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 14 on Unit 14

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



Fitting Models with Derivatives to Experimental Data

- In the differential method, derivatives that appear in the model equation are treated like experimentally measured variables
 - ▶ Usually not highly accurate, there best for initial or quick analysis
 - ▶ Requires estimation of the value of the derivative
- Batch reactors
 - ▶ The experimental data allow calculation of the dependent variable (usually n_i) at several different values of the independent variable, t
 - ▶ Tangent method (historical): plot the data, draw a smooth curve, at each t , draw a tangent, estimate the derivative as the slope of the tangent
 - ▶ Polynomial method: fit a polynomial that yields a smooth curve to the experimental data, at each t , evaluate the derivative of the polynomial and use the result to estimate the derivative
 - ▶ Finite difference method: connect the data points by straight line segments, at each t , estimate the derivative as the slope of the line segment preceding (backward differences) or following (forward differences) the point or as the average of the slopes of the line segments preceding and following (central differences) the point.

$$\left. \frac{dn_i}{dt} \right|_k \approx \frac{(n_i)_k - (n_i)_{k-1}}{(t)_k - (t)_{k-1}} \qquad \left. \frac{dn_i}{dt} \right|_k \approx \frac{(n_i)_{k+1} - (n_i)_k}{(t)_{k+1} - (t)_k}$$

$$\left. \frac{dn_i}{dt} \right|_k \approx \left(\frac{1}{2} \right) \left(\frac{(n_i)_{k+1} - (n_i)_k}{(t)_{k+1} - (t)_k} + \frac{(n_i)_k - (n_i)_{k-1}}{(t)_k - (t)_{k-1}} \right)$$



Differential Data Analysis

- Initial rates

- ▶ Prepare reagents in well-known proportions, start the reaction and only estimate the derivative at the start of the reaction using any of the preceding methods
- ▶ Allows variation of a single concentration while holding all others constant

- PFRs

- ▶ The experimental data typically **do not** allow the calculation of the dependent variable (usually \dot{n}_i) at several different values of the independent variable, z
- ▶ Differential data analysis can only be used if the reactor was operated differentially

- $$\frac{d\dot{n}_i}{dz} \approx \frac{\Delta\dot{n}_i}{\Delta z} = \frac{\dot{n}_i|_{outlet} - \dot{n}_i|_{inlet}}{L}$$

- only valid if the change in \dot{n}_i was small, e. g. 5%
- ▶ When the rate expression is substituted into the design equation, it should be evaluated at the average of the inlet and outlet composition
 - best if the inlet and outlet concentration of each species only differ by a small amount, e. g. 5%

- Results from differential data analysis are more strongly influenced by experimental “noise” than results from integral data analysis (Unit 15)



Questions?



Activity 14.1(a)

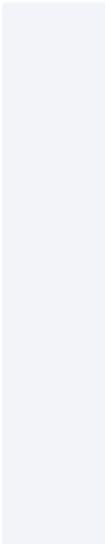
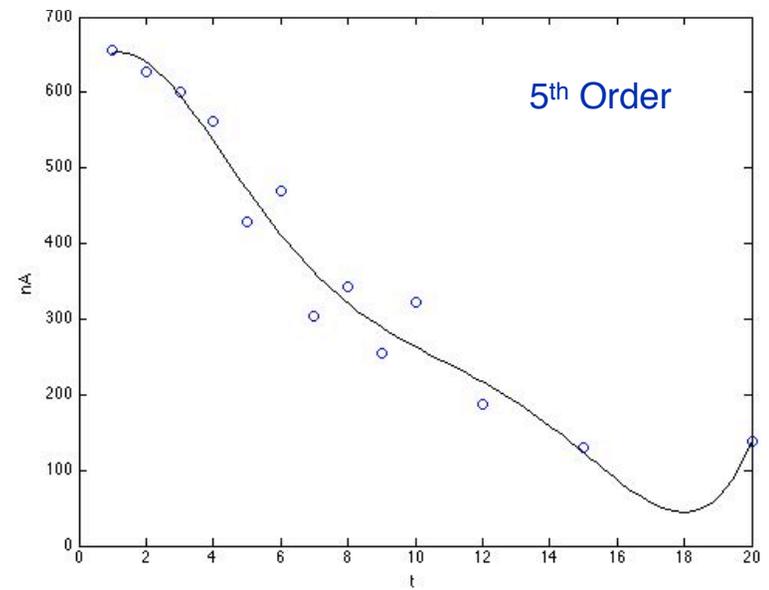
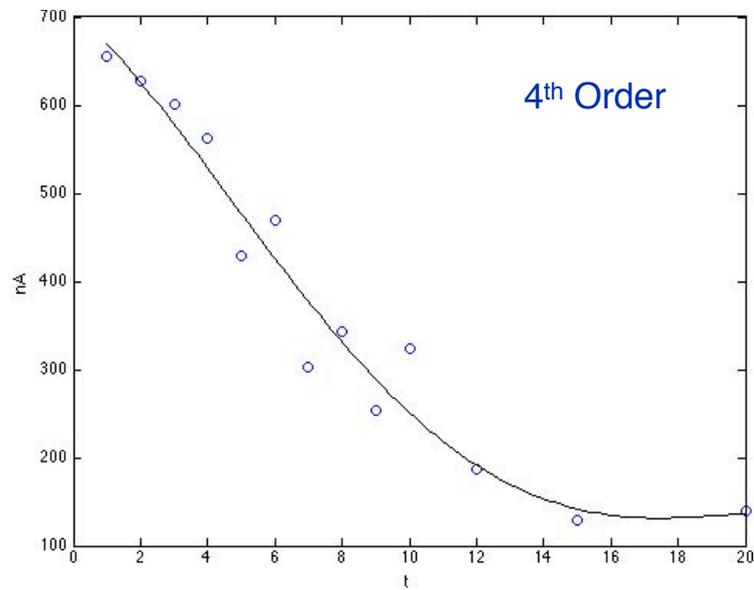
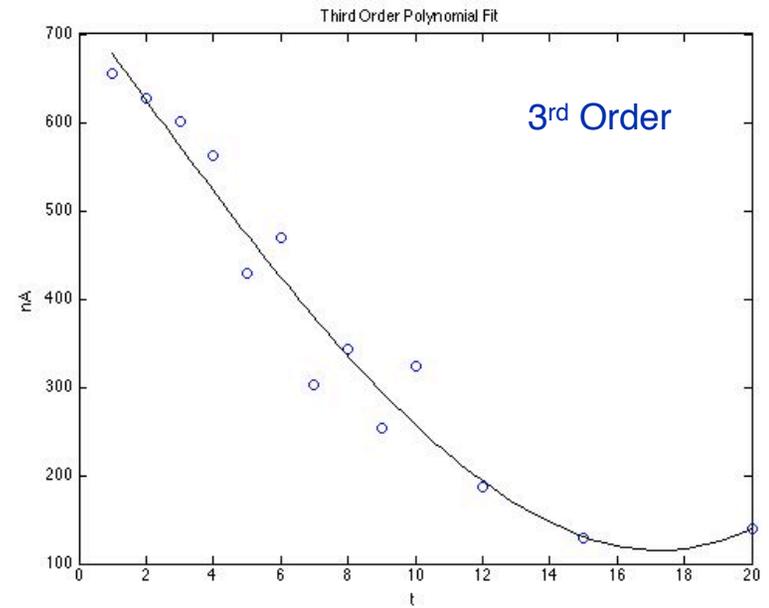
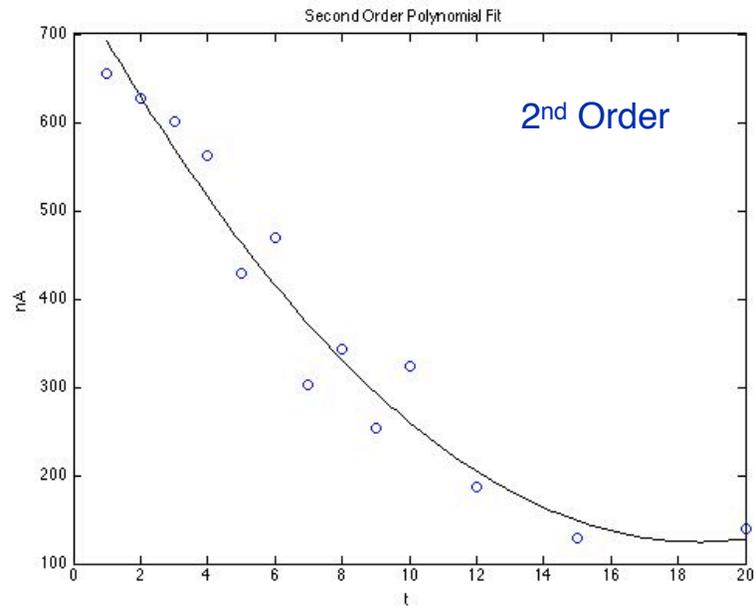
A rate expression is needed for the reaction $A \rightarrow Y + Z$, which takes place in the liquid phase. It doesn't need to be highly accurate, but it is needed quickly. Only one experimental run has been made, that using an isothermal batch reactor. The reactor volume was 750 mL and the reaction was 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 below.

Plot the data, fit a 2nd, 3rd, 4th and 5th order polynomial to the data and plot the polynomials. Choose the best polynomial and use it to estimate dn_A/dt for each experimental data point.

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



Note $n_A = C_A \cdot V$



Activity 14.1(b)

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 below.

Use forward, backward and central differences to estimate dn_A/dt for each experimental data point. When using central differences, use a forward difference for the first data point and a backward difference for the last data point.

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



Finite Differences

Forward

$$\left. \frac{dn_i}{dt} \right|_k \approx \frac{(n_i)_{k+1} - (n_i)_k}{(t)_{k+1} - (t)_k}$$

Backward

$$\left. \frac{dn_i}{dt} \right|_k \approx \frac{(n_i)_k - (n_i)_{k-1}}{(t)_k - (t)_{k-1}}$$

Central

$$\left. \frac{dn_i}{dt} \right|_k \approx \left(\frac{1}{2} \right) \left(\frac{(n_i)_{k+1} - (n_i)_k}{(t)_{k+1} - (t)_k} + \frac{(n_i)_k - (n_i)_{k-1}}{(t)_k - (t)_{k-1}} \right)$$



Finite Differences

Forward

$$\left. \frac{dn_i}{dt} \right|_k \approx \frac{(n_i)_{k+1} - (n_i)_k}{(t)_{k+1} - (t)_k}$$

<i>t</i> (min)	<i>dn_A/dt</i> (mol/min)
1	-27.7500
2	-27.7500
3	-37.5000
4	-133.5000
5	40.5000
6	-166.5000
7	40.5000
8	-89.2500
9	69.0000
10	-68.2500
12	-19.2500
15	1.9500
20	

Backward

$$\left. \frac{dn_i}{dt} \right|_k \approx \frac{(n_i)_k - (n_i)_{k-1}}{(t)_k - (t)_{k-1}}$$

<i>t</i> (min)	<i>dn_A/dt</i> (mol/min)
1	
2	-27.7500
3	-27.7500
4	-37.5000
5	-133.5000
6	40.5000
7	-166.5000
8	40.5000
9	-89.2500
10	69.0000
12	-68.2500
15	-19.2500
20	1.9500

Central

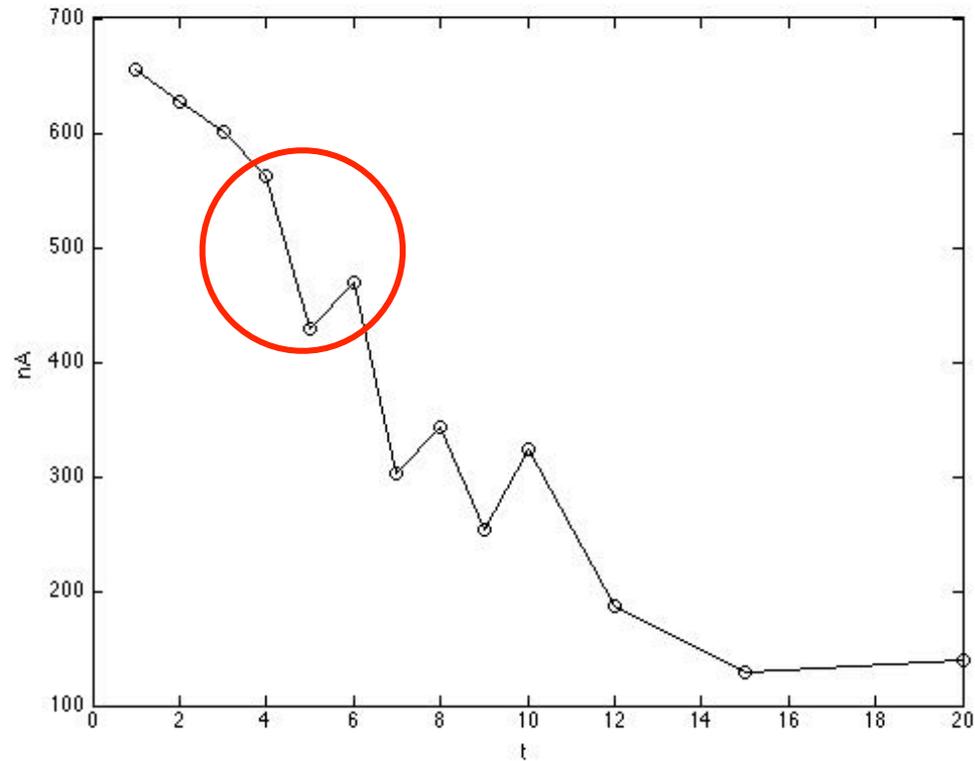
$$\left. \frac{dn_i}{dt} \right|_k \approx \left(\frac{1}{2} \right) \left(\frac{(n_i)_{k+1} - (n_i)_k}{(t)_{k+1} - (t)_k} + \frac{(n_i)_k - (n_i)_{k-1}}{(t)_k - (t)_{k-1}} \right)$$

<i>t</i> (min)	<i>dn_A/dt</i> (mol/min)
1	-27.7500
2	-27.7500
3	-32.6250
4	-85.5000
5	-46.5000
6	-63.0000
7	-63.0000
8	-24.3750
9	-10.1250
10	0.3750
12	-43.7500
15	-8.6500
20	1.9500



n_A vs. t

Effect of Noise in the Data on Finite Differences



Activity 14.1(c)

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 below.

Find the best value for a first order rate coefficient using the differential method of analysis and each of the estimates of dn_A/dt from parts (a) and (b). Comment upon the results.

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



First Order Rate Expression

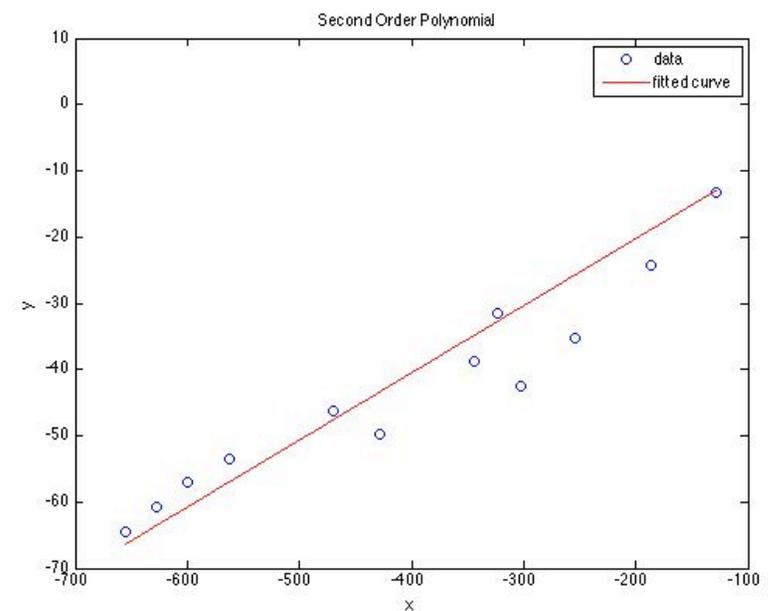
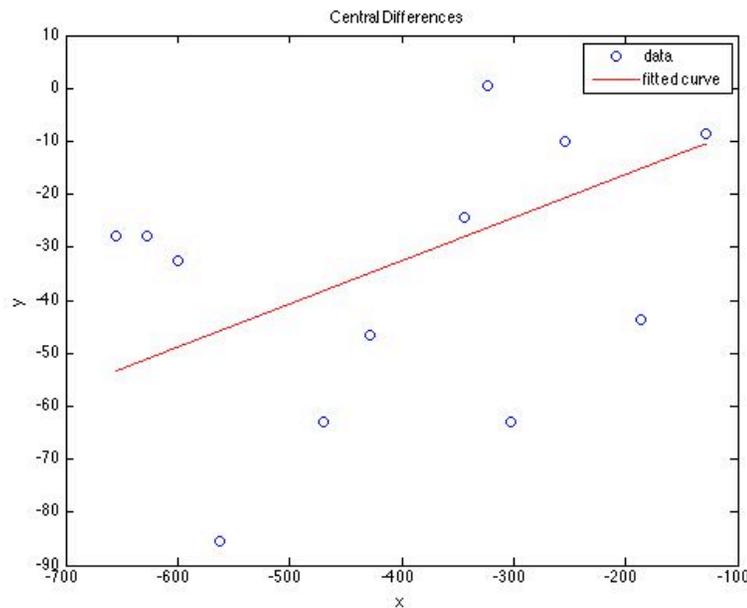
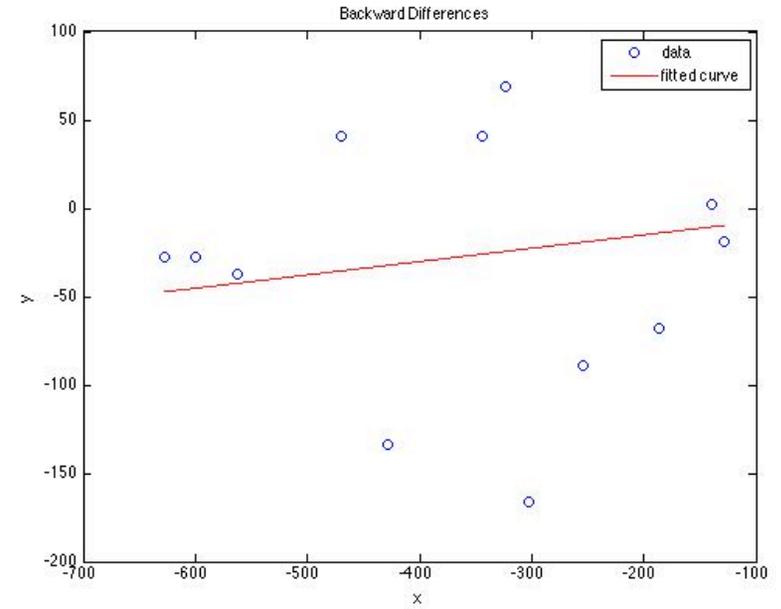
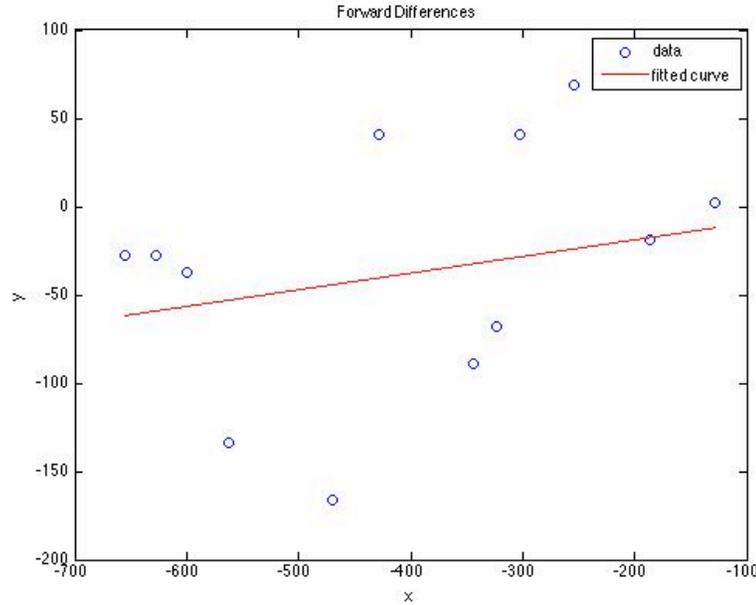
$$\frac{dn_A}{dt} = -kVC_A$$

$$x = -VC_A$$

$$y = \frac{dn_A}{dt}$$

$$m = k$$

$$y = mx$$



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