

Before going to the blackboard, we

- looked at Grad CRE Notes, Diffusion resistance in methanol synthesis catalyst pellets
- the following labs in the desktop software Reactor Lab: D2L1, D2L2, D7L3

n^{th} ORDER, ISOTHERMAL $-r_{A,T} = k_T C_A^n$

$$\frac{d^2\psi}{dz^2} - \phi_n^2 \psi^n = 0$$

$$\phi_n' = L \sqrt{\frac{(n+1)}{2} \frac{k_T S_{a,p} C_{A,es}^{n-1}}{D_{eff}}}$$

WHERE

- $L = R$ SLAB
- $L = R/2$ CYLINDER
- $L = R/3$ SPHERE

CHARACTERISTIC DIFFUSION LENGTH $\rightarrow \frac{\text{VOLUME}}{\text{EXT. AREA}}$

$$-r_{A,OBS} = \eta_n k_T C_{A,es}^n$$

INTERNAL DIFFUSION RESISTANCE & EXTERNAL MASS XFER RESISTANCE "DISGUISE" TRUE KINETICS

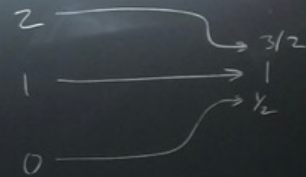
① FOR $n=2$ & $\phi_n \gg 1$, WHAT IS OBSERVED ORDER?

$$-r_{A, \text{OBS}} = \frac{k_T C_A^2}{\sqrt{\frac{(n+1)k_{ps} C_A}{2\phi}}} \propto \frac{C_A^2}{\sqrt{C_A}} = C_A^{3/2} \rightarrow \text{OBSERVED ORDER } n - \left(\frac{n-1}{2}\right)$$

FOR $n=1$ & $\phi_n \gg 1$, OBSERVED ORDER IS 1

FOR $n=0$ " " " " " $1/2$

TRUE ORDER OBSERVED ORDER



n^{th} ORDER COUPLED + w/ 1st ORDER DIFFUSION \rightarrow RXN MORE LIKE 1st ORDER.

FICK'S LAW \rightarrow DIFFUSION CAN BE CONSIDERED 1st ORDER PROCESS
 $\text{FLUX} = -D_{\text{eff}} \frac{dC}{dr} \approx -D_{\text{eff}} \frac{(C_A - 0)}{R}$

② WHAT ABOUT OBSERVED ACTIVATION ENERGY?

FOR $\phi \ll 1$, $\eta \rightarrow 1$, OBS $\Delta E \rightarrow$ TRUE ΔE

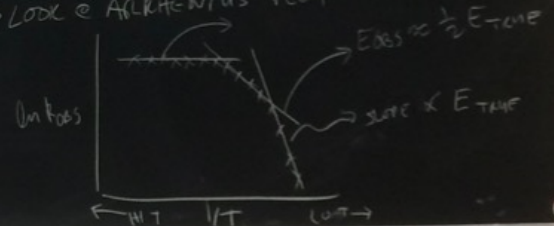
FOR $\phi \gg 1$, $\eta \rightarrow \frac{1}{\phi}$ OBS $\Delta E \rightarrow ?$

$$k_{\text{OBS}} \propto \frac{k_T}{\sqrt{D_{\text{eff}}}} \propto \frac{e^{-E/RT}}{\sqrt{e^{-E/RT}}} \Rightarrow E_{\text{OBS}} \approx \frac{1}{2} E_{\text{TRUE}}$$

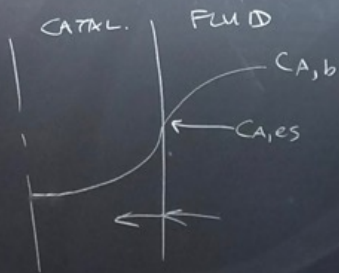
$D_{\text{eff}} \propto T^{3/2}$

\rightarrow LOOK BACK TO PLOT ON 1st SLIDE TODAY

\rightarrow LOOK @ ARRHENIUS PLOT



NOW ADD EXTERNAL MASS XFER RESISTANCE



e.g., 1st ORDER RXN

$$\eta k_T S_a C_{A,es}$$

$\frac{m}{s} \frac{m^2}{kg} \frac{mol}{m^3}$

INTERNAL ACTIVE SITE AREA PER MASS
GEOMETRICAL EXTERNAL AREA PER MASS CATT.

$$= k_m a_{es} (C_{A,b} - C_{A,es}) = -r_{A,obs}$$

$\frac{m}{s} \frac{m^2}{kg} \frac{mol}{m^3}$

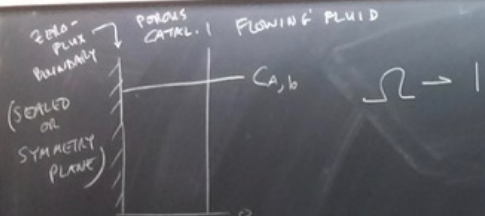
EXTERNAL MASS XFER COEFFICIENT

SOLVE FOR $C_{A,es} = f(C_{A,b})$ & SUBSTITUTE BACK

$$-r_{A,obs} = \Omega k_T S_a C_{A,b}$$

\leftarrow OVERALL EFFECTIVENESS FACTOR

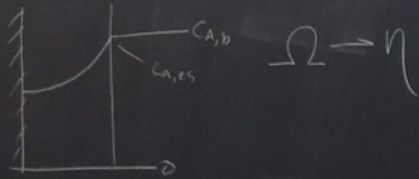
$$\Omega = \frac{\eta k_m a_{es}}{k_m a_{es} + \eta k_T S_a}$$



FAST EXT. M.T.
FAST DIFFUSION

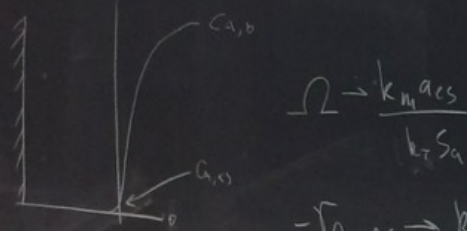
"KINETIC CONTROL"

$$-r_{A,obs} = k_T S_a C_{A,b}$$



FAST EXT. MASS T. } $k_m a_{cs} \gg \eta k_T S_a$
SLOW DIFFUSION

$$-r_{A,obs} = \eta k_T S_a C_{A,b}$$



SLOW EXT. M.T. } $k_m a_{cs} \ll \eta k_T S_a$
FAST RXN

$$-r_{A,obs} = k_m a_{cs} C_{A,b}$$

"EXTERNAL MASS XFER CONTROL"

$$\Omega \rightarrow \frac{k_m a_{cs}}{k_T S_a}$$

$$-r_{A,obs} \rightarrow k_m a_{cs} C_{A,b} \rightarrow (C_{A,b} - C_{A,cs})$$

BUT $C_{A,b} \gg C_{A,cs}$