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 and spans most of the width of the page.

A First Course on Kinetics and Reaction Engineering

Class 13 on Unit 13

Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
 - ▶ A. Rate Expressions
 - ▶ B. Kinetics Experiments
 - 11. Laboratory Reactors
 - 12. Performing Kinetics Experiments
 - ▶ C. Analysis of Kinetics Data
 - 13. CSTR Data Analysis
 - 14. Differential Data Analysis
 - 15. Integral Data Analysis
 - 16. Numerical Data Analysis
- Part III - Chemical Reaction Engineering
- Part IV - Non-Ideal Reactions and Reactors



Testing a Rate Expression Using CSTR Data

- Assuming one reaction is taking place and a steady state reactor, a single mole balance design equation is needed to model the reactor

- ▶ $\dot{n}_i - \dot{n}_i^0 = Vr_{i,j}$

- ▶ i is any one reactant or product; j is the one reaction that is taking place

- Analysis procedure

- ▶ Substitute math function to be tested as rate expression into the design equation above

- ▶ Linearize the resulting equation

- $y = m_1 x_1 + m_2 x_2 + \dots + m_n x_n + b$

- each slope, m_i , must be constant with the same value in every experiment and it must contain at least one unknown parameter from the rate expression
- there must be at least one slope (i. e. $n \geq 1$)
- there does not have to be an intercept, b

- ▶ Calculate values of y and x_i for every experimental data point

- ▶ Use linear least squares to fit the linearized model equation to the experimental data

- ▶ Decide whether the fit is sufficiently accurate

- correlation coefficient
- model plot or parity plot and residuals plots

- ▶ If the fit is accurate, calculate the best values of the rate expression parameters and their uncertainties

- ▶ If the fit is not accurate, choose a different mathematical function to test as a rate expression



Useful Points and Relationships

- The concentrations or partial pressures in the rate expression are evaluated at the outlet conditions, which are the same as the perfectly mixed contents of the reactor where the reaction is taking place
- For liquid phase systems, it can usually be assumed that the volumetric flow rate is constant so the inlet and outlet volumetric flow rates are equal

$$\dot{V}^0 = \dot{V} \quad \dot{V} = \frac{1}{\rho} \left(\sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_i M_i \right)$$

- For ideal gases

$$x_i = \frac{\dot{n}_i}{\dot{n}_{tot}} \quad P_i = x_i P = \frac{\dot{n}_i P}{\dot{n}_{tot}} \quad \dot{V} = \frac{\dot{n}_{tot} RT}{P}$$

- For liquid or gas phase systems

$$C_i^0 = \frac{\dot{n}_i^0}{\dot{V}^0} \quad C_i = \frac{\dot{n}_i}{\dot{V}} \quad \tau = \frac{V}{\dot{V}^0} \quad SV = \frac{1}{\tau} = \frac{\dot{V}^0}{V} \quad \dot{n}_{tot} = \sum_{i=1}^{N_{\text{species}}} \dot{n}_i$$



Questions?



Activity 13.1

- Suppose the liquid phase reaction $A + B \rightarrow Y + Z$ was studied in a 100 L CSTR
- Three kinds of experiments were performed to generate kinetics data
 - ▶ The results are given in the handout, 13_Activity_1_Handout.xlsx, that accompanies this Unit
 - ▶ Experiments to gauge whether the reaction is reversible or not are highlighted in light blue and are summarized below
 - ▶ Experiments to help guess the concentration dependence of the rate are highlighted in light green and are summarized on the next slide
 - ▶ Experiments to generate a large kinetics data set, spanning the conditions of interest are highlighted in light orange and are also summarized on the next slide
- Experiments to gauge reversibility of the reaction (light blue highlight)
 - ▶ 2 experiments
 - One at low temperature (298 K) and one at high temperature (360 K)
 - High concentrations of products ($C_Y = C_Z = 1.0$ M) and low concentrations of reactants ($C_A = C_B = 0.1$ M)
 - Low flow rate (high space time) to get highest conversion possible
 - ▶ Results
 - To within the experimental noise, no product was converted to reactant
 - **The reaction appears to be irreversible**



Experimental Results

- Experiments to scope composition dependence (highlighted in light green)
 - ▶ Problem: we set the inlet concentrations, not the outlet concentration
 - If the space time is high, all of the concentrations will be considerably different at the outlet than they were at the inlet
 - Therefore, use a small space time so that the concentrations change only slightly
 - ▶ 5 experiments, all at the same temperature (325 K) and largest allowed flow (1000 L/min)
 - Base case inlet composition: $C_A = C_B = C_Y = C_Z = 1 \text{ M}$
 - Outlet C_Y is 1.06 M, so concentration changes are small
 - ▶ Results
 - Double inlet C_A or C_B , ΔC_Y is approximately double the base case
 - Double inlet C_Y or C_Z , ΔC_Y is approximately the same as the base case
 - $r = k C_A C_B$ may be a good first guess for the rate expression
- Experiments to generate a large data set spanning conditions of interest (highlighted in light orange)
 - ▶ Five “blocks” of experiments at 305, 320, 330, 345 and 355 K
 - ▶ Within each block want to span a range of concentrations of each reagent by
 - Using different feed compositions
 - Varying space time
 - ▶ A statistical design is preferred
 - I just randomly selected different inlet settings trying to span the range of concentrations
 - For each block I arbitrarily picked inlet concentrations then did a few experiments with different flow rates (to span a range of conversions)
 - Repeated with a second set of inlet concentrations



Activity 13.1a

- The kinetics data for this example consist of five “blocks” of constant temperature experiments
- Data of this kind can be processed in two steps
 - ▶ In the first step, each of the blocks is processed separately
 - Since all of the experiments in the block use the same temperature, the rate coefficient(s) can be treated as a single unknown parameter within any one block
 - The data in a block can be analyzed, and the best value for the rate coefficient(s) at that block temperature can be determined
 - ▶ In the second step, the temperature dependence of the rate coefficient(s) can be determined by fitting the Arrhenius expression to the resulting k vs. block temperature data
- To begin, you have been assigned one of the constant temperature blocks of data to analyze
 - ▶ Test the rate expression suggested by the preliminary experiments ($r = k C_A C_B$) using the data in the block you have been assigned
 - ▶ Determine whether the rate expression is satisfactory
 - If it is, determine the best value for k at the temperature of your block
 - ▶ Determine the best values for the pre-exponential factor and the activation energy



Analysis of a Data Block

- Mole balance on Y



Analysis of a Data Block

- Mole balance on Y
 - $\dot{n}_Y - \dot{n}_Y^0 = Vr_Y$
- Rate expression to test

U
T
E
B



Analysis of a Data Block

- Mole balance on Y
 - $\dot{n}_Y - \dot{n}_Y^0 = Vr_Y$
- Rate expression to test
 - $r_Y = kC_A C_B$
- Substituting



Analysis of a Data Block

- Mole balance on Y
 - $\dot{n}_Y - \dot{n}_Y^0 = Vr_Y$
- Rate expression to test
 - $r_Y = kC_A C_B$
- Substituting
 - $\dot{n}_Y - \dot{n}_Y^0 = kVC_A C_B$
- Linearize the model



Analysis of a Data Block

- Mole balance on Y
 - ▶ $\dot{n}_Y - \dot{n}_Y^0 = Vr_Y$
- Rate expression to test
 - ▶ $r_Y = kC_A C_B$
- Substituting
 - ▶ $\dot{n}_Y - \dot{n}_Y^0 = kVC_A C_B$
- The model is linear
 - ▶ Define
 - $y = \dot{n}_Y - \dot{n}_Y^0$
 - $x = VC_A C_B$
 - $m = k$
 - ▶ The model becomes
 - $y = mx$
- Can fit using linear least squares
 - ▶ Need to calculate y and x for each data point in the block



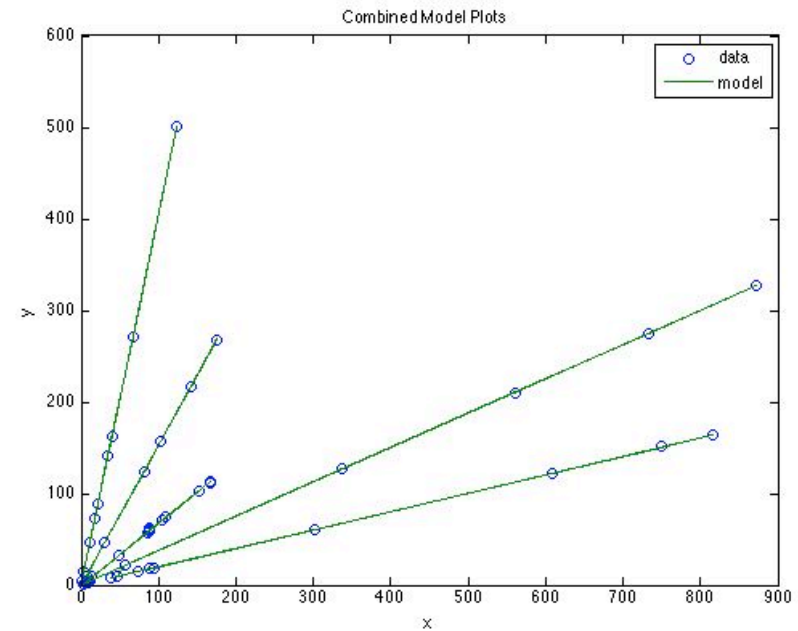
Analysis of a Data Block

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 - ▶ The model becomes
 - $y = mx$
- Can fit using linear least squares
 - ▶ Need to calculate y and x for each data point in the block
- Calculation of y
 - ▶ $\dot{n}_Y = \dot{V}C_Y$
 - ▶ $\dot{n}_Y^0 = \dot{V}^0 C_Y^0$
 - ▶ $\dot{V} = \dot{V}^0$
 - ▶ Given: \dot{V}^0, C_Y^0, C_Y
 - ▶ y can be calculated
- Calculation of x
 - ▶ from a mole table
 - $\dot{n}_A = \dot{n}_A^0 - \dot{n}_Y + \dot{n}_Y^0$
 - $\dot{n}_B = \dot{n}_B^0 - \dot{n}_Y + \dot{n}_Y^0$
 - ▶ $C_A = \frac{\dot{n}_A}{\dot{V}}; C_B = \frac{\dot{n}_B}{\dot{V}}$
 - ▶ Given: V and (from above) \dot{n}_Y^0, \dot{n}_Y
 - ▶ x can be calculated
- Fit block using linear least squares



Step 1 Fitting Results

- Excluded reversibility experiments
 - Apparent conversions were of the same order as experimental noise
- Correlation coefficient ~ 1 for each block
- Small, random deviations of data in model plots
- The rate expression is acceptable
 - Slope of fitted line is equal to rate coefficient
 - Uncertainty in slope equals uncertainty in rate coefficient
- Note, now have values of rate coefficient at each of 5 temperatures
 - In step 2, can make an Arrhenius plot
- Accompanying files
 - Activity_13_1_Results.xlsx shows data grouping/numbering
 - Activity_13_1.m performs calculations



| T (K) | r^2 | k (L/mol/min) | 95% C.L. |
|-------|--------|---------------|----------|
| 305 | 1 | 0.2009 | 0.0004 |
| 315 | 1 | 0.3753 | 0.0003 |
| 325 | 0.999 | 0.6755 | 0.0067 |
| 340 | 1 | 1.5297 | 0.0038 |
| 360 | 0.9999 | 4.0759 | 0.0194 |



Step 2, Find the Arrhenius Parameters

- Simply fit the Arrhenius expression to the results from the first part of the analysis shown at the right
 - ▶ If power-law exponents had been determined in the first part of the analysis and they were not the same for each block temperature, one could separately attempt to fit some functional form for the temperature dependence of each exponent
 - Unlike the rate coefficients where the functional form is known (Arrhenius expression) there isn't any theory to guide selection of a functional form for the exponents

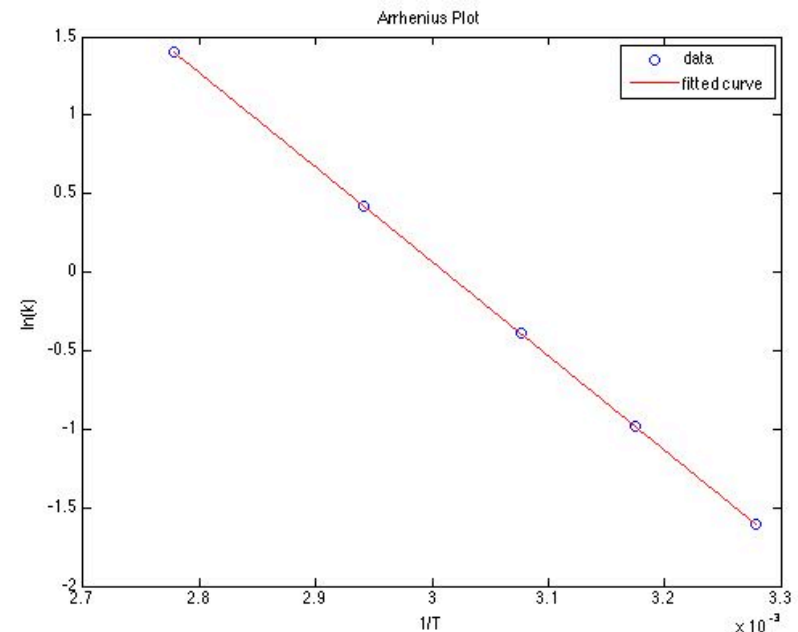
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 - ▶ If power-law exponents had been determined in the first part of the analysis and they were not the same for each block temperature, one could separately attempt to fit some functional form for the temperature dependence of each exponent
 - Unlike the rate coefficients where the functional form is known (Arrhenius expression) there isn't any theory to guide selection of a functional form for the exponents
- The fit is very good
 - ▶ $k_0 = 7.27 \pm 0.18 \times 10^7$ L/mol/min
 - ▶ $E = 49.97 \pm 0.07$ kJ/mol

| T (K) | r ² | k (L/mol/min) | 95% C.L. |
|-------|----------------|---------------|----------|
| 305 | 1 | 0.2009 | 0.0004 |
| 315 | 1 | 0.3753 | 0.0003 |
| 325 | 0.999 | 0.6755 | 0.0067 |
| 340 | 1 | 1.5297 | 0.0038 |
| 360 | 0.9999 | 4.0759 | 0.0194 |



Activity 13.1b

- An alternative approach is to analyze the full set of kinetics data all at once
 - ▶ To do this, the rate expression must be written as $r = k_0 \exp(-E/RT) C_A C_B$ and substituted in the design equation
 - ▶ The rest of the fitting process is analogous, but it uses the entire data set at once instead of processing in constant temperature blocks.
- Test the rate expression using this approach and compare the results to the previous findings



Activity 13.1b

- An alternative approach is to analyze the full set of kinetics data all at once
 - ▶ To do this, the rate expression must be written as $r = k_0 \exp(-E/RT) C_A C_B$
 - ▶ Substitution in the design equation
 - $\dot{n}_Y - \dot{n}_Y^0 = k_0 e^{-E/RT} V C_A C_B$
 - ▶ Linearization



Activity 13.1b

- An alternative approach is to analyze the full set of kinetics data all at once

- ▶ To do this, the rate expression must be written as $r = k_0 \exp(-E/RT) C_A C_B$

- ▶ Substitution in the design equation

$$- \dot{n}_Y - \dot{n}_Y^0 = k_0 e^{-E/RT} V C_A C_B$$

- ▶ Linearization

$$\frac{\dot{n}_Y - \dot{n}_Y^0}{V C_A C_B} = k_0 e^{-E/RT}$$

$$\ln\left(\frac{\dot{n}_Y - \dot{n}_Y^0}{V C_A C_B}\right) = \left(\frac{-E}{R}\right) \frac{1}{T} + \ln(k_0)$$

- This has the form $y = mx + b$ if $y = \ln\left(\frac{\dot{n}_Y - \dot{n}_Y^0}{V C_A C_B}\right)$ $x = \frac{-1}{RT}$

$$m = E \quad b = \ln(k_0)$$

- ▶ Calculate y and x for every data point in the full set and fit $y = mx + b$ to the resulting data

- In general, this approach is not recommended, especially if there are kinetics parameters other than rate coefficients (e. g. power-law exponents)

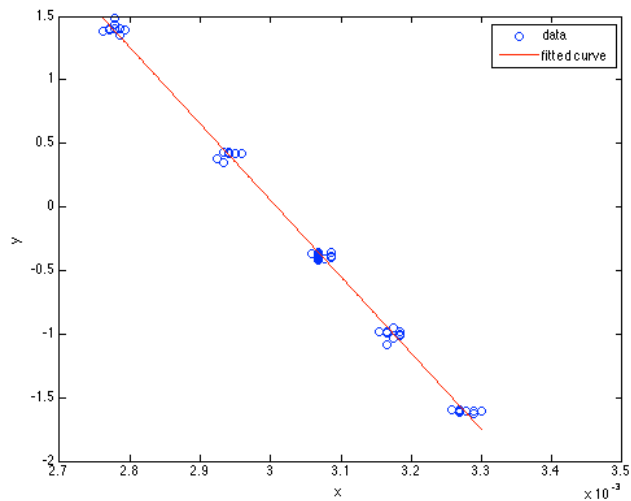
- ▶ The strong exponential temperature dependence can mask weaker concentration dependence of the reaction rate



Activity 13.1b

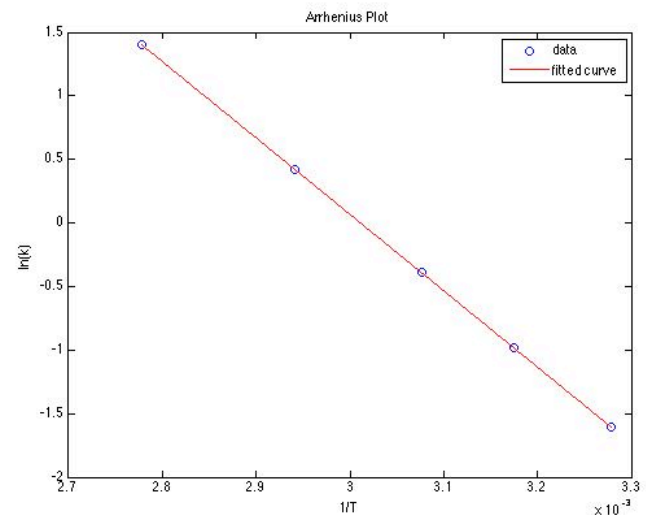
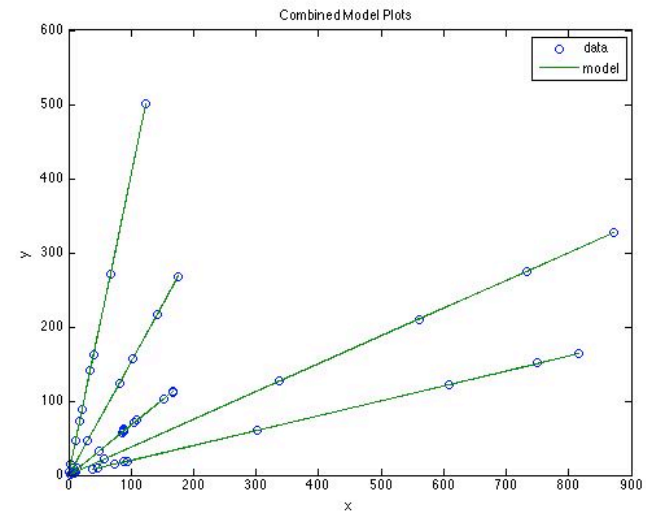
- Results from fitting all at once

- $r^2 = 0.9953$
- $k_0 = 7.21 \pm 2.62 \times 10^7 \text{ L/mol/min}$
- $E = 49.99 \pm 0.99 \text{ kJ/mol}$



- Results from two step fitting

- $k_0 = 7.27 \pm 0.18 \times 10^7 \text{ L/mol/min}$
- $E = 49.97 \pm 0.07 \text{ kJ/mol}$



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