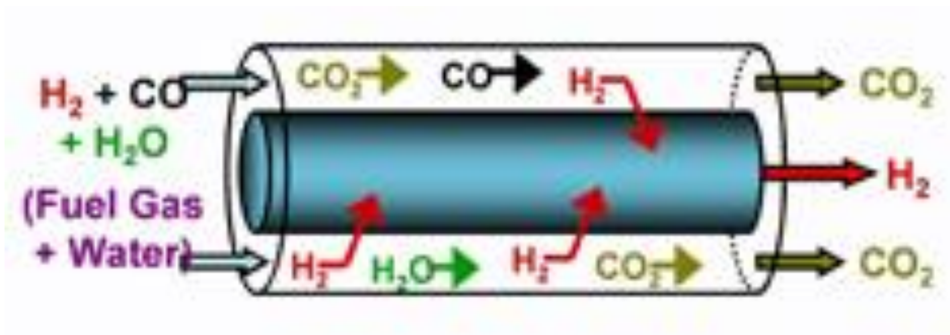
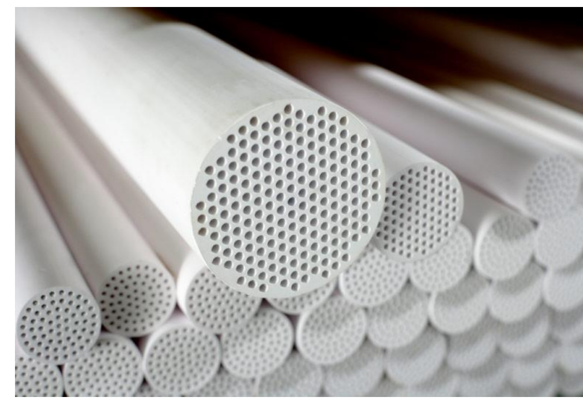
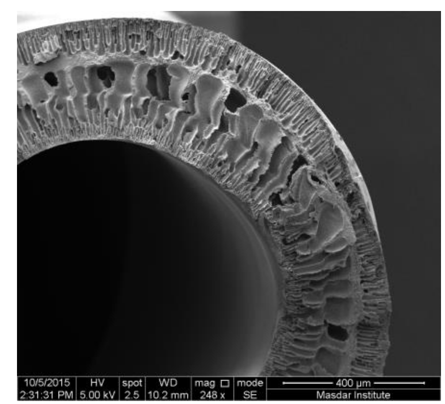
Reactor Design II







Week 2
Membrane Reactors

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COLLEGE OF ENGINEERING - كلية الهندسة
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Introduction

- Chemical Reaction Engineering (CRE) explores the rates and mechanisms of chemical reactions and their application in reactor design.

- This lecture focuses on membrane reactors and their ability to enhance conversion by leveraging thermodynamic principles.

Topics to be Addressed

- - Fundamentals of Membrane Reactors
- - Mole Balances and Rate Laws
- - Stoichiometry in Membrane Reactors
- - Transport Laws and Relative Rates
- - Example Problems and Engineering Analysis

Objectives

- By the end of this lecture, students will be able to:
- - Understand the operational principles of membrane reactors.
- - Apply mole balances and stoichiometry to reactor problems.
- - Analyze example cases of isothermal reactions in membrane reactors.
- - Relate theoretical concepts to practical applications in reactor design.

Introduction

- Membrane reactors provide a unique advantage in shifting equilibrium reactions to achieve higher conversions.

- This session includes theoretical insights, practical implications, and examples to solidify understanding of membrane reactor operations.

Introduction

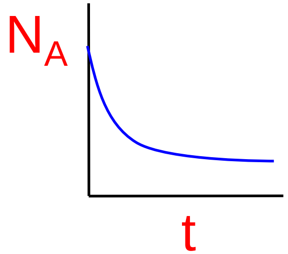
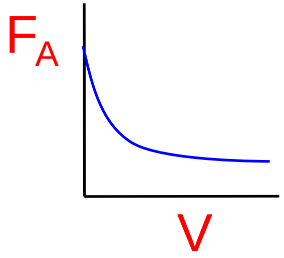
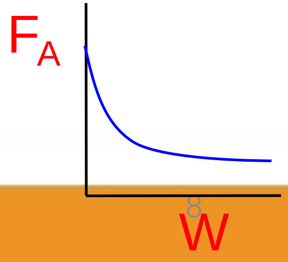
- Membrane reactors can be used to increase conversion when the reaction is thermodynamically limited as well as to increase the selectivity when multiple reactions are occurring.
- Thermodynamically limited reactions are reactions where the equilibrium lie far to the left (i.e., reaction side) and there is little conversion.
- If the reaction is exothermic, increasing the temperature will only drive the reaction further to the left, and decreasing the temperature will result in a reaction rate so slow that there is very little conversion.
- If the reaction is endothermic, increasing the temperature will move the reaction to the right to favor a higher conversion; however, for many reactions these higher temperatures cause the catalyst to become deactivated.

Introduction

- The term membrane reactor describe a number of different types of reactor configurations that contain a membrane. The membrane can either provide a barrier to certain components while being permeable to others.
- Like reactive distillation, the membrane reactor is another technique for driving reversible reactions to the right toward completion in order to achieve very high conversion.
- These high conversion can achieve by having one of the reaction products diffuse out of a semipermeable membrane surrounding the reacting mixture.
- As a result, the reversible reaction will not be able to take place, and the reaction will continue to proceed to the right toward completion.

Reactor Mole Balances Summary

The GMBE applied to the four major reactor types (and the general reaction A→B)

Reactor	Differential	Algebraic	Integral	
Batch	$\frac{dN_A}{dt} = r_A V$		$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$	
CSTR		$V = \frac{F_{A0} - F_A}{-r_A}$		
PFR	$\frac{dF_A}{dV} = r_A$		$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{dr_A}$	
PBR	$\frac{dF_A}{dW} = r'_A$		$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A}$	

$$A + 2B \rightleftarrows C$$

Mole Balance

① Write mole balance on each species.†

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

↓

Rate Law

② Write rate law in terms of concentration.

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

↓

Relative Rates

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

$$\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{1}$$

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

↓

Stoichiometry

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

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

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.

$$\frac{dp}{dW} = -\frac{\alpha}{2p}\frac{F_T}{F_{T0}} \quad \text{with} \quad p = \frac{P}{P_0}$$

↓

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.

† For PBR, use $\frac{dF_A}{dW} = r_A, \quad \frac{dF_B}{dW} = r_B, \quad \frac{dF_C}{dW} = r_C.$

Membrane Reactors

Membrane reactors can be used to achieve conversions greater than the original equilibrium value. These higher conversions are the result of ***Le Chatelier's principle***; you can remove the reaction products and drive the reaction to the right.

To accomplish this, a membrane that is permeable to that reaction product, but impermeable to all other species, is placed around the reacting mixture.

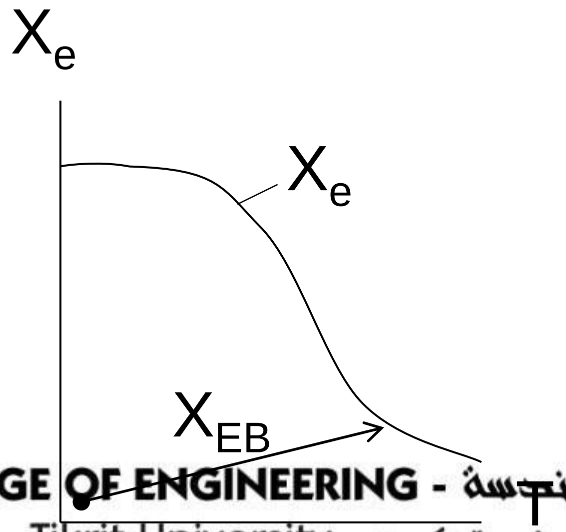
Membrane Reactors

Dehydrogenation Reaction:

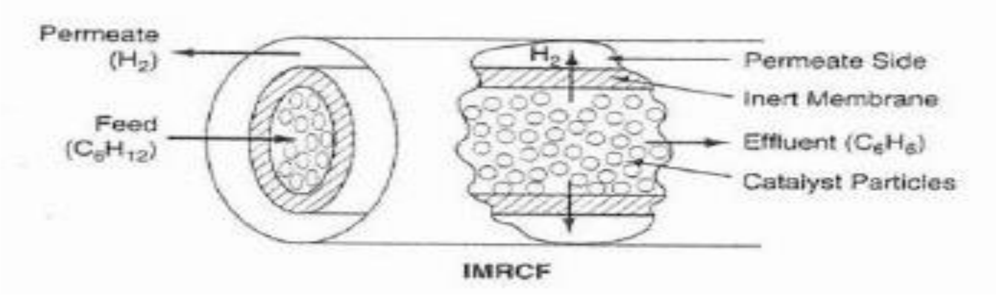
$C_3H_8 \leftrightarrow H_2 + C_3H_6$ $\quad\quad$ $A \leftrightarrow B + C$

Thermodynamically Limited:

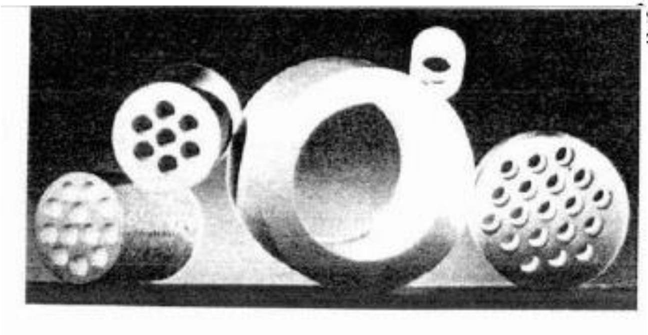
exothermic



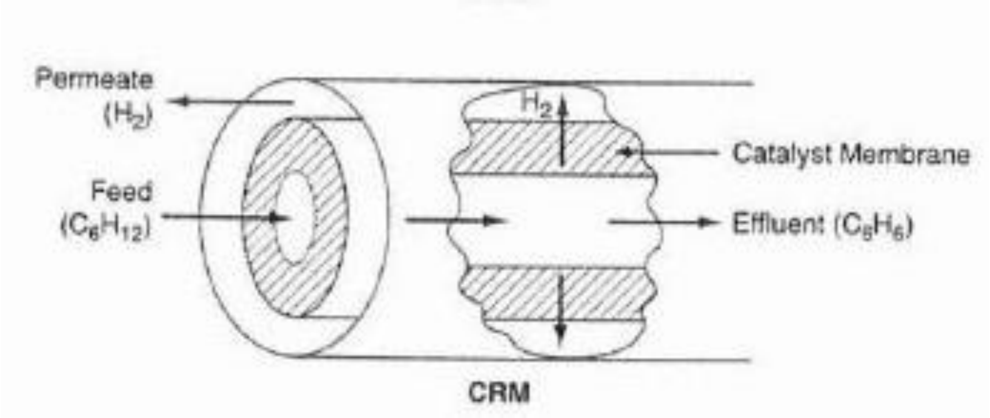
Membrane Reactors



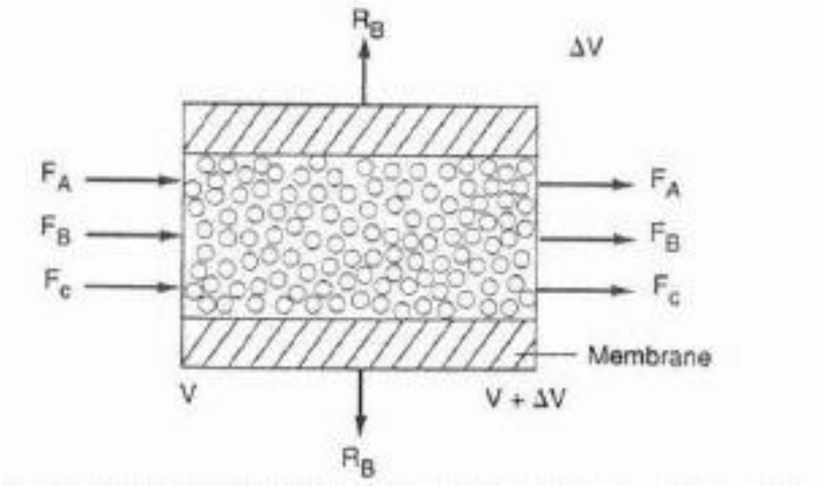
Cross section of IMRCF



Membrane Reactors

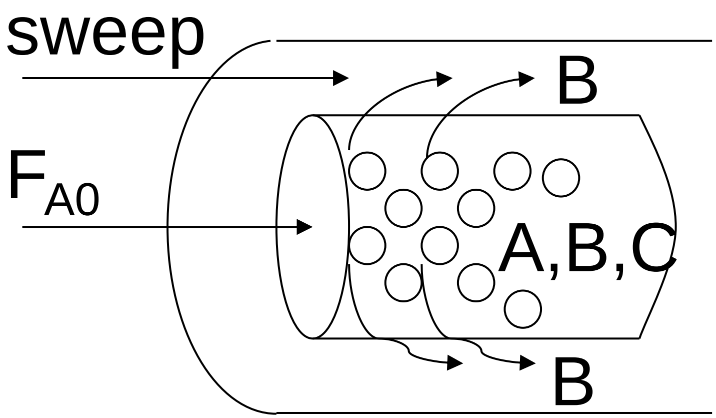


Cross section of CRM



Schematic of IMRCF for mole balance

Membrane Reactors

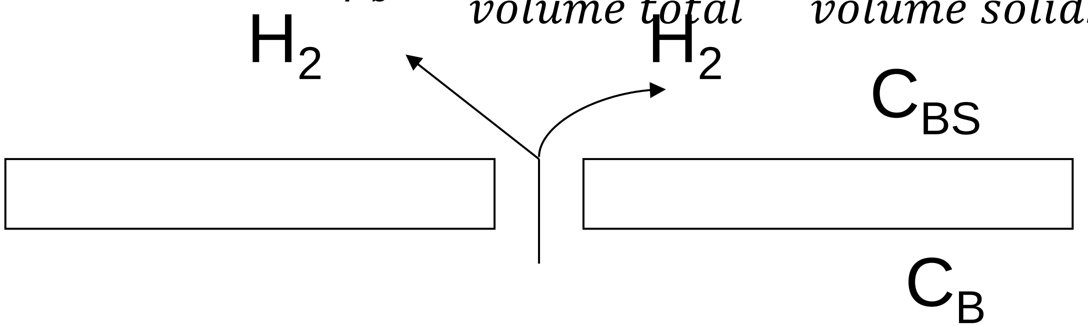


$W = \rho_b V$ = solids weight

$\rho_b = (1-\phi)\rho_C$ = bulk solids density

ρ_C = density of solids

$$\rho_b = \frac{volume\ solids}{volume\ total} * \frac{mass\ of\ solids}{volume\ solids}$$



A,C stay behind since they are too big

Membrane Reactors

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Mole Balance on Species A:

Species A: In – out + generation = 0

$$F_A\Big|_V - F_A\Big|_{V+\Delta V} + r_A \Delta V = 0$$

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

Membrane Reactors

Mole Balance on Species B:

Species B: In – out – out membrane + generation = 0

$$F_B\Big|_V - F_B\Big|_{V+\Delta V} - R_B\Delta V + r_B\Delta V = 0$$

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

$$R_B = \frac{\text{moles of B through sides}}{\text{volume of reactor}}$$

Membrane Reactors

$$W_B = k'_C(C_B - C_{BS}) = \frac{\text{molar flow rate through membrane}}{\text{surface area of membrane}} \left[\frac{mol}{m^2 \cdot s}\right]$$

$$a = \frac{\text{membrane surface area}}{\text{reactor volume}} = \frac{\pi DL}{\frac{\pi D^2}{4} L} = \frac{4}{D} \quad \left[\frac{m^2}{m^3}\right]$$

$$R_B = W_B a = k'_C a[C_B - C_{BS}]$$

$$k_C = k'_C a$$

$$R_B = k_C[C_B - C_{BS}] \quad \left[\frac{mol}{m^3 \cdot s}\right]$$

↑ (C_{BS}) Neglected most of the time

Membrane Reactors

Mole Balances:

$$(1)\quad \frac{dF_A}{dV} = r_A$$

$$(2)\quad \frac{dF_B}{dV} = r_B - R_B$$

$$(3)\quad \frac{dF_C}{dV} = r_C$$

Rate Law:

$$(4)\quad r_A = -k\left[C_A - \frac{C_B C_C}{K_C}\right]$$

Membrane Reactors

Relative Rates:

$$\frac{-r_A}{1} = \frac{r_B}{1} = \frac{r_C}{1}$$

Net Rates:

$$(5) \quad r_A = -r_B, \quad r_A = -r_C$$

Transport Law:

$$(6) \quad R_B = k_C C_B$$

Stoichiometry:

$$(7) \quad C_A = C_{T0}\frac{F_A}{F_T}$$

(isothermal, isobaric)

$$(8) \quad C_B = C_{T0}\frac{F_B}{F_T}$$

$$(9) \quad C_C = C_{T0}\frac{F_C}{F_T}$$

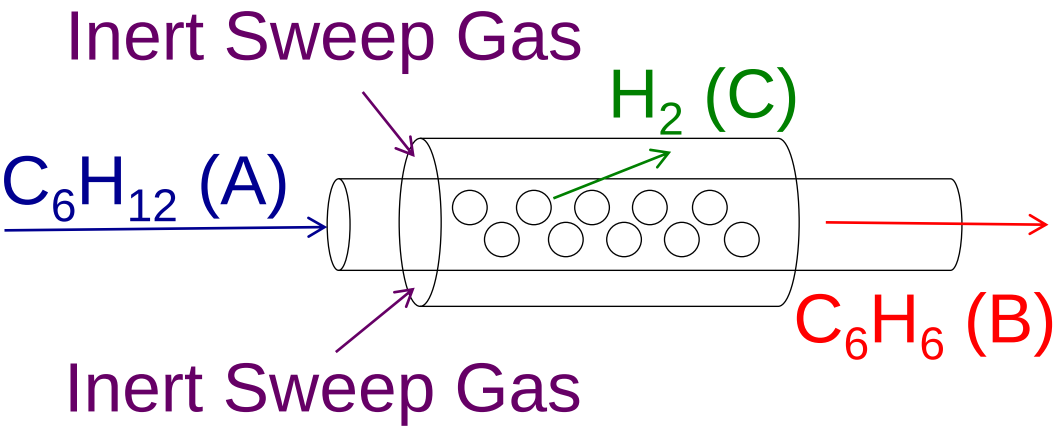
$$(10) \quad F_T = F_A + F_B + F_C$$

Parameters: $C_{TO} = 0.2, \quad F_{A0} = 5, \quad k = 4, \quad K_C = 0.0004, \quad k_C = 8$

Membrane Reactors

Example 1: The following reaction is to be carried out isothermally in a membrane reactor with no pressure drop. The membrane is permeable to product C, but impermeable to all other species.

$$C_6H_{12} \Leftrightarrow C_6H_6 + 3H_2$$
$$A \Leftrightarrow B + 3C$$



For membrane reactors, we cannot use conversion. We have to work in terms of the molar flow rates F_A, F_B, F_C.

Membrane Reactors

Mole Balances

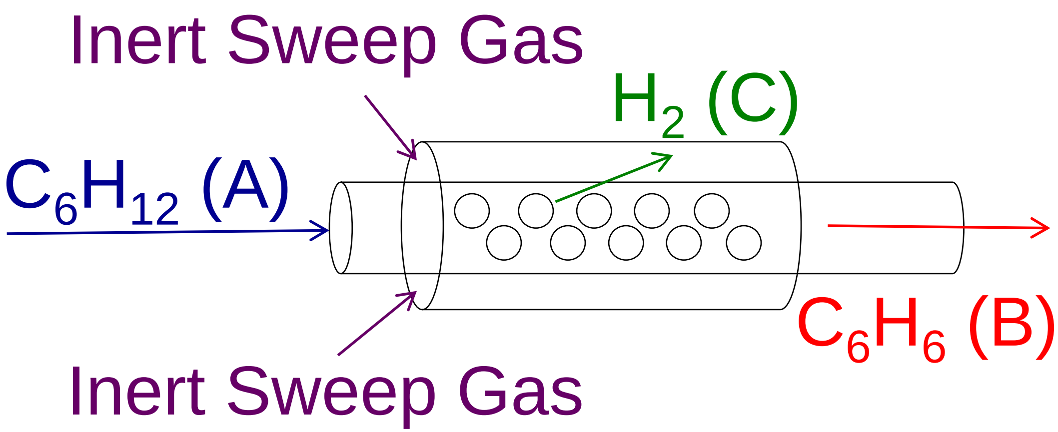
$$C_6H_{12} \Leftrightarrow C_6H_6 + 3H_2$$

$$A \Leftrightarrow B + 3C$$

$$\frac{dF_A}{dW} = r_A'$$

$$\frac{dF_B}{dW} = r_B'$$

$$\frac{dF_C}{dW} = r_C' - k_C C_C$$



Membrane Reactors

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Rate Law:

$$-r_A' = k_A\left[C_A - \frac{C_B C_C^3}{K_C}\right]$$

Relative Rates:

$$\frac{r_A'}{-1} = \frac{r_B'}{1} = \frac{r_C'}{3}$$

Net Rates:

$$r_B' = -r_A'$$
$$r_C' = -3r_A'$$

Membrane Reactors

Stoichiometry:

Isothermal, no Pressure Drop

$$C_{T0} = \frac{P_0}{RT_0}$$

$$C_A = C_{T0}\frac{F_A}{F_T}$$

$$C_B = C_{T0}\frac{F_B}{F_T}$$

$$C_C = C_{T0}\frac{F_C}{F_T}$$

$$F_T = F_A + F_B + F_C$$

Membrane Reactors

Combine: - Use Polymath

Parameters:

$$C_{T0} = 0.2\,\frac{mol}{dm^3}$$

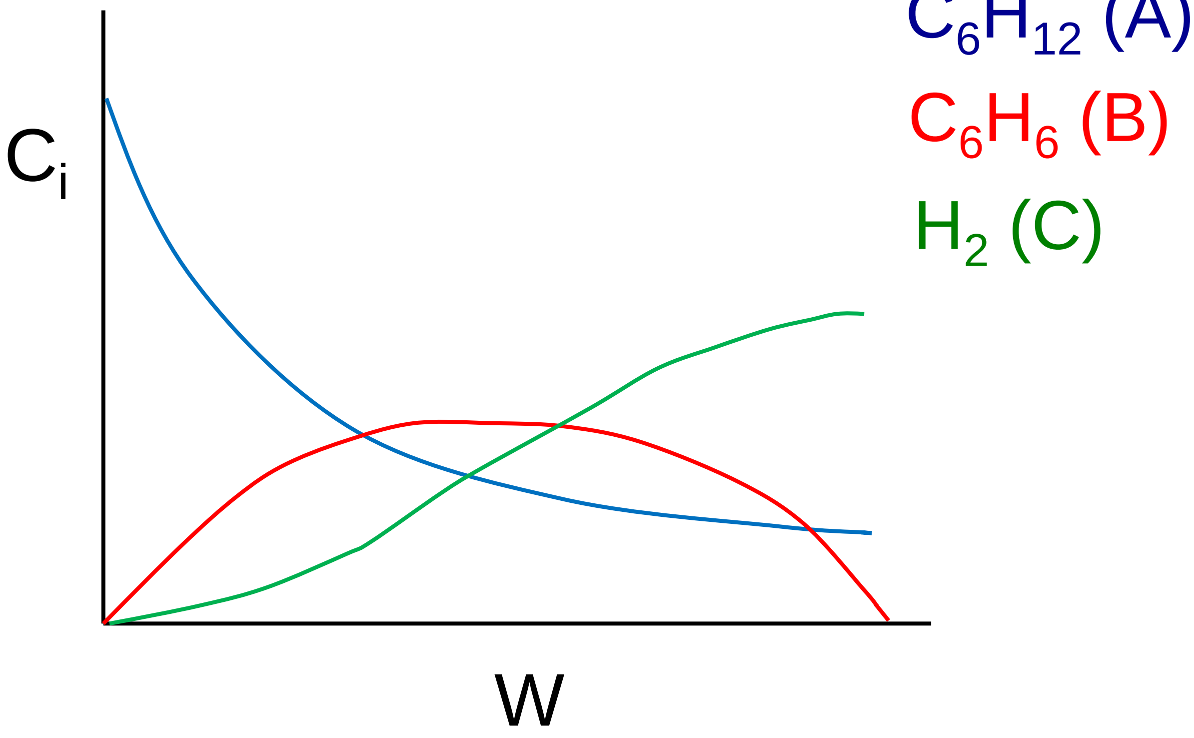
$$F_{A0} = 10\,\frac{mol}{s}$$

$$k_A = 10\,\frac{dm^3}{kg\ cat\ s}$$

$$k_C = 0.5\,\frac{dm^3}{kg\ cat\ s}$$

$$K_C = 200\,\frac{mol^2}{dm^6}$$

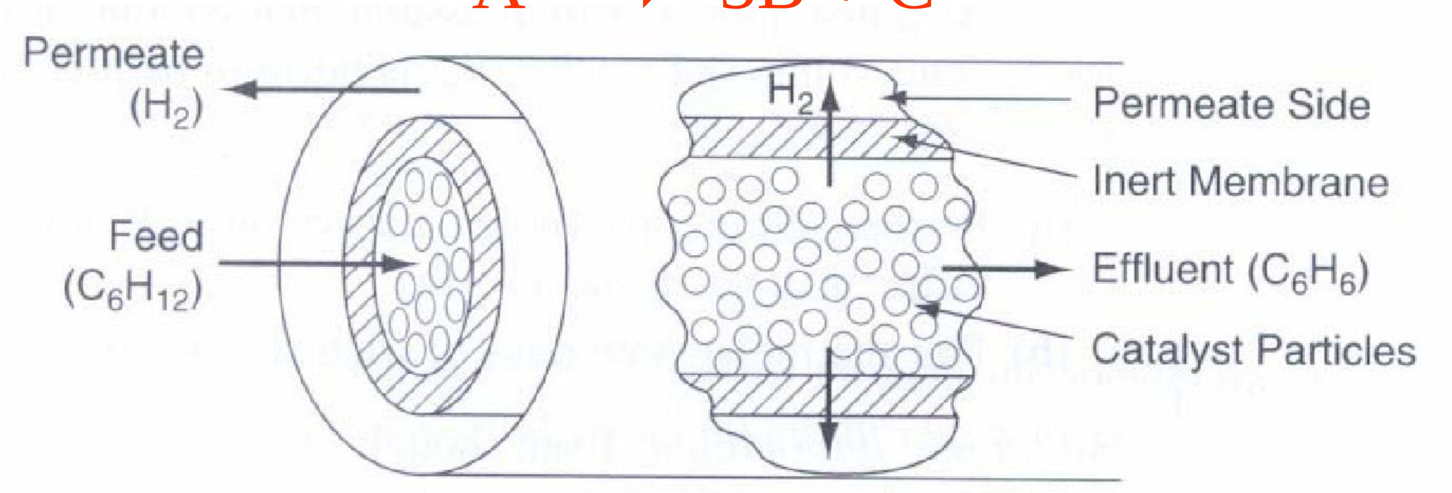
Membrane Reactors



- Inert membrane reactor with catalyst pellets on the feed side (IMRCF)

$$C_6H_{12} \leftrightarrows 3H_2 + C_6H_6$$

$$A \leftrightarrows 3B + C$$

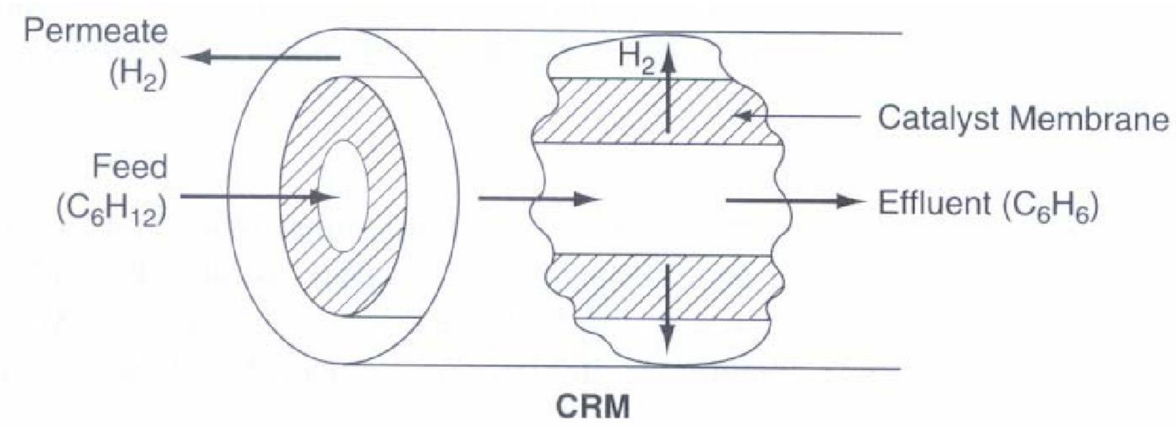


IMRCF

H_2 molecule is small enough to diffuse through the small pore of the membrane while C_6H_{12} and C_6H_6 cannot.

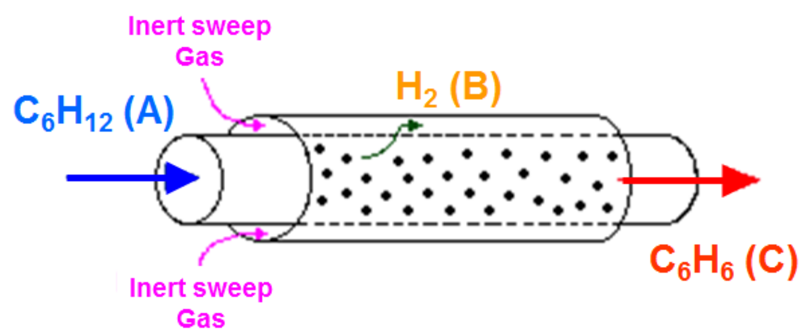
Catalytic membrane reactor (CMR)

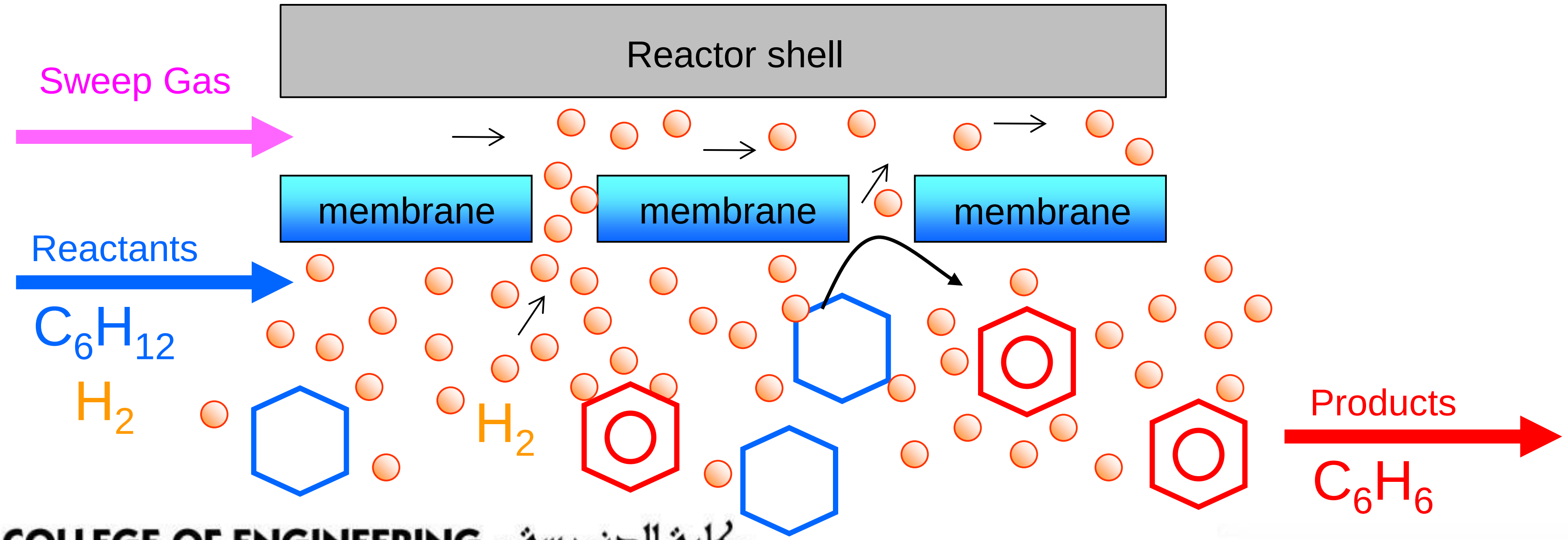
$$C_6H_{12} \leftrightarrows 3H_2 + C_6H_6$$
$$A \leftrightarrows 3B + C$$



Membrane reactors are commonly used in dehydrogenation reactions, where only one of the products (molecular hydrogen) is small enough to pass through the membrane. This raises the conversion for the reaction, making the process more economical.

H_2 diffuses through the membrane while C_6H_6 does not



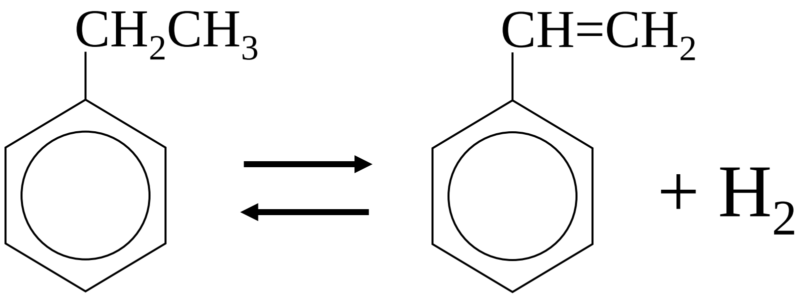


- According to The DOE, an energy saving of 10 trillion Btu/yr could result from the use of catalytic membrane reactors as replacements for conventional reactors for dehydrogenation reactions:

such as the.

$$A \leftrightarrows B + C$$

Dehydrogenation of ethylbenzene to styrene



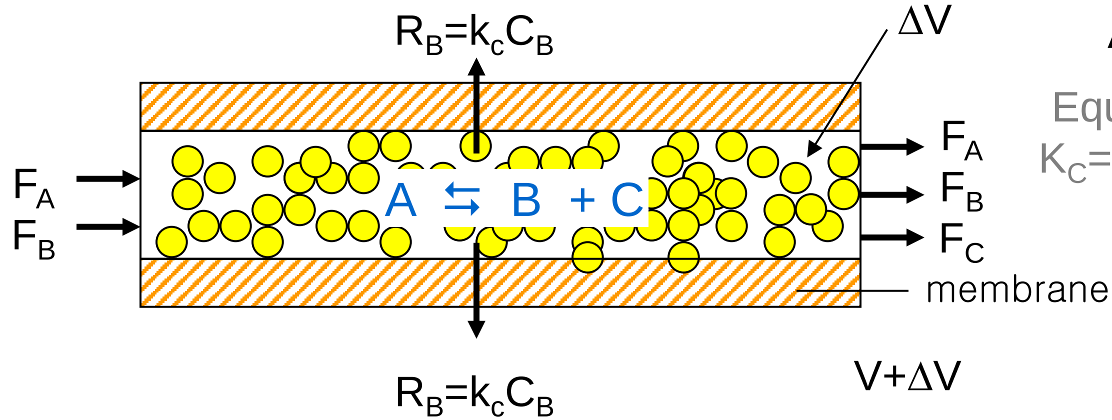
Dehydrogenation of butane to butylene

$$C_4H_{10} \leftrightarrows C_4H_8 + H_2$$

Dehydrogenation of propane to propylene

$$C_3H_8 \leftrightarrows C_3H_6 + H_2$$

The basic algorithm for solving reaction in the membrane reactor



P=8.2 atm
T=227°C
F_{A0}=10mol/min

A ⇆ B + C

Equilibrium constant
K_C=0.05 mol @227°C

1. Mole balance: A, B & C

for a differential mole balance on A in the catalytic bed at steady state

$$F_A|_V - F_A|_{V+\Delta V} + r_A \Delta V = 0$$

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

for a differential mole balance on B in the catalytic bed at steady state

$$F_B|_V - F_B|_{V+\Delta V} - R_B \Delta V + r_B \Delta V = 0$$

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

for a differential mole balance on C in the catalytic bed at steady state

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

The basic algorithm for solving reaction in the membrane reactor

2. Rate law:

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

3. Transport out the sides of the reactor: C_{BS}~0

$$R_B = k_C C_B$$

k_c is a transport coefficient. k_c=f(membrane & fluid properties, tube diameter…) ➡ constant

4. Stoichiometry: P & T = const

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

$$F_T = F_A + F_B + F_C$$

$$-r_A = r_B = r_C$$

$$C_A = C_{T0}\frac{F_A}{F_T}\frac{P}{P_0}\frac{T_0}{T} \qquad C_B = C_{T0}\frac{F_B}{F_T}\frac{P}{P_0}\frac{T_0}{T}$$

$$C_C = C_{T0}\frac{F_C}{F_T}\frac{P}{P_0}\frac{T_0}{T} \qquad C_D = C_{T0}\frac{F_D}{F_T}\frac{P}{P_0}\frac{T_0}{T}$$

The basic algorithm for solving reaction in the membrane reactor

5. Combining and Summarizing:

$$\frac{dF_A}{dV} = r_A; \quad \frac{dF_B}{dV} = -r_A - k_c C_{T0}\left(\frac{F_B}{F_T}\right); \quad \frac{dF_C}{dV} = -r_A$$

$$-r_A = k_c C_{T0}\left[\left(\frac{F_A}{F_T}\right) - \frac{C_{T0}}{K_C}\left(\frac{F_B}{F_T}\right)\left(\frac{F_C}{F_T}\right)\right]$$

$$F_T = F_A + F_B + F_C$$

6. Parameter evaluation: C_{T0}=0.2 mol/L, k=0.7 min^{-1}, K_C=0.05 mol/L, k_c=0.2 min^{-1}
F_{A0}=10 mol/min, F_{B0}=F_{C0}=0

$$C_{T0} = \frac{P_0}{RT_0} = \frac{830.6\ \text{kPa}}{\left[(8.314\,\text{kPa}\cdot\text{dm}^3/(\text{mol}\cdot\text{K})\right](500\text{K})} = 0.2\,\frac{\text{mol}}{\text{dm}^3}$$

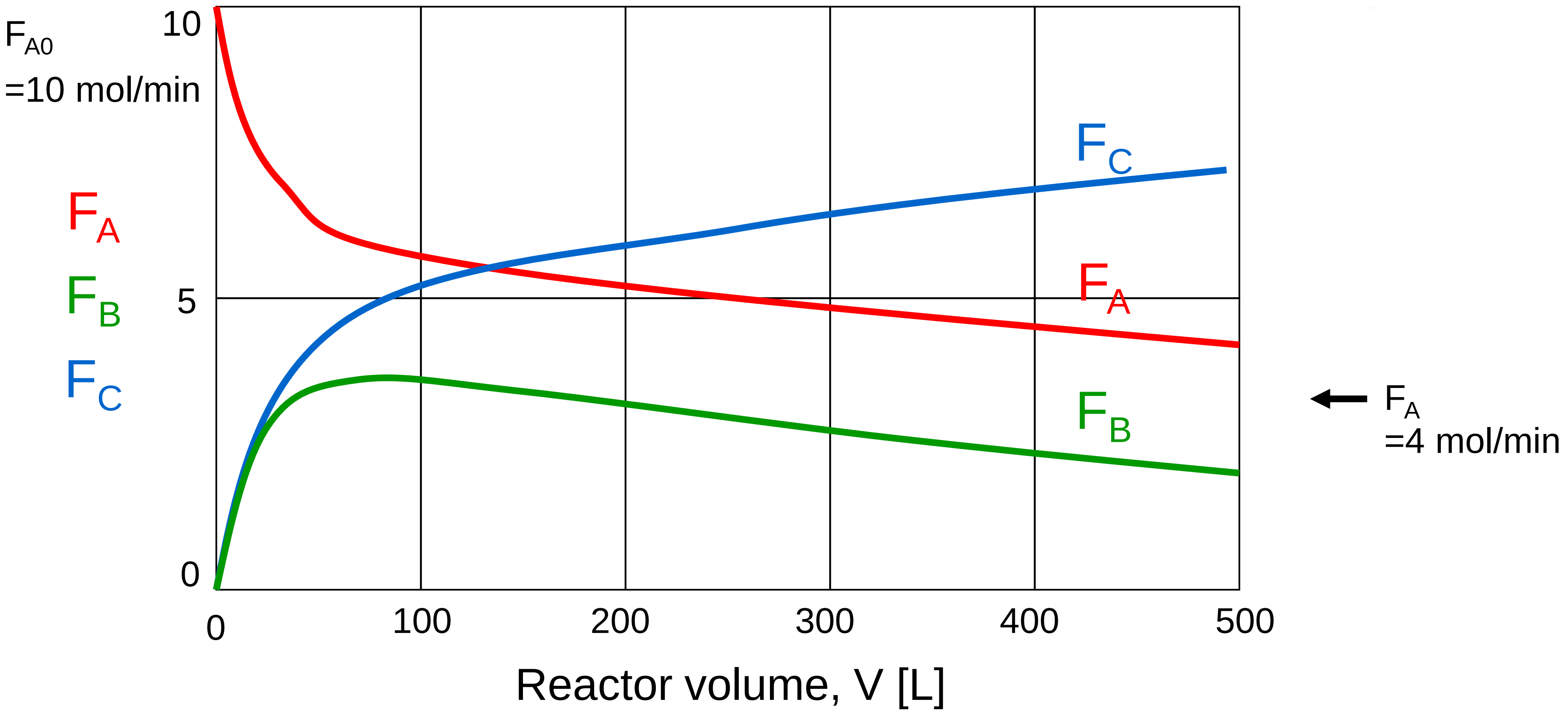
7. Numerical solution: Solve with POLYMATH or MATLAB

The basic algorithm for solving reaction in the membrane reactor

POLMATH solution:

$k_c = 0.2\ min^{-1}$

$A \leftrightarrows B + C$



$$X = \frac{F_{A0} - F_A}{F_{A0}} = \frac{10 - 4}{10} = 0.6$$

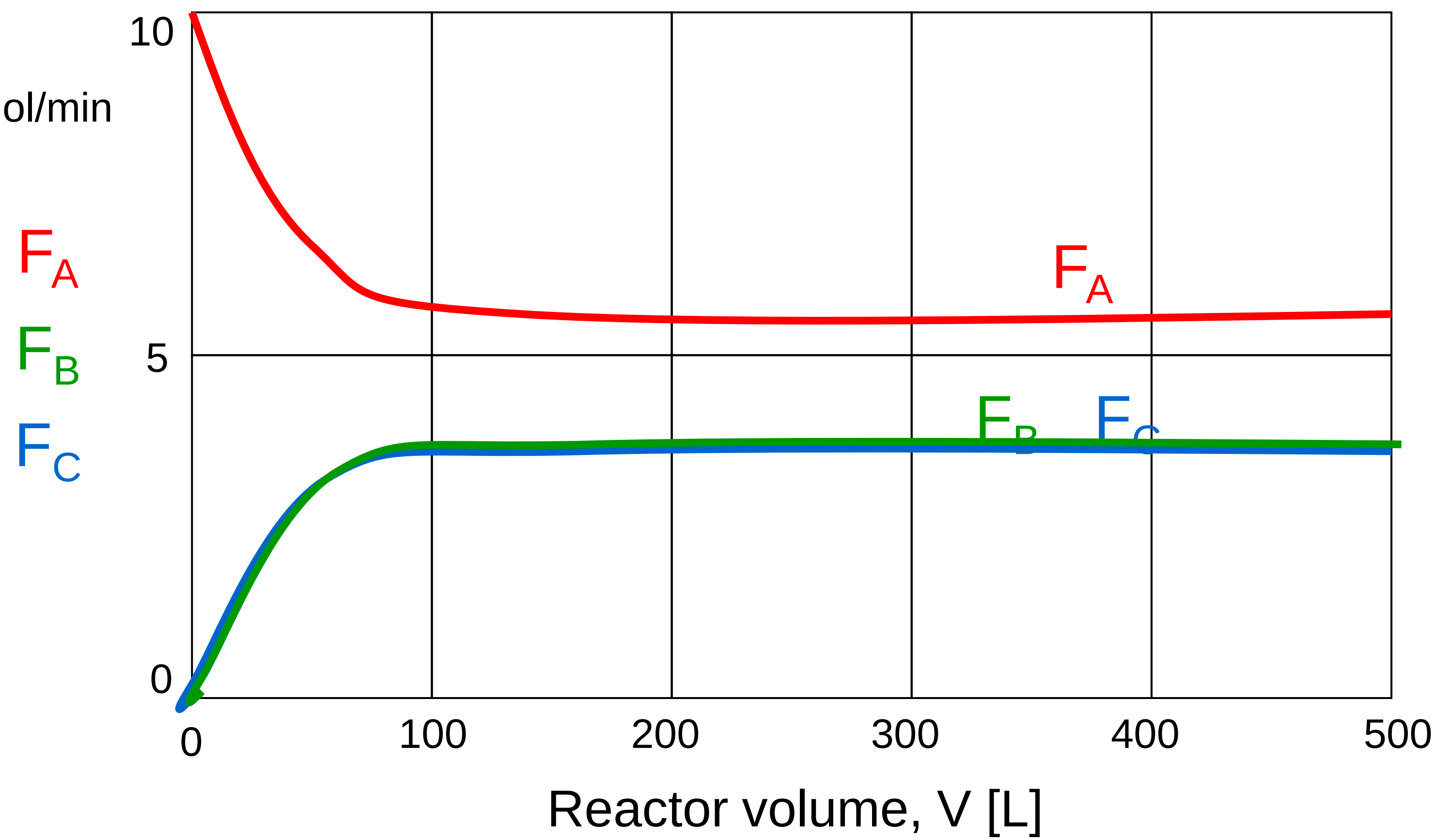
The basic algorithm for solving reaction in the membrane reactor

$A \leftrightarrows B + C$

POLMATH solution:

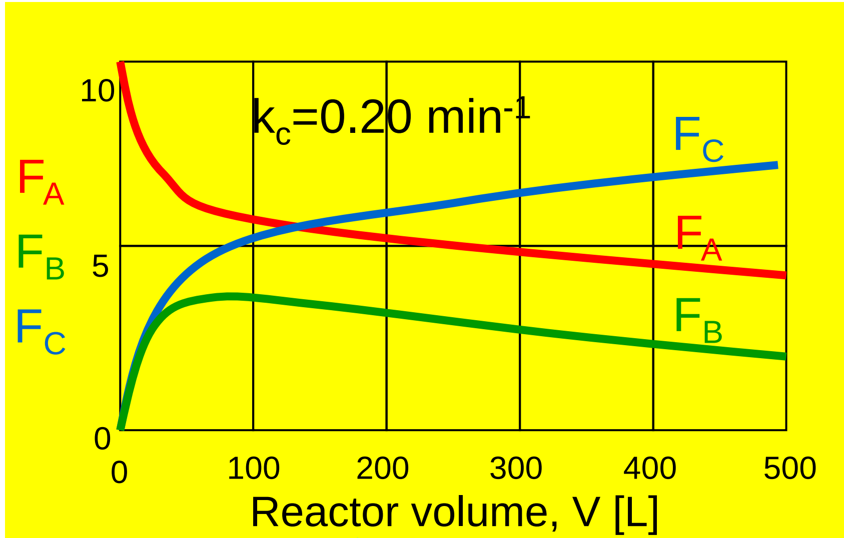
k_c=0.0022 min^{-1}

F_{A0} =10 mol/min

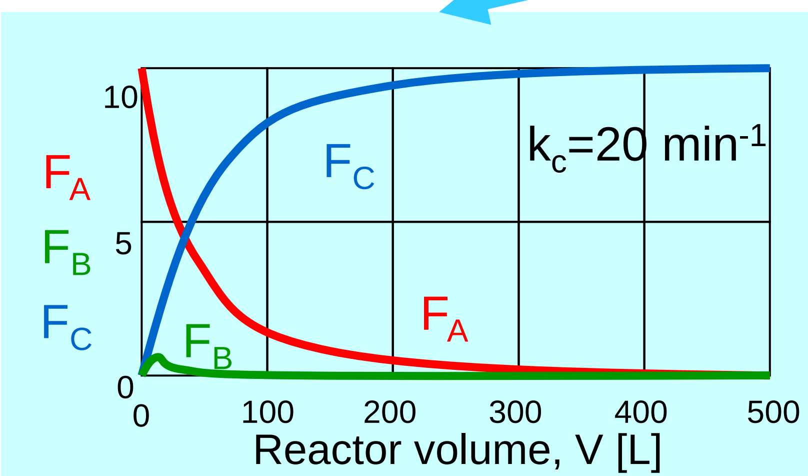


Effects of side stream, $R_B=k_cC_B$ in a membrane reactor

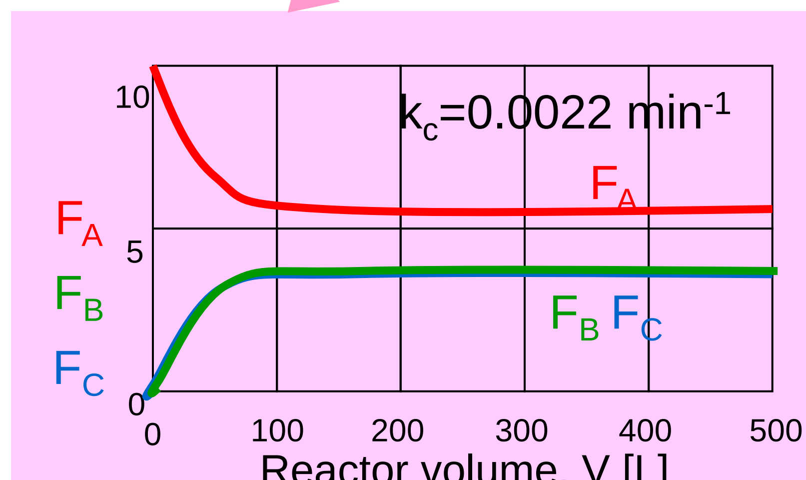
$A \leftrightarrows B + C$



Large side stream

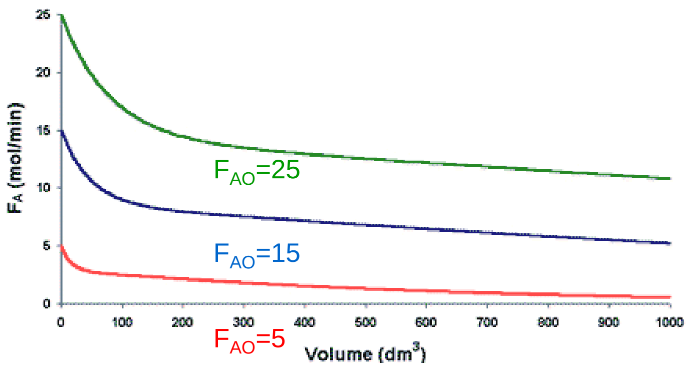


Little side stream

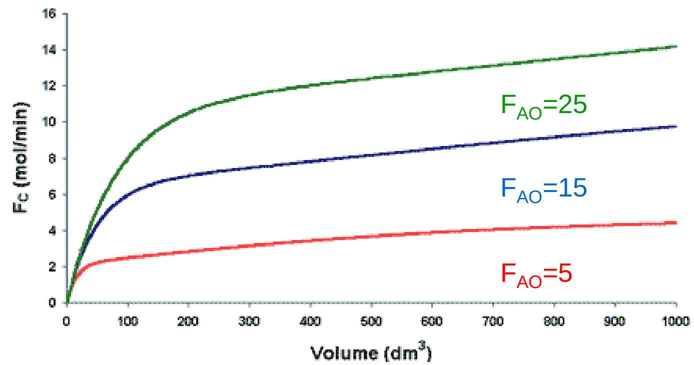


Effects of changing the inlet flowrate, F_{A0}

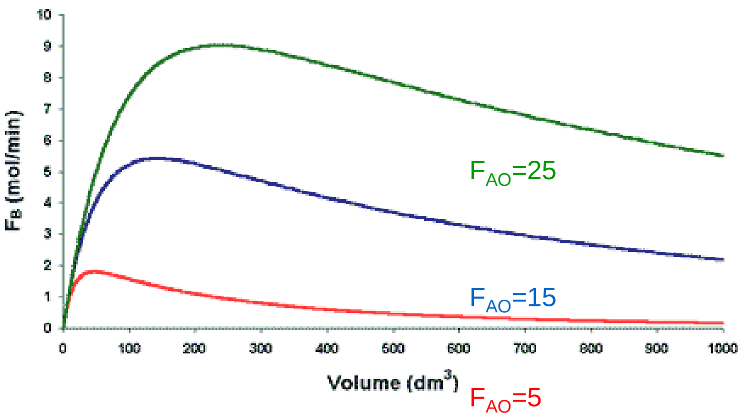
F_A vs Volume with Changing F_{A0}



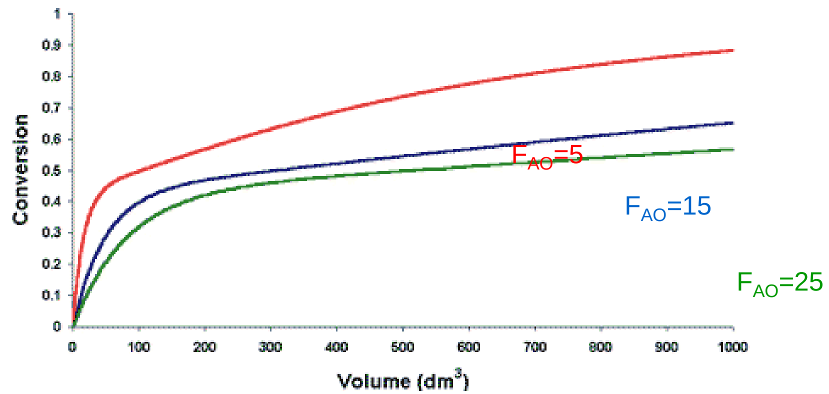
F_C vs Volume with Changing F_{A0}



F_B vs Volume with Changing F_{A0}



Conversion vs Volume with Changing F_{A0}



As expected, our flow rates increase as F_{A0} increases. Interestingly though, conversion actually decreases as F_{A0} increases. Why? Even though more of reactant A enters the reactor as the flow rate increases, it spends less time in the reactor, which causes the decrease in conversion.

Are you ready?

Summary

- In this lecture, we covered:

- - The fundamentals and applications of membrane reactors.
- - Key concepts: mole balances, rate laws, and stoichiometry.
- - Transport laws and their role in reaction dynamics.
- - Practical examples of membrane reactor operations.
- Membrane reactors offer significant advantages in increasing conversion and selectivity, making them essential tools in modern chemical engineering.