Getting started with Simulis® Thermodynamics

Use Case 15: Parameter identification with MS Excel

Software & Services In Process Simulation

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ProSim

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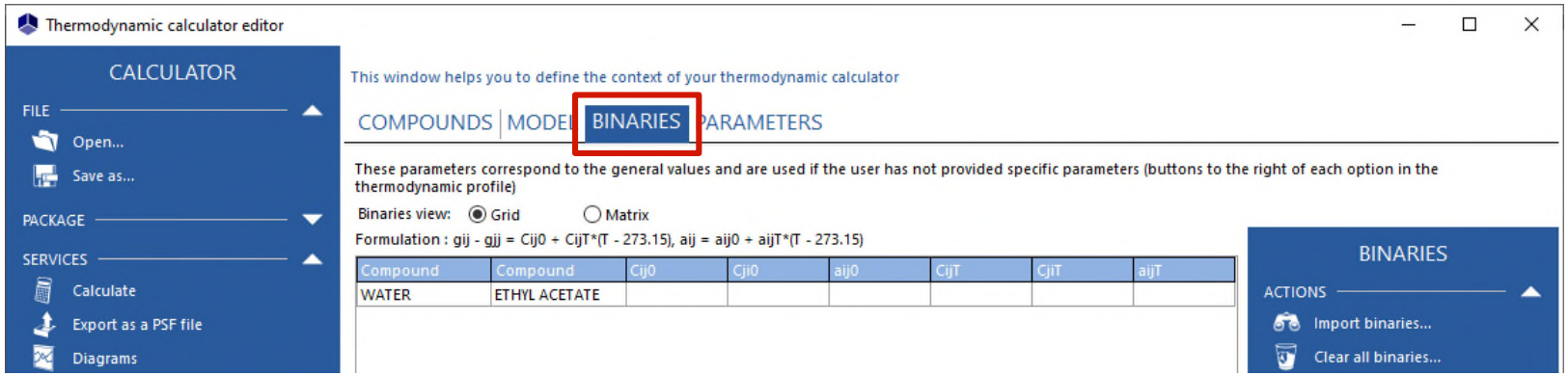
Introduction

It is possible to regress binary interaction parameters of thermodynamic models from experimental data with dedicated Simulis® functions (functions with extension Kij). Example given:

- stCALFlashTPKij()
- stCALGammaLKij()
- …

The use of these functions are directly linked to regression of parameters located in the “BINARIES” tab of the calculator:



Before studying this case, it is recommended to consult “Getting Started with Simulis Thermodynamic, Case 8” that explains how to regress binary interaction parameters from experimental data in Excel

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Introduction

This document presents, with illustration examples, the possibility to regress other types of parameters:

1- Pure components properties

2- Specific binary interaction parameters (BIP)

3- Binary interaction parameters (BIP) for solid-liquid equilibria

The use of a complementary add-in “Simulis Parameters Identification.xla” (or SPI) is necessary

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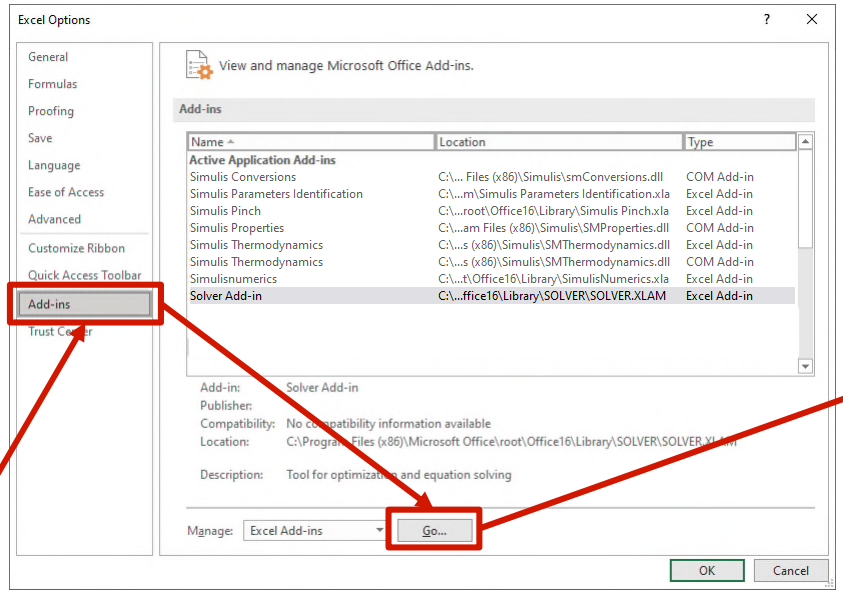
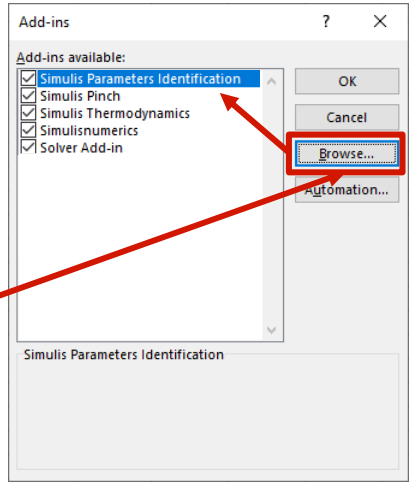
Introduction - SPI Add-In

- Installation of the complementary add-in “Simulis Parameters Identification.xla”:
  - Save the add-in in the folder (to be created if necessary): C:\ProSim
  - In Excel Options
    - Add-ins
    - Go
    - Brose
    - Add the add-in





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Introduction - Excel Solver

- if the Excel Solver is not found:
  - Search the path where is located:
    - SOLVER32.DLL
  - Example given:
    - C:\Program Files (x86)\Microsoft Office\OfficeXX\Library\SOLVER
    - C:\Programmes\Microsoft Office\OfficeXX\Library\SOLVER
    - Or do a search on C:\

- Copy/Paste the DLL "SOLVER32.DLL" in the following folder (needs administrator rights):
  - C:\Windows\SysWOW64 (if 32 bits Excel version)
  - C:\Windows\System32 (if 64 bits Excel version or depending on Windows version)

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Introduction - Examples

- Available examples with this document:
  - Regression of NRTL-SAC parameters (pure component properties)
    - SIMULIS_GS15_EN-parameter-identification_caffeine-solubility.xlsm
  - Regression of specific BIP
    - SIMULIS_GS15_EN-parameter-identification_water-acetone-viscosity.xlsm
  - Regression of BIP for solid-liquid equilibria
    - SIMULIS_GS15_EN-parameter-identification_aspirin-acetone-solubility.xlsm

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1- Pure component properties identification

- Pure component properties
  - All constant properties of one or several components are accessible:
    - *stCALGetProperty(Name, Index, pID, Unit)*

      to get a property value of a component

      (function available in the Simulis Thermodynamics add-in)
    - *stCALSetProperty(Name, Index, pID, Value, Unit)*

      to set a property value of a component

      (function available in the complementary SPI add-in)

With:

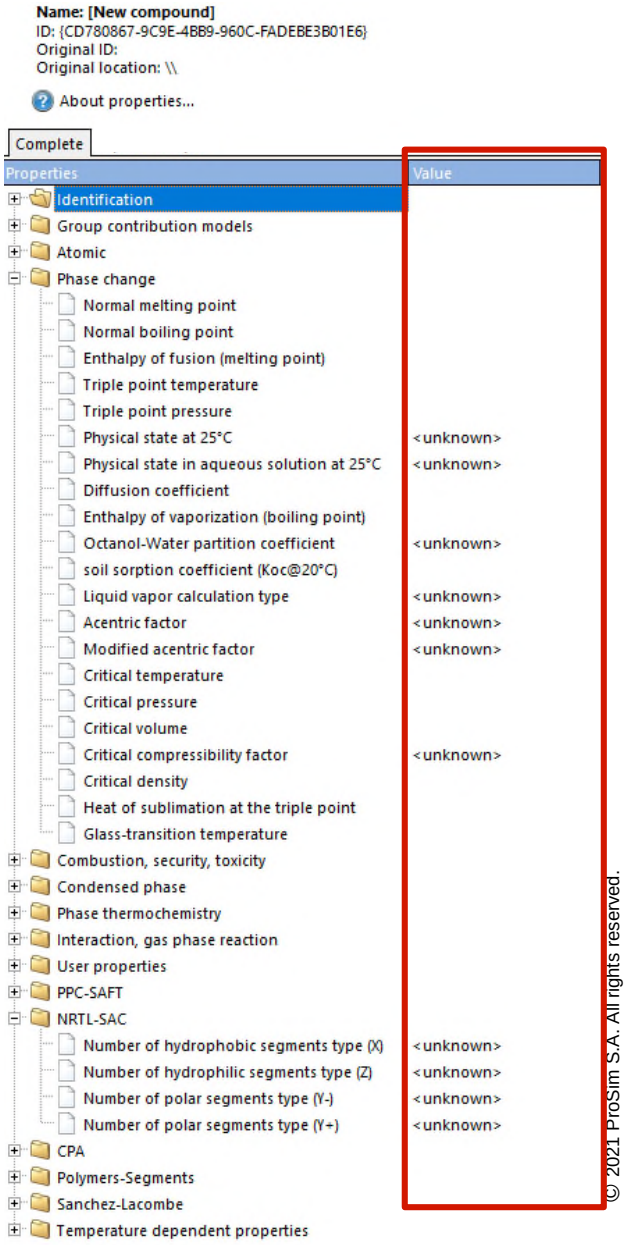
Name : Name of the calculator

Index : Index of the component in the list

pID : Property identifier

Value : Value of the property to be set

Unit : Optional argument



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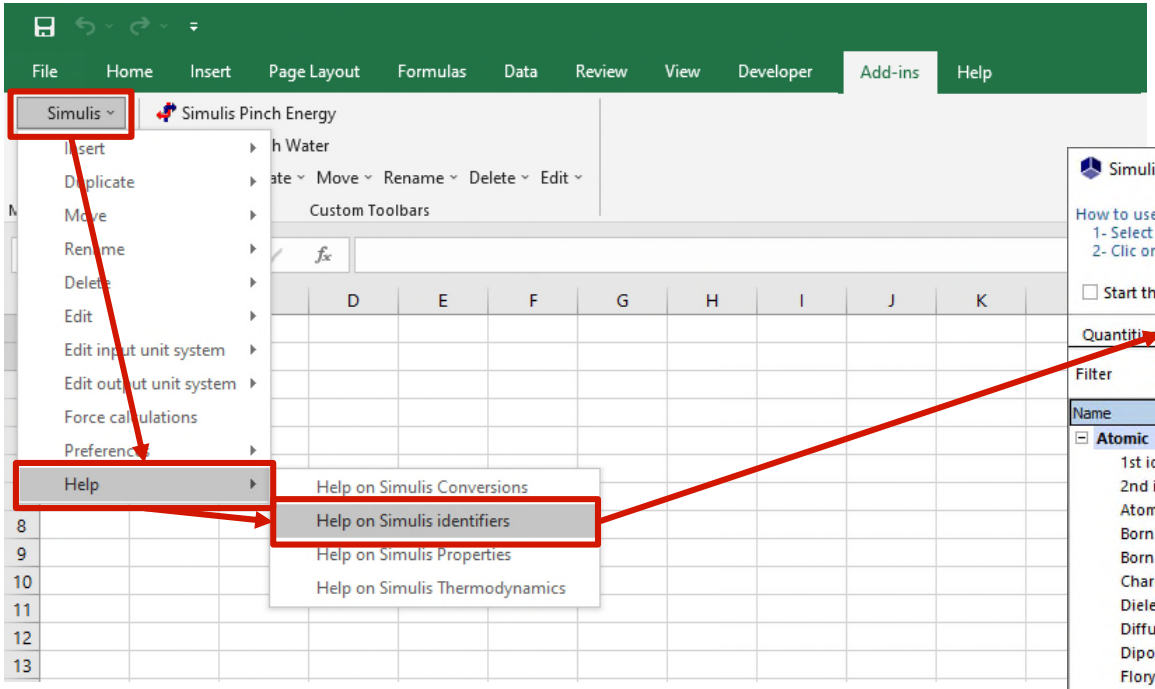
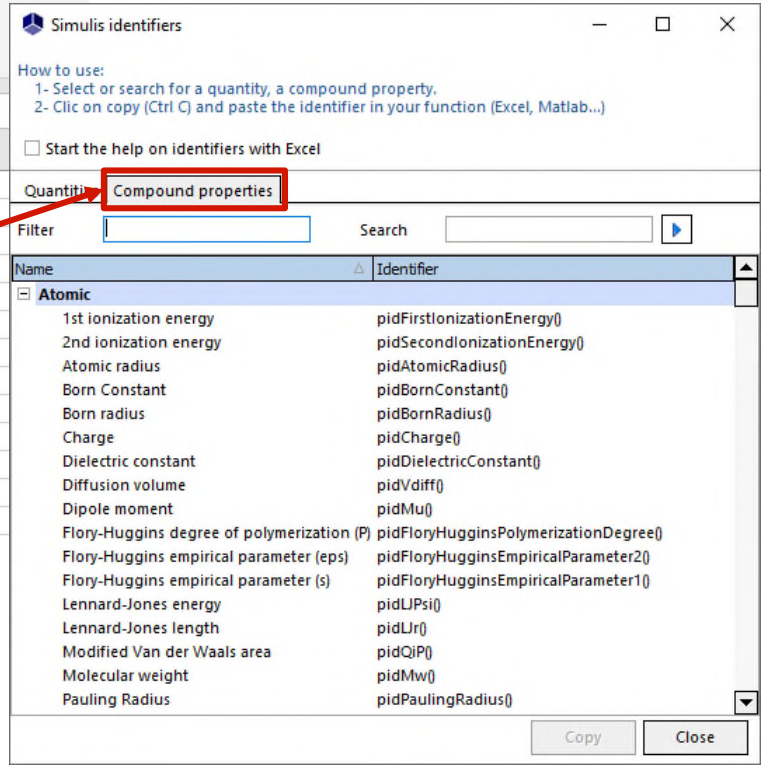
1- Pure component properties identification

- Pure component properties
  - Access to pID property identifier:
    - “Simulis” menu, “Help”, “Help on Simulis identifiers”
    - Simulis identifiers, “Compound properties” tab





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1- Pure component properties identification

- Pure component properties
  - Example: Regress NRTL-SAC parameters of caffeine to represent its solubility in several solvents

    Reference: J. Zhong, N. Tang, B. Asadzadeh, W. Yan, "Measurement and Correlation of Solubility of Theobromine, Theophylline, and Caffeine in Water and Organic Solvents at Various Temperatures", J. Chem. Eng. Data, 62, 2570-2577 (2017)

- Steps to build the Excel file
  - 1- Define the calculator
  - 2- Choice of units
  - 3- Available experimental data
  - 4- Thermodynamic calculations
  - 5- Define the deviation minimization criterion between experimental data and the model
  - 6- Working table of properties to be regressed
  - 7- Define the calculation sequence
  - 8- Use of the solver

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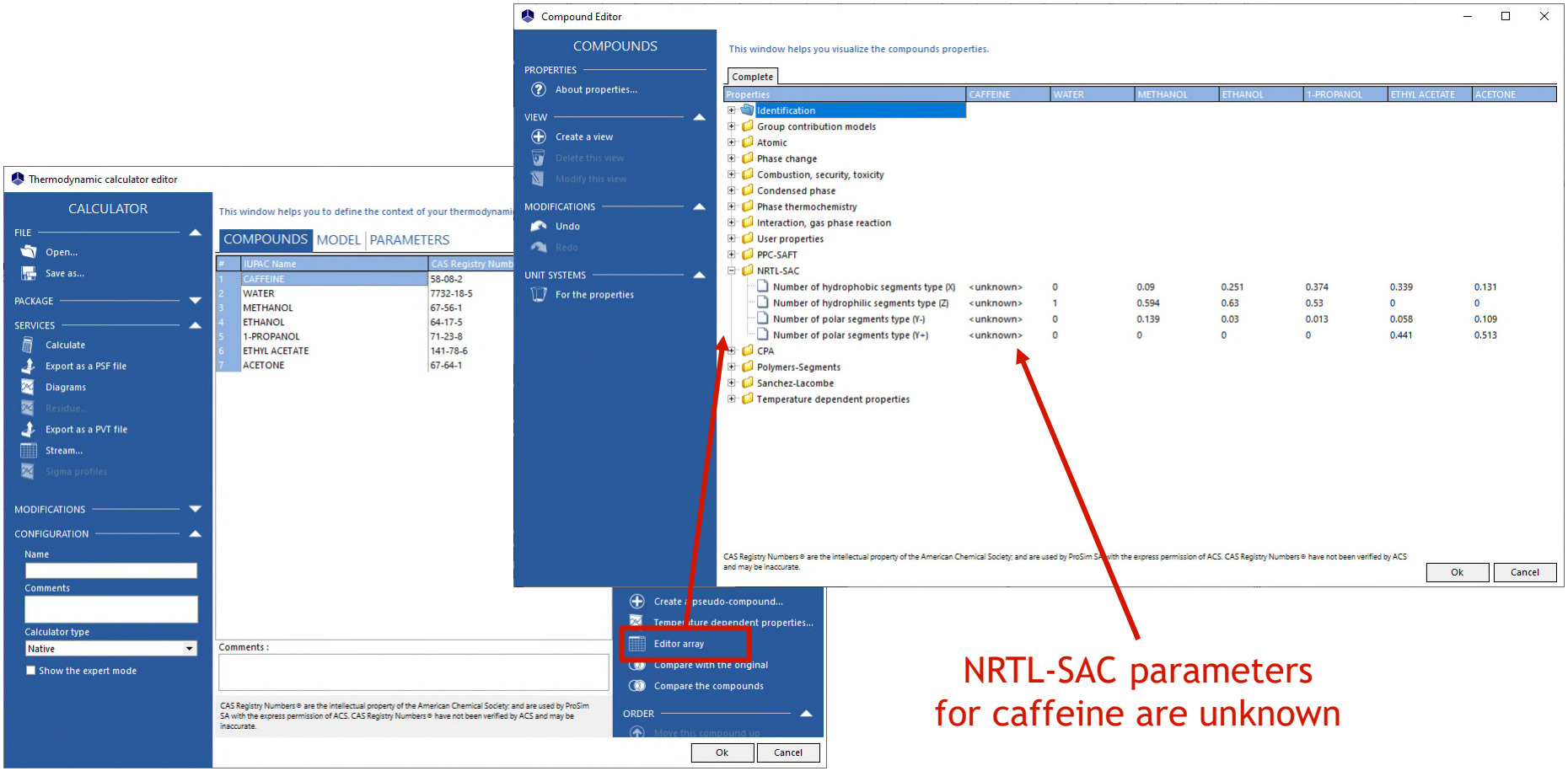
1- Pure component properties identification

- Step 1: Define the calculator
  - Import components CAFFEINE, WATER, METHANOL, ETHANOL, 1-PROPANOL, ETHYL ACETATE, ACETONE
  - Choose NRTL-SAC thermodynamic profile
  - Visualize available NRTL-SAC parameters for the components (with editor array)



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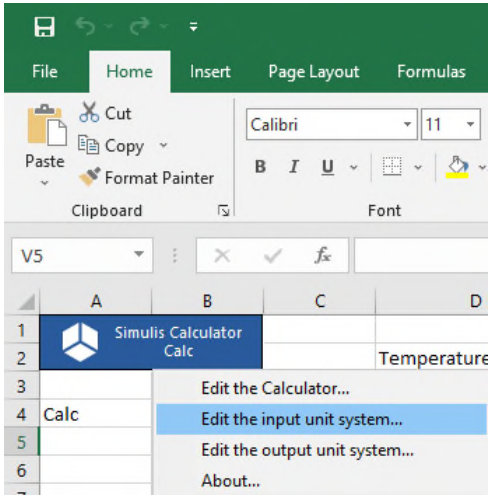
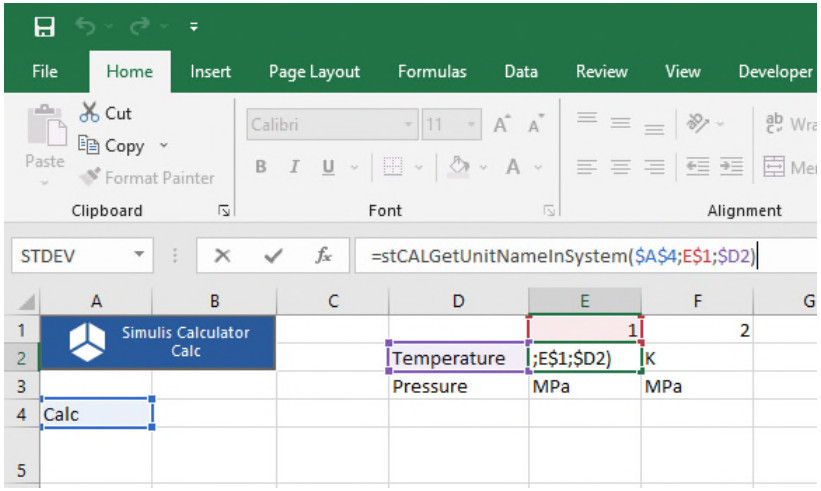
1- Pure component properties identification

- Step 2: Choice of units
  - Right-click on the calculator object
    - Edit the input unit system
    - Edit the output unit system
    - Choose "K" for temperature,
      "MPa" for pressure



- Visualize the units used in the Excel worksheet
  - Simulis function: *stCALGetUnitNameInSystem()*



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1- Pure component properties identification

- Step 3: Available experimental data
  - Enter experimental solubilities available for each solvent (Zhong *et al.*, 2017)
    - Pressure
    - Temperatures
    - Solubilities (molar fractions)

	A	B	C	D	E
4	Calc				
5					
6				1 CAFFEINE	
7				2 WATER	
8				3 METHANOL	
9				4 ETHANOL	
10				5 1-PROPANOL	
11				6 ETHYL ACETATE	
12				7 ACETONE	
13					
14			P (MPa)	0.1	
15					
16			*Data*		
17			T (K)	x1	
18		Solubility in Water	288.01	1.23E-03	
19			298.11	1.61E-03	
20			308.09	2.27E-03	
21			318.11	2.96E-03	
22			328.15	3.98E-03	
23					
24		Solubility in Methanol	288.24	1.34E-03	
25			298.17	1.89E-03	
26			308.17	2.80E-03	
27			318.2	4.26E-03	
28			328.12	6.63E-03	
29					
30		Solubility in Ethanol	288.01	7.80E-04	
31			298.11	1.32E-03	
32			308.09	2.04E-03	
33			318.11	3.22E-03	
34			328.15	4.69E-03	
35					
36		Solubility in 1-Propanol	288.24	1.17E-03	
37			298.17	1.77E-03	
38			308.17	2.82E-03	
39			318.2	4.53E-03	
40			328.12	7.16E-03	

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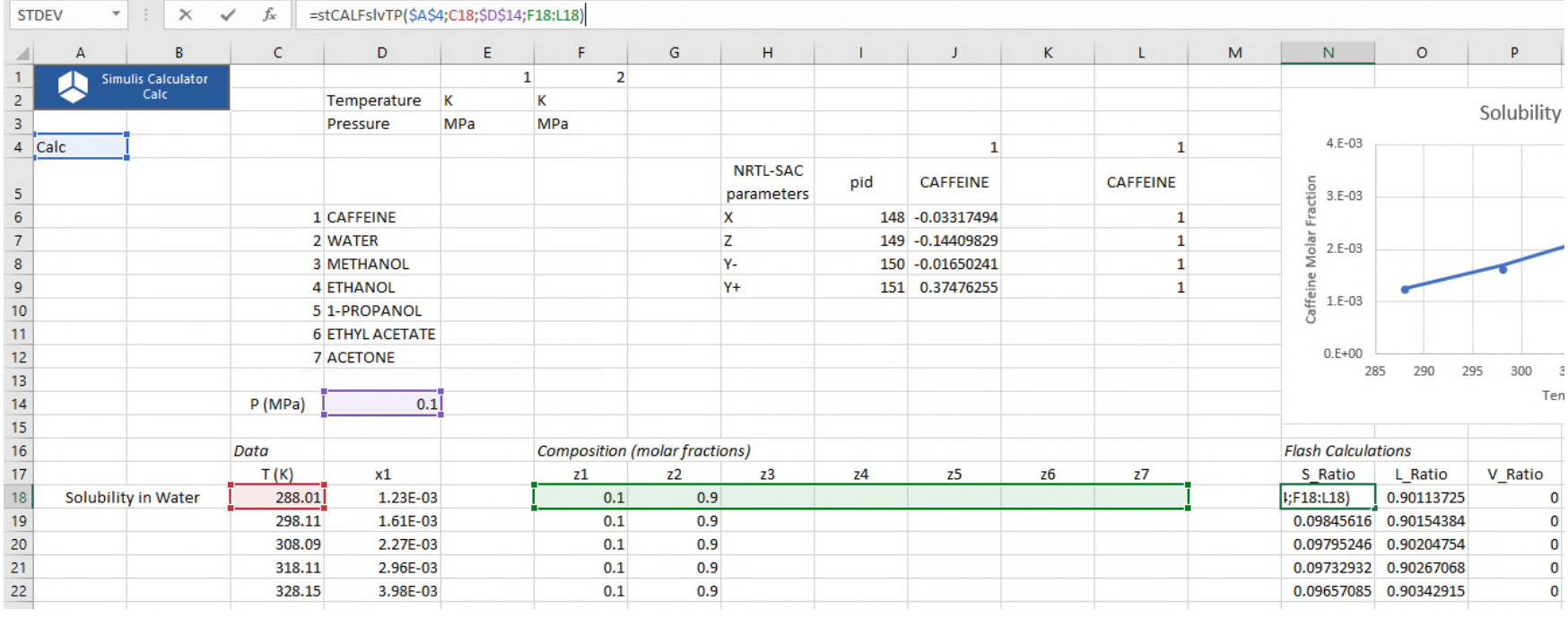
1- Pure component properties identification

- Step 4: Thermodynamic calculations
  - Vapor-liquid-solid equilibrium calculation at given temperature and pressure
    - Simulis function: *stCALFslvTP()*
    - Results as a vector (3*NC+3=24 cells, for 7 components):
      - Solid ratio
      - Liquid ratio
      - Vaporization ratio
      - Fractions (molar or mass) in solid phase
      - Fractions (molar or mass) in liquid phase
      - Fractions (molar or mass) in vapor phase



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1- Pure component properties identification

- Step 5: define the minimization criterion between experimental data and the model
  - Deviation function between experimental solubility and calculated solubility:

$$\%\mathrm{AARD} = \frac{100}{N_p} \sum_{i=1}^{N_p} \frac{\left| x_{1i}^{exp} - x_{1i}^{calc} \right|}{x_{1i}^{exp}}$$

With:

- % AARD : Average Absolute Relative Deviation
- N_p : Number of experimental points
- x_{1i}^{exp} : Experimental solubility of caffeine (molar fraction)
- x_{1i}^{calc} : Calculated solubility of caffeine (molar fraction)

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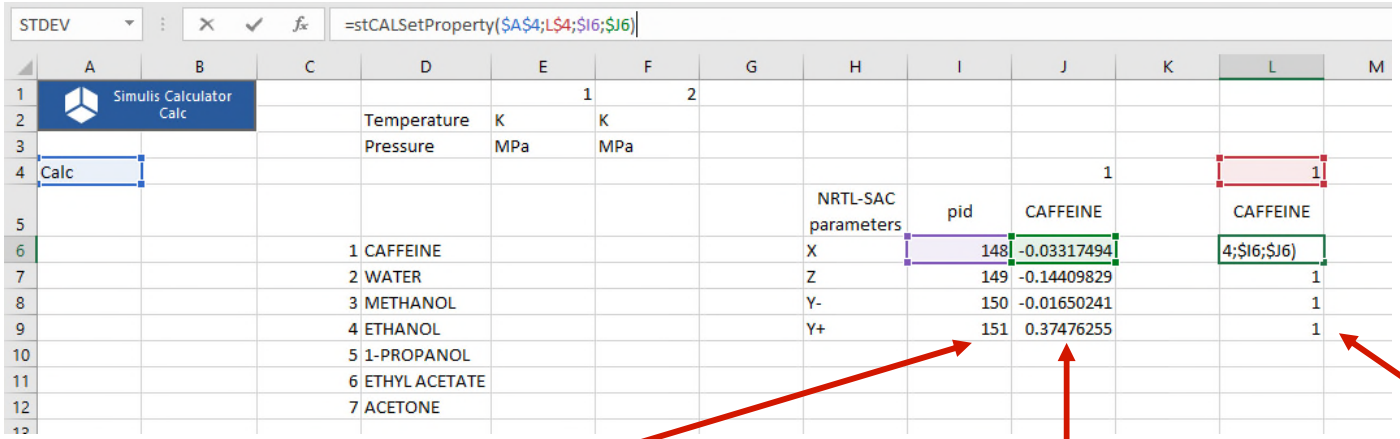
1- Pure component properties identification

- Step 6: Working table of properties to be regressed
  - pID of NRTL-SAC parameters
    - X : pidHydrophobicSegmentCount()
    - Z : pidHydrophilicSegmentCount()
    - Y^- : pidPolarYMinusSegmentCount()
    - Y^+ : pidPolarYPlusSegmentCount()
  - Values of NRTL-SAC parameters
    - Initial (e. g. 0.2; 0.2; 0.2; 0.6), then modified after regression
  - Copy values of NRTL-SAC parameters in the component of the calculator
    - Use of SPI Simulis function: *stCALSetProperty()*
    - Result of this function is “1”



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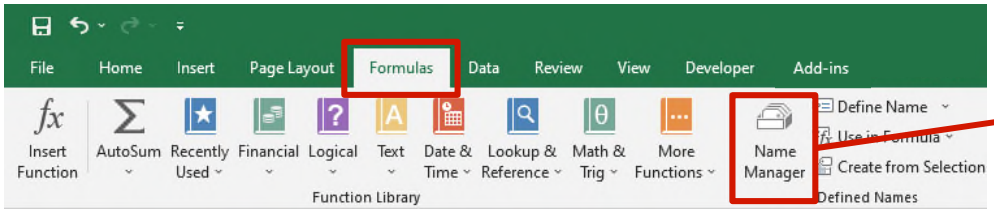
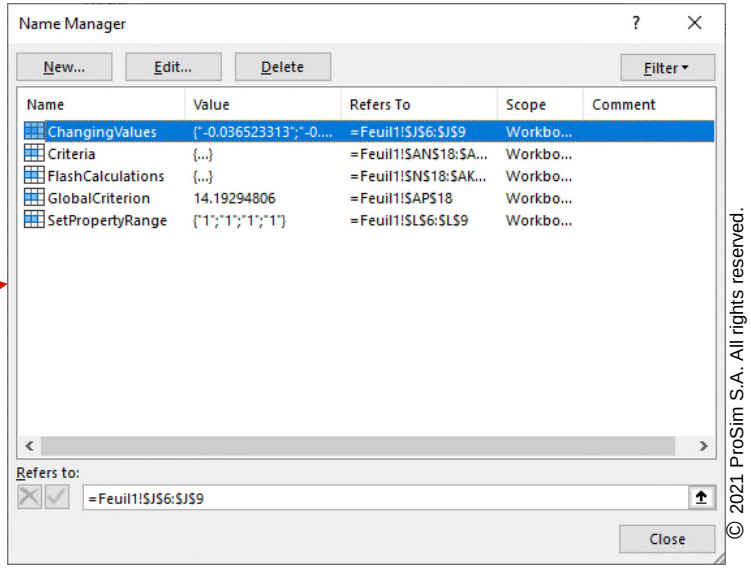
1- Pure component properties identification

- Step 7: Define the calculation sequence
  - Name the cells, *e.g.*:
    - “ChangingValues” for NRTL-SAC parameters table (cells J6 to J9)
    - “SetPropertyRange” for the copy of the values of the properties in the calculator (cells L6 to L9)
    - “FlashCalculations” for flash calculation (cells of columns N to AK)
    - “Criteria” for relative deviations (cells of column AN)
    - “GlobalCriterion” for the criterion to be minimized (cell AP18)
  - Access to named cells:
    - “Formulas” menu, “Name Manager”





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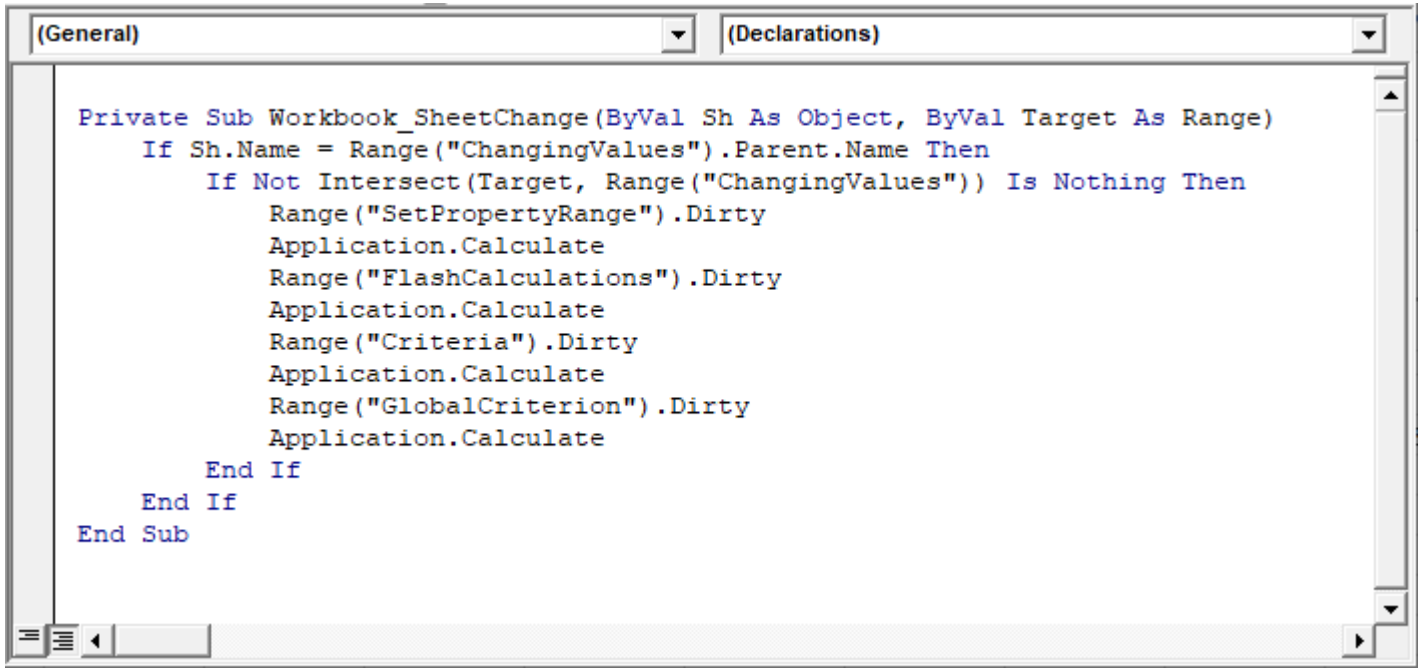
1- Pure component properties identification

- Step 7: Define the calculation sequence
  - Add a VBA macro (click on ALT+F11)
    - Define the order of calculation with the named cells defined previously
    - Once a value of the working table of NRTL-SAC parameters is modified:
      - This property value is pasted in the compound
      - Flash calculation are done
      - Deviations are calculated
      - Global criterion is calculated



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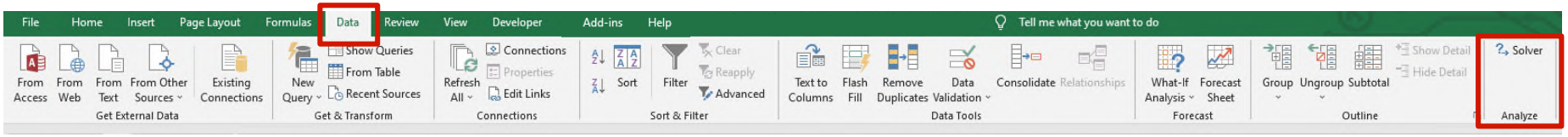
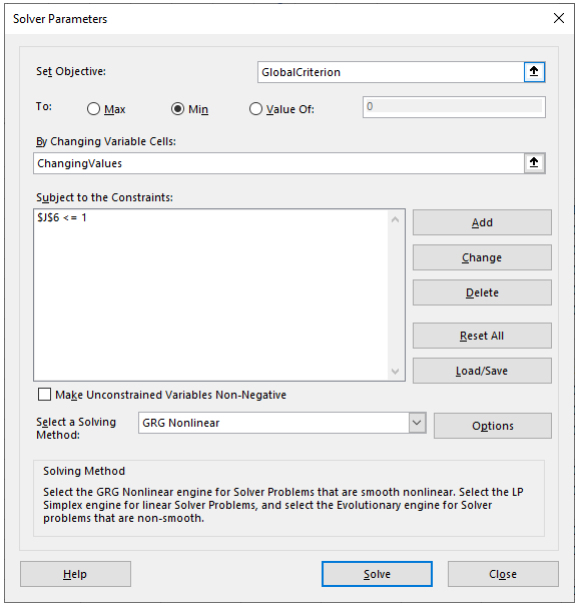
1- Pure component properties identification

- Step 8: Use of the solver
  - Access to the solver
    - “Data” menu, “Solver”



  - Parameters of the solver
    - Minimize global criterion (*GlobalCriterion*)
    - Modifying the table of NRTL-SAC parameters (*ChangingValues*)



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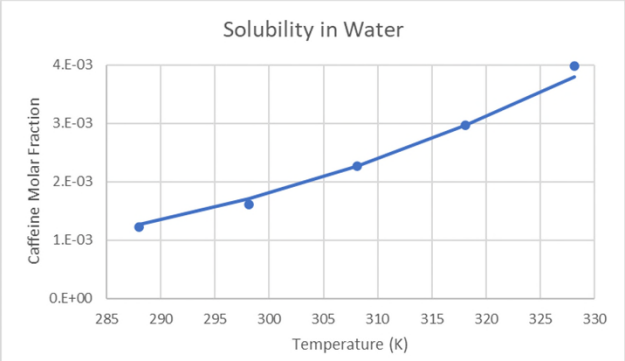
1- Pure component properties identification

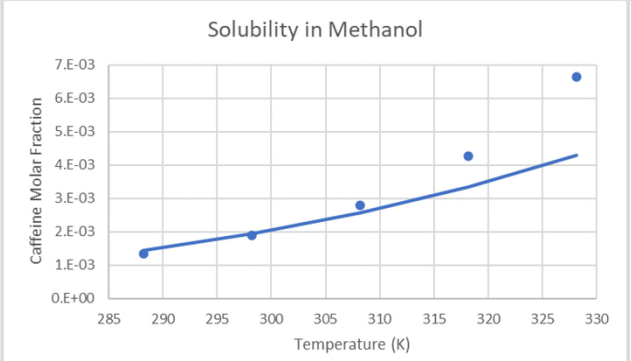
- Results
  - NRTL-SAC parameters of caffeine are obtained
  - Plot of the obtained curves, compared to experimental points

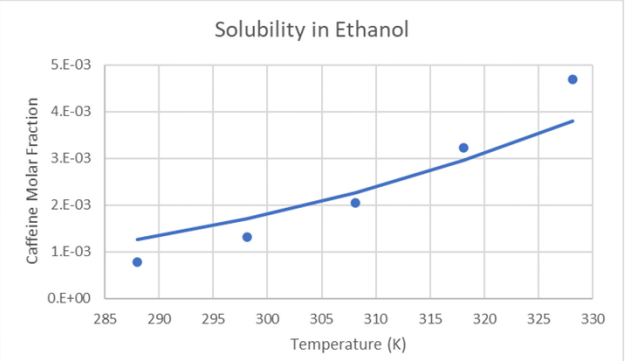
Name: CAFFEINE
ID: {EE6DE16D-F90D-473E-B213-CB5197379AFB}
Original ID: 6853
Original location: Simulis® Compounds Files\Common files\Standard 2017
About properties...

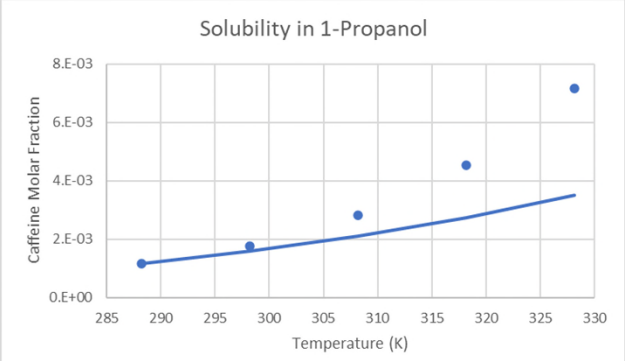
Complete

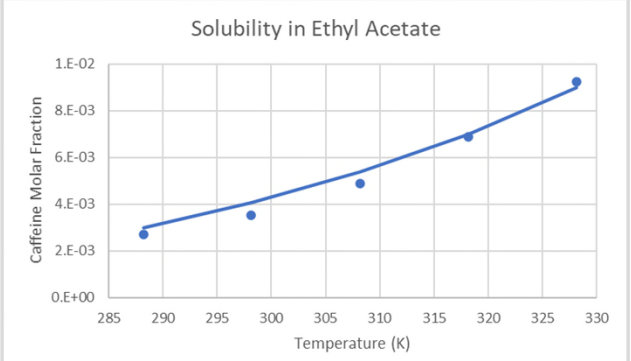
Properties	Value
Phase thermochemistry	
Interaction, gas phase reaction	
User properties	
PPC-SAFT	
NRTL-SAC	
Number of hydrophobic segments type (X)	-0.033174941001269
Number of hydrophilic segments type (Z)	-0.14409829013656
Number of polar segments type (Y-)	-0.016502414531919
Number of polar segments type (Y+)	0.37476254595267

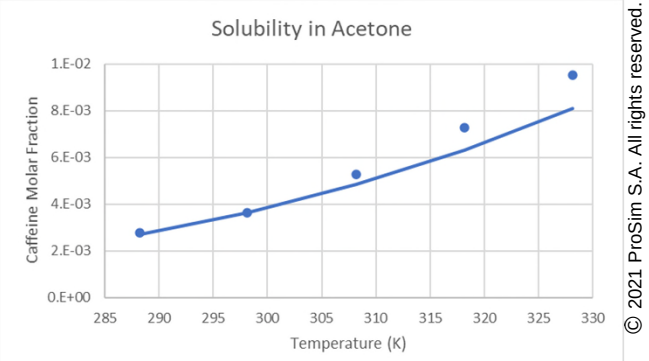












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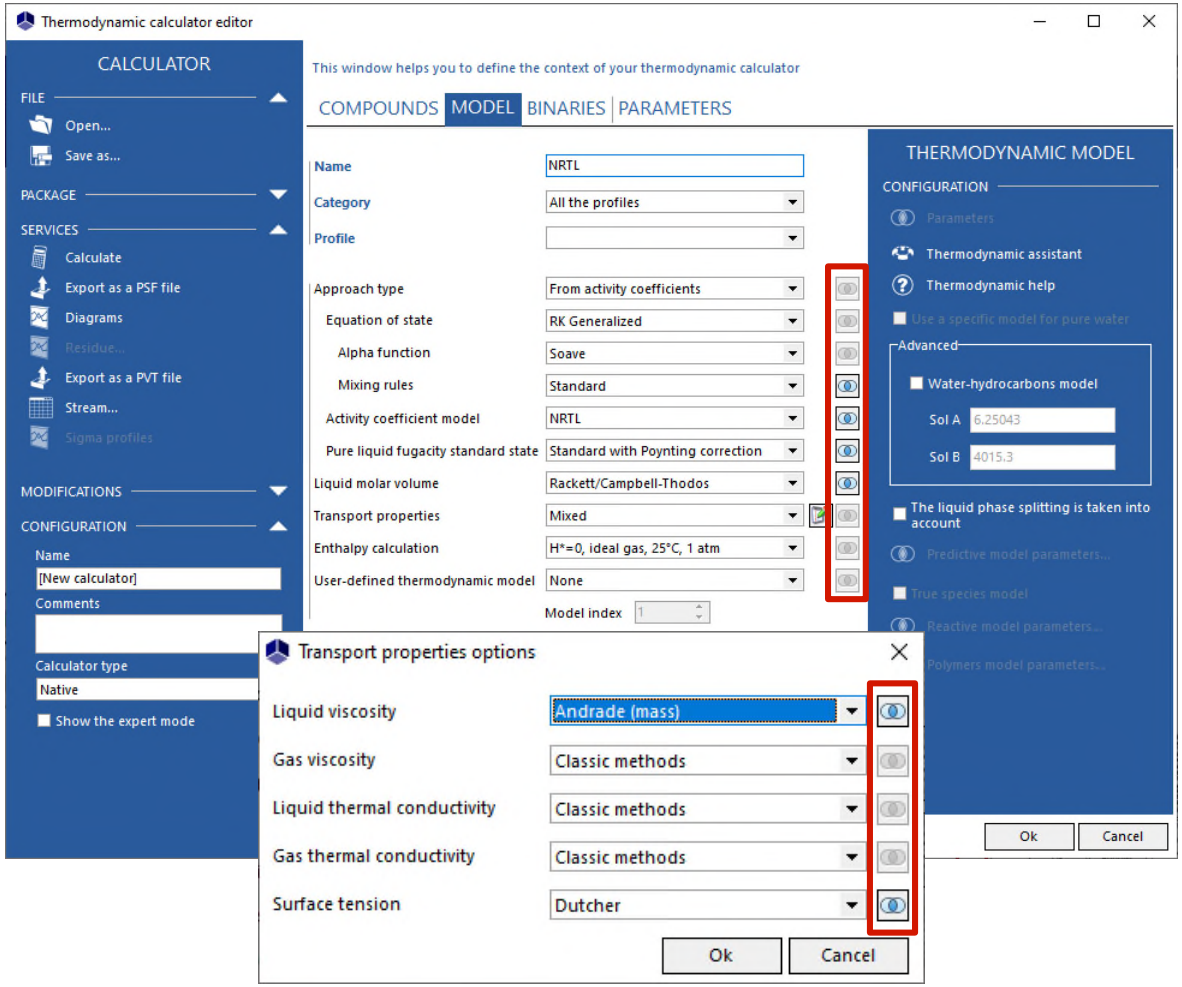
2- Regression of specific binary interaction parameters

- Specific binary interaction parameters (BIP)
  - Possibility to give BIP values, specific for the calculated thermodynamic property, depending on the chosen models

Possible specific binaries

No specific binaries



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2- Regression of specific binary interaction parameters

- Examples of thermodynamic properties and associated models that allow to enter specific binary interaction parameters:
  - Equation of state (in heterogeneous approach):
    - Equation of state: SRK-KD, SRK-CPA, PR-CPA, LKP, BWRS, PPC-SAFT…
    - Mixing rules: Standard, Margules, Van Laar, Soreide-Whitson, Twu, Stryjek-Vera…
  - Equation of state (in homogeneous approach):
    - Complex mixing rules: Wong-Sandler
  - Activity coefficients model:
    - Wilson, Margules
    - NRTLs
    - UNIQUACs
  - Pure liquid fugacity standard state (in heterogeneous approach):
    - Standard with Poynting correction (excess enthalpy calculation)
    - Lois de Henry (MR1 and MR2)
  - Liquid molar volume:
    - Rackett/Campbell-Thodos
  - Liquid viscosity:
    - Andrade (molar or mass)
  - Surface tension:
    - Dutcher

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2- Regression of specific binary interaction parameters

- Specific binary interaction parameters (BIP)
  - All types of binary interaction parameters are accessible:
    - *stCALSetBinariesValues(Name, ICode, Index1, Index2, Values)*

      to set values of binary interaction parameters

      (function available in the complementary SPI add-in)

With:

Name : Name of the calculator

ICode : Code of the thermodynamic property

Index1 : Vector of index for component 1

Index2 : Vector of index for component 2

Values : Values of binary interaction parameters

Note: In the case of a system with 2 components, each vector of index contains only 1 cell

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2- Regression of specific binary interaction parameters

- Specific binary interaction parameters (BIP)
  - Table of available thermodynamics properties codes:

Name used in SPI add-in	ICode	Description
CodeBinGlobal	-1	Global BIP
CodeBinActivityCoefficient	0	Specific BIP for activity coefficient model
CodeBinEnthalpyCalculation	1	Specific BIP for enthalpy calculation model
CodeBinGasStateEquation	2	Specific BIP for gas equation of state model
CodeBinLiquidFugacity	3	Specific BIP for pure liquid fugacity standard state model
CodeBinLiquidMolarVolume	4	Specific BIP for liquid molar volume model
CodeBinMixtureRules	5	Specific BIP for mixing rules model
CodeBinThermoModel	6	Specific BIP for thermodynamic profile model
CodeBinTransferProperties	7	Specific BIP for transport properties model
CodeBinUserModel	8	Specific BIP for user-defined thermodynamic model
CodeBinVaporPressure	9	Specific BIP for vapor pressure model
CodeBinLiquidViscosity	10	Specific BIP for liquid viscosity model
CodeBinVaporViscosity	11	Specific BIP for vapor viscosity model
CodeBinLiquidConductivity	12	Specific BIP for liquid thermal conductivity model
CodeBinVaporConductivity	13	Specific BIP for vapor thermal conductivity model
CodeBinSurfaceTension	14	Specific BIP for surface tension model
CodeBinAlphaFunction	15	Specific BIP for alpha function model

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2- Regression of specific binary interaction parameters

- Specific binary interaction parameters (BIP)
  - Example: Regress specific binary interaction parameters of Andrade model to represent viscosity of a water – acetone mixture

    Reference: B.I. Konobeev, V. V. Lyapin, "Density, Viscosity, and Surface Tension Data on Certain Binary Systems", Zh. Prikl. Khim., 43, 803-810 (1970)

- Steps to build the Excel file
  - 1- Define the calculator
  - 2- Choice of units
  - 3- Available experimental data
  - 4- Thermodynamic calculations
  - 5- Define the deviation minimization criterion between experimental data and the model
  - 6- Working table of properties to be regressed
  - 7- Define the calculation sequence
  - 8- Use of the solver

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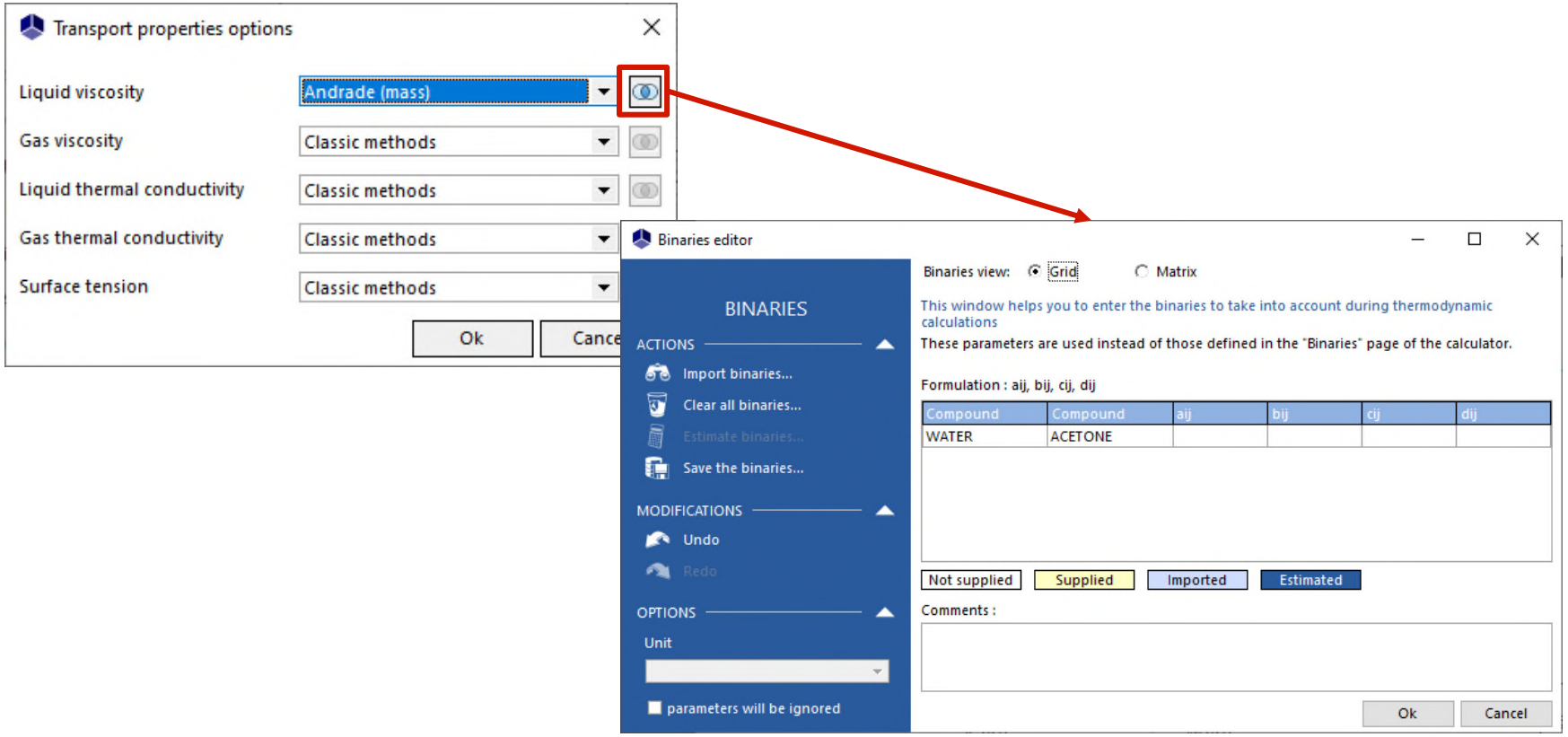
2- Regression of specific binary interaction parameters

- Step 1: Define the calculator
  - Import components WATER, ACETONE
  - Choose NRTL thermodynamic profile
  - Import global BIP from the database in the “BINARIES” tab (phase equilibrium calculations)
  - For transport properties, choose Andrade (mass) for liquid viscosity



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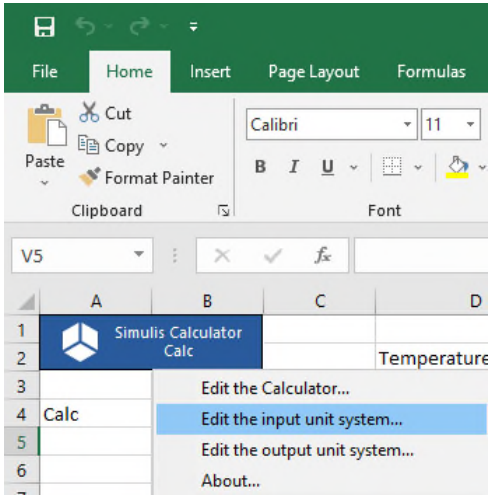
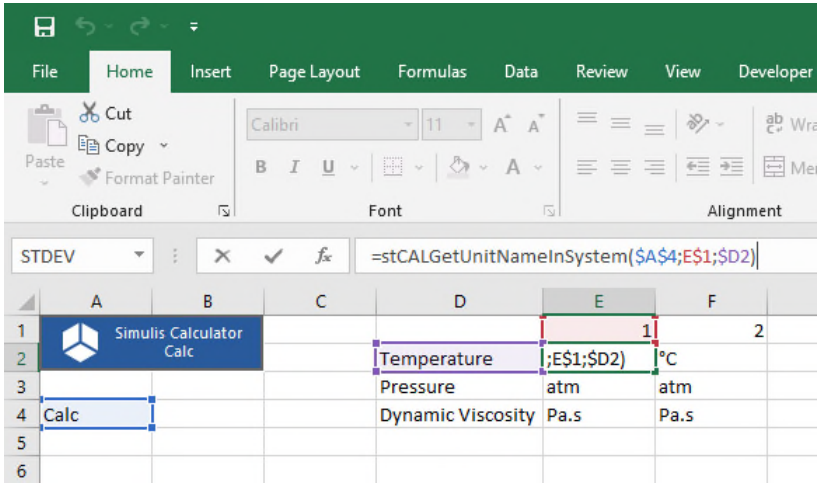
2- Regression of specific binary interaction parameters

- Step 2: Choice of units
  - Right-click on the calculator object
    - Edit the input unit system
    - Edit the output unit system
    - Choose "°C" for temperature,
      "atm" for pressure
      "Pa.s" for dynamic viscosity



  - Visualize the units used in the Excel worksheet
    - Simulis function: *stCALGetUnitNameInSystem()*



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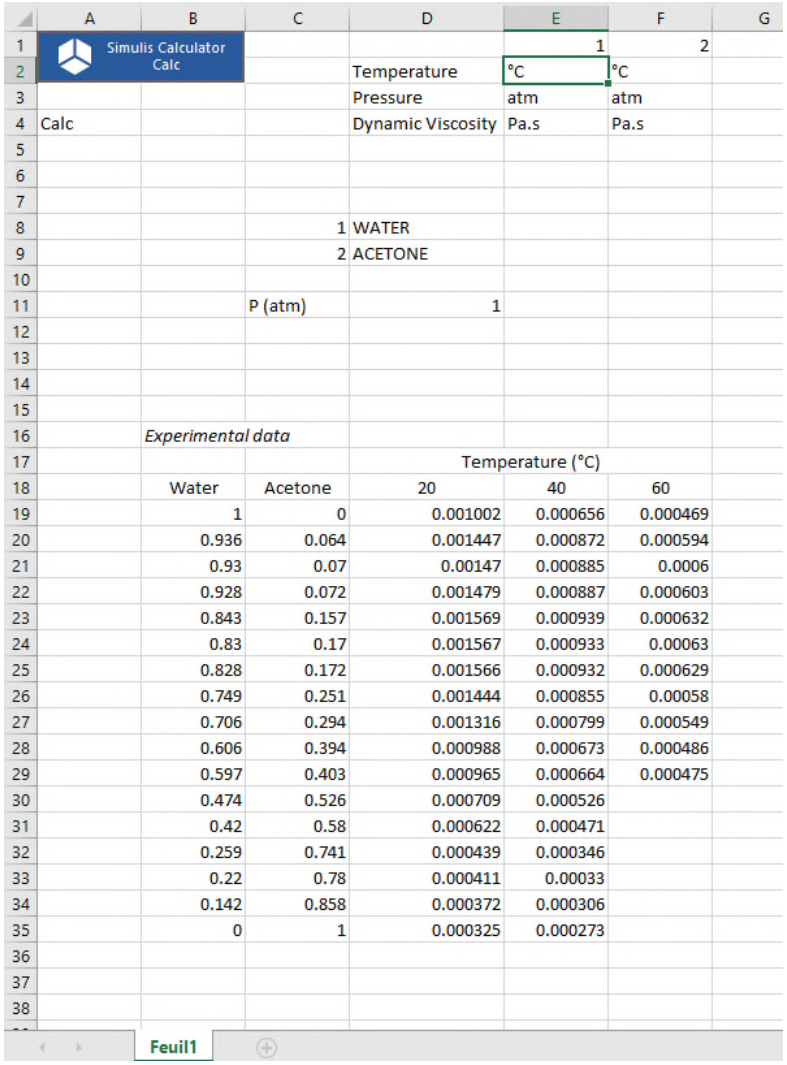
2- Regression of specific binary interaction parameters

- Step 3: Available experimental data
  - Enter experimental viscosities available for the system (Konobeev *et al.*, 1970)
    - Pressure
    - Temperatures
    - Compositions (molar fractions)
    - Viscosities



	A	B	C	D	E	F	G
1	Simulis Calculator Calc				1	2	
2				Temperature	°C	°C	
3				Pressure	atm	atm	
4	Calc			Dynamic Viscosity	Pa.s	Pa.s	
5							
6							
7							
8			1	WATER			
9			2	ACETONE			
10							
11			P (atm)	1			
12							
13							
14							
15							
16		*Experimental data*					
17				Temperature (°C)			
18		Water	Acetone	20	40	60	
19		1	0	0.001002	0.000656	0.000469	
20		0.936	0.064	0.001447	0.000872	0.000594	
21		0.93	0.07	0.00147	0.000885	0.0006	
22		0.928	0.072	0.001479	0.000887	0.000603	
23		0.843	0.157	0.001569	0.000939	0.000632	
24		0.83	0.17	0.001567	0.000933	0.00063	
25		0.828	0.172	0.001566	0.000932	0.000629	
26		0.749	0.251	0.001444	0.000855	0.00058	
27		0.706	0.294	0.001316	0.000799	0.000549	
28		0.606	0.394	0.000988	0.000673	0.000486	
29		0.597	0.403	0.000965	0.000664	0.000475	
30		0.474	0.526	0.000709	0.000526		
31		0.42	0.58	0.000622	0.000471		
32		0.259	0.741	0.000439	0.000346		
33		0.22	0.78	0.000411	0.00033		
34		0.142	0.858	0.000372	0.000306		
35		0	1	0.000325	0.000273		
36							
37							
38							

Feuil1

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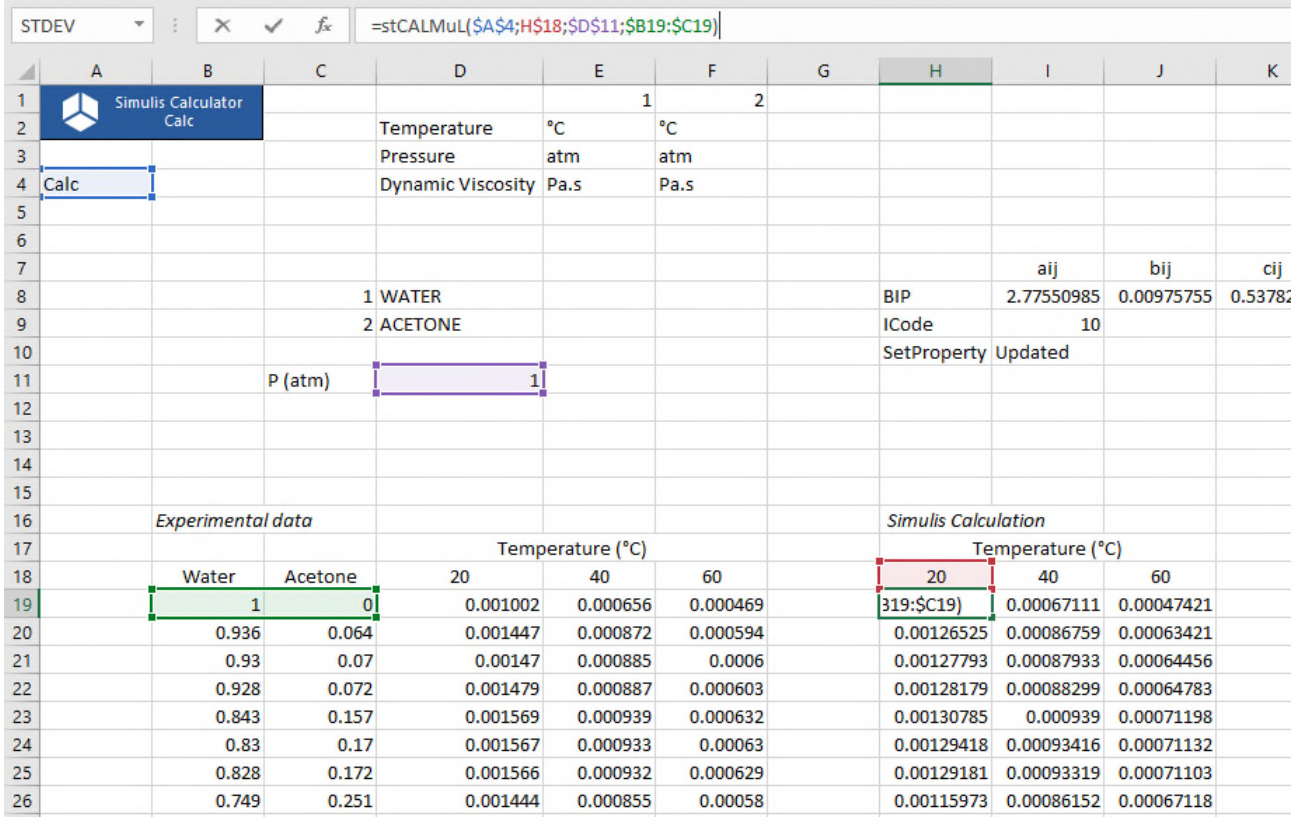
2- Regression of specific binary interaction parameters

- Step 4: Thermodynamic calculations
  - Liquid dynamic viscosity calculation at given temperature and pressure
    - Simulis function: *stCALMuL()*
    - Results:
      - Liquid viscosity of the mixture



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2- Regression of specific binary interaction parameters

- Step 5: define the minimization criterion between experimental data and the model
  - Deviation function between experimental viscosity and calculated viscosity:

$$\%AAD = \frac{100}{N_p} \sum_{i=1}^{N_p} \left| \mu_i^{exp} - \mu_i^{calc} \right|$$

With:

- % AAD : Average Absolute Deviation
- N_p : Number of experimental points
- μ_i^{exp} : Experimental viscosity of the mixture
- μ_i^{calc} : Calculated viscosity of the mixture

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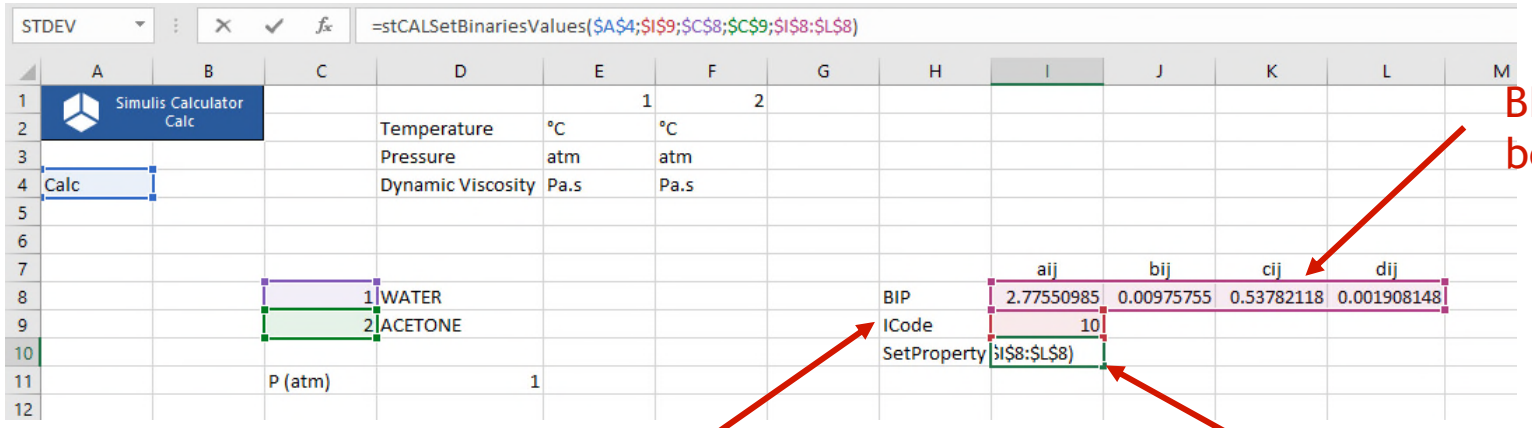
2- Regression of specific binary interaction parameters

- Step 6: Working table of properties to be regressed
  - Values of specific binary interaction parameters of Andrade model
    - Initial (e. g. 0; 0; 0; 0), then modified after regression
  - Code of specific BIP for the thermodynamic property to be modified
    - ICode=10 for liquid viscosity
  - Copy BIP values in the calculator
    - Use of SPI Simulis function: *stCALSetBinariesValues()*
    - Result of this function is “Updated”



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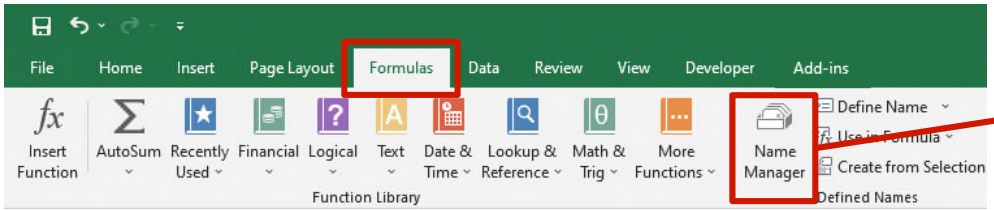
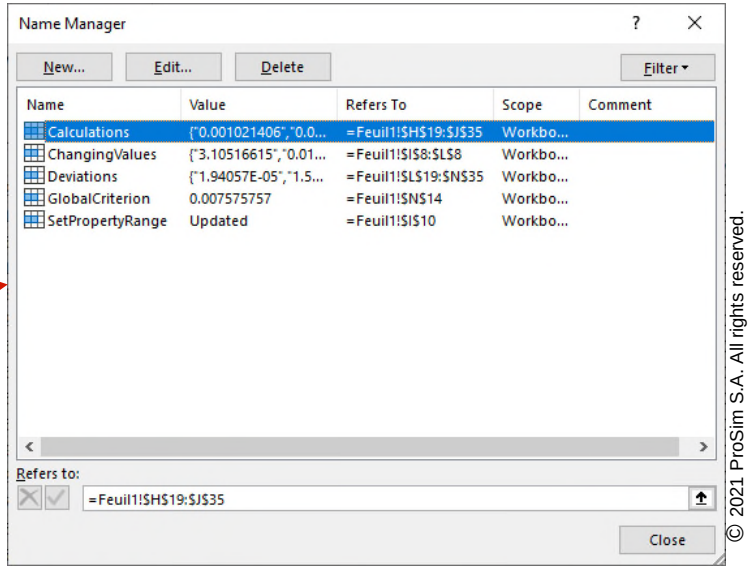
2- Regression of specific binary interaction parameters

- Step 7: Define the calculation sequence
  - Name the cells, e. g. :
    - o "ChangingValues" for the BIP table (cells I8 to L8)
    - o "SetPropertyRange" for the copy of the values of the properties in the calculator (cell I10)
    - o "Calculations" for properties calculations (cells H19 to J35)
    - o "Deviations" for deviations calculations (cells L19 to N35)
    - o "GlobalCriterion" for the criterion to be minimized (cell N14)
  - Access to named cells:
    - o "Formulas" menu, "Name Manager"





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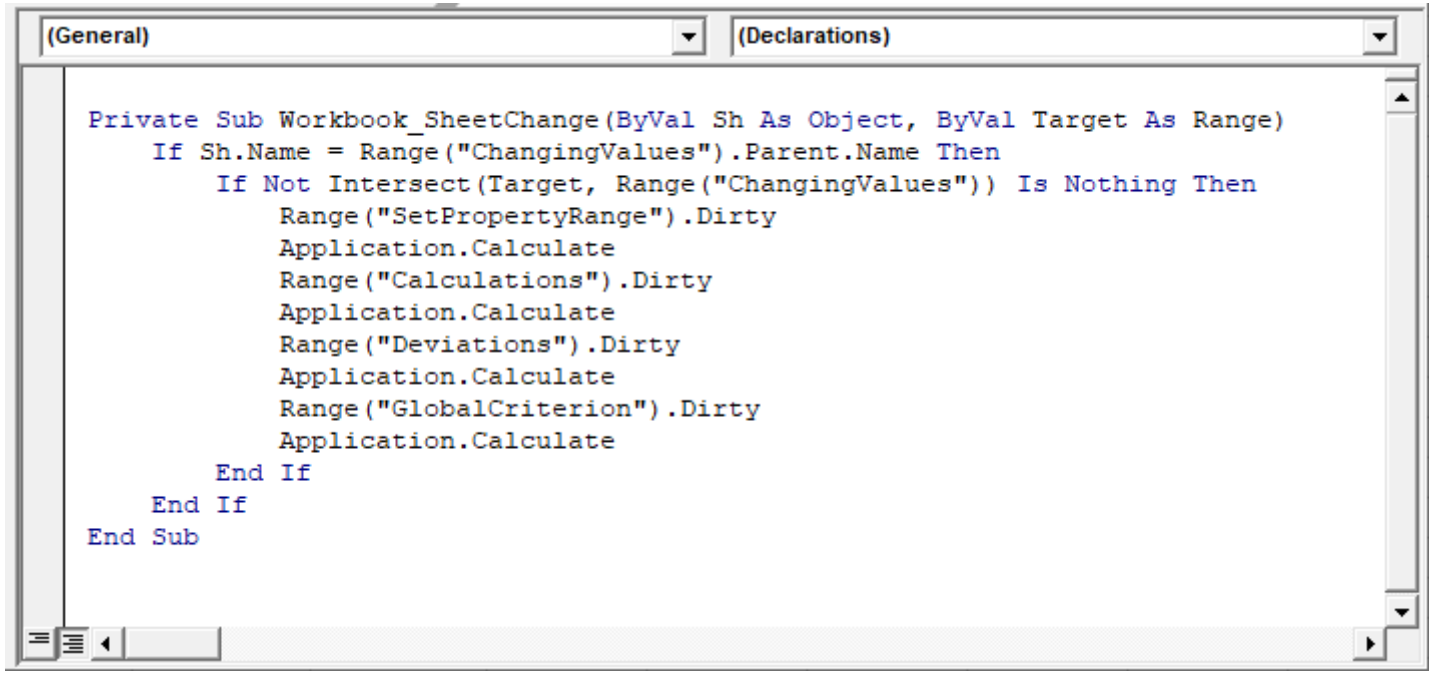
2- Regression of specific binary interaction parameters

- Step 7: Define the calculation sequence
  - Add a VBA macro (click on ALT+F11)
    - Define the order of calculation with the named cells defined previously
    - Once a value of the working table of the BIP is modified:
      - This property value is pasted in the compound
      - Flash calculation are done
      - Deviations are calculated
      - Global criterion is calculated



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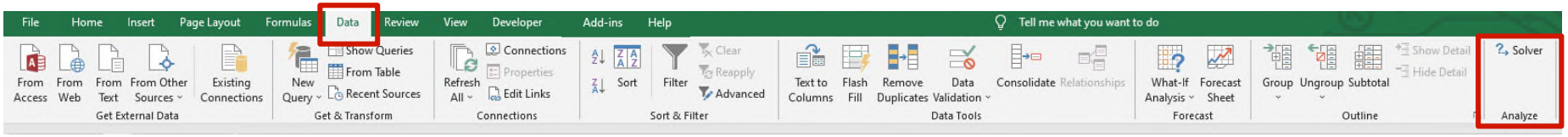
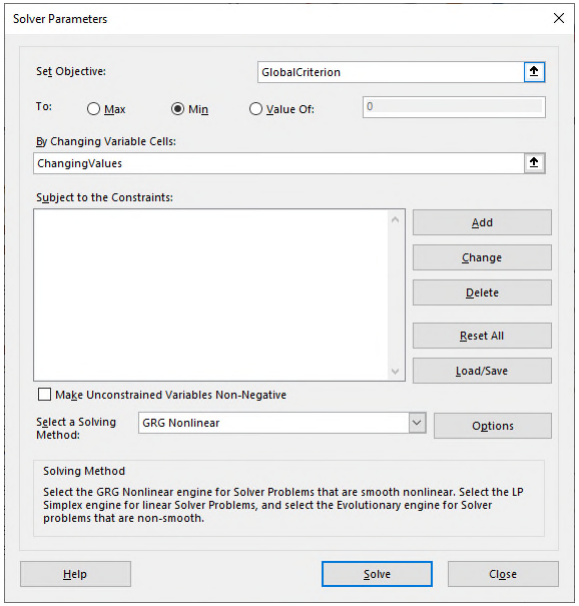
2- Regression of specific binary interaction parameters

- Step 8: Use of the solver
  - Access to the solver
    - “Data” menu, “Solver”



  - Parameters of the solver
    - Minimize global criterion (*GlobalCriterion*)
    - Modifying the table of the BIP (*ChangingValues*)



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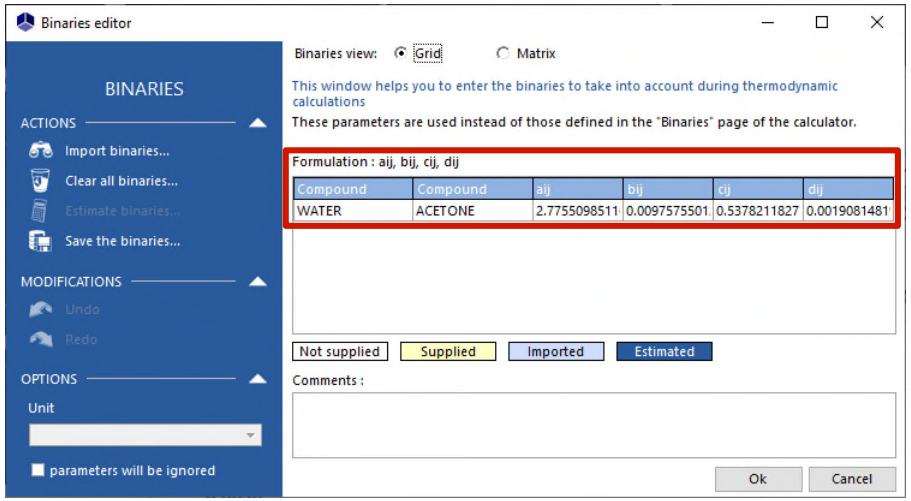
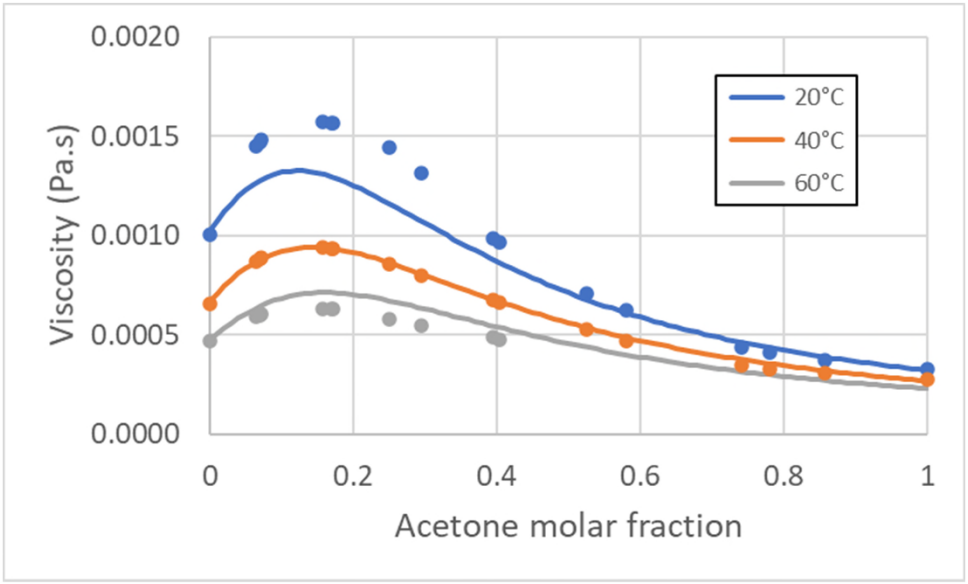
2- Regression of specific binary interaction parameters

- Results
  - Specific binary interaction parameters are obtained to represent the liquid viscosity of the mixture with the Andrade (mass) model



- Plot of the results, compared to experimental points



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3- Regression of binary interaction parameters for solid-liquid equilibria

- Binary interaction parameters (BIP) for solid-liquid equilibria
  - No Simulis function with the Kij extension exists for phase equilibria with solid
  - All types of binary interaction parameters are accessible:
    - *stCALSetBinariesValues(Name, ICode, Index1, Index2, Values)*

      to set values of binary interaction parameters

      (function available in the complementary SPI add-in)

      With:

      Name : Name of the calculator

      ICode : Code of the thermodynamic property

      Index1 : Vector of index for component 1

      Index2 : Vector of index for component 2

      Values : Values of binary interaction parameters

Note: In the case of a system with 2 components, each vector of index contains only 1 cell

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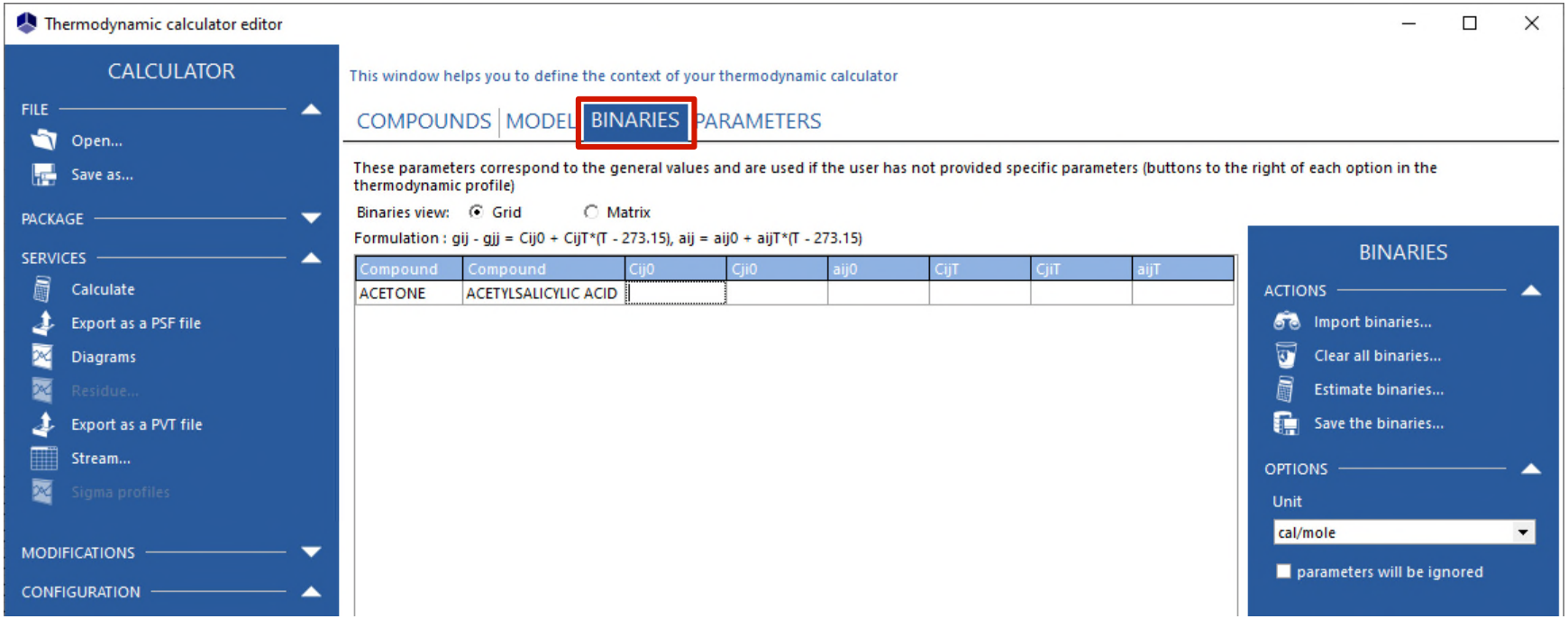
3- Regression of binary interaction parameters for solid-liquid equilibria

- Binary interaction parameters (BIP) for solid-liquid equilibria
  - Access to available thermodynamic code: ICode=-1

Name used in SPI add-in	ICode	Description
CodeBinGlobal	-1	Global BIP

  - ICode=-1 directly corresponds to parameters located in the “BINARIES” tab of the calculator:



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3- Regression of binary interaction parameters for solid-liquid equilibria

- Binary interaction parameters (BIP) for solid-liquid equilibria
  - Example: Regress NRTL binary interaction parameters tor represent the solubility of aspirin in acetone

    Reference: G.D. Maia, M. Giulietti, "Solubility of Acetylsalicylic Acid in Ethanol, Acetone, Propylene Glycol, and 2-Propanol", J. Chem. Eng. Data, 53 (1), 256-258 (2008)

- Steps to build the Excel file
  - 1- Define the calculator
  - 2- Choice of units
  - 3- Available experimental data
  - 4- Thermodynamic calculations
  - 5- Define the deviation minimization criterion between experimental data and the model
  - 6- Working table of properties to be regressed
  - 7- Define the calculation sequence
  - 8- Use of the solver

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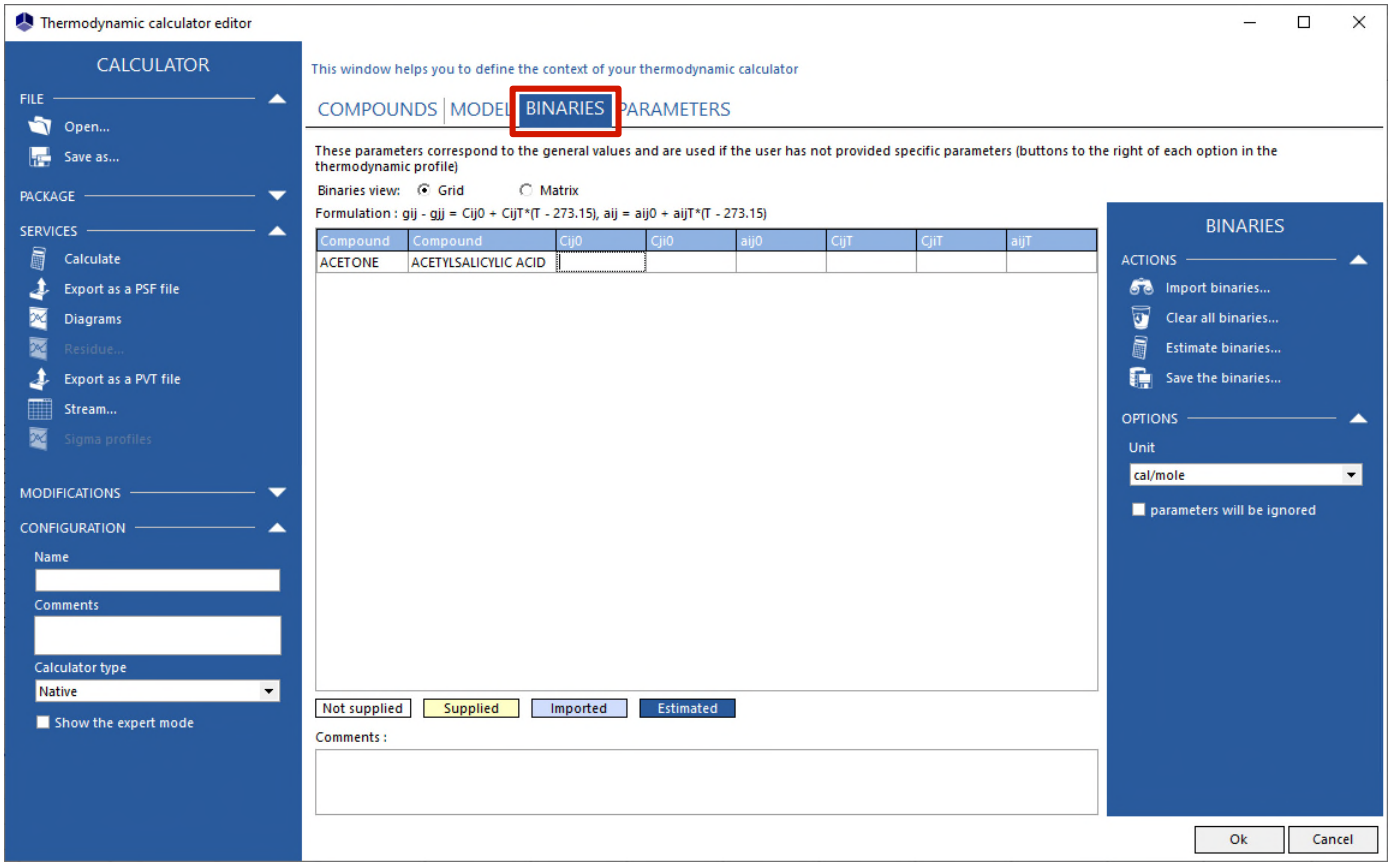
3- Regression of binary interaction parameters for solid-liquid equilibria

- Step 1: Define the calculator
  - Import components ACETONE, ACETYLSALICYLIC ACID
  - Choose NRTL thermodynamic profile
  - Access to global binary interaction parameters, “BINARIES” tab



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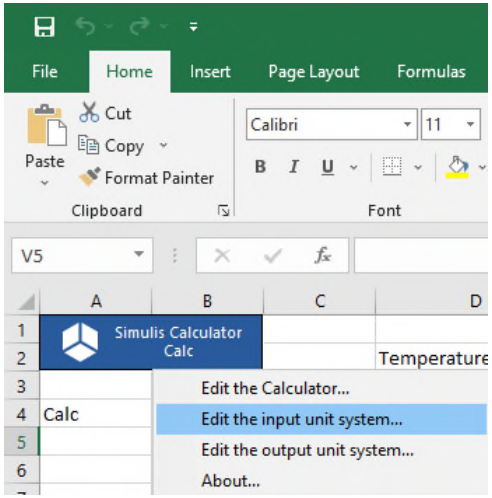
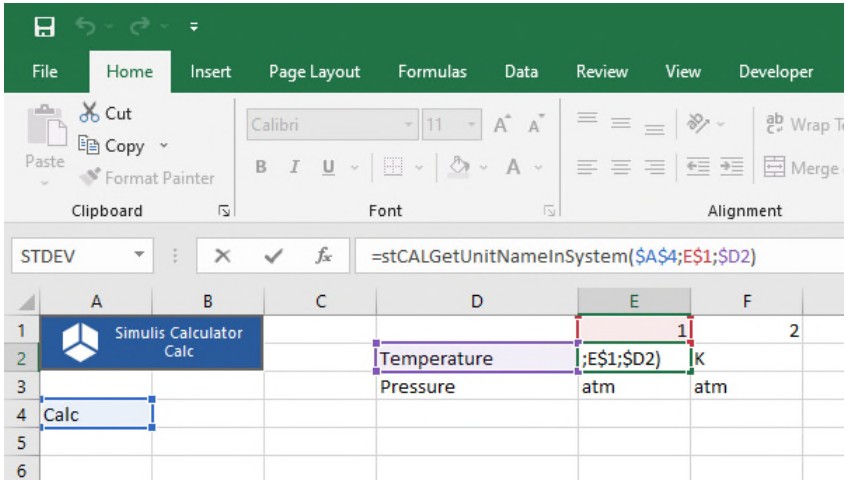
3- Regression of binary interaction parameters for solid-liquid equilibria

- Step 2: Choice of units
  - Right-click on the calculator object
    - Edit the input unit system
    - Edit the output unit system
    - Choose "K" for temperature, "atm" for pressure
  - Visualize the units used in the Excel worksheet
    - Simulis function: *stCALGetUnitNameInSystem()*





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3- Regression of binary interaction parameters for solid-liquid equilibria

- Step 3: Available experimental data
  - Enter experimental solubility available for the system (Maia *et al.*, 2008)
    - Pressure
    - Temperatures
    - Solubilities (molar fractions)

	A	B	C	D
1	Simulis Calculator Calc			
2				Temperature
3				Pressure
4	Calc			
5				
6				
7			1	ACETONE
8			2	ACETYLSALICYLIC ACID
9				
10			P (atm)	1
11				
12				
13		*Experimental Data*		
14		T (K)	x	
15		281.9	0.061	
16		290.6	0.075	
17		297.9	0.088	
18		304.4	0.101	
19		310.6	0.114	
20		315.3	0.127	
21		319.8	0.139	
22		323.3	0.151	
23		326.3	0.162	
24				

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3- Regression of binary interaction parameters for solid-liquid equilibria

- Step 4: Thermodynamic calculations
  - Vapor-liquid-solid equilibrium calculation at given temperature and pressure
    - Simulis function: *stCALFslvTP()*
    - Results as a vector (3*NC+3=9 cells, for 2 components):
      - Solid ratio
      - Liquid ratio
      - Vaporization ratio
      - Fractions (molar or mass) in solid phase
      - Fractions (molar or mass) in liquid phase
      - Fractions (molar or mass) in vapor phase

STDEV =stCALFslvTP(A4;B15;D10;E15:F15)

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	Simulis Calculator Calc				1	2										
2				Temperature	K	K										
3				Pressure	atm	atm										
4	Calc															
5																
6									Cij0	Cji0	aij0	CijT	CjiT	ajiT		
7			1	ACETONE				BIP	-1191.817586	2611.388279	0.2	0	0	0		
8			2	ACETYLSALICYLIC ACID				ICode	-1							
9								Set	Updated							
10		P (atm)		1												
11																
12																
13		*Experimental Data*						*Simulis Thermodynamics Calculations*								
14		T (K)	x		z1	z2		Solid Ratio	Liquid Ratio	Vapor Ratio	xS1	xS2	xL1	xL2	yV1	yV2
15		281.9	0.061		0.5	0.5		);E15:F15)	0.532486104	0	0	1	0.93899164	0.06100836	0	0
16		290.6	0.075		0.5	0.5		0.459652373	0.540347627	0	0	1	0.92533024	0.07466976	0	0
17		297.9	0.088		0.5	0.5		0.451818946	0.548181054	0	0	1	0.91210741	0.08789259	0	0
18		304.4	0.101		0.5	0.5		0.44372252	0.55627748	0	0	1	0.898832	0.101168	0	0
19		310.6	0.114		0.5	0.5		0.43484769	0.56515231	0	0	1	0.88471725	0.11528275	0	0
20		315.3	0.127		0.5	0.5		0.427252621	0.572747379	0	0	1	0.87298523	0.12701477	0	0
21		319.8	0.139		0.5	0.5		0.419177934	0.580822066	0	0	1	0.86084884	0.13915116	0	0
22		323.3	0.151		0.5	0.5		0.412285726	0.587714274	0	0	1	0.85075354	0.14924646	0	0
23		326.3	0.162		0.5	0.5		0.405903212	0.594096788	0	0	1	0.84161371	0.15838629	0	0
24																

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3- Regression of binary interaction parameters for solid-liquid equilibria

- Step 5: define the minimization criterion between experimental data and the model
  - Deviation function between experimental solubility and calculated solubility:

$$\%\mathrm{AARD} = \frac{100}{N_p} \sum_{i=1}^{N_p} \frac{\left| x_{2i}^{exp} - x_{2i}^{calc} \right|}{x_{2i}^{exp}}$$

With:

- % AARD : Average Absolute Relative Deviation
- N_p : Number of experimental points
- x_{2i}^{exp} : Experimental solubility of aspirin (molar fraction)
- x_{2i}^{calc} : Calculated solubility of aspirin (molar fraction)

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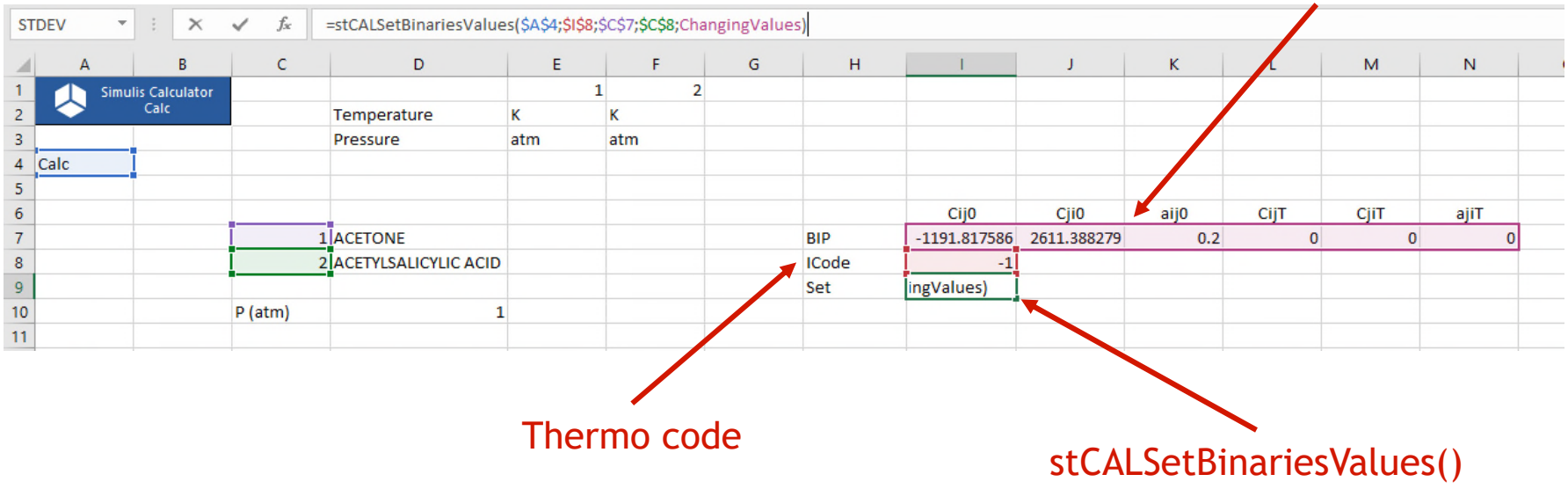
3- Regression of binary interaction parameters for solid-liquid equilibria

- Step 6: Working table of properties to be regressed
  - Values of NRTL binary interaction parameters
    - a_{ij}^0 is fixed to 0.2, only C_{ij}^0 and C_{ji}^0 will be identified
    - Initial (e. g. -1000; 1000), then modified after regression
  - Code of global BIP
    - ICode=-1
  - Copy BIP values in the calculator
    - Use of SPI Simulis function: *stCALSetBinariesValues()*
    - Result of this function is “Updated”



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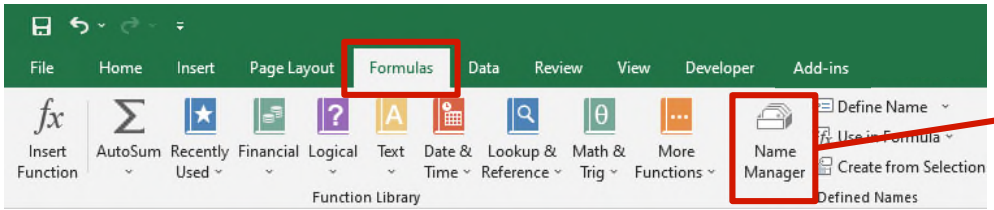
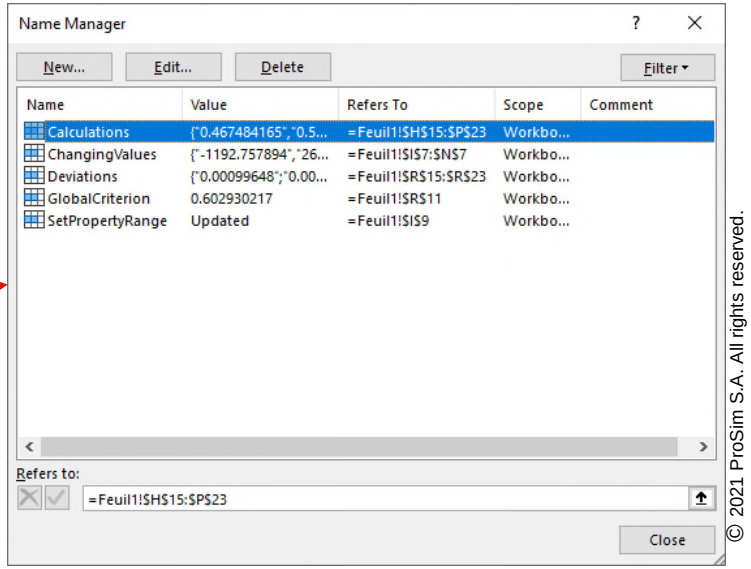
3- Regression of binary interaction parameters for solid-liquid equilibria

- Step 7: Define the calculation sequence
  - Name the cells, e. g. :
    - “ChangingValues” for the BIP table (cells I7 to N7)
    - “SetPropertyRange” for the copy of the values of the properties in the calculator (cell I9)
    - “Calculations” for properties calculations (cells H15 to P23)
    - “Deviations” for deviations calculations (cells R15 to R23)
    - “GlobalCriterion” for the criterion to be minimized (cell R11)
  - Access to named cells:
    - “Formulas” menu, “Name Manager”





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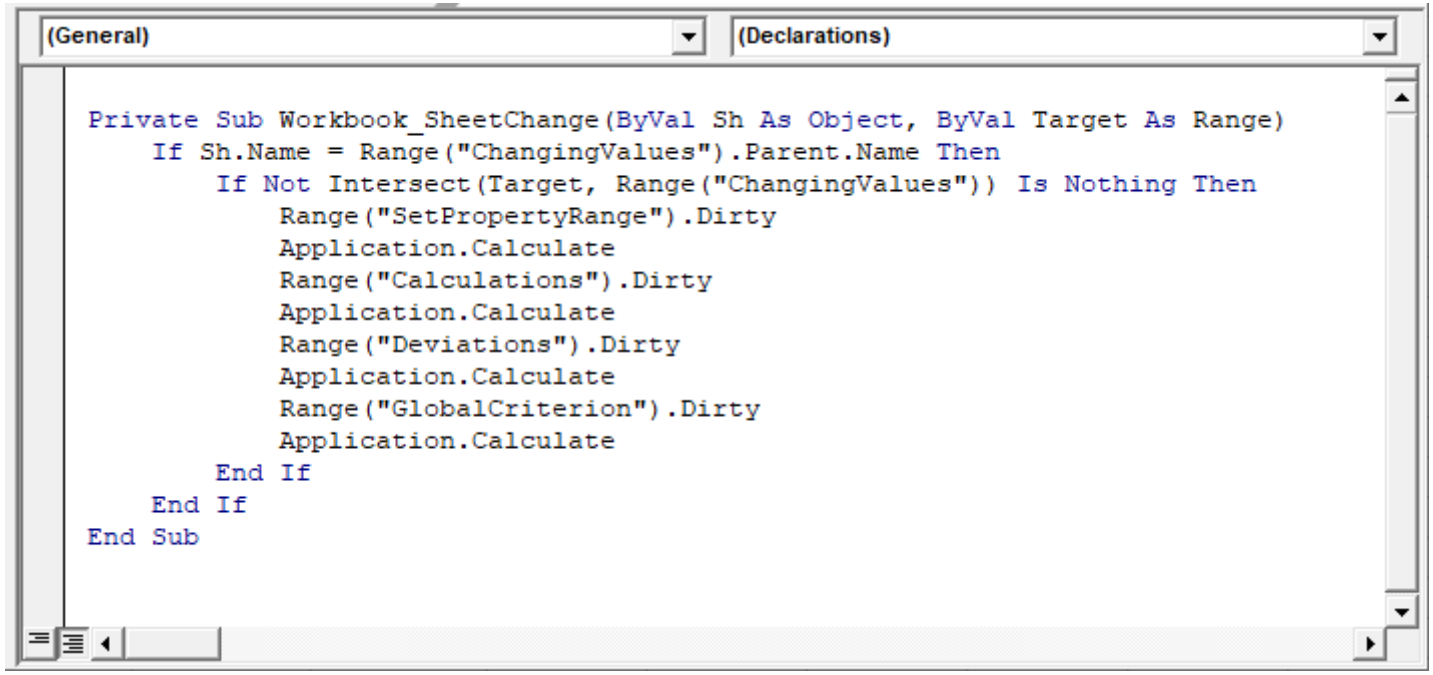
3- Regression of binary interaction parameters for solid-liquid equilibria

- Step 7: Define the calculation sequence
  - Add a VBA macro (click on ALT+F11)
    - Define the order of calculation with the named cells defined previously
    - Once a value of the working table of the BIP is modified:
      - This property value is pasted in the compound
      - Flash calculation are done
      - Deviations are calculated
      - Global criterion is calculated



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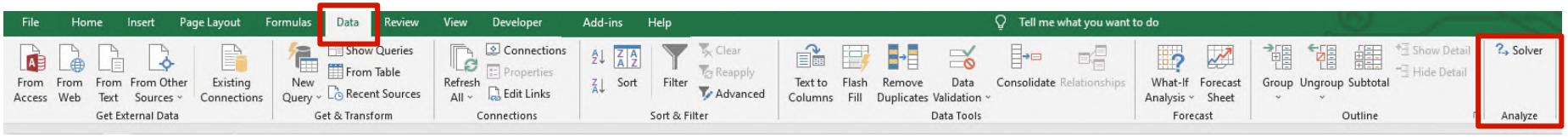
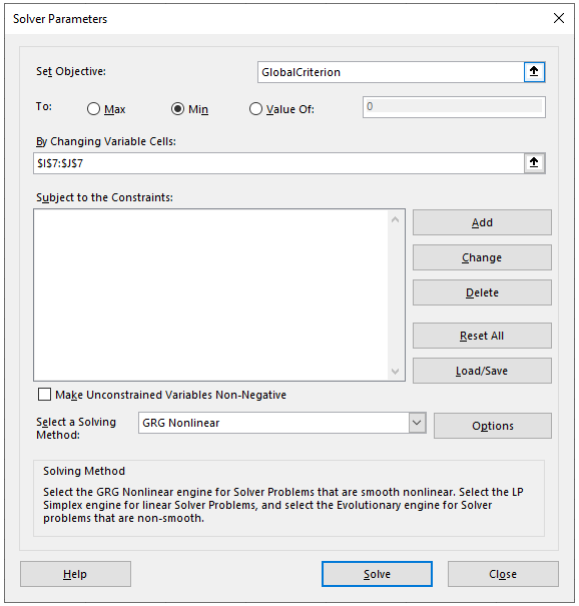
3- Regression of binary interaction parameters for solid-liquid equilibria

- Step 8: Use of the solver
  - Access to the solver
    - o “Data” menu, “Solver”



  - Parameters of the solver
    - o Minimize global criterion (*GlobalCriterion*)
    - o Modifying the C_{ij}^0 and C_{ji}^0 parameters (*I7 and J7*)



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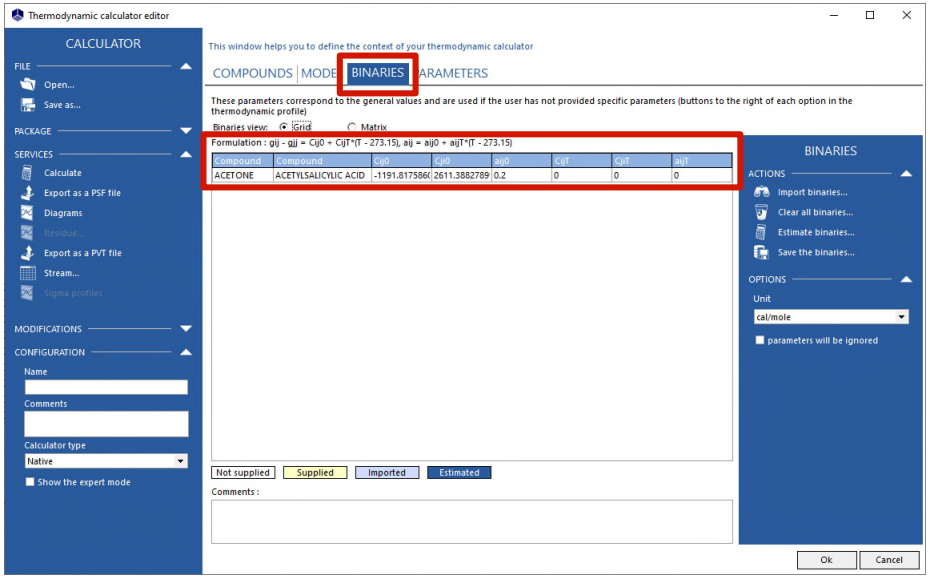
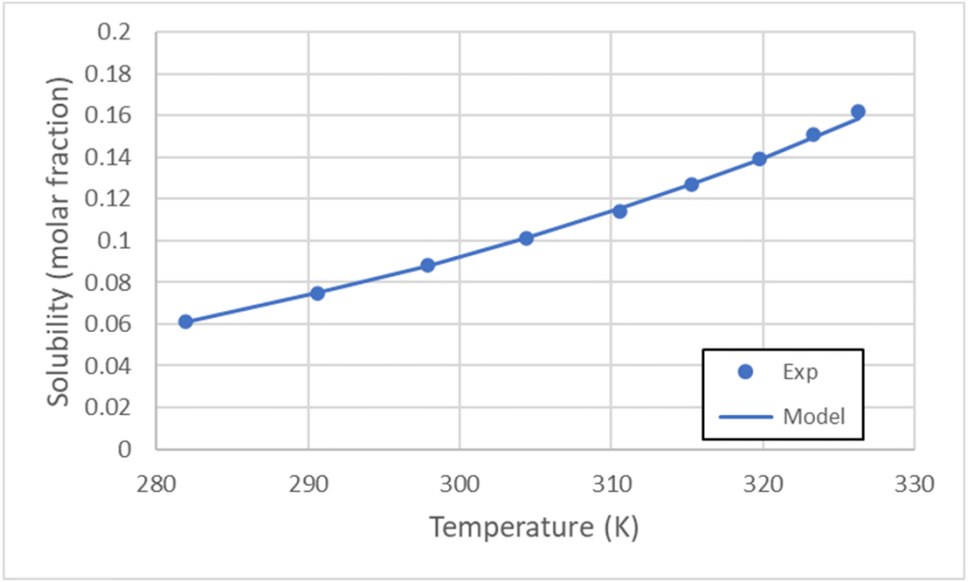
3- Regression of binary interaction parameters for liquid-solid equilibria

- Results
  - NRTL binary interaction parameters are obtained to represent the solubility of aspirin in acetone



- Plot of the results, compared to experimental points



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