$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_S - F_{A0} \sum \Theta_i \int_{T_{i0}}^{T} C_{p_i} dT - F_{A0} X_A \left[\Delta H^\circ_{rxn}(T_R) + \int_{T_R}^{T} \Delta C_{p_{rxn}} dT \right]$$

⇒ Energ. SS, adiabatic, no shaftwork, C_p's are indep. of temperature

$$0 = -F_{A0} \sum \Theta_i C_{p_i}(T - T_{i0}) - F_{A0} X_A \left[\Delta H^\circ_{rxn}(T_R) + \Delta C_{p_R}(T - T_R) \right]$$

$$\therefore -\underset{\cancel{F_{A0}}}{X_A} \left[\Delta H^\circ_{rxn}(T_R) + \Delta C_{p_R}(T - T_R) \right] = \cancel{F_{A0}} \sum \Theta_i C_{p_i}(T - T_{i0})$$

$$\boxed{\therefore -X_A^{EB} = \frac{\cancel{F_{A0}} \sum \Theta_i C_{p_i}(T - T_{i0})}{\Delta H^\circ_{rxn}(T_R) + \Delta C_{p_R}(T - T_R)}}$$

Simplest case ESS, ADIA, no $\dot{W}_S$, C_p indep. of T

$$A \xrightarrow{k} B$$

$-r_A = kC_A$, ideal CSTR

$$\therefore \; -r_A = kC_{A0}\left(1 - X_A^{MB}\right)$$

← mass balance

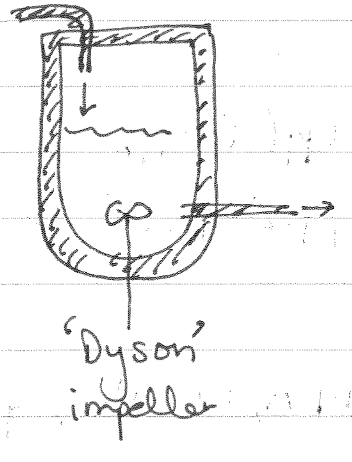
$$v C_{A0} - v C_A = (-r_A) V$$

$$\therefore \; v C_{A0} X_A = k C_{A0} (1 - X_A) V$$

$$\therefore \; X_A = \frac{kV}{v}(1 - X_A)$$

$$\therefore \; X_A = k\tau - k\tau X_A$$

$$\boxed{\therefore \; X_A^{MB} = \frac{k\tau}{1 + k\tau}} \longrightarrow ①$$



* flow conditions known

* reaction constant known (function of temp.)

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

$$\therefore \; X_A^{MB} = \frac{A\exp\left(\frac{-E_a}{RT}\right)\tau}{1 + A\exp\left(\frac{-E_a}{RT}\right)\tau}$$

From the energy balance,

$$X_A^{EB} = \frac{\cancel{F_{A0}} \sum \Theta_i C_{pi} (T - T_{i0})}{-\left[\Delta H_{rxn}^\circ (T_R) + \Delta C_{pR} (T - T_R)\right]}$$

$$\boxed{\therefore \; X_A^{EB} = \frac{\cancel{F_{A0}} \left[C_{pA} (T - T_{A0}) + C_{pB} (T - T_{B0}) \Theta_B\right]}{-\Delta H_{rxn}^\circ (T_R) - (C_{pB} - C_{pA}) (T - T_R)}} \rightarrow ②$$

We have 2 eqns. and an implicit relationship between X_A & T.

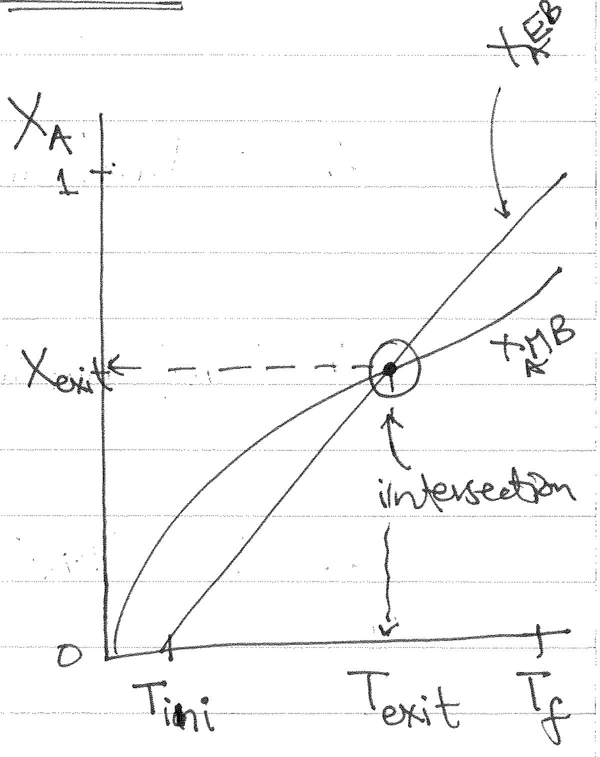
How to proceed :

T(K)	X_A^{EB}	X_A^{MB}
273		
↓		
353		

(e.g.)

populate

Calculate these values using ① & ②



always the case for CSTR

$\boxed{\text{This problem has to be solved graphically.}}$

<u>Now consider a PFR</u>: same conditions

Energy balance remains the same.

$$X_A = \frac{C_{pA}(T - T_{A0}) + \Theta_B C_{pB}(T - T_{B0})}{-\Delta H^\circ_{rxn}(T_R) - (C_{pB} - C_{pA})(T - T_R)}$$

For simplicity, consider the general eqn.

$$X_A = \frac{\sum C_{pi}\Theta_i (T - T_{i0})}{-\left[\Delta H^\circ_{rxn}(T_R) + \Delta C_{p\,rxn}(T - T_R)\right]}$$

$$\therefore -\Delta H^\circ_{rxn}(T_R) X_A - X_A \Delta C_{p\,rxn} T + X_A \Delta C_{p\,rxn} T_R = \sum C_{pi}\Theta_i T - \sum C_{pi}\Theta_i T_{i0}$$

$$\therefore X_A \Delta C_{p\,rxn} T_R + \sum C_{pi}\Theta_i T_{i0} - \Delta H^\circ_{rxn}(T_R) X_A = X_A \Delta C_{p\,rxn} T + \sum C_{pi}\Theta_i T$$

①

$$\boxed{\therefore T = \frac{X_A \Delta C_{p\,rxn} T_R + \sum C_{pi}\Theta_i T_{i0} - \Delta H^\circ_{rxn}(T_R) X_A}{X_A \Delta C_{p\,rxn} + \sum C_{pi}\Theta_i}}$$

all terms separated

~~The problem has to be solved graphically~~.

Now, for our system:

$$T = \frac{X_A(C_{pB}-C_{pA})T_R + (C_{pA}+\Theta_B C_{pB})T_{i0} - \Delta H^\circ_{rxn}(T_R)X_A}{X_A(C_{pB}-C_{pA}) + C_{pA} + \Theta_B C_{pB}}$$

$$\boxed{\therefore\ T = \frac{X_A(C_{pB}-C_{pA})T_R + C_{pA}T_{A0} + \Theta_B C_{pB}T_{B0} - \Delta H^\circ_{rxn}(T_R)X_A}{X_A(C_{pB}-C_{pA}) + C_{pA} + \Theta_B C_{pB}}}$$

$\rightarrow \underline{T_{A0} = T_{B0} = T_0}$

assume pure A

Mass balance for a PFR is:

$$\frac{dX_A}{dV} = \frac{-F_{A0}}{r_A}$$

derive from stoichiometric table

$$\therefore\ \frac{dX_A}{dV} = \frac{+F_{A0}}{+kC_{A0}(1-X_A)\frac{T_0}{T}}$$

$$\therefore\ \frac{dX_A}{dV} = \frac{v_0}{k}\,\frac{1}{(1-X_A)\left(\frac{T_0}{T}\right)}$$

you can see how different inlet temps. are possible

$$\therefore\ \frac{dX_A}{dV} = \left(\frac{v_0}{k}\right)\frac{T}{(1-X_A)T_0}$$

$$\therefore \quad \frac{dX_A}{dV} = \left(\frac{\upsilon_0}{k}\right)\left(\frac{T}{T_0}\right)\left(\frac{1}{1-X_A}\right)$$

$$\& \quad T = \frac{X_A(C_{pB}-C_{pA})T_R + C_{pA}T_0 - \Delta H^\circ_{rxn}(T_R)X_A}{X_A\,((C_{pB}-C_{pA}) + C_{pA}}$$

Methodology :

$$X_{A_{i+1}} = X_{A_i} + \Delta V\left[\left(\frac{\upsilon_0}{k_i}\right)\left(\frac{T_i}{T_0}\right)\left(\frac{1}{1-X_{A_i}}\right)\right]$$

① Start with $X_{A_i} = 0$.

② $$T_i = \frac{X_{A_i}((C_{pB}-C_{pA})T_R + C_{pA}T_0 - \Delta H^\circ_{rxn}(T_R)X_{A_i}}{X_{A_i}(C_{pB}-C_{pA}) + C_{pA}}$$

solve for T_i

iterate

③ Use T_i to solve for k_i using Arrhenius

④ Calculate $X_{A_{i+1}}$, keep ΔV constant.

⑤ set $X_{A_{i+1}} = X_{A_i}$

Therefore

X_A	- - - - - - -
V	- - - - - - - -

Ⓠ1 you can be given a final volume & asked for exit conversion

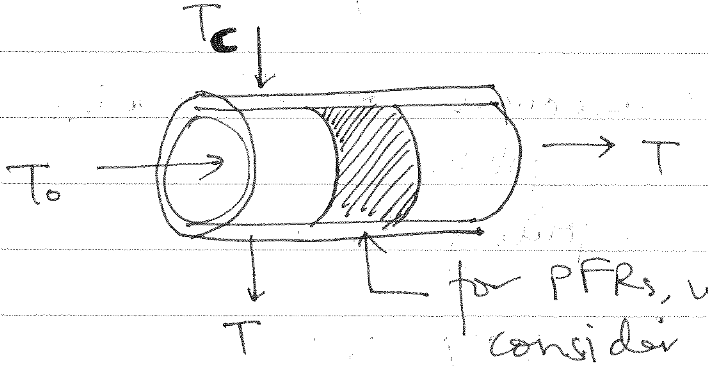
OR

Ⓠ2 you can be given an exit conversion & asked for final volume

$\boxed{\text{Methodology same}}$

Now, let's move into the world of heat exchangers

<u>PFRs</u>



for PFRs, we have to consider unit volume

→ change along length ≡ dV.

Why? Let's consider the general energy balance

$\dot{Q}$'s units ≡ $\frac{\text{Joule}}{s}$

coolant

But, $\dot{Q} = k_c A \Delta T_c$

from Newton's law of cooling (different from Fourier)

$$k_c \equiv \frac{\left(\frac{\text{Joule}}{s}\right)}{m^2 \cdot (K)}$$

$$\therefore \quad k_c = \frac{\text{Joule}}{m^2 \cdot s \cdot K}$$ ← heat transfer coefficient

For heat exchanger, we denote k_c as U

U ≡ accounts for all realities of the system (fouling etc.)

$$\therefore \quad \dot{Q} = UA\Delta T$$

Cases considered so far:

1. Adiabatic CSTR (graphical sol^n.)
2. Adiabatic PFR: (iterative, numerical method)

Now, let's consider reactors with heat exchange.

Recollect:

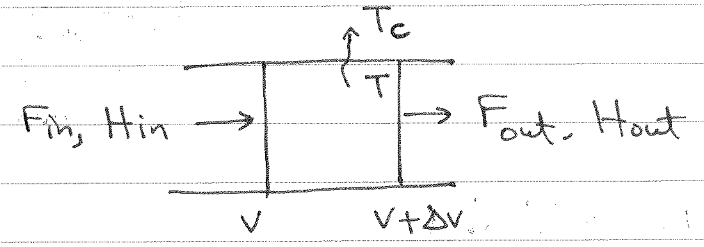
$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_s - F_{A0}\sum \Theta_i \int_{T_{i0}}^{T} C_{pi}\,dT - F_{A0}X_A\left[\Delta H_{rxn}^{\circ}(T_R) + \int_{T_R}^{T}\Delta C_{p\,rxn}\,dT\right]$$

Let's take a step back:

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum F_{i0}H_{i0} - \sum F_i H_i$$

Consider a PFR @ $\underline{\underline{ESS}}$. (no $\dot{W}_s$!)

$$\therefore\ 0 = \dot{Q} + \sum F_{i0}H_{i0} - \sum F_i H_i$$



<u>Energy</u>

$$\begin{Bmatrix}\text{rate of}\\\text{accum.}\end{Bmatrix} = \begin{Bmatrix}\text{rate of}\\\text{input}\end{Bmatrix} - \begin{Bmatrix}\text{rate of}\\\text{output}\end{Bmatrix} + \begin{Bmatrix}\text{rate of}\\\text{generation}\end{Bmatrix} - \begin{Bmatrix}\text{rate}\\\text{of}\\\text{consumptio}\end{Bmatrix}$$

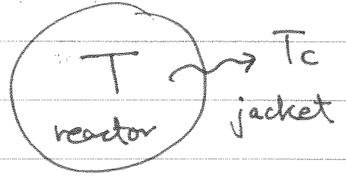
For reactions, we can lump heat changes into the flow terms

$$\therefore\ 0 = \left\{\begin{matrix}\text{energy}\\\text{in}\end{matrix}\right\} - \left\{\begin{matrix}\text{energy}\\\text{out}\end{matrix}\right\}$$

$$\therefore\ 0 = \Delta\dot{Q} + \sum F_i H_i\Big|_V - \sum F_i H_i\Big|_{V+\Delta V}$$

Heat exchangers

For the moment, assume the simplest case



$$\therefore\ \Delta\dot{Q}_{out} = \underbrace{k A (T - T_c)}_{\text{Newton's law of cooling}}$$

$$\Delta\dot{Q} \equiv k A (T - \overset{\text{generic term for coolant}}{T_c})$$

$$(J/s) \equiv \left(\frac{J}{s\,m^2.K}\right)(m^2)\ (K)$$

More generally, $\Delta\dot{Q}_{out} = U \underbrace{\Delta A}_{\text{surface area of volume element}} (T - T_c)$

$$\&\ \Delta A = \Delta V.a$$

i.e. $a = \dfrac{\Delta A}{\Delta V}$ .... exchange area per unit volume

$$\therefore \Delta \dot{Q}_{out} = \alpha \Delta V\, U (T - T_c)$$

$\therefore$ The energy balance becomes:

$$-\alpha \Delta V\, U (T - T_c) + \sum F_i H_i \Big|_V - \sum F_i H_i \Big|_{V+\Delta V} = 0$$

$$\sum F_i H_i \Big|_{V+\Delta V} - \sum F_i H_i \Big|_V = \alpha \Delta V\, U (T_c - T)$$

$$\therefore \frac{\sum F_i H_i \Big|_{V+\Delta V} - \sum F_i H_i \Big|_V}{\Delta V} = \alpha\, U (T_c - T)$$

$$\therefore \frac{d \sum F_i H_i}{dV} = U\alpha (T_c - T)$$

$$\therefore \sum \frac{d F_i H_i}{dV} = U\alpha (T_c - T)$$

$$\therefore \boxed{\sum \left[F_i \frac{dH_i}{dV} + H_i \frac{dF_i}{dV} \right] = U\alpha (T_c - T)} \rightarrow ①$$

For a PFR, from the mole balance:

$$\frac{dF_i}{dV} = r_i$$

r_i: −ve for reactants, +ve for products

& $dH_i = C_{p_i} dT$ → assuming C_{p_i} indep. of T.

make subst. in ①

$$\therefore \sum \left[F_i C_{p_i} \frac{dT}{dV} + H_i r_i \right] = Ua(T_c - T)$$

$$\therefore \sum F_i C_{p_i} \frac{dT}{dV} + \underbrace{\sum H_i r_i}_{\text{let's simplify this term}} = Ua(T_c - T)$$

e.g. $aA + bB \rightarrow cC + dD$

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

$(-r_A) \equiv$ rate of disapperance of A (positive q/ty)

$$\therefore \quad -r_A = \frac{-r_B}{(b/a)} = \frac{r_C}{(c/a)} = \frac{r_D}{(d/a)}$$

$$\therefore \sum H_i r_i = -H_A(-r_A) - H_B(-r_B) + H_C r_C + H_D r_D$$

$$= -H_A(-r_A) - \frac{b}{a}H_B(-r_A) + \frac{c}{a}H_C(-r_A) + \frac{d}{a}H_D(-r_A)$$

$$= (-r_A)\left[-H_A - \frac{b}{a}H_B + \frac{c}{a}H_C + \frac{d}{a}H_D \right]$$

$$= -r_A \left[\Delta H_{rxn} \right]$$

$$\therefore \frac{dT}{dV}\left[\sum F_i C_{pi}\right] + (-r_A)\,\Delta H_{rxn} = U\alpha\,(T_c - T)$$

$$\therefore \frac{dT}{dV} = \frac{U\alpha(T_c - T) - (-r_A)\,\Delta H_{rxn}}{\sum F_i C_{pi}}$$

$$\boxed{\therefore \frac{dT}{dV} = \frac{r_A\,\Delta H_{rxn} - U\alpha(T - T_c)}{\sum F_i C_{pi}}}$$

For PBR,

$d V \cdot \rho_B = dW$

generalized form of energy balance for ESS PFR with heat exchange

From Stoichiometry table

$$F_i = F_{A0}\left[\theta_i \pm s_i X_A\right]$$

stoichiometric coeff.

product/reactant

Also, $\sum F_i C_{pi} = F_{A0}\left[\sum \theta_i C_{pi} + \Delta C_{p\,rxn} X_A\right]$

$$\therefore \frac{dT}{dV} = \frac{r_A\,\Delta H_{rxn} - U\alpha(T - T_c)}{F_{A0}\left[\left(\sum \theta_i C_{pi} +\right)\Delta C_{p\,rxn} X_A\right]}$$

we've derived this before

PFR design

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \longrightarrow \underline{\underline{MB}}$$

$$\frac{dT}{dV} = \frac{-Ua(T-T_c) + r_A \Delta H_{rxn}}{F_{A0}\left[\left(\sum \theta_i C_{pi}\right) + \Delta C_{p\,rxn} X\right]} \longrightarrow \underline{\underline{EB}}$$

$$\boxed{\text{Solve these equations numerically}}$$

ⓠ What is T_c? How do we estimate it?

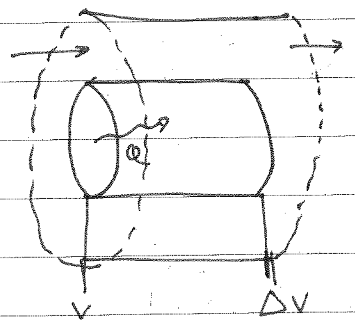
<u>Easiest case</u> ≡ given to you in the problem statement
& you assume it to <u>be constant</u> **

⊛ ** This is possible in cross-flow heat exchangers.

⊛ However, in most cases, coolant flows in parallel or counter to the reactor.

⊛ In this situation, T_c will vary along the length of the reactor.

To analyse this, let us once again solve



$$0 = \left\{\begin{matrix}\text{energy}\\ \text{in}\end{matrix}\right\} - \left\{\begin{matrix}\text{energy}\\ \text{out}\end{matrix}\right\}$$

$$\dot{m}_c H_c\big|_V - \dot{m}_c H_c\big|_{V+\Delta V} + U\alpha(T - T_c)\Delta V = 0$$

Why mass?
because that
is how
coolant's are
sold!
(they're not
pure mixtures)

$$\therefore \quad \frac{\dot{m}_c H_c\big|_V - \dot{m}_c H_c\big|_{V+\Delta V}}{\Delta V} + U\alpha(T - T_c) = 0$$

$$\therefore \quad -\dot{m}_c \frac{dH_c}{dV} + U\alpha(T - T_c) = 0$$

$$\therefore -\dot{m}_c \frac{dH_c}{dV} + U\alpha (T - T_c) = 0$$

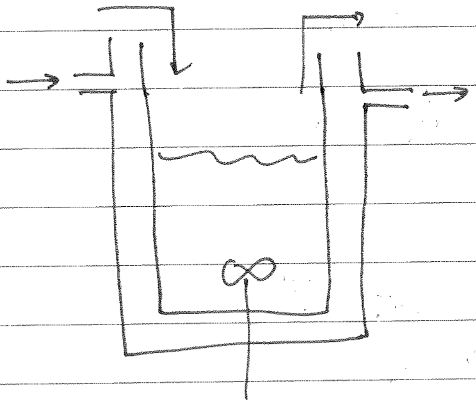
$$\therefore -\dot{m}_c C_{p\,cool} \frac{dT_c}{dV} + U\alpha (T - T_c) = 0$$

$$\boxed{\therefore \frac{dT_c}{dV} = \frac{U\alpha (T - T_c)}{\dot{m}_c C_{p\,cool}}} \Longrightarrow \text{describes coolant temp. variation}$$

∴ Realistically, in these type of systems, one is solving a system of 3 ODEs:

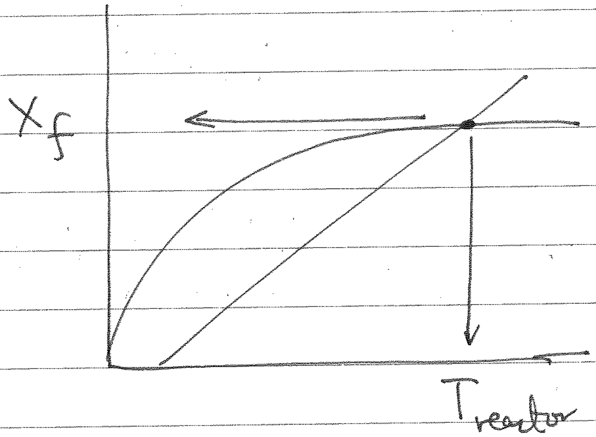
$$\left.\begin{aligned} \frac{dT}{dV} &= \frac{r_A \Delta H_{rxn} - U\alpha (T - T_c)}{F_{A0}\left[(\sum \Theta_i C_{p_i}) + \Delta C_{p\,rxn} X\right]} \\ \frac{dT_c}{dV} &= \frac{U\alpha (T - T_c)}{\dot{m}_c C_{p\,cool}} \\ \frac{dX}{dV} &= \frac{-r_A}{F_{A0}} \end{aligned}\right\} \text{solve together!}$$

What happens in a CSTR?



Assumption:
→ reactor well mixed
→ coolant operated so that it too is homogeneous

Recollect:



CSTR operation occurs @ single pt.

Consider the energy balance:

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_S - F_{A0}\sum \Theta_i C_{pi}(T - T_{i0}) - F_{A0}X_A\Big[\underbrace{\Delta H^\circ_{rxn}(T_R) + \Delta C_{p\,rxn}(T - T_R)}_{=\Delta H_{rxn}}\Big]$$

At ESS,

$$0 = \dot{Q} - \dot{W}_S - F_{A0}\sum \Theta_i C_{pi}(T - T_{i0}) - F_{A0}X_A\left[\Delta H_{rxn}\right]$$

$$\therefore \; X_A^{EB} = \frac{\dot{Q} - \dot{W}_S - F_{A0}\sum \Theta_i C_{pi}(T - T_{i0})}{F_{A0}\Delta H_{rxn}} \quad ①$$

$$X_A^{MB} = \frac{(-r_A)V}{v_0 C_{A0}} = \frac{k C_A^{\alpha} V}{v_0 C_{A0}}$$

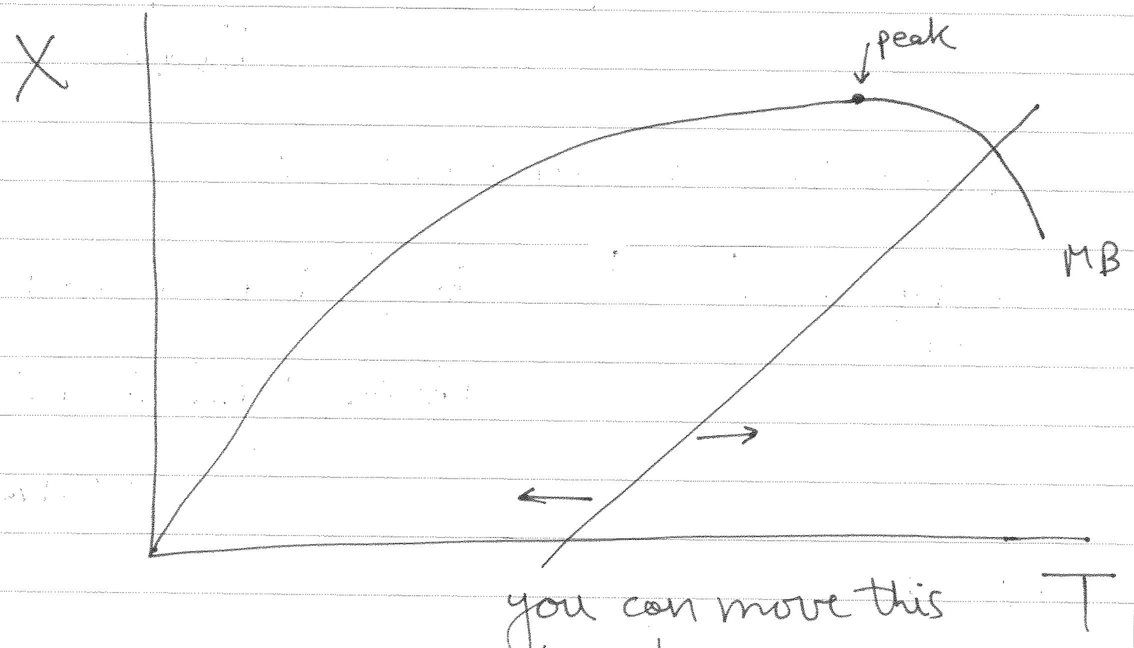
If $r_A = kC_A$ & $A \rightarrow B$

$$X_A^{MB} = \frac{k C_{A0}(1-X_A) V}{v_0 C_{A0}}$$

$$\boxed{\therefore X_A^{MB} = \frac{k\tau}{1+k\tau}} \longrightarrow ②$$

<u>eqns similar</u>

Often, heat might degrade a catalyst & you want to ensure highest conversion



you can move this line by varying T_{i0}, F_{A0} & $\dot{Q}$

$$\& \ \underline{\dot{Q} = U\Delta A(T-T_c)} = \underline{\dot{m}_c C_{p_{cool}}(T_c - T_{c0})}$$