

CHEMICAL ENGINEERING-
IS CHEMISTRY COUPLED WITH
" TRANSPORT PROCESSES "

CONVECTION }
DIFFUSION } MASS TRANSPORT

CONVECTION }
CONDUCTION } ENERGY TRANSPORT
RADIATION }

+ ECONOMICS, ETC.

"HETEROGENEOUS CATALYST"

CATALYST IN DIFFERENT

PHASE THAN REACTANTS & PRODUCTS

↪ USUALLY SOLID CATALYST

VS.

"HOMOGENEOUS CATALYSTS"

CATALYST & REACTANTS IN SAME PHASE

e.g., ORGANOMETALLIC Pt COMPOUND
IN LIQUID SOLUTION

Porous solid catalysts are "heterogeneous catalysts"

They are important because most products involve one at some stage during manufacture.

Since the reaction chemistry happens inside a porous material, transport processes are important.

This is why chemical engineers study them.

CONSIDER 1D "SLAB" GEOMETRY

NO RXN FLUID | RXN + DIFFUSION POROUS CATALYST | NO RXN FLUID

RXN IS $A \rightarrow B$

IF WE KNOW $C_A(r)$ WE CAN CALC. $r_A(r)$

$C_A(r)$

$C_B(r)$

$C_{A,B} \in \text{BULK}$

$C_A(R) = C_{A,e}$ EXTERNAL SURFACE OF LAYER

CONC. GRADIENT DUE TO EXTERNAL MASS XFER RESISTANCE BUT NO RXN HERE

PLANE OF SYMMETRY OR ZERO-FLUX, SEALED BOUNDARY

$r \rightarrow R$

GOAL

TO DESIGN RXR NEED

- RATE = $f(\text{BULK CONC'S \& T})$
- ASSUME WE KNOW "TRUE", "LOCAL" RATE EQN
e.g., $r_{A, \text{TRUE}} = -k_{\text{TRUE}} C_A$
- BUT C_A VARIES WITH POSITION (r)
SO LOCAL RATE VARIES WITH POSITION
- WE NEED "OVERALL", "OBSERVED", "AVERAGE" RATE IN POROUS LAYER AS FUNC OF $C_{A,B}$

IMMEDIATE NEED, GET $C_A(r)$

WE CAN WRITE DIFFUSION EQN FOR EQUIMOLAR COUNTER DIFFUS.

$$\text{DIFFUSIVE FLUX OF A IN } +r \text{ DIRECTION @ } r \left(\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right) = -D_{\text{eff}} \frac{dC_A}{dr} \Big|_r$$

WRITE BAL FOR REACTANT "A" IN DIFFERENTIAL CONTROL VOLUME ELEMENT $\Delta r A_r$ @ ANY POSITION r
ACCUM = IN - OUT + GENERATION BY RXN

$$0 \text{ @ SS} = \left[-D_{\text{eff}} A_r \frac{dC_A}{dr} \Big|_r \right] - \left[-D_{\text{eff}} A_r \frac{dC_A}{dr} \Big|_{r+\Delta r} \right] + r_A A_r \Delta r$$

$\frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$ $\frac{\text{mol}}{\text{m}^3 \cdot \text{s}}$ $\frac{\text{mol}}{\text{s}}$

$\frac{1}{r} A_r$ SINCE CONSTANT HERE $\div \Delta r$ & $\lim \Delta r \rightarrow 0$

$$D_{\text{eff}} \frac{d^2 C_A}{dr^2} + r_A = 0 \quad \left. \begin{array}{l} \text{2nd ORDER} \\ \text{ODE} \end{array} \right\} \rightarrow \text{NEED TWO BOUNDARY CONDITIONS TO SOLVE}$$

- DEFINE $A_r (\text{m}^2)$ AS GEOMETRIC AREA NORMAL TO r AS FUNCTION OF r
SPHERE $A_r = 4\pi r^2$
SLAB $A_r = \text{CONSTANT, e.g., UNIT AREA.}$

- SPECIFY "EQUIMOLAR COUNTER DIFFUSION" & ISOTHERMAL SLAB

↳ MOLES DIFFUSING IN = MOLES DIFFUSING OUT

THE CASE FOR $A \rightleftharpoons B$ BUT NOT $A \rightleftharpoons 2B$

IMMEDIATE NEED, GET $C_A(r)$

WE CAN WRITE DIFFUSION EQN FOR EQUIMOLAR COUNTER DIFFUS.

DIFFUSIVE FLUX OF A IN +r DIRECTION @ r

$$\left(\frac{\text{mol}}{\text{m}^2 \cdot \text{s}}\right) = -D_{\text{eff}} \frac{dC_A}{dr} \Big|_r$$

WRITE BAL FOR REACTANT "A" IN DIFFERENTIAL CONTROL VOLUME ELEMENT Δr @ ANY POSITION r

ACCUM = IN - OUT + GENERATION BY RXN

$$0 = \left[-D_{\text{eff}} A_r \frac{dC_A}{dr} \Big|_r \right] - \left[-D_{\text{eff}} A_r \frac{dC_A}{dr} \Big|_{r+\Delta r} \right] + r_A A_r \Delta r$$

$\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \cdot \text{m}^2 \cdot \text{m}$

$\therefore A_r$ SINCE CONSTANT HERE $\div \Delta r$ & $\lim \Delta r \rightarrow 0$

$$D_{\text{eff}} \frac{d^2 C_A}{dr^2} + r_A = 0 \quad \left. \begin{array}{l} \text{2nd ORDER} \\ \text{ODE} \end{array} \right\} \rightarrow \text{NEED TWO BOUNDARY CONDITIONS TO SOLVE}$$

MAKE THIS EQN DIMENSION LESS

DEFINE $\psi = \frac{C_A}{C_{A,es}} \leftarrow C_A(R)$

$$\lambda = \frac{r}{R}$$

$C_A = \psi C_{A,es} ; r = \lambda R$

SUBSTITUTE INTO ORIG EQN. & SPECIFY

$r_A = -k C_A$

$$\frac{d^2 \psi}{d\lambda^2} - \phi^2 \psi = 0$$

$\phi = \text{THIELE MODULUS}$

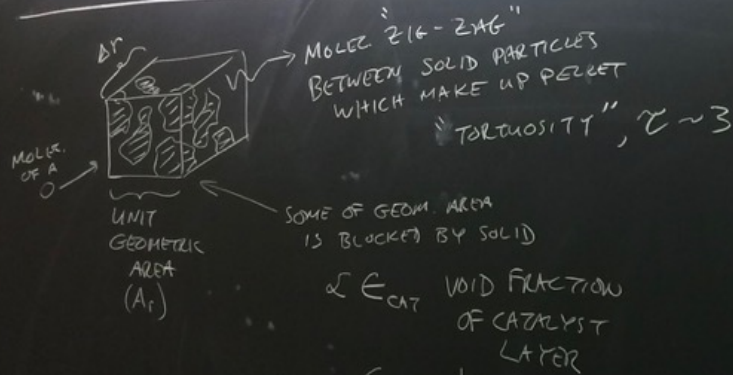
B.C. 1) @ $\lambda=1, \psi=1$

$$\phi = R \sqrt{\frac{k}{D_{\text{eff}}}} \quad \left(\frac{1}{\text{m}} \sqrt{\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \cdot \text{m}^2} \right)$$

2) @ $\lambda=0, \frac{d\psi}{d\lambda} = 0$

= DIMENSIONLESS

WHAT IS D_{eff} ?



FOR RELATIVELY LARGE PORES

$$D_{eff} \approx \epsilon_{cat} \frac{D_{AB}}{\tau} \approx \frac{1}{10} D_{AB}$$

→ VS. D_{AB} BINARY DIFF. COEFFIC IN FREE, OPEN FLUID

THIS IS A BRIEF DESCRIPTION
LOTS MORE DETAIL TO STUDY IF DESIRED
USE N_2 PHYSISORPTION IN BET METHODS
WHICH GIVE PORE VOL VS PORE SIZE
DISTRIBUTIONS

To be continued.

Also see ReactorLab.net, Resources, Grad CRE Notes, Reaction and diffusion in porous catalysts