EXERCISE 1

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

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

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

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

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

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

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

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

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

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

Van't Hoff

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

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

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

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

e) equilibrium conversion (useful)

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

$$X_{eq} = \frac{K_{eq}}{1+K_{eq}}$$

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

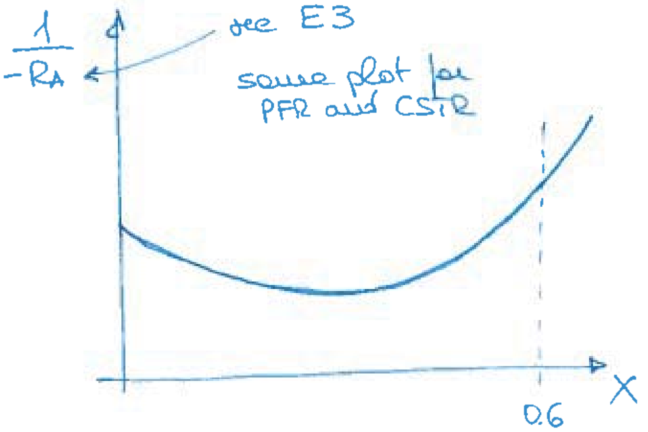
f) ENERGY BALANCE EQUATION

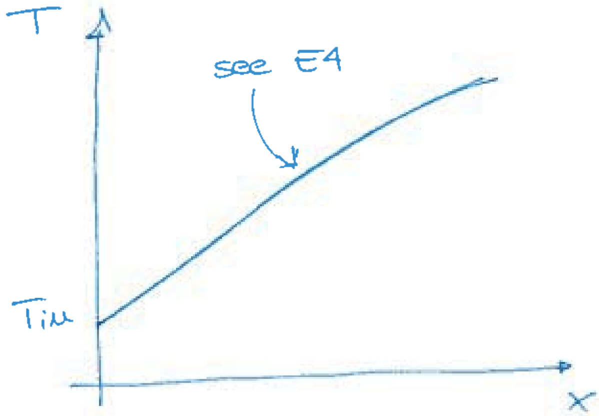
$$\int_{T_{in}}^{T} \widetilde{C_p}^{in}\, dT + \widetilde{\Delta H_R}(T)\, X = 0$$

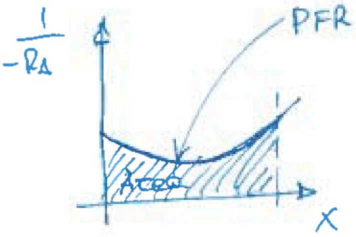
$$C_{p_j} = \text{const} \implies \boxed{T = T_{in} + \frac{-\widetilde{\Delta H_R}^{in}\, X}{\widetilde{C_p}^{in} + \widetilde{\Delta C_p}\, X} \qquad (E\,4)}$$

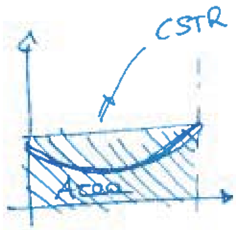
this is the same for PFR and CSTR cases

g) LEVENSPIEL'S PLOT









PFR

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

CSTR

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

PFR $\quad \text{Area} = \int_0^{X_f = 0.60} \frac{dX}{-R_A}$

X_f = is the desired final conversion

CSTR $\quad \text{Area} = \frac{1}{-R_A^f} \cdot X_f$

PFR $\begin{cases} V = \dot{F}_A^{in} \displaystyle\int_0^{X_f} \frac{dX}{-R_A} \\ T = T_{in} + \dfrac{-\widetilde{\Delta H}_R^{in} X}{\widetilde{C_p}_{in} + \Delta\widetilde{C_p} X} \end{cases}$

Alternative approach:

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

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

EX 2.

NON ISOTHERMAL CSTR at constant density

$V = 1135\,\ell$

$A + B + (M) \longrightarrow C + (M)$

M does not partecipate to the reaction (it behaves like an inert species)

$$\begin{cases} \dot{Q}_A^0 = 1360\ \ell/h \\ \dot{Q}_M^0 = 1320\ \ell/h \\ \dot{Q}_B^0 = 6600\ \ell/h \\ \dot{Q}_C^0 = 0 \end{cases} \qquad \begin{cases} \dot{F}_A^0 = 19.50\ \text{kmol}/h \\ \dot{F}_M^0 = 32.60\ \text{kmol}/h \\ \dot{F}_B^0 = 364\ \text{kmol}/h \end{cases}$$

$T_{in} = 29°C$ $\qquad A + B \xrightarrow{K} C \qquad r = K C_A^1 \cdot C_B^0 = K C_A^1 = K C_A$

$T_{MAX} = 53°C$ $\qquad \begin{cases} A = 16.96 \cdot 10^{12}\ h^{-1} \\ E = 72000\ J/mol \end{cases} \quad K = A \exp(-E/RT)$

Specific heats

$\widetilde{Cp}_A = 146\ J/mol\,K$

$\widetilde{Cp}_B = 75$ "

$\widetilde{Cp}_C = 192$ "

$\widetilde{Cp}_D = 82$ "

Formation enthalpies

$\widetilde{H}_A^0 (T_0 = 20°C) = -148918\ J/mol$

$\widetilde{H}_B^0 = -275000$ "

$\widetilde{H}_C^0 = -505360$ "

$$\begin{cases} C_A^0 = \dfrac{\dot{F}_A^0}{Q_{TOT}} = 2.11\ \dfrac{mol}{\ell} \\ C_B^0 = \dfrac{\dot{F}_B^0}{Q_{TOT}} = 39.4\ " \\ C_M^0 = \dfrac{\dot{F}_M^0}{Q_{TOT}} = 3.53\ " \end{cases}$$

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

ENERGY BALANCE $\quad X(T) = - \dfrac{\int_{T_{in}}^{T} \widetilde{Cp}_{in}\, dT}{\widetilde{\Delta H}_R(T)}$

$\tau = \dfrac{V}{Q_{TOT}} = 0.123\ h$

$$\begin{cases} C_A^0 X = K C_A^0 (1 - X)\, \tau \\ X(T) = \dfrac{-\widetilde{Cp}_{in}(T - T_{in})}{\widetilde{\Delta H}_R^0 + \widetilde{\Delta Cp}(T - T_0)} \end{cases}$$

$\widetilde{Cp}_{in} = \sum_{j}^{4} Cp_j\, \vartheta_j^0 \overset{!}{=} \widetilde{Cp}_A \vartheta_A^0 + Cp_B \vartheta_B^0 + Cp_M \vartheta_M^0$

$\widetilde{\Delta Cp} = \sum_{1}^{3}{}_j\, \widetilde{Cp}_j \nu_j = -\widetilde{Cp}_A - \widetilde{Cp}_B + \widetilde{Cp}_C$

$\widetilde{\Delta H}_R^0 = \sum_{1}^{3}{}_j\, \widetilde{H}_R^0 \nu_j \overset{!}{=} -\widetilde{H}_A^0 - \widetilde{H}_B^0 + \widetilde{H}_C^0$

$$\begin{cases} X = \dfrac{K\tau}{1+K\tau} \\[2ex] X = \dfrac{-C_p^{in}(T-T_{in})}{\widetilde{\Delta H_R^0}+\widetilde{\Delta C_p}(T-T_0)} \end{cases} \qquad \begin{cases} X = \dfrac{A\exp(-E/RT)\,\tau}{1+A\exp(-E/RT)\,\tau} \\[2ex] X = \dfrac{-C_p^{in}(T-T_{in})}{\widetilde{\Delta U_R^0}+\widetilde{\Delta C_p}(T-T_0)} \end{cases}$$

NLS of 2 equations (non linear)

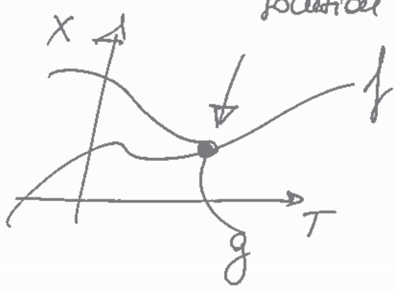
$$\underline{\underline{NLS}} \quad \begin{cases} X - \dfrac{A\exp(-E/RT)\,\mathrm{Tau}}{1+A\exp(-E/RT)\,\mathrm{Tau}} = 0 \\[2ex] X + \dfrac{C_p^{in}(T-T_{in})}{\widetilde{\Delta U_R^0}+\widetilde{\Delta C_p}(T-T_0)} = 0 \end{cases} \qquad \begin{cases} f_1(X,T) = 0 \\[2ex] f_2(X,T) = 0 \end{cases}$$

It can be written as a single NL equation in T

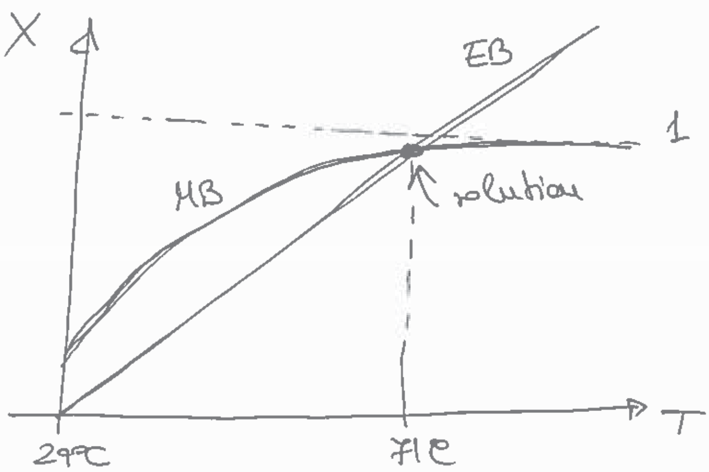
$$\frac{A\exp(-E/RT)\,\tau}{1+A\exp(-E/RT)\,\tau} = -\frac{C_p^{in}(T-T_{in})}{\widetilde{\Delta U_R^0}+\widetilde{\Delta C_p}(T-T_0)}$$

Also a graphical procedure is possible, directly on the equations of the NLS in the following form:

$$\begin{cases} X = f(T) \\ X = g(T) \end{cases}$$



SOLUTION
$T = 71.9°C$
$X = 96.1\,\%$



PRACTICAL SESSION 3

EXERCISE 3

balance equations for a PFR with heat exchange

$$\begin{cases} \dfrac{d\dot{F}_j}{dV} = R_j \\ \dot{F}_{tot}\tilde{C}p_{tot}\dfrac{dT}{dV} = U(Te-T)\dfrac{pw}{A} + \dot{Q}_R \end{cases}$$

$+$

initial conditions $\begin{cases} \dot{F}_j(V=0) = \dot{F}_j^{in} \\ T(V=0) = T^{in} \end{cases}$

Hp: $Te = \text{const}$

$A = \text{const}$ (cross section area) $\Rightarrow dV = A\,dz$

$$\begin{cases} \dfrac{d\dot{F}_j}{dz} = AR_j \\ \dot{F}_{tot}\tilde{C}p_{tot}\dfrac{dT}{dz} = U(Te-T)\cdot\dfrac{pw}{A}\cdot A + \dot{Q}_R A \end{cases}$$

$\dfrac{pw}{A} = \dfrac{\text{perimeter}}{\text{cross section area}} = \dfrac{4}{D}$

$A = \text{cross section area} = \dfrac{\pi D^2}{4}$

$\dot{Q}_R = \text{heat release} = -\widetilde{\Delta H}_R \cdot r$

Implementation in MATLAB

$X_{out} = 99.57\%$

$T_{out} = 366.72°C$

$T_{max} = 911.6°C$ @ $109.8\ m$

Analysis with constraints

$U_{min} = 75.96\ \dfrac{kcal}{m^2 h K}$

$X = 99.6\%$