FACULTY OF APPLIED SCIENCE
Chemical Engineering
Queen's University

CHEE 321: Chemical Reaction Engineering

Module 5: Multiple Reactions (Chapter 6, Fogler)

Course (Content) Organization

Isothermal, Ideal Reactor (Single Reaction) Design

<u>Mole Balance</u>
(Module-1)
In – Out + Con = Acc
$F_{A,in}-F_{A,out}+(r_A)V = dC_A/dt$

<u>Rate Law</u>
(Module-2)
$(r_A) = kC_A^n$

<u>Design Algorithm</u>
(Module-3)
1. GMBE, 2. Rate Law
3. Stoich 4.Combine

<u>Analysis of Rate law</u>
(Module-4)
Kinetics: How to obtain k and rxn order

<u>Multiple Reactions</u>
(Module-5)
Selectivity, Yield

Output

- Reactor Volume
- Reaction Time
- Rate Constant
- Conversion
- Product Composition

Non-Isothermal Reactor Design

(Module-6)

- *Energy Balance*
- *Heat Transfer Rate*
- *Equilibrium Reactions*
- *Multiple Steady State*

$dT/dz = ?$

$T_{in}-T_{out} = ?$

Output

- Temperature Profile
- Heat Removal
- Heating Requirement

Topics to be covered in this Module

- Types of multiple reactions
- Introduction to selectivity and yield
- Qualitative Analyses (Parallel and Series Reactions)
  - Maximizing the reactor operation for single reactant systems
  - Maximizing the reactor operation for two reactant systems
- Algorithm for Reactor Design of Multiple Reactions
  - Mole Balance
  - Net Rates of Reactions
  - Stoichiometry

Multiple Reactions

Types of Multiple Reactions

1. Series Reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Use molar flow rates and concentrations; DO NOT use conversion!

2. Parallel Reactions

$$A \xrightarrow{k_1} B$$

$$A \xrightarrow{k_2} C$$

3. Complex Reactions: Series and Parallel

$$A \xrightarrow{k_1} B + C$$

$$A + C \xrightarrow{k_2} D$$

Cannot use stoichiometric tables to relate change in C_B to change in C_A

4. Independent

$$A \xrightarrow{k_1} C$$

$$B \xrightarrow{k_2} D$$

Selectivity and Yield

Desired Reaction:

$$A \xrightarrow{k_D} D$$

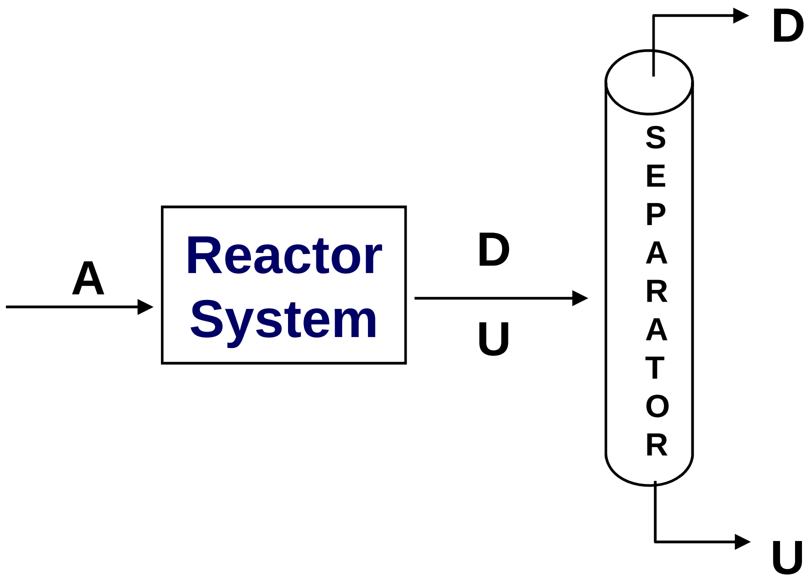
Undesired Reaction:

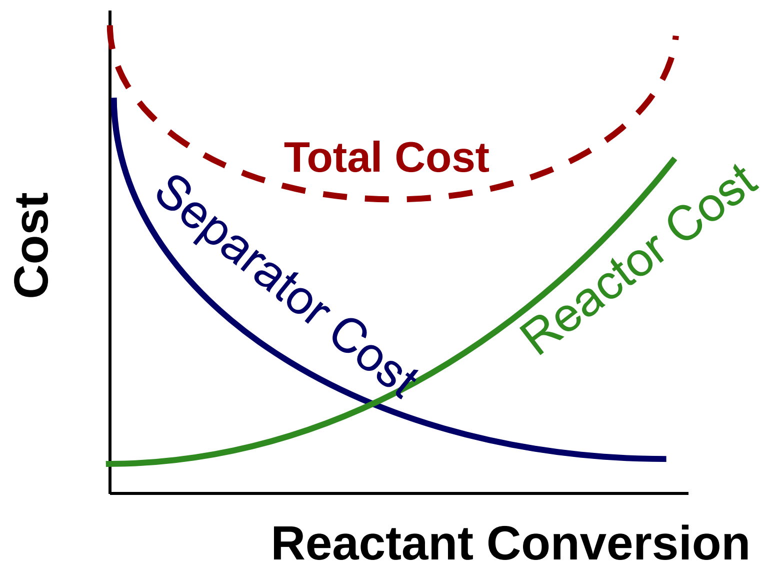
$$A \xrightarrow{k_U} U$$

$$D \xrightarrow{k_{U2}} U$$

	Instantaneous	Global
Selectivity	$S_{DU} = \frac{r_D}{r_U}$	$\tilde{S}_{DU} = \frac{F_D}{F_U}$
Yield	$Y_D = \frac{r_D}{-r_A}$	$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A} = \frac{N_D}{N_{A0} - N_A}$

- What should be the criterion for designing the reactor ?
- Is it necessary that reactor operates such that minimum amount of undesired products are formed ?





Instantaneous vs. Global Yield

- For a CSTR: $\tilde{S}_{DU} = S_{DU}$

  $\tilde{Y}_D = Y_D$

  For proof, see Fogler Ex. 6-1 (pg 308)

- For a PFR, concentrations and rxn rates are changing along reactor length:

  instantaneous yield: $Y_D = \dfrac{r_D}{-r_A} = \dfrac{dF_D}{-dF_A}$

  global yield $\tilde{Y}_D = \dfrac{\text{D formed}}{\text{A reacted}} = \dfrac{F_D}{(F_{A0} - F_A)}$

  for $v = v_0$: $\tilde{Y}_D = \dfrac{-1}{(C_{A0} - C_A)} \displaystyle\int_{C_{A0}}^{C_A} Y_D \, dC_A'$

Series Reactions

Example:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

This series reaction could also be written as

Reaction (1) $A \xrightarrow{k_1} B$

Reaction (2) $B \xrightarrow{k_2} C$

Batch reactor, isothermal, incompressible

Species A: $-\frac{dC_A}{dt} = -r_A = k_1 C_A$, t=0 $C_A=C_{A0}$

$$\boxed{C_A = C_{A0}\exp(-k_1 t)}$$

From Fogler website
http://www.engin.umich.edu/~cre/06chap/frames_learn.htm

Series Reactions

Species B:

$$\frac{dC_B}{dt} = r_B$$

$$r_B = r_{B\,NET} = r_{1B} + r_{2B}$$

$$r_B = k_1 C_A - k_2 C_B$$

$$\frac{dC_B}{dt} = k_1 C_{A0} \exp(-k_1 t) - k_2 C_B$$

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} \exp(-k_1 t)$$

Using the integrating factor, i.f.:

$$\text{i.f.} = \exp \int k_2 dt = \exp(k_2 t)$$

See Appendix A3

$$\frac{d[C_B \exp(k_2 t)]}{dt} = k_1 C_{A0} \exp(k_2 - k_1)t$$

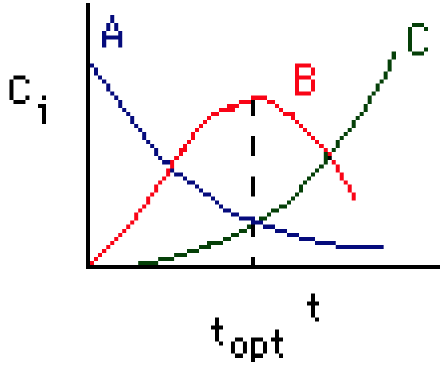
at $t = 0$, $C_B = 0$

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right]$$

Series Reactions

When should you stop the reaction to obtain the maximum amount of B? Let's see.

$$t = t_{opt} \text{ at } \frac{dC_B}{dt} = 0$$



Then

$$t_{opt} = \left(\frac{1}{k_2 - k_1}\right) \ln \frac{k_2}{k_1}$$

What about byproduct C? This can be calculated by integration, or by stoichiometry

$$\frac{dC_C}{dt} = k_2 C_B, \; t = 0 \; C_C = 0$$

And

$$C_C = \frac{C_{A0}}{k_2 - k_1}\left[k_2\left(1 - e^{-k_1 t}\right) - k_1\left(1 - e^{-k_2 t}\right)\right]$$

You would have the same set of equations for an isothermal PFR, replacing t with τ ; see Fogler Ex. 6-4

Parallel Reactions:
Selectivity for Single Reactant Systems

<u>Example (parallel reaction)</u>

Desired Reaction: $A \xrightarrow{k_D} D$ $r_D = k_D C_A^{\alpha_D}$

Undesired Reaction: $A \xrightarrow{k_U} U$ $r_U = k_U C_A^{\alpha_U}$

What is the net rate of reaction of A ??

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D C_A^{\alpha_D}}{k_U C_A^{\alpha_U}} = \frac{k_D}{k_U} C_A^{(\alpha_D - \alpha_U)}$$

Let us examine some reactor operating scenarios to maximize selectivity.

Fogler, 6.2

Parallel Reactions:
Selectivity for Single Reactant Systems

Case 1: $\alpha_D - \alpha_U > 0$

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{(\alpha_D - \alpha_U)}$$

High C_A favors D

How can we accomplish this?

- For gas phase reactions, maintain high pressures
- For liquid-phase reactions, keep the diluent to a minimum

- Batch or Plug Flow Reactors should be used
- CSTR should NOT be chosen

Parallel Reactions: Selectivity for Single Reactant Systems

Case 2: $\alpha_D - \alpha_U < 0$

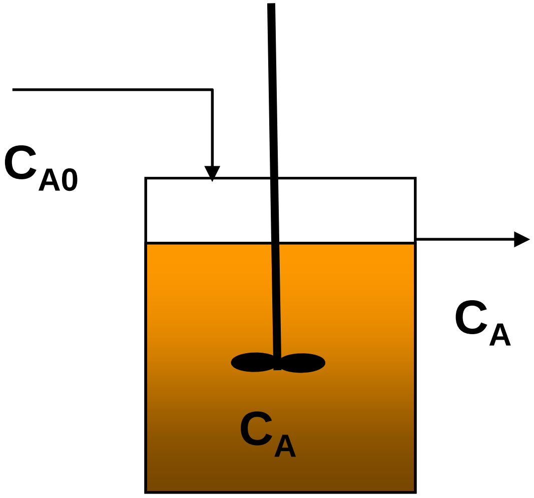
$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U C_A^{(\alpha_U - \alpha_D)}}$$

Low C_A favors D

How can we accomplish this?

- For gas phase reactions, operate at low pressures
- For liquid-phase reactions, dilute the feed

- CSTR is preferred



Reactant concentration maintained at low level

Parallel Reactions:
Selectivity for Single Reactant Systems

Case 3: $\alpha_D - \alpha_U = 0$

Concentration cannot be used operating parameter for selectivity maximization

What now?

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} = \frac{A_D \exp[-E_D/RT]}{A_U \exp[-E_U/RT]} = \frac{A_D}{A_U} \exp[-(E_D - E_U)/RT]$$

(a) If $E_D > E_U$

- Operate reactor at highest possible temperature

(b) If $E_U > E_D$

- Operate reactor at lowest possible temperature

None of these discussions / strategies examine yield. Both must be considered in reactor design!

Parallel Reactions:
Selectivity for Two Reactant Systems

Example

Desired Reaction: $A + B \xrightarrow{k_D} D \qquad r_D = k_D C_A^{\alpha_1} C_B^{\beta_1}$

Undesired Reaction: $A + B \xrightarrow{k_U} U \qquad r_U = k_U C_A^{\alpha_2} C_B^{\beta_2}$

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{(\alpha_1 - \alpha_2)} C_B^{(\beta_1 - \beta_2)}$$

Parallel Reactions: Selectivity for Two Reactant Systems

Case 1: $\alpha_1 > \alpha_2$; $\beta_1 > \beta_2$

Let, ***a*** = $\alpha_1 - \alpha_2$; ***b*** = $\beta_1 - \beta_2$

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^a C_B^b$$

For high S_{DU}, maintain both A & B as high as possible

How can we accomplish this?

- Use Batch reactor
- Use Plug Flow reactor

Parallel Reactions:
Selectivity for Two Reactant Systems

Case 2: $\alpha_1 > \alpha_2$; $\beta_1 < \beta_2$

Let, $\boldsymbol{a} = \alpha_1 - \alpha_2$; $b = \beta_2 - \beta_1$

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} \frac{C_A^a}{C_B^b}$$

$$A + B \xrightarrow{k_D} D \qquad r_D = k_D C_A^{\alpha_1} C_B^{\beta_1}$$

$$A + B \xrightarrow{k_U} U \qquad r_U = k_U C_A^{\alpha_2} C_B^{\beta_2}$$

For high S_{DU}, maintain concentration of A high and of B low

How can we accomplish this? See Fogler Figure 6.3

- Use semi-batch reactor where B is fed slowly
- Use Tubular reactor with side streams of B being fed continuously
- Use series of small CSTR with A fed only to first and B to each reactor

Parallel Reactions:
Selectivity for Two Reactant Systems

Case 3: $\alpha_1 < \alpha_2$; $\beta_1 < \beta_2$

Let, $a = \alpha_2 - \alpha_1$; $b = \beta_2 - \beta_1$

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} \frac{1}{C_A^a C_B^b}$$

For high S_{DU}, maintain both concentration of A and B low

How can we accomplish this?

- For gas phase reactions, operate at low pressures
- For liquid-phase reactions, dilute the feed

- CSTR is preferred

Parallel Reactions: Selectivity for Two Reactant Systems

<u>Case 4</u>: $\alpha_1 < \alpha_2$; $\beta_1 > \beta_2$

Let, $a = \alpha_2 - \alpha_1$; $b = \beta_1 - \beta_2$

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U}\frac{C_B^b}{C_A^a}$$

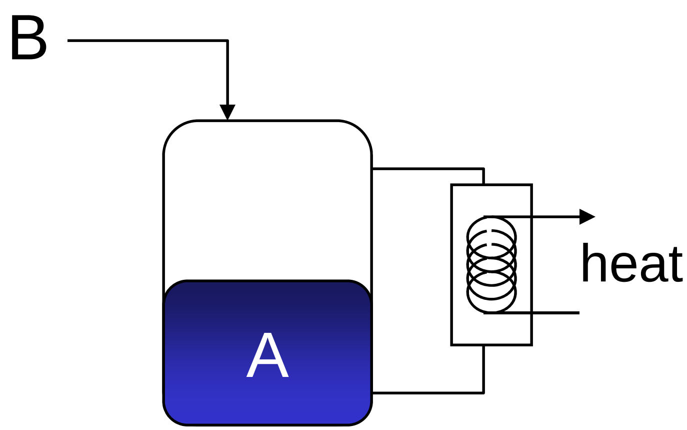
For high S_{DU}, maintain concentration of B high and of A low

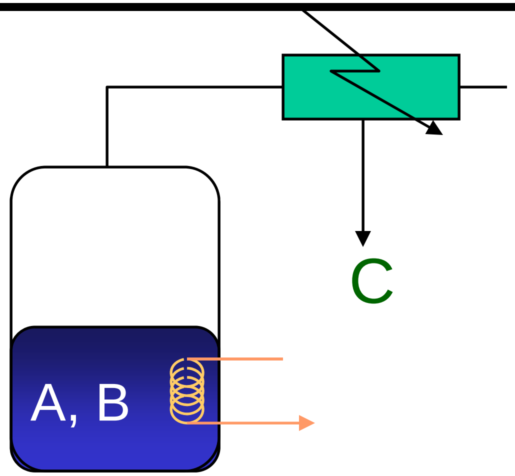
How can we accomplish this?

- Use semi-batch reactor where A is fed slowly
- Use Tubular reactor with side streams of A being fed continuously
- Use series of small CSTR with B fed only to first and A to each reactor

Same as Case 2, with A and B switched…

Why Semi-Batch Reactors?





- B is slowly fed to A contained in the reactor.
- Unwanted products can be minimized
- exothermic reaction can be carried out at controlled rate

- Product C is continuously removed
- Higher conversion for reversible reactions can be obtained

Semi-Batch Reactors - GMBE

1. GMBE on a molar basis

Input - Output + Gen = Accu.

For Species A

$$0 - 0 + (r_A)V = \frac{dN_A}{dt}$$

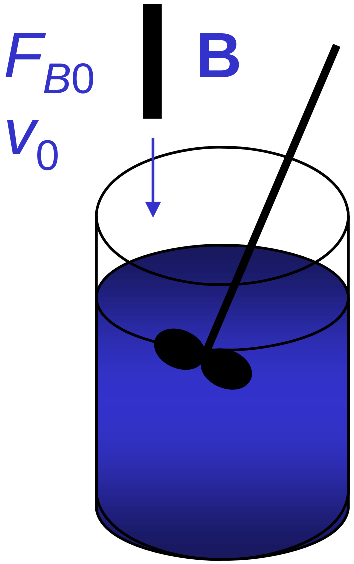
For Species B

$$F_{B0} - 0 + (r_B)V = \frac{dN_B}{dt}$$

Constant Density Systems

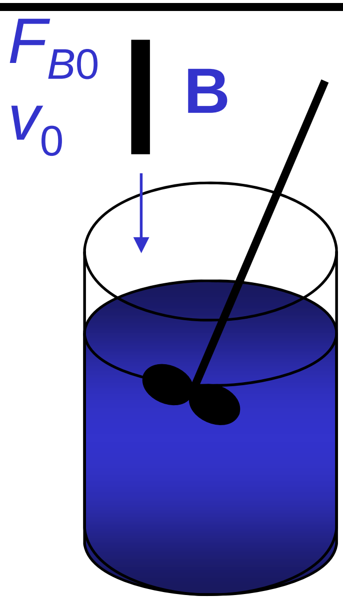
$$V = V_0 + v_0 t$$

Constant Flowrate



Semi-Batch Reactors - GMBE

2. GMBE on a concentration Basis



For Species A (no inflow)

$$0 - 0 + (r_A)V = \frac{dN_A}{dt}$$

$$[N_A = V\,C_A]$$

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

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

Constant flow and density

$$\frac{dV}{dt} = v_0$$

Similarly for Species B

$$F_{B0} - 0 + (r_B)V = \frac{dN_B}{dt}$$

$$[F_{B0} = v_0\,C_{B0}]$$

$$[N_B = V\,C_B]$$

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

Modification to the CRE Algorithm for Multiple Reactions

Fogler, 6.4

- **Mole balance on every species** (not in terms of conversion)
- **Rate Law**: *Net Rate* of reaction for each species,

  e.g., $r_A = \Sigma\, r_{iA}$

- **Stoichiometry**

  a) Liquid Phase, incompressible: $C_A = N_A/V = F_A/v_0$

  b) Gas Phase use

$$C_i = C_{T0} \frac{F_i}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

Variable volumetric flowrate; ideal gas

$$F_T = F_A + F_B + \ldots$$

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

- **Combine** – More difficult: set of algebraic or differential equations for A, B, …

Design Equation for Reactors – Multiple Reactions

	Gas-Phase	Liquid Phase
Batch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
Semi-Batch (B fed)	$\frac{dN_A}{dt} = r_A V$ $\frac{dN_B}{dt} = r_B V + F_{B0}$	$\frac{dC_A}{dt} = r_A - \frac{\upsilon_0 C_A}{V}$ $\frac{dC_B}{dt} = r_B + \frac{\upsilon_0 [C_{B0} - C_B]}{V}$
CSTR	$V = \frac{F_{A0} - F_A}{-r_A}$	$V = \upsilon_0 \frac{[C_{A0} - C_A]}{-r_A}$
PFR	$\frac{dF_A}{dV} = r_A$	$\upsilon_0 \frac{dC_A}{dV} = r_A$
PBR	$\frac{dF_A}{dW} = r'_A$	$\upsilon_0 \frac{dC_A}{dW} = r'_A$

NOTE the design equations are EXACTLY as for a single reaction

but…

Balances must be written for all components

Reaction rates are NET rates of reaction

What are the assumptions for each reactor type?

Net Rate of Reaction

For N reactions, the net rate of formation of species A is:

$$r_A = \sum_{i=1}^{N} r_{iA}$$

For a given reaction i

$$a_i \, A + b_i \, B \rightarrow c_i \, C + d_i \, D$$

$$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$$

NOTE: You can use stoichiometric coefficients to relate relative rates of reaction of species for a specific reaction only

Example: Net Rate of Reaction

- The following reactions follow elementary rate law:

$$(1) \qquad A + 2B \rightarrow 2C$$

$$(2) \qquad 2C + \tfrac{1}{2}B \rightarrow 3D$$

Write net rates of formation of A, B and C

$$k_{1A} = 0.1\left(dm^3/mol\right)^2/min$$

$$k_{2D} = 2\left(dm^3/mol\right)^{3/2}/min$$

Fogler, 6.4.2; see Ex. 6-5

Example: Multiple Gas Phase Reactions in an Isothermal PFR

$$A + 2B \rightarrow C \qquad -r_{1A} = k_{1A} C_A C_B^2$$

$$3C + 2A \rightarrow D \qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

The complex gas phase reactions take place in a PFR. The feed is equal molar in A and B with F_{A0} = 10 mol/min and the volumetric flow rate is 100 dm^3/min. The reactor volume is 1,000 dm^3, there is no pressure drop, the total entering concentration is C_{T0} = 0.2 mol/dm^3 and the rate constants are:

$$k_{1A} = 100\left(\frac{dm^3}{mol}\right)^2 \Big/ min$$

$$k_{2C} = 1{,}500\left(\frac{dm^3}{mol}\right)^4 \Big/ min$$

Plot F_A, F_B, F_C, F_D and $\tilde{S}_{C/D}$ as a function of V

Taken from http://www.engin.umich.edu/~cre/06chap/frames_learn.htm

Gas Phase Multiple Reactions - Algorithm

1. Mole Balance

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

B $$\frac{dF_B}{dV} = r_B$$

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

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

Remember, unlike single-reactions,
for multiple reactions
mole balance for each species
must be written

r_A, r_B, r_C, r_D are all NET rates of reactions

Example (cont'd)

2. Rate Laws

$$A + 2B \rightarrow C \qquad -r_{1A} = k_{1A} C_A C_B^2$$

$$3C + 2A \rightarrow D \qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

Species A

$$r_A = r_{1A} + r_{2A}$$

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

$$r_{2C} = -k_{2C} C_C^3 C_A^2 \Rightarrow \frac{-r_{2A}}{2} = \frac{-r_{2C}}{3} \Rightarrow r_{2A} = -\frac{2}{3}(-r_{2C}) = -\frac{2}{3} k_{2C} C_C^3 C_A^2$$

$$\boxed{r_A = -k_{1A} C_A C_B^2 - \frac{2}{3} k_{2C} C_C^3 C_A^2}$$

Species B

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

Species C

$$r_C = k_{1A} C_A C_B^2 - k_{2C} C_C^3 C_A^2$$

Species D

$$r_D = r_{2D} = -\frac{r_{2C}}{3} = \frac{1}{3} k_{2C} C_C^3 C_A^2$$

Example (cont'd)

3. Stoichiometry

$$C_A = \frac{F_{T0}}{\upsilon_0}\frac{F_A}{F_T}\frac{P}{P_0}\frac{T_0}{T} = C_{T0}\frac{F_A}{F_T}\frac{P}{P_0}\frac{T_0}{T}$$

4. Combine

$$\Delta P = 0,\ P = P_0,\ T = T_0 \quad \Rightarrow \quad C_i = C_{T0}\frac{F_i}{F_T}$$

$$\frac{dF_A}{dV} = -\left[k_{1A}C_{T0}^3\left(\frac{F_A}{F_T}\right)\left(\frac{F_B}{F_T}\right)^2 + \frac{2}{3}k_{2C}C_{T0}^5\left(\frac{F_C}{F_T}\right)^3\left(\frac{F_A}{F_T}\right)^2\right]$$

$$\frac{dF_B}{dV} = -2k_{1A}C_{T0}^3\left(\frac{F_A}{F_T}\right)\left(\frac{F_B}{F_T}\right)^2$$

$$\frac{dF_C}{dV} = k_{1A}C_{T0}^3\left(\frac{F_A}{F_T}\right)\left(\frac{F_B}{F_T}\right)^2 - k_{2C}C_{T0}^5\left(\frac{F_C}{F_T}\right)^3\left(\frac{F_A}{F_T}\right)^2$$

$$\frac{dF_D}{dV} = \frac{1}{3}k_{2C}C_{T0}^5\left(\frac{F_C}{F_T}\right)^3\left(\frac{F_A}{F_T}\right)^2$$

$$F_T = F_D + F_C + F_B + F_A$$

What you should know…

- Qualitative Analyses (Parallel and Series Reactions)
  - Maximizing the reactor operation for single reactant systems
  - Maximizing the reactor operation for two reactant systems
  - Consideration of selectivity and yield

- Algorithm for Reactor Design of Multiple Reactions
  - Mole Balance
  - Net Rates of Reactions
  - Stoichiometry
  - Be able to write the set of equations for the system
    - usually cannot be solved without computer programs
    - be able to sketch the expected qualitative behaviour