Getting started with Simulis® Thermodynamics

Use Case 8: Fitting binary interaction parameters from experimental data in Excel

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Introduction

Some thermodynamic models require binary interaction parameters (BIPs) to correctly predict fluid phase equilibria.

Unfortunately, these BIPs are not always available in the software database or in the literature.

The present document shows how to estimate the BIPs of an Ethanol – Ethyl Acetate mixture, from a small set of experimental data (provided in the attached Excel file), using Simulis Thermodynamics in Excel.

It is to be noted that the accuracy and reliability of the estimated values strongly depend on the set of experimental data. They should be used for the temperature range in which the experimental data were retrieved. Outside this range the predictive capabilities of the model is not guaranteed. Larger are the temperature and pressure ranges, better it is.

To perform this example, it is necessary to have access to the "software component" version of Simulis Thermodynamics, and use it through Excel.
Before studying this case, it is recommended to consult "Getting Started with Simulis Thermodynamic, Case 1" that explains how to insert a Simulis object in Excel, select components and define a thermodynamic system.

Step 1: Create the spreadsheet

- In Excel, create the spreadsheet with the experimental data corresponding to the liquid and vapor phase compositions of the mixture at the thermodynamic equilibrium.

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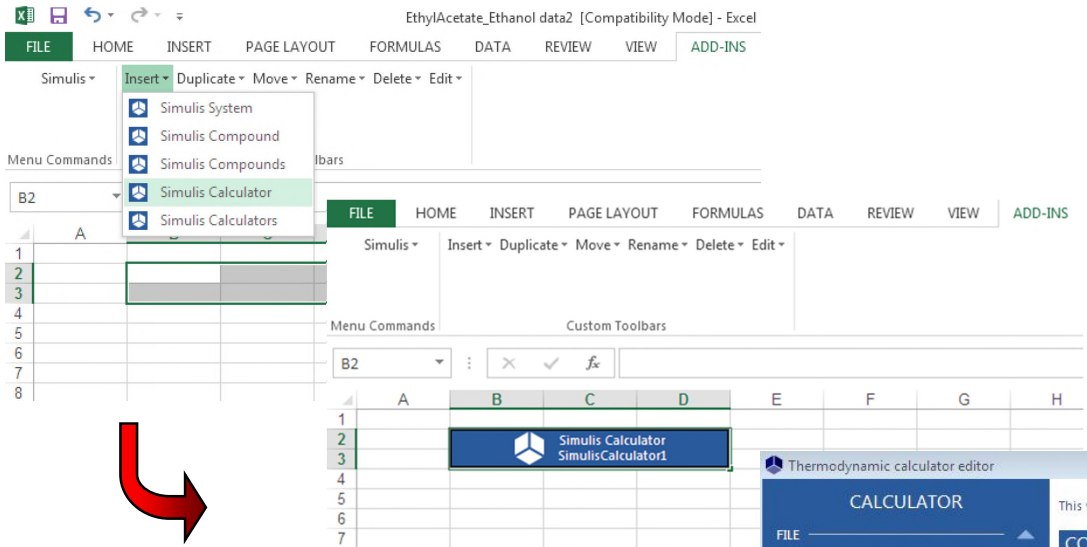
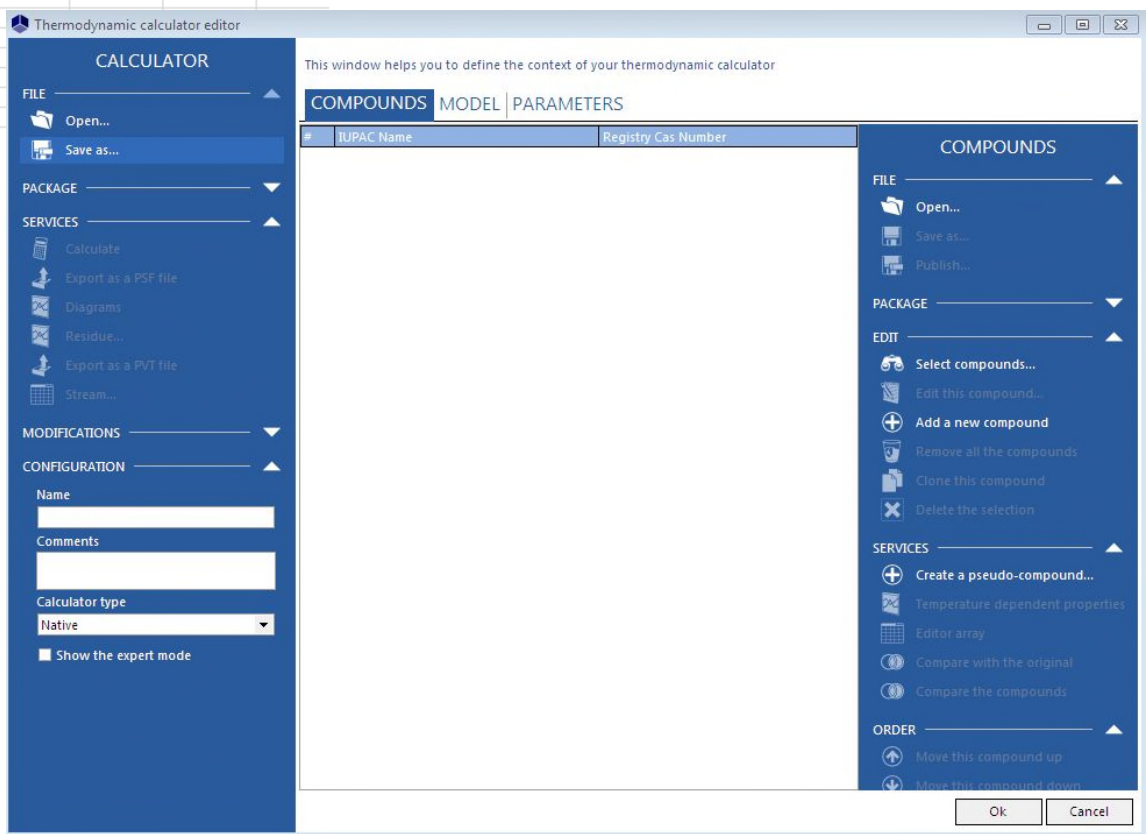
	Experimental data			
Reference	F. Mato *et al.*, *An. Quim. Ser. A*, 1984, Vol. 80, p. 338			
P	760 mmHg			
T	Liquid phase fraction (x)		Vapor phase fraction (y)	
°C	ETHYL ACETATE	ETHANOL	ETHYL ACETATE	ETHANOL
78.30	0.0000	1.0000	0.0000	1.0000
78.30	0.0130	0.9870	0.0300	0.9700
78.00	0.0220	0.9780	0.0500	0.9500
77.80	0.0300	0.9700	0.0660	0.9340
76.70	0.0710	0.9290	0.1340	0.8660
76.10	0.0950	0.9050	0.1760	0.8240
76.00	0.0970	0.9030	0.1750	0.8250
75.20	0.1350	0.8650	0.2300	0.7700
75.10	0.1360	0.8640	0.2320	0.7680
74.40	0.1500	0.8500	0.2490	0.7510
73.40	0.2570	0.7430	0.3510	0.6490
72.70	0.3310	0.6690	0.4100	0.5900
72.80	0.3320	0.6680	0.4040	0.5960
72.60	0.3600	0.6400	0.4220	0.5780
72.20	0.4620	0.5380	0.4950	0.5050
72.10	0.5450	0.4550	0.5450	0.4550
72.20	0.6280	0.3720	0.5920	0.4080
72.40	0.6810	0.3190	0.6350	0.3650
72.70	0.7740	0.2260	0.6810	0.3190
73.40	0.8270	0.1730	0.7280	0.2720
73.60	0.8320	0.1680	0.7630	0.2370
74.40	0.8900	0.1100	0.8380	0.1620
74.60	0.9170	0.0830	0.8650	0.1350
75.30	0.9360	0.0640	0.9000	0.1000
77.10	1.0000	0.0000	1.0000	0.0000

The data set can be either at constant temperature (isotherm) or constant pressure (isobar). Here we are at constant pressure, however the temperature varies only by 1,20 °C which is hardly sufficient to estimate the temperature dependent parameters. It is possible but it is highly recommended to re-run the estimation with additional sets of data.

Step 2: Insert a Simulis Thermodynamics calculator and configure the thermodynamic profile

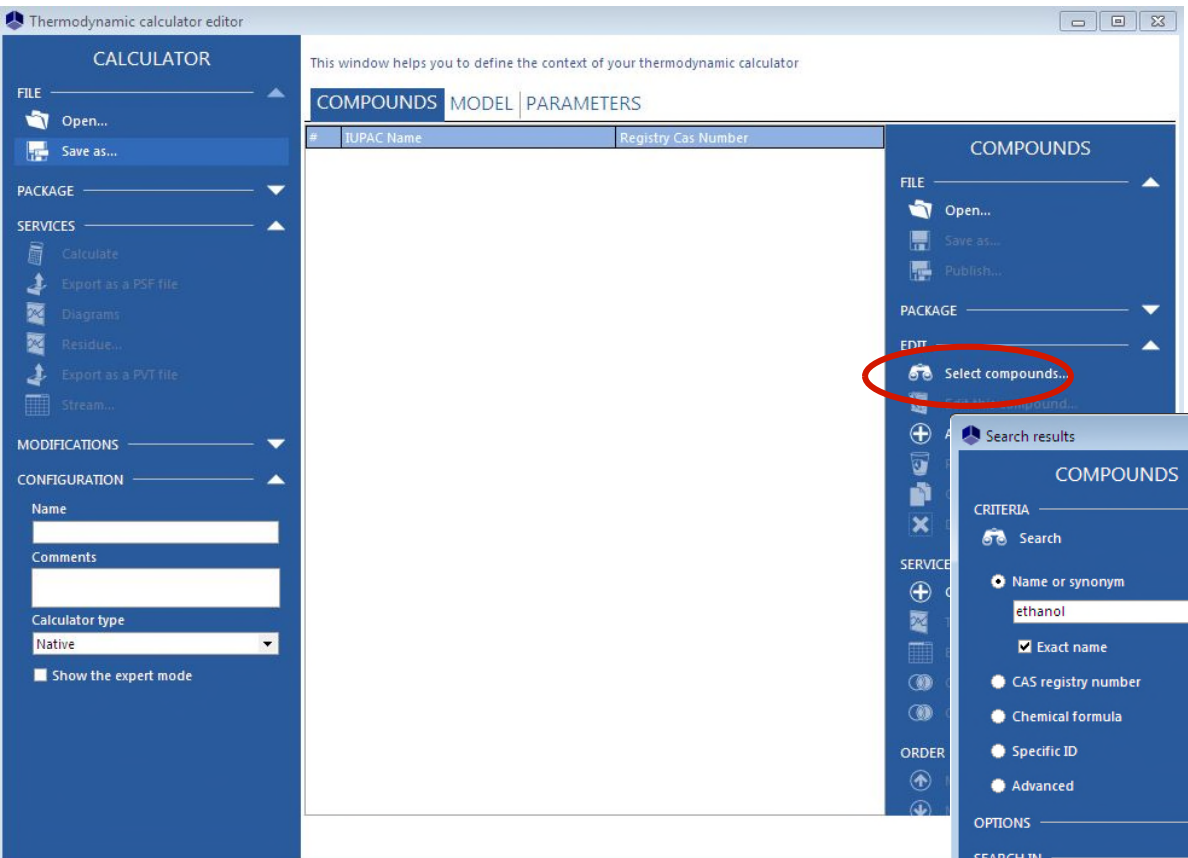


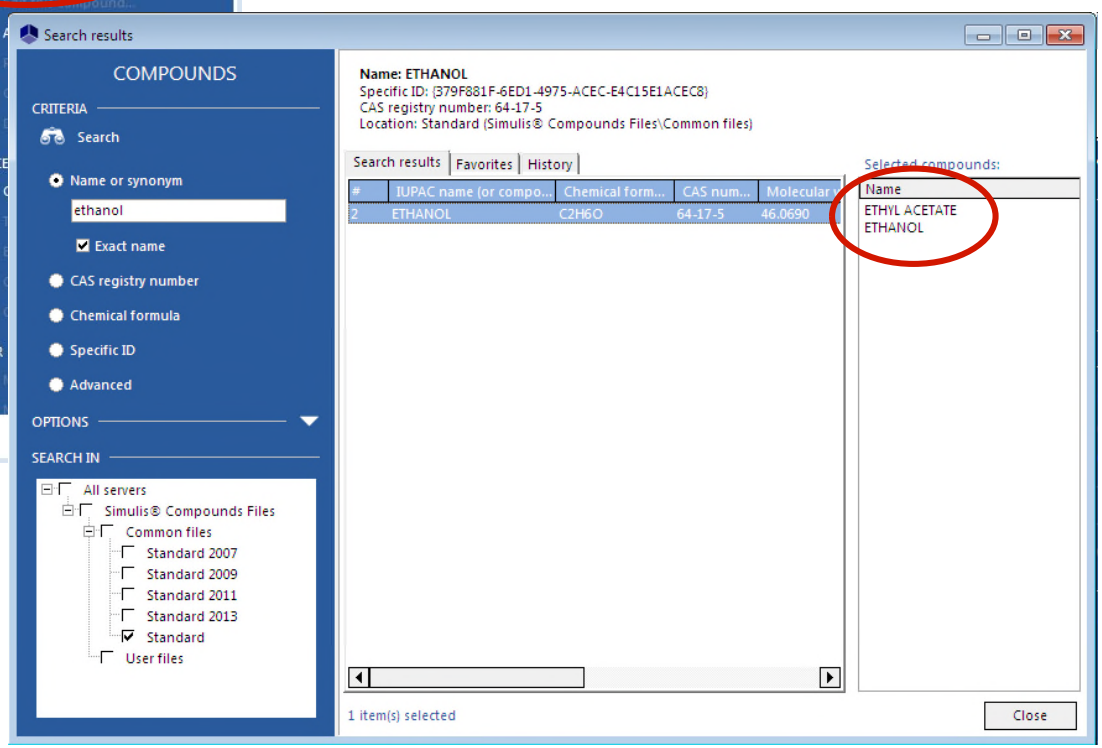


Refer to "*Getting Started with Simulis Thermodynamic, use case 1*" for details on these operations.

Step 2: Insert a Simulis Thermodynamics calculator and define the thermodynamics

Select the components: Ethyl-Acetate and Ethanol

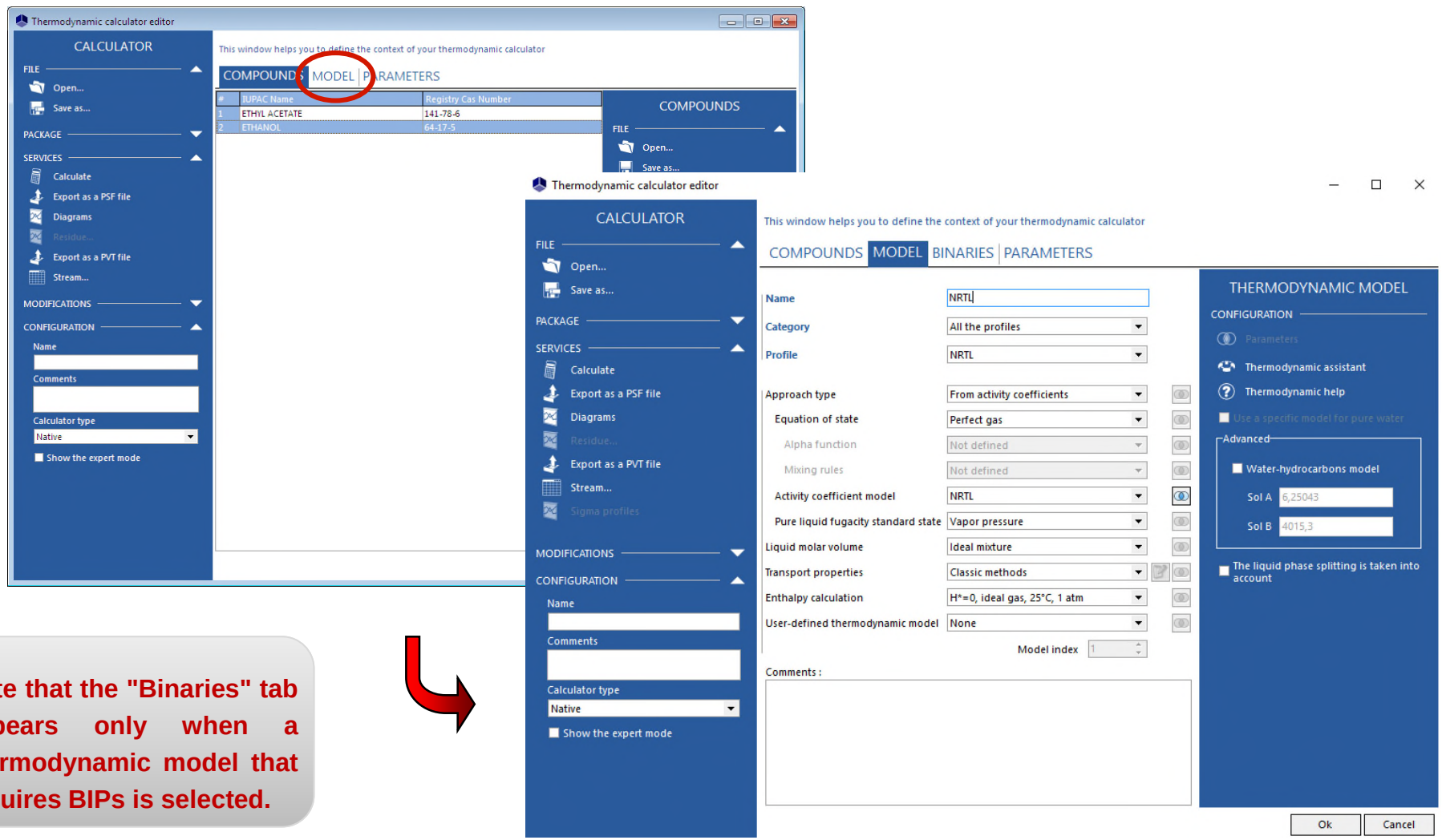




Refer to "*Getting Started with Simulis Thermodynamic, use case 1*" for details on these operations.

Step 2: Insert a Simulis Thermodynamics calculator and define the thermodynamics

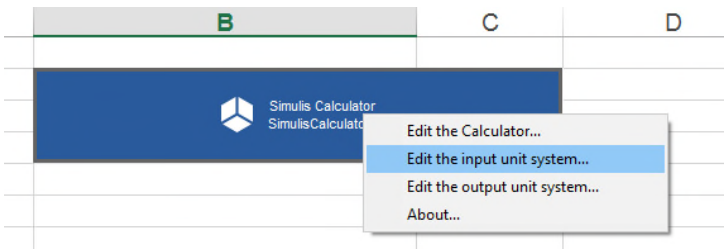
Select the thermodynamic model: NRTL



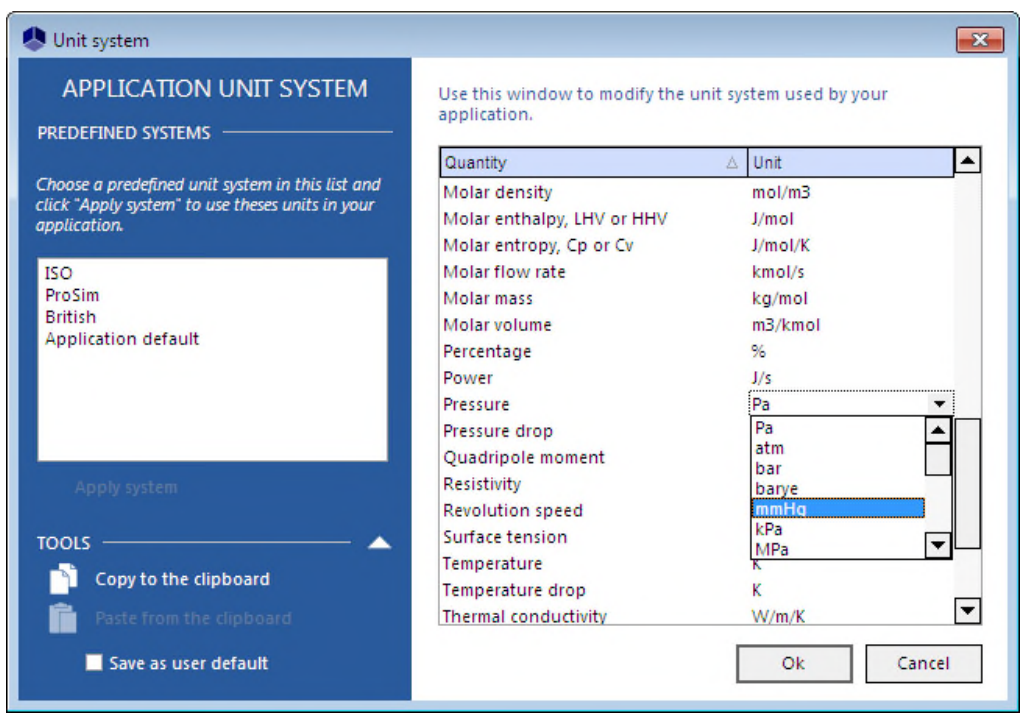
Note that the "Binaries" tab appears only when a thermodynamic model that requires BIPs is selected.

Step 3: Change the unit system

- The default unit system is in Pa and K. Our data are provided in mmHg and °C, therefore we need to adapt the unit system to avoid any conversion calculation.



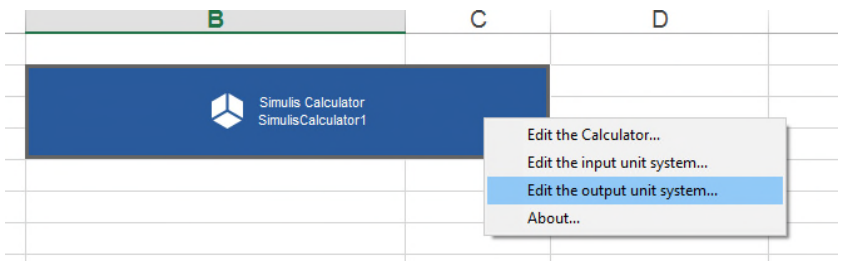
Right-click on the Calculator and select *"Edit the input unit system…".*



The unit system window opens. Scroll down to find "*Pressure*", then select "*Pa*" and change it to "*mmHg*". Repeat the operation for the temperature, then press "*OK*".

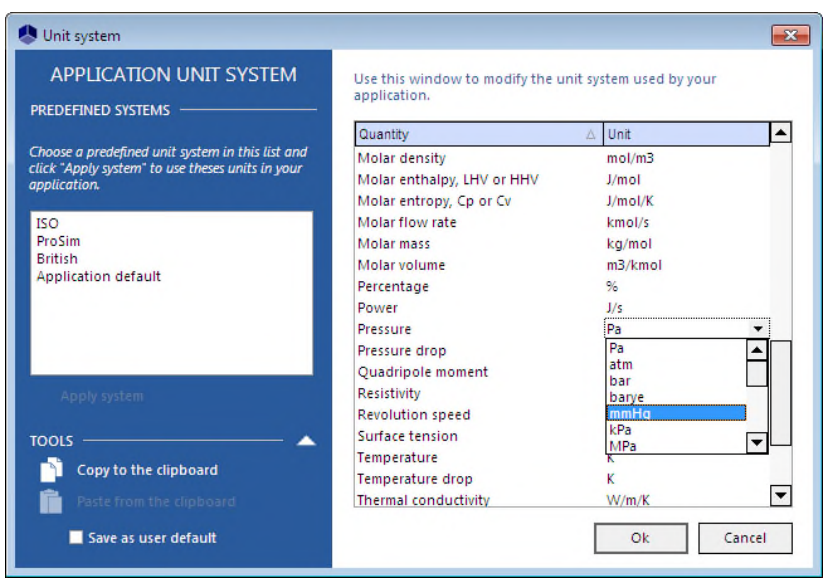
Step 3: Change the unit system

- Repeat the operation for the output unit system.



Right click on the Calculator and select *"Edit the output unit system…".*

If no change is made, the output results of the calculation will be provided in the default unit system.



The unit system window opens. Scroll down to find "*Pressure*", then select "*Pa*" and change it to "*mmHg*". Repeat the operation for the temperature, then press "*OK*".

Step 4: Create a table for binary interaction parameters initialization and results

- This table enables to provide the initialization values for the BIP.
- The NRTL model requires 6 parameters (Cij0, Cji0, aij0, Cij(T), Cji(T), aij(T)). Other models may need more or less parameters. You can check the calculator's “binaries” tab to know the exact number of parameters that are required.

ulis Calculator
ulisCalculator1

Compounds		Binary interaction parameters					
1	2	Cij0	Cji0	aij0	CijT	CjiT	aijT
ETHYL ACETATE	ETHANOL	0	0	0.2	0	0	0

Experimental data				
Reference	F. Mato *et al.*, *An. Quim. Ser. A*, 1984, Vol. 80, p. 338			
P	760	mmHg		
T	Liquid phase fraction (x)		Vapor phase fraction (y)	
°C	ETHYL ACETATE	ETHANOL	ETHYL ACETATE	ETHANOL
78.30	0.0000	1.0000	0.0000	1.0000
78.30	0.0130	0.9870	0.0300	0.9700
78.00	0.0220	0.9780	0.0500	0.9500
77.80	0.0300	0.9700	0.0660	0.9340
76.70	0.0710	0.9290	0.1340	0.8660
76.10	0.0950	0.9050	0.1760	0.8240
76.00	0.0970	0.9030	0.1750	0.8250
75.20	0.1350	0.8650	0.2300	0.7700
75.10	0.1360	0.8640	0.2320	0.7680
74.40	0.1500	0.8500	0.2490	0.7510

1 and 2 correspond to the respective positions of the components in the calculator.

All parameters are set to 0 except a_{ij}^{0} which is generally set to 0.2 for vapor-liquid equilibrium (current case) and 0.3 for liquid phase splitting.

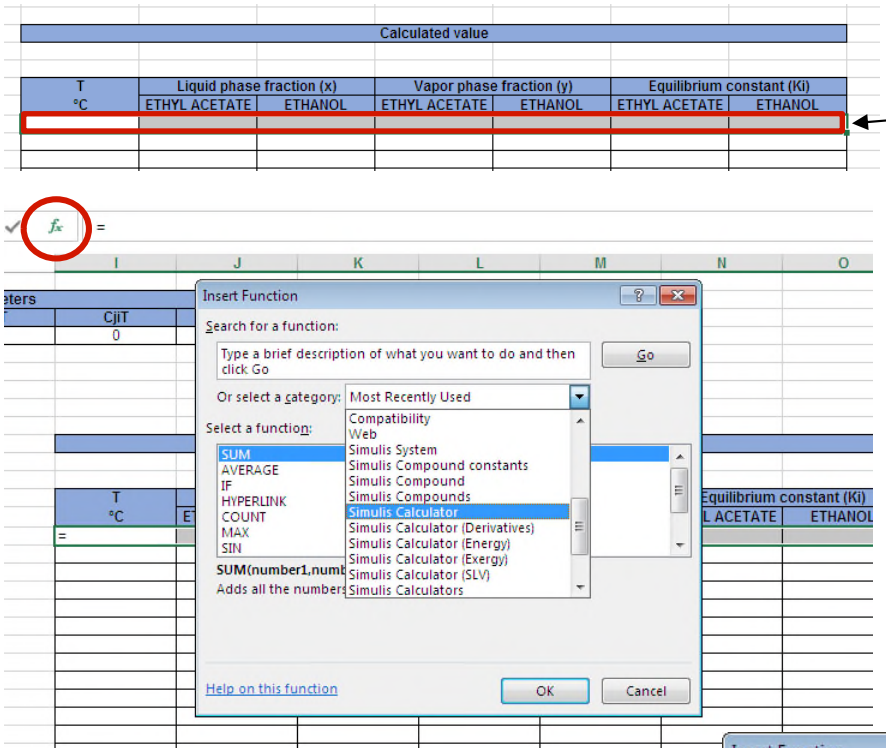
Step 5: Calculate the composition values for the liquid and vapor phases

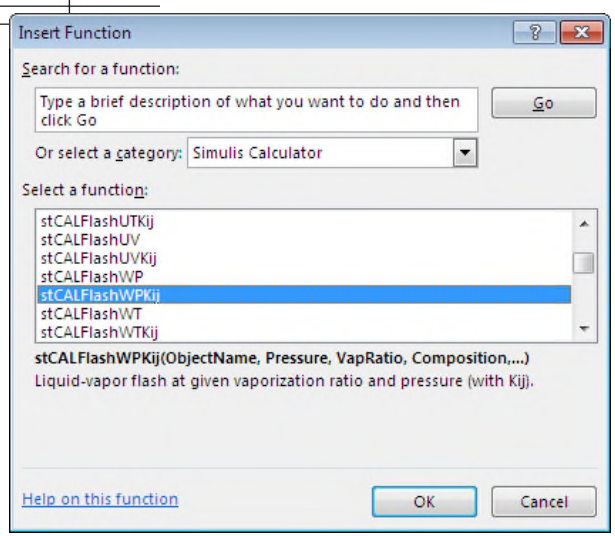
- Set up another table that will show the equilibrium calculation results (temperature, liquid and vapor phase fraction and equilibrium constants).

Binary interaction parameters			
aij0	CijT	CjiT	aijT
0.2	0	0	0

		Calculated value						
e fraction (y)		T	Liquid phase fraction (x)		Vapor phase fraction (y)		Equilibrium constant (Ki)	
ETHANOL		°C	ETHYL ACETATE	ETHANOL	ETHYL ACETATE	ETHANOL	ETHYL ACETATE	ETHANOL
1.0000								
0.9700								
0.9500								
0.9340								
0.8660								
0.8240								
0.8250								
0.7700								
0.7680								
0.7510								
0.6490								
0.5900								
0.5960								
0.5780								
0.5050								
0.4550								
0.4080								
0.3650								
0.3190								
0.2720								
0.2370								
0.1620								
0.1350								
0.1000								
0.0000								

Step 5: Calculate the composition values for the liquid and vapor phases

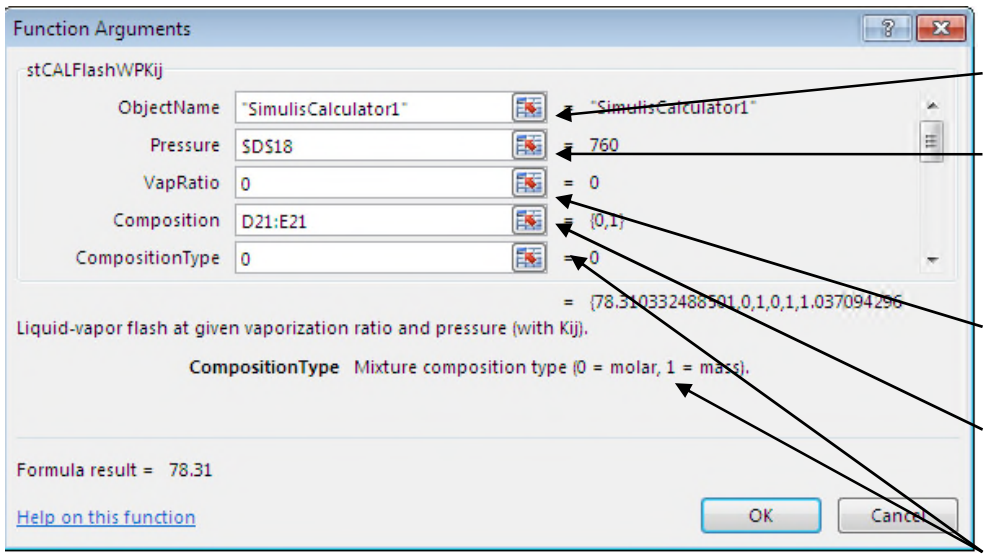


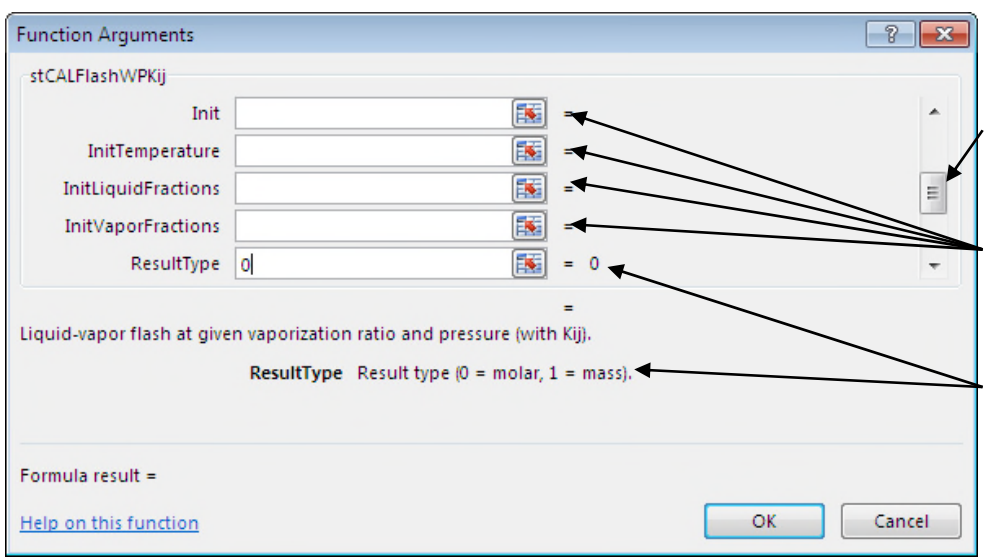


Insert the Simulis calculator function:

1. **Select the first line of the table and click on the MS-Excel insert function button.**
2. **In the "*Insert function*" window category list, select Simulis Calculator.**
3. **In the list of function, select "*stCALFlashWPKij*" which calculates the temperature, liquid and vapor phase fractions and equilibrium constants at given pressure and vapor ratio.**
4. **Set the function arguments (see next page)**

Step 5: Calculate the composition values for the liquid and vapor phases





Enter the name of the calculator.

Select the cell in which the pressure is defined. Insert the "$" sign to keep the selection constant when expanding the function through the table.

Vapor ratio is set to 0 as we will vary the liquid composition (next cell).

Select the cells in which the liquid composition is defined.

Set the composition type to 0 as the composition is molar.

Scroll down to get other arguments of the function…

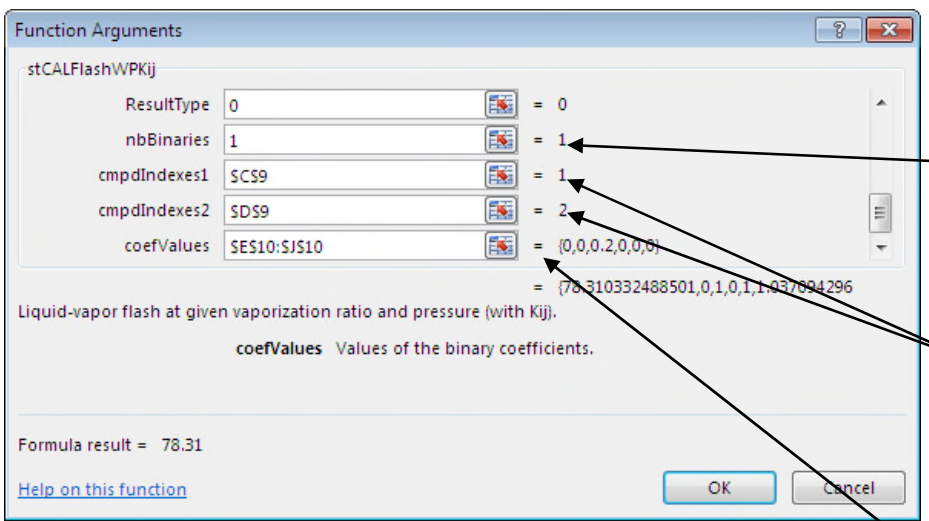
There is no initialization therefore "Init" fields remain blank

Results type is set to 0 as we have molar experimental data

Scroll down to configure the other arguments of the function (see next page)…

Step 5: Calculate the composition values for the liquid and vapor phases

Compounds		Binary interaction parameters					
1	2	Cij0	Cij0	aij0	CijT	CijT	aijT
ETHYL ACETATE	ETHANOL	0	0	0,2	0	0	0



Set the Binaries number to 1 as we calculate only one binary.

These fields define the position of the first and the second component in the Calculator (1 and 2). Insert the "$" sign to keep the selection constant.

This field defines the cells in which the coefficients will be shown. Select the BIP value fields. Insert the "$" sign to keep the selection constant.

When completed, press "*CRTL + SHIFT + ENTER*" to insert the functions in all the selected cells. If you press "*OK*", only the first cell will be configured correctly.

Step 5: Calculate the composition values for the liquid and vapor phases

Calculated value						
T	Liquid phase fraction (x)		Vapor phase fraction (y)		Equilibrium constant (Ki)	
°C	ETHYL ACETATE	ETHANOL	ETHYL ACETATE	ETHANOL	ETHYL ACETATE	ETHANOL
78,31	0,0000	1,0000	0,0000	1,0000	1,0371	1,0000

Select the first line and expand it vertically through the table (or copy-paste it in other lines)

Calculated value						
T	Liquid phase fraction (x)		Vapor phase fraction (y)		Equilibrium constant (Ki)	
°C	ETHYL ACETATE	ETHANOL	ETHYL ACETATE	ETHANOL	ETHYL ACETATE	ETHANOL
78.31	0.0000	1.0000	0.0000	1.0000	1.0371	1.0000
78.30	0.0130	0.9870	0.0135	0.9865	1.0367	0.9995
78.29	0.0220	0.9780	0.0228	0.9772	1.0364	0.9992
78.28	0.0300	0.9700	0.0311	0.9689	1.0361	0.9989
78.24	0.0710	0.9290	0.0735	0.9265	1.0348	0.9973
78.22	0.0950	0.9050	0.0982	0.9018	1.0340	0.9964
78.22	0.0970	0.9030	0.1003	0.8997	1.0339	0.9964
78.18	0.1350	0.8650	0.1394	0.8606	1.0327	0.9949
78.18	0.1360	0.8640	0.1404	0.8596	1.0327	0.9949
78.17	0.1500	0.8500	0.1548	0.8452	1.0322	0.9943
78.06	0.2570	0.7430	0.2643	0.7357	1.0286	0.9901
77.98	0.3310	0.6690	0.3396	0.6604	1.0260	0.9871
77.98	0.3320	0.6680	0.3406	0.6594	1.0260	0.9871
77.95	0.3600	0.6400	0.3690	0.6310	1.0250	0.9860
77.84	0.4620	0.5380	0.4718	0.5282	1.0213	0.9817
77.75	0.5450	0.4550	0.5549	0.4451	1.0182	0.9782
77.66	0.6280	0.3720	0.6375	0.3625	1.0151	0.9745
77.60	0.6810	0.3190	0.6899	0.3101	1.0130	0.9722
77.49	0.7740	0.2260	0.7812	0.2188	1.0094	0.9679
77.42	0.8270	0.1730	0.8330	0.1670	1.0072	0.9655
77.41	0.8320	0.1680	0.8378	0.1622	1.0070	0.9653
77.34	0.8900	0.1100	0.8941	0.1059	1.0046	0.9625
77.31	0.9170	0.0830	0.9202	0.0798	1.0035	0.9612
77.28	0.9360	0.0640	0.9385	0.0615	1.0027	0.9603
77.20	1.0000	0.0000	1.0000	0.0000	1.0000	0.9572

Step 6: Calculate experimental data versus calculated data deviation

- **Create a third table which will show the difference between the experimental data and the calculated data of temperature and vapor fraction for each component. The function is:**

  absolute value of (experimental value – calculated value) / experimental value

Deviation		
On T	On y_1	On y_2
0.00013196		0
2.48008E-05	0.550773122	0.01703422
0.003711947	0.543989321	0.028631017
0.006194515	0.52903184	0.037383406
0.02011339	0.451711093	0.06989525
0.027851503	0.441868313	0.09437964
0.029178401	0.426898162	0.090554156
0.03963369	0.393855982	0.117645293
0.041004942	0.394649607	0.119217069
0.050614066	0.378198817	0.125394814
0.063464989	0.246893493	0.133527914
0.072654147	0.171703299	0.119319241
0.071166377	0.156891196	0.106349066
0.073712646	0.125624233	0.091718731
0.078148245	0.04679454	0.045867915
0.078373899	0.018222931	0.021827467
0.075578095	0.076806704	0.111445022
0.071759223	0.086415753	0.150339734
0.065819614	0.147200598	0.314243284
0.054778175	0.144191076	0.385923173
0.051828634	0.098083752	0.315771742
0.039552805	0.066974037	0.346445945
0.036311044	0.063837286	0.409031501
0.026357877	0.042823267	0.385409407
0.00133061	0	

y_1 is the vapor fraction of Ethyl Acetate, y_2 is the vapor fraction of Ethanol.

In each cell, enter the formula defined above. For the first cell, it will be "=*ABS(F21-L21)/F21*". F21 and L21 define respectively the cells with experimental and calculated values for one temperature (see purple arrows below). Insert corresponding functions for y_1 and y_2 (see red arrows below).

Experimental data						Calculated value							Deviation		
Reference	F. Mato *et al.*, *An. Quim. Ser. A*, 1984, Vol. 80, p. 238														
P	760 mmHg														
T	Liquid phase fraction (x)		Vapor phase fraction (y)			T	Liquid phase fraction (x)		Vapor phase fraction (y)		Equilibrium constant (Ki)		On T	On y_1	On y_2
°C	ETHYL ACETATE	ETHANOL	ETHYL ACETATE	ETHANOL		°C	ETHYL ACETATE	ETHANOL	ETHYL ACETATE	ETHANOL	ETHYL ACETATE	ETHANOL			
78,30	0,0000	1,0000	0,0000	1,0000		78,31	0,0000	1,0000	0,0000	1,0000	1,0371	1,0000	0,0001319		0
78,30	0,0130	0,9870	0,0300	0,9700		78,30	0,0130	0,9870	0,0135	0,9865	1,0367	0,9995	2,48008E-05	0,550773122	0,01703422
78,00	0,0220	0,9780	0,0500	0,9500		78,29	0,0220	0,9780	0,0228	0,9772	1,0364	0,9992	0,003711947	0,543989321	0,028631017
77,80	0,0300	0,9700	0,0660	0,9340		78,28	0,0300	0,9700	0,0311	0,9689	1,0361	0,9989	0,006194515	0,52903184	0,037383406
76,70	0,0710	0,9290	0,1340	0,8660		78,24	0,0710	0,9290	0,0735	0,9265	1,0348	0,9973	0,02011339	0,451711093	0,06989525
76,10	0,0950	0,9050	0,1760	0,8240		78,22	0,0950	0,9050	0,0982	0,9018	1,0340	0,9964	0,027851503	0,441868313	0,09437964
76,00	0,0970	0,9030	0,1750	0,8250		78,22	0,0970	0,9030	0,1003	0,8997	1,0339	0,9964	0,029178401	0,426898162	0,090554156
75,20	0,1350	0,8650	0,2300	0,7700		78,18	0,1350	0,8650	0,1394	0,8606	1,0327	0,9949	0,03963369	0,393855982	0,117645293
75,10	0,1360	0,8640	0,2320	0,7680		78,18	0,1360	0,8640	0,1404	0,8596	1,0327	0,9949	0,041004942	0,394649607	0,119217069
74,40	0,1500	0,8500	0,2490	0,7510		78,17	0,1500	0,8500	0,1548	0,8452	1,0322	0,9943	0,050614066	0,378198817	0,125394814
73,40	0,2570	0,7430	0,3510	0,6490		78,06	0,2570	0,7430	0,2643	0,7357	1,0286	0,9901	0,063464989	0,246893493	0,133527914
72,70	0,3310	0,6690	0,4100	0,5900		77,98	0,3310	0,6690	0,3396	0,6604	1,0260	0,9871	0,072654147	0,171703299	0,119319241
72,80	0,3320	0,6680	0,4040	0,5960		77,98	0,3320	0,6680	0,3406	0,6594	1,0260	0,9871	0,071166377	0,156891196	0,106349066
72,60	0,3600	0,6400	0,4220	0,5780		77,95	0,3600	0,6400	0,3690	0,6310	1,0250	0,9860	0,073712646	0,125624233	0,091718731
72,20	0,4620	0,5380	0,4950	0,5050		77,84	0,4620	0,5380	0,4718	0,5282	1,0213	0,9817	0,078148245	0,04679454	0,045867915
72,10	0,5450	0,4550	0,5450	0,4550		77,75	0,5450	0,4550	0,5549	0,4451	1,0182	0,9782	0,078373899	0,018222931	0,021827467
72,20	0,6280	0,3720	0,5920	0,4080		77,66	0,6280	0,3720	0,6375	0,3625	1,0151	0,9745	0,075578095	0,076806704	0,111445022
72,40	0,6810	0,3190	0,6350	0,3650		77,60	0,6810	0,3190	0,6899	0,3101	1,0130	0,9722	0,071759223	0,086415753	0,150339734
72,70	0,7740	0,2260	0,6810	0,3190		77,49	0,7740	0,2260	0,7812	0,2188	1,0094	0,9679	0,065819614	0,147200598	0,314243284
73,40	0,8270	0,1730	0,7280	0,2720		77,42	0,8270	0,1730	0,8330	0,1670	1,0072	0,9655	0,054778175	0,144191076	0,385923173
73,60	0,8320	0,1680	0,7630	0,2370		77,41	0,8320	0,1680	0,8378	0,1622	1,0070	0,9653	0,051828634	0,098083752	0,315771742
74,40	0,8900	0,1100	0,8380	0,1620		77,34	0,8900	0,1100	0,8941	0,1059	1,0046	0,9625	0,039552805	0,066974037	0,346445945
74,60	0,9170	0,0830	0,8650	0,1350		77,31	0,9170	0,0830	0,9202	0,0798	1,0035	0,9612	0,036311044	0,063837286	0,409031501
75,30	0,9360	0,0640	0,9000	0,1000		77,28	0,9360	0,0640	0,9385	0,0615	1,0027	0,9603	0,026357877	0,042823267	0,385409407
77,10	1,0000	0,0000	1,0000	0,0000		77,20	1,0000	0,0000	1,0000	0,0000	1,0000	0,9572	0,00133061	0	

Step 7: Calculate binary interaction parameters

- **The calculation will use the Excel solver to determine the parameters which will minimize the global deviation criterion. This criterion is defined here as the sum of the square of the deviation values.**

Deviation		
On T	On y_1	On y_2
0.00013196		0
2.48008E-05	0.550773122	0.01703422
0.003711947	0.543989321	0.028631017
0.006194515	0.52903184	0.037383406
0.02011339	0.451711093	0.06989525
0.027851503	0.441868313	0.09437964
0.029178401	0.426898162	0.090554156
0.03963369	0.393855982	0.117645293
0.041004942	0.394649607	0.119217069
0.050614066	0.378198817	0.125394814
0.063464989	0.246893493	0.133527914
0.072654147	0.171703299	0.119319241
0.071166377	0.156891196	0.106349066
0.073712646	0.125624233	0.091718731
0.078148245	0.04679454	0.045867915
0.078373899	0.018222931	0.021827467
0.075578095	0.076806704	0.111445022
0.071759223	0.086415753	0.150339734
0.065819614	0.147200598	0.314243284
0.054778175	0.144191076	0.385923173
0.051828634	0.098083752	0.315771742
0.039552805	0.066974037	0.346445945
0.036311044	0.063837286	0.409031501
0.026357877	0.042823267	0.385409407
0.00133061	0	
Global criterion		3.129135581

Enter the formula below the deviation table:

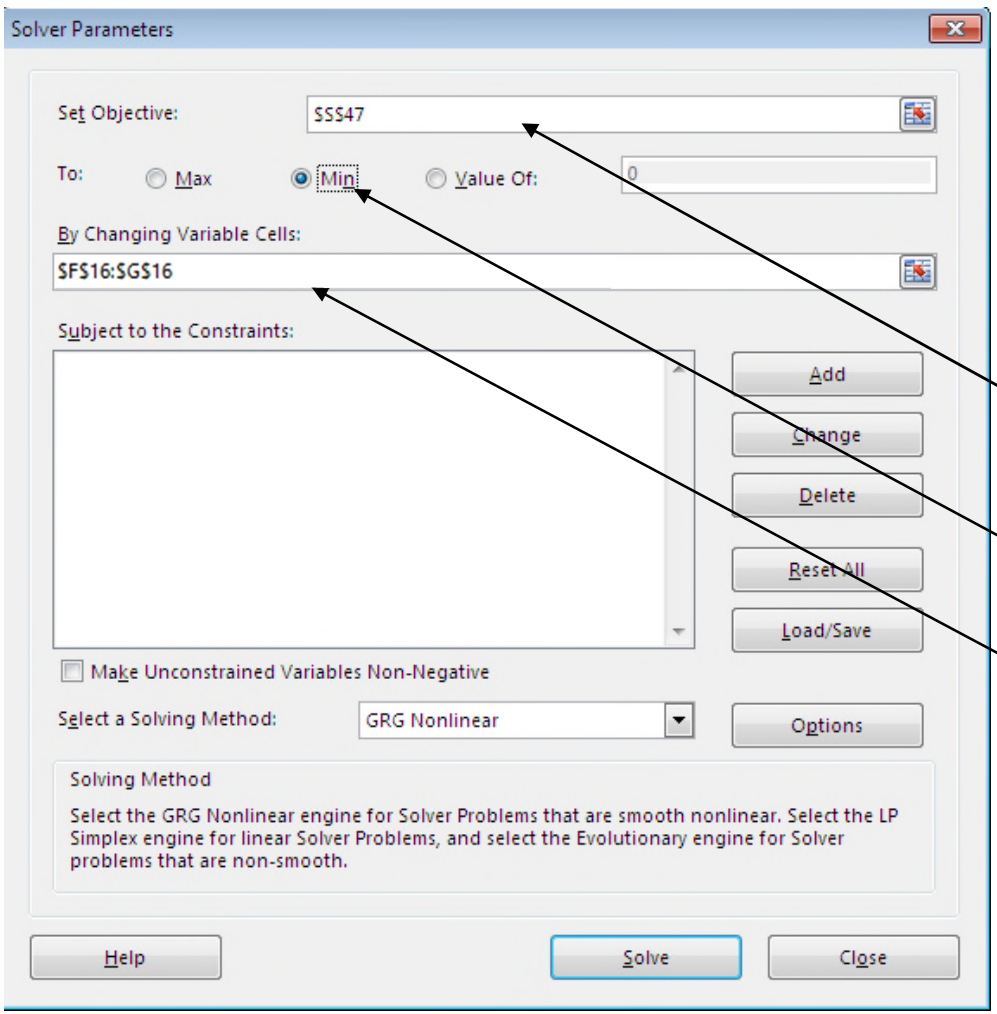
***"=sum.square (T21:V45)"*.**

T21:V45 represents the table cells and will vary according to the design of your spreadsheet.

Press "*Enter*" to obtain the value: 3.129135581

Step 7: Calculate binary interaction parameters

- **Open the solver and minimize the criterion.**



To open the solver window, select "*Tools / Solver*" in the MS Excel menu. (If not activated, select "*Additional add-in*" and check the solver option).

The target cell is the one to be minimized, (the global criterion cell).

Select the Minimization action.

The variable cells are the BIPs cells. Select only C_{ij}^0 and C_{ji}^0 because a_{ij}^0 has to remain at 0.2 and the temperature range corresponding to the experimental data is not wide enough to have a good estimation of C_{ij}^T, C_{ji}^T and a_{ij}^T

Then press "*Solve*"

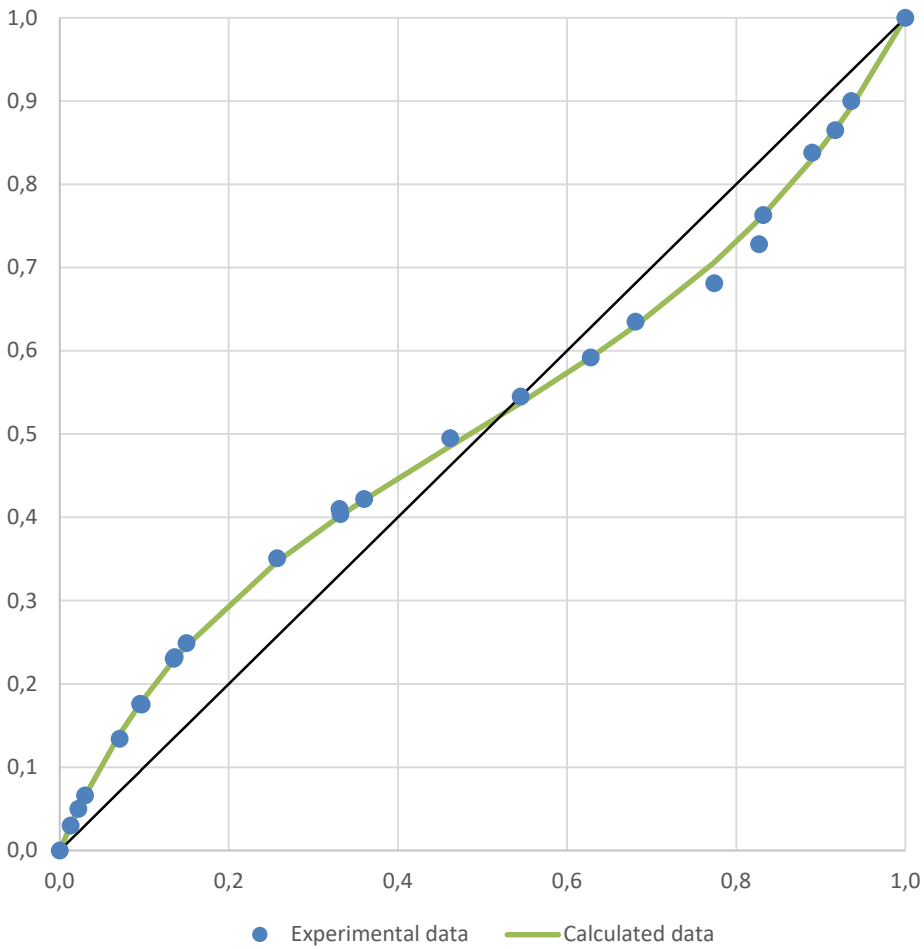
Step 7: Calculate binary interaction parameters

Compounds		Binary interaction parameters					
1	*2*	Cij0	Cji0	aij0	CijT	CjiT	aijT
ETHYL ACETATE	ETHANOL	-48,94021736	635,3978483	0,2	0	0	0

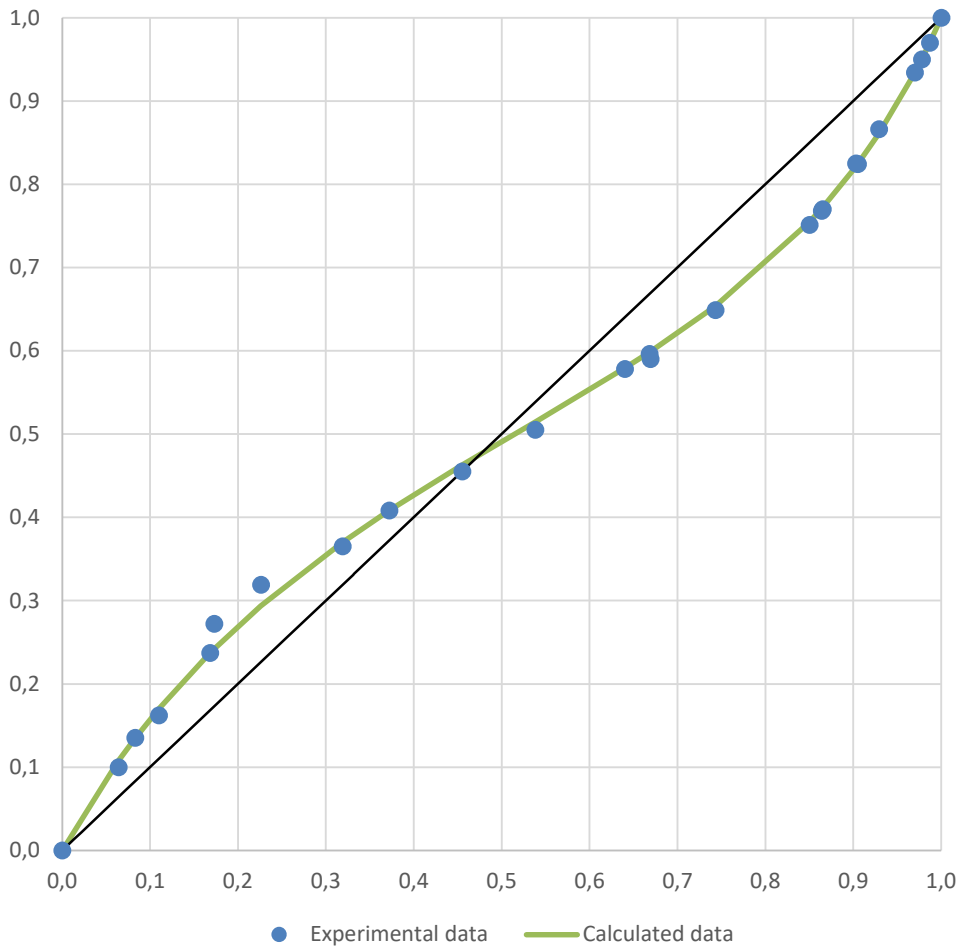
- **BIPs are calculated. The new global criterion is 0,035 (this value depends on the solver parameters).**
- **To verify the consistency of your estimation, plot the curves corresponding to liquid / vapor fractions for each components (x1-y1 and x2-y2) and compare the calculated curves with the experimental curves.**

Step 7: Calculate binary interaction parameters

Ethyl Acetate



Ethanol



Limit of the method

- Number of experimental data
- Number of BIPs to fit
- Number of possible solutions
- Numerical method and parameters of Excel solver

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