ChE 344
Reaction Engineering and Design

Lecture 7: Thursday, Jan 27, 2022

Isothermal reactor design-Multiple reactors

Reading for today's Lecture: Chapter 5.1-5.4

Homework #2 due tomorrow 11:59pm

HW#3 will be posted today, due next Friday

Reading for Lecture 8: Chapter 5.5

Lecture 7: Isothermal reactor design – Reactors in series
Related Text: Chapter 5.1-5.4

For reactors in series with only one reaction we will use the same design equations we were introduced to when we discussed Levenspiel plots (see Lecture 2). However, now we will need to solve the equations rather than having a generated Levenspiel plot already.

We will define the conversion based on the feed to the first reactor (this is the way we were defining it for Levenspiel plots).

$$X = \frac{moles\ A\ reacted\ at\ a\ point\ along\ the\ reactor\ series}{moles\ A\ fed\ to\ the\ initial\ reactor}$$

For a CSTR when we can solve with X (single reaction, etc.):

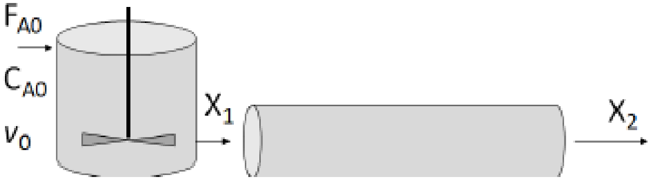
$$V = \frac{F_{A0}(X_{out} - X_{in})}{(-r_A)_{out}}$$

For a PFR when we can solve with X:

$$V = \int_{X_{in}}^{X_{out}} \frac{F_{A0}\,dX}{-r_A}$$

You could also redefine the conversion for each reactor, then at the end determine the overall conversion (not recommended, but technically can also be correct).

Example: CSTR first, followed by a PFR.



Solving for X_1 for the CSTR. Here $X_{in,CSTR} = 0$ and $X_{out,CSTR} = X_1$.

$$V_{CSTR} = \frac{F_{A0}(X_{out} - X_{in})}{(-r_A)_{out}} = \frac{F_{A0}(X_1)}{(-r_A)_{at\ X_1}}$$

Use this mole balance, rate law, and stoichiometry to solve for X_1. Recall for CSTR that $-r_A$ is evaluated at the conversion at the outlet (X_1) since the reactor is well-mixed.

Next, solving for the PFR. Here $X_{in,PFR} = X_1$ and $X_{out,PFR} = X_2$.

$$V = \int_{X_{in}}^{X_{out}} \frac{F_{A0}\,dX}{-r_A} = \int_{X_1}^{X_2} \frac{F_{A0}\,dX}{-r_A}$$

For the PFR r_A is a function of the conversion, which is changing through the reactor, but we are looking for X_2.

Last lecture, using our algorithm to design reactors.

The order we will solve problems:

0. Assumptions
1. Mole balance: Reactor design eqn. in terms of conversion
2. Rate Law: Rate in terms of rate constant, concentrations
3. Stoichiometry: Conc. in terms of conversion
4. Combine: Combine parts 1-3
5. Evaluate: Plug in values to get the answer

Professor Fogler sometimes called this the ‘French menu’ analogy. The analogy is essentially because you are picking from different options.

For example: For your appetizer (mole balance) you can pick from a CSTR, PFR, PBR, or batch reactor. Later we will add some more reactors (semi-batch, membrane reactor) but we have a more selective menu now.

We went through an example of hydrolysis (water addition chemical reaction, liquid phase)

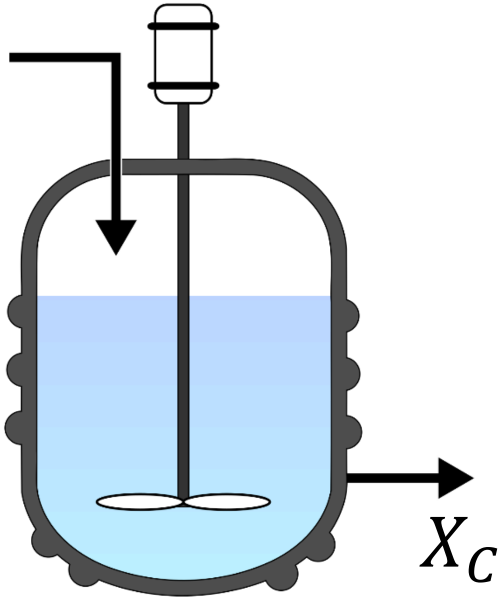
$$\mathrm{A} + \mathrm{B} \rightarrow 2\mathrm{C}$$

Pseudo-first order

$$k' \equiv k C_{B0}$$

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

<u>CSTR</u>



<u>PFR</u>

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

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

$\tau k'$ is also called the Damköhler number. If it is larger, more conversion (either larger k or larger time spent in reactor)

Discuss with your neighbors:

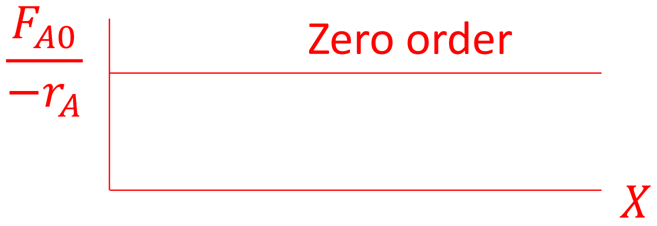
We just saw that even though the PFR had the same volume and inlet volumetric flow rate as the CSTR, it resulted in higher conversion than in the CSTR.
If the reaction was **zero** order in both A and B, and the CSTR conversion in a 1 L reactor was 50%, what would the conversion for a 1 L PFR be? Assume 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	$+\frac{1}{2}F_{A0}X$	$F_C = F_{A0}(\frac{1}{2}X)$

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

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. Combine: 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. Evaluate 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)

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

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

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

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

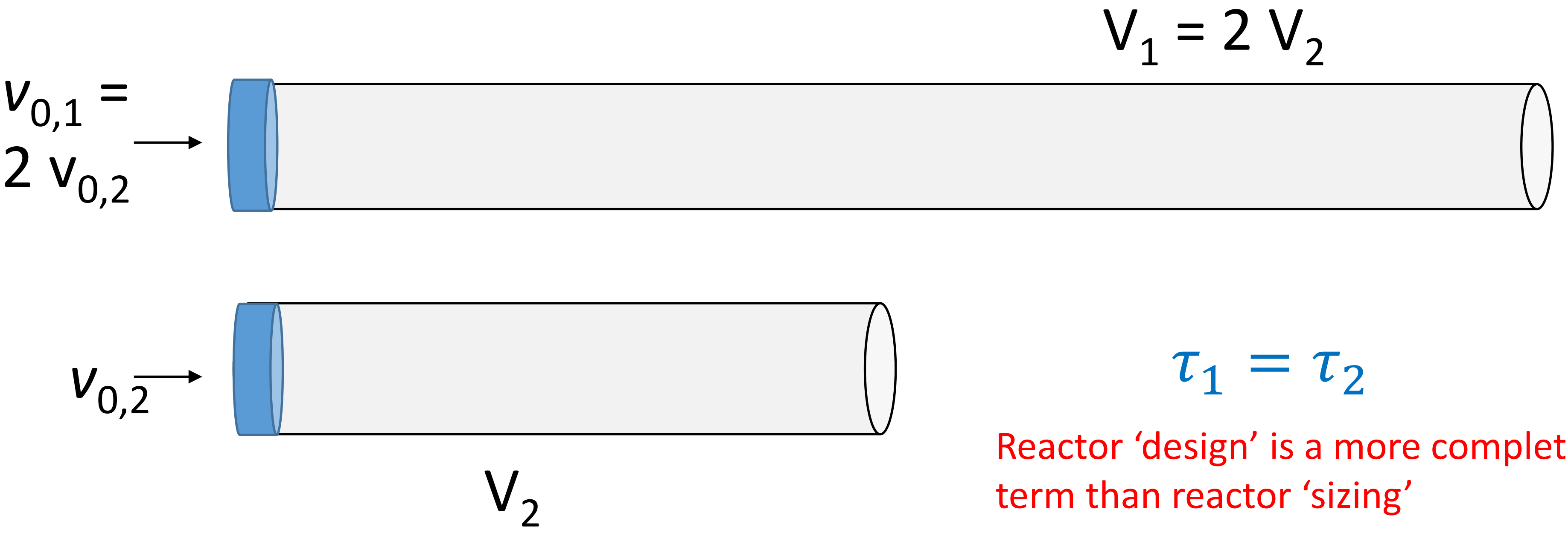
$$\tau = 283.7\ seconds$$

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

Time spent in the reactor (space time).

We've used it for CSTRs and PFRs, both steady state reactors.

For a PFR it is simple to visualize, it is how long it takes the plug to go through the reactor.



$$\tau_1 = \tau_2$$

Reactor 'design' is a more complete term than reactor 'sizing'

For a CSTR, space time is more difficult to visualize, because it is well mixed.

Before we start on new things today, I want to show another analogy you may have noticed, as an aside:

<u>Batch design equation</u>

$$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$$

<u>Plug flow reactor design eqn.</u>

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

$$\frac{dX}{d\tau}\frac{d\tau}{dV} = \frac{dX}{d\tau}\frac{d(V/v_0)}{dV} = \frac{dX}{d\tau}\frac{1}{v_0}$$

$$\frac{dX}{d\tau}\frac{1}{v_0} = \frac{-r_A}{F_{A0}} = \frac{-r_A}{C_{A0}}\frac{1}{v_0}$$

For constant V:

$$\frac{dX}{dt} = \frac{-r_A}{C_{A0}}$$

$$\frac{dX}{d\tau} = \frac{-r_A}{C_{A0}}$$

This is the analogy between time in a batch reactor and space time in a PFR. Basically each plug is a little batch reactor that spends some amount of time in the PFR. (if $v = v_0$)

Putting together our building blocks to be able to size more and more complex combinations of reactors.

Previously, we had a Levenspiel plot and could look at areas under the curve (PFR) or of rectangles of X and $F_{A0}/-r_A$ (CSTR) to size our reactors. But now we want to analytically/numerically find solutions given a rate law.

Where would we use this? If…

- No space to hold a single large enough reactor
- Already have a certain size reactor available
- Want to be able to detect whether the reaction is proceeding correctly at a given point in the conversion
- Want to partially do a reaction, and then separate the products and reactants, or heat/cool the outlet, and continue with the remaining reactants to ‘beat’ equilibrium.

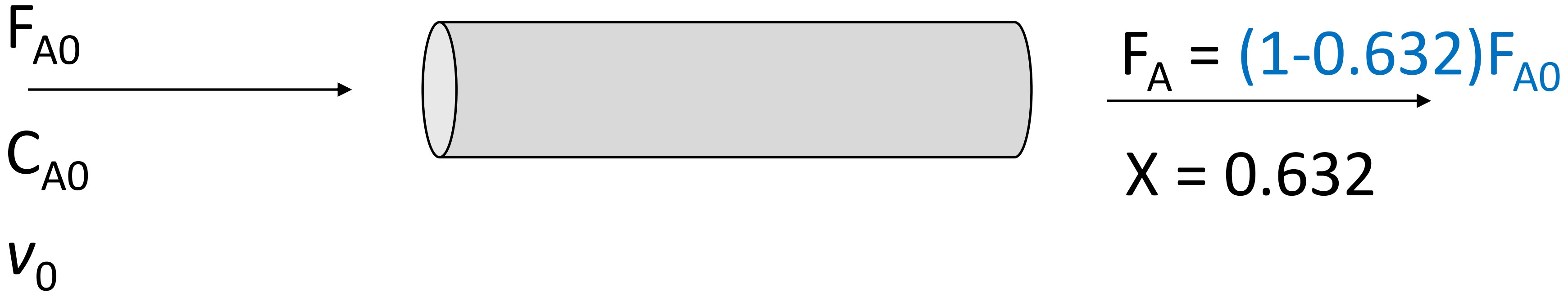
CSTR and PFR in series

We have the elementary gas-phase reaction:

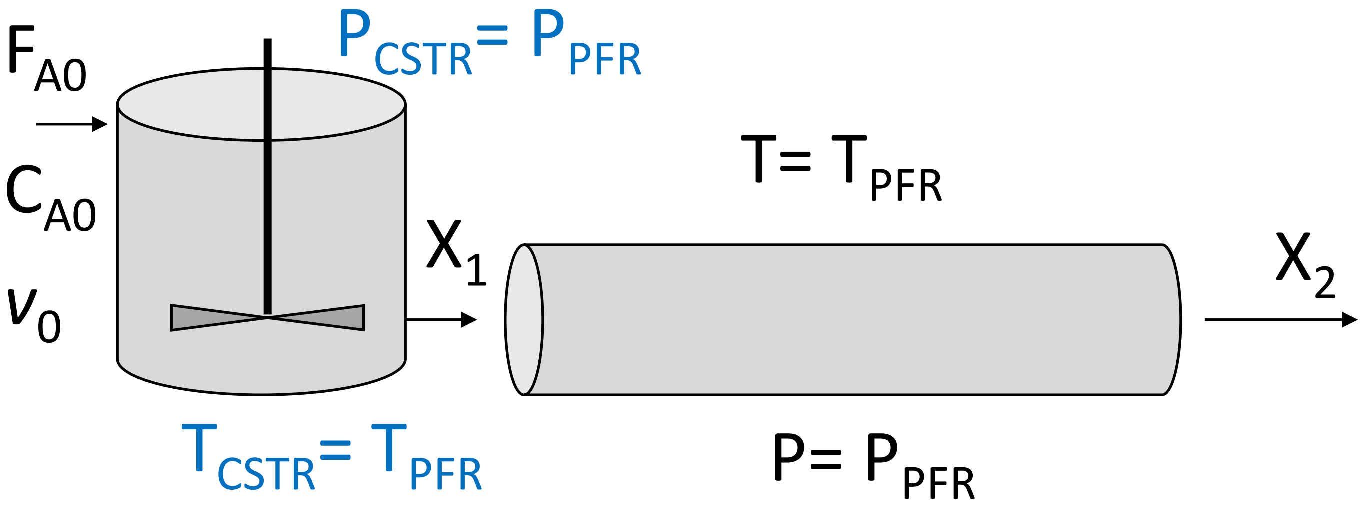
$$A \rightarrow B$$

We have been told it is elementary by someone that has done some studies of the reaction rate beforehand, and we are confident that they have done everything properly. We will learn how we can do that ourselves later in class.

One of our colleagues has been running this reaction before in a PFR, under isothermal and isobaric conditions, and achieves 63.2% conversion with a pure feed of A.



The reactor plant manager wants to put a CSTR upstream of the PFR. They know the CSTR is equal volume to the existing PFR. The same pure feed of A would go into the CSTR.



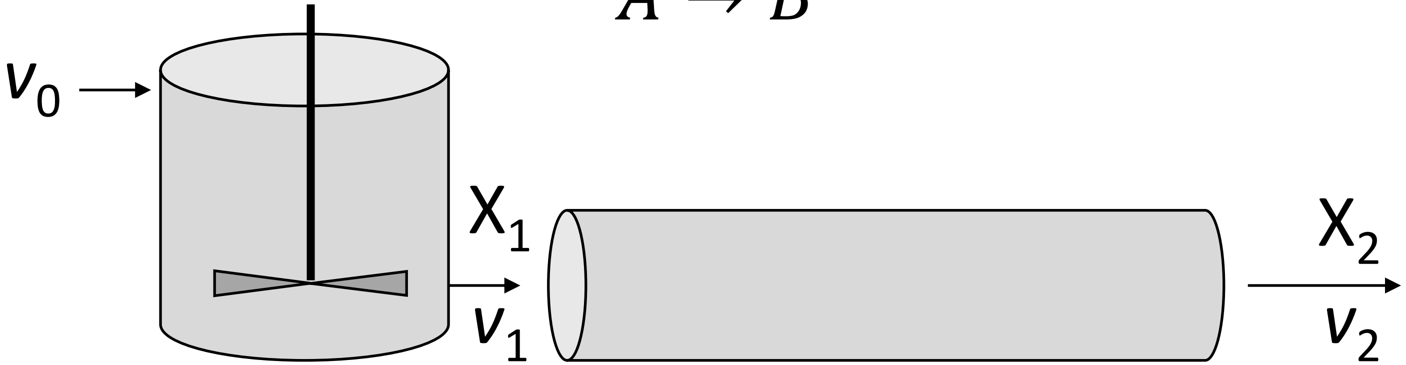
Our task is to find what is the intermediate conversion from the CSTR (X_1) and what is the exit conversion from the PFR (X_2), based on the feed to the first reactor.

We're going to start by looking at the information we have about the PFR by itself. But first…

Discuss with your neighbors:

For our gas-phase reaction in isothermal and isobaric reactors with $P_{PFR} = P_{CSTR}$ and $T_{PFR} = T_{CSTR}$:

$$A \rightarrow B$$



[✓ A) $v_2 = v_1 = v_0$]

B) $v_2 > v_1 = v_0$

C) $v_2 < v_1 = v_0$

D) $v_2 > v_1 > v_0$

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

$\delta = 0$! Also, isothermal and isobaric for entire system. If reactor T, P were different, this would not be the case b/c of ideal gas law (even if they were both isothermal and isobaric)

This should look somewhat familiar…

F_{A0}

C_{A0}

$v_0 = F_{A0}/C_{A0}$

$A \rightarrow B$

X = 0.632

The PFR design equation/mole balance is:

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

The rate law for this reaction is:

$$-r_A = kC_A$$

The stoichiometry for this reaction tells us:

$$C_A = C_{A0}(1 - X)$$

Combine the equations:

$$\frac{dX}{dV} = \frac{kC_A}{F_{A0}} = \frac{kC_{A0}(1 - X)}{F_{A0}} = \frac{k}{v_0}(1 - X)$$

Rearrange so we can integrate:

$$\frac{dX}{(1-X)} = \frac{k}{v_0} dV$$

$$\int_0^X \frac{dX}{(1-X)} = \int_0^V \frac{k}{v_0} dV$$

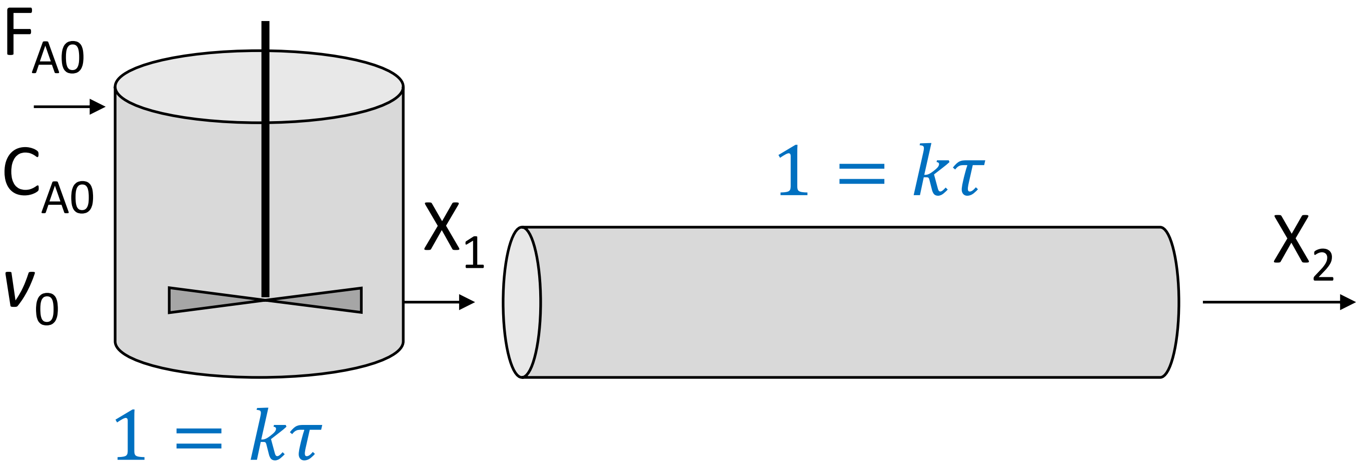
$$\ln \frac{1}{(1-X)} = \frac{k}{v_0} V$$

Remember what V/v_0 is also called? Space time! Evaluate it

$$\ln \frac{1}{(1-0.632)} = 1 = k\tau$$

We can apply this $k\tau$ to the CSTR and PFR in series.

Let’s start with the CSTR and solve for X_1.



The **CSTR** design equation/mole balance is:

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

The rate law for this reaction is:

$$-r_A = kC_A$$

The stoichiometry for this reaction tells us:

$$C_A = C_{A0}(1 - X)$$

Combine

$$V = \frac{F_{A0}X}{-r_A} = \frac{F_{A0}X}{kC_A} = \frac{F_{A0}X}{kC_{A0}(1-X)}$$

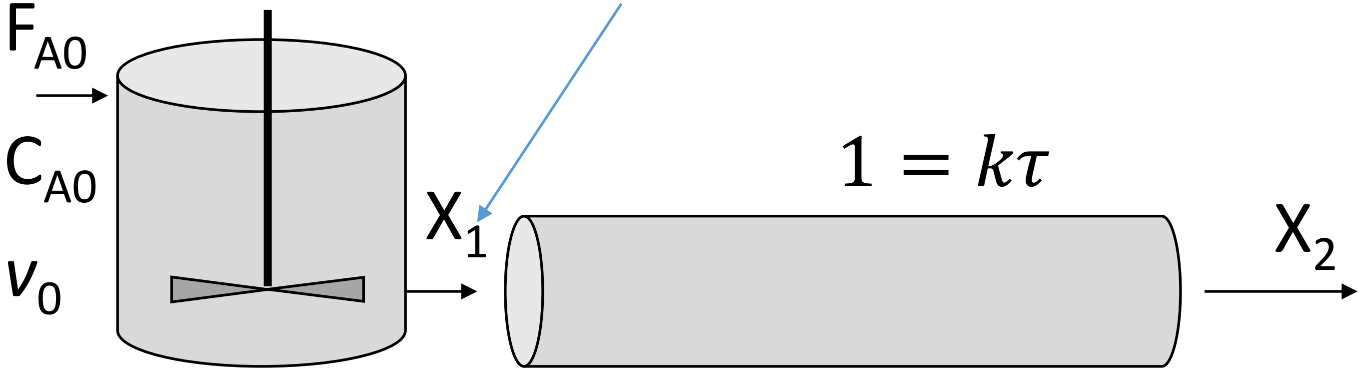
$$V = \frac{v_0 X}{k\,(1-X)}$$

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

$1 = k\tau$, we said

$V_{CSTR} = V_{PFR}$

$$X_1 = 0.5$$



$1 = k\tau$

Now solve for PFR. We can use (almost) the same equation as before!

$$\int_{X_1}^{X_2} \frac{dX}{(1-X)} = \int_0^{V_{PFR}} \frac{k}{v_0} dV$$

X out of CSTR → X_1

$$\int_{0.5}^{X_2} \frac{dX}{(1-X)} = k\tau_{PFR}$$

$$\ln\frac{1}{(1-X_2)} - \ln\frac{1}{(1-0.5)} = 1$$

$$\ln\frac{1}{(1-X_2)} - 0.693 = 1$$

$$\frac{1}{(1-X_2)} = \exp(1.693\ )$$

$$X_2 = 0.816$$

Discuss with your neighbors:

We have a pure gas phase stream of A at a volumetric flow rate of v_0 = 5 L/min and F_{A0} of 0.1 mol/min. The stream enters a PFR and undergoes the reaction $A \rightarrow bB$ at 400 K.

If we add a diluent (inert) to the inlet flow stream such that F_{I0} = 0.1 mol/min, F_{A0} is still 0.1 mol/min, v_0 is still 5 L/min, would it affect $C_A(X)$? Assume ideal gases, isobaric reactor operation, and isothermal.

A) Yes, always

B) No, never

[✓ C) It would only affect C_A if $b \neq 1$]

D) It would affect C_A if b = 1

$$C_{A0} = \frac{F_{A0}}{v_0}$$

$$C_A = C_{A0}\frac{1-X}{1+\varepsilon X}\frac{T_0}{T}\frac{P}{P_0}$$

$$\varepsilon = y_{A0}\delta$$

$$\delta = 0 \text{ iff } b = 1$$

$$y_{A0} = \frac{F_{A0}}{F_{T0}}$$

y_{A0} = 1 (case 1)

y_{A0} = ½ (case 2)

What do industrial reactors actually look like?

For example, your ethylene ICP. If you are making huge quantities of ethylene in a PFR, would you just have one very long or large diameter tube?

Probably not, but if you know τ for the X you want, you could use many smaller diameter pipes in parallel as the ‘reactor’.

Each tube/pipe is a reactor

V_{PFR} is the cross sectional area (A_{CS}) * z (distance/length). So we could calculate the length needed for the set of reactors if for example we want to use 20 7” diameter pipes.

Many reactions are catalytic (>90%) and particularly using heterogeneous catalysts,* and so often packed bed reactors are used (behave like PFRs for the most part).

PBR (aka fixed bed) with pressure drop next lecture.

- Ammonia synthesis
- Sulfuric acid synthesis
- Hydrocarbon (HC) cracking
- CO, NO_x, HC oxidation (3-way cat. converter)
- Steam reforming (make H_2)
- Desulfurization of natural gas (remove H_2S)

*Different phase of catalyst and reactant/product

Catalytic converter