# PRACTICAL SESSION 2

## EX. 1

PARALLEL REACTIONS IN A LIQUID CSTR

$$\begin{cases} A \xrightarrow{k_1} B \\ A \xrightarrow{k_2} C \end{cases}$$

B is the desired product

$k_1 = 0.5\ min^{-1}$

$k_2 = 0.1\ min^{-1}$

$Q = 4\ \frac{l}{min}$

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

SELECTIVITY

$$\sigma_B = \frac{C_B}{C_A^\circ - C_A}$$

YIELD

$$Y_B = \frac{C_B}{C_B^\circ}$$

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

$$\dot{Q}(C_A^\circ - C_A) + (-k_1 C_A - k_2 C_A) V = 0$$

$$\dot{Q}(C_A^\circ - C_A^\circ(1-X)) - C_A^\circ(1-X)(k_1+k_2) V = 0 \qquad k_1+k_2 \overset{let}{=} k$$

$$\dot{Q}X - (1-X) k V = 0 \qquad \tau \overset{let}{=} \frac{V}{Q}$$

$$\tau = \frac{1}{k} \frac{X}{1-X} \qquad \tau(95\%) = 31.67\ min$$

$$C_A^\circ - C_A - k\tau C_A \Rightarrow C_A(\tau) = \frac{C_A^\circ}{1+k\tau}$$

$$C_B^\circ - C_B + k_1 \tau C_A \Rightarrow C_B(\tau) = k_1 \tau C_A(\tau) = \frac{k_1 \tau C_A^\circ}{1+k\tau}$$

$$C_B(\tau) = k_2 \tau C_A(\tau) = \frac{k_2 \tau C_A^\circ}{1+k\tau}$$

$$\sigma_B = \frac{C_B}{C_A^\circ - C_A} = \dots = \frac{k_1}{k_{tot}} \qquad \sigma_C = \frac{k_2}{k_{tot}}$$

$$Y_B = \frac{C_B}{C_{A0}} = \frac{k_1 \tau}{1+k\tau} \qquad Y_C = \frac{k_2 \tau}{1+k\tau}$$

$$\frac{dY_B}{d\tau} = \frac{k_1(1+k\tau) - k_1 \tau k}{(1+k\tau)^2} = \frac{k_1 + k_1 k\tau - k_1 \tau k}{(1+k\tau)^2} = \frac{k_1}{(1+k\tau)^2}$$

no max

# EX. 2

PARALLEL REACTIONS IN A BATCH REACTOR (constant density)

$$\begin{cases} A \to B \\ A \to C \end{cases} \qquad \begin{cases} k_1 = 1.64\ h^{-1} \\ k_2 = 0.13\ h^{-1} \end{cases}$$

$\rho = 800\ kg/m^3$
$T = 100\,^\circ C$
$V = 1\ m^3$
$\tau_D = 1\ h$

$$\begin{cases} C_F(\tau) = C_1 \tau_D + C_2 \tau + C_3 \\ I(\tau) = 15\ \$/kg_B \end{cases}$$

$$\begin{cases} \frac{dC_A}{dt} = -k_1 C_A - k_2 C_A \\ \frac{dC_B}{dt} = k_1 C_A \\ \frac{dC_C}{dt} = k_2 C_C \end{cases}$$

$k_1 + k_2 \overset{def}{=} k$

$$\frac{dC_A}{dt} = -(k_1+k_2) C_A = -k C_A$$

$$C_A = C_A^\circ \exp(-kt)$$

$$\frac{dC_B}{dt} = k_1 C_A = k_1 C_{A0} \exp(-kt)$$

$$C_B - C_B^\circ = k_1 C_{A0} \int_0^\tau \exp(-kt)\,dt = \ldots = \frac{k_1 C_{A0}}{k}\left(1 - \exp(-k\tau)\right)$$

solution

$$\begin{cases} C_A(\tau) = C_A^\circ \exp(-k\tau) \\ C_B(\tau) = \frac{k_1 C_{A0}}{k}\left(1 - \exp(-k\tau)\right) \\ C_C(\tau) = \frac{k_2 C_{A0}}{k}\left(1 - \exp(-k\tau)\right) \end{cases}$$

$$C_A(\tau) = C_A^\circ \exp(-k\tau) \Rightarrow \ln\frac{C_A}{C_A^\circ} = -k\tau \qquad \tau = -\frac{1}{k}\ln\frac{C_A}{C_{A0}}$$

$$\tau = -\frac{1}{k}\ln\frac{C_A^\circ(1-X)}{C_A^\circ} = \ldots = -\frac{1}{k}\ln(1-X)$$

$$\tau(98\%) = -\frac{\ln(1-X)}{k} = 2.18\ h \qquad \frac{Mcycles}{day} = \frac{24}{\tau+\tau_D} = 7.52$$

$$P_{\pi_B} = C_B V \frac{Mcycles}{day} = \ldots = 155.5\ \frac{kmol}{day}$$

Optimal economical conditions

MARGIN = INCOMES - COSTS

$M = I - C$ to be maximized

$$I = I(t) = P_B \cdot Price_B \cdot MW_B =$$

$$= \frac{24\,h}{\tau + \tau_D} \cdot C_B V \cdot 15\,\frac{\#}{Tonne} \cdot MW_B$$

$$= \frac{24 \cdot V \cdot 15\,MW_B}{\tau + \tau_D} C_B = 24 \cdot V \cdot 15 \cdot MW_B \frac{C_B}{\tau + \tau_D}$$

$$I(\tau) = 24\,V \cdot 15 \cdot MW_B \cdot \frac{K_1 C_{B0}}{K} \cdot \frac{1 - \exp(-K_2 \tau)}{\tau + \tau_D} = \beta \frac{1 - \exp(-K_2 \tau)}{\tau + \tau_D}$$

$$C(\tau) = (C_1 \tau_D + C_2 \tau + C_3) \cdot \frac{\text{cycles}}{\text{day}} = \frac{24}{\tau + \tau_D} (C_1 \tau_D + C_2 \tau + C_3)$$

$$M = I - C = \beta \frac{1 - \exp(-K_2 \tau)}{\tau + \tau_D} - 24 \frac{(C_1 \tau_D + C_2 \tau + C_3)}{\tau + \tau_D}$$

$$= \frac{\beta (1 - \exp(-K_2 \tau)) - 24 (C_1 \tau_D + C_2 \tau + C_3)}{\tau + \tau_D}$$

$$\frac{dM}{d\tau} = \frac{(\beta K_1 \exp(-K_1 \tau) - 24 C_2)(\tau + \tau_D) - (\beta (1 - \exp(-K\tau)) - 24 (C_1 \tau_D + C_2 \tau + C_3))}{(\tau + \tau_D)^2}$$

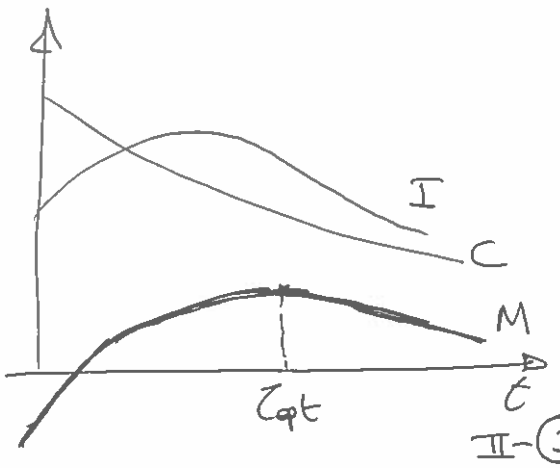
$$= 0$$

algebraic non linear equation $0 = (\beta K_1 \exp(-K_1 \tau) - 24 C_2)(\tau + \tau_D) - (\beta (1 - \exp(-K\tau)) - 24 (C_1 \tau_D + C_2 \tau + C_3))$

↳ must be solved numerically

Alternatively, the M, I and C functions can be plotted and the maximum of M can be read directly

$\tau_{opt} = 1.72\,h$



EX 3.

NON ISOTHERMAL CSTR at constant density

$V = 1135\ \ell$

$A + B + (M) \longrightarrow C + (M)$ M does not participate to the reaction (it behaves like an inert species)

$\dot{Q}_A^\circ = 1340\ \ell/h$
$\dot{Q}_H^\circ = 1320\ \ell/h$
$\dot{Q}_B^\circ = 6600\ \ell/h$
$\dot{Q}_C^\circ = 0$

$\dot{F}_A^\circ = 18.50$ kmol/h
$\dot{F}_H^\circ = 32.60$ kmol/h
$\dot{F}_B^\circ = 364$ kmol/h

$T_{IN} = 29°C$

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

$T_{MAX} = 53°C$

$A = 16.96 \cdot 10^{12}\ h^{-1}$
$E = 72000\ J/mol$
$K = A \exp(-E/RT)$

Specific heats

$\widetilde{c_{pA}} = 146\ J/mol\,K$
$\widetilde{c_{pD}} = 75$ "
$\widetilde{c_{pC}} = 192$ "
$\widetilde{c_{pD}} = 82$ "

Formation enthalpies

$\widetilde{H_A^\circ}(T_0 = 20°C) = -148918\ J/mol$
$\widetilde{H_B^\circ} = -275000$ "
$\widetilde{H_C^\circ} = -505360$ "

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

ENERGY BALANCE $\quad X(T) = -\dfrac{\int_{T_{IN}}^{T} \widetilde{c_{pIN}}\, dT}{\widetilde{\Delta H_R}(T)}$

$C_A^\circ = \dfrac{\dot{F}_A^\circ}{Q_{TOT}} = 2.11\ \dfrac{mol}{\ell}$
$C_B^\circ = \dfrac{\dot{F}_B^\circ}{Q_{TOT}} = 39.9$ "
$C_H^\circ = \dfrac{\dot{F}_H^\circ}{Q_{TOT}} = 3.53$ "

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

$C_A^\circ X = K C_A^\circ (1 - X)\,\tau$

$X(T) = \dfrac{-\widetilde{c_{pIN}}(T - T_{IN})}{\widetilde{\Delta H_R^\circ} + \widetilde{\Delta c_p}(T - T_0)}$

$\widetilde{c_{pIN}} = \sum_j^4 c_{pj}\,\vartheta_j^\circ =$
$= \widetilde{c_{pA}}\vartheta_A^\circ + c_{pB}\vartheta_B^\circ + c_{pH}\vartheta_H^\circ$

$\widetilde{\Delta c_p} = \sum_j^3 \widetilde{c_{pj}}\,\nu_j =$
$= -\widetilde{c_{pA}} - \widetilde{c_{pB}} + \widetilde{c_{pC}}$

$\widetilde{\Delta H_R^\circ} = \sum_j^3 \widetilde{H_R^\circ}\,\nu_j =$
$= -\widetilde{H_A^\circ} - \widetilde{H_B^\circ} + \widetilde{H_C^\circ}$

$$\begin{cases} X = \dfrac{K\tau}{1+K\tau} \\ X = \dfrac{-C_p^{im}(T-T_{im})}{\Delta H_R^\circ + \Delta C_p (T-T_0)} \end{cases} \qquad \begin{cases} X = \dfrac{A\exp(-E/RT)\,\tau}{1+A\exp(-E/RT)\,\tau} \\ X = \dfrac{-C_p^{im}(T-T_{im})}{\Delta H_R^\circ + \Delta C_p (T-T_0)} \end{cases}$$

NLS of 2 equations (non linear)

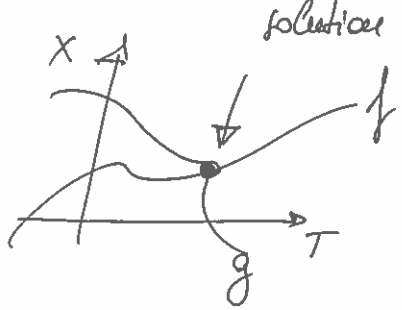
$$\underline{\underline{NLS}} \quad \begin{cases} X - \dfrac{A\exp(-E/RT)\,\text{Tau}}{1+A\exp(-E/RT)\,\text{Tau}} = 0 \\ X + \dfrac{C_p^{im}(T-T_{im})}{\Delta H_R^\circ + \Delta C_p (T-T_0)} = 0 \end{cases} \qquad \begin{cases} f_1(X,T) = 0 \\ f_2(X,T) = 0 \end{cases}$$

It can be written as a simple NL equation in $T$

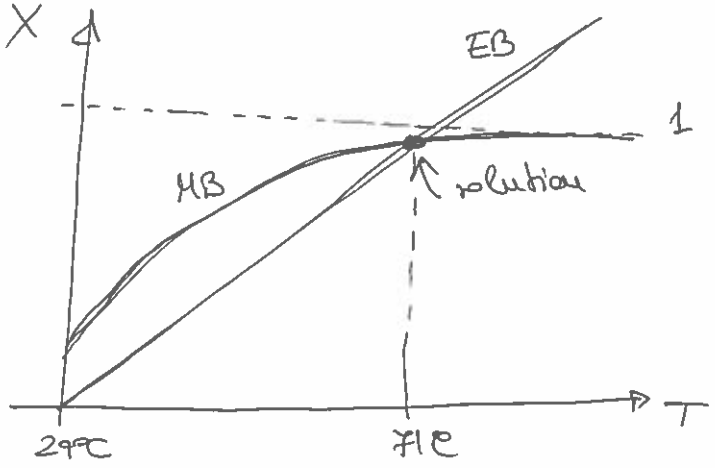
$$\frac{A\exp(-E/RT)\,\tau}{1+A\exp(-E/RT)\,\tau} = -\frac{C_p^{im}(T-T_{im})}{\Delta H_R^\circ + \Delta C_p (T-T_0)}$$

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
$T = 71.9°C$
$X = 96.1\%$



## EX 4

PLUG FLOW REACTOR with constant density

REACTIONS IN SERIES $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

exactly same exercise PC 1 – 6

solutions
$$\begin{cases} C_A(\tau) = C_A^0 \exp(-k_1 \tau) \\ C_B(\tau) = \dfrac{k_1 C_A^0}{k_2 - k_1}\left(\exp(-k_1\tau) - \exp(-k_2\tau)\right) \\ C_C(\tau) = C_A^0 - C_A(\tau) - C_B(\tau) \end{cases}$$

$$\begin{cases} k_1 = 1.99\ s^{-1} \\ k_2 = 1.86\ s^{-1} \end{cases} \qquad C_{A0} = 35.7 \frac{mol}{m^3}$$

$$\tau = 3.23\ s \qquad Y_C = \frac{C_C(\tau)}{C_A^0(\tau)} = 96.8\ \%$$

## EX 5

Same exercise above, only different numbers

i) same analytical solution

ii) same MATLAB code

iii) quasi-steady state hypothesis for species B

If we look at the kinetic constants, we see that the second reaction is more than 1000 times FASTER than the first one

$k_1 = 0.57\ s^{-1}$

$k_2 = 1114\ s^{-1}$

$\frac{k_2}{k_1} \gg 1$ this means that B disappears as soon as it is produced

We can assume it is in quasi steady state

$$\frac{k_2}{k_1} \gg 1 \Rightarrow \frac{dC_B}{d\tau} \sim 0 \Rightarrow k_1 C_A(\tau) = k_2 C_B(\tau)$$

$$\Rightarrow C_B(\tau) = \frac{k_1}{k_2} C_A^0 \exp(-k_1 \tau)$$

This the problem is simplified because we have $C_B(\tau)$ explicitly and we do not have to solve the corresponding ODE equation

$$\begin{cases} \dfrac{dC_A}{d\tau} = -K_1 C_A \\ \dfrac{dC_C}{d\tau} = K_2 \cdot C_B = \dfrac{K_2 K_1}{K_2} C_A^\circ \exp(-K_1\tau) \end{cases}$$

$$\begin{cases} \dfrac{dC_A}{d\tau} = -K_1 C_A \\ \dfrac{dC_C}{d\tau} = K_1 C_A^\circ \exp(-K_1\tau) \end{cases}$$

2 equations

→ it is interesting to observe that $K_2$ does not appear explicitly

Indeed, if $K_2 \gg K_1$, the RDS (RATE DETERMING STEP) is the first reaction

$$\begin{cases} C_A(\tau) = C_A^\circ \exp(-K_1\tau) \\ C_C(\tau) = C_A^\circ (1 - \exp(-K_1\tau)) \\ C_B(\tau) = \dfrac{K_1}{K_2} C_A^\circ \exp(-K_1\tau) \end{cases}$$

← since $\frac{K_1}{K_2} \ll 1$ it is always expected be very small