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, 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 28 on Unit 27**

# 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
  - ▶ **D. Plug Flow Reactors**
    - 25. Reaction Engineering of PFRs
    - 26. Analysis of Steady State PFRs
    - 27. Analysis of Transient PFRs
  - ▶ E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors



# Transient PFR Design Equations

- Mole balance: 
$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \sum_{\substack{j=all \\ \text{reactions}}} \nu_{i,j} r_j - \frac{\pi D^2}{4 \dot{V}} \frac{\partial \dot{n}_i}{\partial t} + \frac{\pi D^2 \dot{n}_i}{4 \dot{V}^2} \frac{\partial \dot{V}}{\partial t}$$

- Energy balance:

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

- Initial conditions

- ▶ Values of the dependent variables ( $\dot{n}_i$  and  $T$ ) at all values of  $z$  in the instant after the change at  $t = 0$

- Boundary conditions

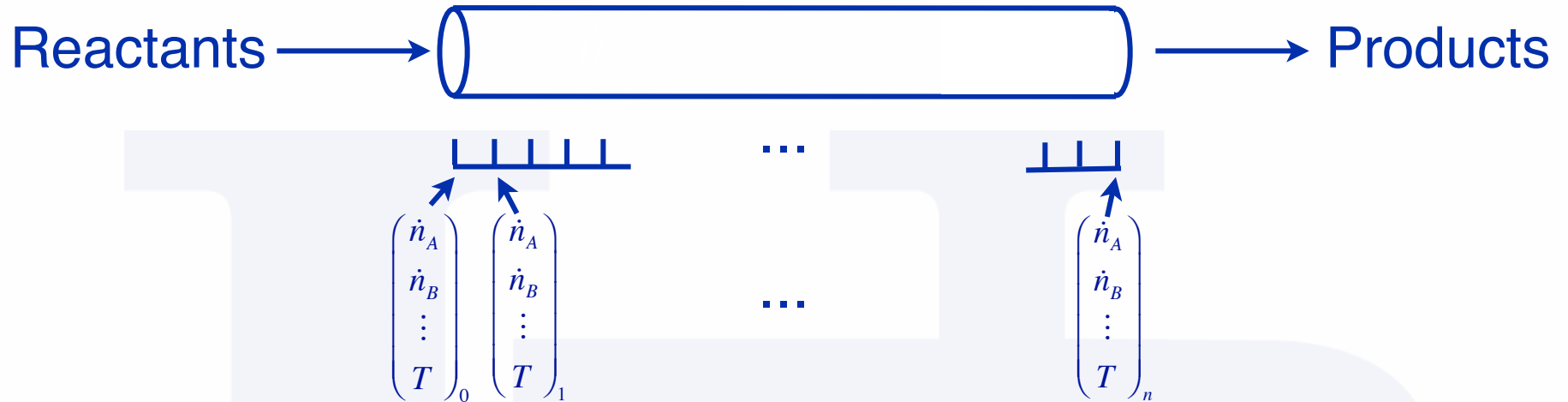
- ▶ Value of the dependent variables at one fixed position (usually the inlet) as a function of time since the change

- Fronts - a special kind of PFR transient

- ▶ The transient is initiated by a step change at the reactor inlet
- ▶ The step change is not “felt” by any of the fluid within the reactor
- ▶ The front moves through the reactor with a velocity equal to the fluid flow rate
- ▶ The concentration and temperature profiles ahead of the front are equal to the steady state profile prior to the step change
- ▶ The concentration and temperature profiles behind the front are equal to the steady state profile at the inlet conditions after the change



# Discretizing the Reactor



- Define a set of discretization points along the length of the reactor
- At each point, introduce variables for the molar flow rates and temperature
  - ▶ Initially (at  $t = 0$ ) the values of each variable is known at every discretization point
  - ▶ Goal is to find values at each point as a function of time

# Convert PDEs to ODEs



...



$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \sum_{j=\text{all reactions}} \nu_{i,j} r_j - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_i}{\partial t} + \frac{\pi D^2 \dot{n}_i}{4\dot{V}^2} \frac{\partial \dot{V}}{\partial t}$$

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

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \sum_{j=\text{all reactions}} \nu_{i,j} r_j - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_i}{\partial t} + \frac{\pi D^2 \dot{n}_i}{4\dot{V}^2} \frac{\partial \dot{V}}{\partial t}$$

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

$$\frac{\Delta \dot{n}_i}{\Delta z} = \frac{\pi D^2}{4} \sum_{j=\text{all reactions}} \nu_{i,j} r_j - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_i}{\partial t} + \frac{\pi D^2 \dot{n}_i}{4\dot{V}^2} \frac{\partial \dot{V}}{\partial t}$$

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

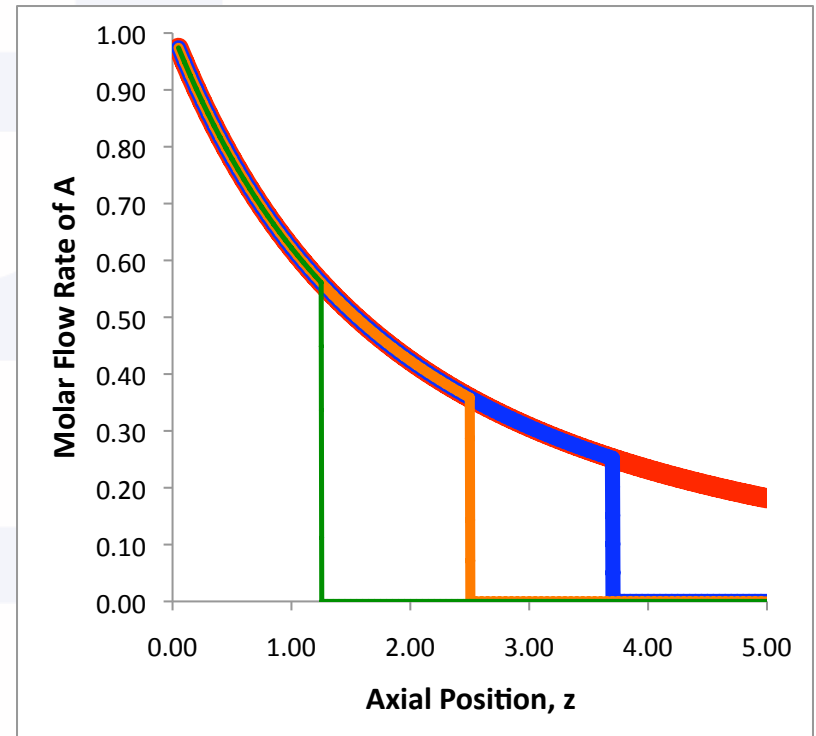
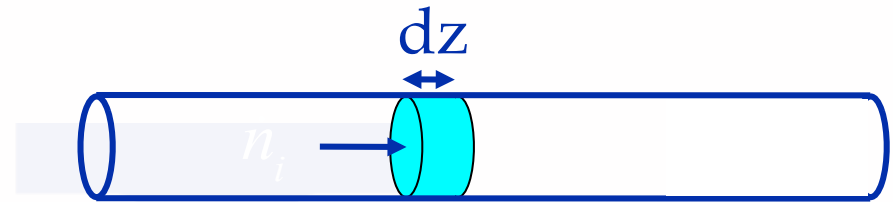
$$\frac{\Delta \dot{n}_i}{\Delta z} = \frac{\dot{n}_i - \dot{n}_i}{z - z}$$

$$\frac{\Delta \dot{n}_i}{\Delta z} = \frac{\dot{n}_i - \dot{n}_i}{z - z}$$



# Transient PFR Analysis Without Solving the Transient Equations

- When a differentially thick fluid element enters the reactor, it does not mix with the element preceding it nor with the one following it
- It could be the first element following a change in the input
- Or it could be the same as millions of elements that entered before it did
- What happens within that element is the same in either case
- A change at the inlet to a PFR propagates through the reactor as a front.

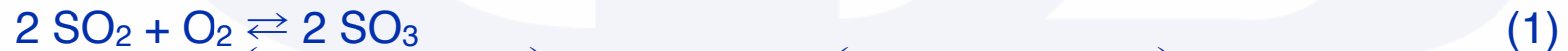


Questions?



# Parallel PFR Tubes Example

A tubular packed bed catalytic reactor is used for the oxidation of SO<sub>2</sub> to SO<sub>3</sub> using air, equation (1). The feed consists of 800 lbmol h<sup>-1</sup> of SO<sub>2</sub> and 4000 lbmol air h<sup>-1</sup> at 850 °F and 2.5 atm. The feed is split equally into 4500 tubes that are 20 ft long and have an inside diameter of 2.7 in. The fluid outside of the tubes is maintained at 800 °F. The catalyst particles have a sphericity of 0.45, a diameter of 0.46 cm, a bed porosity of 0.6 and a density of 35 lb<sub>m</sub> ft<sup>-3</sup>. The overall heat transfer coefficient, based on the inside area is (204 kJ h<sup>-1</sup> m<sup>-2</sup> K<sup>-1</sup>). The fluid viscosity may be assumed to be constant at 0.32 cp. The rate expression is given in equations (2) through (4). What are the outlet temperature and the sulfur dioxide conversion. Selected thermodynamic data are given on the next slide.



$$r_1 = \frac{A_1 \exp\left(\frac{-31 \text{ kcal mol}^{-1}}{RT}\right) P_{\text{SO}_2} P_{\text{O}_2} - A_2 \exp\left(\frac{-53.6 \text{ kcal mol}^{-1}}{RT}\right) P_{\text{SO}_3} P_{\text{O}_2}^{1/2}}{P_{\text{SO}_2}^{1/2}} \quad (2)$$

$$A_1 = 1.745 \times 10^5 \text{ mol s}^{-1} \text{ g}_{\text{cat}}^{-1} \text{ atm}^{-3/2} \quad (3)$$

$$A_2 = 7.59 \times 10^9 \text{ mol s}^{-1} \text{ g}_{\text{cat}}^{-1} \text{ atm}^{-1} \quad (4)$$





# Thermodynamic Data

Species	$\Delta H_{f-i}(298K)$	$C_{p-i} [\text{cal mol}^{-1} \text{K}^{-1}]^* = \alpha_i + \beta_i T + \gamma_i T^2 + \delta_i T^3$			
i	cal mol <sup>-1</sup>	$\alpha_i$	$\beta_i$	$\gamma_i$	$\delta_i$
SO <sub>2</sub>	-70950	5.697	0.016	-1.185E-05	3.172E-09
O <sub>2</sub>	0	6.713	-8.790E-07	4.170E-06	-2.544E-09
SO <sub>3</sub>	-94470	12.13	0.00812		
N <sub>2</sub>	0	7.44	-0.00324	6.400E-06	-2.790E-09



# Identifying and Solving Quantitative Reaction Engineering Problems

- Identifying quantitative reaction engineering problems
  - ▶ In a quantitative reaction engineering problem one is typically given
    - the reactions that are taking place
    - their rate expressions (with values for all of the kinetic parameters appearing in them)
    - the thermal properties of the fluids involved
    - selected specifications for the reactor
    - specifications on how the reactor operates
  - ▶ One is then typically asked
    - either to determine additional reactor specifications or operating procedures needed to meet specified reactor performance criteria
    - or to calculate selected reactor performance metrics
- 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 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 (in the case of steady state PFRs, they will be initial value differential equations)
  - 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 (again, in the case of steady state PFRs, they will be initial value differential equations)
  - Assuming they are written in the form  $\frac{dy}{dx} = f(\underline{y}, x)$ , 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  $f$  given  $x$  and  $\underline{y}$
- ▶ After the design equations have been solved numerically, yielding values for the independent and dependent variables, use the results to calculate any other quantities or plots that the problem asked for



### Reactor Relationships

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

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

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

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

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

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

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

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

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



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- Part I - Chemical Reactions
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  - ▶ C. Continuous Flow Stirred Tank Reactors
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    - 25. Reaction Engineering of PFRs
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    - 27. Analysis of Transient PFRs
  - ▶ **E. Matching Reactors to Reactions**
    - 28. Choosing a Reactor Type
    - 29. Multiple Reactor Networks
    - 30. Thermal Back-Mixing in a PFR
    - 31. Back-Mixing in a PFR via Recycle
    - 32. Ideal Semi-Batch Reactors
- **Part IV - Non-Ideal Reactions and Reactors**

