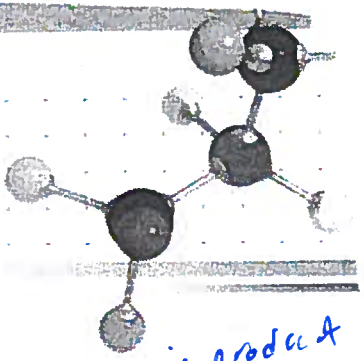
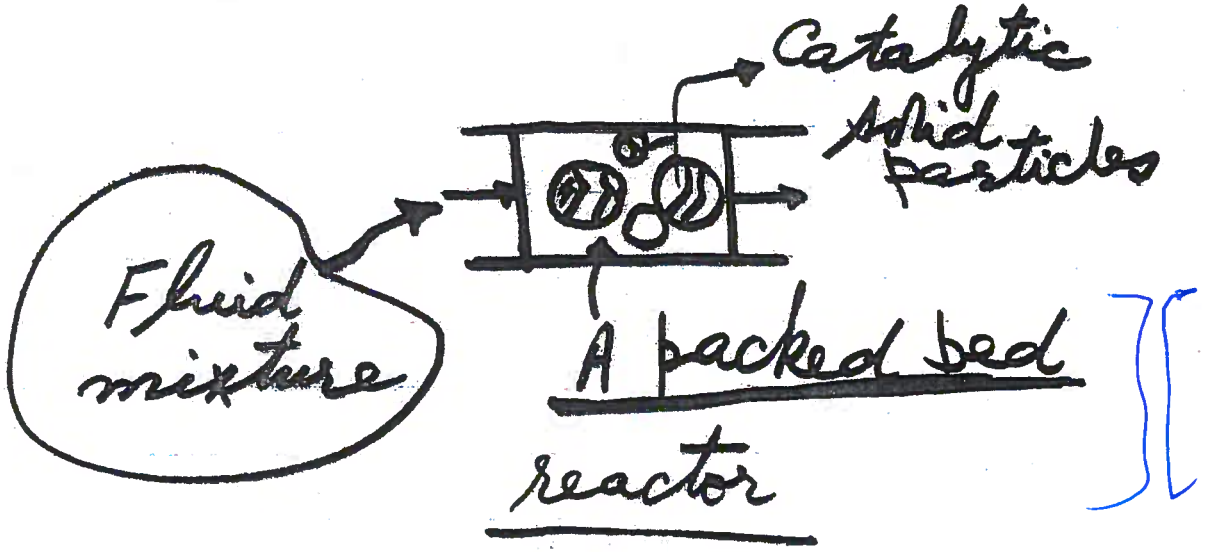
Feb 13

Chapter 3

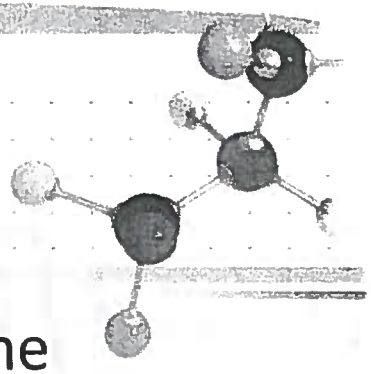
Transport Processes with Reactions Catalyzed by Solids



in product usually P drop due to friction

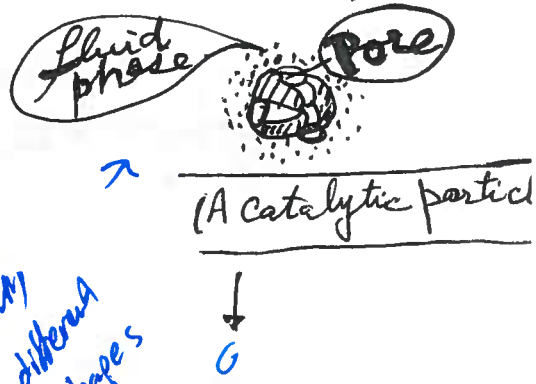


low T = activation Energy low



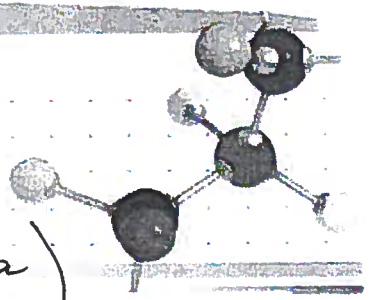
If a chemical reaction is catalyzed by solid particles, the temperature and chemical species concentrations may not be the same (i.e. uniform) everywhere inside the porous particles. The complete catalytic particle and its immediate fluid-phase environment are discussed in this chapter.

NOTE



momentum layer

thermal layer



momentum of boundary layer (kmol / m_f^3)

C_A

(A porous catalytic particle in a packed bed reactor.

boundary layer.

Center of the catalytic pellet

in which there thermal boundry layer it will be vary

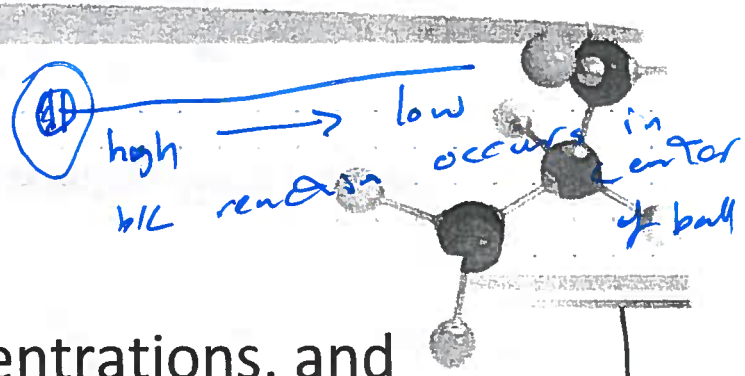
Outer boundary-layer [concentration and thermal (or temp.)] (boundary layers).

same Therml or Conc

Bulk fluid-phase

if the reaction exothermic the thermal gradient will be.

[note: students to read.]



In this system, the chemical species concentrations, and temperature may vary from the 'bulk' fluid-phase region to the center of the catalytic pellet. Therefore, the various transport phenomena of mass and heat transfer are to be accounted for.

→ Here, the particle is considered as:

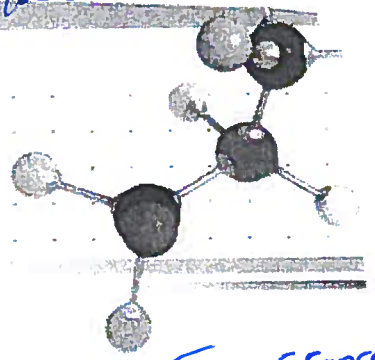
(a) a pseudocontinuum medium,

or

(b) a truly heterogeneous medium. ✓

reaction rate is $C = \frac{V}{\text{surface area}}$

depend if it is endothermic the maximum T will be at bulk flow

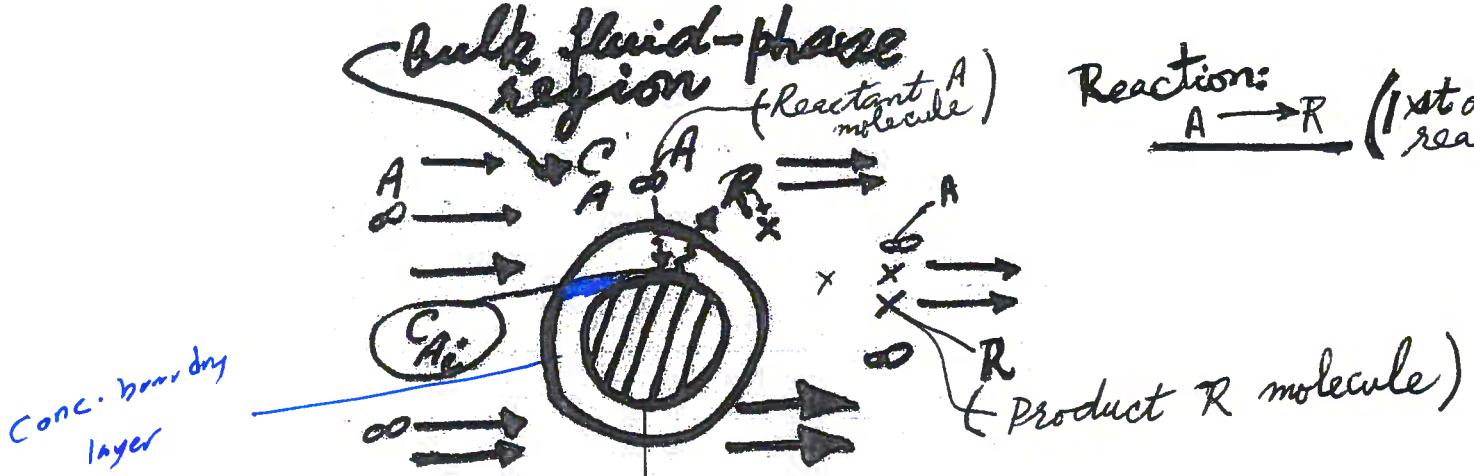


Part (I)

- Interfacial gradient effects
  - ▲ Reaction of a component of a fluid at the surface of a solid.

C_{Aj} = concentration of A at surface

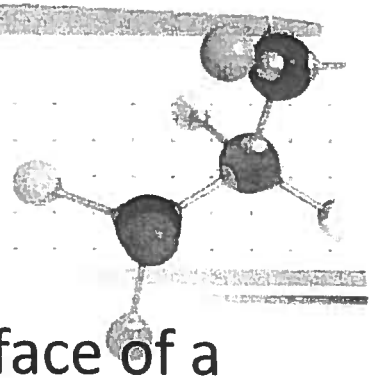
C_A at bulk region



A nonporous solid catalytic particle bathed in reactive fluid mixture (gas or liquid)

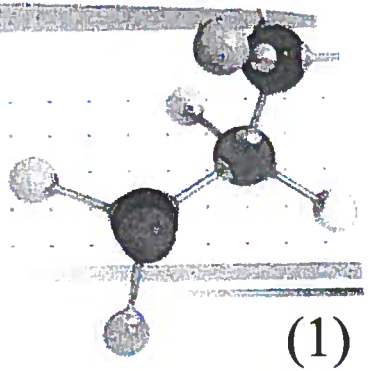
C_{Aj} = only for

[note: students to read this slide]



Say, a catalytic reaction, A→R, takes place on the surface of a catalytic particle shown. Note that the reaction takes place only at the active sites of the exterior surface of the pellet. Also, the overall process is taking place at the steady-state conditions. The overall surface reaction is assumed to be first-order with respect to the concentration of A. The consumption rate of A per unit particle surface area is:

(→ on page 6)



$$\longrightarrow \quad r_{Ai} = k_r C_{Ai} \qquad (1)$$

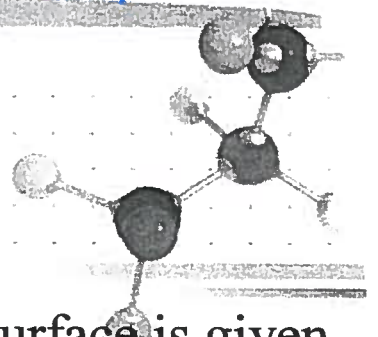
$$\left[\frac{kmol \text{ of A consumed at the interfacial area}}{\text{time-interfacial area}}\right]$$

where k_r = overall surface reaction rate coefficient, $\left[\frac{m_f^3}{hr - m_p^2}\right]$

of the particle surface

C_{Ai} = molar concentration of A at the interface in the fluid-phase, $\left[\frac{kmol}{m_f^3}\right]$.

Kmole = Kg mole
same



The mass transfer of A from the bulk fluid-phase to the particle surface is given by:

$$N_A = k_g \left(C_A - C_{Ai}\right) \quad (2)$$

C_A at particle surface

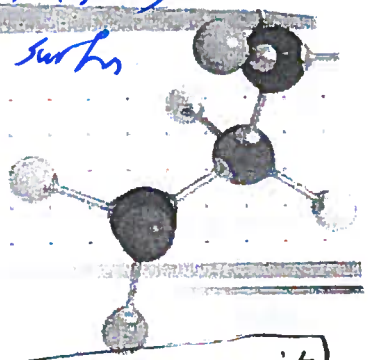
$$\left[\frac{kmol}{hr - m_p^2}\right]$$

where k_g = mass transfer coefficient, $\left[\frac{m_f^3}{hr - m_p^2}\right]$

C_{Ai} = molar concentration of A at the particle interfacial area in the fluid-phase, $\left[\frac{kmol}{m_f^3}\right]$.

C_A = molar concentration of A in the bulk fluid phase, $\left[\frac{kmol}{m_f^3}\right]$.

note reaction can not determined by bulk flow - it is by surface



The steady-state condition at the particle surface requires that

$$r_{Ai} = N_A \left(= r_A\right) \tag{3}$$

note: conversion rate of A per unit particle outer surface area per unit time

r_{Ai}: r of A per area

S#8 — Eq. (1) — r_{Ai} ; N_A — Eq. (2) — S#9

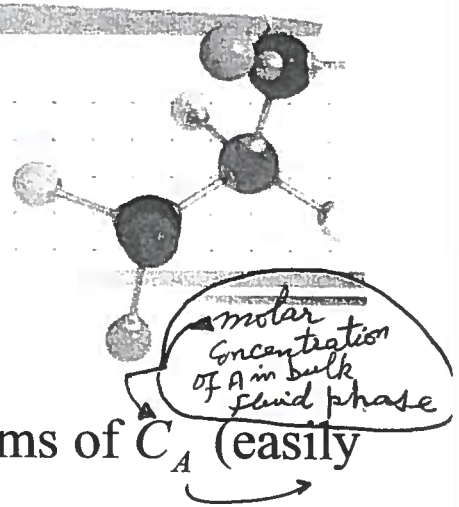
$$k_r C_{Ai} = k_g \left(C_A - C_{Ai}\right) \tag{3a}$$

This equation is solved for C_{Ai} to obtain:

$$C_{Ai} = \left[\frac{k_g}{k_r + k_g}\right] C_A \tag{3b}$$

bit difficult to measure experimentally

Into Eq. (1), S#8:



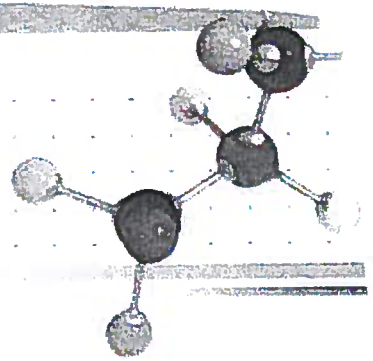
⇓

To eliminate unmeasurable C_{Ai}, C_{Ai} in Eq. (1) is expressed in terms of C_A (easily measurable) using Eq. (3b) to obtain:

$$r_A = r_{Ai} = \left[\frac{1}{k_r} + \frac{1}{k_g}\right]^{-1} C_A \qquad (4)$$

[the apparent reaction rate per unit area per unit time]

↓



Also,

$$r_A = \underbrace{\left[\frac{1}{k_r} + \frac{1}{k_g}\right]^{-1}}_{= k_o} C_A \qquad \text{[from Eq. (4), s \# 11]} \qquad (5)$$

$$= k_o C_A \qquad (5a)$$

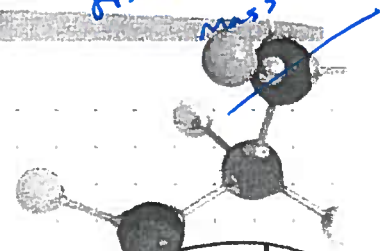
where $k_o = \left[\frac{1}{k_r} + \frac{1}{k_g}\right]^{-1}$ (5b)

= overall rate coefficient, $\left[\frac{m_f^3}{hr - m_p^2}\right]$.

C_{Ai}

C_A not attached to surface

If we know $k_{overall}$ we can find k_g transport mass



reaction rate coefficient or constant at a constant temperature, T [K]

mass transfer coefficient

- The two limiting cases:

(a) The mass transfer is much more rapid than the surface reaction, i.e., $k_g >> k_r$.

Under this condition, $k_o \simeq k_r$ in Eq. (5b). (S#12)

$$k_o = \left[\frac{1}{k_r} + \frac{1}{k_g}\right]^{-1} \simeq \left[\frac{1}{k_r}\right]^{-1} = (k_r^{-1})^{-1} \simeq k_r$$

The apparent rate of the consumption of A is then given by:

$$r_A = k_o C_A \simeq k_r C_A \qquad (6a)$$

the surface reaction process controls the overall process of mass transfer and reaction.

Also, from Eq. (3b),

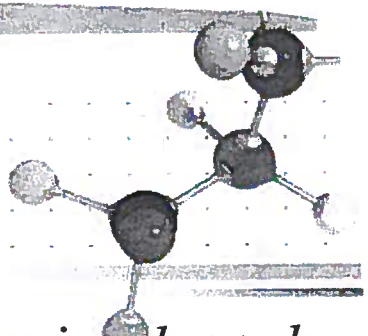
C_{Ai} = on part not attached (S#10) gas phase → or liquid

$$C_{Ai} \simeq C_A \qquad (6b)$$

i.e. there is "almost" no resistance to mass transfer between the exterior surface of the particle and the fluid bulk region

or ↳ thickness of the concentration boundary layer is negligibly small.

If mass transport is high there is more A move and react fast



(b) The surface reaction is much more rapid than the mass transfer, i.e., $k_r >> k_g$.

For this situation, Eq. (5b) leads to:

$$k_o = k_g \tag{7}$$

Into Eq. (5a) to obtain:

$$r_A = k_o C_A = k_g C_A \tag{8}$$

The overall reaction is controlled by mass transfer only.

$$C_{Ai} = \left[\frac{k_g}{k_r + k_g}\right] C_A = \left[\frac{\left(\frac{k_g}{k_r}\right)}{1 + \left(\frac{k_g}{k_r}\right)}\right] C_A \simeq \left[\frac{(k_g/k_r)}{1+0}\right] C_A = \left(\frac{k_g}{k_r}\right) C_A \simeq (0) C_A$$

(for $k_r >> k_g$)

(extremely small)

Also, from Eq. (3b),

S # 10

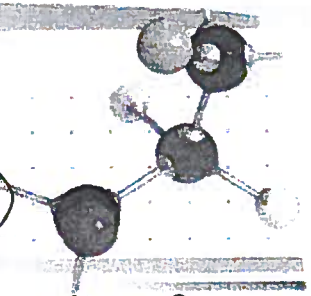
$$C_{Ai} \simeq (0) C_A \simeq 0 \qquad \text{(for } k_r >> k_g\text{)} \tag{9}$$

[indicating that there is "almost" no resistance to the surface reaction; but, resistance to mass transfer exists in the concentration boundary-layer where concentration of A drops from the bulk fluid region concentration, C_A, to its concentration, $C_{Ai} \simeq 0$, at the particle exterior surface].

means $\simeq k_{sr}$ = high

means = chemisob, physisobs are high conv reaction takes place fast

→ NOTE: Students to read this slide carefully.



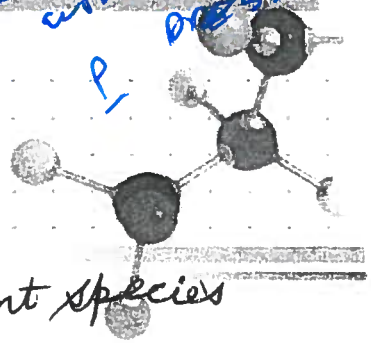
In case (a), the overall reaction is controlled by the surface reaction; therefore, called the "reaction controlling step". In case (b) the overall reaction is controlled by the mass transfer process; therefore, termed as the "mass transfer or diffusion control step".

→ The above procedure may be applied to a second or higher-order reaction. Analysis is, of course, more complex. For the application of Eqs. (6a) and (8) to experimentally determine k_r [intrinsic overall reaction rate coefficient at a temperature] and k_g (mass transfer coefficient), see some useful comments in G. F. Fromant and K. B. Bischoff, Chemical Reactor Analysis and Design, pp.126,127, John Wiley & Sons, New York (1990), or pp. 155, 156 (2011).

P°_{As} = vapor pressure at active site

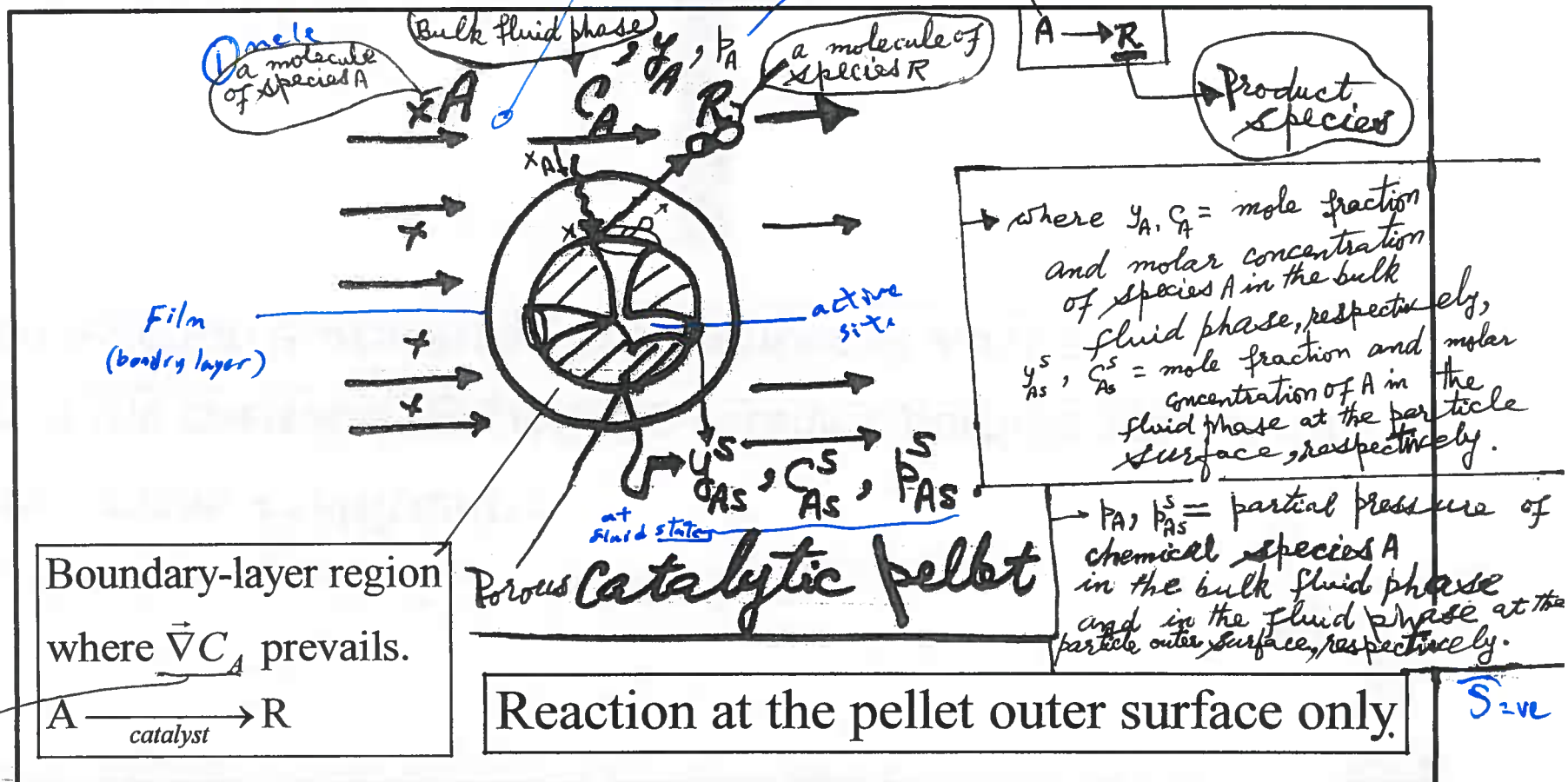
some time mass transfer coefficient as function of applied pressure

P_i



bulk flow region

- Mass and Heat transfer resistances



For example, $\left(\frac{\partial C_A}{\partial r}\right) \neq 0$.

In the spherical coordinate system:

$$\vec{\nabla} C_A = \left[\vec{\delta}_r \frac{\partial}{\partial r} + \vec{\delta}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \vec{\delta}_\phi \frac{1}{r \sin\theta}\frac{\partial}{\partial \phi}\right] C_A = \left[\vec{\delta}_r \frac{\partial C_A}{\partial r} + \vec{\delta}_\theta \frac{1}{r}\frac{\partial C_A}{\partial \theta} + \vec{\delta}_\phi \frac{1}{r \sin\theta}\frac{\partial C_A}{\partial \phi}\right]$$

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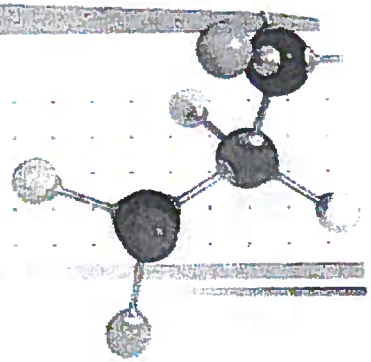
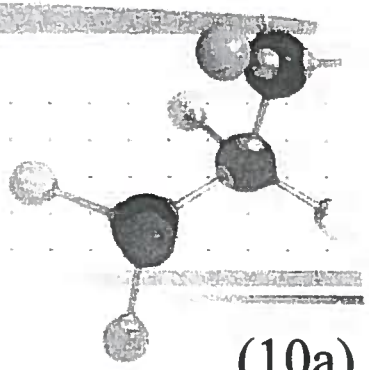


Mass transfer coefficients:

Flux of the chemical species to a catalytic particle accelerating a given reaction is expressed in a number of ways as:



driving force for mass transfer

$$N_A = k_g \left(y_A - y_{As}^S \right) \qquad (10a)$$

$$\left[\frac{kmol}{m_p^2 - s} \right] \quad \left[\frac{kmol}{m_p^2 - s} \right]$$

or

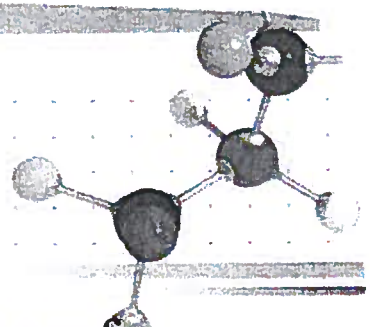
$$= k_g \left(C_A - C_{As}^S \right) \qquad (10b)$$

$$\left[\frac{kmol}{m^2 \cdot s} \right] = \left[\frac{m_f^3}{m_p^2 - s} \right] \quad \left[\frac{kmol}{m_f^3} \right]$$

$$= k_g \left(p_A - p_{As}^S \right) \qquad (10c)$$

$$= \left[\frac{kmol}{m_p^2 - s - bar} \right] \quad [bar]$$

NOTE: Students, please read this slide.



Note that with different driving forces, the units of k_g, the mass transfer coefficient, are different. For the case of equimolar counterdiffusion; e.g., $N_R = -N_A$ or $(N_A + N_R) = 0$, [see sketch]; the mass transfer coefficient, k_g^o, represents the molecular diffusive transport. The values of k_g^o can be obtained from the correlations given in the literature. The mass transfer coefficient, k_g, for the situation other than the equimolar counterdiffusion is evaluated from the equations relating k_g and k_g^o. (when $(N_A + N_R) = 0$)

[Reaction: A → R]

$= \frac{D_{AR}}{\delta_c}$

thickness of concentration boundary layer

and

D_{AR} = molecular diffusivity for the system A-R; i.e. for A or R in the fluid phase mixture of species A and

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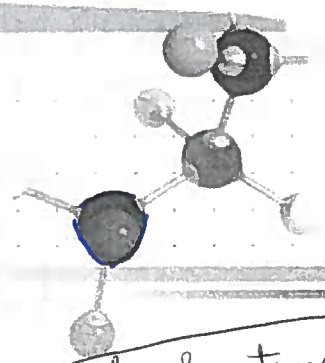
explanation

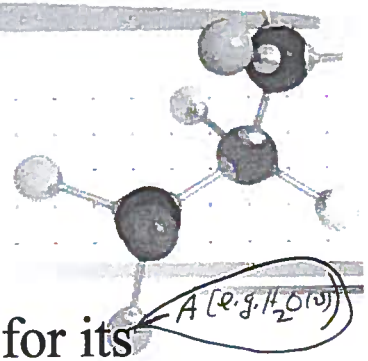


mole fraction of air

$y_B = 1 - y_A$ ← mole fraction of $H_2O(v)$

(Also, see s #22.)

Boundary layer



For the diffusion of A (vapor) through a stagment film of B (air) for its condensation on a cold plate surface, the film theory relates k_g to k_g^o as:

$$k_g = \frac{k_g^o}{(y_B)_{\text{log mean}}} \quad (11)$$

k_g^o → mass transfer coefficient under the condition of low mass transfer rate.

where $(y_B)_{\text{log mean}} = \dfrac{y_B^S - y_B}{\log_e \left[\dfrac{y_B^S}{y_B}\right]}$

y_B → bulk concentration of B

Note that $y_B = 1 - y_A$ (12)

(y_B → mole fraction of B in bulk fluid; y_A → mole fraction of vapor A in the bulk fluid region)

The driving force to be used with k_g, given by Eq. (11), is $(y_A - y_A^S)$.

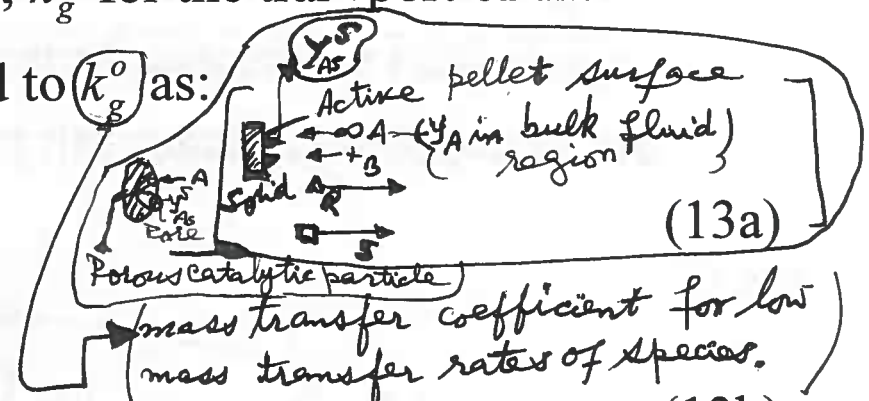
y_A, y_A^S → mole fractions

So, $|N_A| = k_g (y_A - y_A^S)$.

($|N_A|$ → molar flux of vapor A from the bulk fluid (here, (gas+vapor)) mixture region to the surface of the liquid film of the condensate of A, $\frac{\text{kmol}}{\text{m}^2 - \text{s}}$)

For a reaction, $aA + bB \rightleftarrows rR + sS$ or $\underbrace{(-1)}_{\alpha_A=-1}A + \underbrace{\left(-\frac{b}{a}\right)}_{\alpha_B=-\frac{b}{a}}B + \underbrace{\left(\frac{r}{a}\right)}_{\alpha_R=\frac{r}{a}}R + \underbrace{\left(\frac{s}{a}\right)}_{\alpha_S=\frac{s}{a}}S = 0,$ (a limiting reactant)

taking place at the surface of a catalytic pellet; k_g for the transport of the chemical species A to the active pellet surface is related to k_g^o as:



actual mass transfer coefficient

$$k_g = \frac{k_g^o}{y_{fA}} \qquad (13a)$$

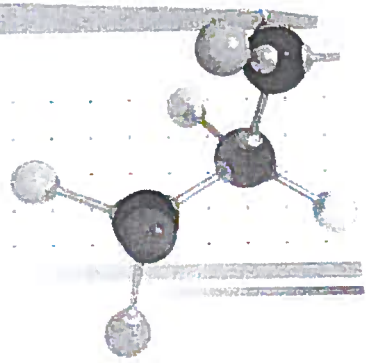
mass transfer coefficient for low mass transfer rates of species.

where $y_{fA} = \dfrac{(1+\delta_A y_A) - (1+\delta_A y_{As}^S)}{\ln\left[\dfrac{1+\delta_A y_A}{1+\delta_A y_{As}^S}\right]}$ (13b)

(See s#24)

⇓

film mole fraction factor



$$\Downarrow$$

$$\rightarrow \text{with } \delta_A = \sum_{j=1}^{all} \alpha_j = \alpha_A + \alpha_B + \alpha_R + \alpha_S = \left(\frac{r}{a}\right) + \left(\frac{s}{a}\right) + (-1) + \left(-\frac{b}{a}\right)$$

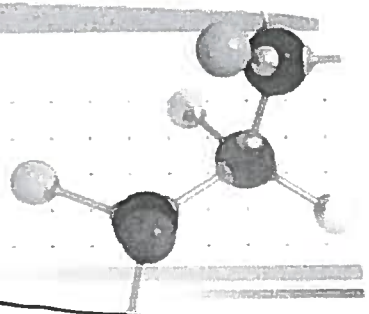
$$= \left[\frac{r}{a} + \frac{s}{a}\right] - \left[1 + \frac{b}{a}\right] \qquad (13c)$$

= change in mixture moles because of the chemical reaction at the catalytic surface per mole of the limiting reactant A consumed.

Euqation (13b) written in terms of the total and partial pressures is called the "film pressure factor, p_{fA}" and is: (S#23)

total pressure; partial pressure of A in the fluid bulk; partial pressure of A in the fluid at the solid surface; gas mixture

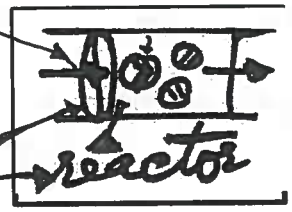
$$p_{fA} = \frac{\left(p_t + \delta_A p_A\right) - \left(p_t + \delta_A p_{As}^S\right)}{\ln\left[\dfrac{p_t + \delta_A p_A}{p_t + \delta_A p_{As}^S}\right]} \qquad (14)$$



The correlations of the mass transfer coefficients in terms of the j_D factor are:

$$j_D = \frac{k_g^o M_m}{G} Sc^{\frac{2}{3}} \qquad (15a)$$

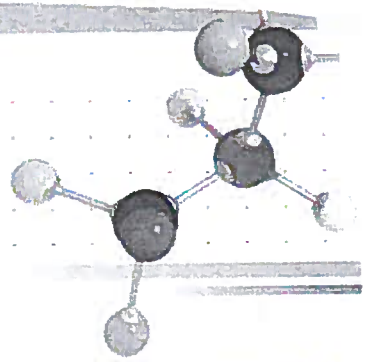
where G = mass superficial velocity through the bed $\left[\frac{kg}{m_r^2 - s}\right]$



M_m = mixture mean molecular weight $\left[\frac{kg}{kmol}\right]$

k_g^o = mass transfer coefficient for the molecular mass diffusion $\left[\frac{kmol}{m_p^2 - s}\right]$

(under the low mass transfer rate conditions)



$$Sc = \left(\frac{\mu}{\rho}\right)_f \left(\frac{1}{D}\right) \qquad (15b)$$

[Schmidt number for mass transfer] [mass diffusivity, $\frac{m^2}{s}$]

where μ, ρ = fluid absolute or dynamic viscosity (μ) and fluid density (ρ). These should be taken at the mean film temperature, pressure, and composition conditions if possible.

s #23

Using Eq. (13a), Eq. (15a) may be written as: (slide #25)

[i.e. insert for k_g from Eq. (13a) into Eq. (15a) to get]

$$j_D = \frac{k_g M_m y_{fA}}{G} Sc^{\frac{2}{3}} \qquad (15c)$$

j_D: dimensionless

$$= \frac{k_g M_m p_{fA}}{p_t G} Sc^{\frac{2}{3}} \qquad (15d)$$

p_t: total pressure

(gases)

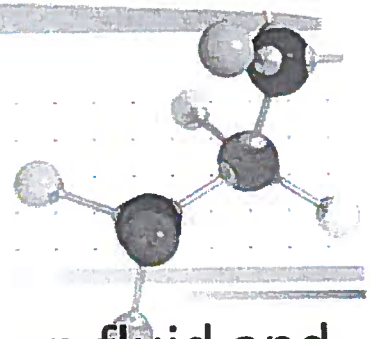
$$\rightarrow \frac{k_g}{p_t}[=]\frac{\text{kmol}}{\text{m}^2\text{-s-bar}}.$$

$$j_D = f(\text{Re}_p) \qquad (16)$$

where $\text{Re}_p = \frac{d_p G}{\mu}$;

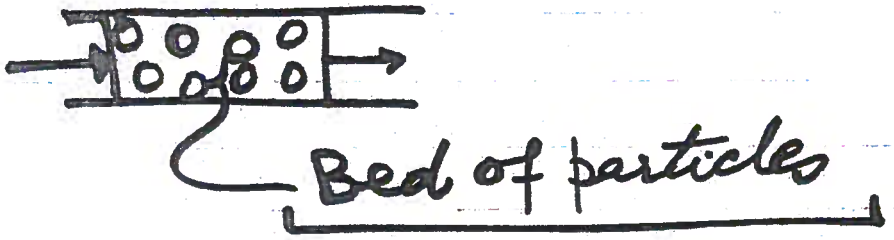
NOTE

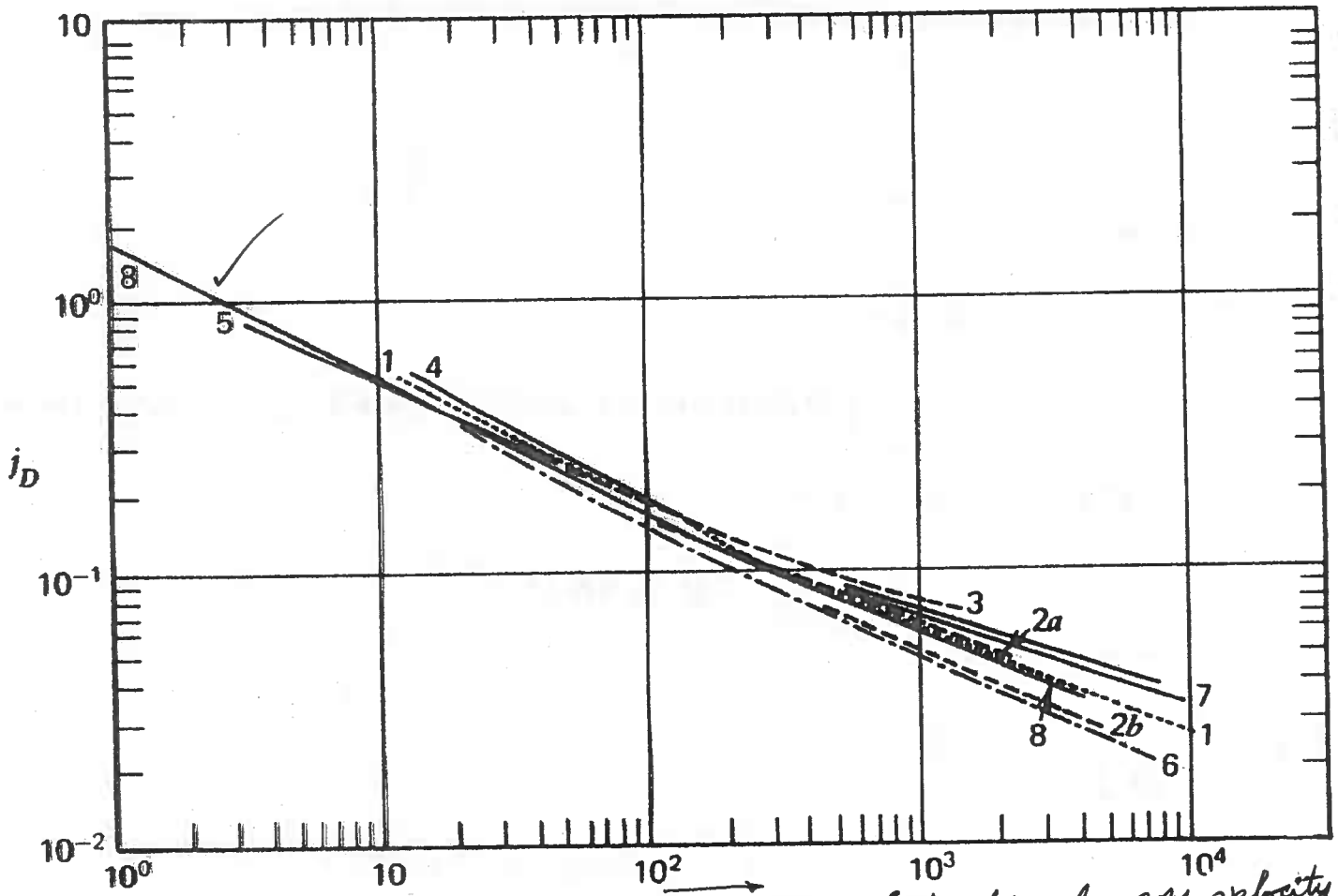
(Reynolds number (based on the particle diameter) for mass transfer)

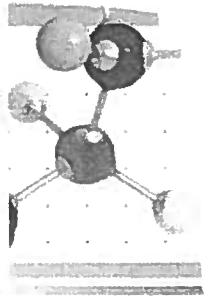


Slide #29

→ Figure 3.2.1-1 shows j_D factor for mass transfer between fluid and particles packed in a bed.







$\text{Re} = \frac{d_p G}{\mu}$ → superficial mass velocity [= total mass flowrate / tube or duct cross-sectional area]

→ increases with an increase in d_p; j_D decreases (i.e., k_g decreases (see p. 27)) → bed void fraction

because

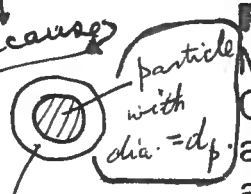
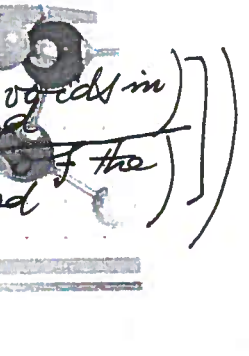


Figure 3.2.1-1
Mass transfer between a fluid and a bed of particles (spheres; $\varepsilon = 0.37$). Curve 1: Gamson et al. (1943), Wilke and Hougen (1945). Curve 2: Taecker and Hougen (1949). Curve 3: McCune and Wilhelm (1949). Curve 4: Ishino and Otake (1951). Curve 5: Bar Ilan and Resnick (1957). Curve 6: DeAcetis and Thodos (1960)., Curve 7: Bradshaw and Bennett (1961). Curve 8: Hougen (1961); Yoshida, Ramaswami, and Hougen (1962).

δ_c = thickness of the conc. boundary layer increases. So, $k_g^\circ = \frac{D_{AB}}{\delta_c}$; hence, k_g and j_D both decrease (see (15d), s # 27).



(definition: $\varepsilon = \left[\frac{\text{(total volume of voids in the packed bed)}}{\text{(total volume of the packed bed)}}\right]$)

For packed beds of spheres with ε (packed bed void fraction) $= 0.37$,

$$j_D = 1.66\left[\mathrm{Re}_p\right]^{-0.51} \qquad \text{(17a)}$$

for $\mathrm{Re}_p \left(= \frac{d_p G}{\mu}\right) < 190$;

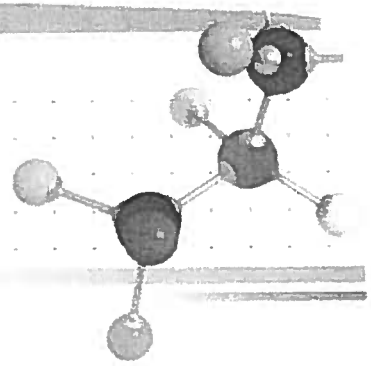
$$j_D = 0.983\left[\mathrm{Re}_p\right]^{-0.41} \qquad \text{(17b)}$$

for $\mathrm{Re}_p > 190$.

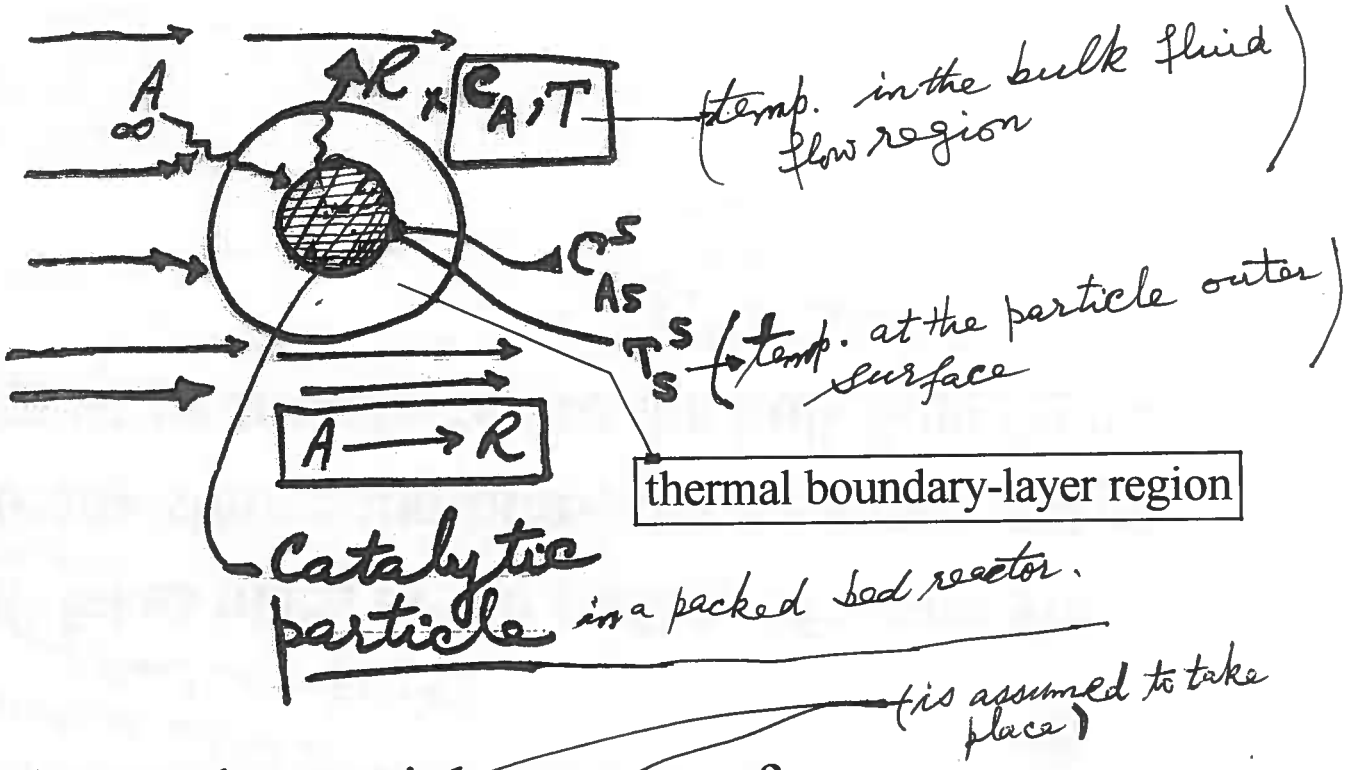
These correlations (17) can be used to calculate k_g.

(See (15d) and (16))

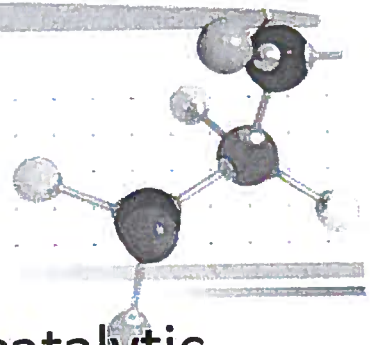
s # 27



- Heat transfer coefficients:



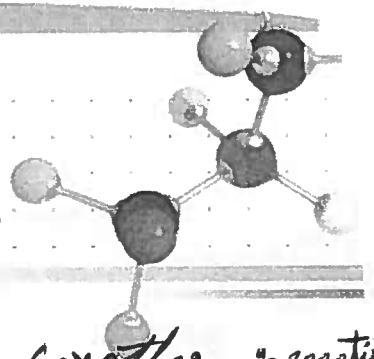
Reaction at the particle outer surface



(reactant species)
(product species)

Say, a reaction, A→R, takes place at the surface of a catalytic particle shown. At steady-state conditions, the heat evolved at the particle surface must be transferred to the bulk fluid phase.

(for an exothermic reaction)



at steady-state conditions

The thermal energy balance at the particle surface leads to:

$$r_A\left(-\Delta H\right) = h_f\, a_m \left(T_s^S - T\right) \qquad (18)$$

$\left[\frac{kJ}{kg\ cat.-s}\right]$

$\Delta H = -\#$ (exothermic reaction)

$= +\#$ (endothermic ")

$\left[\frac{kmol\ \text{of A consumed}}{kg\ cat.-s}\right]$

heat of reaction $\left[\frac{kJ}{kmol}\right]$

for: A → R

T_s^S $[K]$

Bulk fluid temp., $[K]$

external particle surface area per $kg\ cat.$, $\left[\frac{m_p^2}{kg\ cat.}\right]$

heat transfer coefficient for film surrounding the particle, $\left[\frac{kJ}{m_p^2 - s - K}\right]$

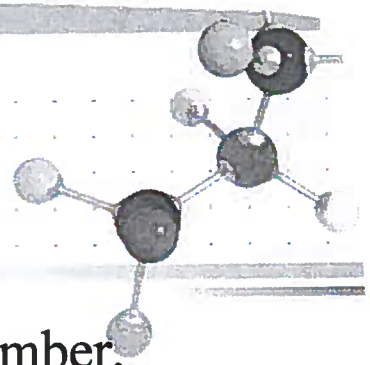
NOTE:

- $h_f = \left(\frac{k_f}{\delta_{th}}\right)$

(for a stagnant film or thermal boundary around a particle)

With an increase in d_p, δ_{th} (thickness of thermal boundary layer) increases; consequently, h_f decreases.

δ_{th} [=] [m_f]; k_f = fluid thermal conductivity [=] $\left[\frac{kJ \cdot m_f}{m_p^2 \cdot s \cdot K}\right]$ (these units are).



The j_H – factor is used to correlate h_f to the particle Reynolds number, $\mathrm{Re}_p \left(= \frac{d_p G}{\mu} \right)$. Relation between j_H and h_f is:

$$j_H = \frac{h_f}{c_p G} \mathrm{Pr}^{\frac{2}{3}} \qquad (19)$$

where $\mathrm{Pr} = \frac{c_p \mu}{\lambda}$

c_p: fluid heat capacity (for heat transfer) $\left[\frac{kJ}{kg-K}\right]$

μ: fluid absolute viscosity $\left(\frac{kg}{m \cdot s}\right)$

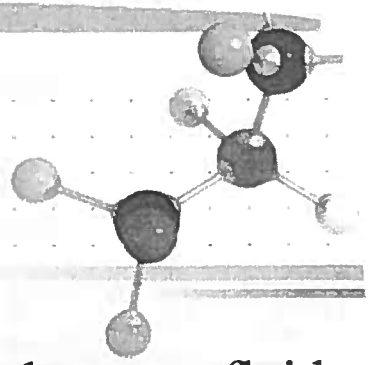
λ: fluid thermal conductivity $\left[\frac{kJ}{m \cdot s \cdot K}\right]$

Pr: Prandtl number (dimensionless)

G: bed superficial mass velocity $\left[\frac{kg}{m_r^2 - s}\right]$

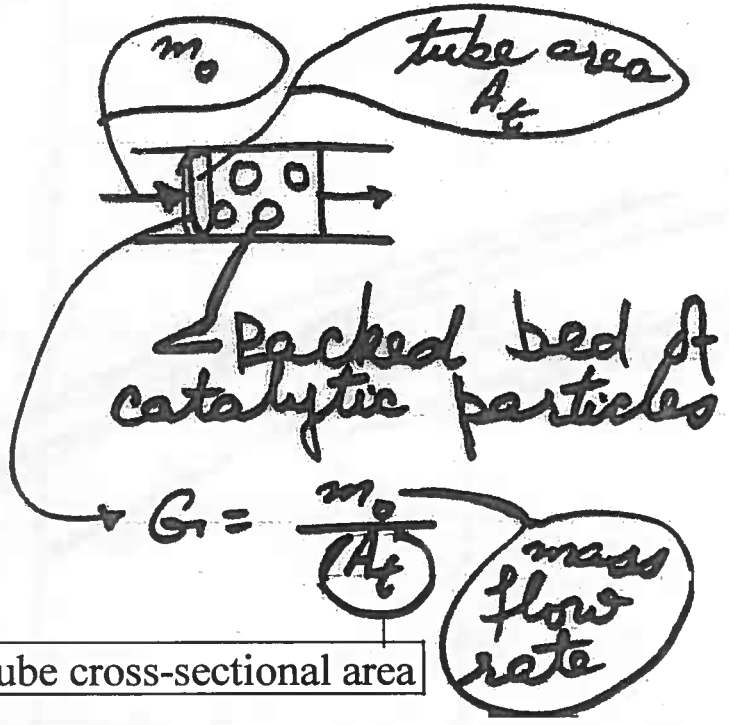
$G = \frac{\text{fluid mass flow rate through the packed bed}}{\text{bed X-area}}$

for example, $A = \frac{\pi}{4} d_t^2$. (19a)



S#36

→ j_H – factor vs. $\mathrm{Re} = \dfrac{d_p G}{\mu}$ is shown in Fig. 3.2.2-1 for heat transfer between fluid and particles packed in a bed.



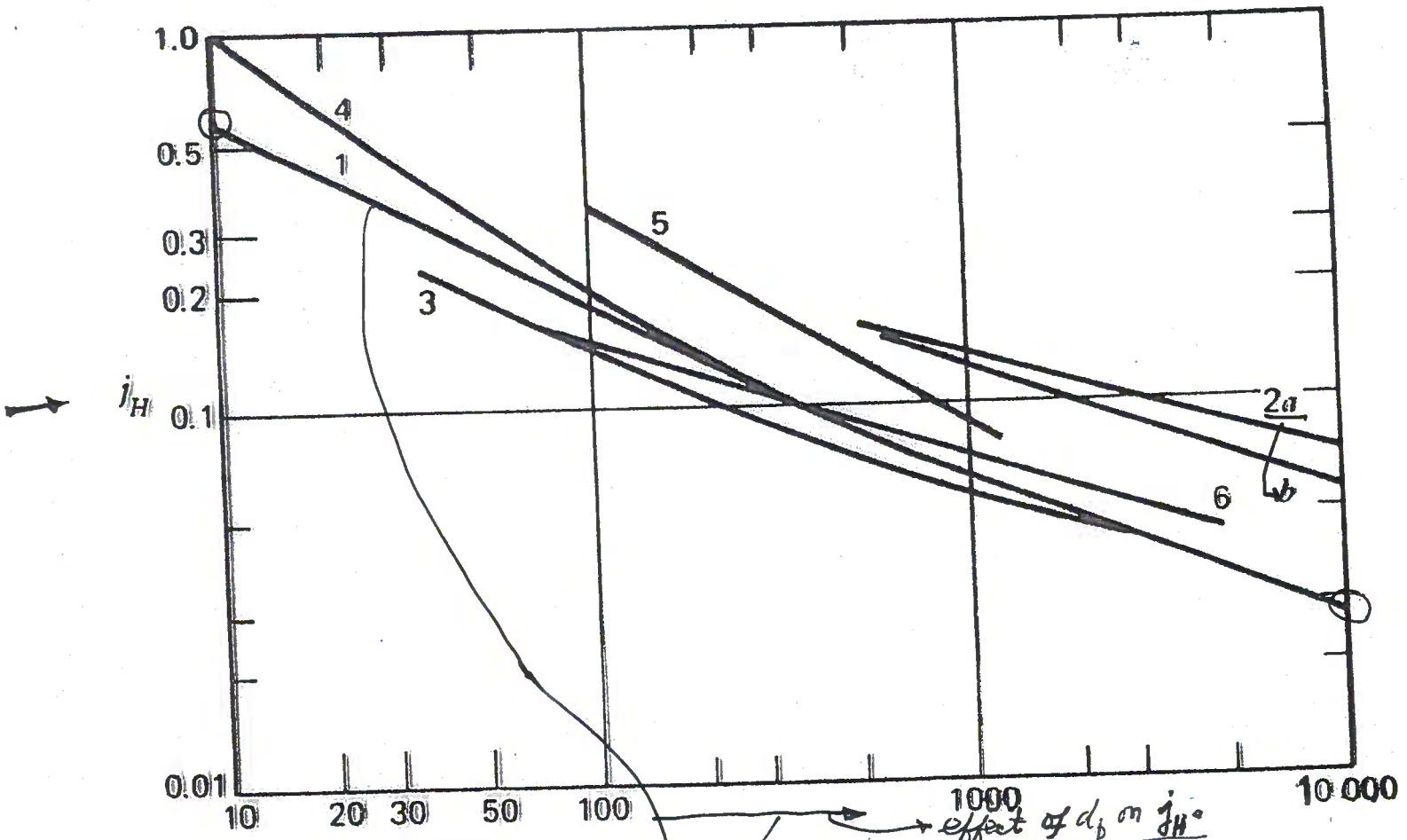


Figure 3.2.2-1
Heat transfer between a fluid and a bed of particles (spheres $\varepsilon = 0.37$). Curve 1: Gamson et al. (1943), Wilke and Hougen (1945). Curve 2: Baumeister and Bennett (*a*) for $d_t/d_p > 20$, (*b*) mean correlation (1958). Curve 3: Glaser and Thodos (1958). Curve 4: deAcetis and Thodos (1960). Curve 5: Sen Gupta and Thodos (1963). Curve 6: Handley and Heggs (1968).

- Multicomponent diffusion in a fluid

The net flux of a chemical species *j* in a multicomponent mixture is given by:

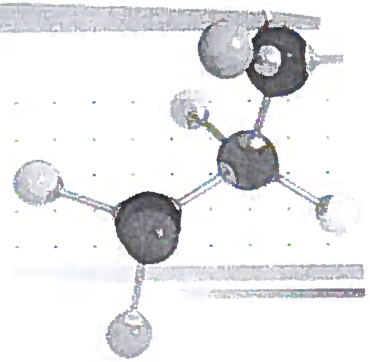
take sum over all chemical species excluding species j

fluid mixture molar concentration

# of chemical species in mixture

$$\vec{N}_j = -\sum_{k=1}^{k=N-1} c_t D_{jk} \vec{\nabla} y_k + y_j \sum_{k=1}^{k=N} \vec{N}_k \qquad (20)$$

flux via molecular diffusion only	flux via bulk or convective flow of mixture



$\Downarrow$

where y_j = mole fraction of a component j

c_t = total mixture molar concentration

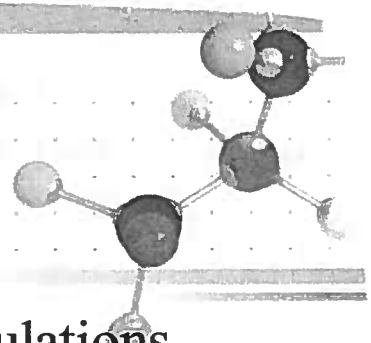
D_{jk} = mass diffusivity of j in the binary mixture of j and k, $\left[\frac{m^2}{s}\right]$.

Note:

For the subject of fluxes in a multicomponent mixture, see Bird et al. Transport Phenomena, pp. 563-572, John Wiley & Sons (1960).

↓

Or: pp. 582–611, John Wiley & Sons (2007, second edition)



S#37

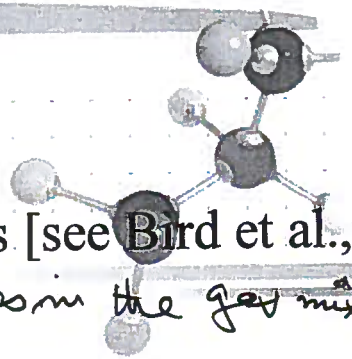
The form of Eq. (20) is very complex for many engineering calculations.

Therefore, a mean effective binary diffusivity for species j is defined as:

$$\vec{N}_j = -c_t D_{jm} \vec{\nabla} y_j + y_j \sum_{k=1}^{k=N} \vec{N}_k \qquad (21)$$

where D_{jm} = effective mass diffusivity of component j in the multicomponent mixture, $\left[\frac{m_f^2}{s}\right]$.

where m for



For the case of an ideal gas mixture, the Stefan-Maxwell equations [see Bird et al., p.570]: (1960 edition) or, p.538 (2007, 2nd edition):

($k=N$: total # of chemical species in the gas mixture)

$$-c_t \vec{\nabla} y_j = \sum_{\substack{k=1 \\ k\neq j}}^{k=N} \frac{1}{D_{jk}} \left(y_k \vec{N}_j - y_j \vec{N}_k \right) \tag{22}$$

• Application of Eq. (22):

(a two component mixture)

Equation (22) applied to a binary mixture for $j=1$:

$$-c_t \vec{\nabla} y_1 = \sum_{k\neq 1}^{k=N=2} \frac{1}{D_{1k}} \left(y_k \vec{N}_1 - y_1 \vec{N}_k \right)$$

(c_t: total gas molar mixture concentration)

$$= \frac{1}{D_{12}} \left(y_2 \vec{N}_1 - y_1 \vec{N}_2 \right)$$

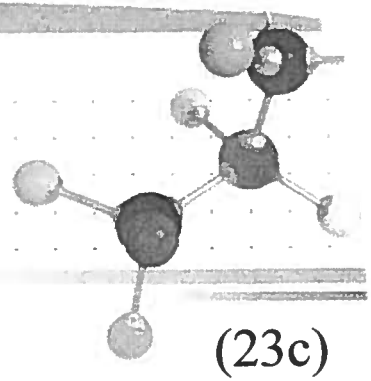
$$\therefore \quad -c_t D_{12} \vec{\nabla} y_1 = \left[(1-y_1) \vec{N}_1 - y_1 \vec{N}_2 \right] \tag{23a}$$

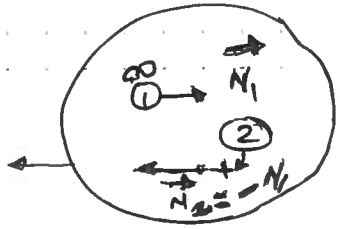
($\because y_1 + y_2 = 1 \rightarrow y_2 = 1 - y_1$)

leads to:

$$\rightarrow \quad \vec{N}_1 = \underbrace{-c_t D_{12} \vec{\nabla} y_1}_{\text{diffusion flux of species 1}} + \underbrace{y_1 \left(\vec{N}_1 + \vec{N}_2 \right)}_{\rightarrow \text{(convective flux) of species 1.}} \tag{23b}$$

[$\vec{N}_1 + \vec{N}_2$ = mixture flux]





→ For an equimolar counterdiffusion, $\vec{N}_2 = -\vec{N}_1$ (23c)

or $$\underbrace{\left(\vec{N}_1 + \vec{N}_2\right) = 0}_{\text{(23d)}}$$

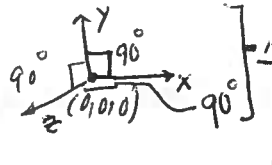
Into Eq. (23b):

→ $$\vec{N}_1 = -c_t D_{12} \vec{\nabla} y_1$$

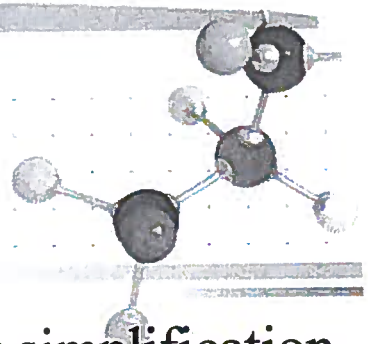
→ $$\vec{\nabla} = \vec{\delta}_x \frac{\partial}{\partial x} + \vec{\delta}_y \frac{\partial}{\partial y} + \vec{\delta}_z \frac{\partial}{\partial z} \quad (24)$$

(in rectangular coordinates)

where $\vec{\delta}_x$, $\vec{\delta}_y$, $\vec{\delta}_z$ unit vectors along x-, y-, and z-coordinates.



Note: z-coordinate ⊥ the plane of this paper sheet surface containing x and y coordinates.



S # 39

S # 40

→ $\vec{\nabla} y_j$ from Eq. (21) is equated to $\vec{\nabla} y_j$ of Eq. (22) to obtain, after simplification,

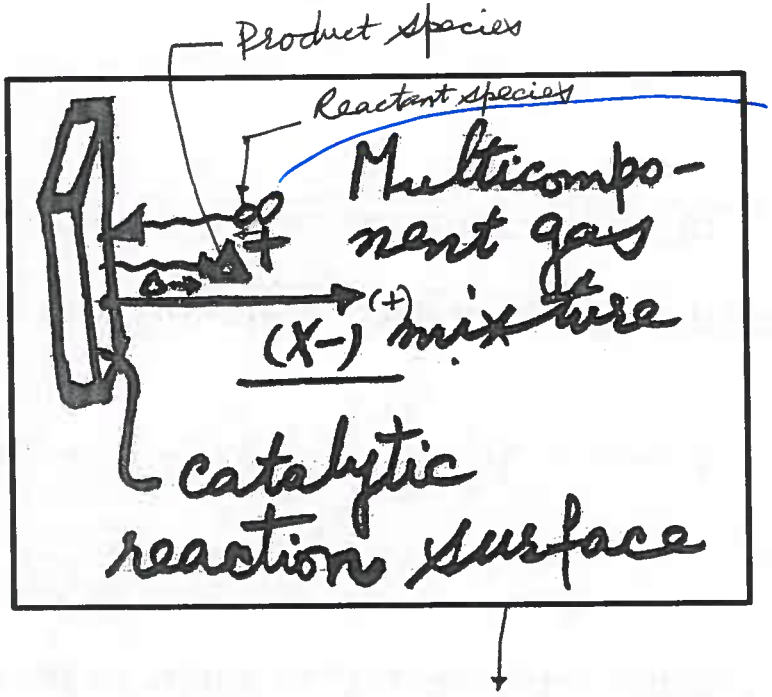
$$\frac{1}{D_{jm}} = \frac{\sum_{k=1}^{k=N} \frac{1}{D_{jk}} \left(y_k - y_j \frac{\vec{N}_k}{\vec{N}_j} \right)}{1 - y_j \sum_{k=1}^{k=N} \left(\frac{\vec{N}_k}{\vec{N}_j} \right)} \qquad (25)$$

D_{jm}: effective mass diffusivity

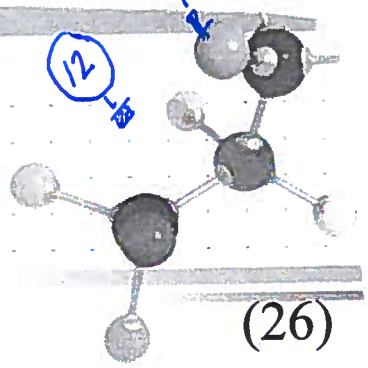
D_{jk} = mass diffusivity of j in the binary mixture (gas) of components j and k.

S#42

- Application of Eq. (25) for a system involving a chemical reaction:



all reactants should have to surface area



Say, a chemical reaction takes place at the catalytic surface,

$$\alpha_1 A_1 + \cdots + \alpha_j A_j + \cdots = 0 \tag{26}$$

or

$$\left(\frac{\alpha_1}{\alpha_j}\right) A_1 + \cdots + 1 \cdot A_j + \left(\frac{\alpha_k}{\alpha_j}\right) A_k + \cdots = 0 \tag{26a}$$

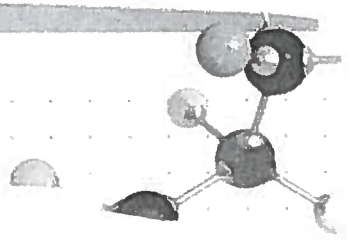
where the stoichiometric coefficient α_j has a negative number value for a reactant species being consumed and a positive number value for a product species being generated.

NOTE

At the steady-state:

$$\left[\begin{array}{l}\text{Production or consumption rate of chemical species } j, \\ r_j \text{ (per unit catalytic surface area)}\end{array}\right]$$

$$= \left[\begin{array}{l}\text{transport flux away or to the catalytic surface of the} \\ \text{speceis j per unit catalytic surface area, } N_j\end{array}\right] \tag{27}$$



S#44

But, for the reaction, Eq. (26),

"rate of reaction, Eq. (26), occurring as whole" at a given reactive mixture temperature and pressure conditions)

$$\frac{r_1}{\alpha_1} = \frac{r_2}{\alpha_2} = \cdots = \frac{r_j}{\alpha_j} = \frac{r_k}{\alpha_k} = \cdots = r = \text{constant} \tag{28}$$

$$\therefore \quad \left(\frac{N_1}{\alpha_1}\right) = \left(\frac{N_2}{\alpha_2}\right) = \cdots = \frac{N_j}{\alpha_j} = \frac{N_k}{\alpha_k} = \cdots = r \tag{29}$$

$$\therefore \quad N_j = r\alpha_j; \qquad N_k = r\alpha_k \tag{29a}$$

Equation (25) is written for one directional transport of the chemical species as:

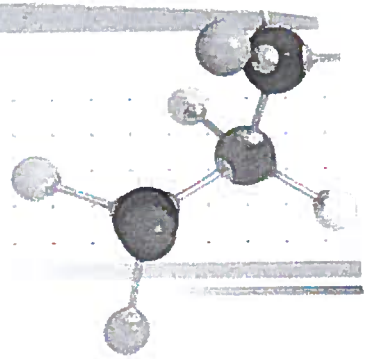
S#42

of it opposite direction

mole flux.

$$\frac{1}{D_{jm}} = \frac{\sum_{k=1}^{k=N} \frac{1}{D_{jk}} \left(y_k - y_j \frac{N_k}{N_j} \right)}{1 - y_j \sum_{k=1}^{k=N} \left(\frac{N_k}{N_j} \right)} \tag{30}$$

↳ molecular diffusivity of j in mixture (multi component)



s #45

Substitute for N_j and N_k from Eq. (29a) into Eq. (30) to obtain:

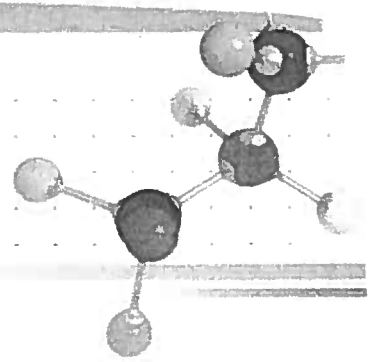
$$\frac{1}{D_{jm}} = \frac{\sum_{\substack{k=1 \\ k\neq j}}^{k=N} \left[\frac{1}{D_{jk}} \left(y_k - \frac{\alpha_k}{\alpha_j} y_j \right) \right]}{1 + y_j \sum_{k=1}^{k=N} \left(-\frac{\alpha_k}{\alpha_j} \right)} \qquad \text{(important equation)} \tag{31a}$$

D_{jm} → molecular mass diffusivity of component j in the multicomponent reactive mixture.

N = total number of chemical species present in the reactive mixture

Now, $\delta_j = \sum_{k=1}^{k=N} \left(-\frac{\alpha_k}{\alpha_j} \right)$ (defined) (31b)

= change in moles of the mixture due to reaction per mole of a reactant j converted completely.



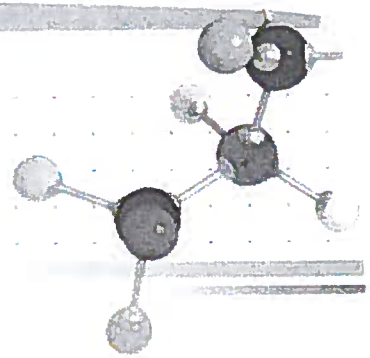
s#46

Equation (31a) can then be written as:

$$\left(\underbrace{\frac{1}{D_{jm}}}_{\text{effective mass diffusivity}}\right) = \frac{\sum_{\substack{k=1 \\ k\neq j}}^{k=N}\left[\frac{1}{D_{jk}}\left(y_k + \left(\frac{\alpha_k}{-\alpha_j}\right)y_j\right)\right]}{1+\delta_j y_j} \qquad (31c)$$

(key important equation)

where D_{jk} = mass diffusivity of j in the binary mixture of j and k.



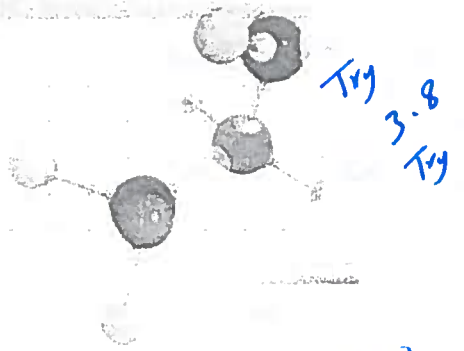
Note: (→ students to read!)

→ For accurate determination of mass diffusivities in multicomponent liquid mixtures, there is no complete theory available. For more information on the theories of ordinary diffusion in liquids, see pp. 513-516 in the reference cited before, i.e., Transport Phenomena by Bird et al. (1960) or pp. 528 – 530 (→ 531 – 533)
(for diffusion in binary liquids)
(for diffusion in colloidal suspensions and " " of polymers)
(→ 2007, second edition)

8/1/05

Feb 25

Packet 4 (7)



Try 3.8 Try

- Diffusion and reaction inside catalytic particles (isothermal conditions)
  - The concept of effectiveness factor:
    - consider a solid pellet as shown with total length along y-direction equal to (2*L*).

binary mixture = diffusion in mixture

S#81

pore area dimensionless fraction = pore area / A area

(pore area) the take r covered by A

A → R Reaction

r

bulk flow

pellet

hence τ = actual distance

r = radius of spherical actual r not measure the distance cus it's zag zag

for A in gas mixture = how A diffuses

Diffusion

$D_{eA} = \frac{D_A \varepsilon_s}{\tau}$

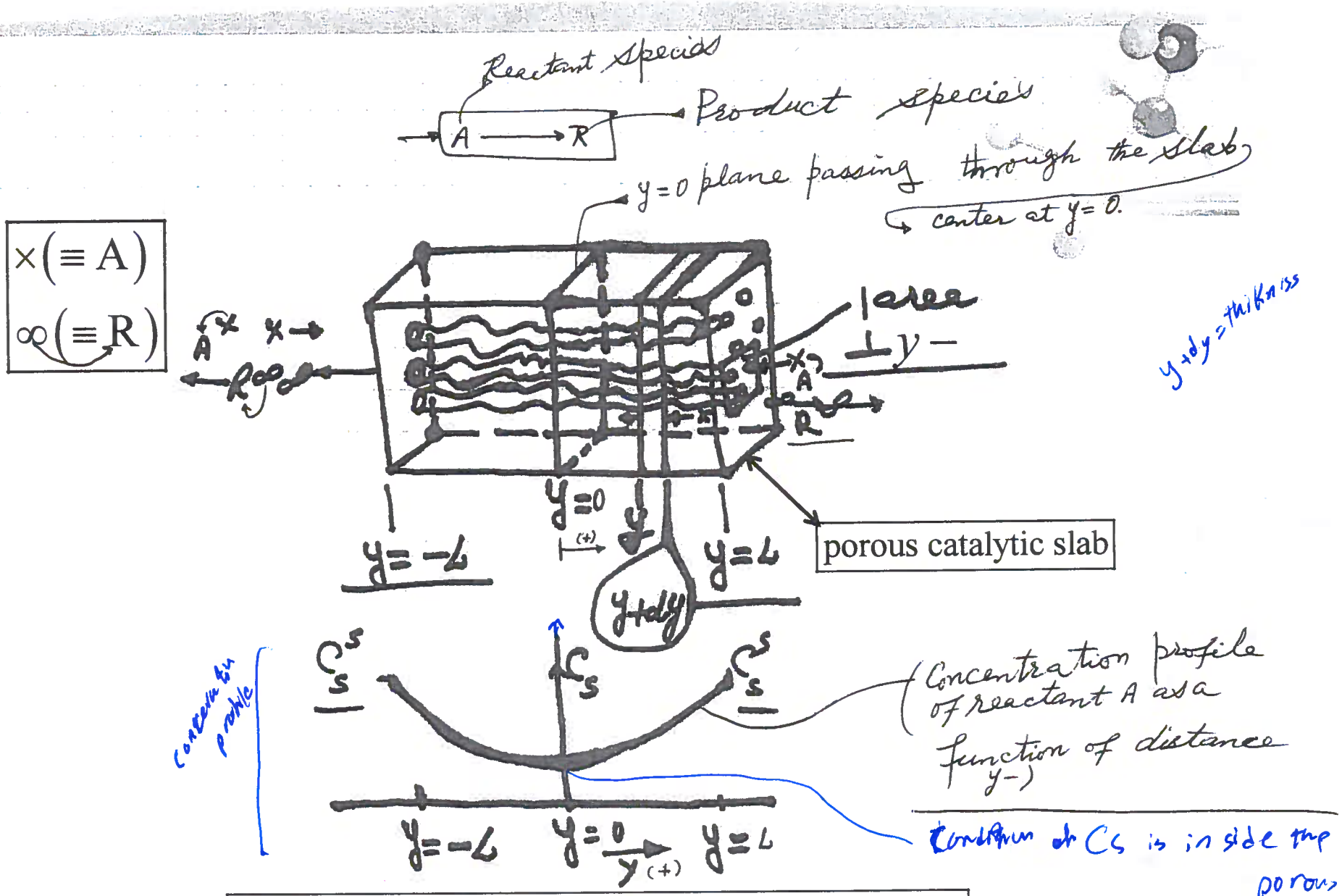
effect diffusion of actual A in mixture in a solid state

τ = tortuosity factor

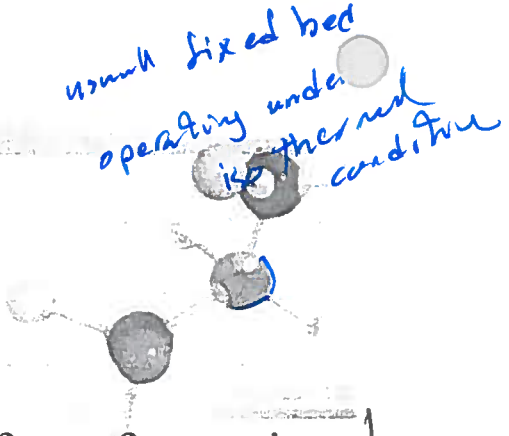
no dimension (dimensionless)

z = 0

z = L



Concentration of A in the pellet, C_s versus y profile



→ Say, a simple first-order reaction, $A \rightarrow R$, is catalyzed by the active surface of pores in the pellet at the isothermal condition. A diffuses toward the central plane at $y = 0$ through tortuous pores while reacting at the walls of the pores. Here, the steady-state, one-dimensional analysis of this process is presented.

The mole balance on the reactant A over the element shown in the slab located between y and $(y + dy)$ planes leads to:

$$D_{eA}\frac{d^2C_s}{dy^2} - (kC_s)\rho_s = 0 \qquad (53)$$

$$\left[\frac{kmol}{kg\ cat.s}\right]\left[\frac{kg\ cat.}{m_p^3\ \text{of pellet vol.}}\right]$$

(second order, ordinary differential equation)

$$D_{eA}\left[\left(\frac{\partial C_s}{\partial y}\bigg|_{y+dy}^{at}\right) - \left(\frac{\partial C_s}{\partial y}\bigg|_{y}^{at}\right)\right] - (kC_s\rho_s)dy = (\epsilon_p\, dy)\frac{\partial C_s}{\partial t}$$

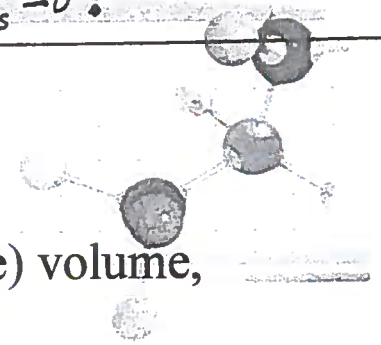
(GO TO TOP OF PAGE 83)

$$D_{eA} \lim_{(dy)\to 0} \left[\frac{\left(\frac{\partial C_s}{\partial y}\right)_{y+dy} - \left(\frac{\partial C_s}{\partial y}\right)_{y}}{dy} \right] - k C_s \rho_s = \rho \frac{\partial C_s}{\partial t}$$

$$D_{eA} \frac{\partial^2 C_s}{\partial y^2} - k C_s \rho_s = \rho \frac{\partial C_s}{\partial t}$$

For the steady state condition, $\frac{\partial C_s}{\partial t} = 0$.

Hence, $D_{eA} \frac{d^2 C_s}{dy^2} - k C_s \rho_s = 0$.



$\Downarrow$

where

C_s = concentration of A in the slab per unit fluid-phase (e.g. gas phase) volume,

$$\left[\frac{kmol \text{ of A}}{m_f^3} \right]$$

k = first-order rate constant $\left[\frac{m_f^3}{kg\ cat. - s} \right]$

ρ_s = pellet density, $\left[\frac{kg\ cat.}{m_p^3 \text{ of pellet volume}} \right]$

D_{eA} = effective diffusivity of A in the pellet accounting for transport of A via all mechanisms of transport, pore tortuosity and constrictions, and fractional y – plane area not available for transport of the species due to the presence of solid grains of the pellet, $\left[\frac{m_f^3}{m_p - s} \right]$.

$= \left(\frac{D_A \epsilon_p}{\tau} \right)$

NOTE

S#82

Note that in obtaining Eq. (53), equimolar counterdiffusion, i.e., $N_R = -N_A$, has been assumed.

→ Equation (53) is solved using the boundary conditions:

$$\left(C_s\big|_{@\,y=L}\right) = C_s^s \quad \rightarrow \tag{54a}$$

$$\left(\frac{dC_s}{dy}\bigg|_{@\,y=0}\right) = 0 \tag{54b}$$

(symmetry of C_s w.r.t. y at $y=0$)

(with respect to y)

→The solution is:

$$\left(\frac{C_s}{C_s^s}\right) = \frac{\cosh\left[L\sqrt{\frac{k\rho_s}{D_{eA}}}\cdot\left(\frac{y}{L}\right)\right]}{\cosh\left[L\sqrt{\frac{k\rho_s}{D_{eA}}}\right]} = \frac{\cosh\left[\phi'\frac{y}{L}\right]}{\cosh[\phi']} \qquad (55)$$

$$\tanh\theta = \frac{e^{\theta}-e^{-\theta}}{e^{\theta}+e^{-\theta}}, \quad \sinh\theta = \frac{e^{\theta}-e^{-\theta}}{2}, \quad [\cosh\theta] = \frac{e^{\theta}+e^{-\theta}}{2}$$

NOTE: One can fix a value of ϕ'. Calculate (C_s/C_s^s) as a function of (y/L) and plot (C_s/C_s^s) vs. (y/L). (55a)

where $\phi' = \left(L\sqrt{\frac{k\rho_s}{D_{eA}}}\right)$, is called the Thiele modulus for the first-order reaction;

→[dimensionless].

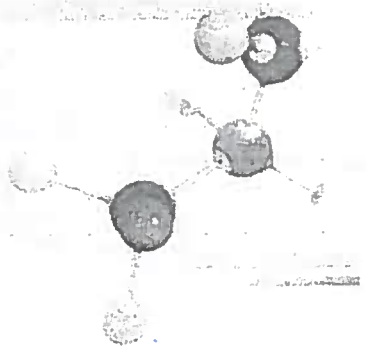


Figure 3.6.1-1 shows $\left[\frac{C_s}{C_s^s}\right]$ *vs.* $\left(\frac{y}{L}\right)$ profiles for a number of values of ϕ'.

Note that the rate $\left[kC_s'\rho_s; \frac{kmol}{m_p^3 - s}\right]$ decreases toward the central plane because of the decrease in C_s with y for each ϕ'.

The pellet internal effectiveness factor is now defined as:

⇓

$$\phi' = \left(L\sqrt{\frac{k\rho_s}{D_{eA}}}\right) = 0.5$$

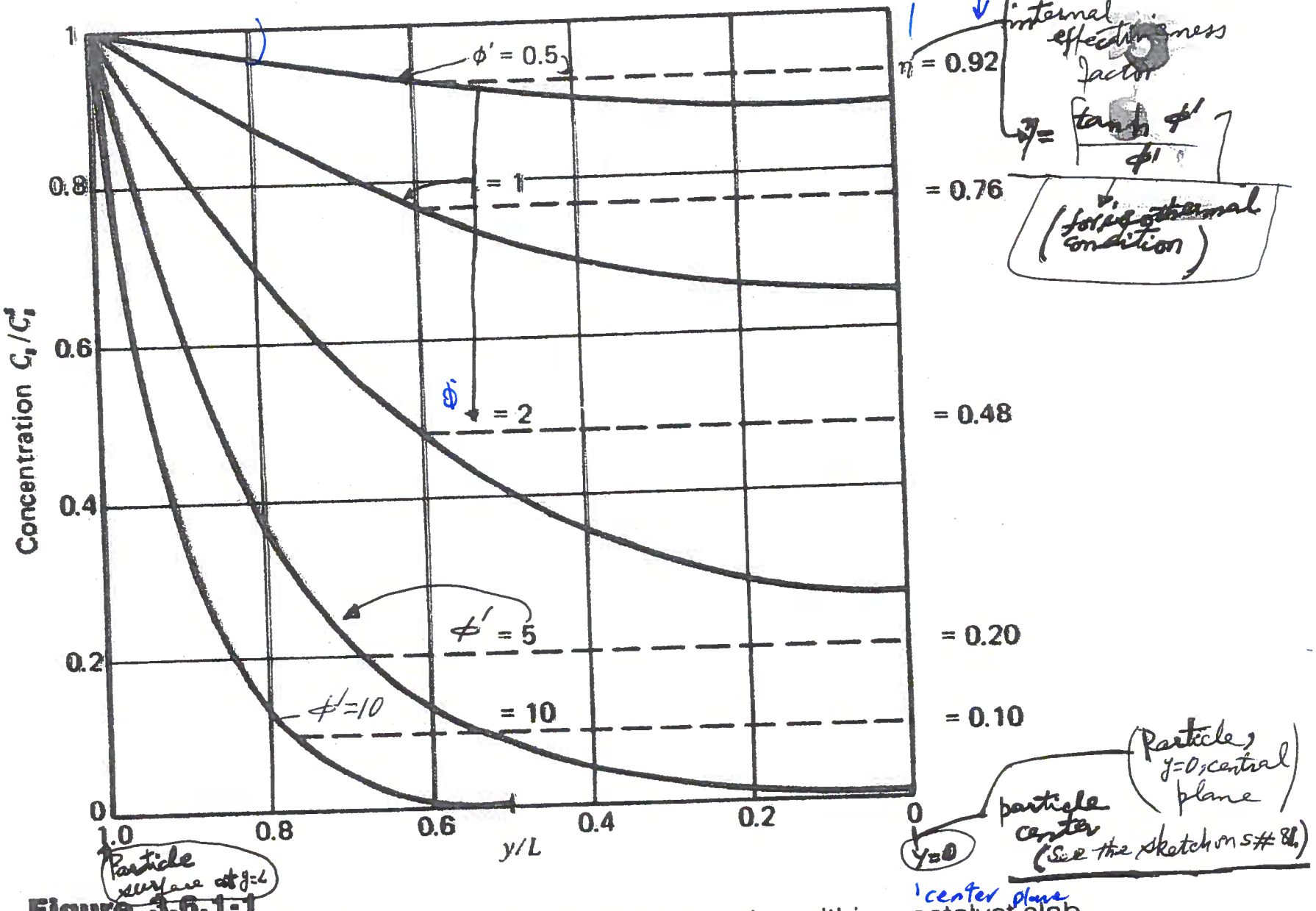


Figure 3.6.1-1
Distribution and average value of reactant concentration within a catalyst slab as a function of the parameter ϕ'. Adapted from Levenspiel (1962).

Internal effectiveness factor

reactant A

$$\eta = \frac{\left(\text{actual consumption rate of A in the entire pellet}\right)}{\left(\begin{array}{l}\text{consumption rate of A in the entire pellet if the temperature, pressure,}\\ \text{and composition conditions everywhere in the pellet were same as at}\\ \text{the pellet surface, i.e., } @\ y = L\end{array}\right)} \qquad (56a)$$

can only for second half then ×2

See s#81 →

$$= \frac{2\left(\int_{y=0}^{y=L}\left[\left(r_A\rho_s\right)\left(1\times dy\right)\right]\right)}{2\left(\int_{y=0}^{y=L}\left[r_A\big|_{@C_s=C_s^s}\right]\rho_s\left(1\times dy\right)\right)} \qquad (56b)$$

($r_A\rho_s$): (Conversion rate of reactant A per unit catalyst volume)

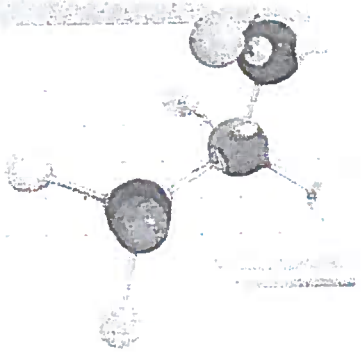
$(1\times dy)$: (volume of a thin particle element of unit x-area and thickness dy)

where r_A = consumption rate of A per unit mass of the catalyst $(= kC_s$, here) (at the same r in the entire particle)

$(1\times dy)$ = volume of the element shown in the slab sketch.

Spatial

(s#81)



Note $\left[\rho_s (1 \times dy)\right] = dW_c$ = mass of the catalyst in the element.

Equation (56b) is reduced to:

(S#88)

$$\eta = \frac{\int_{W_c=0}^{W_c=W_c^t} r_A dW_c}{\left(r_A\big|_{@C_s=C_s^s}\right)\underbrace{\left(\int_0^{W_c^t} dW_c\right)}_{=W_c^t}} \qquad (56c)$$

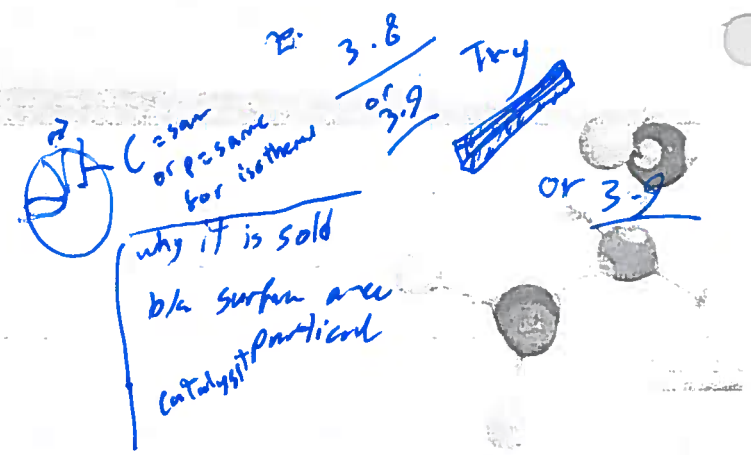
if we divided by W_c^t mass total

conversion rate of A per unit mass of an unfouled catalyst (e.g., a catalyst free of coke deposition)

$$= \frac{\left[\dfrac{\int_0^{W_c^t} r_A dW_c}{W_c^t}\right]}{\left(r_A\big|_{@C_s=C_s^s}\right)} \qquad (56d)$$

Catalyst mass between $y=0$ and $y=L$ planes $\perp$ y coordinate in the catalytic particle

impeca of interg



$$\Downarrow$$

$$\therefore \quad \eta = \frac{\left(r_A\right)_{obs.}}{\left(r_A\big|_{@C_s=C_s^s}\right)} \tag{56e}$$

where $\left(r_A\right)_{obs.}$ = average actual consumption rate of A per unit catalyst mass, $\left[\frac{kmol}{kg\ cat.-s}\right]$

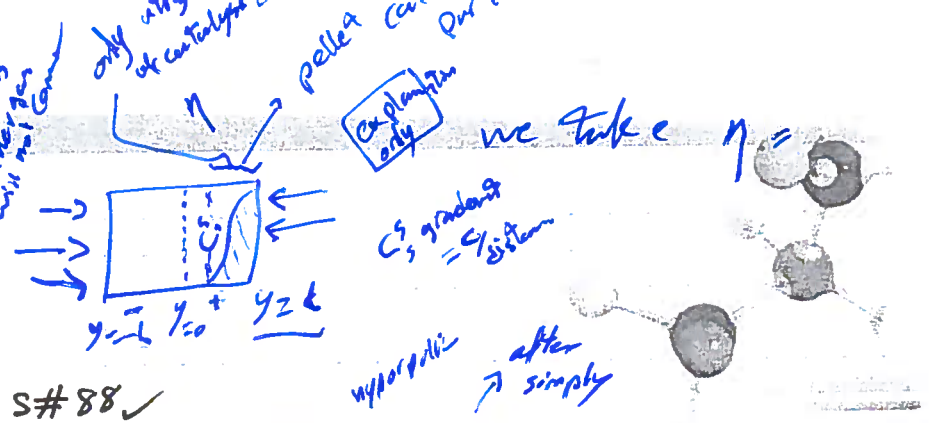
$\left(r_A\big|_{@C_s=C_s^s}\right) = r_A\left(C_s^s\right)$ = consumption rate of A per unit catalyst mass if $C_s = C_s^s$

everywhere inside the pellet, $\left[\frac{kmol}{kg\ cat.-s}\right]$

$= kC_s^s$

W_c^t = total mass of the pellet between $y = 0$ to $y = L$ plane.

$[kg]$

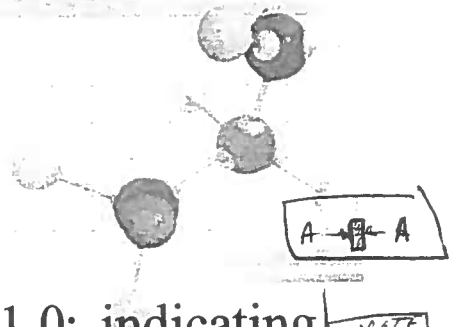


If C_s is substituted from Eq. (55a) into Eq. (56b) or (56d), one obtains:

$$\eta = \frac{[\tanh \phi']}{\phi'} \quad \left[\text{where } \tanh \phi' = \frac{e^{\phi'} - e^{-\phi'}}{e^{\phi'} + e^{-\phi'}}\right] \quad (57)$$

with ϕ' = Thiele modulus = $L\sqrt{\dfrac{k\rho_s}{D_{eA}}}$ (for a first-order reaction) (57a)

→ Note: ρ_s is assumed to be uniform in the pellet.



$\phi' = L\sqrt{\frac{k\rho_s}{D_{eA}}}$

Figure 3.6.1-2 shows η vs. ϕ' (for slab). Note that for $\phi' \to 0, \eta \to 1.0$; indicating negligible resistance to the overall mass transfer process. For $\phi' \to \infty$ (i.e., when ϕ' is >>3)

[may happen because of large value of L, high k, or very small D_{eA} for a catalyst of given density, ρ_s],

$$\rightarrow \quad \eta_\infty \cong \frac{1}{\phi'} \qquad (58)$$

mathematically, because for $\phi' > 3$:

$\tanh \phi' = \left(\frac{e^{\phi'} - e^{-\phi'}}{e^{\phi'} + e^{-\phi'}}\right) \rightarrow 1.0$ in Eq. (57),

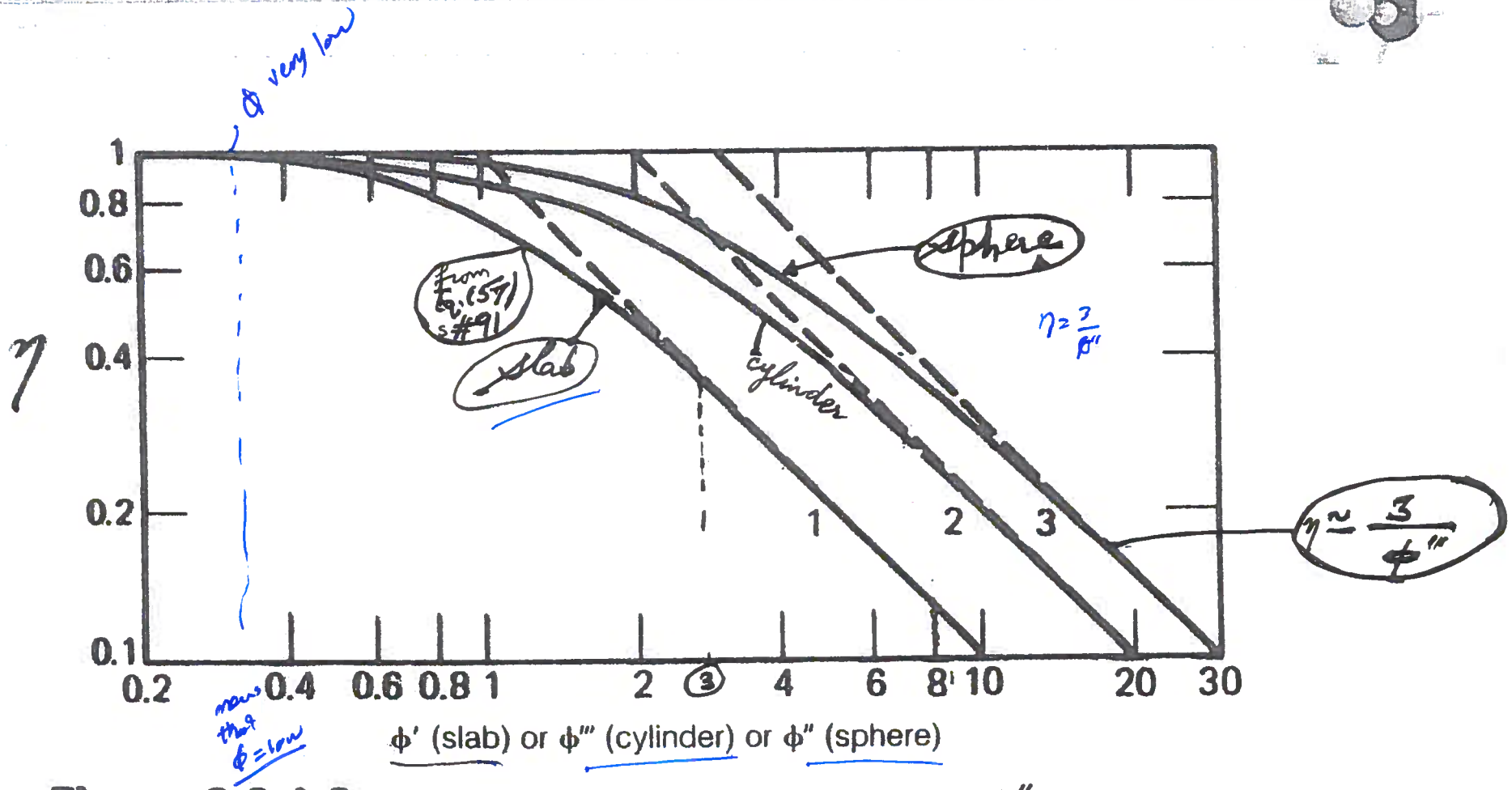
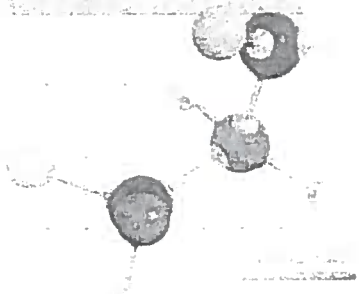


Figure 3.6.1-2
Effectiveness factors for slab (1), cylinder (2), and sphere (3). From Aris (1969).



→ The above procedure can be followed to analyze the first-order reaction and diffusion in a porous catalytic, spherical pellet to obtain:

$$\rightarrow \eta = \frac{3}{\phi''}\left[\frac{\phi'' \coth \phi'' - 1}{\phi''}\right] \qquad (59)$$

$$\coth \phi'' = \frac{e^{\phi''} + e^{-\phi''}}{e^{\phi''} - e^{-\phi''}}$$

→ where $\phi'' = R\sqrt{\frac{k\rho_s}{D_{eA}}}$ (59a)

Thiele modulus

where R = radius of the spherical, porous catalyst pellet

η vs. ϕ'' is also shown in Fig. 3.6.1-2. This is similar to η vs. ϕ' for the slab.

For $\phi'' \rightarrow$ "∞"; Eq. (59) leads to:

$$\eta \simeq \frac{3}{\phi''} \cdot \qquad (59b)$$

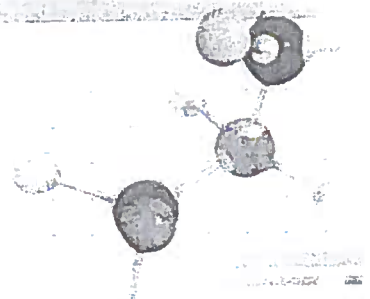


Figure 3.6.1-2 also shows η vs. ϕ''' (thiele modulus) for a cylindrical pellet. All three plots for slab, cylinder, and sphere appear to be similar.

$\frac{4}{3}\pi R^3$ / for volume of spheric

If a new modulus for the spherical pellet is defined as

radius of the pellet

$$\phi = \frac{R}{3}\sqrt{\frac{k\rho_s}{D_{eA}}} \qquad (60a)$$

(rate coefficient for the 1st-order reaction at a temp. T)

V_p = pellet volume

$S_{p.ext}$ = pellet external surface area

$$\frac{R}{3} = \left(\frac{V_p}{S_{p,ext}}\right)\left[\sqrt{\frac{k\rho_s}{D_{eA}}}\right] \qquad (60b)$$

$= \phi''$ (see S#94)

Thiele modulus for a spherical, catalytic pellet

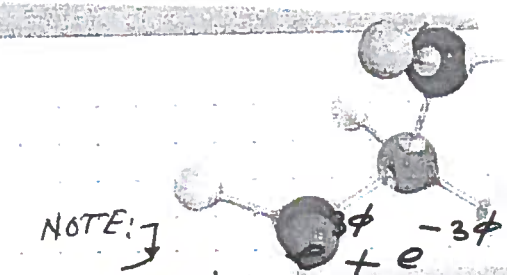
outer surface of catalytic are

$$= \frac{\phi''}{3} \qquad (60c)$$

So,

$$\phi'' = 3\phi \qquad (61)$$

- Into Eq. (59) (S# 94)



NOTE:

$$\coth(3\phi) = \frac{e^{3\phi} + e^{-3\phi}}{e^{3\phi} - e^{-3\phi}}$$

large value of ϕ

$\Downarrow$

We obtain, $\longrightarrow$

$$\eta = \frac{1}{\phi}\left[\frac{(3\phi)\coth(3\phi) - 1}{3\phi}\right] \qquad (62)$$

$\because \coth(3\phi) \to 1.0;$ then $\eta \simeq \frac{1}{\phi}\left[\frac{3\phi - 1}{3\phi}\right] = \frac{1}{\phi}\left[1 - \frac{1}{3\phi}\right]$ (62a)

$\simeq \frac{1}{\phi}$ $\left[\because 1 \gg \left(\frac{1}{3\phi}\right)\right]$ NOTE

$\rightarrow$

$$\eta \simeq \frac{1}{\phi} \qquad (\text{for } \phi \to \text{"}\infty\text{"})$$

Now, η vs. ϕ modulus plots for the sphere and slab match exactly when $\phi \to 0$, and $\phi \to \infty$ [See Fig. 3.6.1-3]. (S# 98)

→ A general modulus, applicable for all pellet shapes, is now defined as:

$$\phi = \frac{V_p}{S_{p,ext}}\sqrt{\frac{k\rho_s}{D_{eA}}} \qquad (63)$$

(k: rate coefficient for the first-order reaction)

$\left(\frac{V_p}{S_{p,ext}} = \frac{\text{pellet volume}}{\text{pellet external area}}\right)$

for determining value of ϕ (dimensionless)

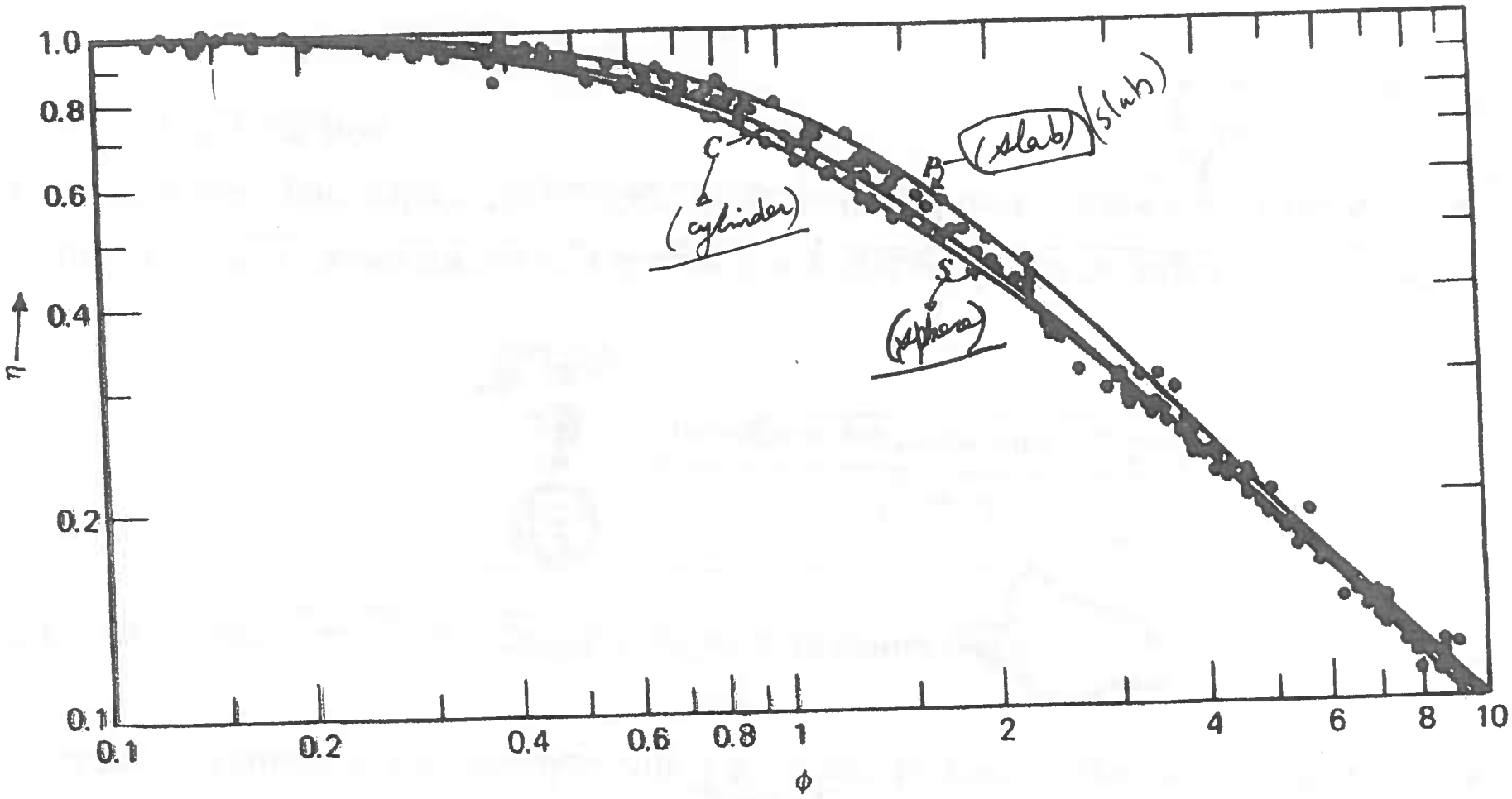
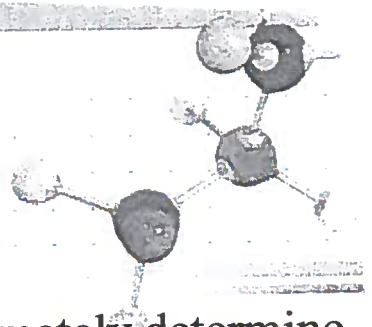


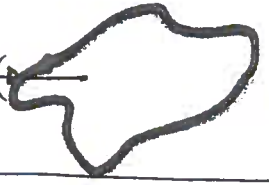
Figure 3.6.1-3
Effectiveness factors for slab (*P*), cylinder (*C*), and sphere (*S*) as functions of the Thiele modulus. Dots represent calculations by Amundson and Luss (1967) and Gunn (1965). From Aris (1965).

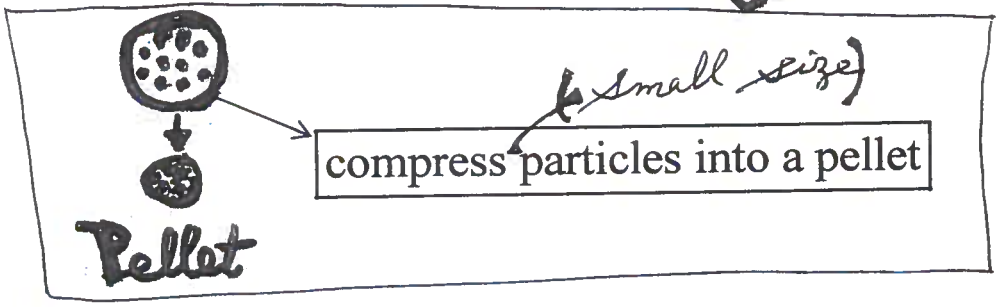
→ NOTE: Students to read this slide.



S# 98

→ With this definition of the modulus, Fig. 3.6.1-3 can be used to approximately determine

→ η for any shape of a catalytic pellet; regular or irregular ().



→ Differences in η values for various shapes, for ϕ around 1, can be larger for non-first-order reactions; particularly for reaction order → 0; and for the Langmuir-Hinshelwood rate form of a reaction.

(See chapter 2 in the textbook.)

A ⟶ R

→ The generalized modulus for an nth order, irreversible reaction is given below:

$$\phi = \frac{V_p}{S_{p,ext}} \sqrt{\frac{n+1}{2} \frac{k\left(C_s^s\right)^{n-1} \rho_s}{D_{eA}}} \qquad \text{(for n>(-1))} \qquad (64)$$

should be more order

↳ 0.5-1 ≈ 0.5

where $r_A = kC_s^n$, $\left[\frac{kmol \text{ of A consumed}}{kg\ cat. - s}\right]$ (64a)

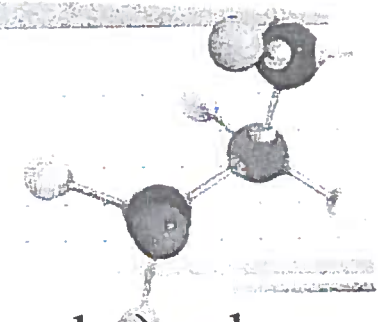
it doesn't mean "n" order is means it is complex

ρ_s = pellet density $\left[\frac{kg}{\text{pellet volume}}\right]$

pellet volume

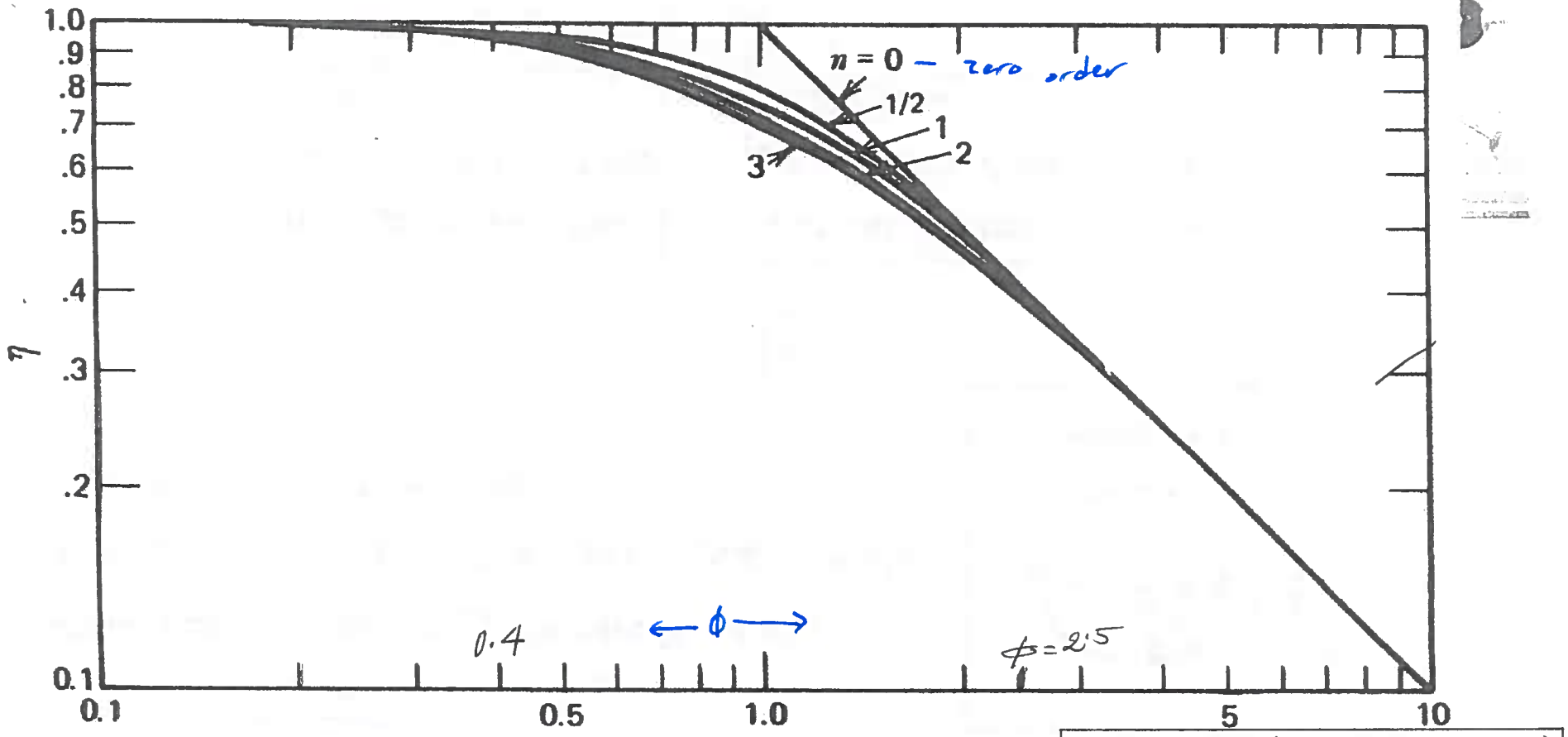
→ $\left(\frac{V_p}{S_{p,ext}}\right) = L$ = pellet characteristic length

pellet external surface area



s#102

Figure 3.6.2-1 shows η vs. ϕ plots for various n (reaction order) values. Note that all curves overlap for $\phi < 0.4$ and $\phi > 2.5$. They differ for $\phi = 0.4 \rightarrow 2.5$.



$$\phi = L\sqrt{\frac{n+1}{2}\,\frac{k\,C_s^{n-1}\,\rho_s}{D_{eA}}}$$

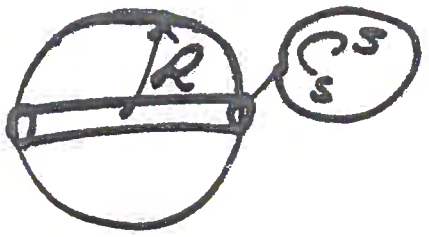
pellet density = $\left(\frac{\text{total pellet mass}}{\text{total pellet volume}}\right)$

effective diffusivity of A

Figure 3.6.2-1
Relationship of η versus generalized modulus for simple-order reactions.

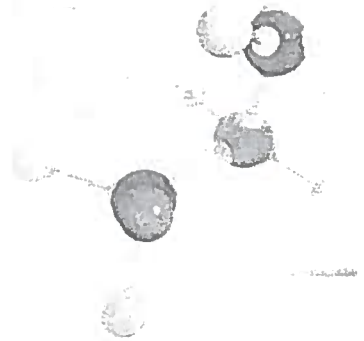
- Diffusional falsification of rate coefficient and activation energy

Actual reaction rate; $r_{A,act}$ for an nth-order, isothermal reaction, A → R, taking place inside a pellet is given by theory as:



A porous catalytic pellet

$$\underbrace{r_{A,act}}_{\text{average reaction rate per unit volume of the catalyst}} = \eta \underbrace{\left[r_{A,s} \right]}_{\text{reaction rate per unit catlyst volume at the pellet external surface species concentration conditions}} \qquad (65)$$



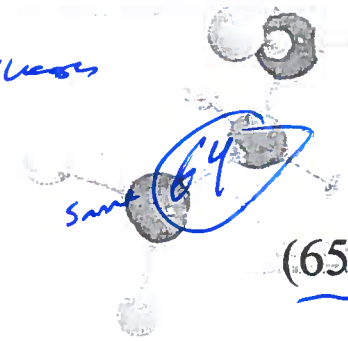
$$r_{A,act} = \eta \left[k \rho_s \left(C_s^s \right)^n \right] \qquad (65a)$$

true reaction order

$\left[\frac{kmol}{cat.vol - s} \right]$ $\left[\frac{kmol}{cat.vol - s} \right]$

valid for high ϕ value (e.g. $\phi > 10$)

internal effectiveness factor, $\eta \simeq \frac{1}{\phi}$ Eq. 64, $S \neq 100$.



$$\Downarrow$$

when we insert what equation

$$r_{A,act} = \frac{S_{p,ext}}{V_p}\sqrt{\frac{2}{n+1}D_{eA}k_V}\cdot\left[C_s^s\right]^{\left(\frac{n+1}{2}\right)} \qquad (65b)$$

$$= \left(\frac{S_{p,ext}}{V_p}\right)\sqrt{\frac{2}{n+1}}D_{eA}^{\frac{1}{2}}k_V^{\frac{1}{2}}\left[C_s^s\right]^{\left(\frac{n+1}{2}\right)}$$

now we mean the barrel relative to energy

$$\left[\frac{kmol}{cat.vol-s}\right]$$

$$= \left(\frac{S_{p,ext}}{V_p}\right)\sqrt{\frac{2}{n+1}}\left[A_D e^{-\frac{E_D}{RT}}\right]^{\frac{1}{2}}\left[A_o e^{-\frac{E}{RT}}\right]^{\frac{1}{2}}\left[C_s^s\right]^{\left(\frac{n+1}{2}\right)} \qquad (65c)$$

$$= \left[\frac{S_{p,ext}}{V_p}\cdot\sqrt{A_D A_o}\cdot\sqrt{\frac{2}{n+1}}\right]e^{-\frac{1}{RT}\left[\frac{E_D+E}{2}\right]}\left[C_s^s\right]^{\left(\frac{n+1}{2}\right)} \qquad (65d)$$

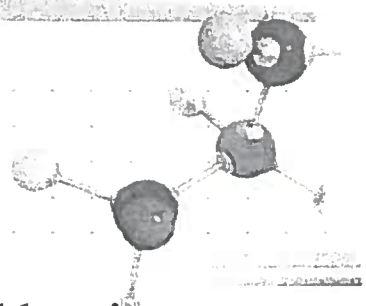
after connect to gether

same unit of diffusivity

Note: $k_V = k\rho_s$ in Eq. (65b). $k\left[=\right] m_f^{3n}/\left(s.kgcat.\left(kmol\ A\right)^{(n-1)}\right)$; $D_{eA}\left[=\right]\frac{m_f^3}{m_p.s}$;

$$k_V\left[=\right]\frac{m_f^{3n}}{m_p^3.s.\left(kmol\ A\right)^{(n-1)}}.$$

$D_{eA} = \frac{m^2}{s}$ or $\frac{cm^2}{s}$



Experimentally, the observed average rate per unit catalyst volume would be given as:

$$r_{A,obs.} = k_{obs}\left(C_s^s\right)^{n_{obs}} \tag{66}$$

$$= A_{o,obs}\, e^{-\frac{E_{obs}}{RT}}\left(C_s^s\right)^{n_{obs}} \tag{66a}$$

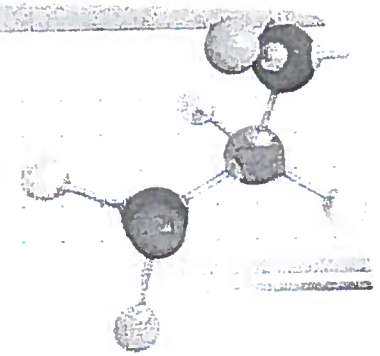
Because, $r_{A,act} = r_{A,obs.}$; comparison of RHS's of Eqs. (65d) and (66a) shows that:

$$E_{obs} = \frac{E_D + E}{2} \tag{67a}$$

$$n_{obs} = \left(\frac{n+1}{2}\right) \tag{67b}$$

where E and n are true reaction activation energy and order of the reaction.

E_D indicates the resistance to the overall reaction process due to diffusion in the pores.



For $E_D << E$; Eq. (67a) becomes:

s#106

$$E_{obs} \simeq \frac{E}{2} \quad \text{or} \quad E \simeq 2E_{obs} \tag{68a}$$

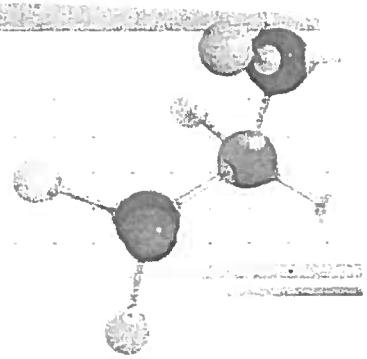
Note that the true activation energy of the chemical reaction, E, is 2 times the activation energy that is experimentally measured. Also,

$$n = 2n_{obs} - 1 \tag{68b}$$

← (from (67b), s#106)

So, the true reaction order is (two times the observed reaction order -1). For the results given in Eqs. (68a) and (68b), the chemical kinetics is referred to as the kinetics falsified by the diffusion inside the catalytic pellet.

students to read!



→ Over the entire range of ϕ, the falsified activation energy is given by:

$$\frac{E_{obs}}{E} = 1 + \frac{1}{2}\left[\frac{d(\ln \eta)}{d(\ln \phi)}\right] \qquad (69a)$$

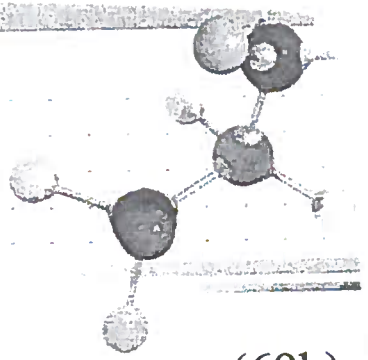
E_{obs} → true activation energy of the chemical reaction

ϕ → Thiele modulus

[Weisz and Prater (1954)]

where E_{obs} = apparent or experimentally determined activation energy,

E = true activation energy of the chemical reaction.



3 shapes usually consider cylinder

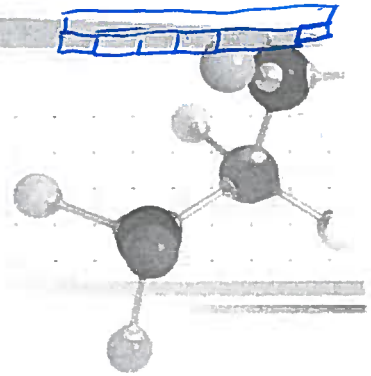
Also,

$$\underbrace{n_{obs}}_{\text{experimentally observed reaction order}} = \underbrace{n}_{\text{true reaction order}} + \frac{n-1}{2}\left[\frac{d\ln\eta}{d\ln\phi}\right] \qquad (69b)$$

[Languasco et al. (1972)]

η = internal effectiveness factor,

ϕ = modulus.



- Weisz-Prater criterion for internal diffusion:

The Weisz-Prater criterion uses the measured reaction rate to determine if the internal diffusion limits the reaction inside a porous catalyst. The Weisz-Prater parameter, C_{WP}, is:

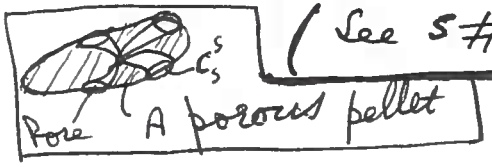
$$C_{WP} = \frac{(r_A)_{obs}\,\rho_s L^2}{D_{eA} C_s^s} \left(= \eta\phi^2 = \Phi\right) \qquad (70a)$$

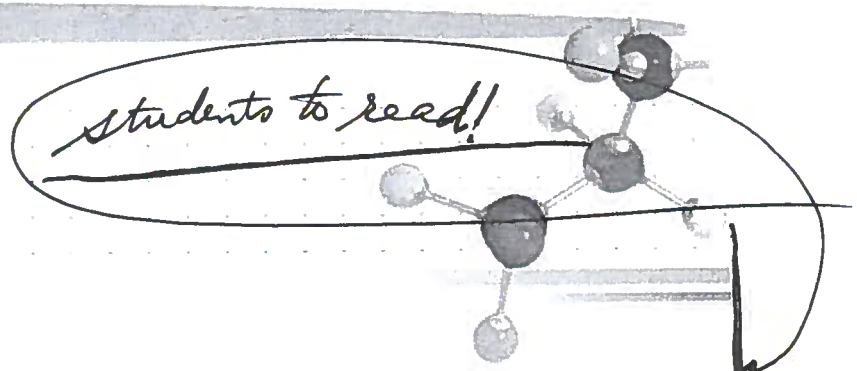
where $L = \dfrac{V_p}{S_{p,ext}}$ $\left[m_p\right]$

pellet volume

pellet external surface area

$(r_A)_{obs}$ = observed reaction rate $\left[\dfrac{kmol}{kg\ cat - s}\right]$





students to read!

ρ_s = pellet density $\left[\frac{kg}{m_p^3}\right]$

D_{eA} = effective diffusivity of A in the pellet $\left[\frac{m_f^3}{m_p - s}\right]$

C_s^s = concentration of reactant A at the pellet external surface conditions "just" in the pore $\left[\frac{kmol}{m_f^3}\right]$.

This criterion states that:

(parameter)

If $C_{WP} \ll 1$, (70b)

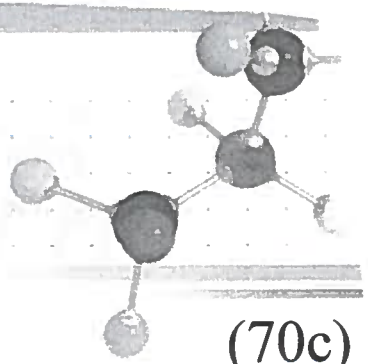
then diffusion resistance in the pores has negligible effect on the overall reaction in the porous pellet. That is, no concentration gradient prevails inside the pellet. Only, intrinsic reaction controls the overall process of reaction inside the pellet.

• free of the transport of species

NOTE

$(\vec{\nabla} C_{A\cdot s}) = \vec{0}$ delta $C_A = \vec{0}$ why $\vec{0}$ instead of 0

$(\vec{\nabla} C_{A,s}) = \vec{0}$ | $\vec{\nabla} C_{A,s} = \left(\vec{i}\frac{d}{dx} + \vec{j}\frac{d}{dy} + \vec{k}\frac{d}{ds}\right)$



If $C_{WP} >> 1$ | (70c)

then, the internal diffusion severely limits the overall consumption of a reactant or production of a desired chemical species.

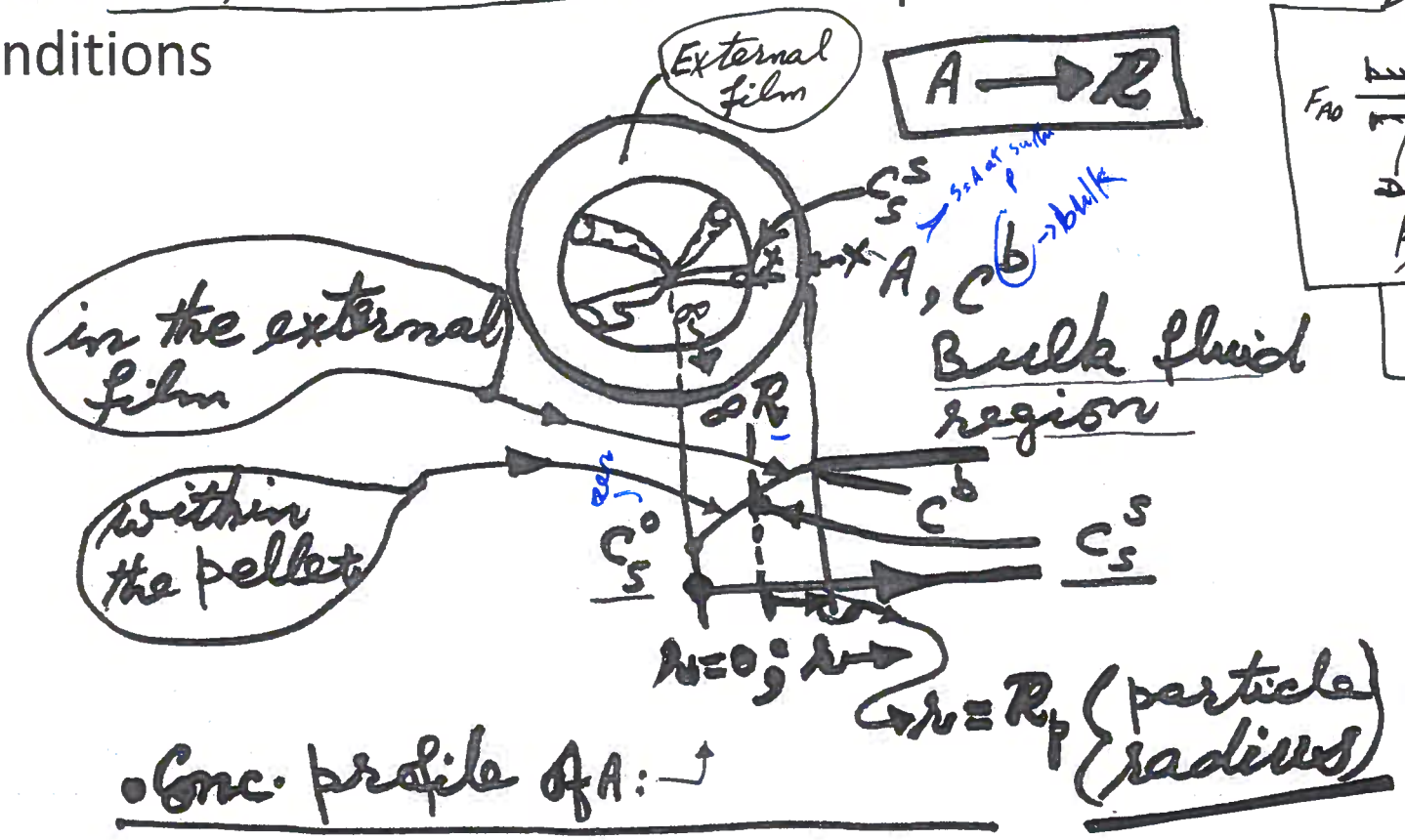
For more information on this topic, see G. F. Froment and K. B. Bischoff, Chemical Reactor Analysis and Design, pp. 166, 167; John Wiley and Sons (1990)

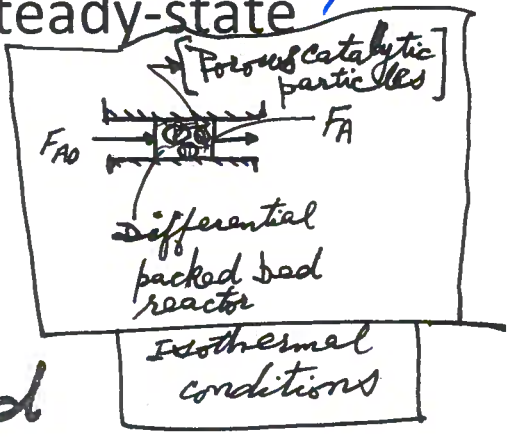
H. S. Fogler, Elements of Chemical Reaction Engineering, pp. 625, 626; Prentice Hall (1992)

- Overall effectiveness factor

  - Combination of external and internal diffusion resistance:

  First-order, isothermal reaction in a pellet under steady-state conditions





→ NOTE: Students to read this slide.

Imagine a first-order reaction taking place in the catalytic, porous pellet shown in the sketch under steady-state, isothermal conditions. The notation here is:

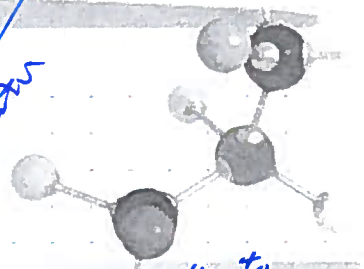
C_s = concentration of the reactant A in the solid porous pellet, $\left[\frac{kmol}{m_f^3}\right]$

C = concentration of the reactant A in the fluid-phase outside the exterior boundary of the pellet, $\left[\frac{kmol}{m_f^3}\right]$

C^b = bulk concentration of A in the bulk fluid region where $\vec{\nabla} C = \vec{0}$, $\left[\frac{kmol}{m_f^3}\right]$ (i.e. the spatial gradient of conc. of A = 0)

C_s^s = concentration of A in the pellet at its external surface, $\left[\frac{kmol}{m_f^3}\right]$

C_s^o = concentration of A in the pellet at its center, $\left[\frac{kmol}{m_f^3}\right]$.



→ At the steady-state conditions:

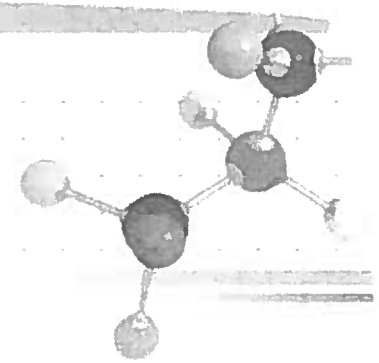
$$\left(\begin{array}{l}\text{total mass transfer rate of A to}\\ \text{the pellet exterior surface}\end{array}\right)=\left(\begin{array}{l}\text{consumption rate of}\\ \text{A in the entire pellet}\end{array}\right) \tag{71}$$

$$\left(\left[k_g\left(C^b-C_s^s\right)\right]S_{p,ext}\right)=\left(\left[\eta\left(r_A^s\rho_s\right)\right]V_p\right) \tag{71a}$$

where k_g = mass transfer coefficient for transfer of A to the surface through the external film, where concentration of A varies from C^b to C_s^s;

$$\left[\frac{m_f^3}{m_p^2-s}\right]$$

⇓



NOTE; Students to read the notation.

⇓

$S_{p,ext}$ = particle external surface area $\left[m_p^2\right]$; V_p = particle volume $\left[m_p^3\right]$

η = internal effectiveness factor [dimensionless]

r_A^s = consumption rate of A via catalytic surface intrinsic chemical kinetics per unit catalyst mass if the entire internal pellet surface is exposed to the concentration of A at the pellet surface, $\left[\frac{kmol\ A}{kg\ cat - s}\right]$.

C_s^s

ρ_s = pellet density, $\left[\frac{kg\ cat}{m_p^3}\right]$

For the first-order reaction,

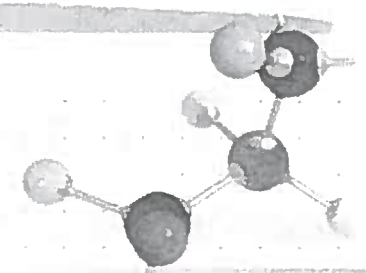
$$r_A^s = kC_s^s \tag{72}$$

Note that determination of C_s^s is usually difficult; therefore, expression for it is obtained in terms of C^b (more easily measured) using Eqs. (71a) and (72). Substituting for r_A^s from Eq. (72) into Eq. (71a) to obtain:

$$\left[k_g\left(C^b - C_s^s\right)S_{p,ext}\right] = \eta\left(kC_s^s\rho_s\right)V_p \tag{73}$$

On simplification of Eq. (73), one obtains:

$$C_s^s = \frac{C^b}{1+\eta\left(\frac{k}{k_g}\right)\rho_s\left(\frac{V_p}{S_{p,ext}}\right)} \tag{73a}$$



So, the total consumption rate of A in the entire pellet,

$$r_{A,p}^{t} = \eta r_A^s \left(\rho_s V_p\right) \quad \text{(pellet mass)} \qquad (74)$$

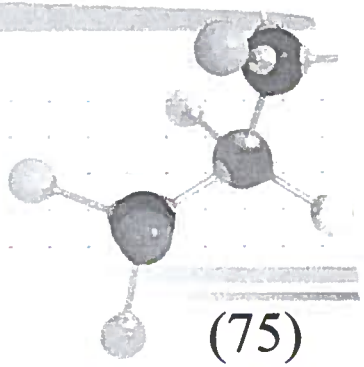
$$\left[\frac{kmol}{s}\right]$$

ρ_s = average, uniform particle density.

$$= k_g \left(C^b - C_s^s\right) S_{p,ext} \qquad (74a)$$

total mass transfer rate of A to the pellet exterior surface

With $r_A^s = kC_s^s$ in Eq. (74),



$$r_{A,p}^{t} = \eta k C_s^s \rho_s V_p \qquad (75)$$

substitute for C_s^s from (73a) (s#117)

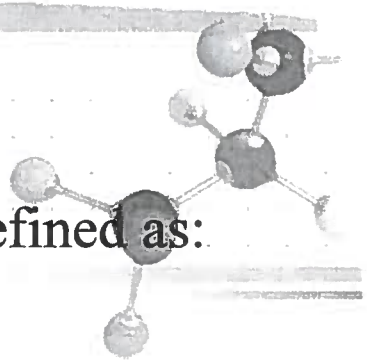
to obtain:

$$r_{A,p}^{t} = \eta r_A^s \left(\rho_s V_p\right) = \eta k C_s^s \left(\rho_s V_p\right)$$

$$= \left[\frac{\eta}{1+\eta\left(\frac{k}{k_g}\right)\rho_s\left(\frac{V_p}{S_{p,ext}}\right)}\right]\left(kC^b \rho_s V_p\right) \qquad (76)$$

→ Note that $\left(kC^b \rho_s V_p\right)$ = consumption rate of A in the entire pellet via first-order reaction if the pellet (exterior and interior) surface were exposed to the bulk fluid-phase concentration of A.

is valid for gas–liquid



→ Now, the global effectiveness factor [for (film + particle)] is defined as:

$$\eta_G = \frac{\left(\text{actual consumption rate of A in the pellet}\right)}{\left(\begin{array}{l}\text{consumption rate of A in the pellet if its entire [interior + exterior]}\\ \text{surface were exposed to the bulk concentration of A}\end{array}\right)} \quad (77)$$

s# 119

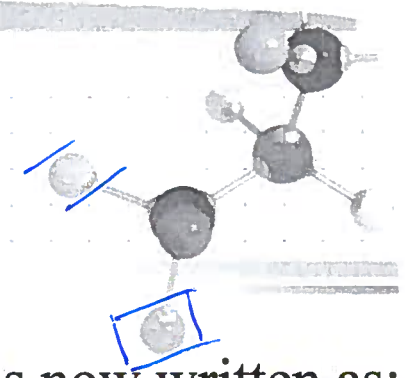
$$= \frac{r_{A,p}^{t}}{\left(kC^{b}\rho_s V_p\right)} \quad (77a)$$

$$= \frac{\left[r_{A,p}^{t}/\left(\rho_s V_p\right)\right]}{kC^{b}} \quad (77b)$$

actual conversion rate of A per unit catalyst mass (→ Eq. (76), s#119)

conversion rate of A per unit catalyst mass if the concentration of A in the pores of the catalyst pellet everywhere = C^b

Hence, $$\eta_G = \frac{\eta}{1+\eta\left(\frac{k}{k_g}\right)\rho_s\left(\frac{V_p}{S_{p,ext}}\right)}$$



Define $\dfrac{V_p}{S_{p,ext}} = L\,(\text{particle characteristic length})$, Eq. (77b) is now written as:

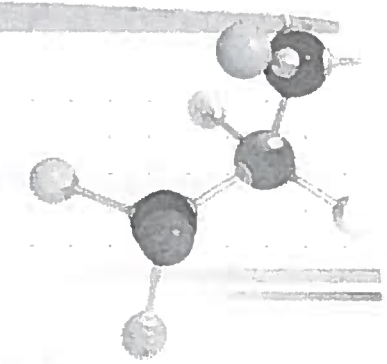
S#120

$$\eta_G = \frac{\eta}{1+\eta\dfrac{k\rho_s L}{k_g}} \tag{78a}$$

← (Take reciprocals of both sides of Eq. (78a) and simplify.)

or

$$\underbrace{\left(\frac{1}{\eta_G}\right)}_{(I)} = \underbrace{\frac{1}{\eta}}_{(II)} + \underbrace{\left(\frac{k\rho_s L}{k_g}\right)}_{(III)} \tag{78b}$$



From the definition of the modulus, ϕ as:

$$\phi = \frac{V_p}{S_{p,ext}} \sqrt{\frac{k\rho_s}{D_{eA}}} \quad \text{for the first-order reaction} \tag{79}$$

$$= L\sqrt{\frac{k\rho_s}{D_{eA}}} \tag{79a}$$

(do at home!)

From (79a), $\left(k\rho_s L\right) = \dfrac{\phi^2 D_{eA}}{L}$ (79b)

S#121

Into (78b) leads to:

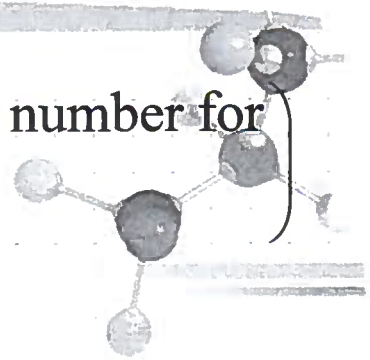
$$\left(\frac{1}{\eta_G}\right) = \frac{1}{\eta} + \phi^2 \frac{D_{eA}}{k_g L} \tag{80a}$$

→ diffusion

→ moment of reactant of A

Defining Sh' (modified Sherwood number, also called the Biot number for mass transfer, B_{i_m}

$= k_g L / D_{eA}$,



Equation (80a) is written as:

(S#122)

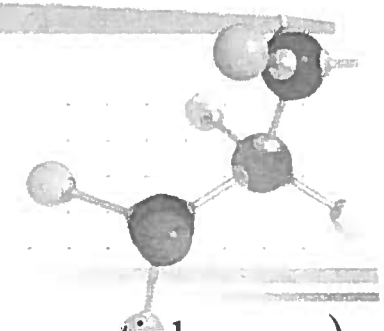
$$\frac{1}{\underbrace{\eta_G}_{I}} = \frac{1}{\underbrace{\eta}_{II}} + \frac{\phi^2}{\underbrace{Sh'}_{III}} \qquad (81)$$

For the first-order reaction:

Term (I) ≡ indicative of the total resistance to the mass transfer and chemical reaction in the pellet

Term (II) ≡ indicative of pellet "internal resistance" because of the species diffusion and chemical reaction occurrence inside the pellet

Term (III) ≡ indicative of film or external resistance because of diffusion of the species in the film.



→ Note that once η_G is known, then r_A (actual reaction rate averaged over particle mass) $\left[\frac{kmol\ A}{kg\ cat - s}\right]$ can be determined simply as:

$$r_A = \eta_G r_A^b \qquad (82)$$

$\left[\frac{kmol\ A}{kg\ cat - s}\right]$ → consumed

where r_A^b = rate of comsumption of A per unit pellet mass if the entire pellet material is exposed to the bulk concentration of A, C^b,

$= kC^b$. (82a)

(here, for the first-order reaction)