

Lecture 11

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Lecture 11 – Thursday

- Block 1: **Mole Balances**
 - Block 2: **Rate Laws**
 - Block 3: **Stoichiometry**
 - Block 4: **Combine**
-
- Determining the **Rate Law** from Experimental Data
 - Integral Method
 - Differential (Graphical) Method
 - Nonlinear Least Regression

Integral Method

Consider the following reaction that occurs in a constant volume **Batch Reactor**: (We will withdraw samples and record the concentration of A as a function of time.)



Mole Balances:

$$\frac{dN_A}{dt} = r_A V$$

Rate Laws:

$$-r_A = kC_A^\alpha$$

Stoichiometry:

$$V = V_0$$

Combine:

$$-\frac{dC_A}{dt} = kC_A^\alpha$$

Finally we should also use the formula to plot reaction rate data in terms of conversion vs. time for 0, 1st and 2nd order reactions.

Derivation equations used to plot 0th, 1st and 2nd order reactions.

These types of plots are usually used to determine the values k for runs at various temperatures and then used to determine the activation energy.

<u>Zeroth order</u>	<u>First Order</u>	<u>Second Order</u>
$\frac{dC_A}{dt} = r_A = -k$	$\frac{dC_A}{dt} = r_A = -kC_A$	$\frac{dC_A}{dt} = r_A = -kC_A^2$
$\text{at } t = 0, C_A = C_{A0}$	$\text{at } t = 0, C_A = C_{A0}$	$\text{at } t = 0, C_A = C_{A0}$
$\Rightarrow C_A = C_{A0} - kt$	$\Rightarrow \ln\left(\frac{C_{A0}}{C_A}\right) = kt$	$\Rightarrow \frac{1}{C_A} - \frac{1}{C_{A0}} = kt$

Integral Method

Guess and check for $\alpha = 0, 1, 2$ and check against experimental plot.

$$\alpha = 0$$

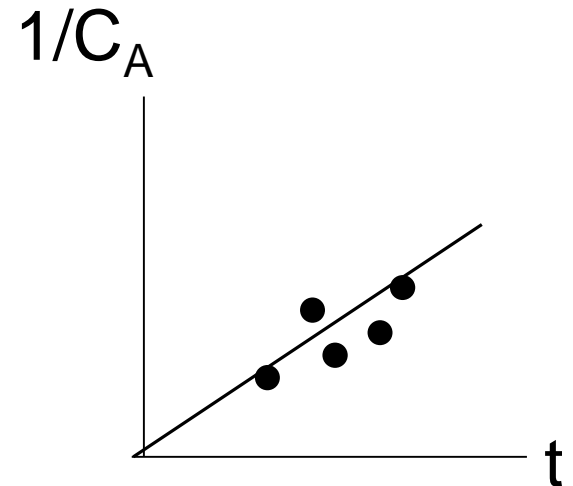
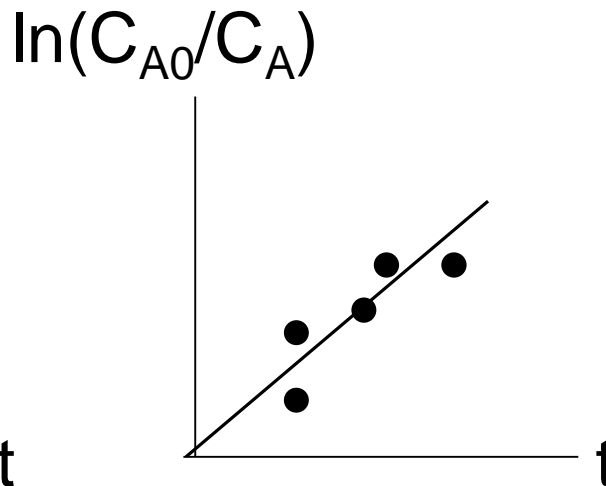
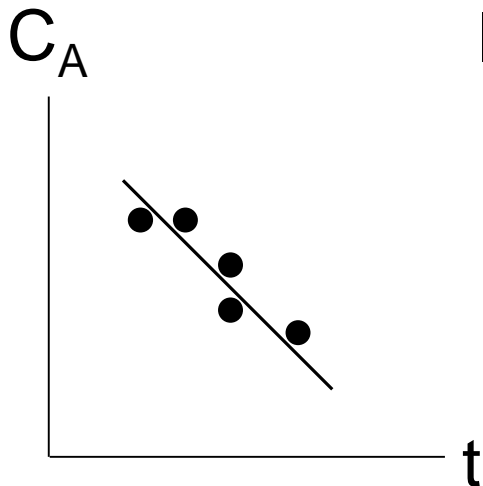
$$r_A = C_{A0} - kt$$

$$\alpha = 1$$

$$\ln\left(\frac{C_{A0}}{C_A}\right) = kt$$

$$\alpha = 2$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

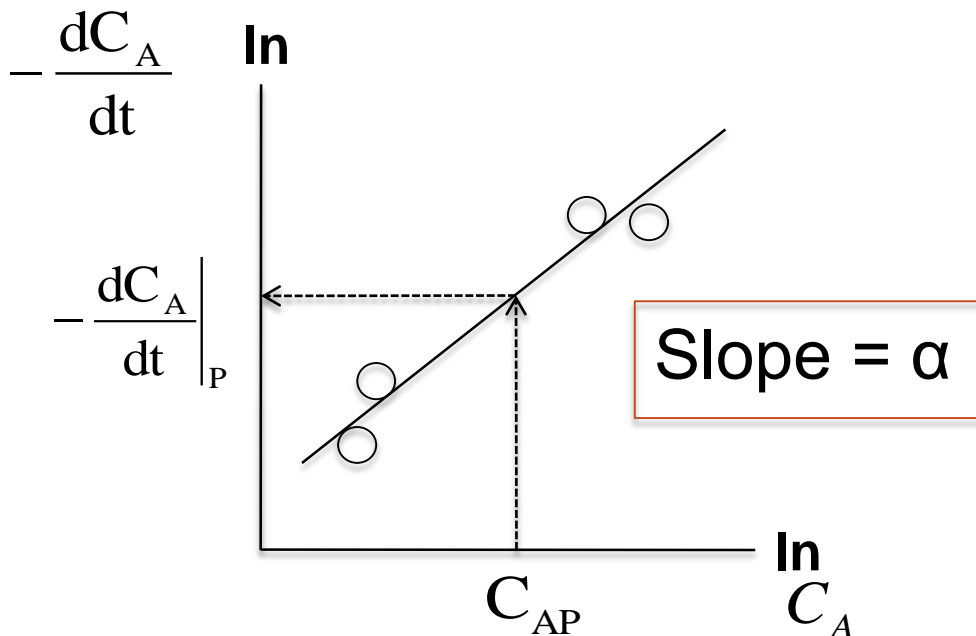


Differential Method

Taking the natural log of $\left[-\frac{dC_A}{dt} = kC_A^\alpha \right]$

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A$$

The reaction order can be found from a ln-ln plot of: $\left(-\frac{dC_A}{dt}\right)$ vs C_A



$$k = \frac{\left(-\frac{dC_A}{dt}\right)\bigg|_P}{C_{AP}^\alpha}$$

Methods for finding the slope of log-log and semi-log graph papers may be found at

<http://www.physics.uoguelph.ca/tutorials/GLP/>

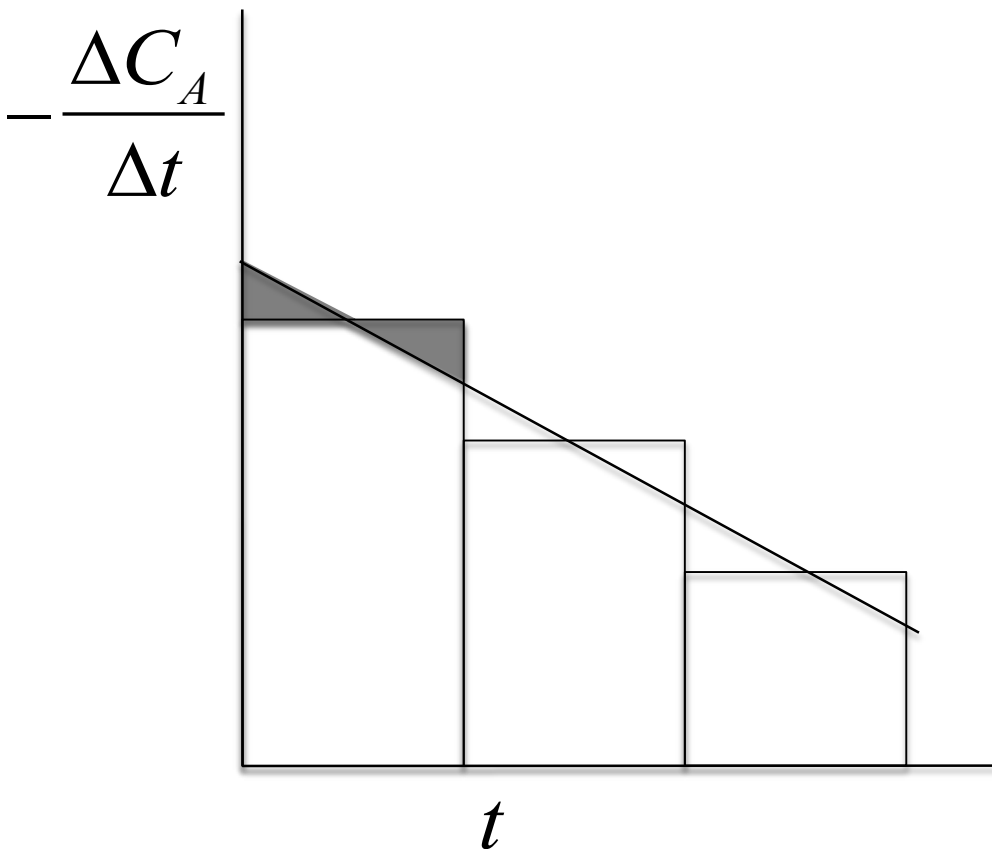
However, we are usually given concentration as a function of time from batch reactor experiments:

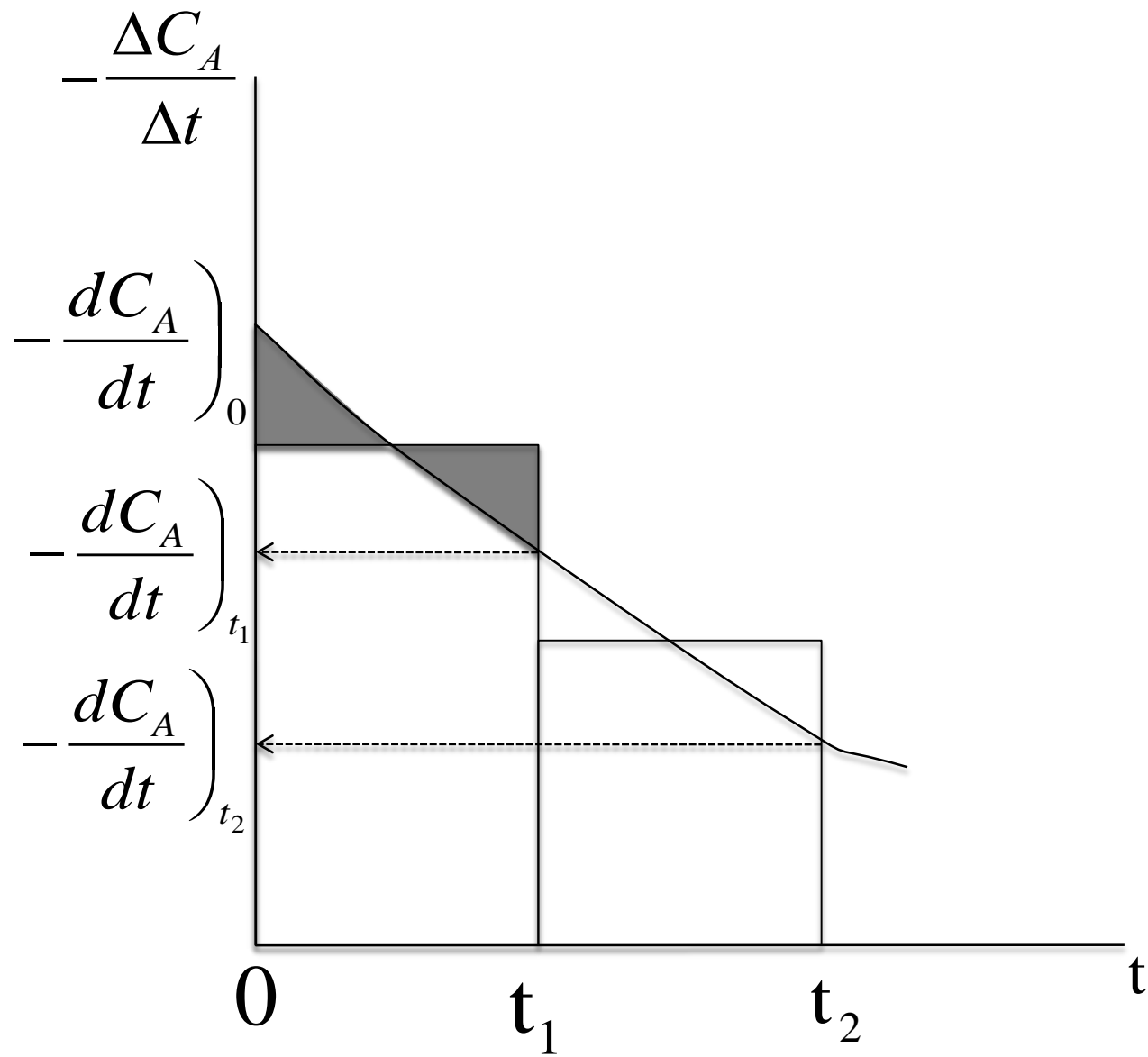
time (s)	0	t_1	t_2	t_3
concentration (moles/dm ³)	C_{A0}	C_{A1}	C_{A2}	C_{A3}

Three ways to determine $(-dC_A/dt)$ from concentration-time data

- Graphical differentiation
- Numerical differentiation formulas
- Differentiation of a polynomial fit to the data

1. Graphical

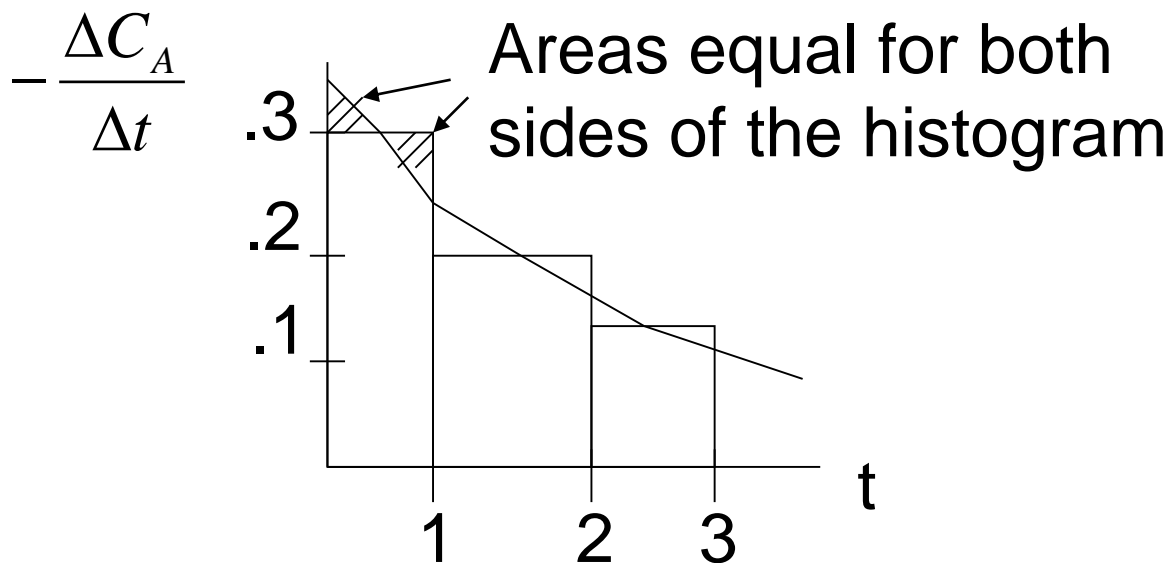




The method accentuates measurement error!

Example – Finding the Rate Law

t(min)	0	1	2	3
$C_A(\text{mol/L})$	1	0.7	0.5	0.35
$-\frac{\Delta C_A}{\Delta t}$	0.3	0.2	0.15	

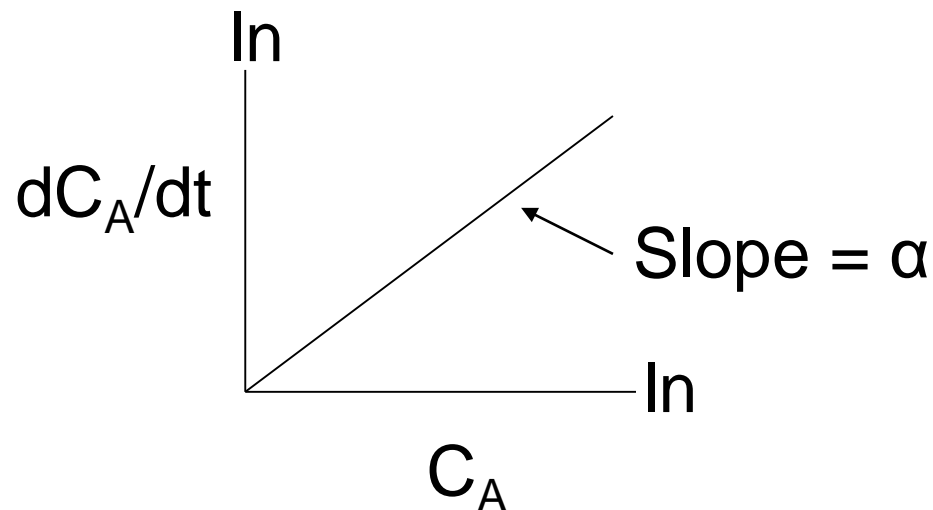


Example – Finding the **Rate Law**

Find $f(t)$ of $-\frac{\Delta C_A}{\Delta t}$ using equal area differentiation

C_A	1	0.7	0.5	0.35
$-dC_A/dt$	0.35	0.25	0.175	0.12

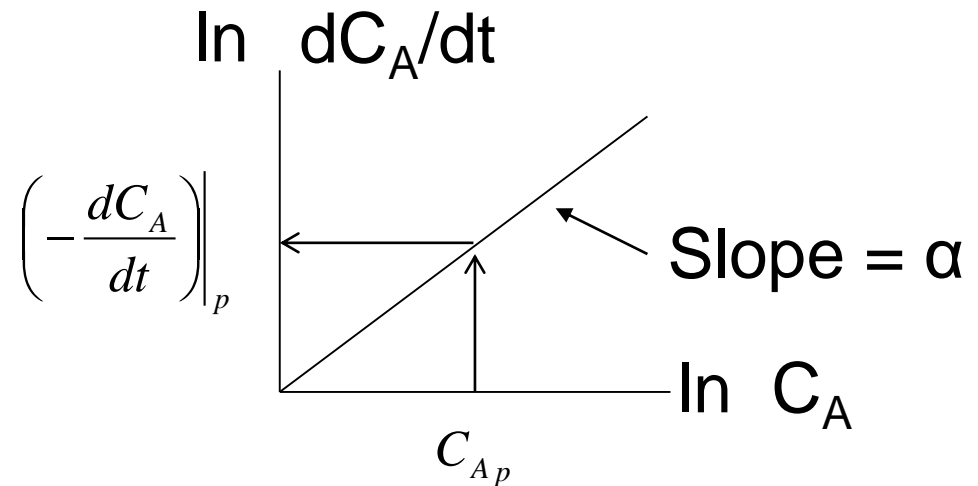
Plot $(-dC_A/dt)$ as a function of C_A



Example – Finding the **Rate Law**

Choose a point, p , and find the concentration and derivative at that point to determine k .

$$k = \frac{\left(-\frac{dC_A}{dt} \right) \Big|_p}{C_{Ap}^\alpha}$$



Non-Linear Least-Square Analysis

We want to find the parameter values (α , k , E) for which the sum of the squares of the differences, the measured rate (r_m), and the calculated rate (r_c) is a minimum.

$$\sigma^2 = \sum_{i=1}^n \frac{(C_{im} - C_{ic})^2}{N - K} = \frac{S^2}{N - K}$$

That is, we want σ^2 to be a minimum.

Non-Linear Least-Square Analysis

For concentration-time data, we can combine the mole balance equation for $-r_A = kC_A^\alpha$ to obtain:

$$\frac{dC_A}{dt} = -kC_A^\alpha$$

$$t = 0 \quad C_A = C_{A0}$$

$$C_{A0}^{1-\alpha} - C_A^{1-\alpha} = (1-\alpha)kt$$

Rearranging to obtain the calculated concentration as a function of time, we obtain:

$$C_{Ac} = C_A = [C_{A0}^{1-\alpha} - (1-\alpha)kt]^{1/(1-\alpha)}$$

Non-Linear Least-Square Analysis

Now we could use Polymath or MATLAB to find the values of α and k that would minimize the sum of squares of differences between the measured (C_{Am}) and calculated (C_{Ac}) concentrations.

That is, for N data points,

$$s^2 = \sum_{i=1}^N (C_{Ami} - C_{Aci})^2 = \sum_{i=1}^N \left[C_{Ami} - [C_{A0}^{1-\alpha} - (1-\alpha)kt_i]^{1/(1-\alpha)} \right]^2$$

Similarly one can calculate the time at a specified concentration, t_c

$$t_c = \frac{C_{A0}^{1-\alpha} - C_A^{1-\alpha}}{k(1-\alpha)}$$

and compare it with the measured time, t_m , at that same concentration.

That is, we find the values of k and α that minimize:

$$s^2 = \sum_{i=1}^N (t_{mi} - t_{ci})^2 = \sum_{i=1}^N \left[t_{mi} - \frac{C_{A0}^{1-\alpha} - C_{Ai}^{1-\alpha}}{k(1-\alpha)} \right]^2$$

Non-Linear Least Squares Analysis

Guess values for α and k and solve for measured data points then sum squared differences:

C_{Am}	1	0.7	0.5	0.35	
C_{Ac}	1	0.5	0.33	0.25	
$(C_{Ac}-C_{Am})$	0	-0.2	-0.17	-0.10	
$(C_{Ac}-C_{Am})^2$	0	0.04	0.029	0.01	0.07

for $\alpha = 2, k = 1 \rightarrow s^2 = 0.07$

for $\alpha = 2, k = 2 \rightarrow s^2 = 0.27$

etc. until s^2 is a minimum

Non-Linear Least Squares Analysis

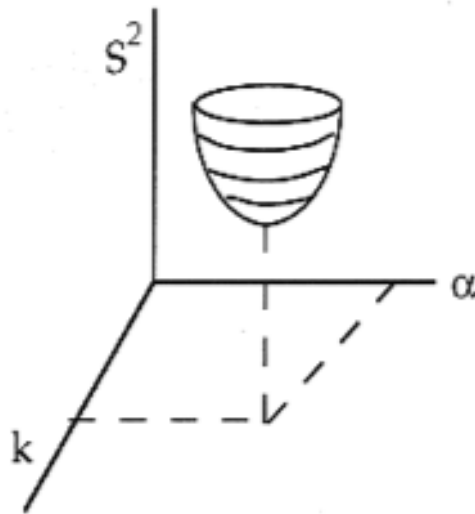
TABLE E5-3.1. REGRESSION OF DATA

<i>Original Data</i>		<i>Guess 1</i>		<i>Guess 2</i>		<i>Guess 3</i>		<i>Guess 4</i>	
		$\alpha = 3$ $k' = 5$	$\alpha = 2$ $k' = 5$	$\alpha = 2$ $k' = 0.2$	$\alpha = 2$ $k' = 0.1$				
<i>t</i> (min)	$C_A \times 10^3$ (mol/dm ³)	t_C	$(t_m - t_C)^2$	t_C	$(t_m - t_C)^2$	t_C	$(t_m - t_C)^2$	t_C	$(t_m - t_C)^2$
1	0 50	0 0	0 0	0 0	0 0	0 0	0 0	0 0	
2	50 38	29.2 433	1.26 2,375	31.6 339	63.2 174				
3	100 30.6	66.7 1,109	2.5 9,499	63.4 1,340	126.8 718				
4	200 22.2	163 1,375	5.0 38,622	125.2 5,591	250 2,540				
		$s^2 = 2916$		$s^2 = 49,895$		$s^2 = 7270$		$s^2 = 3432$	

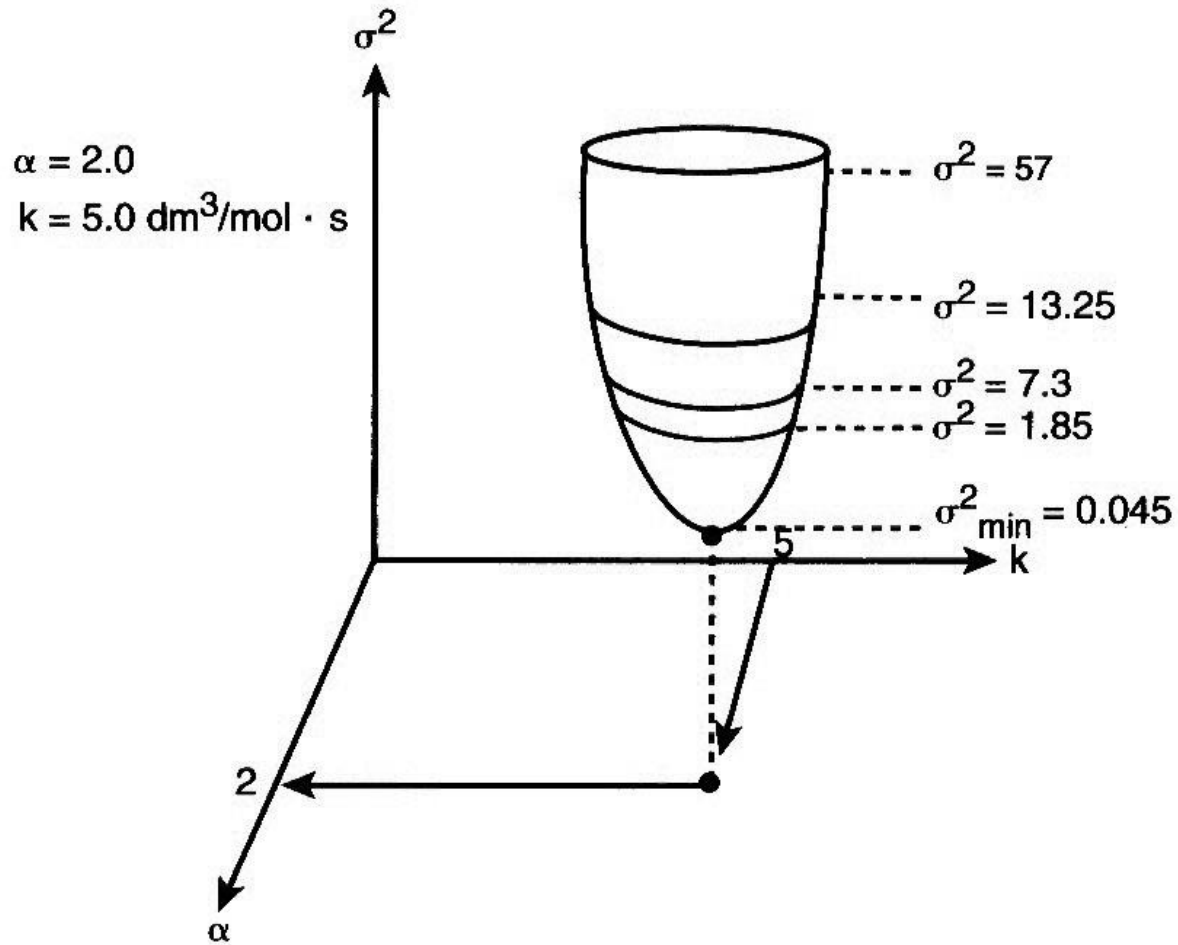
Non-Linear Least Squares Analysis

$$s^2 = \sum_{i=1}^N (C_{Ami} - C_{Aci})^2 = \sum_{i=1}^N \left(C_{Ami} - [C_{A0}^{1-\alpha} - (1-\alpha)kt_i]^{1/1-\alpha} \right)^2$$

We find the values of alpha and k which minimize s^2



$$\sigma^2 = f(k, \alpha)$$



Minimum Sum of Squares

R008 : C005 C05

	t	Ca	C03	C04	C05	C06	C07	C08	C09	C10	C11	C12	C13
01	0	2											
02	.5	1.63											
03	1	1.41											
04	2	1.15											
05	3	1											
06	4	.89											
07													
08													
09													
10													
11													
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Regression Analysis Graph

Report Store Model

Linear & Polynomial | Multiple linear | Nonlinear

Model:

$t = [2^{1-\alpha} - Ca^{1-\alpha}] / (k(1-\alpha))$

e.g. $y = 2 * x^A + B$

Model Parameters Initial Guess:

Model parm	Initial guess
alpha	2
k	.1

Dependent Variable:

Independent Variable/s:

Model Variable/s:

Available Variables:

POLYMATH 6.10 Educational Release - [Nonlinear Report #4]

File Edit Window Help

POLYMATH Report
Nonlinear Regression (mrqmin) 26-Nov-2007

Model: $C02 = A+B*C03$

Variable	Initial guess	Value	95% confidence
A	0.5	-8.38	0.1723379
B	0.5	0.68	0.0519618

Nonlinear regression settings
Max # iterations = 64
Tolerance = 0.0001

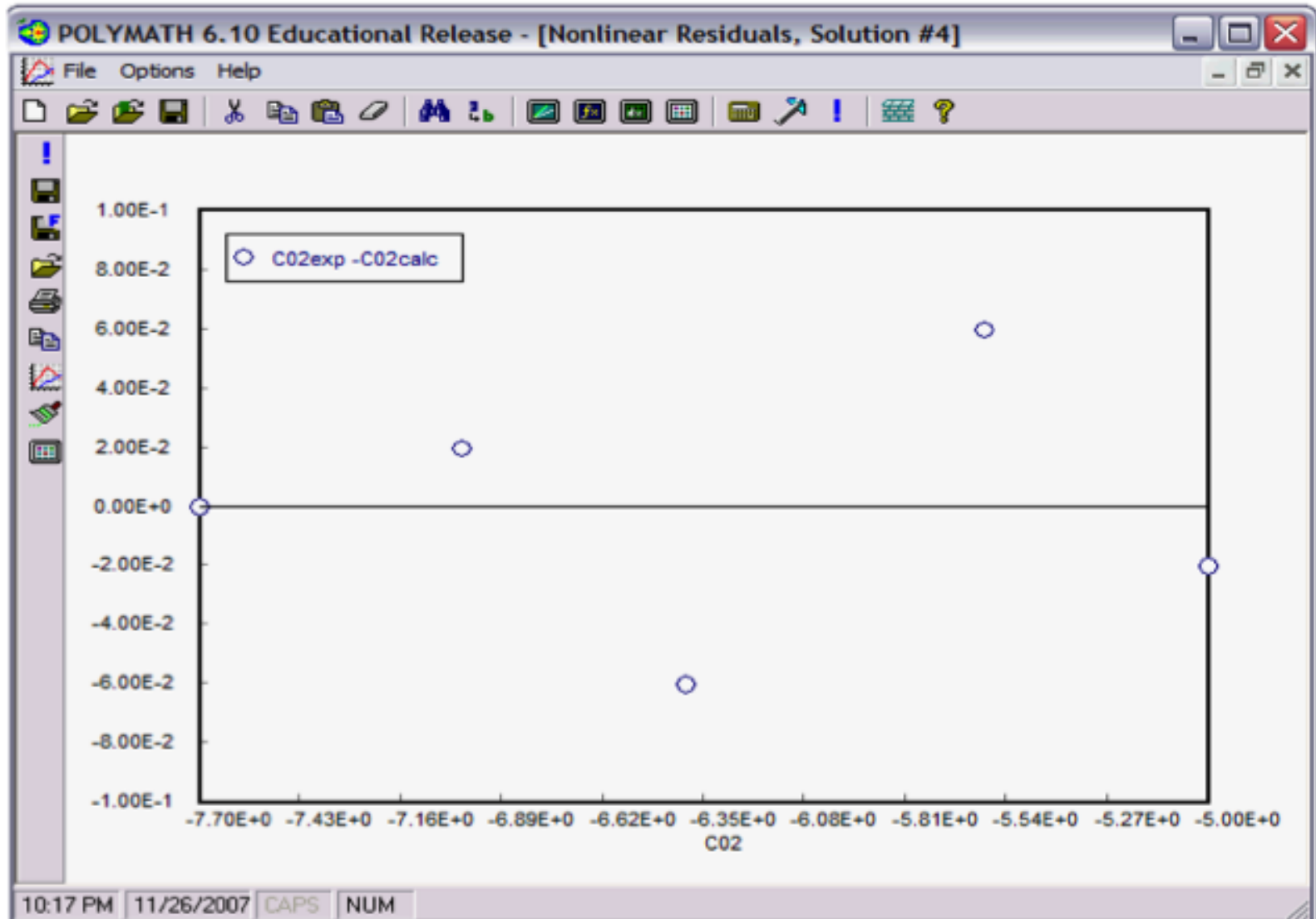
Precision

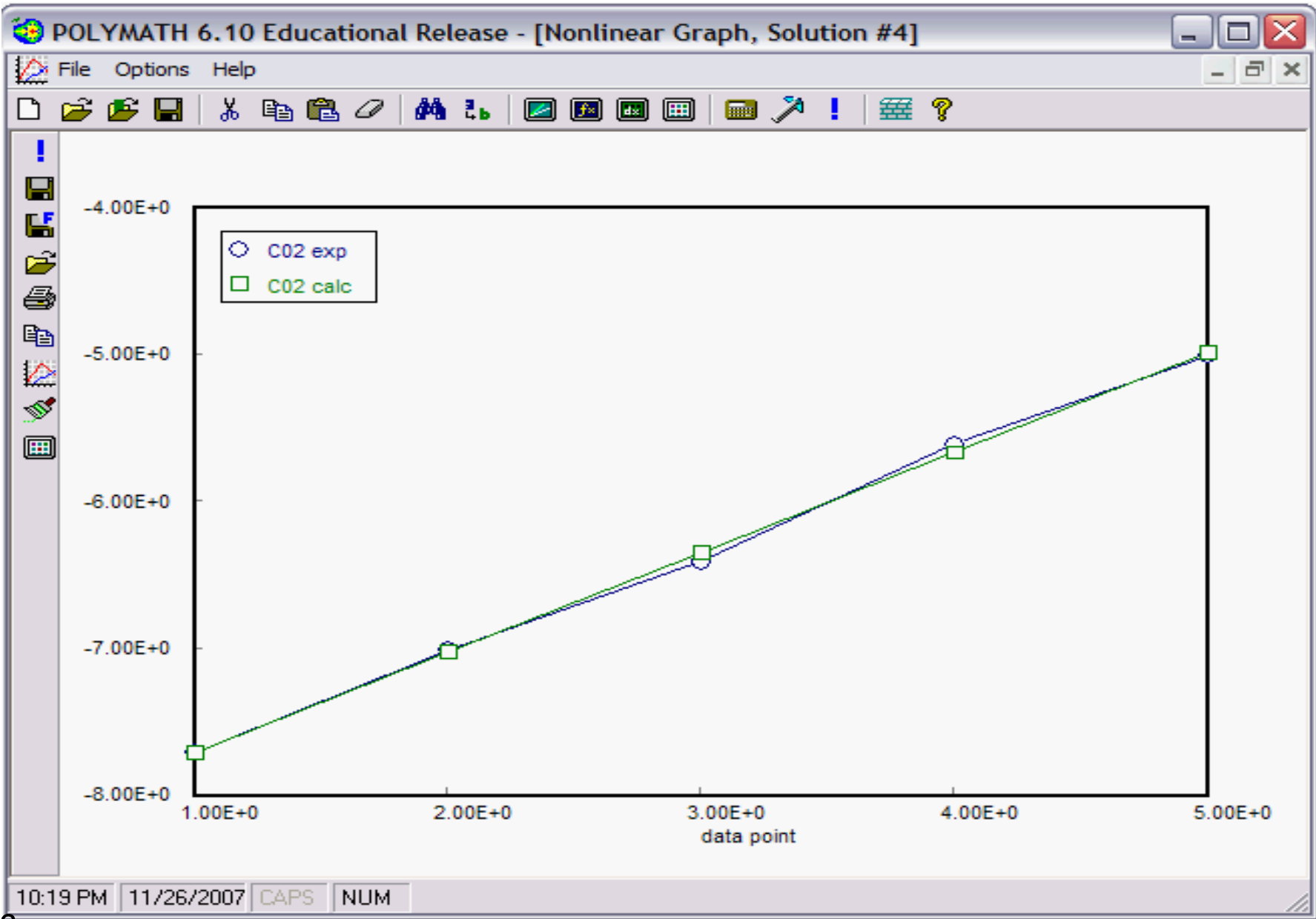
R ²	0.9982729
R ² adj	0.9976972
Rmsd	0.0178885
Variance	0.0026667
Chi-Sq	0.8
Alamda	1.0E-05

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Residuals





End of Lecture 11