The background features a large, stylized blue and grey buffalo mascot. 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. The text is centered horizontally.

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

**Class 41 on Unit 38**

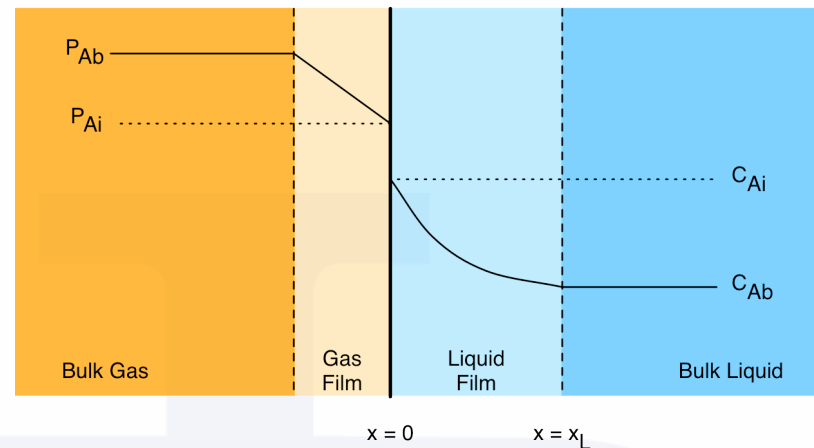
# Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
- Part III - Chemical Reaction Engineering
- **Part IV - Non-Ideal Reactions and Reactors**
  - ▶ A. Alternatives to the Ideal Reactor Models
  - ▶ B. Coupled Chemical and Physical Kinetics
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# Two Film Model for Gas-Liquid Reactions

- Thin films between the bulk fluid and the interface exist in each phase
- In these films mass transport occurs only by diffusion
- At the interface,  $x = 0$ , phase equilibrium is established
  - ▶  $P_{Ai} = h_A C_{Ai}$  (Henry's law)
- Hatta number,  $\gamma$ , represents rate of reaction relative to rate of diffusion
- Liquid effectiveness factor,  $\eta_L$ , is ratio of actual rate to rate if there were no concentration gradients
- Liquid enhancement factor,  $\zeta$ , is ratio of actual gas absorption rate to gas absorption rate if no chemical reaction occurred
- Definitions of  $\gamma$ ,  $\eta_L$  and  $\zeta$  depend upon geometry, form of rate expression and other assumptions
- Expressions at right for geometry shown, reaction first order in A only, non-volatile liquid reactant B, and comparable rates of reaction and diffusion
  - ▶ Change if these conditions change
  - ▶ Often requires numerical solution



$$\gamma = x_L \sqrt{\frac{k}{D_{AL}}} = \frac{\sqrt{kD_{AL}}}{k_L}$$

$$\eta_L = \frac{1}{\gamma Sh \tanh \gamma} \left( 1 - \frac{C_{Ab}}{C_{Ai}} \frac{1}{\cosh \gamma} \right); \quad Sh = \frac{k_L}{A_v D_A}$$

$$\zeta = \frac{\gamma}{\tanh \gamma} \left[ 1 - \frac{C_{Ab}}{C_{Ai}} \left( \frac{1}{\cosh \gamma} \right) \right]$$



Questions?



# Today's Activity

- Take out a sheet of paper and write down three important points from today's class



# Gas-Liquid Batch Reactor

- Consider a batch reactor charged with toluene (liquid) at a specified T, then admit a specified amount of Cl<sub>2</sub> (gas) and agitate vigorously

▶ Assume

- Liquid phase is continuous and perfectly mixed
- Agitation causes formation and dispersion of Cl<sub>2</sub> bubbles such that the number and size of the bubbles are constant, leading to a constant ratio of the interfacial area to the liquid volume, S<sub>v</sub>
- Reaction rate and rate of diffusion of Cl<sub>2</sub> into the liquid are comparable
- Liquid density is constant
  - Gas volume then is constant
  - Gas pressure will change due to changes in gas phase moles and temperature

- ▶ Semi-batch reactor mole balances are used for Cl<sub>2</sub> (A) and toluene (B) in the bulk liquid volume

$$\frac{dn_{A,b}}{dt} = \dot{n}_A - V_{l,b}r(C_{A,b}, C_{B,b}, T_b); \quad n_{A,b}(0) = 0 \quad \frac{dn_{B,g}}{dt} = \dot{n}_B - V_{l,b}r(C_{A,b}, C_{B,b}, T_b); \quad n_{B,g}(0) = n_{B,g}^0$$

- The molar flow rates are found from the fluxes evaluated at interface between the liquid film and the bulk liquid

$$\dot{n}_A = N_A \Big|_{y=y_L} S_V V_{l,b} = -S_V V_{l,b} D_A \frac{\partial C_{A,f}}{\partial y} \Big|_{y=y_L} \quad \dot{n}_B = N_B \Big|_{y=y_L} S_V V_{l,b} = -S_V V_{l,b} D_B \frac{\partial C_{B,f}}{\partial y} \Big|_{y=y_L}$$



- The concentrations in the film, and hence the gradients are found from mole balances on A and B in the liquid film
  - The mole balances on A and B in the film are transient equations
    - ▶ The concentration profile is building up over time
    - ▶ We can make a pseudo-steady state assumption
      - ▶ Set the accumulation term equal to zero
      - ▶ Essentially this assumes that as the bulk composition changes, the gradients in the film accommodate instantaneously

- With the pseudo-steady state assumption, the mole balances take the form

$$D_A \frac{\partial^2 C_{A,f}}{\partial y^2} = r(C_{A,f}, C_{B,f}, T_f) \quad D_B \frac{\partial^2 C_{B,f}}{\partial y^2} = r(C_{A,f}, C_{B,f}, T_f)$$

- Boundary conditions are needed to solve these mole balances on the film

- ▶ @  $y = 0$ ,  $C_{A,f} = C_{A,i} = C_{A,g} = H_{AP} = H_A n_{A,g} RT / V_{\text{gas}}$  and  $\frac{\partial C_{B,f}}{\partial y} = 0$
- ▶ @  $y = y_L$ ,  $C_{A,f} = C_{A,b}$  and  $C_{B,f} = C_{B,b}$

- In order to solve the mole balances on A and B in the film, we need values for  $y_L$  and  $n_{A,g}$

- Since we have made the pseudo-steady state assumption
  - ▶ the flux of A into the film minus the flux of A out of the film is the amount of A that reacted within the film
  - ▶ the flux of B into the film is the amount of B that reacted within the film
  - ▶ these two fluxes are related through the reaction stoichiometry

$$-D_A \frac{\partial C_{A,f}}{\partial y} \Big|_{y=0} - \left( -D_A \frac{\partial C_{A,f}}{\partial y} \Big|_{y=y_L} \right) = D_B \frac{\partial C_{B,f}}{\partial y} \Big|_{y=y_L}$$

- ▶ this gives us an implicit expression for  $y_L$



- We can find  $n_{A,g}$  from a mole balance on the gas

$$\frac{dn_{A,g}}{dt} = D_A S_V V_{l,b} \left. \frac{\partial C_{A,f}}{\partial y} \right|_{y=0} ; n_{A,g}(0) = \frac{P^0 V_g}{RT^0}$$

- **Summary**

- ▶ We have a set of ODEs that we need to solve to find  $n_{B,b}$  (which is related by stoichiometry to the moles of product) for a specified final condition (processing time, conversion of B, etc.)

$$\frac{dn_{A,b}}{dt} = -S_V V_{l,b} D_A \left. \frac{\partial C_{A,f}}{\partial y} \right|_{y=y_L} - V_{l,b} r(C_{A,b}, C_{B,b}, T_b); n_{A,b}(0) = 0$$

$$\frac{dn_{B,g}}{dt} = -S_V V_{l,b} D_B \left. \frac{\partial C_{B,f}}{\partial y} \right|_{y=y_L} - V_{l,b} r(C_{A,b}, C_{B,b}, T_b); n_{B,g}(0) = n_{B,g}^0$$

$$\frac{dn_{A,g}}{dt} = D_A S_V V_{l,b} \left. \frac{\partial C_{A,f}}{\partial y} \right|_{y=0} ; n_{A,g}(0) = \frac{P^0 V_g}{RT^0}$$

- to solve these equations numerically, we will use an initial value ODE solver
- in addition to the initial values and the final condition we will need to provide code that evaluates the right hand side (RHS) of these equations given  $t$ ,  $n_{A,b}$ ,  $n_{B,b}$  and  $n_{A,g}$ 
  - Presumably, we know everything on the RHS of these equations except for the three partial derivatives evaluated at  $y = 0$  and  $y = y_L$
  - To evaluate those partials, our code will need to call a mixed boundary ODE solver to solve the balance equations on the film

$$D_A \frac{\partial^2 C_{A,f}}{\partial y^2} = r(C_{A,f}, C_{B,f}, T_f) \quad D_B \frac{\partial^2 C_{B,f}}{\partial y^2} = r(C_{A,f}, C_{B,f}, T_f)$$

- ▶ @  $y = 0$ ,  $C_{A,f} = C_{A,i} = C_{A,g} = H_A P = H_A n_{A,g} RT / V_{\text{gas}}$  and  $\frac{\partial C_{B,f}}{\partial y} = 0$
- ▶ @  $y = y_L$ ,  $C_{A,f} = C_{A,b}$  and  $C_{B,f} = C_{B,b}$





- ▶ Our mixed boundary ODE solver will need to evaluate the film mole balances; all the necessary quantities are known
- ▶ Our mixed boundary ODE solver will also need the value of  $y_L$ 
  - ▶ It will need to call a non-linear equation solver to solve the stoichiometry constraint

$$-D_A \left. \frac{\partial C_{A,f}}{\partial y} \right|_{y=0} - \left( -D_A \left. \frac{\partial C_{A,f}}{\partial y} \right|_{y=y_L} \right) = D_B \left. \frac{\partial C_{B,f}}{\partial y} \right|_{y=y_L}$$

- ▶ We will need to provide a guess for  $y_L$  to the non-linear equation solver along with code that evaluates the stoichiometry constraint
    - ▶ The code we provide to the non-linear equation solver will have to solve the same mixed boundary ODEs as before, but it will know the value of  $y_L$
    - ▶ It can find  $y_L$  and return the value to the first mixed boundary ODE solver
  - ▶ The mixed boundary ODE solver can return the values of the partials needed by the code we provided to the initial value ODE solver
    - ▶ The initial value ODE solver can calculate  $n_{A,b}$ ,  $n_{B,b}$  and  $n_{A,g}$  versus  $t$
- We made many assumptions; the process above can be modified accordingly
    - ▶ We accounted for the consumption of A and B in the film; if diffusion is very fast compared to reaction, we can drop the rate term from the film mole balances
    - ▶ We assumed that the reaction and diffusion rates were comparable; if reaction is very fast, we can set the concentration of A in the bulk to zero so that all reaction occurs in the film
    - ▶ We assumed A was the only species that is present in both liquid and gas, we could use non-zero Henry's law constants for B and the products, so they all appear in the gas phase
      - This will introduce the need to add a gas phase film mole balance



- ▶ We assumed pseudo-steady state; we could account for accumulation in the film
  - Doing this would not be a trivial exercise
- The alternative is to calculate a liquid effectiveness factor or liquid utilization factor at some average set of conditions
  - ▶ Then the rate in the bulk liquid mole balances would be multiplied by this factor and analytical expressions for the partial derivatives in those balances would be used
    - these analytical expressions would be based on the average conditions, not the actual conditions in the reactor



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