PRACTICAL SESSION 1

EX. 1

CONSTANT VOLUME BATCH REACTOR

$\rho = \text{const}$ $\qquad A \rightarrow B \qquad K = 0.01\ s^{-1}$

$C_A^0 = 2 \frac{mol}{l}$

$r = K C_A \quad \begin{cases} R_A = -K C_A \\ R_B = K C_A \end{cases} \qquad \begin{cases} \frac{dC_A}{dt} = -K C_A \\ \frac{dC_B}{dt} = K C_A \end{cases}$

$$\frac{dC_A}{dt} = -k C_A \Rightarrow -C_A^0 \frac{dX}{dt} = -k C_A^0 (1-X)$$

$$\begin{cases} \frac{dX}{dt} = k(1-X) \\ X(t=0) = 0 \end{cases} \longrightarrow \frac{dX}{X-1} = -k\,dt$$

$$\ln \frac{X-1}{(X-1)_0} = -kt$$

$$\frac{X-1}{-1} = -kt$$

$$\boxed{X = 1 - \exp(-kt)}$$

$$X(\tau) = 1 - \exp(-k\tau)$$

$$\boxed{\tau = -\frac{1}{K} \ln(1-X)}$$

$\tau(X = 90\%) = 230\ s$

$\tau(X = 99.9\%) = 691\ s$

EX 2.

CONSTANT VOLUME BATCH REACTOR

$$A \rightarrow B \qquad r = k C_A^{\mu}, \quad \mu \neq 1$$

$$\frac{dC_A}{dt} = -k C_A^{\mu} \Rightarrow -C_A^{\circ}\frac{dX}{dt} = -k C_{A0}^{\mu}(1-X)^{\mu}$$

$$\begin{cases} \dfrac{dX}{dt} = k C_{A0}^{\mu-1}(1-X)^{\mu} \\ X(t=0) = 0 \end{cases} \qquad (1-X)^{-\mu}dX = k C_{A0}^{\mu-1}dt$$

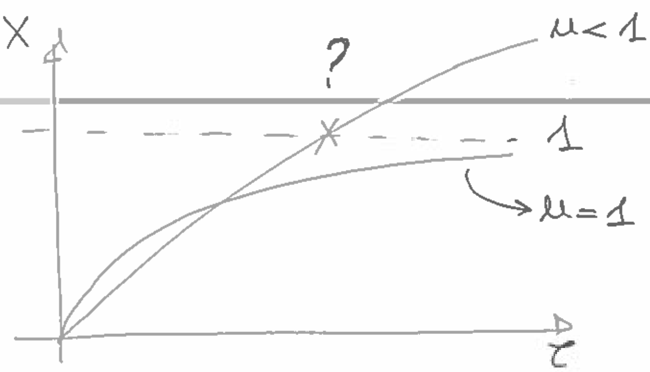
$$\int (1-X)^{-\mu}dX = k C_{A0}^{\mu-1} t$$

$$\int (1-X)^{-\mu}dX = \underset{\substack{\uparrow \\ y \overset{def}{=} 1-X}}{\ldots\ldots} = -\int y^{-\mu}dy = -\left[\frac{y^{-\mu+1}}{-\mu+1}\right]$$

$$-\left[\frac{(1-X)^{-\mu+1}}{-\mu+1}\right]_0^X = k C_{A0}^{\mu-1} t$$

$$-\left[\frac{(1-X)^{-\mu+1} - 1}{-\mu+1}\right] = \frac{(1-X)^{-\mu+1} - 1}{\mu - 1} = k C_{A0}^{\mu-1} t$$

$$\tau(X) = \frac{(1-X)^{-\mu+1} - 1}{k C_{A0}^{\mu-1}(\mu-1)} \qquad \begin{cases} \mu = 1/2 & \tau(90\%) = 193\,s \\ \mu = 2 & \tau(90\%) = 950\,s \end{cases}$$



! BE CAREFUL

EX. 3

CSTR at constant density

$$A + B \longrightarrow C \qquad r = k C_A C_B \qquad \begin{cases} k = 0.05 \ \frac{l}{mol\, s} \\ C_{A0} = 3 \ \frac{mol}{l} \\ C_{B0} = 4 \ \frac{mol}{l} \end{cases}$$

$$F_A^0 - F_A + R_A V = 0 \implies Q\left(C_{A0} - C_A\right) + R_A V = 0$$

$$Q\left(C_{A0} - C_{A0}(1-X)\right) - k C_{A0}(1-X) C_{A0} (\vartheta_B^0 - X) V = 0$$

$$Q C_{A0} X - k C_{A0}^2 (1-X)(\vartheta_B^0 - X) V = 0 \qquad \tau \stackrel{def}{=} \frac{V}{Q} \qquad \vartheta_B^0 = \frac{C_B^0}{C_A^0}$$

$$X - k C_{A0} (1-X)(\vartheta_B^0 - X)\, \tau = 0$$

$$\tau = \frac{X}{k C_{A0} (1-X)(\vartheta_B^0 - X)} = \dots = \frac{X}{k(1-X)(C_B^0 - C_{A0} X)}$$

$$\tau(95\%) = 330\, s$$

Observation

$$\begin{cases} C_B = C_{B0} - C_{A0} X \\ C_A = C_{A0} - C_{A0} X \end{cases}$$

$$C_B - C_A = C_{B0} - C_{A0} \stackrel{def}{=} \Delta C_0 = const$$

$$C_B = C_A + \Delta C_0$$

$$C_B^0 = C_A^0 + \Delta C_0 \implies C_B^0 - X C_A^0 = \dots = C_A^0(1-X) + \Delta C_0$$

$$\tau = \frac{X}{k(1-X)\left(C_A^0(1-X) + \Delta C_0\right)}$$

EX. 4

CONSTANT DENSITY CSTR

$$A \rightleftharpoons B \qquad r = k_f C_A - k_b C_B \qquad \begin{cases} k_f = 0.5 \text{ min}^{-1} \\ k_b = 0.1 \text{ min}^{-1} \end{cases}$$

$$\begin{cases} C_A^o = 1 \text{ mol/l} \\ C_B^o = 0 \end{cases}$$

Equilibrium

$$k_f C_{Aeq} = k_b C_{Beq}$$

$$k_f \cancel{C_{A0}} (1 - X_{eq}) = k_b \cancel{C_{A0}} X_{eq}$$

$$X_{eq} = \frac{k_f}{k_f + k_b} \qquad X_{eq} = 5/6 > 50\% \quad \checkmark$$

Residence time

$$\dot{Q}(C_A^o - C_A) + R_A V = 0$$

$$\dot{Q} C_{A0} X - (k_f C_A - k_b C_B) V = 0$$

$$C_{A0} X - (k_f C_{A0}(1-X) - k_b C_A^o X)\tau = 0$$

$$X - (k_f(1-X) - k_b X)\tau = 0$$

$$\boxed{\tau = \frac{X}{k_f(1-X) - k_b X}} \qquad \tau(50\%) = 2.5 \text{ min}$$

EX. 5

CSTR with non constant density

$A \rightarrow 3B$ $\qquad r = K C_A^2$ $\qquad K = 0.5 \dfrac{l}{\text{min mol}}$

$$\begin{cases} C_A^\circ = 3 \dfrac{\text{mol}}{l} \\ C_B^\circ = 0 \\ F_A^\circ = 0.2 \dfrac{\text{mol}}{s} \end{cases}$$

$$\dot{F}_A^\circ - \dot{F}_A + R_A V = 0$$

$$C_j = C_{A0} \frac{\vartheta_j^\circ + \nu_j X}{1 + \varepsilon X} \gamma^*$$

$$\gamma^* = \frac{T^\circ P}{T P_0} = \ldots = 1$$

$$\varepsilon = \frac{F_A^\circ}{F_{tot}^\circ} \delta = 1 \cdot (3-1) = 2$$

$$C_A = C_{A0} \frac{1 - X}{1 + 2X}$$

$$\dot{Q} = \dot{Q}_0 (1 + \varepsilon X) / \gamma^*$$
$$\overset{1}{=} \dot{Q}_0 (1 + 2X)$$

$$\dot{Q}_0 C_{A0} - \dot{Q} C_A - K C_A^2 V = 0$$

$$\dot{Q}_0 C_{A0} - \dot{Q}_0 (1+2X) C_{A0} \frac{1-X}{1+2X} - K C_{A0}^2 \frac{(1-X)^2}{(1+2X)^2} V = 0$$

$$\dot{Q}_0 C_{A0} - \dot{Q}_0 C_{A0} (1-X) - K C_{A0} \cdot C_{A0} \frac{(1-X)^2}{(1+2X)^2} \cdot V = 0$$

$$1 - (1-X) - K C_{A0} \frac{(1-X)^2}{(1+2X)^2} \cdot \tau = 0$$

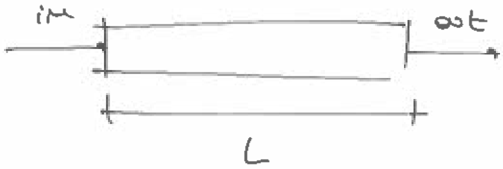
$$X - K C_{A0} \frac{(1-X)^2}{(1+2X)^2} \tau = 0$$

$$\boxed{\tau = \frac{X (1+2X)^2}{K C_{A0} (1-X)^2}} \qquad V = \frac{\dot{F}_A^\circ}{K C_{A0}^2} \frac{(1+2X)^2}{(1-X)^2}$$

$$\tau(95\%) = 734.7 \text{ min}$$

EX 6

REACTIONS IN SERIES IN A PFR (constant density)



$L = 100\ m$

$d = 0.08\ m$

$T = 750\ °C$

$P = 3\ bar$

$\dot{F}_A^\circ = 20\ \frac{kmol}{h}$

$\dot{F}_B^\circ = \dot{F}_C^\circ = 0$

$$\dot{Q} = \frac{\dot{F}_A^\circ \cdot MW_A}{\rho}$$

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad \begin{cases} r_1 = k_1 C_A \\ r_2 = k_2 C_B \end{cases}$$

$$\begin{cases} \frac{dC_A}{dt} = -k_1 C_A \\ \frac{dC_B}{dt} = k_1 C_A - k_2 C_B \\ \frac{dC_C}{dt} = k_2 C_B \end{cases} + \text{ICs} \begin{cases} C_A(0) = C_A^\circ = \dot{F}_A^\circ / \dot{Q} \\ C_B(0) = C_B^\circ = 0 \\ C_C(0) = C_C^\circ = 0 \end{cases}$$

$$\frac{dC_A}{dt} = -k_1 C_A \implies C_A = C_{A0} \exp(-k_1 t)$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \implies \frac{dC_B}{dt} = k_1 C_{A0} \exp(-k_1 t) - k_2 C_B$$

$$C_B = C_{B\,hom} + C_{Bp} \qquad C_{Bp} = A \exp(-k_1 t)$$

$$\frac{dC_{B\,hom}}{dt} = -k_2 C_{B\,hom}$$

$$C_{B\,hom} = B \cdot \exp(-k_2 t)$$

$$-Ak_1 \exp(-k_1 t) = k_1 C_{A0} \exp(-k_1 t) + A \exp(-k_1 t) k_2$$

$$-Ak_1 = k_1 C_{A0} + A k_2$$

$$A = \frac{k_1 C_{A0}}{k_2 - k_1}$$

$$C_B = C_{B\,hom} + C_{Bp}$$

$$C_B = B \exp(-k_2 t) + \frac{k_1 C_{A0}}{k_2 - k_1} \exp(-k_1 t)$$

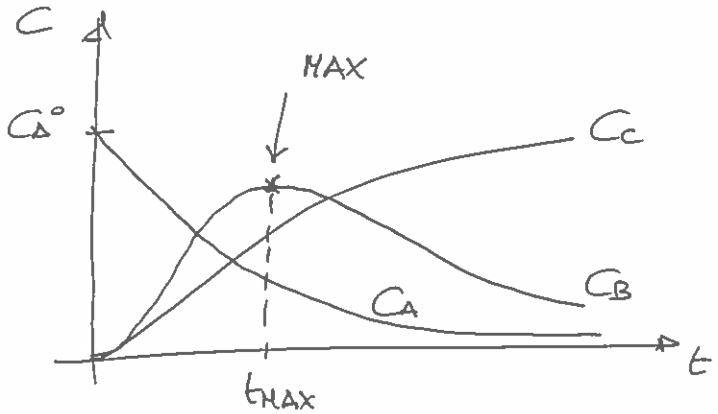
initial condition $\quad C_B(t=0)=0 \qquad 0 = B + \dfrac{k_1 C_{A0}}{k_2-k_1}$

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

$$C_{tot} = C_B + C_A + C_C = \text{const} \Rightarrow C_C(t) = C_{tot} - C_A - C_B$$

solution

$$\begin{cases} C_A(t) = C_{A0}\exp(-k_1 t) \\ C_B(t) = \dfrac{k_1 C_{A0}}{k_2-k_1}\left(\exp(-k_1 t) - \exp(-k_2 t)\right) \\ C_C(t) = C_A^\circ - C_A(t) - C_B(t) \end{cases}$$



$$\begin{cases} C_{A0} = 35.7\ \dfrac{mol}{m^3} \\ \tau = \dfrac{L}{V} = 3.23\,s \\ \eta_C = \dfrac{C_C(\tau)}{C_A^\circ} = \dfrac{C_C(\tau)}{C_A^\circ} = 96.8\% \\ k_1 = 1.49\ s^{-1} \\ k_2 = 1.86\ s^{-1} \end{cases}$$

$$C_B(t) = \alpha\left(\exp(-k_1 t) - \exp(-k_2 t)\right) \quad , \quad \alpha = \frac{k_1 C_{A0}}{k_2-k_1}$$

$$\frac{dC_B}{dt} = \alpha\left(-k_1\exp(-k_1 t) + k_2\exp(-k_2 t)\right) = 0$$

$$k_1\exp(-k_1 t) = k_2\exp(-k_2 t)$$

$$\ln k_1 - k_1 t = \ln k_2 - k_2 t$$

$$t_{MAX} = \frac{\ln\frac{k_2}{k_1}}{k_2-k_1} = \dots = \frac{\ln\frac{k_1}{k_2}}{k_1-k_2}$$

! maximum position

EX 7

SERIES REACTION IN A CONSTANT VOLUME BATCH REACTOR

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$T = 500\,K$

$V = 0.50\ m^3$

$N_A^\circ = 20\ kmol$

$\tau_D = 1\,h$

$$C_{A0} = \frac{N_A^\circ}{V} = 40\ \frac{kmol}{m^3}$$

$$\begin{cases} k_1 = 1.75\ h^{-1} \\ k_2 = 0.0297\ h^{-1} \end{cases}$$

$$\begin{cases} \dfrac{dC_A}{dt} = -k_1 C_A \\ \dfrac{dC_B}{dt} = k_1 C_A - k_2 C_B \\ \dfrac{dC_C}{dt} = k_2 C_B \end{cases} \Longrightarrow \begin{cases} C_A(t) = C_A^\circ \exp(-k_1 t) \\ C_B(t) = \dfrac{k_1 C_A^\circ}{k_2 - k_1}\left(\exp(-k_1 t) - \exp(-k_2 t)\right) \\ C_C(t) = C_A^\circ - C_B - C_A \end{cases}$$

Max. yield of B $\quad Y_B = \dfrac{C_B}{C_A^\circ} = \dfrac{k_1}{k_2 - k_1}\left(\exp(-k_1 t) - \exp(-k_2 t)\right)$

same position of maximum of B
see previous problem

$$t_{\substack{MAX \\ yield\,B}} = \frac{\ln \frac{k_2}{k_1}}{k_2 - k_1} \qquad t_{\substack{MAX \\ yield\,B}} = 2.37\,h$$

Max. production of B

$$P_B \stackrel{def}{=} N_B(\tau)\ N_{cycles/day} = C_B(\tau)\,V \cdot \frac{24\,h}{\tau + \tau_D}$$

$$= \frac{24 \cdot k_1 C_{A0} V}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_1 t)\right] / (\tau + \tau_D)$$

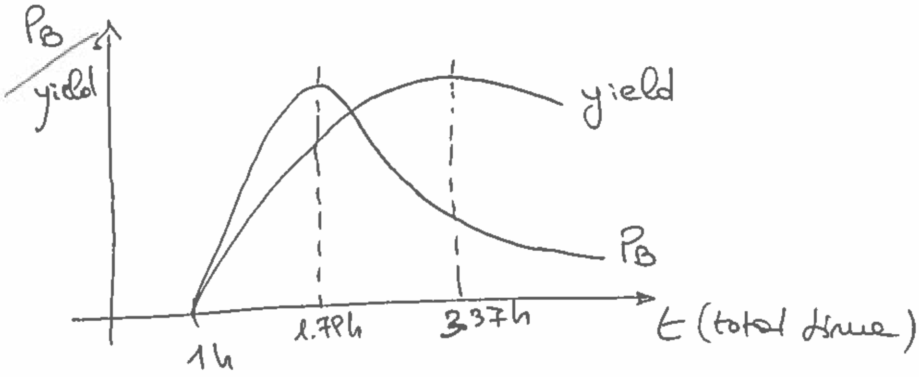
$$\propto \frac{\exp(-k_1 t) - \exp(-k_2 t)}{\tau + \tau_D}$$

$$\frac{dP_B}{d\tau} = \alpha\ \frac{\left(-k_1 \exp(-k_1 \tau) + k_2 \exp(-k_2 \tau)\right)(\tau + \tau_D) - \left(\exp(-k_1 \tau) - \exp(-k_2 \tau)\right)}{(\tau + \tau_D)^2} = 0$$

$$\left(-k_1 \exp(-k_1 \tau) + k_2 \exp(-k_2 \tau)\right)(\tau + \tau_D) - \left(\exp(-k_1 \tau) - \exp(-k_2 \tau)\right) = 0$$

non linear algebraic equation to solve in τ

$$\left(-k_1 \exp(-k_1\tau) + k_2 \exp(-k_2\tau)\right)(\tau+\tau_D) - \left(\exp(-k_1\tau) - \exp(-k_2\tau)\right) = 0$$



instead of solving the equation above, one can plot the P_B function and find the maximum position on it

$$\tau_{\substack{max \\ production}} = 0.79\,h$$

EXERCISE 8

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

inlet mixture
$$\begin{cases} T_{in} = 330\ K \\ \dot{F}_{tot}^{in} = 163\ kmol/h \\ C_A^{in} = 9.30\ kmol/m^3 \\ x_A^{in} = 0.90 \\ x_B^{in} = 0 \\ x_I^{in} = 0.10 \end{cases}$$

thermodynamic data
$$\begin{cases} \Delta H_R(T_0) = \Delta H_R^0 = -6900\ J/mol \\ T_0 = 300\ K \\ C_{pA} = 131\ J/mol/K \\ C_{pB} = 171\ J/mol/K \\ C_{pI} = 161\ J/mol/K \end{cases}$$

kinetics
$$\begin{cases} k_f(T_f^*) = 31.1\ 1/h \\ T_f^* = 360\ K \\ E = 65700\ J/mol \end{cases}$$

thermodynamic equilibrium
$$\begin{cases} K_{eq}(T_{eq}^*) = 3.03 \\ T_{eq}^* = 60\ °C = 333\ K \end{cases}$$

SOLUTION

a) preliminary calculations

$$\begin{cases} \dot{F}_A^{in} = x_A^{in} \cdot \dot{F}_{tot}^{in} = 146.7\ kmol/h \\ \dot{F}_B^{in} = x_B^{in} \cdot \dot{F}_{tot}^{in} = 0 \\ \dot{F}_I^{in} = x_I^{in} \cdot \dot{F}_{tot}^{in} = 16.3\ kmol/h \end{cases} \qquad \begin{cases} \vartheta_A = \dfrac{x_A^{in}}{x_A^{in}} = 1 \\ \vartheta_B = \dfrac{x_B^{in}}{x_A^{in}} = 0 \\ \vartheta_I = \dfrac{x_I^{in}}{x_A^{in}} = 0.111 \end{cases}$$

$$\widetilde{C}_p^{in} = \sum_j \vartheta_j \widetilde{C}_{pj} = 148.8\ J/mol/K$$

$$\widetilde{\Delta C}_p = \widetilde{C}_{pB} - \widetilde{C}_{pA} = 40\ J/mol/K$$

$$\Delta H_R^{in} = \Delta H_R^0 + \widetilde{\Delta C}_p (T_{in} - T_0) = -5700\ J/mol$$

$$\Delta H^* = \Delta H(T_{eq}^*) = \widetilde{\Delta H_R^\circ} + \widetilde{\Delta C_p}(T_{eq}^* - T_0) = -5580 \ J/mol$$

b) <u>kinetics</u>

$$k_f(T_f^*) = k_f^* = A \exp\left(-\frac{E}{RT_f^*}\right)$$

$$k_f(T) = A \exp(-E/RT)$$

$$\boxed{k_f(T) = k_f^* \exp\left(-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_f^*}\right)\right) \qquad (E1)}$$

c) <u>equilibrium constant</u>

$$\frac{d \ln K_{eq}}{dT} = \frac{\widetilde{\Delta H_R}}{RT^2} \qquad \widetilde{\Delta H_R} = \Delta H_R^\circ + \widetilde{\Delta C_p}(T - T_0)$$

$$\ln K_{eq} = C' + \frac{\widetilde{\Delta C_p}}{R} \ln T - \frac{\widetilde{\Delta H_0^R} - \widetilde{\Delta C_p} T_0}{RT}$$

$$\ln \frac{K_{eq}}{K_{eq}^*} = -\left(\frac{\Delta H_R^*}{R} - \frac{\widetilde{\Delta C_p}}{R} T^*\right)\left(\frac{1}{T} - \frac{1}{T^*}\right) + \frac{\widetilde{\Delta C_p}}{R} \ln \frac{T}{T^*}$$

$$\boxed{K_{eq} = K_{eq}^* \cdot \exp\left[-\left(\frac{\Delta H_R^*}{R} - \frac{\widetilde{\Delta C_p}}{R} T^*\right)\left(\frac{1}{T} - \frac{1}{T^*}\right) + \frac{\widetilde{\Delta C_p}}{R} \ln \frac{T}{T^*}\right] \qquad (E2)}$$

in case $\widetilde{\Delta C_p} = 0 \implies K_{eq} = K_{eq}^* \exp\left(-\frac{\Delta H_R^\circ}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right)$

~~[illegible]~~ Van't hoff

d) <u>formation rate of reference species</u>

$$R_A = -k_f \cdot C_A + k_b C_B = -k_f C_A^\circ (1 - X) + k_b C_A^\circ X$$

$$k_b = \frac{k_f}{K_{eq}}$$

$$= \ldots = k_f C_A^\circ \left(-1 + X\left(1 + \frac{1}{K_{eq}}\right)\right)$$

$$\boxed{-R_A = k_f C_A^\circ \left(1 - \left(1 + \frac{1}{K_{eq}}\right) X\right) \qquad (E3)}$$

e) <u>equilibrium conversion (useful)</u>

$$k_f \cdot C_A^{eq} = k_b C_B^{eq} \rightarrow k_f C_A^{0}(1-X_{eq}) = k_b C_A^{0} X_{eq}$$

$$X_{eq} = \frac{K_{eq}}{1+K_{eq}}$$! be careful $K_{eq} = K_{eq}(T) \rightarrow X_{eq} = X_{eq}(T)$

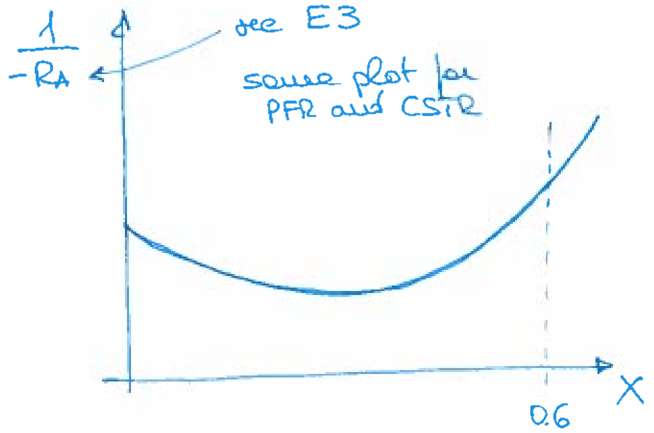
f) <u>ENERGY BALANCE EQUATION</u>

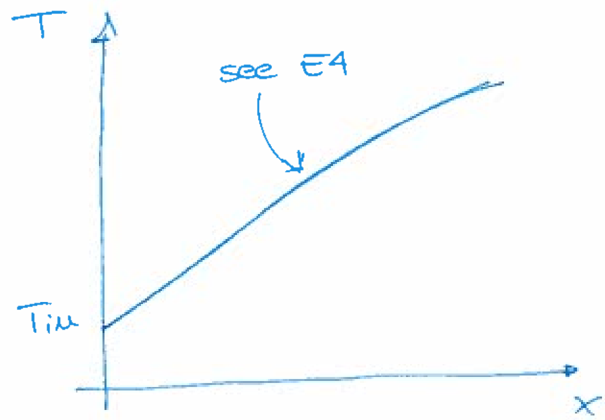
$$\int_{T_{in}}^{T} \widetilde{C_p}^{in}\, dT + \widetilde{\Delta H_R}(T)\, X = 0$$

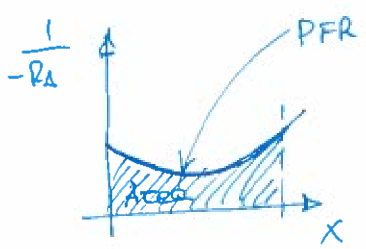
$$C_{p_j} = \text{const} \Longrightarrow \boxed{T = T_{in} + \frac{-\widetilde{\Delta H_R}^{in} X}{\widetilde{C_p}_{in} + \Delta\widetilde{C_p} X} \qquad (E4)}$$

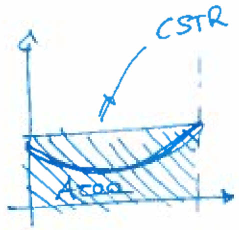
this is the same for PFR and CSTR cases

g) <u>LEVENSPIEL'S PLOT</u>









<u>PFR</u>

$V = \text{Area} \cdot F_A^{in}$

<u>CSTR</u>

$V = \text{Area} \cdot F_A^{in}$

<u>PFR</u> $$\text{Area} = \int_{0}^{X_f = 0.60} \frac{dX}{-R_A}$$

X_f = is the desired final conversion

<u>CSTR</u> $$\text{Area} = \frac{1}{-R_A^f} \cdot X_f$$

$$
\text{PFR}\quad
\begin{cases}
V = \dot{F}_A^{in} \displaystyle\int_0^{X_f} \frac{dX}{-\dot{R}_A} \\[2ex]
T = T_{in} + \dfrac{-\widetilde{\Delta H}_R^{in}\, X}{\widetilde{C_p}_{in} + \Delta \widetilde{C_p}\, X}
\end{cases}
$$

Alternative approach:

$$
\text{PFR}\quad
\begin{cases}
\dfrac{dX}{dV} = -\dfrac{\dot{R}_A}{\dot{F}_A^{in}} \\[2ex]
\dfrac{dT}{dV} = \dfrac{\dot{Q}_R}{\dot{F}_A^{in}\left(\widetilde{C_p}^{in} + \Delta \widetilde{C_p}\, X\right)}
\end{cases}
\quad + \quad \text{ICs}
\begin{cases}
X(V=0) = 0 \\
T(V=0) = T_{in}
\end{cases}
$$

$$
\dot{Q}_R = \text{heat release} = \dot{R}_A\, \widetilde{\Delta H}_R
$$