Polymath tutorial on non-linear regression (*Example 10-3*)

The following table shows the raw data for performing nonlinear regression using Polymath (refer Table E10-3.1, Elements of chemical reaction engineering, 5th edition)

P_E	P_{EA}	P_H	Rate
1	1	1	1.04
1	1	3	3.13
1	1	5	5.21
3	1	3	3.82
5	1	3	4.19
0.5	1	3	2.391
0.5	0.5	5	3.867
0.5	3	3	2.199
0.5	5	1	0.75

Determine the model parameters for each of the rate law equation given below

a) $-r'_E = \dfrac{k\,P_E P_H}{1+K_{EA}\,P_{EA}+K_E P_E}$

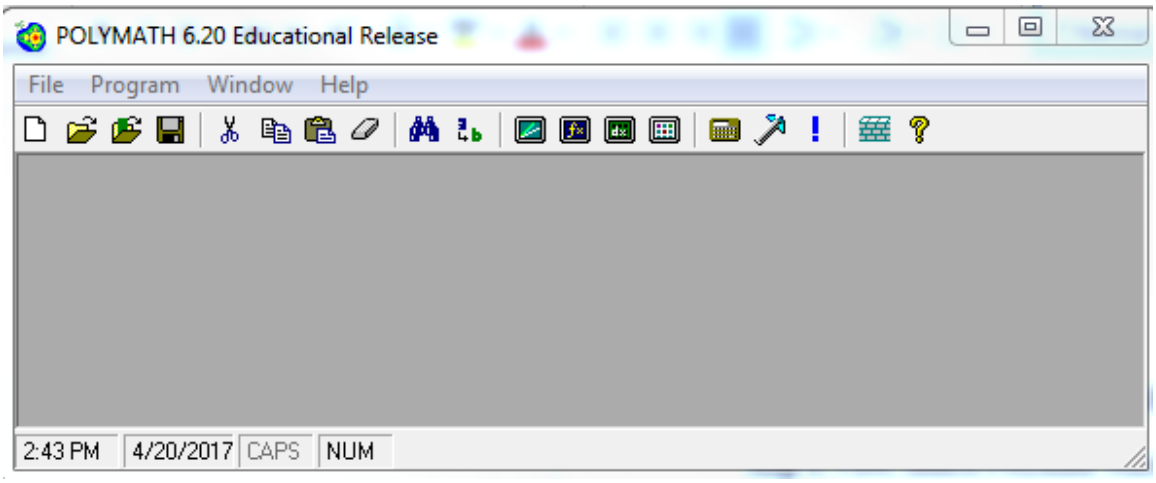
b) $-r'_E = \dfrac{k\,P_E P_H}{1+K_E P_E}$

c) $-r'_E = \dfrac{k\,P_E P_H}{(1+K_E P_E)^2}$

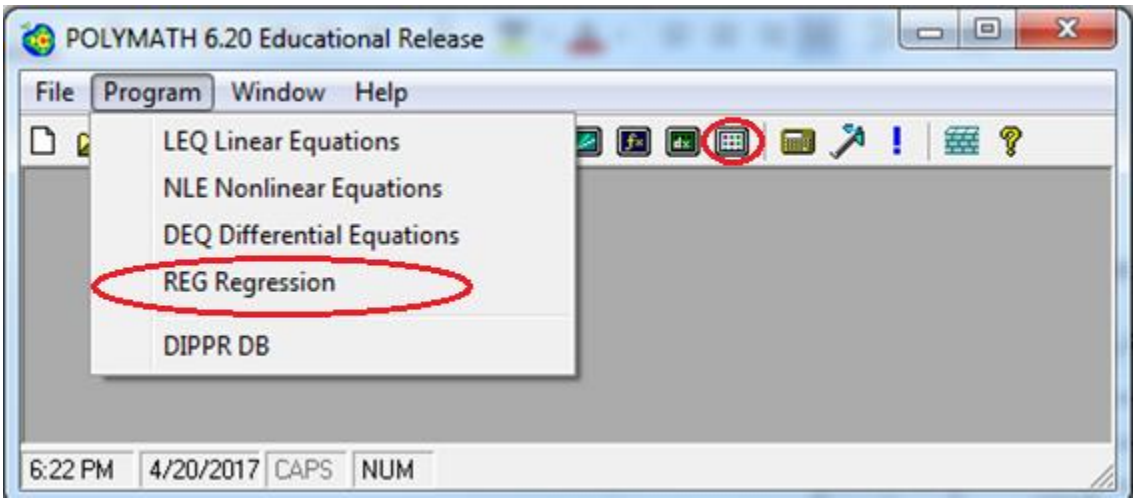
d) $-r'_E = k\,P_E^a P_H^b$

Step 1: First make sure you have polymath installed. If you don't have it then refer to the installation instruction present on http://www.umich.edu/~elements/5e/software/polymath.html

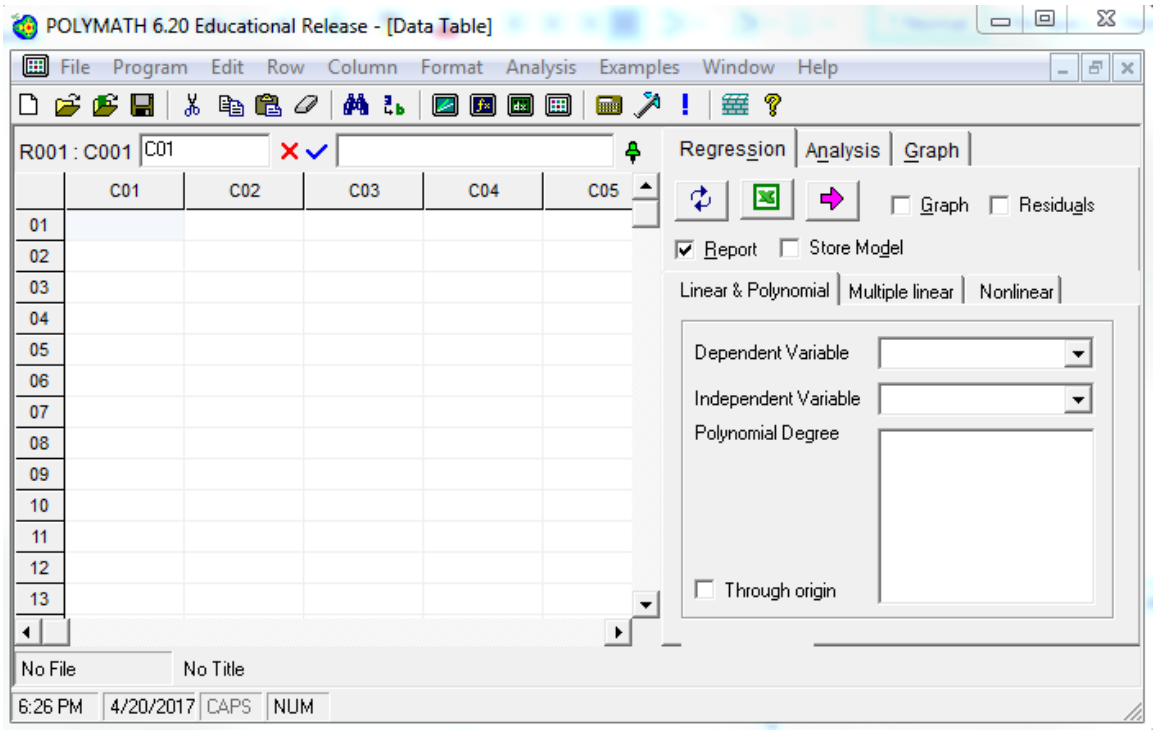
When you open Polymath, following window would appear



Step 2: Click on the “Program” tab present on the toolbar. Select "REG Regression". The shortcut button for nonlinear regression solver is also present on the menu bar as shown by red circle in below screenshot

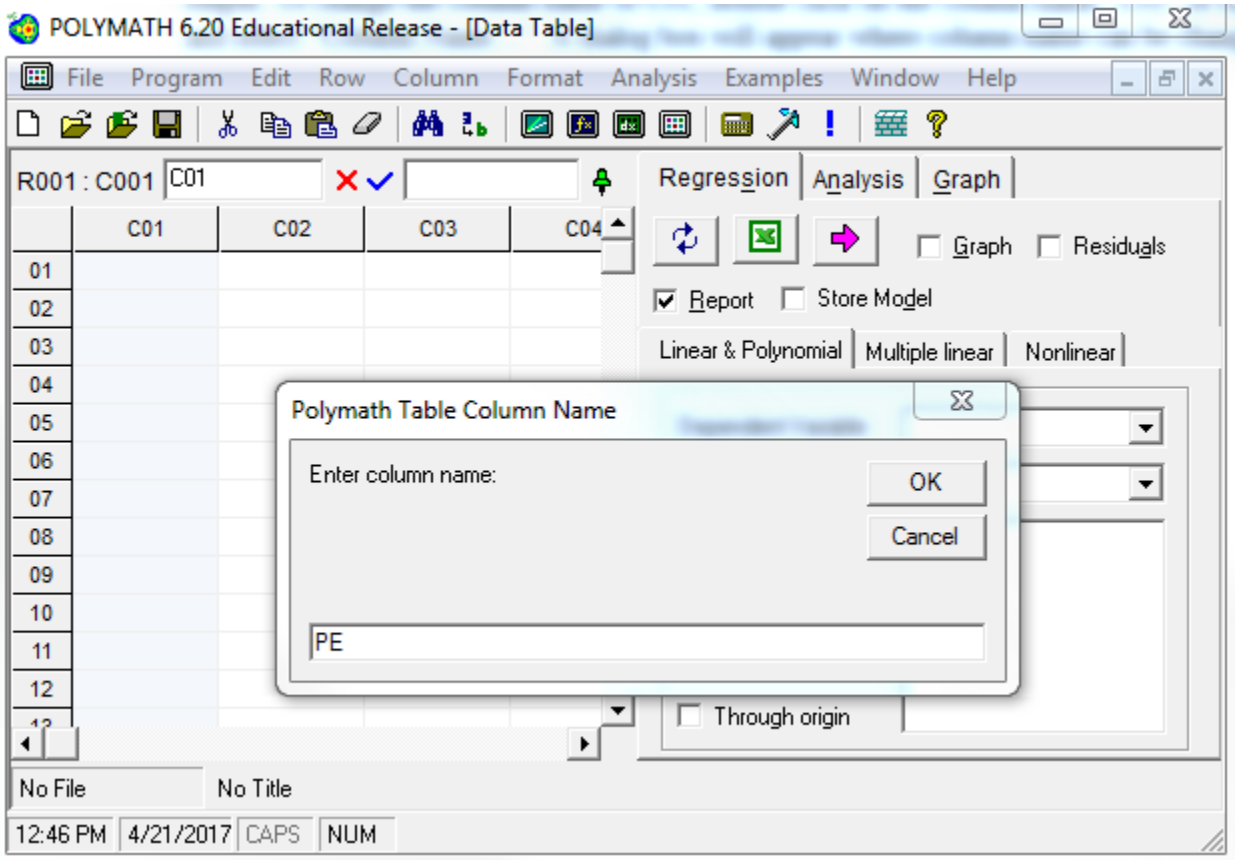


This will open up a spreadsheet which looks like this:



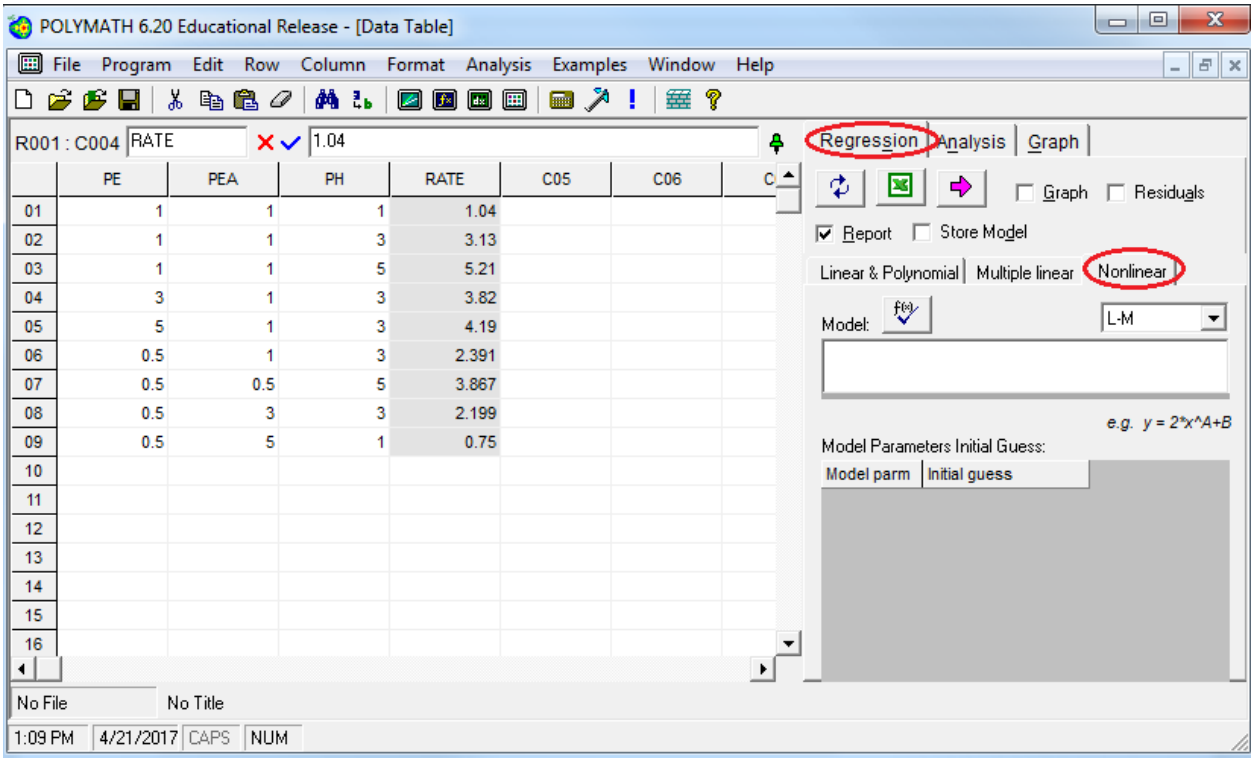
Step 3: Before inserting the data into the spreadsheet, it is recommended to change the column name with the name of the variable mentioned in the data table. This would make it easy to comprehend the polymath output. To change the column name of C01, double click on the column name "C01" or right click on C01 and select "Column Name…" A dialog box will appear where column name can be changed

Enter the column name as PE and click Ok



Similarly, rename C02 to PEA, C03 to PH and C04 to Rate

Step 4: To input the data for PE, select the first cell (row 01, column PE) and enter the first data. Similarly, enter the remaining data of PE in subsequent rows. Repeat this procedure to input the data for PEA, PH and Rate. For nonlinear regression, click on the Regression tab on the right side of the window, and select the "Nonlinear" regression tab under the "Report" and "Store Model" check boxes. The Spreadsheet should look like this:



Part (a)

Step 5: Now, you need to input the model form you wish your equation to match. In this case, there are 4 equations for rate law. We will first do the nonlinear regression for the part (a) and then repeat the same for part (b) to (d).

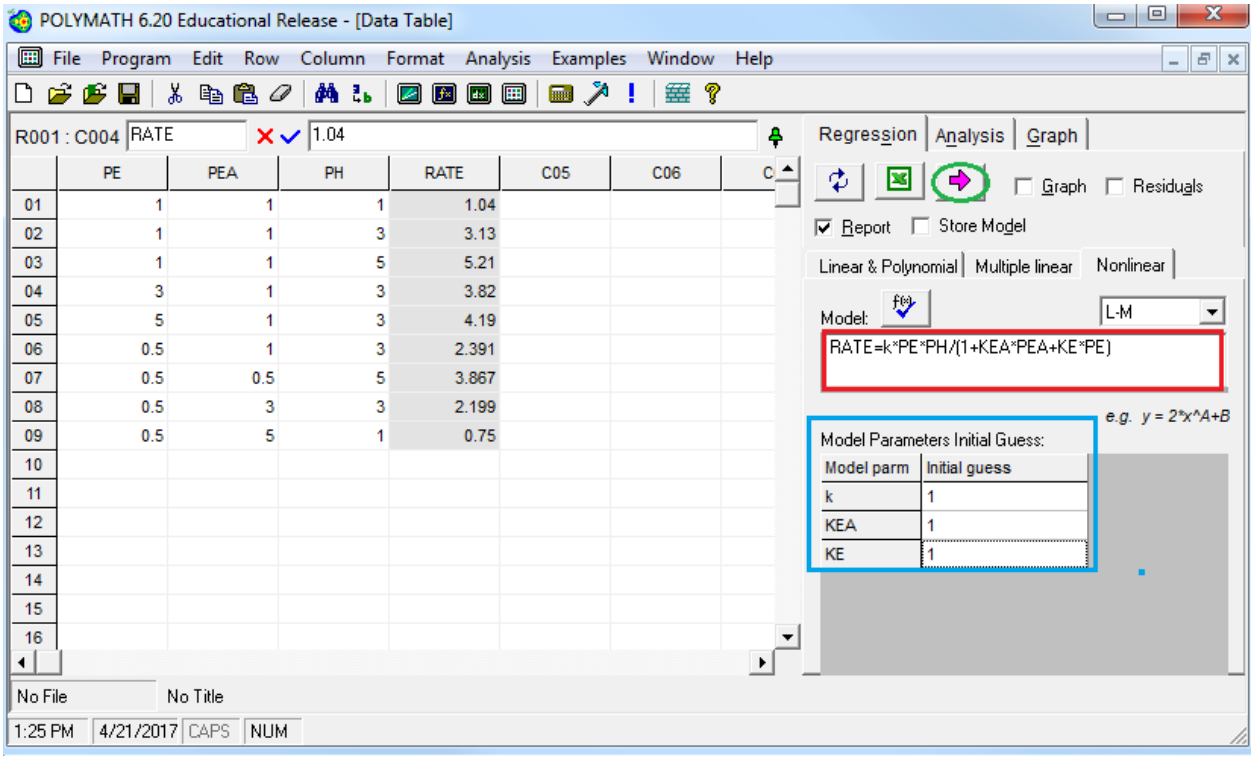
For part (a), the rate expression is given by

$$Rate=k*PE*PH/(1+KEA*PEA+KE*PE)$$

To input the model, place the cursor in the rectangular box below "Model:" and type the Rate equation as shown in the below screen shot.

Next, you need to provide initial guesses for the parameters in your model, in this case, k, KEA, and KE. (Note: The solution Polymath provides may be very sensitive to the initial value guesses, so if the first regression solution is not very good, you may want to change the initial guesses and rerun the regression).

Let's put 1 as initial guess for all the model parameters. To input the initial guess, select the cell corresponding to each parameter under section "Model Parameters Initial Guess" and then enter the guess value



Now select what you want polymath to output by checking the boxes on the right side of the window. The options are Graph, Residuals, Report, and Store Model.

Step 6: Click on the pink arrow to have Polymath perform the regression. If you selected "Report" you will see a screen like this that details the statistical results (such as R^2, Variance etc.) from the regression analysis.

Nonlinear Report #1

File Edit Help

POLYMATH Report
Nonlinear Regression (L-M) 21-Apr-2017

Model: RATE = k*PE*PH/(1+KEA*PEA+KE*PE)

Variable	Initial guess	Value	95% confidence
k	1.	3.34788	0.2922517
KEA	1.	0.0428419	0.0636262
KE	1.	2.21108	0.2392585

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	0.998321
R^2adj	0.9977614
Rmsd	0.0191217
Variance	0.0049361

General

Sample size	9
Model vars	3
Indep vars	3
Iterations	12

Source data points and calculated data points

	PE	PH	PEA	RATE	RATE calc	Delta RATE
1	1	1	1	1.04	1.028876	0.0111244
2	1	3	1	3.13	3.086627	0.0433733
3	1	5	1	5.21	5.144378	0.0656221
4	3	3	1	3.82	3.9253	-0.1053004
5	5	3	1	4.19	4.150869	0.0391314
6	0.5	3	1	2.391	2.33749	0.0535101
7	0.5	5	0.5	3.867	3.935052	-0.0680519
8	0.5	3	3	2.199	2.247839	-0.0488395
9	0.5	1	5	0.75	0.7216039	0.0283961

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From the above report

$$k = 3.348$$

$$K_{EA} = 3.348$$

$$K_E = 3.348$$

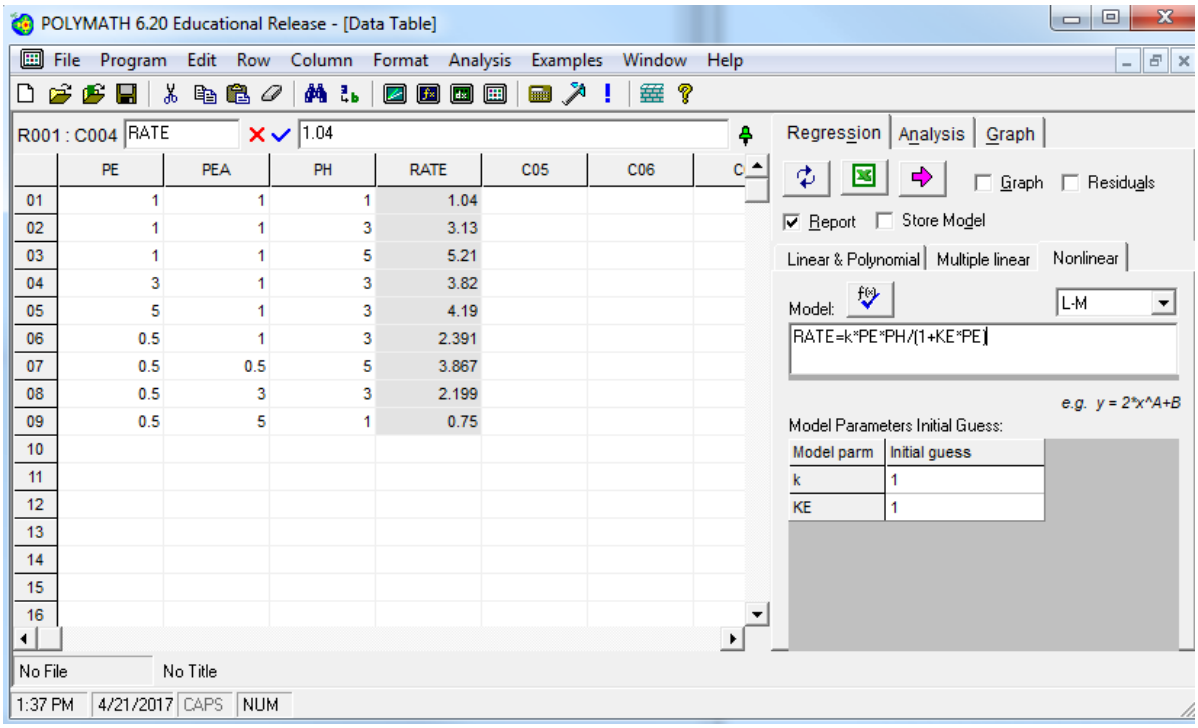
Part (b)

Step 7: Go back to step 5 and enter the RATE equation as

RATE=k*PE*PH/(1+KE*PE)

with

Initial Guess: k= 1, KE= 1



Step 8: Click on the pink arrow  to have Polymath perform the regression

Nonlinear Report #2

File Edit Help

POLYMATH Report
Nonlinear Regression (L-M) 21-Apr-2017

Model: RATE = k*PE*PH/(1+KE*PE)

Variable	Initial guess	Value	95% confidence
k	1.	3.186785	0.287998
KE	1.	2.101336	0.2638835

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	0.9975978
R^2adj	0.9972547
Rmsd	0.022872
Variance	0.0060534

General

Sample size	9
Model vars	2
Indep vars	2
Iterations	5

Source data points and calculated data points

	PE	PH	RATE	RATE calc	Delta RATE
1	1	1	1.04	1.027552	0.0124478
2	1	3	3.13	3.082657	0.0473433
3	1	5	5.21	5.137761	0.0722388
4	3	3	3.82	3.926757	-0.1067567
5	5	3	4.19	4.154263	0.0357374
6	0.5	3	2.391	2.331034	0.0599658
7	0.5	5	3.867	3.885057	-0.018057
8	0.5	3	2.199	2.331034	-0.1320342
9	0.5	1	0.75	0.7770114	-0.0270114

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From the above report,

$$k = 3.187$$

$$K_E = 2.1$$

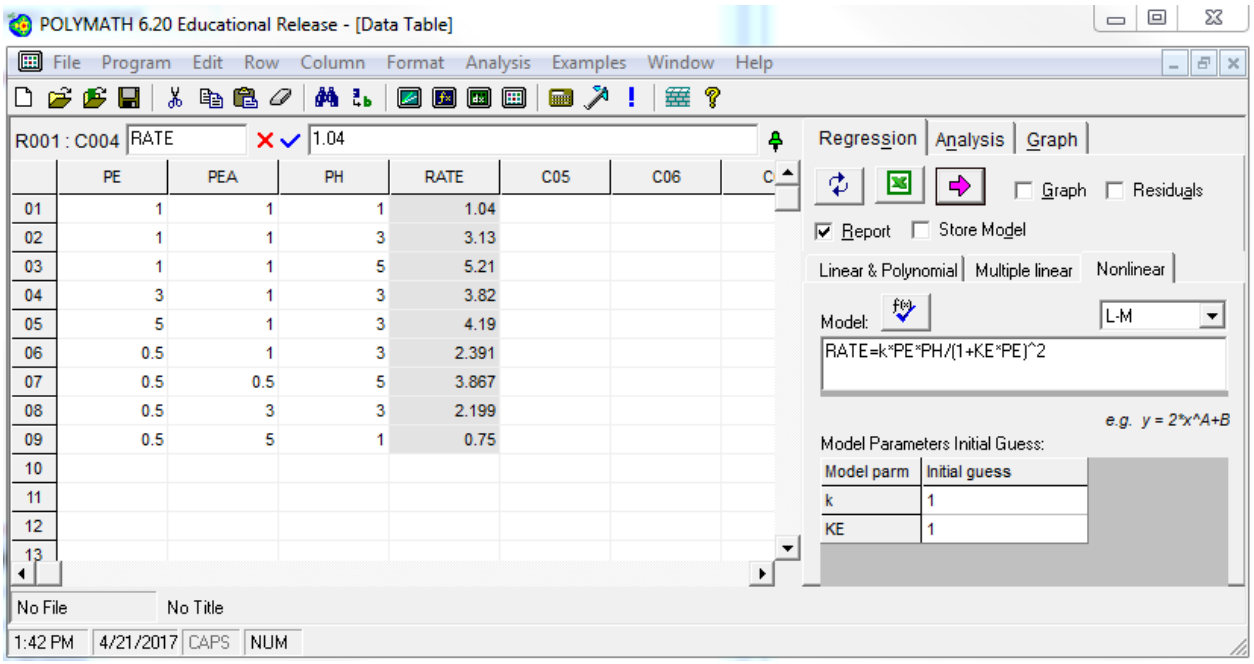
Part (c)

Step 9: Go back to step 7 and enter the RATE equation as

RATE=k*PE*PH/(1+KE*PE)

with

Initial Guess: k= 1, KE= 1



Step 10: Click on the pink arrow  to have Polymath perform the regression

Nonlinear Report #3

File Edit Help

POLYMATH Report
Nonlinear Regression (L-M) 21-Apr-2017

Model: RATE = k*PE*PH/(1+KE*PE)^2

Variable	Initial guess	Value	95% confidence
k	1.	2.008776	0.2661838
KE	1.	0.3616652	0.0623045

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	0.9752762
R^2adj	0.9717442
Rmsd	0.0733772
Variance	0.0623031

General

Sample size	9
Model vars	2
Indep vars	2
Iterations	9

Source data points and calculated data points

	PE	PH	RATE	RATE calc	Delta RATE
1	1	1	1.04	1.083405	-0.0434051
2	1	3	3.13	3.250215	-0.1202152
3	1	5	5.21	5.417025	-0.2070253
4	3	3	3.82	4.158759	-0.3387591
5	5	3	4.19	3.820566	0.3694335
6	0.5	3	2.391	2.160957	0.230043
7	0.5	5	3.867	3.601595	0.265405
8	0.5	3	2.199	2.160957	0.038043
9	0.5	1	0.75	0.720319	0.029681

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From the above report,

$$k = 2.009$$

$$K_E = 0.3617$$

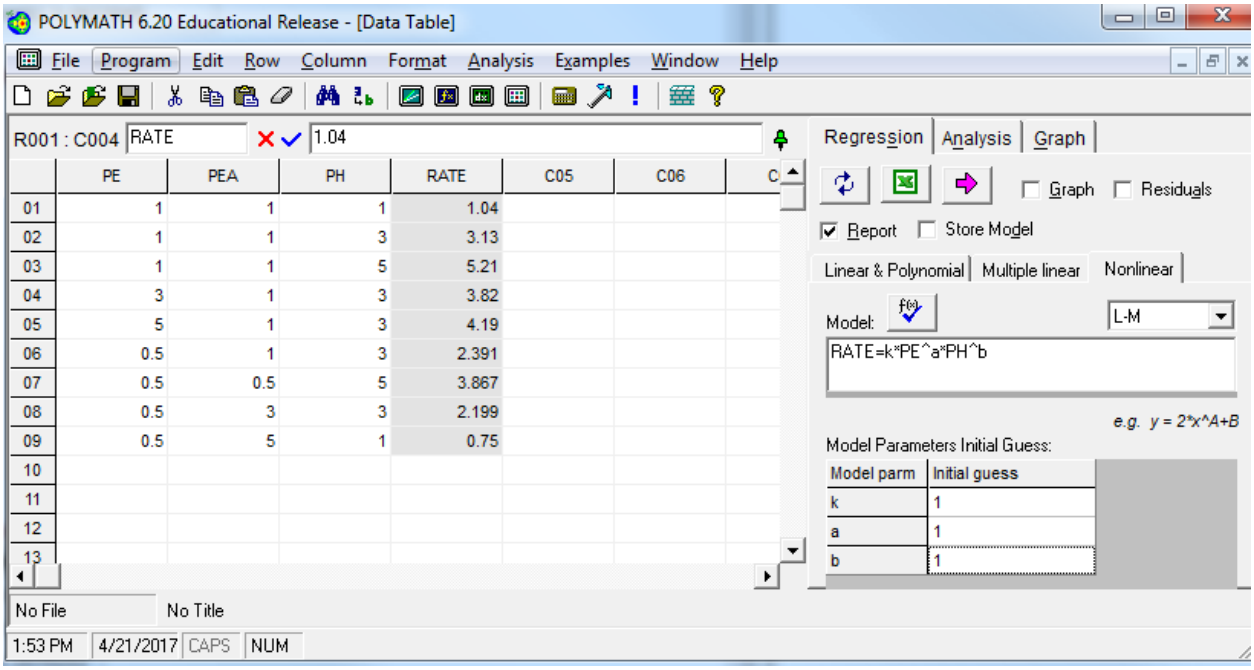
Part (d)

Step 11: Go back to step 9 and enter the RATE equation as

RATE=k*PE^a*PH^b

with

Initial Guess: k= 1, a=1, b=1



Step 12: Click on the pink arrow  to have Polymath perform the regression

Nonlinear Report #4

File Edit Help

POLYMATH Report
Nonlinear Regression (L-M) 21-Apr-2017

Model: RATE = k*PE^a*PH^b

Variable	Initial guess	Value	95% confidence
k	1.	0.8940237	0.2505474
a	1.	0.2584412	0.0704628
b	1.	1.061554	0.2041339

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	0.9831504
R^2adj	0.9775338
Rmsd	0.0605757
Variance	0.0495372

General

Sample size	9
Model vars	3
Indep vars	2
Iterations	6

Source data points and calculated data points

	PE	PH	RATE	RATE calc	Delta RATE
1	1	1	1.04	0.8940237	0.1459763
2	1	3	3.13	2.869717	0.2602829
3	1	5	5.21	4.935641	0.2743591
4	3	3	3.82	3.811947	0.0080529
5	5	3	4.19	4.349924	-0.1599245
6	0.5	3	2.391	2.399057	-0.0080569
7	0.5	5	3.867	4.12615	-0.25915
8	0.5	3	2.199	2.399057	-0.2000569
9	0.5	1	0.75	0.7473955	0.0026045

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From the above report,

$$k = 0.894$$

$$a = 0.258$$

$$b = 1.062$$