Chemical Reactor Design

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Chapter 6

Chemical Reaction Engineering

Multiple Reactions

Introduction

❀ Seldom is the reaction of interest the only one that occurs in a chemical reactor. Typically, multiple reactions will occur, some desired and some undesired. One of the key factors in the economic success of a chemical plant is minimization of undesired side reactions that occur along with the desired reaction.

❀ In this chapter, we discuss reactor selection and general mole balances for multiple reactions. First, we describe the four basic types of multiple reactions: series, parallel, independent, and complex.

❀ Next, we define the selectivity parameter and discuss how it can be used to minimize unwanted side reactions by proper choice of operating conditions and reactor selection.

Objectives

🌸 Define different types of <u>selectivity</u> and <u>yield</u>

🌼 Choose a reaction system

that would <u>maximize the selectivity of the desired product</u>

given the rate laws for all the reactions occurring in the system.

🌸 <u>Size reactors to maximize the selectivity</u>

and to determine the species concentrations in a batch reactor,

semi-batch reactor, CSTR, PFR, and PBR, systems.

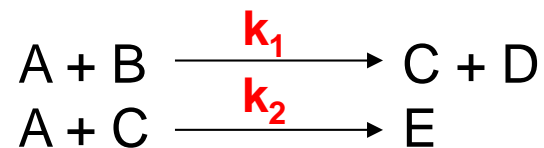# 6.1 Definition of Multiple Reaction
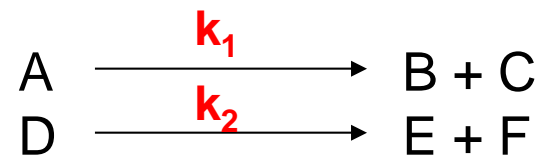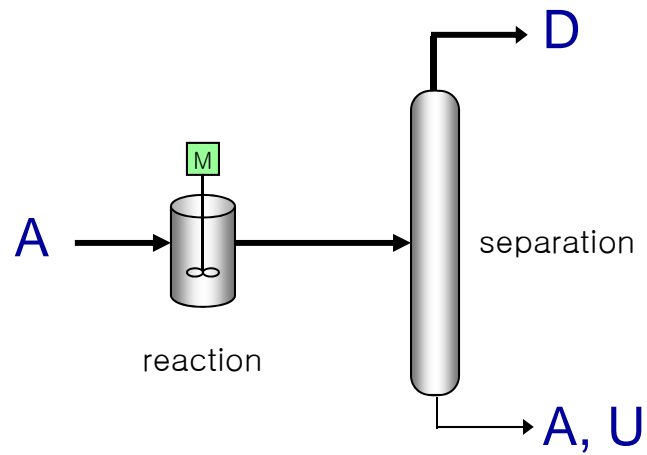
✿ Parallel rxns (competing rxns)

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$
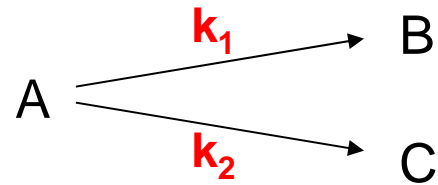
✿ Series rxns (consecutive rxns)

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

✿ Complex rxns (Parallel + Series rxns)

$$A + B \xrightarrow{k_1} C + D$$
$$A + C \xrightarrow{k_2} E$$

✿ Independent rxns

$$A \xrightarrow{k_1} B + C$$
$$D \xrightarrow{k_2} E + F$$

Examples of Multiple Reaction

❀ Parallel rxns *(Oxidation of ethylene to ethylene oxide)*

$$CH_2=CH_2 + O_2 \quad \xrightarrow{k_1} \quad 2CO_2 + 2H_2O$$

$$\xrightarrow{k_2} \quad \underset{O}{CH_2\text{-}CH_2}$$

❀ Series rxns *(rxn of EO with NH₃)*

$$\underset{O}{CH_2\text{-}CH_2} + NH_3 \longrightarrow HOCH_2CH_2NH_2 \quad \text{(Monoethanolamine)}$$

$$\xrightarrow{EO} (HOCH_2CH_2)_2NH \xrightarrow{EO} (HOCH_2CH_2)_3N$$

Diethanolamine   Triethanolamine

❀ Complex rxns *(formation of 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 rxns *(The cracking of crude oil to form gasoline)*

$$C_{15}H_{32} \longrightarrow C_{12}H_{26} + C_3H_6$$
$$C_8H_{18} \longrightarrow C_6H_{14} + C_2H_4$$

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Desired and Undesired Reaction

k_D

A → D (*Desired Product*)

k_U

A → U (*Undesired Product*)

Competing or side rxn

The economic incentive

Maximize the formation of D

Minimize the formation of U

D

M

A → reaction → separation

A, U
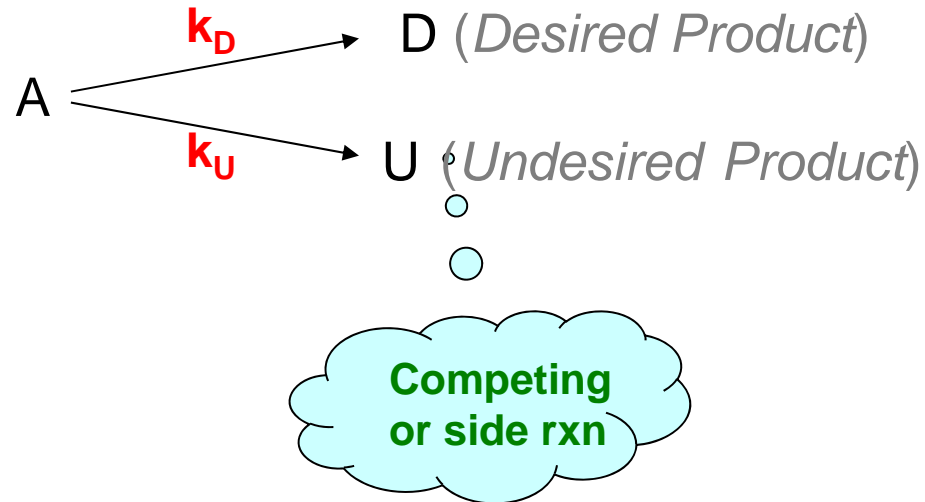
Rxn-separation system producing both D & U

cost

Total cost

Reaction cost

Separation cost

Low   High
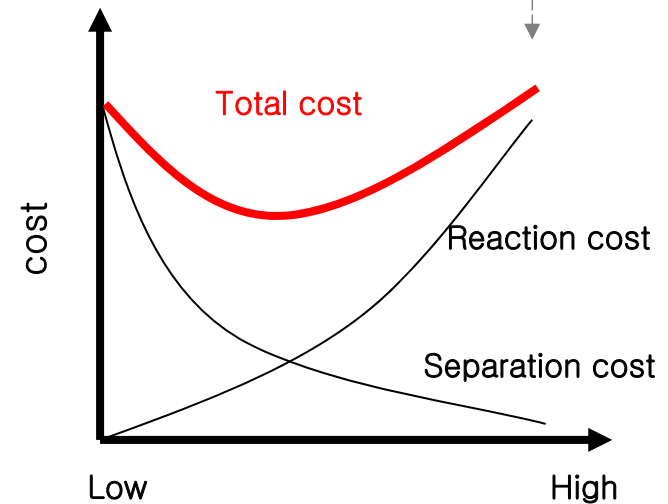
Efficiency of a reactor system

A → D (*Desired Product*) with rate constant k_D

A → U (*Undesired Product*) with rate constant k_U
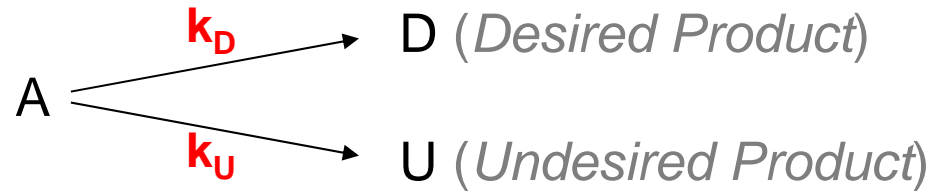
The rate laws are

$$-r_A = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2}$$

$$r_D = k_D C_A^{\alpha_1}$$

$$r_U = k_U C_A^{\alpha_2}$$

Selectivity tells us how one product is favored over another when we have multiple reactions.

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2} = \frac{\text{Rate of formation of D}}{\text{Rate of formation of U}}$$

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Overall Selectivity, $\widetilde{S}_{DU}$

For Flow Reactor

$$\widetilde{S}_{D/U} = \frac{F_D}{F_U} = \frac{\text{Exit molar flow rate of desired product}}{\text{Exit molar flow rate of undesired product}}$$
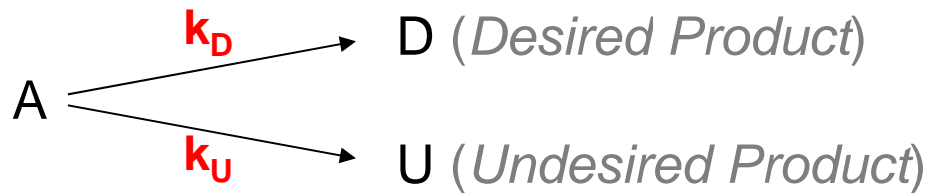
For Batch Reactor

$$\widetilde{S}_{D/U} = \frac{N_D}{N_U} = \frac{\text{No. of moles of desired product at the end of rxn time}}{\text{No. of moles of undesired product at the end of rxn time}}$$

Mission: Develop a relationship between $\widetilde{S}_{D/U}$ and $S_{D/U}$ in a CSTR

Solution

A $\xrightarrow{\textbf{k}_\textbf{D}}$ D (*Desired Product*)

A $\xrightarrow{\textbf{k}_\textbf{U}}$ U (*Undesired Product*)

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

$$\widetilde{S}_{D/U} - \frac{F_D}{F_U}$$

Mole balance of D and U yields $F_D = r_D V$ and $F_U = r_U V$, respectively

$$\widetilde{S}_{D/U} = \frac{F_D}{F_U} = \frac{r_D V}{r_U V} = \frac{r_D}{r_U} = S_{D/U}$$

$$\boxed{\widetilde{S}_{D/U} = S_{D/U}}$$

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Yields

<u>Instantaneous Yield (Basis: Reaction Rate)</u>

$$Y_D = \frac{r_D}{-r_A}$$

<u>Overall Yield (Basis: Mole or Molar Flow Rate)</u>

For a batch system: $\widetilde{Y}_D - \dfrac{N_D}{N_{Ao} - N_A} = \dfrac{\text{Mole of desired product formed at the end of reaction}}{\text{Number of moles of key reactant consumed}}$

For a flow system: $\widetilde{Y}_D = \dfrac{F_D}{F_{Ao} - F_A}$

Note

Different definitions for selectivity and yield

Check carefully to ascertain the definition intended by the author

From an *economic standpoint*,
overall selectivities and yields are important
in determining profits

The instantaneous selectivities give insights
in choosing reactors and reaction schemes
that will help maximize the profit

6.2 Parallel Reactions

$$k_D \rightarrow D \ (\textit{Desired Product})$$

$$A$$

$$k_U \rightarrow U \ (\textit{Undesired Product})$$
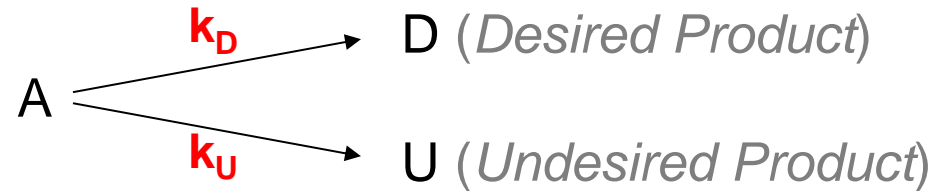
The rate laws are

$$-r_A = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2}$$

$$r_D = k_D C_A^{\alpha_1}$$

$$r_U = k_U C_A^{\alpha_2}$$

We want to maximize $S_{D/U}$.

$$\boxed{S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}} = \frac{\text{Rate of formation of D}}{\text{Rate of formation of U}}$$

α_1 and α_2 are positive reaction orders

$$A \begin{array}{c} \xrightarrow{k_D} \text{D (\textit{Desired Product})} \\ \xrightarrow{k_U} \text{U (\textit{Undesired Product})} \end{array}$$
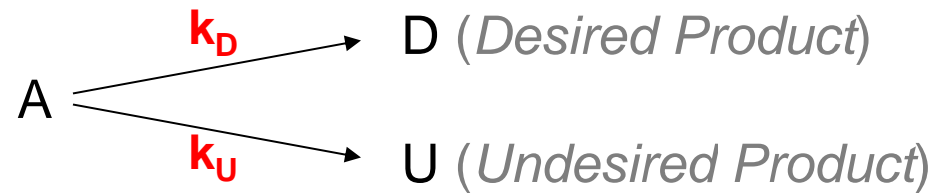
$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

✿ **Case 1:** $\alpha_1 > \alpha_2$, $a = \alpha_1 - \alpha_2$

$$\boxed{S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^a}$$

Maximize $S_{D/U}$

- keeping the concentration of reactant A as high as possible during the rxn

- in gas phase rxn, we should run it w/o inerts and at high pressures to keep C_A high

- in liquid phase rxn, the use of diluents should be keep to a minimum

- use a batch or plug-flow reactor

A
$\xrightarrow{k_D}$ D (*Desired Product*)

$\xrightarrow{k_U}$ U (*Undesired Product*)
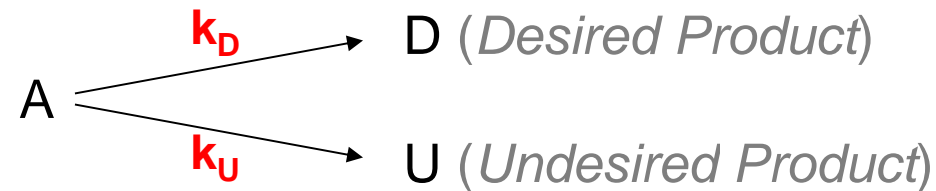
$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

❀ **Case 2:** $\alpha_2 > \alpha_1$, $b = \alpha_2 - \alpha_1$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} \frac{1}{C_A^b}$$

Maximize $S_{D/U}$

- keeping the concentration of reactant A as low as possible during the rxn

- in gas phase rxn, we should run it with inerts and at low pressures to keep C_A low

- in liquid phase rxn, the use of diluents should be keep to a maximum

- use a CSTR or recycle reactor (product stream act as a diluent)

Maximizing S_{DU} for one reactant
Whether the reaction should be run at high or low T?

$$S_{D/U} \sim \frac{k_D}{k_U} = \frac{A_D}{A_U} e^{-\frac{E_D - E_U}{RT}}$$

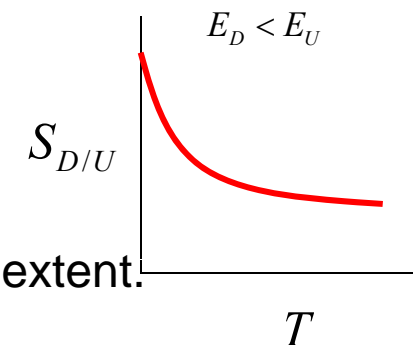$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

✿ Case 3: $E_D > E_U$

- k_D (r_D) increases more rapidly with increasing temp. than does the k_U.

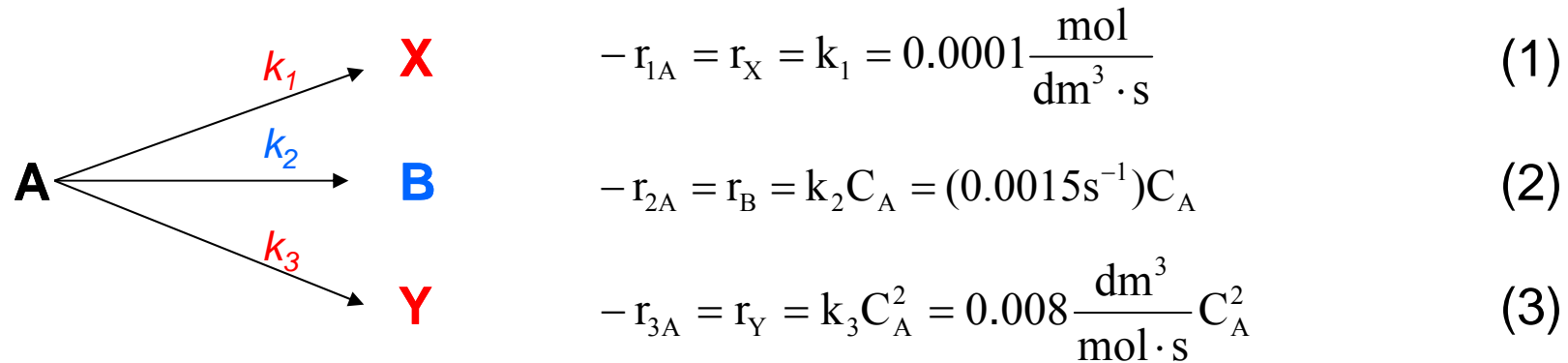- keeping the temperature as high as possible to maximize S_{DU}.

$E_D > E_U$

$S_{D/U}$

T
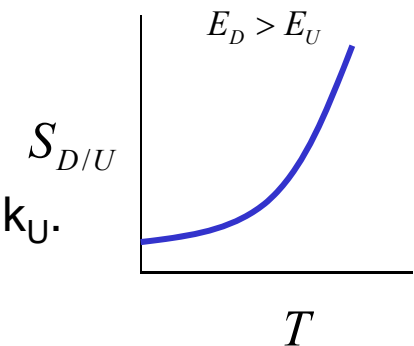
✿ Case 4: $E_U > E_D$

- keeping the temperature as low as possible to maximize S_{DU}

- not so low that the desired rxn does not proceed to any significant extent.

$E_D < E_U$

$S_{D/U}$

T

Maximizing $S_{B/XY}$ for the Trambouze Reaction

Reactant A decomposes by three simultaneous reactions to form three products, B (desired), X (undesired), and Y (undesired). These liquid phase reactions, along with the appropriate rate laws, are called the **Trambouze reactions**.

$$k_1 \rightarrow X \qquad -r_{1A} = r_X = k_1 = 0.0001 \frac{mol}{dm^3 \cdot s} \qquad (1)$$

$$A \; k_2 \rightarrow B \qquad -r_{2A} = r_B = k_2 C_A = (0.0015 s^{-1}) C_A \qquad (2)$$

$$k_3 \rightarrow Y \qquad -r_{3A} = r_Y = k_3 C_A^2 = 0.008 \frac{dm^3}{mol \cdot s} C_A^2 \qquad (3)$$

How and under what conditions (e.g., reactor types, temperature, concentrations) should the reaction be carried out to maximize the selectivity of B ?

➤ The specific reaction rates are given @ *300K*
➤ *E_1=10,000, E_2=15,000, and E_3=20,000 kcal/mole*
➤ *C_{A0}=0.4M, v_0=2.0 dm³/s*

$$S_{B/(X+Y)} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 + k_3 C_A^2}$$

Maximizing $S_{B/XY}$ for the Trambouze Reaction

C_A	$S_{B/(X+Y)}$
0	0
0.025	0.357143
0.05	0.625
0.075	0.775862
0.1	0.833333
0.125	0.833333
0.15	0.803571
0.175	0.76087
0.2	0.714286
0.225	0.668317
0.25	0.625
0.275	0.585106
0.3	0.54878
0.325	0.515873
0.35	0.486111
0.375	0.459184
0.4	0.434783
0.425	0.412621
0.45	0.392442
0.475	0.374016
0.5	0.357143

$$S_{B/(X+Y)} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 + k_3 C_A^2}$$

$$S_{B/(X+Y)} = (0.0015 * C_A)/(0.0001 + 0.008 * C_A^2)$$

$$S_{B/(X+Y)} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 + k_3 C_A^2}$$

$S_{B/(X+Y)}$

C_A (mol/dm³)

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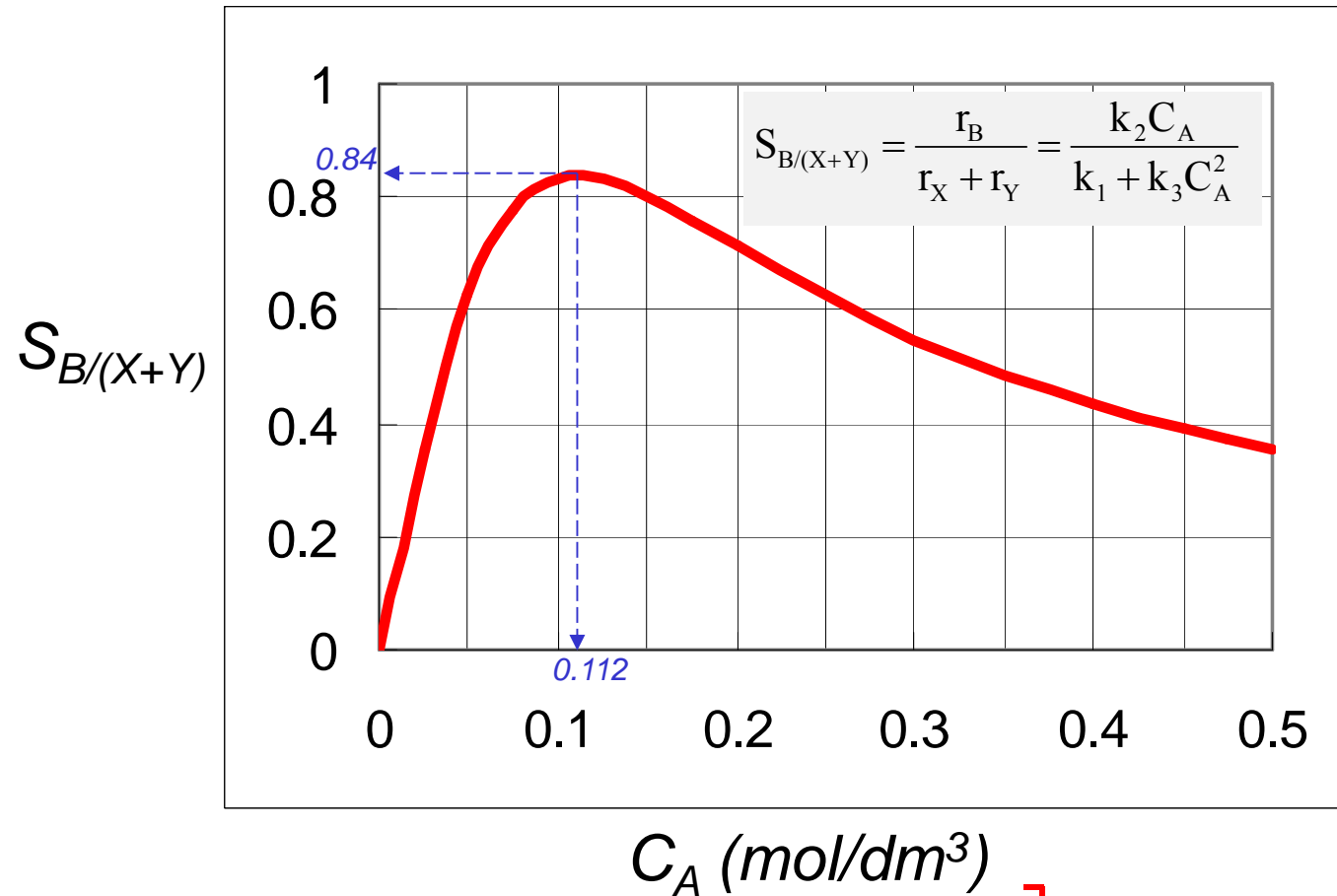
Maximizing $S_{B/XY}$ for the Trambouze Reaction

As we see, the selectivity reaches a maximum at a concentration C_A^*. Because the concentration changes down the length of a PFR, we cannot operate at this maximum. Consequently, we will use a CSTR and design it to operate at this maximum. To find the maximum C_A^*, we differentiate $S_{B/(X+Y)}$ w.r.t. C_A, set the derivative to zero, and solve for C_A^*. That is,

$$S_{B/(X+Y)} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 + k_3 C_A^2}$$

$$\frac{dS_{B/(X+Y)}}{dC_A} = 0 = \frac{k_2\left[k_1 + k_3 C_A^{*2}\right] - k_2 C_A^*\left[2k_3 C_A^*\right]}{\left[k_1 + k_3 C_A^{*2}\right]^2}$$

$$C_A^* = \sqrt{\frac{k_1}{k_3}} = \sqrt{\frac{0.0001(mol/dm^3 \cdot s)}{0.008(dm^3/mol \cdot s)}} = 0.1118 mol/dm^3$$

$$S_{B/XY} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A^*}{k_1 + k_3 C_A^{*2}} = \frac{k_2\sqrt{\dfrac{k_1}{k_3}}}{k_1 + k_3\left(\sqrt{\dfrac{k_1}{k_3}}\right)^2} = \frac{k_2\sqrt{\dfrac{k_1}{k_3}}}{2k_1} = \frac{k_2}{2\sqrt{k_1 k_3}} = 0.8385$$

Maximizing $S_{B/XY}$ for the Trambouze Reaction

We now calculate this CSTR volume and conversion. The net rate of formation of A from reactions (1), (2), and (3) is

$$- r_A = k_1 + k_2 C_A + k_3 C_A^2$$

$$A \begin{array}{l} \xrightarrow{k_1} X \quad r_X = k_1 \\ \xrightarrow{k_2} B \quad r_B = k_2 C_A \\ \xrightarrow{k_3} Y \quad r_Y = k_3 C_A^2 \end{array}$$
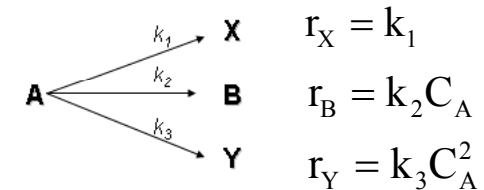
CSTR volume for this liquid-phase reaction, $\upsilon = \upsilon_0$

$$V = \frac{\upsilon_0 [C_{A0} - C_A^*]}{- r_A} = \frac{\upsilon_0 [C_{A0} - C_A^*]}{[k_1 + k_2 C_A^* + k_3 C_A^{*2}]} = 1567.6 \, dm^3 \qquad \text{CSTR volume for maximum selectivity}$$

$$\tau = \frac{V}{\upsilon_0} = \frac{C_{A0} - C_A^*}{- r_A^*} = \frac{C_{A0} - C_A^*}{k_1 + k_2 C_A^* + k_3 C_A^{*2}} = 783.8s$$

$$k_1 = 0.0001 \, mol/dm^3 \cdot s$$
$$k_2 = 0.0015 \, s^{-1}$$
$$k_3 = 0.008 \, dm^3 /mol \cdot s$$
$$\upsilon_0 = 2.0 \, dm^3 /s$$
$$C_{A0} = 0.4 \, mol/dm^3$$
$$C_A^* = 0.112 \, mol/dm^3$$

Maximizing $S_{B/XY}$ for the Trambouze Reaction

Maximum the selectivity w.r.t. temperature

$$S_{B/XY} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A^*}{k_1 + k_3 C_A^{*2}} = \frac{k_2}{2\sqrt{k_1 k_3}} = \frac{A_2}{2\sqrt{A_1 A_3}} \, exp\left[\frac{\frac{E_1 + E_3}{2} - E_2}{RT}\right]$$

Case 1: $\dfrac{E_1 + E_3}{2} < E_2$ Run @ high temperature (w/o side rxn)

Case 2: $\dfrac{E_1 + E_3}{2} > E_2$ Run @ low temperature (with insured conversion)

For the activation energies given above $\dfrac{E_1 + E_3}{2} = E_2 = 15{,}000$

So the selectivity for this combination of activation energies is independent of temperature !

Maximizing $S_{B/XY}$ for the Trambouze Reaction

What is the conversion of A in the CSTR?

$$X^* = \frac{C_{A0} - C_A^*}{C_{A0}} = \frac{0.4 - 0.112}{0.4} = \boxed{0.72}$$

If greater than 72% conversion of A is required, then the CSTR operated with a reactor concentration of 0.112 mol/dm^3 should be followed by a PFR because the concentration and selectivity will decrease continuously from C_A^* as we move down the PFR to an exit concentration C_{Af}. Hence the system

$$\left[CSTR \Big|_{C_A^*} + PFR \Big|_{C_A^*}^{C_{Af}} \right]$$

Would be the highest selectivity while forming more the desired product B, beyond what was formed at C_A^* in a CSTR.

How can we increase the conversion and still have a high selectivity $S_{B/(X+Y)}$?

Maximizing $S_{B/XY}$ for the Trambouze Reaction

Optimum CSTR followed by a PFR.

The exit concentration of X, Y, and B can be found from the CSTR mole balances

Species X:
$$V = \frac{v_0 C_X}{r_X} = \frac{v_0 C_X}{k_1} \rightarrow C_X = k_1 \tau = (0.0001)(783) = \boxed{0.0783\, mol\,/\,dm^3}$$

Species B:
$$V = \frac{v_0 C_B}{r_B} = \frac{v_0 C_B}{k_2 C_A^*} \rightarrow C_B = k_2 \tau C_A^* = (0.0015)(0.112)(783) = \boxed{0.132\, mol\,/\,dm^3}$$

Species Y:
$$V = \frac{v_0 C_Y}{r_Y} = \frac{v_0 C_Y}{k_3 C_A^{*2}} \rightarrow C_Y = k_3 \tau C_A^{*2} = (0.008)(0.112)^2(783) = \boxed{0.0786\, mol\,/\,dm^3}$$

$$F_X = v_0 C_X = 0.156 \text{ mol}\,/\,s, \quad F_B = v_0 C_B = 0.264 \text{ mol}\,/\,s, \quad F_Y = v_0 C_Y = 0.157 \text{ mol}\,/\,s$$

Let's check to make sure the sum of all the species in solution equals the initial concentration C_{A0} = 0.4.

$$C_A + C_X + C_B + C_Y = 0.112 + 0.0783 + 0.132 + 0.0786 = 0.4 \;////\; QED$$

Maximizing $S_{B/XY}$ for the Trambouze Reaction

The reason we want to use a PFR after we reach the maximum selectivity, $S_{B/XY}$, is that the PFR will continue to gradually reduce C_A. Thus, more B will be formed than if another CSTR were to follow. If 90% conversion were required, then the exit concentration would be C_{Af}=(1-0.9)(0.4 mol/dm³)=0.04 mol/dm³.

The PFR mole balances for this liquid-phase reaction ($v=v_0$) are

$$\upsilon_0 \frac{dC_A}{dV} = \frac{dC_A}{d\tau} = r_A, \quad \frac{dC_X}{d\tau} = r_X, \quad \frac{dC_B}{d\tau} = r_B, \quad \frac{dC_Y}{d\tau} = r_Y$$

Combining mole balances with their respective rate laws yields

$$\frac{dC_A}{d\tau} = -k_1 - k_2 C_A - k_3 C_A^2 \quad (\text{at } \tau = 0, \text{ then } C_A = 0.112 \text{ mol}/\text{dm}^3)$$

$$\frac{dC_X}{d\tau} = k_1 \quad (\text{at } \tau = 0, \text{ then } C_X = 0.0783 \text{ mol}/\text{dm}^3)$$

$$\frac{dC_B}{d\tau} = k_2 C_A \quad (\text{at } \tau = 0, \text{ then } C_B = 0.132 \text{ mol}/\text{dm}^3)$$

$$\frac{dC_Y}{d\tau} = k_3 C_A^2 \quad (\text{at } \tau = 0, \text{ then } C_Y = 0.0786 \text{ mol}/\text{dm}^3)$$

τ=0, the entering concentrations to the PFR are the exit concentrations from CSTR.

Maximizing $S_{B/XY}$ for the Trambouze Reaction

The conversion can be calculated

$$X = \frac{C_{A0} - C_A}{C_{A0}}$$

We will use Polymath to plot the exit concentrations as a function of τ and then determine the volume ($V=v_0\tau$) for 90% conversion (C_A=0.04 mol/dm³) and then find C_X, C_B, and C_Y at this volume. This volume turns out to be approximately 600 dm³.

At the exit of the PFR, C_A=0.037, C_X=0.11, C_B=0.16, and C_Y=0.09 all in mol/dm³.

One now has to make a decision as to whether adding the PFR to increase the conversion of A from 0.72 to 0.9 and the molar flow rate of B from 0.26 to 0.32 mol/s is worth not only the added cost of the PFR, but also the decrease in selectivity. This reaction was carried out isothermally; nonisothermal multiple reactions will be discussed in Chapter 8.

PFR concentration & selectivity profiles for the Trambouze Reaction

POLYMATH Results
Example 6-2 Maximizing the Selectivity for the Trambouze Reactions 08-12-2004, Rev5.1.232

ODE Report (RKF45)

**Differential equations as entered by the user**
[1] $d(Ca)/d(tau) = -k1-k2*Ca-k3*Ca^2$
[2] $d(Cx)/d(tau) = k1$
[3] $d(Cb)/d(tau) = k2*Ca$
[4] $d(Cy)/d(tau) = k3*Ca^2$

**Explicit equations as entered by the user**
[1] $Cao = 0.4$
[2] $X = 1-Ca/Cao$
[3] $k1 = 0.0001$
[4] $k2 = 0.0015$
[5] $k3 = 0.008$
[6] $Sbxy = Cb/(Cx+Cy)$

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
tau	0	0	300	300
Ca	0.112	0.0376688	0.112	0.0376688
Cx	0.0783	0.0783	0.1083	0.1083
Cb	0.132	0.132	0.1634944	0.1634944
Cy	0.0786	0.0786	0.0914368	0.0914368
Cao	0.4	0.4	0.4	0.4
X	0.72	0.72	0.905828	0.905828
k1	1.0E-04	1.0E-04	1.0E-04	1.0E-04
k2	0.0015	0.0015	0.0015	0.0015
k3	0.008	0.008	0.008	0.008
Sbxy	0.8413002	0.8185493	0.8413002	0.8185493

PFR concentration & selectivity profiles for the Trambouze Reaction

PFR concentration & selectivity profiles for the Trambouze Reaction

POLYMATH 5.1 – [Differential Equations Solution #2]

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POLYMATH Results

No Title   05-21-2007, Rev5.1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
tau	0	0	300	300
Ca	0.112	0.0376688	0.112	0.0376688
Cx	0.0783	0.0783	0.1083	0.1083
Cb	0.132	0.132	0.1634944	0.1634944
Cy	0.0786	0.0786	0.0914368	0.0914368
Cao	0.4	0.4	0.4	0.4
X	0.72	0.72	0.905828	0.905828
k1	1.0E-04	1.0E-04	1.0E-04	1.0E-04
k2	0.0015	0.0015	0.0015	0.0015
k3	0.008	0.008	0.008	0.008
Sbxy	0.8413002	0.8185493	0.8413002	0.8185493

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(Ca)/d(tau) = -k1-k2*Ca-k3*Ca^2
[2] d(Cx)/d(tau) = k1
[3] d(Cb)/d(tau) = k2*Ca
[4] d(Cy)/d(tau) = k3*Ca^2

Explicit equations as entered by the user

[1] Cao = 0.4
[2] X = 1-Ca/Cao
[3] k1 = 0.0001
[4] k2 = 0.0015
[5] k3 = 0.008
[6] Sbxy = Cb/(Cx+Cy)

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PFR concentration & selectivity profiles for the Trambouze Reaction
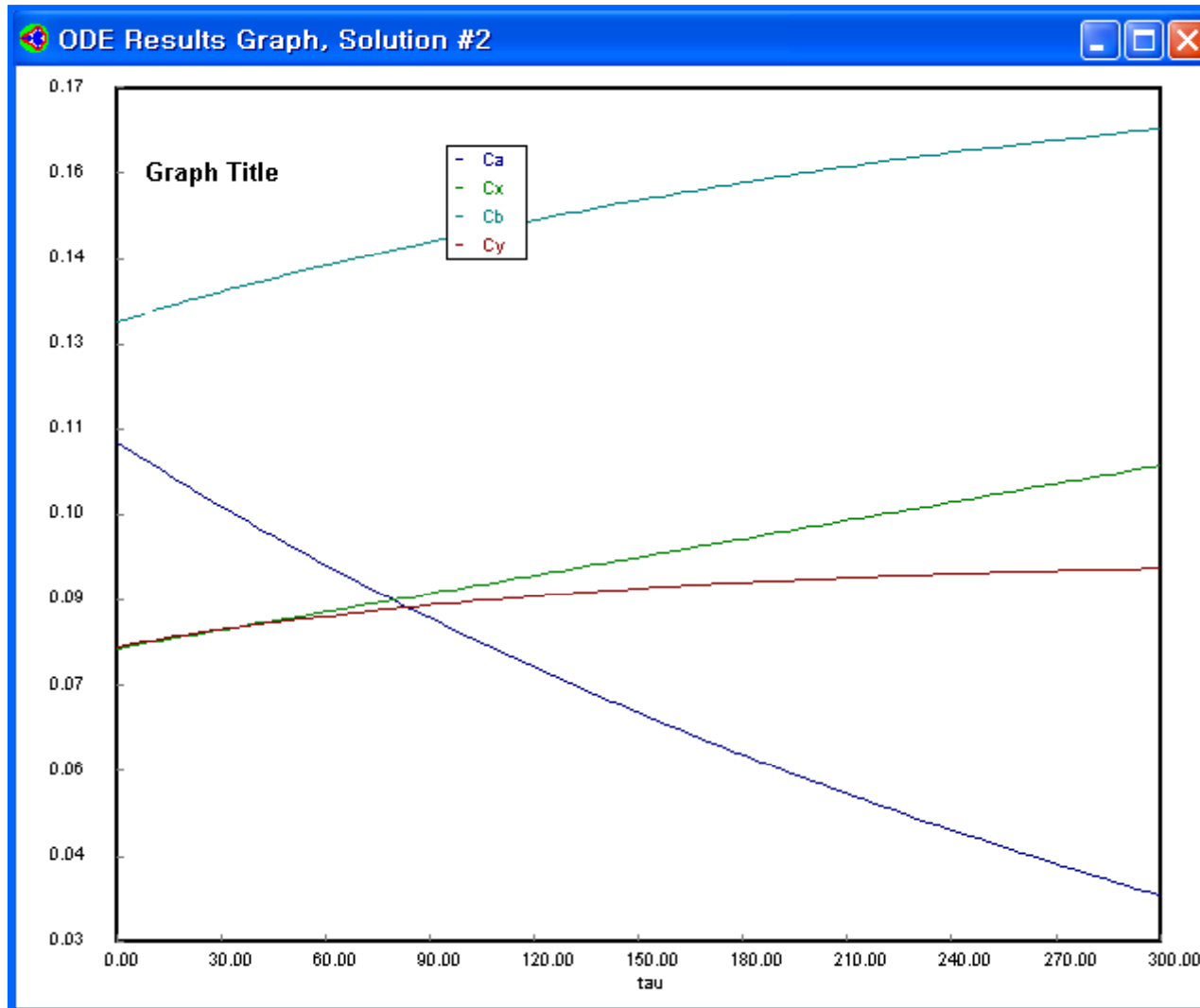
PFR concentration & selectivity profiles for the Trambouze Reaction
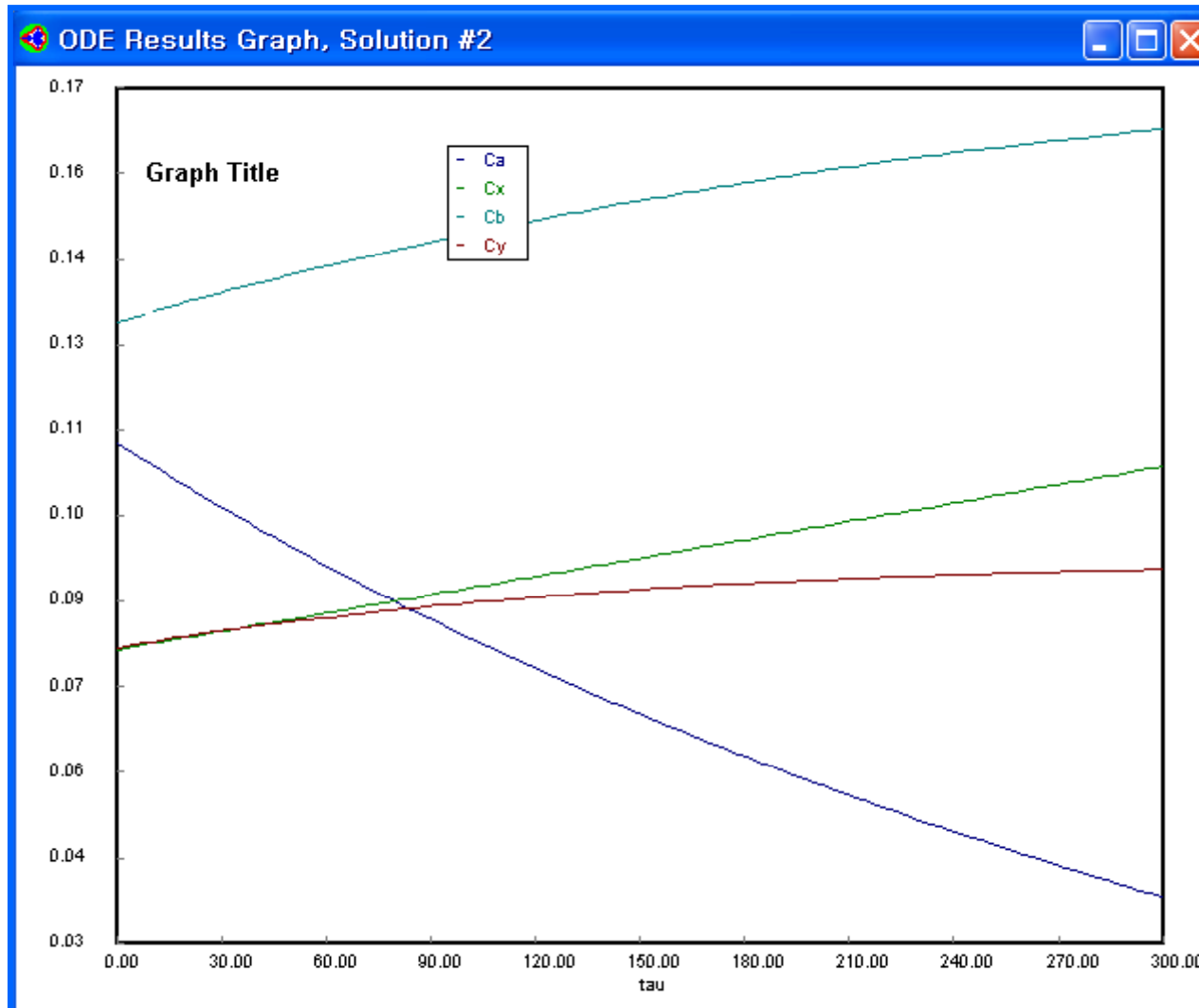
Two simultaneous reactions with two reactants

$$A + B \quad \overset{k_1}{\nearrow} \quad D \text{ (\textit{Desired Product})}$$
$$\quad \underset{k_2}{\searrow} \quad U \text{ (\textit{Unwanted Product})}$$
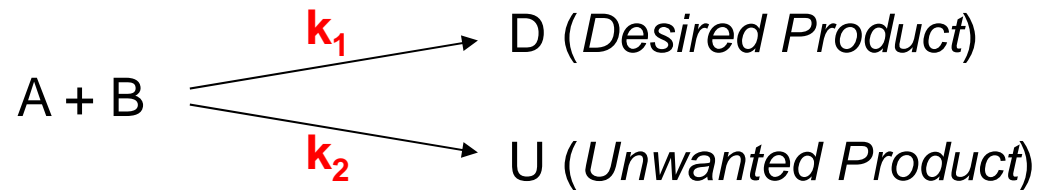
The rate laws are

$$- r_A = k_1 C_A^{\alpha_1} C_B^{\beta_1} + k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$

$$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

Rate selectivity parameter

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2}$$

Rate selectivity parameter (= Instantaneous selectivity) is to maximized by choosing reactor schemes.

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Reactor Selection Criteria

- Selectivity
- Yield
- Temperature control
- Safety
- Cost

Figure 6-3
Different reactors and schemes for maximizing the desired product
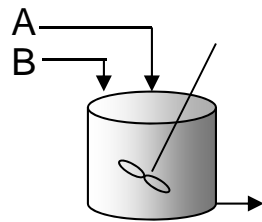
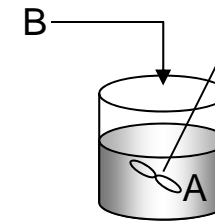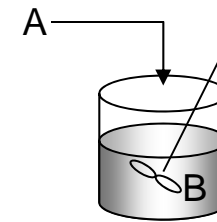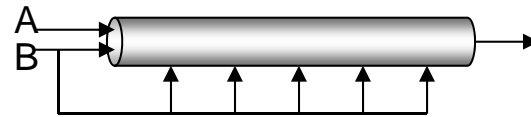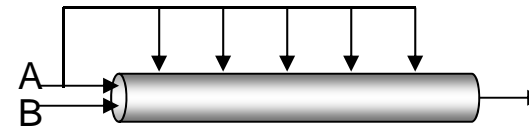(a) CSTR

(b) tubular reactor
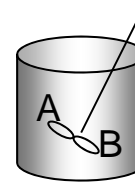
(c) batch

(d) semi-batch 1
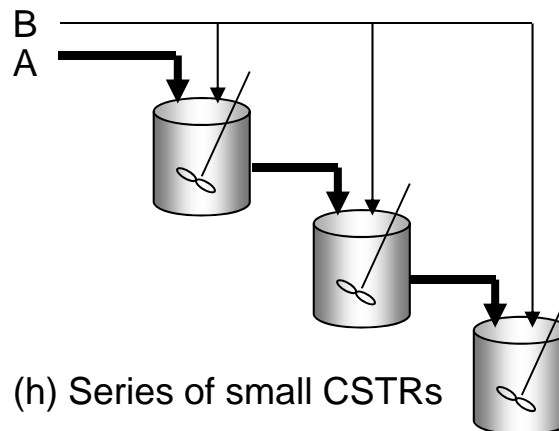
(e) semi-batch 2

(f) Tubular reactor with side streams

(g) Tubular reactor with side streams

(h) Series of small CSTRs

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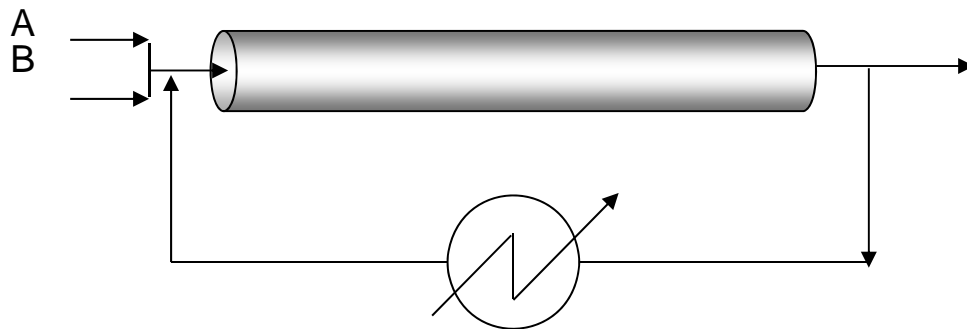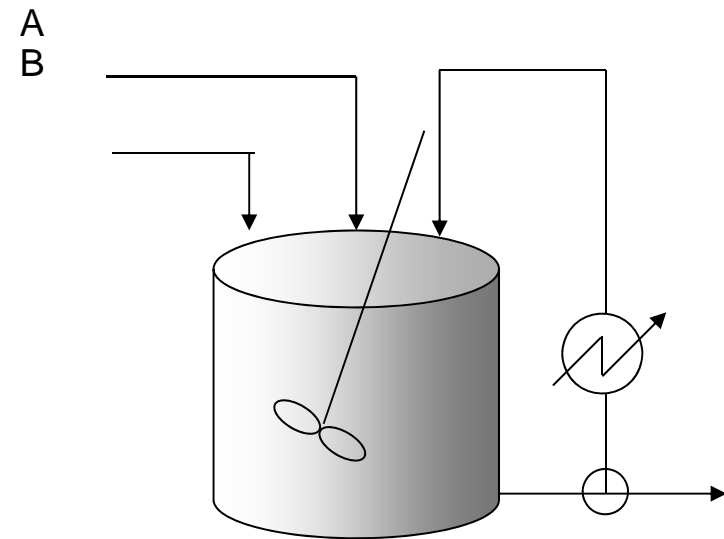
Figure 6-3

Different reactors and schemes for maximizing the desired product

The two reactors with recycle shown in (i) and (j) can be used for highly exothermic reactions. Here recycle stream is cooled and returned to the reactor to dilute and cool the inlet stream thereby avoiding hot spots and run-away reactions. The PFR with recycle is used for gas-phase reactions, and the CSTR is used for liquid-phase reactions.
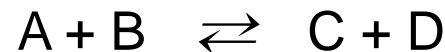

(i) Tubular reactor with recycle

(j) CSTR with recycle

Figure 6-3

## Different reactors and schemes for maximizing the desired product

The last two reactors, (k) and (l), are used for thermodynamically limited reactions where the equilibrium lies far to the left (reactant side)

$$A + B \rightleftarrows C + D$$

And one of the products must be removed (e,g., C) for the reaction to continue to completion. The membrane reactor (k) is used for thermodynamically limited gas-phase reactions, while reactive distillation (l) is used for liquid-phase reaction when one of the products has a high volatility (e.g., C) than the other species in the reactor.
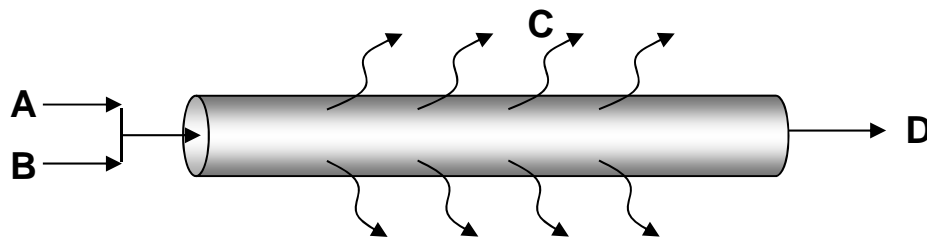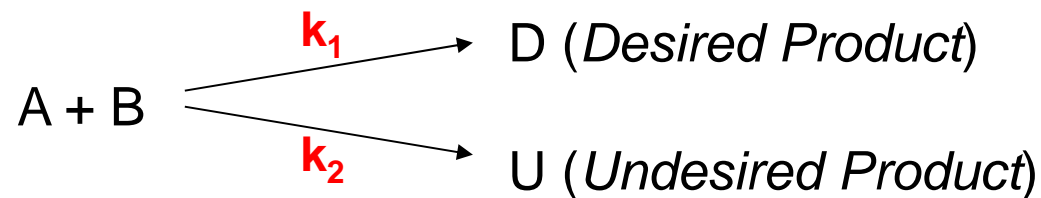

(k) Membrane reactor
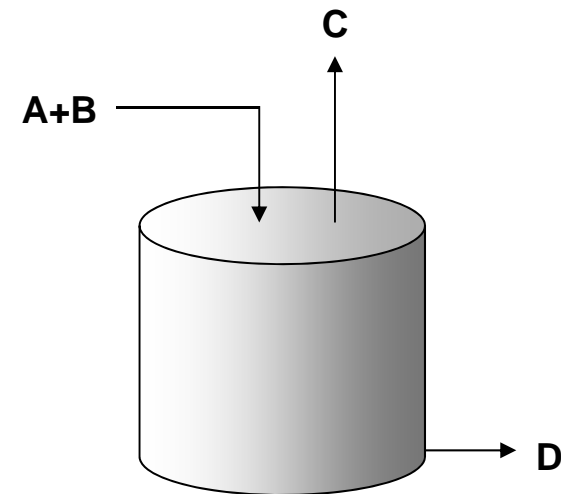
(l) Reactive distillation

Example 6-3: Minimizing unwanted products for two reactants

For the parallel reactions, consider all possible combinations of reaction orders and select the reaction scheme that will maximize $S_{D/U}$.

$$A + B \xrightarrow{k_1} D\ (Desired\ Product)$$
$$A + B \xrightarrow{k_2} U\ (Undesired\ Product)$$

$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$
$$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

Case I : $\alpha_1 > \alpha_2$, $\beta_1 > \beta_2$, $a = \alpha_1 - \alpha_2 > 0$, $b = \beta_1 - \beta_2 > 0$
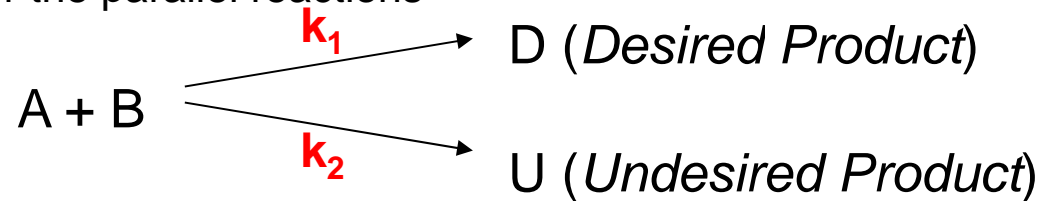
the rate selectivity parameter

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^a C_B^b$$

To maximize the S_{DU}, maintain the concentration of both A and B as high as possible

✪ a tubular reactor (Figure 6.3 (b))

✪ a batch reactor (Figure 6.3 (c))

✪ high pressures (if gas phase), and reduce inerts

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Example 6-3: Minimizing unwanted products for two reactants

for the parallel reactions

A + B
$\xrightarrow{k_1}$ D (*Desired Product*)
$\xrightarrow{k_2}$ U (*Undesired Product*)

$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$
$$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

Case II : $\alpha_1 > \alpha_2$, $\beta_1 < \beta_2$, $a = \alpha_1 - \alpha_2 > 0$, $b = \beta_2 - \beta_1 > 0$

the rate selectivity parameter

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1 C_A^a}{k_2 C_B^b}$$

To maximize the S_{DU}, maintain C_A high and C_B low.

✪ a semibatch reactor in which B is fed slowly into A. (Figure 6.3(d))

✪ a tubular reactor with side stream of B continually (Figure 6.3(f))

✪ a series of small CSTRs with A fed only to the first reactor and small B fed to each reactor. (Figure 6.3(h))

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Example 6-3: Minimizing unwanted products for two reactants

for the parallel reaction

$$A + B \quad \xrightarrow{k_1} \quad D \ (\textit{Desired Product})$$
$$\xrightarrow{k_2} \quad U \ (\textit{Undesired Product})$$
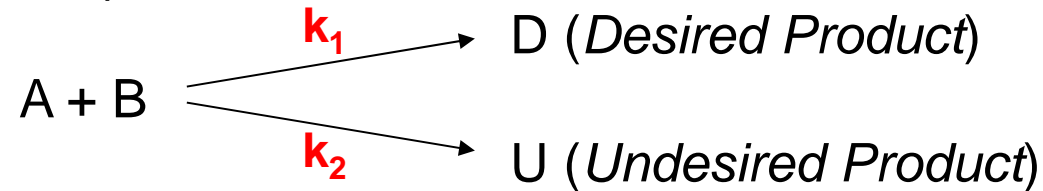
$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$
$$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

Case III : $\alpha_1 < \alpha_2$, $\beta_1 < \beta_2$, $a = \alpha_2 - \alpha_1 > 0$, $b = \beta_2 - \beta_1 > 0$

the rate selectivity parameter

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1}{k_2 C_A^a C_B^b}$$

To maximize the S_{DU}, maintain the concentration of both A and B as low as possible

✪ a CSTR (Figure 6.3(a))

✪ a tubular reactor in which there is a large recycle ratio (Figure 6.3(i))

✪ a feed diluted with inert material

✪ low pressures (if gas phase)

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Example 6-3: Minimizing unwanted products for two reactants

for the parallel reaction

$$A + B \xrightarrow{\ \ k_1\ \ } D\ (Desired\ Product)$$

$$A + B \xrightarrow{\ \ k_2\ \ } U\ (Undesired\ Product)$$
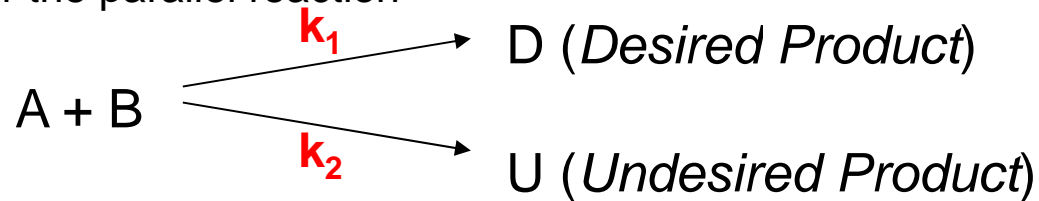
$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$

$$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

Case IV : $\alpha_1 < \alpha_2$, $\beta_1 > \beta_2$, $a = \alpha_2 - \alpha_1 > 0$, $b = \beta_1 - \beta_2 > 0$

the rate selectivity parameter

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1 C_B^b}{k_2 C_A^a}$$

To maximize the S_{DU}, maintain the concentration of both A and B as high as possible

✪ a semibatch reactor in which A is slowly fed to a large amount of B (Figure 6.3(e))

✪ a membrane reactor or tubular reactor with side stream of A (Figure 6.3(g))

✪ a series of small CSTRs with fresh A fed to each reactor (Figure 6.3(h))

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

❀ In parallel rxns, maximize the desired product

ⓘ by adjusting the reaction conditions (e.g. C_A, C_B)

ⓘ by choosing the proper reactor

❀ In series rxns, maximize the desired product

ⓘ by adjusting the space-time for a flow reactor
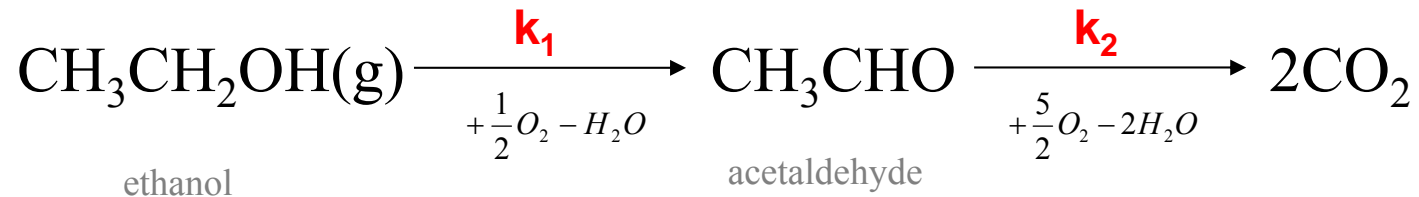
ⓘ by choosing real-time for a batch reactor

Maximizing the desired product in series reaction

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

Desired Product
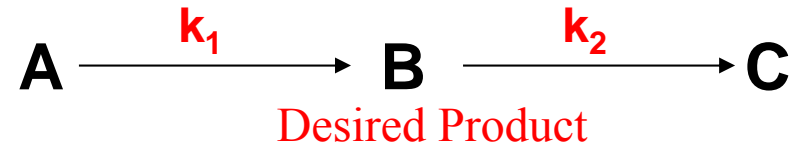
❀ If the first reaction is slow and second reaction is fast, it will be extremely difficult to produce species B.

❀ If the first reaction (formation of B) is fast and the reaction to form C is slow, a large yield of B can be achieved.

❀ However, if the reaction is allowed to proceed for a long time in a batch reactor or if the tubular flow reactor is too long, the desired product B will be converted to C.

❀ In no other type reaction is exactness in the calculation of the time needed to carry out the reaction more important than in series reactions.

Example 6-4: Maximizing the yield of the intermediate product

The oxidation of ethanol to form acetaldehyde is carried out on a catalyst of 4 wt% Cu-2wt% Cr on Al_2O_3. Unfortunately, acetaldehyde is also oxidized on this catalyst to form carbon dioxide. The reaction is carried out in a dilute concentrations (ca. 0.1% ethanol, 1% O_2, and 98.9% N_2). Consequently, the volume change with the reaction can be neglected. Determine the concentration of acetaldehyde as a function of space time.

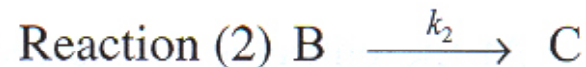$$CH_3CH_2OH(g) \xrightarrow[+\frac{1}{2}O_2 - H_2O]{k_1} CH_3CHO \xrightarrow[+\frac{5}{2}O_2 - 2H_2O]{k_2} 2CO_2$$

ethanol   acetaldehyde

The rxns are irreversible and first-order in ethanol and acetaldehyde, respectively.

Solution

Because O_2 is in excess, we can write the preceding series reaction as

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

The preceding series reaction can be written as

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

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

1. **Mole balance on A:**

$$\frac{dF_A}{dW} = r'_A \qquad \text{(E6-4.1)}$$

   a. **Rate law:**

$$-r'_A = k_1 C_A$$

   b. **Stoichiometry** (Dilute concentrations: $y_{A0} = 0.001$) $\therefore v = v_0$

$$F_A = C_A v_0$$

c. **Combining**, we have

$$v_0 \frac{dC_A}{dW} = -k_1 C_A \qquad \text{(E6-4.2)}$$

Let $\tau' = W/v_0 = \rho_b V/v_0 = \rho_b \tau$, where ρ_b is the bulk density of the catalyst.

d. Integrating with $C_A = C_{A0}$ at $W = 0$ gives us

$$C_A = C_{A0} e^{-k_1 \tau'} \qquad \text{(E6-4.3)}$$

2. **Mole balance on B:**

$$\frac{dF_B}{dW} = r'_{B_{net}} \qquad \text{(E6-4.4)}$$

a. **Rate law** (net):

$$r'_{B_{net}} = r'_{B_{rxn1}} + r'_{B_{rxn2}}$$

$$r'_{B_{net}} = k_1 C_A - k_2 C_B \qquad \text{(E6-4.5)}$$

b. **Stoichiometry:**

$$F_B = v_0 C_B$$

c. **Combining** yields

$$v_0 \frac{dC_B}{dW} = k_1 C_A - k_2 C_B \qquad \text{(E6-4.6)}$$

Substituting for C_A, dividing v_0 into W and rearranging, we have

$$\frac{dC_B}{d\tau'} + k_2 C_B = k_1 C_{A0} e^{-k_1 \tau'}$$

d. **Using** the integrating factor gives us

$$\frac{d(C_B e^{+k_2 \tau'})}{d\tau'} = k_1 C_{A0} e^{(k_2 - k_1)\tau'}$$

At the entrance to the reactor, $W = 0$, $\tau' = W/v_0 = 0$, and $C_B = 0$. Integrating, we get

$$C_B = k_1 C_{A0} \left(\frac{e^{-k_1 \tau'} - e^{-k_2 \tau'}}{k_2 - k_1} \right) \tag{E6-4.7}$$

The concentrations of A, B, and C are shown in Figure E6-4.1.

3. **Optimum yield.** The concentration of B goes through a maximum at a point along the reactor. Consequently, to find the optimum reactor length, we need to differentiate Equation (E6-4.7):

$$\frac{dC_B}{d\tau'} = 0 = \frac{k_1 C_{A0}}{k_2 - k_1} \left(-k_1 e^{-k_1 \tau'} + k_2 e^{-k_2 \tau'} \right) \tag{E6-4.8}$$
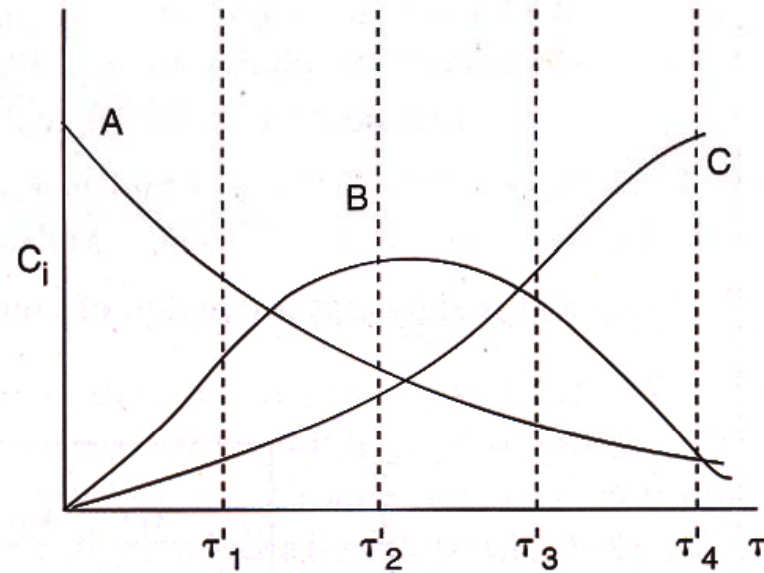
Figure E6-4.1 Concentration profiles down a PBR in terms of space time $\tau' = W/v_0$. [*Note:* $\tau' = \rho_b(W/\rho_b)/v_0 = \rho_b(V/v_0) = \rho_b\tau$.]

Solving for τ'_{opt} gives

$$\tau'_{opt} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \qquad (E6\text{-}4.9)$$

$$W_{opt} = \frac{v_0}{k_1 - k_2} \ln \frac{k_1}{k_2} \qquad (E6\text{-}4.10)$$

The corresponding conversion of A at the maximum C_B is

$$X_{opt} = \frac{C_{A0} - C_A}{C_{A0}} = 1 - e^{-k_1 \tau'_{opt}}$$

Using Equation (E6-4.9) to substitute for τ'_{opt}

$$X_{\text{opt}} = 1 - \exp\left[-\ln\left(\frac{k_1}{k_2}\right)^{k_1/(k_1-k_2)}\right] = 1 - \left(\frac{k_1}{k_2}\right)^{k_1/(k_2-k_1)} \qquad \text{(E6-4.11)}$$

4. Mole Balance on C:

$$\frac{dC_C}{d\tau'} = r'_C = k_2 C_B = \frac{k_1 k_2 C_{A0}}{k_2 - k_1}[e^{-k_1\tau'} - e^{-k_2\tau'}] \qquad \text{(E6.4-12)}$$

At the entrance to the reactor, no C is present, so the boundary condition is
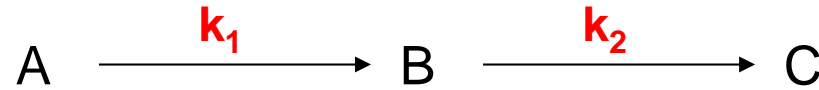
$$\tau' = 0 \quad C_C = 0$$

$$C_C = \frac{C_{A0}}{k_2 - k_1}[k_2[1 - e^{-k_1\tau'}] - k_1[1 - e^{-k_2\tau'}]] \qquad \text{(E6.4-13)}$$

Note as $t \to \infty$ then $C_C = C_{A0}$ as expected

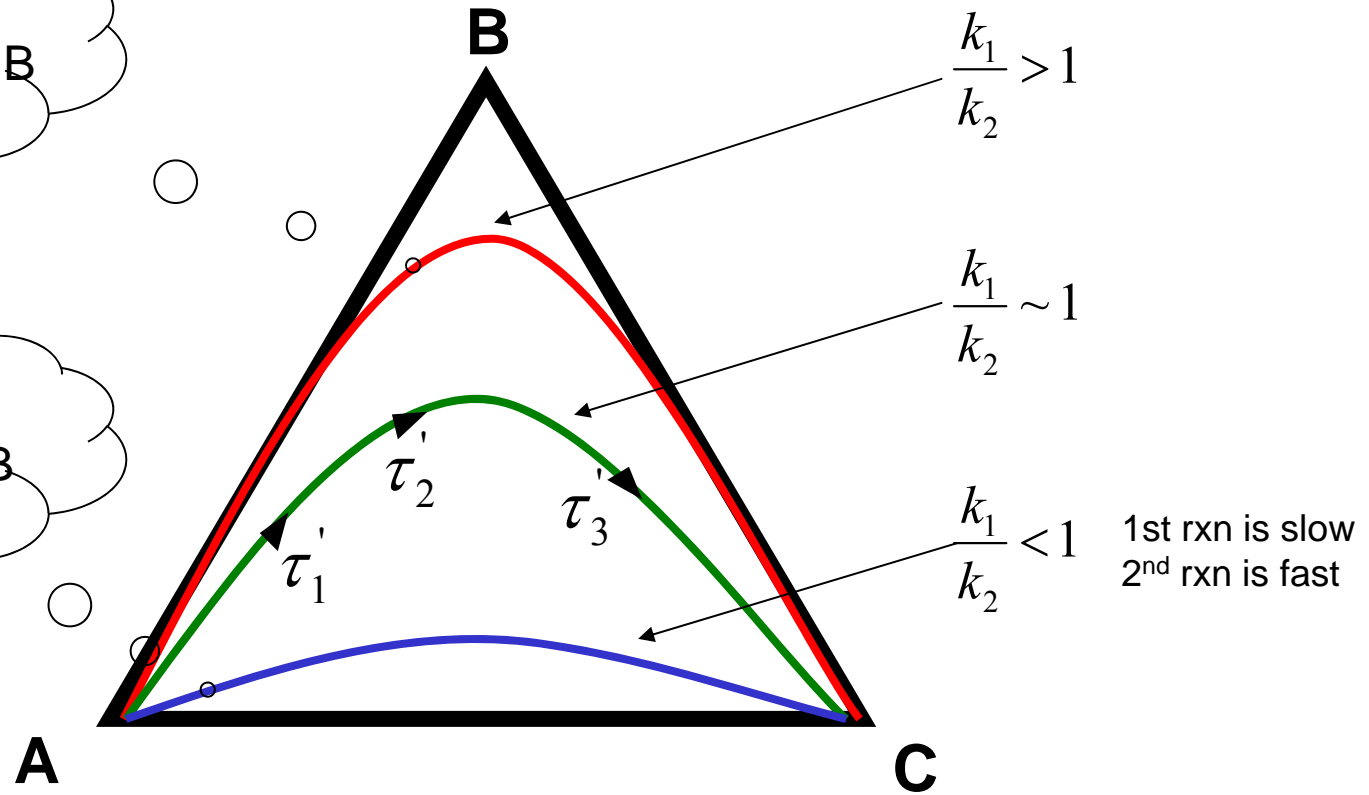We note that the concentration of C, C_C, could have also been obtained from the overall mole balance

$$C_C = C_{A0} - C_A - C_B \qquad \text{(E6.4-14)}$$

Reaction paths for different ks in series reaction

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

For $k_1/k_2>1$, a
Large quantity of B
Can be obtained

For $k_1/k_2<1$, a
Little quantity of B
Can be obtained

B

$\dfrac{k_1}{k_2}>1$

$\dfrac{k_1}{k_2}\sim 1$

$\dfrac{k_1}{k_2}<1$

1st rxn is slow
2nd rxn is fast

τ_1'

τ_2'

τ_3'

A

C

Long rxn time in batch or long tubular reactor
→ B will be converted to C

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