Small Washcoat Diffusion Resistance, Further Developments

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Review and Preview

- Asymptotic solution for small dimensionless diffusion resistance, D_{inv}.
  - Introduced at 2014 CLEERS
  - "An Asymptotic Solution for Washcoat Pore Diffusion in Catalytic Monoliths", Bissett, Emission Control Science and Technology, Vol. 1, No. 1, pp. 3-16 (2015)
- Summary
  - Alternative to approaches using Thiele modulus, ad hoc linearization
  - Recognize that "standard" approach (no washcoat gradients) is $D_{inv} = 0$ limit.
  - Generalize to $O(D_{inv})$ to capture dominant effects of small diffusion resistance.
  - Practical aftertreatment regime of catalyst effectiveness, $D_{eff} \approx O(10^{-6}\ m^2/s)$
  - Permits all features common to standard approach
    - Large, fully nonlinear reaction system
    - Many species, coverages
  - Also dual washcoat layers
  - Equivalent computational speed
- Preview
  - How does this asymptotic solution fit with other approximations using Thiele modulus?
  - Small concentrations and mass transport limits

Connections with Thiele modulus

- Asymptotic solution of nonlinear reaction/diffusion equations
  - No linearizations to obtain effectiveness factors or internal mass transfer coefficients
  - Large systems of reactions, species, coverages
- However, can still do "simplest problem", single-species, linear reactant:

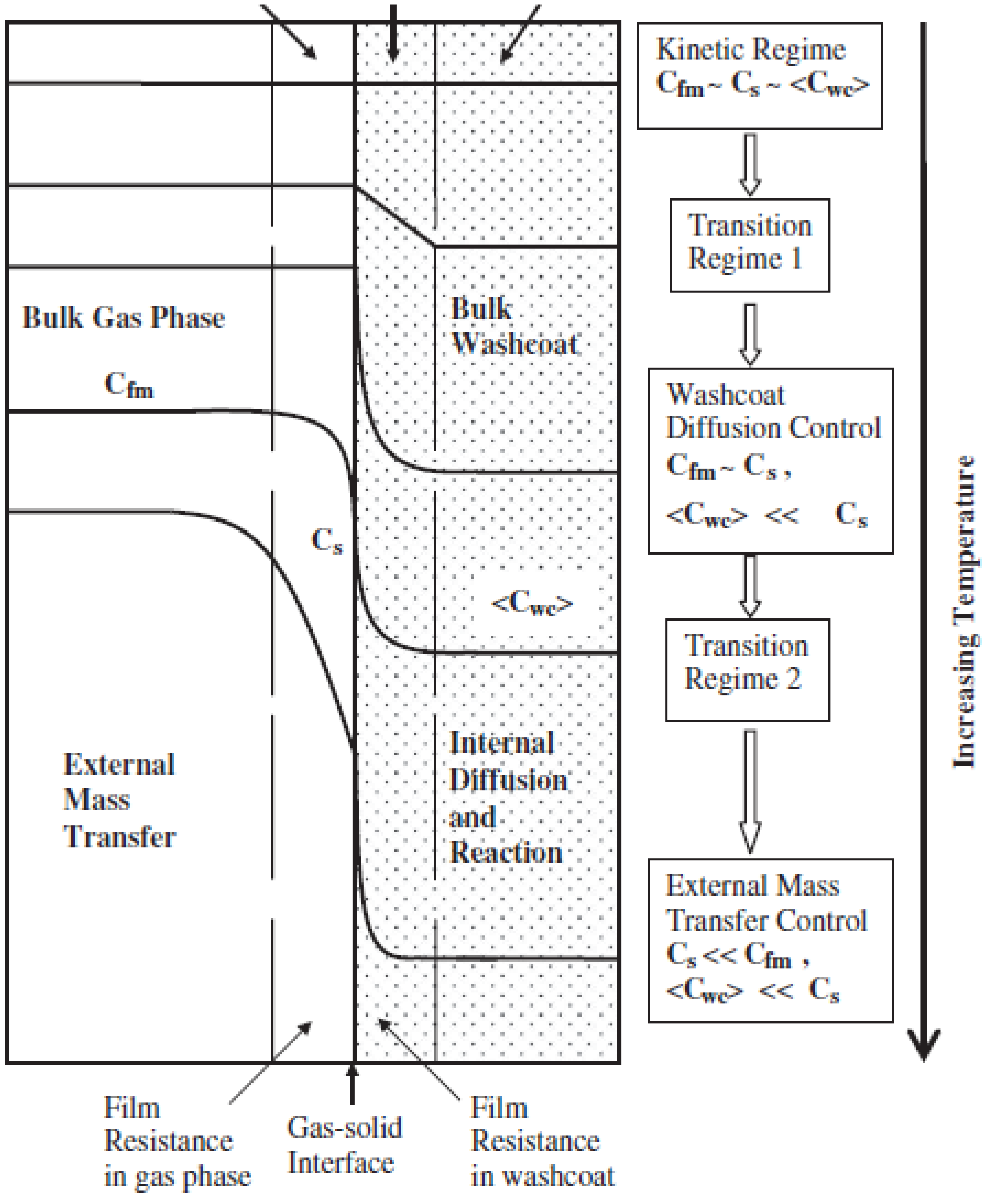
$$\frac{\partial^2 \omega}{\partial x^2} = \varphi^2 \omega \qquad 0 < x < 1$$

$$\frac{\partial \omega}{\partial x} = Bi(\omega - \omega_g) \qquad x = 0$$

$$\frac{\partial \omega}{\partial x} = 0 \qquad x = 1$$

  - Thiele modulus, φ, satisfies $\varphi^2 = D_{inv}(-R/\omega)$ with rate constant, $k = -R/\omega$
  - Biot number, $Bi = D_{inv} K$, controls size of gradients on each side of interface
  - D_{inv} << 1 limit requires both φ and Bi small
  - Sometimes done with simpler B.C., $\omega = 1$ at $x = 0$, but this obscures key points.
  - Complete asymptotic analysis
    - Inspired by figure in "Overall mass transfer coefficients and controlling regimes in catalytic monoliths", Joshi et al., Chemical Engineering Science, Vol. 65, pp. 1729-1747(2010), Figure 2.

Figure 2 from Joshi, et al. (2010)



Breakdown for all asymptotic regimes for single linear reactant

- Full solution available,
  - e.g., “The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts, Volume I, The Theory of the Steady State” Aris, Oxford University Press (1975)
- Either from full solution or governing equations. Simple exercise
- First divide into Bi regimes, then φ
- Some regimes are “distinguished limits”, some are transitional sublimits

$Bi = O(1)$

$\varphi^2 \ll 1$	$\omega(x) \sim \omega_g\left[1-\varphi^2\left(1/Bi + x - x^2/2\right)\right]$	$\omega_g \approx \omega_s \approx \bar{\omega}$
$\varphi^2 = O(1)$	$\omega(x) = \dfrac{\omega_g}{\cosh\varphi + (\varphi/Bi)\sinh\varphi}\cosh(\varphi(1-x))$	$\omega_g > \omega_s > \bar{\omega}$
$\varphi^2 \gg 1$	$\omega(x) \sim \dfrac{\omega_g Bi}{\varphi}\exp(-\varphi x)$	$\omega_g \gg \omega_s \gg \bar{\omega}$

- Down: increasing temperature
- Blue: kinetic control, $\omega_g \approx \bar{\omega}$
- Red: mass transfer control, $\omega_g \gg \omega_s$
- Mass transfer control =>
  - Kinetics fast enough that channel gas “sees” no surface concentration
  - Channel gas satisfies $W\dfrac{\partial \omega_g}{\partial z} = -K\omega_g$
  - Reactor output independent of local solution of reaction/diffusion problem in washcoat

$Bi >> 1$

$\varphi^2 \ll 1$	$\omega(x) \sim \omega_g\left[1-\varphi^2\left(1/Bi + x - x^2/2\right)\right]$	$\omega_g \approx \omega_s \approx \overline{\omega}$
$\varphi^2 = O(1)$	$\omega(x) \sim \dfrac{\omega_g}{\cosh\varphi}\cosh(\varphi(1-x))$	$\omega_g \approx \omega_s > \overline{\omega}$
$Bi \gg \varphi^2 \gg 1$	$\omega(x) \sim \omega_g \exp(-\varphi x)$	$\omega_g \approx \omega_s \gg \overline{\omega}$
$\varphi^2 = O(Bi)$	$\omega(x) \sim \dfrac{\omega_g}{(1+\varphi/Bi)}\exp(-\varphi x)$	$\omega_g > \omega_s \gg \overline{\omega}$
$\varphi^2 \gg Bi$	$\omega(x) \sim \dfrac{\omega_g Bi}{\varphi}\exp(-\varphi x)$	$\omega_g \gg \omega_s \gg \overline{\omega}$

- Corresponds to Joshi paper figure ($D_{eff} \approx O(10^{-7}\ m^2/s)$)
  - e.g., $\omega_g \approx \omega_s \gg \overline{\omega}$ only occurs when $Bi >> 1$
- As temperature (φ^2) increases, $\omega_s >> \omega$ before $\omega_g >> \omega_s$
- Kinetic and transport control occur in only 1 extreme regime each

Bi << 1

$\varphi^2 \ll Bi$	$\omega(x) \sim \omega_g\left[1-\varphi^2\left(1/Bi+x-x^2/2\right)\right]$	$\omega_g \approx \omega_s \approx \bar{\omega}$
$\varphi^2 = O(Bi)$	$\omega(x) \sim \dfrac{\omega_g}{1+\varphi^2/Bi}\left[1+\varphi^2\left(\dfrac{\varphi^2/(3Bi)}{1+\varphi^2/Bi}-x+x^2/2\right)\right]$	$\omega_g > \omega_s \approx \bar{\omega}$
$Bi \ll \varphi^2 \ll 1$	$\omega(x) \sim \dfrac{\omega_g Bi}{\varphi^2}\left\{1-Bi/\varphi^2-\varphi^2\left[1/6-(1-x)^2/2\right]\right\}$	$\omega_g \gg \omega_s \approx \bar{\omega}$
$\varphi^2 = O(1)$	$\omega(x) \sim \dfrac{\omega_g Bi}{\varphi \sinh \varphi}\cosh(\varphi(1-x))$	$\omega_g \gg \omega_s > \bar{\omega}$
$\varphi^2 \gg 1$	$\omega(x) \sim \dfrac{\omega_g Bi}{\varphi}\exp(-\varphi x)$	$\omega_g \gg \omega_s \gg \bar{\omega}$

- Our case of interest (D_{inv} << 1) : $Bi = D_{inv}K \ll 1$ and $\varphi^2 = D_{inv}(R/\omega) = O(Bi)$
  - Closest regime to "standard", $D_{inv} = 0$
  - 1st and 3rd rows are included sublimits of 2nd row
- Mass transport limitation achieved even while $\varphi^2 << O(1)$
- Solution in washcoat does not affect reactor output (ω_g) for $\omega_g >> \omega_s$

D_{inv} << 1 for large nonlinear systems

- Review from asymptotic solution (e.g. single layer)

$$K\left[\omega_s(\bar{\omega},\bar{R})-\omega_g\right]=\bar{R}, \qquad \bar{R}=R(\bar{\omega})$$

  – used in determining $\bar{\omega}$

  – Solution: $\omega(x)=\bar{\omega}+D_{inv}\bar{R}\left[1/6-(1-x)^2/2\right]$

- Consider reactant, i, $\bar{R}_i<0$, $\varphi_i^2=-D_{inv,i}\bar{R}_i/\bar{\omega}_i=O(D_{inv})$
  – If we increase φ_i^2 greater than $O(D_{inv})$:
    - “Simplest problem” ➔ mass transfer limit before $O(1)$
    - In general problem, cannot make rate more negative than $-K_i\omega_{gi}$
    - Instead, decrease $\bar{\omega}_i\to 0$
    - Flat profiles, ($D_{inv}\ll 1$, $\bar{R}$ bounded, $O(1)$) ➔ $\omega_s\to 0$
    - Transport limitation. Do not need detailed washcoat solution.
- Asymptotic solution depends on approximately flat profiles
  – Breakdown with increasing φ_i^2 manifests as $\omega(x)<0$

Small concentration problem

- Can’t get, don’t need (mass transport) accurate asymptotic solution for $\varphi_i^2 = O(1)$ or larger
- Can’t tolerate negative concentrations
- Several strategies attempted
  - Dual layer hardest, especially layer 1 reactant, layer 2 product
  - Must respect asymptotic solution for $\varphi_i^2 << 1$, where needed and applicable
  - Can introduce/manipulate higher-order terms: D_{inv}^2 and higher
- Best strategy so far – hyperbolic functions from “simplest problem”

Maintain positive washcoat profiles

- Each species handled individually (suppress subscript)
- For products, rates positive, no changes required:
  - Layer 1: $\omega(x) = \bar{\omega}^{(1)} + D_{inv}^{(1)} \bar{R}^{(1)} [1/6 - (1-x)^2/2] + D_{inv}^{(1)} \bar{R}^{(2)} (x - 1/2)$
  - Layer 2: $\omega(x) = \bar{\omega}^{(2)} + D_{inv}^{(2)} \bar{R}^{(2)} [1/6 - (2-x)^2/2]$
- Positivity requires arguments from algebraic equations for $\bar{\omega}^{(1)}$ and $\bar{\omega}^{(2)}$
- For reactants, $\bar{R} < 0$
  - Layer 1: $\omega(x) = \bar{\omega}^{(1)} \varphi^{(1)} \dfrac{\cosh(\varphi^{(1)}(1-x))}{\sinh \varphi^{(1)}} + D_{inv}^{(1)} \bar{R}^{(2)} \dfrac{\sinh(\varphi^{(1)}(x - 1/2))}{\varphi^{(1)} \cosh(\varphi^{(1)}/2)}$
  - Layer 2: $\omega(x) = \bar{\omega}^{(2)} \varphi^{(2)} \dfrac{\cosh(\varphi^{(2)}(2-x))}{\sinh \varphi^{(2)}}$
  - When expanded for small φ, these agree with original formulas.
  - Maintains $\omega(x) \geq 0$ for all φ
  - Downsides: hyperbolic evaluations and increased nonlinearity of profiles

Review and Conclusions

- Considerable experience in complex, challenging problems since last year. Current release of GT-Suite.
- Increasing Thiele modulus cannot not make the rate larger than the finite external mass transfer limit. It makes the washcoat concentrations small.
- Clarified how mass transport limit and small Biot number allows us to finesse large concentration gradients of large Thiele modulus
- Avoid negative concentrations for large Thiele modulus by adding higher-order terms that convert washcoat profiles from simpler linear functions of the rates to hyperbolic functions.
- Plan a research note to archive hyperbolic function modification