Chemical Reaction Engineering
Chapter 14 : Mass transfer limitations in reacting systems

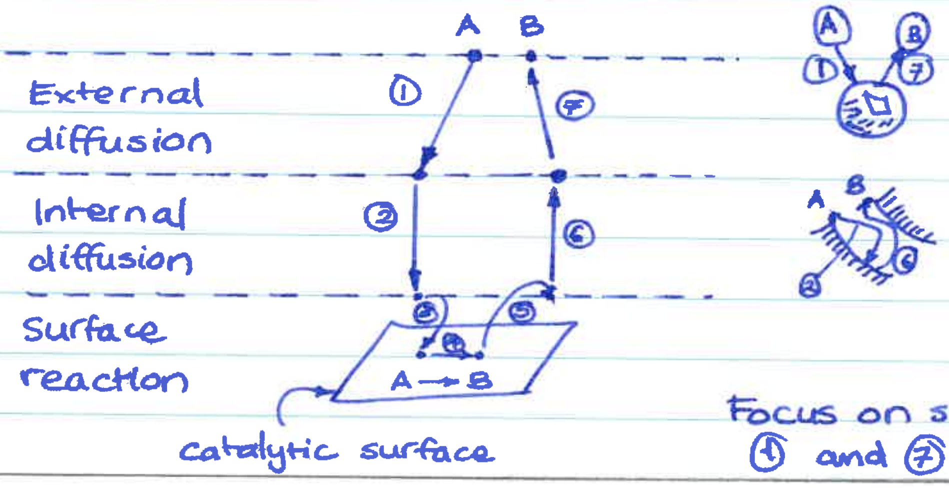
Industrial reactions at high temperature

→ limited by rate of mass transfer between bulk fluid and the catalytic surface

Mass transfer : Any process in which diffusion plays a role.

⇒ Rate laws cannot be applied directly

⇒ Need to consider fluid velocity and fluid properties while writing molar balances



Focus on steps ① and ⑦

Notes on
Elements of chemical reaction engineering, H. Scott Fogler
- Ranjeet Utikar

Diffusion fundamentals

Molar flux with no diffusion

$$W_{Az} = \frac{C_A v}{A_c} = \frac{F_{Az}}{A_c}$$

$$\frac{mol}{m^2\,s} \qquad \frac{mol}{\cancel{m^3}}\;\frac{\cancel{m^3}}{s}\;\frac{1}{m^2}$$

F_{Az} : uniform at a given cross section → plug flow assumption

⇒ Need to develop mole balance that incorporates both diffusion and reaction.

Diffusion: Spontaneous intermingling or mixing of atoms or molecules by random thermal motion.

⇒ Gives rise to motion of species relative to motion of mixture

⇒ From regions of high conc. to regions of low conc.

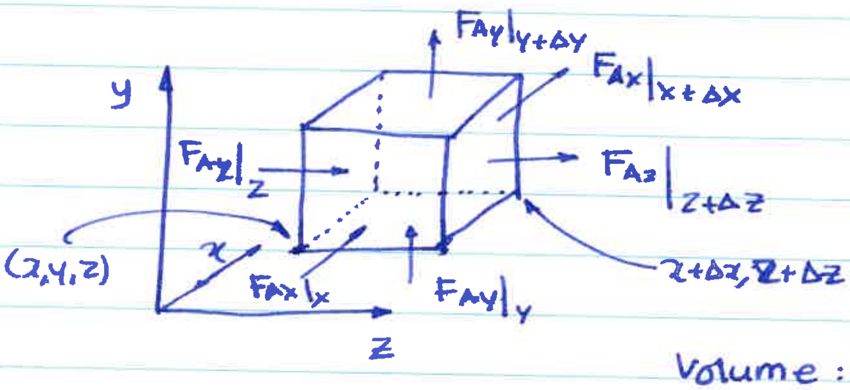
↑ In absence of other gradients

⇨ Diffusion results in a molar flux of the species (A), W_A (moles/area time), in the direction of the concentration gradient

$$W_A = i\,W_{Ax} + j\,W_{Ay} + k\,W_{Az}$$

rectangular co-ordinates.

Mole balance in rectangular co-ordinates



Volume : $\Delta x \Delta y \Delta z = \Delta V$

$$F_{Ax} = W_{Ax}\,\Delta z\,\Delta y$$
$$F_{Ay} = W_{Ay}\,\Delta x\,\Delta z$$
$$F_{Az} = W_{Az}\,\Delta x\,\Delta y$$

$$\begin{bmatrix}\text{molar}\\ \text{flow rate}\\ \text{in}\end{bmatrix}_{z} - \begin{bmatrix}\text{molar}\\ \text{flow}\\ \text{rate out}\end{bmatrix}_{z+\Delta z} + \begin{bmatrix}\text{molar}\\ \text{flow}\\ \text{rate in}\end{bmatrix}_{y} - \begin{bmatrix}\text{molar}\\ \text{flow rate}\\ \text{out}\end{bmatrix}_{y+\Delta y} +$$

$$\begin{bmatrix}\text{molar}\\ \text{flow}\\ \text{rate in}\end{bmatrix}_{x} - \begin{bmatrix}\text{molar}\\ \text{flow rate}\\ \text{out}\end{bmatrix}_{x+\Delta x} + \begin{bmatrix}\text{rate}\\ \text{of gen-}\\ \text{ration}\end{bmatrix} = \begin{bmatrix}\text{rate}\\ \text{of}\\ \text{accumulation}\end{bmatrix}$$

$$\Delta x \Delta y\, W_{Az}\Big|_{z} - \Delta x \Delta y\, W_{Az}\Big|_{z+\Delta z} +$$

$$\Delta x \Delta z\, W_{Ay}\Big|_{y} - \Delta x \Delta z\, W_{Ay}\Big|_{y+\Delta y} +$$

$$\Delta z \Delta y\, W_{Ax}\Big|_{x} - \Delta z \Delta y\, W_{Ax}\Big|_{x+\Delta x} +$$

$$r_A\, \Delta x \Delta y \Delta z = \Delta x \Delta y \Delta z \frac{\partial C_A}{\partial t} \quad \text{——} ①$$

r_A : rate of generation of A per unit volume $\frac{\text{mol}}{\text{m}^3\ \text{h}}$

Dividing ① by $\Delta x \Delta y \Delta z$ and taking limit as they go to zero

$$\boxed{-\frac{\partial W_{Ax}}{\partial x} - \frac{\partial W_{Ay}}{\partial y} - \frac{\partial W_{Az}}{\partial z} + r_A = \frac{\partial C_A}{\partial t}} \quad \text{——} ②$$

In cylindrical co-ordinates

$$-\frac{1}{r}\frac{\partial}{\partial r}(rW_{Ar}) - \frac{\partial W_{Az}}{\partial z} + r_A = \frac{\partial C_A}{\partial t} \quad ③$$

Molar flux

$$\begin{tikzcd} W_A \arrow[r] \arrow[dr] & J_A \\ & B_A \end{tikzcd}$$

J_A : Molecular diffusion flux relative to bulk motion of fluid due to conc. gradient

B_A : Flux resulting from bulk motion of fluid

$$W_A = J_A + B_A \quad ④$$

$$B_A = y_A(\Sigma W_i)$$

Total flux of all molecules

mole fraction of A

$$W_A = J_A + y_A \Sigma W_i \quad ⑤$$

For A → B (two component system)

$$W_A = J_A + y_A(W_A + W_B)$$

W_A ⇒ is w.r.t. fixed co-ordinate system

↳ = conc. of A × particle velocity of A, U_A

$$W_A = U_A C_A$$

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

particle velocity: Vector avg. of millions of molecules of A at a given point

similarly

$$W_B = U_B C_B$$

$$\therefore\ B_A = y_A \sum W_i$$

$$B_A = C_A U$$

$C = \sum y_i C_i$

$C_i = y_i C$

$\sum y_i U_i = U$

↗ molar avg. vel

$$W_A = J_A + C_A U \quad \text{— ⑥}$$

Fick's First law

⇒ How molar diffusive flux is related to conc. gradient

Fourier's law (thermal conduction)

$q = -k_t \nabla T$ $\qquad$ k_t: thermal conductivity

$$\nabla = i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}$$

For mass transfer : Fick's law

$$J_A = -D_{AB} \nabla C_A \quad \text{—} ⑦$$

D_{AB}: Diffusivity of A in B (m^2/s)

combining ⑥ and ⑦

$$W_A = -D_{AB} \nabla C_A + C_A U$$

In one dimension,

$$W_{Az} = -D_{AB} \frac{dC_A}{dz} + C_A U_z \quad \text{—} ⑧$$

Binary diffusion

→ Most systems have more than two components
  ↳ Analysis is complicated

→ Can be simplified into a binary system → each species diffuses through another single species

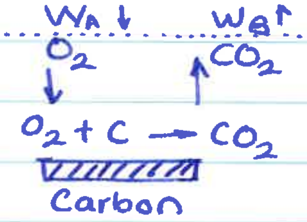
→ effective diffusivity.

Evaluating molar flux

→ A diffusing in B

$$W_A = -D_{AB}\nabla C_A + y_A(W_A + W_B)$$

① Equimolar counter diffusion (EMCD



$$W_A = -W_B$$

$$W_A = J_A = -D_{AB}\nabla C_A$$

② Species A diffusing through stagnant species B ($W_B = 0$)

→ Solid boundary with adjacent stagnant fluid layer

$$W_A = J_A + y_A W_A$$

$$W_A = \frac{J_A}{1 - y_A} = -\frac{D_{AB}\nabla C_A}{1 - y_A}$$

$$W_A = -D_{AB}c\,\nabla \ln(1 - y_A)$$

③ Bulk flow of A >> molecular diffusion

$$W_A = B_A = y_A(W_A + W_B) = C_A U$$

plug flow model

④ Small bulk flow $J_A >> B_A$

$$W_A = -\mathcal{D}_{AB} \nabla C_A = J_A$$

⑤ Knudsen diffusion:

Occurs in porous catalyst where diffusing molecule collides more often with catalyst walls/pore walls than with each other

$$W_A = J_A = -\underset{\substack{\uparrow\\ \text{Knudsen diffusivity.}}}{\mathcal{D}_K} \nabla C_A$$

Diffusion and convective transport

$$\underset{\substack{\uparrow\\ \text{molar flow}\\ \text{rate of A in}\\ \text{z dir.}}}{F_{Az}} = \underset{\substack{\uparrow\\ \text{molar}\\ \text{flux in}\\ \text{z}}}{W_{Az}} \underset{\substack{\uparrow\\ \text{cross-}\\ \text{sectional}\\ \text{area normal to flow}}}{A_C}$$

$$W_{Az} = -\mathcal{D}_{Az} \frac{dC_A}{dz} + C_A U_z$$

$$F_{Az} = W_{Az} A_c = \left[-\mathcal{D}_{Az} \frac{dC_A}{dz} + C_A U_z\right] A_c \tag*{—⑨}$$

similar expressions for F_{Ay} and F_{Ax}.

substituting in equation ②

$$\mathcal{D}_{AB}\left[\frac{\partial^2 C_A}{\partial x^2}+\frac{\partial^2 C_A}{\partial y^2}+\frac{\partial^2 C_A}{\partial z^2}\right]-U_x\frac{\partial C_A}{\partial x}-U_y\frac{\partial C_A}{\partial y}-U_z\frac{\partial C_A}{\partial z}$$

$$+\,r_A=\frac{\partial C_A}{\partial t}$$

in one dimension :

$$\boxed{\mathcal{D}_{AB}\frac{\partial^2 C_A}{\partial z^2}-U_z\frac{\partial C_A}{\partial z}+r_A=\frac{\partial C_A}{\partial t}} \quad \text{——} \ ⑩$$

Need boundary conditions to solve eq. ⑩

Boundary conditions :

1. Conc. at boundary :

@ $z=0$ $\quad C_A = C_{A0}$

→ For instantaneous reactions, $C_{AS}=0$

Conc. of reactant at boundary.

@ $z=L$ $\quad \frac{dC_A}{dz}=0 \; ; \; C_A^{L-}=C_A^{L+}$

↳ Dankwert's boundary condition.

② Specify flux at boundary

(a) No mass transfer to boundary

$W_A = 0$ ← wall of non-reacting pipe

$$\frac{dC_A}{dr} = 0 \quad @\ r = R$$

(b) molar flux to surface = rate of reaction at surface

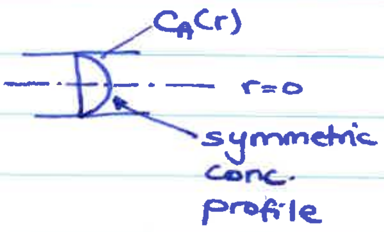
$$W_A\Big|_{surface} = -r_A''\Big|_{surface}$$

(c) molar flux to boundary = convective transport across boundary layer

$$W_A\Big|_{boundary} = \underset{\text{mass transfer coefficient}}{k_c}\,(\underset{\text{bulk conc.}}{C_{Ab}} - \underset{\text{surface conc.}}{C_{As}})$$

③ Planes of symmetry

$$\frac{dC_A}{dr} = 0 \quad @\ r = 0$$



For tubular reactor eq. ⑩ becomes

$$\frac{dF_A}{dV} = \frac{d(A_c W_{Az})}{d(A_c z)} = \frac{dW_{Az}}{dz} = r_A \quad — ⑪$$

Temperature and pressure dependence of D_{AB}

- → Predicting gas diffusivity
  - ↳ Fuller's correlation
- — Data in Perry's handbook

Phase	order of mag cm²/s	m²/s	T & P dependence
Gas			
Bulk	10^{-1}	10^{-5}	$D_{AB}(T_1, P_1)\frac{P_1}{P_2}\left(\frac{T_2}{T_1}\right)^{1.75} = D_{AB}(T_2, P_2)$
Knudsen	10^{-2}	10^{-6}	$D_{AB}(T_2, P_2) = D_A(T_1)\left(\frac{T_2}{T_1}\right)^{1/2}$
liquid	10^{-5}	10^{-9}	$D_{AB}(T_2) = D_{AB}(T_1)\left(\frac{\mu_1}{\mu_2}\right)\left(\frac{T_2}{T_1}\right)$
solid	10^{-9}	10^{-13}	$D_{AB}(T_2) = D_{AB}(T_1) \cdot \exp\left[\frac{E_D}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right]$

Knudsen, liquid, & solid D are independent of P

Steps in modelling diffusion to a reacting surface

⇒ Diffusion of species through stagnant film in which no reaction takes place

⇒ A reacts instantaneously upon reaching the surface $C_{As} \cong 0$

⇒ Rate of diffusion through stagnant film = rate of reaction on the surface

Steps:

① Perform differential mole balance
  ↳ Equation for W_{Az}

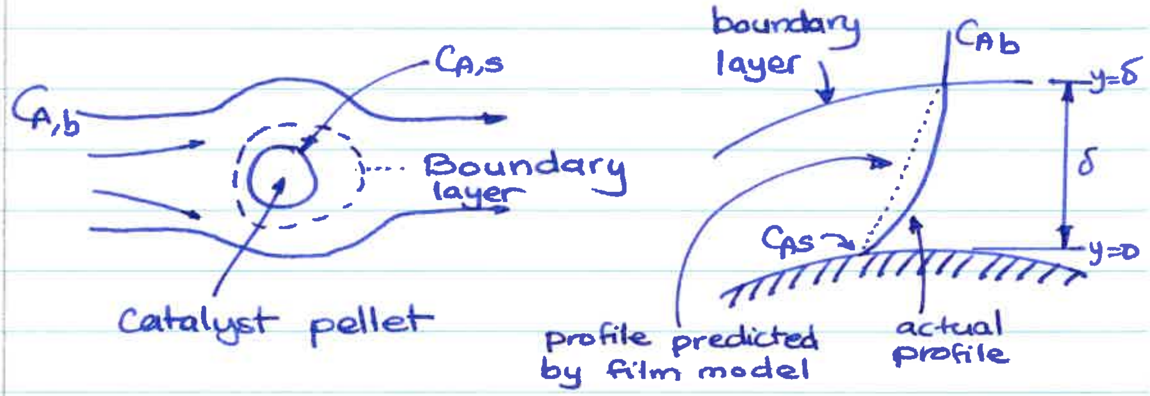
② Replace W_{Az} by appropriate expression for conc. gradient

③ State boundary conditions

④ Solve for conc. profile

⑤ solve for molar flux

Diffusion through a stagnant film



→ Flow past a single catalytic pellet

→ reaction takes place only on external catalyst surface and not in fluid surrounding it.

hydrodynamic boundary layer: distance from solid object to where the fluid velocity is 99% of the bulk velocity U_o

mass transfer boundary layer: distance at which conc. of diffusing species is 99% of the bulk concentration.

→ Nearly all the resistance is in BL

→ Assume fluid layer next to solid as stagnant film (hypothetical) of thickness δ

→ We can not measure δ

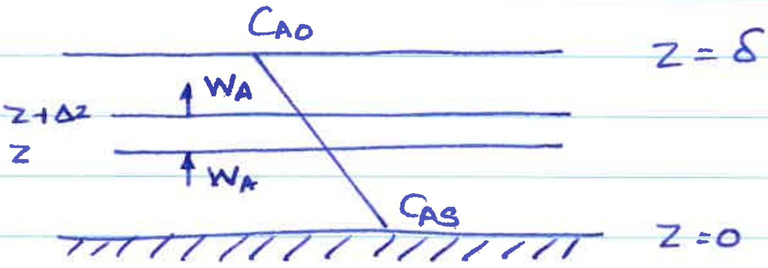
→ All the resistance to mass transfer is within the film

→ properties at the outer edge of the film are identical to those of bulk fluid.

For film thickness << radius of pellet

→ curvature effects can be neglected

→ problem reduces to 1D diffusion



In − out + generation = Accumulation

$$W_{Az}\big|_z - W_{Az}\big|_{z+\Delta z} + 0 = 0$$

dividing by Δz and taking limit as $\Delta z \rightarrow 0$

$$\frac{dW_{Az}}{dz} = 0$$ — ⑫

For diffusion through stagnant film at dilute concentrations,

$$J_A >> y_A (W_A + W_B)$$

$$W_{Az} = -D_{AB}\frac{dC_A}{dz}$$ .... Also for EMCD

∴ ⑫ becomes

$$\frac{d^2 C_A}{dz^2} = 0$$

BCs:

$z = 0$ $C_A = C_{As}$

$z = \delta$ $C_A = C_{Ab}$

Integrating twice

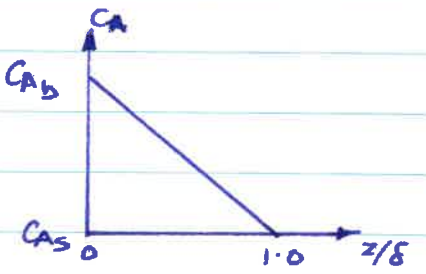
$$C_A = k_1 z + k_2$$

$\Rightarrow C_{As} = k_2$

$\frac{(C_{Ab} - C_{As})}{\delta} = k_2$

substituting BCs

$$\boxed{C_A = C_{As} + (C_{Ab} - C_{As})\frac{z}{\delta}}$$ — ⑬



surface flux

$$W_{Az}\Big|_{\delta} = -D_{AB}\frac{dC_A}{dz}\Big|_{\delta}$$

$$W_{Az} = \frac{D_{AB}}{\delta}\left[C_{Ab} - C_{As}\right] \quad \text{———} \quad ⑭$$

At steady state

Flux of A to the surface = rate of reaction of A on surface

Mass transfer coefficient

$$\boxed{k_c = \frac{D_{AB}}{\delta}}$$

Varies around the sphere.
(consider mean thickness

$$\therefore \quad W_{Az} = k_c\left[C_{Ab} - C_{As}\right] \quad \text{———} \quad ⑮$$

$$W_{Az} = \text{Flux} = \frac{\text{driving force}}{\text{resistance}} = \frac{\left[C_{Ab} - C_{As}\right]}{(1/k_c)}$$

mass transfer resistance

Correlations for mass transfer coefficient

- → For similar geometries the heat transfer and mass transfer correlations are analogous.
- → k_c analogous to h (heat transfer coefficient)

Forced convection → h correlated in terms of Nu, Re, Pr

Nusselt's Number

$$Nu = \frac{h d_p}{k_t}$$

Reynold's number

$$Re = \frac{U \rho d_p}{\mu}$$

Prandtl Number

$$Pr = \frac{\mu C_p}{k_t}$$

$$= \left(\frac{\mu}{\rho}\right)\left(\frac{\rho C_p}{k_t}\right) = \frac{\nu}{\alpha_t}$$

h : htc $(J/m^2 s\,K)$ $(W/m^2 K)$

α_t : Thermal diffusivity (m^2/s)

μ : viscosity (kg/ms)

ρ : density (kg/m^3)

d_p : diameter (m)

k_t : Thermal conductivity $(J/K\,ms)$

U : free stream vel. (m/s)

C_p : heat capacity $(J/kg \cdot K)$

ν : kinematic viscosity (m^2/s)

Ranz - Marshall correlation : heat transfer for flow around sphere

$$\boxed{Nu = 2 + 0.6\, Re^{1/2}\, Pr^{1/3}} \quad — ⑯$$

For sphere immersed in stagnant fluid

$Nu = 2 \quad \Rightarrow Re = 0$

At high Re (boundary layer is still laminar)

$Nu \mathrel{\hat{=}} 0.6\, Re^{1/2}\, Pr^{1/3}$

For mass transfer

$Sh \longrightarrow Nu \quad ; \quad Sc \longrightarrow Pr$

Sherwood Number

$$Sh = \frac{k_c d_p}{D_{AB}} \longleftarrow \frac{\text{convective mass transfer}}{\text{Diffusion rate}}$$

Schmidt Number

$$Sc = \frac{\nu}{D_{AB}} \longleftarrow \frac{\text{momentum diffusivity}}{\text{mass diffusivity}}$$

Frössling correlation

$$\boxed{Sh = 2 + 0.6\, Re^{1/2}\, Sc^{1/3}} \qquad (17)$$

Mass transfer to a single particle

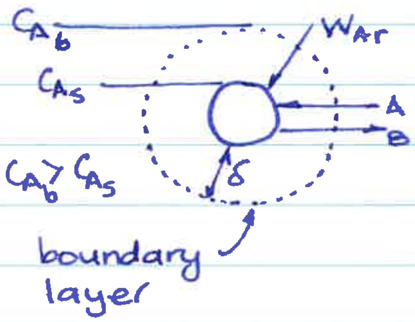
(a) Rapid reaction on surface of catalyst

consider isomerization reaction

$$A \longrightarrow B$$

$$-r''_{As} = \frac{k_r C_{As}}{1 + K_A C_{As} + K_B C_{Bs}}$$

Langmuir Hinshelwood



At high temp. (weak adsorption)

$$(K_B C_{Bs} + K_A C_{As}) \ll 1$$

$$-r''_{As} = k_r C_{As}$$

molar flux to surface = rxn rate @ surface

$$W_{Ar}\big|_{surface} = -r''_{As}$$

$$W_A = k_c(C_{Ab} - \underset{\text{not measurable}}{C_{As}}) = k_r \underset{\text{not measurable}}{C_{As}} \qquad \text{—⑱}$$

rearranging.

$$C_{As} = \frac{k_c C_{Ab}}{k_c + k_r}$$

$$W_A = -r''_{As} = \frac{k_r k_c C_{Ab}}{k_c + k_r} \qquad \text{—⑲}$$

$$\frac{k_r k_c}{k_c + k_r} = k_{eff} \leftarrow \text{effective transport coefficient}$$

$$W_A = -r''_{As} = k_{eff} C_{Ab}$$

→ <u>Mass transfer limitation</u>

$k_c \ll k_r$

$k_{eff} = k_c$

$$W_A = -r''_{As} \simeq k_c C_{Ab}$$

To increase reaction rate

→ Increase C_{Ab} or k_c

$$Sh = 2 + 0.6\,Re^{1/2}\,Sc^{1/3}$$

For most liquids. Sc is sufficiently large

$$\therefore \quad Sh = 0.6\,Re^{1/2}\,Sc^{1/3}$$

$$\therefore \quad k_c = 0.6\left(\frac{D_{AB}}{d_p}\right)\left(\frac{U d_p}{\nu}\right)^{1/2}\left(\frac{\nu}{D_{AB}}\right)^{1/3}$$

$$\boxed{k_c = 0.6\left(\frac{D_{AB}^{2/3}}{\nu^{1/6}}\right)\left(\frac{U^{1/2}}{d_p^{1/2}}\right)} \quad \text{— (20)}$$

physical properties of fluid

⇒ depend on P&T

function of flow conditions and particle size

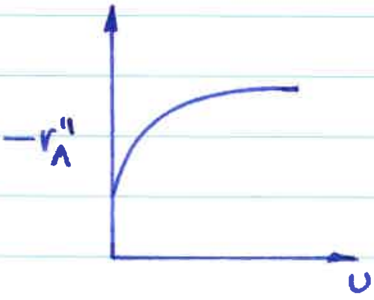
$D_{AB} \propto T$

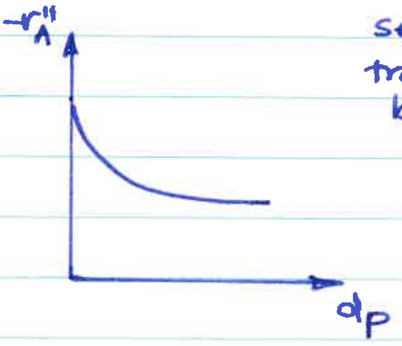
$\nu \propto T^{3/2}$ ... for gases

ν decreases exponentially for liquids

$$\left(\frac{U_2}{U_1}\right)^{0.5} = 2^{0.5} = 1.41$$

→ doubling the velocity increases mass transfer coeff. by 41%





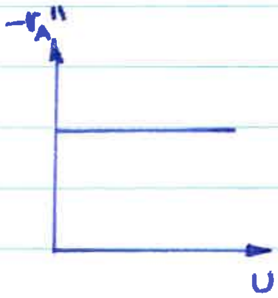
Slow reaction

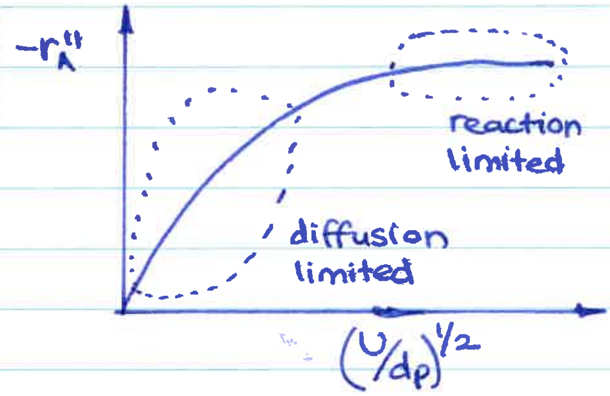
$$k_{eff} = \frac{k_c k_r}{k_c + k_r} \qquad k_r << k_c$$

$$k_{eff} = k_r$$

$$W_A = -r_A'' \cong k_r C_{Ab}$$

may be affected by particle size in some cases





At low U

→ mass transfer BL is large

→ diffusion limits reaction

→ For fixed velocity mass transfer limitation can be overcome by using small particles → Increased ΔP

→ When obtaining reaction rate data one must operate at sufficiently large U or small particles → No mass transfer limitation

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Mass transfer limited reactions in packed bed

- → High temperature reactions
- → Surface reaction is rapid
- → overall reaction rate is limited by the rate of transfer of reactant from the bulk to the surface
- → Mass transfer limited reactions behave/respond very differently to changes in temperature and flow conditions compared to rate limited reactions.

Consider following reaction

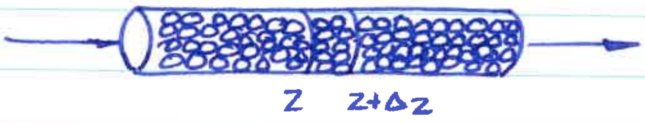
$$aA + bB \longrightarrow cC + dD$$

steady state mole balance

$$\begin{bmatrix}\text{molar}\\ \text{rate in}\end{bmatrix} - \begin{bmatrix}\text{molar}\\ \text{rate out}\end{bmatrix} + \begin{bmatrix}\text{molar rate}\\ \text{of generation}\end{bmatrix} = \begin{bmatrix}\text{molar rate of}\\ \text{accumulation}\end{bmatrix}$$

$$F_{Az}\Big|_{z} - F_{Az}\Big|_{z+\Delta z} + r''_A(A_c\Delta z)a_c = 0$$

$$F_{Az}\big|_{z} - F_{Az}\big|_{z+\Delta z} + r_A'' a_c (A_c \Delta z) = 0 \quad \text{—— (21)}$$



r_A'' : rate of generation per unit of catalytic surface area $\frac{\text{mol}}{\text{s m}^2}$

a_c : external surface area of catalyst per unit volume of catalyst bed $\frac{\text{m}^2}{\text{m}^3}$

$$a_c = \frac{\text{vol. of solid}}{\text{vol. of bed}} \times \frac{\text{surface area}}{\text{vol. of solid}}$$

$$a_c = (1-\Phi)\left[\frac{\pi d_p^2}{\pi d_p^3/6}\right] = \frac{6(1-\Phi)}{d_p}$$

Φ : bed porosity [-]

d_p : particle diameter m

A_c : cross sectional area of tube containing catalys m^2

Dividing (21) by Δz and taking limit as $\Delta z \to 0$

$$-\frac{1}{A_c}\frac{dF_{Az}}{dz} + r_A'' a_c = 0 \quad \text{—— (22)}$$

→ Express F_{Az} and r_A'' in terms of concentration

$$F_{Az} = W_{Az} A_c$$

$$= (J_{Az} + B_{Az}) A_c$$

In almost all packed beds

$\underset{\text{diffusion}}{J_{Az}} << \underset{\text{Bulk flow}}{B_{Az}}$ ... Axial diffusion can be neglected

Neglecting dispersion -

$F_{Az} = A_c B_{Az} = U C_A A_c$ —— ㉓

U : superficial velocity

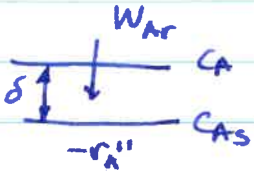
For constant superficial velocity eq. ㉒ becomes

$- U \dfrac{dC_A}{dz} + r_A'' a_c = 0$ —— ㉔

For reactions at steady state

$$\left[\begin{array}{l}\text{molar flux of}\\ \text{A to the part-}\\ \text{icle surface}\end{array}\right] = \left[\begin{array}{l}\text{rate of disappearance}\\ \text{of A on the}\\ \text{surface}\end{array}\right]$$

$$-r_A'' = W_{Ar}$$



$$-r_A'' = W_{Ar} = k_c\,(C_A - C_{As})$$

k_c: mass transfer coefficient (m/s)

$$k_c = \frac{\mathcal{D}_{AB}}{\delta}$$

C_A : Bulk conc. of A (mol/m³)

C_{As}: Conc of A ~~on~~ at surface (mol/m³)

∴ Eq. ㉔ becomes

$$-U\frac{dC_A}{dz} - k_c\,(C_A - C_{As})\,a_c = 0$$

In most mass transfer limited reactions

$C_A \gg C_{As}$ (Surface conc. is negligible w.r.t. bulk conc)

$$\therefore \quad -u\frac{dC_A}{dz} = k_c a_c C_A$$

Integrating with the limit

at $z = 0$; $C_A = C_{A0}$

$$\frac{C_A}{C_{A0}} = \exp\left(-\frac{k_c a_c}{u} z\right) \quad \text{— (25)}$$

corresponding variation in reaction rate along the length

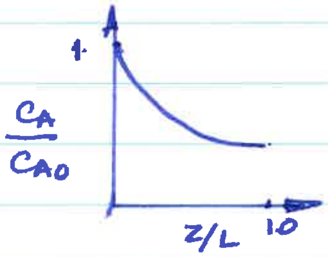
$$-r_A'' = k_c C_{A0} \exp\left(\frac{-k_c a_c}{u} z\right)$$

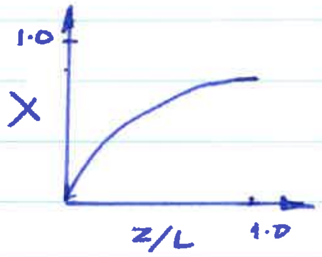
conversion at length L $\quad X = \frac{C_{A0} - C_{AL}}{C_{A0}}$

Evaluating (25) at $z = L$ $\quad \frac{C_{AL}}{C_{A0}} = 1 - X$

$$\frac{C_{AL}}{C_{A0}} = \exp\left(\frac{-k_c a_c}{u} L\right)$$

$$\therefore \quad \boxed{\ln \frac{1}{1-X} = \frac{k_c a_c}{u} L} \quad \text{—— (26)}$$





Effect of flowrate on conversion

For flow through packed bed

$$Sh' = 1.0\,(Re')^{1/2}\,Sc^{2/3} \quad \ldots$$ Thoenes and Kramers

$$0.25 < \Phi < 0.35$$
$$40 < Re' < 4000$$
$$1 < Sc < 4000$$

$$\left[\frac{k_c d_p}{D_{AB}}\left(\frac{\Phi}{1-\Phi}\right)\frac{1}{\gamma}\right] = \left[\frac{U d_p \rho}{\mu(1-\Phi)\gamma}\right]^{1/2}\left(\frac{\mu}{\rho D_{AB}}\right)^{1/3}$$

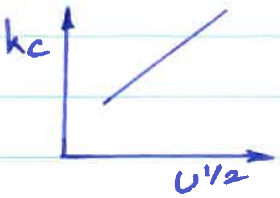
Φ : porosity $\qquad d_p = \left(\frac{6}{\pi}\right) V_p^{1/3}$

γ : shape factor

$$Sh' = \frac{Sh\ \Phi}{(1-\Phi)\gamma} \ ; \quad Re' = \frac{Re}{(1-\Phi)\gamma}$$

For constant fluid properties and particle diameters

$$k_c \propto U^{1/2}$$



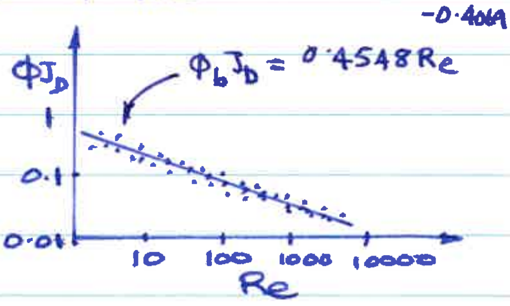
In case of differential reactor (Fixed conc. C_A)

$$-r_A'' \propto k_c C_A \propto U^{1/2}$$

→ As gas velocity increases, reaction becomes rate limited and is independent of the superficial velocity.

Most mass transfer correlations are reported in terms of the Colburn $\overline{J}$ factor as a function of Re

$$J_D = \frac{Sh}{Sc^{1/3}\,Re}$$



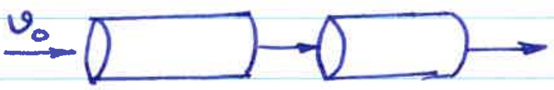
$$\phi J_D = \frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}}$$

– packed bed –

Parameter sensitivity

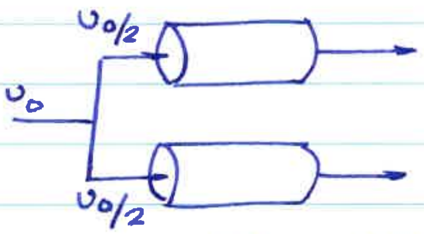
$$k_c \propto \left(\frac{\mathcal{D}_{AB}^{2/3}}{\nu^{1/6}}\right)\left(\frac{U^{1/2}}{d_p^{1/2}}\right)$$

case 1 : Series Vs parallel



$X = 0.865$

- Series arrangement -



$x = ?$

- parallel arrangement

→ mass transfer limited reaction

→ current conversion $X = 0.865$

→ Can we sp separate the two reactors?

→ lower ΔP

→ Neglect effect of temperature.

$$\ln\left(\frac{1}{1-X}\right) = \frac{k_c a_c}{U} L$$

Arrangement ① Undivided system

$$\ln\left(\frac{1}{1-x_1}\right) = \frac{k_{c1} a_c}{U_1} L_1 \quad \text{— (a)}$$

$$x_1 = 0.865$$

arrangement ② divided system

$$\ln\left(\frac{1}{1-x_2}\right) = \frac{k_{c2} a_c}{U_2} L_2 \quad \text{— (b)}$$

$$x_2 = ?$$

Taking ratio of (b) and (a)

$$\frac{\ln\left(\frac{1}{1-x_2}\right)}{\ln\left(\frac{1}{1-x_1}\right)} = \frac{k_{c2}}{k_{c1}} \left(\frac{L_2}{L_1}\right) \frac{U_1}{U_2}$$

$$L_2 = \frac{1}{2} L_1 \; ; \; U_2 = \frac{1}{2} U_1$$

$$k_c \propto U^{1/2} \Rightarrow \frac{k_{c2}}{k_{c1}} = \left(\frac{U_2}{U_1}\right)^{1/2}$$

$$\therefore \ln\left(\frac{1}{1-x_2}\right) = \ln\left(\frac{1}{1-x_1}\right) \frac{L_2}{L_1} \left(\frac{U_1}{U_2}\right)^{1/2}$$

$$\therefore \ln\left(\frac{1}{1-x_2}\right) = \left(\ln \frac{1}{1-0.865}\right)\left(\frac{1}{2}\right)\sqrt{2} = 1.414$$

$$x_2 = 0.76$$

→ Divided arrangement has small ΔP

→ but conversion decreases from 0.865 to 0.76

Case ② Increase temperature for increasing conversion

Rule of thumb: Reaction rate doubles every 10°c. The reaction rate can be increased by a factor of 2^{10} by increasing temperature from 400°c to 500°c

→ Is this correct?

⇒ Mass transfer controlled reaction

→ Surface reaction rates increase more rapidly with temperature compared to diffusion rates

⇒ Increasing temperature will only increase the degree to which reaction is mass transfer limited.

scenario 1 : $T = 400\,^\circ C$ $X = 0.865$

scenario 2 : $T = 500\,^\circ C$ $X = ?$

$$\frac{\ln\left(\frac{1}{1-X_2}\right)}{\ln\left(\frac{1}{1-X_1}\right)} = \frac{k_{c2}}{k_{c1}}\left(\frac{L_2}{L_1}\right)\frac{U_1}{U_2} = \frac{k_{c2}}{k_{c1}}\left(\frac{U_1}{U_2}\right)$$

$L_1 = L_2$ yes

$$F_{TO} = \vartheta_{01}\left(\frac{P_{01}}{RT_{01}}\right) = \vartheta_{02}\left(\frac{P_{02}}{RT_{02}}\right)$$

If P is constant

$$\frac{\vartheta_{01}}{T_{01}} = \frac{\vartheta_{02}}{T_{02}}$$

$\vartheta = A_c U$

$\therefore U_2 = \frac{T_2}{T_1} U_1$

Dependence of k_c on T

$$k_c \propto \left(\frac{U}{d_p}\right)^{1/2}\left(\frac{D_{AB}^{2/3}}{\nu^{1/6}}\right)$$

d_p : const.

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{U_2}{U_1}\right)^{1/2}\left(\frac{D_{AB2}}{D_{AB1}}\right)^{2/3}\left(\frac{\nu_1}{\nu_2}\right)^{1/6}$$

For gas phase :

$$\mathcal{D}_{AB} \propto T^{1.75}$$

$$\mu \propto T^{1/2} \; ; \; \rho \propto T^{-1}$$

$$\nu = \frac{\mu}{\rho} \propto T^{3/2}$$

$$\therefore \quad \frac{\ln\left(\frac{1}{1-X_2}\right)}{\ln\left(\frac{1}{1-X_1}\right)} = \frac{U_1}{U_2}\,\frac{k_{c_2}}{k_{c_1}} = \left(\frac{U_1}{U_2}\right)^{1/2}\left(\frac{\mathcal{D}_{AB2}}{\mathcal{D}_{AB1}}\right)^{2/3}\left(\frac{\nu_1}{\nu_2}\right)^{1/6}$$

$$= \left(\frac{T_1}{T_2}\right)^{1/2}\left[\left(\frac{T_2}{T_1}\right)^{1.75}\right]^{2/3}\left[\left(\frac{T_1}{T_2}\right)^{3/2}\right]^{1/6}$$

$$= \left(\frac{T_1}{T_2}\right)^{1/2}\left(\frac{T_1}{T_2}\right)^{6/7}\left(\frac{T_1}{T_2}\right)^{1/4} = \left(\frac{T_2}{T_1}\right)^{5/12}$$

For case ② $= \left(\frac{773}{673}\right)^{5/12} = 1.059$

$$\therefore \quad \ln\left(\frac{1}{1-X_2}\right) = 1.059 \ln\left(\frac{1}{1-0.865}\right) = 1.059(2)$$

$$\Rightarrow \quad X = 0.88$$

→ Increasing the temperature from 400°C to 500°C increases the conversion by only 1.7%