ChE 344
Reaction Engineering and Design

Lecture 15: Tuesday, Mar 8, 2022

Non-isothermal reactor design: Reactor staging,

Heat exchange

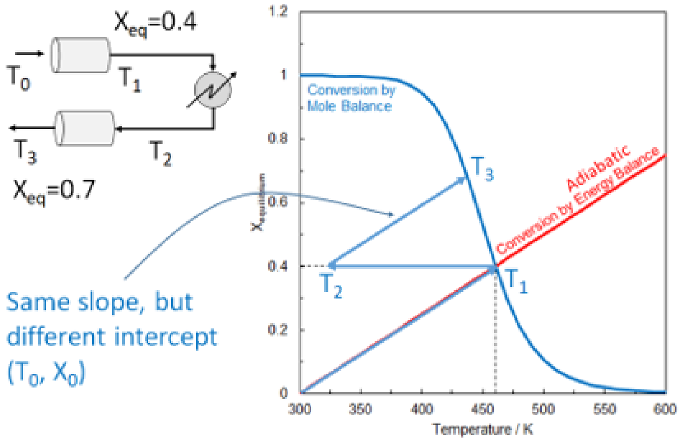
Reading for today’s Lecture: Chapter 11.6, 12.1

Reading for Lecture 16 : Chapter 12.1, 12.2, 12.4

Lecture 15: Non-isothermal Reactor Design
Related Text: Chapter 11.6, 12.1

Interstage heat exchangers

For an exothermic reaction, $A \rightleftarrows B$ we can view the equilibrium conversion vs. the conversion from the adiabatic energy balance. The intercept (T1) is the maximum conversion you can achieve in a single adiabatic reactor. However, by cooling the reactants/products, you can get a higher conversion in a second reactor.



For a heat exchanger coupled with a reactor (PFR)

From PFR energy balance

$$\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - Ua(T - T_a)}{\sum F_i C_{P,i}} = \frac{r_A \Delta H_{rxn} - Ua(T - T_a)}{F_{A0}\left[\sum \theta_i C_{P,i} + \Delta C_P X\right]} = \frac{Q_g - Q_r}{\sum F_i C_{P,i}}$$

T_a is the temperature of the heat exchanger fluid at volume V.

Q_g is the heat 'generated' by the reaction, and Q_r is the heat 'removed' by the heat exchanger (positive if $T > T_a$, negative if $T < T_a$).

U is the heat transfer coefficient with units of J/m^2·s·K

a is the shape factor, or heat transfer area divided by unit reactor volume.

From PFR mole balance

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

Can solve this coupled set of equations for PFR design.

Progress in expanding our reactor repertoire

For Midterm 1, **isothermal** CSTRs, PFRs/PBRs, batch reactors, isobaric flow with a single reaction.

Isobaric flow reactors:

$$P = P_0 \quad \text{or more rigorously} \quad \frac{dP}{dV} = 0 \qquad \frac{dP}{dW} = 0$$

Then we introduced **pressure drop** for packed bed reactors which we modeled using the Ergun equation (for gases here).

$$\frac{dp}{dW} = -\frac{\alpha}{2}\frac{1}{p}\frac{T}{T_0}\frac{F_T}{F_{T0}}$$

We needed to solve a coupled set of equations when adding the Ergun equation because this pressure drop influenced our volumes for gases, and thus concentrations.

Next we added to our menu a new set of reactors

Semi-batch (Lecture 9) and **membrane reactors** (Lecture 10)

We also added the concept of using **experimental data to determine rate laws** (Lecture 11) and **multiple reactions** (Lecture 12).

The most recent step was to study the effect if the reactors are not isothermal (Lecture 13-14)

Isothermal reactors:

$T = T_0$ or more rigorously $\dfrac{dT}{dV} = 0$

Many of the reactions that are run in reality may be exothermic or endothermic, which we know can change the temperature of the reactants/products.

For our **adiabatic reactors** from the energy balance, assuming

- No heat in/out
- No shaft work
- Steady state

$$X_{adiabatic} = \frac{\sum \theta_i C_{P,i}[T - T_0]}{-\left[\Delta H_{rxn}\left(T_{ref}\right) + \Delta C_P\left(T - T_{ref}\right)\right]}$$

Note on ΔH_{rxn}: In derivation, X is of limiting reactant, so we wrote reaction as:

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

$$\nu_A = -1$$

$$\nu_C = +c/a$$

$$\sum \nu_i H_i = \Delta H_{rxn}$$

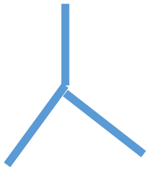
Then we can solve this along with the mole balance equation if we know something about the

- rate law (e.g., $r = kC_A^{\alpha}$)
- rate law parameter dependence on T (k, K_C)
- stoichiometry

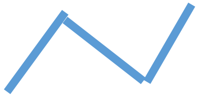
Example problem: Isomerization of n-C_4H_{10} (butane)

Example 11-3 Fogler

Liquid phase, elevated pressure



n-C_4H_{10} A



Want to make

iso-C_4H_{10} B

i-C_5H_{12}(inert) also fed

F_{T0} = 163 kmol/hr

T_0 = 330 K, but NOT isothermal! Adiabatic reactor

90% nC4, 10% i-C5

$$A \rightleftarrows B$$

$$k_f(360K) = 31.1\ 1/hr$$

ΔH_{rxn} = -6900 J/mol C4, E_a = 65.7 kJ/mol; K_C = 3.03 @ 60 °C;

C_{A0} = 9.3 kmol/m^3

$\overset{A}{C_{P,n\text{-}C4}} = \overset{B}{C_{P,i\text{-}C4}}$ = 141 J/mol·K; $\overset{\text{inert}}{C_{P,i\text{-}C5}}$ = 161 J/mol·K

From our mole balance algorithm:

$$15.77 m^3/hr \int_0^X \frac{1}{k_f\left((1-X)-\frac{X}{K_C}\right)} dX = V_{PFR}$$

Recall we CANNOT solve this just yet, because some of these parameters in the integral are a function of X!

Using our adiabatic energy balance equation we got (for this particular reactor):

$$T = (43.4\ K)X + 330\ K$$

May call it X_{EB} or $X_{adiabatic}$ to indicate its from the EB

$$k_f(T) = k_f(360\ K)\exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{360\ K}\right)\right]$$

$$= 31.1\ hr^{-1}\exp\left[-\frac{65700\ J/mol}{8.314\ J/mol\cdot K}\left(\frac{1}{T} - \frac{1}{360\ K}\right)\right]$$

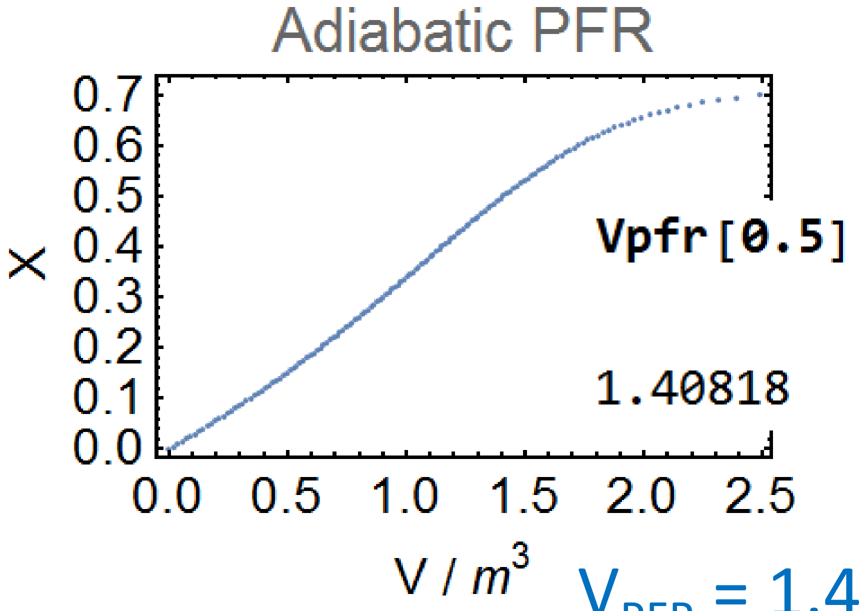
$$K_C(T) = K_C(333\ K)\exp\left[-\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right]$$

$$= 3.03\exp\left[-\frac{-6900\ J/mol}{8.314\ J/mol\cdot K}\left(\frac{1}{T} - \frac{1}{333\ K}\right)\right]$$

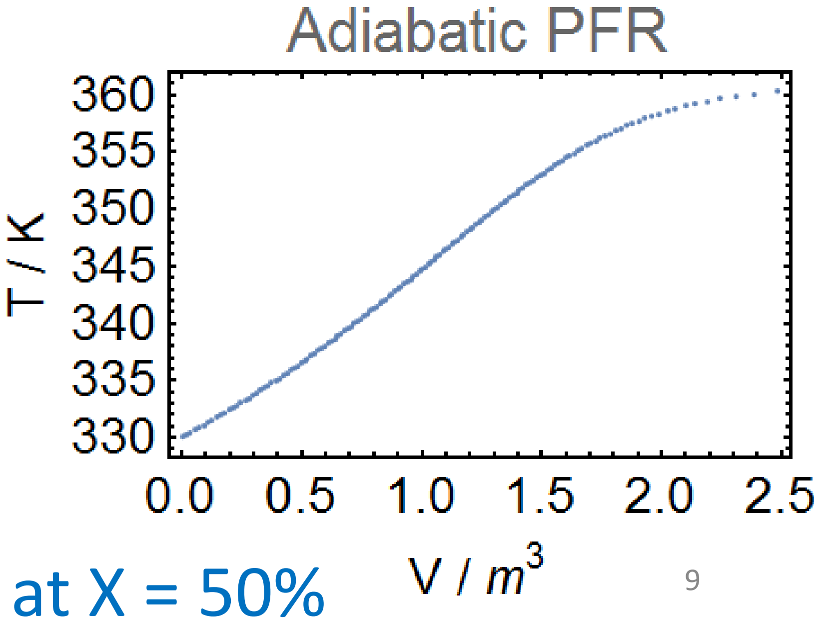
We now can solve our mole balance equation because we know how k_f and K_C are related to T, and how T is related to X

Here solving/plotting in Mathematica, but full problem solved on page 563 in book using Polymath (full code on Canvas)

```
(* Define kf and Kc *)

kf[T_] := 31.1 * Exp[-65700 / 8.314 * (1 / T - 1 / 360)]

Kc[T_] := 3.038 Exp[6900 / 8.314 * (1 / T - 1 / 333)]

(* T = f(X) *)

T[x_] := 43.3 * x + 330

Vpfr[xx_] := 15.77 * NIntegrate[1 / (kf[T[x]] * ((1 - x) - x / Kc[T[x]])), {x, 0, xx}]
```



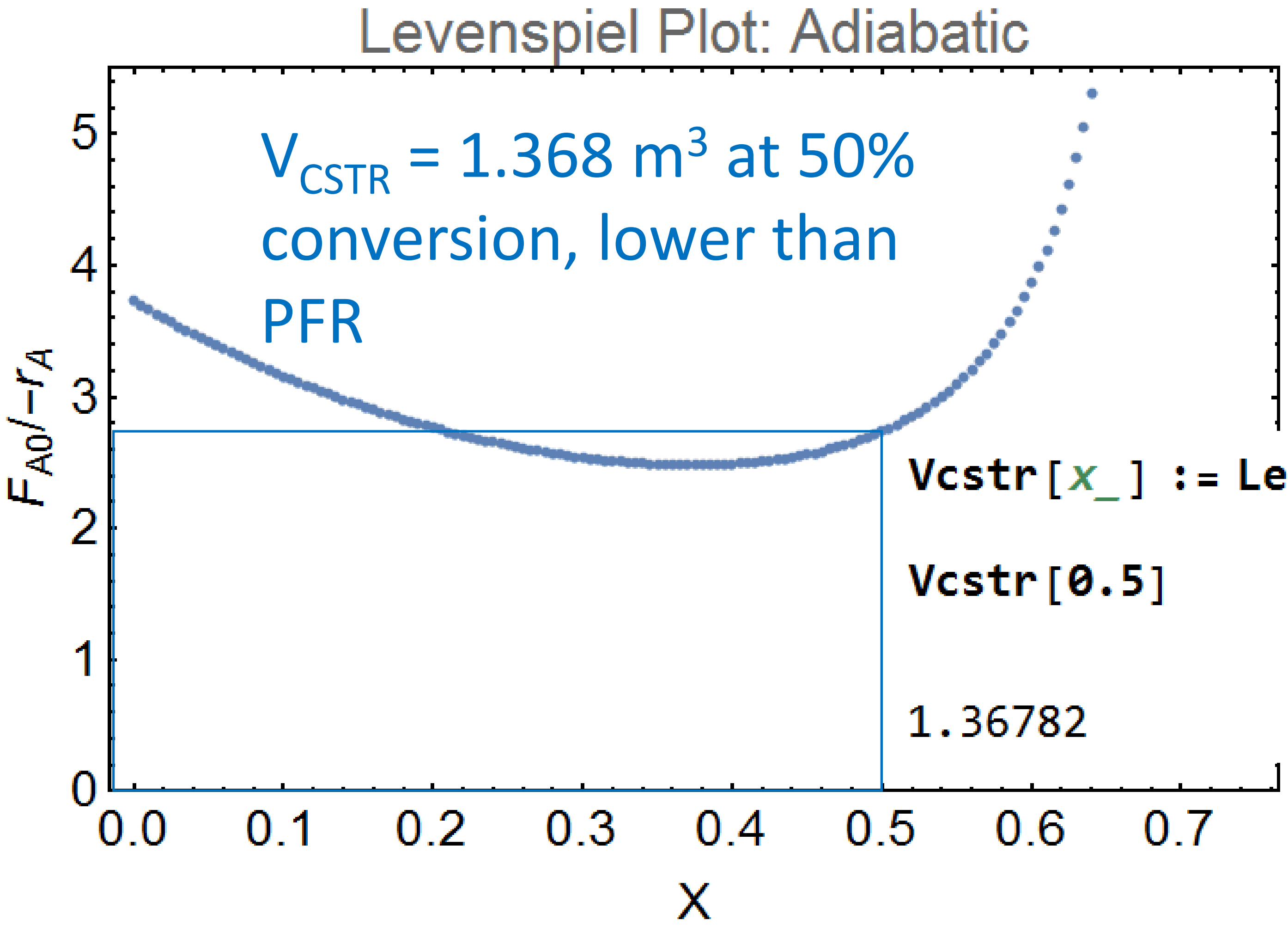
```
Vpfr[0.5]

1.40818
```



V_{PFR} = 1.408 m^3 at X = 50%

Levenspiel Plot

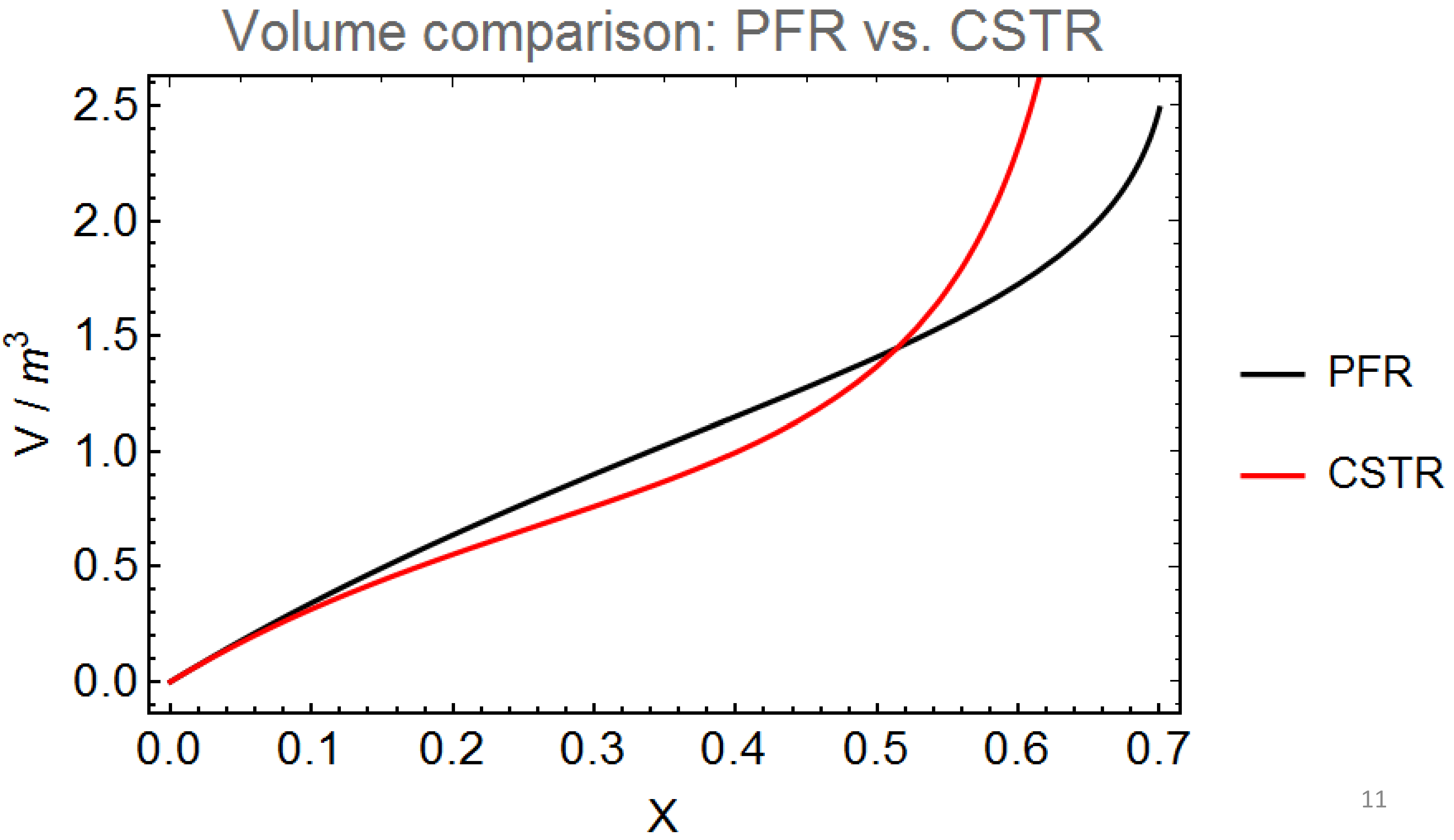
```
(* Want to plot Fa0/-ra as the y axis,
first define it *)

LevYpfr[x_] := 15.77 / (kf[T[x]] * ((1 - x) - x / Kc[T[x]]))
```



V_{CSTR} = 1.368 m^3 at 50% conversion, lower than PFR

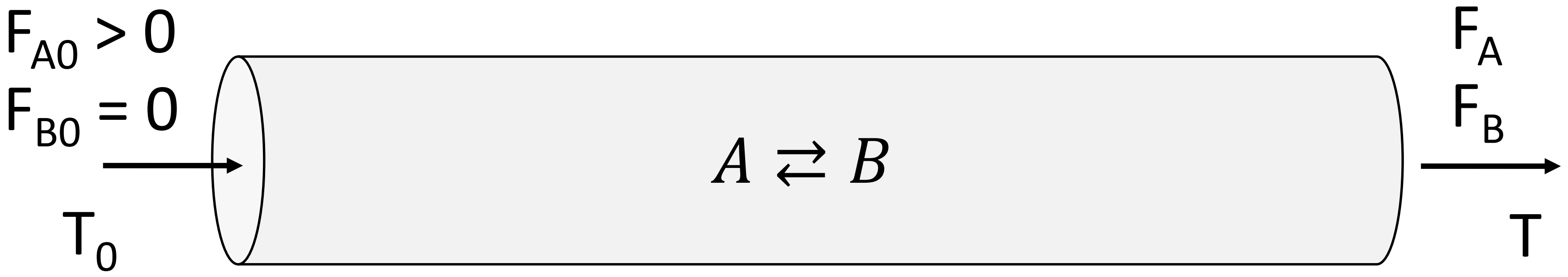
```
Vcstr[x_] := LevYpfr[x] * x

Vcstr[0.5]

1.36782
```

Plotting the V_{CSTR} and V_{PFR} functions together to compare volumes at different conversions



Discuss with your neighbors:

For an adiabatic reactor, if $T > T_0$, which is true?



$k(T_0)$ $K_C(T_0)$

$k(T)$ $K_C(T)$

[✓ A) $k(T) > k(T_0)$; $K_C(T) < K_C(T_0)$]

Exothermic:
$X > 0$, $T > T_0$, $\Delta H_{rxn}<0$

B) $k(T) > k(T_0)$; Cannot tell about $K_C(T_0)$ vs. $K_C(T)$

C) $k(T) > k(T_0)$; $K_C(T) > K_C(T_0)$

D) $k(T) < k(T_0)$

$$K_C(T) = K_C(T_0)\exp\left[-\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$

$$A \rightleftarrows B$$

At **equilibrium**, no net reaction

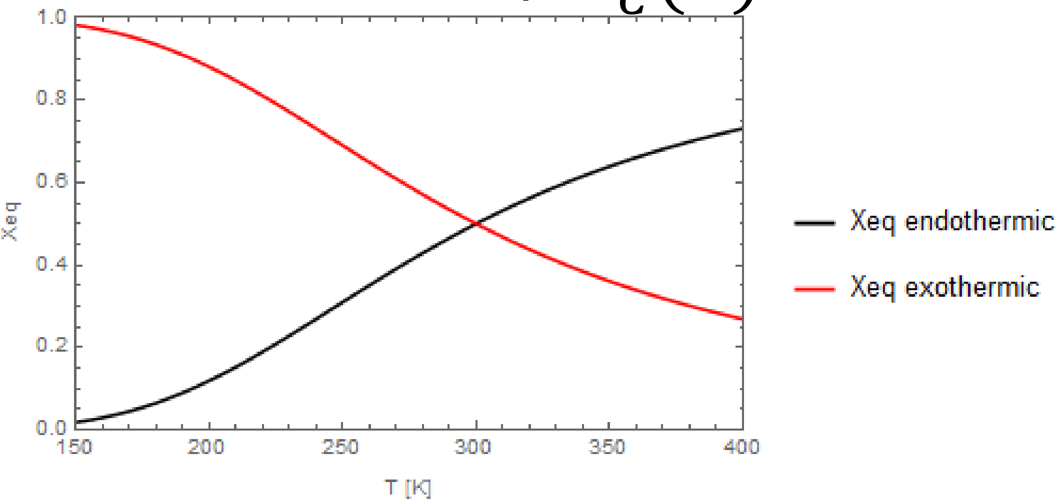
$$k_f C_{A,eq} = k_r C_{B,eq} \qquad K_C = \frac{k_f}{k_r}$$

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

$$C_B = C_{A0}(X)$$

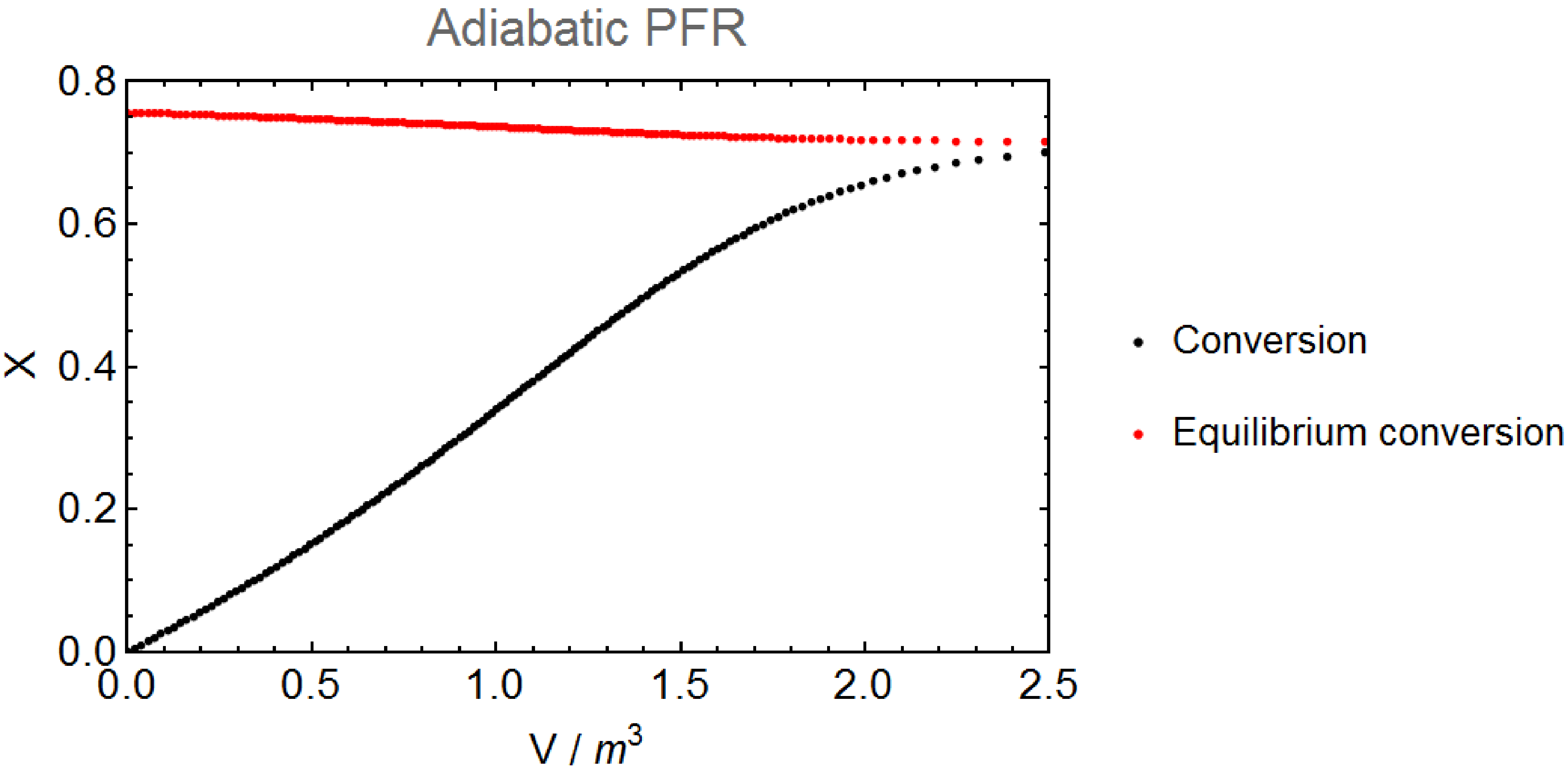
$$K_C C_{A0}(1-X_{eq}) = C_{A0}X_{eq}$$

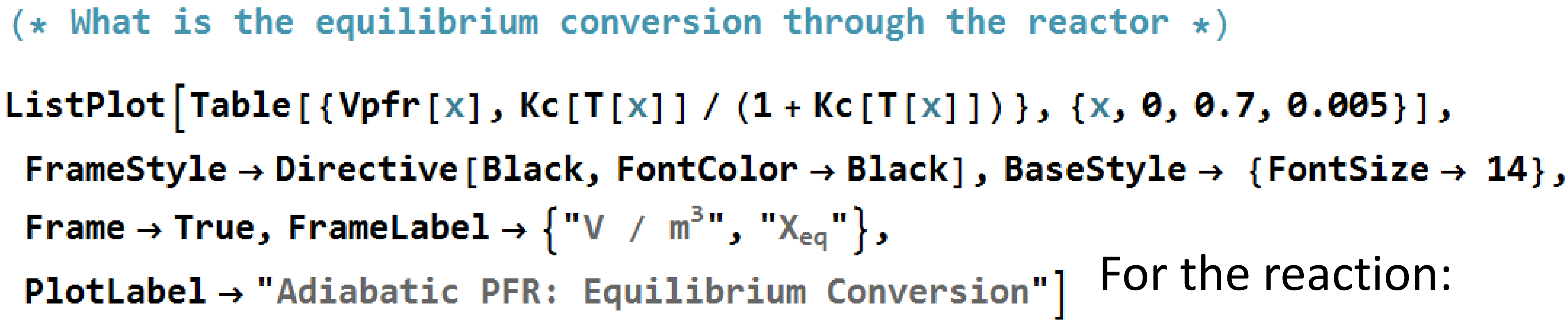
$$X_{eq}(T) = \frac{K_C(T)}{1+K_C(T)}$$



Taking products out or cofeeding will change X_{eq}. But also, we could control the T!

Plotting the equilibrium vs. reactor conversion as a function of reactor volume for our butane reactor.

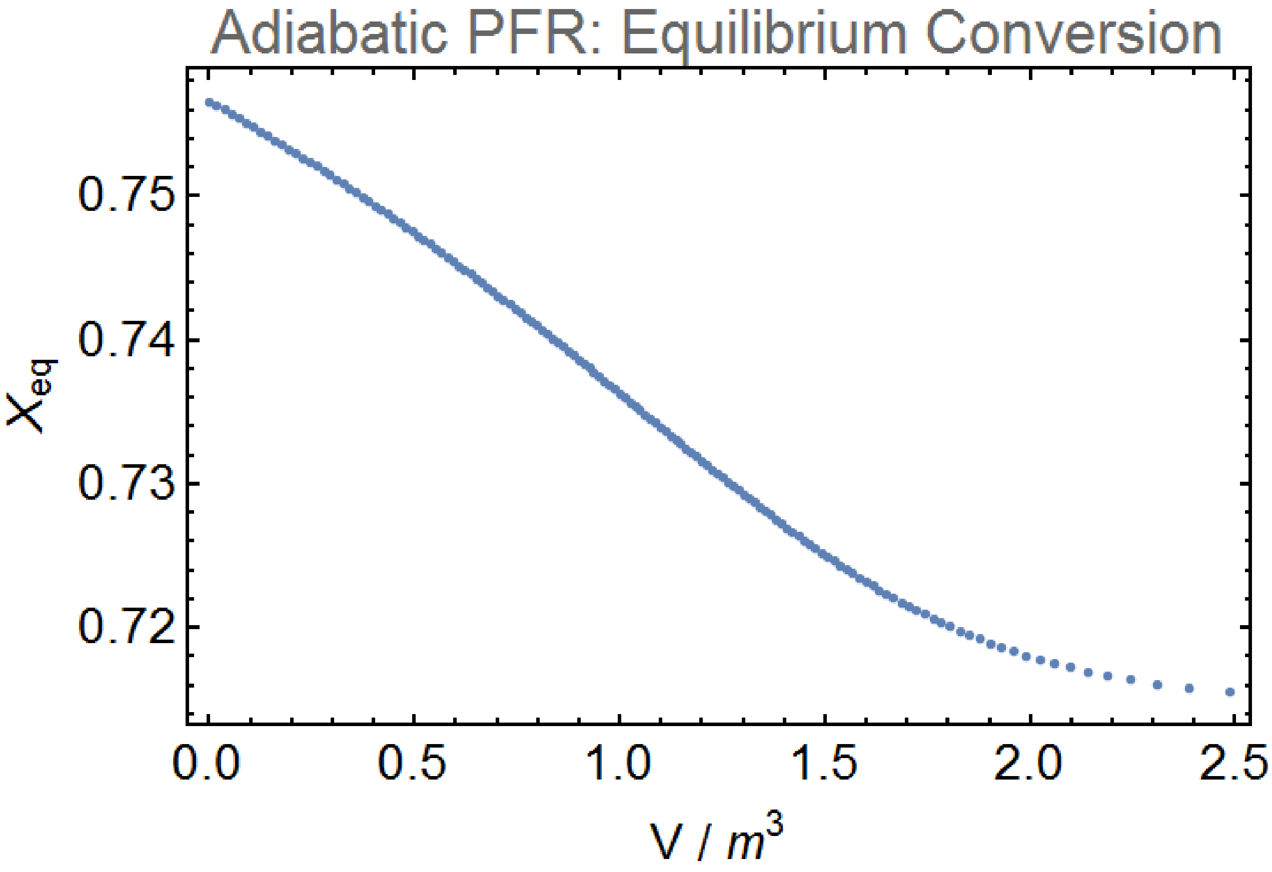




```
(* What is the equilibrium conversion through the reactor *)

ListPlot[Table[{Vpfr[x], Kc[T[x]] / (1 + Kc[T[x]])}, {x, 0, 0.7, 0.005}],
 FrameStyle → Directive[Black, FontColor → Black], BaseStyle → {FontSize → 14},
 Frame → True, FrameLabel → {"V / m^3", "X_eq"},
 PlotLabel → "Adiabatic PFR: Equilibrium Conversion"]
```

For the reaction:

$$A \rightleftarrows B$$



$$K_C = \frac{C_{B,eq}}{C_{A,eq}}$$

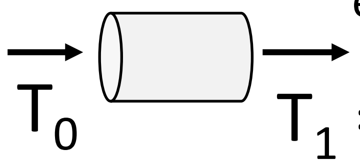
$$X_{eq} = \frac{K_C}{1 + K_C}$$

Continuing adiabatic reactor design

Exothermic

$$A \rightleftarrows B$$

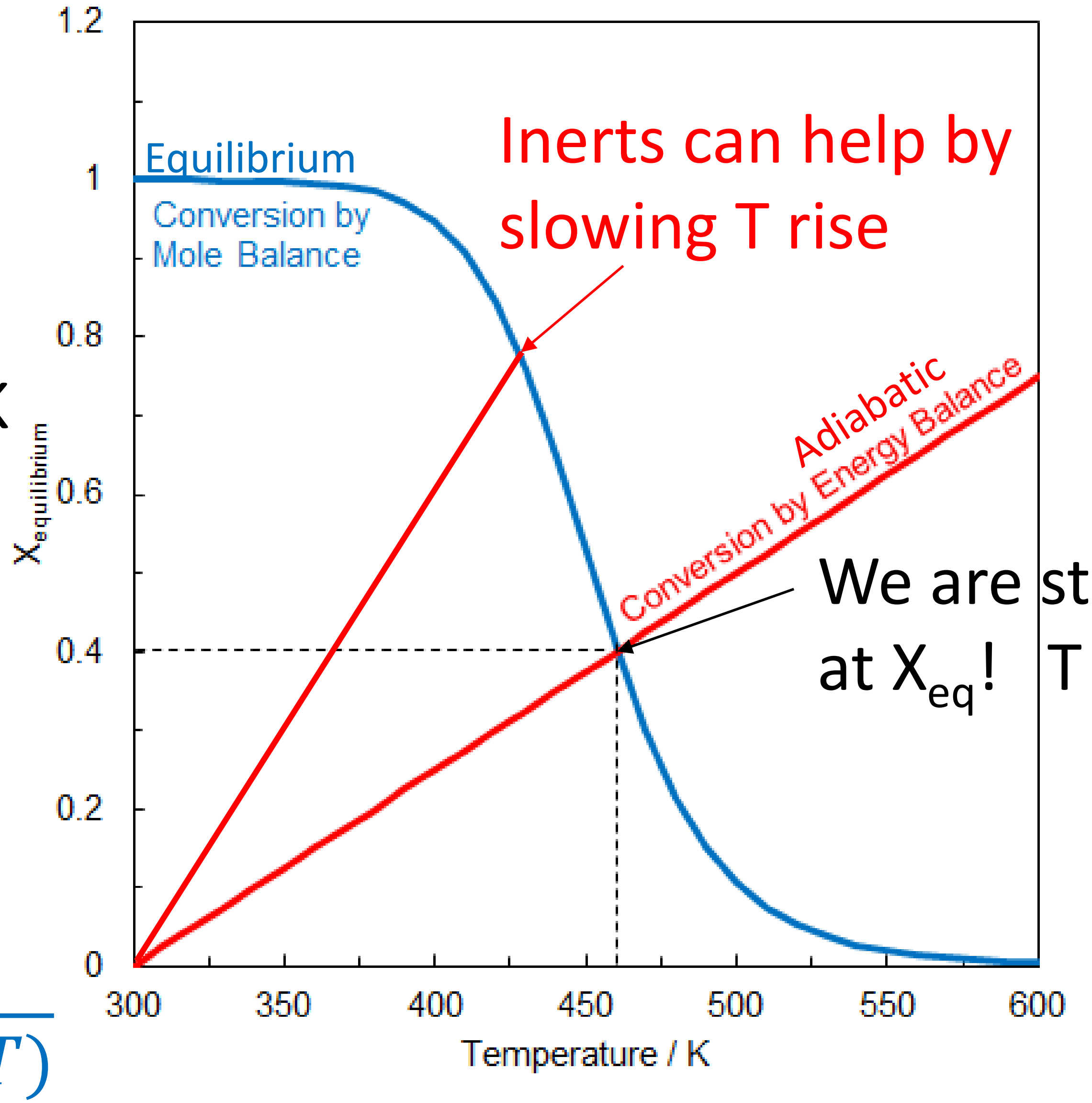
Single adiabatic reactor



T_0

$X_{eq}=0.4$

T_1 = 460 K



Inerts can help by slowing T rise

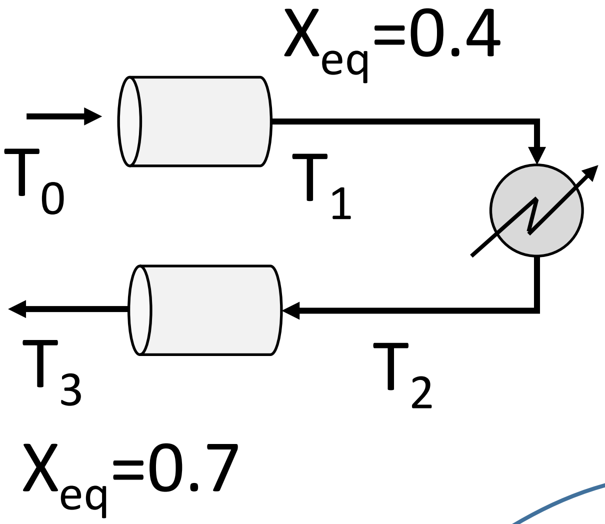
We are stuck at X_{eq}! $T = T_1$

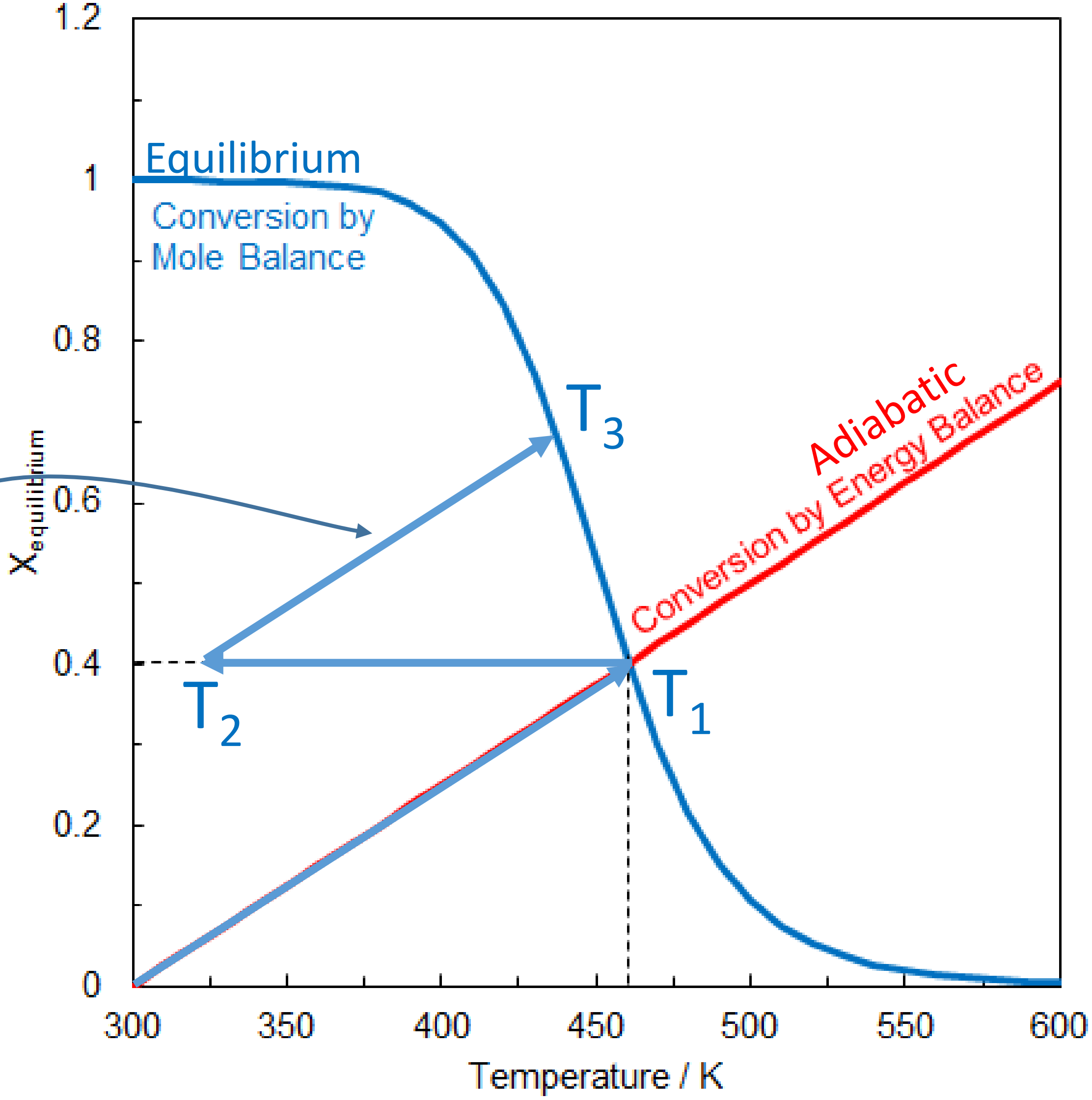
$$X_{adiabatic,EB} = \frac{\sum \theta_i C_{P,i}[T - T_0]}{-[\Delta H_{rxn}(T)]}$$

$$X_{eq}(T) = \frac{K_C(T)}{1 + K_C(T)}$$

What if we cooled in between reactors?

$$A \rightleftarrows B$$



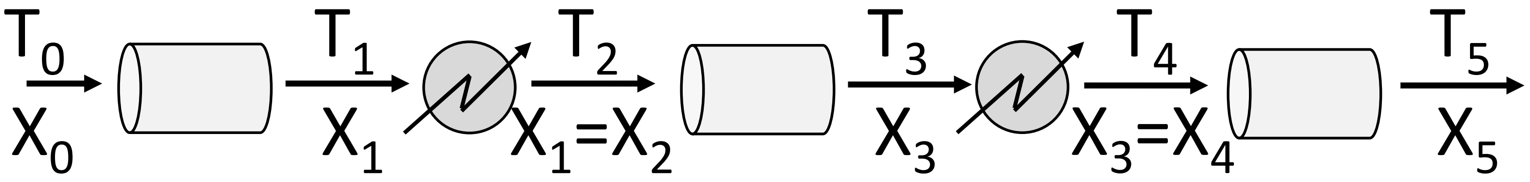


Same slope, but different intercept (T_0, X_0)

Interstage cooling

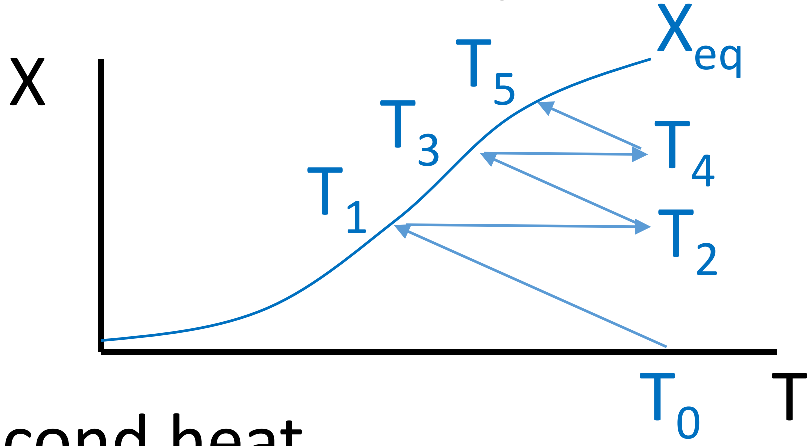
Discuss with your neighbors:

For a series of adiabatic reactors, what should the interstage heat exchangers do to the fluid to maximize X?



$A \rightleftarrows B$

Endothermic



A) First heat exchanger cool, second heat

B) First heat exchanger heat, second cool

[✓ C) Both heat]

D) Both cool

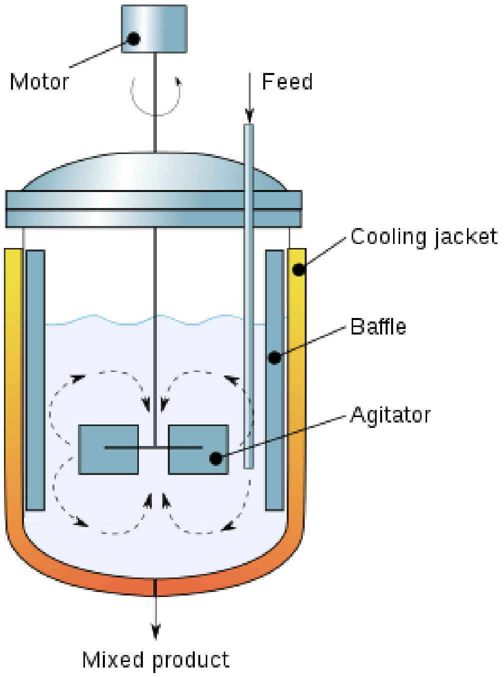
What if we want to control the temperature of our reactor?

We may want to do this for:

Safety

What if the reactor gets too hot?

http://umich.edu/~safeche/



Control equilibrium/selectivity/conversion

Keep your reactor working

- Polymer production
- Catalytic regeneration (avoid sintering)

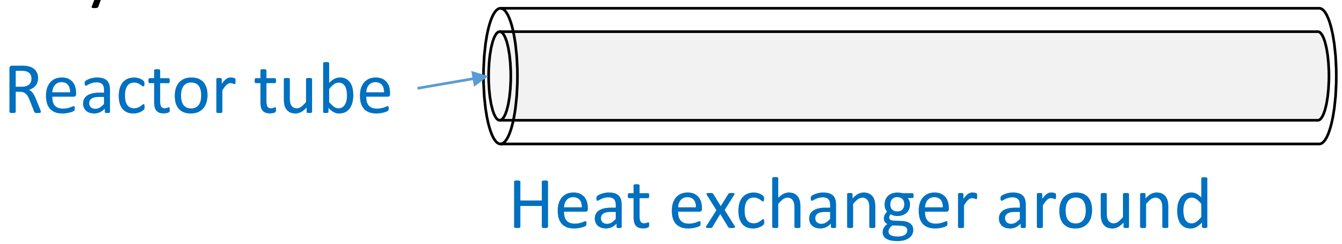
Easier to model/take rate data

Isothermal reactors much easier to deal with!

Often, we will control the temperature with **heat exchangers**

We used these for interstage (in between reactors), but we can also have a heat exchanger integrated with our reactor

PFR today



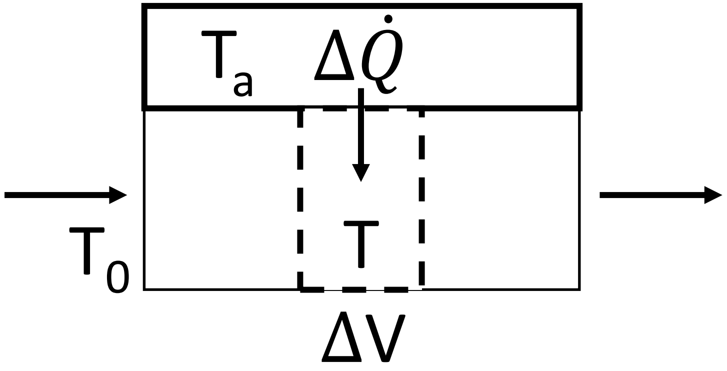
There will be an additional heat term that we previously did not include for adiabatic reactors

Eventually…

- We will need an energy balance on heat exchanging fluid and reactor
- For CSTRs, we will find that there are multiple steady states
- Dealing with multiple reactions each with a ΔH_{rxn}

Industrial reactors will generally have heat exchangers (no longer adiabatic): Recall our energy balance

$$F_{A0}\left[\left(\sum -\theta_i C_{P,i}[T-T_0]\right) - \left[\Delta H_{rxn}(T_{ref}) + \Delta C_P(T-T_{ref})\right]X\right] + \dot{Q} - \cancelto{0}{\dot{W}_{shaft}} = \cancelto{0}{\frac{d\hat{E}_{sys}}{dt}}$$



No mass transport through walls, only heat

Reactor with coolant/heating adjacent to reactant volume.

$\dot{Q} \neq 0$. In reactant slug have a $\Delta\dot{Q}$ term from V to V+ΔV.

T_a is the cooling/heating material temp.

How does heat transfer?

Need a temperature gradient

$$\Delta\dot{Q} = U\Delta A(T_a - T)$$

U is the heat transfer coefficient with units of J/m^2·s·K

ΔA is the heat transfer area with respect to ΔV

$$\Delta A \equiv \underbrace{a}_{\substack{\mathit{shape\ factor,}\\ \frac{\mathit{heat\ transfer\ area}}{\mathit{unit\ reactor\ volume}}}} \Delta V$$

For example, if heat exchanger surrounds a tubular reactor:

a very small diameter tube reactor (large a)

vs.

a very large diameter tube (small a)

$$a = \frac{\pi \Delta L D}{\frac{\pi}{4}\Delta L D^2}$$

Energy balance on a reactor element ΔV

In – out + gen – cons = accumulation = 0

$$\sum F_i H_i\Big|_V - \sum F_i H_i\Big|_{V+\Delta V} + Ua\Delta V(T_a - T) = 0$$

This is the balance on the reactor volume ΔV. This time we have a term outside the sums that is non-zero, that has ΔV

$$\frac{\sum F_i H_i|_V - \sum F_i H_i|_{V+\Delta V}}{\Delta V} + Ua(T_a - T) = 0$$

Limit as ΔV goes to zero,

$$-\frac{d[\sum F_i H_i]}{dV} + Ua(T_a - T) = 0$$

Product rule of derivatives

$$Ua(T_a - T) = \frac{d[\sum F_i H_i]}{dV} = \sum F_i \frac{dH_i}{dV} + \sum H_i \frac{dF_i}{dV}$$

$$H_i(T) = H_i{}^0(T_{ref}) + \int_{T_{ref}}^{T} C_{P,i}\,dT$$

$$\frac{dH_i}{dV} = \frac{dH_i}{dT}\frac{dT}{dV} = C_{P,i}\frac{dT}{dV}$$

To evaluate the $\frac{dF_i}{dV}$ terms, we will need to consider more details about the reactor.
This is different than for our adiabatic case where we had a general equation that applied to several different reactor types. (Adiabatic had same EB for CSTR/PFR)

For PFR we get relation between flow rate and volume from our mole balance:

$$\frac{dF_i}{dV} = r_i$$

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

$$\frac{dF_A}{dV} = r_A;$$

$$\frac{dF_B}{dV} = r_B = \frac{b}{a}r_A; \frac{dF_C}{dV} = r_C = -\frac{c}{a}r_A; \frac{dF_D}{dV} = r_D = -\frac{d}{a}r_A$$

$$\frac{dF_i}{dV} = -\nu_i r_A$$

Plugging back into our energy balance for a PFR

$$Ua(T_a - T) = \sum F_i \left(C_{P,i} \frac{dT}{dV} \right) + \sum H_i(-\nu_i r_A)$$

$$Ua(T_a - T) = \sum F_i C_{P,i} \frac{dT}{dV} - \sum H_i \nu_i r_A$$

$$Ua(T_a - T) = \frac{dT}{dV} \sum \left[F_i C_{P,i} \right] - r_A \Delta H_{rxn}$$

-Heat 'removed' Heat 'generated'

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + r_A \Delta H_{rxn}}{\sum F_i C_{P,i}}$$

$$F_i = F_{A0}(\theta_i + \nu_i X)$$

PFR mole balance design equation:

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

PFR energy balance with heat exchanger:

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + r_A \Delta H_{rxn}}{\sum F_i C_{P,i}} = \frac{r_A \Delta H_{rxn} - Ua(T - T_a)}{F_{A0}\left[\sum \theta_i C_{P,i} + \Delta C_P X\right]}$$

$$F_i = F_{A0}(\theta_i + \nu_i X)$$

Now we have two non-linear coupled ODEs, can solve with software of our choice if we assume T_a is constant everywhere in the reactor.

ΔH_{rxn} at T, $r_A \Delta H_{rxn}$ is positive (negatives cancel) for proceeding exothermic reaction

For an exothermic reaction in a PFR, how much total heat must be removed to maintain isothermal operation? $A \rightarrow B$

F_{A0} = 1 mol min^{-1}

X = 0.5

T_0 = 300 K

$\Delta H_{rxn} = -20\ kJ\ mol^{-1}$

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

$$\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - Ua(T - T_a)}{\sum F_i C_{P,i}}$$

$$total\ heat\ removed = \int Ua(T - T_a)dV$$

For dT/dV = 0 $\quad F_{A0}\frac{dX}{dV} = \frac{-Ua(T - T_a)}{\Delta H_{rxn}}$

Total $Q_{removed} = -1\ mol\ min^{-1}(0.5)(-20\ kJ\ mol^{-1})$

Total $Q_{removed} = 10\ kJ\ min^{-1}$

If isothermal, E.B. is

$$\frac{dT}{dV} = 0 = \frac{r_A \Delta H_{rxn} - Ua(T - T_a)}{\sum F_i C_{P,i}}$$

$$0 = r_A \Delta H_{rxn} - Ua(T - T_a)$$

$$r_A = \frac{Ua(T - T_a)}{\Delta H_{rxn}}$$

Mole balance is

$$F_{A0} \frac{dX}{dV} = -r_A = -\frac{Ua(T - T_a)}{\Delta H_{rxn}}$$

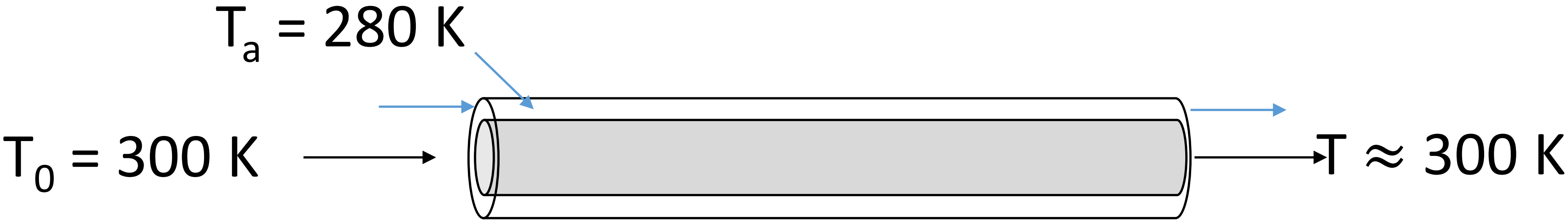
Rearrange, then take integral

$$F_{A0} \Delta H_{rxn} dX = -Ua(T - T_a) dV$$

$$\int F_{A0} \Delta H_{rxn} dX = -\int Ua(T - T_a) dV$$

$$Total\ rem. = \int Ua(T - T_a)dV = -1\ mol\ min^{-1}(0.5)(-20\ kJ\ mol^{-1}) = 10 kJ min^{-1}$$

Where would this heat be coming from? From the heating fluid, which may be flowing co or counter-current



Here co-current

In reality, if the heating fluid is removing heat, it itself must be heating up, so $T_a = f(V)$

If T_a is not constant, we will need an energy balance on the heating/cooling element (next Tuesday)