

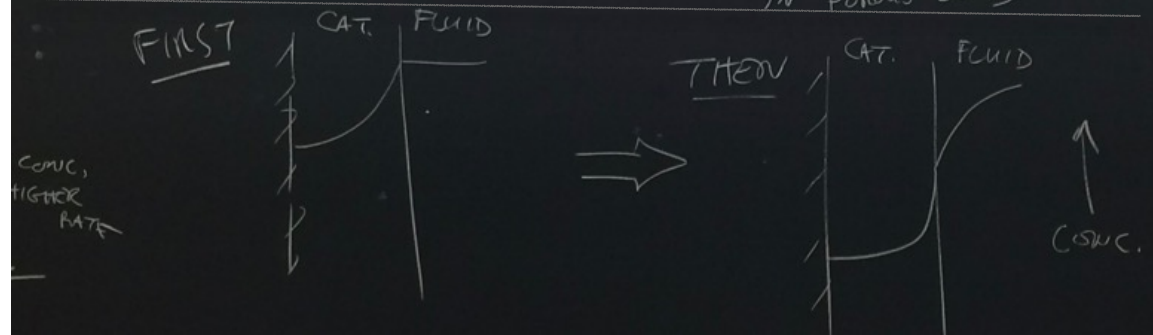
As $k_T \uparrow$, WHICH DO GET FIRST?

OR
EXT. CONC. GRADIENTS
INT. CONC. GRADIENTS

← EXTERNAL MASS XFER RESISTANCE OR
← INTERNAL DIFFUSION RESISTANCE

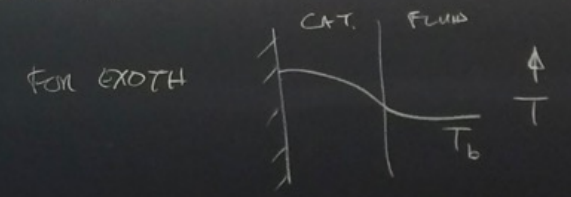
THINK OF k_m vs D_{eff} EXT. M.T. COEFFIC.

OR THINK OF FLOWING FLUID vs STAENANT FLUID IN POROUS SOLID



As $k_T \uparrow$, WHICH DO YOU GET 1ST?

EXT. TEMPERATURE GRADIENTS OR INTERNAL T " ?



DEPENDS ON THERMAL CONDUCT. OF SOLID...

IF HIGH, CAN GET T GRAD EXT. 1ST

FOR ISOTHERMAL, n^{th} ORDER
CATALYSTS $\eta \leq 1$

CAN WE EVER GET $\eta > 1$
WITH OTHER CASES?

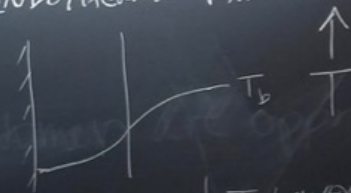
i.e., TRANSPORT RESISTANCE
INCREASES RATE!

TWO CASES WHERE $\eta > 1$ POSSIBLE

(1) (ISOTHERMAL) Hmmm... REACT. CONC. LOWER INSIDE...
HOW COULD RATE BE HIGHER...?

(2) (NON ISOTHERMAL) \rightarrow EXOTHERMIC RXN WITH SIGNIFICANT
INT. OR EXT. HEAT XFER RESIST. \rightarrow T INSIDE HIGHER
THAN BULK T

ENDOTHERMIC RXN

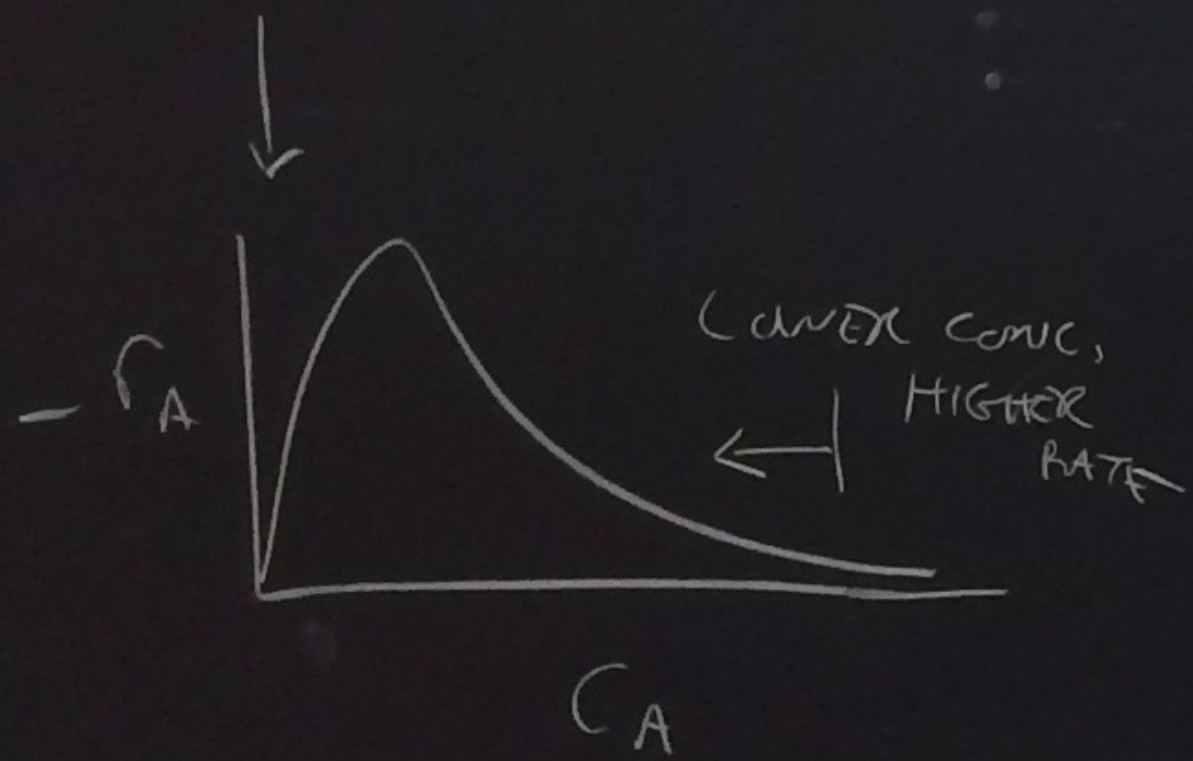


\leftarrow T LOWER THAN T_{bulk}
WITH SIGNIF. HEAT XFER
RESIST. SO RATE LOWER,
THAN RATE EVAL. @ T_{bulk} .
 $\therefore \eta \leq 1$

OR
EXT. CON
GRAD
INT. C
GRA

$$-r_A = kC_A$$

$$-r_A = \frac{kC_A}{(1+K_C C_A)^2}$$



e.g.)
ONIC SELF-INHIBITING RXN

CATALYST LOSE ACTIVITY OVER TIME → DEACTIVATE (HOPEFULLY SLOWLY!)

- POISONS IN FLUID → e.g. SULFUR, LEAD
 - CHEMICAL POISONS → CHEM. CHANGE SITES
 - PHYSICAL POISONS → COVER & BLOCK SITES

- SIDE REACTIONS THAT DEPOSIT MATERIAL
THAT COVERS & BLOCKS SITES

e.g. CARBONACEOUS "COKE" IN PETROLEUM REFINING

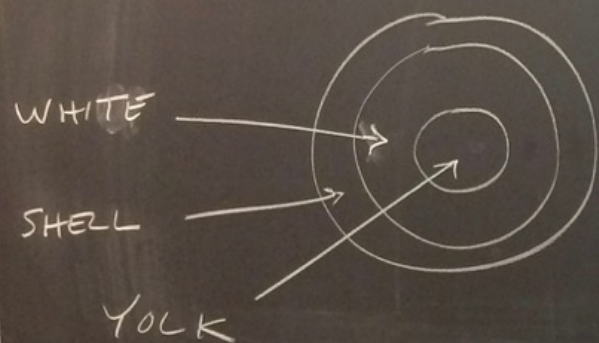
- THERMAL SINTERING

- CHANGE IN STRUCTURE OF ACTIVE SITES
 - " " CONFIGURATION OF SURFACE ATOMS THAT MAKE
A SITE

- INCREASE IN SIZE OF CATALYST PARTICLES → $\frac{\text{SURFACE}}{\text{VOL}}$ ↓ = $\frac{\text{ACTIVITY}}{\text{EXPENSE \$}}$

NOW, NOT ALL CATALYSTS ARE UNIFORMLY ACTIVE SPATIALLY

CONSIDER THE "EGG MODEL" OF CATALYST PELLET



3 ZONES HERE (COULD BE 1, 2, ... 4...)

- SOME COULD BE ACTIVE
- " " " NOT ACTIVE
- " " HAVE DIFFERENT D_{eff}

etc.

WHY?

- FOR EXAMPLE, PUT ALL ACTIVE SITES IN YOLK TO PROTECT FROM CHEMICAL POISONS
- FOR EXAMPLE, PUT SITES IN YOLK TO GET HIGHER RATE WITH NEGATIVE ORDER KINETICS

(1) ACTIVE | FLUID (1ST ORDER ISOTH) CASE (1) HAS $\phi_0 = 10$; CASE (2) HAS OUTER $\frac{1}{2}$ OF LAYER DEACTIVATED \rightarrow SAME LOCAL S_a ($\frac{m^2}{kg}$) or ($\frac{mol}{m^3}$) IN INNER $\frac{1}{2}$ etc.

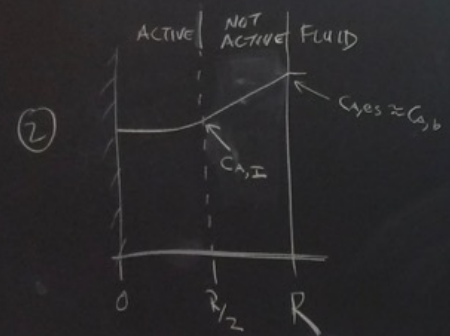
WHAT IS $\frac{-r_{A,obs}(2)}{-r_{A,obs}(1)}$?

$-r_{A,obs}(2) = \eta(2) k_T S_a \theta(2) \underbrace{(P R A_r)}_{\text{TOTAL CAT. MASS}} C_{A,es}$

$-r_{A,obs}(1) = \eta(0) k_T S_a \theta(0) (P R A_r) C_{A,es}$

\rightarrow SAME Defn

$$= \frac{\eta(2) \theta(2)}{\eta(0) \theta(0)} = \frac{\eta(2) (\frac{1}{2})}{\frac{\tanh \phi_0}{\phi_0} (1)}$$



$-r_{A,obs}(2) = A_r D_{eff} \frac{(C_{A,es} - C_{A,I})}{(R/2)}$

$\& -r_{A,obs}(2) = \eta(I) k_T S_a (1) P \left(\frac{R}{2}\right) A_r C_{A,I}$

SET EQUAL, SOLVE FOR $C_{A,I} = f(C_{A,es})$ &

SUBSTITUTE TO GET $-r_{A,obs}(2) = f'(C_{A,es})$

CAN WE SAY ANYTHING ABOUT η_I ?

... WE KNOW VALUE OF η_0

$\phi = L \sqrt{\frac{k_T S_a P}{D_{eff}}}$

$\phi_I = \frac{R}{2} \sqrt{\frac{k_T S_a P}{D}} = \frac{1}{2} \Rightarrow \phi_I = \frac{1}{2} \phi_0$

$\phi_0 = R \sqrt{\frac{k_T S_a P}{D}} \quad \eta_I = \frac{\tanh \phi_I}{\phi_I}$