

Polymath tutorial to determine the Rate-Law parameters (Example 10-1)

The following table shows the raw data for performing nonlinear regression to determine model parameters (refer Table 10-6)

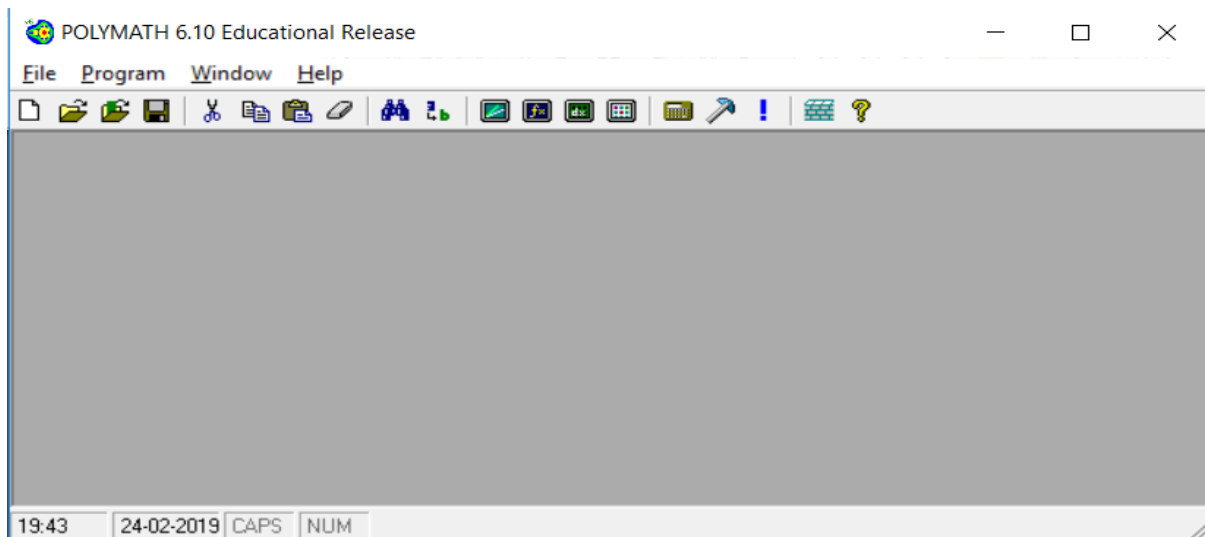
RATE	PT	PH2	PM	PB
71	1	1	1	0
71.3	1	1	4	0
41.6	1	1	0	1
19.7	1	1	0	4
42	1	1	1	1
17.1	1	1	0	5
71.8	1	1	0	0
142	1	2	0	0
284	1	4	0	0
47	0.5	1	0	0
71.3	1	1	0	0
117	5	1	0	0
127	10	1	0	0
131	15	1	0	0
133	20	1	0	0
41.8	1	1	1	1

The nonlinear equation is given by

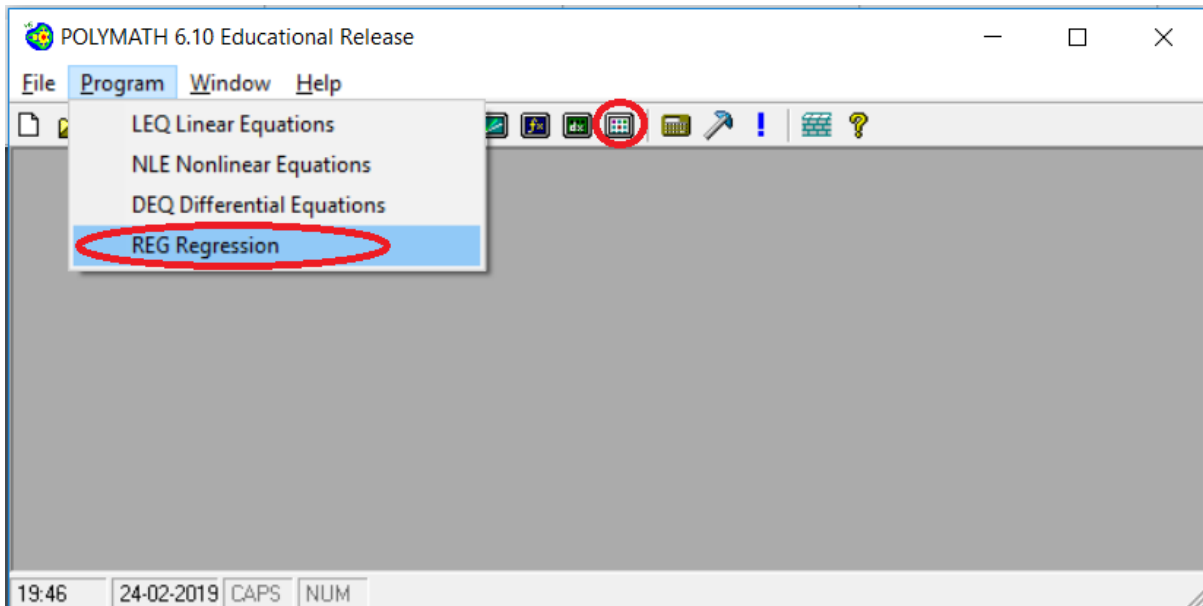
$$Rate = \frac{k P_T P_{H_2}}{1 + K_B P_B + K_T P_T}$$

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>

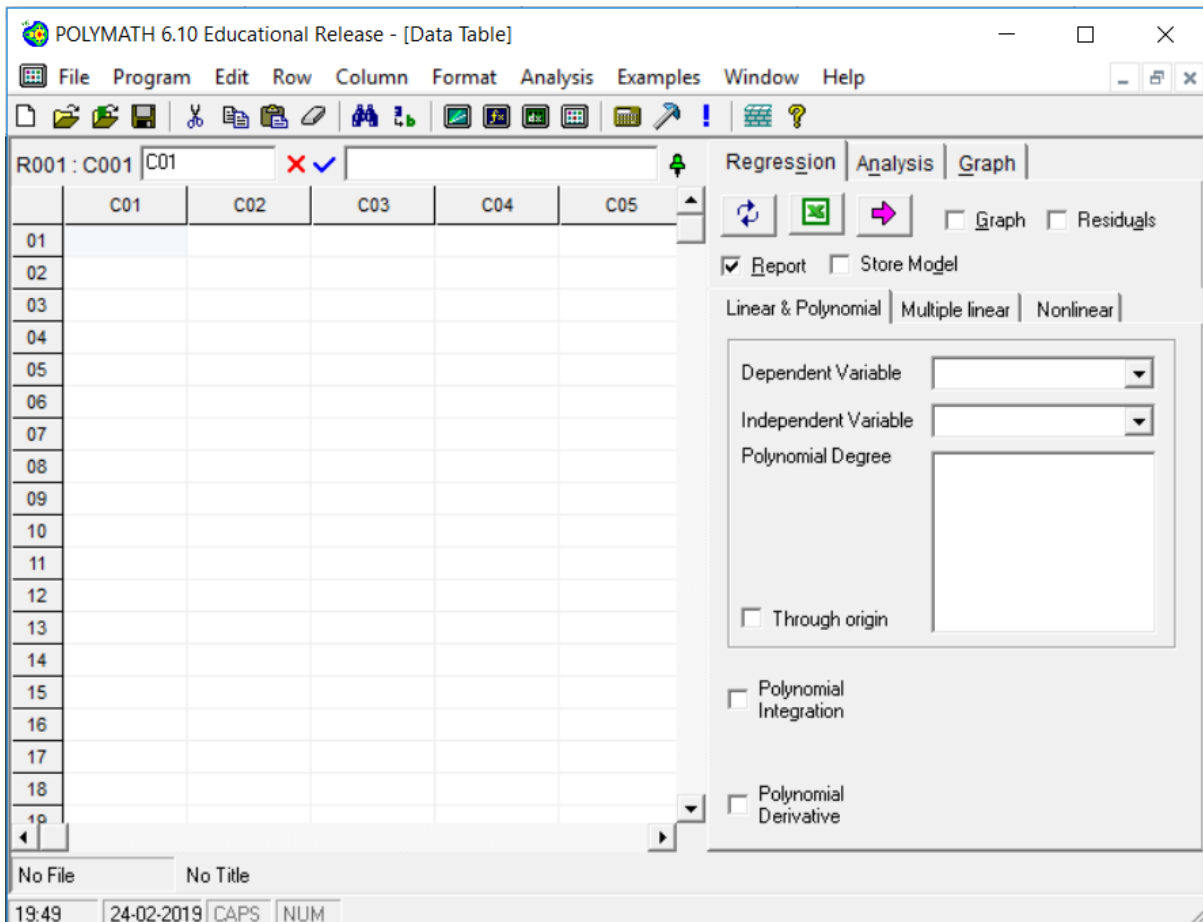
When you open Polymath, following window would appear



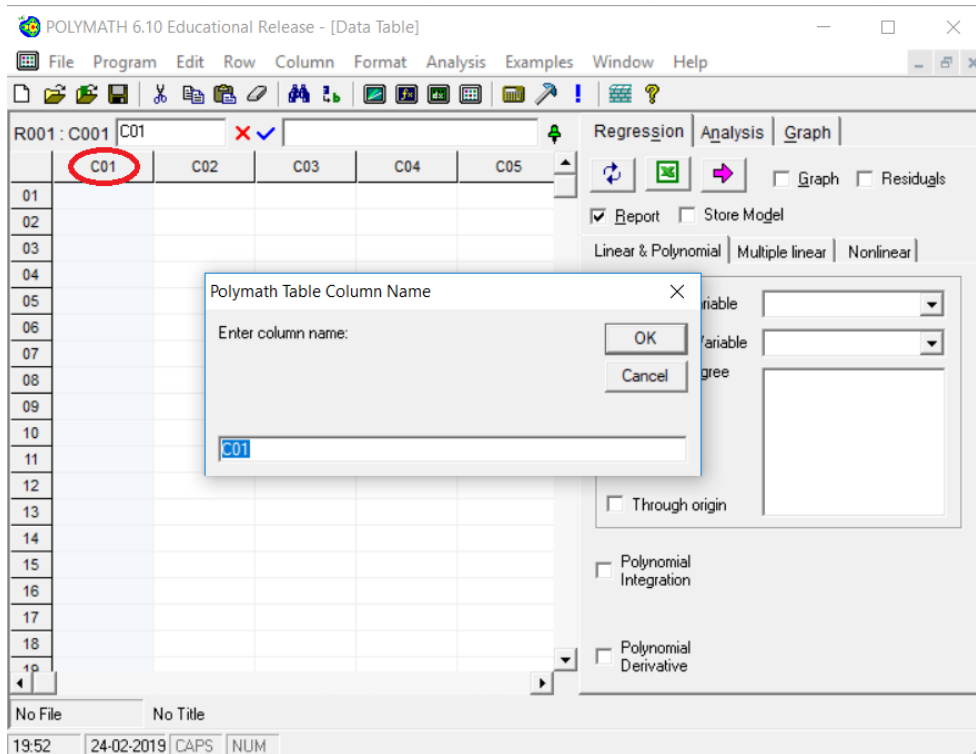
Step 2: To use the nonlinear regression solver in Polymath, first click on the "Program" tab present on the toolbar and select "REG Regression". The shortcut button for nonlinear equation solver is also present on the menu bar as shown by red circle in below screenshot



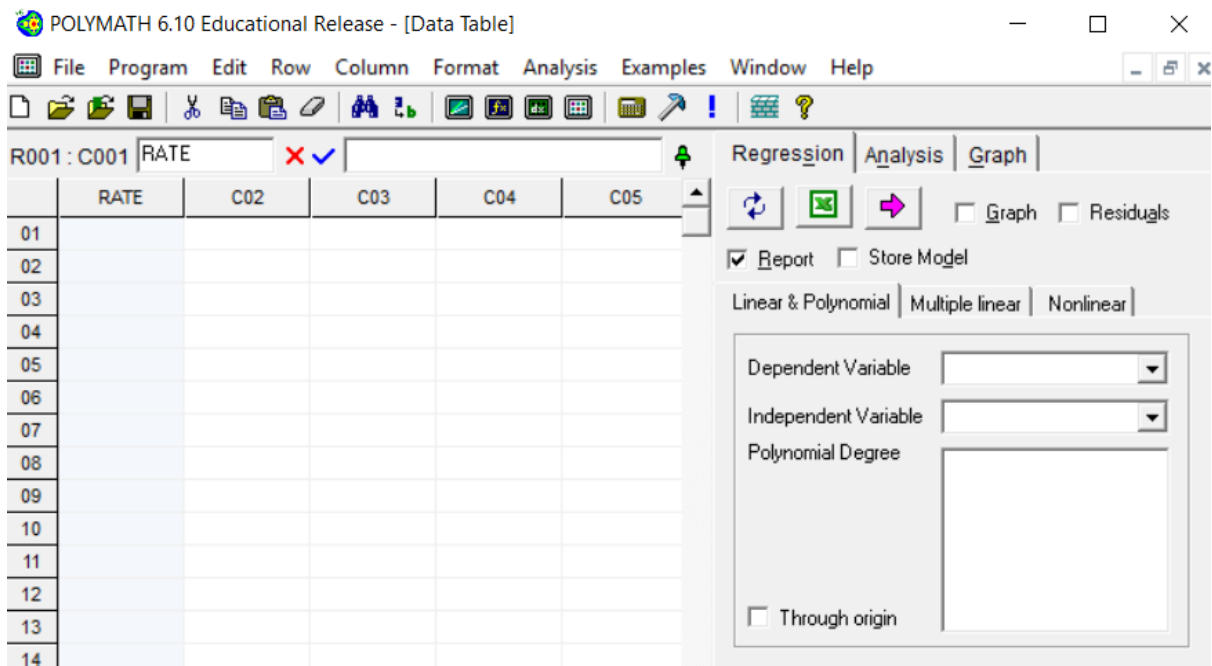
This will open up another window, which looks like this



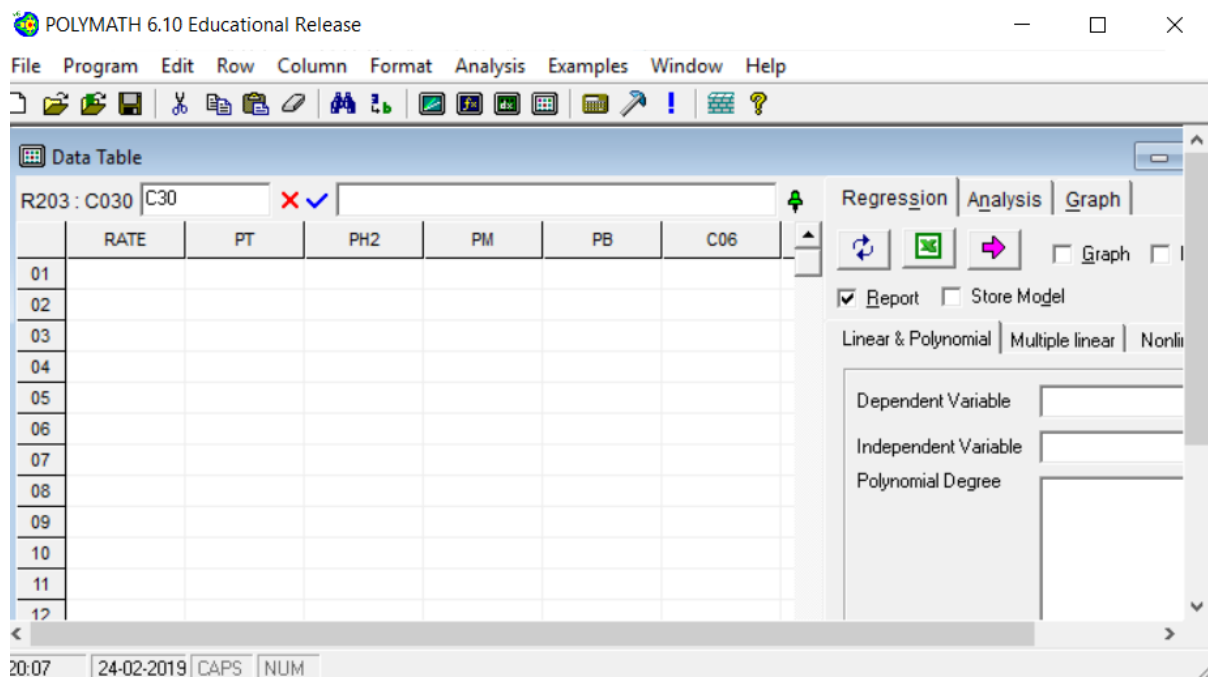
Step 3: Before inserting the data into the spreadsheet, it is recommended to change the column name with the name of the variable mentioned in the data table. This would make it easy to comprehend the polymath output. To change the column name of C01, double click on the column name “C01” or right click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



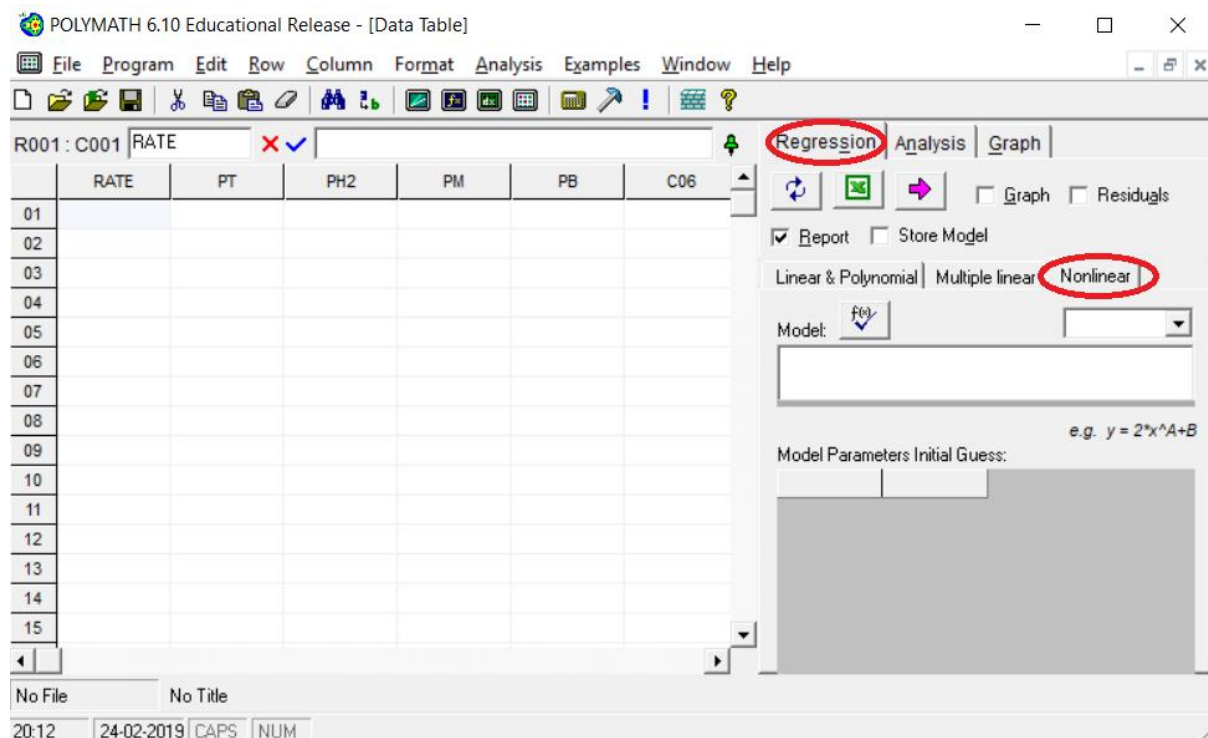
Change the column name to RATE and click Ok. You will find that 1st column name is changed to RATE



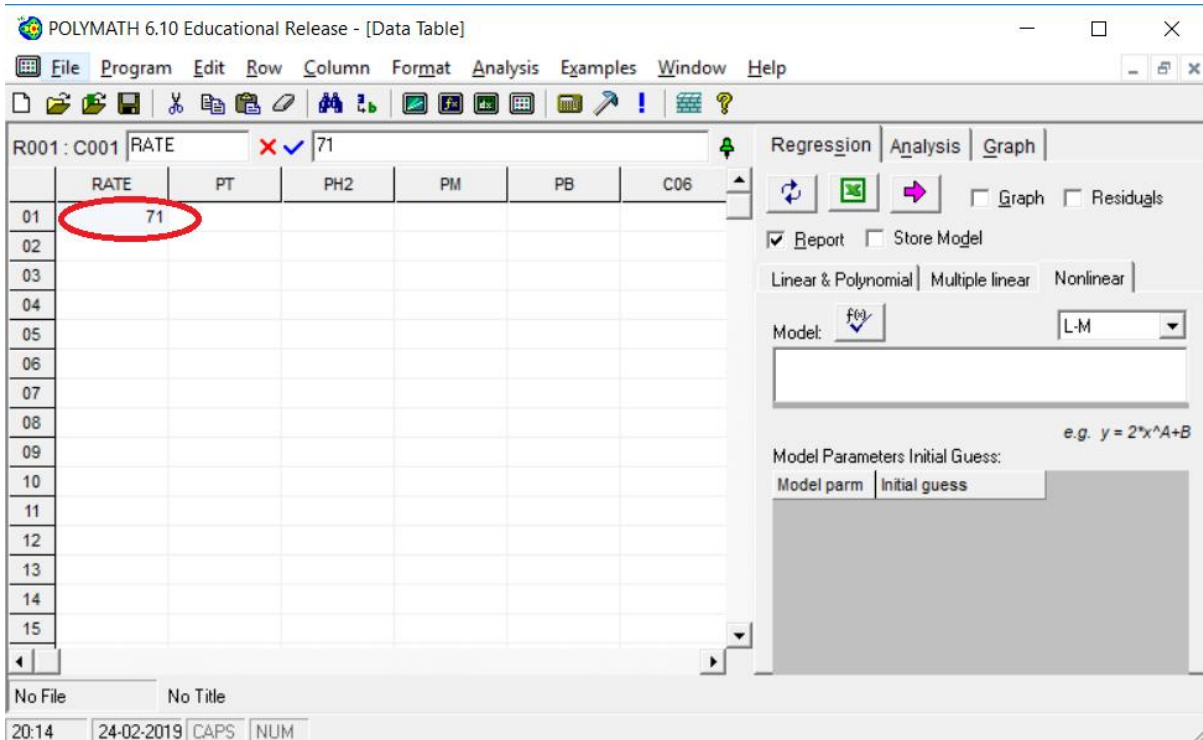
Similarly, rename C02, C03, C04, & C05 to PT, PH2, PM, & PB respectively



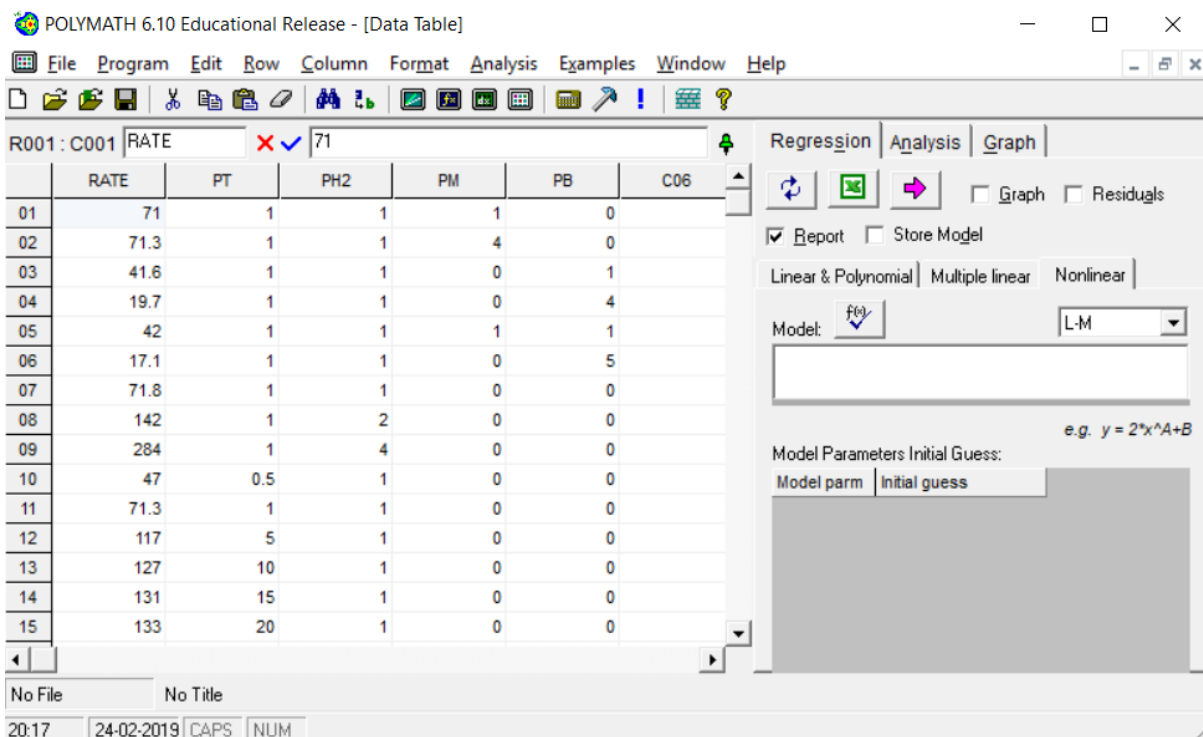
Step 4: For using nonlinear regression solver, click on the Regression tab on the right side of the window, and select the "Nonlinear" regression tab below the "Report" and "Store Model" check boxes. The window should look like this:



Step 5: To input the data for RATE, select the first cell (row 01, column RATE) and enter the first data as shown below:



Similarly, enter the remaining data of RATE in subsequent rows. Repeat this procedure to input the data for PT, PH2, PM, & PB (from Table 10-6). After entering the data, the spreadsheet would look like this:



Step 6: Now, you need to input the model form you wish your equation to match. In this case, the form is $\text{RATE} = k \cdot \text{PT} \cdot \text{PH}_2 / (1 + \text{KB} \cdot \text{PB} + \text{KT} \cdot \text{PT})$, where RATE, PT, PH₂, & PB are columns in the data table that we are using. k, KB, and KT are the model parameters which you need to fit. To input the model, place the cursor in the rectangular box below "Model:" and type the equation as shown in the below screen shot.

The screenshot shows the POLYMATH 6.10 Educational Release interface. The main window displays a data table with columns RATE, PT, PH₂, PM, PB, and C06. The Regression dialog box is open, showing the model equation $\text{RATE} = k \cdot \text{PT} \cdot \text{PH}_2 / (1 + \text{KB} \cdot \text{PB} + \text{KT} \cdot \text{PT})$ entered in the "Model:" field. The regression method is set to "L-M".

	RATE	PT	PH ₂	PM	PB	C06
01	71	1	1	1	0	0
02	71.3	1	1	4	0	0
03	41.6	1	1	0	1	0
04	19.7	1	1	0	4	0
05	42	1	1	1	1	0
06	17.1	1	1	0	5	0
07	71.8	1	1	0	0	0
08	142	1	2	0	0	0
09	284	1	4	0	0	0
10	47	0.5	1	0	0	0
11	71.3	1	1	0	0	0
12	117	5	1	0	0	0
13	127	10	1	0	0	0
14	131	15	1	0	0	0
15	133	20	1	0	0	0
16	41.8	1	1	1	1	0

Step 7: Next, we need to select an appropriate regression analysis routine. To select, click on the drop-down menu present over the top right of the rectangular box as shown and select the regression method. By default, Polymath choose "L-M" as regression method. In this case, we will also choose the same method for regression.

The screenshot shows the POLYMATH 6.10 Educational Release interface. The main window displays the same data table as in Step 6. The Regression dialog box is open, showing the model equation $\text{RATE} = k \cdot \text{PT} \cdot \text{PH}_2 / (1 + \text{KB} \cdot \text{PB} + \text{KT} \cdot \text{PT})$ entered in the "Model:" field. The regression method is set to "L-M", which is highlighted in a red circle in the original image.

	RATE	PT	PH ₂	PM	PB	C06
01	71	1	1	1	0	0
02	71.3	1	1	4	0	0
03	41.6	1	1	0	1	0
04	19.7	1	1	0	4	0
05	42	1	1	1	1	0
06	17.1	1	1	0	5	0
07	71.8	1	1	0	0	0
08	142	1	2	0	0	0
09	284	1	4	0	0	0
10	47	0.5	1	0	0	0
11	71.3	1	1	0	0	0
12	117	5	1	0	0	0
13	127	10	1	0	0	0
14	131	15	1	0	0	0
15	133	20	1	0	0	0
16	41.8	1	1	1	1	0

Step 8: Next, you need to provide initial guesses for the parameters in your model, in this case, k, KB, and KT (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 144 as initial guess for k, 1.4 as initial guess for KB, and 1.03 as initial guess for KT. To input the initial guess, select the cell corresponding to each parameter under section "Model Parameters Initial Guess" and then enter the guess value.

POLYMATH 6.10 Educational Release - [Data Table]

File Program Edit Row Column Format Analysis Examples Window Help

R018 : C004 PM

	RATE	PT	PH2	PM	PB	C06
01	71	1	1	1	0	
02	71.3	1	1	4	0	
03	41.6	1	1	0	1	
04	19.7	1	1	0	4	
05	42	1	1	1	1	
06	17.1	1	1	0	5	
07	71.8	1	1	0	0	
08	142	1	2	0	0	
09	284	1	4	0	0	
10	47	0.5	1	0	0	
11	71.3	1	1	0	0	
12	117	5	1	0	0	
13	127	10	1	0	0	
14	131	15	1	0	0	
15	133	20	1	0	0	
16	41.8	1	1	1	1	
17						
18						
19						

Regression Analysis Graph

Report Store Model

Linear & Polynomial Multiple linear Nonlinear

Model: $f(x)$ L-M

RATE=k*PT*PH2/(1+KB*PB+KT*PT)

Model Parameters Initial Guess:

Model parm	Initial guess
k	144
KB	1.4
KT	1.03

Dependent Variable RATE

Now select what you want polymath to output by checking the boxes on the upper right side of the window. The options are Graph, Residuals, Report, and Store Model. You can check multiple boxes also at the same time.

POLYMATH 6.10 Educational Release - [Data Table]

File Program Edit Row Column Format Analysis Examples Window Help

R018 : C004 PM

	RATE	PT	PH2	PM	PB	C06
01	71	1	1	1	0	
02	71.3	1	1	4	0	
03	41.6	1	1	0	1	
04	19.7	1	1	0	4	
05	42	1	1	1	1	
06	17.1	1	1	0	5	
07	71.8	1	1	0	0	
08	142	1	2	0	0	
09	284	1	4	0	0	
10	47	0.5	1	0	0	
11	71.3	1	1	0	0	
12	117	5	1	0	0	
13	127	10	1	0	0	
14	131	15	1	0	0	
15	133	20	1	0	0	
16	41.8	1	1	1	1	
17						

Regression Analysis Graph

Report Store Model


Linear & Polynomial Multiple linear Nonlinear

Model: $f(x)$ L-M

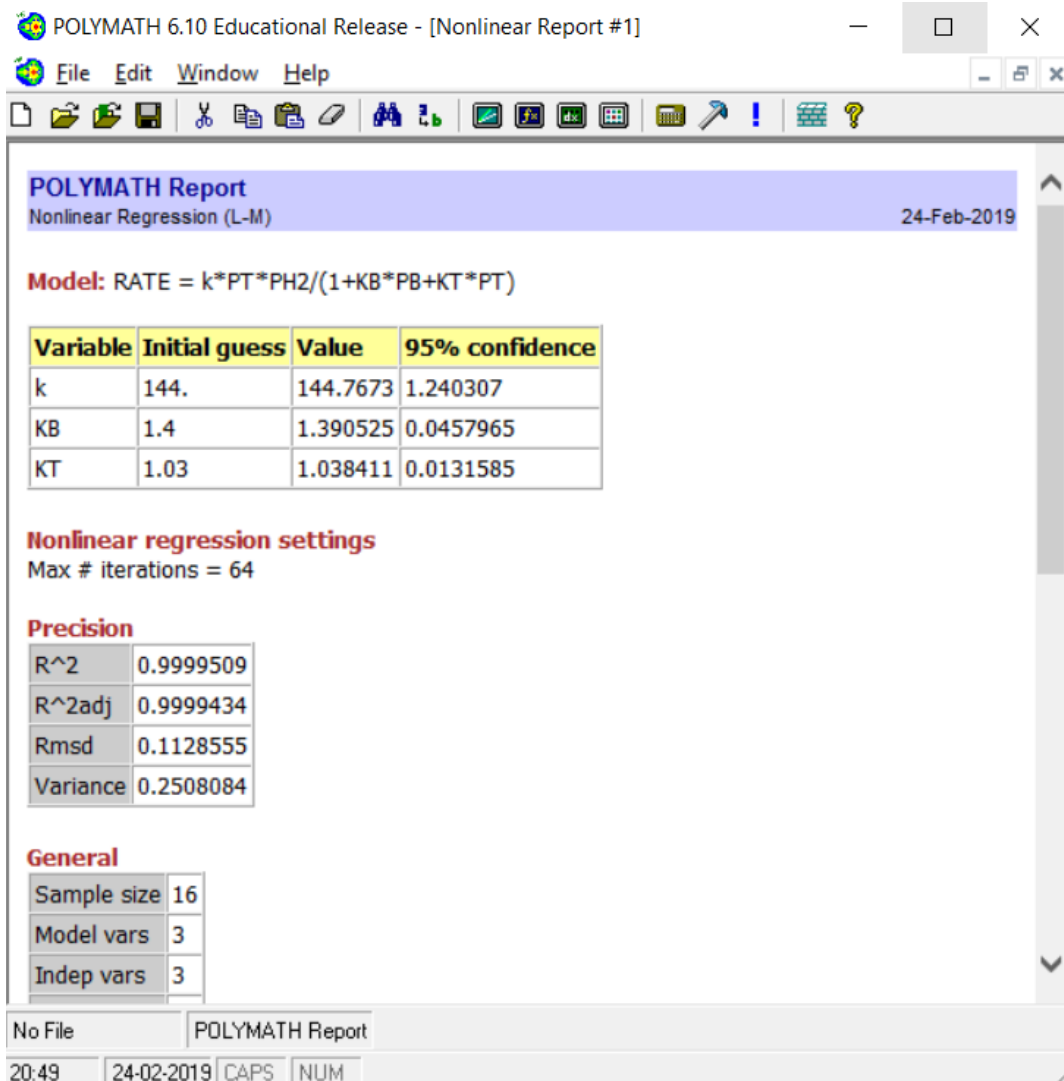
RATE=k*PT*PH2/(1+KB*PB+KT*PT)

Model Parameters Initial Guess:

Model parm	Initial guess
k	144
KB	1.4
KT	1.03

Click on the pink arrow  to have Polymath perform the regression.

Step 9: If you checked the box for "Report" you will see a screen like this that details the statistics from the regression analysis. The R² value obtained is 0.999 which indicates a very good fit



POLYMATH Report
Nonlinear Regression (L-M) 24-Feb-2019

Model: $\text{RATE} = k \cdot \text{PT} \cdot \text{PH}_2 / (1 + \text{KB} \cdot \text{PB} + \text{KT} \cdot \text{PT})$

Variable	Initial guess	Value	95% confidence
k	144.	144.7673	1.240307
KB	1.4	1.390525	0.0457965
KT	1.03	1.038411	0.0131585

Nonlinear regression settings
Max # iterations = 64

Precision

R ²	0.9999509
R ² adj	0.9999434
Rmsd	0.1128555
Variance	0.2508084

General

Sample size	16
Model vars	3
Indep vars	3

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From the above report,

k= 144.77
KB= 1.39
KT= 1.038

Step 10: If you checked the box for "Graph" you will see a screen like this that plots both experimental and model calculated values.

