Multiple Reactions

- We have largely considered single reactions so far in this class.
- How many industrially important processes involve a single reaction?
- The job of a chemical engineer is therefore to design...
Multiple Reactions

- We need to develop tools that will allow us to quantify how well (or how poorly) we are doing at producing a desired product.

- There are three concepts that we need to develop for multiple reactions:
  - Conversion (similar to single reactions)
    - $X_j =$
  - Selectivity
    - $S_j =$
  - Yield
    - $Y_j =$
Multiple Reactions

So far, we have exclusively looked at simple systems with only one reaction occurring. However, many reaction systems of practical relevance involve multiple reactions occurring at the same time, either in parallel or in series (i.e. sequentially).

Let’s look at steam cracking of ethane (~ 80 billion tons/a world production!):

\[
\begin{align*}
C_2H_6 & \rightarrow C_2H_4 + H_2 & \text{(I) ethene (ethylene) formation} \\
C_2H_6 & \rightarrow C_2H_2 + 2 H_2 & \text{(II) acetylene formation} \\
C_2H_4 & \rightarrow C_2H_2 + H_2 & \text{(III) acetylene formation from ethylene} \\
C_2H_6 + H_2 & \rightarrow 2 CH_4 & \text{(IV) methane formation} \\
3 C_2H_6 & \rightarrow C_6H_6 + 6 H_2 & \text{(V) benzene formation} \\
C_2H_6 & \rightarrow 2 C(s) + 3 H_2 & \text{(VI) coke formation} \\
C_2H_2 & \rightarrow 2 C(s) + H_2 & \text{(VII) coke formation (explosion!)} \\
C(s) + H_2O & \rightarrow CO + H_2 & \text{(VIII) coke gasification}
\end{align*}
\]

We distinguish between parallel reactions and series reactions.
Conversion, Selectivity, Yield

Simple example: \( A \rightarrow B; \ A \rightarrow C \)

Conversion: \( X_j = \)

Selectivity: \( S_B = \)

or: \( S_B = \)

Yield: \( Y_B = X_A \cdot S_B \)

Production rate: \( F_B = Y_B F_A 0 \)  
(and similar for \( C \))

Typically, **selectivity** is the crucial quantity!

(caveat: note the formulation with mol numbers, not concentrations! → Why?!)  
(preferred form!)

(remark: you must be sure that you know all products!)

Why?
Selectivity: Complications...

Selectivity:

\[ S_B = \frac{N_B - N_{B,0}}{v_B} \cdot \frac{v_A}{N_A - N_{A,0}} \]

Definition ambiguous if product formed from more than one reactant!

Example: Andrussov process (HCN synthesis)

(1)

(2)

(3)

Conversions of methane and ammonia can be very different. Extent to which reaction proceeds via (2) or (3) rather than (1) will be different. Hence:

\[ S_{\text{HCN,CH}_4} \neq S_{\text{HCN,NH}_3} \]

Selectivity needs a reference point!
$S_i$: even more problems...

Selectivity:

$S_B = \frac{n_{C_2H_6}}{n_{C_2H_6} + n_{CO_2}}$

What if I don't know the reaction equations (hence no $\nu_i$)?

(Of Often the case for very complex reactant mixtures, networks of many parallel and series reactions!)

(Simplified) Example: Methane Coupling

$2 \text{CH}_4 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O} \quad (1)$

$\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \quad (2)$

Assume equal amounts of methane react along (1) & (2):

$1 \text{ mol CH}_4 \rightarrow 0.25 \text{ mol C}_2\text{H}_6 + 0.5 \text{ mol CO}_2.$

If we did not know the reaction equations

we might be tempted to calculate: $S_{C} = \frac{n_{C}}{n_{C} + n_{CO_2}} = 0.25 / 0.75 = \frac{1}{3}$.

But we reacted equal amounts of CH$_4$ along both pathways: shouldn't $S_{C} = 0.5$ ?!

“atom selectivity”:

$S_{j,i} = \frac{n_{j,i}}{n_{j,i} + n_{j,i+1}}$
"differential" selectivity:
\[ S'_B = \frac{dN_B}{dN_A} \cdot \frac{v_A}{v_B} \]
Also called "instantaneous" selectivity in batch reactors...

...or "local" selectivity in (plug) flow reactors:
\[ S'_B = \]

And for once we can also use concentrations!
\[ S'_B = \frac{dN_B}{dN_A} \cdot \frac{v_A}{v_B} = \]

( Why ?? )
Selectivity: Parallel Reactions

Let's look at a reactant, which can form a desired product D, and an undesired side-product U in parallel reactions.

Two problems:
- “repair” of low S generally not possible
- undesired side-product usually needs to be separated
Parallel Reactions: Selectivity II

\[ r_D = k_D C_A^d = k_{0,D} \exp\left\{\frac{-E_D}{RT}\right\} C_A^d \]

\[ r_U = k_U C_A^u = k_{0,U} \exp\left\{\frac{-E_U}{RT}\right\} C_A^u \]

Differential Selectivity:

\[ S' = v_D \frac{r_D}{(v_D r_D + v_U r_U)} \]

\[ (S')^{-1} = 1 + \frac{v_U r_U}{v_D r_D} \]

\[ (S')^{-1} \sim \frac{v_D}{v_U} \frac{r_U}{r_D} = \frac{v_{DU}}{v_{OD}} \frac{k_{0U}}{k_{0D}} \exp\left\{-\frac{(E_U - E_D)}{RT}\right\} C_A^{(u-d)} \]

\[ S' \sim \exp\left\{-\frac{(E_D - E_U)}{RT}\right\} C_A^{(d-u)} \]

(I) \ d > u \quad S' \ increases \ with \quad \rightarrow \quad \text{PFR (BR) > CSTR}

\quad \text{no dilution}

\quad \text{high pressure}

(II) \ d < u \quad S' \ increases \ with \quad \rightarrow \quad \text{CSTR}

\quad \text{or PFR w/high recycle}

\quad \text{dilution}

\quad \text{low pressure}

(III) \ E_D < E_U \quad S' \ decreases \ with

(IV) \ E_D > E_U \quad S' \ increases \ with
Differential and Total S

Parallel reactions, different rctn orders

\[ A \xrightarrow{k_1} D \quad r_1 = k_1 C_A^d \]
\[ A \xrightarrow{k_2} U \quad r_2 = k_2 C_A^u \]

(Reactor) Selectivity:
\[ S_D = \]

Local selectivity:
\[ S_D' = \]

Hence we calculate \( N_D \):
\[ N_D = \]

(or equivalently with \( F_j \))

\[ S_D = \frac{F_B}{F_{A0} - F_{Ae}} = -\frac{1}{F_{A0} - F_{Ae}} \int_{F_{A0}}^{F_{Ae}} S_D' \, dF_A \]

For \( \dot{V} = \text{const.} \)
\[ S_D = -\frac{1}{C_{A0} - C_{Ae}} \int_{C_{A0}}^{C_{Ae}} S_D' \, dC_A \]

**total S = integral average of local S**
PFR vs CSTR

\[ S_D' = \frac{1}{C_{A0} - C_{Ae}} \int_{C_{A0}}^{C_{ Ae}} S_D' \, dC_A \]

**Why?**

If reaction order of desired reaction > reaction order of side reaction, PFR better, otherwise CSTR better.
Parallel Reaction Networks

More interesting case:
Network of many parallel reactions, some with higher r.o., some with lower r.o. than desired reaction

Optimum yield for CSTR first, followed by PFR

(Exact shape of $S' - C_A$ curve, and hence also precise sizing of reactors is dependent on specific network!)
Conversion in Multireaction Systems

Let's again consider the simple parallel reaction system:

\[ A \rightarrow B, \quad r_1 = k_1 C_A \]
\[ A \rightarrow C, \quad r_2 = k_2 C_A \]

How can we express the concentrations \( C_A, C_B, C_C \) in terms of \( X_A \)?

We can't - at least not directly! We have to distinguish between \( X_{A,1} \) and \( X_{A,2} \)!

While we still can define \( X_A = (N_{A_0} - N_A)/N_{A_0} \), we have to distinguish between the different pathways to do our 'book-keeping' (i.e. mass balances) for \( B \) and \( C \):

\[ B: \quad C_B = C_{A_0} X_{A,1} \]
\[ C: \quad C_C = C_{A_0} X_{A,2} \]
\[ A: \quad C_A = \]

but also:

\[ C_A = \]

Everything else remains unchanged - we now simply have one more quantity to keep track of, i.e. the different \( X_{ji} \)!
Series Reactions: Selectivity

Very common: partial vs total oxidation reactions

(April) all oxidation reactions follow a sequence of successively “deeper” oxidation.

Example: Ethane oxidation

\[
\begin{align*}
C_2H_6 + \frac{1}{2} O_2 & \rightarrow C_2H_4 + H_2O \quad \text{(oxidative dehydrogenation)} \\
C_2H_4 + O_2 & \rightarrow 2 \text{CO} + 2 \text{H}_2 \quad \text{(syngas formation)} \\
\text{CO} + \text{H}_2 + O_2 & \rightarrow \text{CO}_2 + H_2O \quad \text{(combustion)}
\end{align*}
\]

Let’s assume a PFR for A \(\rightarrow\) B \(\rightarrow\) C, with 1st order kinetics:

\[
\begin{align*}
r_A &= \quad, \quad r_B &=
\end{align*}
\]

Plugging this into the PFR design equation, we get:

\[
\begin{align*}
C_A(\tau) &= \quad, \quad C_B(\tau) = \\
C_C(\tau) &= \quad
\end{align*}
\]

Check the derivation in the textbook (p. 160ff)!
You should be able to derive this yourself.

So, what does this look like?
Series Reactions: CSTR

What about the same series reaction in a CSTR?

(Same procedure: rate laws into design equation, substitute $C_{B0}$ and $C_{C0}$ by expressions in terms of $C_{A0}$)

\[
C_A = \frac{C_{A0}}{1} \quad C_B = \frac{C_{A0} k_1 \tau}{1} \quad C_C = \frac{C_{A0} k_1 k_2 \tau^2}{1}
\]

So, what does this look like?
How is it different from a PFR?

- For series reactions, there is always an optimum residence time to achieve a maximum yield towards the intermediate product.
- For positive order kinetics, the optimum yield in the PFR is always greater than that in a CSTR.

How can we rationalize this?
How about the BR?
Maximum in $C_B$  -> optimum in residence time!

How can I calculate the optimum? Look for $dC_B/d\tau = 0$!

**PFR:**
(log mean rate constant)$^{-1}$

**CSTR:**
(geometric mean rate constant)$^{-1}$

What if $C$ and not $B$ is the desired product?
Example:

We wish to produce a product B from a reactant A in a PFR with $V = 4 \text{ l/min}$ and $C_{A0} = 2 \text{ mol/l}$. However, another reaction is also occurring, forming an undesired product C. (Both reactions are irreversible, 1st order, with $k_B = 0.5 \text{ min}^{-1}$ and $k_C = 0.1 \text{ min}^{-1}$).

(a) Assuming a series reaction $A \rightarrow B \rightarrow C$, calculate the maximum achievable yield of B, as well as the necessary reactor volume.

(b) Assuming parallel reactions $A \rightarrow B$ and $A \rightarrow C$, calculate the reactor volume necessary to achieve the same conversion of A as in (a). What is the yield of B in this case?

Procedure:

(a) Calculate $\tau_{opt}$, from there $C_B(\tau_{opt})$ and $C_A(\tau_{opt})$. From these you obtain $S_{B,max}$ and $X_{A,max}$.

(b) Calculate $\tau(X_A=0.865)$, from there: $V = 13.36 \text{ l}$. With $\tau$ from the equation for $C_B$ in a PFR/series reactions...

Check it in LDS, examples 4-2 and 4-3, incl. the CSTR case!