

Mole Balance of a differential reactor

The volumetric flow rate through the catalyst bed is monitored. Entering and exiting conc. are also monitored in this reactor

w → wt. of catalyst

F_{A0} , F_{Af} → Inlet and outlet reactant (A) molar flow rates

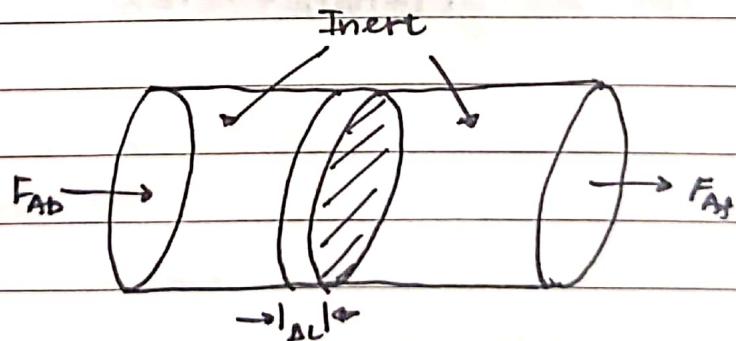
r_A → Rate of r_A

v_0 , v_f → Volumetric flow rates of reactants initially and finally respectively

C_{A0} , C_A → Initial and final conc. of reactant

C_P → Product conc.

Differential reactor is used to determine rate of r_A as a fn. of conc. of partial pressure of reactant. It is tube containing very small amt. of catalyst in the form of disc.



- Conversion of the reactant in the catalyst is extremely small, so the inlet and outlet conc. are nearly same.
- The reactor is assumed to be gradientless, and the rate of r_A is uniform throughout the rea

, As the conversion is very low, so the heat change during the r_n is also negligible, hence assumed to isothermal.

Conditions of differential reactor:

- , Reactants shouldn't bypass the catalyst bed
- , Catalyst should be long in order to maintain same rate of r_n for a suff. long time.

Flow Rate In - Flow Rate Out + Rate of generation = Rate of Accumulation

$$F_{A0} - F_{Af} + \frac{\text{rate of } r_n \times \text{mass of cat.}}{\text{mass of cat.}} = 0$$

$$\Rightarrow -r_A = \frac{F_{A0} - F_{Af}}{w}$$

$$\text{In terms of conc., } -r_A = \frac{C_{A0}V_0 - C_A V_F}{w}$$

$$\text{In terms of product conversion, } -r_A = \frac{F_{A0} \chi_A}{w} = \frac{F_p}{w}$$

χ_A - conversion of pdt. to reactant

F_p - molar flow rate of pdt.

When stoichiometric co-eff of A and P are equal,

$$F_{A0} \chi_A = F_p$$

For const. volumetric flow,

$$-r_A = \frac{w_0}{w} \frac{(C_{A0} - C_A)}{C_A} = \frac{w_0 \rho}{w}$$

For very little catalyst and large vol. flow rate,
 $(C_{A0} - C_A)$ is small

$$-r_A = f(C_{Ab}), \quad C_{Ab} = \frac{C_{A0} + C_A}{2}$$

∴ Rate is a fn. of avg. reactant conc. within
the catalyst bed.

However, very little conversion is assumed for
differential reactor

$$C_{Ab} \approx C_{A0}$$

$$\therefore -r_A = f(C_{A0})$$

All the design eqn's for ideal catalytic or fluid
solid m. can be obtained from their homogeneous
reactors analogues, by substituting reactor vol. v
with catalyst wt. w

$$V = \frac{w}{\rho_B}, \quad \rho_B \rightarrow \text{bulk density of catalyst}$$

For an ideal batch reactor, the diff. form of
design of heterogeneous reaction is,

$$-r_A w = N_{A0} \frac{dx_A}{dt}$$

Temperature Dependence of Rate law

Specific rate const. k follows Arr. temp. dependence and increases exponentially with temp.

Adsorption is an exothermic rxn; higher the temp. smaller is adsorption eq. const. Thus, denominator of catalytic rate law approaches 1.

For surface rxn controlled irreversible rxn, $A \rightarrow B$

The rate law is $-r_A = \frac{kP_A}{1 + k_A P_A + k_B P_B}$

At high temp i.e., lower surface coverage, $1 \gg k_A P_A + k_B P_B$

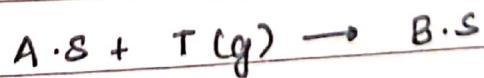
$$-r_A = kP_A$$

For a rev. rxn,

$$-r_A = k \left(P_A - \frac{P_B}{k_p} \right)$$

To reduce catalyst wt., temp. should be increased.

Rate law Parameters



Rate law for surface rxn, $-r_A = \frac{k P_A P_T}{1 + k_A P_A + k_B P_B}$

$k, k_A, k_B \rightarrow$ Rate law parameters

Linearising the rate law,

$$\frac{P_A P_T}{-r_A} = \frac{1}{K} + \frac{K_A P_A}{K} + \frac{K_B P_B}{K}$$

Can be solved using three sets of experimental data to determine three unknowns.

Catalyst Deactivation

Sintering or Ageing : Loss of catalytic activity due to loss of active surface area, resulting from prolonged exposure to high gas phase temperature. Active surface area maybe lost either by crystal agglomeration and growth of metals deposited on the support. A change in surface area also might result in this.

Fouling or coking : Results from carbonaceous material deposited on surface of catalyst.

Poisoning : Occurs when Poisoning molecules are irreversibly chemisorbed to active sites.

Diffusional Resistance to Mass Transfer on Heterogeneous Run.

External Resistance: During diff. resistance of reactants/products between the bulk and external surface of catalyst.

Internal Resistance: During diff. of reactants/pdr. from external pellet surface to interior of pore.

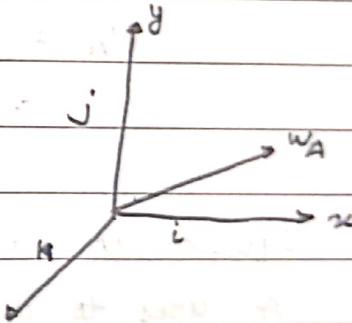
Fundamentals of Diffusion

Diffusion: Movement of diffusion species from high to low conc. relative to bulk movement.

Molar flux of species A,

$$W_A = i w_{Ax} + j w_{Ay} + k w_{Az}$$

$w_A \rightarrow$ mole/area · time



$$W_A = J_A + B_A$$

$J_A \rightarrow$ Diffusional Flux relative to bulk flow,

$B_A \rightarrow$ Bulk flow

$v_A \rightarrow$ Total molar velocity of A

$v' \rightarrow$ Avg molar velocity of A due to bulk motion.

$v_A - v' \rightarrow$ Velocity due to diffusion

$$v_A = v' + (v_A - v'), \quad c_A v_A = c_A v' + c_A (v_A - v')$$

$$w_A = c_A \left(\frac{v_A c_A + v_B c_B}{c} \right) + J_A$$

$$w_A = c_A u_A = (\text{moles/cc}) (\text{cm/s}) \rightarrow \text{moles/cm}^2\text{s}$$

$$w_A = \frac{c_A}{C} (c_A u_A + c_B u_B) + J_A = y_A (w_A + w_B) + J_A \quad - \textcircled{1}$$

From Fick's 1st law of diffusion,

$$J_A = -D_{AB} C \nabla y_A$$

C \rightarrow conc. in moles/dm³

D_{AB} \rightarrow Diffusivity of A in B (dm²/s)

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

Using J_A in $\textcircled{1}$,

$$\begin{aligned} w_A &= y_A (w_A + w_B) + J_A \\ &= c_A u' + (-D_{AB} C \nabla y_A) \end{aligned}$$

Equimolar Counter Diffusion (EMCD) : If one mole of A goes to a given direction, one mole of B goes to opp. direction.

$$\text{So, } w_A = -w_B$$

$$\therefore w_A = -D_{AB} C \nabla y_A$$

Dilute conc. : Here, bulk motion is considered to be small so $y(w_A + w_B)$ can be neglected, $w_A = J_A$

This eqn. can be applied to porous catalyst system, where pore radii is very small.

Diffusion under this cond. is called Knudsen diff.

Diffusion occurs when mean free path of reactant gas molecule is greater than the diameter of pore. Here reacting molecules collide more often with pore wall than with each other and molecules of diff. species don't affect each other.

The flux of A for Knudsen Diff., when bulk flow is neglected,

$$w_A = J_A = -D_K C \nabla y_A$$

Diffusion through stagnant gas : When A is a solute gas in mixture of A and B and B is stagnant, then $w_B = 0$

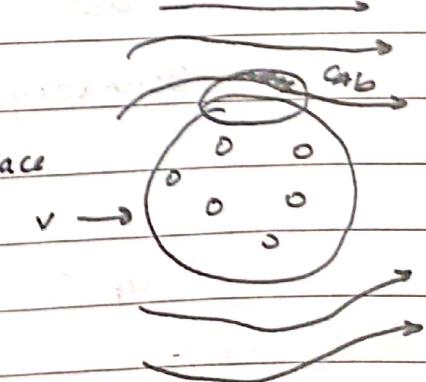
$$w_A = J_A + y_A (w_A + w_B) = J_A + y_A w_A$$

Diffusion through catalyst particle

Species A is in dil. conc., diffusing at steady state from bulk fluid through a stagnant film of B of thickness δ to external surface of catalyst.

C_{Ab} is conc. of A at external boundary
 C_{As} is conc. of A at external bottom surface

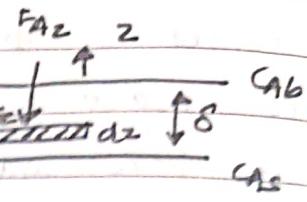
Curvature is neglected.



Mole Balance of A

F_{Az} → molar flow rate at $z = 0$

F_{Az+dz} → molar flow rate at $z + dz$



Considering only diffusion,

$$F_{Az} - F_{Az+dz} = 0$$

$$dz \rightarrow 0, \frac{dF_{Az}}{dz} = 0$$

If A_c is area of cross-section of dz , $F_{Az} = W_{Az} \cdot A_c$

$$\frac{dW_{Az}}{dz} = 0 \quad \text{---(1)}$$

We have considered dilute soln. \Rightarrow in z -dir only.

$$W_A = - D_{AB} \frac{dC_A}{dz}$$

$$\frac{dW_A}{dz} = - D_{AB} \frac{d^2C_A}{dz^2} = 0 \quad (\text{CF from (1)})$$

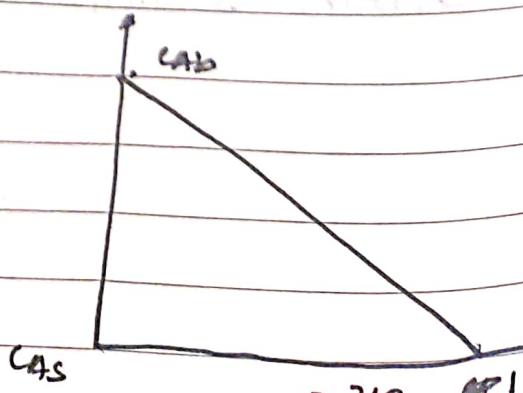
$$\frac{d^2C_A}{dz^2} = 0 \Rightarrow C_A = k_1 z + k_2$$

Boundary cond., At $z = 0$, $C_A = C_{Ab} \Rightarrow k_2 = C_{Ab}$

At $z = \delta$, $C_A = C_{As} \Rightarrow k_1 = \frac{C_{As} - C_{Ab}}{\delta}$

$$C_A = \frac{C_{As} - C_{Ab}}{\delta} z + C_{Ab}$$

$$\frac{C_A - C_{Ab}}{C_{As} - C_{Ab}} = \frac{z}{\delta}$$



Determination of molar flux of A diffusing through stagnant film, dilute soln. and EMCD:

① For dilute soln. and EMCD:

$$W_A = -D_{AB} \frac{dc_A}{dz} \quad \text{--- (1)}$$

$$c_A = (c_{AS} - c_{Ab}) \frac{z}{\delta} + c_{Ab}$$

$$\Rightarrow W_A = D_{AB} \frac{(c_{Ab} - c_{AS})}{\delta}$$

$$= \frac{D_{AB}}{\delta} (y_{Ab} - y_{AS}) \left(\frac{T_0}{T} \right) \quad \text{Total molar}$$

② For stagnant film,

$$W_A = -D_{AB} \frac{dc_A}{dz} + y_A w_A \quad (w_B = 0, B_A = y_A w_A)$$

$$w_A (y_A - 1) = D_{AB} \frac{dc_A}{dz} = D_{AB} c \frac{dy_A}{dz}$$

$$w_A \int dz = D_{AB} c \int \frac{dy_A}{y_{Ab} \frac{dy_A}{y_A - 1}}$$

Boundary cond., $z = \delta$, $y_A = y_{AS} (y_{AS})$

$$z = 0, y_A = y_{Ab}$$

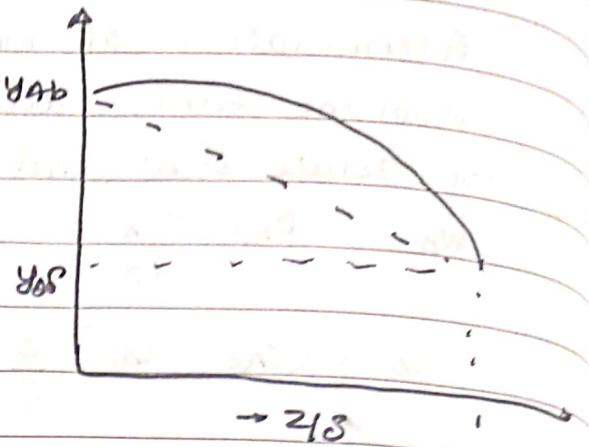
$$\therefore w_A \delta = D_{AB} c \ln \frac{1 - y_{Ab}}{1 - y_{AS}}$$

∴ Flux through stagnant film \geq Flux through dilute soln.

$$y_A = y_{Ab} - (y_{Ab} - y_{A\infty}) \frac{z}{\delta}$$

And for stagnant film,

$$y_A = 1 - (1 - y_{Ab}) \left(\frac{1 - y_{A\infty}}{1 - y_{Ab}} \right)^{2/\delta} y_{A\infty}$$

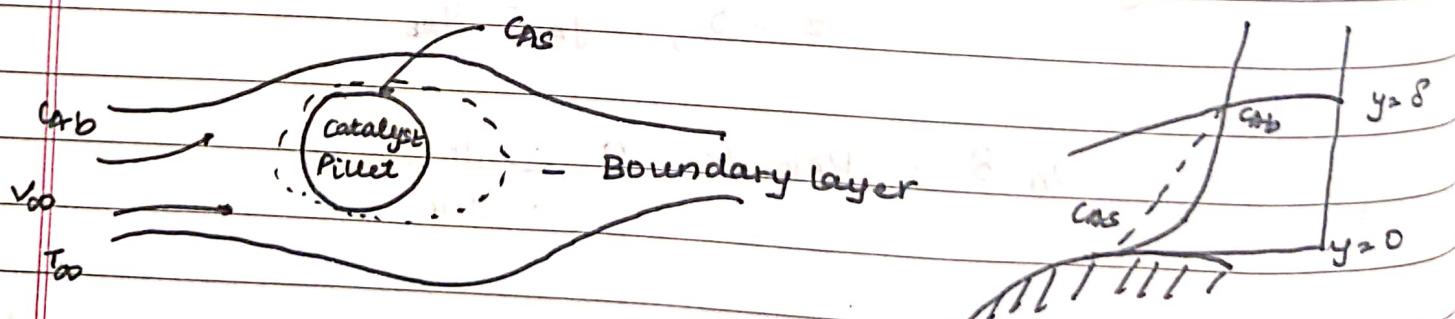


External Resistance to Mass Transfer

We consider flow past a single catalyst pellet. Reaction takes place only on the catalyst and not in the fluid surrounding.

Hydrodynamic boundary layer is defined as distance from a solid object where fluid vel. is 99% of bulk velocity

Mass transfer BL is defined as distance from a solid object to where the conc. of diffusing species reaches 99% of bulk conc.



Mass Transfer co-efficient

For either dilute soln. or BMS, mass flux at single point can be written as

$$W_{A(0)} = \frac{D_{AB}}{8} (C_{AB} - C_A)$$

$$k_c^* = \frac{D_{AB}}{8}, \quad k_c^* \rightarrow \text{local HTC at a point}$$

$$k_c = \int k_c^* \frac{dA}{A}$$

Avg. molar flux from bulk fluid to surface is,

$$W_A = k_c (C_{AB} - C_A)$$

$$\Pr = \frac{\rho \mu}{k_e} = \left(\frac{\mu}{\rho} \right) \left(\frac{\rho c_p}{k_e} \right) = \frac{\text{Kinematic visc.} (\nu)}{\text{Thermal diff.} (\alpha_e)}$$

$$Nu = 2 + 0.6 Re^{1/2} \Pr^{1/3}$$

For stagnant film, $Re = 0$, $Nu = 2$

For higher Reynolds Number, BL is laminar,

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

Analogy, Nu analogous to Sh (Sherwood No.)

$$Sh = \frac{k_c d}{D_{AB}}, \quad h \text{ analogous to } k_c$$

k_c is analogous to D_{AB}

$$Sc = \frac{\nu}{D_{AB}} \Rightarrow Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$$

↳ Frossling correlation

Mass Transfer to a Single Particle

There are two limiting cases for m: with diffusion.

- ① R_m is so rapid, rate of diffusion to surface limits rate r_A' rate.
- ② R_m is so slow compared to rate of diffusion that almost no conc. gradient exists b/w bulk and surface.

Consider, $A \rightarrow B$

$$-r_A' = \frac{k_r C_{AS}}{1 + k_A C_A + k_B C_B}$$

At high temp, denom $\rightarrow 1$

$$-r_A' = k_r C_{AS}$$

Boundary cond.,

$$\text{At surface, } w_A = -r_A'$$

$$\text{At Boundary layer, } w_A = k_c (C_{AB} - C_{AS})$$

$$\therefore w_A = k_c (C_{AB} - C_{AS}) = -r_A' = k_r C_{AS} \quad \text{(2)}$$

$$C_{AS} = \frac{k_c C_A}{k_r + k_o}$$

\therefore Rate of m: on surface is

$$w_A = -r_A' = \frac{k_c k_r}{k_r + k_o} C_A = k_{eff} C_A$$

Eff. Transport Co-eff.

Rapid r_m , (Mass transfer is slower)

When rate of mass transfer from surface limits the overall rate of r_m :

$$k_r \gg k_o, \frac{k_o}{k_r} \ll 1$$

$$\text{Thus, } -r_A' = \frac{k_o C_A}{1 + k_o/k_r} \approx k_o C_A$$

For gas phase catalytic r_m and most liq., S_c is large, thus 2 can be ignored in Frossing relation

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

$$\frac{k_o d}{D_{AB}} = 0.6 \frac{Re}{r} \left(\frac{d u}{r} \right)^{1/2} \left(\frac{r}{D_{AB}} \right)^{1/3}$$

$$\Rightarrow k_o = 0.6 \left(\frac{D_{AB}}{r^{1/6}} \right)^{2/3} \left(\frac{u^{1/2}}{d^{1/2}} \right)$$

fn. of temp.
and pressure

$$r \propto T^{2/3} (\text{gas})$$

r dec. exp. for liquids

D_{AB} inc. with inc. in T

fn. of flow of gas
and particle size
of catalyst.

Slow r_m :

Here, rate const. is smaller compared to HTC

$$k_r \ll k_o, -r_A' = k_r \alpha A$$

↳ Independent of rel. of fluid
and particle size.

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At low velocity, mass transfer boundary layer thickness is large, hence diffusion limits the mass transfer.

As the velocity past the solid particle increases, the BL thickness decreases and MT across BL can't limit the mass transfer.

