CBE 40445

10/2/20

TEST #2 REVIEW

CHAPTERS 4, 5, 6

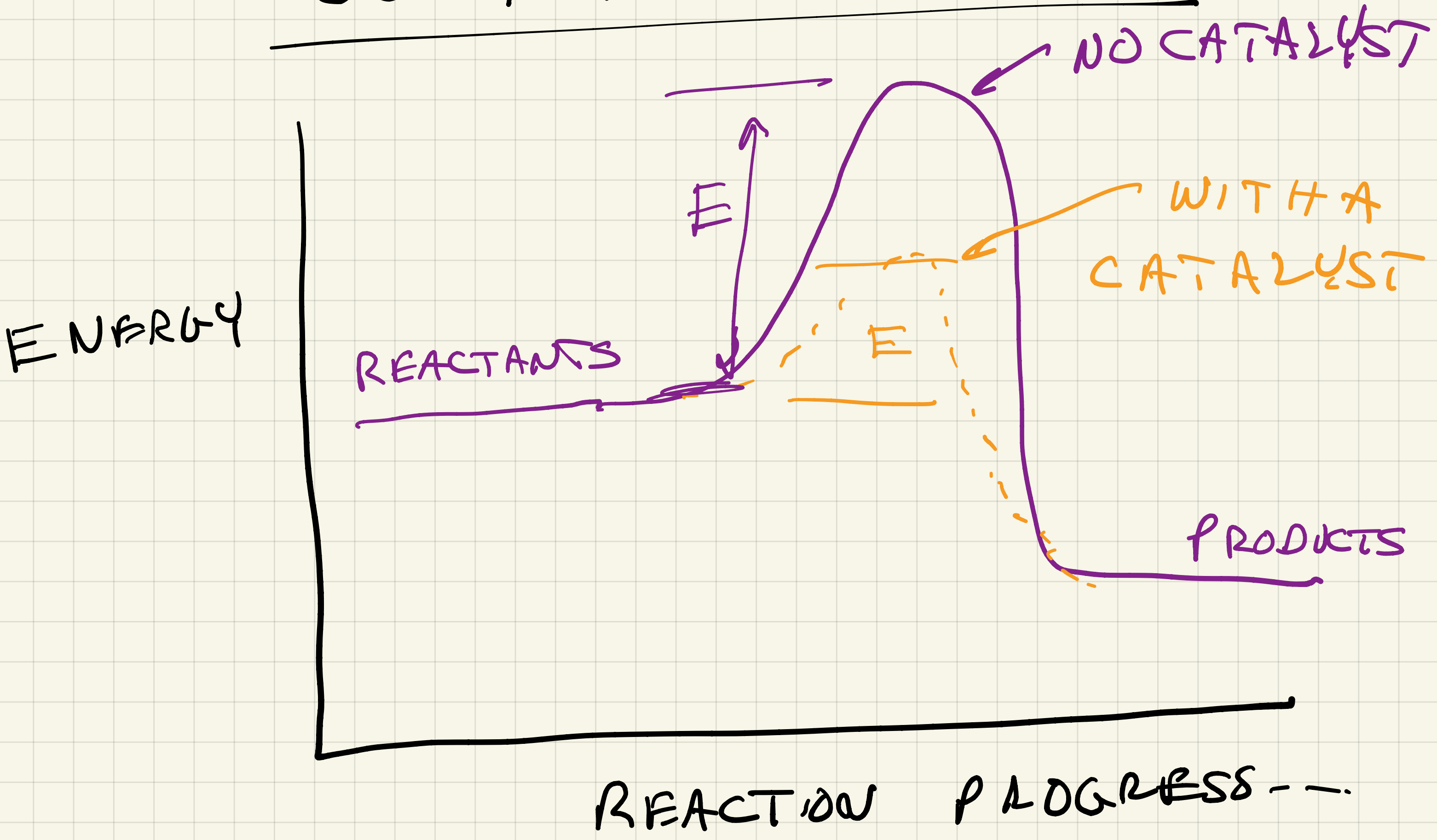
EXAMINATION AND QUANTIFICATION OF HETEROGENEOUS CATALYSTS

- COMPLEX REACTION SCHEMES
- SURFACE SITES INVOLVED
- INTERMEDIATE COULD BE AT STEADY-STATE

MASS TRANSFER EFFECTS IN HETEROGENEOUS CATALYSTS

- QUANTIFICATION OF INTERNAL + EXTERNAL DIFFUSION LIMITATIONS
- $0 = D_A \frac{d^2 C_A}{dy^2} - k C_A$

MOST IMPORTANT IDEA



ACTIVATION ENERGY IS REDUCED

$$\frac{\exp\left(\frac{-25{,}000}{(1.987)300}\right)}{\exp\left(\frac{-35{,}000}{1.987(300)}\right)}$$

$$= 2\times10^{7} \quad !!$$

LANGMUIR ADSORPTION

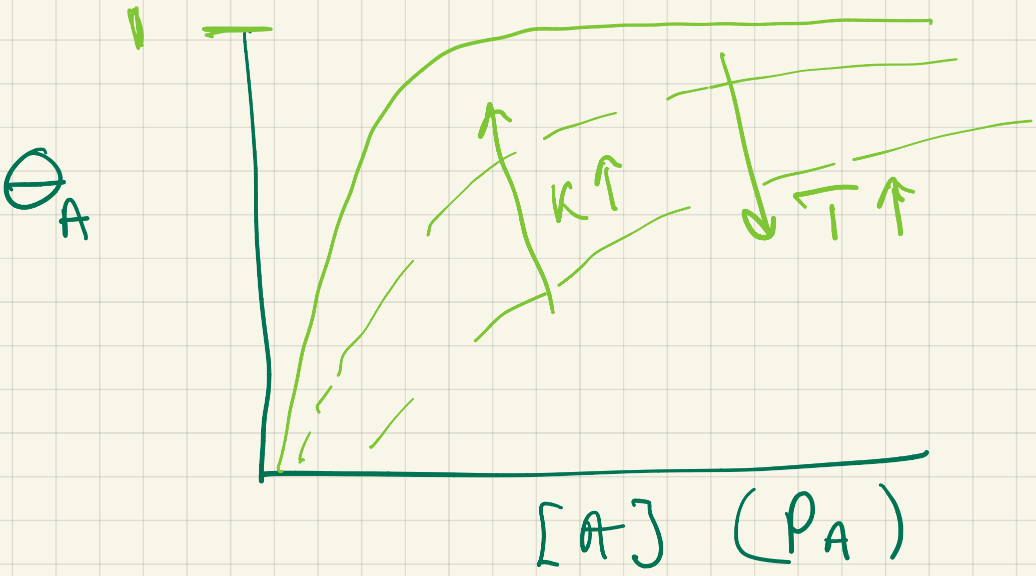
- PHYSICAL ADSORPTION (CONDENSATION
- 1 LAYER ON IDENTICAL SITES

$$A + * \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} A^* \qquad K_{ads} = \frac{k_{ads}}{k_{de}} = \frac{[A^*]}{[A][*]}$$

$$[*]_0 = [*] + [A^*] \qquad \theta_A = \frac{A^*}{[*]_0}$$

$$\theta_A = \frac{K_{ads}[A]}{1 + K_{ads}[A]}$$

$$\Delta G = \underset{\substack{\uparrow \\ \text{NEGATIVE}}}{\Delta H} - T\underset{\substack{\uparrow \\ \text{NEGATIVE}}}{\Delta S}$$



RATE EXPRESSION FOR CATALYZED REACTION

$$A \longrightarrow M$$

① $$A + * \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} A^*$$ ADSORPTION

② $$A^* \xrightarrow{k_2} M + *$$ SURFACE REACTION

$$r = k_2[A^*]$$

HOW DO WE GET AN EXPRESSION FOR A^* ?

$$[*]_0 = [*] + [A^*]$$

USE THIS EQ FOR $[*]$

ASSUME $[A^*] \rightarrow$ STEADY STATE

$$\frac{d[A^*]}{dt} = 0 = k_{ads}[A][*] - k_{des}[A^*] - k_2[A^*]$$

$$[A^*] = \frac{K_{ads}[A][*]_0}{1 + \frac{k_2}{k_{des}} + K_{ads}[A]} \qquad K_{ads} = \frac{k_{ads}}{k_{des}}$$

$$r = \frac{k_2 \; K_{ads} \; [A][*]_0}{1 + \frac{k_2}{k_{des}} + K_{ads}[A]}$$

$$A + B \longrightarrow M$$

2ND ORDER

$$r = \frac{k_3 K_{adsA} K_{adsB} [*_0][A][B]}{\left(\underbrace{1 + K_{ads_A}[A] + K_{ads}[B]}_{\text{SITE BALANCE}}\right)^2}$$

EFFECT OF ADSORPTION ON ACTIVATION ENERGY

SEE 9/18

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2$$

$$r = 2k_2 [O_2][*]$$

FOR HIGH SURFACE COVERAGE

$$r = \frac{2k_2 [*_0][O_2]}{K_1 [CO]}$$

APPARENT RATE CONST

$$\frac{2k_2}{K_1}$$

$$E_{APP} = E_2 - \Delta H_{ADS\,CO}$$

$$+ \quad - \, (-)$$

$$E_{APP} \cong -\Delta H_{ADS\,CO}$$

BUT THEN THE COUNTER EXAMPLE

$$A \rightarrow M$$

$$A + * \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} A* \xrightarrow{k_2} M + *$$

$$r = \frac{k_2 K_{ads} [*]_0 [A]}{1 + K_{ads} [A]}$$

LOW COVERAGE

$$r \hat{=} k_2 K_{ads} [*]_0 [A]$$

$$E_{APP} = \underset{(+)}{E_2} + \underset{(-)}{\Delta H_{Ads}}$$

$$E_{APP} \sim + \text{ OR } -$$

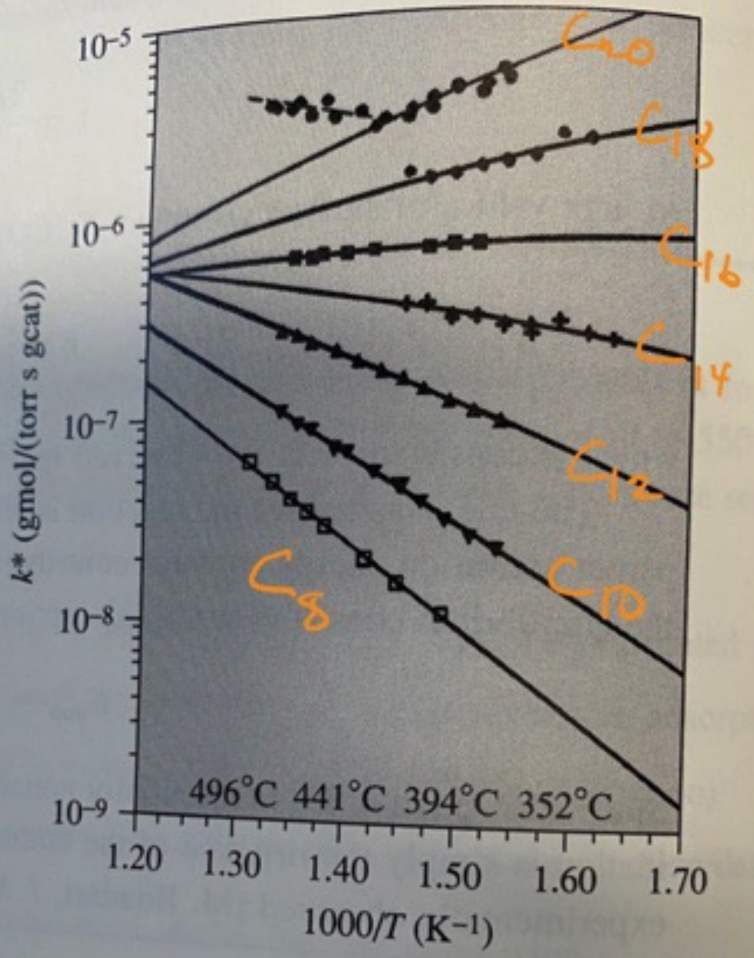


Figure 5.3.1 |
Temperature dependen

TRANSPORT LIMITATIONS IN HETEROGENEOUS CATALYSTS

INTERNAL DIFFUSION LIMITATIONS

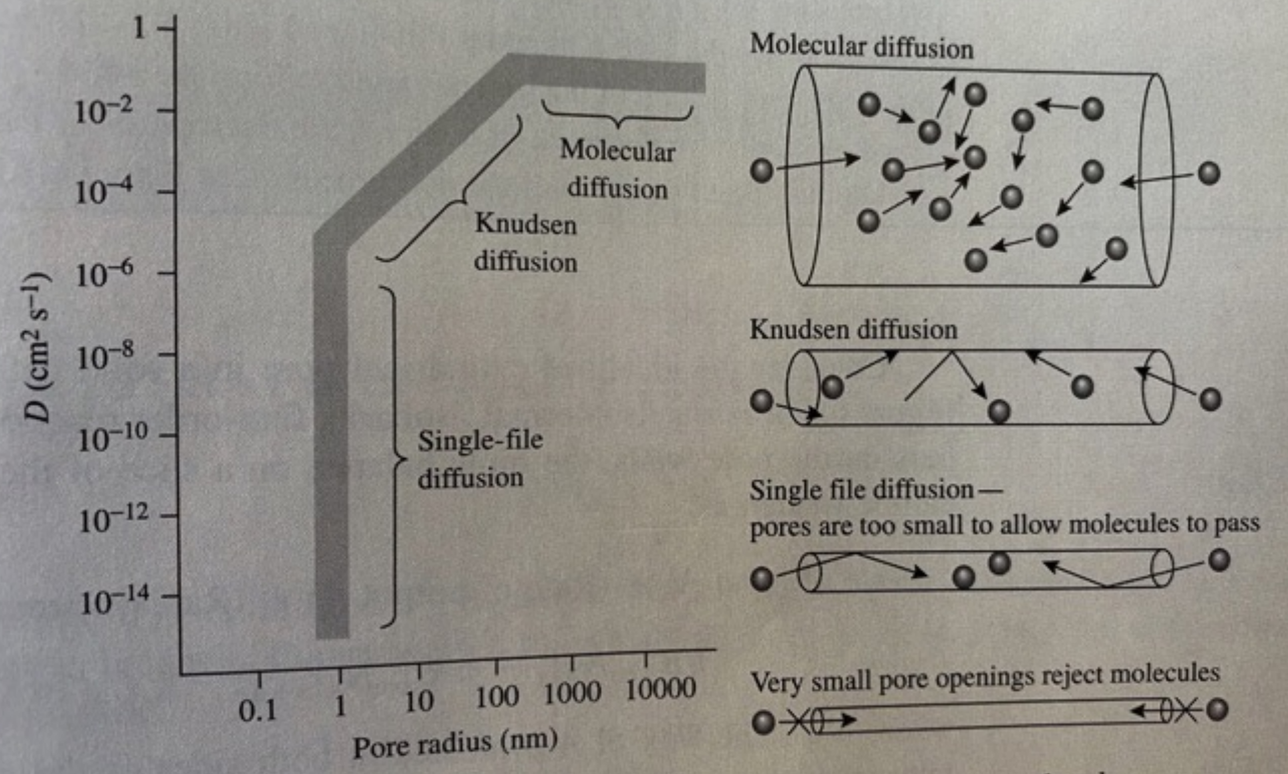
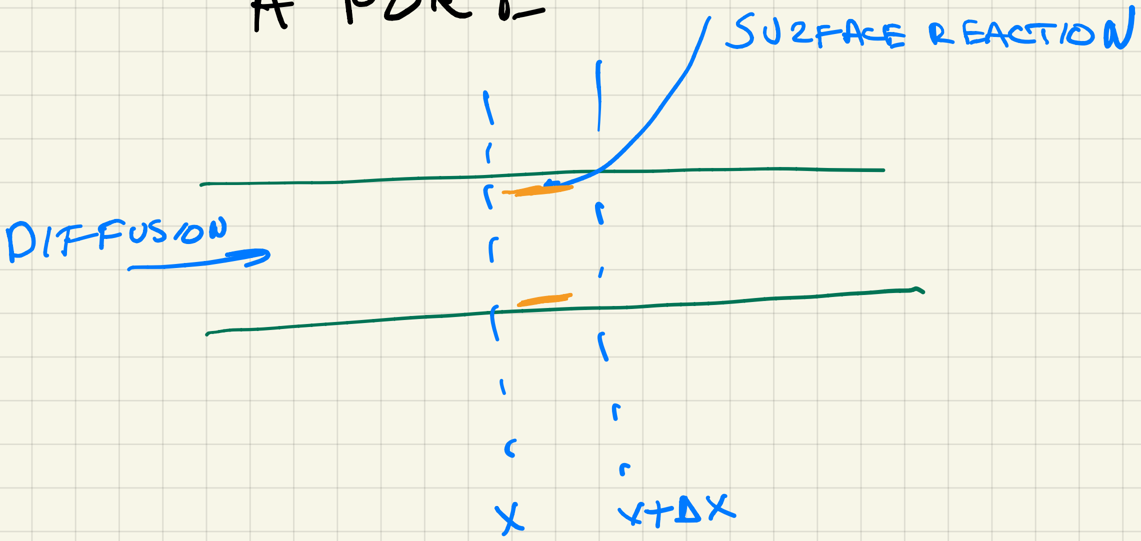


Figure 6.3.1 | Influence of pore size on diffusivity of gas-phase molecules.

REACTION WILL BE OCCURING INSIDE CATALYST.

LET'S CONSIDER REACTION & DIFFUSION TOGETHER IN A PORE



MASS BALANCE

RATE OF ACCUMULATION = RATE AT WHICH A FLOWS INTO SLICE AT x=x − RATE AT WHICH A FLOWS OUT OF SLICE AT x=x+Δx + RATE AT WHICH A IS CREATED BY REACTION

$$0 = N_A\Big|_{x} \pi R_p^2 - N_A\Big|_{x+\Delta x} \pi R_p^2 - \underset{\substack{\text{SURFACE RATE CONST} \\ \left(\frac{\ell}{\text{TIME}}\right)}}{k_s} C_A \underbrace{(2\pi R_p)\Delta x}_{\text{SURFACE AREA INSIDE PORE}}$$

WITH "USUAL" SIMPLIFICATIONS

$$\frac{d^2 C_A}{dx^2} - \frac{k}{D_{TA}} C_A = 0$$

NONDIMENSIONAL:

$$\frac{d^2 \theta}{dX^2} - \frac{k L^2}{D_{TA}} \theta = 0$$

$$\phi^2 = \frac{k L^2}{D_{TA}}$$

$\theta = 0$ @ $X = 0$

$\frac{d\theta}{dX} = 0$ @ $X = 1$

$$\theta = \frac{\cosh(\phi(1-X))}{\cosh \phi}$$

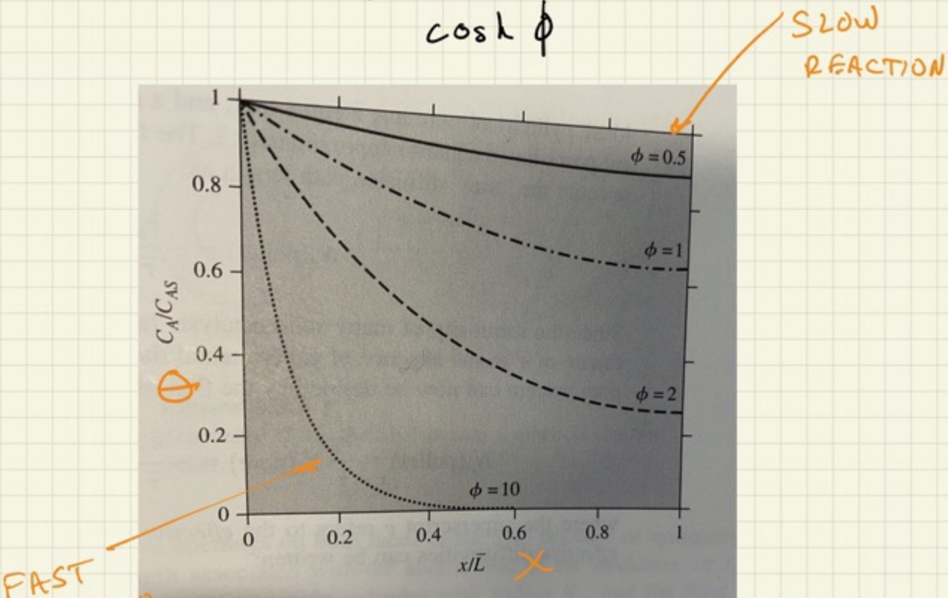


Figure 6.3.4 | Effect of Thiele modulus on the normalized concentration profiles in a catalyst pore with first-order surface reaction.

EFFECTIVENESS FACTOR

$$\eta = \frac{r_{OBSERVED}}{r_{MAX}}$$

$C(x) < C_s$ IN SOME OR ALL OF CATALYST

C_s IN ENTIRE VOLUME OF CATALYST PELLET

$$= \frac{S_p \int_0^r k C_A(r) r^2 dr}{V_p k C_s}$$

RATHER THAN CALCULATE SURFACE INTEGRAL, USUALLY EASIER TO CALCULATE C_A FLUX AT SURFACE

$$r_{OBSERVED} = 4 \pi R_p D^{e}_{TA} \left. \frac{dC_A}{dr} \right|_{r=R_p}$$

IF WE PICK A LENGTH THAT IS GENERALIZED FOR DIFFERENT GEOMETRIES...

$$L_p = \frac{V_p}{S_p}$$

$$\phi_0 = L_p \sqrt{\frac{k}{D^e_{TA}}}$$

LARGE ϕ IS DIFFUSION LIMITED

	L_p
SLAB	L
CYLINDER	$R_p/2$
SPHERE	$R_p/3$

$$\eta = \frac{\tanh \phi_0}{\phi_0}$$

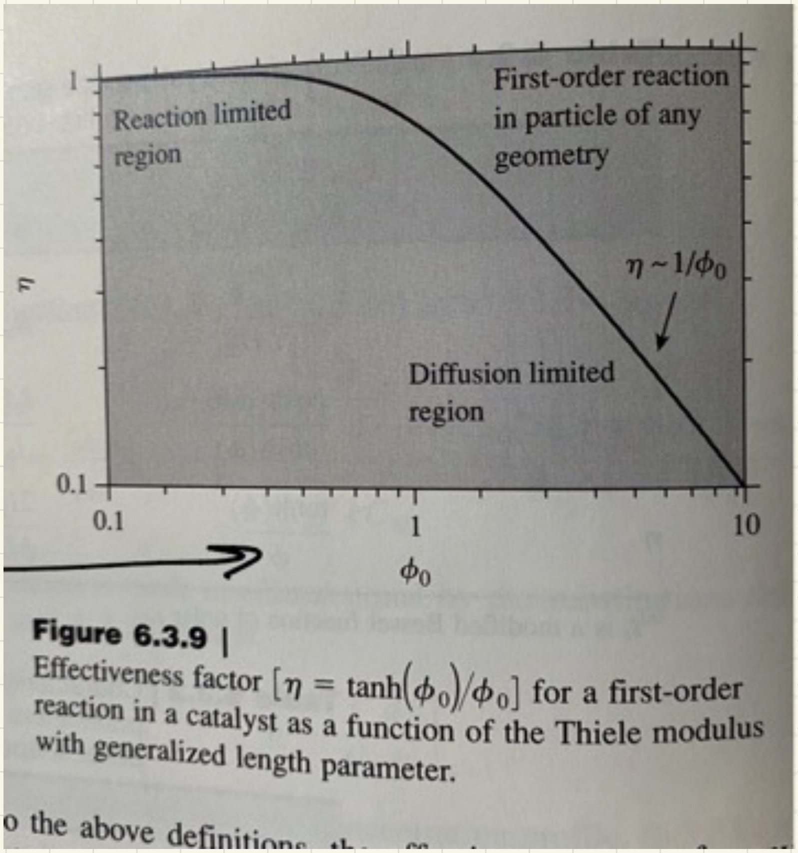
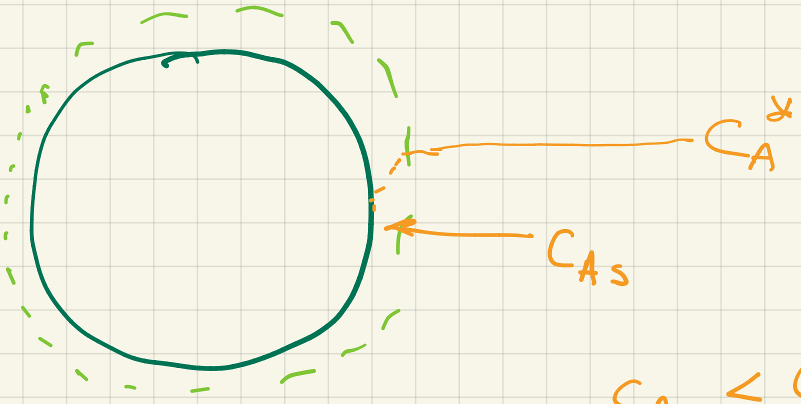


Figure 6.3.9 |
Effectiveness factor $[\eta = \tanh(\phi_0)/\phi_0]$ for a first-order reaction in a catalyst as a function of the Thiele modulus with generalized length parameter.

o the above definitions

EXTERNAL RESISTANCE



$C_{As} < C_A^*$

CHARACTERIZE EXTERNAL RESISTANCE WITH MASS TRANSFER COEFFICIENT

$$Sh \equiv \frac{\bar{k}_c L_p}{D_{A\,(\text{LIQUID OR GAS})}}$$

$$Sh = 2 + 0.6\, Re^{1/2}\, Sc^{1/3}$$

$$Re \equiv \frac{L_p\, u^\infty \rho}{\mu}$$

$$Sc \equiv \frac{\mu/\rho}{D_A}$$

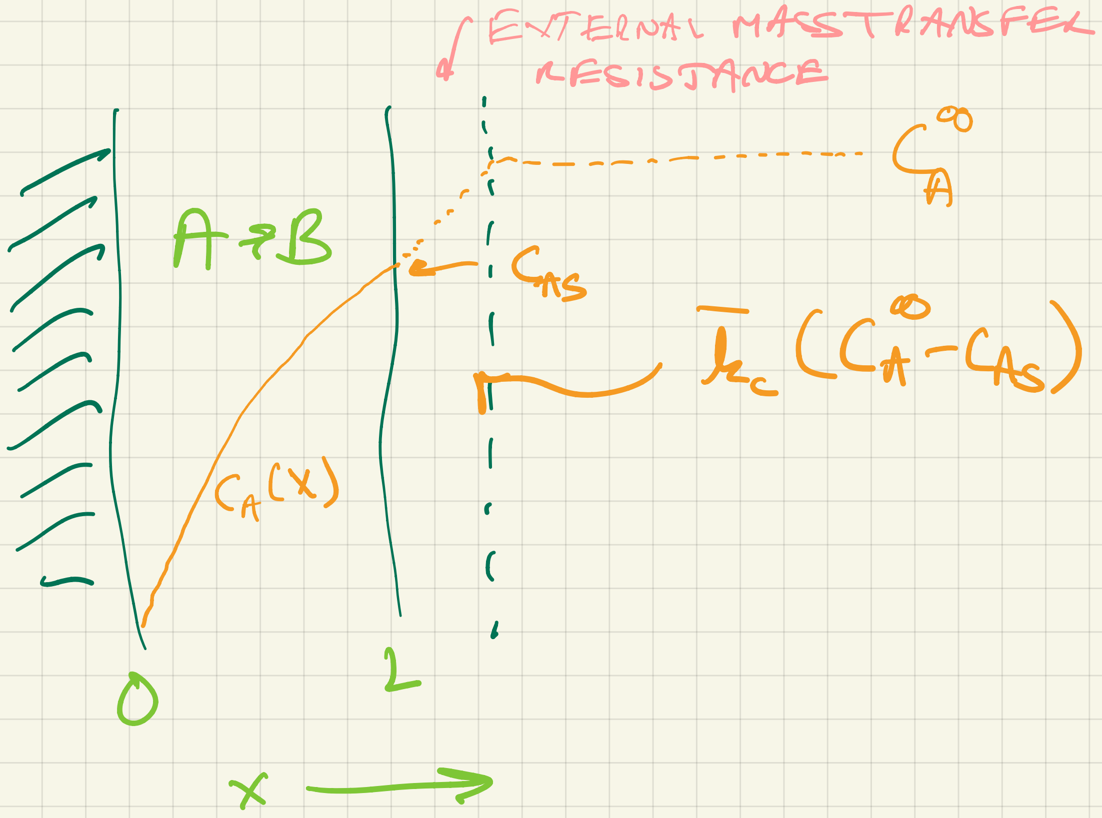
EXAMINATION OF COMBINED EXTERNAL + INTERNAL RESISTANCE FROM SOLUTIONS TO "EXACT" EQUATIONS

CONSIDER 1ST ORDER REACTION

SLAB GEOMETRY

$$A \longrightarrow B$$

$$r = k C_A$$



$$0 = D_{TA}^{\circ} \cdot \frac{\partial^2 C_A}{\partial x^2} - k C_A$$

SOLVE INSIDE PELLET WITH A BOUNDARY CONDITION THAT ACCOUNTS FOR EXTERNAL MASS TRANSFER

$$\eta \equiv \frac{x}{L} \qquad (0 - 1)$$

$$\Theta \equiv \frac{C_A}{C_A^{\infty}}$$

$$\phi^2 \equiv \frac{k L}{D_{TA}^{\circ}}$$

REACTION RATE CONSTANT

$$Bi \equiv \frac{L \bar{k}_c}{D_{TA}}$$

MASS TRANSFER COEFFICIENT

$$0 = \frac{d^2\theta}{d\eta^2} - \phi^2 \theta$$

$$\left.\frac{\partial \theta}{\partial \eta}\right|_{\eta=1} = -Bi\left(\theta(1) - 1\right)$$

FLUX INSIDE PELLET = FLUX TO SURFACE OF PELLET

$$\theta'(\eta=0) = 0$$

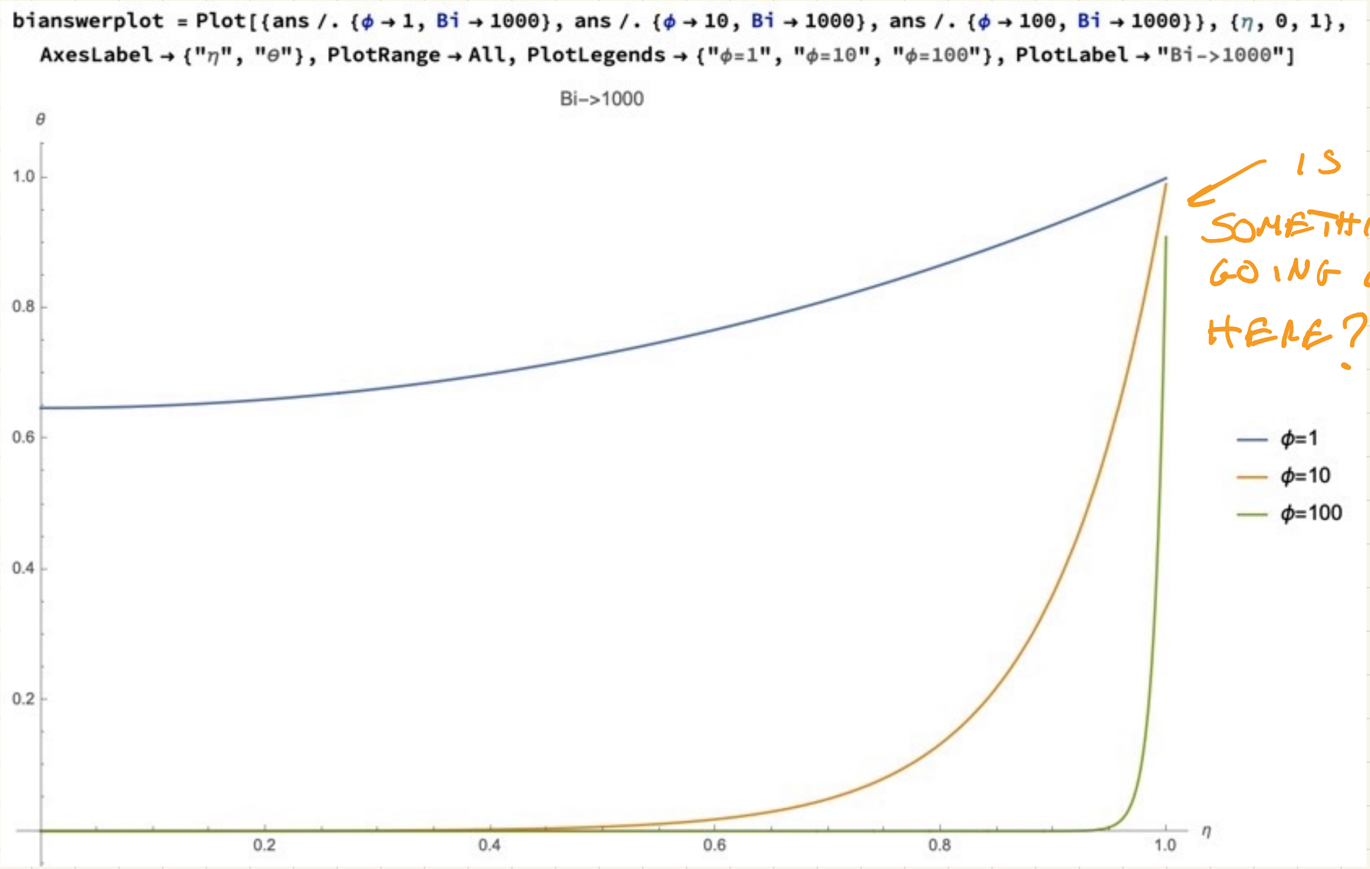
NO FLUX PAST THE "BOUNDARY"

FOR A CYLIDER OR SPHERE, THIS IS A SYMMETRY CONDITION ACROSS $\eta=0$

$$\theta(\eta) = \frac{Bi \cosh(\eta\phi)}{Bi \cosh(\phi) + \phi \sinh(\phi)}$$

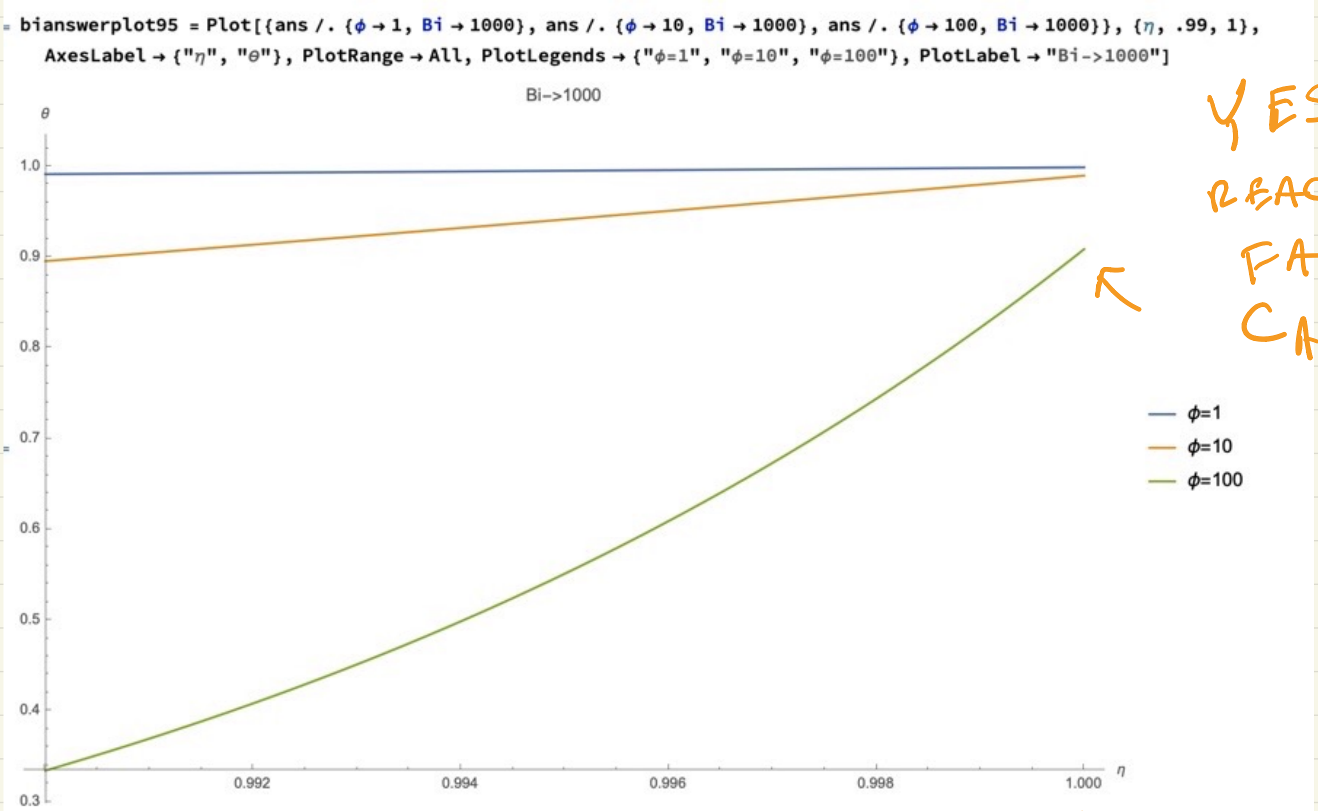
FOR $Bi = 1000$ $\quad Bi \equiv \frac{L \bar{k}_c}{D_{TA}}$

EXTERNAL MASS TRANSFER IS NOT LIMITING UNTIL VERY HIGH REACTION RATES



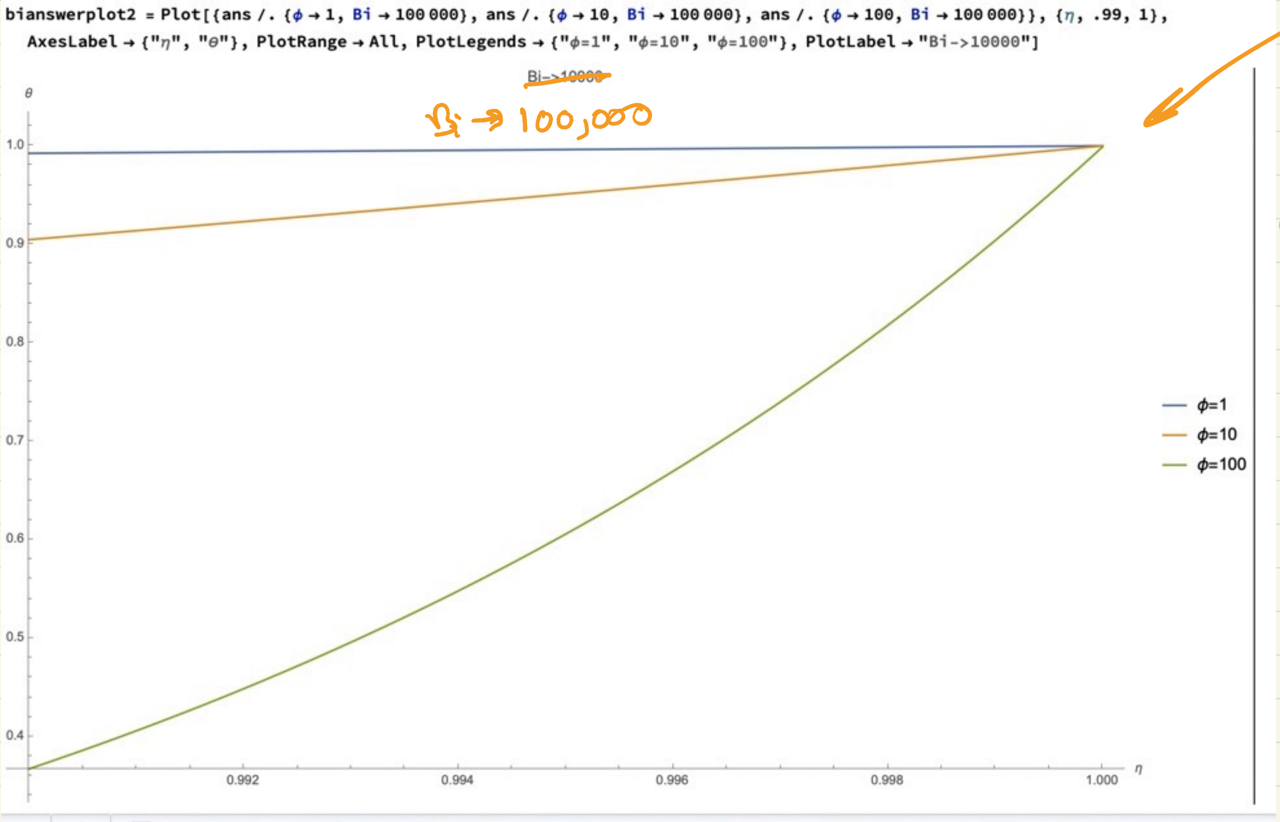
```
bianswerplot = Plot[{ans /. {ϕ → 1, Bi → 1000}, ans /. {ϕ → 10, Bi → 1000}, ans /. {ϕ → 100, Bi → 1000}}, {η, 0, 1},
  AxesLabel → {"η", "θ"}, PlotRange → All, PlotLegends → {"ϕ=1", "ϕ=10", "ϕ=100"}, PlotLabel → "Bi->1000"]
```

IS SOMETHING GOING ON HERE?



```
bianswerplot95 = Plot[{ans /. {ϕ → 1, Bi → 1000}, ans /. {ϕ → 10, Bi → 1000}, ans /. {ϕ → 100, Bi → 1000}}, {η, .99, 1},
  AxesLabel → {"η", "θ"}, PlotRange → All, PlotLegends → {"ϕ=1", "ϕ=10", "ϕ=100"}, PlotLabel → "Bi->1000"]
```

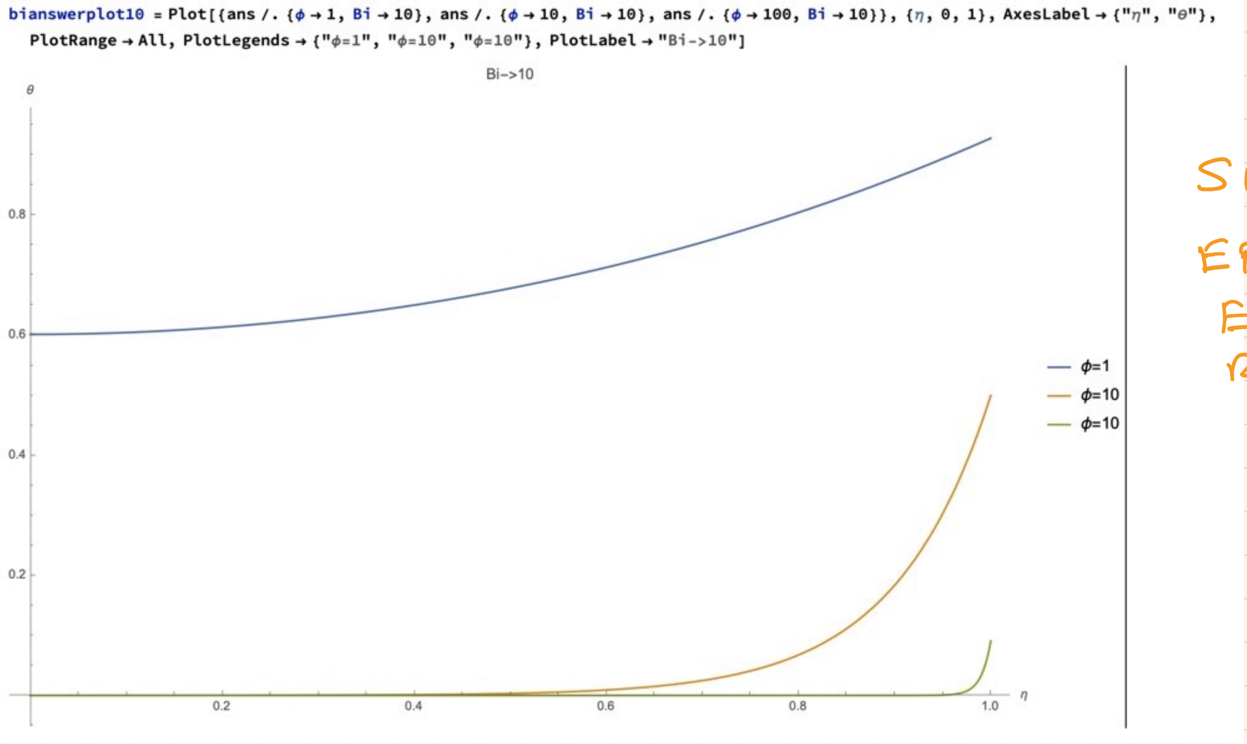
YES, IF REACTION IS FAST $C_{AS} < 1$



```
bianswerplot2 = Plot[{ans /. {ϕ → 1, Bi → 100 000}, ans /. {ϕ → 10, Bi → 100 000}, ans /. {ϕ → 100, Bi → 100 000}}, {η, .99, 1},
  AxesLabel → {"η", "θ"}, PlotRange → All, PlotLegends → {"ϕ=1", "ϕ=10", "ϕ=100"}, PlotLabel → "Bi->10000"]
```

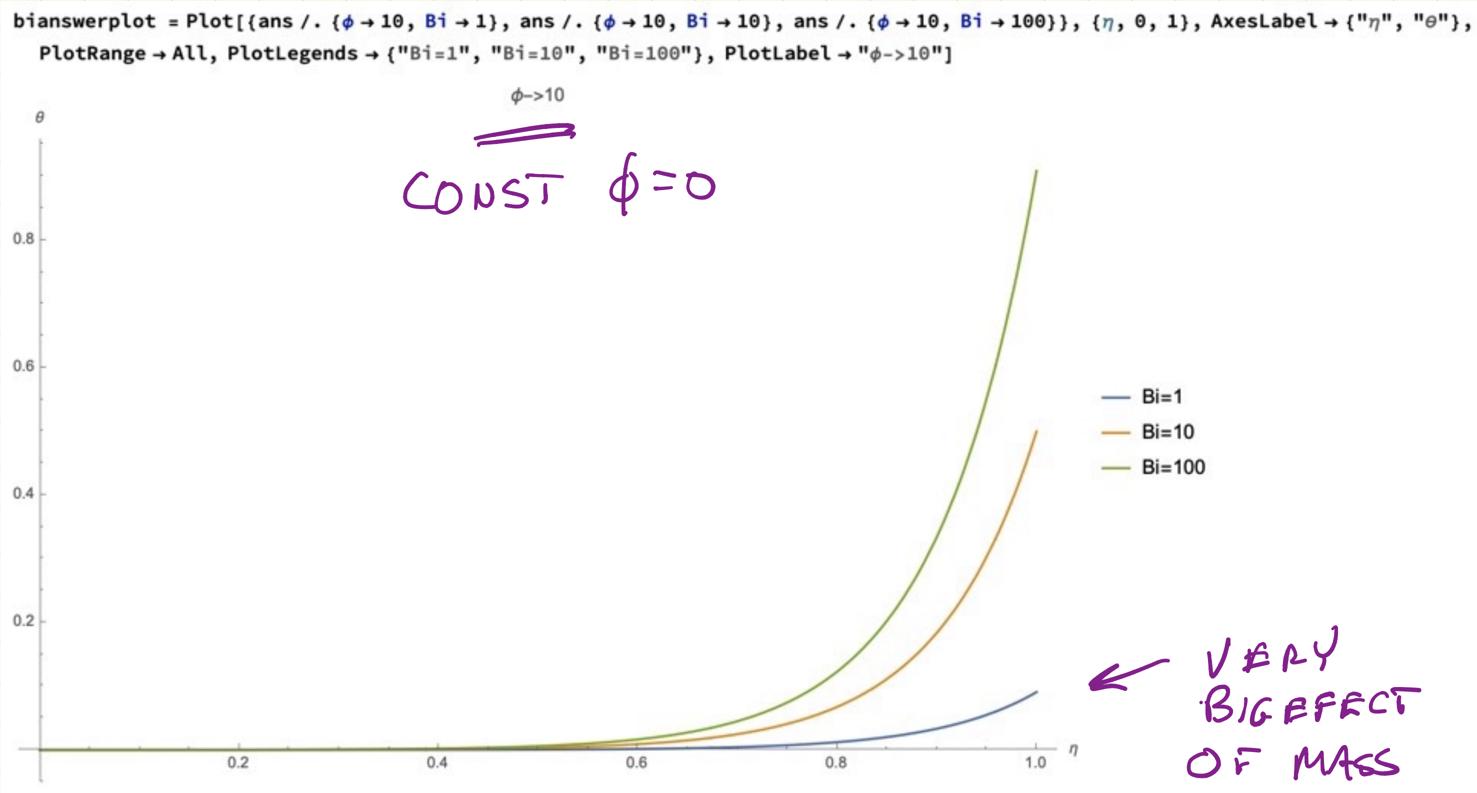
AT $Bi = 100,000$ WE GET $C_{AS} = 1$

A MORE MODERATE Bi



```
bianswerplot10 = Plot[{ans /. {ϕ → 1, Bi → 10}, ans /. {ϕ → 10, Bi → 10}, ans /. {ϕ → 100, Bi → 10}}, {η, 0, 1}, AxesLabel → {"η", "θ"},
  PlotRange → All, PlotLegends → {"ϕ=1", "ϕ=10", "ϕ=10"}, PlotLabel → "Bi->10"]
```

SUBSTANTIAL EFFECT OF EXTERNAL RESISTANCE



```
bianswerplot = Plot[{ans /. {ϕ → 10, Bi → 1}, ans /. {ϕ → 10, Bi → 10}, ans /. {ϕ → 10, Bi → 100}}, {η, 0, 1}, AxesLabel → {"η", "θ"},
  PlotRange → All, PlotLegends → {"Bi=1", "Bi=10", "Bi=100"}, PlotLabel → "ϕ->10"]
```

CONST $\phi = 0$

VERY BIG EFECT OF MASS TRANSFER RESISTANCE

WHAT IS FLUX TO SURFACE

$$\left.\frac{\partial \theta}{\partial \eta}\right|_{\eta=1} = \frac{Bi\, \phi \sinh(\phi)}{Bi \cosh(\phi) + \phi \sinh(\phi)}$$

THIS IS A FAMILAR FORM

IF $\phi >> 1$ FLUX $\rightarrow$ Bi

$$\theta(1) = 0 \,, \quad (C_s = 0)$$

MASS TRANSFER IS CONTROLLING

IF $Bi \rightarrow \infty$

FLUX $= \phi \tanh \phi$

OR

$$\eta = \frac{FLUX}{\phi^2} = \frac{\tanh \phi}{\phi}$$

SAME RESULT AS BEFORE

MORE GENERALLY

$$\eta = \frac{\left.\frac{\partial \psi}{\partial \eta}\right|_{\eta=1}}{\phi^2} = \frac{Bi}{\phi^2 + Bi \coth\phi}$$

$$= \frac{\tanh\phi}{\phi\left(1 + \frac{\phi \tanh\phi}{Bi}\right)}$$

WHAT DOES THIS SAY ABOUT REACTION RATE

$D^e_{JA} \frac{\partial C_A}{\partial x} \Rightarrow$ RATE OF C_A GOING INTO CATALYST

$$\left.\frac{\partial \theta}{\partial \eta}\right|_{\eta=1} = \frac{Bi\, \phi \sinh(\phi)}{Bi \cosh(\phi) + \phi \sinh(\phi)}$$

MAKE DIMENSIONAL :

$$D^{e}_{TA}\frac{dC_A}{dx} = \frac{C^{\infty}}{L} D_{TA}\frac{\partial\theta}{\partial\eta} =$$

$$= \frac{\bar{k}_c C^{\infty}}{1 + \frac{\bar{k}_c}{kL}\coth\left[\frac{kL^2}{D^{e}_{TA}}\right]}$$

$Lk >> k_c$

JUST EXTERNAL MASS TRANSFER

FLUX $= \bar{k}_c C^{\infty}$

$k_c >> Lk$

FLUX $= k C^{\infty} L \tanh\left[\frac{kL^2}{D_{TA}}\right]$

YOU CAN PHYSICALLY REDUCE EXTERNAL MASS TRANSFER RESISTANCE BY "STIRRING FASTER"

$$Sh = 2 + 0.6\, Re^{1/2}\, Sc^{1/3}$$

USUALLY MASS TRANSFER HAS LIMITED RANGE ~ FACTOR ~ 5-10