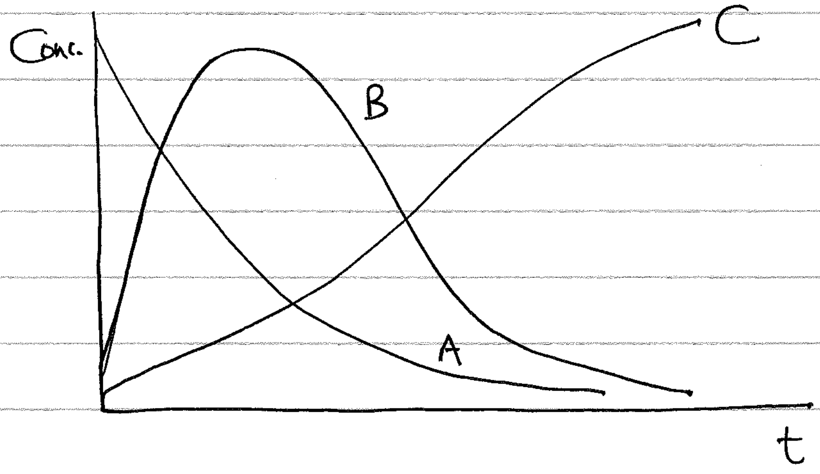
Let us revisit the series reactions case:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \quad \text{.... \underline{batch reactors}}$$

$$C_A = C_{A0} \exp(-k_1 t)$$

$$C_B = \left(\frac{k_1 C_{A0}}{k_1 - k_2}\right)\left[\exp(-k_2 t) - \exp(-k_1 t)\right]$$

$$C_C = C_{A0} + \left(\frac{C_{A0}}{k_1 - k_2}\right)\left[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)\right]$$



$$S_{B/C} = \frac{r_B}{r_C} \quad \text{.... definition of instantaneous selectivity}$$

$$\therefore \; S_{B/C} = \frac{k_1 C_A - k_2 C_B}{k_2 C_B}$$

$$\therefore \quad -k_1 C_A C_B = k_1 C_A^2 - k_2 C_A C_B$$

$$\therefore \quad -k_1 C_B = k_1 C_A - k_2 C_B$$

$$\therefore \quad (k_2 - k_1) C_B = k_1 C_A$$

$$\therefore \quad C_B = \left(\frac{k_1}{k_2 - k_1}\right) C_A$$

$$\therefore \quad \frac{k_1 C_{A0}}{k_1 - k_2}\left\{\exp(-k_2 t^*) - \exp(-k_1 t^*)\right\} = \frac{k_1}{k_2 - k_1} C_{A0} \exp(-k_1 t^*)$$

$$\hookrightarrow \boxed{t^* = S_{B/C} \text{ is maximum (or optimum)}}$$

$$\therefore \quad \exp(-k_2 t^*) - \exp(-k_1 t^*) = -\exp(-k_1 t^*)$$

$$\therefore \quad \exp(-k_2 t^*) = 0$$

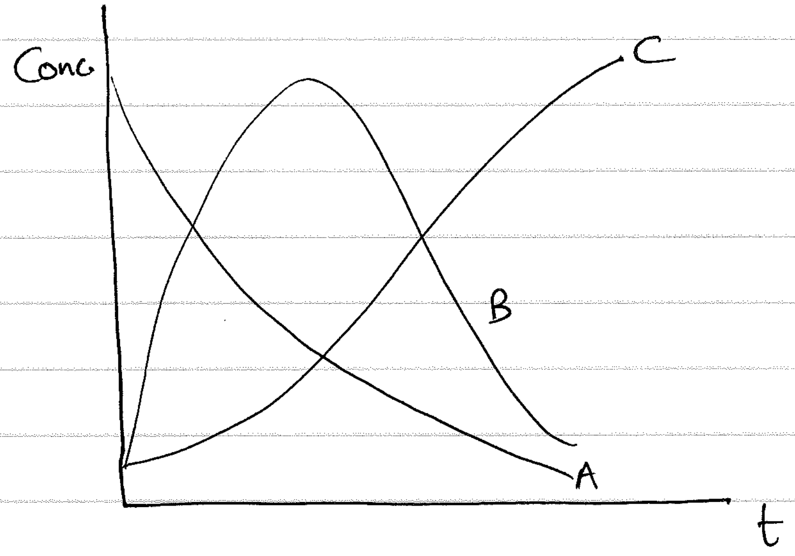
$$\therefore \quad \underbrace{t^* \to \infty}$$

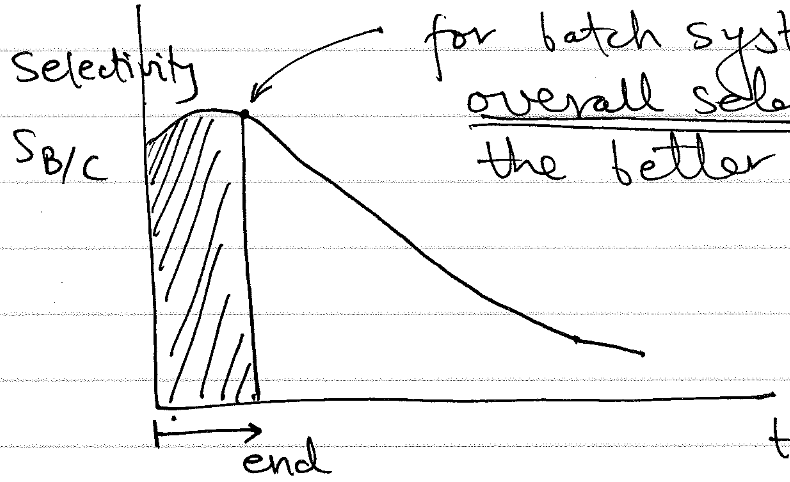
What does this mean?

$S_{B/C}$ is a monotonically decreasing function & @ $t \to \infty$, it is at its lowest value (not maximum!)

* In this case, one must solve the problem graphically.

For batch reactors:





for batch systems, <u>overall selectivity</u> is the better metric

$$\therefore \quad \tilde{S}_{B/C} = \frac{C_B}{C_C} \Longrightarrow \text{maximise this!}$$

$$\therefore \quad \frac{C_B}{C_C} = \frac{\frac{k_1 C_{A0}}{k_1 - k_2}\left\{ \exp(-k_2 t) - \exp(-k_1 t) \right\}}{C_{A0} + \frac{C_{A0}}{k_1 - k_2}\left\{ k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t) \right\}}$$

$$\therefore \frac{d\tilde{S}_{B/C}}{dt} = \frac{d}{dt}\left(\frac{C_B}{C_C}\right) = 0$$

$$\therefore C_C C_B' - C_B C_C' = 0$$

$$\therefore C_C(k_1 C_A - k_2 C_B) = C_B(k_2 C_B)$$

$$\therefore k_1 C_A C_C - k_2 C_B C_C = k_2 C_B^2$$

$$\therefore \text{At } t_{opt}, \quad \underbrace{k_1 C_A C_C = k_2 C_B^2 - k_2 C_B C_C}_{\text{a lot of math!}}$$

$$\boxed{\text{OR: solve graphically!}}$$

Often, we might choose to maximize yields.

This is a batch system ≡ we are looking at overall yields

$$\therefore \quad S_{B/C} = \frac{k_1}{k_2}\left(\frac{C_A}{C_B}\right) - 1$$

Now, C_A, C_B & $C_c = f(t)$

$$\therefore \quad S_{B/C} = f(t)$$

$\therefore \quad \frac{dS_{B/C}}{dt} = 0$ for maximising selectivity

$$\therefore \quad \frac{dS_{B/C}}{dt} = \frac{d}{dt}\left\{\frac{k_1}{k_2}\frac{C_A}{C_B} - 1\right\}$$

$$\therefore \quad \frac{dS_{B/C}}{dt} = \frac{k_1}{k_2}\frac{d}{dt}\left(\frac{C_A}{C_B}\right)$$

$$\therefore \quad \frac{dS_{B/C}}{dt} = \frac{k_1}{k_2}\left\{\frac{C_B C_A' - C_A C_B'}{C_B^2}\right\}$$

For maxima $\frac{dS_{B/C}}{dt} = 0$

$$\therefore \quad C_B C_A' = C_A C_B'$$

$$\therefore \quad C_B(-k_1 C_A) = C_A(k_1 C_A - k_2 C_B)$$

$\therefore$ Series reactions $\Rightarrow$ assume volumes don't change

$$\tilde{Y}_B = \frac{C_B}{C_{A_0}}$$

$$\therefore \quad \tilde{Y}_B = \frac{k_1 C_{A_0}}{k_1 - k_2}\left(\exp(-k_2 t) - \exp(-k_1 t)\right) \times \frac{1}{C_{A_0}}$$

$$\therefore \quad \frac{d\tilde{Y}_B}{dt} = \frac{k_1}{k_1 - k_2}\frac{d}{dt}\left(\exp(-k_2 t) - \exp(-k_1 t)\right)$$

At $t = t_{opt}$, $\dfrac{d\tilde{Y}_B}{dt} = 0$

$$\therefore \quad -k_2 \exp(-k_2 t) + k_1 \exp(-k_1 t) = 0 \quad \ldots @\, t_{opt}$$

$$\therefore \quad \frac{\exp(-k_2 t_{opt})}{\exp(-k_1 t_{opt})} = \frac{k_1}{k_2}$$

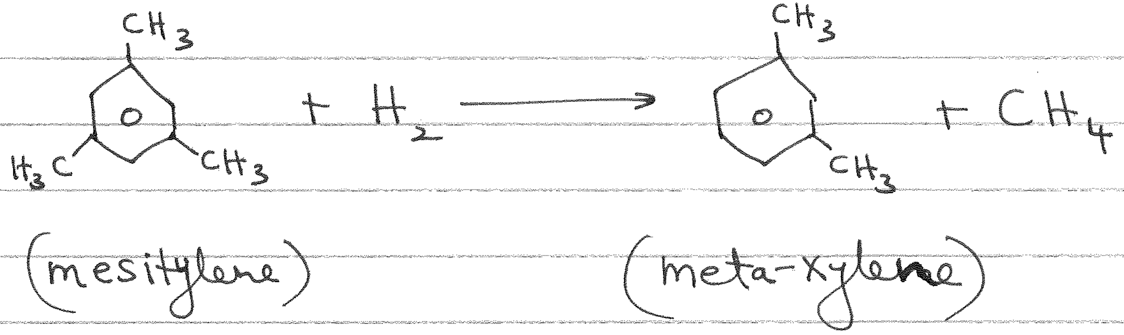
$$\therefore \quad -k_2 t_{opt} + k_1 t_{opt} = \ln\left(\frac{k_1}{k_2}\right)$$

$$\boxed{t_{opt} = \frac{1}{k_1 - k_2}\ln\left(\frac{k_1}{k_2}\right)} \quad \ldots\ldots \text{ similar to } \frac{dC_B}{dt} = 0 \text{ \underline{case}.}$$

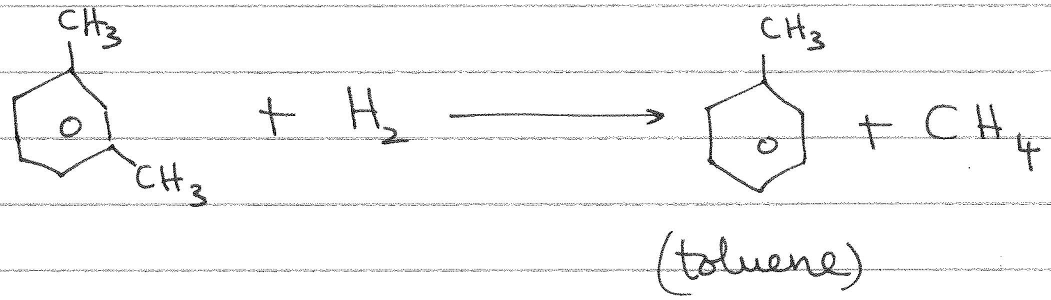
Multiple reactions in a PFR/PBR :

Hydrodealkylation of mesitylene:-

Reaction 1



Reaction 2



Let us re-write this system using simpler nomenclature :

$$M + H \xrightarrow{k_1} X + A$$

alkane!

$$X + H \xrightarrow{k_2} T + A$$

This rxn. is being undertaken in a PFR.

Also, $$\left.\begin{aligned} -r_1 &= k_1 C_M C_H^{1/2} \\ -r_2 &= k_2 C_X C_H^{1/2} \end{aligned}\right\}$$ rate expressions

Let us recollect some of our design eqns. for a PFR:

$$v = V_0 \left(\frac{P_0 T}{T P_0}\right) \left(1 + \varepsilon X\right)$$

What is our basis species?

For multiple reactions, let's rewrite the eqn.:

ⓐ What was $\underline{(1+\varepsilon X)}$?

$$\frac{N_T}{N_{T0}} = 1 + \varepsilon X$$ .... we had derived this earlier in the course

$$\therefore \quad v = v_0 \left(\frac{P_0 T}{T P_0}\right) \left(\frac{N_T}{N_{T0}}\right)$$

For the PFR, assume:

$$P = P_0 \quad \& \quad T = T_0$$

$$\therefore \quad \upsilon = \frac{\upsilon_0 N_T}{N_{T_0}}$$

Re-write the equation:

$$M + H \longrightarrow X + A$$
$$X + H \longrightarrow T + A$$

Add the rxns.:

$$\underbrace{M + X + 2H}_{4 \text{ moles}} \longrightarrow \underbrace{X + T + 2A}_{4 \text{ moles}}$$

$$\therefore \quad \Delta = 0 \implies \varepsilon = 0$$

$$\therefore \quad N_T = N_{T_0}$$

$$\therefore \quad \upsilon = \upsilon_0$$

The design eqn. becomes:

$$\frac{dN_i}{dV} = r_i$$ ... for species i (signs change based on prod. or react.)

$$\therefore \; v_o \frac{dC_H}{dV} = r_H$$

$$-r_H = k_1 C_M C_H^{1/2} + k_2 C_X C_H^{1/2}$$

$$\therefore \; -r_H = (k_1 C_M + k_2 C_X) C_H^{1/2}$$

$$\therefore \; v_o \frac{dC_H}{dV} = -(k_1 C_M + k_2 C_X) C_H^{1/2}$$

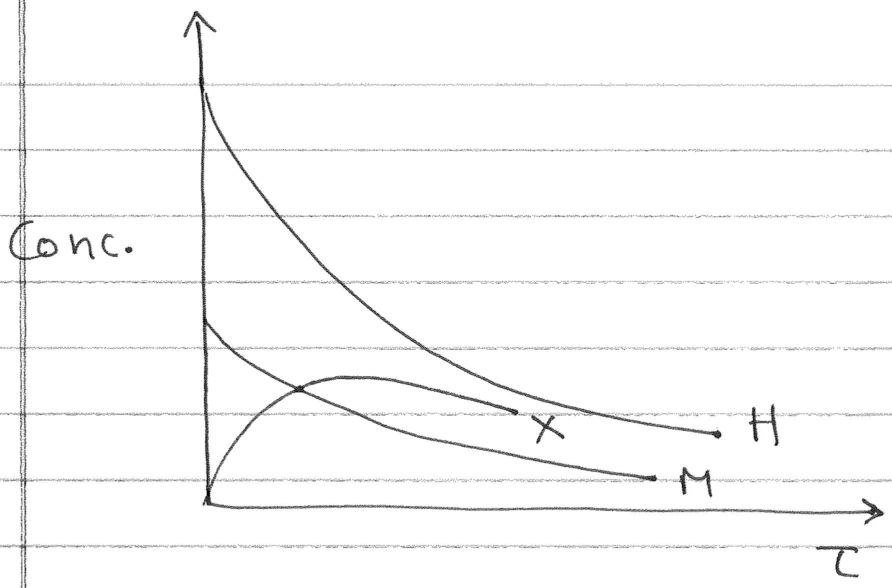
What is $\frac{V}{v_o}$? Residence time!

$$\therefore \; \frac{dC_H}{d\tau} = -(k_1 C_M + k_2 C_X) C_H^{1/2}$$

Similarly, $\frac{dC_M}{d\tau} = -k_1 C_M C_H^{1/2}$

$$\frac{dC_X}{d\tau} = (k_1 C_M - k_2 C_X) C_H^{1/2}$$

This is a system of differential equations that must be solved numerically.



What happens if the reaction is taking place on a packed-bed?

$$\frac{dN_i}{dW} = r_i'$$

{The ks are adjusted suitably}

$$v = v_0\left(\frac{P_0}{P}\right)$$

What is P/P_0? Remember Ergun!

$$y = P/P_0$$

& $$\frac{dy}{dW} = \frac{-\alpha}{2y}\left(\frac{T}{T_0}\right)\left(1+\varepsilon X\right)$$

Recollect: $\alpha = \dfrac{2\beta_o}{A_c \rho_{cat}(1-\phi) P_o}$

$$\beta_o = \frac{G(1-\phi)}{\rho_o g_c D_p \phi^3}\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right]$$

$$\& \; G = \frac{\dot{m}}{A_c} \quad \text{(mass flux)}$$

For this system,

$$\frac{dy}{dW} = \frac{-\alpha}{2y}$$

$$v = \frac{v_o}{y}$$

$$\& \; \frac{dN_i}{dW} = r_i \quad \text{i.e. } \frac{d(vC_i)}{dW} = r_i$$

$$\left.\begin{array}{l} \therefore \; v_o \dfrac{d\left(C_i/y\right)}{dW} = r_i \longrightarrow ① \\[2ex] \dfrac{dy}{dW} = \dfrac{-\alpha}{2y} \longrightarrow ② \end{array}\right\} \text{solve numerically}$$

You may have been curious about the $(1+\varepsilon X)$ term?

How would have that panned out?

→ Assume H_2 as the basis species!

$$\begin{tikzcd} & \text{rxn. 1} \\ H_2 \arrow[ur, bend left] \arrow[dr, bend right] & \\ & \text{rxn. 2} \end{tikzcd}$$

} X is overall conversion

Here, we break up the conversion into its components.

$$X_H^{\text{overall}} = \frac{\overbrace{(N_{H_o} - N_H)}^{\text{moles reacted}}}{N_{H_o}}$$

$$X_H^{\text{overall}} = \frac{\left\{\begin{matrix}\text{moles reacted}\\ \text{in rxn. 1}\end{matrix}\right\} + \left\{\begin{matrix}\text{moles reacted}\\ \text{in rxn. 2}\end{matrix}\right\}}{N_{H_o}}$$

$$\therefore X_H^{\text{overall}} = \underset{\substack{\downarrow \\ \text{conversion} \\ \text{in rxn. 1}}}{X_{H_1}} + \underset{\substack{\downarrow \\ \text{conversion} \\ \text{in rxn. 2}}}{X_{H_2}}$$

$$\therefore \; N_H = N_{Ho} - X_H^{overall} N_{Ho}$$

$$\therefore \; N_H = N_{Ho} - \left(X_{H_1} + X_{H_2}\right) N_{Ho}$$

$$\therefore \; \underbrace{N_H}_{\text{final}} = \underbrace{N_{Ho}}_{\text{initial}} - \underbrace{X_{H_1} N_{Ho}}_{\substack{\text{change}\\ \text{due to}\\ \text{rxn. 1}}} - \underbrace{X_{H_2} N_{Ho}}_{\substack{\text{change}\\ \text{due to}\\ \text{rxn. 2}}}$$

Similarly,

$$N_M = N_{Mo} - X_{H_1} N_{Ho} \qquad \text{(mesitylene)}$$

$$\& \; N_X = N_{Xo} + X_{H_1} N_{Ho} - X_{H_2} N_{Ho} \qquad \text{(m-xylene)}$$

The design eqn. is:

$$\frac{dX_H^{overall}}{dV_{PFR}} = \left(\frac{-r_H}{N_{Ho}}\right)$$

$$\& \; -r_H = \left(k_1 C_M + k_2 C_X\right) C_H^{1/2}$$

The system of ODEs is more complex, but we can still solve this numerically like before.

* All eqns. on this page will be involved.

Special case: Membrane reactors

Do you remember when we said using semi-batch or membrane reactors was good?

$$A + B \xrightarrow{k_1} D \qquad -r_1 = k_1 C_A^2 C_B$$

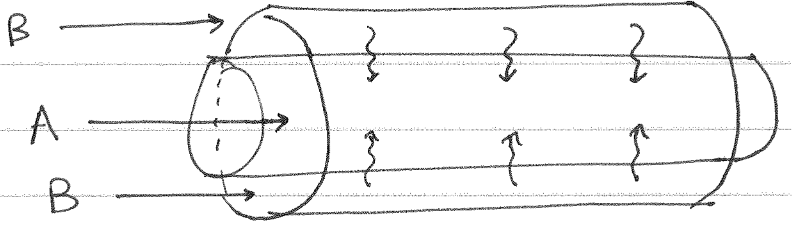
$$A + B \xrightarrow{k_2} U \qquad -r_2 = k_2 C_A C_B^2$$

$$S_{D/U} = \frac{(-r_1)}{(-r_2)} = \frac{r_1}{r_2} = \frac{k_1}{k_2}\frac{C_A^2 C_B}{C_A C_B^2}$$

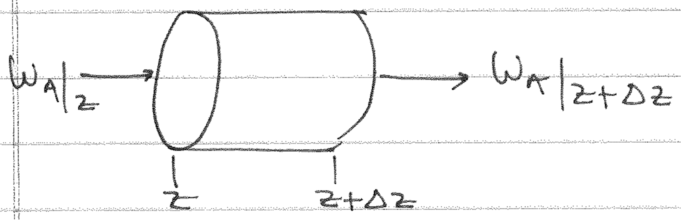
$$\therefore \quad S_{D/U} = \left(\frac{k_1}{k_2}\right) C_A \left(\frac{1}{C_B}\right)$$

To maximise $S_{D/U}$, C_A as high as possible

C_B as low as possible



Let us try & solve this system.

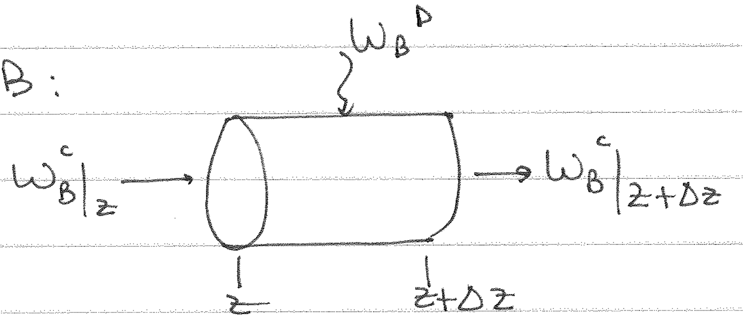


$$0 = W_A|_z A_c - W_A|_{z+\Delta z} A_c + (r_1+r_2) A_c \Delta z$$

$$\therefore \quad \frac{dW_A}{dz} = r_1 + r_2$$

$$\boxed{\therefore \quad \frac{d(\upsilon C_A)}{dV} = r_1 + r_2} \longrightarrow ①$$

For B:



$$\therefore \quad 0 = W_B^c|_z A_c - W_B^c|_{z+\Delta z} A_c + (r_1+r_2) A_c \Delta z + J_B A_s$$

$$A_s = 2\pi r \Delta z$$

$$\therefore \quad -\frac{dW_B^c}{dz} + 2\pi r J_B + r_1 + r_2 = 0$$

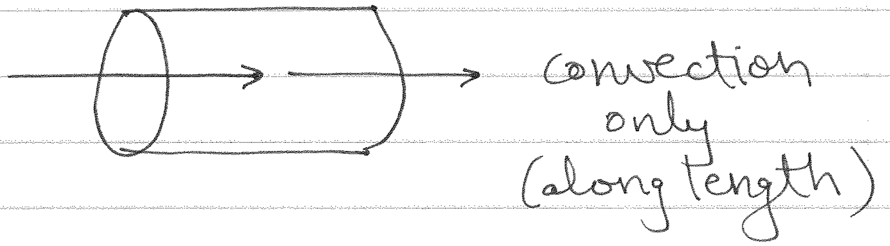
Remember our discussion of mass transfer?

$$\begin{Bmatrix}\text{Total}\\\text{flux}\end{Bmatrix} = \begin{Bmatrix}\text{diffusive}\\\text{flux}\end{Bmatrix} + \begin{Bmatrix}\text{convective}\\\text{flux}\end{Bmatrix}$$

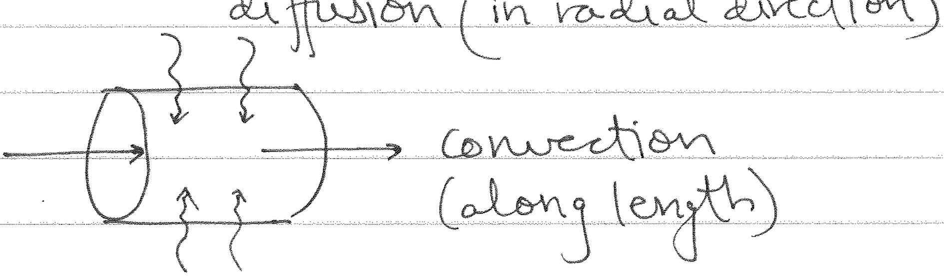
$\frac{\text{moles}}{m^2 \cdot s}$

$$\boxed{\therefore \quad W_i = J_i + x_i W}$$

<u>For A</u> :



<u>For B</u> :



$$W_i = \frac{\text{moles}}{m^2 \cdot S} = \frac{\upsilon \cdot \text{Conc.}}{A_c}$$

$$J_i = -D\frac{dC_i}{dm}$$

thickness of membrane

If we assume membrane is very thin,

$$J_i \approx \left(\frac{-D}{dm}\right)\Delta C_i$$

which can we rewritten as

$$J_i = \left(\frac{D}{\delta}\right)\cdot\left(C_{out_i} - C_{in_i}\right)$$

Note: From ideal gas law: $P = CRT$

$$\boxed{\begin{aligned} &\therefore \quad P_i = x_i P \\ &\& \quad C_i = x_i C = \frac{x_i P}{RT} \end{aligned}}$$

$$\therefore J_i = \frac{D}{\delta RT}\left(P_{out_i} - P_{in_i}\right)$$

$$\therefore J_i \approx K\left(P_{out_i} - P_{in_i}\right)$$

you may see this expression as well

$$\therefore -\frac{d(v C_B)}{dV} + 2\pi r J_B + (r_1 + r_2) = 0$$

in pressure terms $$\left\{ \therefore -\frac{d(v C_B)}{dV} + 2\pi r K \left(P_B^{out} - P_B^{in}\right) + (r_1 + r_2) = 0 \right.$$

OR : $$\boxed{-\frac{d(v C_B)}{dV} + \frac{2\pi r D}{\delta}\left(C_B^{out} - C_B\right) + (r_1 + r_2) = 0} \rightarrow ②$$

$$v = v_0 \left(\frac{P_0 T}{T_0 P}\right)(1 + \varepsilon X) \longrightarrow ③$$

choose the basis species appropriately & solve the system of ODEs

Assumptions: * $P_0 = P$ (no pressure drop)

* isothermal

simplifies system $\Rightarrow$ v_0 comes out of ODE & $v = v_0(1 + \varepsilon X)$