A First Course on Kinetics and Reaction Engineering

Class 20 on Unit 19

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
    - 18. Reaction Engineering of Batch Reactors
    - 19. Analysis of Batch Reactors
    - 20. Optimization of Batch Reactor Processes
  - C. Continuous Flow Stirred Tank Reactors
  - D. Plug Flow Reactors
  - E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors

Modeling a Process Step for a Batch Reactor

- Write a mole balance design equation for every reactant and product
  - $\frac{dn_i}{dt} = V \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j$
- Write an energy balance
  - $\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all \\ species}} \left(n_i \hat{C}_{p,i} \right) + V \sum_{\substack{j=all \\ reactions}} \left(r_j \Delta H_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt}$
  - May not be needed if the reactor operates isothermally
- If there is heat transfer to a heat transfer fluid of uniform temperature
  - set $\dot{Q} = UA\left(T_e - T\right)$ in the energy balance
  - If the heat is from a heat transfer fluid's phase change, check that the flow rate of the heat transfer fluid is at least equal to the minimum value
    - $\dot{Q} = \dot{m}_{\min}\left(\Delta \tilde{H}_v\left(T_e\right)\right)$
    - determine the proper value of *U* based upon geometry, etc.
  - If the heat is sensible heat from heat transfer fluid that is perfectly mixed, write an energy balance on the heat transfer fluid
    - $\dot{m}\tilde{C}_{p,e}\left(T_e^0 - T_e\right) - \dot{Q} = \rho_e V_e \tilde{C}_{p,e} \frac{dT_e}{dt}$
    - set $\dot{Q} = UA\left(T_e - T\right)$ in both energy balances
    - determine the proper value of *U* based upon geometry, etc.
- Solve the resulting set of design equations

Simplifications and Solution

- Simplification of the energy balance on the reaction volume
  - $$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all \\ species}} \left(n_i \hat{C}_{p,i} \right) + V \sum_{\substack{j=all \\ reactions}} \left(r_j \Delta H_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt}$$
  - If the reactor is adiabatic, the heat term equals zero
  - The work term almost always equals zero (no shafts or moving boundaries except agitator)
  - The derivative of the volume with respect to time may almost always be set equal to zero
  - The derivative of the pressure with respect to time
    - may almost always be set to zero for liquids
    - is re-written using the ideal gas law (for ideal gases)
- Numerical solution of the set of design equations (initial value ordinary differential equations)
  - Write the equations in the following (vector) form: $\frac{d\underline{y}}{dt} = \underline{f}\left(\underline{y}, t\right); \quad \underline{y}\left(t=0\right) = \underline{y}^0$
  - Use software of your choice to solve numerically; no matter what software you use you will need to provide
    - the initial values of the dependent variables, that is, the values of each y_i at $t = 0$
    - the final value of either t or one of the dependent variables
    - code that evaluates each of the functions, f_i, given a value for t, values for each of the dependent variables, y_i, and information given in the problem specification and other reference sources such as handbooks

Major AFCoKaRE Problem Types and How to Identify Them

- Reaction Mechanism Problems
  - In a reaction mechanism problem one is typically given a macroscopically observed (also called overall or apparent) reaction along with a mechanism and asked to generate a rate expression for the macroscopically observed reaction rate.
- Age Function Problems
  - In an age function problem one is typically given data for the response of a laboratory reactor to either a step change or an impulse stimulus and asked to use those data to determine whether the laboratory reactor obeys the assumptions of one of the ideal flow reactor models (CSTR or PFR).
- Kinetics Data Analysis Problems
  - In a kinetics data analysis problem, one is typically given a set of kinetics data for a given reaction, the type of ideal reactor used to gather those data and a description of the reactor and how it was operated. One is then asked either to find a rate expression that describes the data, or, more commonly to test whether a given rate expression gives an accurate representation of the data.
- Qualitative Reaction Engineering Problems
  - In a qualitative reaction engineering problem, one is typically given the reaction(s) that is(are) taking place and some information about them along with the type of reactor being used and some information about how that reactor is operated. One is then usually asked to qualitatively describe or sketch how one (or more) quantities will vary during the operation of the reactor. In particular, one is not asked to calculate quantities or to plot calculated quantities (as opposed to making a qualitative sketch).

- 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 parameters appearing in them), the thermal properties of the fluids involved, selected specifications for the reactor and specifications on how the reactor operates. One is then typically asked either to determine additional reactor specifications or operating procedures to meet specified reactor performance criteria, or, to calculate the selected reactor performance metrics.

A General Approach to Solving Quanitative 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 19.1

A gas mixture contains 1500 ppm of A, 1000 ppm of B and 7% C. The remainder of the gas is inert (non-reactive). A 3 L reactor steel reactor is charged with this mixture at 1115 K and 1.7 atm. Reactions (1) and (2) take place adiabatically with rates given by equations (3) and (4). The pre-exponential factors for reactions (1) and (2) are 6.1 x 10^{16} L mol^{-1} s^{-1} and 5.5 x 10^{13} s^{-1}, respectively; the activation energies are 250 and 320 kJ/mol, respectively. Calculate the parts per million of B after 0.5, 1 and 5 seconds. You may assume the heats of reactions (1) and (2) to be constant and equal to -1700 kJ/mol and -800 kJ/mol, respectively. The heat capacities of the gases may be taken to equal that of the inert, 32 J mol^{-1} K^{-1}, and to be independent of temperature.

$$4\,A + 4\,B + C \rightarrow 4\,Y + 6\,Z \quad (1)$$

$$4\,A + 5\,C \rightarrow 4\,B + 6\,Z \quad (2)$$

$$r_1 = k_{0,1} \exp\left\{\frac{-E_1}{RT}\right\} C_A C_B \quad (3)$$

$$r_2 = k_{0,2} \exp\left\{\frac{-E_2}{RT}\right\} C_A \quad (4)$$

Solution

- 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

Solution

- Read through the problem statement and determine
  - the type of reactor being used: a batch reactor
  - whether it operates transiently or at steady state: batch reactors are always transient
  - whether it is heated/cooled, isothermal or adiabatic: it operates adiabatically
  - (if the reactor is a PFR) whether there is a significant pressure drop: not applicable
- 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

Solution

- Given
  - y_A = 1500/1000000; y_B = 1000/1000000, y_C = 0.07, y_Y = y_Z = 0, V = 3 L, T^0 = 1115 K, P^0 = 1.7 atm, $k_{0,1} = 6.1 \times 10^{16}$ L mol^{-1} s^{-1}, $k_{0,2} = 5.5 \times 10^{13}$ s^{-1}, E_1 = 250 kJ mol^{-1}, E_2 = 320 kJ mol^{-1}, ΔH_1 = -1700 kJ mol^{-1}, ΔH_2 = -800 kJ mol^{-1}, $\hat{C}_{p,i}$ = 32 J mol^{-1} K^{-1}
  - V is extensive, so it is not necessary to assume a basis
- Asked to find
  - y_B (expressed as ppm) at t = 0.5, 1 and 5 s

Solution

- Read through the problem statement and determine
  - the type of reactor being used: a batch reactor
  - whether it operates transiently or at steady state: batch reactors are always transient
  - whether it is heated/cooled, isothermal or adiabatic: it operates adiabatically
  - (if the reactor is a PFR) whether there is a significant pressure drop: not applicable
- 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

Reactor Relationships

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

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

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

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

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

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

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

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

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

Solution

$$4\,A + 4\,B + C \rightarrow 4\,Y + 6\,Z$$
$$4\,A + 5\,C \rightarrow 4\,B + 6\,Z$$

- Given
  - $y_A = 1500/1000000$; $y_B = 1000/1000000$, $y_C = 0.07$, $y_Y = y_Z = 0$, $V = 3$ L, $T^0 = 1115$ K, $P^0 = 1.7$ atm, $k_{0,1} = 6.1 \times 10^{16}$ L mol^{-1} s^{-1}, $k_{0,2} = 5.5 \times 10^{13}$ s^{-1}, $E_1 = 250$ kJ mol^{-1}, $E_2 = 320$ kJ mol^{-1}, $\Delta H_1 = -1700$ kJ mol^{-1}, $\Delta H_2 = -800$ kJ mol^{-1}, $\hat{C}_{p,i} = 32$ J mol^{-1} K^{-1}
  - V is extensive, so it is not necessary to assume a basis
- Asked to find
  - y_B (expressed as ppm) at t = 0.5, 1 and 5 s
- Mole balances

$$\frac{dn_A}{dt} = V\left(\nu_{A,1} r_1 + \nu_{A,2} r_2\right) = V\left(-4r_1 - 4r_2\right)$$

$$\frac{dn_B}{dt} = V\left(\nu_{B,1} r_1 + \nu_{B,2} r_2\right) = V\left(-4r_1 + 4r_2\right)$$

$$\frac{dn_C}{dt} = V\left(\nu_{C,1} r_1 + \nu_{C,2} r_2\right) = V\left(-r_1 - 5r_2\right)$$

$$\frac{dn_Y}{dt} = V\left(\nu_{Y,1} r_1 + \nu_{Y,2} r_2\right) = 4Vr_1$$

$$\frac{dn_Z}{dt} = V\left(\nu_{Z,1} r_1 + \nu_{Z,2} r_2\right) = V\left(6r_1 + 6r_2\right)$$

Solution

- Read through the problem statement and determine
  - the type of reactor being used: a batch reactor
  - whether it operates transiently or at steady state: batch reactors are always transient
  - whether it is heated/cooled, isothermal or adiabatic: it operates adiabatically
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$$\dot{n}_i^0+V\sum_{\substack{j=\text{all}\\ \text{reactions}}}\nu_{i,j}r_j=\dot{n}_i+\frac{d}{dt}\left(\frac{\dot{n}_iV}{\dot{V}}\right);$$

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

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

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

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

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

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

Solution

$4\,A + 4\,B + C \rightarrow 4\,Y + 6\,Z$

$4\,A + 5\,C \rightarrow 4\,B + 6\,Z$

- Given
  - $y_A = 1500/1000000$; $y_B = 1000/1000000$, $y_C = 0.07$, $y_Y = y_Z = 0$, $V = 3$ L, $T^0 = 1115$ K, $P^0 = 1.7$ atm, $k_{0,1} = 6.1 \times 10^{16}$ L mol^{-1} s^{-1}, $k_{0,2} = 5.5 \times 10^{13}$ s^{-1}, $E_1 = 250$ kJ mol^{-1}, $E_2 = 320$ kJ mol^{-1}, $\Delta H_1 = -1700$ kJ mol^{-1}, $\Delta H_2 = -800$ kJ mol^{-1}, $\hat{C}_{p,i} = 32$ J mol^{-1} K^{-1}
  - V is extensive, so it is not necessary to assume a basis
- Asked to find
  - y_B (expressed as ppm) at t = 0.5, 1 and 5 s
- Mole balances

$$\frac{dn_A}{dt} = V\left(\nu_{A,1}r_1 + \nu_{A,2}r_2\right) = V\left(-4r_1 - 4r_2\right)$$

$$\frac{dn_Y}{dt} = V\left(\nu_{Y,1}r_1 + \nu_{Y,2}r_2\right) = 4Vr_1$$

$$\frac{dn_B}{dt} = V\left(\nu_{B,1}r_1 + \nu_{B,2}r_2\right) = V\left(-4r_1 + 4r_2\right)$$

$$\frac{dn_Z}{dt} = V\left(\nu_{Z,1}r_1 + \nu_{Z,2}r_2\right) = V\left(6r_1 + 6r_2\right)$$

$$\frac{dn_C}{dt} = V\left(\nu_{C,1}r_1 + \nu_{C,2}r_2\right) = V\left(-r_1 - 5r_2\right)$$

- Energy Balance

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

$$0 = \frac{dT}{dt}\left(n_A + n_B + n_C + n_Y + n_Z + n_I\right)\hat{C}_{p,i} + V\left(r_1\Delta H_1 + r_2\Delta H_2\right) - V\frac{dP}{dt}$$

- 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 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 **they are differential 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

- 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 they are differential 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
        - independent variable: t
        - dependent variables: n_A, n_B, n_C, n_Y, n_Z, T, P
        - 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
            - there are 7 dependent variables and 6 equations
            - express P in terms of the other dependent variables using the ideal gas law

- The derivative of the pressure can be eliminated by use of the ideal gas law

$$V\frac{dP}{dt} = V\frac{d}{dt}\left(\frac{n_{total}RT}{V}\right)$$

$$= V\frac{R}{V}\frac{d}{dt}\left(n_{total}T\right)$$

$$= R\frac{d}{dt}\left(\left(n_A + n_B + n_C + n_Y + n_Z + n_I\right)T\right)$$

$$= R\left(\left(n_A + n_B + n_C + n_Y + n_Z + n_I\right)\frac{dT}{dt} + T\left(\frac{dn_A}{dt} + \frac{dn_B}{dt} + \frac{dn_C}{dt} + \frac{dn_Y}{dt} + \frac{dn_Z}{dt} + \cancel{\frac{dn_I}{dt}}\right)\right)$$

- Recall $\frac{dn_A}{dt} = V\left(-4r_1 - 4r_2\right)$ $\quad \frac{dn_B}{dt} = V\left(-4r_1 + 4r_2\right)$ $\quad \frac{dn_C}{dt} = V\left(-r_1 - 5r_2\right)$

$$\frac{dn_Y}{dt} = 4Vr_1 \qquad \frac{dn_Z}{dt} = V\left(6r_1 + 6r_2\right)$$

- Substitute

$$V\frac{dP}{dt} = R\left(\left(n_A + n_B + n_C + n_Y + n_Z + n_I\right)\frac{dT}{dt} + TV\left(r_1 + r_2\right)\right)$$

- Substitute in the energy balance

$$0 = \frac{dT}{dt}\left(n_A + n_B + n_C + n_Y + n_Z + n_I\right)\hat{C}_{p,I} + V\left(r_1\Delta H_1 + r_2\Delta H_2\right)$$
$$-R\left(\left(n_A + n_B + n_C + n_Y + n_Z + n_I\right)\frac{dT}{dt} + TV\left(r_1 + r_2\right)\right)$$

Solution

$4\,A + 4\,B + C \rightarrow 4\,Y + 6\,Z$

$4\,A + 5\,C \rightarrow 4\,B + 6\,Z$

- Given
  - $y_A^0 = 1500/1000000$; $y_B^0 = 1000/1000000$, $y_C^0 = 0.07$, $y_Y^0 = y_Z^0 = 0$, $V = 3$ L, $T^0 = 1115$ K, $P^0 = 1.7$ atm, $k_{0,1} = 6.1 \times 10^{16}$ L mol^{-1} s^{-1}, $k_{0,2} = 5.5 \times 10^{13}$ s^{-1}, $E_1 = 250$ kJ mol^{-1}, $E_2 = 320$ kJ mol^{-1}, $\Delta H_1 = -1700$ kJ mol^{-1}, $\Delta H_2 = -800$ kJ mol^{-1}, $\hat{C}_{p,i} = 32$ J mol^{-1} K^{-1}
  - V is extensive, so it is not necessary to assume a basis
- Asked to find
  - y_B (expressed as ppm) at t = 0.5, 1 and 5 s
- Mole balances

$$\frac{dn_A}{dt} = V\left(\nu_{A,1}r_1 + \nu_{A,2}r_2\right) = V\left(-4r_1 - 4r_2\right)$$

$$\frac{dn_Y}{dt} = V\left(\nu_{Y,1}r_1 + \nu_{Y,2}r_2\right) = 4Vr_1$$

$$\frac{dn_B}{dt} = V\left(\nu_{B,1}r_1 + \nu_{B,2}r_2\right) = V\left(-4r_1 + 4r_2\right)$$

$$\frac{dn_Z}{dt} = V\left(\nu_{Z,1}r_1 + \nu_{Z,2}r_2\right) = V\left(6r_1 + 6r_2\right)$$

$$\frac{dn_C}{dt} = V\left(\nu_{C,1}r_1 + \nu_{C,2}r_2\right) = V\left(-r_1 - 5r_2\right)$$

- Energy Balance

$$\frac{dT}{dt} = \frac{-V\left(r_1\left(\Delta H_1 - RT\right) + r_2\left(\Delta H_2 - RT\right)\right)}{\left(\hat{C}_{p,I} - R\right)\left(n_A + n_B + n_C + n_Y + n_Z + n_I\right)}$$

- 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 they are differential 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
    - independent variable: t
    - dependent variables: n_A, n_B, n_C, n_Y, n_Z, T, P
    - 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
      - there are 7 dependent variables and 6 equations
      - express P in terms of the other dependent variables using the ideal gas law
- 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 $\frac{d}{dx}\underline{y} = \underline{f}\left(x,\underline{y}\right)$ 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 $\frac{d}{dx}\underline{y} = \underline{f}\left(x,\underline{y}\right)$ 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 $\underline{y}$

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- Initial values
  - At t = 0

$$n_i(0) = y_i^0 n_{total}^0 \qquad n_{total}^0 = \frac{P^0 V}{RT^0}$$

$$T(0) = T^0$$

- Code to evaluate the right hand sides of the equations (given independent and dependent variables)
  - In addition to the quantities given in the problem statement, need r_1 and r_2

$$r_1 = k_{0,1} \exp\left\{\frac{-E_1}{RT}\right\} C_A C_B \qquad C_A = \frac{n_A}{V} \qquad C_B = \frac{n_B}{V}$$

$$r_2 = k_{0,2} \exp\left\{\frac{-E_2}{RT}\right\} C_A$$

- Final value of either the independent variable or one of the dependent variables
  - Three cases: t = 0.5 s, t = 1 s and t = 5 s

- 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

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$$y_B = \frac{n_B(t)}{n_A(t)+n_B(t)+n_C(t)+n_Y(t)+n_Z(t)+n_I(t)}$$

$$n_I(t) = n_I(0) = y_I^0 n_{total}^0 \qquad y_I^0 = 1 - y_A^0 - y_B^0 - y_C^0 - y_Y^0 - y_Z^0$$

$$ppm_B = 10^6 y_B$$

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
    - 18. Reaction Engineering of Batch Reactors
    - 19. Analysis of Batch Reactors
    - 20. Optimization of Batch Reactor Processes
  - C. Continuous Flow Stirred Tank Reactors
  - D. Plug Flow Reactors
  - E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors