

## Lecture # 26 CHE331A

### Multiple steady states in a CSTR

Goutam Deo

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- ❑ Energy balance in ideal reactors
- ❑ Adiabatic flow reactors
- ❑ Non-adiabatic PFR
- ❑ Reversible reactions in adiabatic reactors
- ❑ CSTR with heat effects



# Design and analysis of the CSTR with heat effects

►  $C_{P,0} \left( \frac{UA}{F_{A0}C_{P,0}} \right) T_a + C_{P,0}T_0 - C_{P,0} \left( \frac{UA}{F_{A0}C_{P,0}} + 1 \right) T - X\Delta h_{Rxn}(T) = 0$

► Define two parameters:

$$\kappa = \left( \frac{UA}{F_{A0}C_{P,0}} \right) \quad \text{and} \quad T_c = \frac{\kappa T_a + T_0}{1 + \kappa}$$

► Then,  $-X\Delta h_{Rxn}(T) = C_{P,0}(1 + \kappa)(T - T_c)$

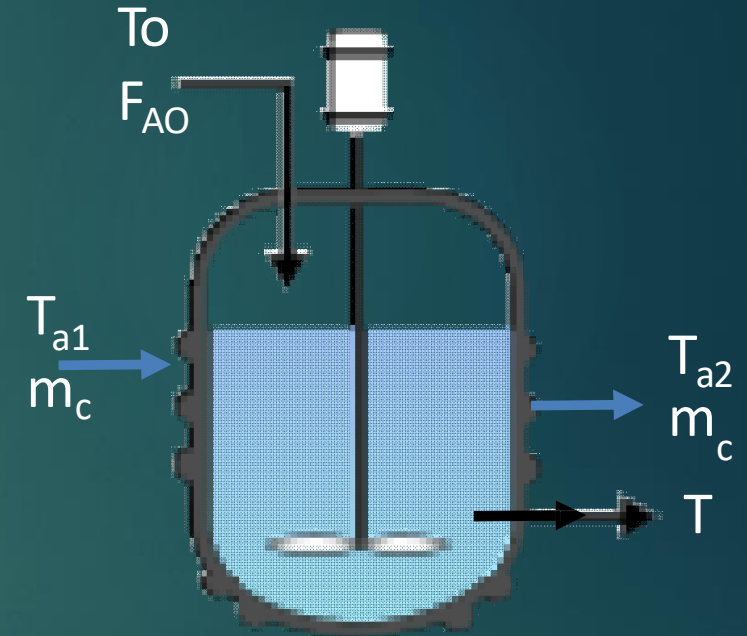
► Thus, we can find  $X$  or  $T$  from the above

$$X_{EB} = \frac{C_{P,0}(1 + \kappa)(T - T_c)}{-\Delta h_{Rxn}(T)}$$

OR

$$T = T_c + \frac{-X\Delta h_{Rxn}(T)}{C_{P,0}(1 + \kappa)}$$

► The mol balance equation is given by:  $V = \frac{F_{A0}X}{-r_A(X,T)}$



# Designing/Analyzing a CSTR with known $X$ (or $V$ ) so that we can determine $V$ and $T$ (or $X$ and $T$ )

## Case I

$X$  known to determine  $V$  and  $T$

- Calculate  $T$  from Energy Balance (EB)

$$\circ T = T_C + \frac{-X\Delta h_{Rxn}(T)}{C_{P,0}(1+\kappa)} \quad \text{OR}$$

$$\circ T = \frac{-F_{A0}X\Delta h_{Rxn}(T) + UA T_a + F_{A0}C_{P,0}T_0}{UA + F_{A0}C_{P,0}}$$

- Calculate  $k$  from the value of  $T$  determined
- Calculate  $V$  from the mol balance (MB) equation  $V = \frac{F_{A0}X}{-r_A(X,T)}$

## Case III

$V$  known to determine  $X$  and  $T$

- MB and EB equations are to be solved simultaneously ( $X_{EB}$  and  $X_{MB}$  vs  $T$ )

- For example, MB equation

$$\circ X_{MB} = \frac{k\tau}{1+k\tau} = \frac{\tau A \exp\left(-\frac{E}{RT}\right)}{1 + \tau A \exp\left(-\frac{E}{RT}\right)} \quad (1^{\text{st}} \text{ order})$$

- And, EB equation

$$\circ X_{EB} = \frac{UA(T-T_a) + F_{A0} \sum [\theta_i C_{P,i}(T-T_0)]}{F_{A0}(-\Delta h_{Rxn}(T))}$$



# Knowing V and calculating X and T

► Production of Propylene glycol in CSTR,  $V = 40.1 \text{ ft}^3$  and  $\dot{v}_0 = 326.3 \frac{\text{ft}^3}{\text{h}}$

► MB equation for CSTR:  $X_{MB} = \frac{\tau A \exp\left(-\frac{E}{RT}\right)}{1 + \tau A \exp\left(-\frac{E}{RT}\right)} = \frac{(2.084 \cdot 10^{12}) \exp(-16306/T)}{1 + (2.084 \cdot 10^{12}) \exp(-16306/T)}$

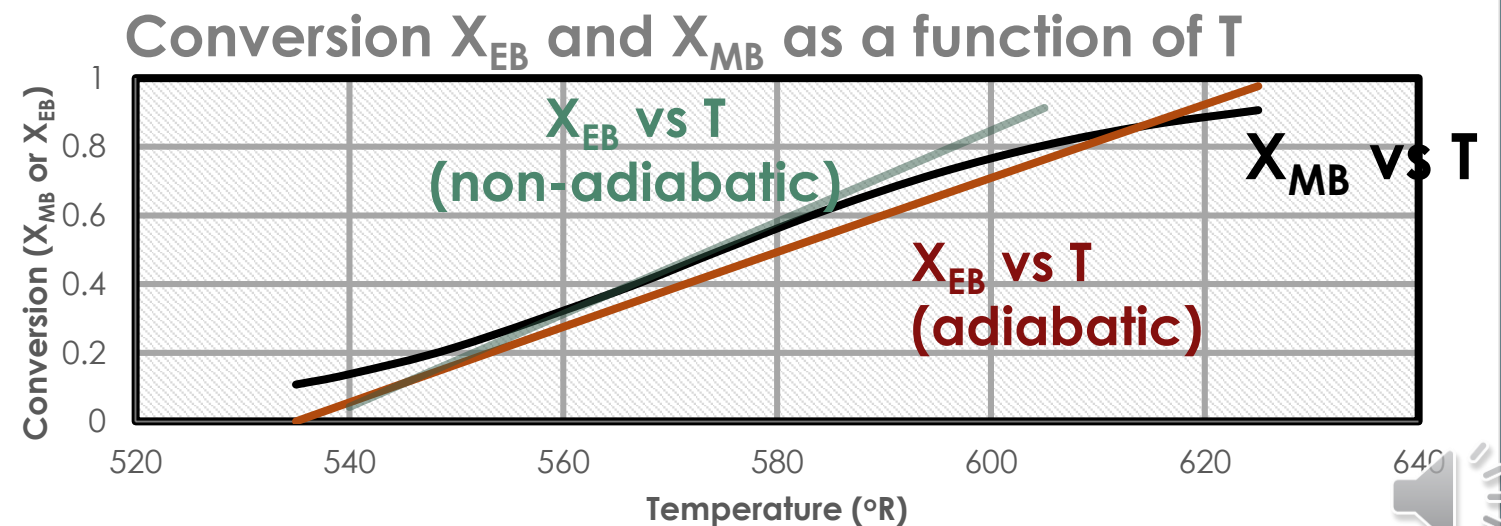
► EB equation:  $X_{EB} = \frac{UA(T - T_a) + F_{A0} \sum [\theta_i C_{P,i} (T - T_o)]}{F_{A0} (-\Delta h_{Rxn}(T))} = \frac{92.9(T - 545) + 403.3(T - 535)}{36400 + 7(T - 528)}$

► For adiabatic case,  $U = 0$

○  $X = 0.85$  and  $T = \sim 620 \text{ }^\circ\text{R}$

► For non-adiabatic,

○  $X = 0.36$  and  $T = \sim 564 \text{ }^\circ\text{R}$



# Further analysis of the Energy Balance equation for the CSTR with heat effects

- ▶ Energy balance equation:  $-X\Delta h_{Rxn}(T) = C_{P,0}(1 + \kappa)(T - T_c)$
- ▶ In terms of rate:  $-\left(\frac{-r_{AV}}{F_{A0}}\right)\Delta h_{Rxn}(T) = C_{P,0}(1 + \kappa)(T - T_c)$
- ▶ LHS is the heat generated term, G(T):
  - $G(T) = -\left(\frac{-r_{AV}}{F_{A0}}\right)\Delta h_{Rxn}(T)$  and
- ▶ RHS is the heat removal (by flow and heat exchange) R(T):
  - $R(T) = C_{P,0}(1 + \kappa)(T - T_c)$
- ▶ G(T) and R(T) can be analyzed for different operating conditions





# The heat generated term, $G(T)$ , in the CSTR

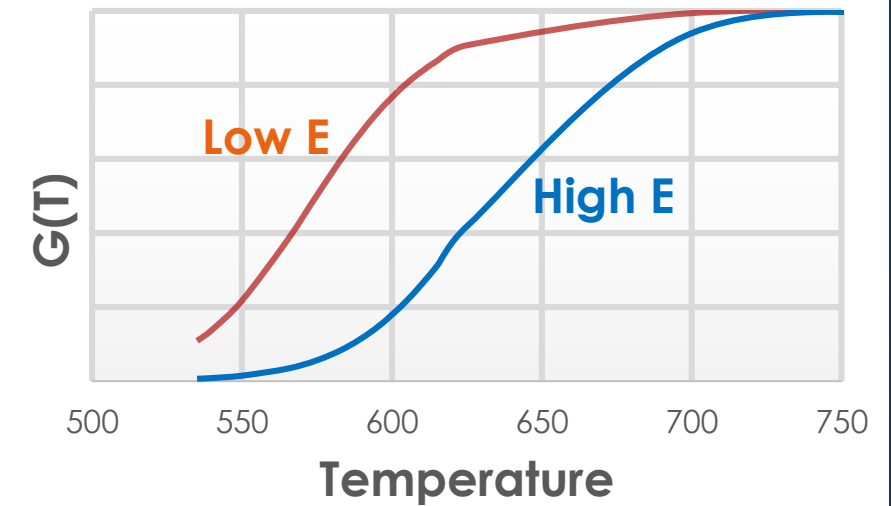
- ▶ The heat generated term,  $G(T)$ , is

$$G(T) = -X\Delta h_{Rxn}(T) = -\left(\frac{-r_A V}{F_{A0}}\right)\Delta h_{Rxn}(T)$$

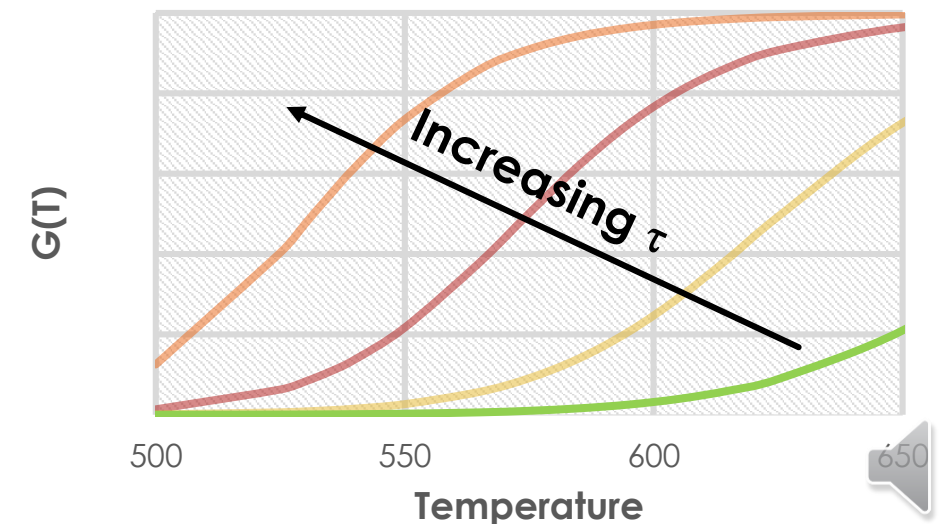
$$G(T) = -\left(\frac{\Delta h_{Rxn}(T)\tau A \exp(-\frac{E}{RT})}{1 + \tau A \exp(-\frac{E}{RT})}\right)$$

- ▶ At low temps  $G(T) = -\Delta h_{Rxn}(T)\tau A \exp(-\frac{E}{RT})$
- ▶ At high temps  $G(T) = -\Delta h_{Rxn}(T)$
- ▶ Depends on  $k$  ( $A$  or  $E$ ) and  $\tau$

Effect of activation energy on  $G(T)$



Effect of space time on  $G(T)$



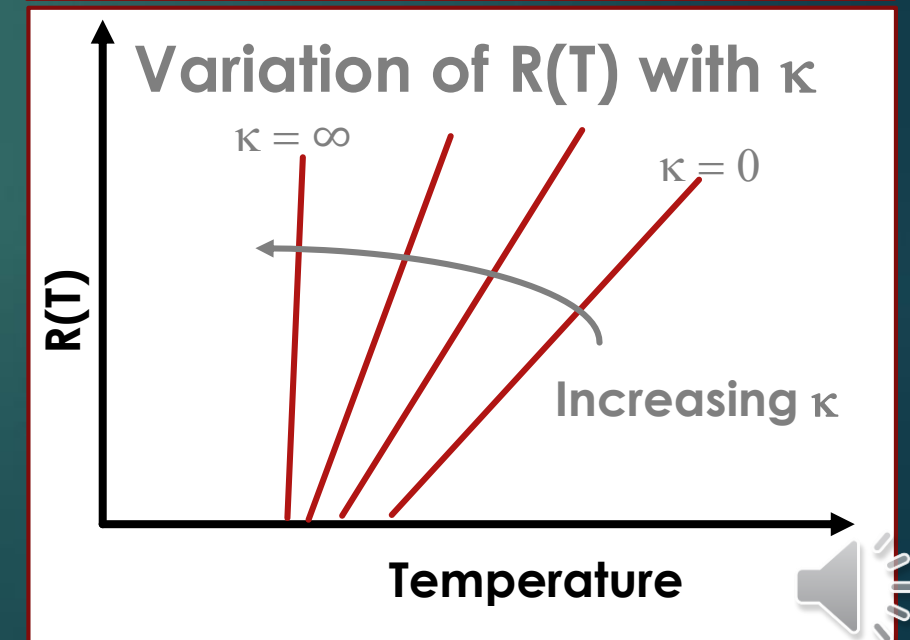
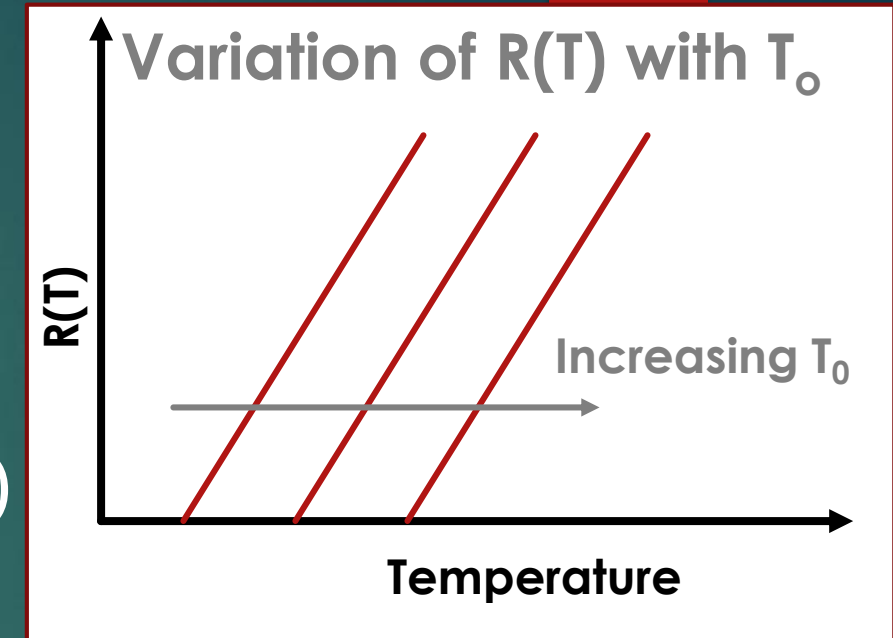
# The heat removal term, $R(T)$ , in the CSTR with heat effects

- ▶ The heat removal term is given by:

$$R(T) = C_{P,0}(1 + \kappa)(T - T_c)$$

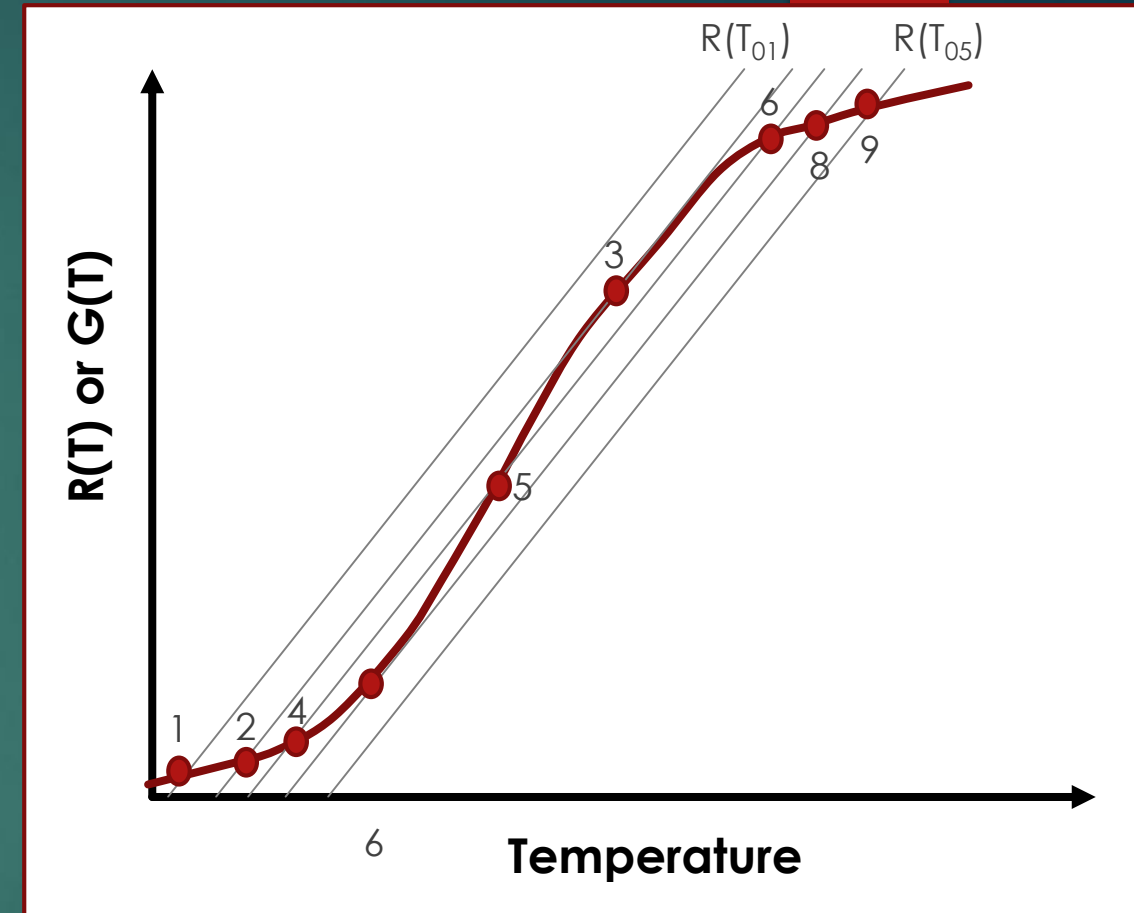
- Depends on  $\kappa$  (*non adiabatic parameter*) and  $T_c$  (or  $T_0$ )
- ▶  $R(T)$  increases linearly with  $T \rightarrow$  slope of  $C_{P,0}(1 + \kappa)$ 
  - Increasing  $T_0$  (inlet temp) shifts line to the right
  - Increasing  $\kappa$  (decreasing molar flowrate and/or heat-transfer area) increases the slope

$$\kappa = 0, T_c = T_0 \text{ and } \kappa = \infty, T_c = T_a$$



# The presence of multiple steady states in the non-isothermal CSTR

- ▶ Intersection of the  $G(T)$  and  $R(T)$  curves is the temperature at which the CSTR will operate under steady state
- ▶ The  $R(T)$  curve depends on the operating conditions:  $R(T) = C_{P,0}(1 + \kappa)(T - T_c)$
- ▶ The  $G(T)$  curve depends on the reaction parameters:  $G(T) = -X\Delta h_{Rxn}(T)$
- ▶ Multiple steady states are possible under certain conditions
  - $R(T_{01})$  to  $R(T_{05})$  increasing  $T_{01}$  to  $T_{05}$
  - Steady states change from 1 to 2 to 3 to 2 to 1  $\rightarrow$  depends on shape of  $G(T)$



Other useful terms associated with multiple steady states:

1. ignition-extinction curve
2. Stability
3. Runaway reactions





# Energy Balance for a Batch Reactor

- ▶ Energy balance:  $\sum_{inlet} \dot{E} - \sum_{outlet} \dot{E} + \dot{Q} - \dot{W} = \frac{d(E)_{CV}}{dt}$
- ▶ With no inlet and outlet flow:  $\dot{Q} - \dot{W} = \frac{d(E)_{CV}}{dt}$  assuming ideal solutions
- ▶  $(E)_{cv} = \sum_i E_i N_i = \sum_i u_i N_i = \sum_i N_i (h_i - P v_i) = \sum_i N_i h_i - P \sum_i v_i = \sum_i N_i h_i - PV$
- ▶ Neglecting changes in PV with time,  $(E)_{CV} = [\sum_i N_i h_i]_{CV}$
- ▶ Thus,  $\dot{Q} - \dot{W} = \frac{d(E)_{CV}}{dt} = \left[ \sum_i N_i \frac{dh_i}{dt} + \sum_i h_i \frac{dN_i}{dt} \right]_{CV}$

$$\frac{dh_i}{dt} = C_{P,i} \frac{dT}{dt} \quad \text{and} \quad \frac{dN_i}{dt} = r_i V = v_i V (-r_A) \quad \rightarrow \quad \text{Further,} \quad \sum_i v_i h_i = \Delta h_{rxn}$$

$$\dot{Q} - \dot{W} = \left[ \sum_i N_i \frac{dh_i}{dt} + \sum_i h_i \frac{dN_i}{dt} \right]_{CV} = \left[ \sum_i N_i C_{P,i} \frac{dT}{dt} + (-r_A V) \Delta h_{rxn} \right]_{CV}$$



# Energy Balance for a Batch Reactor ... continued

- ▶ We have  $\dot{Q} - \dot{W} = \left[ \sum_i N_i C_{P,i} \frac{dT}{dt} + (-r_A V) \Delta h_{rxn} \right]_{CV}$
- ▶ Rearranging:  $\frac{dT}{dt} = \frac{\dot{Q} - \dot{W} + (-\Delta h_{rxn})(-r_A V)}{\sum_i N_i C_{P,i}}$
- ▶ This is preferred when number of moles is used instead of conversion
- ▶ In terms of conversion:  $N_i = N_{A0}(\theta_i + v_i X)$ , Further
- ▶ And  $\sum_i N_i C_{P,i} = N_{A0} \sum_i (\theta_i C_{P,i} + v_i C_{P,i} X) = N_{A0} [\sum_i (\theta_i C_{P,i}) + \Delta C_P X]$ 
$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W} + (-\Delta h_{rxn})(-r_A V)}{N_{A0} [\sum_i (\theta_i C_{P,i}) + \Delta C_P X]}$$
- ▶ For liquid-phase reactions,  $\Delta C_{P,i}$  is very small and  $\sum_i \theta_i C_{P,i} = C_{P,s}$ 
  - $\sum_i N_i C_{P,i} = N_{A0} \sum_i \theta_i C_{P,i} = N_{A0} C_{P,s}$
  - Where  $C_{P,s}$  is the heat capacity of the solution



# Energy Balance for a Batch Reactor ... adiabatic ops

- ▶ Previously: 
$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W} + (-\Delta h_{rxn})(-r_A V)}{N_{A0}[\sum_i(\theta_i C_{P,i}) + \Delta C_P X]}$$
- ▶ For adiabatic operations and neglecting the stirrer work:  $\dot{Q} = 0 = \dot{W}$
- ▶ 
$$\frac{dT}{dt} = \frac{(-\Delta h_{rxn})(-r_A V)}{N_{A0}[\sum_i(\theta_i C_{P,i}) + \Delta C_P X]} \rightarrow N_{A0}[\sum_i(\theta_i C_{P,i}) + \Delta C_P X] \frac{dT}{dt} = (-\Delta h_{rxn})(-r_A V)$$
- ▶ Substituting:  $\sum_i \theta_i C_{P,i} = C_{P,s}$  and the mol balance equation:  $-r_A V = N_{A0} \frac{dX}{dt}$
- ▶ We have:  $[C_{P,s} + \Delta C_P X] \frac{dT}{dt} = (-\Delta h_{rxn}) \frac{dX}{dt}$  which needs to be integrated
- ▶ Resulting equation: 
$$X = \frac{C_{P,s}(T - T_0)}{(-\Delta h_{rxn})} \quad \text{OR} \quad T = T_0 + \frac{X(-\Delta h_{rxn})}{C_{P,s}}$$
- ▶ Also a linear relationship between T and X as seen for the flow reactors
  - Similar strategies can be applied

