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,

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

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

From the data table,

$k1$ = 0.00043, $T1$ =312.5

$k2$ = 0.00103, $T2$ =318.47

Substitute the value of $k1, T1$ in equation (1) to obtain equation (2). Substitute the value of $k2$, $T2$ in equation (1) to obtain equation (3)

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

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

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

$$a1\,x + b1\,y = beta1$$

$$a2\,x + b2\,y = beta2$$

Where $a1, a2$ are coefficient of variable x, $b1, b2$ are coefficient of variable y and $beta1, beta2$ are the constant for two equations respectively.

For your equation the name of the two variable are $\ln A\ and\ E/R$. Rearrange equations 2 and 3 in the Polymath format, we get

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

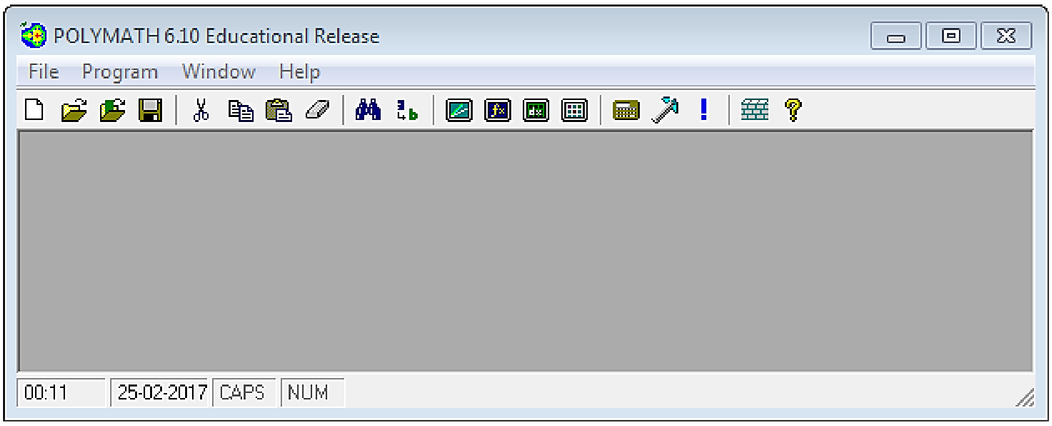
and

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

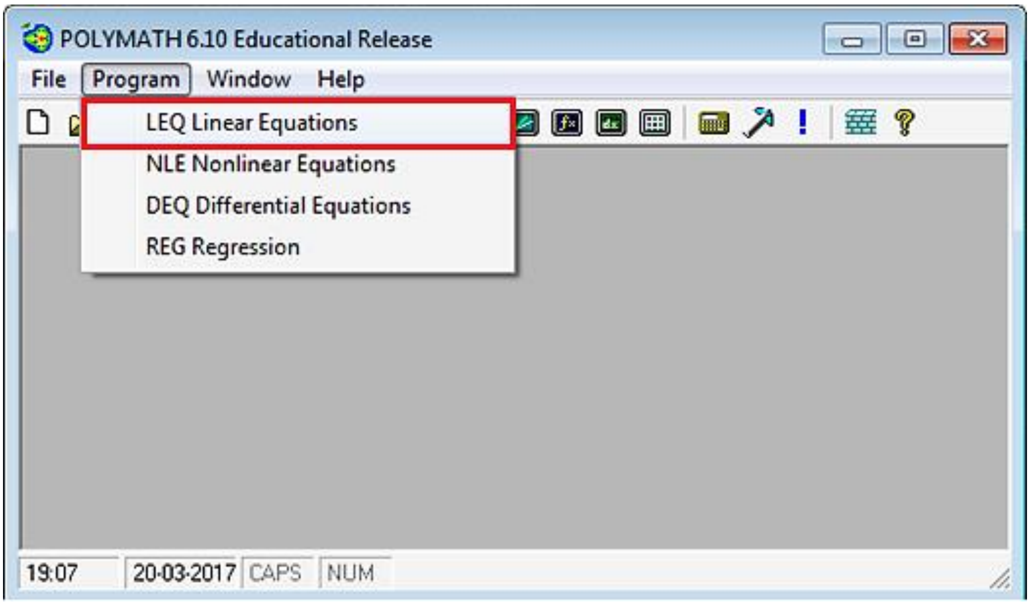
From the above 2 equation, we have
$a1$=1,$a2 = 1, b1 = -0.0032, b2 = -0.00314, beta1 = -7.75173, beta2 = -6.8782$

Step 1: Open the polymath software. If you don't have it, then refer to the installation instruction available at http://www.umich.edu/~elements/5e/software/polymath.html

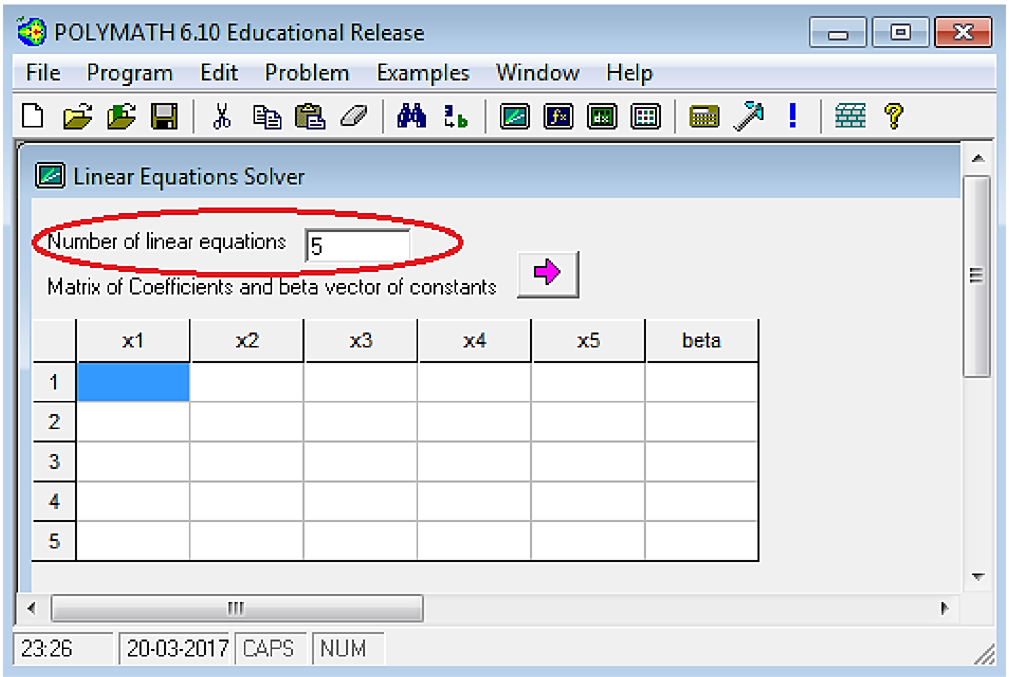
You will see the following window when you open the polymath



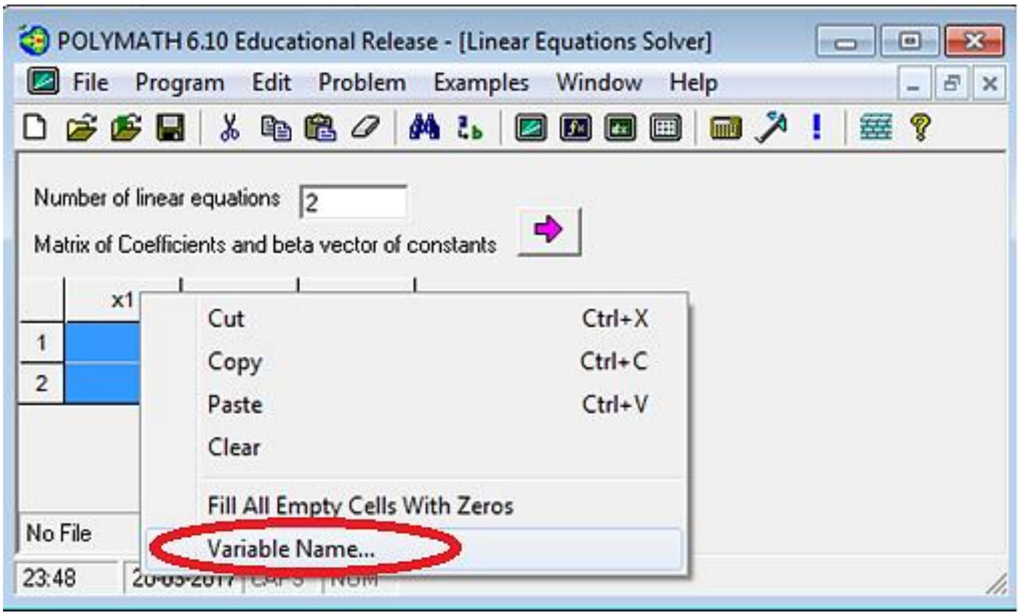
Step 2: To use the linear solver in Polymath, first click on the "Program" tab present on the toolbar. This will bring up a list of options from which you need to select. In this case we need to solve linear equations so select "LEQ Linear Equations". The shortcut button () is also present on the menu bar



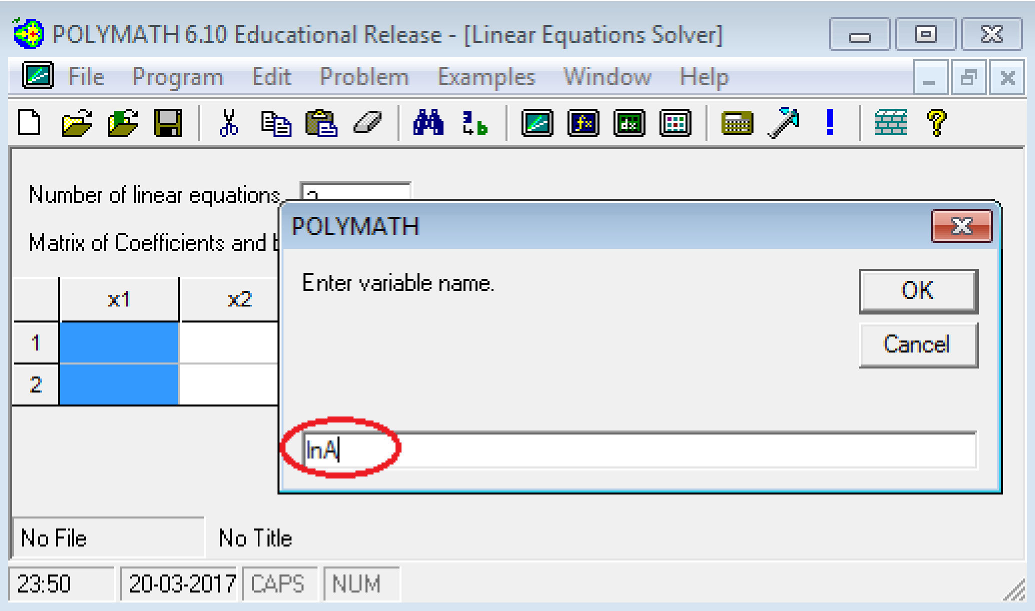
Step 3: This will bring up another window, which looks like this. Each row corresponds to an equation, and each column corresponds to a variable name i.e. x1, x2, ..., x5, and beta, where "beta" is the constants in the right hand side of the equations. The number of equation must be equal to number of 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.



Step 4: To change the variable name, first select the column x1, then right click and select "Variable Name…"

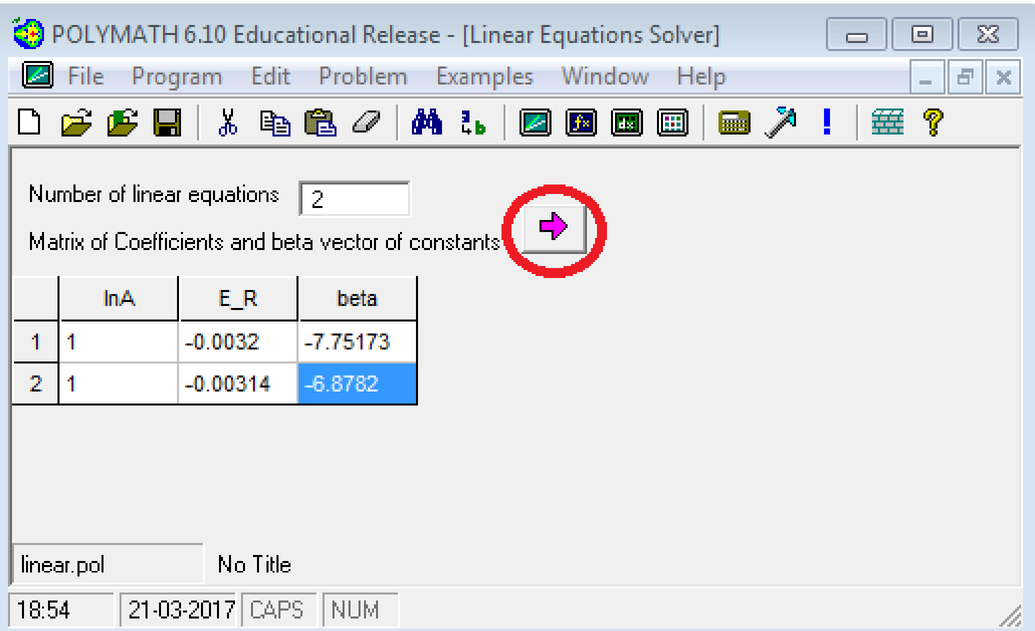


Step 5: Now replace the 1st variable name from x1 to lnA and press Ok

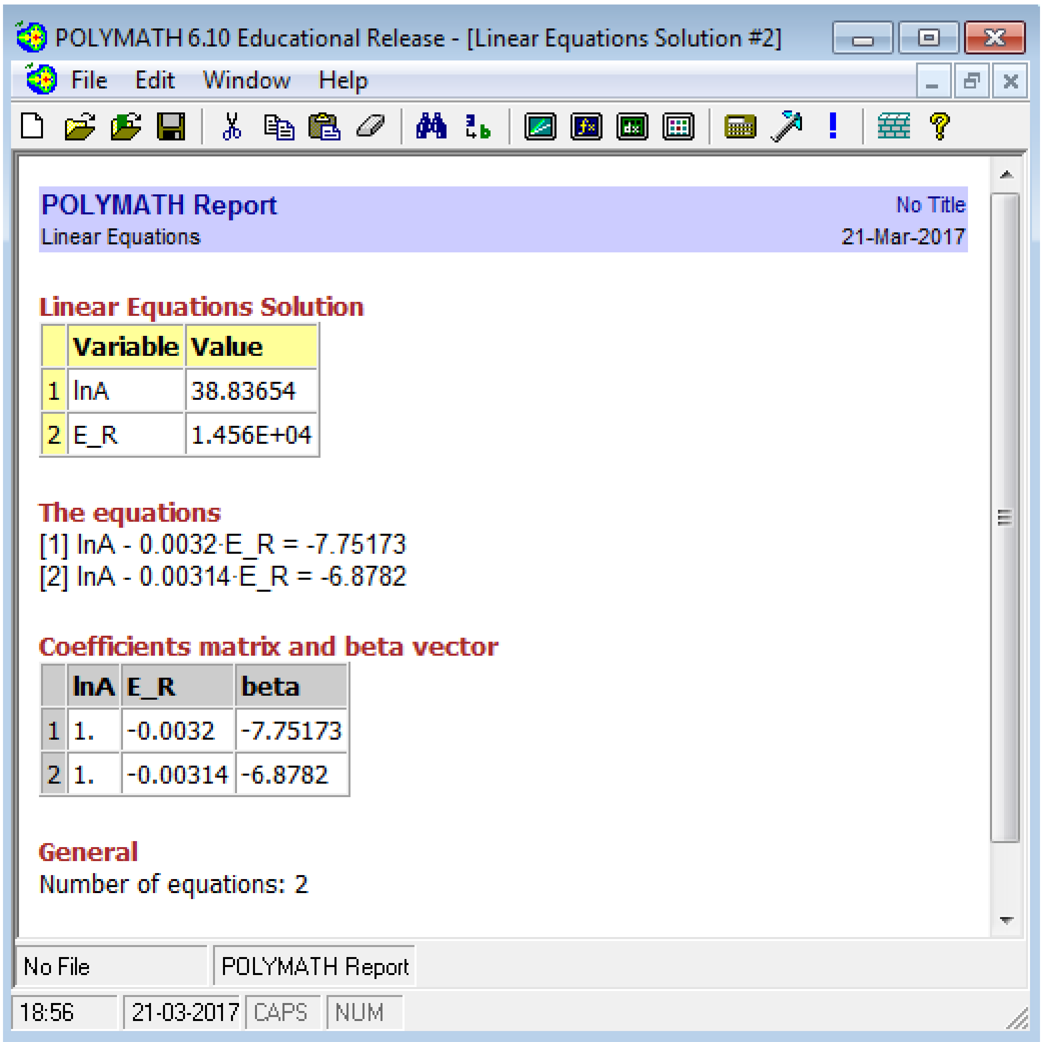


Step 6: Similarly, rename second variable x2 to E_R (as E/R can't be entered). The first row under a variable name contains coefficient of that variable in 1st equation and second row contains coefficient of the same variable in the second equation.

In this case, $a1$ *and* $a2$ are coefficient of $\ln A$ with $a1 = a2 = 1$ in both the equation, so enter the value of a1 in 1st row and a2 in second row under column $\ln A$. $b1$ *and* $b2$ are coefficient of E_R with $b1 = -0.0032$ *and* $b2 = -0.00314$. 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. $beta1 = -7.75173$ *and* $beta2 = -6.8782$ in respective rows. After all the values are entered, click on pink arrow  to run the program



Step 7: You will find that Polymath report is generated which reports the value of ln A= 38.84 and E/R = 1.456 E04



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

Or,

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

Step 8: Now redo **Steps 1 to 7** using the following values of k and T to determine the parameters A and E

k (s^{-1})	T (K)
0.00355	328
0.00717	333