6. Multiple Reactions

- **Selectivity and Yield**
- **Reactions in Series**

  - To give maximum selectivity
- **Algorithm for Multiple Reactions**
- **Applications of Algorithm**
- **Multiple Reactions-Gas Phase**

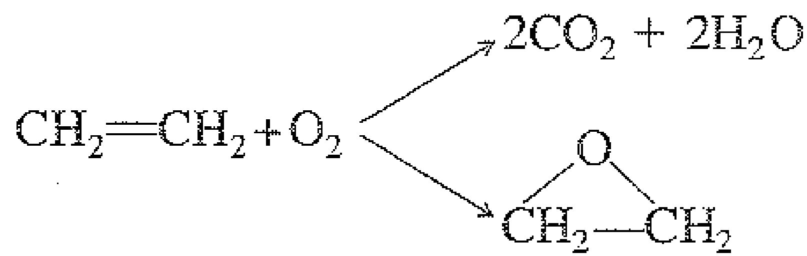
0. Types of Multiple Rxns I

- **Parallel Reactions**

$$A \xrightarrow{k_1} B$$

$$A \xrightarrow{k_2} C$$

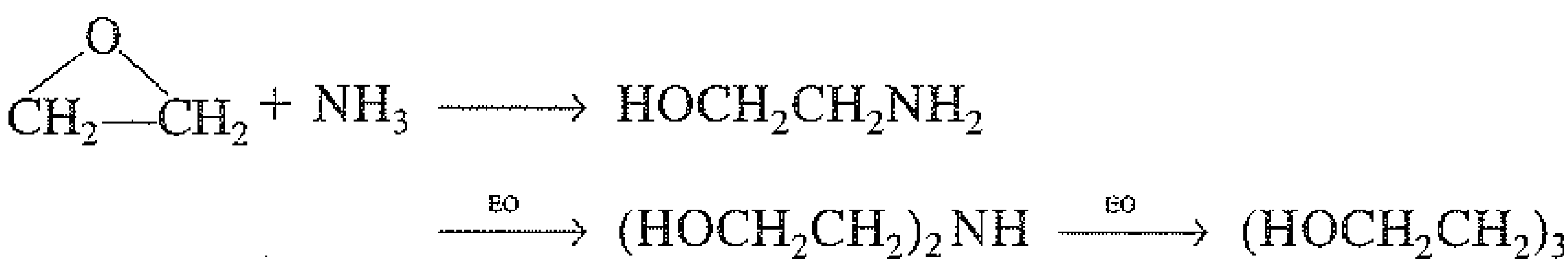
- Oxidation of ethylene



- **Series Reactions**

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

- Reaction of EO with ammonia



0. Types of Multiple Rxns II

- **Complex Reactions: Series and Parallel aspects combined**

$$A \xrightarrow{k_1} 2B + C$$

$$A + 2C \xrightarrow{k_2} 3D$$

- Formation butadiene from ethanol

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

$$C_2H_5OH \longrightarrow CH_3CHO + H_2$$

$$C_2H_4 + CH_3CHO \longrightarrow C_4H_6 + H_2O$$

- **Independent Reactions**

$$A \xrightarrow{k_1} B$$

$$C \xrightarrow{k_2} D$$

- Cracking crude oil

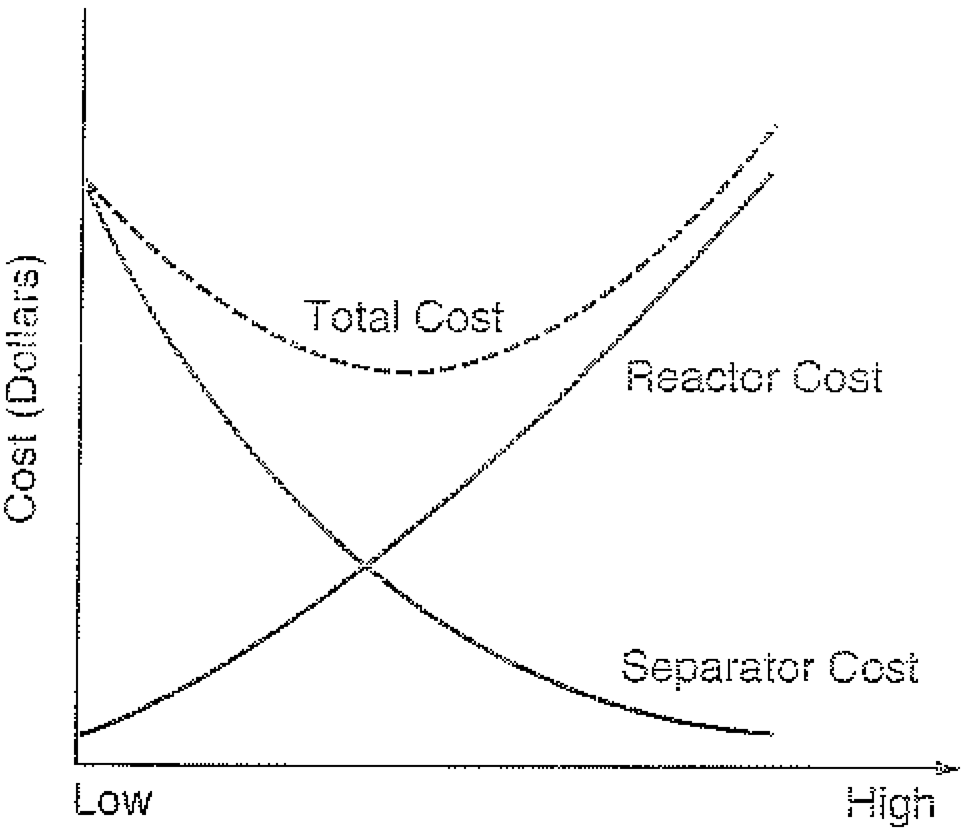
$$C_{15}H_{32} \longrightarrow C_{12}C_{26} + C_3H_6$$

$$C_8H_{18} \longrightarrow C_6H_{14} + C_2H_4$$

1. Selectivity and Yield I

- **Two types of selectivity**

	Instantaneous	Overall
Selectivity	$S_{DU} = \dfrac{r_D}{r_U}$	$\tilde{S}_{DU} = \dfrac{F_D}{F_U}$
Yield	$Y_D = \dfrac{r_D}{-r_A}$	$\tilde{Y}_D = \dfrac{F_D}{F_{A0} - F_A}$
Example	$A + B \xrightarrow{k_1} D$, desired product, $r_D = k_1 C_A^2 C_B$ $A + B \xrightarrow{k_2} U$, undesired product, $r_U = k_2 C_A C_B$ $S_{DU} = \dfrac{r_D}{r_U} = \dfrac{k_1 C_A^2 C_B}{k_2 C_A C_B} = \dfrac{k_1}{k_2} C_A$	


Total Cost
Reactor Cost
Separator Cost
Cost (Dollars)
Low
High

1. Selectivity and Yield II

○ **Self Test 1**

- 3 species were found in a CSTR, C_{A0} = 2moles/dm^3

Run	T (°C)	C_A (mole/dm^3)	C_B (mole/dm^3)	C_C (mole/dm^3)
1	30	1.7	0.01	0.29
2	50	1.4	0.03	0.57
3	70	1.0	0.1	0.90
4	100	0.5	1.25	1.25
5	120	0.1	1.80	0.1
6	130	0.01	1.98	0.01

1. Selectivity and Yield III

- **Self Test 2**

  - At low temperatures

  1) Little conversion of A

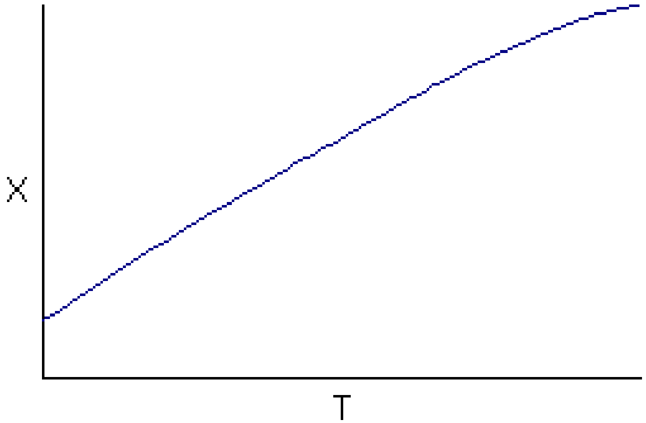
  2) Little B formed

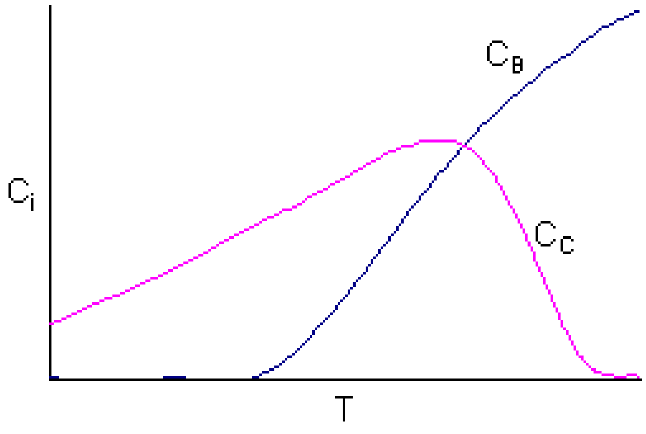
  3) Mostly C formed (but not too much because of the low conversion - 15 to 30% - of A)

  - At high temperatures

  1) Virtually complete conversion of A

  2) Mostly B formed





1. Selectivity and Yield IV

- **Self Test 3**
  - **Data suggest 2 reactions**

$$(1) \quad A \xrightarrow{k_1} B \qquad -r_{1A} = k_1 C_A = C_A A_1 \; e^{-E_1/RT} = r_B$$

$$(2) \quad A \xrightarrow{k_2} C \qquad -r_{2A} = k_2 C_A = C_A A_2 \; e^{-E_2/RT} = r_C$$

  - **Reaction (1) is dominant at high temperatures**

$k_1 = A_1 \; e^{-E_1/RT}$ **with $k_1 » k_2$, $A_1 » A_2$**

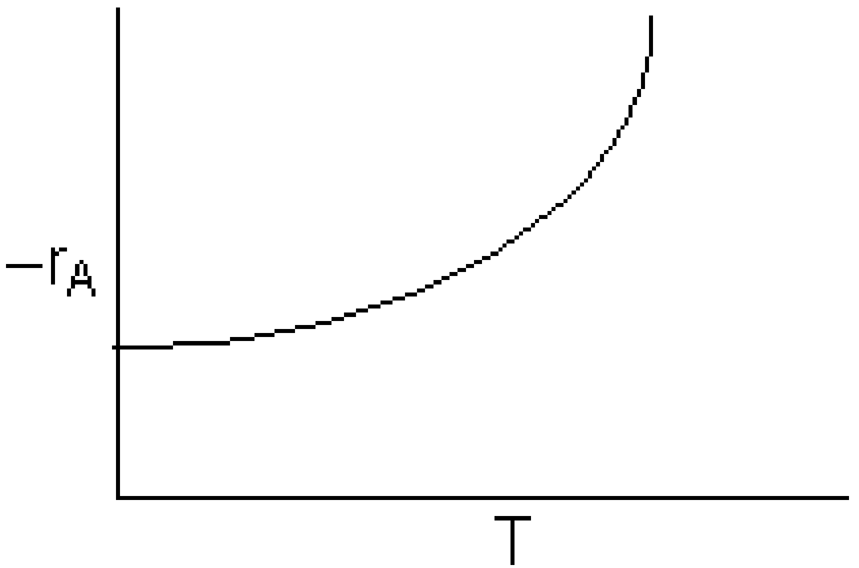
  - **Reaction (2) is dominant at low temperatures**

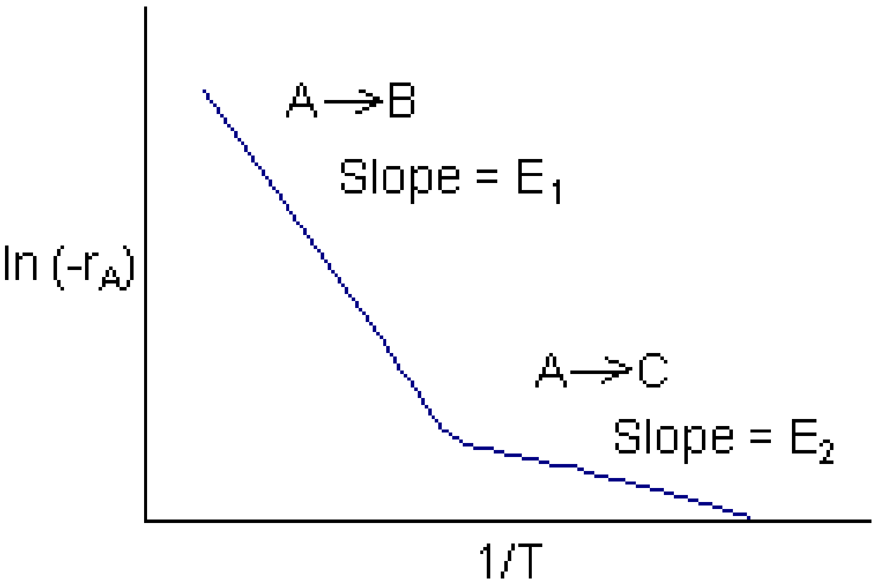
$k_2 » k_1$, $E_2 > E_1$

$$-r_A = (k_1 + k_2) C_A = \left(A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT}\right) C_A$$

1. Selectivity and Yield V

- **Self Test 4**





2. Parallel Reactions I

$$\mathrm{A} \xrightarrow{k_1} \mathrm{D(Desired)}, \quad r_\mathrm{D} = k_1 C_\mathrm{A}^{\alpha}$$

$$\mathrm{A} \xrightarrow{k_2} \mathrm{U(Undesired)}, \quad r_\mathrm{U} = k_2 C_\mathrm{A}^{\beta}$$

- **The net rate of disappearance of A**

$$r_\mathrm{A} = r_\mathrm{D} + r_\mathrm{U}$$

- **Instantaneous selectivity**

$$S_\mathrm{D/U} = \frac{r_\mathrm{D}}{r_\mathrm{U}} = \frac{k_1 C_\mathrm{A}^{\alpha}}{k_2 C_\mathrm{A}^{\beta}} = \frac{k_1}{k_2} C_\mathrm{A}^{(\alpha\text{-}\beta)}$$

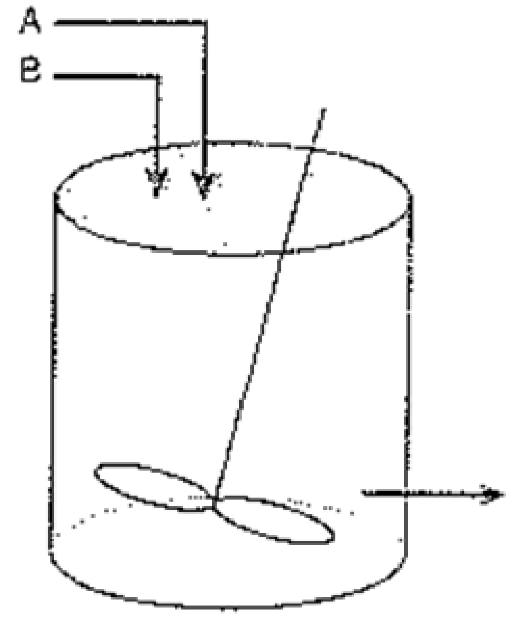
- If $\alpha > \beta$ use high concentration of A. Use PFR.

- If $\alpha < \beta$ use low concentration of A. Use CSTR.

※ Reactor Selection I

○ **Criteria**

- **Selectivity**
- **Yield**
- **Temperature control**
- **Safety**
- **Cost**



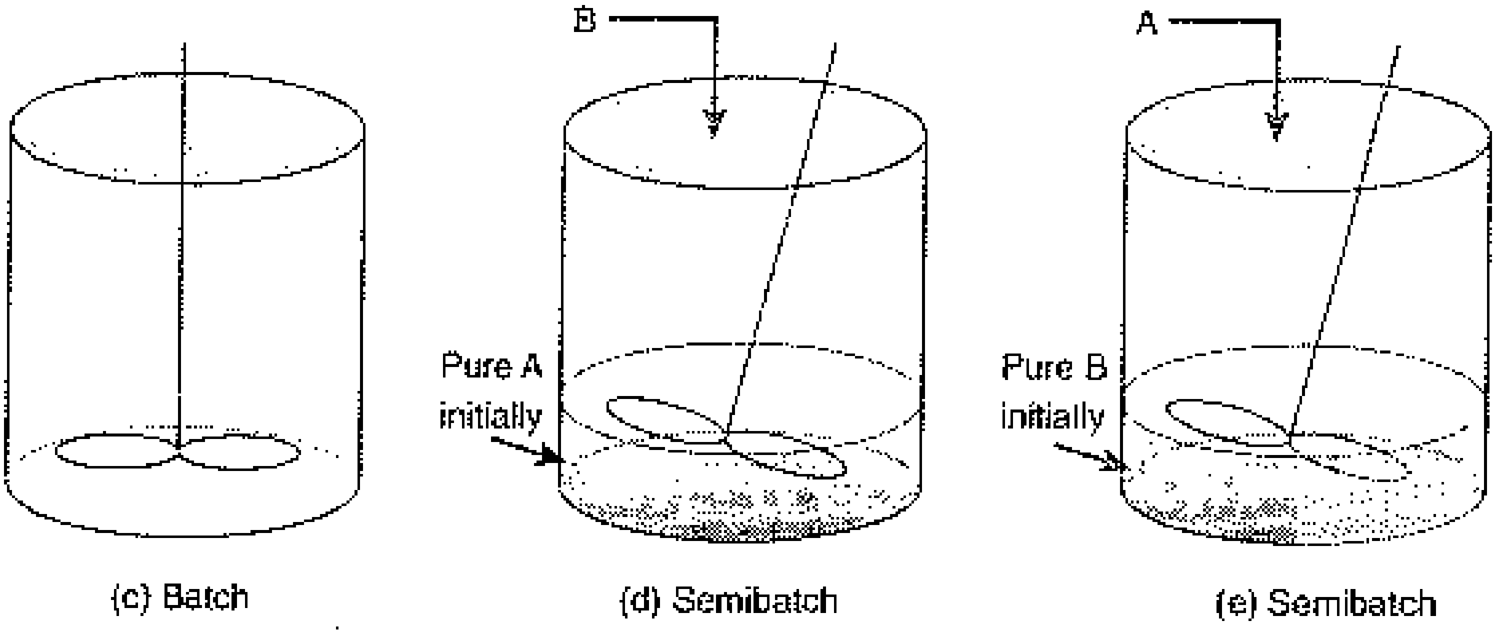
(a) CSTR

(b) Tubular reactor

※ Reactor Selection II

○ **Application of Batch**

- **High A with low B (d)**
- **High B with low A (e)**

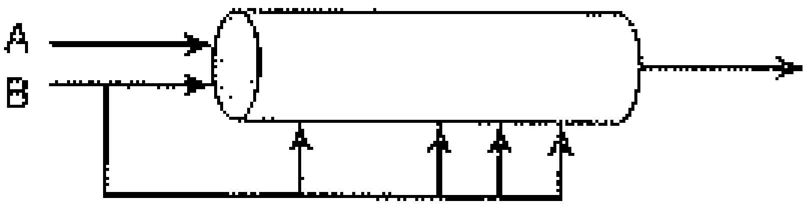


※ Reactor Selection III

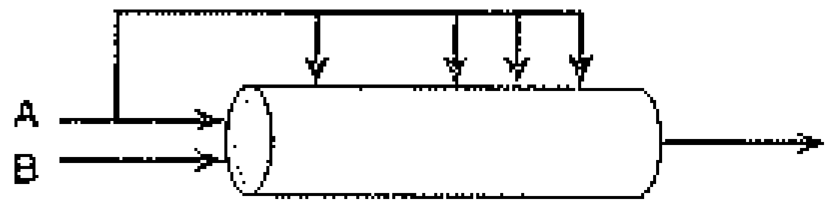
○ **Application of PFR (Membrane)**

- High A with low B (f)

- High B with low A (g)



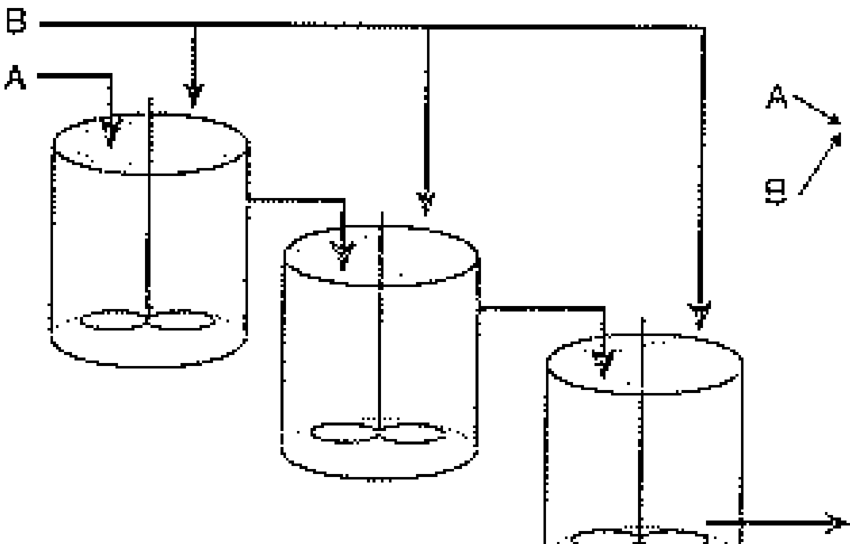
(f) A membrane reactor or a tubular reactor with side streams



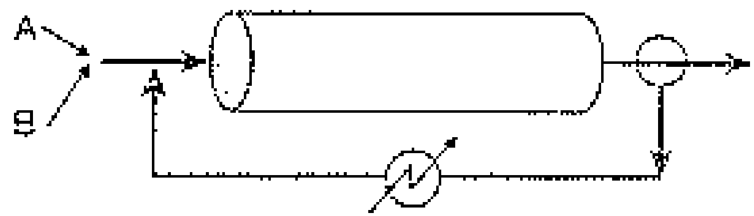
(g) A membrane reactor or a tubular reactor with side streams

※ Reactor Selection IV

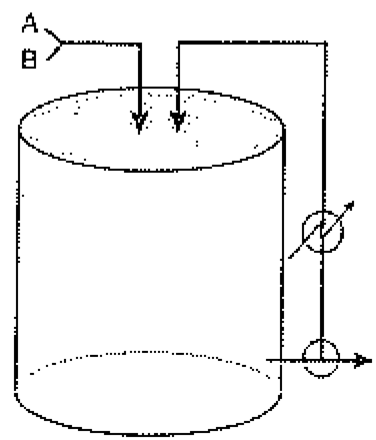
- **Low A & B with temp. control**



(h) Series of small CSTRs



(i) Tubular reactor with recycle

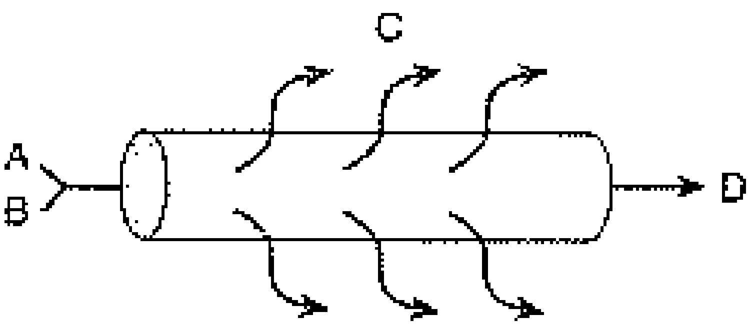


(j) CSTR with recycle

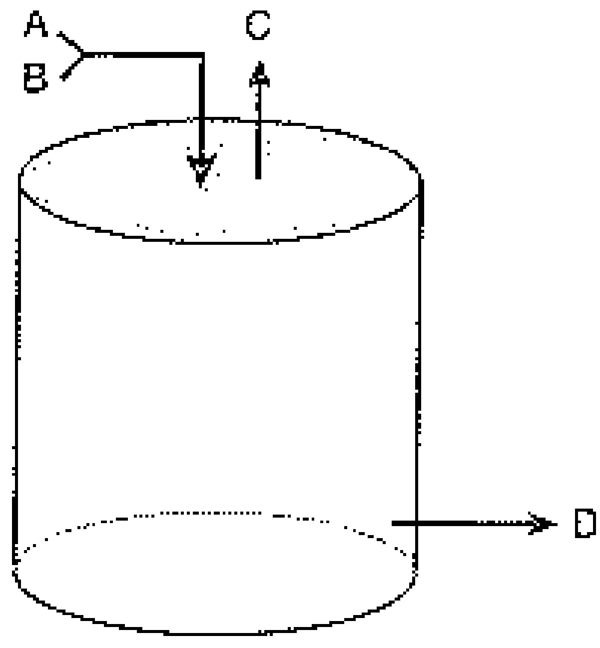
※ Reactor Selection V

○ **Reversible reaction**

- Shift equilibrium by removing C



(k) Membrane reactor



(l) Reactive distillation

2. Parallel Reactions II

- **Maximizing the Selectivity - Parallel Reactions 1**
  - **Determine the instantaneous selectivity, $S_{D/U}$, for the liquid phase reactions:**

$$A + B \longrightarrow D \qquad r_D = k_1 C_A^2 C_B$$

$$A + B \longrightarrow U_1 \qquad r_{U_1} = k_2 C_A C_B$$

$$A + B \longrightarrow U_2 \qquad r_{U_2} = k_3 C_A^3 C_B$$

$$S_{D/U_1U_2} = \frac{r_D}{r_{U_1} + r_{U_2}} = \frac{k_1 C_A^2 C_B}{k_2 C_A C_B + k_3 C_A^3 C_B} = \frac{k_1 C_A}{k_2 + k_3 C_A^2}$$

Sketch the selectivity as a function of the concentration of A. Is there an optimum and if so what is it?

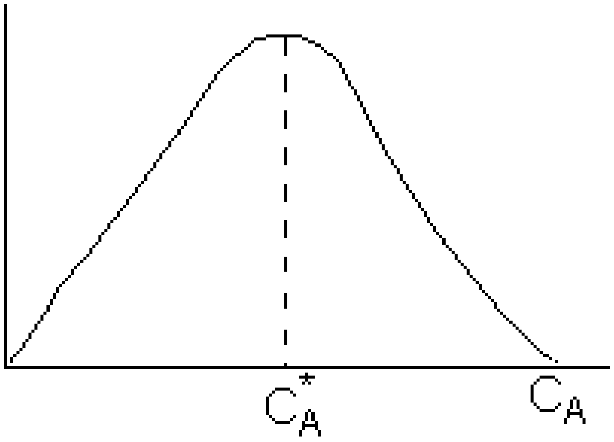
2. Parallel Reactions III

- **Maximizing the Selectivity - Parallel Reactions 2**

$$S_{D/U_1U_2} = \frac{r_D}{r_{U_1} + r_{U_2}} = \frac{k_1 C_A^2 C_B}{k_2 C_A C_B + k_3 C_A^3 C_B} = \frac{k_1 C_A}{k_2 + k_3 C_A^2}$$

$$\frac{dS}{dC_A} = 0 = k_1\left[k_2 + k_3 C_A^{*2}\right] - k_1 C_A^*\left[2k_3 C_A^*\right] S_{D/U_1U_2}$$

$$C_A^* = \sqrt{\frac{k_2}{k_3}}$$



Use CSTR with exit concentration C_A^*

3. Series Reactions (p. 283)

- **Example: Series reaction in a batch reactor 1**

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

- This series reaction could also be written as

- **Reaction (1)** $A \xrightarrow{k_1} B$ **:** $-r_{1A}=k_1C_A$
- **Reaction (2)** $B \xrightarrow{k_2} C$ **:** $-r_{2B}=k_2C_B$

- Mole balance on every species

- **Species A** Batch Reactor $V = V_0$

$$\frac{1}{V_0}\frac{dN_A}{dt} = r_A$$

3. Series Reactions II

- **Example: Series reaction in a batch reactor 2**
  - **Net rate of reaction of A, $r_A = r_{1A} + 0$**
  - **Rate law,** $r_{1A} = -k_{1A} C_A$
  - **Relative rates,** $r_{1B} = -r_{1A}$

$$\frac{dC_A}{dt} = -k_{1A} C_A$$

  - **Integrating with $C_A = C_{A0}$ at $t = 0$ and then rearranging**

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

3. Series Reactions III

- **Example: Series reaction in a batch reactor 3**
  - **Net species B:** $$\frac{dC_B}{dt} = r_B$$
  - **Net rate of reaction of B** $$r_B = r_{B\,NET} = r_{1B} + r_{2B}$$
  - **Rate law, $r_{2B} = -k_2 C_B$**
  - **Relative rates** $$r_B = k_1 C_A - k_2 C_B$$
    $$\frac{dC_B}{dt} = k_1 C_{A0} \exp(-k_1 t) - k_2 C_B$$
  - **Combine**
    $$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} \exp(-k_1 t)$$
    ☜ **1st order ODE**

3. Series Reactions IV

- **Example: Series reaction in a batch reactor 4**

- Using the integrating factor, i.f.: (p 1012, A 3)

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

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

- **at t = 0, C_B = 0**

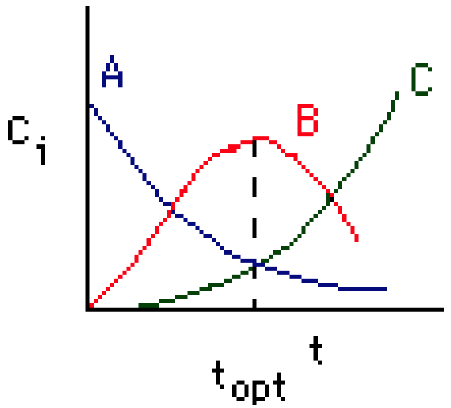
$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right]$$

3. Series Reactions V

- **Example: Series reaction in a batch reactor 5**
  - **- Optimization of the desired product B**

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

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

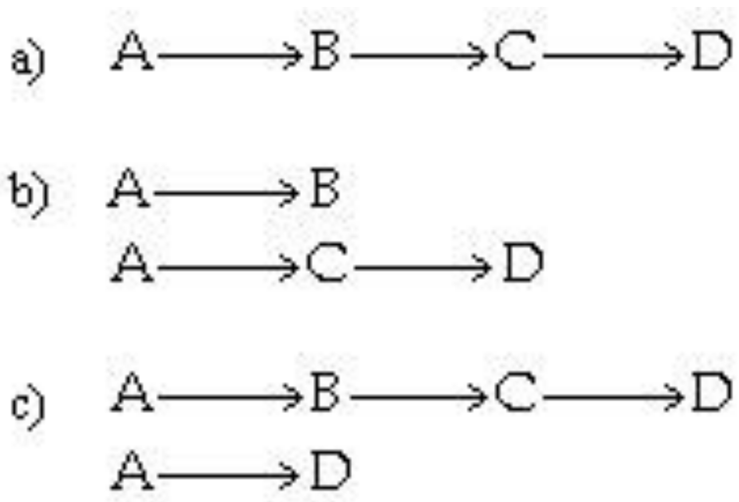


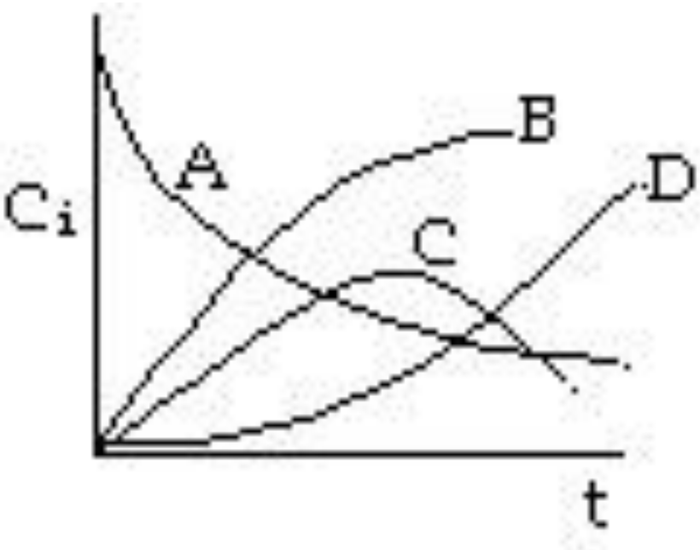
- **- Species C, $C_C = C_{A0} - C_B - C_A$**

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

3. Series Reactions VI

- **Self Test 1**
  - **Concentration-time trajectories**
  - **Which of the following reaction pathways best describes the data:**





3. Series Reactions VII

○ **Self Test 2**

- **Concentration-time trajectories**
- **Sketch the concentration-time trajectory for the reaction**

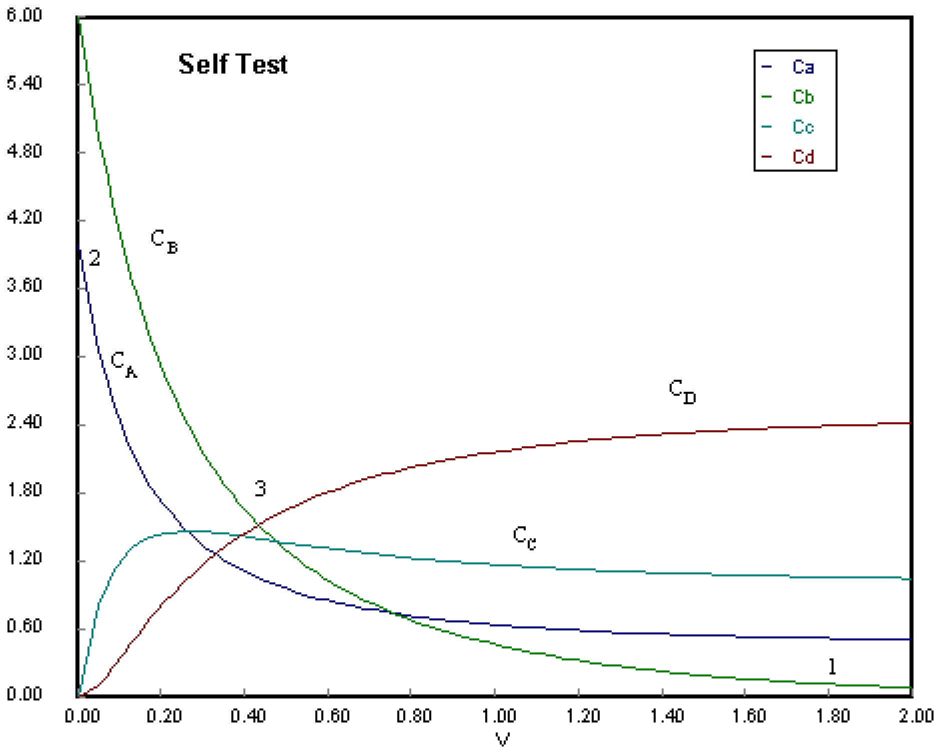
1) $A + B \longrightarrow C$

2) $B + C \longrightarrow D$

$C_{A0} = 4 \ \text{mol}/\text{dm}^3$.

$C_{B0} = 6 \ \text{mol}/\text{dm}^3$

$C_{C0} = C_{D0} = 0$



4. Algorithm for Complex Reactions I

Multiple Reactions

Reactions

1 Number each reaction

(1) $A + 2B \longrightarrow C$

(2) $3A + C \longrightarrow 2D$

↓

Mole Balance

2 Write mole balance on each and every species

$$\frac{dF_A}{dW} = r'_A, \quad \frac{dF_B}{dW} = r'_B, \quad \frac{dF_C}{dW} = r'_C, \quad \text{and} \quad \frac{dF_D}{dW} = r'_D$$

↓

Net Rate Laws

3 Write the net rate of reaction for each species

$$r'_A = r'_{1A} + r'_{2A}, \; r'_B = r'_{1B} + r'_{2B}, \; r'_C = r'_{1C} + r'_{2C}, \; \text{and} \; r'_D = r'_{1D} + r'_{2D}$$

4 Write rate law for one species in every reaction

$$r'_{1A} = -k_{1A} C_A C_B^2 \quad \text{and} \quad r'_{2A} = -k_{2A} C_A C_C$$

5 In each reaction relate the rates of reaction of each species to one another

$$r'_{1B} = 2r'_{1A}, \; r'_{1C} = -r'_{1A}, \; r'_{2B} = 0, \; r'_{1D} = 0, \; r'_{2C} = r'_{2A}/3 \; \text{and} \; r'_{2D} = -\tfrac{2}{3} r'_{2A}$$

6 Combine net rates, rate laws, and relative rates to write the net rates in terms of concentrations

$$r'_A = -k_{1A} C_A C_B^2 - k_{2A} C_A C_C, \quad r'_B = -2k_{1A} C_A C_B^2$$

$$r'_C = k_{1A} C_A C_B^2 - k_{2A} C_A C_C / 3), \quad r'_D = \tfrac{2}{3} k_{2A} C_A C_C$$

4. Algorithm for Complex Reactions II

Stoichiometry

7 For isothermal ($T = T_0$) *gas-phase* reactions, write the concentrations in terms of molar flow rates

$$\text{e.g., } C_A = C_{T_0}\frac{F_A}{F_T}y,\; C_B = C_{T_0}\frac{F_B}{F_T}y \;\text{ with }\; F_T = F_A + F_B + F_C + F_D$$

For *liquid-phase* reactions, just use concentrations as they are, e.g., C_A, C_B

Pressure Drop

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

$$\frac{dy}{dW} = -\frac{\alpha}{2y}\frac{F_T}{F_{T_0}}\frac{T}{T_0}, \;\text{ with }\; y = \frac{P}{P_0}$$

Combine

9 Use an ODE solver (e.g, Polymaht) to combine steps 1 through 8 to solve for the profiles of molar flow rates, concentration, and pressure, for example

4. Algorithm for Complex Reactions III

- **Mole Balances (p 327)**

Reactor Type	Gas Phase	Liquid Phase
Batch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
Semibatch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A - \frac{\upsilon_0 C_A}{V}$
	$\frac{dN_B}{dt} = r_B V + F_{B0}$	$\frac{dC_B}{dt} = r_B + \frac{\upsilon_0 \left[C_{B0} - C_B\right]}{V}$
CSTR	$V = \frac{F_{A0} - F_A}{-r_A}$	$V = \upsilon_0 \frac{\left[C_{A0} - C_A\right]}{-r_A}$
PFR	$\upsilon_0 \frac{dC_A}{dV} = r_A$	$\frac{dF_A}{dV} = r_A$
PBR	$\upsilon_0 \frac{dC_A}{dW} = r'_A$	$\frac{dF_A}{dW} = r'_A$

4. Algorithm for Complex Reactions IV

○ **Rates 1**

- Number every reaction (1) $2A \rightarrow B$

(2) $A + 3B \rightarrow 2C$

- Rate laws for every reaction

$$(1) \quad r_{1A} = -k_{1A} C_A^2$$

$$(2) \quad r_{2A} = -k_{2A} C_A C_B \quad \text{(non elementary)}$$

- Relative rates for each reaction for a given reaction *i*

$$(i) \quad \mathrm{a}_i\mathrm{A} + \mathrm{b}_i\mathrm{B} \rightarrow \mathrm{c}_i\mathrm{C} + \mathrm{d}_i\mathrm{D}$$

4. Algorithm for Complex Reactions V

○ **Rates 2**

- Relative rates for each reaction 2

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

$$RXN\ 1: \frac{r_{1A}}{-2} = \frac{r_{1B}}{1}$$

$$r_{1B} = \frac{-r_{1A}}{2} = \frac{k_{1A}}{2} C_A^2$$

$$RXN\ 2: \frac{r_{2A}}{-1} = \frac{r_{2B}}{-3} = \frac{r_{2C}}{2}$$

$$r_{2B} = 3r_{2A}$$

$$r_{2C} = -2r_{2A}$$

4. Algorithm for Complex Reactions VI

- **Rates 3**

  - Net rate of formation for species A that appears in N reactions

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

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

$$r_B = r_{1B} + r_{2B} = \frac{1}{2}k_{1A}C_A - 3k_{2A}C_A C_B$$

$$r_C = r_{1C} + r_{2C} = 0 + 2k_{2A}C_A C_B$$

4. Algorithm for Complex Reactions VII

- **Stoichiometry**
  - **Net rate of formation for species A that appears in N reactions**
  - **NOTE: We could use the gas phase mole balance for liquids and then just express the concentration as Flow $C_A = F_A/v_0$ Batch $C_A = N_A/V_0$**

$$C_i = C_{T0} \frac{F_i}{F_T} \frac{T_{0y}}{T}$$

$$F_T = \sum F_i = F_A + F_B + \ldots.$$

4. Algorithm for Complex Reactions VIII

- **Self Test**
  - **- Writing net rates of formation**
    - **The reactions are elementary. Write the net rates of formation for A, B, C and D**

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

(2) $2C + \frac{1}{2}B \rightarrow 3D$ $\quad k_{2D} = 2\left(dm^3/mol\right)^{3/2}/min$

Sol) A

$$r_A = r_{1A} + r_{2A} = r_{1A} + 0$$

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

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

4. Algorithm for Complex Reactions IX

- **Self Test 2**

B

$$r_B = r_{1B} + r_{2B}$$

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

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

$$\frac{r_{2B}}{-1/2} = \frac{r_{2D}}{3}$$

$$r_{2B} = -\frac{1}{6} r_{2D}$$

$$r_{2D} = k_{2D} C_B^{1/2} C_C^2$$

$$r_{2B} = -\frac{1}{6} k_{2D} C_B^{1/2} C_C^2$$

$$\boxed{r_B = -2k_{1A} C_A C_B^2 - \frac{1}{6} C_B^{1/2} C_C^2}$$

4. Algorithm for Complex Reactions X

- **Self Test 3**

C $r_C = r_{1C} + r_{2C}$

$$\frac{r_{1C}}{2} = \frac{r_{1A}}{-1}$$

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

$$\frac{r_{2C}}{-2} = \frac{r_{2D}}{3}$$

$$r_C = 2k_{1A} C_A C_B^2 - \frac{2}{3} k_{2D} C_C^2 C_B^{1/2}$$

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

4. Algorithm for Complex Reactions XI

- **Self Test 4**

D $$r_D = r_{1D} + r_{2D} = r_{2D}$$

$$\boxed{r_D = k_{2D} C_C^2 C_B^{1/2}}$$

- These net rates of reaction are now coupled with the appropriate mole balance of A, B, C, and D and solved using a numerical software package.

- **For example for a PFR:**

$$\frac{dF_A}{dV} = -k_{1A} C_A C_B^2$$

$$\frac{dF_B}{dV} = -2k_{1A} C_A C_B^2 - \frac{1}{6} C_B^{1/2} C_C^2$$

5. Applications of Algorithm I

$$A + 2B \rightarrow C \quad \textbf{(1)} \quad -r_{1A} = k_{1A} C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined wrt species A.

$$3C + 2A \rightarrow D \quad \textbf{(2)} \quad -r_{2C} = k_{2C} C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined wrt species C.

5. Applications of Algorithm II

- **Example A: Liquid phase PFR 1**

- The complex liquid phase reactions follow elementary rate laws

(1) $A + 2B \rightarrow C$ $\qquad$ $-r_{1A} = k_{1A}C_AC_B^2$

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

- Equal molar in A and B with F_{A0} = 200 mol/min and the volumetric flow rate is 100 dm^3/min. The reaction volume is 50 dm^3 and the rate constants are

$$k_{1A} = 10\left(\frac{dm^3}{mol}\right)^2 \Big/ min \qquad k_{2C} = 15\left(\frac{dm^3}{mol}\right)^4 \Big/ min$$

- Plot F_A, F_B, F_C, F_D and $S_{C/D}$ as a function of V

5. Applications of Algorithm III

- **Example A: Liquid phase PFR 2**

  - Solution

  - **Mole balances**

(1) $$\frac{dF_A}{dV} = r_A \qquad (F_{A0} = 200 \ \text{mol/min})$$

(2) $$\frac{dF_B}{dV} = r_B \qquad (F_{B0} = 200 \ \text{mol/min})$$

(3) $$\frac{dF_C}{dV} = r_C \qquad V_F = 50 \ \text{dm}^3$$

(4) $$\frac{dF_D}{dV} = r_D$$

5. Applications of Algorithm IV

- **Example A: Liquid phase PFR 3**

- Solution

- **Net rates**

(5) $$r_A = r_{1A} + r_{2A}$$

(6) $$r_B = r_{1B}$$

(7) $$r_C = r_{1C} + r_{2C}$$

(8) $$r_D = r_{2D}$$

- **Rate laws**

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

(10) $$r_{2C} = -k_{2C} C_A^2 C_C^3$$

5. Applications of Algorithm V

- **Example A: Liquid phase PFR 4**

  - Solution

  - **Relative rates**

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1} \qquad \text{Reaction 1}$$

(11) $$r_{1B} = 2\ r_{1A}$$

(12) $$r_{1C} = -r_{1A}$$

$$\frac{r_{2A}}{-2} = \frac{r_{2C}}{-3} = \frac{r_{2D}}{1} \qquad \text{Reaction 2}$$

(13) $$r_{2A} = \frac{2}{3} r_{2C}$$

(14) $$r_{2D} = -\frac{1}{3} r_{2C}$$

5. Applications of Algorithm VI

- **Example A: Liquid phase PFR 5**

  - Solution

  - **Selectivity**
  - ***If* one were to write $S_{C/D} = F_C/F_D$ in the Matlab program, Matlab would not execute because at V = 0 $F_C = 0$ resulting in an undefined volume (infinity) at V = 0. To get around this problem we start the calculation 10^{-4} dm^3 from the reactor entrance where F_D will note be zero and use the following IF statement.**

$$(15) \quad \tilde{S}_{C/D} = \text{if } (V > 0.001) \text{ then } \left(\frac{F_C}{F_D}\right) \text{ else } (0)$$

5. Applications of Algorithm VII

- **Example A: Liquid phase PFR 6**
  - **- Solution**
    - **Stoichiometry**

(16) $C_A = F_A / \upsilon_0$

(17) $C_B = F_B / \upsilon_0$

(18) $C_C = F_C / \upsilon_0$

(19) $C_D = F_D / \upsilon_0$

Parameters

(20) $\upsilon_0 = 100 \ \ dm^3/min$

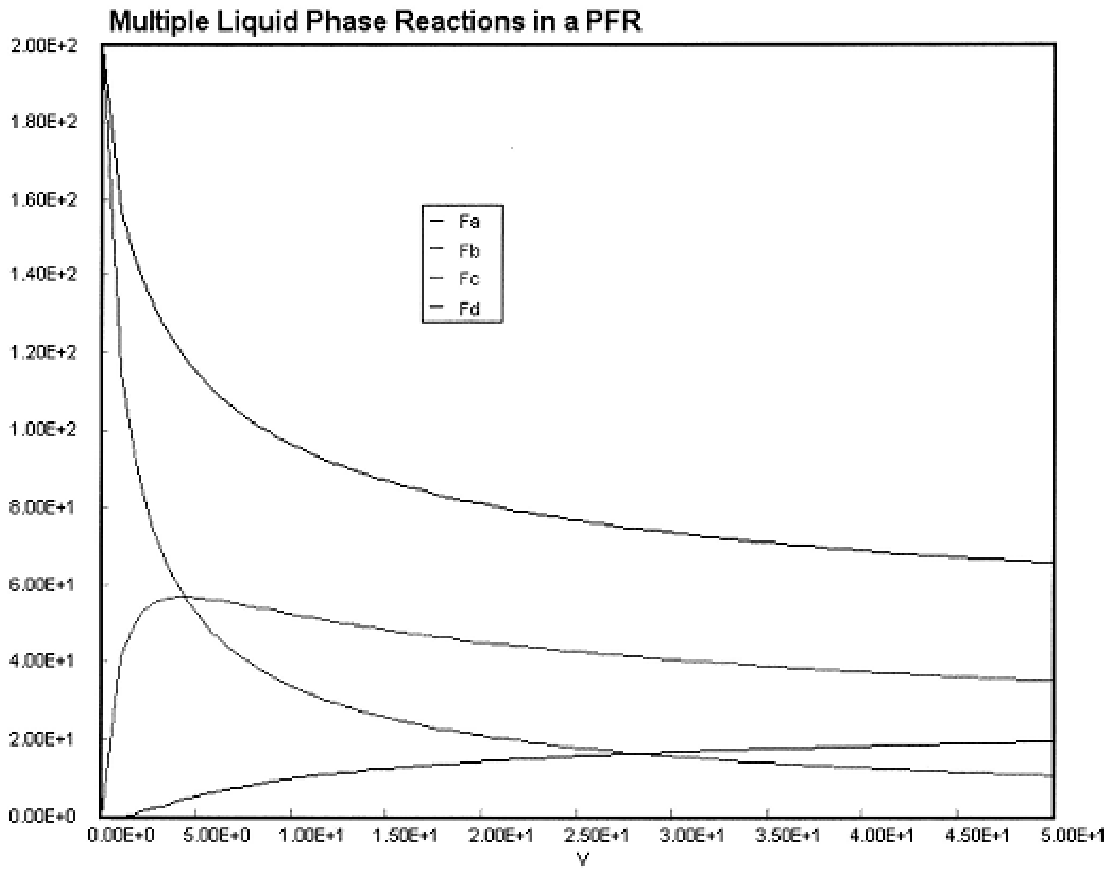
(21) $k_{1A} = 10 \ \ \left(dm^3/mol\right)^2 / min$

(22) $k_{2C} = 15 \ \ \left(dm^3/mol\right)^4 / min$

5. Applications of Algorithm VIII

- **Example A: Liquid phase PFR 7**

  - Solution



5. Applications of Algorithm IX

- **Example B: Liquid phase CSTR 1**
  - Same rxns, rate laws, and rate constants as example A

    $A + 2B \rightarrow C$ (1) $-r_{1A} = k_{1A}C_AC_B^2$ NOTE: The specific reaction rate k_{1A} is defined wrt species A

    $3C + 2A \rightarrow D$ (2) $-r_{2C} = k_{2C}C_C^3C_A^2$ NOTE: The specific reaction rate k_{2C} is defined wrt species C
  - Liquid phase reactions take place in a 2,500 dm^3 CSTR.
    - equal molar in A and B with F_{A0} = 200 mol/min,
    - v_0 = 100 dm^3/min, V_0 = 50 dm^3.
  - Find the concentrations of A, B, C, and D exiting the reactor along with the exiting selectivity.
  - Plot F_A, F_B, F_C, F_D and $S_{C/D}$ as a function of V

5. Applications of Algorithm X

- **Example B: Liquid phase CSTR 2 – Solution**

- Liquid CSTR

- **Mole balances**

$$(1) \quad f(C_A) = \upsilon_0 C_{A0} - \upsilon_0 C_A + r_A V$$

$$(2) \quad f(C_B) = \upsilon_0 C_{B0} - \upsilon_0 C_B + r_B V$$

$$(3) \quad f(C_C) = - \upsilon_0 C_C + r_C V$$

$$(4) \quad f(C_D) = - \upsilon_0 C_D + r_D V$$

- **Net rates**

$$(5) \quad r_A = r_{1A} + r_{2A}$$

$$(6) \quad r_B = r_{1B}$$

$$(7) \quad r_C = r_{1C} + r_{2C}$$

$$(8) \quad r_D = r_{2D}$$

5. Applications of Algorithm XI

- **Example B: Liquid phase CSTR 2 – Solution 2**
  - **Rate laws**
  - **Net rates**

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

(10) $$r_{2C} = -k_{2C} C_A^2 C_C^3$$

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1}$$ Reaction 1

(11) $$r_{1B} = 2\ r_{1A}$$

(12) $$r_{1C} = -r_{1A}$$

$$\frac{r_{2A}}{-2} = \frac{r_{2C}}{-3} = \frac{r_{2D}}{1}$$ Reaction 2

(13) $$r_{2A} = \frac{2}{3} r_{2C}$$

(14) $$r_{2D} = -\frac{1}{3} r_{2C}$$

5. Applications of Algorithm XII

- **Example B: Liquid phase CSTR 2 – Solution 3**
  - **Selectivity**

(15) $$S_{C/D} = \frac{F_C}{(F_D + 0.001)}$$

  - **Parameters**

(16) $$\upsilon_0 = 100 \ \ dm^3/min$$

(17) $$k_{1A} = 10 \ \ (dm^3/mol)^2/min$$

(18) $$k_{2C} = 15 \ \ (dm^3/mol)^4/min$$

(19) $$V = 2{,}500 \ \ dm^3$$

(20) $$C_{A0} = 2.0$$

(21) $$C_{B0} = 2.0$$

5. Applications of Algorithm XIII

- **Example C: Gas phase PFR, no pressure drop**

- Same rxns, rate laws, and rate constants as example A

A + 2B → C (1) $-r_{1A} = k_{1A}C_AC_B^2$ NOTE: The specific reaction rate k_{1A} is defined wrt species A

3C + 2A → D (2) $-r_{2C} = k_{2C}C_C^3C_A^2$ NOTE: The specific reaction rate k_{2C} is defined wrt species C

- The complex gas phase reactions take place in a PFR.

- **feed is equal molar in A and B with F_{A0} = 10 mol/min**
- **volumetric flow rate is 100 dm^3/min.**
- **reactor volume 1,000 dm^3, no pressure drop**
- **total entering concentration is C_{T0} = 0.2 mol/dm^3**

5. Applications of Algorithm XIV

- **Example C: Gas phase PFR, no pressure drop 2**
  - **The complex gas phase reactions take place in a PFR.**
    - **rate constants**

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

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

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

5. Applications of Algorithm XV

- **Example C: Gas phase PFR, no pressure drop 3**

Sol)

- Gas phase PFR, no pressure drop

- **Mole balances**

(1) $$\frac{dF_A}{dV} = r_A \qquad (F_{A0} = 10)$$

(2) $$\frac{dF_B}{dV} = r_B \qquad (F_{B0} = 10)$$

(3) $$\frac{dF_C}{dV} = r_C \qquad V_f = 1,000$$

(4) $$\frac{dF_D}{dV} = r_D$$

5. Applications of Algorithm XVI

- **Example C: Gas phase PFR, no pressure drop 4**

Sol)

- Gas phase PFR, no pressure drop 2

- **Net rates**

(5) $$r_A = r_{1A} + r_{2A}$$

(6) $$r_B = r_{1B}$$

(7) $$r_C = r_{1C} + r_{2C}$$

(8) $$r_D = r_{2D}$$

- **Rate law**

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

(10) $$r_{2C} = -k_{2C} C_A^2 C_C^3$$

5. Applications of Algorithm XVII

○ **Example C: Gas phase PFR, no pressure drop 5**

Sol)

- Gas phase PFR, no pressure drop 3

• **Relative rates**

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1} \qquad \text{Reaction 1}$$

(11) $$r_{1B} = 2\ r_{1A}$$

(12) $$r_{1C} = -r_{1A}$$

$$\frac{r_{2A}}{-2} = \frac{r_{2C}}{-3} = \frac{r_{2D}}{1} \qquad \text{Reaction 2}$$

(13) $$r_{2A} = \frac{2}{3} r_{2C}$$

(14) $$r_{2D} = -\frac{1}{3} r_{2C}$$

5. Applications of Algorithm XVIII

- **Example C: Gas phase PFR, no pressure drop 6**

Sol) - Gas phase PFR, no pressure drop 4

- **Selectivity**

(15) $S_{C/D} = \text{if } (V > 0.0001) \text{ then } \left(\frac{F_C}{F_D}\right) \text{ else } (0)$

- **Stoichiometry**

(16) $C_A = C_{T0}\left(\frac{F_A}{F_T}\right)y$

(17) $C_B = C_{T0}\left(\frac{F_B}{F_T}\right)y$

(18) $C_C = C_{T0}\left(\frac{F_C}{F_T}\right)y$

(19) $C_D = C_{T0}\left(\frac{F_D}{F_T}\right)y$

(20) $y = 1$

(21) $F_T = F_A + F_B + F_C + F_D$

5. Applications of Algorithm XIX

- **Example C: Gas phase PFR, no pressure drop 7**

Sol) - Gas phase PFR, no pressure drop 5

- **Parameters**

$$C_{T0} = 0.2 \ \ mol/dm^3 \quad (22)$$

$$y = 1 \quad (23)$$

$$k_{1A} = 100 \ \left(dm^3/mol\right)^2 / min \quad (24)$$

$$k_{2C} = 1{,}500 \left(dm^3/mol\right)^4 / min \quad (25)$$

5. Applications of Algorithm XX

- **Example C: Gas phase PFR, no pressure drop 8**

Sol) - Gas phase PFR, no pressure drop 5