

# Introduction to Chemical Reactors

August 2013

## 3. Multiple Reactions

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## Objectives and sources

- Extend the models for reactor design to chemical systems of multiple reactions (in **series**, **parallel** and their **combinations**).
- Calculate the conditions for **maximum yield** and **selectivity** of a given product.
- Identify the best reactor and its operating conditions for a given objective, e.g. maximise yield.
- Schmidt: Chapter 4

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## 3.1 Introduction and basic concepts

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Multiple reactions can be in

- *series*,
- *parallel*, or
- *combination of series and parallel*.

In reactors with multiple competing reactions we are interested not only in maximising the *conversion*,  $X$ , of the desired reaction, but also the *selectivity*,  $S_J$ , and/or *yield*,  $Y_J$ , of a given product.

Unfortunately, there is generally a trade-off between  $X$  and  $S_J$  ( $Y_J$ ).

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## Motivation

Virtually all industrial/commercial processes involve systems of multiple reactions.

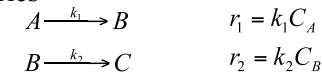
In a **single reaction system** the objective is often to **increase the reaction rate** (thus minimising the reactor volume or the residence time). This is generally achieved **by increasing the temperature** of operation.

However, in a **multiple reaction system** the problem is to create a reactor configuration to

- **maximise** the production of a **desired product**, or
- **minimise** the production of **undesired ones**.

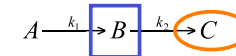
## Types of multiple reactions

### 1. Reactions in series



Main  
product

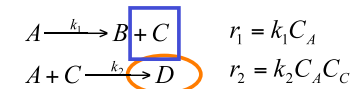
byproduct



### 2. Reactions in parallel



### 3. Complex systems of reaction: series and parallel



## Selectivity ( $S_J$ )

$$S_J = \frac{\text{moles of desired product J formed}}{\text{moles of all products formed}}$$

So, for example, for a reaction where  $A \rightarrow B$

$$S_J = \frac{N_J}{N_{A0} - N_A} = \frac{F_J}{F_{A0} - F_A} \quad \rho \text{ constant} = \frac{C_J}{C_{A0} - C_A}$$

## Yield ( $Y_J$ )

$$Y_J = \frac{\text{moles of desired product J formed}}{\text{moles of reactant fed}}$$

$$Y_J = \frac{N_J}{N_{A0}} = \frac{F_J}{F_{A0}} \quad \rho \text{ constant} = \frac{C_J}{C_{A0}}$$

... and for a reaction where  $A \rightarrow B$

$$Y_J = S_J X_A$$

Table 4.1 from Schmidt 2<sup>nd</sup> ed.

Process	Reaction	$\tau$	$P$	$T$	$X$	$S$	Catalyst
fermentation	sugar $\rightarrow$ C <sub>2</sub> H <sub>5</sub> OH + 2CO <sub>2</sub>	1 week	1 atm	35°C	100%	50%	yeast
methanol synthesis	CO + 2H <sub>2</sub> $\rightarrow$ CH <sub>3</sub> OH	1 min	50	250	90	99	Cu/ZnO
steam cracking	C <sub>2</sub> H <sub>6</sub> $\rightarrow$ C <sub>2</sub> H <sub>4</sub> + H <sub>2</sub>	1 sec	2	850	70	85	none
ethylene oxidation	C <sub>2</sub> H <sub>4</sub> + $\frac{1}{2}$ O <sub>2</sub> $\rightarrow$ C <sub>2</sub> H <sub>4</sub> O	5 sec	2	280	10	60-90	Ag
FCC reactor	C <sub>16</sub> $\rightarrow$ C <sub>8</sub> + C <sub>8</sub> <sup>+</sup>	10 sec	2	450			zeolite
FCC regenerator	C + O <sub>2</sub> $\rightarrow$ CO <sub>2</sub>	1 min	2	550	100	100	none
hydrotreating	C <sub>24</sub> + H <sub>2</sub> $\rightarrow$ 2C <sub>12</sub>	1 min	30				Co-Mo
steam reforming	CH <sub>4</sub> + H <sub>2</sub> O $\rightarrow$ CO + 3H <sub>2</sub>	1 sec	—	250		99	Ni
NH <sub>3</sub> synthesis	N <sub>2</sub> + 3H <sub>2</sub> $\rightarrow$ 2NH <sub>3</sub>	10 sec	200	250	50	100	Fe
auto catalytic converter	CO $\rightarrow$ CO <sub>2</sub> , NO $\rightarrow$ N <sub>2</sub>	0.1 sec	1	400	95		Pt-Rh-Pd
maleic anhydride	C <sub>4</sub> H <sub>10</sub> + O <sub>2</sub> $\rightarrow$ C <sub>4</sub> H <sub>4</sub> O <sub>3</sub>	10 sec	2	400			VPO
NH <sub>3</sub> oxidation	NH <sub>3</sub> + $\frac{5}{4}$ O <sub>2</sub> $\rightarrow$ NO + H <sub>2</sub> O	10 <sup>-3</sup> sec	10	900	90	90	Pt-Rh
HCN synthesis	CH <sub>4</sub> + NH <sub>3</sub> + O <sub>2</sub> $\rightarrow$ HCN	10 <sup>-3</sup> sec	2	1100	70	70	Pt-Rh
steam reforming	CH <sub>4</sub> + H <sub>2</sub> O $\rightarrow$ CO + 3H <sub>2</sub>	1 sec	—	800	90	100	Ni
cyclohexane oxidation	c-C <sub>6</sub> H <sub>12</sub> $\rightarrow$ adipic acid	1 h	1	150	5	80	Co homog.
p-xylene oxidation	xylene $\rightarrow$ terephthalic acid	20 min	1	150	80	99	
water-gas shift	CO + H <sub>2</sub> O $\rightarrow$ CO <sub>2</sub> + H <sub>2</sub>	1 sec	—	250	80	100	Cu/ZnO
autothermal reform	CH <sub>4</sub> + $\frac{1}{2}$ O <sub>2</sub> $\rightarrow$ CO + 2H <sub>2</sub>	10 <sup>-3</sup> sec	—	1000	95	95	Rh
formaldehyde	CH <sub>3</sub> OH + $\frac{1}{2}$ O <sub>2</sub> $\rightarrow$ HCHO	10 <sup>-2</sup> sec	—	400	98	98	Fe-Mo

Notes: All values are very approximate. Selectivities are based on carbon atoms in the major reactant.

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## A notation for multiple reactions

$$\sum_{j=1}^S v_{ij} A_j = 0$$

$i = 1, 2, \dots, R$  (reactions)

$j = 1, 2, \dots, S$  (species)

$v_{ij}$  = stoichiometric coefficient of species  $j$  in reaction  $i$ ; negative if  $j$  is a reactant; positive if  $j$  is a product

$$r = k \prod_{j=1}^S C_j^{m_j}$$

$m_j$  = order of the reaction with respect to the  $j^{\text{th}}$  species

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The reactor design equations derived for the single reaction case are applicable to each of the species present in the multiple reactions, so we do not have to re-derive them!

All we have to do is to account for the presence of each species in all the reactions ...

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## Summary of reactor design equations – multiple reactions

	differential form	algebraic form	integral form
Batch	$\frac{dC_j}{dt} = \sum_{i=1}^R v_{ij} r_i$		$t = -C_{j0} \int_0^X \frac{dX}{\sum_{i=1}^R v_{ij} r_i(X)}$
CSTR	$\frac{dC_j}{dt} = \frac{1}{\tau} (C_{j0} - C_j) + \sum_{i=1}^R v_{ij} r_i$	$C_{j0} - C_j = -\tau \sum_{i=1}^R v_{ij} r_i$	$V = \frac{-F_{j0} X}{\sum_{i=1}^R v_{ij} r_i}$
PFR	$\frac{dC_j}{d\tau} = \sum_{i=1}^R v_{ij} r_i$		$V = -F_{j0} \int_0^X \frac{dX}{\sum_{i=1}^R v_{ij} r_i(X)}$

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One design equation is created for each of the species present in the system.

We end up with a system of  $n$  simultaneous equations in  $n$  unknowns (the concentrations of the species as a function of time).

In some cases the yield/selectivity of a species is non-monotonic, i.e. it has a maximum value in the range of  $X = 0.0 \dots 1.0$ .

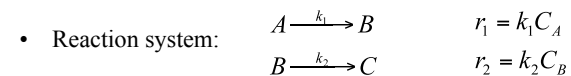
## 3.2 Multiple reactions in series

In the case of a PFR we get a system of simultaneous differential equations.

Let's solve a system of two 1<sup>st</sup> order reactions in series (the simplest case). The same method is applicable to more complicated systems, i.e. more than two reactions of any order.

### Series reactions in a PFR

$$\frac{dC_j}{d\tau} = \sum_{i=1}^R \nu_{ij} r_i$$



Mole Balances for PFR:

$$\begin{aligned} \frac{dC_A}{d\tau} &= -r_1 = -k_1 C_A \\ \frac{dC_B}{d\tau} &= r_1 - r_2 = k_1 C_A - k_2 C_B \\ \frac{dC_C}{d\tau} &= r_2 = k_2 C_B \end{aligned}$$

BCs:  $C_A = C_{A0} \quad ; \quad C_{B0} = C_{C0} = 0$

## Series reactions in a PFR (2)

Solve eqn. 1 (separable)  $\frac{dC_A}{C_A} = -k_1 d\tau \Rightarrow C_A = C_{A0} \exp[-k_1 \tau]$

Solve eqn. 2. Subst.  $C_A$  into eqn. 2;  $\frac{dC_B}{d\tau} + k_2 C_B = k_1 C_{A0} \exp[-k_1 \tau]$

not separable, use Integrating Factor  $IntFact = \exp\left[\int k_2 d\tau\right] = e^{k_2 \tau}$

and get:

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

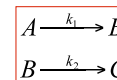
To get  $C_C$  we could substitute  $C_B$  into eqn. 3 and solve, but we notice that  $(C_{A0} - C_A) = C_B + C_C$ . Hence, solve for  $C_C$  and get:

$$C_C = C_{A0} \left[ 1 - \frac{k_2}{k_2 - k_1} \exp[-k_1 \tau] + \frac{k_1}{k_2 - k_1} \exp[-k_2 \tau] \right]$$

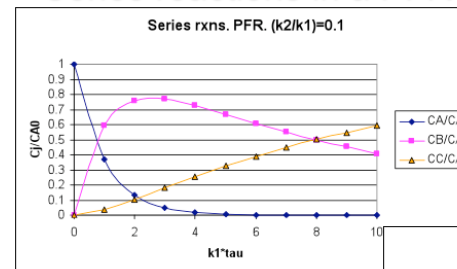
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## Series reactions in a PFR (3)

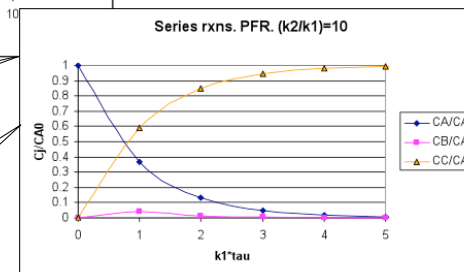


Dimensionless plot  
 $C_A/C_{A0}, C_B/C_{A0}, C_C/C_{A0}$   
vs.  
 $k_1 \tau$



They have a maximum  $C_B$

Looks like  $A \rightarrow C$



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## Maximum yield of B in PFR (series reactions)

$$Y_{B \text{ } \rho \text{ constant}} = \frac{C_B}{C_{A0}}$$

There is an optimum  $\tau$  to maximise  $C_B$

$$\frac{d}{d\tau}(C_B) = 0 = \frac{d}{d\tau} \left( C_{A0} \frac{k_1}{k_2 - k_1} (e^{-k_1 \tau} - e^{-k_2 \tau}) \right) \Rightarrow \tau_{opt} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

substitute  $\tau_{opt}$  into expression for  $C_B$  to get  $C_{B \max}$

$$C_{B \max} = C_{A0} \left( \frac{k_1}{k_2} \right)^{\frac{k_2}{k_2 - k_1}}$$

$$Y_{B \max} = \frac{C_{B \max}}{C_{A0}} = \left( \frac{k_1}{k_2} \right)^{\frac{k_2}{k_2 - k_1}}$$

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In the case of a CSTR operating at steady-state we get a system simultaneous algebraic equations.

Let's solve a system of two 1<sup>st</sup> order reactions in series (the simplest case). The same method is applicable to more complicated systems, i.e. more than two reactions of any order.

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## Series reactions in a CSTR

$$C_{j0} - C_j = -\tau \sum_{i=1}^R \nu_{ij} r_i$$

- Reaction system:  $A \xrightarrow{k_1} B$   $r_1 = k_1 C_A$   
 $B \xrightarrow{k_2} C$   $r_2 = k_2 C_B$

- Mole Balances for CSTR:
 
$$C_A - C_{A0} = -\tau(k_1 C_A)$$

$$C_B - C_{B0} = \tau(k_1 C_A - k_2 C_B)$$

$$C_C - C_{C0} = \tau(k_2 C_B)$$
- Solve:
 
$$C_A = \frac{C_{A0}}{(1 + k_1 \tau)}$$

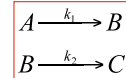
$$C_B = \frac{k_1 C_{A0} \tau}{(1 + k_1 \tau)(1 + k_2 \tau)}$$

$$C_C = \frac{k_1 k_2 C_{A0} \tau^2}{(1 + k_1 \tau)(1 + k_2 \tau)}$$

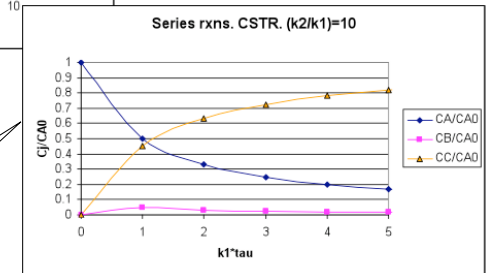
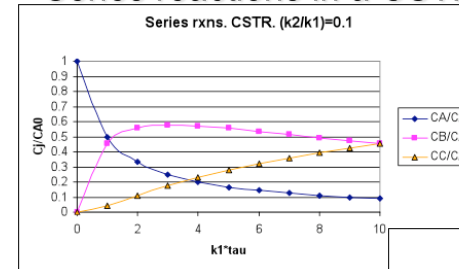
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## Series reactions in a CSTR (2)



Dimensionless plot  
 $C_A/C_{A0}, C_B/C_{A0}, C_C/C_{A0}$   
 vs.  
 $k_1 \tau$



Looks like  
 $A \rightarrow C$

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## Maximum yield of B in CSTR (series reactions)

$$Y_{B \text{ } \rho \text{ constant}} = \frac{C_B}{C_{A0}}$$

There is an optimum  $\tau$  to maximise  $C_B$

$$\frac{d}{d\tau}(C_B) = 0 = \frac{d}{d\tau} \left( \frac{k_1 C_{A0} \tau}{(1 + k_1 \tau)(1 + k_2 \tau)} \right) \Rightarrow \tau_{opt} = \frac{1}{\sqrt{k_1 k_2}}$$

substitute  $\tau_{opt}$  into expression for  $C_B$  to get  $C_{B \max}$

$$C_{B \max} = \frac{k_1 C_{A0}}{\left( k_1^{1/2} + k_2^{1/2} \right)^2}$$

$$Y_{B \max} = \frac{C_{B \max}}{C_{A0}} = \frac{k_1}{\left( k_1^{1/2} + k_2^{1/2} \right)^2}$$

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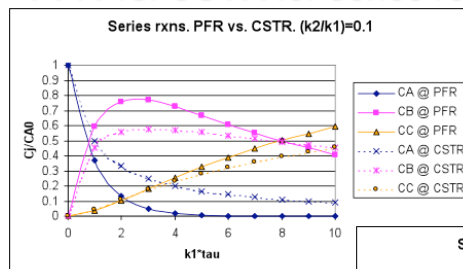
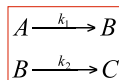
The behaviour of PFRs and CSTRs operating with multiple reactions in series is qualitatively similar.

But are PFR and CSTR identical with respect to multiple reactions?

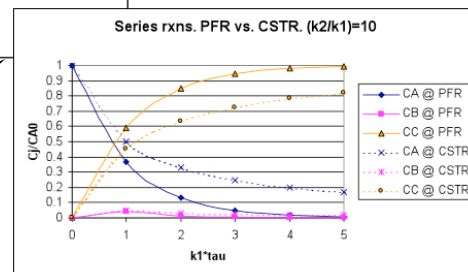
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## PFR vs. CSTR for series reactions



The PFR gives higher yield than the CSTR (for positive order reactions).



The CSTR has always B present (reacting into C), whereas in a PFR initially there is only A

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## PFR vs. CSTR for series reactions (2)

1. There is an **optimum residence time** in a continuous reactor or an **optimum reaction time** in a batch reactor to maximise yield of an intermediate.
2. The PFR will always give a higher maximum yield of an intermediate than a CSTR if all the series reactions obey positive-order kinetics.

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## 3.3 Multiple reactions in parallel

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Multiple reactions in parallel are addressed identically to reactions in series:

One design equation is created for each of the species present in the system.

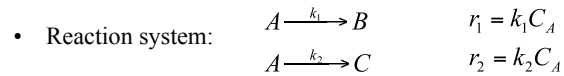
Again, we end up with a system of  $n$  simultaneous equations in  $n$  unknowns (the concentrations of the species as a function of time): PFRs result in a system of simultaneous differential equations, and steady-state CSTRs in a system of simultaneous algebraic equations.

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## Parallel reactions in a PFR

$$\frac{dC_j}{d\tau} = \sum_{i=1}^R \nu_{ij} r_i$$



- Mole Balances for PFR:

$$\frac{dC_A}{d\tau} = -r_1 - r_2 = -k_1 C_A - k_2 C_A$$

$$\frac{dC_B}{d\tau} = r_1 = k_1 C_A$$

$$\frac{dC_C}{d\tau} = r_2 = k_2 C_A$$

$$\text{BCs: } C_A = C_{A0} \quad ; \quad C_{B0} = C_{C0} = 0$$

## Parallel reactions in a PFR (2)

Solve eqn. 1 (separable)  $\frac{dC_A}{C_A} = -(k_1 + k_2) d\tau \Rightarrow C_A = C_{A0} \exp[-(k_1 + k_2)\tau]$

Solve eqn. 2: subst.  $C_A$  into eqn. 2;  $\frac{dC_B}{d\tau} = k_1 C_{A0} \exp[-(k_1 + k_2)\tau]$

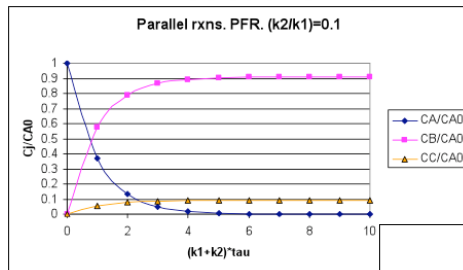
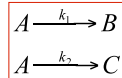
It is separable, integrate and get:  $C_B = C_{A0} \frac{k_1}{k_1 + k_2} (1 - \exp[-(k_1 + k_2)\tau])$

Similarly, eqn. 3 is separable, solve and get:

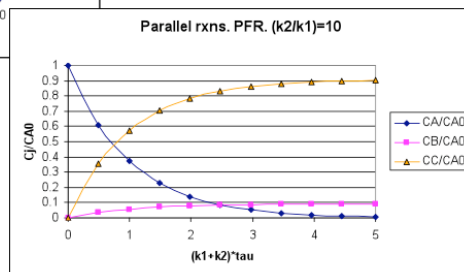
$$C_C = C_{A0} \frac{k_2}{k_1 + k_2} (1 - \exp[-(k_1 + k_2)\tau])$$

The selectivity to form B is:  $S_{B \text{ } \rho \text{ constant}} = \frac{C_B}{C_B + C_C} = \frac{k_1}{k_1 + k_2}$

## Parallel reactions in a PFR (3)



Dimensionless plot  
 $C_A/C_{A0}, C_B/C_{A0}, C_C/C_{A0}$   
vs.  
 $(k_1 + k_2) \tau$

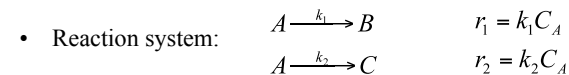


from expression  
for  $C_A(\tau)$

$$\tau = \frac{1}{(k_1 + k_2)} \ln \left( \frac{C_{A0}}{C_A} \right)$$

## Parallel reactions in a CSTR

$$C_{j0} - C_j = -\tau \sum_{i=1}^R \nu_{ij} r_i$$



- Mole Balances for CSTR:

$$C_A - C_{A0} = -\tau(k_1 + k_2)C_A$$

$$C_B - C_{B0} = \tau k_1 C_A$$

$$C_C - C_{C0} = \tau k_2 C_A$$

$$C_A = C_{A0} \quad ; \quad C_{B0} = C_{C0} = 0$$

Solve:

$$C_A = \frac{C_{A0}}{1 + (k_1 + k_2)\tau}$$

$$C_B = \frac{k_1 \tau C_{A0}}{1 + (k_1 + k_2)\tau}$$

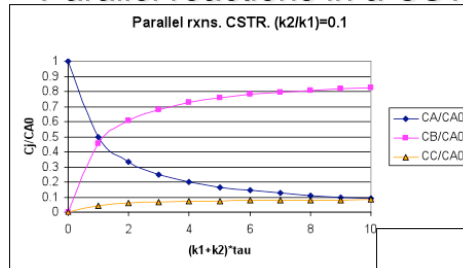
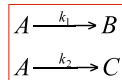
$$C_C = \frac{k_2 \tau C_{A0}}{1 + (k_1 + k_2)\tau}$$

Selectivity to form B  
identical to PFR case:

$$S_{B \text{ } \rho \text{ constant}} = \frac{C_B}{C_B + C_C} = \frac{k_1}{k_1 + k_2}$$



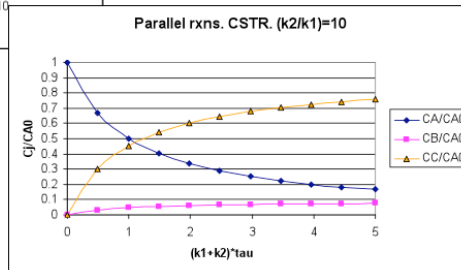
## Parallel reactions in a CSTR (2)



Dimensionless plot  
 $C_A/C_{A0}, C_B/C_{A0}, C_C/C_{A0}$   
 vs.  
 $(k_1 + k_2) \tau$

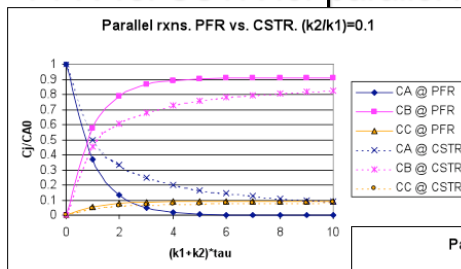
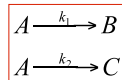
from expression  
 for  $C_A(\tau)$

$$\tau = \frac{(C_{A0} - C_A)}{C_A(k_1 + k_2)}$$



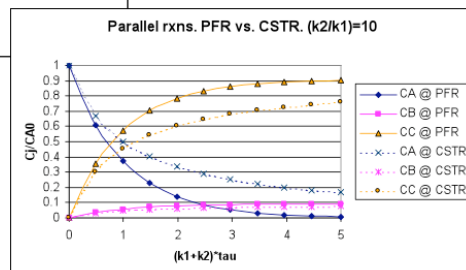
Similarly to the case of multiple reactions in series, PFRs and CSTRs are qualitatively similar but quantitatively different.

## PFR vs. CSTR for parallel reactions



For parallel, irreversible,  
 first-order reactions:

- the  $\tau$  is smaller in a PFR
- selectivity is identical



## 3.4 Instantaneous selectivity and yield

## Instantaneous (differential) selectivity and yield

An alternative definition of selectivity and yield is in terms of the **rates of formation** of the species (rather than the concentrations or molar flowrates), i.e.

$$s_J = \frac{\text{rate of formation of product J}}{\text{rate of formation of all products}} \quad y_{J/A} = \frac{\text{rate of formation of product J}}{\text{rate of depletion of reaction A}}$$

$$s_J = \frac{dC_J}{\sum_{i=1}^{prods} dC_i} \quad y_{J/A} = -\frac{dC_J}{dC_A}$$

*Note: sometimes the selectivity is defined in terms of the formation of unwanted products, rather than formation of all products.*

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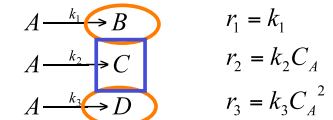
## 3.5 Reactor selection for systems of multiple reactions

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## Example: Trambouze reactions

Parallel reaction system:



Selectivity  
(instantaneous):

$$s_C = \frac{dC_C}{dC_B + dC_C + dC_D} = \frac{k_2 C_A}{k_1 + k_2 C_A + k_3 C_A^2}$$

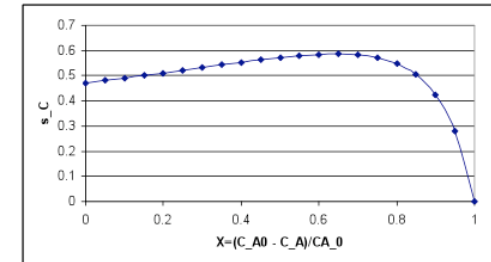
$$k_1 = 1; k_2 = 4; k_3 = 2;$$

$$C_{A0} = 2.0$$

Plotting  $s_C$  vs.  $X$   
(with  $C_A = C_{A0} [1 - X]$ )

$$\begin{aligned} s_{C,\max} @ X_{\max} &= 0.646 \\ C_{A,\max} &= 0.708 \\ s_{C,\max} &= 0.586 \end{aligned}$$

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## Choice of reactors for multiple reactions

- Series reactions
  - If an intermediate product is desired: there is an optimum  $\tau$  for  $Y_{\max}$ .  
PFR gives higher  $Y_{\max}$  if reactions have positive order,  
CSTR gives higher  $Y_{\max}$  if reactions have negative order
  - If a final product is desired:  
PFR requires shorter time and produces less intermediates (for +ve order)
- Parallel reactions
  - Reactions with same order: PFR and CSTR give equal Selectivity
- Series-parallel reactions
  - Solve mass balance equations!

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## Summary

For systems of multiple reactions we must solve  $R$  simultaneous mass balance equations.

### Series reactions

- There is:
  - an optimum residence time in a continuous reactor or
  - an optimum reaction time in a batch reactorto maximise yield of an intermediate.
- The PFR will always give a higher maximum yield of an intermediate for positive-order kinetics.

### Parallel reactions

- $\tau$  is smaller in a PFR, selectivity is identical in PFR and CSTR.