ChE 344
Reaction Engineering and Design

Lecture 6: Tuesday, January 25, 2022

Isothermal Reactor Design

Reading for today's Lecture: Chapter 5.1-5.4

Reading for Lecture 7: Chapter 5.1-5.4

Homework #2 due Friday 11:59pm

Lecture 6: Isothermal reactor design
Related Text: Chapter 5.1-5.4

The order we will solve problems:

0. Assumptions
1. Mole Balance: Reactor design equation for the selected reactors
2. Rate Law: To get reaction rate as a function of rate constant and concentrations
3. Stoichiometry: To get concentration as a function of conversion
4. Combine: Parts 1-3
5. Evaluate: Use values to get numerical answer

Concept of pseudo-orders:

If a concentration does not change significantly with conversion then we can in some cases approximate it as constant. For example if B is in large excess compared to A such that C_B remains constant with conversion (here for liquid reaction).

$$-r_A = kC_B C_A \approx kC_{B0}C_A = kC_{B0}C_{A0}(1-X) = k'C_{A0}(1-X)$$

where $k' \equiv kC_{B0}$. k' is a pseudo-first order rate constant here.

Recall space time:

$$\frac{V}{v_0} = \tau$$

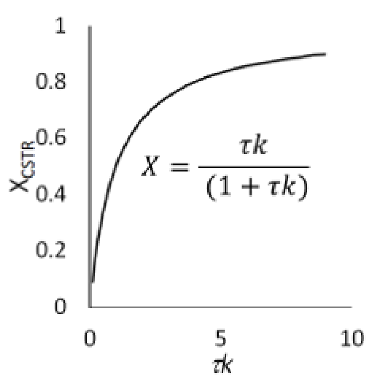
For first order (or pseudo first-order) reactions we get out a term that is called the Damköhler number, or Da_1, which is the ratio of the reaction rate to convection rate).

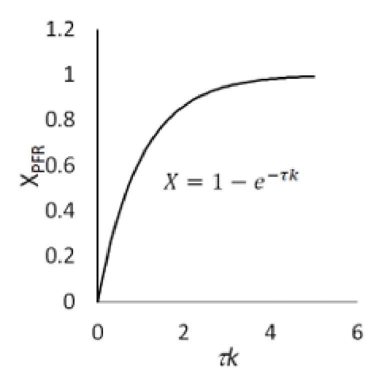
$$Da_1 = k\tau$$

This shows up in the solution for the first order PFR and CSTR:

$$X_{CSTR} = \frac{\tau k}{(1+\tau k)}$$

$$X_{PFR} = 1 - e^{-\tau k}$$





Review on rate laws:

If we know we have an elementary reaction:

$$aA + bB \rightarrow cC + dD$$

$r_j = \nu_j r$ where r is the rate of reaction (per 'mol rxn'). Thus:

Stoich here needed even if not elementary

ν_j is stoichiometric coefficient of *j*

b/c elementary as written

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} = r = kC_A^a C_B^b$$

You could of course re-write this reaction as:

$$\frac{a}{a}A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

or

$$\frac{a}{b}A + \frac{b}{b}B \rightarrow \frac{c}{b}C + \frac{d}{b}D$$

But this won't change the rate law.

Last few lectures, stoichiometry to relate conc. of different species to conversion of the limiting reactant (here it is ‘A’).

$$\overset{1}{\cancel{\frac{a}{a}}}A+\frac{b}{a}B\rightarrow\frac{c}{a}C+\frac{d}{a}D$$

$$\delta=\frac{d}{a}+\frac{c}{a}-\frac{b}{a}-\frac{a}{a}=\frac{d+c-b-a}{a}$$

The denominator is why δ changes with lim. reactant/ definition of X

<u>Batch</u>

$C_j = N_j/V$

<u>Flow</u>

$C_j = F_j/v$

For all cases, N_j and F_j of reactants/products change with X. For gas-phase, where V or *v* is not constant, volume will change if $\delta \neq 0$. Recall $\varepsilon = y_{A0}\,\delta$, so for gas phase if volume is changing:

plus

Product

$$C_C=C_{A0}\frac{\theta_C+\frac{c}{a}X}{1+\varepsilon X}\frac{T_0}{T}\frac{P}{P_0}$$

Discuss with your neighbors:

What is C_B as a function of conversion of A for the following isothermal, reversible, gas-phase reaction in a constant volume batch reactor for a stoichiometric feed?

$$\delta = \frac{c-b-a}{a}$$

b/c 'A' lim reactant

$$4A + B \underset{k_r}{\overset{k_f}{\rightleftarrows}} 3C$$

If elementary rate law

$$\frac{-r_A}{4} = \frac{-r_B}{1} = \frac{r_C}{3} = r = kC_A^4 C_B^1$$

A) $C_B = C_{A0}\frac{\frac{1}{4}-\frac{1}{4}X}{1-\frac{2}{5}X}$

B) $C_B = C_{A0}\frac{4-4X}{1-\frac{5}{2}X}$

C) $C_B = C_{A0}\left(\frac{1}{4}-\frac{1}{4}X\right)$

D) $C_B = 4C_{A0}(1-X)$

Reversible won't affect it.

Even though $\delta = \frac{3}{4} - \frac{1}{4} - 1 = -\frac{1}{2}$, constant V

$$\varepsilon = \frac{4}{5}\left(-\frac{1}{2}\right) = -2/5$$

Stoichiometric means θ_B=1/4

b/a = 1/4

y_{A0} = 4/5 (not needed since const. V)

We will do an example today of making acetic acid from water and acetic anhydride. At one point we did this in ChE 460 at UM (when I was an undergrad).

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$
$$A \quad + B \quad \rightarrow 2C$$

This is an example of a hydrolysis reaction (water addition). Hydrolysis is important for biology (breaking down carbs), making soap, or breaking down cellulose/hemicellulose.

Then, we will look at a gas-phase reaction in a plug flow reactor (if there is time).

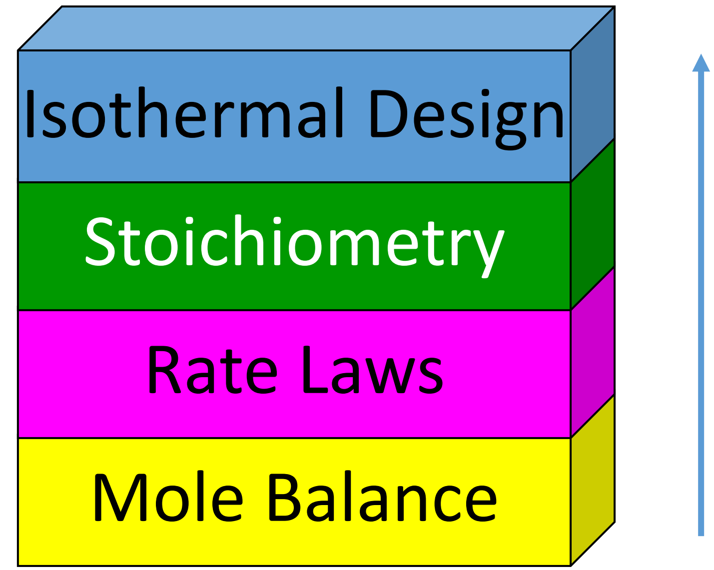
We will put together our building blocks to be able to size isothermal reactors for this and other reactions

Combine to size reactors or get X

C_j is a function of X

r_A is a function of conc./temp

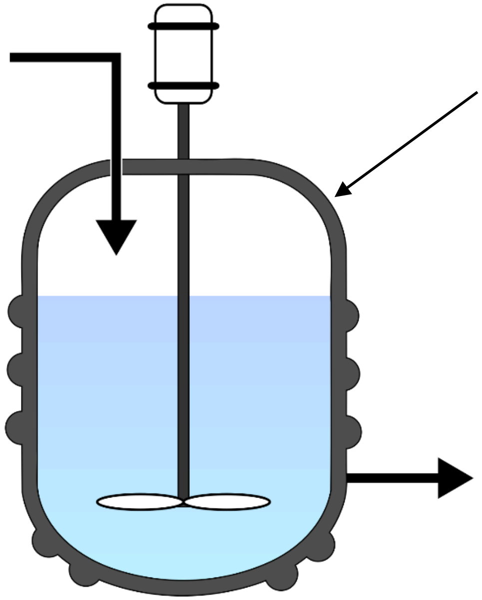
Design equations and conversion



The order we will solve problems: (algorithm)

0. Assumptions
1. Mole balance
2. Rate Law
3. Stoichiometry
4. Combine
5. Evaluate

Reminder on V for reactors. For a liquid phase reaction, usually this is the volume of the liquid where the reaction is occurring (not necessarily the same as the container itself).



So when we are sizing a liquid CSTR, we mean what volume of the physical reactor is needed if it is filled up. (i.e., going from a 10 L to 20 L CSTR wouldn't change things if you still only have 10 L of liquid inside)

Unless we state otherwise, you can assume these are the same (i.e., a 10 L CSTR means V = 10 L, 20 L CSTR means V = 20 L, etc.).

What about for gases?

"Gases fill the volume of whatever container they're in, school."

Liquid phase hydrolysis of acetic anhydride in a CSTR.

The volumetric flow rate in is 3.3×10^{-3} L/s.

The inlet flow is 1 M acetic anhydride (7.8 v%), 51.2 M water (92.2 v%).

The reaction is elementary with k of 1.95×10^{-4} L/(mol s)

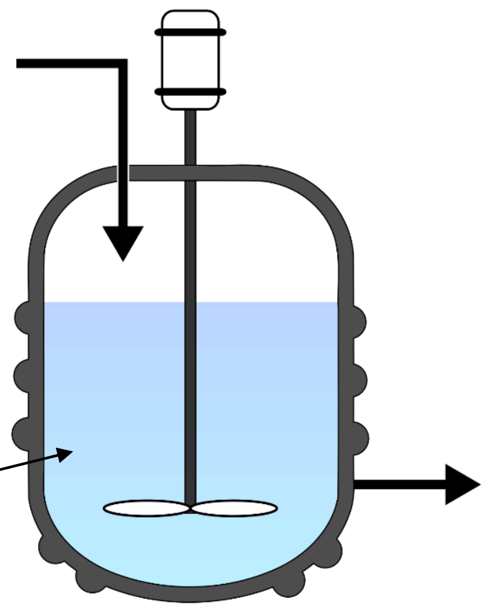
1 L liquid isothermal continuous stirred tank reactor (CSTR).

$$A + B \rightarrow 2C$$

$C_{A0} = 1$ M

$C_{B0} = 51.2$ M

$v_0 = 3.3 \times 10^{-3}$ L/s



V = 1 L of liquid

Question:

What is X (of acetic anhydride)?

0. <u>Assumptions</u>

Isothermal so $T = T_0$, liquid so $v = v_0$

We are assuming $C_{C0} = 0$ (no acetic acid in the inlet stream)

1. <u>Mole balance</u>

CSTR mole balance (conversion is wrt limiting reactant "A")

$$V = \frac{F_{A0}X}{-r_A}$$

2. <u>Rate law</u>

Functions of conversion

$$-r_A = kC_BC_A$$

3. <u>Stoichiometry</u>

Symbol	In	Change	Out
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	$F_{B0} = \theta_B F_{A0}$	$-F_{A0}X$	$F_B = F_{A0}(\theta_B - X)$
C	0	$+2F_{A0}X$	$F_C = F_{A0}(2X)$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X)$$

$$C_B = \frac{F_B}{v} = \frac{F_{A0}(\theta_B - X)}{v_0} = C_{A0}(\theta_B - X)$$

$$\theta_B = \frac{51.2\ M}{1\ M} = 51.2$$

Remember the conversion X is at most going to be 1. Since 51.2 is fairly large compared to 1, we can approximate:

$$C_B = C_{A0}(\theta_B - X) \approx C_{A0}(\theta_B) = C_{B0}$$

Large excess of B (don't just assume this if it is slightly excess)

4. <u>Combine</u>

$$-r_A = kC_BC_A \approx kC_{B0}C_A = \underbrace{kC_{B0}}_{\text{Pseudo-first order rate constant}}C_{A0}(1-X)$$

$$k' \equiv kC_{B0} = \left(1.95 \times 10^{-4}\,\frac{L}{mol\ s}\right)(51.2\ M) = 0.01\ s^{-1}$$

We call this a pseudo-first order rate constant because our reaction appears to be first order (only in A). It has the same units as a first order rate constant (inverse time)

$$-r_A \approx k'C_A = k'C_{A0}(1-X)$$

4. Continue combining with mole balance

$$V = \frac{F_{A0}X}{-r_A} = \frac{F_{A0}X}{k'C_{A0}(1-X)} = \frac{v_0\cancel{C_{A0}}X}{k'\cancel{C_{A0}}(1-X)}$$

$$\frac{V}{v_0}k' = \frac{X}{(1-X)}$$

Recall: Space time ($\tau = \frac{V}{v_0}$)

$$\tau k' = \frac{X}{(1-X)}$$

$$\tau k'(1-X) = X$$

$$\tau k'(1) = X(1+\tau k')$$

$$X = \frac{\tau k'}{(1+\tau k')}$$

5. <u>Evaluate</u>: Plugging in your values for space time and the pseudo-first order constant:

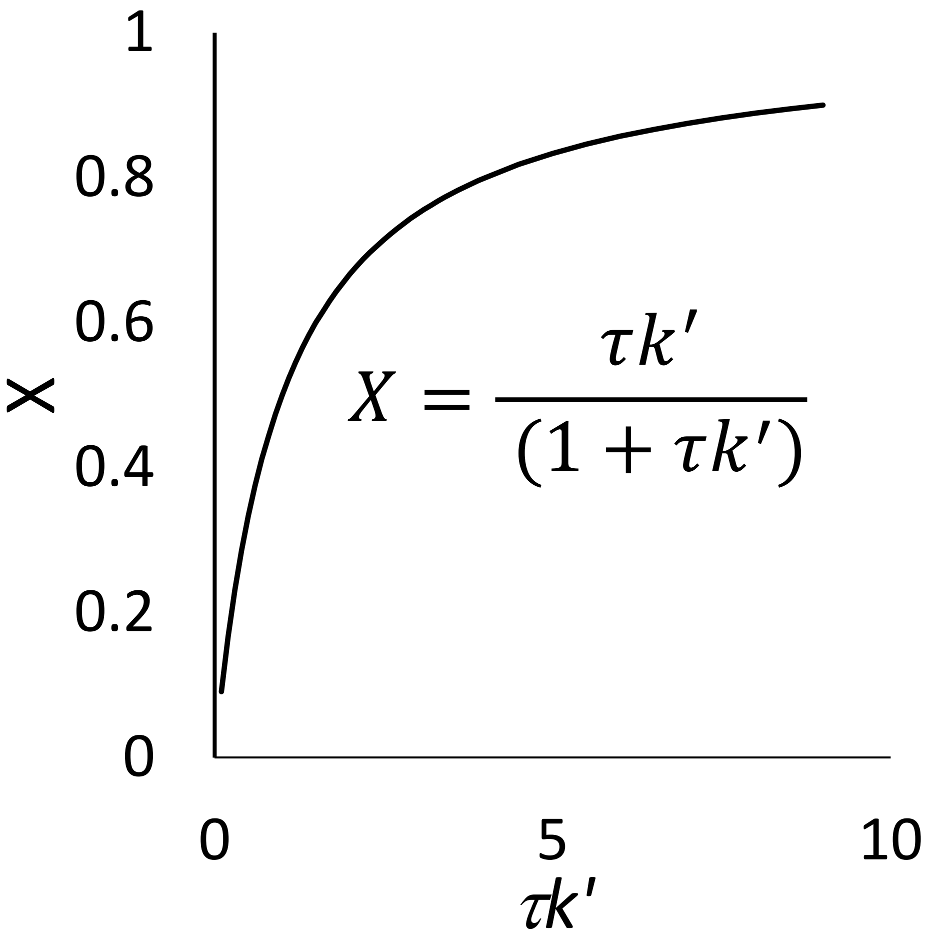
$$\frac{V}{v_0}k' = \frac{1L}{3.3\times 10^{-3}L\, s^{-1}}0.01s^{-1} = 3.03 = \tau k'$$

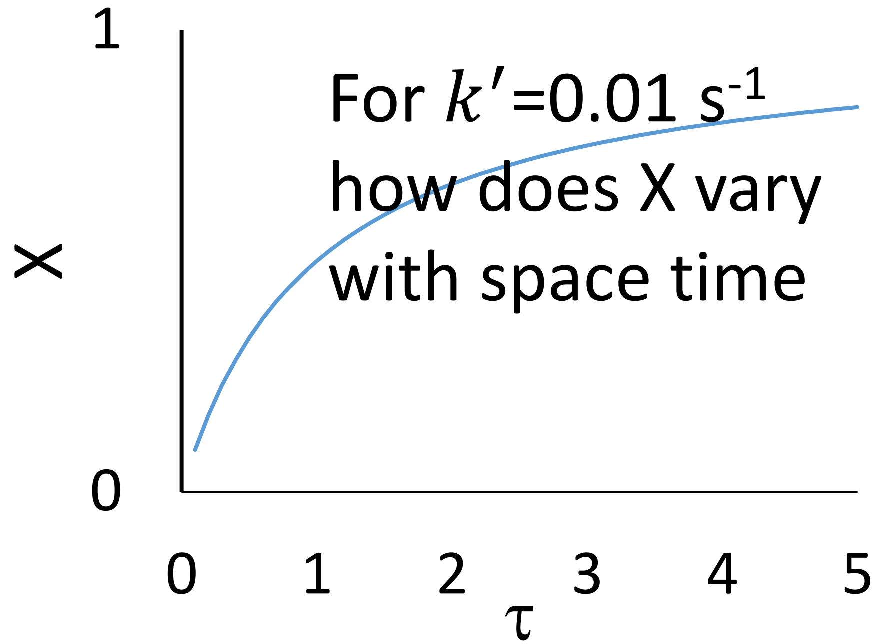
$$X = \frac{3.03}{(1+3.03)} = 0.75$$

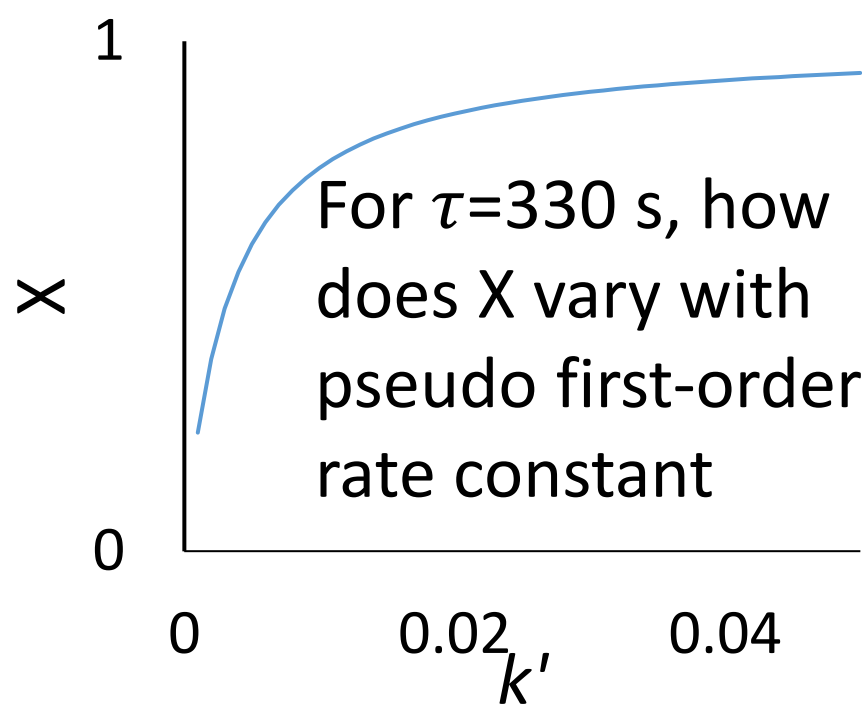
If we didn't make the assumption $C_B = C_{B0}$, we would have gotten essentially the same X (but more complicated math).

The term $\tau k'$ or τk where k or k' is first order is called the Damköhler number (Da_1 = reaction rate/convection rate)

How does conversion vary with Da$_1$? τ? k'?

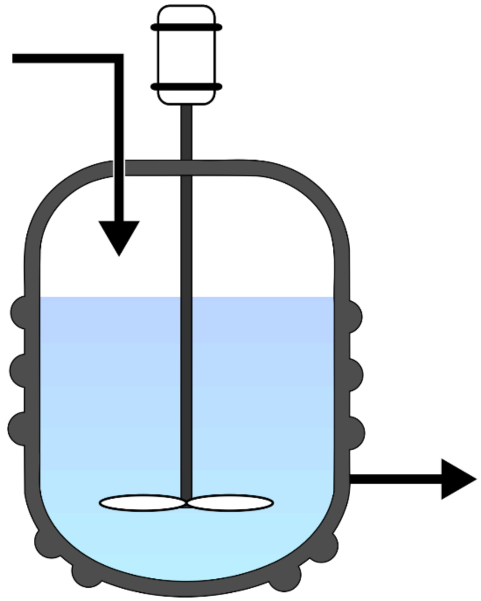






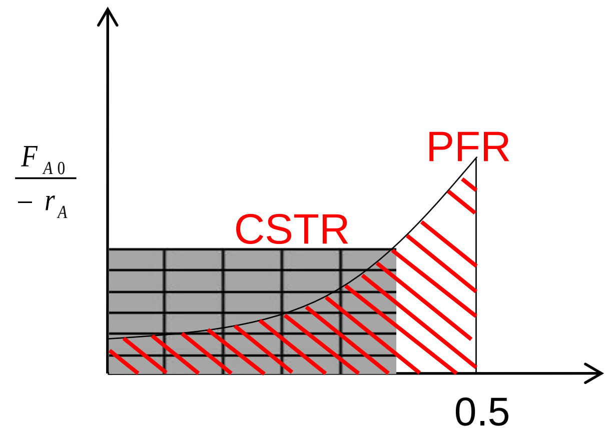
If we run this same pseudo-first order reaction in a PFR instead of a CSTR, if the volume is the same (1 L), which conversion would be higher, exiting the PFR or exiting the CSTR?

C_{A0} = 1 M
C_{B0} = 51.2 M
v_0 = 3.3 x 10^{-3} L/s



V_{CSTR} = 1 L

X_{CSTR} = 0.75



A + B → 2C

PFR higher X for positive order (with same V)

C_{A0} = 1 M
C_{B0} = 51.2 M
v_0 = 3.3 x 10^{-3} L/s

V_{PFR} = 1 L

X_{PFR}?

Now, the same liquid-phase reaction but in a plug flow reactor (PFR) instead of a CSTR.
The volumetric flow rate in and concentrations are the same.
The reaction rate constant is the same.

$$A + B \rightarrow 2C$$

C_{A0} = 1 M
C_{B0} = 51.2 M
$v_0 = 3.3 \times 10^{-3}$ L/s

What is X_{PFR}?

V_{PFR} is 1 L

0. Assumptions

Same as before, except now an ideal PFR
Isothermal so $T = T_0$, liquid so $v = v_0$
We are assuming $C_{C0} = 0$ (no acetic acid in the inlet stream)

1. Mole balance

PFR mole balance (conversion is wrt limiting reactant "A")

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

2. Rate law

$$-r_A = kC_BC_A \approx k'C_A$$

3. Stoichiometry (remember, still liquid)

Species	In	Change	Out
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	$F_{B0} = \theta_B F_{A0}$	$-F_{A0}X$	$F_B = F_{A0}(\theta_B - X)$
C	0	$+2F_{A0}X$	$F_C = F_{A0}(2X)$

$$C_A = C_{A0}(1 - X) \qquad C_B \approx C_{B0}$$

4. Combine: Mole balance, rate law, stoichiometry

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \qquad -r_A \approx k'C_A \qquad C_A = C_{A0}(1-X)$$

$$\frac{dX}{dV} = \frac{k'C_{A0}(1-X)}{F_{A0}} = \frac{k'\,(1-X)}{v_0}$$

$$\frac{dX}{(1-X)} = \frac{k'}{v_0}dV \longrightarrow \int_0^{X_{PFR}} \frac{dX}{(1-X)} = \frac{k'}{v_0}\int_0^{V_{PFR}} dV$$

$$\ln\left(\frac{1}{1-X_{PFR}}\right) = \frac{k'V_{PFR}}{v_0} = \tau k' \qquad X_{PFR} = 1 - e^{-\tau k'}$$

$$-\ln(1-X_{PFR}) = \ln\left(\frac{1}{1-X_{PFR}}\right)$$

5. Evaluate: (same space time as CSTR if $V_{PFR} = V_{CSTR}$)

$$\tau k' = 3.03 \qquad X_{PFR} = 1 - e^{-3.03} = 0.95$$

$X_{CSTR} = 0.75$

Discuss with your neighbors:

We just saw that even though the PFR had the same volume and inlet volumetric flow rate as the CSTR, it resulted in higher conversion than in the CSTR.

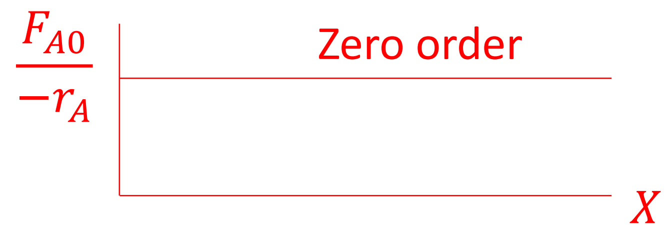
If the reaction was **zero** order in both A and B, and the CSTR conversion in a 1 L reactor was 50%, what would the conversion for a 1 L PFR be? Assume isothermal, isobaric.

A) $X = 50\%$

B) $63.3\% > X > 50\%$

C) $X > 63.3\%$

D) $X < 50\%$



Zero order the PFR vs. CSTR will give the same conversion.

If it is pseudo-zero order (i.e., the concentration drops slightly, but can estimate as negligible), then the conversion in the PFR would be *slightly* higher than 50%.

Now lets solve a gas-phase elementary reaction

(k = 0.15 s^{-1} M^{-1}). Here, isothermal, isobaric.

$$2NOCl \rightarrow 2NO + Cl_2$$

$$2A \rightarrow 2B + C$$

Pure NOCl

C_{A0} = 0.2 M

v_0 = 10 L/s

What does V_{PFR} need to be to get 90% conversion?

1. Mole balance

PFR mole balance (conversion is wrt limiting reactant "A")

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

2. Rate law

$$-\frac{r_A}{2} = \frac{r_B}{2} = r_C = kC_A^2$$

3. Stoichiometry

A → B + ½ C

Species	In	Change	Out
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	0	$+F_{A0}X$	$F_B = F_{A0}(X)$
C	0	$+½F_{A0}X$	$F_C = F_{A0}(½X)$

$$v = v_0(1+\varepsilon X)\frac{\cancel{T}}{\cancel{T_0}}\frac{\cancel{P_0}}{\cancel{P}}$$

Isothermal, isobaric, gas-phase

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$$

4. <u>Combine</u>: Mole balance, rate law, stoichiometry

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \qquad -\frac{r_A}{2} = kC_A^2 \qquad C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$$

$$\frac{dX}{dV} = \frac{2kC_{A0}^2(1-X)^2}{F_{A0}(1+\varepsilon X)^2} = \frac{2kC_{A0}(1-X)^2}{v_0(1+\varepsilon X)^2}$$

$$\frac{(1+\varepsilon X)^2}{(1-X)^2}dX = \frac{2kC_{A0}}{v_0}dV \rightarrow \int_0^X \frac{(1+\varepsilon X)^2}{(1-X)^2}dX = \frac{2kC_{A0}}{v_0}\int_0^V dV$$

$$\int_0^X \frac{(1+\varepsilon X)^2}{(1-X)^2}dX =$$

$$2\varepsilon(1+\varepsilon)\ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2}{1-X}X \quad = 2C_{A0}k\tau$$

5. <u>Evaluate</u> V to achieve 90% conversion

C_{A0} = 0.2 M

v_0 = 10 L/s

k = 0.15 s^{-1} M^{-1}

X = 0.9

$$\delta = \frac{1}{2} + 1 - 1 = \frac{1}{2}$$

y_{A0} = 1 (pure A in)

$$\varepsilon = y_{A0}\delta = \frac{1}{2}$$

$$2\varepsilon(1+\varepsilon)\ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2}{1-X}X = 2kC_{A0}\tau$$

$$1(1.5)\ln(1-0.9) + \frac{1}{4}(0.9) + \frac{(1.5)^2}{1-0.9}(0.9) = 2kC_{A0}\tau$$

$$17.02 = 2kC_{A0}\tau$$

$$\tau = 283.7\ seconds$$

$$V = \tau v_0 = (283.7\ s)\left(10\,\frac{L}{s}\right) = 2837\ L$$