The background features a large, stylized blue and grey buffalo mascot logo. The buffalo is facing forward with its mouth open, showing its teeth. Below the buffalo's head, the word "BUFFALO" is written in a large, bold, white, italicized font with a grey outline.

# **A First Course on Kinetics and Reaction Engineering**

**Class 24 on Unit 23**

# Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
- **Part III - Chemical Reaction Engineering**
  - ▶ A. Ideal Reactors
  - ▶ B. Perfectly Mixed Batch Reactors
  - ▶ **C. Continuous Flow Stirred Tank Reactors**
    - 21. Reaction Engineering of CSTRs
    - 22. Analysis of Steady State CSTRs
    - **23. Analysis of Transient CSTRs**
    - 24. Multiple Steady States in CSTRs
  - ▶ D. Plug Flow Reactors
  - ▶ E. Matching Reactors to Reactions
- **Part IV - Non-Ideal Reactions and Reactors**



# Transient Behavior

- While processes may be designed to operate at steady state, occasionally they still need to be started up or shut down.
  - ▶ Maintenance of equipment
  - ▶ Interruption of feed, heating or cooling
- Definitions
  - ▶ System response: values of the dependent variables (outlet molar flow rates and outlet temperature) as a function of time
  - ▶ Operating parameters: everything else in the design equations
    - particularly quantities that can change easily (either intentionally or unexpectedly)
- As soon as an operating parameter of a CSTR is changed, the reactor enters a period of transient behavior
  - ▶ During transient behavior, the outlet molar flow rates and the outlet temperature change over time
- The transient behavior will end
  - ▶ When (if) the system reaches a new steady state
    - The outlet molar flow rates and temperature approach steady state values over time
    - The steady state corresponds to the new operating parameters (those in effect after the most recent change)
  - ▶ When another operating parameter is changed (causing a new period of transient behavior to begin)
  - ▶ Never; the system could go into a state where the response variables undergo sustained periodic oscillations



# A General Approach to Solving Quantitative Reaction Engineering Problems

- Read through the problem statement and determine
  - ▶ the type of reactor being used
  - ▶ whether it operates transiently or at steady state
  - ▶ whether it is heated/cooled, isothermal or adiabatic
  - ▶ (if the reactor is a PFR) whether there is a significant pressure drop
- Read through the problem statement a second time
  - ▶ assign each quantity given in the problem statement to the appropriate variable symbol
  - ▶ if all of the given quantities are intensive, select a value for one extensive variable as the basis for your calculations
  - ▶ determine what quantities the problem asks for and assign appropriate variable symbols to them
- Write a mole balance equation for each reactant and product; expand all summations and continuous products, and eliminate all zero-valued and negligible terms
- Write an energy balance design equation (unless the reactor is isothermal and the problem does not ask any questions related to heat transfer); expand all summations and continuous products, and eliminate all zero-valued and negligible terms
  - ▶ if information about the heat transfer fluid, beyond its temperature, is provided, write an energy balance on the heat transfer fluid



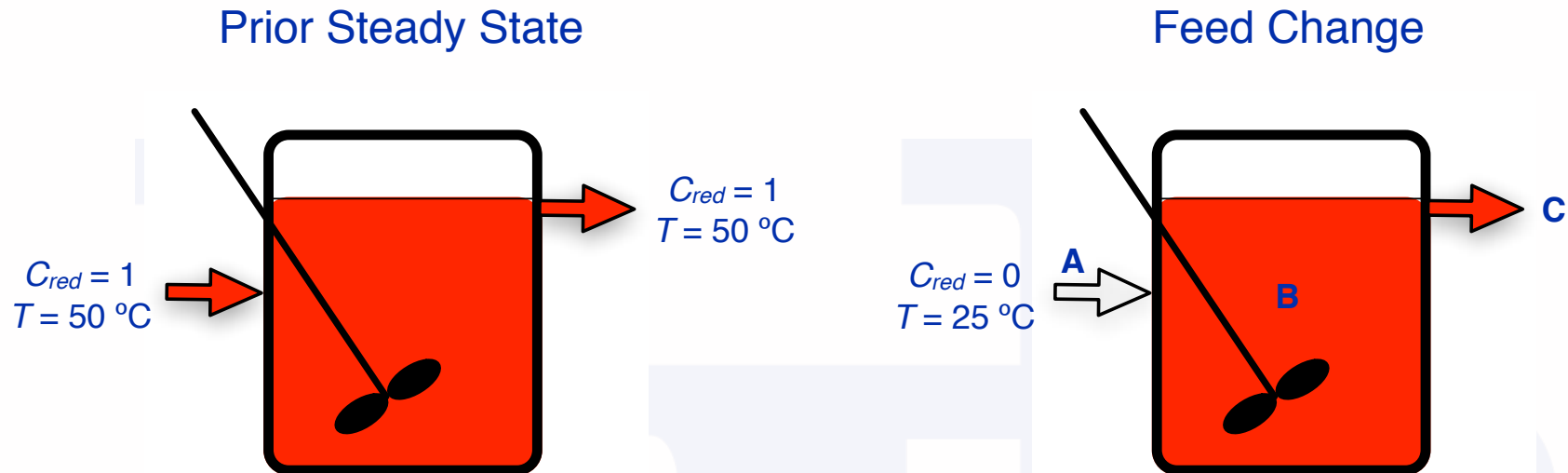
- If the reactor is a PFR and there is a significant pressure drop, write a momentum balance; expand all summations and continuous products, and eliminate all zero-valued and negligible terms
- Identify the type of the design equations
  - ▶ if they are algebraic, identify the unknowns
    - the number of unknowns must equal the number of equations
  - ▶ if they are differential, identify the independent and dependent variables
    - if the number of dependent variables is greater than the number of equations, choose one dependent variable and express it and its derivatives in terms of the remaining dependent variables
- Determine what you will need to provide in order to solve the design equations numerically and show how to do so
  - ▶ For algebraic equations written in the form  $0 = \underline{f}(\underline{x})$  you must provide a guess for  $x$  and code that evaluates  $\underline{f}$  given  $\underline{x}$
  - ▶ For initial value ordinary differential equations written in the form  $\frac{d}{dx}\underline{y} = \underline{f}(x, \underline{y})$  you must provide initial values of  $x$  and  $\underline{y}$ , a final value for either  $x$  or one element of  $\underline{y}$ , and code that evaluates  $\underline{f}$  given  $x$  and  $\underline{y}$
  - ▶ For boundary value differential equations (without a singularity) written in the form  $\frac{d}{dx}\underline{y} = \underline{f}(x, \underline{y})$  you must provide the lower and upper limits of  $x$ , boundary conditions that must be satisfied for each dependent variable and code that evaluates  $\underline{f}$  given  $x$  and  $\underline{y}$
- After the design equations have been solved numerically, yielding values for the unknowns (algebraic equations) or the independent and dependent variables (differential equations), use the results to calculate any other quantities or plots that the problem asked for



Questions?

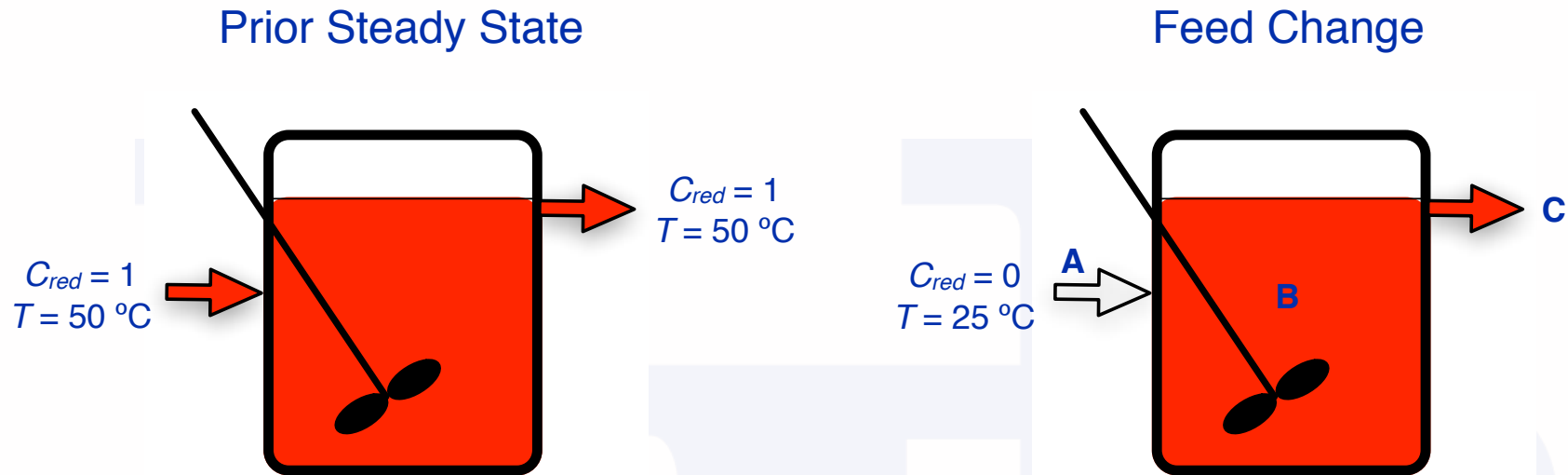


# Activity 23.1



- Suppose a stirred tank is operating at steady state as shown on the left (there's no reaction), when the inlet composition is suddenly changed
  - ▶ The inlet concentration of red coloring changes from 1 to 0 mol L<sup>-1</sup>
  - ▶ The temperature of the inlet flow stream changes from 50 °C to 25 °C
- Assuming the transient will continue until a new steady state is reached, describe how the concentration of red coloring and the temperature will vary at the points labeled A, B and C if the fluid is a constant density liquid

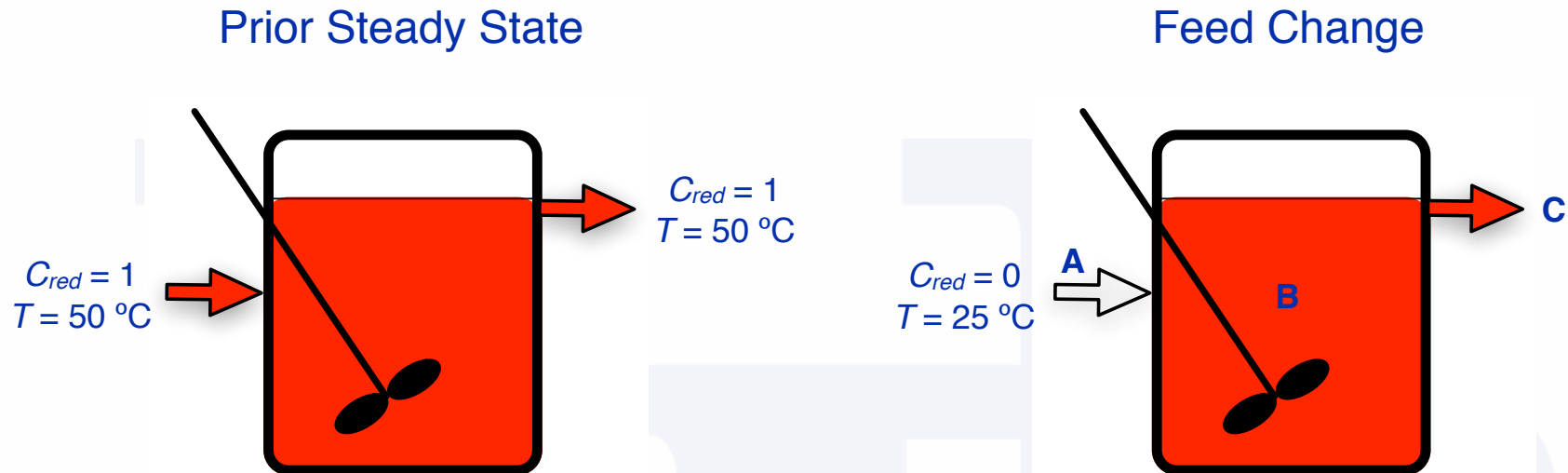
# Qualitative Analysis



- At point A
  - ▶  $C_{red}$  will be constant and equal to  $0\text{ mol L}^{-1}$
  - ▶  $T$  will be constant and equal to  $25\text{ }^{\circ}\text{C}$
- At point B
  - ▶  $C_{red}$  will initially equal  $1\text{ mol L}^{-1}$ , and it will continually decrease until it becomes equal to  $0\text{ mol L}^{-1}$
  - ▶  $T$  will initially equal  $50\text{ }^{\circ}\text{C}$ , and it will continually decrease until it becomes equal to  $25\text{ }^{\circ}\text{C}$
- At point C
  - ▶  $C_{red}$  and  $T$  will be the same as they are at point B



# Activity 23.1



- Suppose a stirred tank is operating at steady state as shown on the left (there's no reaction), when the inlet composition is suddenly changed
  - ▶ The inlet concentration of red coloring changes from 1 to 0 mol L<sup>-1</sup>
  - ▶ The temperature of the inlet flow stream changes from 50 °C to 25 °C
- Write a transient mole balance on the red coloring

### Reactor Relationships

$$\tau = \frac{V}{\dot{V}^0}; \quad SV = \frac{1}{\tau}; \quad \frac{dn_i}{dt} = V \left( \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j \right); \quad \dot{Q} - \dot{W} = \left( \sum_{\substack{i=\text{all} \\ \text{species}}} n_i \hat{C}_{p,i} \right) \frac{dT}{dt} + V \left( \sum_{\substack{j=\text{all} \\ \text{reactions}}} r_j \Delta H_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt};$$

$$\dot{n}_i^0 + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j = \dot{n}_i + \frac{d}{dt} \left( \frac{\dot{n}_i V}{\dot{V}} \right);$$

$$\dot{Q} - \dot{W} = \sum_{\substack{i=\text{all} \\ \text{species}}} \left( \dot{n}_i \int_{T^0}^T \hat{C}_{p,i} dT \right) + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} (r_j \Delta H_j(T)) + V \left( \sum_{\substack{i=\text{all} \\ \text{species}}} \frac{\dot{n}_i \hat{C}_{p,i}}{\dot{V}} \right) \frac{dT}{dt} - P \frac{dV}{dt} - V \frac{dP}{dt};$$

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \left[ \left( \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j \right) - \frac{\partial}{\partial t} \left( \frac{\dot{n}_i}{\dot{V}} \right) \right]; \quad \frac{\partial P}{\partial z} = -\frac{G}{g_c} \left( \frac{4}{\pi D^2} \right) \frac{\partial \dot{V}}{\partial z} - \frac{2fG^2}{\rho D};$$

$$\frac{\partial P}{\partial z} = -\frac{1-\varepsilon}{\varepsilon^3} \frac{G^2}{\rho \Phi_s D_p g_c} \left[ \frac{150(1-\varepsilon)\mu}{\Phi_s D_p G} + 1.75 \right];$$

$$\pi DU (T_c - T) = \frac{\partial T}{\partial z} \left( \sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_i \hat{C}_{p,i} \right) + \frac{\pi D^2}{4} \left( \sum_{\substack{j=\text{all} \\ \text{reactions}}} r_j \Delta H_j \right) + \frac{\pi D^2}{4} \left[ \frac{\partial T}{\partial t} \left( \sum_{\substack{i=\text{all} \\ \text{species}}} \frac{\dot{n}_i \hat{C}_{p,i}}{\dot{V}} \right) - \frac{\partial P}{\partial t} \right];$$

$$\frac{dn_i}{dt} = \dot{n}_i + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j; \quad \dot{Q} - \dot{W} = \sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_i (\hat{h}_i - \hat{h}_{i,\text{stream}}) + \frac{dT}{dt} \sum_{\substack{i=\text{all} \\ \text{species}}} (n_i \hat{C}_{p,i}) + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} (r_j \Delta H_j) - \frac{dP}{dt} V - P \frac{dV}{dt};$$

$$-D_{ax} \frac{d^2 C_i}{dz^2} + \frac{d}{dz} (u_s C_i) = \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j; \quad D_{er} \left( \frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) - \frac{\partial}{\partial z} (u_s C_i) = \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j;$$

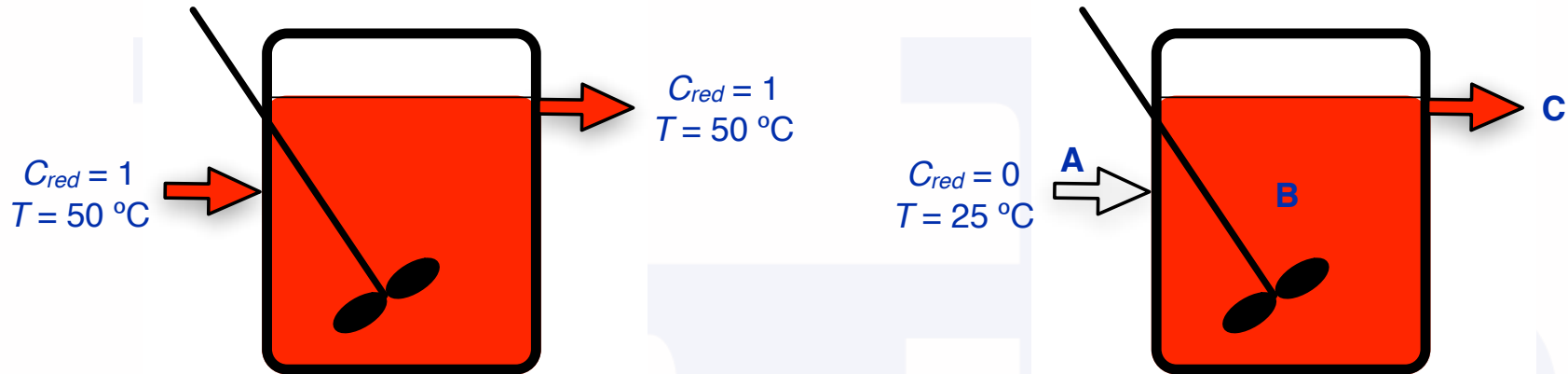
$$\lambda_{er} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) - u_s \rho_{\text{fluid}} \tilde{C}_{p,\text{fluid}} \frac{\partial T}{\partial z} = \sum_{\substack{j=\text{all} \\ \text{reactions}}} r_j \Delta H$$



# Mole Balance

Prior Steady State

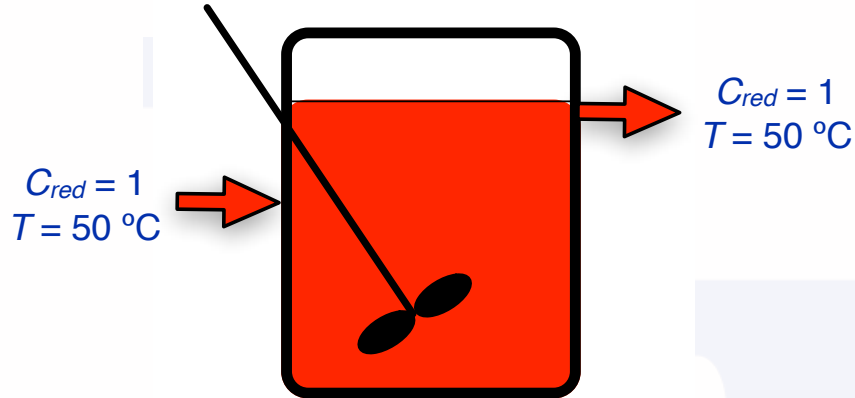
Feed Change



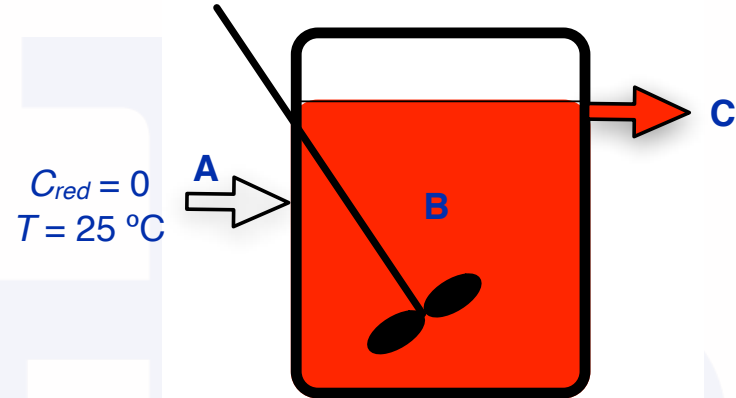
- General mole balance: 
$$\frac{V}{\dot{V}} \frac{d\dot{n}_{red}}{dt} + \frac{\dot{n}_{red}}{\dot{V}} \frac{dV}{dt} - \frac{\dot{n}_{red} V}{\dot{V}^2} \frac{d\dot{V}}{dt} = \dot{n}_{red}^0 - \dot{n}_{red} + V \sum_{\substack{j = \text{all} \\ \text{reactions}}} v_{red,j} r_j$$

# Mole Balance

Prior Steady State



Feed Change

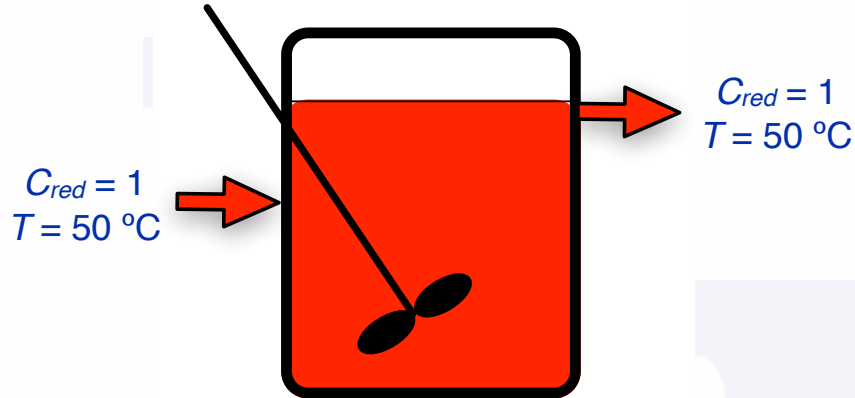


- General mole balance: 
$$\frac{V}{\dot{V}} \frac{d\dot{n}_{red}}{dt} + \frac{\dot{n}_{red}}{\dot{V}} \frac{dV}{dt} - \frac{\dot{n}_{red} V}{\dot{V}^2} \frac{d\dot{V}}{dt} = \dot{n}_{red}^0 - \dot{n}_{red} + V \sum_{j=\text{all reactions}} \nu_{red,j} r_j$$
  - ▶ No reaction, so last term equals zero
  - ▶ Constant density fluid and reactor initially full, so  $V$  and  $\dot{V}$  are constant
    - Their derivatives are then equal to zero
- Mole balance after simplification: 
$$\frac{V}{\dot{V}} \frac{d\dot{n}_{red}}{dt} = \dot{n}_{red}^0 - \dot{n}_{red} \Rightarrow \frac{d\dot{n}_{red}}{dt} = \frac{\dot{V}}{V} (\dot{n}_{red}^0 - \dot{n}_{red})$$
  - ▶ What initial condition is needed to solve this equation?

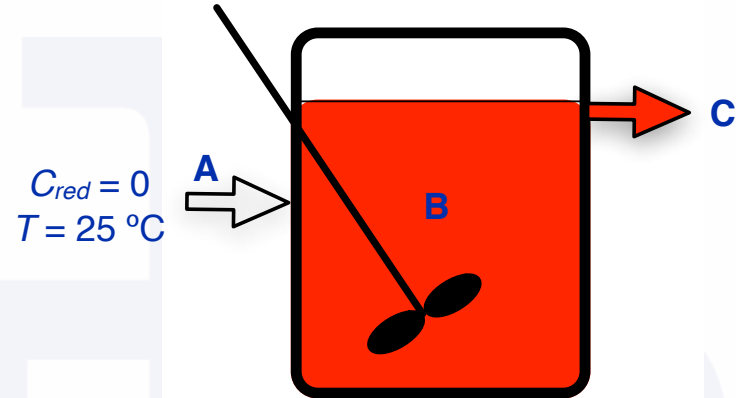


# Mole Balance

Prior Steady State

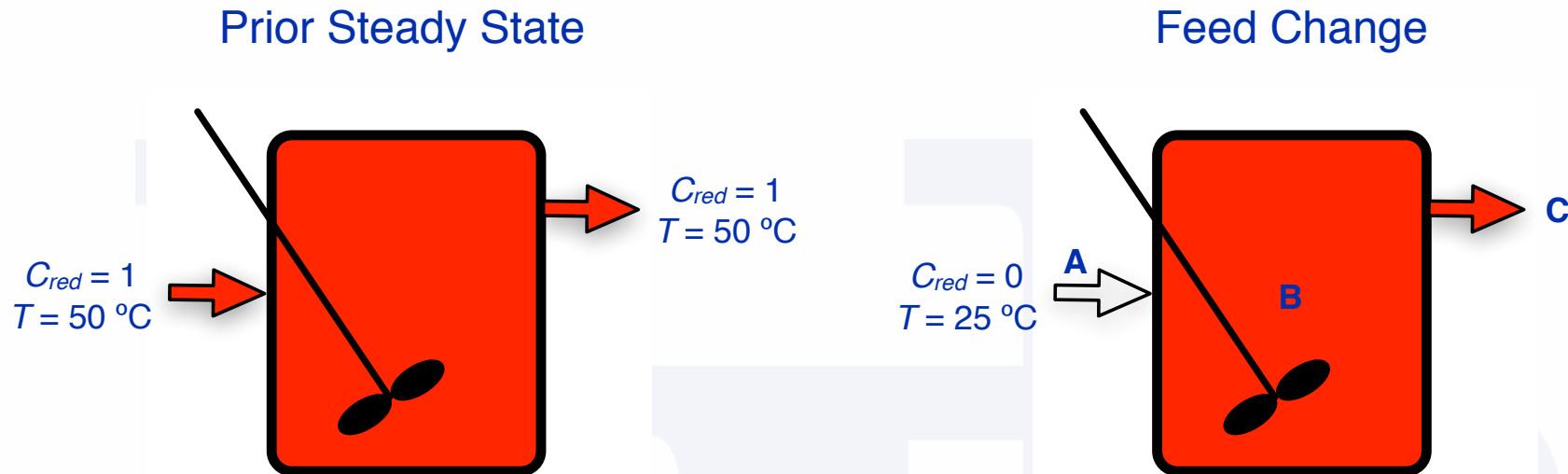


Feed Change



- General mole balance: 
$$\frac{V}{\dot{V}} \frac{d\dot{n}_{red}}{dt} + \frac{\dot{n}_{red}}{\dot{V}} \frac{dV}{dt} - \frac{\dot{n}_{red} V}{\dot{V}^2} \frac{d\dot{V}}{dt} = \dot{n}_{red}^0 - \dot{n}_{red} + V \sum_{j=\text{all reactions}} \nu_{red,j} r_j$$
  - ▶ No reaction, so last term equals zero
  - ▶ Constant density fluid and reactor initially full, so  $V$  and  $\dot{V}$  are constant
    - Their derivatives are then equal to zero
- Mole balance after simplification: 
$$\frac{V}{\dot{V}} \frac{d\dot{n}_{red}}{dt} = \dot{n}_{red}^0 - \dot{n}_{red} \Rightarrow \frac{d\dot{n}_{red}}{dt} = \frac{\dot{V}}{V} (\dot{n}_{red}^0 - \dot{n}_{red})$$
  - ▶ Initial condition is the value of  $\dot{n}_{red}$  at  $t = 0$
  - ▶  $C_{red}(t = 0) = 1 \text{ mol L}^{-1} \Rightarrow \dot{n}_{red}(t = 0) = \dot{V} C_{red}(t = 0) = \dot{V} (1 \text{ mol L}^{-1})$

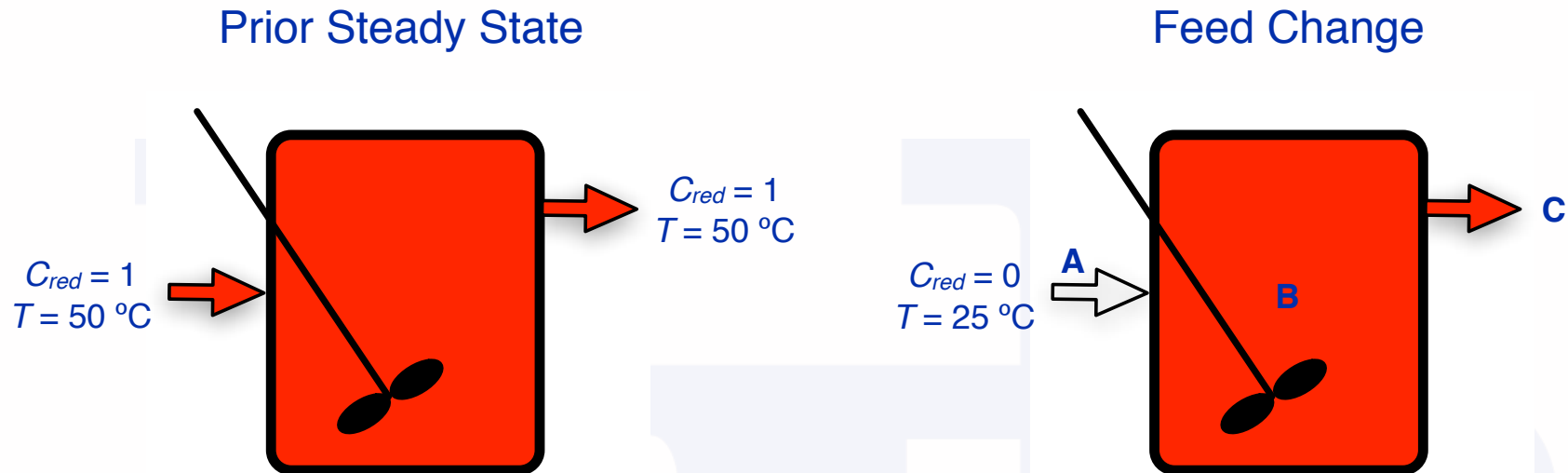
# Activity 23.1



- Suppose a stirred tank is operating at steady state as shown on the left, when the inlet composition is suddenly changed
  - The inlet concentration of red coloring changes from 1 to 0 mol L<sup>-1</sup>
  - The temperature of the inlet flow stream changes from 50 °C to 25 °C
- Assuming the transient will continue until a new steady state is reached, describe how the concentration of red coloring and the temperature will vary at the points labeled A, B and C if ***the fluid is an ideal gas***
- Write a transient mole balance on the red coloring
  - What initial condition is needed to solve this equation?



# Qualitative Analysis



- At point A
  - ▶  $C_{red}$  will be constant and equal to 0
  - ▶  $T$  will be constant and equal to  $25\text{ }^{\circ}\text{C}$
- At point B
  - ▶  $C_{red}$  will initially equal  $1\text{ mol L}^{-1}$ , and it will continually decrease until it becomes equal to  $0\text{ mol L}^{-1}$
  - ▶  $T$  will initially equal  $50\text{ }^{\circ}\text{C}$ , and it will continually decrease until it becomes equal to  $25\text{ }^{\circ}\text{C}$
- At point C
  - ▶  $C_{red}$  and  $T$  will be the same as they are at point B

### Reactor Relationships

$$\tau = \frac{V}{\dot{V}^0}; \quad SV = \frac{1}{\tau}; \quad \frac{dn_i}{dt} = V \left( \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j \right); \quad \dot{Q} - \dot{W} = \left( \sum_{\substack{i=\text{all} \\ \text{species}}} n_i \hat{C}_{p,i} \right) \frac{dT}{dt} + V \left( \sum_{\substack{j=\text{all} \\ \text{reactions}}} r_j \Delta H_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt};$$

$$\dot{n}_i^0 + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j = \dot{n}_i + \frac{d}{dt} \left( \frac{\dot{n}_i V}{\dot{V}} \right);$$

$$\dot{Q} - \dot{W} = \sum_{\substack{i=\text{all} \\ \text{species}}} \left( \dot{n}_i \int_{T^0}^T \hat{C}_{p,i} dT \right) + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} (r_j \Delta H_j(T)) + V \left( \sum_{\substack{i=\text{all} \\ \text{species}}} \frac{\dot{n}_i \hat{C}_{p,i}}{\dot{V}} \right) \frac{dT}{dt} - P \frac{dV}{dt} - V \frac{dP}{dt};$$

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \left[ \left( \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j \right) - \frac{\partial}{\partial t} \left( \frac{\dot{n}_i}{\dot{V}} \right) \right]; \quad \frac{\partial P}{\partial z} = -\frac{G}{g_c} \left( \frac{4}{\pi D^2} \right) \frac{\partial \dot{V}}{\partial z} - \frac{2fG^2}{\rho D};$$

$$\frac{\partial P}{\partial z} = -\frac{1-\varepsilon}{\varepsilon^3} \frac{G^2}{\rho \Phi_s D_p g_c} \left[ \frac{150(1-\varepsilon)\mu}{\Phi_s D_p G} + 1.75 \right];$$

$$\pi DU (T_c - T) = \frac{\partial T}{\partial z} \left( \sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_i \hat{C}_{p,i} \right) + \frac{\pi D^2}{4} \left( \sum_{\substack{j=\text{all} \\ \text{reactions}}} r_j \Delta H_j \right) + \frac{\pi D^2}{4} \left[ \frac{\partial T}{\partial t} \left( \sum_{\substack{i=\text{all} \\ \text{species}}} \frac{\dot{n}_i \hat{C}_{p,i}}{\dot{V}} \right) - \frac{\partial P}{\partial t} \right];$$

$$\frac{dn_i}{dt} = \dot{n}_i + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j; \quad \dot{Q} - \dot{W} = \sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_i (\hat{h}_i - \hat{h}_{i,\text{stream}}) + \frac{dT}{dt} \sum_{\substack{i=\text{all} \\ \text{species}}} (n_i \hat{C}_{p,i}) + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} (r_j \Delta H_j) - \frac{dP}{dt} V - P \frac{dV}{dt};$$

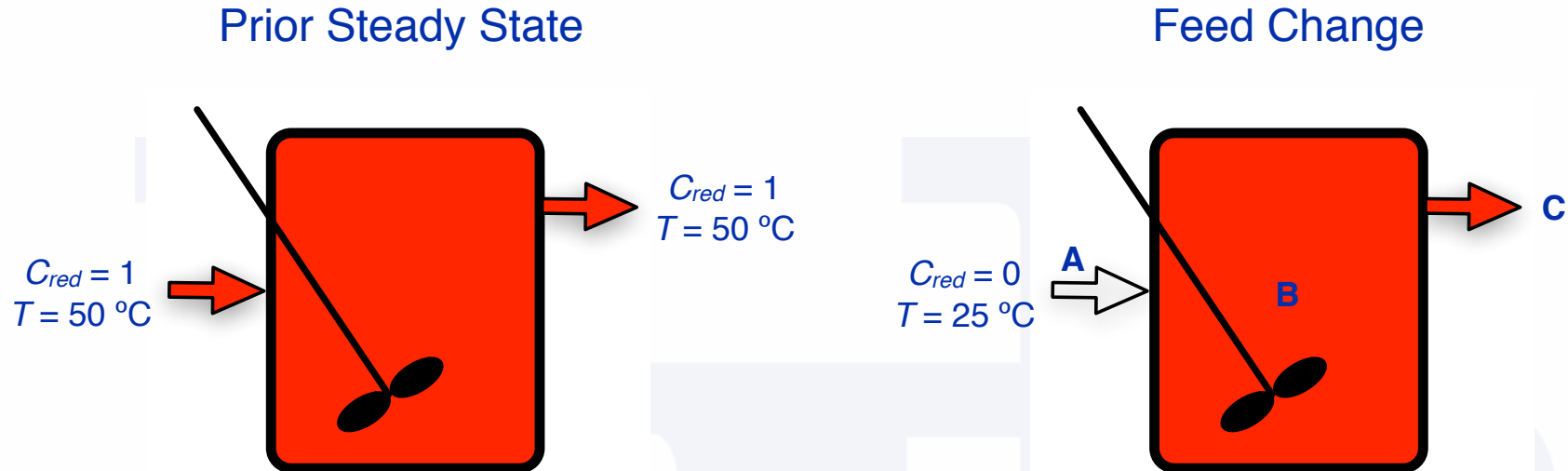
$$-D_{ax} \frac{d^2 C_i}{dz^2} + \frac{d}{dz} (u_s C_i) = \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j; \quad D_{er} \left( \frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) - \frac{\partial}{\partial z} (u_s C_i) = \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j;$$

$$\lambda_{er} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) - u_s \rho_{\text{fluid}} \tilde{C}_{p,\text{fluid}} \frac{\partial T}{\partial z} = \sum_{\substack{j=\text{all} \\ \text{reactions}}} r_j \Delta H$$





# Transient Mole Balance



- General mole balance: 
$$\frac{V}{\dot{V}} \frac{d\dot{n}_{red}}{dt} + \frac{\dot{n}_{red}}{\dot{V}} \frac{dV}{dt} - \frac{\dot{n}_{red} V}{\dot{V}^2} \frac{d\dot{V}}{dt} = \dot{n}_{red}^0 - \dot{n}_{red} + V \sum_{j=\text{all reactions}} \nu_{red,j} r_j$$
  - ▶ As before
    - no reaction so last term is zero
    - reaction volume is constant so its derivative is zero
  - ▶ The temperature is changing; pressure and total molar flow rates are constant
    - the volumetric flow rate must also change over time

$$\frac{V}{\dot{V}} \frac{d\dot{n}_{red}}{dt} - \frac{\dot{n}_{red} V}{\dot{V}^2} \frac{d\dot{V}}{dt} = \dot{n}_{red}^0 - \dot{n}_{red}$$

# Two Approaches to Solving

$$\frac{V}{\dot{V}} \frac{d\dot{n}_{red}}{dt} - \frac{\dot{n}_{red} V}{\dot{V}^2} \frac{d\dot{V}}{dt} = \dot{n}_{red}^0 - \dot{n}_{red}$$

- Express the volumetric flow rate in terms of the other dependent variables and eliminate its derivative

- ▶  $\dot{V} = \frac{\dot{n}_{tot} RT}{P} \Rightarrow \frac{d\dot{V}}{dt} = \frac{\dot{n}_{tot} R}{P} \frac{dT}{dt}$

- ▶  $\frac{dT}{dt} = f(\dot{n}_{red}, T)$  where  $f$  is a known analytic function of the dependent variables (from the energy balance)

- ▶ Substituting the known function eliminates the derivative of  $\dot{V}$  from the ODE at the top of the page

- Add another differential equation

- ▶  $\frac{d\dot{V}}{dt} = \frac{\dot{n}_{tot} R}{P} \frac{dT}{dt}$

- ▶ Some ODE solvers (including fsolve in MATLAB) allow the ODEs to be written in matrix form

- $\underline{M} \frac{d\underline{z}}{dt} = \underline{f}(t, \underline{z})$

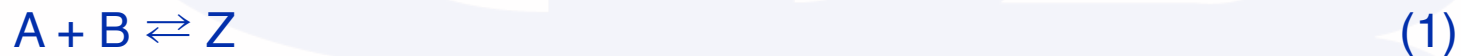
- ▶ Otherwise substitute as above in the original ODE (top of page) and substitute  $f$  from above in the ODE here to get the equations in the desired form for numerical solution

- $\frac{d\underline{z}}{dt} = \underline{f}(t, \underline{z})$



## Activity 23.2

Example 22.1 described a steady state CSTR where the rate of liquid-phase reaction (1) is adequately described by the rate expression given in equation (2). Reactant A is fed to a steady state CSTR at a rate of  $0.01 \text{ lbmol min}^{-1}$ , and reactant B is fed at a rate of  $0.25 \text{ lbmol min}^{-1}$ . This corresponds to an inlet volumetric flow rate of  $0.08 \text{ ft}^3 \text{ min}^{-1}$ . The CSTR has a fluid volume of  $18 \text{ ft}^3$ , and it operates adiabatically. The heat of reaction may be taken to be constant and equal to  $-1.7 \times 10^4 \text{ BTU lbmol}^{-1}$ . The heat capacities of A, B and Z are equal to  $1000$ ,  $180$  and  $1200 \text{ BTU lbmol}^{-1} \text{ }^\circ\text{R}^{-1}$ , respectively, and they may be considered to be independent of temperature. If this reactor was operating at  $650 \text{ }^\circ\text{R}$  and the volumetric flow rate was suddenly doubled, how would the conversion change?



$$r_1 = \left(1.2 \times 10^{14} \text{ ft}^3 \text{ lbmol}^{-1} \text{ min}^{-1}\right) \exp\left\{\frac{-23000 \text{ }^\circ\text{R}}{T}\right\} C_A C_B$$

$$\times \left[ 1 - \frac{C_Z}{\left(6.5 \times 10^{-13} \text{ ft}^3 \text{ lbmol}^{-1}\right) \exp\left\{\frac{20000 \text{ }^\circ\text{R}}{T}\right\} C_A C_B} \right] \quad (2)$$



# A General Approach to Solving Quantitative Reaction Engineering Problems

- Read through the problem statement and determine
  - ▶ the type of reactor being used
  - ▶ whether it operates transiently or at steady state
  - ▶ whether it is heated/cooled, isothermal or adiabatic
  - ▶ (if the reactor is a PFR) whether there is a significant pressure drop
- Read through the problem statement a second time
  - ▶ assign each quantity given in the problem statement to the appropriate variable symbol
  - ▶ if all of the given quantities are intensive, select a value for one extensive variable as the basis for your calculations
  - ▶ determine what quantities the problem asks for and assign appropriate variable symbols to them
- Write a mole balance equation for each reactant and product; expand all summations and continuous products, and eliminate all zero-valued and negligible terms
- Write an energy balance design equation (unless the reactor is isothermal and the problem does not ask any questions related to heat transfer); expand all summations and continuous products, and eliminate all zero-valued and negligible terms
  - ▶ if information about the heat transfer fluid, beyond its temperature, is provided, write an energy balance on the heat transfer fluid



- If the reactor is a PFR and there is a significant pressure drop, write a momentum balance; expand all summations and continuous products, and eliminate all zero-valued and negligible terms
- Identify the type of the design equations
  - ▶ if they are algebraic, identify the unknowns
    - the number of unknowns must equal the number of equations
  - ▶ if they are differential, identify the independent and dependent variables
    - if the number of dependent variables is greater than the number of equations, choose one dependent variable and express it and its derivatives in terms of the remaining dependent variables
- Determine what you will need to provide in order to solve the design equations numerically and show how to do so
  - ▶ For algebraic equations written in the form  $0 = \underline{f}(\underline{x})$  you must provide a guess for  $\underline{x}$  and code that evaluates  $\underline{f}$  given  $\underline{x}$
  - ▶ For initial value ordinary differential equations written in the form  $\frac{d}{dx}\underline{y} = \underline{f}(x, \underline{y})$  you must provide initial values of  $\underline{y}$ , a final value for either  $x$  or one element of  $\underline{y}$ , and code that evaluates  $\underline{f}$  given  $x$  and  $\underline{y}$
  - ▶ For boundary value differential equations (without a singularity) written in the form  $\frac{d}{dx}\underline{y} = \underline{f}(x, \underline{y})$  you must provide the lower and upper limits of  $x$ , boundary conditions that must be satisfied for each dependent variable and code that evaluates  $\underline{f}$  given  $x$  and  $\underline{y}$
- After the design equations have been solved numerically, yielding values for the unknowns (algebraic equations) or the independent and dependent variables (differential equations), use the results to calculate any other quantities or plots that the problem asked for



### Reactor Relationships

$$\tau = \frac{V}{\dot{V}^0}; SV = \frac{1}{\tau}; \frac{dn_i}{dt} = V \left( \sum_{j=\text{all reactions}} v_{i,j} r_j \right); \dot{Q} - \dot{W} = \left( \sum_{i=\text{all species}} n_i \hat{C}_{p,i} \right) \frac{dT}{dt} + V \left( \sum_{j=\text{all reactions}} r_j \Delta H_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt};$$

$$\dot{n}_i^0 + V \sum_{j=\text{all reactions}} v_{i,j} r_j = \dot{n}_i + \frac{d}{dt} \left( \frac{\dot{n}_i V}{\dot{V}} \right);$$

$$\dot{Q} - \dot{W} = \sum_{i=\text{all species}} \left( \dot{n}_i \int_{T^0}^T \hat{C}_{p,i} dT \right) + V \sum_{j=\text{all reactions}} (r_j \Delta H_j(T)) + V \left( \sum_{i=\text{all species}} \frac{\dot{n}_i \hat{C}_{p,i}}{\dot{V}} \right) \frac{dT}{dt} - P \frac{dV}{dt} - V \frac{dP}{dt}$$

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \left[ \left( \sum_{j=\text{all reactions}} v_{i,j} r_j \right) - \frac{\partial}{\partial t} \left( \frac{\dot{n}_i}{\dot{V}} \right) \right]; \frac{\partial P}{\partial z} = -\frac{G}{g_c} \left( \frac{4}{\pi D^2} \right) \frac{\partial \dot{V}}{\partial z} - \frac{2fG^2}{\rho D};$$

$$\frac{\partial P}{\partial z} = -\frac{1-\varepsilon}{\varepsilon^3} \frac{G^2}{\rho \Phi_s D_p g_c} \left[ \frac{150(1-\varepsilon)\mu}{\Phi_s D_p G} + 1.75 \right];$$

$$\pi DU (T_c - T) = \frac{\partial T}{\partial z} \left( \sum_{i=\text{all species}} \dot{n}_i \hat{C}_{p,i} \right) + \frac{\pi D^2}{4} \left( \sum_{j=\text{all reactions}} r_j \Delta H_j \right) + \frac{\pi D^2}{4} \left[ \frac{\partial T}{\partial t} \left( \sum_{i=\text{all species}} \frac{\dot{n}_i \hat{C}_{p,i}}{\dot{V}} \right) - \frac{\partial P}{\partial t} \right];$$

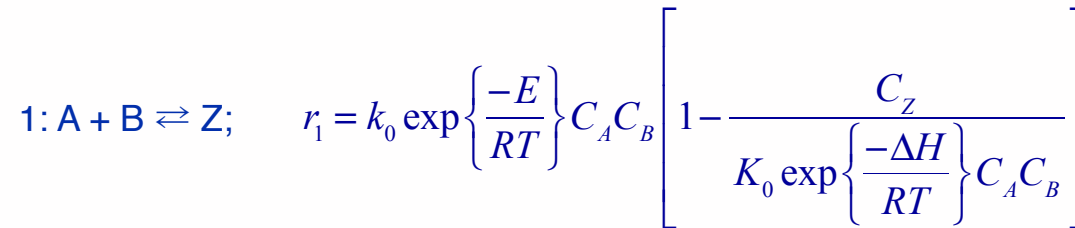
$$\frac{dn_i}{dt} = \dot{n}_i + V \sum_{j=\text{all reactions}} v_{i,j} r_j; \dot{Q} - \dot{W} = \sum_{i=\text{all species}} \dot{n}_i (\hat{h}_i - \hat{h}_{i,\text{stream}}) + \frac{dT}{dt} \sum_{i=\text{all species}} (n_i \hat{C}_{p,i}) + V \sum_{j=\text{all reactions}} (r_j \Delta H_j) - \frac{dP}{dt} V - P \frac{dV}{dt};$$

$$-D_{ax} \frac{d^2 C_i}{dz^2} + \frac{d}{dz} (u_s C_i) = \sum_{j=\text{all reactions}} v_{i,j} r_j; D_{er} \left( \frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) - \frac{\partial}{\partial z} (u_s C_i) = \sum_{j=\text{all reactions}} v_{i,j} r_j;$$

$$\lambda_{er} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) - u_s \rho_{fluid} \tilde{C}_{p,fluid} \frac{\partial T}{\partial z} = \sum_{j=\text{all reactions}} r_j \Delta H$$

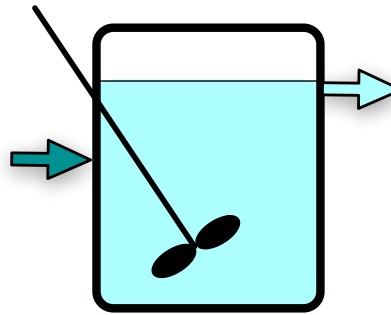


# Schematic Diagram



## Initial Steady State

$$\begin{aligned} \dot{V}^0 &= 0.08 \text{ ft}^3 \text{ min}^{-1} \\ T^0 &= 650 \text{ }^\circ\text{R} \\ \dot{n}_A^0 &= 0.01 \text{ lbmol min}^{-1} \\ \dot{n}_B^0 &= 0.25 \text{ lbmol min}^{-1} \\ \dot{n}_Z^0 &= 0 \text{ lbmol min}^{-1} \end{aligned}$$

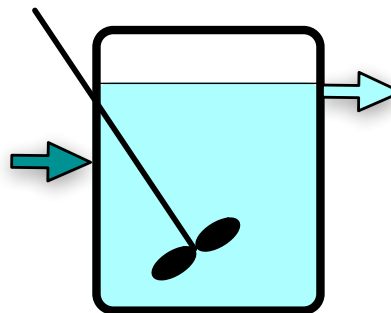


$$\begin{aligned} \dot{V} &= \dot{V}^0 \text{ (constant } \rho \text{ liquid)} \\ T &= 653 \text{ }^\circ\text{R} \\ \dot{n}_A &= 0.0005 \text{ lbmol min}^{-1} \\ \dot{n}_B &= 0.2405 \text{ lbmol min}^{-1} \\ \dot{n}_Z &= 0.0095 \text{ lbmol min}^{-1} \end{aligned}$$

$$\begin{aligned} V &= 18 \text{ ft}^3 \\ \dot{Q} &= 0 \\ \dot{W} &\approx 0 \end{aligned}$$

## Change of Operating Parameters

$$\begin{aligned} \dot{V}^0 &= 0.16 \text{ ft}^3 \text{ min}^{-1} \\ T^0 &= 650 \text{ }^\circ\text{R} \\ \dot{n}_A^0 &= 0.02 \text{ lbmol min}^{-1} \\ \dot{n}_B^0 &= 0.5 \text{ lbmol min}^{-1} \\ \dot{n}_Z^0 &= 0 \text{ lbmol min}^{-1} \end{aligned}$$



$$\begin{aligned} \dot{V} &= \dot{V}^0 \text{ (constant } \rho \text{ liquid)} \\ T &= \\ \dot{n}_A &= \\ \dot{n}_B &= \\ \dot{n}_Z &= \end{aligned}$$

# Solution

- A set of four ODEs
  - ▶ Independent variable is t
  - ▶ Dependent variables are  $\dot{n}_A$ ,  $\dot{n}_B$ ,  $\dot{n}_Z$  and T
- Solve for many different final values of t and plot corresponding conversion
- Only variable quantity in ODEs is  $r_1$

$$r_1 = k_0 \exp\left\{\frac{-23000 \text{ }^\circ\text{R}}{T}\right\} C_A C_B$$

$$\times \left[ 1 - \frac{C_Z}{K_0 \exp\left\{\frac{20000 \text{ }^\circ\text{R}}{T}\right\} C_A C_B} \right]$$

$$\frac{d\dot{n}_A}{dt} = \frac{\dot{V}}{V} (\dot{n}_A^0 - \dot{n}_A - Vr_1)$$

$$\dot{n}_A(t=0) = 0.0005 \text{ lbmol min}^{-1}$$

$$\frac{d\dot{n}_B}{dt} = \frac{\dot{V}}{V} (\dot{n}_B^0 - \dot{n}_B - Vr_1)$$

$$\dot{n}_B(t=0) = 0.2405 \text{ lbmol min}^{-1}$$

$$\frac{d\dot{n}_Z}{dt} = \frac{\dot{V}}{V} (\dot{n}_Z^0 - \dot{n}_Z + Vr_1)$$

$$\dot{n}_Z(t=0) = 0.0095 \text{ lbmol min}^{-1}$$

- Solving will give  $\dot{n}_A$ ,  $\dot{n}_B$ ,  $\dot{n}_Z$  and T at each time
  - ▶ Calculate  $f_A$  at each time and plot

$$f_A = \frac{\dot{n}_A^0 - \dot{n}_A}{\dot{n}_A^0}$$

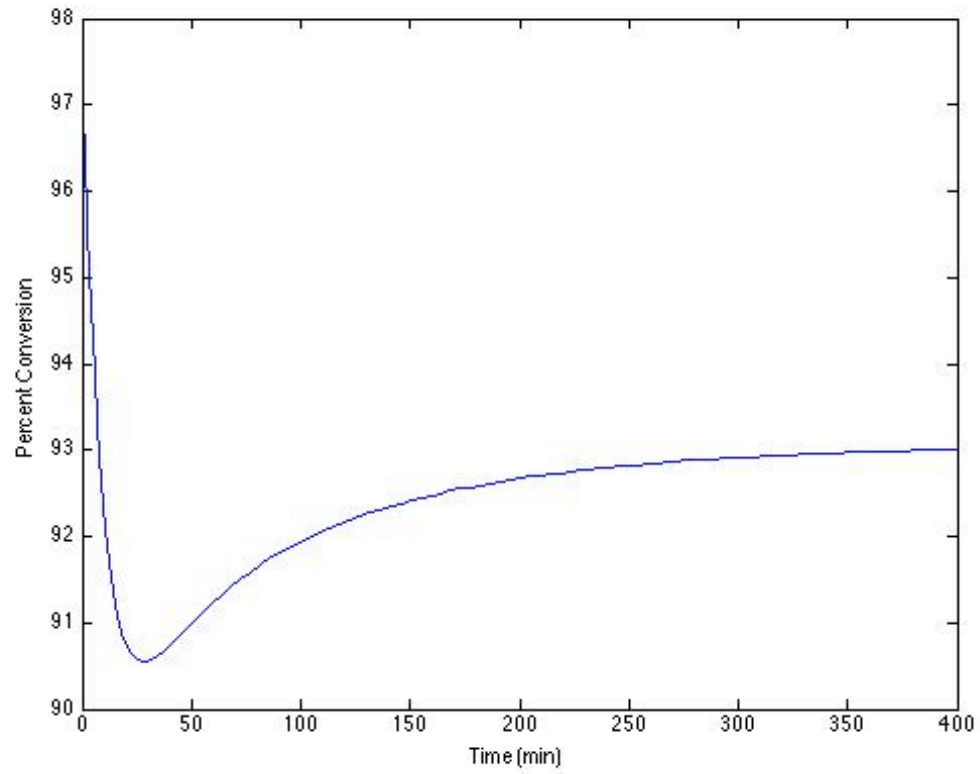
$$\frac{dT}{dt} = \frac{-\left(\dot{n}_A^0 \hat{C}_{p,A} + \dot{n}_B^0 \hat{C}_{p,B} + \dot{n}_Z^0 \hat{C}_{p,Z}\right)(T - T^0) - Vr_1 \Delta H_1(T)}{\frac{\dot{V}}{V} \left(\dot{n}_A \hat{C}_{p,A} + \dot{n}_B \hat{C}_{p,B} + \dot{n}_Z \hat{C}_{p,Z}\right)}$$

$$T(t=0) = 653 \text{ }^\circ\text{R}$$





# Results



# Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
- **Part III - Chemical Reaction Engineering**
  - ▶ A. Ideal Reactors
  - ▶ B. Perfectly Mixed Batch Reactors
  - ▶ **C. Continuous Flow Stirred Tank Reactors**
    - 21. Reaction Engineering of CSTRs
    - 22. Analysis of Steady State CSTRs
    - 23. Analysis of Transient CSTRs
    - 24. Multiple Steady States in CSTRs
  - ▶ D. Plug Flow Reactors
  - ▶ E. Matching Reactors to Reactions
- **Part IV - Non-Ideal Reactions and Reactors**

