Multiple Reactions

- Carefully read over sections in Chapters 6 and 8 pertaining to multiple reactions, reactions with mass transfer, and transient operation of flow reactors
  - ~ Pay special attention to the many examples which illustrate key design strategies

Multiple Reactions

- Parallel $A \xrightarrow{k_1} B$, $A \xrightarrow{k_2} C$
- Series $A \xrightarrow{k_1} B \xrightarrow{k_2} C$
- Complex $A + B \xrightarrow{k_1} C + D$, $A + C \xrightarrow{k_2} E$
- Independent $A \xrightarrow{k_1} B + C$, $D \xrightarrow{k_2} E + F$

Multiple Reactions

- Selectivity

$$A \xrightarrow{k_1} D \qquad A \xrightarrow{k_2} U \qquad \text{or} \qquad A \xrightarrow{k_1} D \xrightarrow{k_2} U$$

Instantaneous Selectivity: $S_{D/U} = \frac{r_D}{r_U}$

Overall Selectivity: $\tilde{S}_{D/U} = \frac{F_D}{F_U} \quad \left(= \frac{N_D}{N_U} \right)$

$\frac{F_D}{F_U}$: Flow Reactor; $\frac{N_D}{N_U}$: Batch Reactor

Multiple Reactions

- Reaction Yield

$$A \xrightarrow{k_1} D \qquad A \xrightarrow{k_2} U \qquad \text{or} \qquad A \xrightarrow{k_1} D \xrightarrow{k_2} U$$

Instantaneous Yield: $Y_{D/A} = \frac{r_D}{-r_A}$

Overall Yield: $\tilde{Y}_{D/A} = \frac{F_D}{F_{A0} - F_A} \quad \left(= \frac{N_D}{N_{A0} - N_A} \right)$

$\frac{F_D}{F_{A0} - F_A}$: Flow Reactor; $\frac{N_D}{N_{A0} - N_A}$: Batch Reactor

Maximizing Selectivity and Yield*

- Sample reactor types for maximizing selectivity and yield…

* See page 296 of text (Fogler, ***Essentials***) for further details

Maximizing Selectivity and Yield

- Example: Consider pair of competitive reactions

$$A \xrightarrow{k_D} D$$

$$A \xrightarrow{k_U} U$$

where

$$r_D = k_D C_A^{\alpha_1} \qquad r_U = k_U C_A^{\alpha_2}$$

- Then

$$S_{D/U} \equiv \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

Maximizing Selectivity and Yield

- Example…

$$A \xrightarrow{k_D} D \qquad A \xrightarrow{k_U} U \qquad S_{D/U} \equiv \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

- Case 1: $\alpha_1 > \alpha_2 \quad \Rightarrow \quad S_{D/U} \propto C_A^a, \quad a = \alpha_1 - \alpha_2$

  ~ Maintain high concentration of *A*
  - Plug flow reactor or batch reactor
  - No diluents
  - High pressure (if gas phase reaction)

Maximizing Selectivity and Yield

- Example…

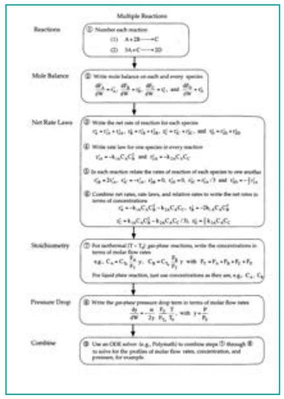
$$A \xrightarrow{k_D} D \qquad A \xrightarrow{k_U} U \qquad S_{D/U} \equiv \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

- Case 2: $\alpha_1 < \alpha_2 \quad \Rightarrow \quad S_{D/U} \propto \frac{1}{C_A^b}, \quad b = \alpha_2 - \alpha_1$

  ~ Maintain low concentration of *A*
  - CSTR
  - Diluents

Design Procedure for Multiple Reactions

- Procedure outline…



Design Procedure for Multiple Reactions

- Writing net rates of formation

reaction 1 $\quad A + B \rightarrow 3C + D \qquad r_A = r_{1A} + r_{2A} + r_{3A} + \ldots$

reaction 2 $\quad A + 2C \rightarrow 3E \qquad r_B = r_{1B} + r_{2B} + r_{3B} + \ldots$

reaction 3 $\quad 2B + 3E \rightarrow 4F \qquad \vdots$

$\vdots$

$$r_J = \sum_i r_{iJ}$$

species index (J); reaction index (i)

$$\frac{r_{1A}}{-a_1} = \frac{r_{1B}}{-b_1} = \frac{r_{1C}}{c_1} = \frac{r_{1D}}{d_1} \quad \Rightarrow \frac{r_{1A}}{-1} = \frac{r_{1B}}{-1} = \frac{r_{1C}}{3} = \frac{r_{1D}}{1}$$

$$\frac{r_{2A}}{-a_2} = \frac{r_{2C}}{-c_2} = \frac{r_{2E}}{e_2} \quad \Rightarrow \frac{r_{2A}}{-1} = \frac{r_{2C}}{-2} = \frac{r_{2E}}{3}$$

$\vdots$

Design Procedure for Multiple Reactions

- CSTR Example:
  - ~ Consider isothermal, isobaric conversion of benzene with side reaction

principal reaction (1) ⟶ $C_6H_6 + 2H_2 \rightarrow C_6H_{10} \quad \Rightarrow \quad B + 2H \rightarrow C$

side reaction (2) ⟶ $C_6H_{10} + H_2 \rightarrow C_6H_{12} \quad \Rightarrow \quad C + H \rightarrow CH$

- ~ Kinetics:

reaction 1: benzene to cyclohexene $-r'_{1B} = \dfrac{0.07128 P_{C_6H_6} P_{H_2}^{0.5}}{1 + 0.0264 P_{C_6H_6}}$ moles benzene converted per kg catalyst per h

reaction 2: cyclohexene to cyclohexane $-r'_{2C} = \dfrac{0.0028 P_{C_6H_{10}} P_{H_2}}{1 + 0.07 P_{C_6H_{10}}}$ moles cyclohexene converted per kg catalyst per h

CHG 3127: The Design Procedure: Multiple Reactions

Design Procedure for Multiple Reactions

- CSTR Example…
  - ~ Modifications to design approach

C. Design Equations:

benzene mole balance: $F_B - F_{B0} = r'_B W = r'_{1B} W$

hydrogen mole balance: $F_H - F_{H0} = r'_H W = (r'_{1H} + r'_{2H}) W = (2r'_{1B} + r'_{2C}) W$

cyclohexene mole balance: $F_C - F_{C0} = r'_C W = (r'_{1C} + r'_{2C}) W = (-r'_{1B} + r'_{2C}) W$

cyclohexane mole balance: $F_{CH} - F_{CH0} = r'_{CH} W = r'_{2CH} W = -r'_{2C} W$

$B + 2H \rightarrow C$

$C + H \rightarrow CH$

CHG 3127: The Design Procedure: Multiple Reactions

Design Procedure for Multiple Reactions

- CSTR Example…
  - ~ Modifications to design approach…

D. Rate Laws and Net Rates of Formation:

net benzene production: $r_B = r_{1B}$

net hydrogen production: $r_H = r_{1H} + r_{2H}$

$$\frac{r_{1B}}{-1} = \frac{r_{1H}}{-2} = \frac{r_{1C}}{1} \Rightarrow r_{1H} = 2r_{1B},\ r_{1C} = -r_{1B}$$

net cyclohexene production: $r_C = r_{1C} + r_{2C}$

$$\frac{r_{2C}}{-1} = \frac{r_{2H}}{-1} = \frac{r_{2CH}}{1} \Rightarrow r_{2H} = r_{2C},\ r_{2CH} = -r_{2C}$$

net cyclohexane production: $r_{CH} = r_{2CH}$

$B + 2H \rightarrow C$

$C + H \rightarrow CH$

Design Procedure for Multiple Reactions

- CSTR Example…
  - ~ Modifications to design approach…

E. Stoichiometry:

$$C_j = C_{T0}\frac{F_j}{F_T}\frac{P}{P_0}\frac{T_0}{T} = C_{T0}\frac{F_j}{F_T} \quad \text{(isothermal, isobaric)}$$

where

$$P_j = C_j RT \quad \text{and} \quad F_T = \sum_{\text{all species present}} F_j$$

$B + 2H \rightarrow C$

$C + H \rightarrow CH$

Design Procedure for Multiple Reactions

- CSTR Example: VBA Code

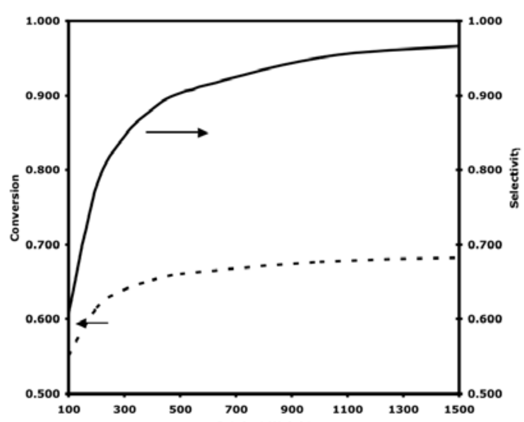
```
Public Function r_Benzene(ByVal f_b As Double, ByVal f_h As Double,
                          ByVal f_c As Double, ByVal f_ch As Double) As Double
      Dim F_tot, p_b, p_h As Double
      F_tot = f_b + f_c + f_h + f_ch
      p_h = pressure_Calc(f_h, F_tot)
      p_b = pressure_Calc(f_b, F_tot)
       r_Benzene = 0.07128 * p_b * p_h ^ 0.5 / (1 + 0.0264 * p_b)
End Function

Public Function r_Cyclohexene(ByVal f_b As Double, ByVal f_h As Double,
                              ByVal f_c As Double, ByVal f_ch As Double) As Double
       Dim F_tot, p_c, p_h As Double
      F_tot = f_b + f_c + f_h + f_ch
      p_h = pressure_Calc(f_h, F_tot)
      p_c = pressure_Calc(f_c, F_tot)
       r_Cyclohexene = 0.0028 * p_c * p_h / (1 + 0.04 * p_c)
End Function

Public Function pressure_Calc(ByVal F_i As Double, ByVal F_tot As Double) As Double
   Dim p As Double
   p = Range("'Benzene CSTR Design.xls'!P_tot").Value
   pressure_Calc = p * F_i / F_tot
End Function
```


Design Procedure for Multiple Reactions

- CSTR Example: Selectivity…

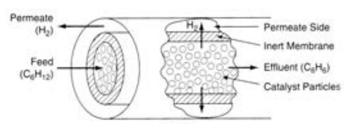


Design Procedure for Multiple Reactions

- Determining overall reaction rates… your turn

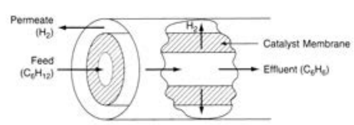
Reaction with Mass Transfer

- Membrane reactor systems



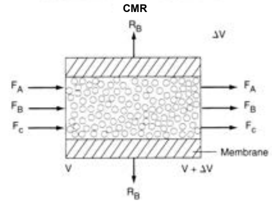
IMRCF

IMRCF: 'Inert Membrane Reactor with Catalyst Pellets on Feed Side'



CMR

CMR: 'Catalytic Membrane Reactor'



From Folger (4th Ed): p 208

Reaction with Mass Transfer

- Membrane reactor systems: example
  - ~ Consider reactions

$$A + B \xrightarrow{k_{1A}} D \quad (1)$$

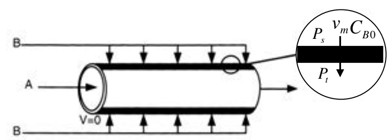
$$A + B \xrightarrow{k_{2A}} U \quad (2)$$

  - ~ Kinetics

$$-r_{1A} = k_{1A} C_A^2 C_B$$
$$-r_{2A} = k_{2A} C_A C_B^2 \quad \Rightarrow S_{D/U} = \frac{k_{1A} C_A}{k_{2A} C_B}$$

← selectivity improved by minimizing B relative to A

  - ~ Employ membrane reactor, gradually feed B



From Folger (4th Ed): p 348

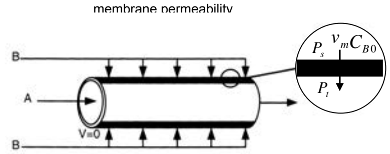
Reaction with Mass Transfer

- Membrane reactor systems: example…

Bulk volumetric flow across membrane:

$$v_m = K\left[P_s - P_t\right] a V_t$$

- v_m: total volumetric flow rate across membrane
- K: membrane permeability
- P_s: shell-side pressure
- P_t: tube-side pressure
- a: membrane inner surface area for flow/unit volume of inner flow volume
- V_t: total inner flow volume



Reaction with Mass Transfer

- Membrane reactor systems: example…

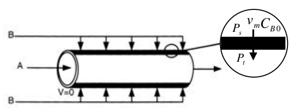
Transport of species B through reactor:

$$\frac{dF_B}{dV} = r_B + R_B, \quad R_B = C_{B0}\frac{v_m}{V_t} = \frac{F_{B0}}{V_t}$$

R_B: molar flow rate of B across membrane/unit inner flow volume

C_{B0}: concentration of B at reactor inlet, shell side

F_{B0}: molar flow rate of B at reactor inlet, shell side



CHG 3127: The Design Procedure: Multiple Reactions

Reaction with Mass Transfer

- Membrane reactor systems: example…

A. Problem specification:
assume performance problem
(volume specified - determine selectivity)

B. Operating conditions:
isothermal
isobaric

CHG 3127: The Design Procedure: Multiple Reactions

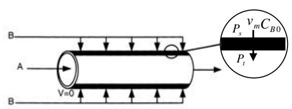
Reaction with Mass Transfer

- Membrane reactor systems: example…

C. Species mole balance equations:

$$A + B \xrightarrow{k_{1A}} D \quad (1)$$

$$A + B \xrightarrow{k_{2A}} U \quad (2)$$



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

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

$$\frac{dF_D}{dV} = r_D$$

$$\frac{dF_U}{dV} = r_U$$

Reaction with Mass Transfer

- Membrane reactor systems: example…

D. Rate laws and net rates of reaction:

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-1} = \frac{r_{1D}}{1} \qquad \frac{r_{2A}}{-1} = \frac{r_{2B}}{-1} = \frac{r_{2U}}{1}$$

$$r_A = r_{1A} + r_{2A} = -k_{1A} C_A^2 C_B - k_{2A} C_A C_B^2$$

$$r_B = r_{1B} + r_{2B} = r_{1A} + r_{2A} = -k_{1A} C_A^2 C_B - k_{2A} C_A C_B^2$$

$$r_D = r_{1D} = -r_{1A} = k_{1A} C_A^2 C_B$$

$$r_U = r_{2U} = -r_{2A} = k_{2A} C_A C_B^2$$

$$A + B \xrightarrow{k_{1A}} D \quad (1)$$

$$A + B \xrightarrow{k_{2A}} U \quad (2)$$

Reaction with Mass Transfer

- Membrane reactor systems: example…

E. Transport law:

$$v_m = K\left[P_s - P_t\right]aV_t,\ R_B = C_{B0}\frac{v_m}{V_t} \qquad \left(R_B = \frac{F_{B0}}{V_t}\ \text{here}\right)$$

F. Stoichiometry (isothermal, isobaric operation):

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

$$C_D = C_{T0}\frac{F_D}{F_T} \quad C_U = C_{T0}\frac{F_U}{F_T}$$

Reaction with Mass Transfer

- Membrane reactor systems: example…

G. Parameter specifications:

$C_{T0} = 0.8$ mol/Liter

$F_{A0} = 4$ mol/s

$F_{B0} = 4$ mol/s

$k_{1A} = 2$ Liter^2/mol^2·s

$k_{2A} = 3$ Liter^2/mol^2·s

Combine and solve…