ChE 344
Reaction Engineering and Design

Lecture 16: Thursday, Mar 10, 2022

9:30am-11:30am

Flow reactors with heat exchange

Reading for today's Lecture: Chapter 12.1-12.2

Reading for Lecture 17: Chapter 12.4-12.6

Lecture 16: Non-isothermal Reactor Design-PFR with heat exchangers
Related Text: Chapter 12.1-12.2

<u>PFR heat exchanger energy balance on **reactor**</u>

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

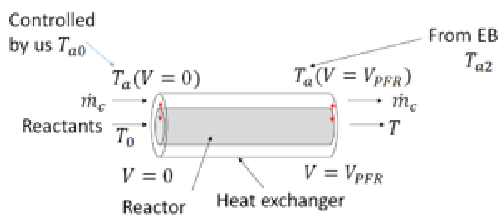
T_a is the temperature of the heat exchanger fluid at volume V.
Q_g is the heat 'generated' by the reaction, and Q_r is the heat 'removed' by the heat exchanger (positive if $T > T_a$, negative if $T < T_a$).
U is the heat transfer coefficient with units of $J/m^2 \cdot s \cdot K$
a is the shape factor, or heat transfer area divided by unit reactor volume.

<u>PBR heat exchanger energy balance</u>

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_b}(T_a - T) + r_A' \Delta H_{rxn}}{\sum F_i C_{P,i}}$$

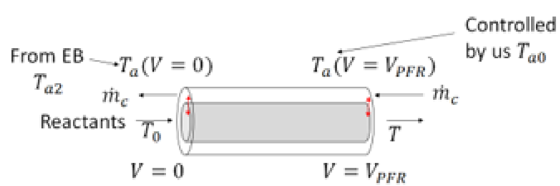
<u>**Co**-current heat exchanger balance on **heat exchanger fluid**</u>

$$\frac{-Ua(T_a - T)}{\dot{m}_c C_{P,c}} = \frac{dT_a}{dV}$$



<u>**Counter**-current heat exchanger balance on **heat exchanger fluid**</u>

$$\frac{Ua(T_a - T)}{\dot{m}_c C_{P,c}} = \frac{dT_a}{dV}$$



For counter-current we need to **<u>iteratively solve</u>** by guessing a T_{a2}, then solving for T_{a0} and comparing to our actual T_{a0}, then modifying our T_{a2} guess.

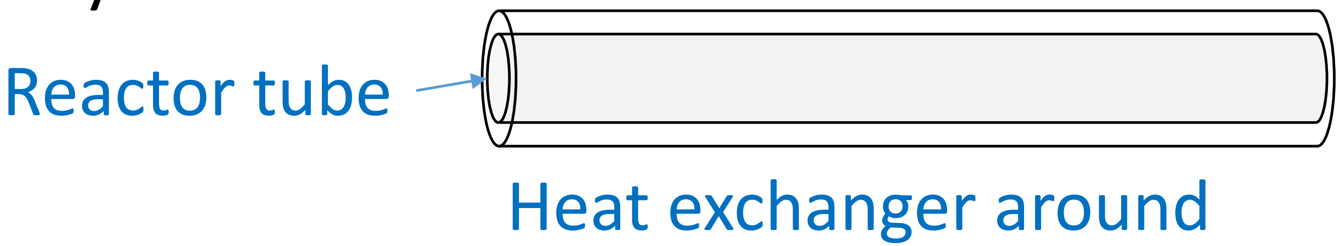
To solve, need to simultaneously solve the coupled i) mole balance equation ii) heat exchanger energy balance on the reactor, iii) energy balance on the heat exchanger fluid.

"Lecture 16-Heat exchanger T profiles.nb" goes through the setup for a zero-order, irreversible reaction.

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



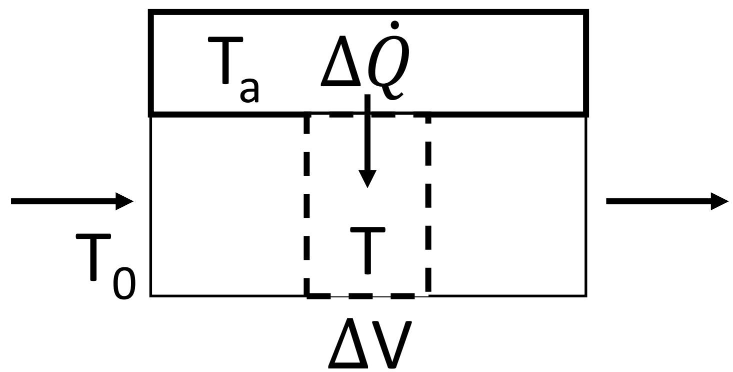
There will be an additional heat term that we previously did not include for adiabatic reactors

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

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



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

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

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

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

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

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

$Q_r \equiv Ua(T - T_a)$

$-Q_r$

-Heat 'removed'

Heat 'generated' Q_g

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

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

PFR mole balance design equation:

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

PFR energy balance with heat exchanger:

Q_g $\qquad$ $Q_r \equiv Ua(T - T_a)$

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

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

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

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

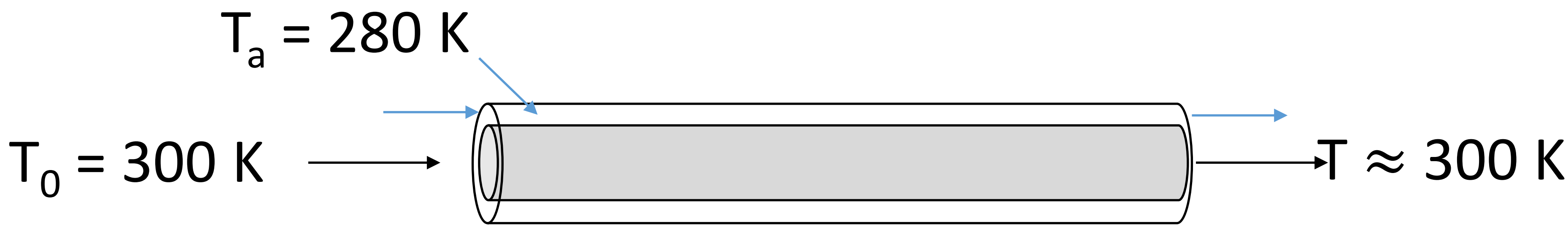
Rearrange, then take integral

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

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

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

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

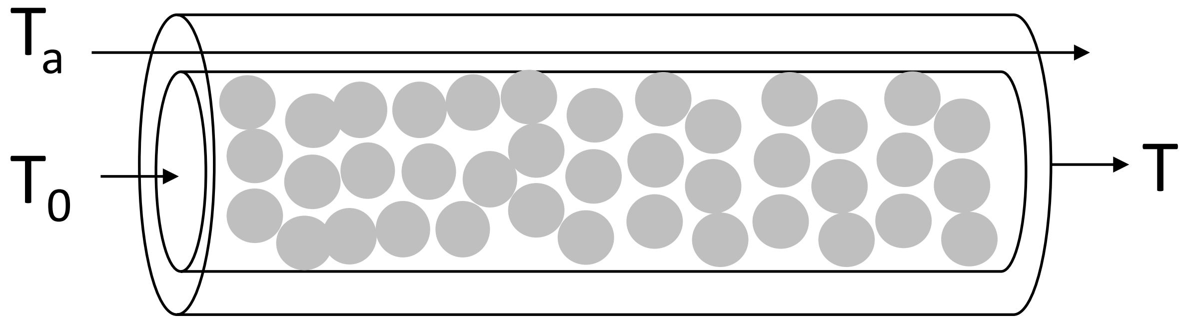


Here co-current

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

Quick aside on heat exchanger with P**B**R



For a packed bed reactor, we may use catalyst weight (W) instead of reactor volume (V)

$$W = V\rho_b$$

Catalyst bed density

$$\frac{dT}{dW} = \frac{dT}{dV}\frac{dV}{dW} = \frac{dT}{dV}\frac{1}{\rho_b}$$

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_b}(T_a - T) + r'_A \Delta H_{rxn}}{\sum F_i C_{P,i}}$$

Lets consider an example:

In a PFR where $A \rightarrow B$, where the reaction is zero-order in A, endothermic and $C_{P,A} = C_{P,B}$:

Sketch X as a function of space time or V, assuming:

a. Isothermal reactor at T_0

b. Adiabatic reactor at inlet T_0

c. Reactor with heat exchanger with fluid at $T_a = T_0$

d. Reactor with heat exchanger with fluid at $T_{a0} = T_0$ at inlet, but heat exchanger fluid cools as it passes along reactor

We will sketch them on the same plot for comparison

Conceptual question:

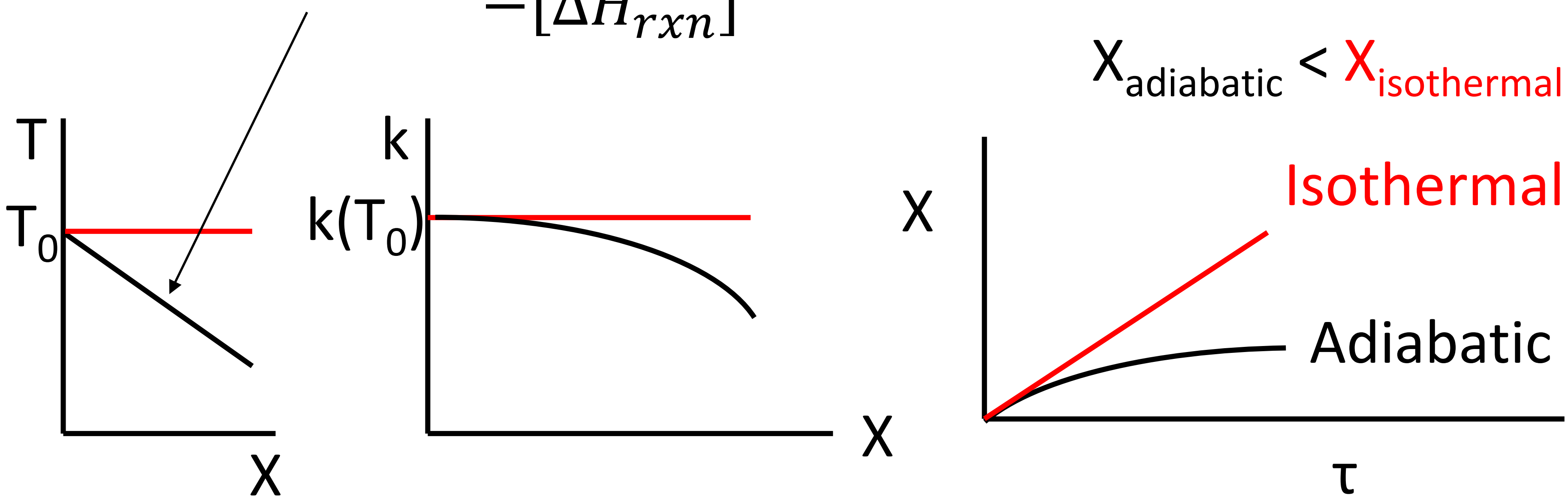
In a PFR where A → B, where the reaction is zero-order in A, <u>endothermic</u> and $C_{P,A} = C_{P,B}$:

Sketch X as a function of space time or V, assuming:

a. Isothermal reactor at T_0

b. Adiabatic reactor at inlet T_0

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



Discuss with your neighbors:

In a PFR where A → B, where the reaction is zero-order in A, endothermic and $C_{P,A} = C_{P,B}$:

At a finite space time or V what is the order of the conversions from low to high?

a. Isothermal reactor at T_0

b. Adiabatic reactor at inlet T_0

c. Reactor with heat exchanger with fluid at $T_a = T_0$

A) $X_{heat\ exchanger} > X_{adiabatic} > X_{isothermal}$

B) $X_{isothermal} > X_{adiabatic} > X_{heat\ exchanger}$

C) $X_{isothermal} > X_{heat\ exchanger} > X_{adiabatic}$

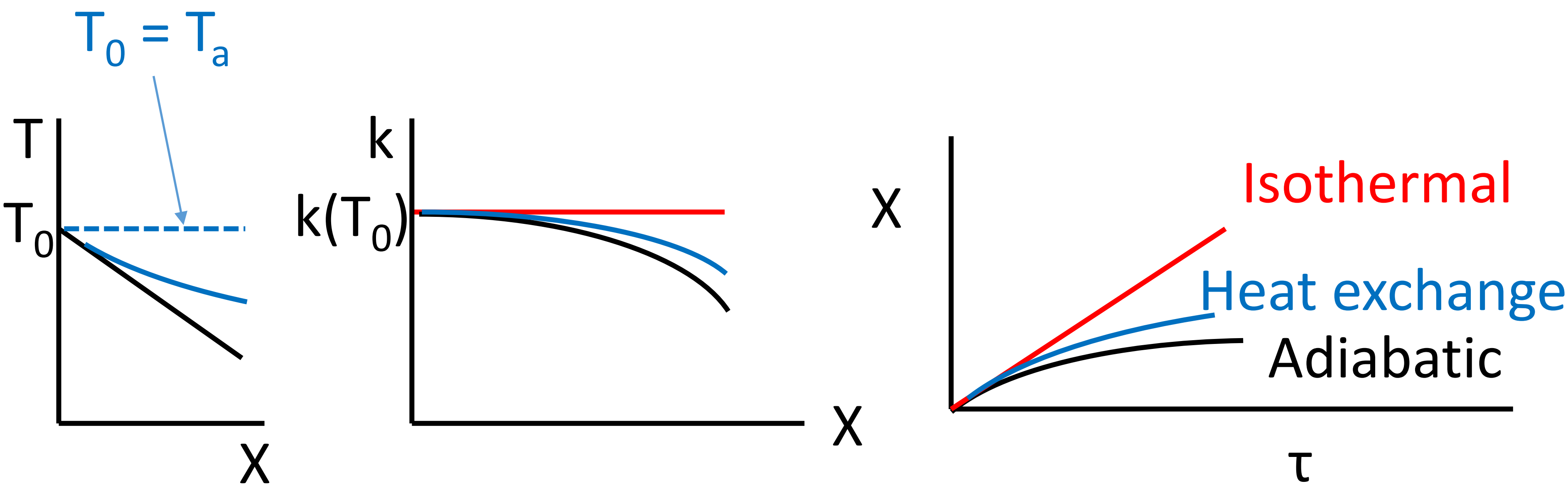
D) $X_{heat\ exchanger} > X_{isothermal} > X_{adiabatic}$

In a PFR where A → B, where the reaction is zero-order in A, endothermic and $C_{P,A} = C_{P,B}$:

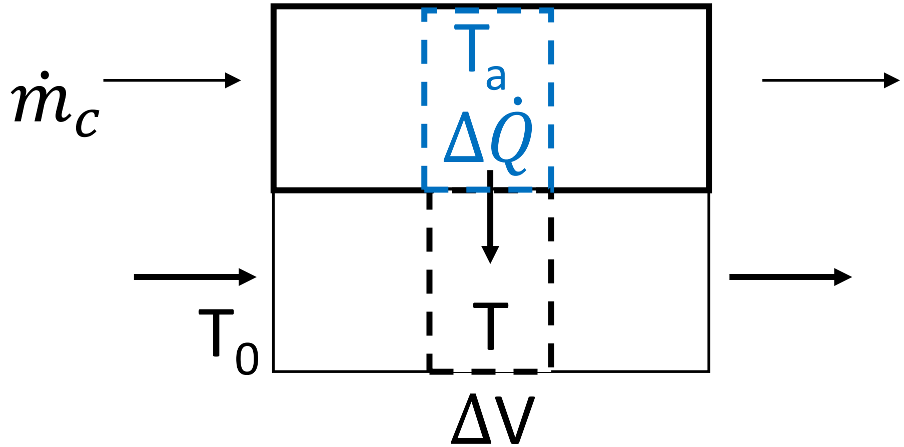
Sketch X as a function of space time or V, assuming:

c. Reactor with heat exchanger with fluid at $T_a = T_0$

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



For a heat exchanger with coolant, what if coolant temperature (T_a) is not constant?



Energy balance on co-current coolant flow: Same Ua, opp sign

$$\dot{m}_c H_c\Big|_V - \dot{m}_c H_c\Big|_{V+\Delta V} - Ua\Delta V(T_a - T) = 0$$

$$\frac{\dot{m}_c H_c|_V - \dot{m}_c H_c|_{V+\Delta V}}{\Delta V} - Ua(T_a - T) = 0$$

$\dot{m}_c$ is <u>mass</u> flow rate of heat exchange fluid (e.g. [=] kg/hr)

H_c is <u>mass</u> enthalpy of heat exchange fluid (e.g. [=] kJ/kg)

Take the limit as ΔV goes to zero,

$$-\frac{d\dot{m}_c H_c}{dV} - Ua(T_a - T) = 0$$

$$-Ua(T_a - T) = \frac{d\dot{m}_c H_c}{dV} = \dot{m}_c \frac{dH_c}{dV} + H_c \frac{d\dot{m}_c}{dV} \overset{0}{}$$

$$H_c(T_a) = H_c{}^0(T_{ref}) + \int_{T_{ref}}^{T_a} C_{P,c} dT$$

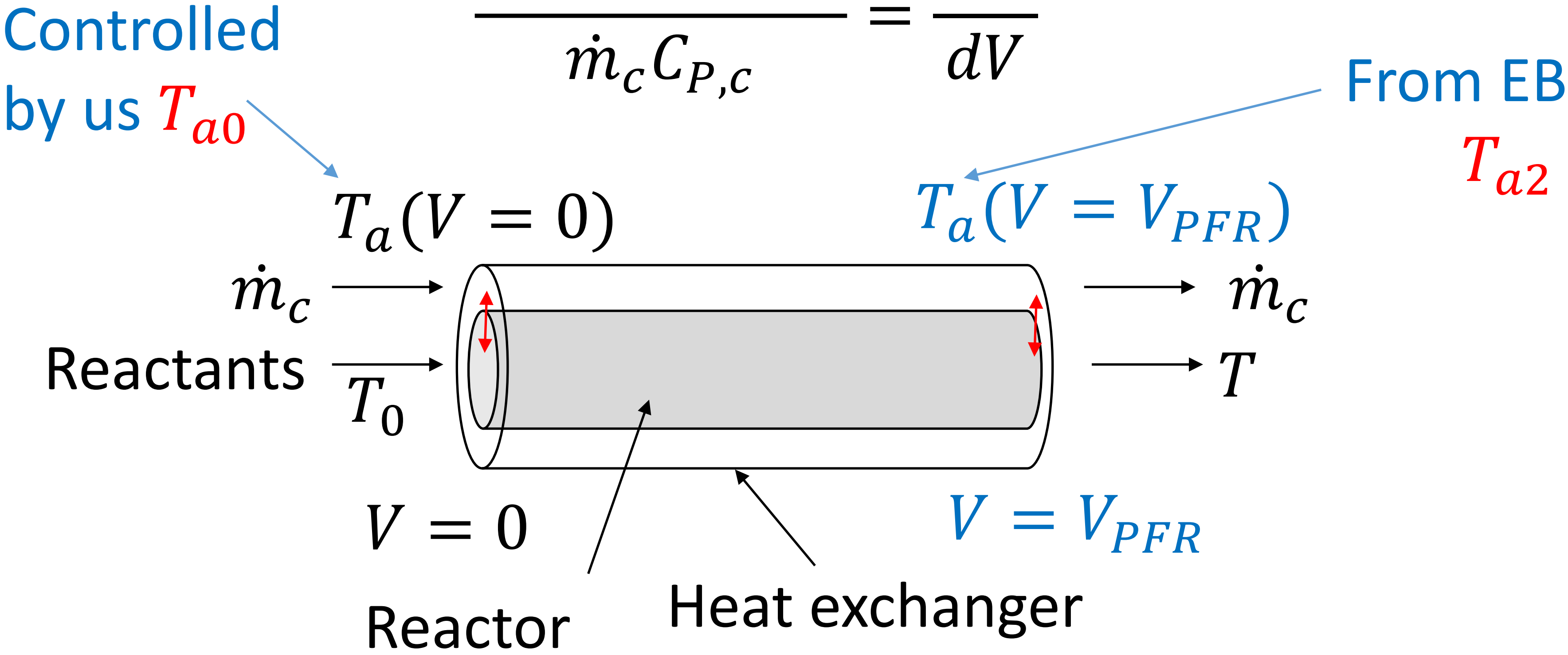
$$\frac{dH_c}{dV} = \frac{dH_c}{dT_a}\frac{dT_a}{dV} = C_{P,c}\frac{dT_a}{dV}$$

$$-Ua(T_a - T) = \dot{m}_c C_{P,c} \frac{dT_a}{dV} + H_c(0)$$

$C_{P,c}$ is <u>mass</u> heat capacity of heating fluid [=] kJ kg^{-1} K^{-1}

This is for the coolant temperature, down the reactor (co-current):

$$\frac{-Ua(T_a - T)}{\dot{m}_c C_{P,c}} = \frac{dT_a}{dV}$$



Balance on the reactor fluid:

This will also be changing now!

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

Discuss with your neighbors:

PFR: A → B, zero-order in A, endothermic and $C_{P,A} = C_{P,B}$:

What is the order of the conversions from low to high?

a. Isothermal reactor at T_0

b. Adiabatic reactor at inlet T_0

c. Reactor with heat exchanger with fluid at $T_a = T_0$

d. Reactor with heat exchanger with fluid at $T_a = T_0$ at inlet, but heat exchanger fluid cools as it passes along reactor

A) $X_{isothermal} > X_{H.E.,Ta} > X_{heat\ exchanger,Ta(V)} > X_{adiabatic}$

B) $X_{isothermal} > X_{heat\ exchanger,Ta(V)} > X_{H.E.,Ta} > X_{adiabatic}$

C) $X_{isothermal} > X_{H.E.,Ta} = X_{heat\ exchanger,Ta(V)} > X_{adiabatic}$

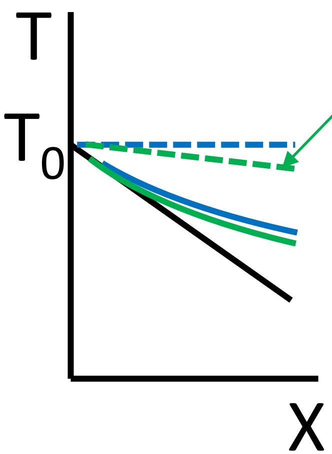
D) $X_{isothermal} > X_{H.E.,Ta} > X_{heat\ exchanger,Ta(V)} = X_{adiabatic}$

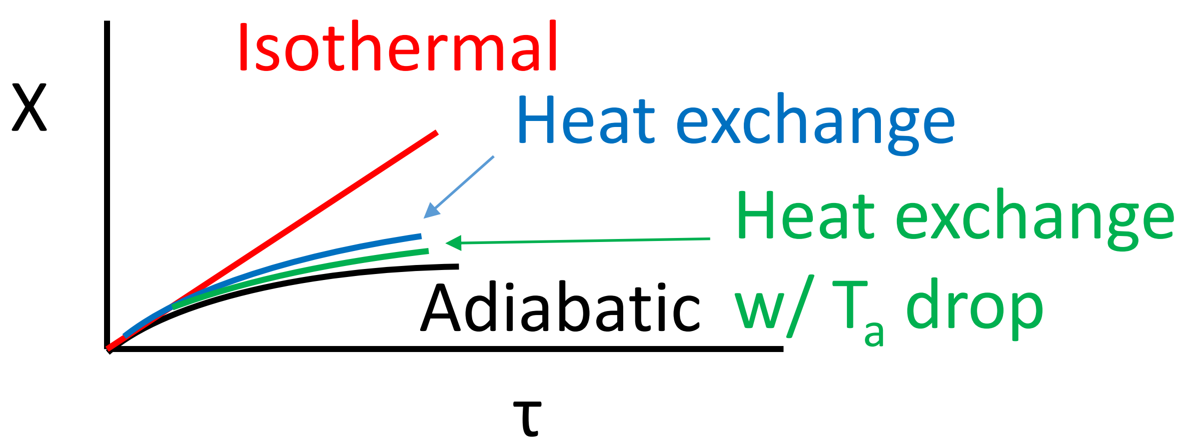
PFR: A → B, zero-order in A, <u>endothermic</u> and $C_{P,A} = C_{P,B}$:

Sketch X as a function of space time, assuming:

d. Reactor with heat exchanger with fluid at $T_a = T_0$ at inlet, but heat exchanger fluid cools as it passes along reactor

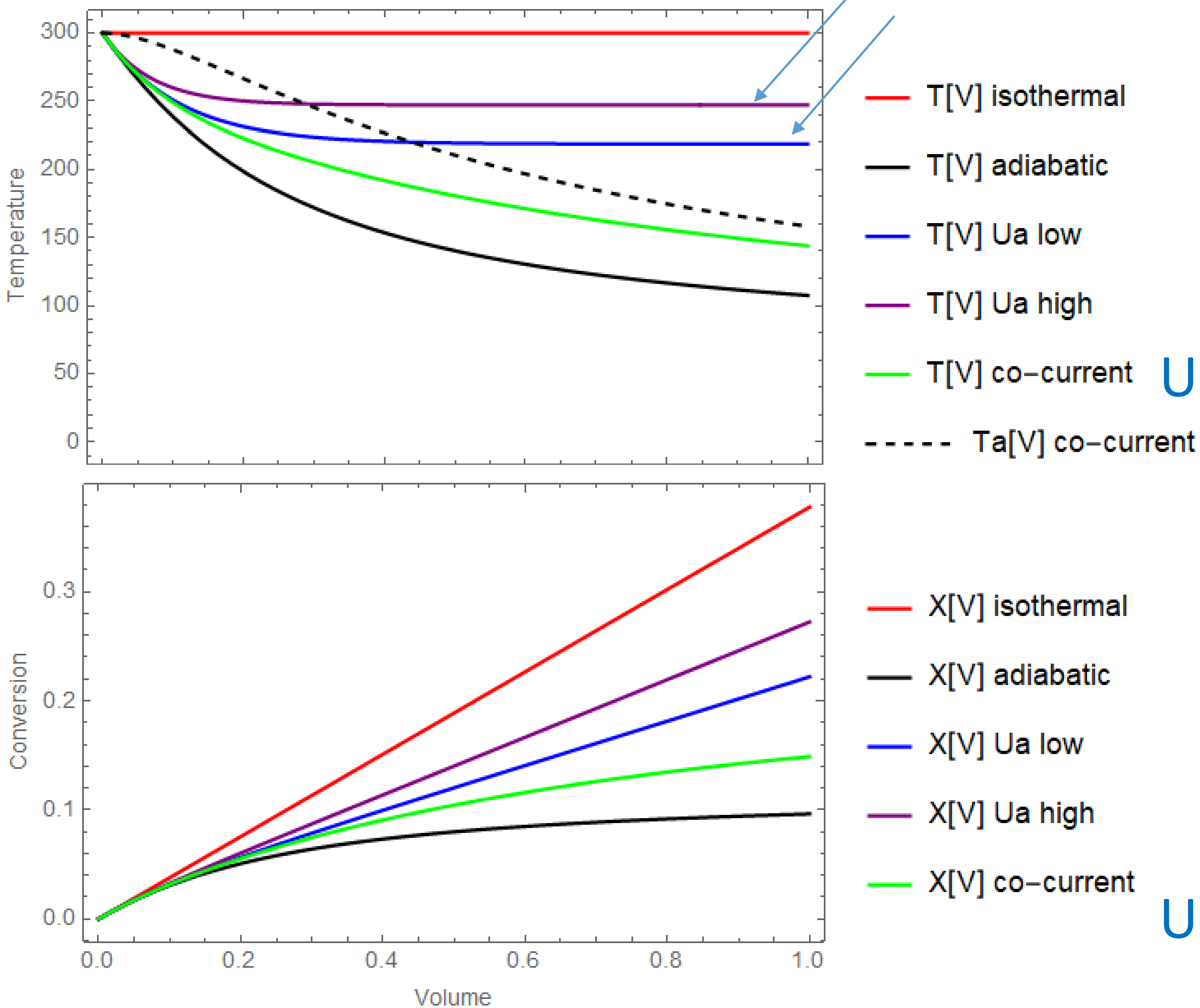
$$\frac{-Ua(T_a - T)}{\dot{m}_c C_{P,c}} = \frac{dT_a}{dV}$$





If $\dot{m}_c C_{P,c}$ is moderate:

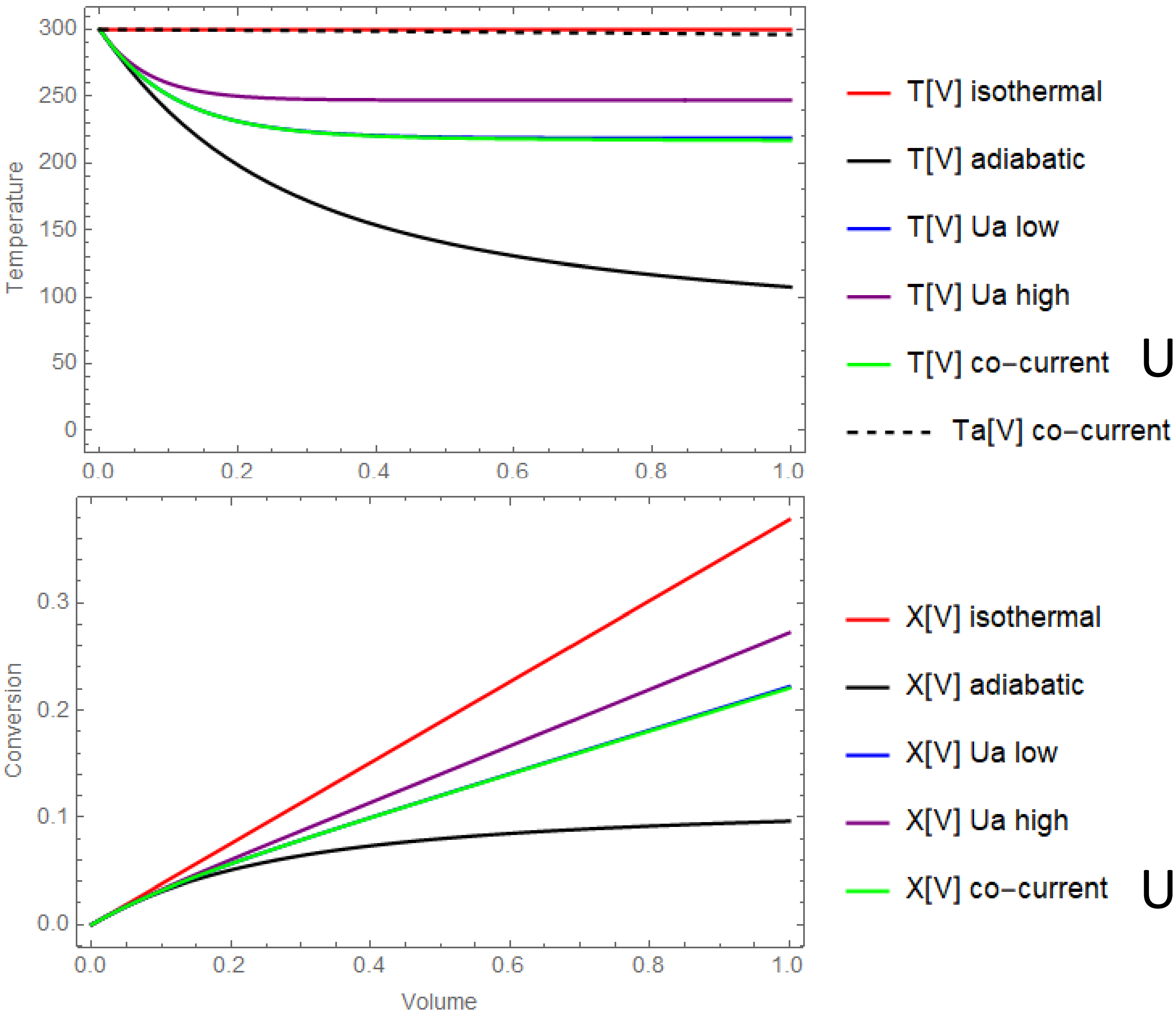
Once (T_a-T) is large enough heat removal = gen.!



Ua low

Ua low

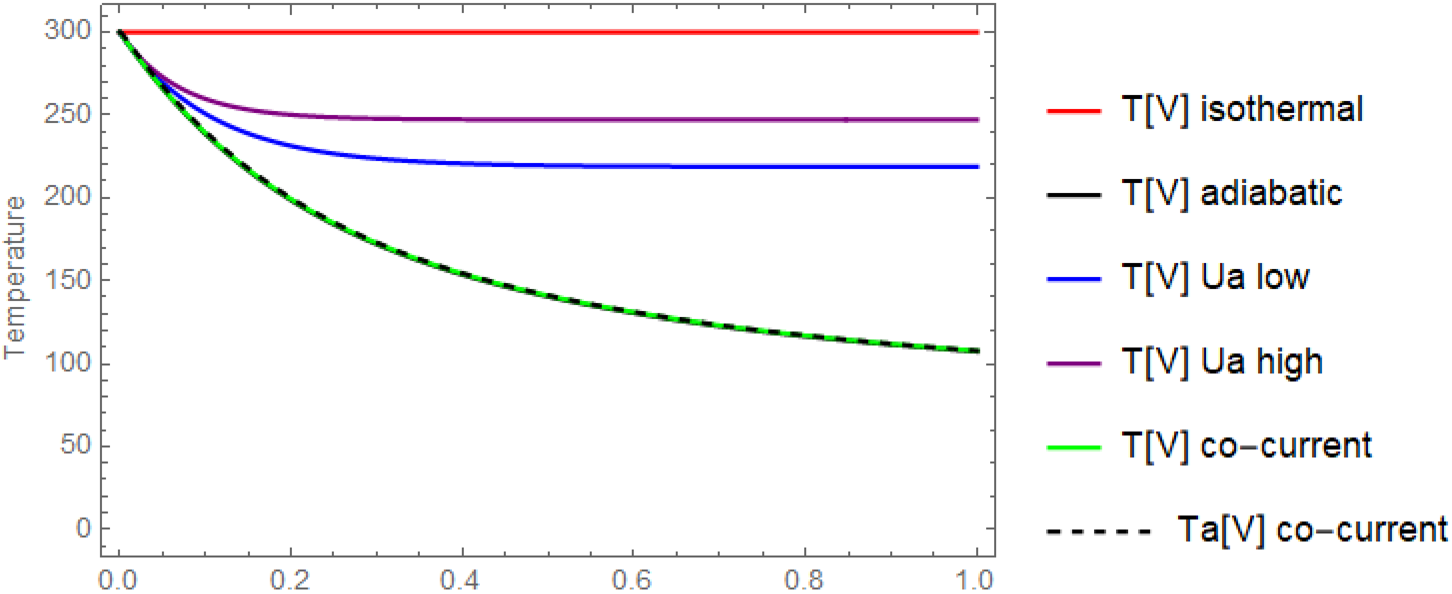
If $\dot{m}_c C_{P,c}$ is very large, T_a remains constant

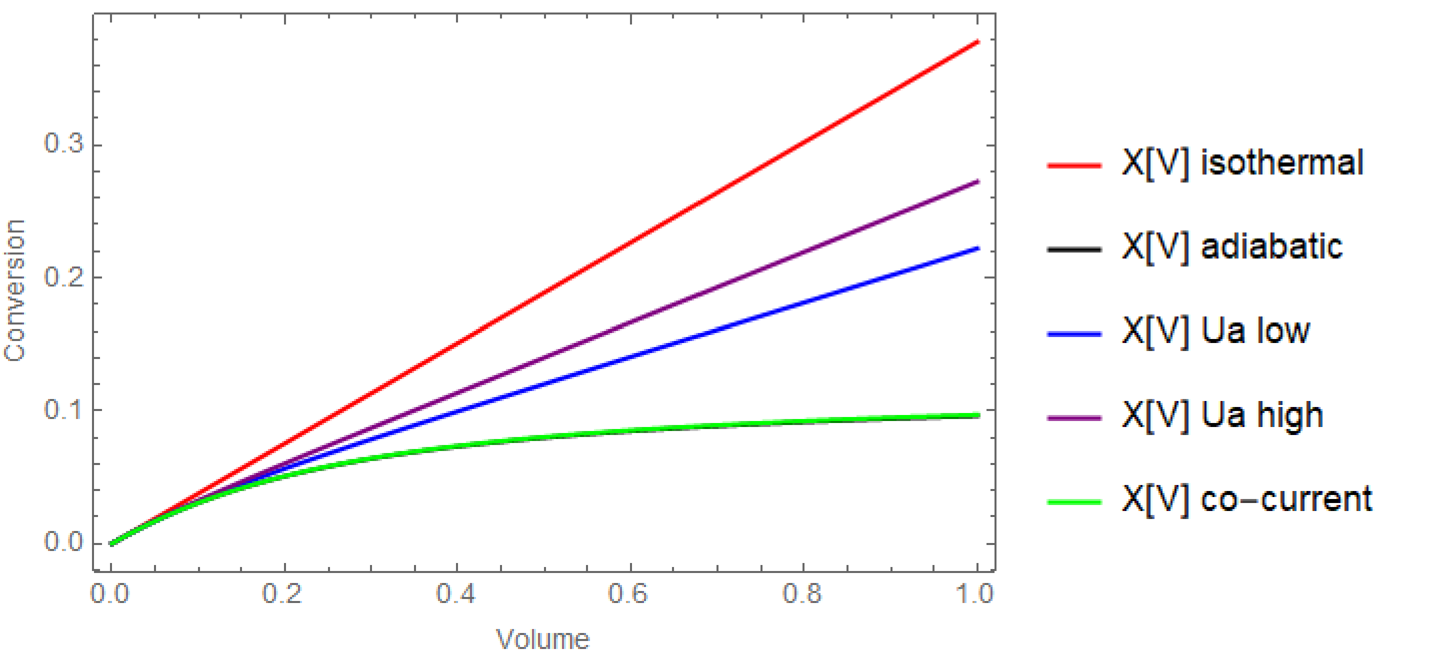


Ua low

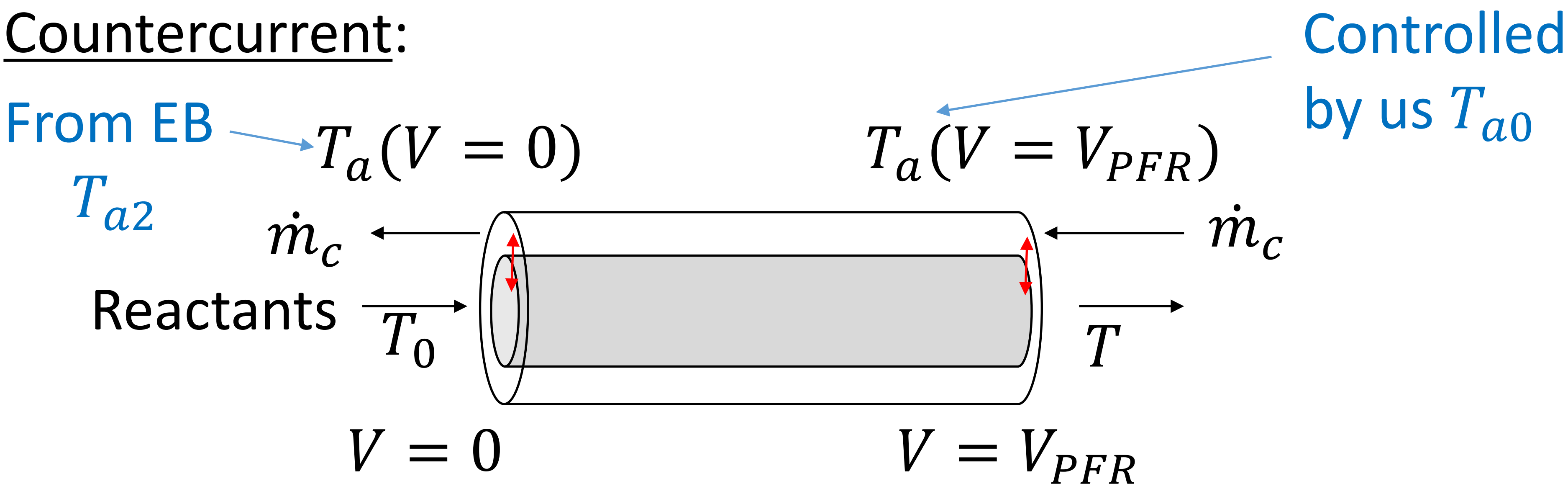
Ua low

If $\dot{m}_c C_{P,c}$ is very small, similar to adiabatic





Countercurrent:



Energy balance on heating fluid for countercurrent:

$$\frac{Ua(T_a - T)}{\dot{m}_c C_{P,c}} = \frac{dT_a}{dV}$$

EB reacting fluid:

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

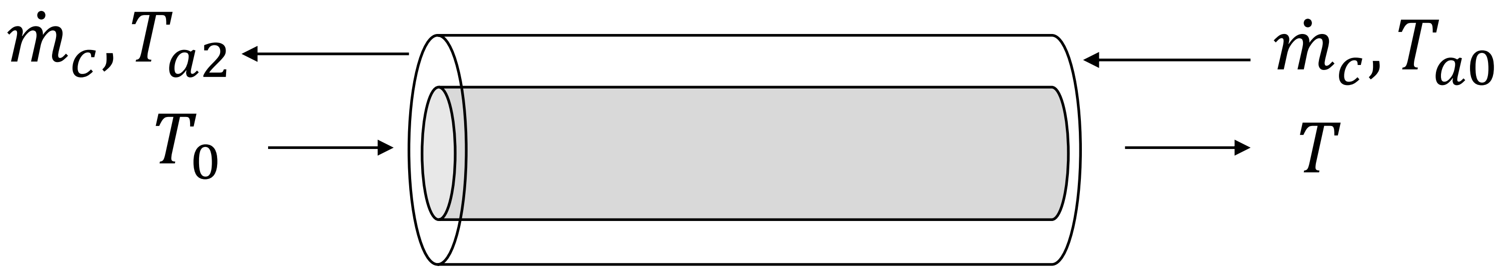
Mole balance:

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

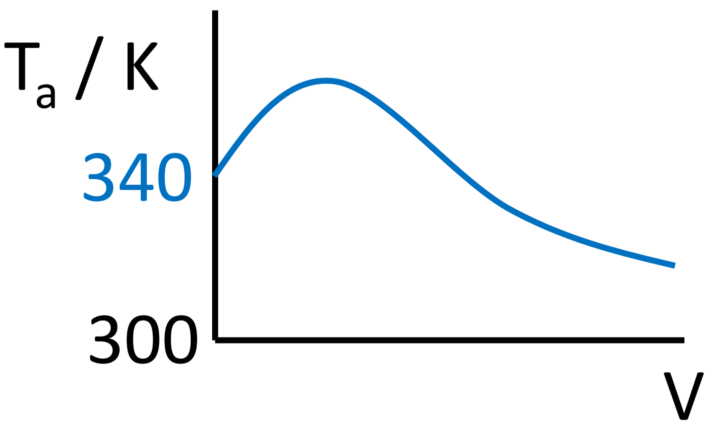
Because you do not know $T_a(V=0) = T_{a2}$ for counter current, it is harder to solve (need to do trial and error).

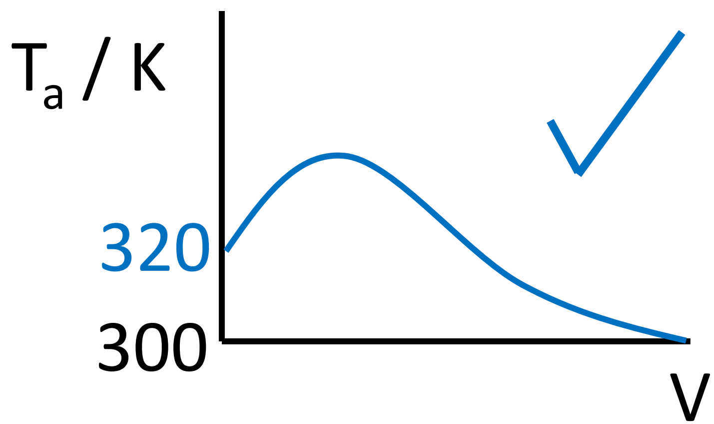
Example:

Countercurrent heat exchanger, exothermic reaction with T_{a0} = 300 K and known value of T_0.



Guess value of T_{a2}, solve for T_{a0}. Start with T_{a2} = 340 K





Guess a new value of T_{a2} (320 K), solve for new T_{a0} to see if it matches