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 2/14/2013

- 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.)

A → Products

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.

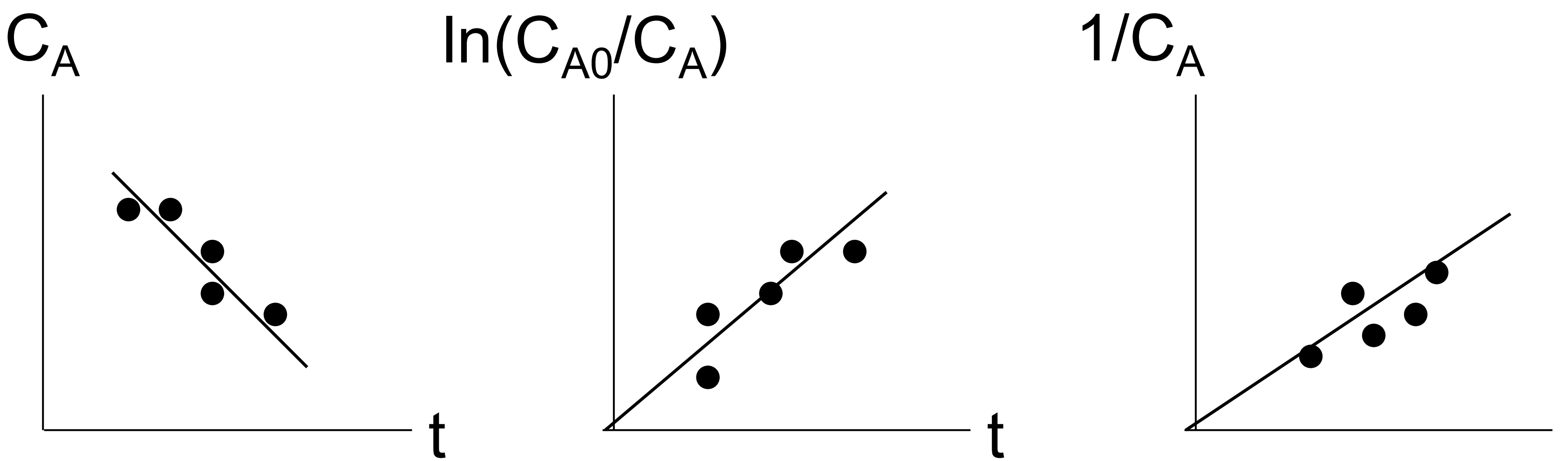
These types of plots are usually used to determine the values k for runs at various temperatures and then used to determine the activation energy.

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

Integral Method

Guess and check for α = 0, 1, 2 and check against experimental plot.

$\alpha = 0$	$\alpha = 1$	$\alpha = 2$
$r_A = C_{A0} - kt$	$\ln\left(\frac{C_{A0}}{C_A}\right) = kt$	$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$

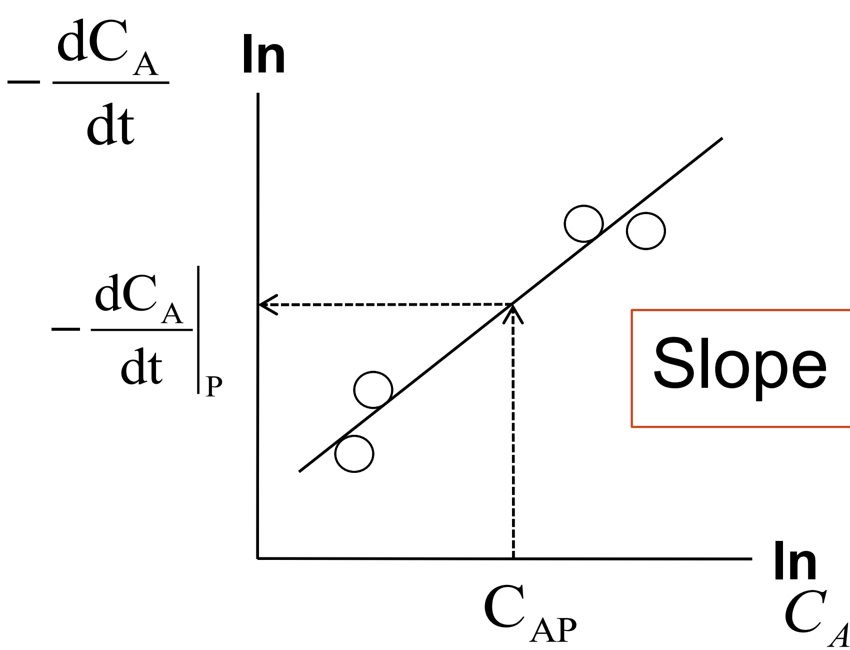


Differential Method

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: $\left(-\frac{dC_A}{dt}\right) \; vs \;\; C_A$



Slope = α

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

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

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

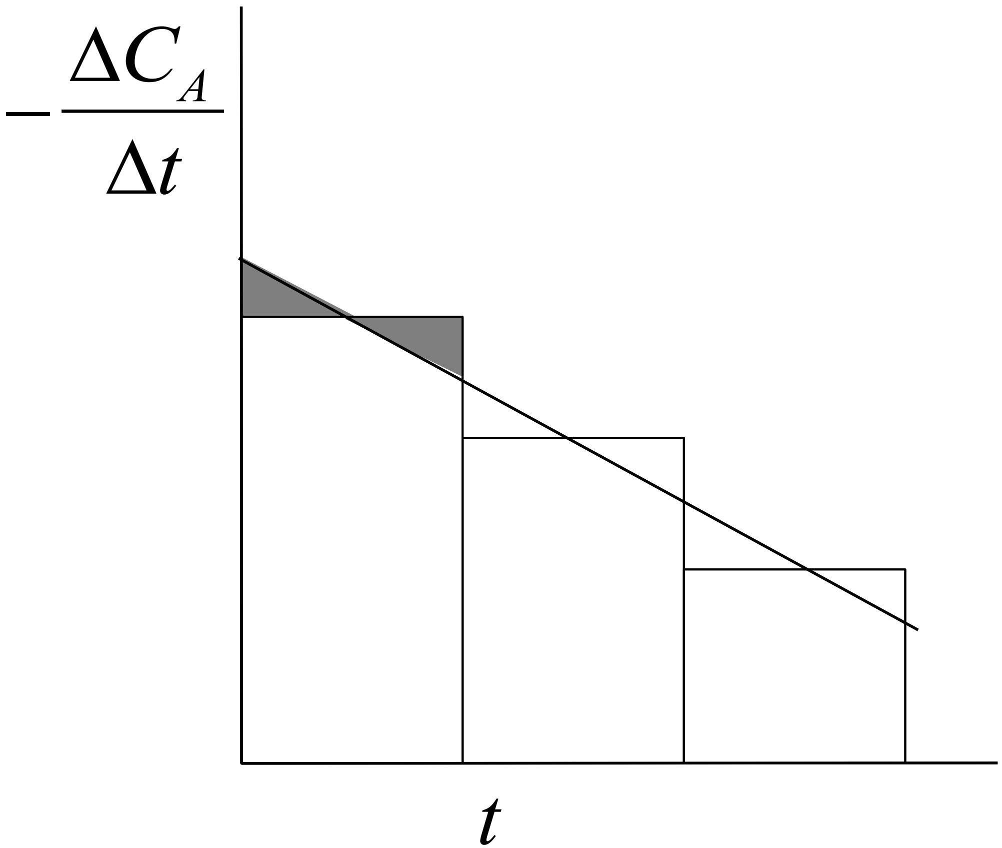
However, we are usually given concentration as a function of time from batch reactor experiments:

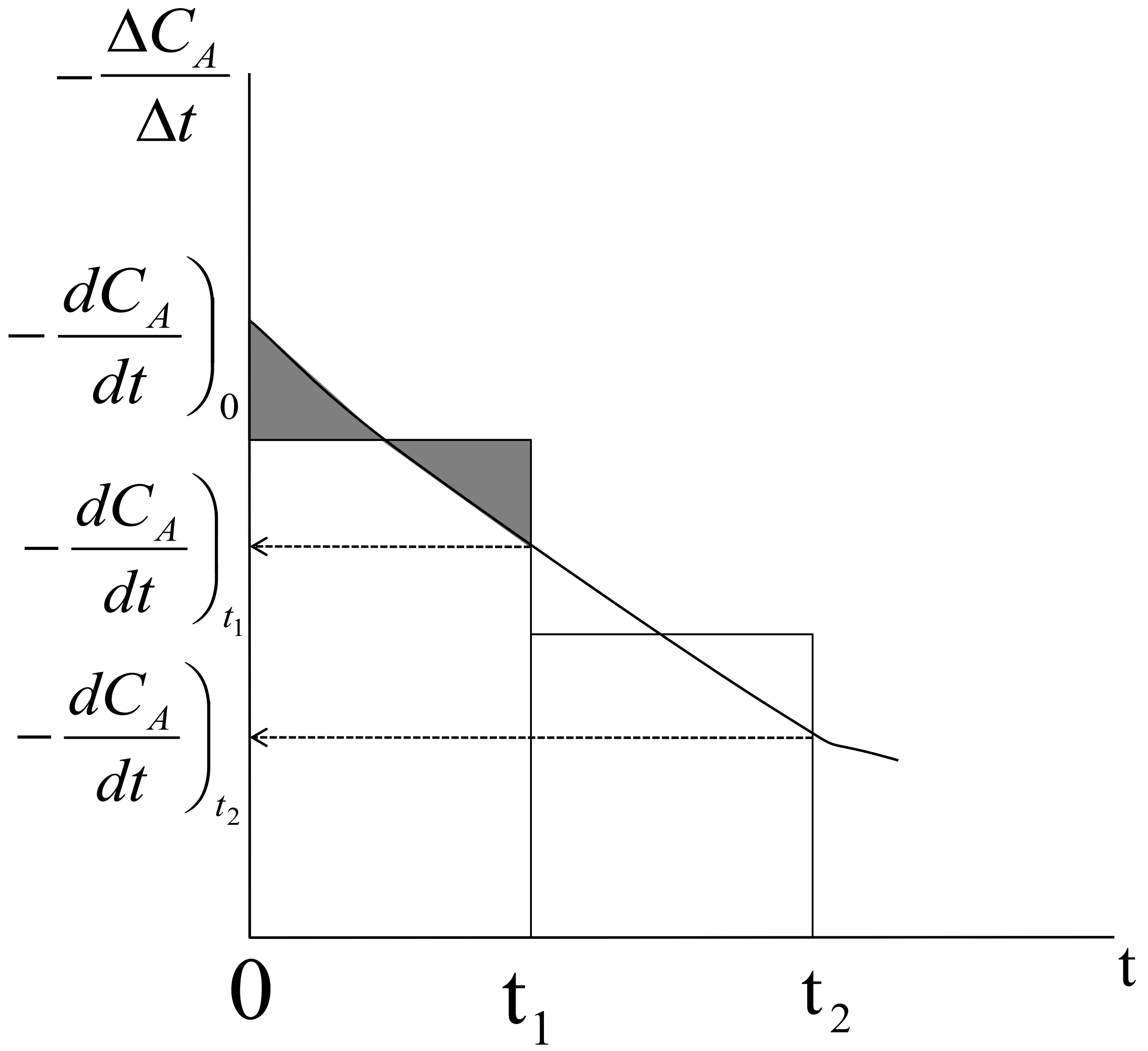
time (s)	0	t_1	t_2	t_3
concentration (moles/dm^3)	C_{A0}	C_{A1}	C_{A2}	C_{A3}

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



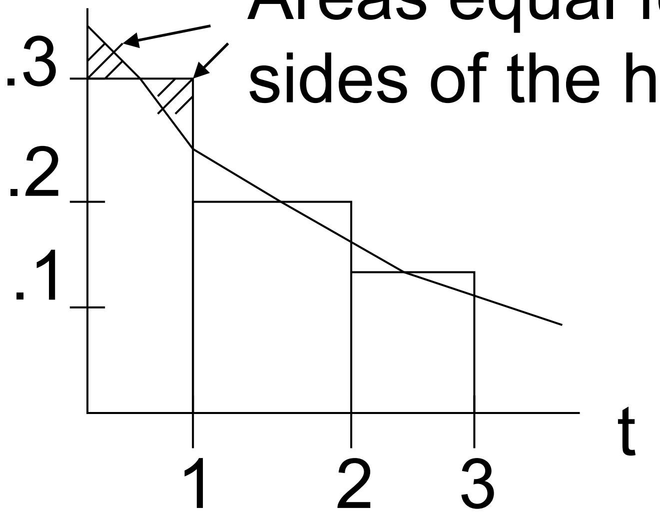


The method accentuates measurement error!

Example – Finding the Rate Law

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

$-\frac{\Delta C_A}{\Delta t}$



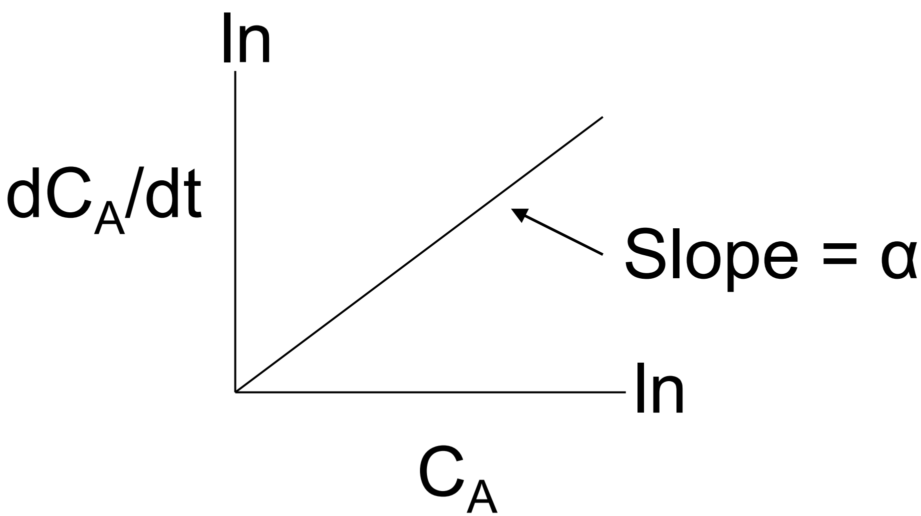
Areas equal for both sides of the histogram

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

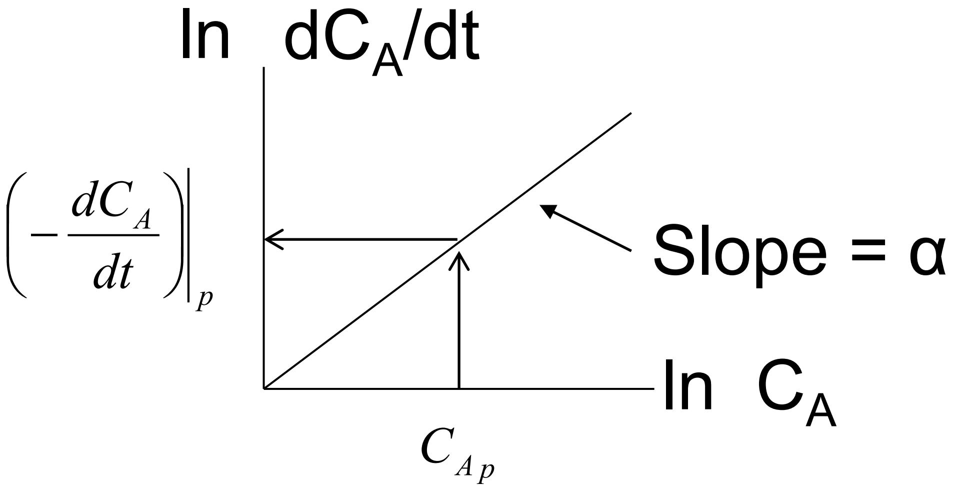
Plot ($-dC_A/dt$) as a function of C_A



Example – Finding the Rate Law

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

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



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.

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

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:

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

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

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

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,

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

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

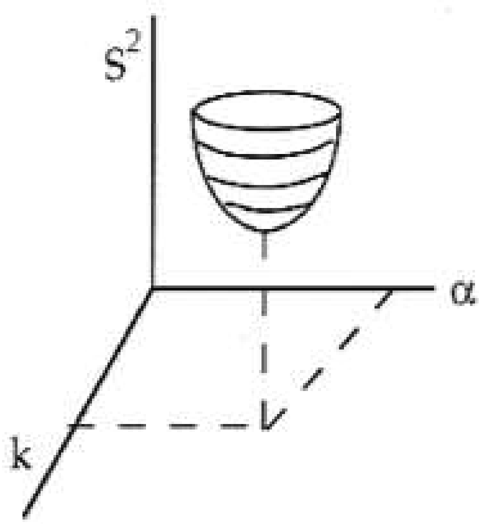
TABLE E5-3.1. REGRESSION OF DATA

	Original Data		*Guess 1*		*Guess 2*		*Guess 3*		*Guess 4*	
			$\alpha = 3$, $k' = 5$		$\alpha = 2$, $k' = 5$		$\alpha = 2$, $k' = 0.2$		$\alpha = 2$, $k' = 0.1$	
	t (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
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
				$s^2 = 2916$		$s^2 = 49{,}895$		$s^2 = 7270$		$s^2 = 3432$

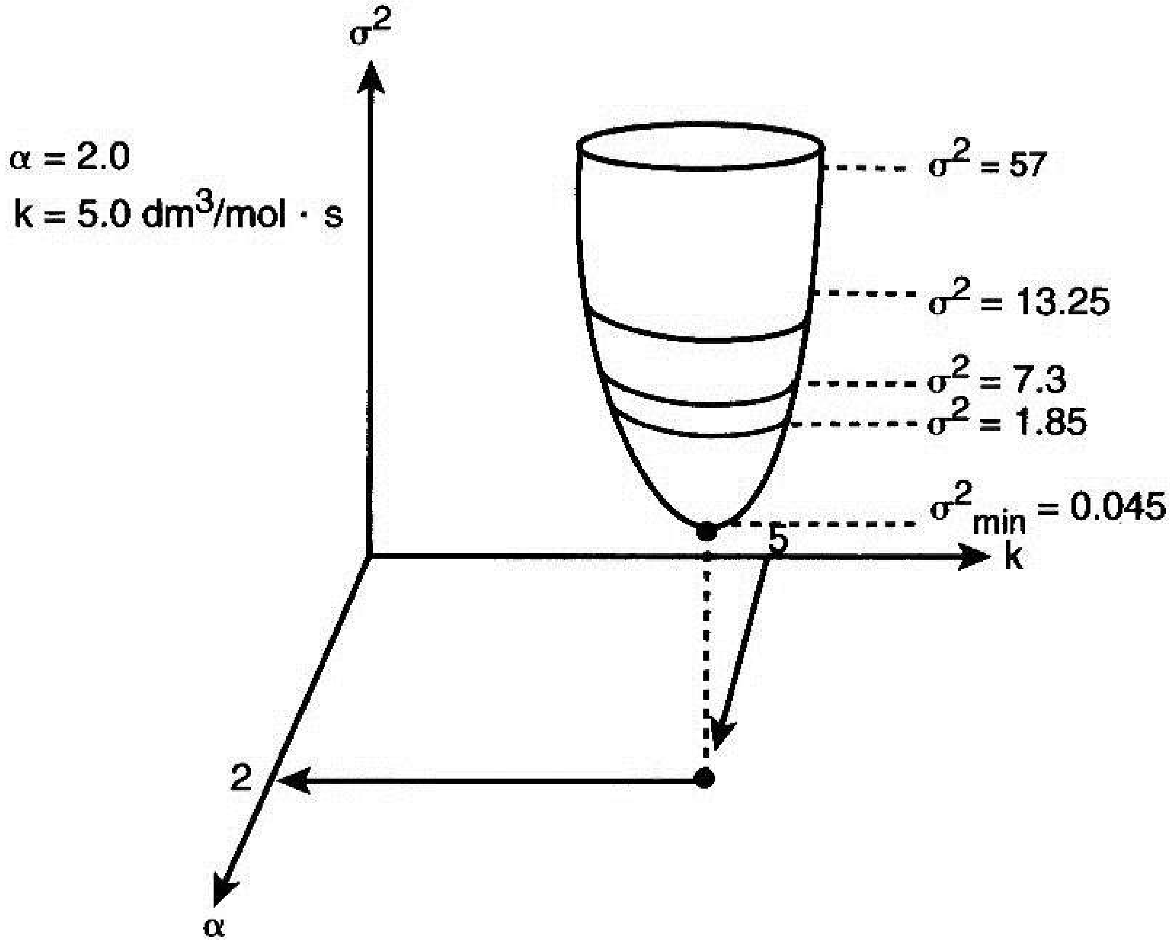
Non-Linear Least Squares Analysis

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

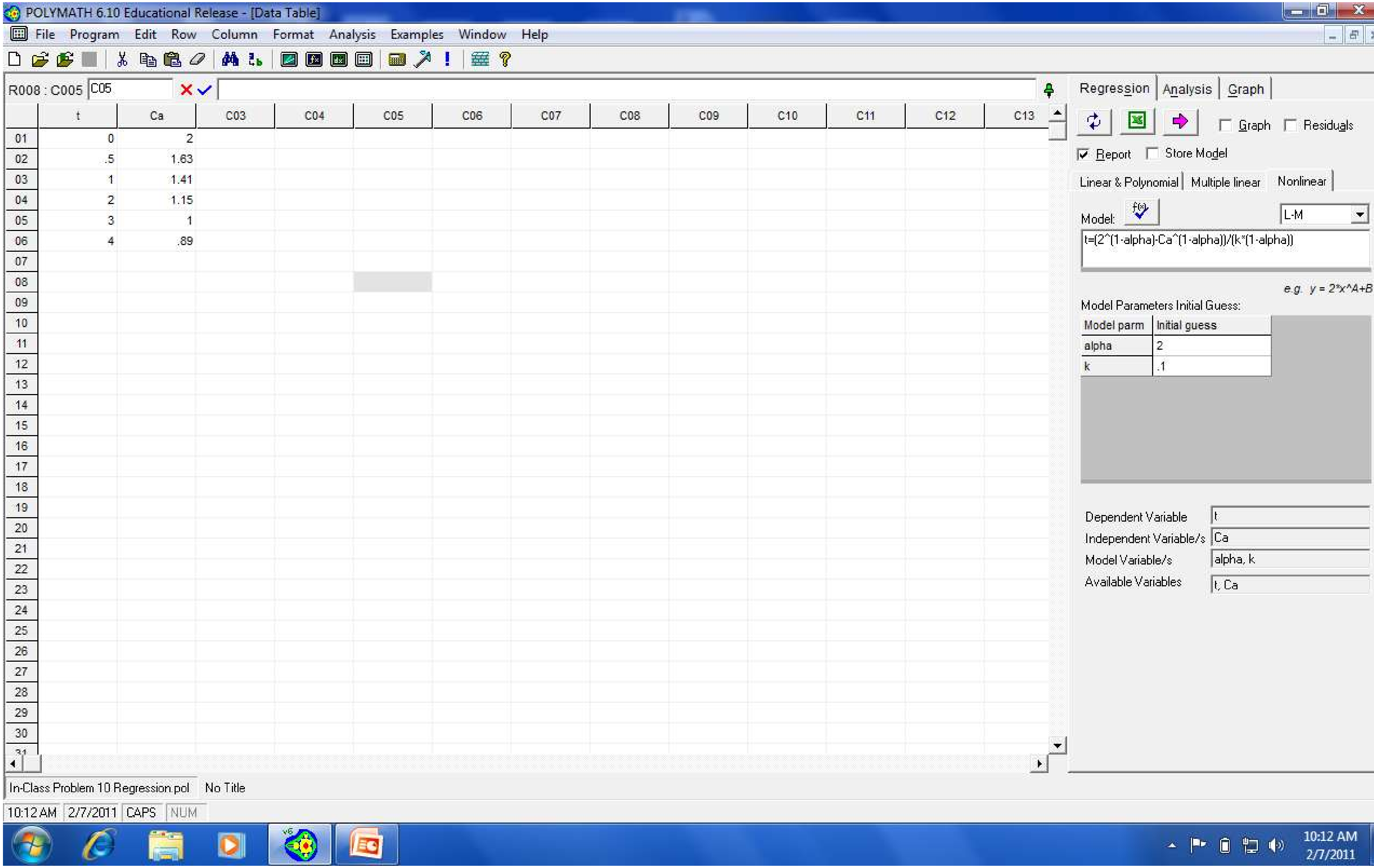
We find the values of alpha and k which minimize s^2



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



Minimum Sum of Squares


POLYMATH 6.10 Educational Release - [Data Table]
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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
Regression Analysis Graph
Graph Residuals
Report Store Model
Linear & Polynomial Multiple linear Nonlinear
Model:
L-M
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 t
Independent Variable/s Ca
Model Variable/s alpha, k
Available Variables t, Ca
In-Class Problem 10 Regression.pol No Title
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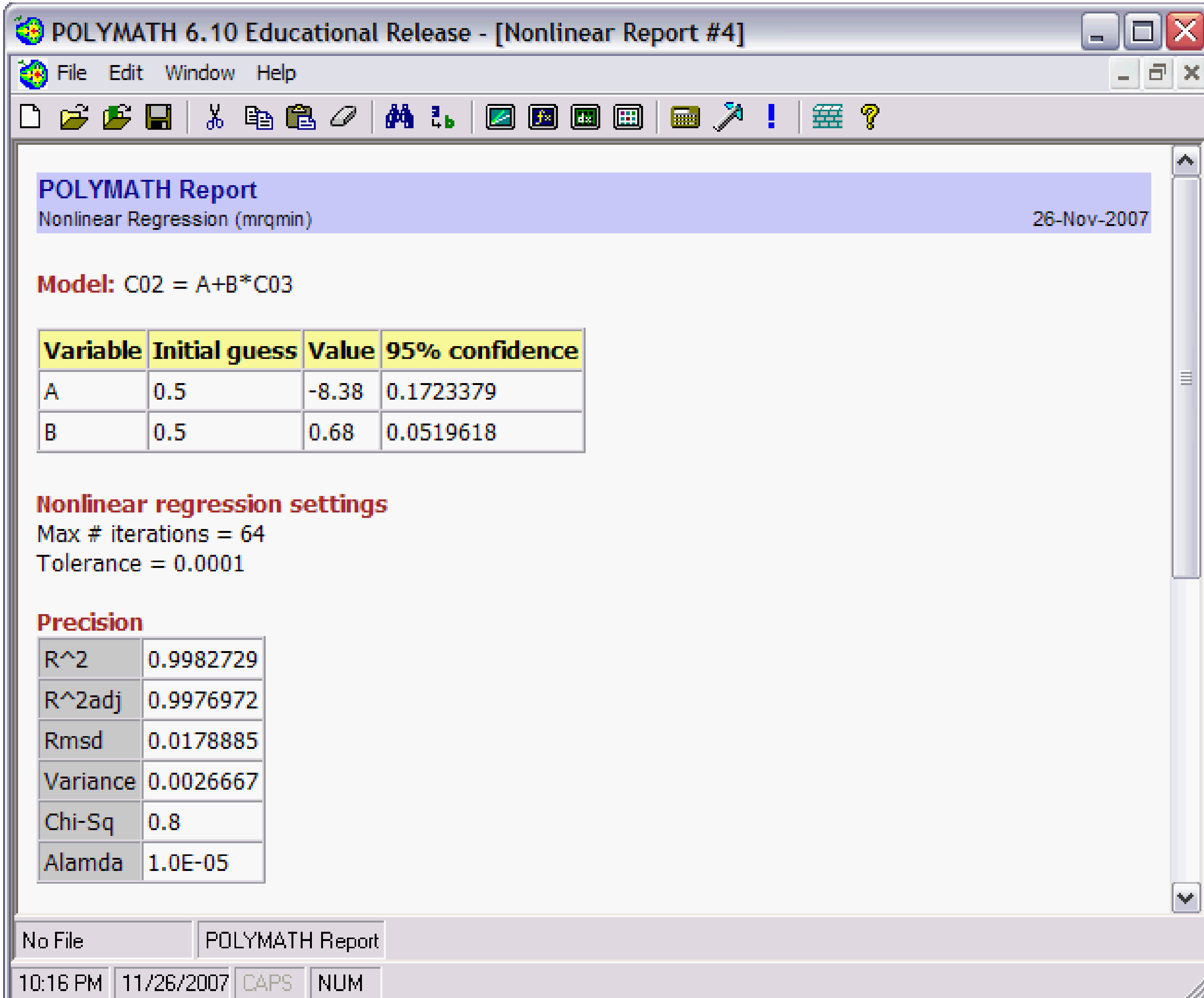


POLYMATH Report

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

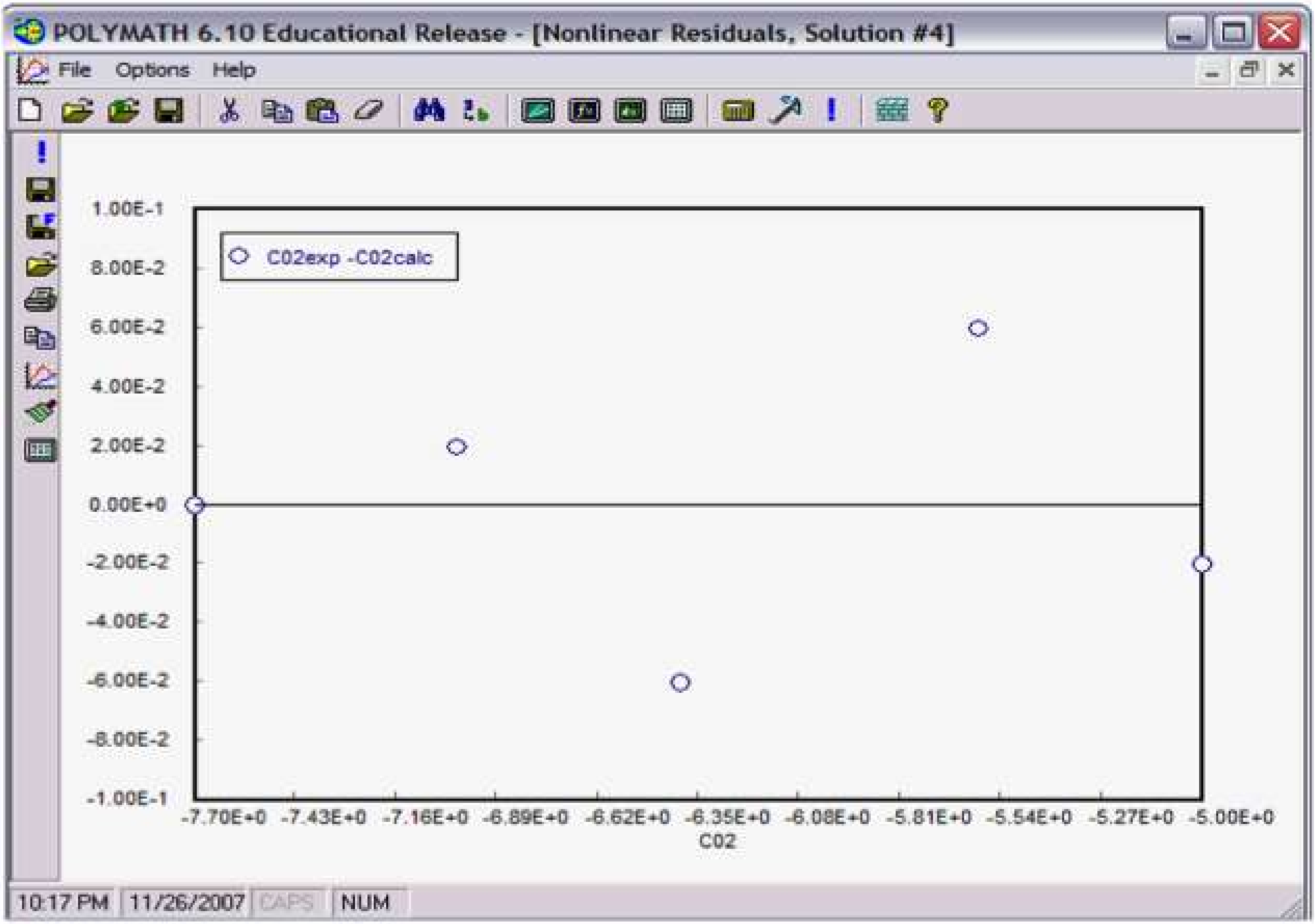
Max # iterations = 64

Tolerance = 0.0001

Precision

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

Residuals



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File Options Help
1.00E-1
8.00E-2
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4.00E-2
2.00E-2
0.00E+0
-2.00E-2
-4.00E-2
-6.00E-2
-8.00E-2
-1.00E-1
C02exp -C02calc
-7.70E+0 -7.43E+0 -7.16E+0 -6.89E+0 -6.62E+0 -6.35E+0 -6.08E+0 -5.81E+0 -5.54E+0 -5.27E+0 -5.00E+0
C02
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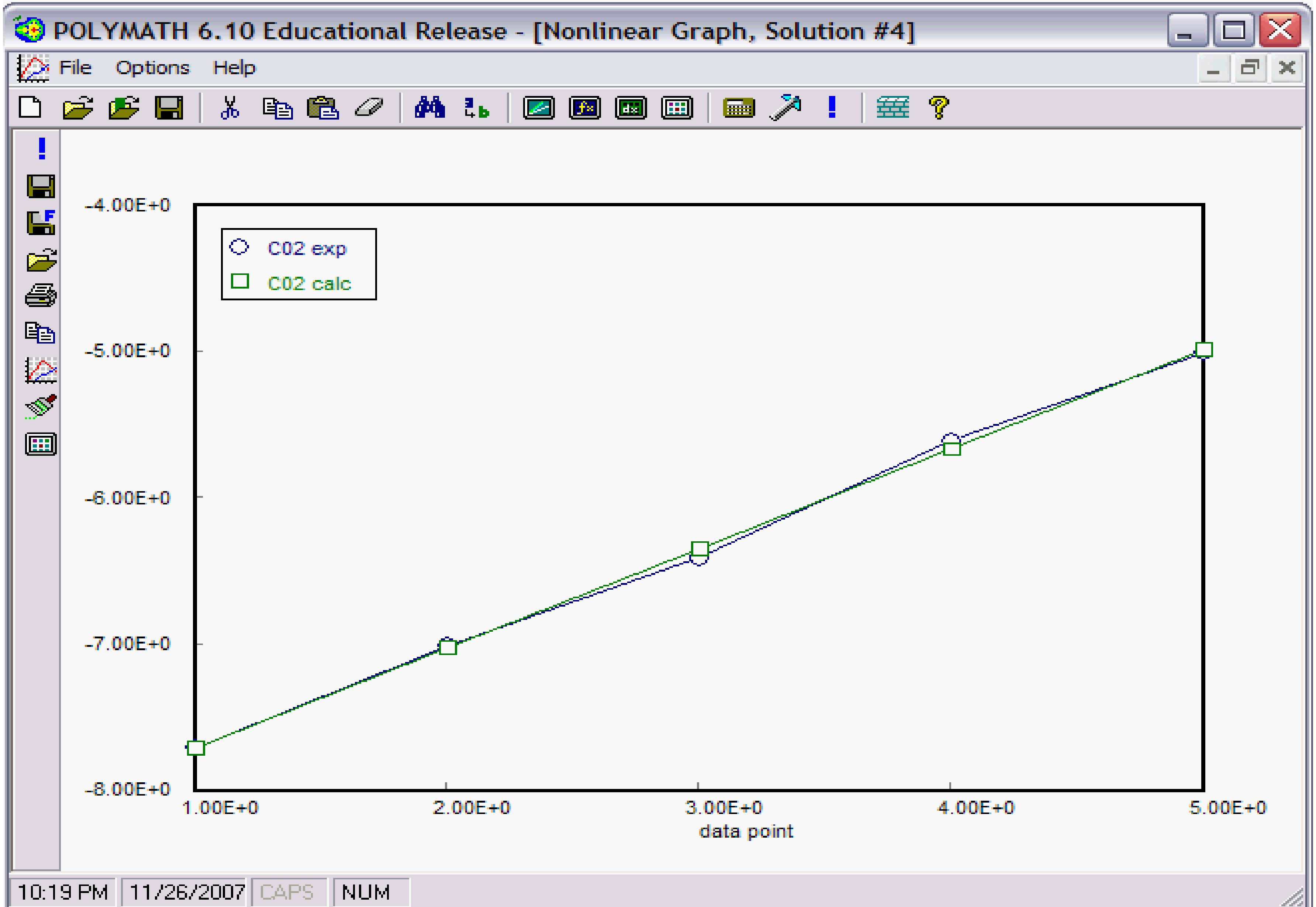
POLYMATH 6.10 Educational Release - [Nonlinear Graph, Solution #4]
File Options Help
C02 exp
C02 calc
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-7.00E+0
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2.00E+0
3.00E+0
4.00E+0
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data point
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End of Lecture 11