

Polymath tutorial on Linear Equation Solver

Chapter 3: Rate Laws

Example 3-1 Determination of the Activation Energy

Use the data in the following table to determine A and E/R using linear equation solver

k (s⁻¹)	T (K)
0.00043	312.5
0.00103	318.47

The equation is given as

$$k = Ae^{-\frac{E}{R}\left(\frac{1}{T}\right)}$$

To find the parameter A & (E/R), we can make the above equation linear by taking logarithm on both side,

$$\ln(k) = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \quad (1)$$

So, you have 2 variables i.e. A and (E/R) and you need 2 equation to solve it

From the data table,

$$k_1 = 0.00043, T_1 = 312.5$$

$$k_2 = 0.00103, T_2 = 318.47$$

Substitute the value of k_1, T_1 in equation (1) to obtain equation (2). Substitute the value of k_2, T_2 in equation (1) to obtain equation (3)

$$\ln(0.00043) = \ln A - \frac{E}{R}\left(\frac{1}{312.5}\right) \quad (2)$$

$$\ln(0.00103) = \ln A - \frac{E}{R}\left(\frac{1}{318.47}\right) \quad (3)$$

To use Polymath Linear equation solver, you need to rearrange your equation in the form

$$a_1 x + b_1 y = \text{beta}_1$$

$$a_2 x + b_2 y = \text{beta}_2$$

Where a_1, a_2 are coefficient of variable x , b_1, b_2 are coefficient of variable y and $\text{beta}_1, \text{beta}_2$ are the constant for two equations respectively.

For your equation the variable x is $\ln A$ and variable y is E/R . Rearrange equations 2 and 3 in the Polymath format, we get

$$1 * \ln A - 0.0032 \left(\frac{E}{R}\right) = -7.75173$$

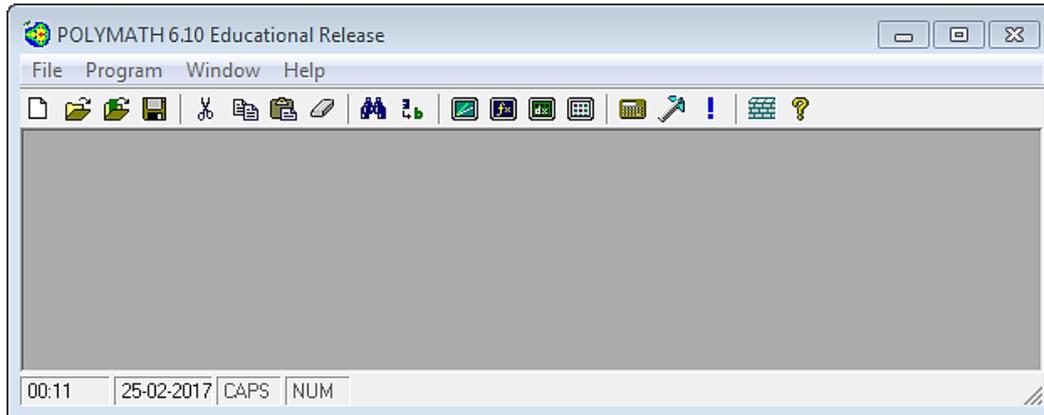
and

$$1 * \ln A - 0.00314 \left(\frac{E}{R}\right) = -6.8782$$

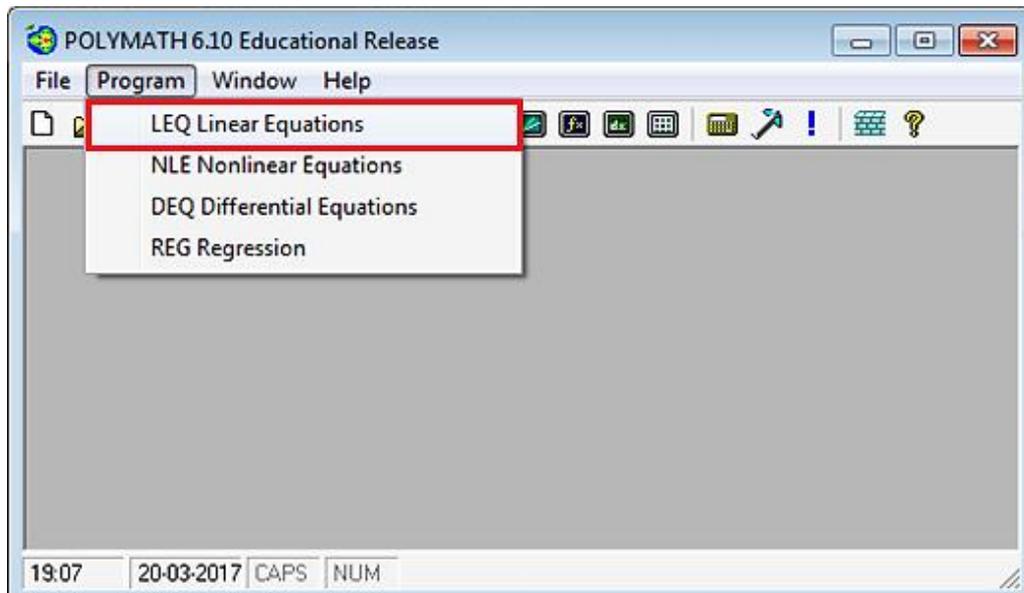
From the above 2 equation, we have

$$a_1=1, a_2 = 1, b_1 = -0.0032, b_2 = -0.00314, \beta_1 = -7.75173, \beta_2 = -6.8782$$

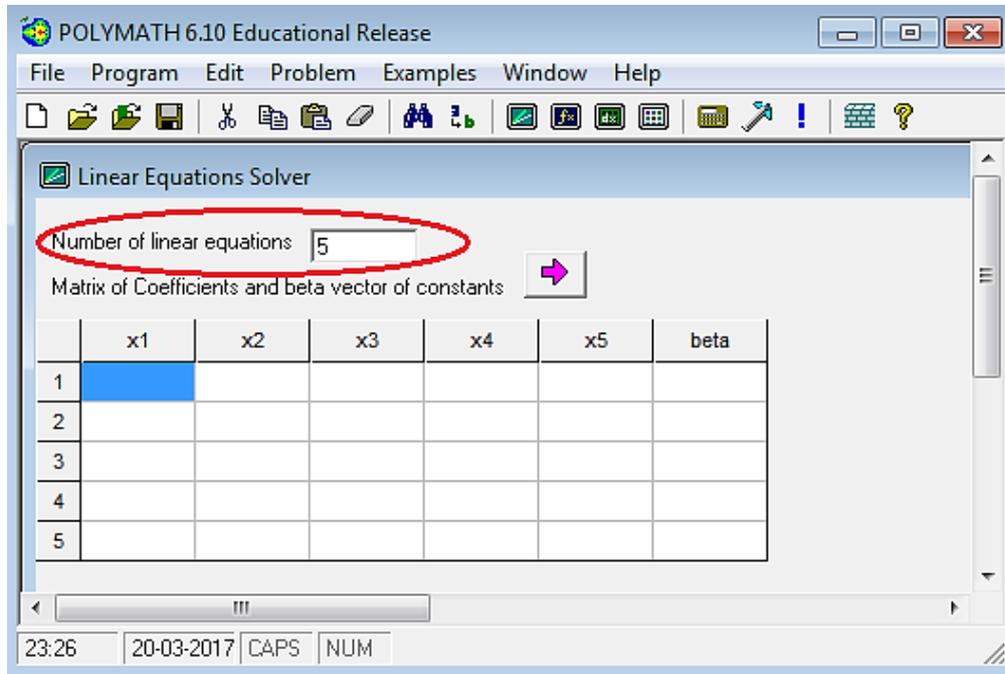
First, launch Polymath which you can download from <http://www.polymath-software.com> You will see a window that looks like this.



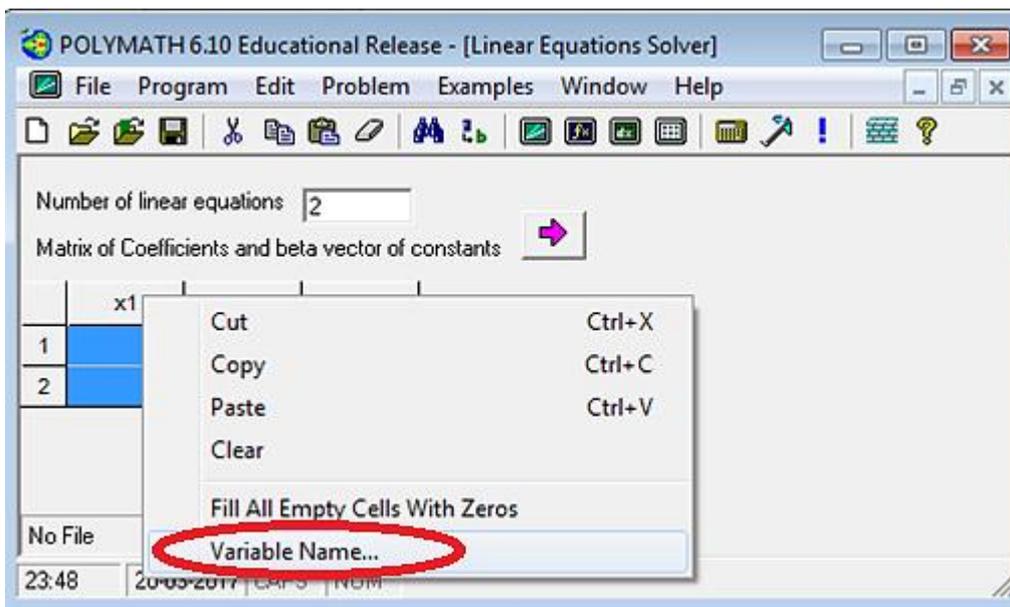
To use the linear solver in Polymath, first click on the “Program” tab present on the toolbar. This will bring up a list of options from which you need to select. In this case we need to solve linear equations so select "LEQ Linear Equations". The shortcut button () is also present on the menu bar



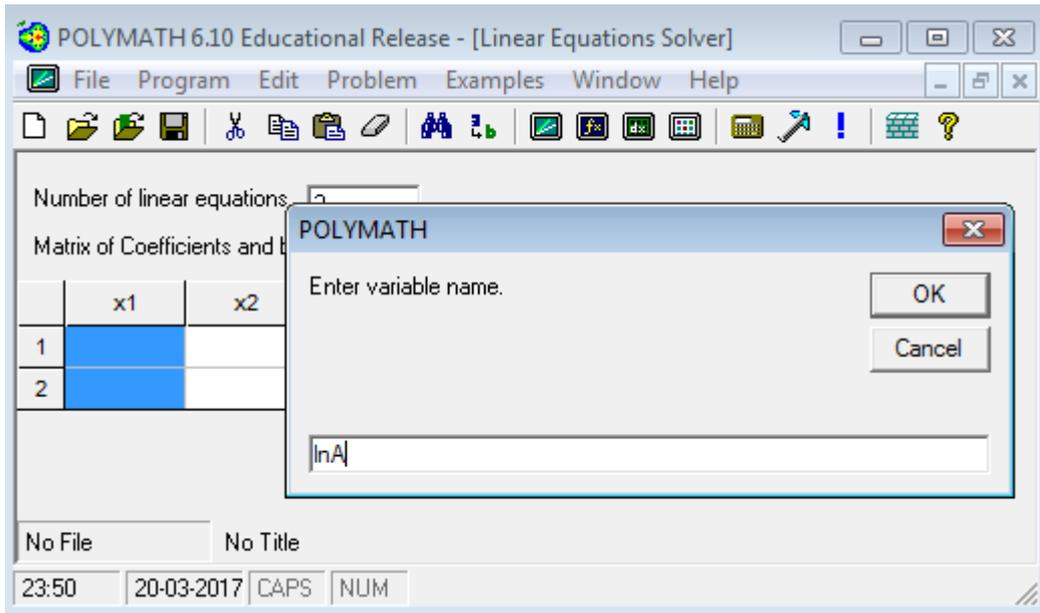
This will bring up another window, which looks like this. Each row corresponds to an equation, and each column corresponds to a variable name i.e. x1, x2, ..., x5, and beta, where “beta” is the constants in the right hand side of the equations. The number of equation must be equal to number of variable. In the current figure, there are 5 equations and 5 variable, however, in our case, there are only 2 variable and 2 equation. So, change the Number of linear equations from 5 to 2.



To change the variable name, first select the column x1, then right click and select “Variable Name...”

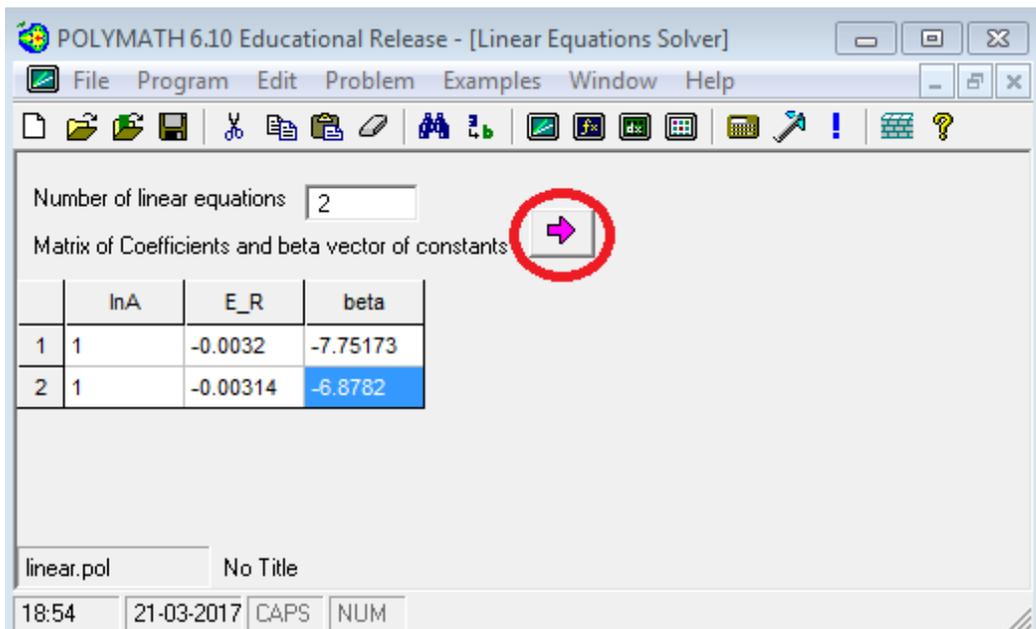


Now replace the 1st variable name from x1 to lnA and press Ok

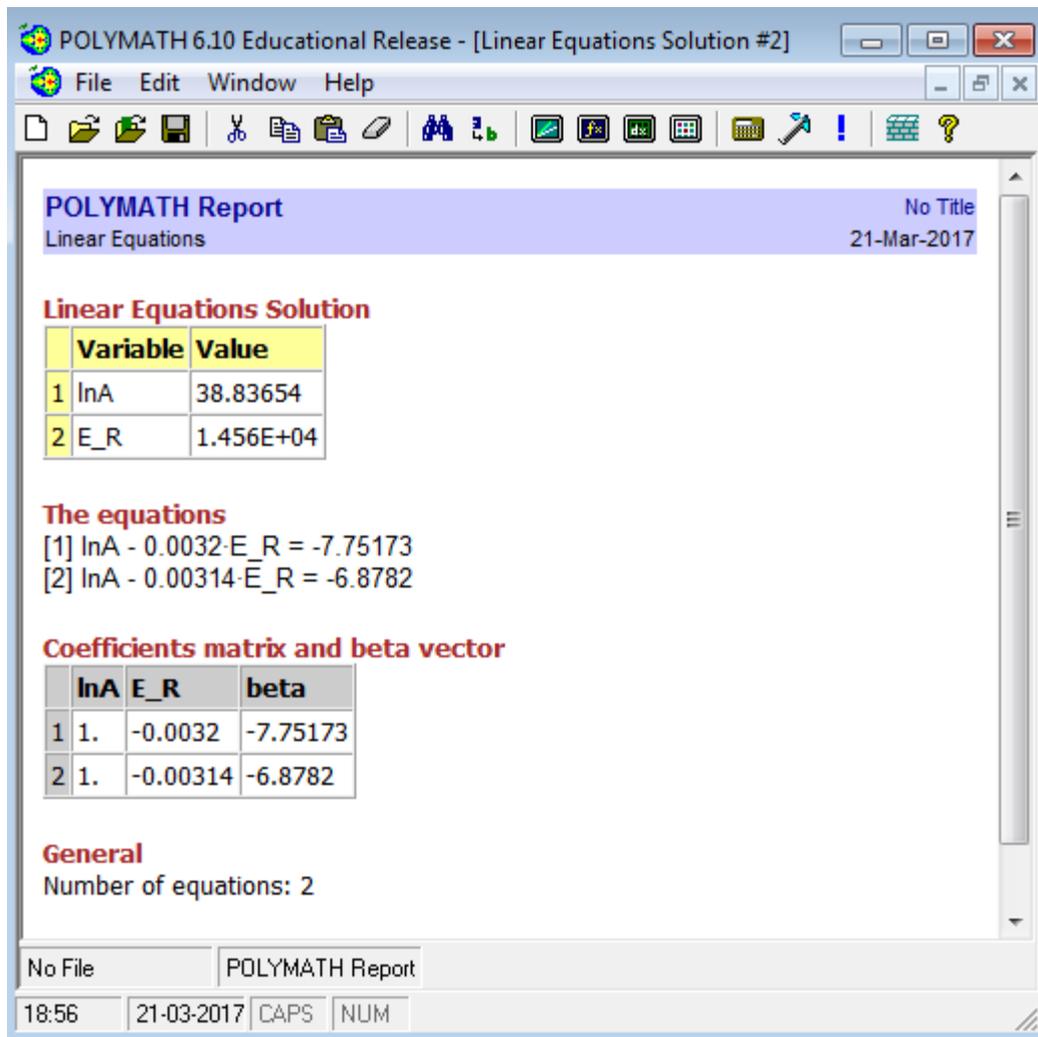


Similarly, rename second variable x2 to E_R (as E/R can't be entered). The first row under a variable name contains coefficient of that variable in 1st equation and second row contains coefficient of the same variable in the second equation.

In this case, a_1 and a_2 are coefficient of $\ln A$ with $a_1 = a_2 = 1$ in both the equation, so enter the value of a_1 in 1st row and a_2 in second row under column $\ln A$. b_1 and b_2 are coefficient of E_R with $b_1 = -0.0032$ and $b_2 = -0.00314$. Enter these values in corresponding rows under column E_R . Under column beta, enter the beta values (RHS constant) for both the equation i.e. $beta_1 = -7.75173$ and $beta_2 = -6.8782$ in respective rows. After all the values are entered, click on pink arrow  to run the program



You will find that Polymath report is generated which reports the value of $\ln A = 38.84$ and $E/R = 1.456 \text{ E}04$



Thus, $A = \exp(38.84) = 7.38 \times 10^{16}$ and $\frac{E}{R} = 1456$

Or,

$$k = 7.38 \times 10^{16} e^{\frac{-1456}{T}}$$