Lecture 9

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Lecture 9 – Thursday 2/7/2013

Balances in terms of molar flow rates

- Block 1: **Mole Balances**
  - Balance Equation on Every Species
- Block 2: **Rate Laws**
  - Relative Rates
  - Transport Laws
- Block 3: **Stoichiometry**
- Block 4: **Combine**

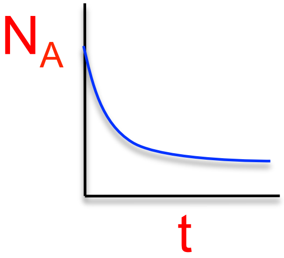
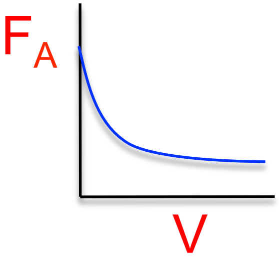
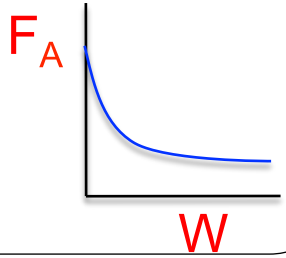
- **Membrane Reactors:**

Used for thermodynamically limited reactions

Review Lecture 1

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.[†]

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

Rate Law

② Write rate law in terms of concentration.

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

Relative Rates

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

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

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

Stoichiometry

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

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

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

(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 $\frac{dF_A}{dW} = r_A,\ \frac{dF_B}{dW} = r_B,\ \frac{dF_C}{dW} = r_C.$

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.

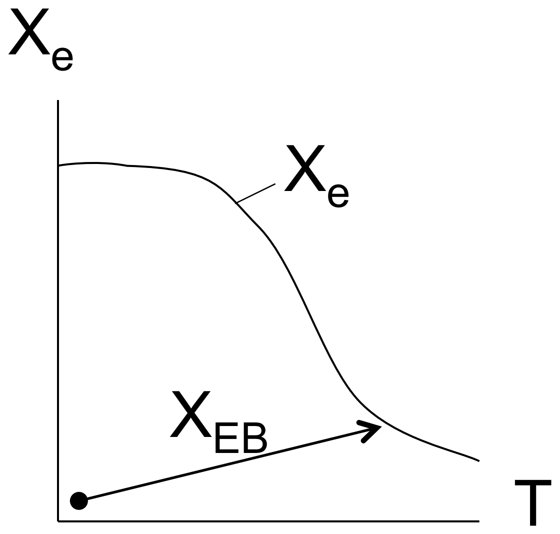
Membrane Reactors

Dehydrogenation Reaction:

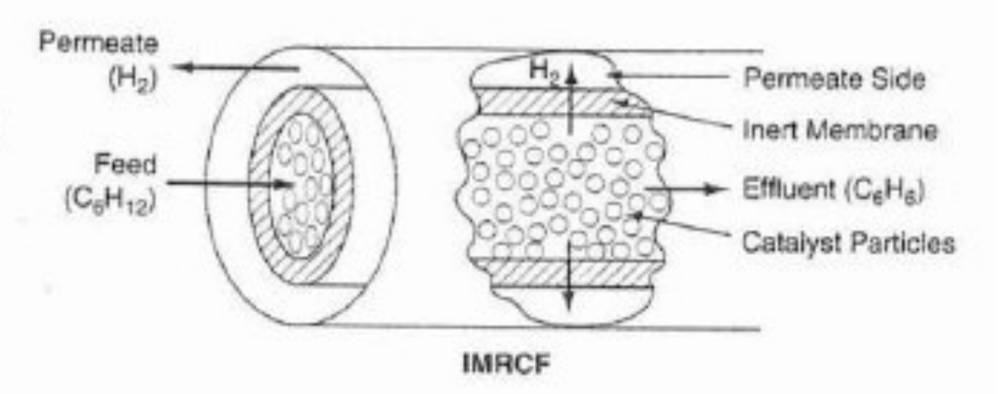
$C_3H_8 \leftrightarrow H_2 + C_3H_6$ $A \leftrightarrow B + C$

Thermodynamically Limited:

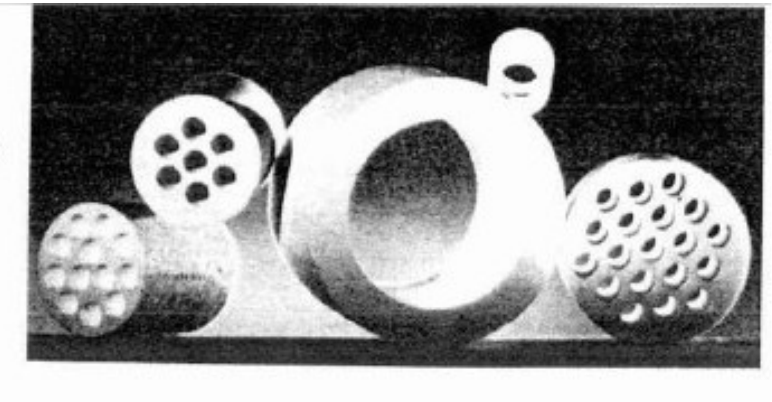
exothermic



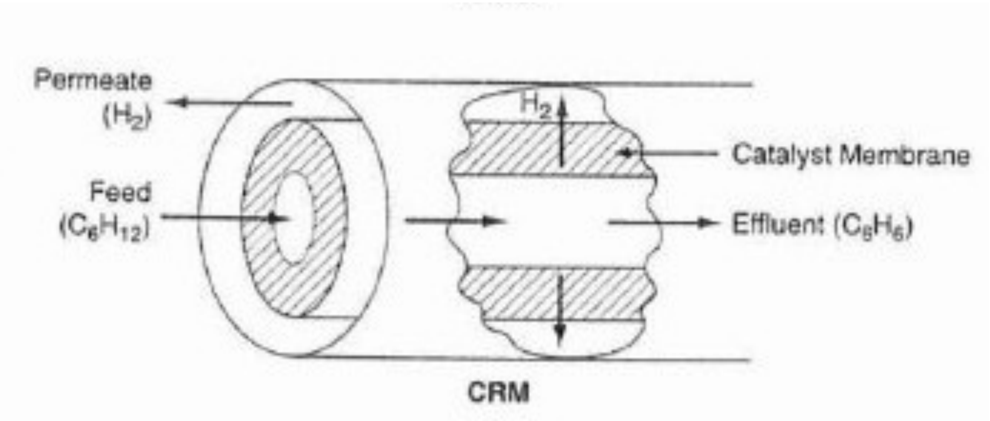
Membrane Reactors



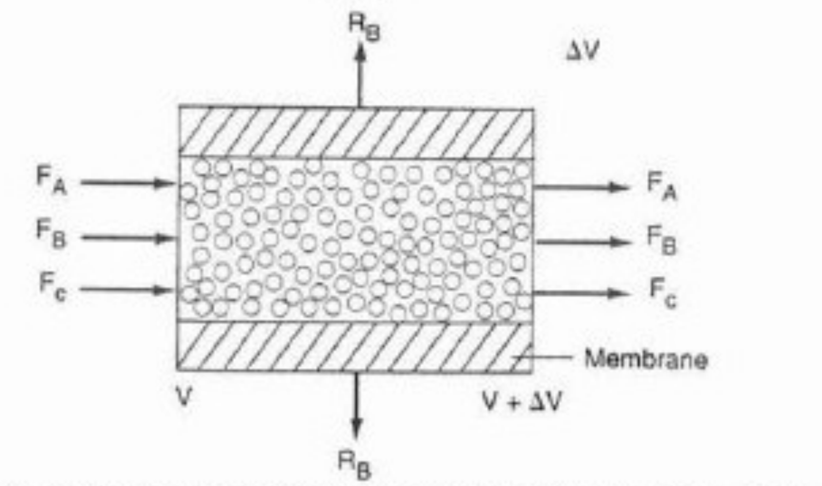
Cross section of IMRCF



Membrane Reactors

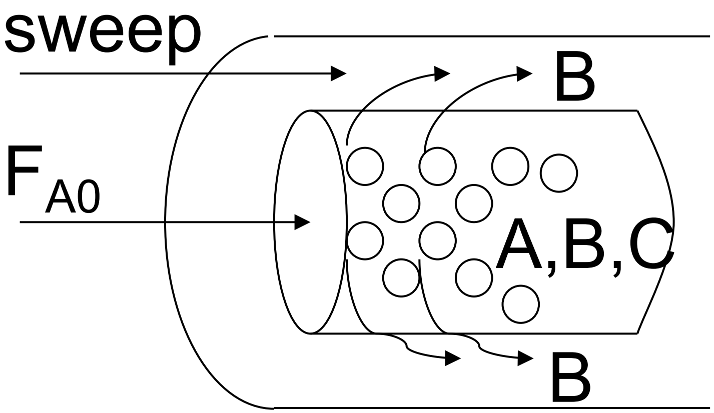


Cross section of CRM



Schematic of IMRCF for mole balance

Membrane Reactors

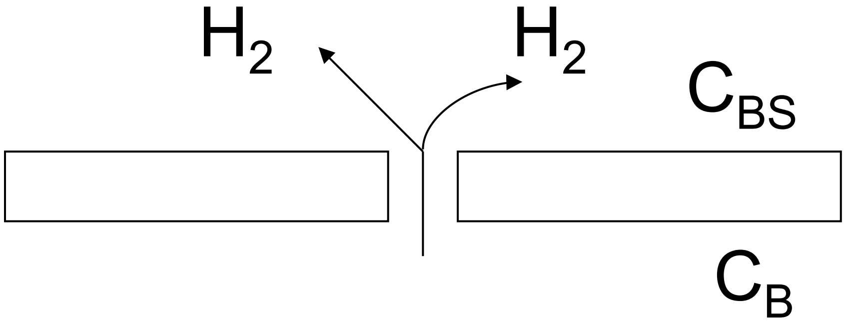


$W = \rho_b V =$ *solids weight*

$\rho_b = (1\text{-}\phi)\rho_C =$ *bulk solids density*

$\rho_C =$ *density of solids*

$\rho\downarrow b = volume\ solids/volume\ total * mass\ of\ solids/volume\ solids$



A,C stay behind since they are too big

Membrane Reactors

Mole Balance on Species A:

Species A: In – out + generation = 0

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

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

Membrane Reactors

Mole Balance on Species B:

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

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

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

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

Membrane Reactors

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

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

$$R_B = W_B a = k_C^{'} a\left[C_B - C_{BS}\right]$$

$$k_C = k_C^{'} a$$

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

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)

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

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

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

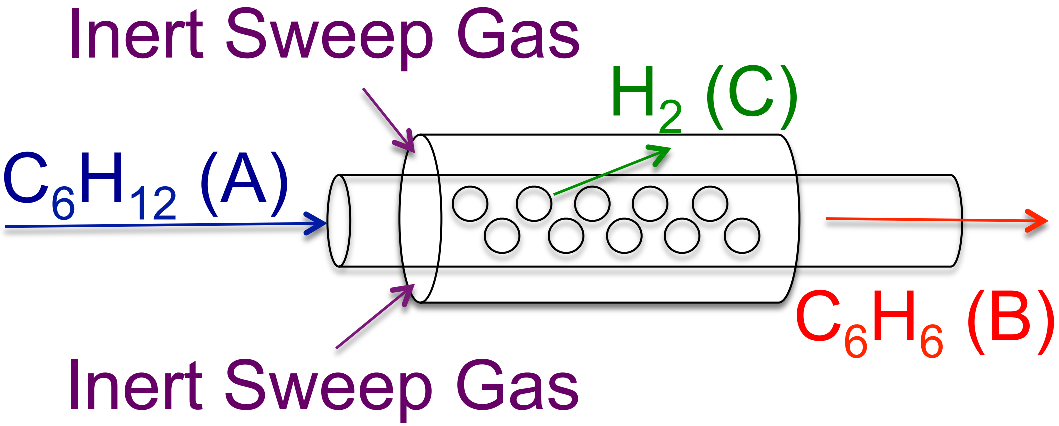
Parameters: $C_{TO} = 0.2, \; F_{A0} = 5, \; k = 4, \; K_C = 0.0004, k_C = 8$

Membrane Reactors

<u>Example</u>: 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

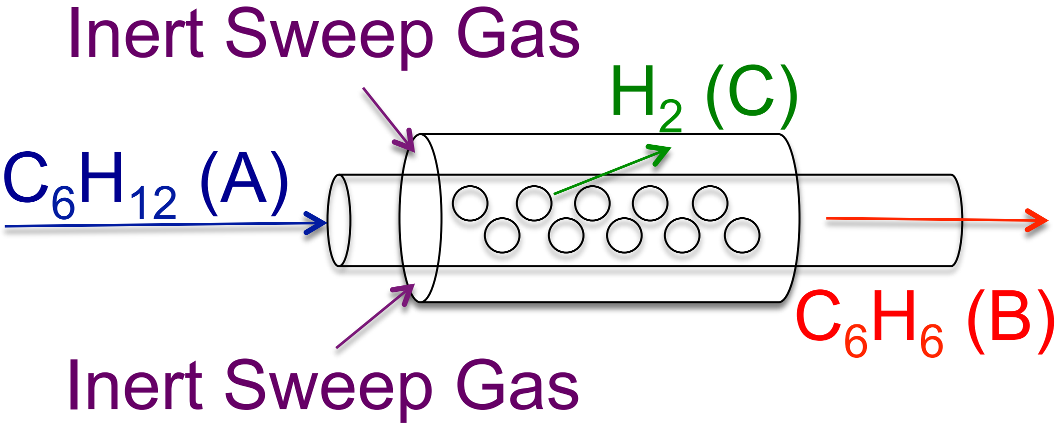
$$C_6H_{12} \Leftrightarrow C_6H_6 + 3H_2$$

$$A \Leftrightarrow B + 3C$$

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

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

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



Membrane Reactors

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:

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

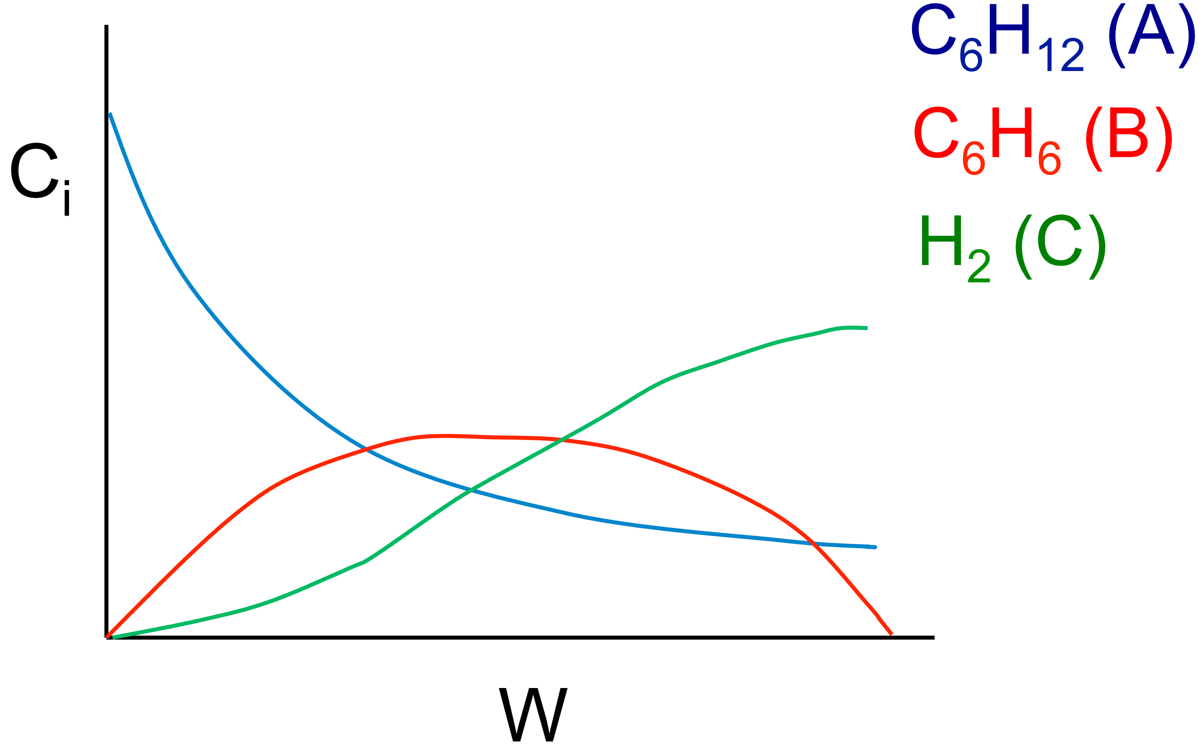
$$F_{A0} = 10\frac{mol}{s}$$

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

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

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

Membrane Reactors



End of Lecture 9