

# Getting started with Simulis® Thermodynamics

## Use Case 15: Parameter identification with MS Excel

Software & Services In Process Simulation

*We guide You to efficiency*



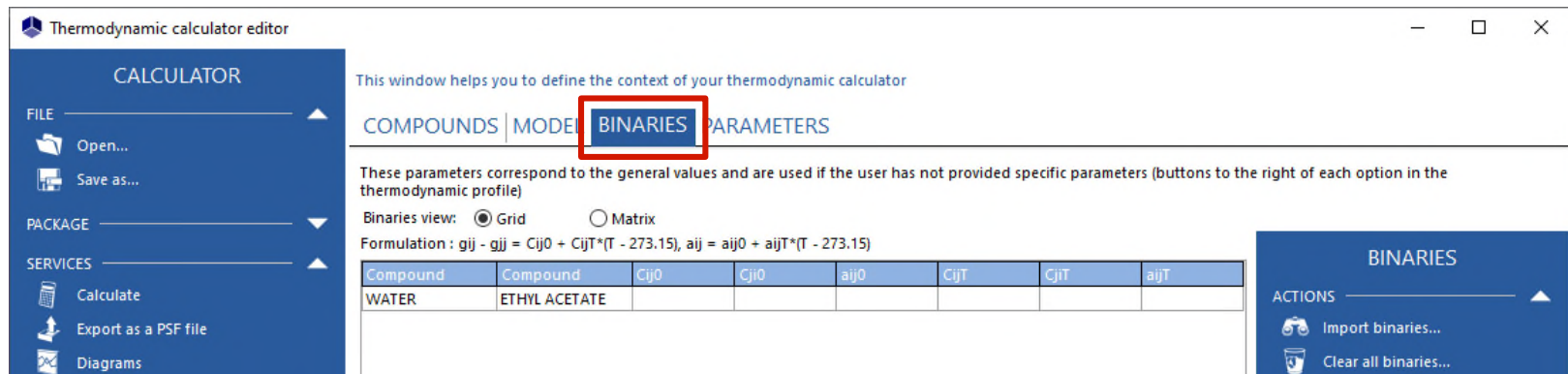
ProSim

# 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*

# Introduction

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

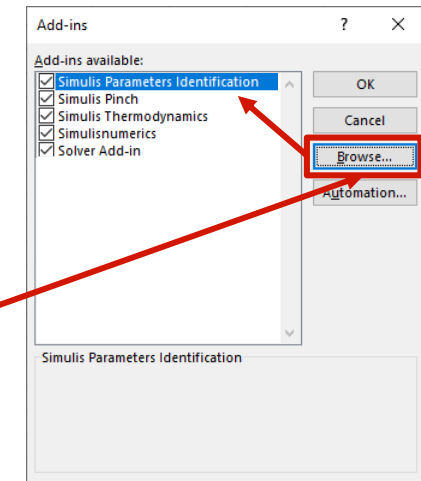
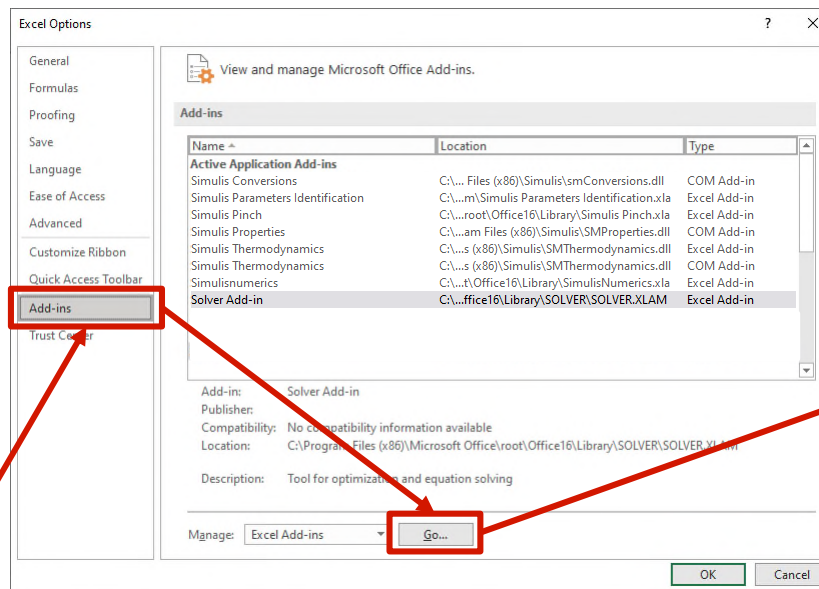
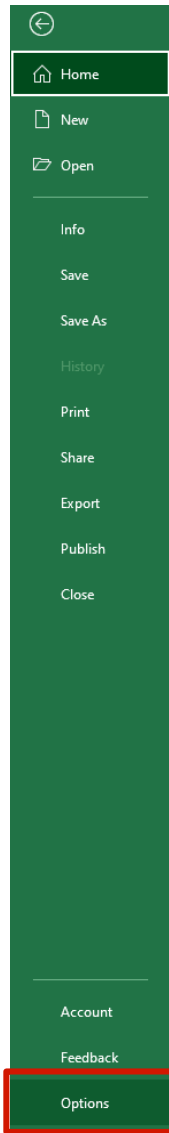
- 1- Pure components properties
- 2- Specific binary interaction parameters (BIP)
- 3- Binary interaction parameters (BIP) for solid-liquid equilibria

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

# 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



# 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)



# 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](#)

# 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

Name: [New compound]  
ID: {CD780867-9C9E-4B89-960C-FADEBE3B01E6}  
Original ID:  
Original location: \\

? About properties...

Complete	Properties	Value
+	Identification	
+	Group contribution models	
+	Atomic	
+	Phase change	
	Normal melting point	
	Normal boiling point	
	Enthalpy of fusion (melting point)	
	Triple point temperature	
	Triple point pressure	
	Physical state at 25°C	< unknown >
	Physical state in aqueous solution at 25°C	< unknown >
	Diffusion coefficient	
	Enthalpy of vaporization (boiling point)	
	Octanol-Water partition coefficient	< unknown >
	soil sorption coefficient (Koc@20°C)	
	Liquid vapor calculation type	< unknown >
	Acentric factor	< unknown >
	Modified acentric factor	< unknown >
	Critical temperature	
	Critical pressure	
	Critical volume	
	Critical compressibility factor	< unknown >
	Critical density	
	Heat of sublimation at the triple point	
	Glass-transition temperature	
+	Combustion, security, toxicity	
+	Condensed phase	
+	Phase thermochemistry	
+	Interaction, gas phase reaction	
+	User properties	
+	PPC-SAFT	
+	NRTL-SAC	
	Number of hydrophobic segments type (X)	< unknown >
	Number of hydrophilic segments type (Z)	< unknown >
	Number of polar segments type (Y-)	< unknown >
	Number of polar segments type (Y+)	< unknown >
+	CPA	
+	Polymers-Segments	
+	Sanchez-Lacombe	
+	Temperature dependent properties	

# 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

The screenshot illustrates the steps to access the Simulis identifiers window. In the background, the Excel ribbon is visible with the 'Simulis' menu highlighted. The 'Simulis' dropdown menu is open, and the 'Help' option is selected, which has opened a sub-menu. In this sub-menu, 'Help on Simulis identifiers' is highlighted. A red arrow points from this option to the 'Simulis identifiers' window in the foreground. In this window, the 'Compound properties' tab is selected under the 'Quantity' section. Another red arrow points from the 'Help on Simulis identifiers' option to this tab. The window displays a list of properties and their corresponding identifiers.

Name	Identifier
<b>Atomic</b>	
1st ionization energy	pidFirstIonizationEnergy()
2nd ionization energy	pidSecondIonizationEnergy()
Atomic radius	pidAtomicRadius()
Born Constant	pidBornConstant()
Born radius	pidBornRadius()
Charge	pidCharge()
Dielectric constant	pidDielectricConstant()
Diffusion volume	pidVdiff()
Dipole moment	pidMu()
Flory-Huggins degree of polymerization (P)	pidFloryHugginsPolymerizationDegree()
Flory-Huggins empirical parameter (eps)	pidFloryHugginsEmpiricalParameter2()
Flory-Huggins empirical parameter (s)	pidFloryHugginsEmpiricalParameter1()
Lennard-Jones energy	pidLJpsi()
Lennard-Jones length	pidLJr()
Modified Van der Waals area	pidQIP()
Molecular weight	pidMw()
Pauling Radius	pidPaulingRadius()

Buttons: Copy, Close



# 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

# 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)

**Thermodynamic calculator editor**

**CALCULATOR**

FILE: Open..., Save as...

PACKAGE: [Dropdown]

SERVICES: Calculate, Export as a PSF file, Diagrams, Residue, Export as a PVT file, Stream..., Sigma profiles

MODIFICATIONS: [Dropdown]

CONFIGURATION: [Dropdown]

Name: [Text field]

Comments: [Text field]

Calculator type: Native [Dropdown]

☒ Show the expert mode

**COMPOUNDS**

IUPAC Name	CAS Registry Number
1 CAFFEINE	58-08-2
2 WATER	7732-18-5
3 METHANOL	67-56-1
4 ETHANOL	64-17-5
5 1-PROPANOL	71-23-8
6 ETHYL ACETATE	141-78-6
7 ACETONE	67-64-1

**Compound Editor**

This window helps you visualize the compounds properties.

Properties: Complete

Properties	CAFFEINE	WATER	METHANOL	ETHANOL	1-PROPANOL	ETHYL ACETATE	ACETONE
Identification							
Group contribution models							
Atomic							
Phase change							
Combustion, security, toxicity							
Condensed phase							
Phase thermochemistry							
Interaction, gas phase reaction							
User properties							
PPC-SAFT							
NRTL-SAC							
Number of hydrophobic segments type (X)	<unknown>	0	0.09	0.251	0.374	0.339	0.131
Number of hydrophilic segments type (Z)	<unknown>	1	0.594	0.63	0.53	0	0
Number of polar segments type (Y-)	<unknown>	0	0.139	0.03	0.013	0.058	0.109
Number of polar segments type (Y+)	<unknown>	0	0	0	0	0.441	0.513
CPA							
Polymers-Segments							
Sanchez-Lacombe							
Temperature dependent properties							

CAS Registry Numbers® are the intellectual property of the American Chemical Society; and are used by ProSim SA with the express permission of ACS. CAS Registry Numbers® have not been verified by ACS and may be inaccurate.

Ok Cancel

**Editor array**

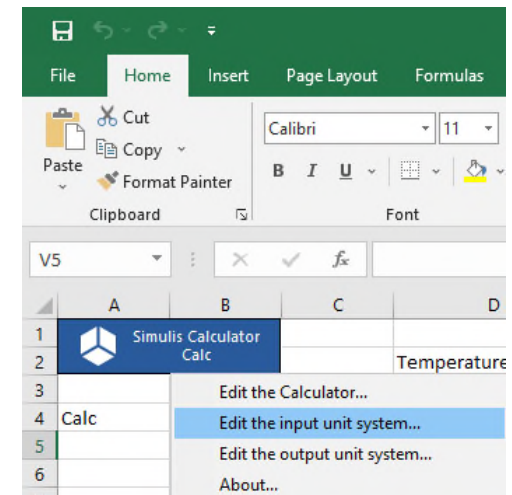
NRTL-SAC parameters for caffeine are unknown

# 1- Pure component properties identification

## ■ Step 2: Choice of units

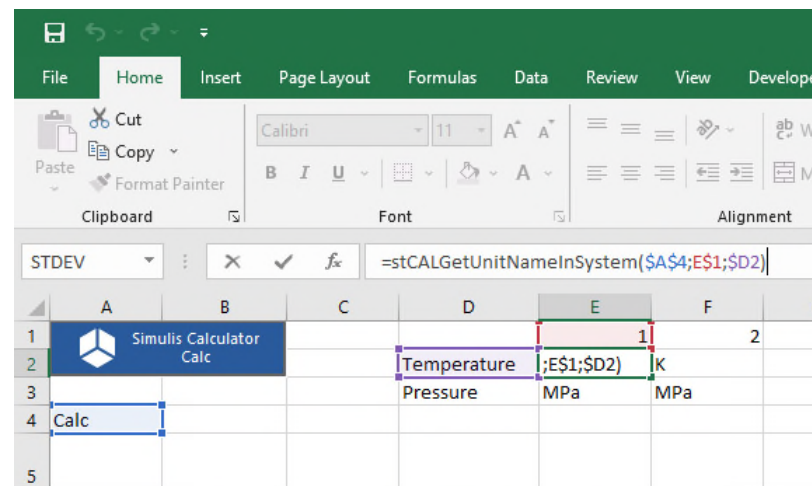
- Right-click on the calculator object

- 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()`



# 1- Pure component properties identification

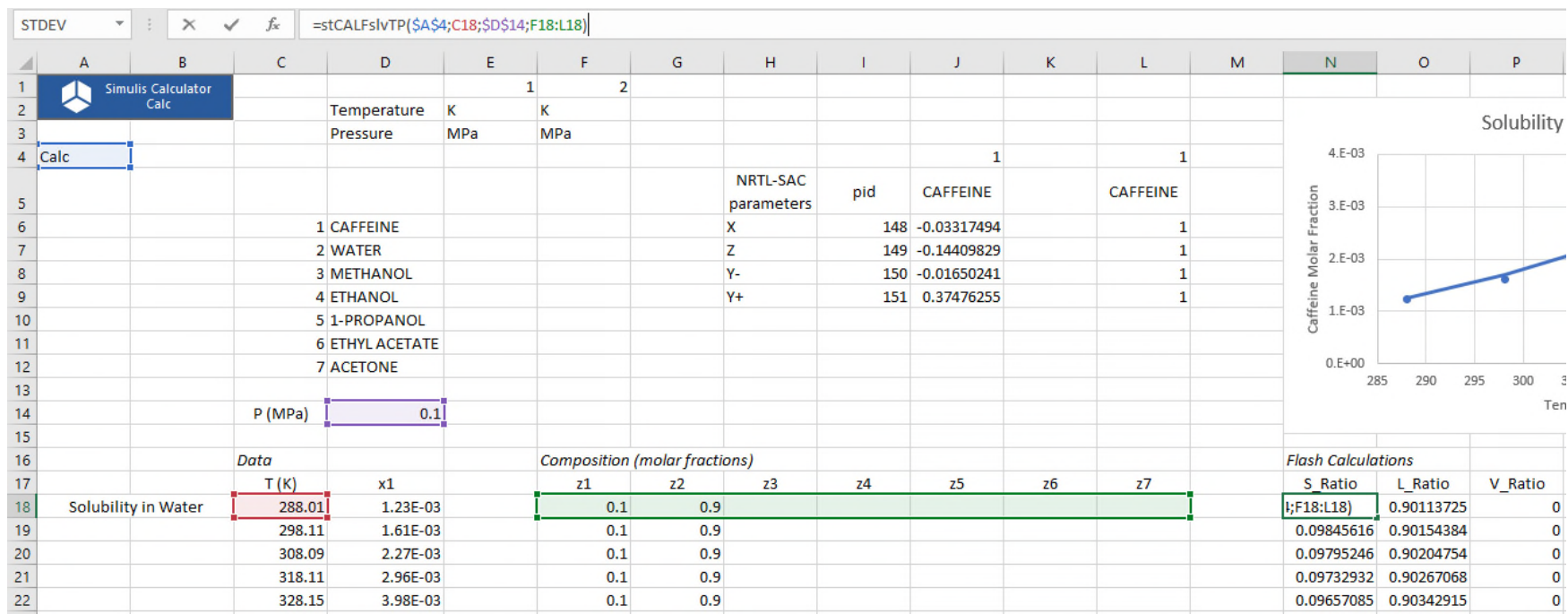
- Step 3: Available experimental data
  - Enter experimental solubilities available for each solvent (Zhong *et al.*, 2017)
    - Pressure
    - Temperatures
    - Solubilities (molar fractions)

	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	



# 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 ( $3 \cdot NC + 3 = 24$  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





# 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:

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

With:

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

# 1- Pure component properties identification

- Step 6: Working table of properties to be regressed
  - pid of NRTL-SAC parameters
    - X : pidHydrophobicSegmentCount()
    - Z : pidHydrophilicSegmentCount()
    - Y<sup>-</sup> : pidPolarYMinusSegmentCount()
    - Y<sup>+</sup> : 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”

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Simulis Calculator Calc				1	2							
2				Temperature	K	K							
3				Pressure	MPa	MPa							
4	Calc									1		1	
5								NRTL-SAC parameters	pid	CAFFEINE		CAFFEINE	
6				1 CAFFEINE				X	148	-0.03317494		4;\$I6;\$J6	
7				2 WATER				Z	149	-0.14409829			1
8				3 METHANOL				Y-	150	-0.01650241			1
9				4 ETHANOL				Y+	151	0.37476255			1
10				5 1-PROPANOL									
11				6 ETHYL ACETATE									
12				7 ACETONE									

pid NRTL-SAC parameters

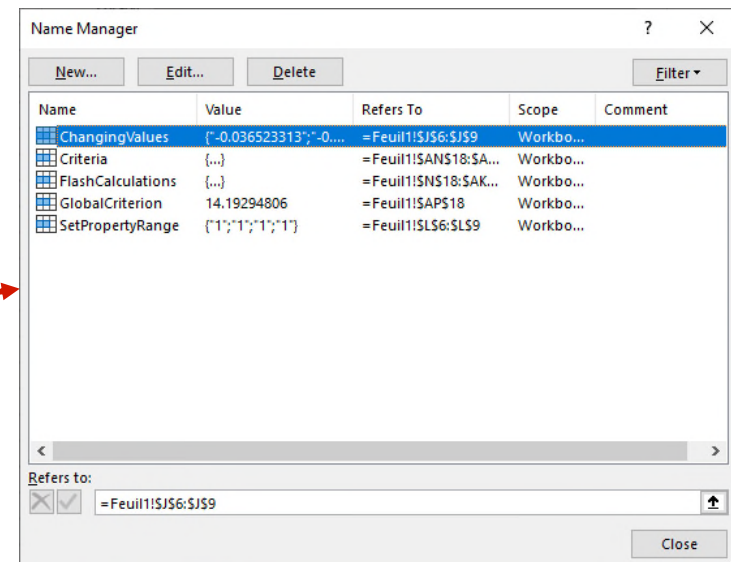
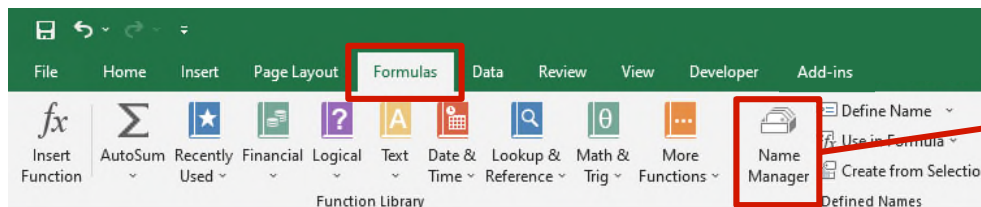
NRTL-SAC parameters Values

stCALSetProperty()

# 1- Pure component properties identification

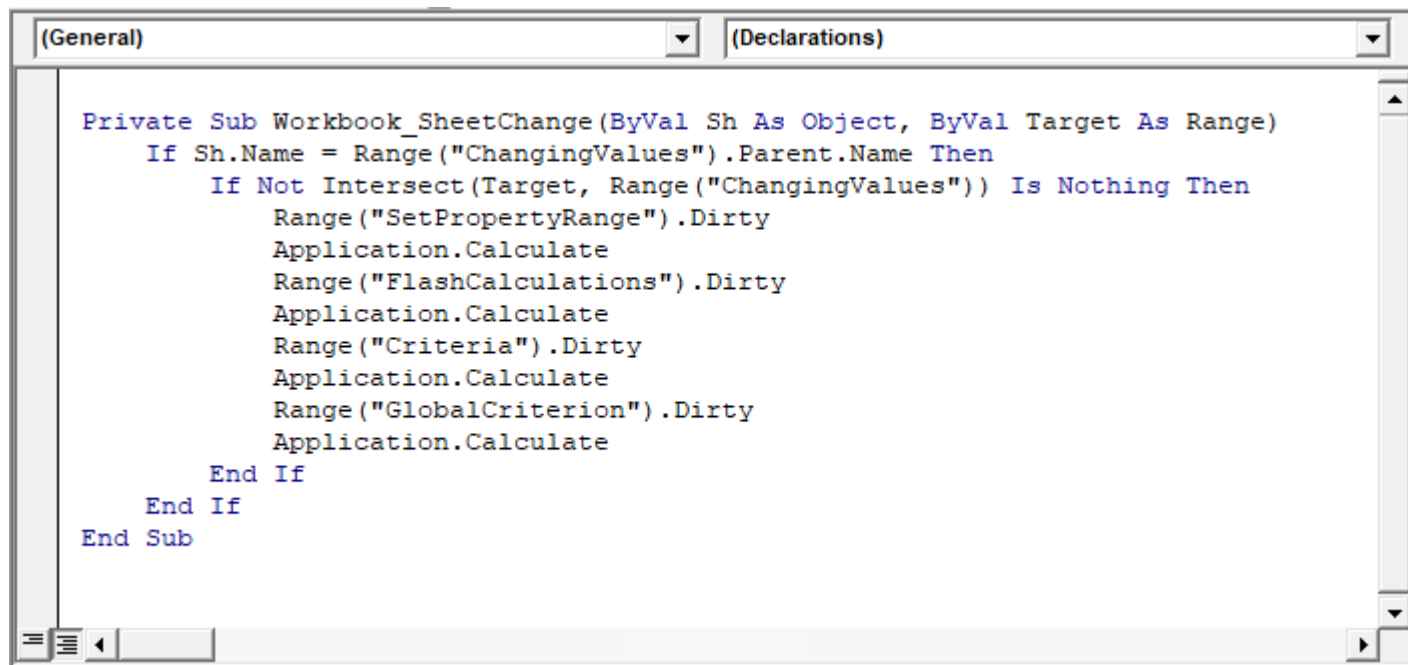
## ■ Step 7: Define the calculation sequence

- 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”



# 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

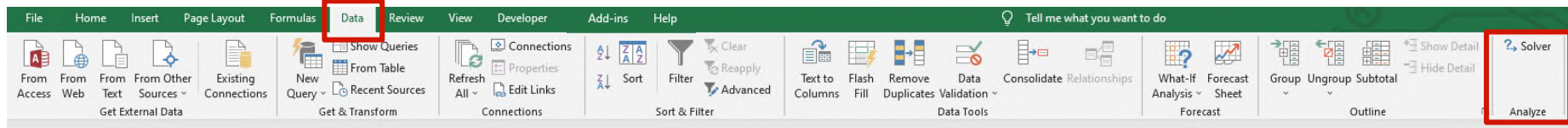


The screenshot shows the VBA Editor window with the 'Declarations' tab selected. It contains a VBA macro named 'Workbook\_SheetChange' that triggers when a cell in the 'ChangingValues' range is edited. The macro performs a series of calculations and updates in a specific order: it marks the 'SetPropertyRange' as dirty and calculates, then the 'FlashCalculations' range, then the 'Criteria' range, and finally the 'GlobalCriterion' range, each time marking it as dirty and calculating. The macro is enclosed in a 'Private Sub' and 'End Sub' block, with 'If' and 'End If' statements for conditional execution.

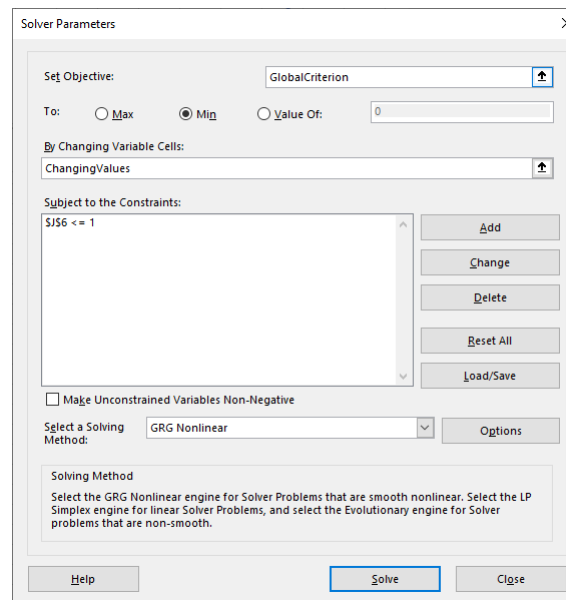
```
Private Sub Workbook_SheetChange(ByVal Sh As Object, ByVal Target As Range)
    If Sh.Name = Range("ChangingValues").Parent.Name Then
        If Not Intersect(Target, Range("ChangingValues")) Is Nothing Then
            Range("SetPropertyRange").Dirty
            Application.Calculate
            Range("FlashCalculations").Dirty
            Application.Calculate
            Range("Criteria").Dirty
            Application.Calculate
            Range("GlobalCriterion").Dirty
            Application.Calculate
        End If
    End If
End Sub
```

# 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*)





# 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

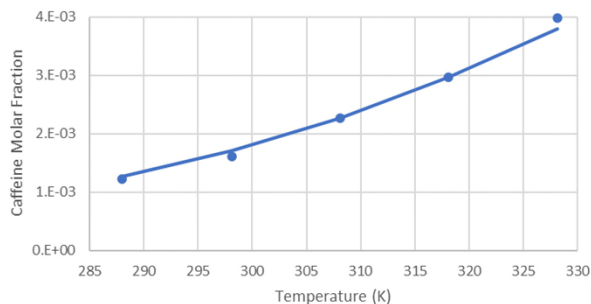
Original location: Simulis® Compounds Files\Common files\Standard 2017

About properties...

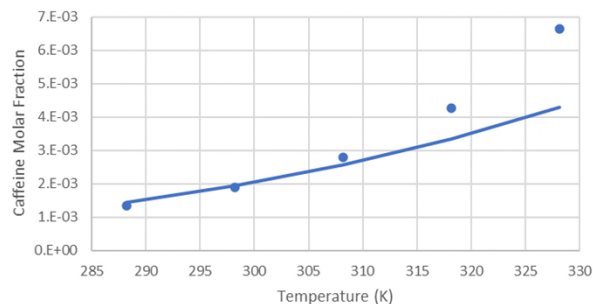
Complete

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

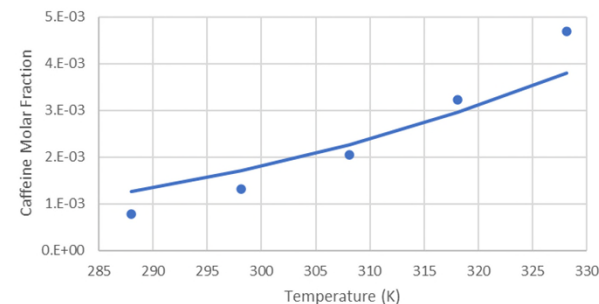
Solubility in Water



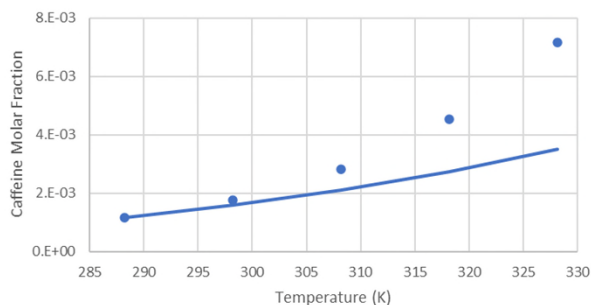
Solubility in Methanol



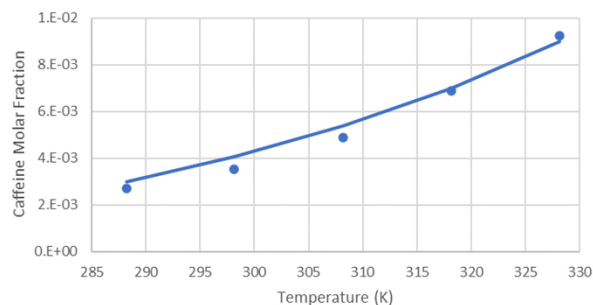
Solubility in Ethanol



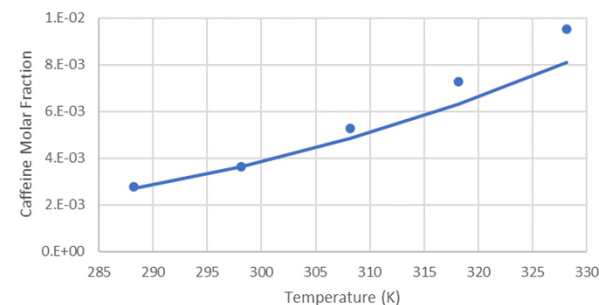
Solubility in 1-Propanol



Solubility in Ethyl Acetate



Solubility in Acetone



## 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

Thermodynamic calculator editor

This window helps you to define the context of your thermodynamic calculator

COMPOUNDS MODEL BINARIES PARAMETERS

**CALCULATOR**

FILE

- Open...
- Save as...

PACKAGE

SERVICES

- Calculate
- Export as a PSF file
- Diagrams
- Residue...
- Export as a PVT file
- Stream...
- Sigma profiles

MODIFICATIONS

CONFIGURATION

Name

[New calculator]

Comments

Calculator type

Native

☐ Show the expert mode

Name

NRTL

Category

All the profiles

Profile

Approach type

From activity coefficients

Equation of state

RK Generalized

Alpha function

Soave

Mixing rules

Standard

Activity coefficient model

NRTL

Pure liquid fugacity standard state

Standard with Poynting correction

Liquid molar volume

Rackett/Campbell-Thodos

Transport properties

Mixed

Enthalpy calculation

H\*=0, ideal gas, 25°C, 1 atm

User-defined thermodynamic model

None

Model index

1

**THERMODYNAMIC MODEL**

CONFIGURATION

Parameters

Thermodynamic assistant

Thermodynamic help

☐ Use a specific model for pure water

Advanced

☐ Water-hydrocarbons model

Sol A

6.25043

Sol B

4015.3

☐ The liquid phase splitting is taken into account

Predictive model parameters...

☐ True species model

Reactive model parameters...

Polymers model parameters...

Ok

Cancel

**Transport properties options**

Liquid viscosity

Andrade (mass)

Gas viscosity

Classic methods

Liquid thermal conductivity

Classic methods

Gas thermal conductivity

Classic methods

Surface tension

Dutcher

Ok

Cancel

## 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**

## 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



## 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



## 2- Regression of specific binary interaction parameters

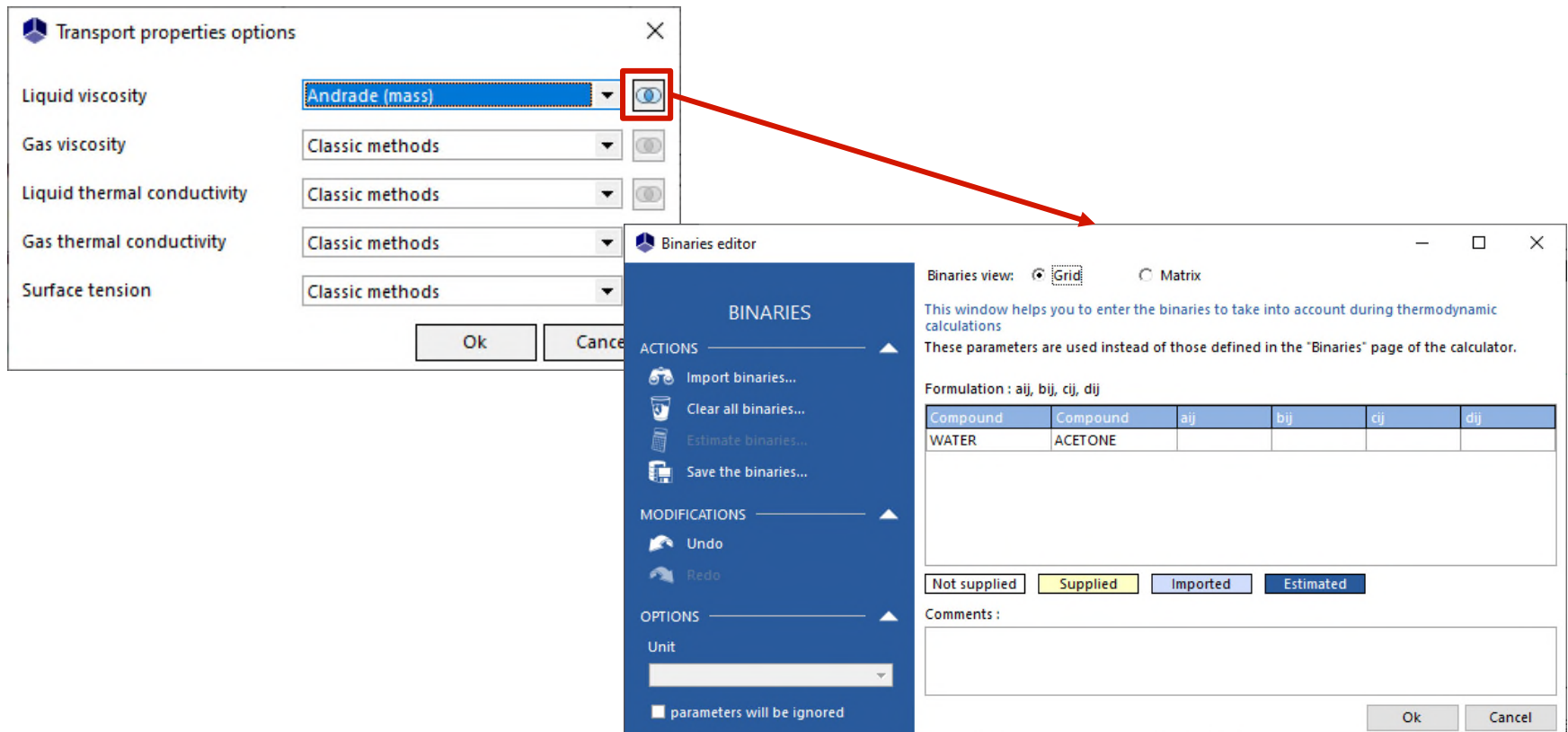
- Specific binary interaction parameters (BIP)
  - Example: Regress specific binary interaction parameters of Andrade model to represent viscosity of a water - acetone mixture

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

## 2- Regression of specific binary interaction parameters

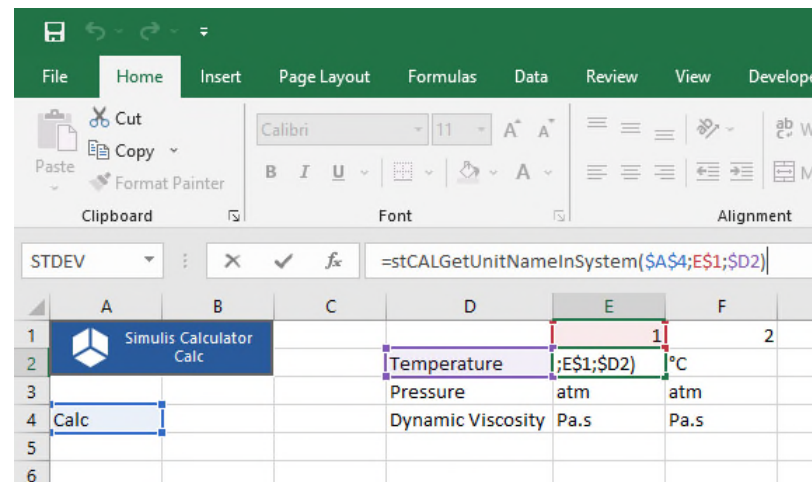
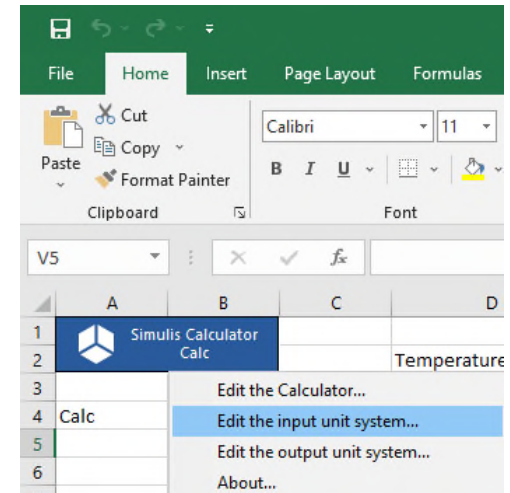
- Step 1: Define the calculator
  - Import components WATER, ACETONE
  - Choose NRTL thermodynamic profile
  - Import global BIP from the database in the “BINARIES” tab (phase equilibrium calculations)
  - For transport properties, choose Andrade (mass) for liquid viscosity



# 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()`



	A	B	C	D	E	F
1	Simulis Calculator				1	2
2				Temperature	°C	
3				Pressure	atm	atm
4	Calc			Dynamic Viscosity	Pa.s	Pa.s
5						
6						

# 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				1	2	
2	Calc			Temperature	°C	°C	
3				Pressure	atm	atm	
4				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							
17							
18							
19							
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37							
38							
39							



## 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

STDEV    X    ✓    f_x    =stCALMuL(\$A\$4;H\$18;D\$11;\$B19:\$C19)											
	A	B	C	D	E	F	G	H	I	J	K
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									aij	bij	cij
8			1 WATER					BIP	2.77550985	0.00975755	0.53782
9			2 ACETONE					ICode	10		
10								SetProperty	Updated		
11			P (atm)		1						
12											
13											
14											
15											
16		Experimental data						Simulis Calculation			
17				Temperature (°C)					Temperature (°C)		
18		Water	Acetone	20	40	60		20	40	60	
19		1	0	0.001002	0.000656	0.000469		319:\$C19)	0.00067111	0.00047421	
20		0.936	0.064	0.001447	0.000872	0.000594		0.00126525	0.00086759	0.00063421	
21		0.93	0.07	0.00147	0.000885	0.0006		0.00127793	0.00087933	0.00064456	
22		0.928	0.072	0.001479	0.000887	0.000603		0.00128179	0.00088299	0.00064783	
23		0.843	0.157	0.001569	0.000939	0.000632		0.00130785	0.000939	0.00071198	
24		0.83	0.17	0.001567	0.000933	0.00063		0.00129418	0.00093416	0.00071132	
25		0.828	0.172	0.001566	0.000932	0.000629		0.00129181	0.00093319	0.00071103	
26		0.749	0.251	0.001444	0.000855	0.00058		0.00115973	0.00086152	0.00067118	



## 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:

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

With:

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

## 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”

STDEV    X    ✓    f<sub>x</sub>    =stCALSetBinariesValues(\$A\$4;\$I\$9;\$C\$8;\$C\$9;\$I\$8:\$L\$8)

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Simulis Calculator				1	2							
2	Calc			Temperature	°C	°C							
3				Pressure	atm	atm							
4				Dynamic Viscosity	Pa.s	Pa.s							
5													
6													
7													
8			1	WATER				BIP	aij	bij	cij	dij	
9			2	ACETONE				ICode	2.77550985	0.00975755	0.53782118	0.001908148	
10								SetProperty	10				
11			P (atm)		1								
12													

BIP values to be regressed

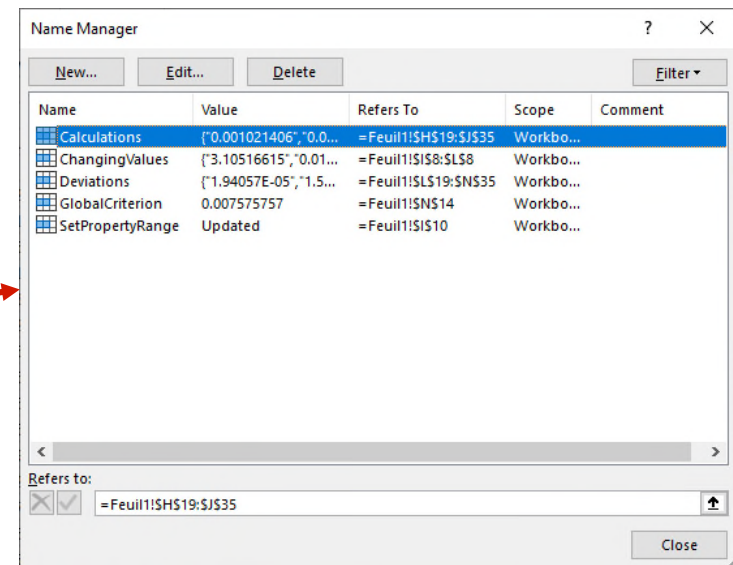
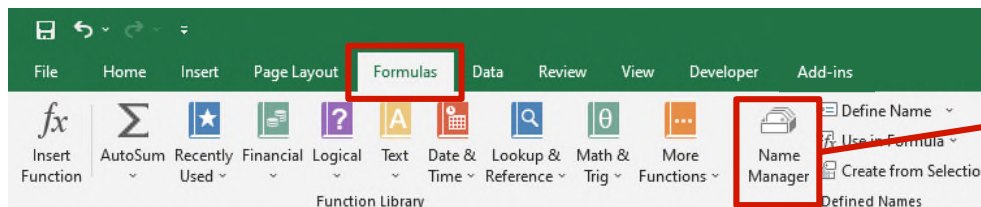
Thermo code

stCALSetBinariesValues()

## 2- Regression of specific binary interaction parameters

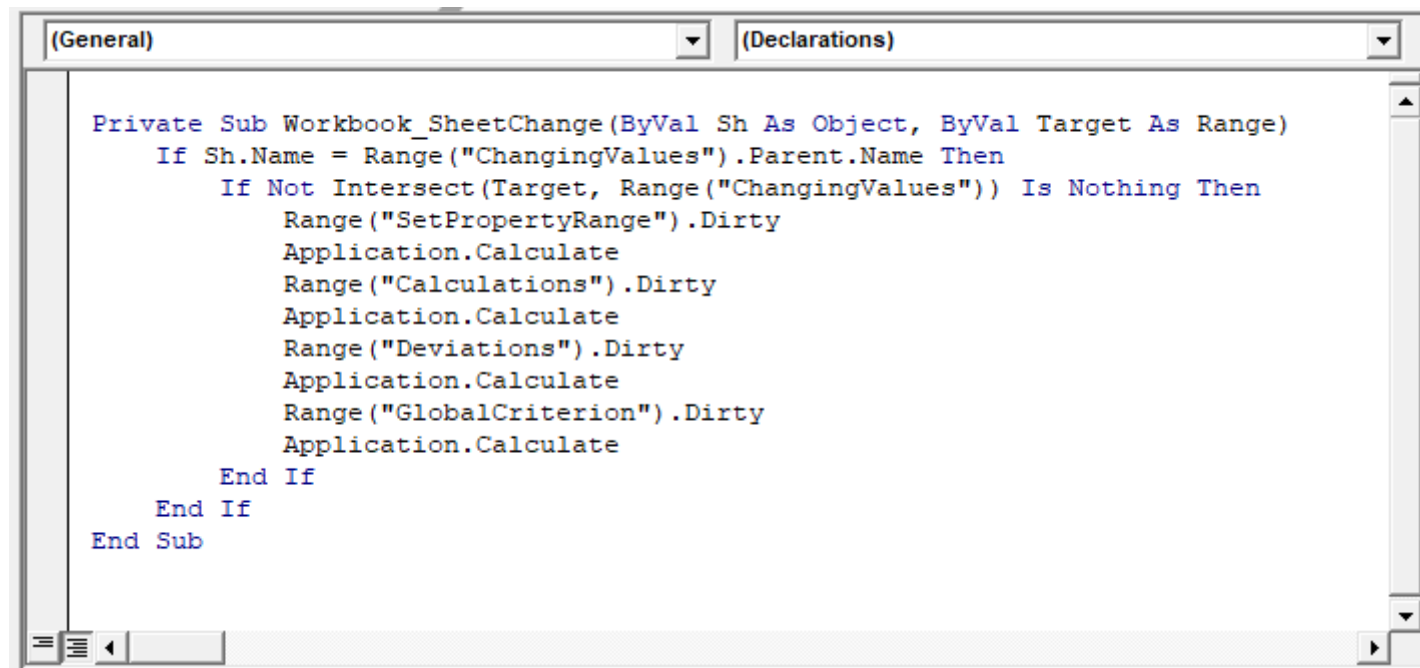
### ■ Step 7: Define the calculation sequence

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



## 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



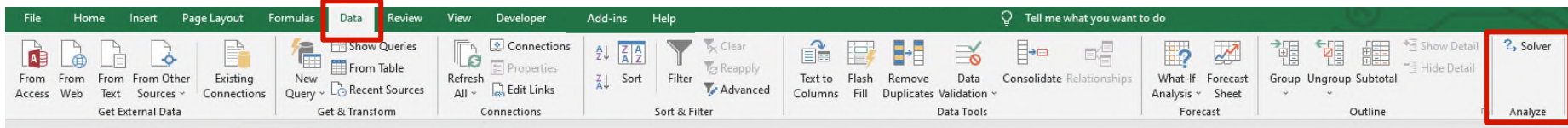
The screenshot shows the VBA Editor window with the 'Declarations' tab selected. It contains a VBA macro named 'Workbook\_SheetChange' that triggers when a cell in the 'ChangingValues' range is changed. The macro performs a series of calculations and updates in a specific order: it marks the 'SetPropertyRange' as dirty and calculates it, then marks 'Calculations' as dirty and calculates it, then marks 'Deviations' as dirty and calculates it, and finally marks 'GlobalCriterion' as dirty and calculates it.

```
(General) (Declarations)

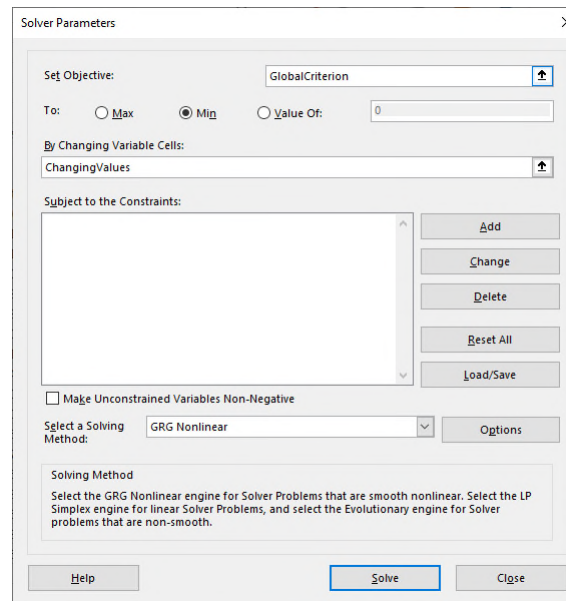
Private Sub Workbook_SheetChange(ByVal Sh As Object, ByVal Target As Range)
    If Sh.Name = Range("ChangingValues").Parent.Name Then
        If Not Intersect(Target, Range("ChangingValues")) Is Nothing Then
            Range("SetPropertyRange").Dirty
            Application.Calculate
            Range("Calculations").Dirty
            Application.Calculate
            Range("Deviations").Dirty
            Application.Calculate
            Range("GlobalCriterion").Dirty
            Application.Calculate
        End If
    End If
End Sub
```

# 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*)





## 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

**Binaries editor**

Binaries view: ☒ Grid ☐ Matrix

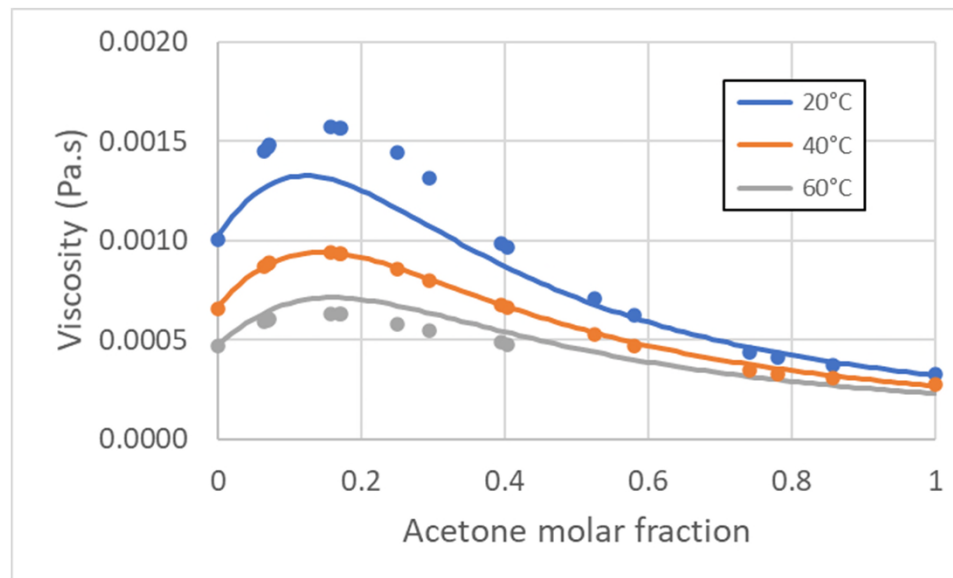
This window helps you to enter the binaries to take into account during thermodynamic calculations  
These parameters are used instead of those defined in the "Binaries" page of the calculator.

Formulation :  $a_{ij}$ ,  $b_{ij}$ ,  $c_{ij}$ ,  $d_{ij}$

Compound	Compound	$a_{ij}$	$b_{ij}$	$c_{ij}$	$d_{ij}$
WATER	ACETONE	2.7755098511	0.0097575501	0.5378211827	0.0019081481

Comments :

- Plot of the results, compared to experimental points



# 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

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

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- 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:

The screenshot shows the 'Thermodynamic calculator editor' window. The 'BINARIES' tab is selected and highlighted with a red box. The interface includes a left sidebar with menu items like FILE, PACKAGE, SERVICES, MODIFICATIONS, and CONFIGURATION. The main area displays the 'BINARIES' tab with a table of parameters for 'ACETONE' and 'ACETYL SALICYLIC ACID'. The table has columns for Compound, Cij0, Cji0, aij0, CijT, CjiT, and aijT. The 'ACETONE' row is highlighted. Below the table, there is a section for 'Formulation' with the equation:  $g_{ij} - g_{ji} = C_{ij}0 + C_{ij}T(T - 273.15)$ ,  $a_{ij} = a_{ij}0 + a_{ij}T(T - 273.15)$ . On the right, there is a 'BINARIES' panel with 'ACTIONS' (Import binaries..., Clear all binaries..., Estimate binaries..., Save the binaries...) and 'OPTIONS' (Unit: cal/mole, parameters will be ignored).

Thermodynamic calculator editor

CALCULATOR

FILE

- Open...
- Save as...

PACKAGE

SERVICES

- Calculate
- Export as a PSF file
- Diagrams
- Residue...
- Export as a PVT file
- Stream...
- Sigma profiles

MODIFICATIONS

CONFIGURATION

This window helps you to define the context of your thermodynamic calculator

COMPOUNDS | MODEL | **BINARIES** | PARAMETERS

These parameters correspond to the general values and are used if the user has not provided specific parameters (buttons to the right of each option in the thermodynamic profile)

Binaries view: ☒ Grid ☐ Matrix

Formulation :  $g_{ij} - g_{ji} = C_{ij}0 + C_{ij}T(T - 273.15)$ ,  $a_{ij} = a_{ij}0 + a_{ij}T(T - 273.15)$

Compound	Compound	Cij0	Cji0	aij0	CijT	CjiT	aijT
ACETONE	ACETYL SALICYLIC ACID						

BINARIES

ACTIONS

- Import binaries...
- Clear all binaries...
- Estimate binaries...
- Save the binaries...

OPTIONS

Unit

cal/mole

☐ parameters will be ignored

# 3- Regression of binary interaction parameters for solid-liquid equilibria <sup>37</sup>

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

Reference: G.D. Maia, M. Giuliatti, "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

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

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

Thermodynamic calculator editor

Calculator

FILE

- Open...
- Save as...

PACKAGE

SERVICES

- Calculate
- Export as a PSF file
- Diagrams
- Residue...
- Export as a PVT file
- Stream...
- Sigma profiles

MODIFICATIONS

CONFIGURATION

Name

Comments

Calculator type

Native

Show the expert mode

COMPOUNDS | MODEL | **BINARIES** | PARAMETERS

This window helps you to define the context of your thermodynamic calculator

These parameters correspond to the general values and are used if the user has not provided specific parameters (buttons to the right of each option in the thermodynamic profile)

Binaries view: ☒ Grid ☐ Matrix

Formulation :  $g_{ij} - g_{jj} = C_{ij}^0 + C_{ij}^T(T - 273.15)$ ,  $a_{ij} = a_{ij}^0 + a_{ij}^T(T - 273.15)$

Compound	Compound	$C_{ij}^0$	$C_{ji}^0$	$a_{ij}^0$	$C_{ij}^T$	$C_{ji}^T$	$a_{ij}^T$
ACETONE	ACETYLSALICYLIC ACID						

Unit

cal/mole

parameters will be ignored

Not supplied Supplied Imported Estimated

Comments :

Ok Cancel

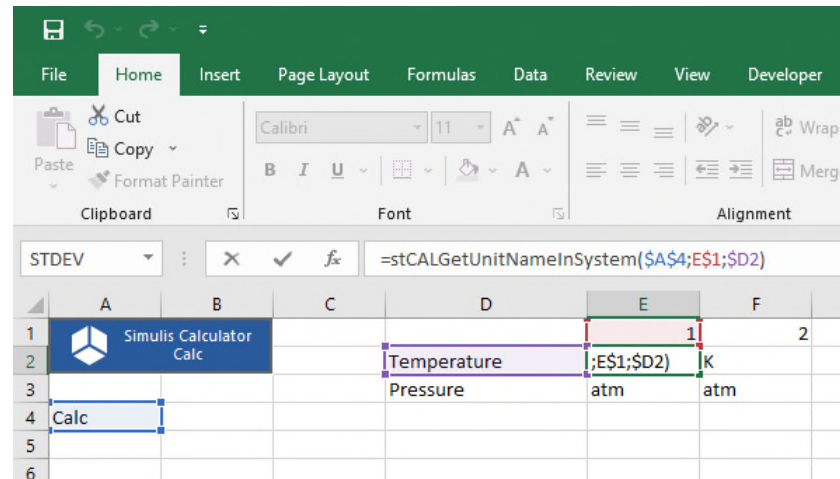
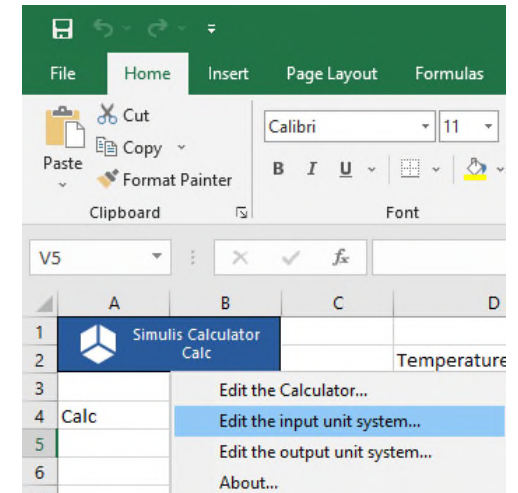


# 3- Regression of binary interaction parameters for solid-liquid equilibria

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## 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()`



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

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- 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				

# 3- Regression of binary interaction parameters for solid-liquid equilibria <sup>41</sup>

- 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(\$A\$4:B15;\$D\$10:E15:F15)																		
1	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P		
2	Simulis Calculator Calc			Temperature	K	1	2											
3				Pressure	atm	atm												
4	Calc																	
5																		
6																		
7				1 ACETONE				BIP	Cij0	Cji0	aij0	CijT	CjiT	ajiT				
8				2 ACETYSALICYLIC ACID				ICode	-1191.817586	2611.388279	0.2	0	0	0				
9								Set	-1									
10				P (atm)		1			Updated									
11																		
12																		
13																		
14		Experimental Data						Simulis Thermodynamics Calculations										
15		T (K)	x		z1	z2		Solid Ratio	Liquid Ratio	Vapor Ratio	xS1	xS2	xL1	xL2	yv1	yv2		
16		281.9	0.061		0.5	0.5		0.532486104	0.532486104	0	0	1	0.93899164	0.06100836	0	0		
17		290.6	0.075		0.5	0.5		0.459652373	0.540347627	0	0	1	0.92533024	0.07466976	0	0		
18		297.9	0.088		0.5	0.5		0.451818946	0.548181054	0	0	1	0.91210741	0.08789259	0	0		
19		304.4	0.101		0.5	0.5		0.44372252	0.55627748	0	0	1	0.898832	0.101168	0	0		
20		310.6	0.114		0.5	0.5		0.43484769	0.56515231	0	0	1	0.88471725	0.11528275	0	0		
21		315.3	0.127		0.5	0.5		0.427252621	0.572747379	0	0	1	0.87298523	0.12701477	0	0		
22		319.8	0.139		0.5	0.5		0.419177934	0.580822066	0	0	1	0.86084884	0.13915116	0	0		
23		323.3	0.151		0.5	0.5		0.412285726	0.587714274	0	0	1	0.85075354	0.14924646	0	0		
24		326.3	0.162		0.5	0.5		0.405903212	0.594096788	0	0	1	0.84161371	0.15838629	0	0		

# 3- Regression of binary interaction parameters for solid-liquid equilibria <sup>42</sup>

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

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

With:

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



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

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- 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”

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	Simulis Calculator				1	2								
2	Calc			Temperature	K	K								
3				Pressure	atm	atm								
4														
5														
6														
7			1	ACETONE				BIP	-1191.817586	2611.388279	0.2	0	0	0
8			2	ACETYLSALICYLIC ACID				ICode	-1					
9								Set	ingValues)					
10			P (atm)		1									
11														

Thermo code

stCALSetBinariesValues()

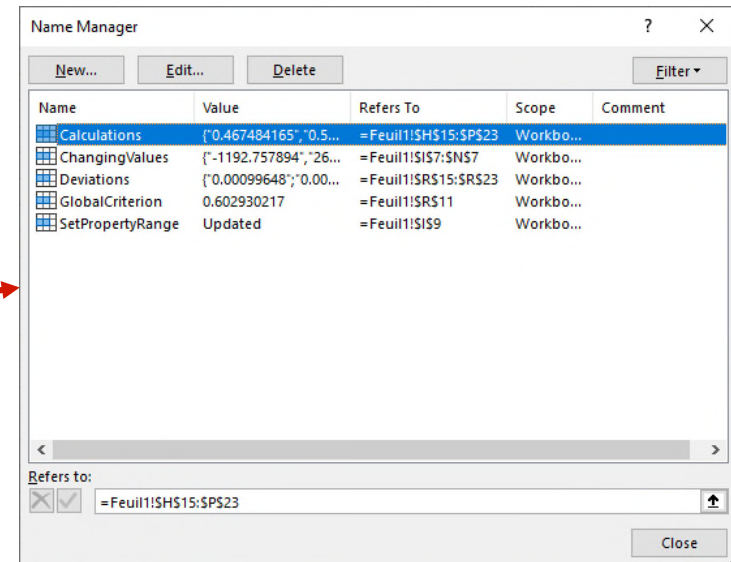
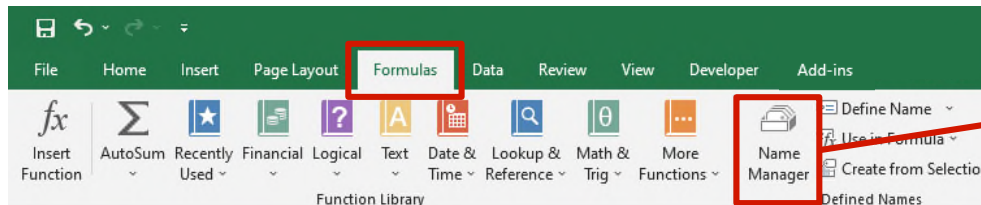
BIP values to be regressed

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

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## ■ Step 7: Define the calculation sequence

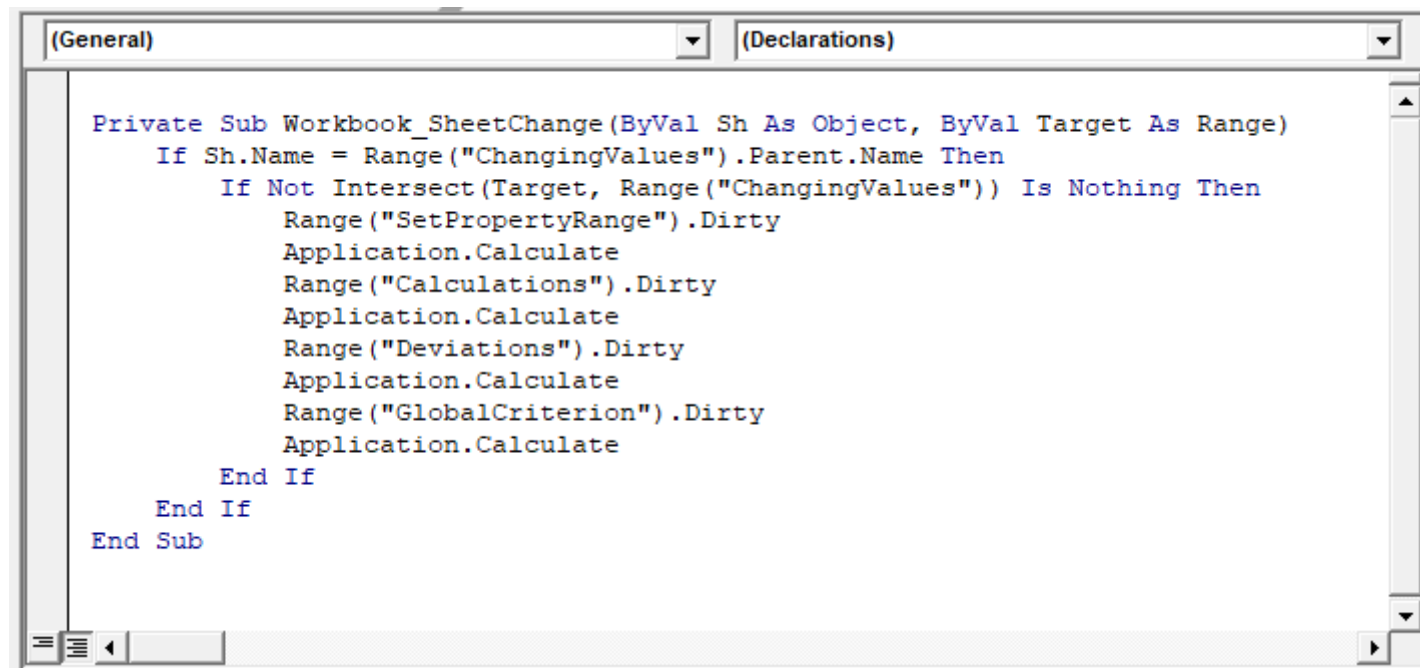
- Name the cells, e. g. :
  - “**ChangingValues**” for the BIP table (cells I7 to N7)
  - “**SetPropertyRange**” for the copy of the values of the properties in the calculator (cell I9)
  - “**Calculations**” for properties calculations (cells H15 to P23)
  - “**Deviations**” for deviations calculations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



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

45

- 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



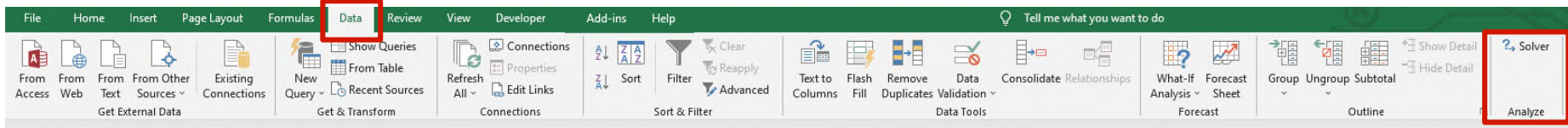
The screenshot shows the VBA editor window with the 'Declarations' tab selected. It contains a VBA macro named 'Workbook\_SheetChange' that triggers when a cell in the 'ChangingValues' range is changed. The macro performs a series of calculations and updates in a specific order: it marks the 'SetPropertyRange' as dirty and calculates it, then marks 'Calculations' as dirty and calculates it, then marks 'Deviations' as dirty and calculates it, and finally marks 'GlobalCriterion' as dirty and calculates it.

```
Private Sub Workbook_SheetChange(ByVal Sh As Object, ByVal Target As Range)
    If Sh.Name = Range("ChangingValues").Parent.Name Then
        If Not Intersect(Target, Range("ChangingValues")) Is Nothing Then
            Range("SetPropertyRange").Dirty
            Application.Calculate
            Range("Calculations").Dirty
            Application.Calculate
            Range("Deviations").Dirty
            Application.Calculate
            Range("GlobalCriterion").Dirty
            Application.Calculate
        End If
    End If
End Sub
```

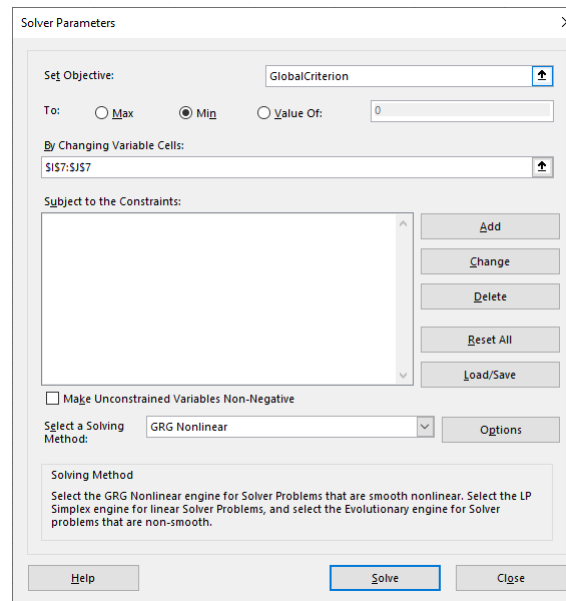
# 3- Regression of binary interaction parameters for solid-liquid equilibria

46

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



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



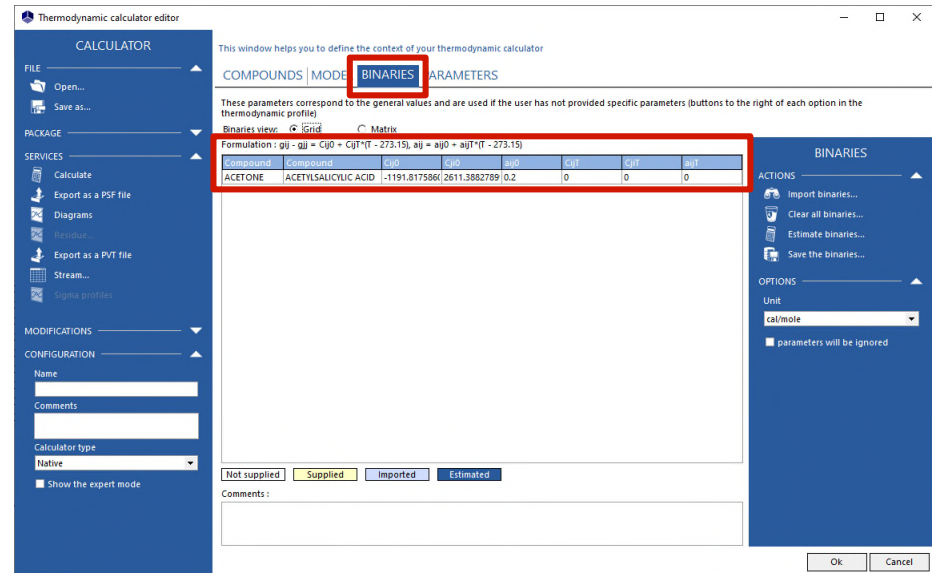


# 3- Regression of binary interaction parameters for liquid-solid equilibria

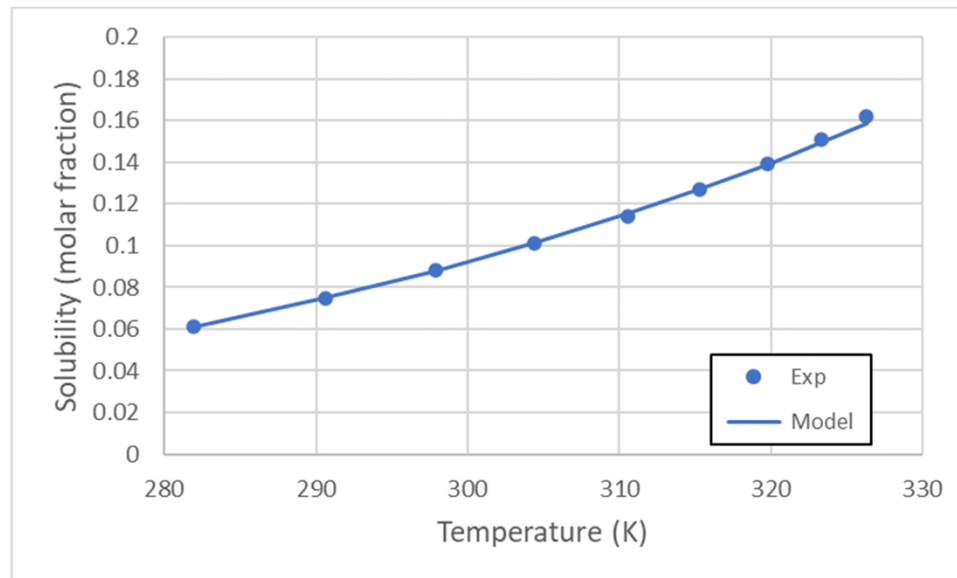
47

## 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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