

# Chemical Reaction Engineering

## Lecture 7

# Design structure for isothermal reactors

Mole balance equations



Rate laws  
*rate vs concentration*



Stoichiometry  
*(to find concentration vs X)*



Combine and Evaluate

## 1. MOLE BALANCES

PFR  

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

CSTR  

$$V = \frac{F_{A0}X}{-r_A}$$

BATCH  

$$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$$

## 2. RATE LAWS

$$-r_A = kC_A$$

$$-r_A = \frac{kC_A}{1 + K_A C_A}$$

$$-r_A = k \left[ C_A - \frac{C_B C_C}{K_e} \right]$$

## 3. STOICHIOMETRY

FLOW  

$$C_A = \frac{F_A}{v}$$

$$F_A = F_{A0}(1 - X)$$

BATCH  

$$C_A = \frac{N_A}{V}$$

$$N_A = N_{A0}(1 - X)$$

LIQUID  
Constant flow rate

$$v = v_0$$

IDEAL GAS  
Variable flow rate

$$v = v_0 (1 + \epsilon X) \frac{P_0 T}{P T_0}$$

IDEAL GAS  
Variable volume

$$V = V_0 (1 + \epsilon X) \frac{P_0 T}{P T_0}$$

LIQUID OR GAS  
Constant volume

$$V = V_0$$

$$C_A = C_{A0}(1 - X)$$

$$C_A = \frac{C_{A0}(1 - X) \frac{P}{P_0} \frac{T_0}{T}}{(1 + \epsilon X)}$$

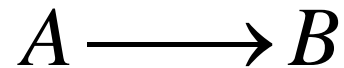
$$C_A = \frac{C_{A0}(1 - X) \frac{P}{P_0} \frac{T_0}{T}}{(1 + \epsilon X)}$$

$$C_A = C_{A0}(1 - X)$$

## 4. COMBINE (First Order Gas-Phase Reaction in a PFR)

# Example: batch operation

- Calculate time necessary to achieve given conversion  $X$  for irreversible 2<sup>nd</sup> order reaction run in a batch reactor.



- Mole balance:  $N_{A0} \frac{dX}{dt} = -r_A V_0$
- Rate law:  $-r_A = kC_A^2$
- Stoichiometry:  $C_A = C_{A0}(1 - X)$
- Combining:  $\frac{dX}{dt} = kC_{A0}(1 - X)^2$   
$$t = \frac{1}{kC_{A0}} \frac{X}{(1 - X)}$$

# Typical reaction times

- 1<sup>st</sup> order reaction: 
$$t = \frac{1}{k} \ln \frac{1}{(1-X)}$$
- 2<sup>nd</sup> order reaction: 
$$t = \frac{1}{kC_{A0}} \frac{X}{(1-X)}$$

Order of magnitude time to achieve 90% conversion in a batch reactor:

| <i>Reaction Time</i><br>$t_R$ | <i>First-Order</i><br>$k \text{ (s}^{-1}\text{)}$ | <i>Second-Order</i><br>$kC_{A0} \text{ (s}^{-1}\text{)}$ |
|-------------------------------|---|--|
| Hours                         | $10^{-4}$   | $10^{-3}$  |
| Minutes                       | $10^{-2}$   | $10^{-1}$  |
| Seconds                       | 1   | 10   |
| Milliseconds                  | 1000  | 10,000   |

| <i>Activity</i>                                  | <i>Time (h)</i> |
|--|-----------------|
| 1. Charge feed to the reactor and agitate, $t_f$ | 1.5–3.0         |
| 2. Heat to reaction temperature, $t_e$           | 0.2–2.0         |
| 3. Carry out reaction, $t_R$                     | (varies)        |
| 4. Empty and clean reactor, $t_c$                | 0.5–1.0         |
| Total time excluding reaction                    | 3.0–6.0         |

# Typical reaction times

Typical cycle time in a batch reactor:

| <i>Activity</i>                                  | <i>Time (h)</i> |
|--|-----------------|
| 1. Charge feed to the reactor and agitate, $t_f$ | 1.5–3.0         |
| 2. Heat to reaction temperature, $t_e$           | 0.2–2.0         |
| 3. Carry out reaction, $t_R$                     | (varies)        |
| 4. Empty and clean reactor, $t_c$                | 0.5–1.0         |
| Total time excluding reaction                    | 3.0–6.0         |

# CSTR

CSTR with a liquid-phase reaction:

- single CSTR mole balance:

design equation: 
$$V = \frac{F_{A0} X}{(-r_A)_{exit}}$$

space time: 
$$\tau = \frac{V}{v_0} = \frac{C_{A0} X}{(-r_A)_{exit}}$$

- rate law (1<sup>st</sup> order) 
$$-r_A = kC_A$$

- Stoichiometry: 
$$C_A = C_{A0} (1 - X)$$

# CSTR

$$V = \frac{F_{A0} X}{(-r_A)_{exit}} \quad \tau = \frac{V}{v_0} = \frac{C_{A0} X}{(-r_A)_{exit}}$$

$$-r_A = kC_A$$

$$C_A = C_{A0} (1 - X)$$

- Combining

$$\tau = \frac{1}{k} \left( \frac{X}{1 - X} \right)$$

$$X = \frac{\tau k}{1 + \tau k}$$

$$C_A = \frac{C_{A0}}{1 + \tau k}$$

Dahmköhler number

# CSTR

- **Dahmköhler number** is a ratio of the rate of the reaction at the entrance to the rate of the convective transport.

$$Da = \frac{-r_A V}{F_{A0}}$$

- For a 1<sup>st</sup> order irreversible reaction:

$$Da = \frac{-r_A V}{F_{A0}} = \frac{kC_{A0} V}{v_0 C_{A0}} = \tau k$$

- For a 2<sup>nd</sup> order irreversible reaction:

$$Da = \frac{-r_A V}{F_{A0}} = \frac{kC_{A0}^2 V}{v_0 C_{A0}} = \tau k C_{A0}$$

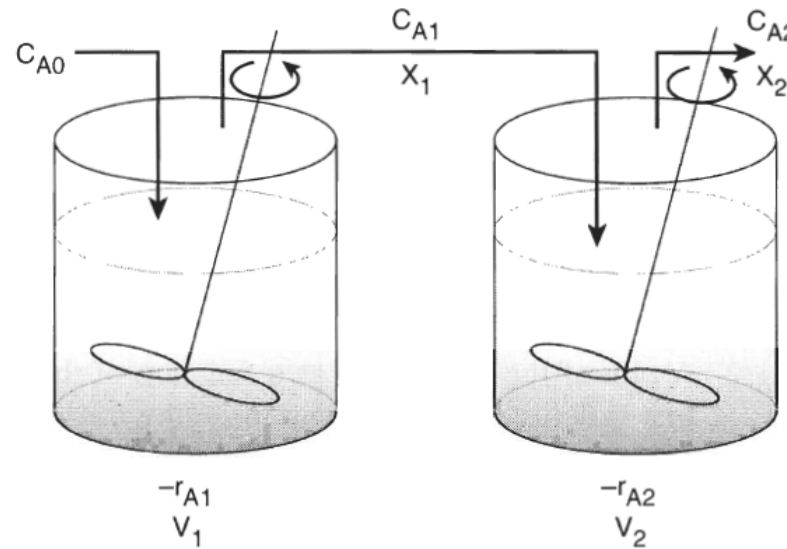
- Gives a quick estimate of the degree of conversion

$$Da < 0.1 \quad \Rightarrow \quad X < 10\%$$

$$Da > 10 \quad \Rightarrow \quad X > 90\%$$



# CSTR in Series



- concentration flowing to the 2<sup>nd</sup> reactor  $C_{A1} = \frac{C_{A0}}{1 + \tau_1 k_1}$
- design equation the 2<sup>nd</sup> reactor  $V = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{v_0 (C_{A1} - C_{A2})}{k_2 C_{A2}}$
- so,  $C_{A2} = \frac{C_{A0}}{(1 + \tau_1 k_1)(1 + \tau_2 k_2)}$
- if the reactors have the same size and temperature:  $C_{A2} = \frac{C_{A0}}{(1 + \tau k)^2}$

# CSTR in Series

- in terms of Damköler number

$$C_{A2} = \frac{C_{A0}}{(1 + Da)^2}$$

- for n reactors

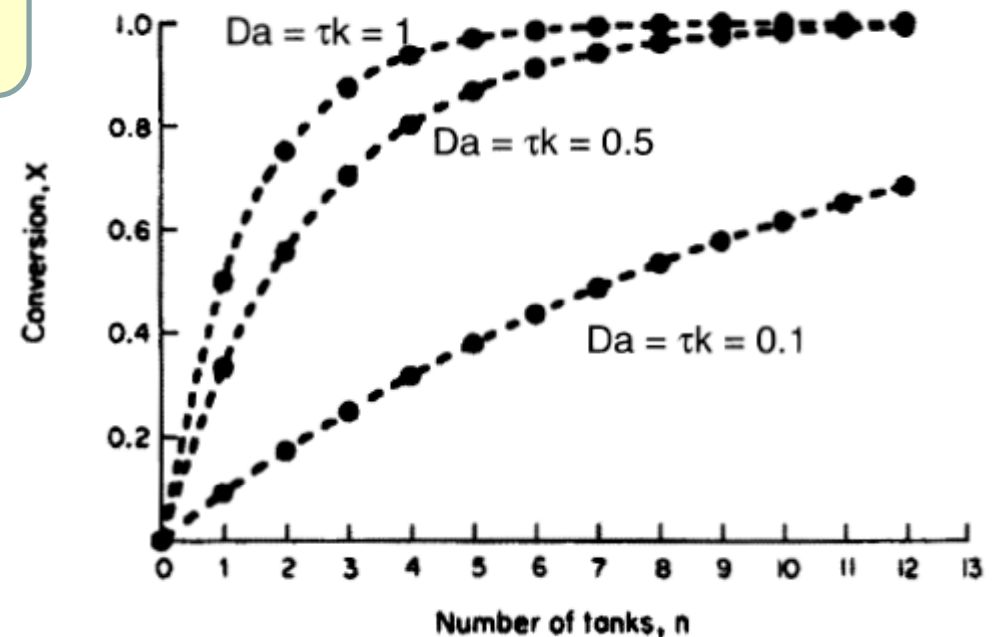
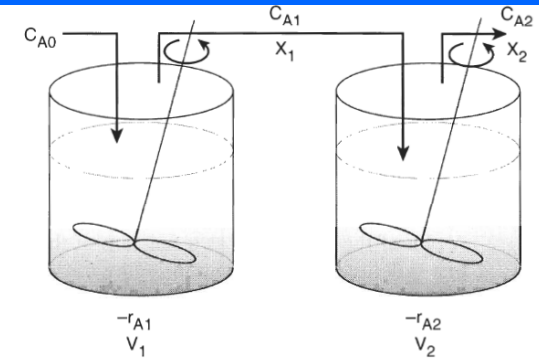
$$C_{A2} = \frac{C_{A0}}{(1 + Da)^n}$$

- conversion:

$$C_{A0}(1 - X) = \frac{C_{A0}}{(1 + Da)^n}$$

$$X = 1 - \frac{1}{(1 + Da)^n}$$

- when the Damköler number is above 1, a high conversion is achieved in few reactors

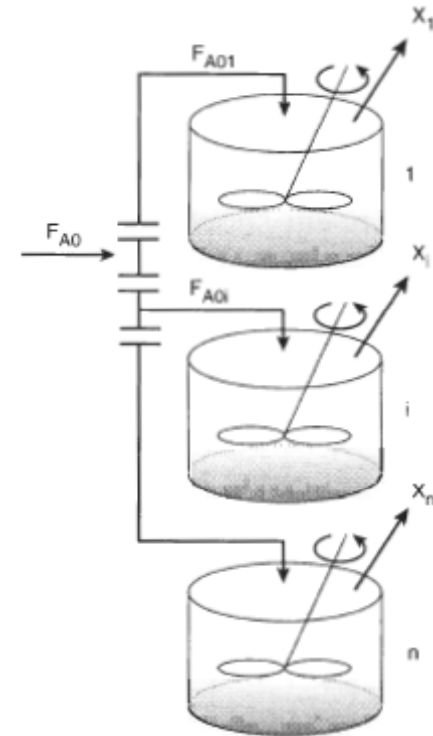


# CSTRs in parallel

- Let's consider identical reactors with the feed equally distributed, than conversion factors and the reaction rates are the same

$$V_i = F_{A0i} \left( \frac{X}{-r_A} \right) \quad \text{or} \quad \frac{V}{n} = \frac{F_{A0}}{n} \left( \frac{X}{-r_A} \right)$$

- So, the situation is identical to a single reactor with the size equal to the total volume of all reactors.



# Tubular reactors: liquid phase

- Design equation  $F_{A0} \frac{dX}{dV} = -r_A$

- in the absence of pressure drop  $V = F_{A0} \int_0^X \frac{dX}{-r_A}$

- Let's consider a 2<sup>nd</sup> order reaction  $A \rightarrow \text{products}$

- rate law:  $-r_A = kC_A^2$

- stoichiometry:  $C_A = C_{A0}(1 - X)$

$$V = \frac{F_{A0}}{kC_{A0}^2} \int_0^X \frac{dX}{(1 - X)^2} = \frac{v_0}{kC_{A0}} \frac{X}{(1 - X)}$$

$$X = \frac{\tau k C_{A0}}{1 + \tau k C_{A0}} = \frac{\text{Da}_2}{1 + \text{Da}_2}$$

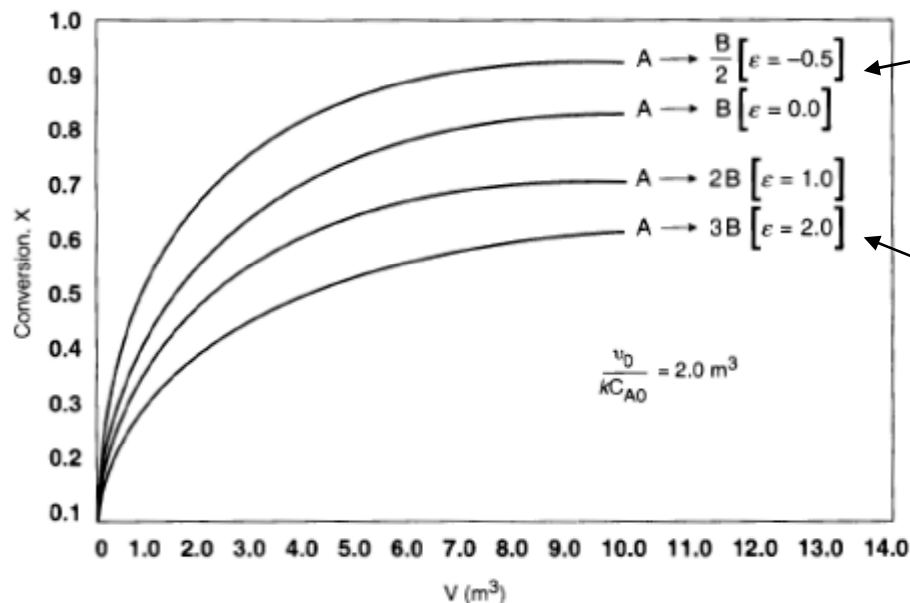
# Tubular reactors: gas phase

- For T, P constant, the concentration is a function of conversion

- stoichiometry: 
$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\epsilon X)} = \frac{C_{A0}(1-X)}{(1+\epsilon X)}$$

- rate law: 
$$-r_A = kC_A^2$$

- combining: 
$$V = \frac{F_{A0}}{kC_{A0}^2} \int_0^X \frac{(1+\epsilon X)^2 dX}{(1-X)^2}$$



if  $\epsilon < 0$ : i.e. number of moles  $\downarrow$ :  
volumetric flow rate  $\downarrow$ , **the residence time**  $\uparrow$ , **so X**  $\uparrow$

if  $\epsilon > 0$ : i.e. number of moles  $\uparrow$ :  
flow rate  $\uparrow$ , **the residence time**  $\downarrow$ , **so X**  $\downarrow$

# Pressure drop in Reactors

- in the liquid phase pressure drop doesn't lead to any significant volume and therefore concentration changes can be neglected.
- in the gas phase can be an important factor

volumetric flow:  $v = v_0 (1 + \varepsilon X) \frac{P_0 T}{P T_0}$

$$C_j = \frac{F_j}{v} = \frac{F_{A0} (\Theta_j + \nu_j X)}{v_0 (1 + \varepsilon X) \frac{P_0 T}{P T_0}} = \frac{C_{A0} (\Theta_j + \nu_j X)}{(1 + \varepsilon X)} \frac{P T_0}{P_0 T}$$

# Pressure drop in Reactors

- to account for a pressure drop we have to use differential form of the equation

$$F_{A0} \frac{dX}{dW} = -r_A$$

- rate law:  $-r_A = kC_A^2$        $2A \rightarrow B + C$

- stoichiometry:  $C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} \frac{P}{P_0} \frac{T_0}{T}$

$$r_A = k \left[ \frac{C_{A0}(1-X)}{(1+\varepsilon X)} \frac{P}{P_0} \frac{T_0}{T} \right]^2$$

- for isothermal operation:

$$\frac{dX}{dW} = \frac{1}{F_{A0}} k \left[ \frac{C_{A0}(1-X)}{(1+\varepsilon X)} \frac{P}{P_0} \frac{T_0}{T} \right]^2 = \frac{kC_{A0}}{v_0} \left[ \frac{(1-X)}{(1+\varepsilon X)} \frac{P}{P_0} \right]^2$$

# Ergun equation

- pressure drop in a packed porous bed is described by Ergun equation:

$$\frac{dP}{dz} = -\frac{G}{\rho g_c D_p} \left( \frac{1-\phi}{\phi^3} \right) \left[ \underbrace{\frac{150(1-\phi)\mu}{D_p}}_{\text{dominant for laminar flow}} + \underbrace{1.75G}_{\text{dominant for turbulent flow}} \right]$$

dominant for laminar flow

dominant for turbulent flow

$\phi$  porosity=volume of void/total volume

$D_p$  particle diameter

$G = \rho u$  superficial mass velocity,  $\rho$  – gas density

$g_c$  conversion factor, =1 for metric system

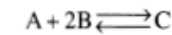
- in terms of catalyst weight:  $W = (1-\phi)Az\rho_c$



# Mole Balance in terms of Concentration and Molar Flow Rates

- Working in terms of **number of moles** ( $N_A$ ,  $N_B, \dots$ ) or **molar flow rates** ( $F_A$ ,  $F_B$  etc) rather than conversion could be more convenient at some instances (e.g. multiple reactions and membrane reactors)
- The difference in calculation: we will write mole balance for **each and every species** in the reactor

# Isothermal reaction design algorithm



Mole balance for every species

Mole Balance

① Write mole balance on each species<sup>7</sup>

$$\text{e.g., } \frac{dF_A}{dV} = r_A, \quad \frac{dF_B}{dV} = r_B, \quad \frac{dF_C}{dV} = r_C$$

Rate law in terms of concentration

Rate Law

② Write rate law in terms of concentration

$$\text{e.g., } -r_A = k_A \left( C_A C_B^2 - \frac{C_C}{K_C} \right)$$

Rate of reactions for every species from stoichiometry

Stoichiometry

③ Relate the rates of reaction of each species to one another

$$\text{e.g., } r_B = 2r_A, \quad r_C = -r_A$$

Concentration for every species

Stoichiometry

④ (a) Write the concentrations in terms of molar flow rates for isothermal *gas-phase* reactions

$$\text{e.g., } C_A = C_{T0} \frac{F_A}{F_T} \frac{P}{P_0}, \quad C_B = C_{T0} \frac{F_B}{F_T} \frac{P}{P_0}$$

$$\text{with } F_T = F_A + F_B + F_C$$

(b) For *liquid-phase* reactions use concentration, e.g.,  $C_A, C_B$

Calculate pressure drop if necessary

Pressure Drop

⑤ Write the *gas-phase* pressure drop term in terms of molar flow rates

$$\frac{dy}{dW} = -\frac{\alpha}{2y} \frac{F_T}{F_{T0}}, \quad \text{with } y = \frac{P}{P_0}$$

Combine and use ODE solver

Combine

⑥ Use an ODE solver or a nonlinear equation solver (e.g., Polymath) to combine Steps ① through ⑤ to solve for, for example, the profiles of molar flow rates, concentration and pressure.

# Mole balance: Liquid phase

- For liquid phase with no volume change, concentration is the preferred variable

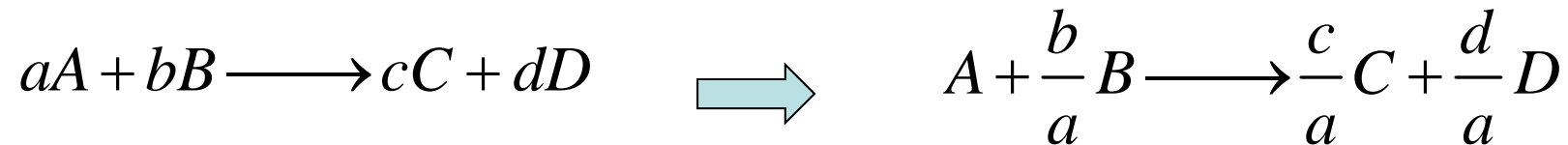


TABLE 4-5. MOLE BALANCES FOR LIQUID-PHASE REACTIONS

|       |                                      |     |   |
|-------|--------------------------------------|-----|---|
| Batch | $\frac{dC_A}{dt} = r_A$              | and | $\frac{dC_B}{dt} = \frac{b}{a}r_A$        |
| CSTR  | $V = \frac{v_0(C_{A0} - C_A)}{-r_A}$ | and | $V = \frac{v_0(C_{B0} - C_B)}{-(b/a)r_A}$ |
| PFR   | $v_0 \frac{dC_A}{dV} = r_A$          | and | $v_0 \frac{dC_B}{dV} = \frac{b}{a}r_A$    |
| PBR   | $v_0 \frac{dC_A}{dW} = r'_A$         | and | $v_0 \frac{dC_B}{dW} = \frac{b}{a}r'_A$   |

# Mole balance: Gas phase

- For e.g. PFR, for every species  $\frac{dF_j}{dV} = r_j$

- Generic power rate law  $-r_A = k_A C_A^\alpha C_B^\beta$  for isothermal operation

- Concentration in terms of flow rates

$$C_j = C_{T0} \frac{F_j}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

- The pressure drop equation

$$\frac{dy}{W} = \frac{-\alpha}{2y} \frac{F_T}{F_{T0}}$$

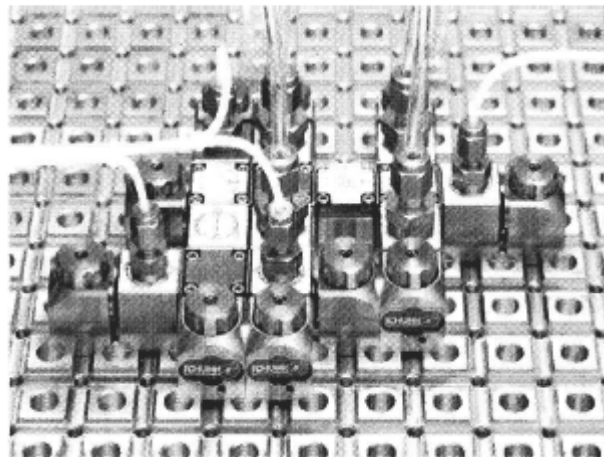
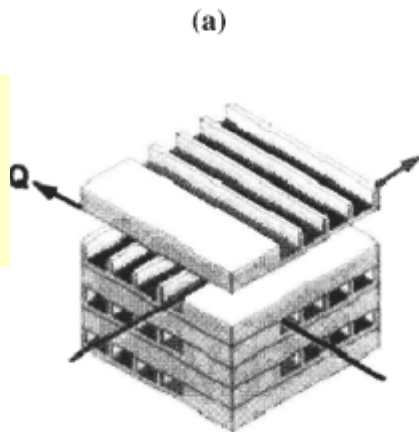
- The total flow rate

$$F_T = \sum_{j=1}^N F_j$$

# Microreactors

- characterized by high surface area to volume ratios
- thus, heat and mass transfer resistances are reduced or eliminated
- surface catalyzed reactions can be facilitated
- hot spots in highly exothermic reactions can be eliminated
- highly exothermic reactions can be carried out isothermally
- leak or microexplosion in a single unit causes a minimal damage to the system
- shorter residence times and narrower residence time distribution

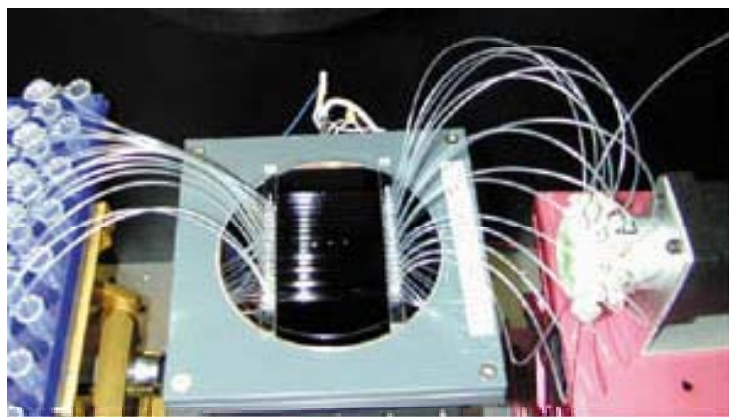
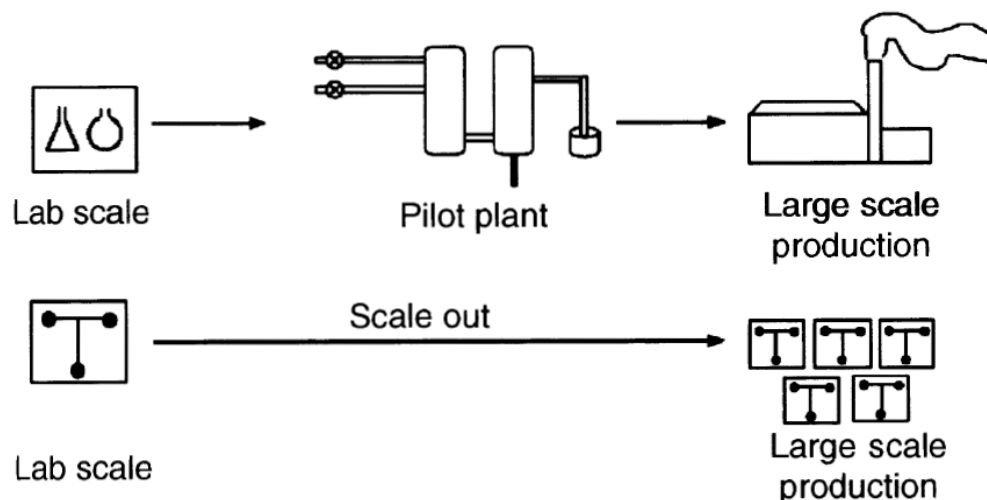
microreactor  
with a heat  
exchanger



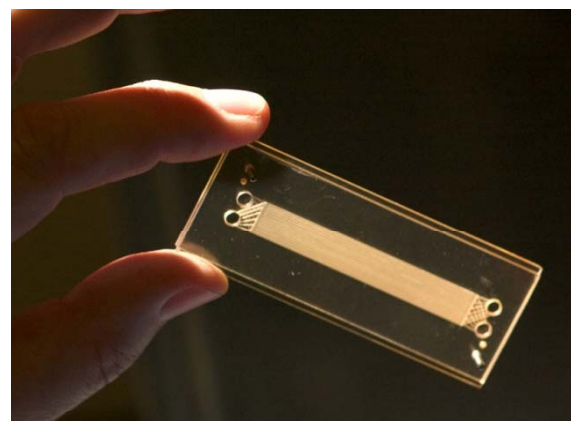
microplant  
with reactor,  
valves and  
mixers

# Chemical synthesis with microreactors

- Advantages:
  - scale-out instead of scale-up
  - flexible
  - easy to change the production volume



Univ. of Texas microreactor for biodiesel production: cost reduction 40c/gallon

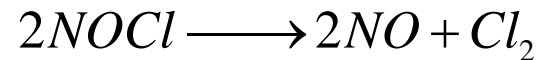
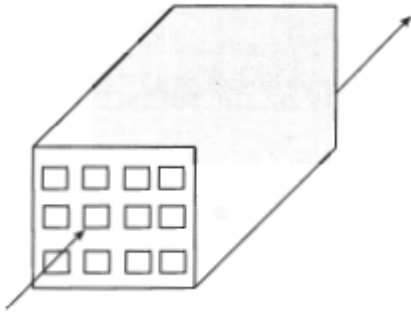


G. Jovanovic, Univ. of Oregon, microreactor for biodiesel production:

# Chemical synthesis with microreactors

- not every reaction benefits from microreactor
- however:
  - exothermic reactions are usually easier to control in microreactors due to better temperature control (reactions involving explosives, regionselective reactions)
  - photochemical reactions can be easier arranged to absorb more light
  - multistep reactions (e.g. peptide synthesis)
  - biphasic reactions (gas-liquid)
  - synthesis of analytically pure components

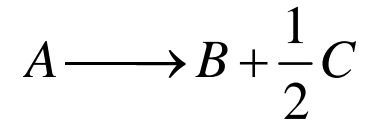
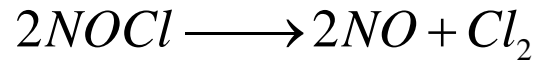
# Microreactor: example



- Gas reaction carried out at 425°C and 1641kPa. Pure NOCl is fed and the reaction follows elementary rate law. It's desired to produce 20 t/year in a bank of 10 microreactors in parallel. Each microreactor has 100 channels, each 0.2mm sq and 250mm long. Plot the molar flow rate as a function of volume down the length of the reactor.
- The rate constant  $k=0.29 \text{ dm}^3/\text{mol}\cdot\text{s}$  at 500K,  $E=24 \text{ kcal/mol}$
- To produce 20 t per year at 85% conversion requires  $2.26 \times 10^{-5} \text{ mol/s}$  per channel



# Example



- Mole balance  $\frac{dF_A}{dV} = r_A \quad \frac{dF_B}{dV} = r_B \quad \frac{dF_C}{dV} = r_C$

- Rate law  $-r_A = kC_A^2$

- Stoichiometry  $r_B = 2r_C = -r_A$

$$C_A = C_{T0} \frac{F_A}{F_T}; \quad C_B = C_{T0} \frac{F_B}{F_T}; \quad C_C = C_{T0} \frac{F_C}{F_T}$$

$$F_T = F_A + F_B + F_C$$

# Example

**POLYMATH 5.1**

File Edit Program Window Examples Help

Open Save LEQ NLE DEQ REG Calculate Units Const Setup

**Ordinary Differential Equations Solver**

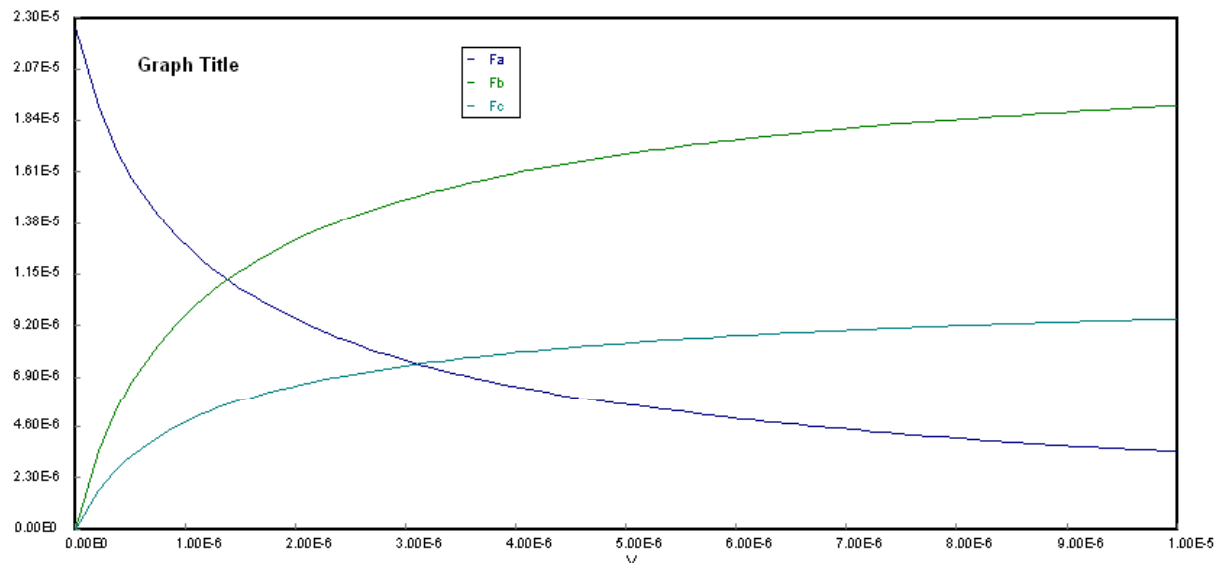
Indep Var  Initial Value

Solve with  Final Value

Comments

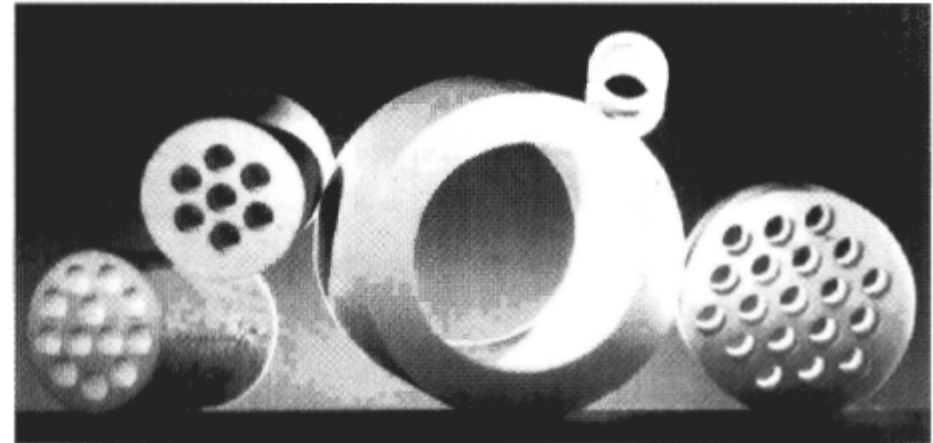
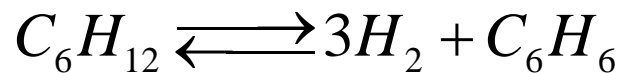
|    | Differential equations / explicit equations    | Initial value |
|----|--|---------------|
| 1  | $d(Fa)/d(V) = ra$                              | 2.26e-5       |
| 2  | $d(Fb)/d(V) = rb$                              | 0             |
| 3  | $d(Fc)/d(V) = rc$                              | 0             |
| 4  | $T = 698$                                      | n.a.          |
| 5  | $Ct0 = 1641/8.314/T$                           | n.a.          |
| 6  | $Ft = Fa + Fb + Fc$                            | n.a.          |
| 7  | $Ca = Ct0 * Fa / Ft$                           |               |
| 8  | $E = 24000$                                    |               |
| 9  | $k = 0.29 * \exp(E / (1.987 * (1/500 - 1/T)))$ |               |
| 10 | $Fa0 = 0.0000226$                              |               |
| 11 | $v0 = Fa0 / Ct0$                               |               |
| 12 | $ra = -k * Ca^2$                               |               |
| 13 | $X = 1 - Fa / Fa0$                             |               |
| 14 | $rb = -ra$                                     |               |
| 15 | $rc = -ra / 2$                                 |               |

Differential Equations: 3 Auxiliary Equations: 12



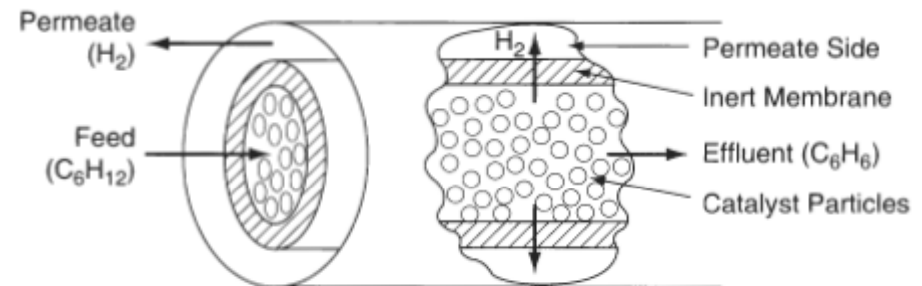
# Membrane reactors

- used to **increase conversion** when the reaction is thermodynamically limited (e.g. with small  $K$ )
- or to **increase selectivity** in when multiple reactions are occurring



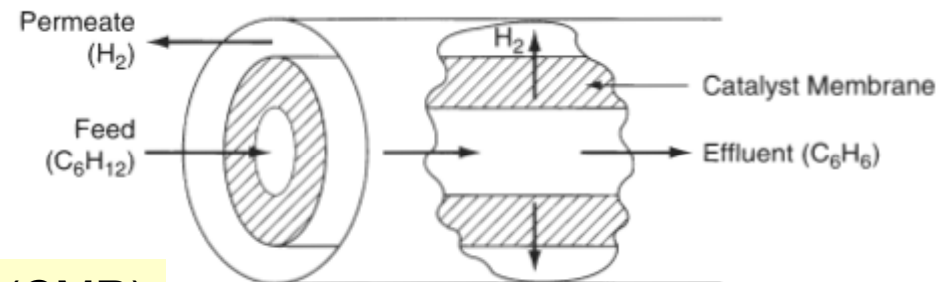
(a)

(b)



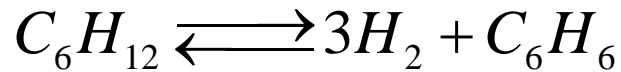
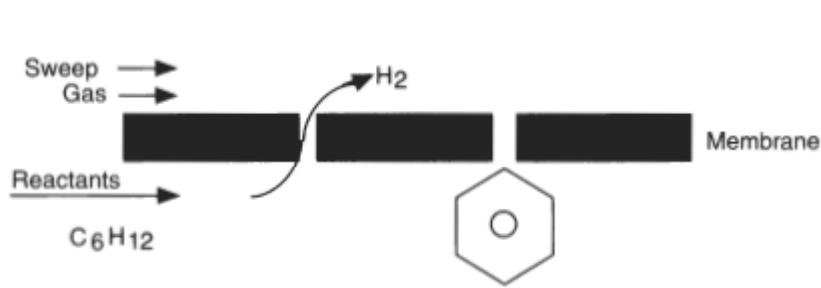
inert membrane reactor with catalyst pellet on the feed side (IMRCF)

(c)

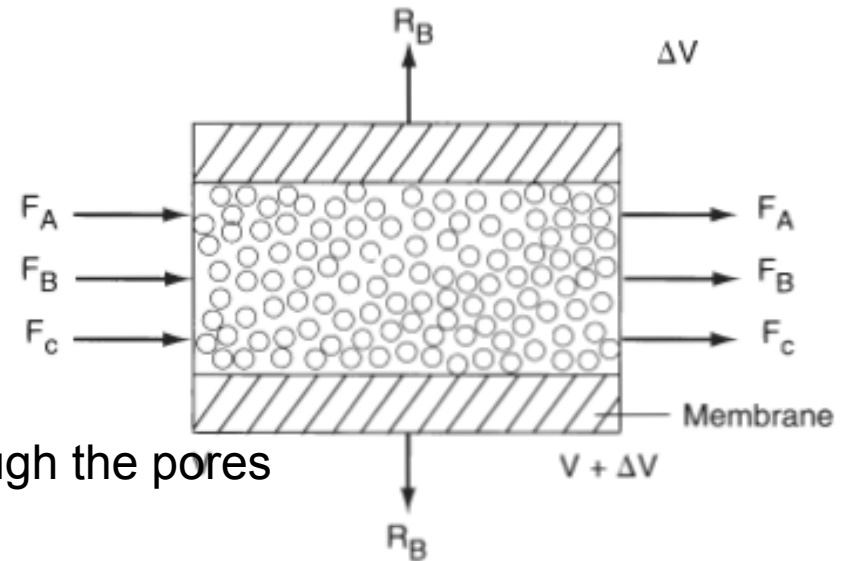
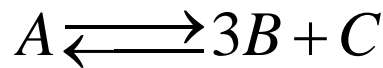


catalyst membrane reactor (CMR)

# Membrane reactors



H<sub>2</sub> leaves through the pores



- Mole balances:

$$\frac{dF_A}{dV} = r_A$$

$$\frac{dF_C}{dV} = r_C$$

generation

$$F_{B|V} - F_{B|V+\Delta V} - R_B \Delta V + r_B \Delta V = 0$$

$$\frac{dF_B}{dV} = r_B - R_B$$

IN by flow

OUT by diffusion

OUT by flow

no accumulation

# Membrane reactors

$$\frac{dF_B}{dV} = r_B - R_B$$

$$R_B = W_B a = k'_c a (C_B - C_{BS})$$

Diffusion flux

area per volume

mass transfer coefficient

concentration in the sweep gas channel

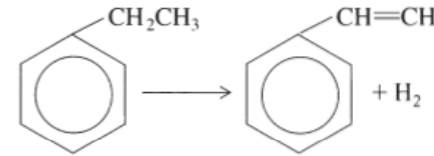
$$a = \frac{\pi DL}{\pi LD^2 / 4} = \frac{4}{D}$$

- Assuming  $C_{BS}=0$  and introducing  $k_c = k'_c a \Rightarrow R_B = k_c C_B$

# Example: Dehydrogenation reaction

- Typical reactions:

- dehydrogenation of ethylbenzene to styrene;
- dehydrogenation of butane to butene
- dehydrogenation of propane to propene



- Problem: for a reaction of type  $A \rightleftharpoons B + C$  where an equilibrium constant  $K_c = 0.05 \text{ mol/dm}^3$ ; temperature  $227^\circ\text{C}$ , pure A enters chamber at 8.2 atm and  $227^\circ\text{C}$  at a rate of 10 mol/min
  - write differential mole balance for A, B, C
  - Plot the molar flow rate as a function of space and time
  - calculate conversion at  $V = 400 \text{ dm}^3$ .
- Assume that the membrane is permeable for B only, catalyst density is  $\rho_b = 1.5 \text{ g/cm}^3$ , tube inside diameter 2cm, reaction rate  $k = 0.7$  and transport coefficient  $k_c = 0.2 \text{ min}^{-1}$ .

# Example

- Mole balance:

$$\frac{dF_A}{dV} = r_A \quad \frac{dF_B}{dV} = r_B - R_B \quad \frac{dF_C}{dV} = r_C$$

- Rate law

$$-r_A = k \left( C_A - \frac{C_B C_C}{K_C} \right)$$

- Transport out of the reactor

$$R_B = k_c C_B$$

- Stoichiometry

$$C_A = C_{T0} \frac{F_A}{F_T} \quad C_B = C_{T0} \frac{F_B}{F_T} \quad C_C = C_{T0} \frac{F_C}{F_T}$$

$$C_A = C_{T0} = \frac{P_0}{RT_0} = 0.2 \text{ mol/dm}^3$$

$$r_B = r_C = -r_A$$

# Example

- POLYMATH solution

**POLYMATH 5.1**

File Edit Program Window Examples Help

Open Save LEQ NLE DEQ REG Calculate Units Const Setup

**Ordinary Differential Equations Solver**

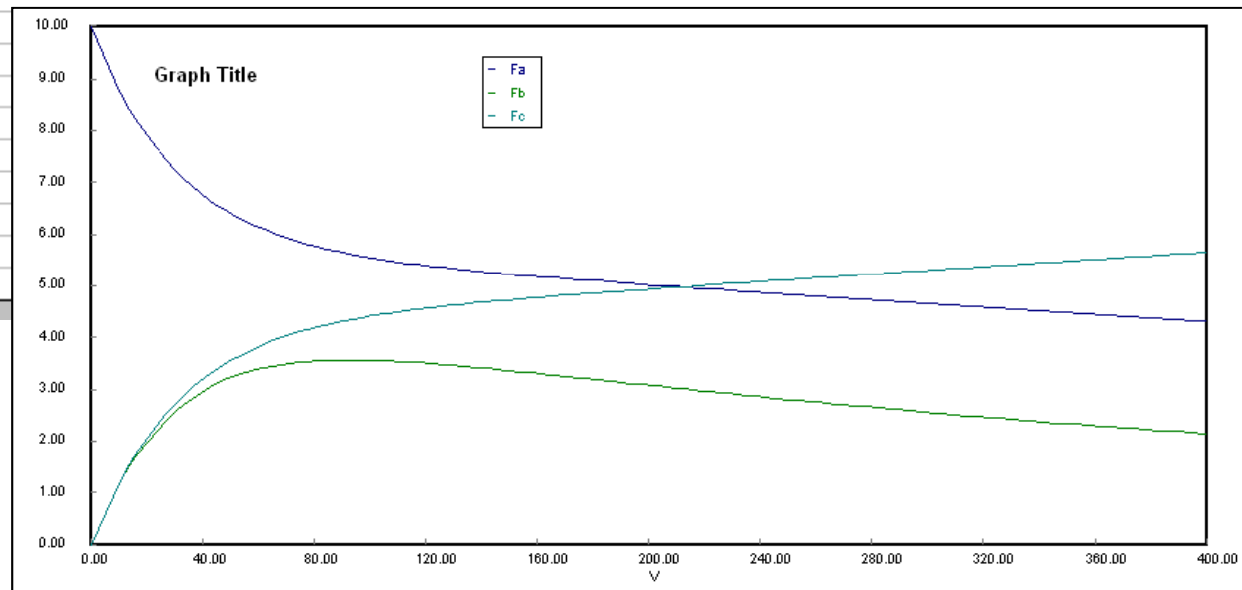
Indep Var  Initial Value

Solve with  Final Value

Comments

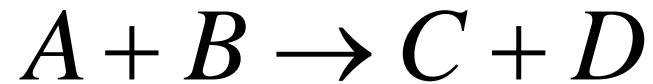
Differential equations / explicit equations

|    |  |
|----|--|
| 1  | $d(F_a)/d(V) = r_a$  |
| 2  | $d(F_b)/d(V) = -r_a - k_c \cdot C_{to} \cdot F_b / F_t$                                |
| 3  | $d(F_c)/d(V) = -r_a$   |
| 4  | $k_c = 0.2$  |
| 5  | $C_{to} = 0.2$   |
| 6  | $F_t = F_a + F_b + F_c$  |
| 7  | $k = 0.7$  |
| 8  | $K_c = 0.05$   |
| 9  | $r_a = -k \cdot C_{to} \cdot ((F_a/F_t) - C_{to}/K_c \cdot (F_b/F_t) \cdot (F_c/F_t))$ |
| 10 |  |

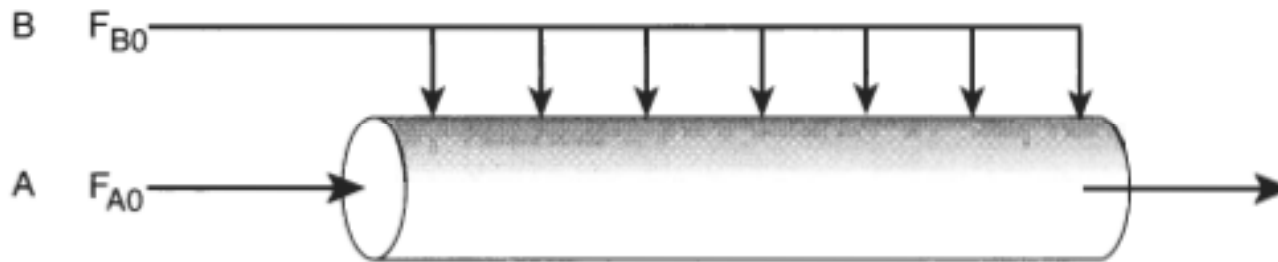




# Use of Membrane reactors to enhance selectivity

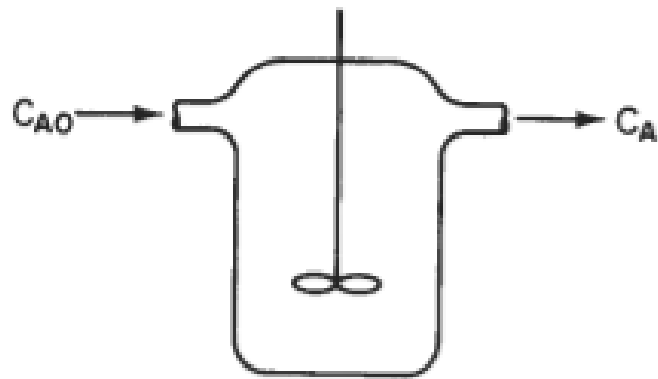


- **B** is fed uniformly through the membrane

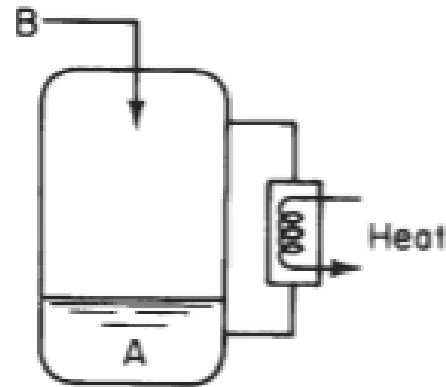


$$\frac{dF_B}{dV} = r_B + R_B$$

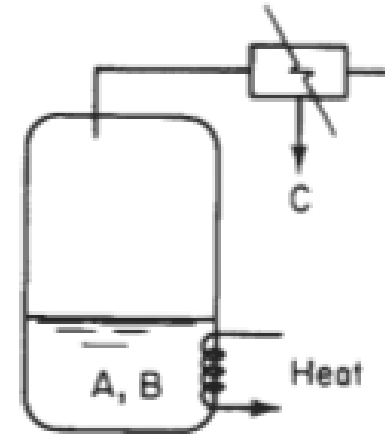
# Unsteady state operation of stirred reactors



reactor start-up



semibatch  
w. cooling



reactive distillation

- during the start up of a reactor:
- slow addition of component **B** to a large quantity of **A** e.g. when reaction is highly exothermic or unwanted side reaction can occur at high concentration of **B**
- one of the products is vaporized and withdrawn continuously.

# Startup of CSTR

- Conversion doesn't have any meaning in startup so we have to use concentrations

$$F_{A0} - F_A + r_A V = \frac{dN_A}{dt}$$

- For liquid phase with constant overflow

$$C_{A0} - C_A + r_A \tau = \tau \frac{dC_A}{dt}, \quad \tau = \frac{V_0}{v_0}$$

- For the 1<sup>st</sup> order reactions

$$-r_A = kC_A, \quad \frac{dC_A}{dt} + \frac{1 + \tau k}{\tau} C_A = \frac{C_{A0}}{\tau}$$

$$C_A = \frac{C_{A0}}{1 + \tau k} \left\{ 1 - \exp \left[ - (1 + \tau k) \frac{t}{\tau} \right] \right\}$$

- e.g. to reach 99% steady state concentration

$$C_{AS} = \frac{C_{A0}}{1 + \tau k}, \quad t_s = 4.6 \frac{\tau}{1 + \tau k}$$

$\nearrow t_s = 4.6\tau$   
 $\searrow t_s = 4.6/k$

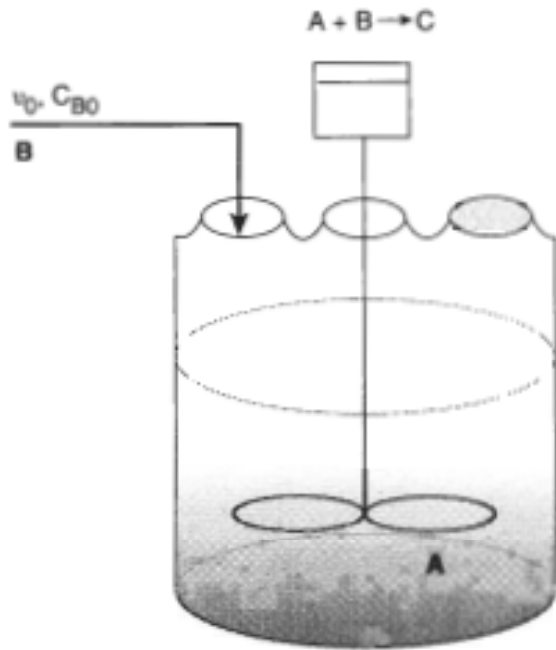
# Semibatch reactors

- semibatch reactors could be used e.g. to improve selectivity



- selectivity: 
$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} \frac{C_A}{C_B}$$

# Semibatch equations



- For component **A**:

$$r_A V = \frac{dN_A}{dt} = \frac{d(C_A V)}{dt} = \frac{V dC_A}{dt} + \frac{C_A dV}{dt}$$

$$V = V_0 + v_0 t$$

$$-v_0 C_A + r_A V = \frac{V dC_A}{dt} \quad \Rightarrow \quad \frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A$$

- For component **B**:

$$r_A V = \frac{dN_B}{dt} = r_B V + F_{B0}$$

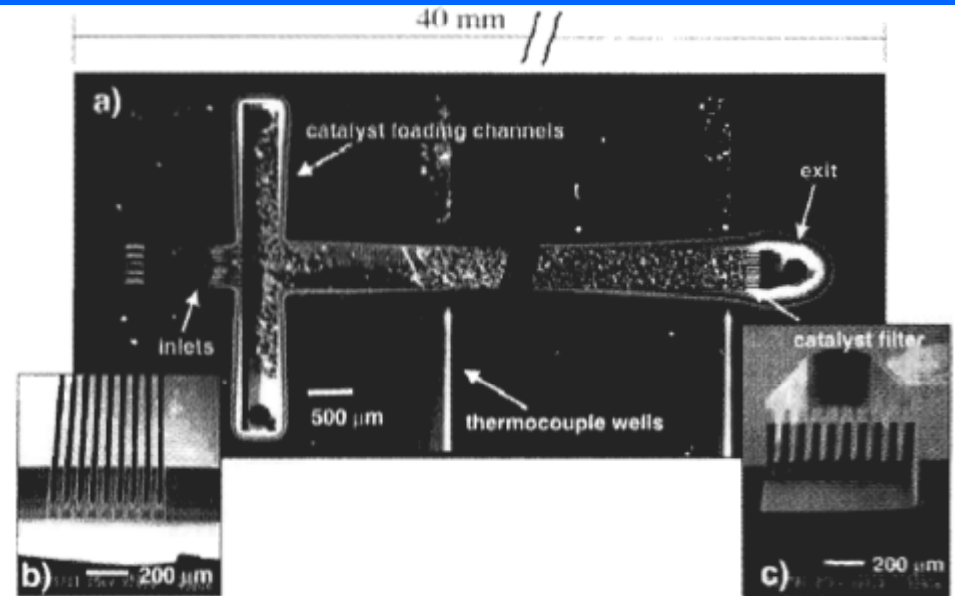
$$\frac{V dC_A}{dt} + \frac{C_A dV}{dt} = r_B V + v_0 C_{B0}$$

$$\frac{dC_B}{dt} = r_B + \frac{v_0}{V} (C_{B0} - C_A)$$

# Problems

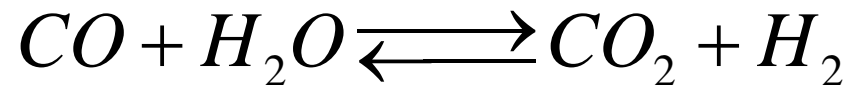
- **P4-19:** A microreactor is used to produce a phosgene in a gas phase. The microreactor is 20mm long, 500  $\mu\text{m}$  in diameter and packed with catalyst particles 35  $\mu\text{m}$  in diameter. The entering pressure is 830 kPa and the entering flow to each reactor is equimolar. Molar flow rate for  $\text{CO}_2$  is  $2 \times 10^{-5} \text{ mol/s}$ , the volumetric flow  $2.83 \times 10^{-7} \text{ m}^3/\text{s}$ , the weight of catalyst in one microreactor  $W = 3.5 \times 10^{-6} \text{ kg}$ . the reactor is kept isothermal at  $120^\circ\text{C}$ . The rate law:

$$-r'_A = k_A C_A C_B$$



# Problems

- **P4-26:** A large component in the processing train for fuel cell technology is the water gas shift membrane reactor, where  $H_2$  can diffuse out the sides of the membrane while the other gases cannot.



- Based on the following information plot the concentration and molar flow rates of each of the reacting species down the length of the membrane reactor. Assume: the volumetric feed is  $10\text{dm}^3/\text{min}$  at  $10\text{atm}$ ; equil molar feed of CO and water vapour with  $C_{T0}=0.4\text{mol}/\text{dm}^3$ , equilibrium constant  $K_e=1.44$ , reaction rate  $k=1.37\text{ dm}^6/\text{mol}\cdot\text{kg cat}\cdot\text{min}$ , mass transfer coefficient for  $H_2$   $k_c=0.1\text{dm}^3/\text{mol}\cdot\text{kg cat}\cdot\text{min}$ . Compare with PFR.

# Home problem analysis

P3-13, Hippo's digestion



# Home problem 3-13: nitroaniline synthesis

- the disappearance rate of orthonitrochlorobenzene

$$r_a = -\frac{d[ONCB]}{dt} = -k[ONCB][NH_3]$$

- Stoichiometric table:

|          |   |          | Change      | Remaining*              | Concentration**         |
|----------|---|----------|-------------|-------------------------|-------------------------|
| ONCB     | A | $F_{A0}$ | $-F_{A0}X$  | $F_{A0}(1-X)$           | $C_{A0}(1-X)$           |
| $NH_3$   | B | $F_{B0}$ | $-2F_{A0}X$ | $F_{A0}(\Theta_B - X)$  | $C_{A0}(\Theta_B - X)$  |
| NA       | C | $F_{C0}$ | $F_{A0}X$   | $F_{A0}(\Theta_C + X)$  | $C_{A0}(\Theta_C + X)$  |
| $NH_4Cl$ | D | $F_{D0}$ | $2F_{A0}X$  | $F_{A0}(\Theta_D + 2X)$ | $C_{A0}(\Theta_D + 2X)$ |

\*) ONCB is a limiting reagent (from stoichiometry)

\*\*\*) reaction in liquid, thus the volume is constant

# Home problem 3-13: nitroaniline synthesis

- the disappearance rate of orthonitrochlorobenzene in terms of conversion

$$r_a = -k[ONCB][NH_3] = -kC_{A0}^2(1-X)(\Theta_B - X)$$

- rate of the reaction at 188°C, 25°C, 288°C when X=0.9:

$$k(T) = Ae^{-E/RT} \quad \Rightarrow \quad k(T_2) = k(T_1)e^{-\frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]}$$

$$k(188^\circ C) = 1.7 \cdot 10^{-3}$$

$$r_a = 3.2 \cdot 10^{-4}$$

$$k(25^\circ C) = k(188^\circ C)e^{-\frac{11273 \text{ cal/mol} \cdot 4.187 \text{ J/cal}}{8.31} \left[ \frac{1}{25+273} - \frac{1}{25+188} \right]} = 2 \cdot 10^{-6}$$

$$r_a = 3.7 \cdot 10^{-7}$$

$$k(288^\circ C) = 1.5 \cdot 10^{-2}$$

$$r_a = 2.85 \cdot 10^{-3}$$

# Home problem 3-13: nitroaniline synthesis

- find the reactor volume for CSTR at  $X=0.9$ :

$$V = \frac{F_{A0}X}{-r_a} = \frac{vC_{A0}X}{-r_a}$$

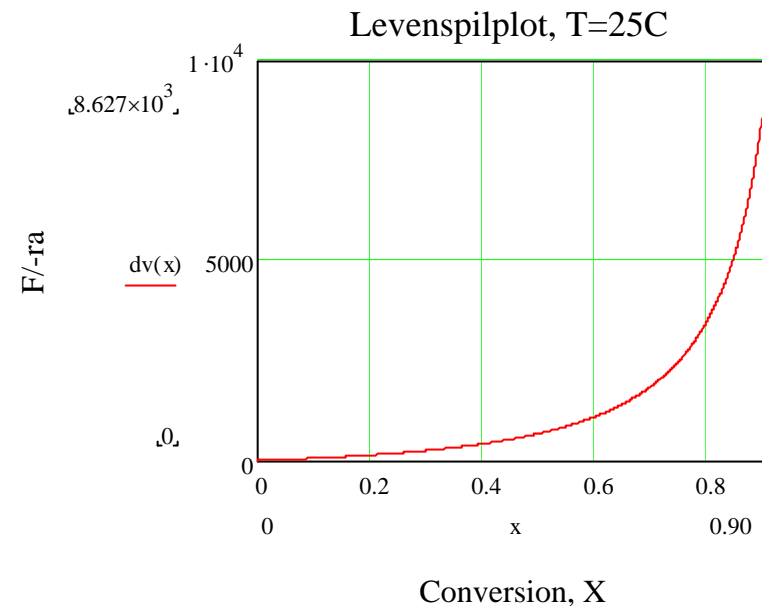
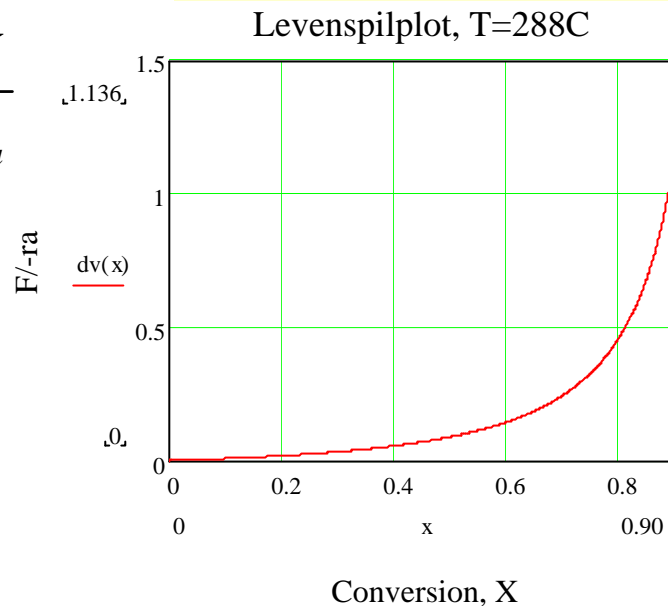
|       | Reaction rate       | Volume ( $X=0.9$ )           |
|-------|---------------------|------------------------------|
| 25°C  | $3.7 \cdot 10^{-7}$ | $8.6 \cdot 10^3 \text{ m}^3$ |
| 188°C | $3.2 \cdot 10^{-4}$ | 10.2 m <sup>3</sup>          |
| 288°C | $2.9 \cdot 10^{-3}$ | 1.14 m <sup>3</sup>          |

- find the reactor volume for PFR at  $X=0.9$ :

at 288°C:  $V=0.15 \text{ m}^3$

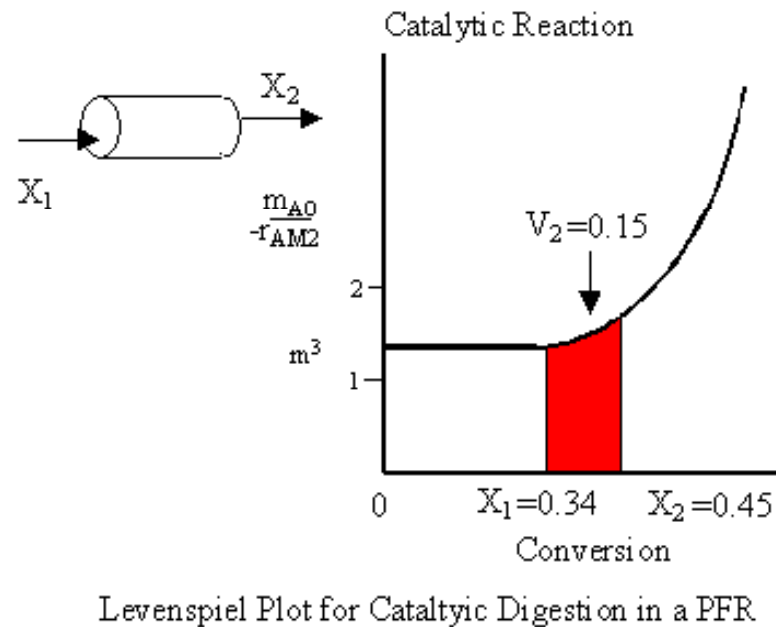
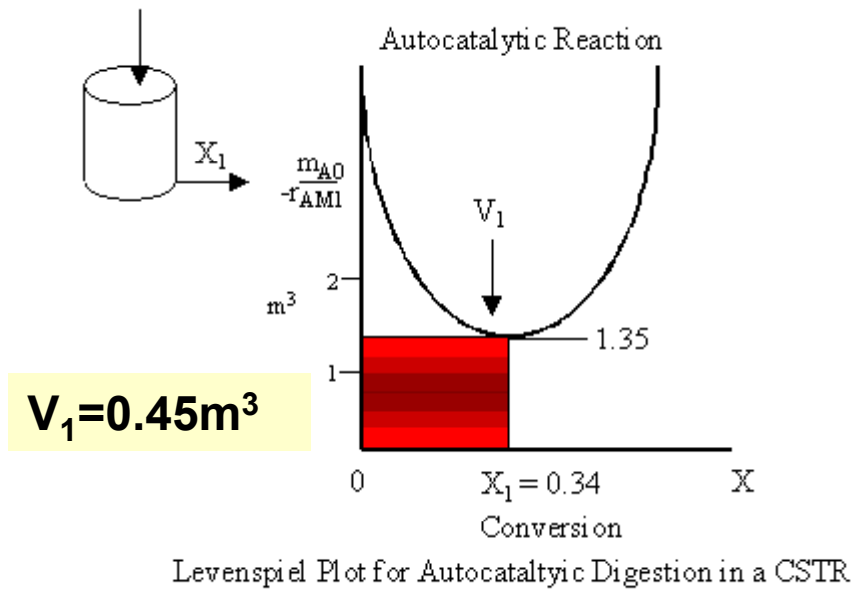
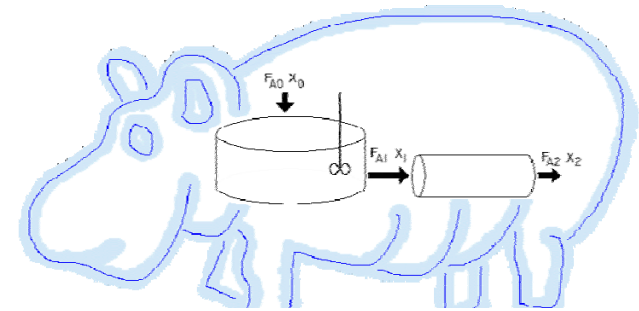
at 25°C:  $V=1.14 \cdot 10^3 \text{ m}^3$

$$V = vC_{A0} \int_0^X \frac{dX}{-r_a}$$



# Hippo's stomach

- Our starting point:  
 $X_0=0$ ;  $X_1=0.34$   $X_2=0.45$ ;
- Fitting the data



- flow rate 40 kg/day, with density of grass 365kg/m<sup>3</sup>,  
 volumetric rate 0.13 m<sup>3</sup>/day

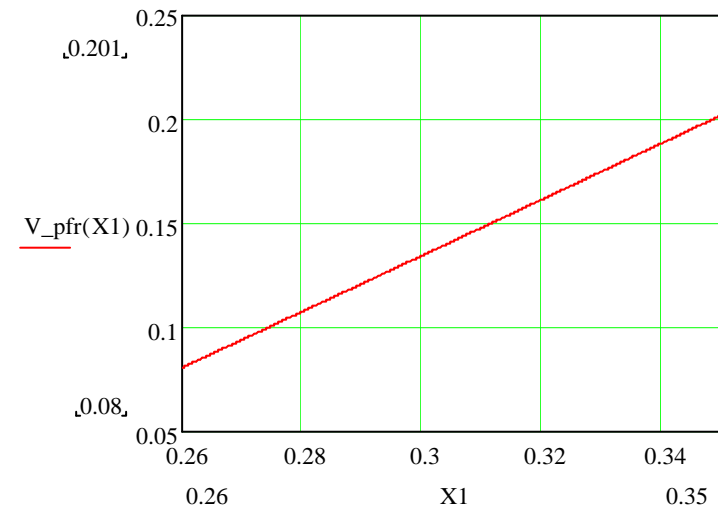
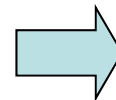
# Hippo's digesting problem

- The hippo has picked up a river fungus and now the effective volume of the CSTR stomach compartment is only 0.2 m<sup>3</sup>. The hippo needs 30% conversion to survive. Will the hippo survive?

CSTR: 
$$V = \frac{F_{A0} X_1}{-r_A} \quad X_1 = \frac{V_{02} X_{01}}{V_{01}} = \frac{0.2 \cdot 0.45}{0.34} = 0.26$$

PFR: 
$$\frac{F_{A0}}{-r_{A2}} = \frac{0.075 \text{ m}^3 (1 + 16.5(1 - X))}{(1 - X)}$$

$$V(X) = \int_{0.26}^X \frac{0.075 \cdot (1 + 16.5(1 - x))}{1 - x} dx$$



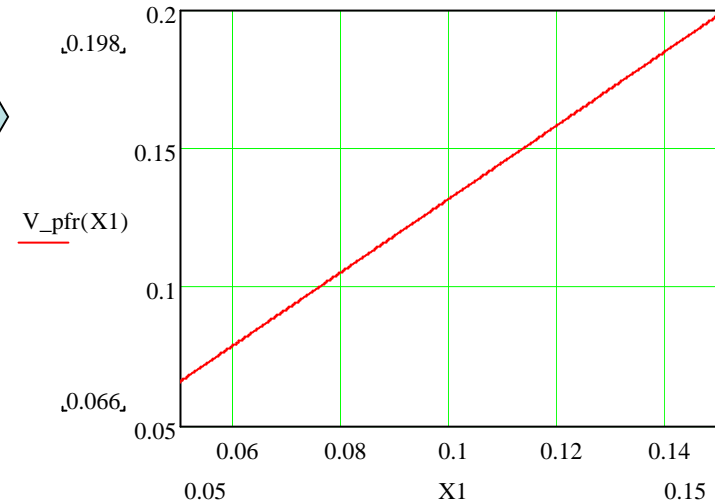
if  $V_{pfr} = 0.15 \text{ m}^3$  as before,  $X_1 \sim 0.31$ , so the hippo **survives**

# Hippo's digesting problem

- The hippo had to have surgery to remove a blockage. Unfortunately, the surgeon, Dr. No, accidentally reversed the CSTR and PFR during the operation. **Oops!!** What will be the conversion with the new digestive arrangement? Can the hippo survive?

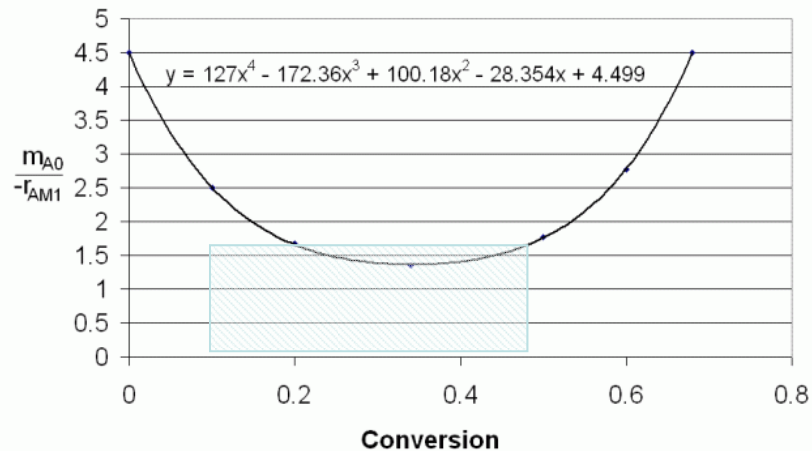
PFR: 
$$V(X) = \int_{0.0}^{X_1} \frac{0.075 \cdot (1 + 16.5(1-x))}{1-x} dx$$

if  $V_{pfr} = 0.15 \text{ m}^3$  as before,  $X_1 \sim 0.11$



Autocatalytic Reaction

CSTR:



$$V = \frac{F_{A0} (X_2 - X_1)}{-r_A}$$

if  $V_{pfr} = 0.45 \text{ m}^3$  as before,  $X_2 \sim 0.42$

