

Mass Transfer with m in a porous catalyst

Bulk diffusivity is a fn: of molecular velocity (\bar{v})
and the mean free path of molecules (λ) (is
a fn: of temp. and pressure)

Knudsen diffusivity is a fn: of molecular
velocity and pore radius (α).

$$D_{AB} = \frac{1}{3} \bar{v} \lambda \quad (\lambda \sim 1/P) \quad D_K = \frac{2}{3} \alpha \bar{v} \text{ cm}^2/\text{s}$$

For gases, at atmospheric pressure, $\lambda = 1000 \text{ \AA}$
order of magnitude. So diffusion in micropore
($< 2 \text{ nm}$) is Knudsen diffusivity

$$D_K = 9 \cdot f \times 10^3 \alpha \left(\frac{T}{M} \right)^{1/2}$$

↑ Temp
↓ Molecular wt. of A
→ Pore radius

Combined diffusivity,

$$D = \frac{1}{\frac{1}{D_{AB}} + \frac{1}{D_K}}$$

when pore radius is large, the eqn reduces to
 $D = D_{AB}$

Effective diffusivity

Pores of catalyst pellet are in st. or cylindrical.
 Hence it's not possible to determine diffusion at each and every point.

Hence, effective diffusivity is defined as avg. diff. taking place at any position r of a spherical pellet.

We consider only radial variation in conc. The radial flux, W_{AR} is based on total area (solid + void) normal to diffusion.

Effective diffusivity takes into consideration,

- Varying cross sectional area of pores
- Path being tortuous
- Not all the area normal to direction of flux are available for molecule to diffuse

$$D_e = \frac{D \phi_p \cdot \sigma}{\tau} \quad \text{combined diffusivity}$$

σ = Actual distance a molecule travels b/w two points

Shortest distance b/w those two points

ϕ_p = Pellet porosity = $\frac{\text{Volume of void space}}{\text{Total vol. (void + solid)}}$

σ = constriction factor (account for variation in cross section area normal to diff.)

$$\sigma = f(\beta), \quad \beta = \frac{\text{Area } A_2}{\text{Area } A_1}$$



Single cylindrical Pore (1st Order Rxn)

Flat Plate Geometry

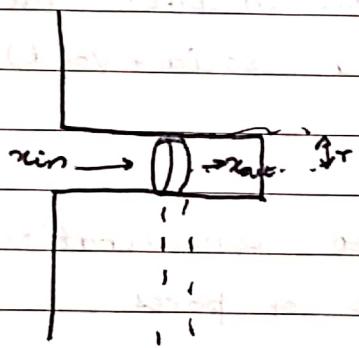
Considering a single cylindrical pore with reactant A diffusing into the pore,



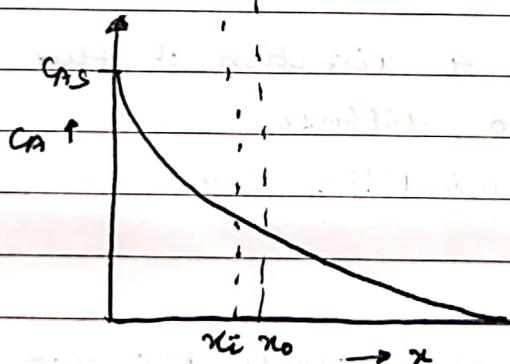
$$-\frac{1}{S} \frac{dN_A}{dt} = k_s C_A$$

mole flux

$$N_A = -D_{AB} \frac{dC_A}{dx} \quad \text{as } C_A \text{ decreased with } x$$



Pore radius is r , x axis is taken to denote the length of pore



C_A0 is conc. of A at the pore mouth and is assumed there is almost no conc. experienced at the end of pore

Hole Balance :

Out + In + Disappearance = Accumulation

$$A(N_A)_{\text{out}} - A(N_A)_{\text{in}}$$

$$-\pi r^2 D \left(\frac{dC_A}{dx_0} \right) + \pi r^2 D \left(\frac{dC_A}{dx_i} \right) + k_s C_A (2\pi r \Delta x) = 0$$

\downarrow Area \downarrow Diff.

$\pi r^2 N_A \rightarrow$ Total Flux throughout cross-sectional area
 $N_A = -D \frac{dC_A}{dx}$ (Fick's 1st law)

$$\pi r^2 N_A = -\pi r^2 D \frac{dC_A}{dx} \rightarrow \text{Rate const. based on surface}$$

$\frac{dC_A}{dx} + k_s C_A = 0$

$2\pi r A x = S.A$ of 1x elem

$$\frac{dC_A}{dx_0} - \frac{dC_A}{dx_i} - \frac{2k_s}{rD} C_A = 0$$

$$\text{As } \Delta x \rightarrow 0, \frac{d^2 C_A}{dx^2} - \frac{2k_s}{rD} C_A = 0 \quad \text{(2)}$$

$k_s \rightarrow$ Based on unit surface area

$k \rightarrow$ Based on unit vol.

$$k V = k_s S$$

$$\therefore k = \frac{S}{V} k_s = \frac{2k_s}{r}$$

The eqn. becomes,

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

The diff. eqn. can be solved by taking the auxiliary eqn.,

$$C_A = M_1 e^{mx} + M_2 e^{-mx}$$

$$m = \sqrt{\frac{k}{rD}} = \sqrt{\frac{2k_s}{rD}}, \quad M_1, M_2 \text{ are const.}$$

The BC's are, At $x=0, C_A = C_{AS}$

At $x=L, \frac{dC_A}{dx} = 0$ (No flux at L)

$$\frac{dc_A}{dx} = M_1 e^{mLx} - M_2 e^{-mLx}$$

using BC,

$$m(M_1 e^{mL} - M_2 e^{-mL}) = 0$$

$$\therefore M_1 e^{mL} = M_2 e^{-mL} \quad \textcircled{1}$$

$$C_{AS} = M_1 + M_2 \Rightarrow M_1 = C_{AS} - M_2 \quad \textcircled{2}$$

On solving \textcircled{1}, \textcircled{2},

$$M_2 = \frac{C_{AS} e^{mL}}{e^{mL} + e^{-mL}}$$

$$M_1 = \frac{C_{AS} e^{-mL}}{e^{mL} + e^{-mL}}$$

$$\text{Thus, } \frac{c_A}{C_{AS}} = \frac{e^{m(L-x)} + e^{-m(L-x)}}{e^{mL} + e^{-mL}} = \frac{\cosh m(L-x)}{\cosh mL}$$

The cont. drop in conc. of reactant on moving onto the pores is dependent on the dimensionless quantity mL , called Thiele modulus.

To account for variations in conc. ; also rate of m' from interior of pores, a factor, called, effectiveness factor (η) is introduced.

$$\eta = \frac{r_p}{r_s} = \frac{\text{global rate with diffusion}}{\text{Rate without diffusion}}$$

Observed rate (overall rate)

Rate at surface (Pore diff. is considered)

$$= \frac{r_A \text{ with diff.}}{r_A \text{ without diff.}} = \frac{C_A}{C_{A0}} \text{ for 1st order}$$

$$\eta_{\text{1st order}} = \frac{\tanh mL}{mL}$$

For small mL ($mL < 0.5$), $\eta \approx 1$

This means that, pore diffusion is negligible or drop in conc. of reactant within pore is very small. Moreover, for small values of mL , $\eta \approx 1$, i.e either short pore length or slow reactions or rapid diffusion.

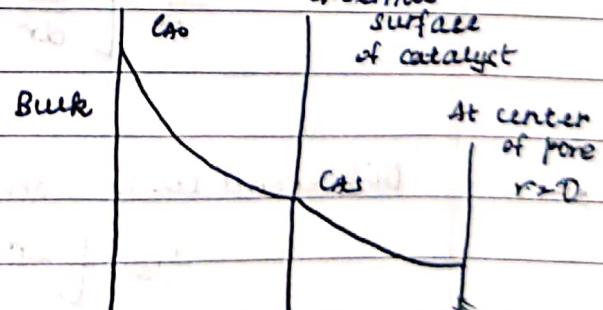
For large mL ($mL > 5$), $\eta \approx \frac{1}{mL}$

This means that the reactant conc. drops rapidly within the pore and diffusion strongly influences the rate of r_p , this is termed as strong pore resistance.

For 1st order r_p ,

$$-r_A = k C_A = k C_{A0} \eta$$

$$mL = L \sqrt{\frac{k}{D}}$$



For no resistance to pore, $\eta \approx 1$, $-r_A = k C_{A0}$

For strong pore resistance, $\eta \approx \frac{1}{mL}$, $-r_A = \frac{k C_{A0}}{mL} = \frac{\sqrt{kD} C_{A0}}{L}$

Pore diffusion in a Spherical Pellet

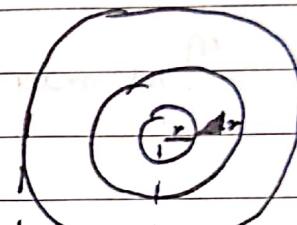
Let us consider a spherical pellet, where a diff. shell of thickness Δr is considered.

Pellet is assumed to be isothermal and has uniform properties. Porosity is uniform

Mole balance

$$-4\pi r^2 D_e \left(\frac{dC_A}{dr} \right) - 4\pi r^2 D_e \left(\frac{dC_A}{dr_{r+\Delta r}} \right)$$

$$= 4\pi r^2 \Delta r P_p k_i C_A$$



Assume effective diffusivity is independent of conc.

$k_i C_A \rightarrow$ rate of m.w.r.t unit mass of catalyst

$$\frac{1}{\Delta r} \left[-r^2 \left(\frac{dC_A}{dr} \right) + r^2 \left(\frac{dC_A}{dr_{r+\Delta r}} \right) \right] = \frac{P_p k_i C_A}{D_e}$$

Taking $\Delta r \rightarrow 0$

$$\frac{1}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{dC_A}{dr} \right) \right] = \frac{P_p k_i C_A}{D_e}$$

Differentiating on both sides,

$$\frac{1}{r^2} \left[2r \frac{dC_A}{dr} + r^2 \frac{d^2 C_A}{dr^2} \right] = \frac{P_p k_i C_A}{D_e}$$

$$\frac{d^2 C_A}{dr^2} + \frac{2}{r} \frac{dC_A}{dr} - \frac{P_p k_i C_A}{D_e} = 0$$

The BC's, At $r=0$, $\frac{dc_A}{dr} = 0$
 $r=R$, $c_A = c_{AS}$

The differential eqn: can be solved and after integ.,
the soln: of eqn:, $c_A = \frac{c_1}{r} \cosh \sqrt{\frac{P_p k_1}{D_e}} r + \frac{c_2}{r} \sinh \sqrt{\frac{P_p k_1}{D_e}} r$

using BC's, $c_1 = 0$, $c_2 = \frac{c_{AS}}{\sinh \sqrt{\frac{P_p k_1}{D_e}} R}$

$$\therefore \frac{c_A}{c_{AS}} = \frac{R \sinh (3\phi_s \cdot r/R)}{\sinh 3\phi_s}$$

where $P_s = \frac{R P_A}{3} \sqrt{\frac{k_1 P_p}{D_e}}$ & Thiele Module
for spherical pellet

Determination of Rate for whole pellet (r_p)

At steady state,

Rate of diff. = Rate of m' in catalyst.

Rate of diffusion per unit wt. of catalyst

$$Q = 4\pi R^2 D_e \left(\frac{dc_A}{dr} \right)_{r=R} = 4\pi R^2 D_e \left(\frac{dc_A}{dr} \right)_{r=R}$$

$$= \frac{3}{R P_p} D_e \left(\frac{dc_A}{dr} \right)_{r=R}$$

$$\eta = \frac{r_p}{r_0} = \frac{3Pe}{RP_p k_r C_{AS}} \left(\frac{dC_A}{dr}_{r=R} \right)$$

$$= \frac{1}{\phi_s} \left[\frac{1}{\tanh(3\phi_s)} - \frac{1}{3\phi_s} \right]$$

It is observed that, for particular ϕ_s , the effectiveness factor η greater in flat plate than for sphere, i.e., diffusion is more in flat plate than sphere, or in other way, diffusional resistance is less in flat plate than sphere.

Hence, flat plate is better than spherical catalyst pellet particle.

For flat plate, thiele modulus is

$$\phi_L = L \sqrt{\frac{k}{Pe}} = L \sqrt{\frac{k P_p}{Pe}} \text{ for unit mass}$$

$$\eta = \frac{\tan \phi_L}{\phi_L}$$

For spherical plate, thiele modulus is,

$$\phi_s = \frac{R}{3} \sqrt{\frac{k_1 P_p}{D_c}}, \quad \eta = \frac{1}{\phi_s} \left[\frac{1}{\tanh(3\phi_s)} - \frac{1}{3\phi_s} \right]$$

For non-spherical particles, $R_{non-sp} = 3 \frac{V_p}{S_p} = R$

R is the radius of spherical pellet having same vol. as non-spherical particle.

In general, $\phi = L \sqrt{\frac{k_1 P_p}{D_e}}$

when $\eta > 0.9$, pore diff. can be neglected and $\phi < 1$
 determining effective factor for pellet catalyst.

Bulk Diff (D_{AB})

Knudsen Diff (D_K)

Combined diffusivity → calculate D_e
 (Eff. diff.)

Calculate ϕ

Calculate η

Physical Significance of Thiele Modulus

$$\phi = \frac{R}{3} \sqrt{\frac{k_1 P_p}{D_e}}$$

Thiele Modulus \propto rate const. k_1
 \propto Diffusivity (D_e)

Hence, it can be said that ϕ gives a measure of extent of reaction to extent of diff., $\frac{k_1}{D_e}$

When diff is more, D_e is high, ϕ is kinetically controlled. But when rate of rxn is higher than diff., and reaction is diff. controlled

Moreover, $\phi \propto$ char. length of pellet

Determination of effectiveness factor for rev.
1st order rev.



let k_1, k_2 be forward and rev. rate const. respectively

$$-\frac{dC_A}{dt} = k_1 C_A - k_2 C_B \quad \text{--- (1)}$$

At const. vol., since moles are const,

$$C_B = C_{B_0} + (C_{A_0} - C_A) \quad \text{--- (2)}$$

$$\begin{aligned} -\frac{dC_A}{dt} &= k_1 C_A - k_2 (C_{B_0} + C_{A_0} - C_A) \\ &= C_A (k_1 + k_2) - k_2 (C_{B_0} + C_{A_0}) \end{aligned} \quad \text{--- (3)}$$

$$\text{At eq.}, \quad k_1 C_{A_{eq}} = k_2 C_{B_{eq}}$$

$$\frac{C_{B_{eq}}}{C_{A_{eq}}} = \frac{k_1}{k_2} = K \leftarrow \text{eq. const.}$$

$$K = \frac{k_1}{k_2}$$

$$\begin{aligned} -\frac{dC_A}{dt} &= k_1 C_A + \frac{k_1}{K} C_A - \frac{k_1}{K} C_{B_0} - \frac{k_1}{K} C_{A_0} \\ &= k_1 \left[\frac{K+1}{K} C_A - \frac{1}{K} (C_{A_0} + C_{B_0}) \right] \end{aligned} \quad \text{--- (4)}$$

$$K = \frac{C_{B_{eq}}}{C_{A_{eq}}} = \frac{C_{B_0} + C_{A_0} - C_{A_{eq}}}{C_{A_{eq}}}$$

$$\Rightarrow \frac{C_{B_0} + C_{A_0}}{C_{A_{eq}}} - 1 = k$$

$$(C_{B_0} + C_{A_0}) = C_{A_{eq}} (K+1)$$

$$\therefore -\frac{dc_A}{dt} = k_1 \left[\frac{\kappa+1}{\kappa} c_A - \frac{1}{\kappa} c_{Aq} (\kappa+1) \right] \\ = \left(\frac{\kappa+1}{\kappa} \right) k_1 (c_A - c_{Aq})$$

$$K_p = \frac{\kappa+1}{\kappa} \cdot k_1 \rightarrow c_A' = c_A - c_{Aq}$$

Hence, the mass balance of reactant for spherical pellet catalyst and for 1st order rev. is;

$$-4\pi r^2 D_e \left(\frac{dc_A'}{dr} \right) - \left(-4\pi r^2 D_e \left(\frac{dc_A'}{dr_{r+dr}} \right) \right) = 4\pi r^2 \Delta r P_p k_1 c_A'$$

Taking limit $\Delta r \rightarrow 0$,

$$\frac{d^2 c_A'}{dr^2} + \frac{2}{r} \frac{dc_A'}{dr} - \frac{P_p k_1 c_A'}{D_e} = 0$$

At BC, $\frac{dc_A'}{dr} = 0$ At $r=0$, $c_A' = c_{Ae}$ at $r=r_s$

$$\phi_s' = \frac{R}{B} \star \sqrt{\frac{k_1 (\kappa+1) P_p}{K D_e}}$$

As $\frac{\kappa+1}{\kappa} > 1$, $\phi_s' > \phi_s$ (Thiele module for rev. m)

$$\eta > \eta'$$

Significance of Intrapellet Diffusion

Isothermal effectiveness factor is considered

with normal pellet sizes ($\frac{1}{8}$ to $\frac{1}{2}$ inch), η is 0.7 to 1 for intrinsically slow m_i .

For fast m_i , $\eta \approx 0.1$. Hence, for intrapellet diffusion, η can be evaluated for diff. m_i s, temp and pellet sizes.

r_p is rate measured at given bulk conc.

Consider external resistance to mass transfer \Rightarrow , i.e $C_{ab} = C_e$

Weitz provided a criterion for deciding from these measurements and D_e , whether intrapellet diff. resistance can be disregarded.

If $\Phi_s \leq \frac{1}{3}$, η is close to 1, so the criterion can be written as,

$$r_s \sqrt{\frac{k_i P_p}{D_e}} \leq 1 \quad \text{or} \quad r_s^2 \frac{k_i P_p}{D_e} \leq 1$$

For 1st order m_i ,

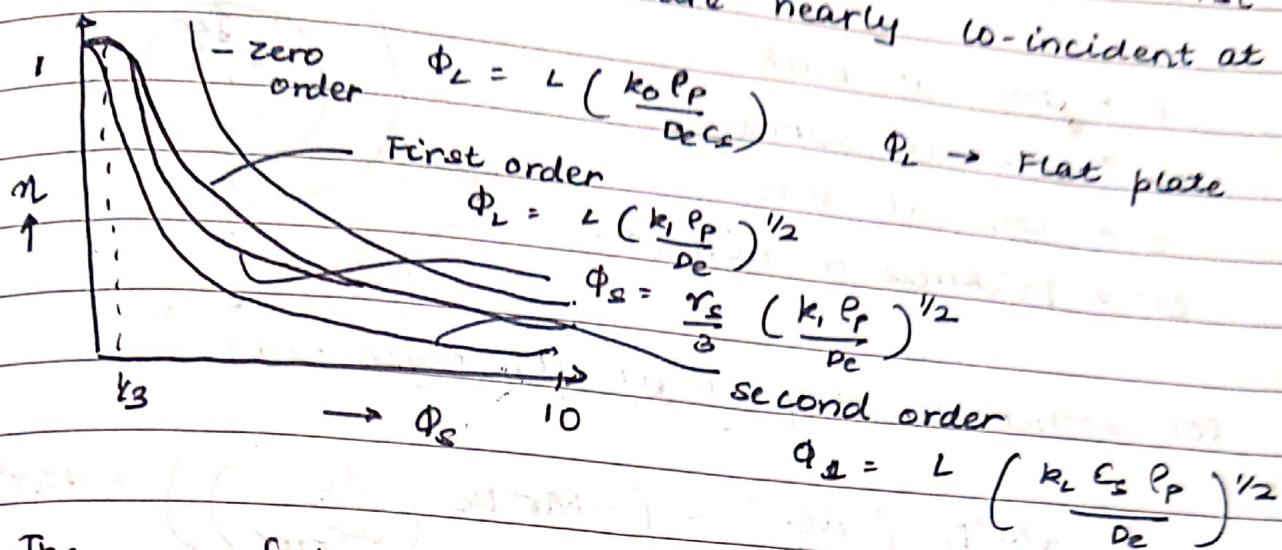
let $C_{wp} = r_s^2 \frac{r_p P_p}{C_s D_e} \rightarrow$ Weitz Prater criterion

If $C_{wp} \leq 1$, the m_i isn't internal diffusion

$C_{wp} > 1$, then r_p is influenced by intrapellet

$$C_{wp} = \eta \times \phi^2 = \frac{\text{Observed (actual) } m_i \text{ rate}}{\text{Diff. rate}}$$

Plot of ϕ_c vs η shows that the curves of first and higher order rxn's are nearly co-incident at $\phi_c \leq \frac{1}{3}$



The usefulness of the Weitz Prater criterion is that, it becomes satisfactory as an approx criterion for most solid catalytic rxn kinetics, even though it's derived for first order kinetics.

Mass and Heat transfer with Reaction

When a rxn takes place, heat of rxn makes a diff in the surface of catalyst and core

The rate of rxn in a catalyst pellet is largely dependent on this temp. gradient.

$$\eta = \frac{\text{Actual rate of } \dot{m}}{\text{Rate at surface of pellet}} = \frac{r_p}{r_s}$$

$$r_p = \eta \times r_s = \eta \cdot f(T_s, C_s)$$

If heat transfer is taken into consideration,

η is called non-isothermal effectiveness factor

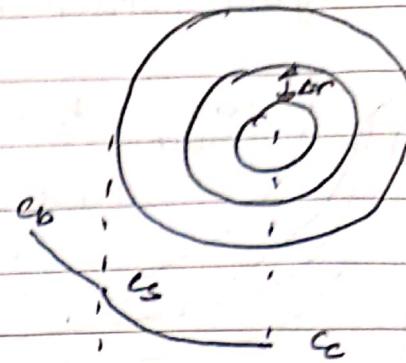
Non-Isothermal effectiveness factor

$C_b \rightarrow$ Conc. at bulk

$C_s \rightarrow$ conc. at surface

$C_c \rightarrow$ conc. at core

$\Delta r \rightarrow$ thickness of diff. vol.



For isothermal eff. (η , HT, MT neglected)

$$-4\pi r^2 D_c \left(\frac{dC}{dr} \right) - \left(-4\pi r^2 D_c \left(\frac{dC}{dr_{\text{eff or}}} \right) \right) = 4\pi r^2 \rho_r p_{\text{eff}}$$

After diff., the eqn' is transformed to,

$$\frac{d^2 C_A}{dr^2} + \frac{2}{r} \frac{dC_A}{dr} - \frac{\rho_r k_r C_A}{D_c} = 0$$

Similarly for HT,

$$-4\pi r^2 K_e \left(\frac{dT}{dr} \right) - \left(-4\pi r^2 K_e \left(\frac{dT}{dr_{\text{eff or}}} \right) \right) = 4\pi r^2 \rho_r p_r k_e C_H$$

$\Delta H \rightarrow$ heat of m.

$K_e \rightarrow$ effective thermal diffusivity

K_e is independent of temp.

After diff.,

$$\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} - \frac{\rho_r k_r C}{K_e} \Delta H = 0$$

At the BC's, $r=0, \frac{dT}{dr} = 0$

$$r = r_s, T = T_s$$

Again, comparing eqn. ② with eqn. ①,

$$\text{De} \left(\frac{d^2 C}{dr^2} + \frac{2}{r} \frac{dc}{dr} \right) = \frac{k_e}{\Delta H} \left(\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} \right)$$

After integrating and using BC's,

$$T - T_s = - \frac{\Delta H \text{De}}{k_e} (C - C_s)$$

This was derived by Damkoehler and applicable to any form of rate expression.

Max. temp. rise will occur in a pellet when rate of consumption of reactant will be equal to rate of diff. of reactant.

$$\text{For } C = 0, \quad T - T_s = \frac{\Delta H \text{De}}{k_e} C_s$$

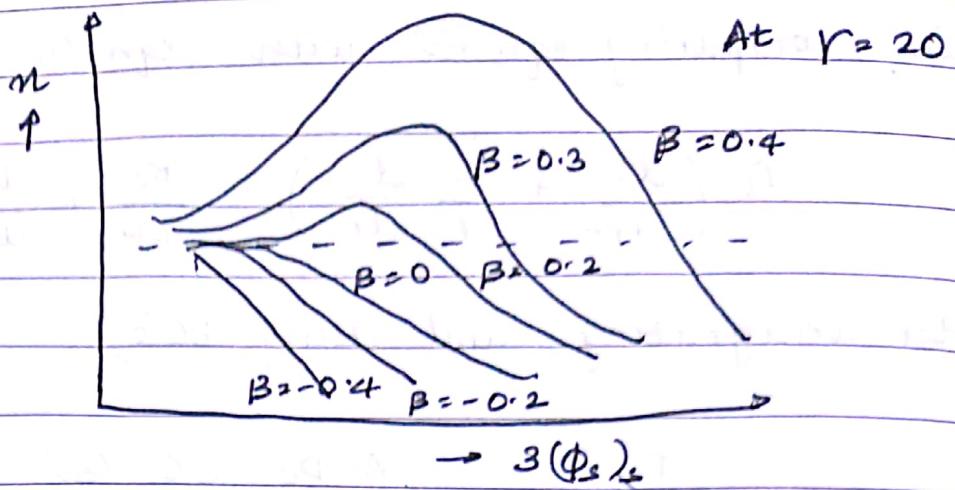
∴ Max Temp. rise depends on ΔH

η is dependent on three dimensionless parameters.

$$\textcircled{1} \text{ Thiele modulus, } \beta (\Phi_0)_s = r_s \sqrt{\frac{(k)_c P_p}{D_e}}$$

$$\textcircled{2} \text{ Arrhenius number, } \alpha = \frac{E}{R g T_s}$$

$$\textcircled{3} \text{ Heat of reaction parameter, } \beta = - \frac{\Delta H \text{De} C_s}{k_e T_s}$$



The curve $\beta = 0$ corresponds to isothermal m .
 For $\beta > 0$, m is exothermic
 $\beta < 0$, m is endothermic

For $\beta > 0$, temp goes into the pellet. The increase in rate of m accompanying the temp. rise can be more than offset the decrease in rate due to drop in conc. $\eta > 1$

while $\eta > 1$, rate of m per pellet increases, which increases production per unit mass of catalyst.

For large η ,

- There will be large increase in temp. towards the center of pellet, resulting in sintering and catalyst deactivation.
- The desired pdt. may subject to further m to unwanted pdt or undesirable side pdt.
- If undesirable m have higher E_A , rise in temp may reduce selectivity of desired pdt.

- For an endothermic m' , temp. decreases with progress of m' and rate decreased. Hence, $m < 1$
- As rate decreased in temp., heat transfer resistance is diminished.
- Decrease in rate going into the pellet for endothermic m' means that mass transfer is of little imp., reaction resistance is rate controlling.