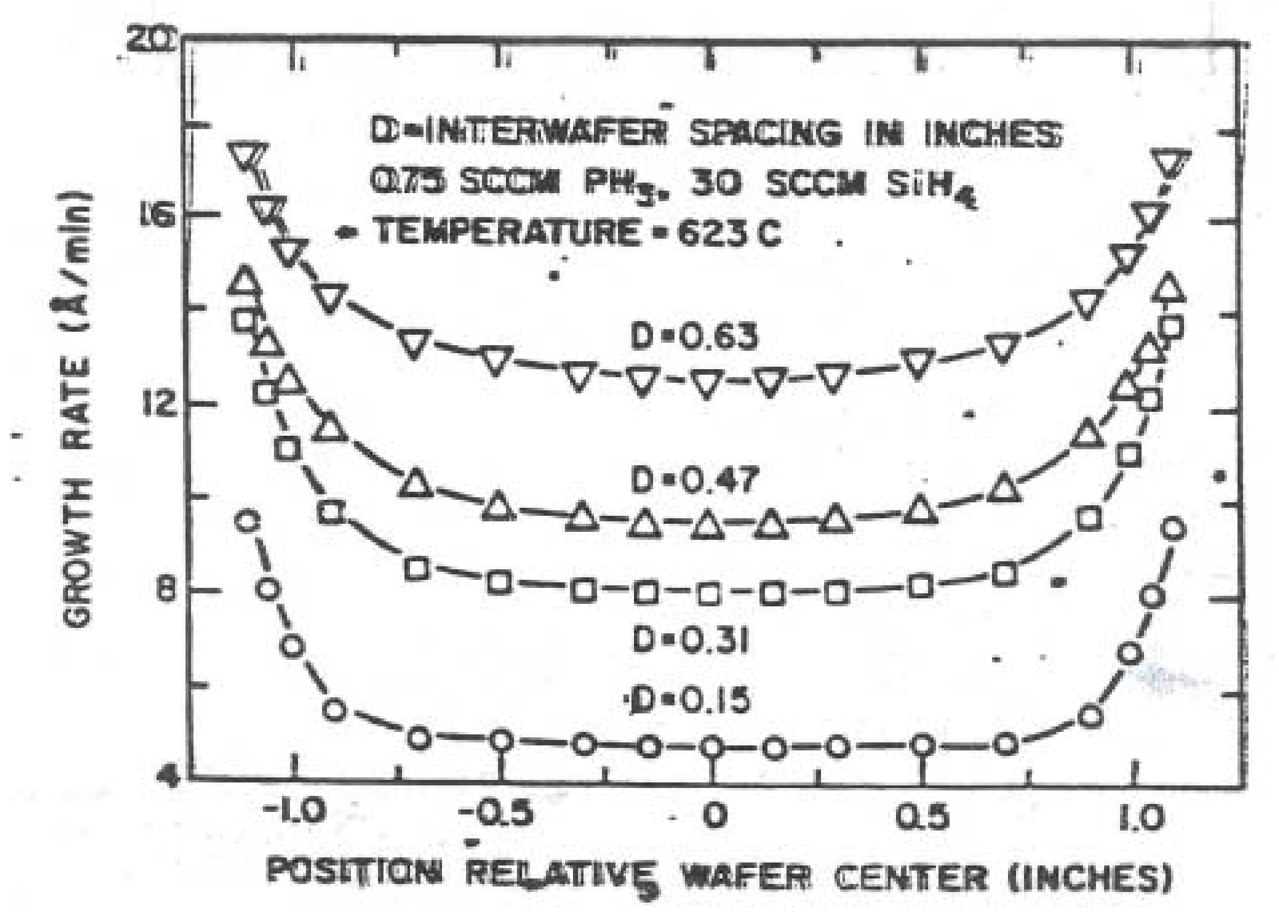
➡

$$\boxed{\eta = \frac{2\, I_1(\Phi)}{\Phi\, I_o(\Phi)} = f(\Phi)}$$

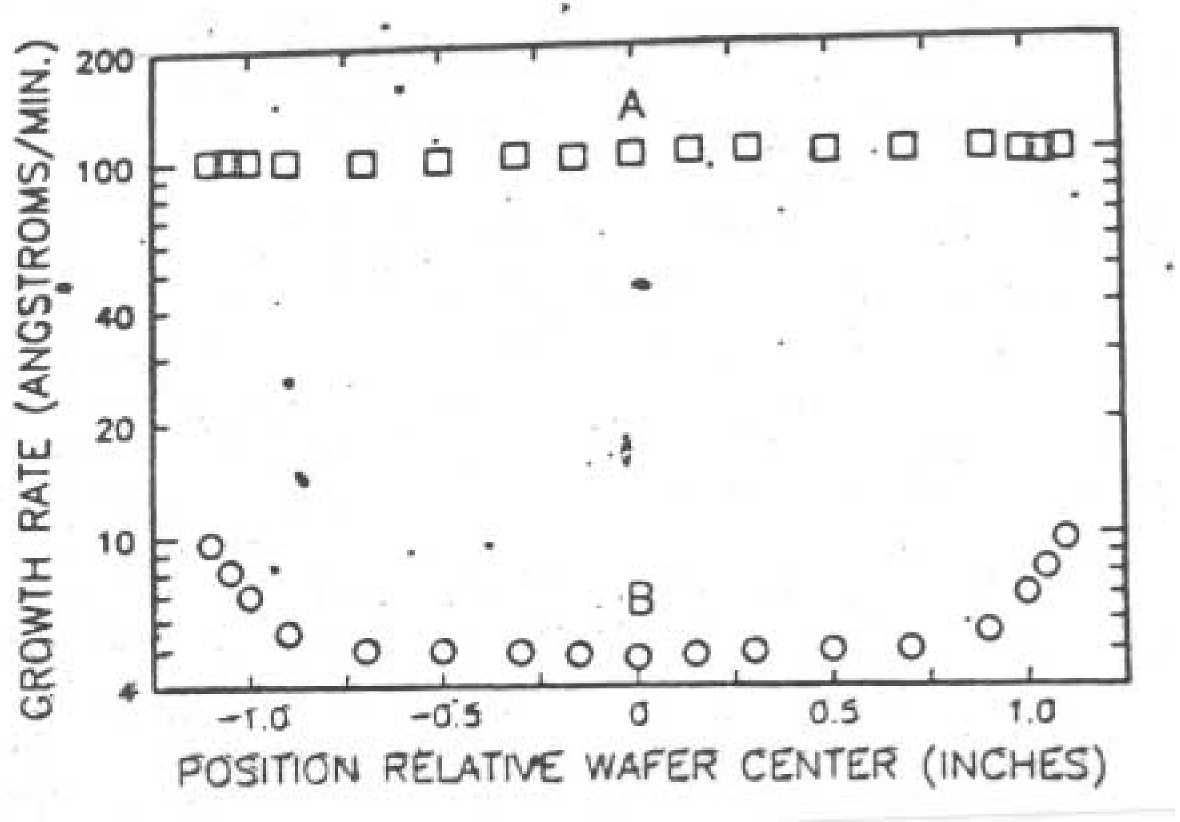
$\Phi << 1 \quad \Rightarrow \quad \eta \to 1 \quad \Rightarrow$ *uniform deposition (rxn limited)*

$\Phi >> 1 \quad \Rightarrow \quad \eta \to 0 \quad \Rightarrow$ *nonuniform deposition (diffusion limited)*

Growth Rate distribution as a function of wafer spacing



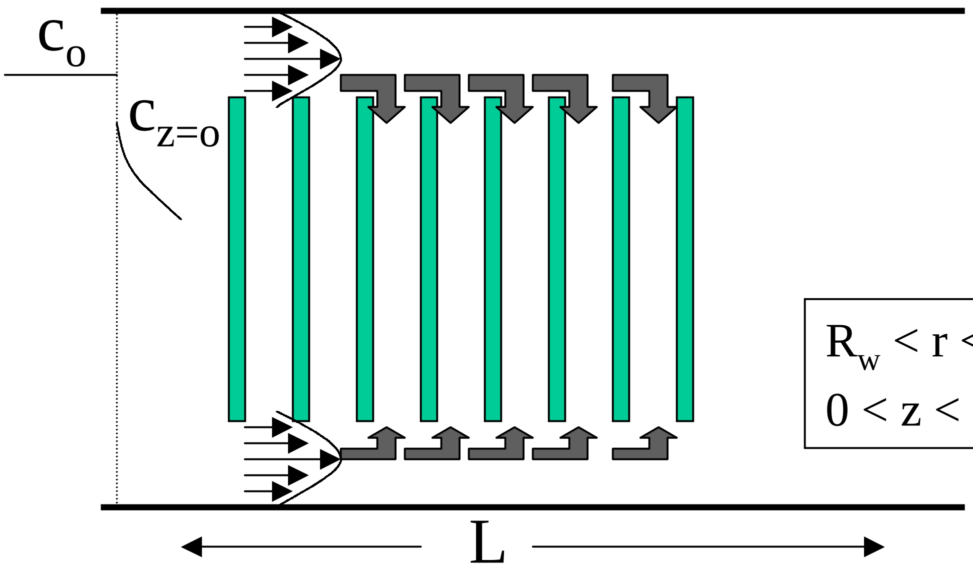
Growth Rate distribution as a function of Φ



$A \quad \Phi << 1 \;\Rightarrow\; \eta \to 1 \;\Rightarrow\; uniform \;\; deposition \;\; (rxn \;\; limited)$

$B \quad \Phi >> 1 \;\Rightarrow\; \eta \to 0 \;\Rightarrow\; nonuniform \;\; deposition \;\; (diffusion \;\; limited)$

Annular Region



$$D_i\nabla^2 c_i - \vec{u}\cdot\nabla c_i + \cancel{R_i} = \cancel{\frac{\partial c_i}{\partial t}}$$

No homogeneous
Gas phase rxns

Steady
state

$R_w < r < R_t$
$0 < z < L$

Boundary Conditions:

$$-D\frac{\partial c}{\partial r} = r_s \quad @ \quad r = R_t$$

$$D\frac{\partial c}{\partial r} = \eta k_s c\frac{2\pi R_w^2}{2\pi R_w \Delta} = \eta k_s c\frac{R_w}{\Delta} \quad @ \quad r = R_w$$

Dankwertz Boundary
Conditions: →

$$\left\{\begin{array}{l} -D\left.\frac{\partial c}{\partial z}\right|_{z=0} = u_z(c_o - c|_{z=0}) \quad @ \quad z = 0 \\ \left.\frac{\partial c}{\partial z}\right|_{z=L} = 0 \quad @ \quad z = L \end{array}\right.$$

r-averaged Eqns. in the Annular Region

$$\boxed{D\left[\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial c}{\partial r}+\frac{\partial^2 c}{\partial z^2}\right]-\underset{0}{\cancel{u_r}}\frac{\partial c}{\partial r}-u_z\frac{\partial c}{\partial z}=0}$$

- We are mostly interested in wafer-to-wafer changes (z variation) and do not care about profiles in the annulus.
- We will average over the r dimension and obtain a single r-averaged equation for C(z) where

$$\boxed{let \quad C(z)=\frac{\int_{R_w}^{R_t}\int_0^{2\pi} rc(r,z)drd\theta}{\int_{R_w}^{R_t}\int_0^{2\pi} rdrd\theta}=\frac{2}{(R_t^2-R_w^2)}\int_{R_w}^{R_t} rc(r,z)dr}$$

$$\boxed{\overline{u}_z=\frac{\int_{R_w}^{R_t}\int_0^{2\pi} ru_z(r)drd\theta}{\int_{R_w}^{R_t}\int_0^{2\pi} rdrd\theta}=\frac{2}{(R_t^2-R_w^2)}\int_{R_w}^{R_t} ru_z dr}$$

Look how boundary conditions in r end up in the differential equation for C(z) as if they are in the gas phase (i.e, the domain of diff eq.); surface reactions at radial walls appear as if they are gas phase reactions

$$D\int_{R_w}^{R_t}\frac{\partial}{\partial r}r\frac{\partial c}{\partial r}dr+\int_{R_w}^{R_t}\frac{\partial^2 c}{\partial z^2}rdr-\int_{R_w}^{R_t}ru_z\frac{\partial c}{\partial z}dr=0$$

$$D\left[r\frac{\partial c}{\partial r}\right]_{r=R_w}^{r=R_t}+\frac{\left(R_t^2-R_w^2\right)}{2}D\frac{d^2C}{dz^2}-\frac{\left(R_t^2-R_w^2\right)}{2}\bar{u}_z\frac{dC}{dz}=0$$

$$-\left(R_tk_sC+\eta\frac{k_sCR_w^2}{\Delta}\right)+\frac{\left(R_t^2-R_w^2\right)}{2}D\frac{d^2C}{dz^2}-\frac{\left(R_t^2-R_w^2\right)}{2}\bar{u}_z\frac{dC}{dz}=0$$

$$D\frac{d^2C}{dz^2}-\bar{u}_z\frac{dC}{dz}-\left[\frac{2k_sR_t}{\left(R_t^2-R_w^2\right)}+2\eta\frac{k_sR_w^2}{\Delta\left(R_t^2-R_w^2\right)}\right]C=0$$

Looks like

$$D\frac{d^2c}{dz^2}-u_z\frac{dc}{dz}+R_{gas}=0$$

Dimensional analysis

$$\Theta = \frac{C}{C_b} \qquad \zeta = \frac{z}{L}$$

$$\frac{D}{\bar{u}_z L}\frac{d^2\Theta}{d\zeta^2} - \frac{d\Theta}{d\zeta} - \left[\frac{2k_s R_t L}{\bar{u}_z\left(R_t^2 - R_w^2\right)} + \eta\frac{2k_s R_w^2 L}{\Delta\bar{u}_z\left(R_t^2 - R_w^2\right)}\right]\Theta = 0$$

$$Pe = \frac{\bar{u}_z L}{D} = \frac{\textit{convective transport}}{\textit{diffusive transport}}$$

$$Da_1 = \frac{2k_s R_t L}{\bar{u}_z\left(R_t^2 - R_w^2\right)} = \frac{\textit{reaction rate (deposition on walls)}}{\textit{convection rate}}$$

$$Da_2 = \frac{2k_s R_w^2 L}{\Delta\bar{u}_z\left(R_t^2 - R_w^2\right)} = \frac{\textit{reaction rate (deposition on wafers)}}{\textit{convection rate}}$$

$$\frac{1}{Pe}\frac{d^2\Theta}{d\zeta^2} - \frac{d\Theta}{d\zeta} - \left[Da_1 + \eta Da_2\right]\Theta = 0$$

Boundary conditions and Solution

$$\frac{d\Theta}{d\zeta} = 0 \quad @ \quad \zeta = 1$$

$$-\frac{1}{Pe}\frac{d\Theta}{d\zeta} = (1-\Theta) \quad @ \quad \zeta = 0$$

$$\Theta = \frac{2[(1+\beta)exp\{M(1+\beta)+M(1-\beta)\zeta\}-(1-\beta)exp\{M(1+\beta)\zeta+M(1-\beta)\}}{(1+\beta)^2\, exp\{M(1+\beta)\}-(1-\beta)^2\, exp\{M(1-\beta)\}}$$

$$where \quad \beta = \sqrt{1+\frac{4(Da_1+\eta Da_2)}{Pe}} \quad and \quad M = \frac{Pe}{2}$$

Dankwertz “continuous flow systems” *Chemical Engineering Science* **2** (1), 1 (1953).

Limiting Cases: PFR limit

- Pe→∞ (i.e., D →0 or u_z →∞)

  small diffusion rate compared to convection

  ⇒ Plug flow reactor (PFR) limit

$$\boxed{\beta = \sqrt{1+\frac{4(Da_1+\eta Da_2)}{Pe}} \rightarrow 1 \quad and \quad M \rightarrow \infty \quad Da^* = (Da_1+\eta Da_2)}$$

$$\boxed{M(1-\beta) = \frac{1}{2}Pe\left[1-\sqrt{1+\frac{4(Da_1+\eta Da_2)}{Pe}}\right] = -\frac{2\,Da^*}{\sqrt{1+\frac{4Da^*}{Pe}}} \quad = -Da^*}$$

$$\boxed{lim_{Pe\rightarrow\infty}\, \Theta = e^{-Da^*\zeta}}$$

Limiting Cases: PFR limit

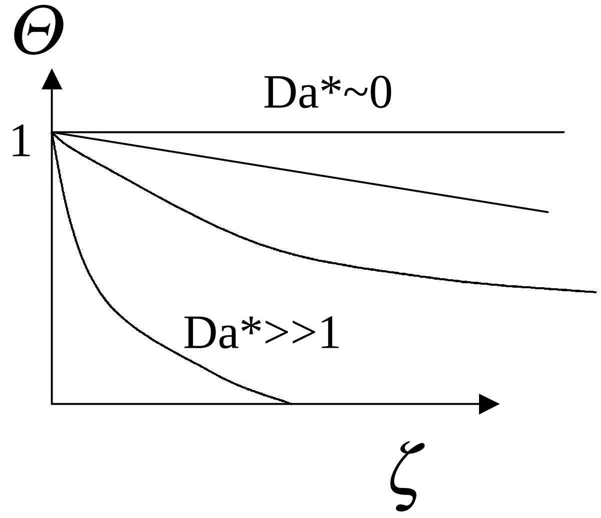
- Another way of seeing this is to look at Pe→∞ of the differential equation and boundary condition at $\zeta=0$

$$\boxed{\frac{1}{Pe}\frac{d^2\Theta}{d\zeta^2}-\frac{d\Theta}{d\zeta}-\left[Da_1+\eta Da_2\right]\Theta=0}$$

$$\boxed{\begin{array}{l}-\dfrac{1}{Pe}\dfrac{d\Theta}{d\zeta}=(1-\Theta)\quad @\quad \zeta=0\\ becomes\quad \Theta=1\quad @\quad \zeta=0\end{array}}$$

$$\boxed{\frac{d\Theta}{d\zeta}=-Da^*\Theta}$$

$$\boxed{\Theta=e^{-Da^*\zeta}}$$



Limiting Cases: CSTR limit

- Pe→0 (i.e., D →∞ or u_z →0)

  small flow rate (convection) compared to diffusion

  ⇒ Continuous stirred tank reactor (CSTR) limit

$$\frac{d^2\Theta}{d\zeta^2} - Pe\left\{\frac{d\Theta}{d\zeta} - Da^* \Theta\right\} = 0$$

$$as \quad Pe \rightarrow 0 \quad \frac{d^2\Theta}{d\zeta^2} = 0$$

$$\frac{d\Theta}{d\zeta} = 0 \quad @ \quad \zeta = 1$$

$$-\frac{1}{Pe}\frac{d\Theta}{d\zeta} = (1-\Theta) \quad @ \quad \zeta = 0$$

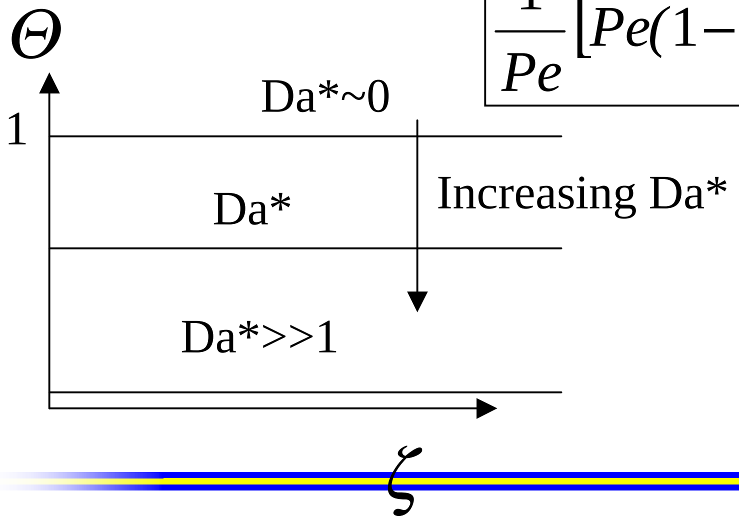
$$as \quad Pe \rightarrow 0 \quad \frac{d\Theta}{d\zeta} = 0 \quad @ \quad \zeta = 0$$

$$\boxed{lim_{Pe\rightarrow 0}\, \Theta = cons\,tan\,t}$$

Limiting Cases: CSTR limit

- To find the concentration we average over z-direction too

$$\boxed{\begin{gathered}\frac{1}{Pe}\int_0^1 \frac{d^2\Theta}{d\zeta^2}d\zeta - \int_0^1 \frac{d\Theta}{d\zeta}d\zeta - Da^*\int_0^1 \Theta d\zeta = 0 \\ \frac{1}{Pe}\left[\left.\frac{d\Theta}{d\zeta}\right|_{\zeta=1} = \left.\frac{d\Theta}{d\zeta}\right|_{\zeta=0}\right] + \Theta(1) - \Theta(0) - Da^*\Theta = 0 \\ \frac{1}{Pe}\left[Pe(1-\Theta)-0\right] - Da^*\Theta = 0\end{gathered}}$$



$$\boxed{\Theta = \frac{1}{1+Da^*}}$$

← CSTR limit

Wafer-to-wafer uniformity

Uniformity index often defined as

$$U = \frac{R_{max} - R_{min}}{R_{avg}} = \frac{C_{max} - C_{min}}{C_{avg}} = \frac{\Theta_{max} - \Theta_{min}}{\Theta_{avg}}$$

- U=0 : good uniformity
- U × 100 = % is variance with respect to average
- As U increases uniformity degrades
- For fixed Da* as Pe↑ U also ↑
- Pe ↑ means D ↓
- Since D ~ 1/P ⇒ lower P ⇒ better uniformity

$$\boxed{Pe = \frac{\bar{u}_z L}{D} = \frac{convective\,transport}{diffusive\,transport}}$$

Deposition Rate

- Often we are interested in deposition rate, R_D in thickness/time, e.g., Å/s, Å/min, nm/s, nm/min, μm/min, etc.

$$deposition\ flux\,(\#/cm^2s)\times film\ area\,(cm^2) = film\ density\,(\#/cm^3)\times \dot{V}\ \ (cm^3/s)$$

$$\boxed{r_s A = N_f A R_D = N_f A \frac{dh}{dt}}$$

$$\boxed{R_D = \frac{r_s}{N_f} = \frac{kc}{N_f}}$$

$$\boxed{N_f = \frac{\rho_f}{M_{wf}} N_{Avogadro}}$$