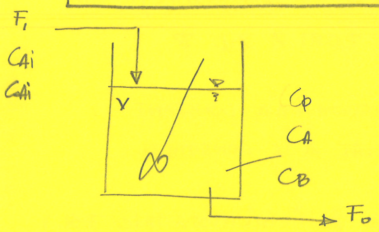
CSTR 'first' order irreversible reaction



Assume that two chemical species A and B are in a solvent feedstream entering a liquid phase chemical reactor

- the reactor is maintained at constant temperature
- The two species react to form a third species P

WE ARE INTERESTED IN THE REACTOR CONCENTRATION AS A FUNCTION OF TIME

Total mass balance

$$\frac{dM}{dt} = \frac{dV\rho_o}{dt} = F_i\rho_i - F_o\rho_o$$

V/t, M/V, V/t, M/V

⤳ WE CAN ASSUME THAT THE LIQUID PHASE DENSITY IS NOT A FUNCTION OF THE CONCENTRATION

$$\rho_i = \rho_o \rightsquigarrow \boxed{\frac{dV}{dt} = F_i - F_o}$$

$$\frac{dM}{dt} = \rho(F_i - F_o)$$

M/V

Component mass balance

let C_A, C_B and C_P the molar concentrations of species A, B, P

Assume the stoichiometric equation $\boxed{A + 2B \longrightarrow P}$

Assuming that there is no component P in the feed, we have

$$* \quad \frac{dVC_A}{dt} = F_iC_{Ai} - F_oC_A + Vr_A$$

V M/V, V/t, M/V

$$* \quad \frac{dVC_B}{dt} = F_iC_{Bi} - F_oC_B + Vr_B$$

V/t, M/V, V M/Vt

$$* \quad \frac{dVC_P}{dt} = -F_oC_P + Vr_P$$

$\boxed{F_iC_{Pi} = 0}$

r_A, r_B and r_P ARE GENERATION RATES OF SPECIES A, B AND P PER UNIT VOLUME

C_{Ai} AND C_{Bi} ARE INLET CONCENTRATIONS OF A AND B

$$r_A \; \frac{\text{moles of } A}{\text{volume time}}$$

WE CAN ASSUME THAT THE RATE OF REACTION OF A (PER UNIT VOLUME) IS 2nd ORDER AND A FUNCTION OF THE CONCENTRATION OF BOTH A AND B

$$* \quad r_A = -KC_AC_B$$

⤳ K is THE REACTION RATE CONSTANT

(-) INDICATES THAT A IS CONSUMED

AS ONE MOLE OF A REACTS WITH TWO MOLES OF B (STOICHIOMETRIC EQ.) TO PRODUCE ONE MOLE OF P, WE HAVE

RATE OF GENERATION OF B (PER UNIT VOLUME)

$$* \quad r_B = -2KC_AC_B$$

RATE OF GENERATION OF P (PER UNIT VOLUME)

$$* \quad r_P = KC_AC_B$$

Thus, we can write

$$* \quad dVC_A/dt = V\,dC_A/dt + C_A\,dV/dt = F_iC_{Ai} - F_oC_A + V(-KC_AC_B)$$

$$\rightsquigarrow \frac{dC_A}{dt} = \frac{F_iC_{Ai} - F_oC_A - VKC_AC_B}{V} - \frac{C_A}{V}\frac{dV}{dt}$$

WITH $dV/dt = F_i - F_o$

$$\rightsquigarrow \frac{dC_A}{dt} = \frac{F_iC_{Ai}}{V} - \cancel{\frac{F_oC_A}{V}} - KC_AC_B - \frac{C_A}{V}F_i + \cancel{\frac{C_A}{V}F_o}$$

$$= F_i/V\,(C_{Ai} - C_A) - KC_AC_B$$

SIMILARLY FOR B AND P

$$* \quad \frac{dC_B}{dt} = \frac{F_i}{V}(C_{Bi} - C_B) - 2KC_AC_B$$

$$* \quad \frac{dC_P}{dt} = -\frac{F_i}{V}C_P + KC_AC_B$$

AND, OF COURSE, WE HAVE

$$* \quad \frac{dV}{dt} = F_i - F_o$$

The model consists of 4 first order differential eqn.

- 4 STATE VARIABLES

To solve the equations, initial conditions must be provided

$V(0)$, $C_A(0)$, $C_B(0)$, $C_P(0)$

AND THE INPUTS AS FUNCTIONS OF TIME

$F_i(t)$, $C_{Ai}(t)$, $C_{Bi}(t)$

The reactor model has four 1st order differential equations

$$\frac{dC_A}{dt} = \frac{F_i}{V}(C_{Ai} - C_A) - K C_A C_B$$

$$\frac{dC_B}{dt} = \frac{F_i}{V}(C_{Bi} - C_B) - 2K C_A C_B$$

$$\frac{dC_P}{dt} = -\frac{F_i}{V} C_P + K C_A C_B$$

$$\frac{dV}{dt} = F_i - F_o$$

It's possible to formulate some symplifying assumptions to to make the analysis easier

→ CONSTANT VOLUME

$$\boxed{\frac{dV}{dt} \approx 0}$$

THIS IS THE SIMPLEST AND OFTEN MOST REALISTIC ASSUMPTION

It's also possible to assume that one of reactant is maintained in large excess, thus constant

→ IF SPECIES B IS IN LARGE EXCESS, C_B IS NEARLY CONSTANT

* $\boxed{dC_B/dt \approx 0}$
* $r_A = -K C_A C_B \approx -k_1 C_A$ WITH $k_1 = C_B K$

The resulting model consists of only two states

$$\frac{dC_A}{dt} = \frac{F_i}{V}(C_{Ai} - C_A) - k_1 C_A$$

$$\frac{dC_P}{dt} = \underbrace{\frac{F_i}{V}(C_{Pi} - C_P)}_{=0} + k_1 C_A$$

$=0$ IF WE ASSUME NO P IN THE FEED

The dynamics of A also decoupled

Models can contain a large number of parameters and variables

→ THERE MAY BE DIFFERENCES IN VALUE BY ORDERS OF MAGNITUDE

It is often desirable for analysis purposes to develop models consisting of dimensionless parameters and variables

CONSIDER AS AN EXAMPLE $\frac{dC_A}{dt} = \frac{F}{V}(C_{Ai} - C_A) - kC_A$

IT SEEMS NATURAL TO CONSIDER A SCALED CONCENTRATION $x = C_A/C_{A0}$ WHERE C_{A0} IS SOME NOMINAL, FOR EXAMPLE STEADY STATE CONCENTR.

$$\frac{d\,C_A/C_{A0}}{dt} = \frac{F}{V}\left(\frac{C_{Ai}}{C_{A0}} - \frac{C_A}{C_{A0}}\right) - k\frac{C_A}{C_{A0}}$$

$$\rightarrow \frac{dx}{dt} = \frac{F}{V}(x_i - x) - kx, \qquad \text{with } x_i = \frac{C_{Ai}}{C_{A0}}$$

$$= \frac{F}{V}x_i - x\left(\frac{F}{V} + k\right)$$

IT IS ALSO NATURAL TO CHOOSE A SCALED TIME $\tau = t/t^*$ WITH t^* SOME PARAMETER TO BE DETERMINED

FROM $dt = t^* d\tau$ WE HAVE

$$\frac{dx}{d\tau \cdot t^*} = \frac{F}{V}x_i - x\left(\frac{F}{V} + k\right)$$

THAT IS $\frac{dx}{d\tau} = \frac{F}{V}t\,x_i - x\,t\left(\frac{F}{V} + k\right)$

Damkholer number

IF WE LET t BE $\frac{V}{F}$, WE CAN WRITE $\frac{dx}{d\tau} = x_i - x\left(1 + \overbrace{k\frac{V}{F}}\right)$

Assuming that the feed concentration is maintained constant $x_f = 1$ and letting $\alpha = Vk/F$, we have

$$\frac{dx}{dt} = 1 - x + \alpha x$$

a single parameter

CONSIDER THE MODELLING EQUATIONS

$$\frac{dV}{dt} = F_i - F_o$$

$$\frac{dC_A}{dt} = \frac{F_i}{V}(C_{Ai} - C_A) - KC_AC_B$$

$$\frac{dC_B}{dt} = \frac{F_i}{V}(C_{Bi} - C_B) - 2KC_AC_B$$

$$\frac{dC_P}{dt} = -\frac{F_i}{V}C_P - KC_AC_B$$

- WE HAVE 4 STATE VARIABLES

$x = [V, C_A, C_B, C_P]$

- WE HAVE 4 INPUT VARIABLES

$u = [F_i, F, C_{Ai}, C_{Bi}]$

- 1 PARAMETER $\theta = [K]$

WE CAN WRITE

$$\begin{bmatrix} \dot{V} \\ \dot{C_A} \\ \dot{C_B} \\ \dot{C_P} \end{bmatrix} = \begin{bmatrix} F_i - F \\ F_i/V(C_{Ai} - C_A) - KC_AC_B \\ F_i/V(C_{Bi} - C_B) - 2KC_AC_B \\ -F_i/V C_P + KC_AC_B \end{bmatrix}$$

OR

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \\ \dot{x}_4 \end{bmatrix} = \begin{bmatrix} u_1 - u_2 \\ u_1/x_1(u_3 - x_2) - p_1x_2x_3 \\ u_1/x_1(u_4 - x_3) - 2p_1x_2x_3 \\ -u_1/x_1(x_4) + p_1x_2x_3 \end{bmatrix} = \begin{bmatrix} f_1(x,u|p) \\ f_2(x,u|p) \\ f_3(x,u|p) \\ f_4(x,u|p) \end{bmatrix}$$

$$
\begin{aligned}
d(x_1 - x_s)/dt &= \\
d(x_2 - x_2)/dt &= \\
&\vdots \\
d(x_n - x_{ns})/dt &=
\end{aligned}
\begin{bmatrix}
\partial f_1/\partial x_1|_{ss} & \partial f_1/\partial x_2|_{ss} & \cdots & \partial f_1/\partial x_n|_{ss} \\
\partial f_2/\partial x_1|_{ss} & \partial f_2/\partial x_2|_{ss} & \cdots & \partial f_2/\partial x_n|_{ss} \\
\vdots & \vdots & & \vdots
\end{bmatrix}
$$

$$\frac{\partial f_1}{\partial x_1} = 0 \ast \frac{\partial f_1}{\partial x_2} = 0 \ast \frac{\partial f_1}{\partial x_3} = 0 \ast \frac{\partial f_1}{\partial x_4} = 0$$

$$\frac{\partial f_2}{\partial x_1} = -\frac{u_1(u_3 - x_2)}{x_1^2} \ast \frac{\partial f_2}{\partial x_2} = -\frac{u_1}{x_1} - p_1 x_3 \ast \frac{\partial f_2}{\partial x_3} = -p_1 x_2 \ast \frac{\partial f_2}{\partial x_4} = 0$$

$$\frac{\partial f_3}{\partial x_1} = -\frac{u_1(u_4 - x_3)}{x_1^2} \ast \frac{\partial f_3}{\partial x_2} = -2p_1 x_3 \ast \frac{\partial f_3}{\partial x_3} = -\frac{u_1}{x_1} - 2p_1 x_2$$

$$\partial f_3/\partial x_4 = \frac{u_1}{x_1}$$

$$\frac{\partial f_4}{\partial x_1} = \frac{+u_1 x_4}{x_1^2} \qquad \frac{\partial f_4}{\partial x_2} = p_1 \qquad \frac{\partial f_4}{\partial x_3} = p_1 x_2 \qquad \frac{\partial f_4}{\partial x_4} = -u_1/x_1$$

$$
\begin{bmatrix}
0 & 0 & 0 & 0 \\
-\frac{u_1(u_3 - x_2)}{x_1^2} & -\frac{u_1}{x_1} - p_1 x_3 & -p_1 x_2 & 0 \\
-\frac{u_1(u_4 - x_3)}{x_1^2} & -2p_1 x_3 & -\frac{u_1}{x_1} - 2p_1 x_2 & u_1/x_1 \\
\frac{u_1 x_4}{x_1^2} & p_1 & p_1 x_2 & -u_1/x_1
\end{bmatrix}
$$

A

$$\frac{\partial f_1}{\partial u_1} = 1 \qquad \frac{\partial f_1}{\partial u_2} = -1 \qquad \frac{\partial f_1}{\partial u_3} = 0 \qquad \frac{\partial f_1}{\partial u_4} = 0$$

$$\frac{\partial f_2}{\partial u_1} = \frac{1}{x_1}(u_3 - x_2) \qquad \frac{\partial f_2}{\partial u_2} = 0 \qquad \frac{\partial f_2}{\partial u_3} = \frac{u_1}{x_1} \qquad \frac{\partial f_2}{\partial u_4} = 0$$

$$\frac{\partial f_3}{\partial u_3} = \frac{1}{x_1}(u_4 - x_3) \qquad \frac{\partial f_3}{\partial u_2} = 0 \qquad \frac{\partial f_3}{\partial u_3} = 0 \qquad \frac{\partial f_4}{\partial u_4} = \frac{u_1}{x_1}$$

$$\frac{\partial f_4}{\partial u_1} = -\frac{x_4}{x_1} \qquad \frac{\partial f_4}{\partial u_2} = 0 \qquad \frac{\partial f_4}{\partial u_3} = 0 \qquad \frac{\partial f_4}{\partial u_4} = 0$$

$$\underbrace{\begin{bmatrix} 1 & -1 & 0 & 0 \\ 1/x_1 (u_3 - x_2) & 0 & u_1/x_1 & 0 \\ 1/x_1 (u_4 - x_3) & 0 & 0 & u_1/x_1 \\ -x_4/x_1 & 0 & 0 & 0 \end{bmatrix}}_{B}$$

$$\underbrace{\begin{bmatrix} d(x_1 - x_1^s)/dt \\ d(x_2 - x_2^s)/dt \\ d(x_3 - x_3^s)/dt \\ d(x_4 - x_4^s)/dt \end{bmatrix}}_{\dot{x}'} = A \underbrace{\begin{bmatrix} x_1 - x_1^s \\ x_2 - x_2^s \\ x_3 - x_3^s \\ x_4 - x_4^s \end{bmatrix}}_{x'} + B \begin{bmatrix} u_1 - u_1^s \\ u_2 - u_2^s \\ u_3 - u_3^s \\ u_4 - u_4^s \end{bmatrix}$$