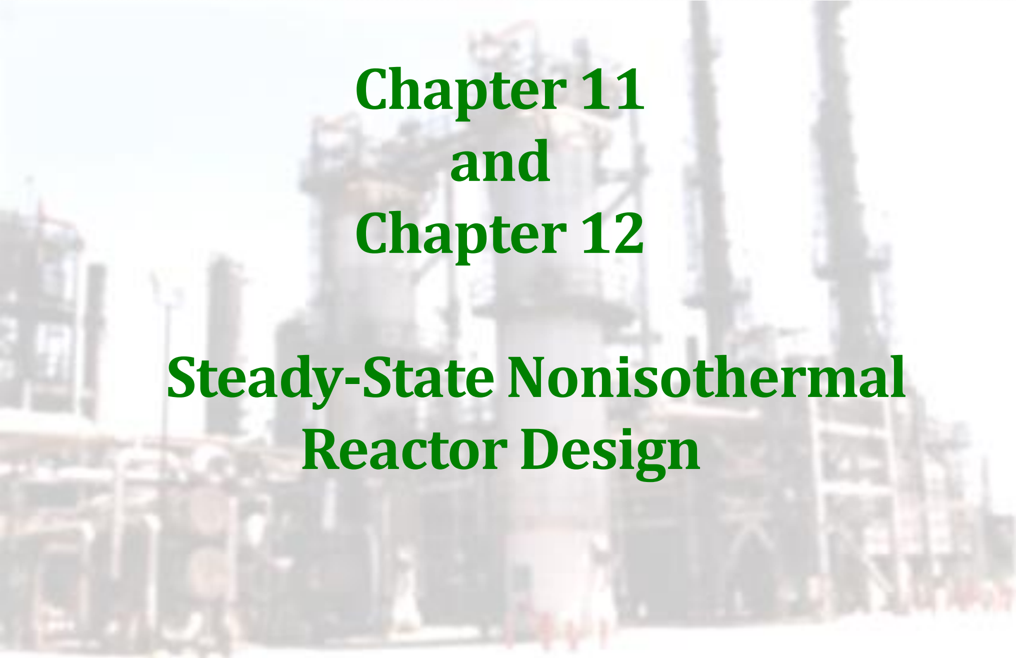


Chapter 11
and
Chapter 12

Steady-State Nonisothermal Reactor Design

> **If you can't stand the heat, get out of the kitchen.**
>
> *Harry S Truman*

THE UNIVERSITY OF JORDAN

Learning Outcomes

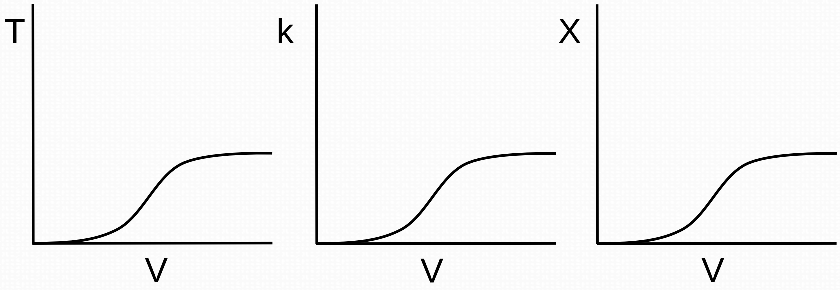
- After completing chapters 11 and 12, you will be able to
  - Describe the algorithm for CSTRs, PFRs, and PBRs that are not operated isothermally.
  - Size adiabatic and nonadiabatic CSTRs, PFRs, and PBRs.
  - Use reactor staging to obtain high conversions for highly exothermic reversible reactions.
  - Carry out an analysis to determine the Multiple Steady States (MSS) in a CSTR along with the ignition and extinction temperatures.

THE UNIVERSITY OF JORDAN

Energy Balance, Rationale and Overview

Let’s calculate the volume necessary to achieve a conversion, X, in a PFR for a first-order, **exothermic** and **adiabatic** reaction.

The temperature profile might look something like this:



Energy Balance, Rationale and Overview

Mole Balance:

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

Rate Law:

$$r_A = -k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] C_A$$

Stoichiometry:

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

Combine:

$$\frac{dX}{dV} = \frac{k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]}{F_{A0}} C_{A0}(1 - X)$$

Energy Balance, Rationale and Overview

$$\frac{dX}{dV} = \frac{k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]}{F_{A0}} C_{A0}(1 - X)$$

We cannot solve this equation because we don't have X either as a function of V or T.

We need another equation. That equation is:

The Energy Balance

User Friendly Equations Relate T and X or F_i

1. Adiabatic CSTR, PFR, Batch or PBR

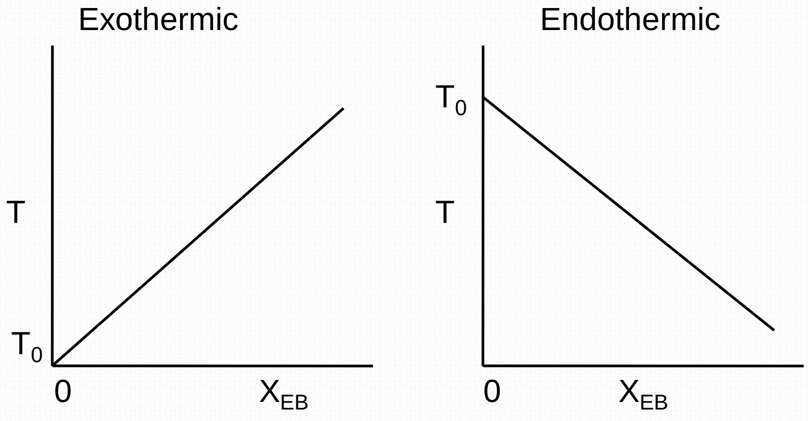
$$\dot{W}_S = 0 \qquad \Delta\hat{C}_P = 0$$

$$X_{EB} = \frac{\sum \Theta_i C_{P_i}(T - T_0)}{-\Delta H^o_{Rx}}$$

$$X = \frac{\sum \Theta_i C_{P_i}(T - T_0)}{-\Delta H_{Rx}}$$

$$T = T_0 + \frac{(-\Delta H^o_{Rx}) X_{EB}}{\sum \Theta_i C_{P_i}}$$

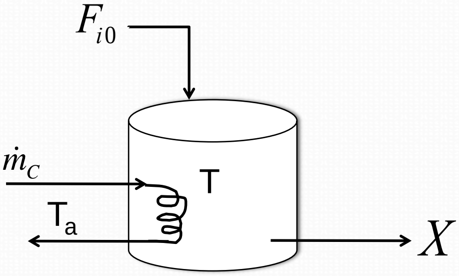
Adiabatic



User Friendly Equations Relate T and X or F_i

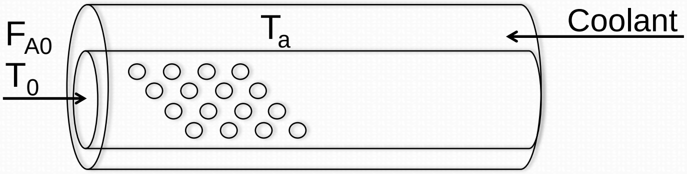
2. CSTR with heat exchange: UA(T_a-T) and a large coolant flow rate

$$X_{EB} = \frac{\left(\frac{UA}{F_{A0}}(T - T_a)\right) + \sum \Theta_i C_{P_i}(T - T_0)}{-\Delta H^o_{Rx}}$$



User Friendly Equations Relate T and X or F_i

3. PFR/PBR with heat exchange



3A. PFR in terms of conversion

$$\frac{dT}{dV} = \frac{\overbrace{r_A \Delta H_{Rx}(T)}^{Q_g} - \overbrace{Ua(T - T_a)}^{Q_r}}{F_{A0}\left(\sum \Theta_i C_{Pi} + \Delta C_p X\right)} = \frac{Q_g - Q_r}{F_{A0}\left(\sum \Theta_i C_{Pi} + \Delta C_p X\right)}$$

User Friendly Equations Relate T and X or F_i

3B. PBR in terms of conversion

$$\frac{dT}{dW}=\frac{r_A'\Delta H_{Rx}(T)-\dfrac{Ua}{\rho_b}(T-T_a)}{F_{A0}\left(\sum\Theta_i C_{Pi}+\Delta C_p X\right)}$$

3C. PBR in terms of molar flow rates

$$\frac{dT}{dW}=\frac{r_A'\Delta H_{Rx}(T)-\dfrac{Ua}{\rho_b}(T-T_a)}{\sum F_i C_{P_i}}$$

User Friendly Equations Relate T and X or F_i

3D. PFR in terms of molar flow rates

$$\frac{dT}{dV}=\frac{r_A\Delta H_{Rx}(T)-Ua(T-T_a)}{\sum F_i C_{P_i}}=\frac{Q_g-Q_r}{\sum F_i C_{P_i}}$$

4. Batch reactor

$$\frac{dT}{dt}=\frac{(r_A V)(\Delta H_{Rx})-UA(T-T_a)}{\sum N_i C_{P_i}}$$

User Friendly Equations Relate T and X or F_i

5. For **Semibatch** or unsteady **CSTR**

$$\frac{dT}{dt}=\frac{\dot{Q}-\dot{W}_S-\sum_{i=1}^{n}F_{i0}\left(C_{P_i}\left(T-T_{i0}\right)+\left[-\Delta H_{Rx}\left(T\right)\right]\left(-r_AV\right)\right)}{\sum_{i=1}^{n}N_iC_{P_i}}$$

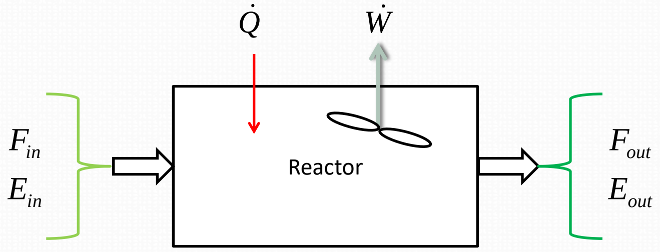
6. For multiple reactions in a **PFR**

$$\frac{dT}{dV}=\frac{\sum_{i=1}^{q}r_{ij}\Delta H_{Rx_{ij}}-Ua\left(T-T_a\right)}{\sum_{j=1}^{m}F_iC_{Pj}}$$

(q reactions and m species)

Let's look where these User Friendly Equations came from.

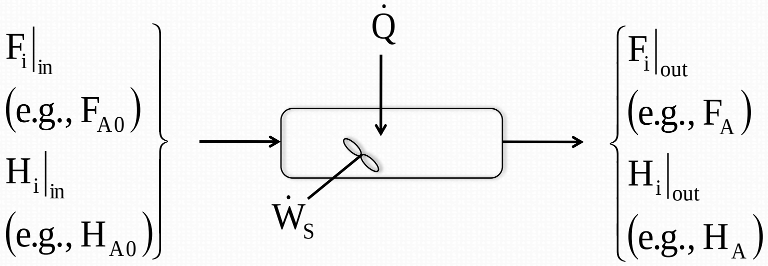
Energy Balance
Reactor with no Spatial Variations



Rate of accumulation of energy ***within*** the system	=	Rate of flow of heat ***to*** the system ***from*** the surroundings	-	Rate of work ***done by*** the system ***on*** the surroundings	+	Rate of energy added to the system by mass flow ***into*** the system	-	Rate of energy leaving system by mass flow ***out*** of the system
$\frac{d\hat{E}_{sys}}{dt}$	=	$\dot{Q}$	-	$\dot{W}$	+	$F_{in}E_{in}$	-	$F_{out}E_{out}$
(J/s)		(J/s)		(J/s)		(J/s)		(J/s)

THE UNIVERSITY OF JORDAN

Energy Balance



Energy Balance on an open system: schematic.

$$\dot{Q}-\dot{W}_S+\sum F_{i0}E_{i0}\big|_{in}-\sum F_iE_i\big|_{out}=\frac{dE_{system}}{dt} \quad (1)$$

THE UNIVERSITY OF JORDAN

NOW, we are going to do to put the above equation into a usable form.

1. Replace U_i by $U_i=H_i-PV_i$
2. Express H_i in terms of heat capacities
3. Express F_i in terms of either conversion or rates of reaction
4. Define ΔH_{Rx}
5. Define ΔC_P
6. Manipulate so that the overall energy balance is in terms of the User Friendly Equations.

Introduction to Heat Effects

- Assumptions:

$$E_i = U_i + \overset{=0}{\cancel{PE_i}} + \overset{=0}{\cancel{KE_i}}$$ Other energies small compared to internal

$$\dot{W} = \text{flow work} + \text{shaft work}$$

$$\text{flow work} = -\sum F_{i0}P_0\tilde{V}_{i0} + \sum F_i P\tilde{V}_i \qquad \left(\tilde{V} = \frac{m^3}{mol}\right)$$

Recall:

$$H_i = U_i + P\tilde{V}_i$$

Introduction to Heat Effects

Substituting for $\dot{W}$

$$\sum F_{i0}U_{i0} - \sum F_i U_i + \dot{Q} - \left[-\sum F_{i0}P_0\tilde{V}_{i0} + \sum F_i P\tilde{V}_i + \dot{W}_S\right] = \frac{dE_{sys}}{dt}$$

$$\sum F_{i0}\left[\overbrace{U_{i0} + P_0\tilde{V}_{i0}}^{H_{i0}}\right] - \sum F_i\left[\overbrace{U_i + P\tilde{V}_i}^{H_i}\right] + \dot{Q} - \dot{W}_S = \frac{dE_{sys}}{dt}$$

$$\boxed{\sum F_{i0}H_{i0} - \sum F_i H_i + \dot{Q} - \dot{W}_S = \frac{dE_{sys}}{dt}}$$

Steady State: $\dot{Q} - \dot{W}_S + \sum F_{i0}H_{i0} - \sum F_i H_i = 0$

Introduction to Heat Effects

General Energy Balance :

$$\boxed{\dot{Q}-\dot{W}_S+\sum F_{i0}H_{i0}-\sum F_iH_i=\frac{dE_{system}}{dt}}$$

For Steady State Operation:

$$\boxed{\dot{Q}-\dot{W}_S+\sum F_{i0}H_{i0}-\sum F_iH_i=0}$$

Introduction to Heat Effects

$$\sum F_{i0}H_{i0}=F_{A0}\sum \Theta_i H_{i0}$$

$$\sum F_iH_i=F_{A0}\sum\left(\Theta_i+\upsilon_i X\right)H_i=F_{A0}\sum \Theta_i H_i+F_{A0}X\overbrace{\sum \upsilon_i H_i}^{\Delta H_{Rx}}$$

$$\dot{Q}-\dot{W}_S+F_{A0}\left(\sum \Theta_i\left(H_{i0}-H_i\right)-X\Delta H_{Rx}\right)=0$$

Introduction to Heat Effects

For No Phase Changes

$$H_i(T) = H_i^0(T_R) + \int_{T_R}^{T} C_{Pi}\,dT$$

Enthalpy of formation at temperature T_R

Constant Heat Capacities

$$\rightarrow H_i(T) = H_i^0(T_R) + C_{Pi}(T - T_R)$$

$$H_i - H_{i0} = C_{Pi}(T - T_0)$$

$$\sum \upsilon_i H_i = \sum \upsilon_i H_i^0 + \sum \upsilon_i C_{Pi}(T - T_R)$$

Heat of reaction at temperature T

Introduction to Heat Effects

$$\sum \upsilon_i H_i = \sum \upsilon_i H_i^0 + \sum \upsilon_i C_{Pi}(T - T_R)$$

$$\Delta H_R(T) = \Delta H_R^o(T_R) + \Delta \hat{C}_P(T - T_R)$$

$$\sum \upsilon_i \hat{C}_{Pi} = \Delta \hat{C}_P = \frac{d}{a}\hat{C}_{PD} + \frac{c}{a}\hat{C}_{PC} - \frac{b}{a}\hat{C}_{PB} - \hat{C}_{PA}$$

Substituting back into the Energy Balance

$$\dot{Q} - \dot{W}_S - F_{A0}X\left[\Delta H_R^o(T_R) + \Delta \hat{C}_P(T - T_R)\right] - F_{A0}\sum \Theta_i \tilde{C}_{Pi}(T - T_{i0}) = 0$$

Introduction to Heat Effects

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

$$\boxed{\Delta H_{Rx} = \frac{d}{a} H_D + \frac{c}{a} H_C - \frac{b}{a} H_B - H_A}$$

$$\boxed{\Delta C_P = \frac{d}{a} C_{PD} + \frac{c}{a} C_{PC} - \frac{b}{a} C_{PB} - C_{PA}}$$

Adiabatic Energy Balance

$$\dot{Q} - \dot{W}_S - F_{A0} X \left[\Delta H_R^o \left(T_R \right) + \Delta \hat{C}_P \left(T - T_R \right) \right] - F_{A0} \sum \Theta_i \tilde{C}_{Pi} \left(T - T_{i0} \right) = 0$$

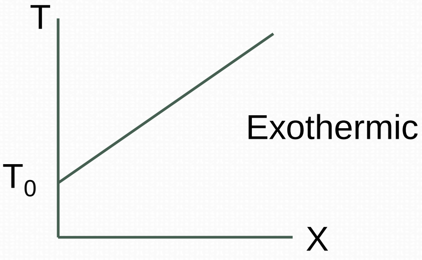
Adiabatic (Q=0) and no Work $(\dot{W}_S = 0)$

$$T = \frac{- X \left[\Delta H_R^o (T_R) - \Delta \hat{C}_P T_R \right] + T_0 \sum \Theta_i \tilde{C}_{Pi}}{\sum \Theta_i \tilde{C}_{Pi} + X \Delta \hat{C}_P}$$

$$\rightarrow X = \frac{\sum_{i=1}^{n} \Theta_i \tilde{C}_{pi} (T - T_{i0})}{-\left[\Delta H_{RX}^{\circ} (T_R) + \Delta \hat{C}_p (T - T_R) \right]}$$

$$if \qquad \Delta C_P = 0$$

$$T = T_0 + \frac{-\Delta H_{Rx}^0 X}{\sum \theta_i C_{Pi}}$$



Example 1: Adiabatic PFR

$$A \leftrightarrow B$$

1) Mole Balance: $\frac{dX}{dV} = -\frac{r_A}{F_{A0}}$

2) Rate Laws:

$$r_A = -k\left[C_A - \frac{C_B}{k_C}\right] \qquad k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

$$\Delta C_P = 0 \qquad k_C = k_{C2} \exp\left[\frac{\Delta H_X^0}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right]$$

Example 1: Adiabatic PFR

$$A \leftrightarrow B$$

3) Stoichiometry: $C_A = C_{A0}(1 - X)\frac{T_0}{T}$

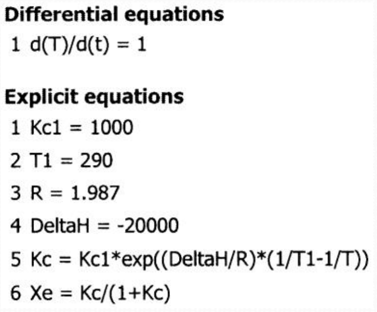
$$C_B = C_{A0} X \frac{T_0}{T}$$

4) Energy Balance

$$T = T_0 + \frac{-\Delta H_{Rx}^0 X}{\sum \theta_i C_{Pi}}$$

First need to calculate the maximum conversion which is at the *adiabatic equilibrium conversion*.

Example 1: Adiabatic PFR



Differential equations

1 d(T)/d(t) = 1

Explicit equations

1 Kc1 = 1000

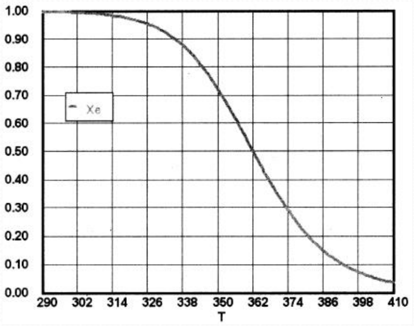
2 T1 = 290

3 R = 1.987

4 DeltaH = -20000

5 Kc = Kc1*exp((DeltaH/R)*(1/T1-1/T))

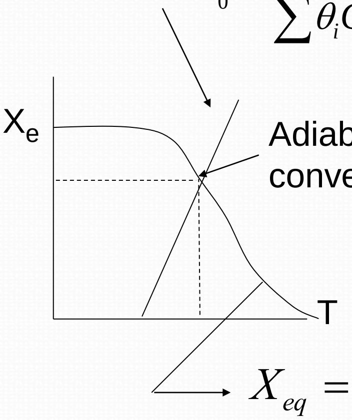
6 Xe = Kc/(1+Kc)



Example 1: Adiabatic PFR

$A \leftrightarrow B$

$$T = T_0 + \frac{-\Delta H_X^0 X}{\sum \theta_i C_{Pi}}$$



Adiabatic equilibrium conversion and temperature

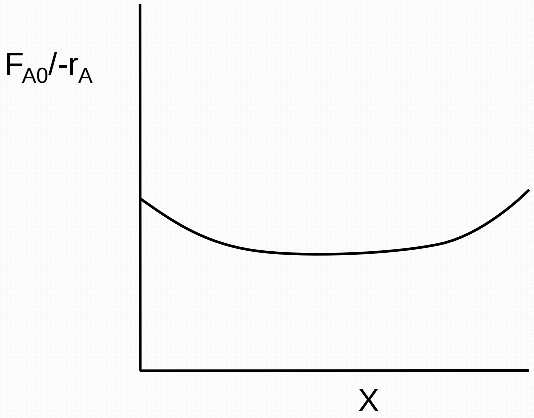
$$X_{eq} = \frac{K_C}{1+K_C}$$

Example 1: Adiabatic PFR

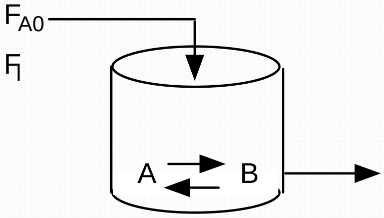
We can now form a table.

Set X ⇨ calculate T ⇨ $-r_A$, and $F_{A0}/-r_A$,

increment X, then plot $F_{A0}/-r_A$ vs. X:



Example 2: Adiabatic CSTR



Elementary liquid phase reaction carried out in a CSTR

The feed consists of both – Inert I and Species A with the ratio of inert I to species A being 2 to 1.

Example 2: Adiabatic CSTR

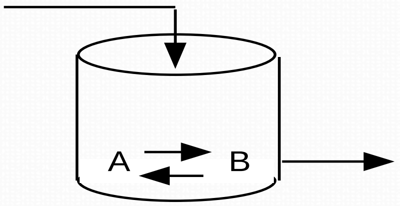
a) Assuming the reaction is irreversible for CSTR, A → B, ($K_C = \infty$) what reactor volume is necessary to achieve 80% conversion?

b) If the exiting temperature to the reactor is 360K, what is the corresponding reactor volume?

c) Make a Levenspiel Plot and then determine the PFR reactor volume for 60% conversion and 95% conversion. Compare with the CSTR volumes at these conversions.

d) Now assume the reaction is reversible, make a plot of the equilibrium conversion as a function of temperature between 290K and 400K.

Example 2: Adiabatic CSTR



$F_{A0} = 5\frac{mol}{min}$

$T_0 = 300\ K$

$F_I = 10\frac{mol}{min}$

$\Delta H_{Rxn} = -20000\frac{cal}{mol\ A}$ (exothermic)

$T = ?$
$X = ?$

1) Mole Balances: $V = \dfrac{F_{A0}X}{-r_A\big|_{exit}}$

Example 2: Adiabatic CSTR

2) Rate Laws:

$$-r_A = k\left[C_A - \frac{C_B}{K_C}\right]$$

$$k = k_1 e^{\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T}\right)}$$

$$K_C = K_{C1}\exp\left[\frac{\Delta H_{Rx}}{R}\left(\frac{1}{T_2}-\frac{1}{T}\right)\right]$$

3) Stoichiometry:

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

$$C_B = C_{A0}X$$

Example 2: Adiabatic CSTR

4) Energy Balance

Adiabatic, $\Delta C_p=0$

$$T = T_0 + \frac{(-\Delta H_{Rx})X}{\sum \Theta_i C_{P_i}} = T_0 + \frac{(-\Delta H_{Rx})X}{C_{P_A} + \Theta_I C_{P_I}}$$

$$T = 300 + \left[\frac{-(-20{,}000)}{164+(2)(18)}\right]X = 300 + \frac{20{,}000}{164+36}X$$

$$\boxed{T = 300 + 100\ X}$$

Example 2: Adiabatic CSTR

Irreversible for Parts (a) through (c)

$$-r_A = kC_{A0}(1-X)\,(\text{i.e., } K_C = \infty)$$

(a) Given X = 0.8, find T and V

$$\begin{tikzcd}
\text{Given } X \arrow[r, "Calc"] & T \arrow[r, "Calc"] \arrow[d] & k \arrow[r, "Calc"] & -r_A \arrow[r, "Calc"] & V \\
 & Calc\ \ K_C \arrow[urr] & & &
\end{tikzcd}$$

(if reversible)

Example 2: Adiabatic CSTR

Given X, Calculate T and V

$$V = \frac{F_{A0}X}{-r_A\big|_{exit}} = \frac{F_{A0}X}{kC_{A0}(1-X)}$$

$$T = 300 + 100(0.8) = 380\text{K}$$

$$k = 0.1\exp\frac{10{,}000}{1.989}\left[\frac{1}{298} - \frac{1}{380}\right] = 3.81$$

$$V = \frac{F_{A0}X}{-r_A} = \frac{(5)(0.8)}{(3.81)(2)(1-0.8)} = 2.82\,\text{dm}^3$$

Example 2: Adiabatic CSTR

(b) Given T = 360 K, Calculate X and V

$$\begin{tikzcd}
\text{Given } X \arrow[r, "\text{Calc}"] & T \arrow[r, "\text{Calc}"] \arrow[d] & k \arrow[r, "\text{Calc}"] & -r_A \arrow[r, "\text{Calc}"] & V \\
& \text{Calc } K_C \arrow[ru] & & &
\end{tikzcd}$$

(if reversible)

$$-r_A = kC_{A0}(1-X)\ \text{(Irreversible)}$$

$$T = 360K$$

$$X = \frac{T-300}{100} = 0.6$$

$$k = 1.83\,\text{min}^{-1}$$

$$V = \frac{(5)(0.6)}{(1.83)(2)(0.4)} = 2.05\,dm^3$$

Example 2: Adiabatic CSTR

(c) Levenspiel Plot

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

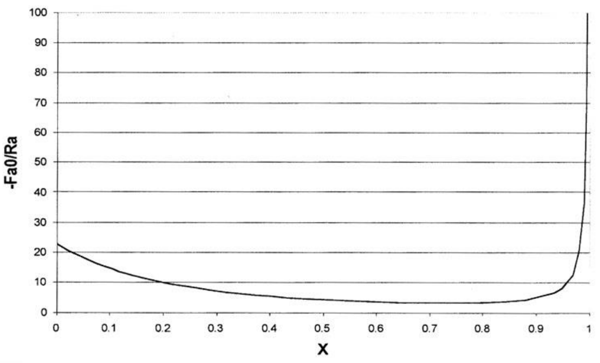
$$T = 300 + 100X$$

$$\text{Choose } X \xrightarrow{Calc} T \xrightarrow{Calc} k \xrightarrow{Calc} -r_A \xrightarrow{Calc} \frac{F_{A0}}{-r_A}$$

Example 2: Adiabatic CSTR

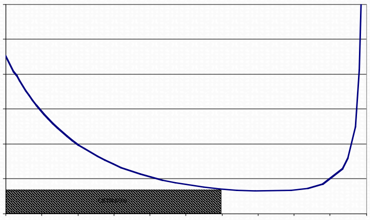
(c) Levenspiel Plot

X	T(K)	$\frac{F_{A0}}{-r_A}\left(dm^3\right)$
0	300	25
0.1	310	14.4
0.2	320	9.95
0.4	340	5.15
0.6	360	3.42
0.8	380	3.87
0.9	390	4.16
0.95	395	8.0

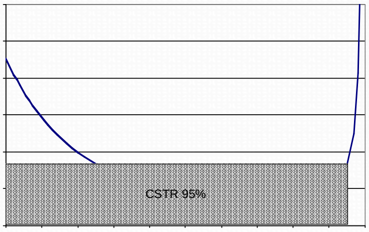


Example 2: Adiabatic CSTR

CSTR X = 0.6 T = 360 K

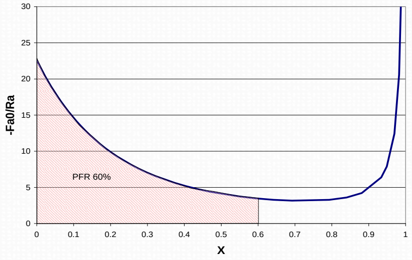


CSTR X = 0.95 T = 395 K

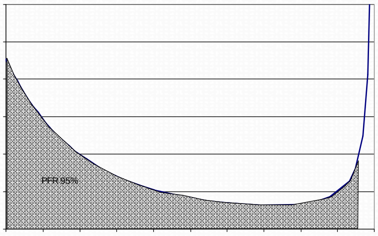


Example 2: Adiabatic **CSTR**

PFR X = 0.6



PFR X = 0.95



Example 2: Adiabatic **CSTR** Summary

CSTR	X = 0.6	T = 360	V = 2.05 dm^3
PFR	X = 0.6	T_{exit} = 360	V = 5.28 dm^3
CSTR	X = 0.95	T = 395	V = 7.59 dm^3
PFR	X = 0.95	T_{exit} = 395	V = 6.62 dm^3

PFR with Heat Effects

Energy Balance in terms of Enthalpy

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

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

$$\frac{-d\sum F_i H_i}{dV} = -\left[\sum F_i \frac{dH_i}{dV} + \sum H_i \frac{dF_i}{dV}\right]$$

PFR with Heat Effects

$$\frac{dF_i}{dV} = r_i = \upsilon_i(-r_A)$$

$$H_i = H_i^0 + C_{Pi}(T - T_R)$$

$$\frac{\mathrm{dH_i}}{\mathrm{dV}} = \mathrm{C_{Pi}}\frac{\mathrm{dT}}{\mathrm{dV}}$$

$$\frac{-d\sum F_i H_i}{dV} = -\left[\sum F_i C_{Pi}\frac{dT}{dV} + \sum H_i \upsilon_i(-r_A)\right]$$

$$\sum \upsilon_i H_i = \Delta H_{Rx}$$

PFR with Heat Effects

$$-\left[\sum C_{Pi} F_i \frac{dT}{dV} + \Delta H_{Rx}(-r_A)\right] + Ua(T_a - T) = 0$$

$$\sum F_i C_{Pi} \frac{dT}{dV} = \Delta H_{Rx} r_A - Ua(T - T_a)$$

$$\boxed{\frac{dT}{dV} = \frac{(-\Delta H_{Rx})(-r_A) - Ua(T - T_a)}{\sum F_i C_{Pi}}}$$

Heat generated

Heat removed

$$\frac{dT}{dV} = \frac{(-r_A)(-\Delta H_{Rx}) - Ua(T - T_a)}{\sum F_i C_{P_i}}$$

$$\sum F_i C_{P_i} = F_{A0}\left[\sum \Theta_i C_{P_i} + \Delta C_P X\right], \text{ if } \Delta C_P = 0 \text{ then}$$

$$\frac{dT}{dV} = \frac{(-r_A)(-\Delta H_{Rx}) - Ua(T - T_a)}{F_{A0} \sum \Theta_i C_{P_i}}$$

Need to determine T_a

User Friendly Equations

A. Constant T_a e.g., $T_a = 300K$

B. Variable T_a Co-Current

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}C_{P_{cool}}}, @V = 0 \quad T_a = T_{ao}$$

C. Variable T_a Counter Current

$$\frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m}C_{P_{cool}}}, @V = 0 \quad T_a = ? \ \text{Guess}$$

Guess T_a at V = 0 to match $T_{a0} = T_{a0}$ at exit, i.e., $V = V_f$

Heat Exchanger Energy Balance Variable T_a Co-current

Coolant Balance:

In - Out + Heat Added = 0

$$\dot{m}_C H_C\big|_V - \dot{m}_C H_C\big|_{V+\Delta V} + Ua\Delta V(T - T_a) = 0$$

$$-\dot{m}_C \frac{dH_C}{dV} + Ua(T - T_a) = 0$$

$$H_C = H_C^0 + C_{PC}(T_a - T_r) \Rightarrow \frac{dH_C}{dV} = C_{PC}\frac{dT_a}{dV}$$

$$\boxed{\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_C C_{PC}}, @V = 0 \quad T_a = T_{a0}}$$

Heat Exchanger Energy Balance Variable T_a Counter-current

In - Out + Heat Added = 0

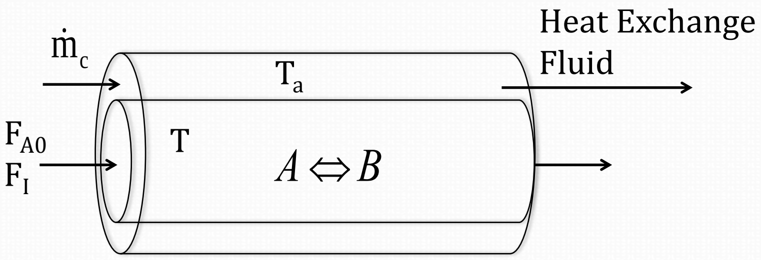
$$\dot{m}_C H_C\big|_{V+\Delta V} - \dot{m}_C H_C\big|_V + Ua\Delta V\left(T - T_a\right) = 0$$

$$\dot{m}_C \frac{dH_C}{dV} + Ua\left(T - T_a\right) = 0$$

$$\boxed{\frac{dT_a}{dV} = \frac{Ua\left(T_a - T\right)}{\dot{m}_C C_{PC}}}$$

Heat Exchanger
Example – Constant T_a

Elementary liquid phase reaction carried out in a PFR



The feed consists of both inerts I and species A with the ratio of inerts to the species A being 2 to 1.

THE UNIVERSITY OF JORDAN

Heat Exchanger

Example – Constant T_a

1) Mole Balance: (1) $$\frac{dX}{dV} = -r_A / F_{A0}$$

2) Rate Laws: (2) $$r_A = -k\left[C_A - \frac{C_B}{K_C}\right]$$

(3) $$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

(4) $$K_C = K_{C2} \exp\left[\frac{\Delta H_{Rx}}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right]$$

THE UNIVERSITY OF JORDAN

Heat Exchanger

Example – Constant T_a

3) Stoichiometry:

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

$$C_B = C_{A0} X$$

4) Heat Effects:

$$\frac{dT}{dV} = \frac{(\Delta H_R)(-r_A) - Ua(T - T_a)}{F_{A0}\sum \theta_i C_{Pi}}$$

$$(\Delta C_P = 0)$$

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

$$\sum \theta_i C_{Pi} = C_{PA} + \theta_I C_{PI}$$

Heat Exchanger

Example – Constant T_a

Parameters: $\Delta H_R,\ E,\ R,\ T_1,\ T_2,$

$k_1,\ k_{C2},\ Ua,\ T_a,\ F_{A0},$

$C_{A0},\ C_{PA},\ C_{PI},\ \theta_I,$

$rate = -r_A$

Derive the user-friendly Energy Balance for a PBR

$$\int_0^W \frac{Ua}{\rho_B}(T_a - T)dW + \sum F_{i0}H_{i0} - \sum F_i H_i = 0$$

Differentiating with respect to W:

$$\frac{Ua}{\rho_B}(T_a - T) + 0 - \sum \frac{dF_i}{dW}H_i - \sum F_i \frac{dH_i}{dW} = 0$$

THE UNIVERSITY OF JORDAN

Derive the user-friendly Energy Balance for a PBR

Mole Balance on species i:

$$\frac{dF_i}{dW} = r_i' = \upsilon_i\left(-r_A'\right)$$

Enthalpy for species i:

$$H_i = H_i^{o}(T_R) + \int_{T_R}^{T} C_{Pi}\,dT$$

THE UNIVERSITY OF JORDAN

Derive the user-friendly Energy Balance for a PBR

Differentiating with respect to W:

$$\frac{dH_i}{dW} = 0 + C_{Pi}\frac{dT}{dW}$$

$$\frac{Ua}{\rho_B}(T_a - T) + r_A'\sum \upsilon_i H_i - \sum F_i C_{Pi}\frac{dT}{dW} = 0$$

Derive the user-friendly Energy Balance for a PBR

$$\frac{Ua}{\rho_B}(T_a - T) + r_A{}' \sum \upsilon_i H_i - \sum F_i C_{Pi} \frac{dT}{dW} = 0$$

$$\sum \upsilon_i H_i = \Delta H_R(T)$$

$$F_i = F_{A0}(\Theta_i + \upsilon_i X)$$

Final Form of the Differential Equations in Terms of Conversion:

A:

$$\boxed{\frac{dT}{dW} = \frac{\frac{Ua}{\rho_B}(T_a - T) + r_A{}' \Delta H_R(T)}{F_{A0}\left[\sum \Theta_i \tilde{C}_{Pi} + \Delta \hat{C}_P X\right]} = f(X,T)}$$

Derive the user-friendly Energy Balance for a PBR

Final form of terms of Molar Flow Rate:

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_B}(T_a - T) + r_A{}' \Delta H}{F_i C_{Pi}}$$

B:

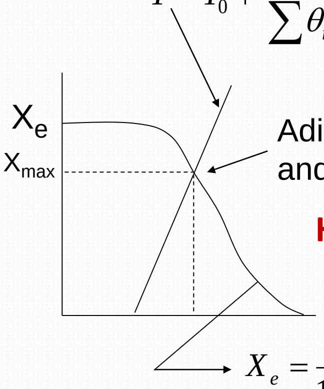
$$\boxed{\frac{dX}{dW} = \frac{-r_A{}'}{F_{A0}} = g(X,T)}$$

Reversible Reactions

Gas Phase Heat Effects

Adiabatic and ΔC_P=0

$$T = T_0 + \frac{-\Delta H_X^0 X}{\sum \theta_i C_{Pi}}$$

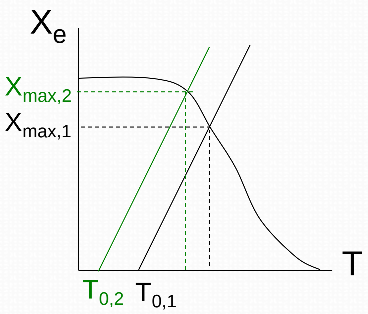


Adiabatic equilibrium conversion and temperature

$$X_e = \frac{K_C}{1+K_C}$$

How to increase the conversion?

How to increase the conversion X_{max}?



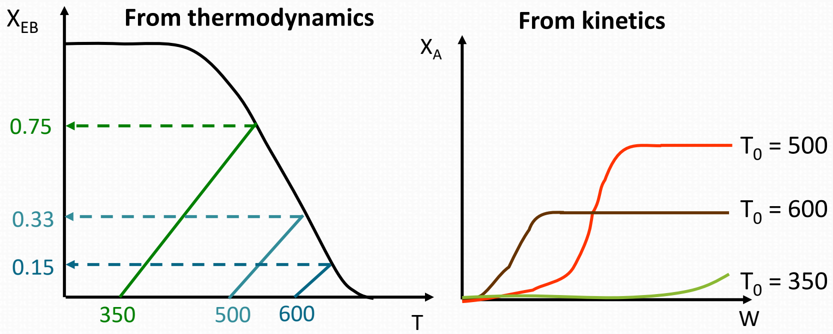
1. By decreasing the feed temperature from $T_{0,1}$ to $T_{0,2}$, the maximum conversion will increase from $X_{max,1}$ to $X_{max,2}$

But, does decreasing T_0 always increase X_{max}?

Optimum Feed Temperature

For a reversible and exothermic reaction, the feed temperature should be optimized to maximize the conversion

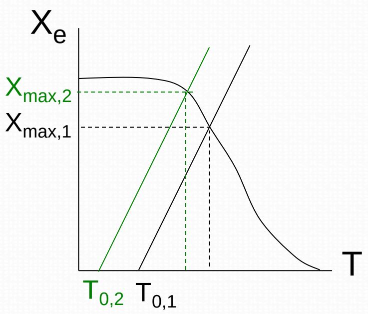
High T_0: reaction reaches equilibrium fast, but X_A is low



Low T_0 would give high $X_{A,e}$ but the specific reaction rate k is so small that most of the reactant passes through the reactor without reacting (never reach $X_{A,e}$)

There is an optimum inlet temperature!

How to increase the conversion X_{max}?

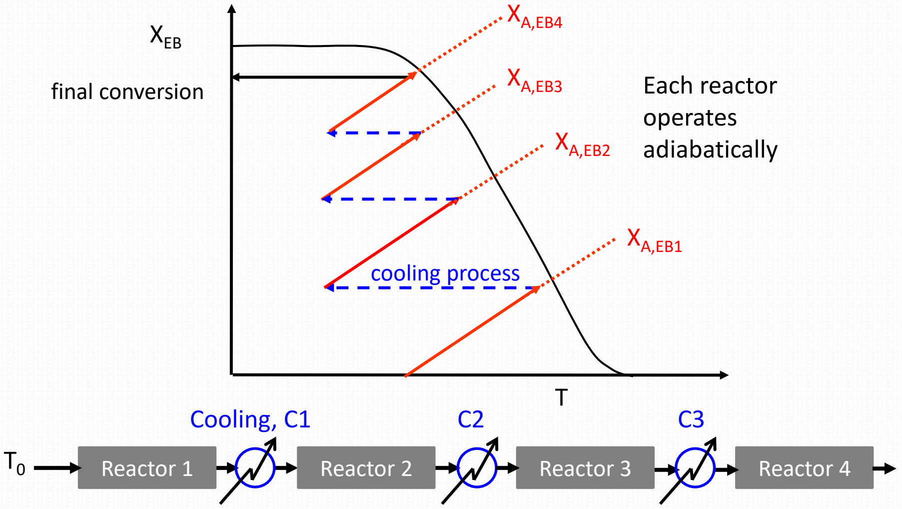


1. By decreasing the feed temperature from $T_{0,1}$ to $T_{0,2}$, the maximum conversion will increase from $X_{max,1}$ to $X_{max,2}$

What else can we do?

Reactor staging with interstage Cooling/Heating

a) With interstage cooling:



Each reactor operates adiabatically

Endothermic reactions are similar, but with heating instead of cooling

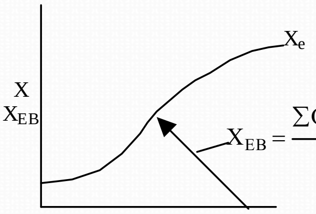
Endothermic Reaction

b) With interstage heating:

PFR $A \Leftrightarrow B$

$$\frac{dX}{dV} = \frac{k\left(1-\left(1+\frac{1}{K_C}\right)X\right)}{\upsilon_0} \quad , \quad X_e = \frac{K_C}{1+K_C}$$

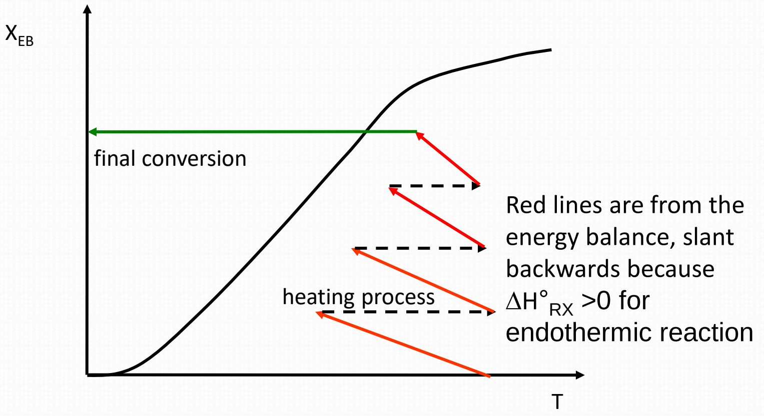
$$T = T_0 + \frac{(-\Delta H_{Rx})X}{C_{P_A} + \Theta_I C_{P_I}}$$



$$X_{EB} = \frac{\Sigma \Theta_i C_{P_i}(T-T_0)}{-\Delta H_{Rx}} = \frac{C_{P_A} + \Theta_I C_{PI}(T-T_0)}{-\Delta H_{Rx}}$$

Endothermic Reactions with interstage heating

The equilibrium conversion increases with increasing temperature, so use interstage heating to increase the conversion



Red lines are from the energy balance, slant backwards because $\Delta H^\circ_{RX} > 0$ for endothermic reaction

---

Application to CSTR

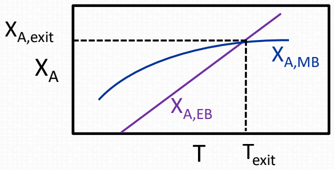
Case 1: Given F_{A0}, C_{A0}, A, E, C_{pi}, H°_i, and X (or T), calculate T (or X) & V

a) Solve EB for T at the exit ($T_{exit} = T_{inside\ reactor}$)
b) Calculate $k = Ae^{-E/RT}$ where T was calculated in step a
c) Plug the k calculated in step b into the design equation to calculate V_{CSTR}

Case 2: Given F_{A0}, C_{A0}, A, E, C_{pi}, H°_i, and V, calculate T & X

a) Solve EB for T as a function of X
b) Solve CSTR design equation for X as a function of T (plug in $k = Ae^{-E/RT}$)
c) Plot X_{EB} vs. T & X_{MB} vs. T on the same graph. The intersection of these 2 lines is the conditions (T and X) that satisfies the energy & mass balance

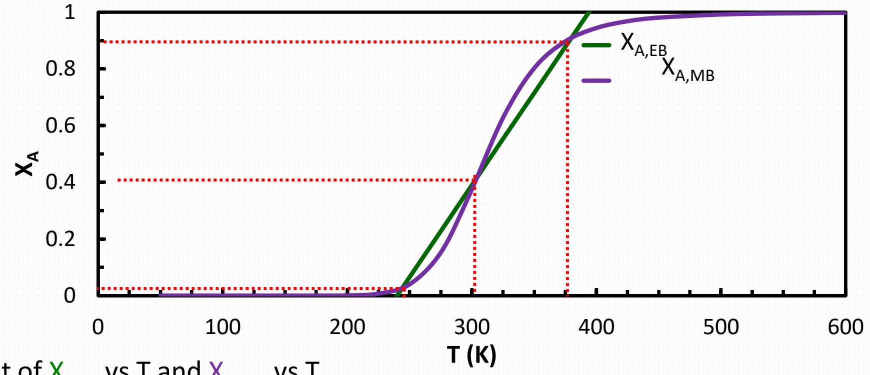
X_{EB} = conversion determined from the EB equation
X_{MB} = conversion determined using the design equation



Intersection is T and X that satisfies both equations

THE UNIVERSITY OF JORDAN

Multiple Steady States in CSTR



- Plot of $X_{A,EB}$ vs T and $X_{A,MB}$ vs T
- Intersections are the T and X_A that satisfy both the mass balance and energy balance
- Multiple sets of conditions are possible for the same reaction in the same reactor with the same inlet conditions!

Reactor must operate near one of these steady states- this requires knowledge of their stability!

THE UNIVERSITY OF JORDAN

Consider a jacketed CSTR with constant heat capacity, negligible shaft work, ΔC_P=0, first order kinetics, all feeds at the same temperature (T_{i0}=T_0), constant T_a in jacket, and an overall heat transfer coefficient

$$\dot{Q} = UA(T_a - T)$$

$$\text{TEB}: 0 = \dot{Q} - F_{A0}\sum_{i=1}^{n}\Theta_i C_{p,i}[T - T_{i0}] - \Delta H_{RX}(T)F_{A0}X_A$$

Substituting for $\dot{Q} = UA(T_a - T)$ and $\Delta H_{RX}(T) = \Delta H_{RX}^{\circ}(T_R)$ since $\Delta C_P = 0$

$$\rightarrow 0 = UA(T_a - T) - F_{A0}\sum_{i=1}^{n}\Theta_i C_{p,i}[T - T_{i0}] - \Delta H_{RX}^{\circ}(T_R)F_{A0}X_A$$

Bring terms that remove heat to other side of equation:

$$\rightarrow F_{A0}\sum_{i=1}^{n}\Theta_i C_{p,i}[T - T_{i0}] - UA(T_a - T) = -\Delta H_{RX}^{\circ}(T_R)F_{A0}X_A$$

$$\rightarrow \underbrace{\sum_{i=1}^{n}\Theta_i C_{p,i}[T - T_{i0}] - \frac{UA(T_a - T)}{F_{A0}}}_{\text{Heat removed term} \equiv R(T)} = \underbrace{-\Delta H_{RX}^{\circ}(T_R)X_A}_{\text{Heat generated term} \equiv G(T)}$$

A steady-state occurs when R(T) = G(T)

THE UNIVERSITY OF JORDAN

Even More Terms…

$$\overbrace{\sum_{i=1}^{n}\Theta_i C_{p,i}[T-T_{i0}]-\frac{UA(T_a-T)}{F_{A0}}}^{\text{Heat removed term} \equiv R(T)}=\overbrace{-\Delta H_{RX}^{\circ}(T_R)X_A}^{\text{Heat generated term} \equiv G(T)}$$

$$C_{P0}=\sum\Theta_i C_{Pi}$$

$$V=\frac{F_{A0}X_A}{-r_A}\rightarrow\frac{-r_A V}{F_{A0}}=X_A$$

Substitute $\rightarrow C_{p0}[T-T_{i0}]-\frac{UA(T_a-T)}{F_{A0}}=-\Delta H_{RX}^{\circ}(T_R)\left(\frac{-r_A V}{F_{A0}}\right)$

More substitutions: $\kappa=\frac{UA}{C_{p0}F_{A0}}$ $\quad T_c=\frac{T_0F_{A0}C_{p0}+UAT_a}{UA+C_{p0}F_{A0}}=\frac{\kappa T_a+T_0}{1+\kappa}$

$$\Delta H_{RX}^{\circ}=\Delta H_{RX}^{\circ}(T_R)$$

$$\rightarrow C_{p0}(1+\kappa)[T-T_C]=-\Delta H_{RX}^{\circ}\left(\frac{-r_A V}{F_{A0}}\right)$$

Heat removed: $R(T)=C_{p0}(1+\kappa)[T-T_C]$

Heat generated: $G(T)=-\Delta H_{RX}^{\circ}\left(\frac{-r_A V}{F_{A0}}\right)$

THE UNIVERSITY OF JORDAN

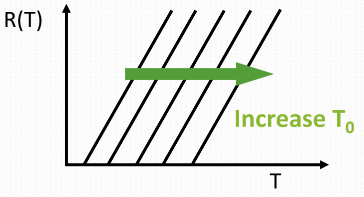
Heat Removal Term and T_0

$$\overbrace{C_{p0}(1+\kappa)[T-T_C]}^{\text{Heat removed: } R(T)}=\overbrace{-\Delta H_{RX}^{\circ}\left(\frac{-r_A V}{F_{A0}}\right)}^{\text{Heat generated } G(T)}$$

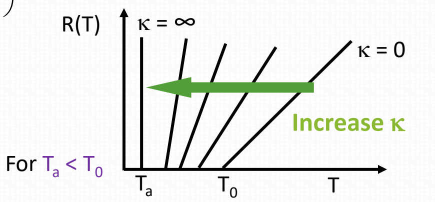
$$\kappa=UA/C_{p0}F_{A0}$$

$$T_c=\frac{\kappa T_a+T_0}{1+\kappa}$$

R(T) line has slope of $C_{P0}(1+\kappa)$



When T_0 increases, slope stays same & line shifts to right



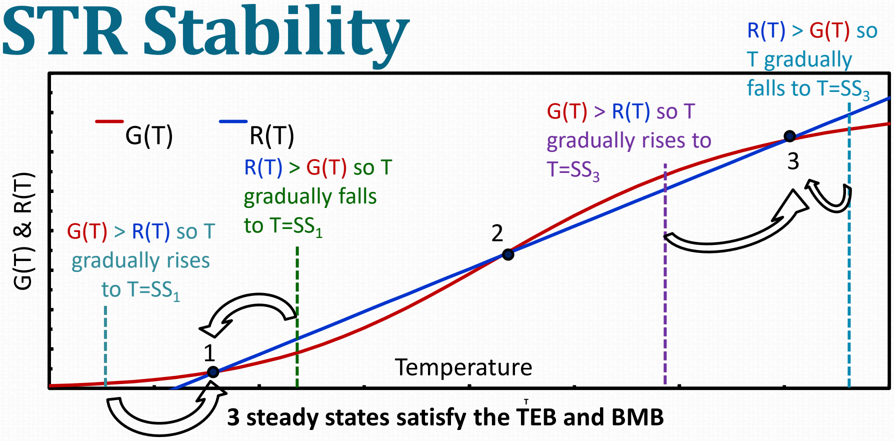
When κ increases from lowering F_{A0} or increasing heat exchange, slope and x-intercept moves

$T_a<T_0$: x-intercept shifts left as κ↑

$T_a>T_0$: x-intercept shifts right as κ↑

κ=0, then $T_C=T_0$ κ=∞, then $T_C=T_a$

CSTR Stability



R(T) > G(T) so T gradually falls to T=SS$_3$

G(T) > R(T) so T gradually rises to T=SS$_3$

R(T) > G(T) so T gradually falls to T=SS$_1$

G(T) > R(T) so T gradually rises to T=SS$_1$

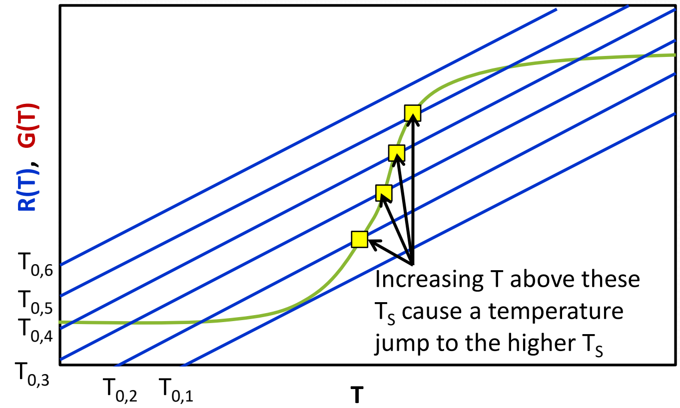
3 steady states satisfy the TEB and BMB

- Suppose a disturbance causes the reactor T to drift to a T between SS$_1$ & SS$_2$
- Suppose a disturbance causes the reactor T to drift to a T between SS$_2$ & SS$_3$
- Suppose a disturbance causes the reactor T to drop below SS$_1$
- Suppose a disturbance causes the reactor T to rise above SS$_3$

SS$_1$ and SS$_3$ are locally stable (return to them after temp pulse)
SS$_2$ is an unstable- do not return to SS$_2$ if there is a temp pulse

---

Multiple Steady States and T$_0$

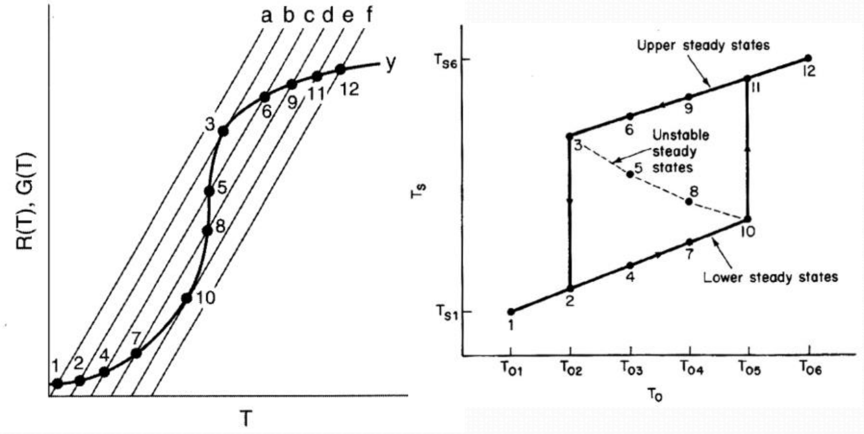


Increasing T above these T$_S$ cause a temperature jump to the higher T$_S$

- Changing the inlet T will shift the steady state temperature (T$_S$)
- Notice that the number of steady state temperatures depends on T$_0$

THE UNIVERSITY OF JORDAN

Multiple Steady States (MSS)



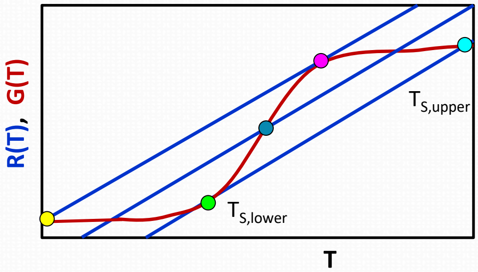
Finding Multiple Steady States with T_0 varied

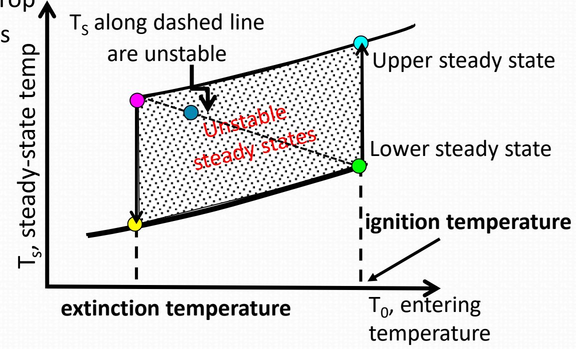
THE UNIVERSITY OF JORDAN

Temperature Ignition-Extinction Curve

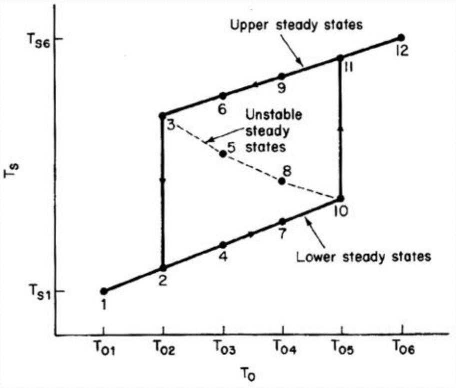
- Slight increase in T above $T_{S,green}$ causes reactor T to jump to $T_{S,cyan}$
- Ignition temp: T where jump from $T_{S,lower}$ to $T_{S,upper}$ occurs
- Slight decrease in T below $T_{S,magenta}$ causes reactor T to drop to $T_{S,yellow}$
- Extinction temp: T where drop from $T_{S,upper}$ to $T_{S,lower}$ occurs

Plot T_S vs T_0



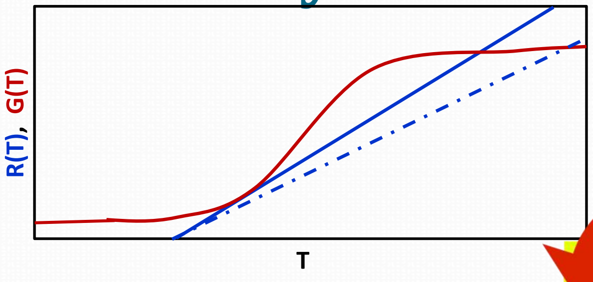


Multiple Steady States (MSS)



Temperature ignition-extinction curve

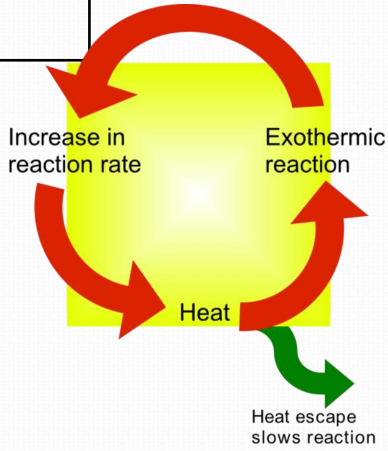
Runaway Reaction



Ignition temperature is very important: once T_0 exceeds $T_{ignition}$, transition to the upper steady state will occur

- undesirable
- dangerous

Runaway reaction
R(T) only intersects with upper steady state



Increase in reaction rate

Exothermic reaction

Heat

Heat escape slows reaction