

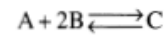
# Lecture 8

Mole balance: calculations of microreactors, membrane reactors and unsteady state in tank reactors

# 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
- The difference in calculation: we will write mole balance for **each and every species** in the reactor

# Isothermal reaction design algorithm



Mole Balance

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

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

Rate Law

② Write rate law in terms of concentration

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

Stoichiometry

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

e.g.,  $r_B = 2r_A$ ,  $r_C = -r_A$

Stoichiometry

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

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

with  $F_T = F_A + F_B + F_C$

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

Pressure Drop

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

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

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

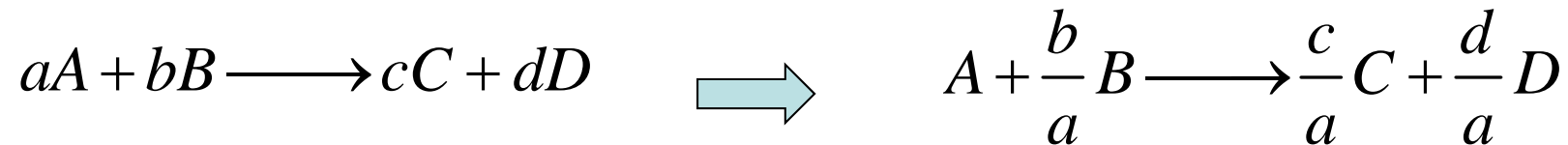


TABLE 4-5. MOLE BALANCES FOR LIQUID-PHASE REACTIONS

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

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

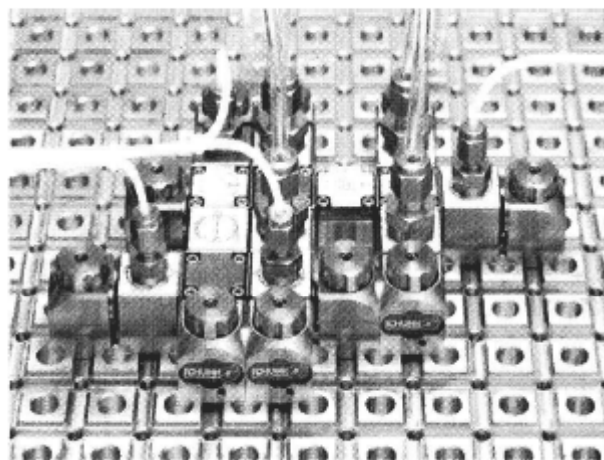
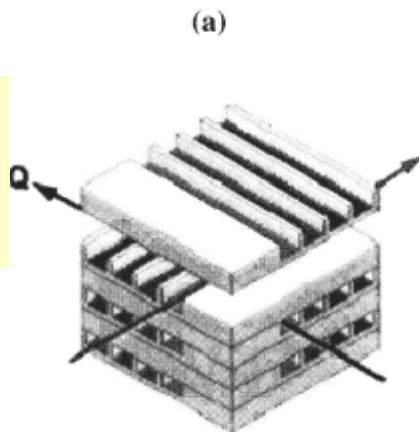
- The total flow rate

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

# 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

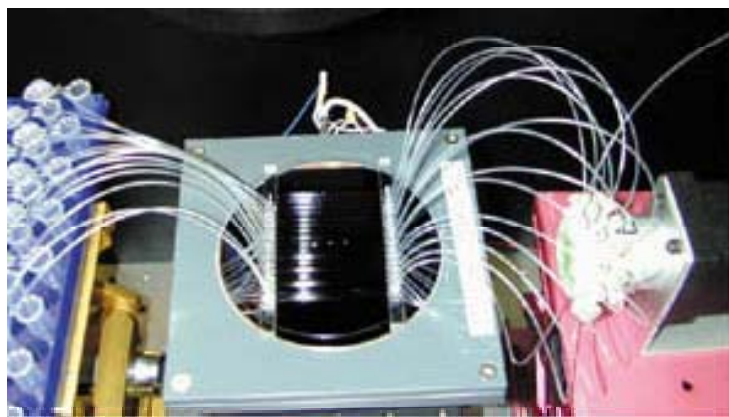
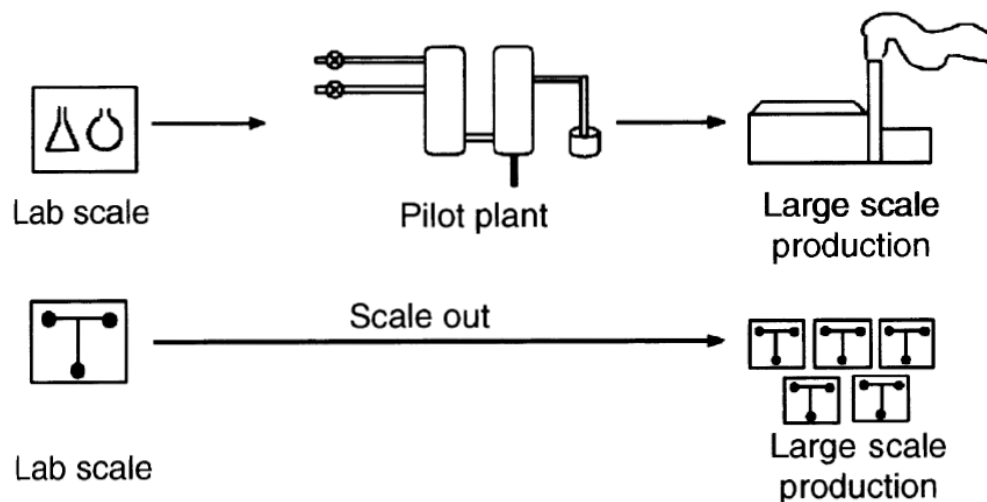
microreactor  
with a heat  
exchanger



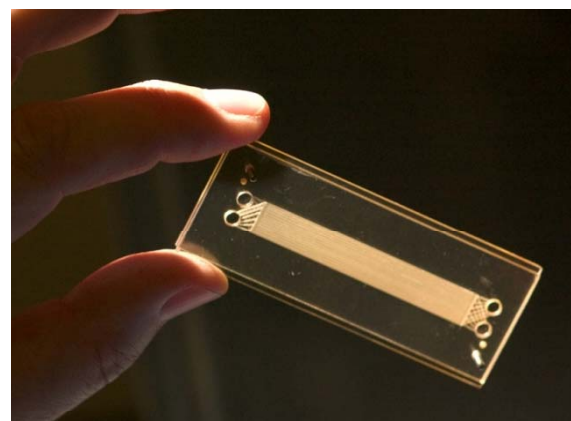
microplant  
with reactor,  
valves and  
mixers

# 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



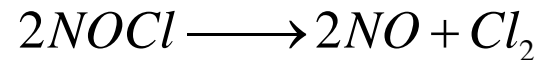
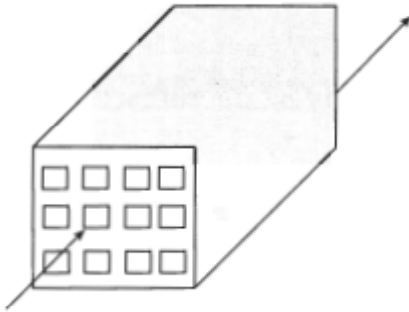
G. Jovanovic, Univ. of Oregon, microreactor for biodiesel production:

# 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

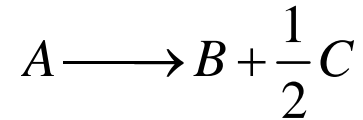
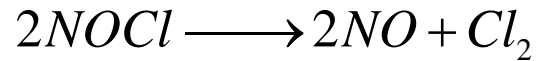


# Microreactor: example



- 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



Ordinary Differential Equations Solver

Indep Var  Initial Value

Solve with  Final Value

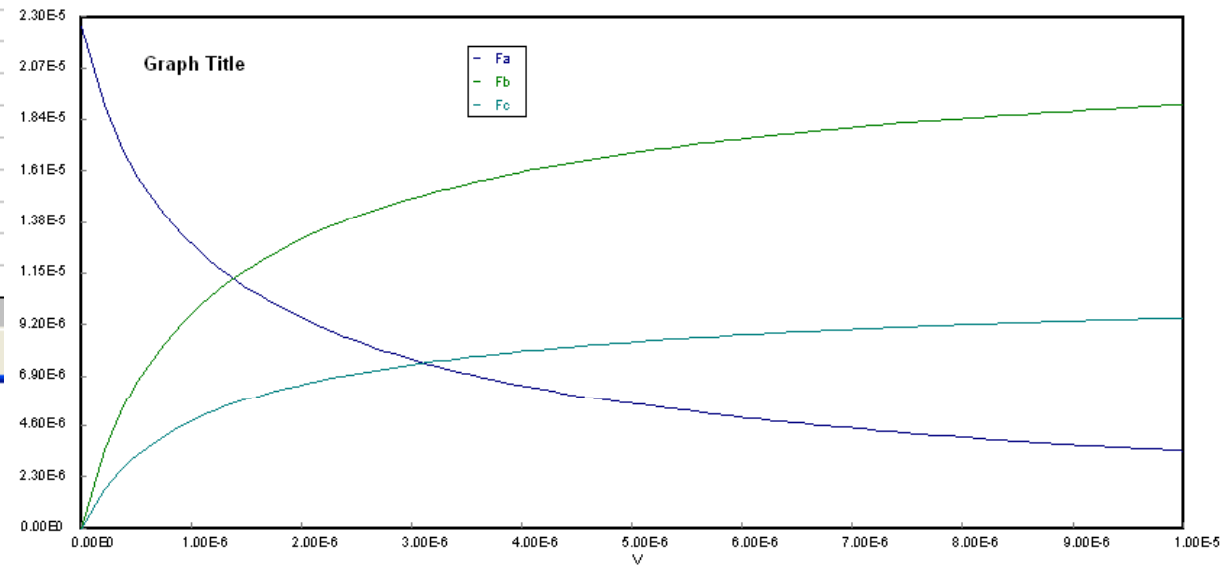


Comments

	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	$rc = -ra / 2$	

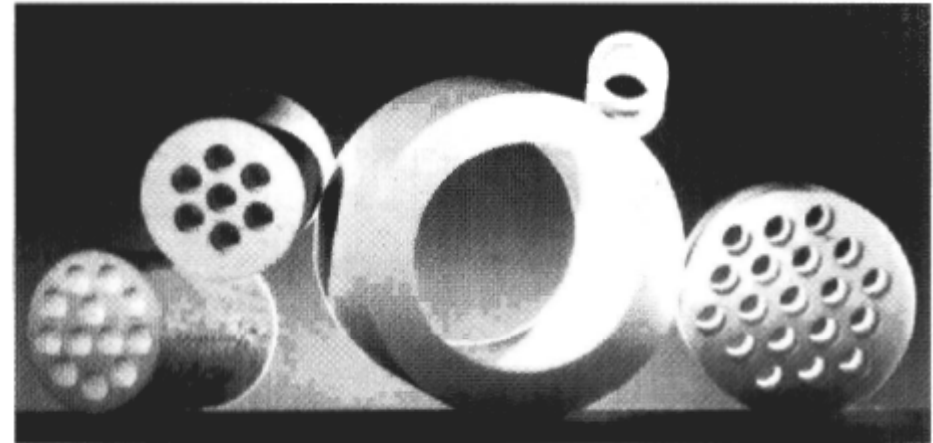
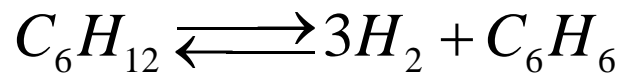
3.00E-6  
2.30E-6  
2.07E-6  
1.84E-6  
1.61E-6  
1.38E-6  
1.15E-6  
9.20E-6  
6.90E-6  
4.60E-6  
2.30E-6  
0.00E0

Differential Equations: 3 Auxiliary Equations: 12



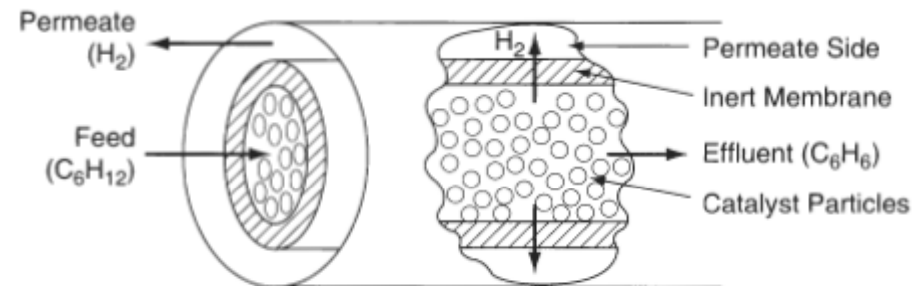
# Membrane reactors

- 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



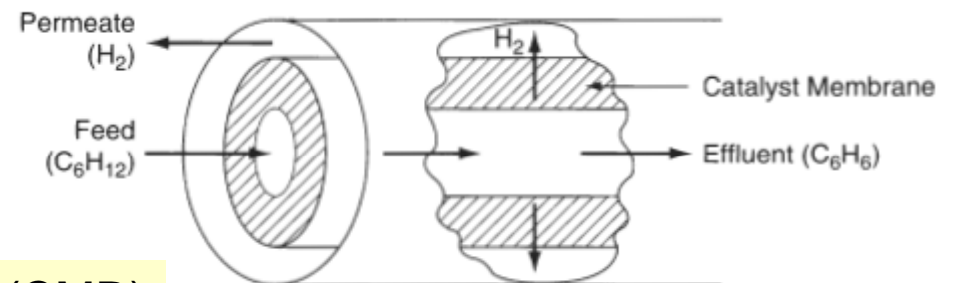
(a)

(b)



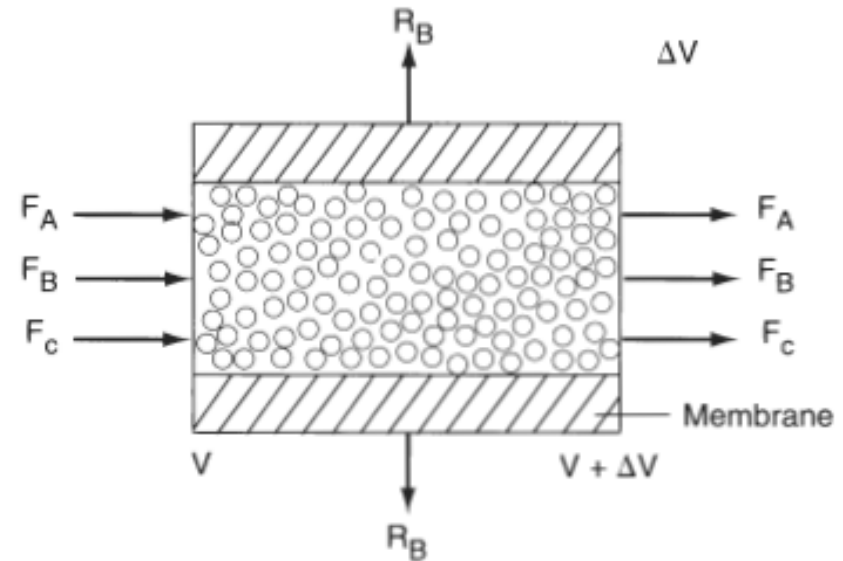
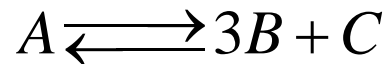
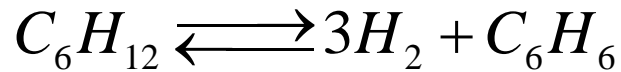
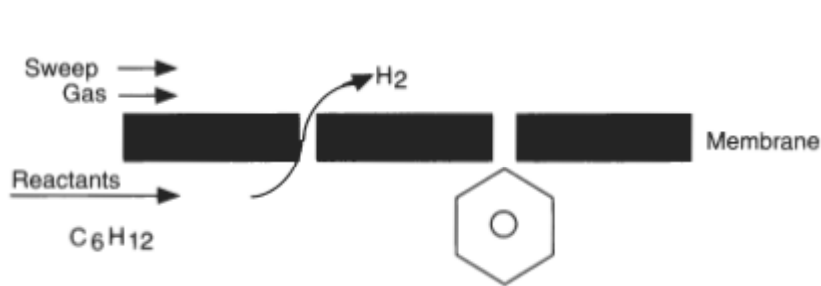
inert membrane reactor with catalyst pellet on the feed side (IMRCF)

(c)



catalyst membrane reactor (CMR)

# Membrane reactors



- 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

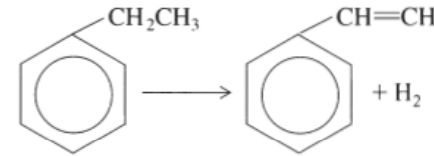
$$a = \frac{\pi DL}{\pi LD^2 / 4} = \frac{4}{D}$$

- 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

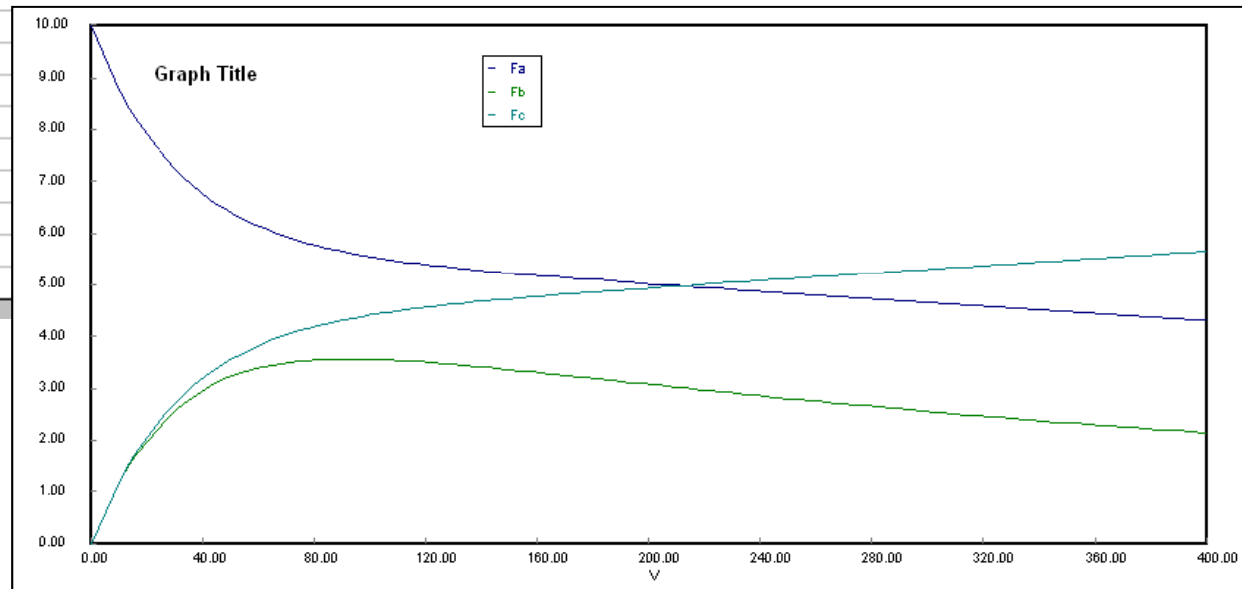
**Ordinary Differential Equations Solver**

Indep Var  Initial Value

Solve with  Final Value

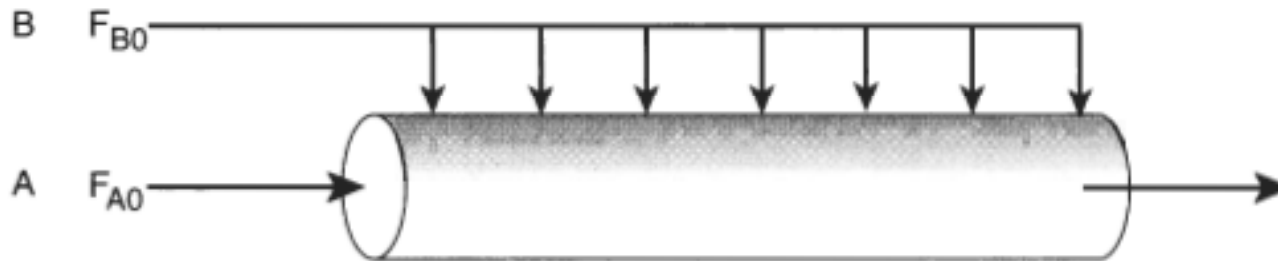
Comments

Differential equations / explicit equations	
1	$d(Fa)/d(V) = ra$
2	$d(Fb)/d(V) = -ra - kc \cdot Cto \cdot Fb / Ft$
3	$d(Fc)/d(V) = -ra$
4	$kc = 0.2$
5	$Cto = 0.2$
6	$Ft = Fa + Fb + Fc$
7	$k = 0.7$
8	$Kc = 0.05$
9	$ra = -k \cdot Cto \cdot ((Fa/Ft) - Cto/Kc \cdot (Fb/Ft) \cdot (Fc/Ft))$
10	



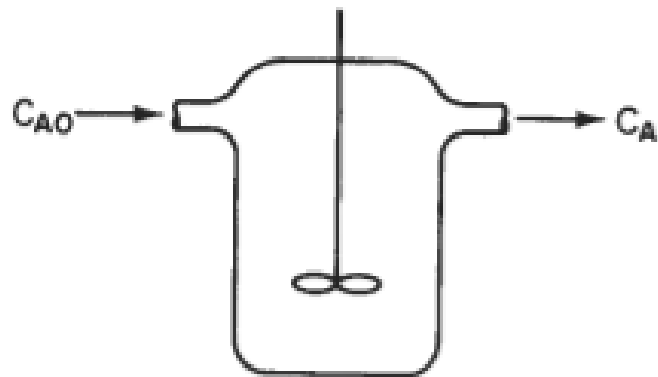
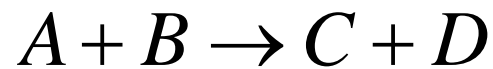
# Use of Membrane reactors to enhance selectivity

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

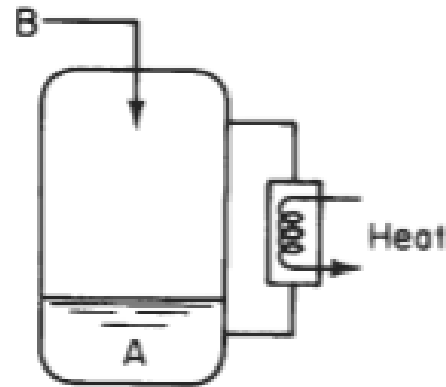


$$\frac{dF_B}{dV} = r_B + R_B$$

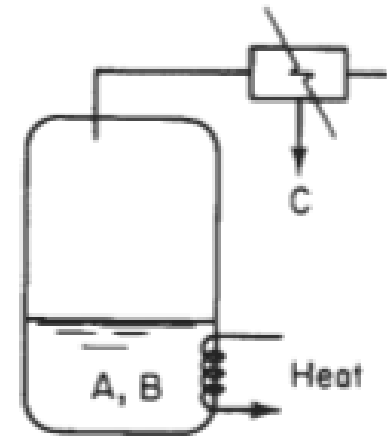
# Unsteady state operation of stirred reactors



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

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

for small k:

$$t_s = 4.6\tau$$

for large k:

$$t_s = 4.6/k$$

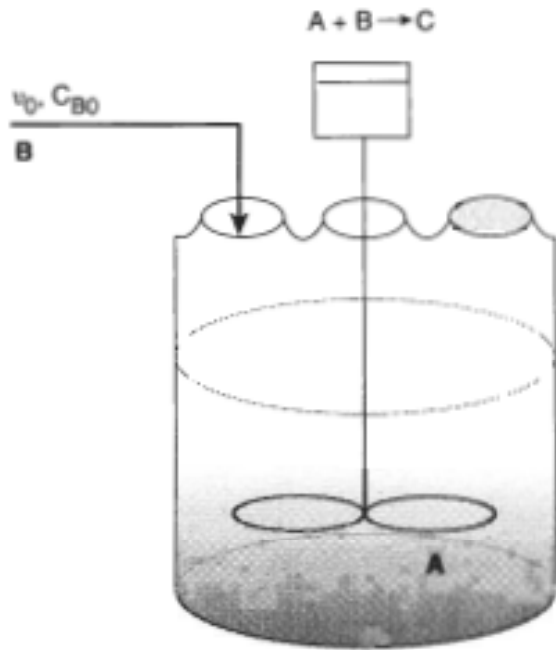
# Semibatch reactors

- 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**:

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

$$V = V_0 + v_0 t$$

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

- For component **B**:

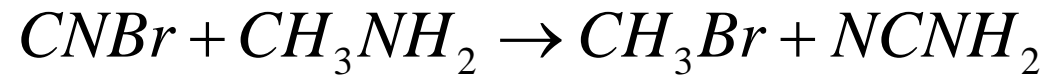
$$r_A V = \frac{dN_B}{dt} = r_B V + F_{B0}$$

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

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

# Example 4.9

- Isothermal semibatch reactor with 2<sup>nd</sup> order reaction



$$V_0 = 5 \text{ dm}^3$$

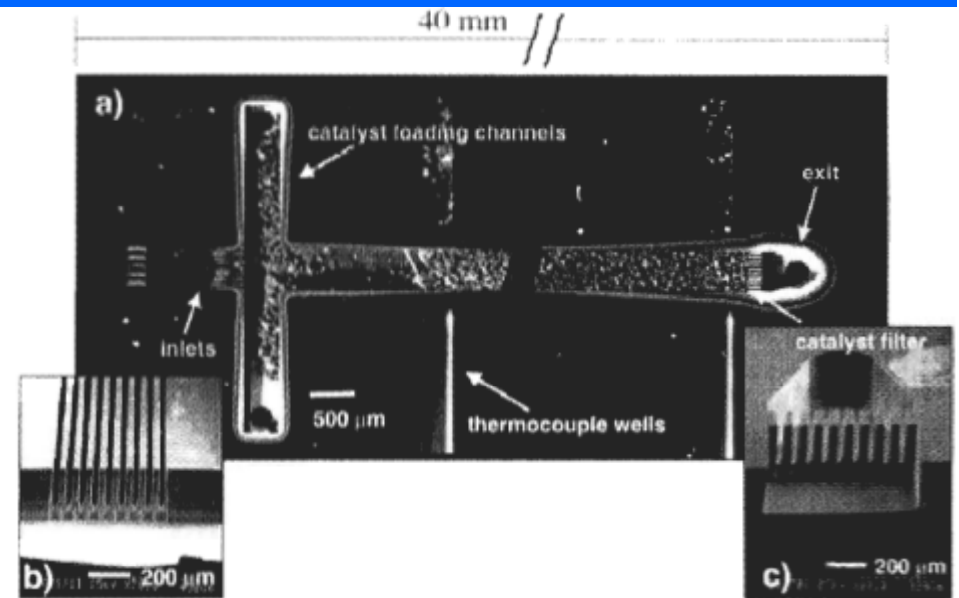
$$C_0(\text{CNBr}) = 0.05 \text{ mol} / \text{ dm}^3$$

$$k = 2.2 \text{ dm}^3 / \text{ s} \cdot \text{ mol}$$

# 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:

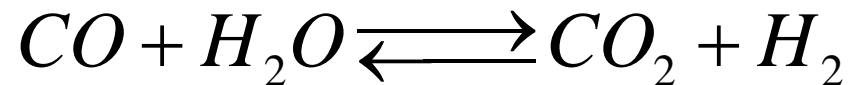
$$-r'_A = k_A C_A C_B$$





# 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.