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 entire graphic is centered on the page.

A First Course on Kinetics and Reaction Engineering

Class 15 on Unit 15

Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
 - ▶ A. Rate Expressions
 - ▶ B. 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



Integral Data Analysis

- Distinguishing features of integral data analysis
 - ▶ The model equation is a differential equation
 - ▶ The differential equation is integrated to obtain an algebraic equation which is then fit to the experimental data
- Before it can be integrated, the differential model equation must be re-written so the only variable quantities it contains are the dependent and independent variables
 - ▶ For a batch reactor, n_i and t
 - ▶ For a PFR, \dot{n}_i and z
 - ▶ Be careful with gas phase reactions where the number of moles changes
 - P and n_{tot} (in a batch reactor) or \dot{V} and \dot{n}_{tot} (in a PFR) will be variable quantities
- Often the integrated form of the PFR design equation cannot be linearized
 - ▶ Use non-linear least squared (Unit 16)
 - ▶ If there is only one kinetic parameter
 - Calculate its value for every data point
 - Average the results and find the standard deviation
 - If the standard deviation is a small fraction of the average and if the deviations of the individual values from the average are random
 - The model is accurate
 - The average is the best value for the parameter and the standard deviation is a measure of the uncertainty



Half-life Method

- Useful for testing rate expressions that depend, in a power-law fashion, upon the concentration of a single reactant

$$\triangleright r_A = -k(C_A)^\alpha$$

- The half-life, $t_{1/2}$, is the amount of time that it takes for the concentration of the reactant to decrease to one-half of its initial value.
- The dependence of the half-life upon the initial concentration can be used to determine the reaction order, α

- ▶ if the half-life does not change as the initial concentration of A is varied, the reaction is first order ($\alpha = 1$)

$$- t_{1/2} = \frac{0.693}{k}$$

- ▶ otherwise, the half-life and the initial concentration are related

$$- t_{1/2} = \frac{(2^{\alpha-1} - 1)}{k(\alpha - 1)(C_A^0)^{\alpha-1}} \quad \Rightarrow \quad \ln(t_{1/2}) = (1 - \alpha)\ln(C_A^0) + \ln\left(\frac{(2^{\alpha-1} - 1)}{k(\alpha - 1)}\right)$$

- the reaction order can be found from the slope of a plot of the log of the half-life versus the log of the initial concentration



Requirements for Linear Least Squares

$$\ln(k) = \left(\frac{-E}{R}\right)\frac{1}{T} + \frac{1}{2}\ln(T) + \ln(k_0) \quad \nrightarrow \quad y = m_1x_1 + m_2x_2 + b$$

$$\ln(k) - \frac{1}{2}\ln(T) = \left(\frac{-E}{R}\right)\frac{1}{T} + \ln(k_0) \quad \Rightarrow \quad y = m_1x_1 + b$$

- The model must be of the form $y = m_1x_1 + m_2x_2 + \dots + m_nx_n + b$
 - ▶ m_2 through m_n may equal zero
 - ▶ b may equal zero
- The non-zero slopes, m_1 through m_n , and the intercept, b , (if not equal to zero) **must each contain a unique unknown constant**
 - ▶ They may not contain quantities that change from one data point to the next
 - ▶ **They cannot be known constants**
- The response variable, y , and the set variables, x_1 through x_n , must be unique quantities that change from one data point to the next
- If the original data are quantities other than y and x_1 through x_n , then values for y and x_1 through x_n , must be calculated for each data point
- The model equation must be fit to the corresponding x and y data
 - ▶ The slope and intercept are not found by plotting the data; they are found by fitting the model to the data
- The fitted model must be assessed to determine whether it is sufficiently accurate



Questions?



Activity 15.1

A rate expression is needed for the reaction $A \rightarrow Y + Z$, which takes place in the liquid phase. It doesn't need to be highly accurate, but it is needed quickly. Only one experimental run has been made, that using an isothermal batch reactor. The reactor volume was 750 mL and the reaction was run at 70 °C. The initial concentration of A was 1M, and the concentration was measured at several times after the reaction began; the data are listed in the table on the right.

Find the best value for a first order rate coefficient using the *integral* method of analysis.

t (min)	C_A (M)
1	0.874
2	0.837
3	0.800
4	0.750
5	0.572
6	0.626
7	0.404
8	0.458
9	0.339
10	0.431
12	0.249
15	0.172
20	0.185



Solution

- Read through the problem statement and each time you encounter a quantity, assign it to the appropriate variable



Solution

- Read through the problem statement and each time you encounter a quantity, assign it to the appropriate variable.
 - ▶ $V = 750 \text{ mL}$
 - ▶ $T = (70 + 273.15) \text{ K}$
 - ▶ $C_A^0 = 1 \text{ mol L}^{-1}$
 - ▶ t_i and $C_{A,i}$ are given for each of the data points, i
- Write the mole balance design equation for the reactor used in the experiments. This equation will be used to model each of the experiments, i



Solution

- Read through the problem statement and each time you encounter a quantity, assign it to the appropriate variable.
 - ▶ $V = 750 \text{ mL}$
 - ▶ $T = (70 + 273.15) \text{ K}$
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 - ▶ t_i and $C_{A,i}$ are given for each of the data points, i
- Write the mole balance design equation for the reactor used in the experiments. This equation will be used to model each of the experiments, i
 - ▶ Mole balance on A: $\frac{dn_A}{dt} = Vr_A$
- Substitute the rate expression to be tested into the design equation



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 - ▶ Mole balance on A: $\frac{dn_A}{dt} = Vr_A$
- Substitute the rate expression to be tested into the design equation
 - ▶ Rate expression: $r_A = -kC_A$
 - ▶ Mole balance after substitution: $\frac{dn_A}{dt} = -kVC_A$
- Integrate the mole balance
 - ▶ Identify the dependent and independent variables



Solution

- Read through the problem statement and each time you encounter a quantity, assign it to the appropriate variable.
 - ▶ $V = 750 \text{ mL}$
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- Integrate the mole balance
 - ▶ Identify the dependent and independent variables: n_A and t
 - ▶ Identify any other variable quantities appearing in the mole balance



Solution

- Read through the problem statement and each time you encounter a quantity, assign it to the appropriate variable.
 - ▶ $V = 750 \text{ mL}$
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- Integrate the mole balance
 - ▶ Identify the dependent and independent variables: n_A and t
 - ▶ Identify any other variable quantities appearing in the mole balance: C_A
 - ▶ Express the other variables in terms of the dependent variable and the independent variable



Solution

- Read through the problem statement and each time you encounter a quantity, assign it to the appropriate variable.
 - ▶ $V = 750 \text{ mL}$
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 - ▶ Identify the dependent and independent variables: n_A and t
 - ▶ Identify any other variable quantities appearing in the mole balance: C_A
 - ▶ Express the other variables in terms of the dependent variable and the independent variable

$$- C_A = \frac{n_A}{V}$$



- ▶ Substitute for the other variables in the design equation



- ▶ Substitute for the other variables in the design equation: $\frac{dn_A}{dt} = -kn_A$
- ▶ Separate the variables



- ▶ Substitute for the other variables in the design equation: $\frac{dn_A}{dt} = -kn_A$
- ▶ Separate the variables: $\frac{dn_A}{n_A} = -kdt$
- ▶ Integrate the design equation



▶ Substitute for the other variables in the design equation: $\frac{dn_A}{dt} = -kn_A$

▶ Separate the variables: $\frac{dn_A}{n_A} = -kdt$

▶ Integrate the design equation:

$$- \int_{n_A^0}^{n_A} \frac{dn_A}{n_A} = -k \int_0^t dt$$

$$- \ln\left(\frac{n_A}{n_A^0}\right) = -kt$$

- Linearize the integrated design equation



▶ Substitute for the other variables in the design equation: $\frac{dn_A}{dt} = -kn_A$

▶ Separate the variables: $\frac{dn_A}{n_A} = -kdt$

▶ Integrate the design equation:

$$- \int_{n_A^0}^{n_A} \frac{dn_A}{n_A} = -k \int_0^t dt$$

$$- \ln\left(\frac{n_A}{n_A^0}\right) = -kt$$

- Linearize the integrated design equation

▶ Model is linear, $y = m \cdot x$

$$- y = \ln\left(\frac{n_A}{n_A^0}\right)$$

$$- x = -t$$

$$- m = k$$

- Calculate the values of y and x for each experimental data point



▶ Substitute for the other variables in the design equation: $\frac{dn_A}{dt} = -kn_A$

▶ Separate the variables: $\frac{dn_A}{n_A} = -kdt$

▶ Integrate the design equation:

$$- \int_{n_A^0}^{n_A} \frac{dn_A}{n_A} = -k \int_0^t dt$$

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- Linearize the integrated design equation

▶ Model is linear, $y = m \cdot x$

$$- y = \ln\left(\frac{n_A}{n_A^0}\right)$$

$$- x = -t$$

$$- m = k$$

- Calculate the values of y and x for each experimental data point

▶ $n_A^0 = VC_A^0$

▶ $n_A = VC_A$

- Fit the linear model to the corresponding x-y data



▶ Substitute for the other variables in the design equation: $\frac{dn_A}{dt} = -kn_A$

▶ Separate the variables: $\frac{dn_A}{n_A} = -kdt$

▶ Integrate the design equation:

$$- \int_{n_A^0}^{n_A} \frac{dn_A}{n_A} = -k \int_0^t dt$$

$$- \ln\left(\frac{n_A}{n_A^0}\right) = -kt$$

• Linearize the integrated design equation

▶ Model is linear, $y = m \cdot x$

$$- y = \ln\left(\frac{n_A}{n_A^0}\right)$$

$$- x = -t$$

$$- m = k$$

• Calculate the values of y and x for each experimental data point

▶ $n_A^0 = VC_A^0$

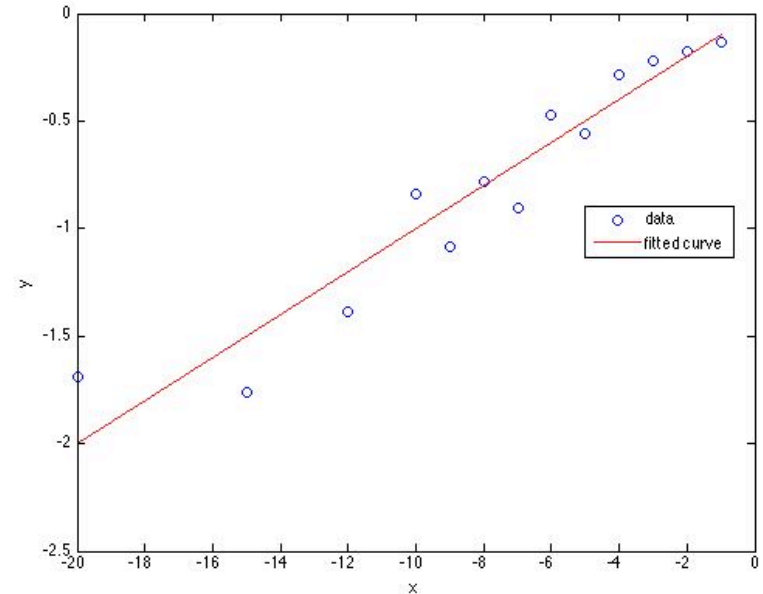
▶ $n_A = VC_A$

• Fit the linear model to the corresponding x-y data

▶ $r^2 = 0.91$

▶ $m = 0.10 \pm 0.01 \text{ min}^{-1}$

• Decide if the fit is acceptable and report the values and uncertainties for the kinetic parameters



Notice the Solution Process

- Read through the problem statement and each time you encounter a quantity, assign it to the appropriate variable
- Write the mole balance design equation for the reactor used in the experiments
- Substitute the rate expression to be tested into the design equation
- Integrate the mole balance
 - ▶ Identify the dependent and independent variables
 - ▶ Identify any other variable quantities appearing in the mole balance
 - ▶ Express the other variables in terms of the dependent variable and the independent variable
 - ▶ Substitute for the other variables in the design equation so only the dependent and independent variables remain
 - ▶ Separate the variables
 - ▶ Integrate the design equation
- Linearize the integrated design equation
- Calculate the values of y and x for each experimental data point
- Fit the linear model to the corresponding x - y data
- Decide if the fit is acceptable and report the values and uncertainties for the kinetic parameters



Comparison of Differential and Integral Analysis

- Differential Analysis (Activity 14.1c)

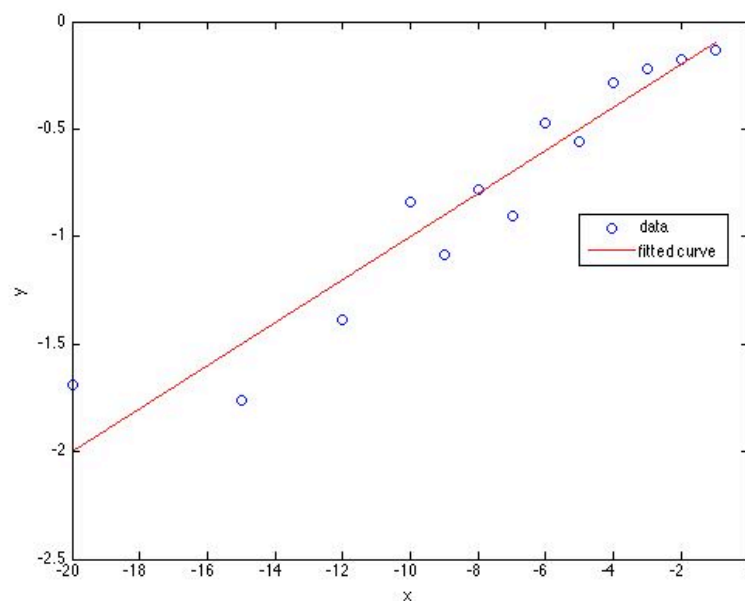
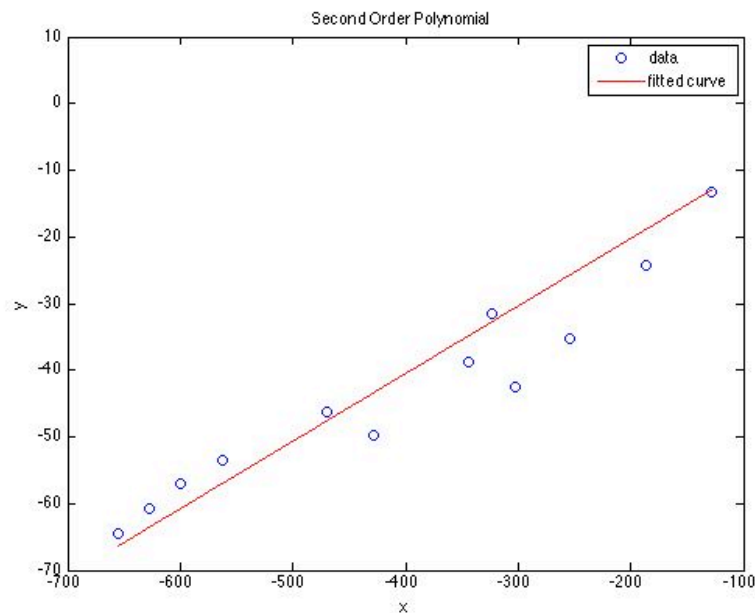
- ▶ Second order polynomial used to approximate dn_A/dt
 - Top right model plot
 - $r^2 = 0.85$
 - $m = 0.10 \pm 0.01 \text{ min}^{-1}$
- ▶ Best finite differences (central differences)
 - $r^2 = 0.16$
 - $m = 0.08 \pm 0.03 \text{ min}^{-1}$

- Integral Analysis (Activity 15.1)

- ▶ Bottom right model plot
- ▶ $r^2 = 0.91$
- ▶ $m = 0.10 \pm 0.01 \text{ min}^{-1}$

- When data are noisy

- ▶ Integral analysis is preferred
 - fit once
- ▶ Polynomial approximation is second best
 - fit twice
- ▶ Finite differences approximation should be avoided



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