The SOLUTION Module

- The SOLUTION module permits you to create, display and edit private non-ideal solution databases using a wide variety of solution models. – The private databases may be imported into the EQUILIB and PHASE DIAGRAM modules and used together with other databases.

- Before reading this slide show you should **first read the “Solution Introduction” slide show**.

- It is also strongly recommended that you **read Sections 1 and 2 completely before advancing to later sections**. Although Sections 1 and 2 describe the creation of a database using a simple one-lattice polynomial model, these sections introduce in detail most of the features and the structure of the SOLUTION module.

DESCRIPTION OF SOLUTION MODELS IN SOLUSAGE

ONE-LATTICE POLYNOMIAL MODEL ("model 1") Sections 1, 2

- One lattice.
- Random mixing.
- Interaction parameters expressed as polynomials (Redlich-Kister, simple or Legendre) in terms of either site fractions or equivalent site fractions.
- Interpolation of binary parameters into ternary systems using either Kohler, Toop or Muggianu techniques or combinations thereof.

ONE-LATTICE REDLICH-KISTER/MUGGIANU MODEL ("model 7") (Section 3)

- One lattice.
- Random mixing.
- This is a restricted version of the One-Lattice Polynomial Model.
- This is a one-lattice version of the Compound Energy Formalism.
- Interaction parameters expressed as Redlich-Kister polynomials in terms of site fractions.
- Interpolation of binary parameters into ternary systems using Muggianu technique.

COMPOUND ENERGY FORMALISM (CEF) ("models 12/20") (Section 5)

- From 2 to 5 sublattices.
- Number of sites on each sublattice fixed, independent of composition.
- Random mixing on each sublattice.
- Interaction parameters expressed as Redlich-Kister polynomials in terms of site fractions.
- Interpolation of binary parameters into ternary systems using Muggianu technique.

TWO-LATTICE POLYNOMIAL MODEL ("model 4") Section 7

- Two sublattices
- Random mixing on each sublattice
- Specifically designed for (but not limited to) ionic liquid solutions in which the ratio R of the number of sites on the two sublattices varies with composition when all ionic charges on a sublattice are not the same.
- Interaction parameters expressed as polynomials (Redlich-Kister, simple or Legendre) in terms of equivalent site fractions to take account of possible variable R.
- Interpolation of binary parameters into ternary systems using either Kohler, Toop or Muggianu techniques or combinations thereof.
- If R is constant then this model is the same as the Compound Energy Formalism with two sublattices, but without being limited to Redlich-Kister polynomials nor to the Muggianu interpolation technique.

TWO-LATTICE POLYNOMIAL MODEL WITH FIRST-NEAREST-NEIGHBOUR SHORT-RANGE-ORDERING ("model 9") Section 8

- Same as the Two-Lattice Polynomial Model but takes account of short-range-ordering between first-nearest-neighbour pairs; in a solution (A,B)(X,Y) the model calculates the equilibrium numbers of nearest-neighbour A-X, A-Y, B-X and B-Y pairs which minimize the Gibbs energy.

ONE-LATTICE MODIFIED QUASICHEMICAL MODEL ("model 3") Section 9

- One lattice.
- In a system (A,B) short-range-ordering is treated by calculating the equilibrium numbers of nearest-neighbour A-A, B-B and A-B pairs which minimize the Gibbs energy.
- Interaction parameters express the Gibbs energy change of pair exchange reactions (such as A-A + B-B = 2 A-B) as polynomials in terms of either site fractions or equivalent site fractions.
- Interpolation of binary parameters into ternary systems using analogies of either the Kohler, Toop or Muggianu techniques or combinations thereof.

TWO-LATTICE MODIFIED QUASICHEMICAL MODEL REVISED ("model 98") or OLD ("model 99") Section 10

- Two-sublattices
- Short-range-ordering (SRO) taken into account both between sublattices (first-nearest-neighbour SRO) and within each sublattice (second-nearest-neighbour SRO).
- The end-members of the model are quadruplets, each consisting of two species from each sublattice.
- Reduces exactly to the Two-Lattice Polynomial Model if SRO is suppressed, or to the One-Lattice Modified Quasichemical Model if one sublattice contains only vacancies, or to the One-Lattice Polynomial Model if SRO is suppressed and one sublattice contains only vacancies.
- The REVISED model incorporates minor improvements to the OLD model and should always be used except when editing a file created previously with the OLD version.

IONIC LIQUID MODEL ("model 13") Section 13

- Two sublattices with variable ratio of sites depending upon composition.
- Random mixing.
- This is the Ionic Liquid Model developed by Hillert, Sundman, Jansson and Agren (refs. 16, 17) which is frequently used in Calphad.

UNIFIED INTERACTION PARAMETER FORMALISM ("model 2") Section 12

- One lattice.
- Random mixing.
- This is the Wagner Interaction Parameter Formalism for dilute solutions corrected to be consistent with the Gibbs-Duhem equation and other necessary thermodynamic relationships.

PITZER MODEL ("model 5") Section 19

- Standard Pitzer model for relatively concentrated aqueous solutions.
- Interaction parameters for ions and neutral solutes as functions of temperature.

Table of contents

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1. Opening a New File and Entry of Data for a binary solution

with the One-lattice Polynomial Model ("model #1")

Example: Binary liquid Ag-Cu solution

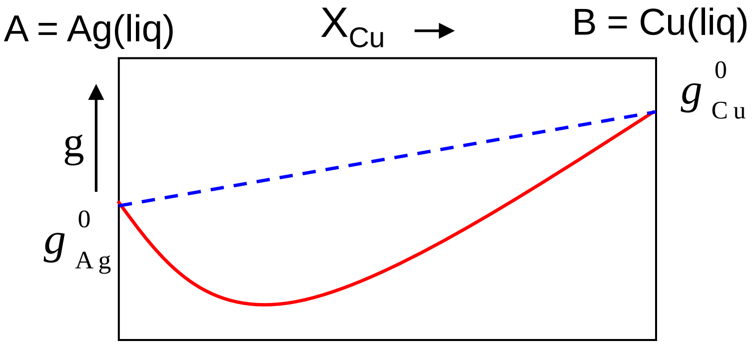
The **One-lattice Polynomial Model (model #1)**

assumes that the **species** (A = Ag, B = Cu) mix randomly on a single lattice (Bragg-Williams model)

$\Delta s^{ideal} = -R\,(X_A \ln X_A + X_B \ln X_B)$ where X_i = molar site fractions of species

Molar Gibbs energy for a binary solution:

$$g = (X_A g_A^0 + X_B g_B^0) - T\Delta s^{ideal} + g^E$$



where: g_i^0 = molar Gibbs energy of an "end-member" consisting of one mole of species i

where: the excess molar Gibbs energy g^E is expressed as a polynomial in either:

(i) Redlich-Kister form: $$g^E = \sum {}^{i}L_{AB} X_A X_B (X_A - X_B)^i \qquad i \geq 0 \qquad [1]$$

or (ii) Simple polynomial form: $$g^E = \sum q_{AB}^{ij} X_A^i X_B^j \qquad i, j \geq 0 \qquad [2]$$

or (iii) Legendre polynomial form: $$g^E = \sum q_{AB}^{i} X_A X_B P_i (X_A - X_B) \qquad i \geq 0 \qquad [3]$$

where P_i is the Legendre polynomial of order i (see ref. (1))

Note: In the general case, the option exists to replace the molar site fractions X_i in these polynomial expansions by "equivalent site fractions" Y_i (see Slide 1.19)

For Ag-Cu liquid solution:

$$g^E = X_A X_B (17384.4 - 4.46430\ T) + (1660.8 - 2.31510\ T) X_A X_B (X_A - X_B)^1 \ \text{J/mol} \qquad [4]$$

Opening a new pair of files, SoluSoln.fdb and SoluSoln.sln

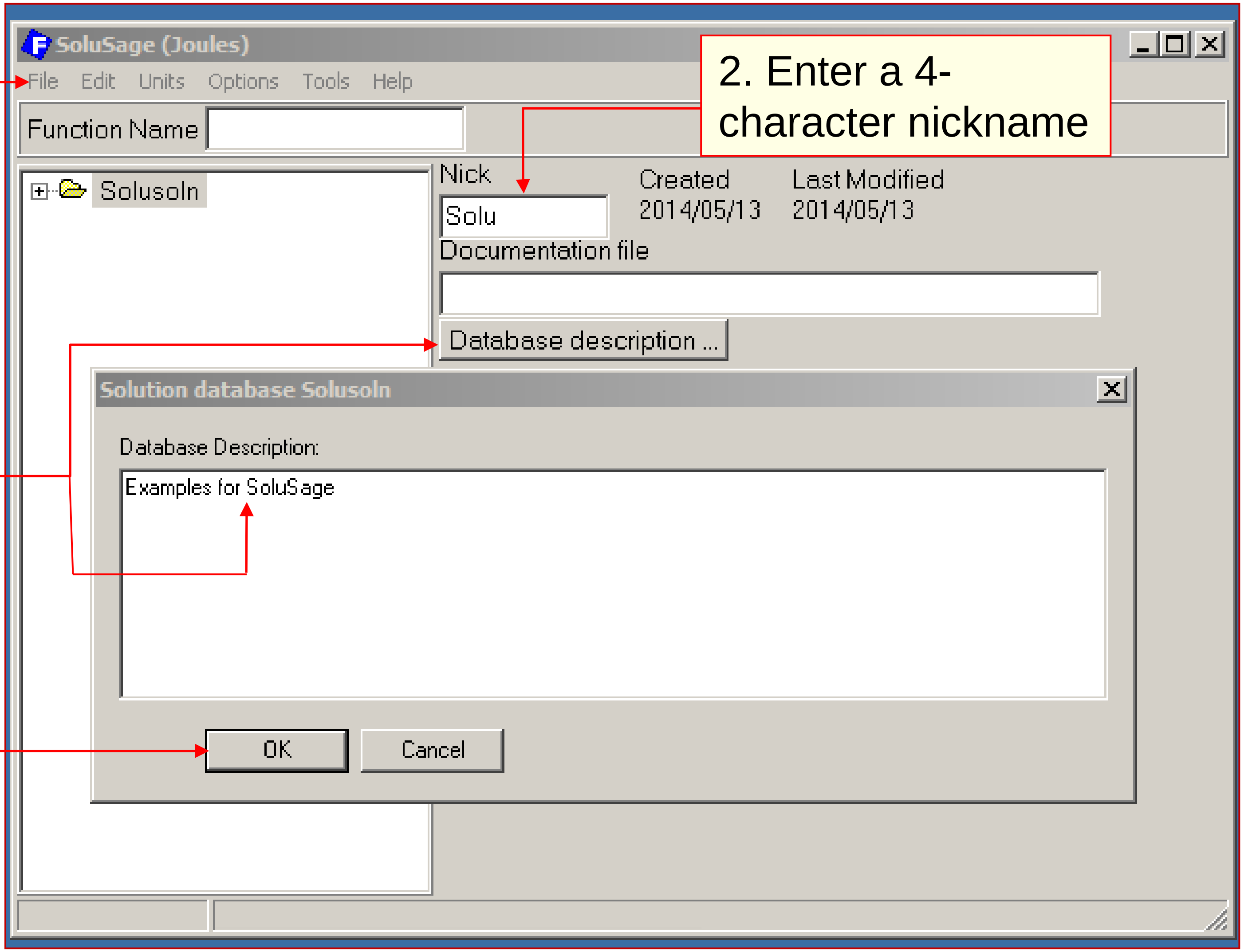
Note: A file may contain several solution phases

1. Click on «File → New»

2. Enter a 4-character nickname

3,4. Enter a description if desired

5. Click on OK

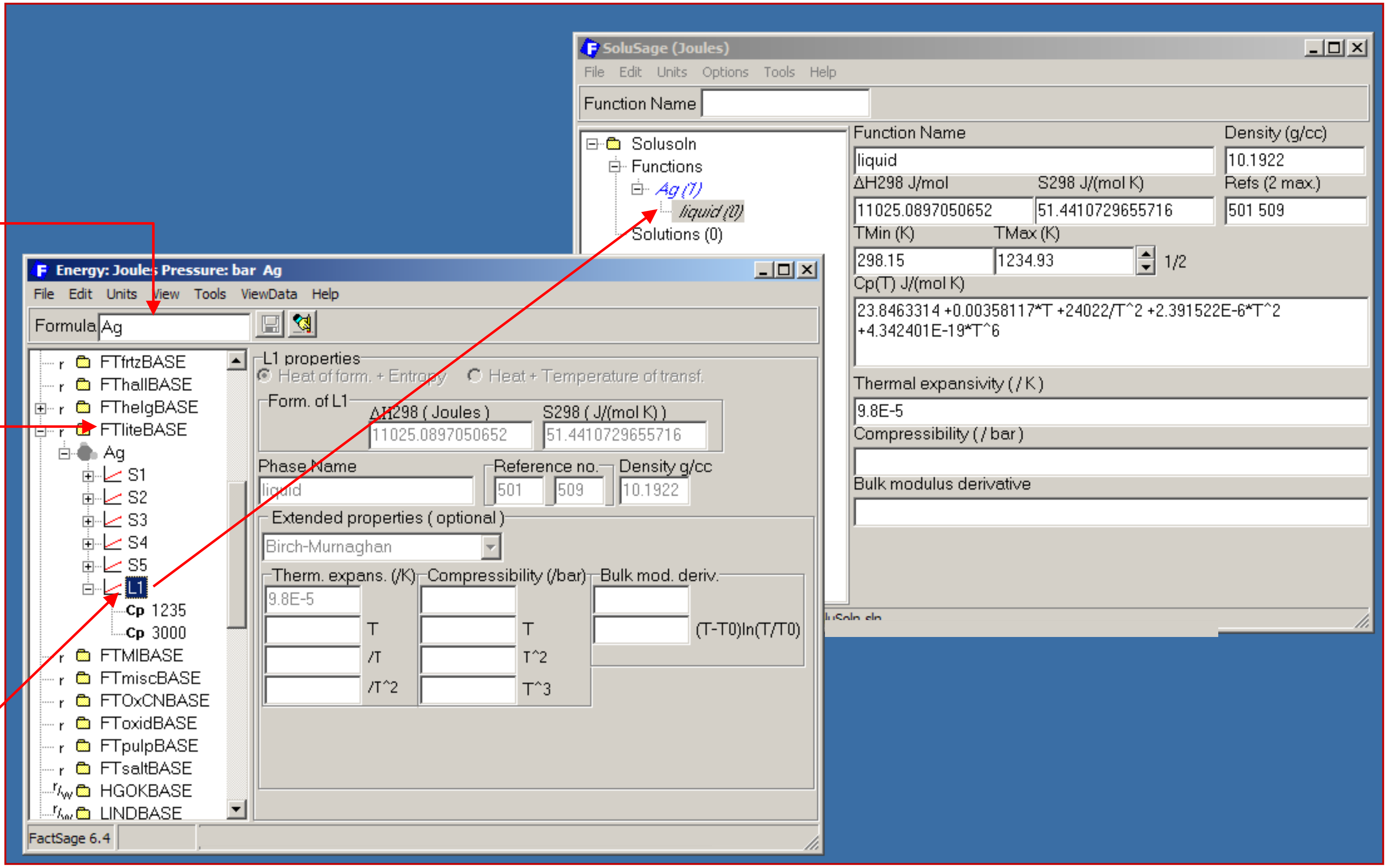


Creating a "Function" containing data for pure liquid Ag

1. Open the **COMPOUND** program and enter **Ag** in the formula box

2. Click on **FTliteBASE** and then on **Ag** to expand the tree view

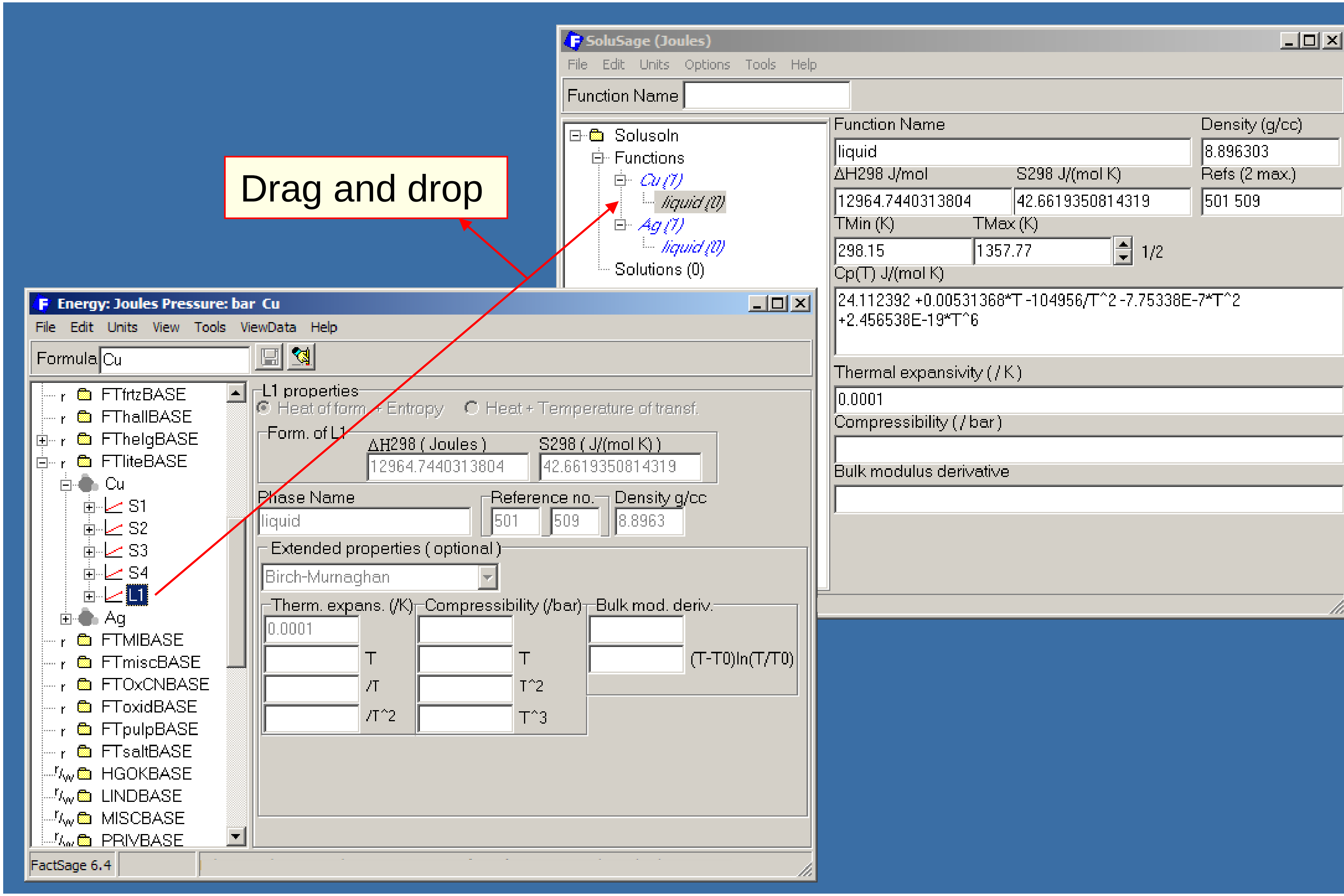
3. Click on **L1** and then **drag and drop** into **Functions**



<u>(Note:</u> If you do not have access to the FTlite database, you can use FactPS or any other database.)

- This creates a **"FUNCTION"** called **Ag#liquid** in the SoluSoln.fdb file. This "function" contains **<u>all</u>** the data for liquid Ag found in the FTlite database (H, S, Cp, density, expansivity, etc.) **<u>except</u>** magnetic properties. (See Section 14).
- For more on creating functions, see Section 6.

Creating a function Cu#liquid for pure liquid Cu

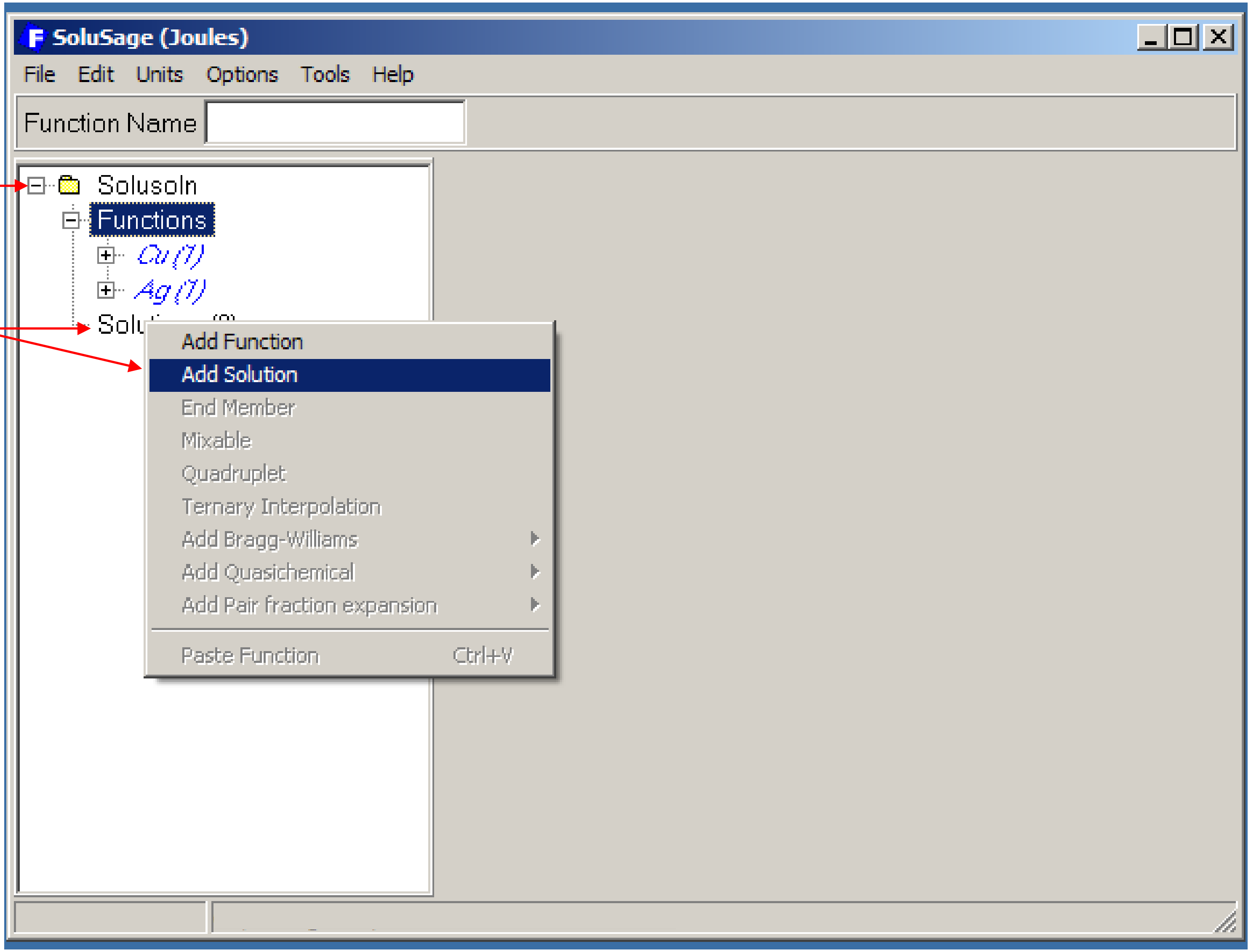


(see previous slide)

Creating a new solution phase within the file SoluSoln.sln

1. Click.

2,3. Right click.



Name the phase and choose the solution model

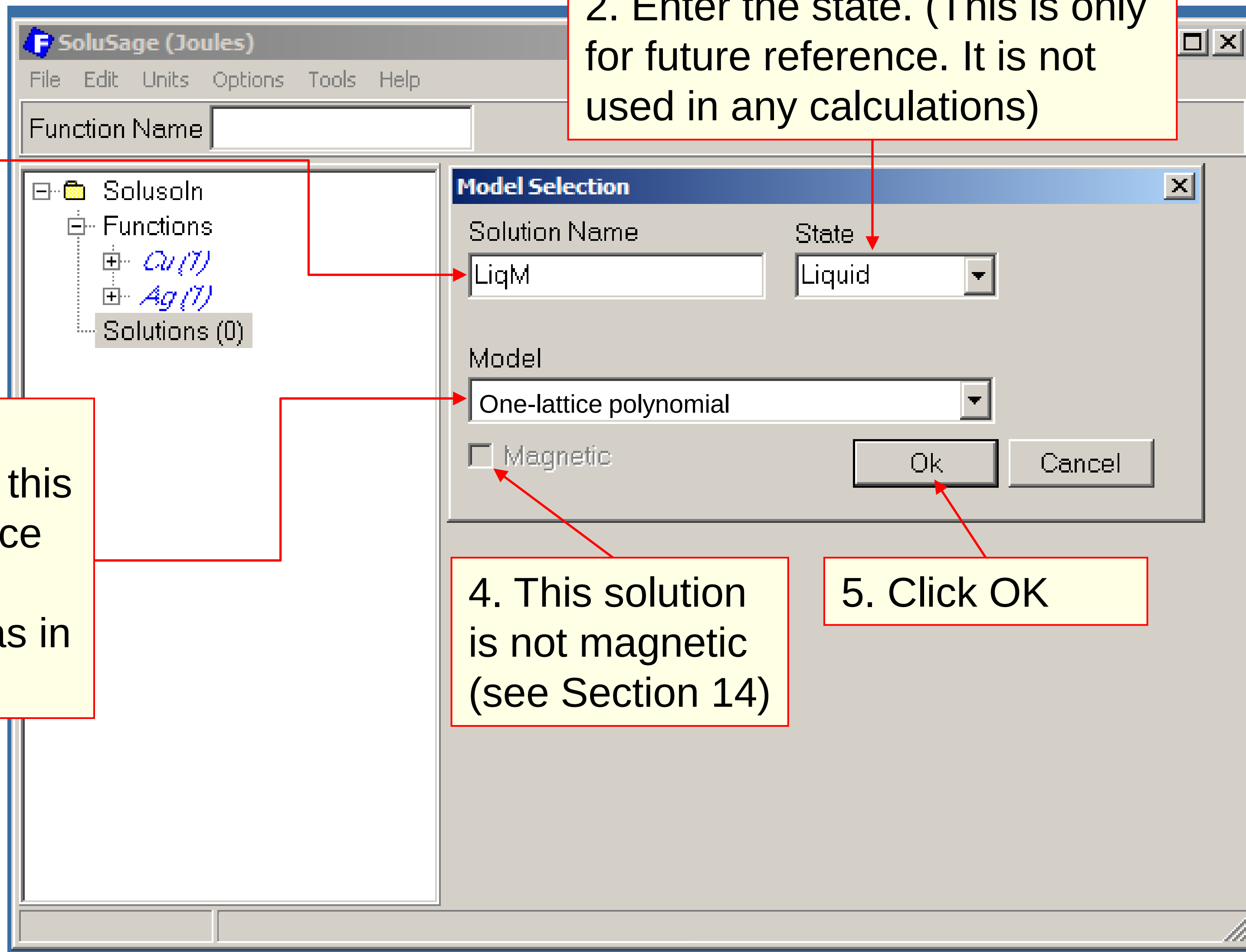
1. Enter a 4-character name of your choice for the solution phase (liquid metal)

2. Enter the state. (This is only for future reference. It is not used in any calculations)

3. Choose the solution model: in this case, one-sublattice with polynomial expansion for g^E as in slide…

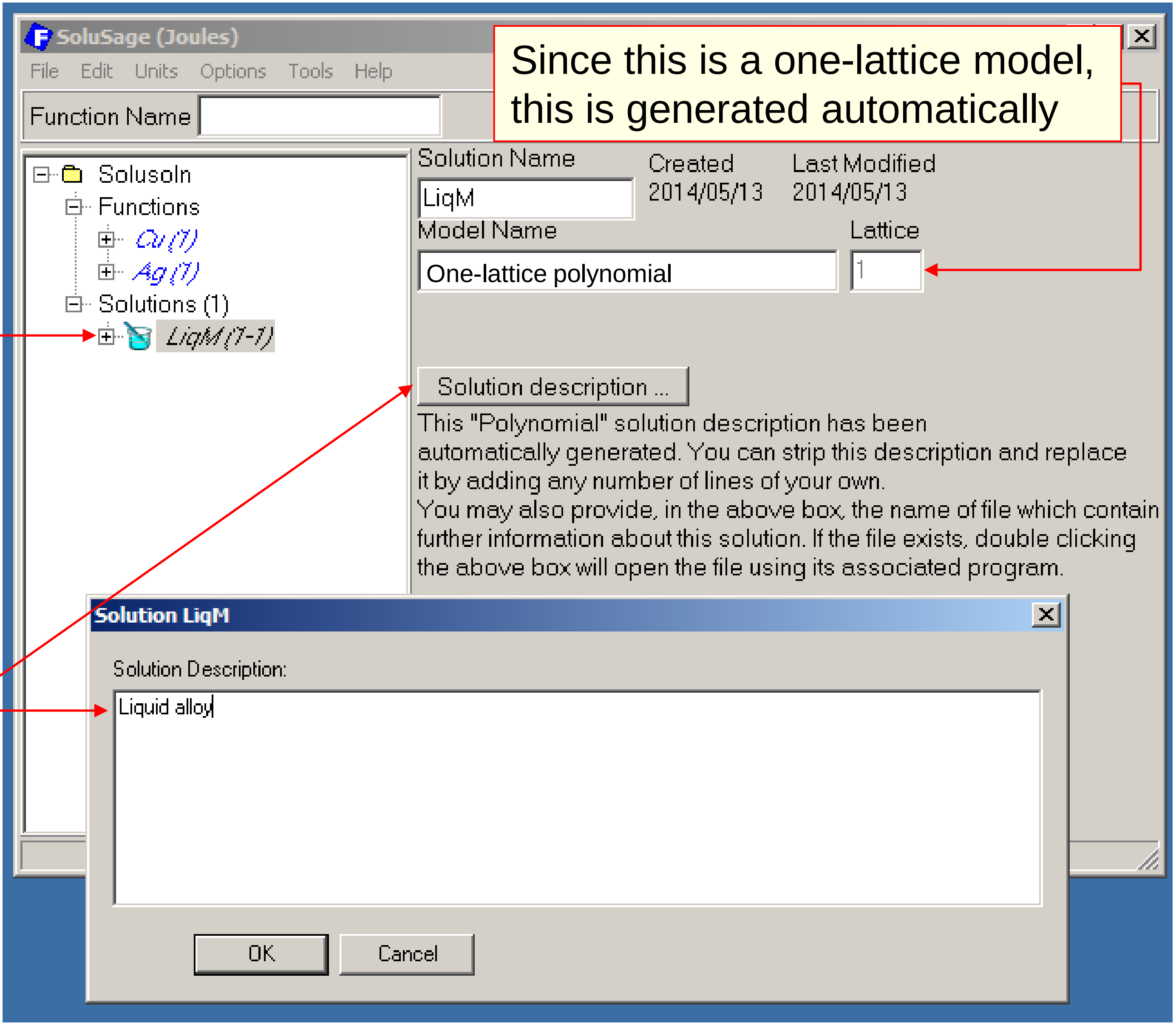
4. This solution is not magnetic (see Section 14)

5. Click OK



Since the phase was identified as «liquid», this symbol appears

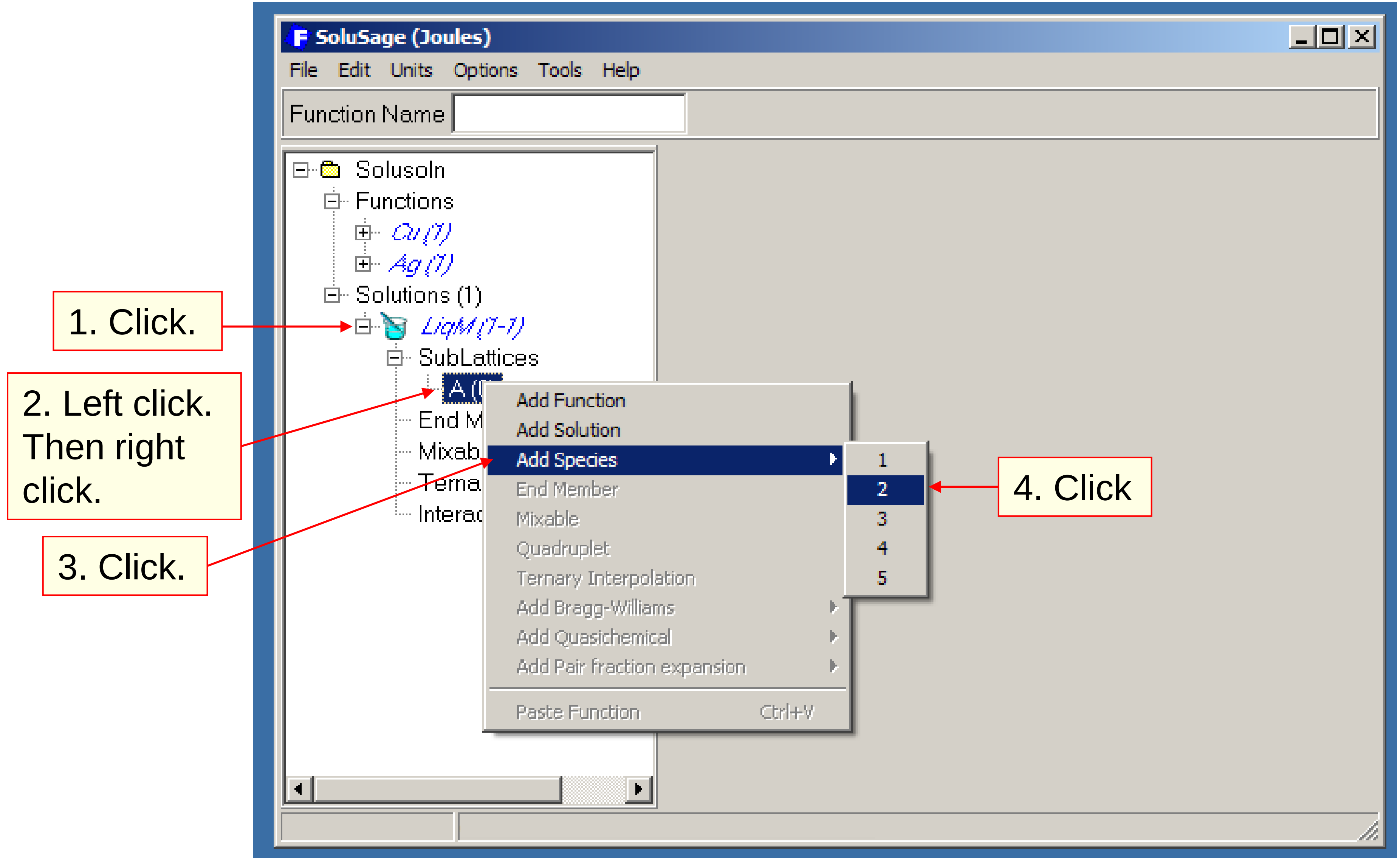
Since this is a one-lattice model, this is generated automatically



1,2. Enter a description. The first word (up to the first space) will appear on all FactSage outputs as the «full name» of the phase. (To show the full name on the tree view, click on «Options», then on «Show full solution name».)

Defining the number of species in the solution (2 in this example)

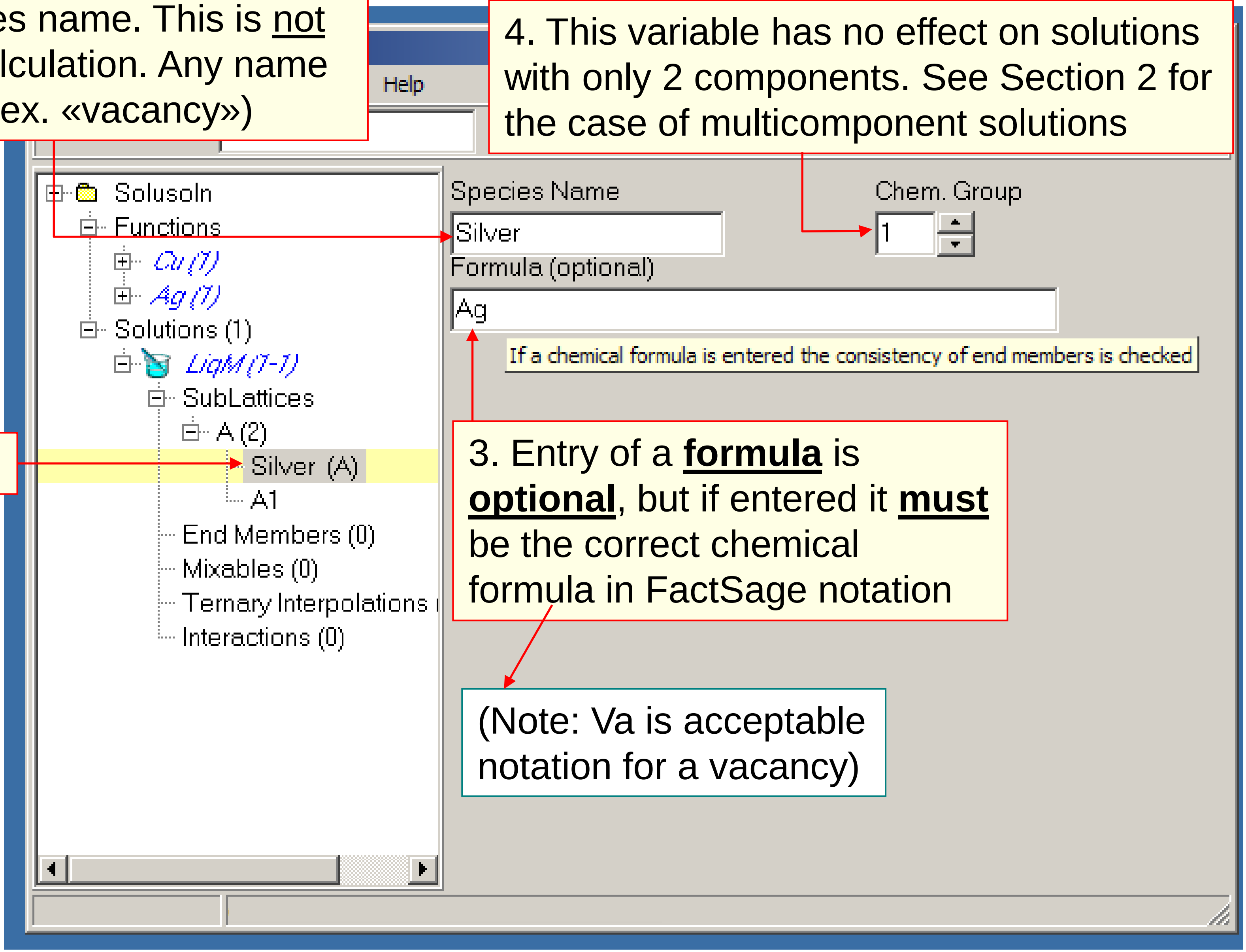
There are 2 **species** which mix on the lattice (a binary solution)



Identifying the first species (Ag)

2. Enter species name. This is not used in any calculation. Any name is acceptable (ex. «vacancy»)

4. This variable has no effect on solutions with only 2 components. See Section 2 for the case of multicomponent solutions

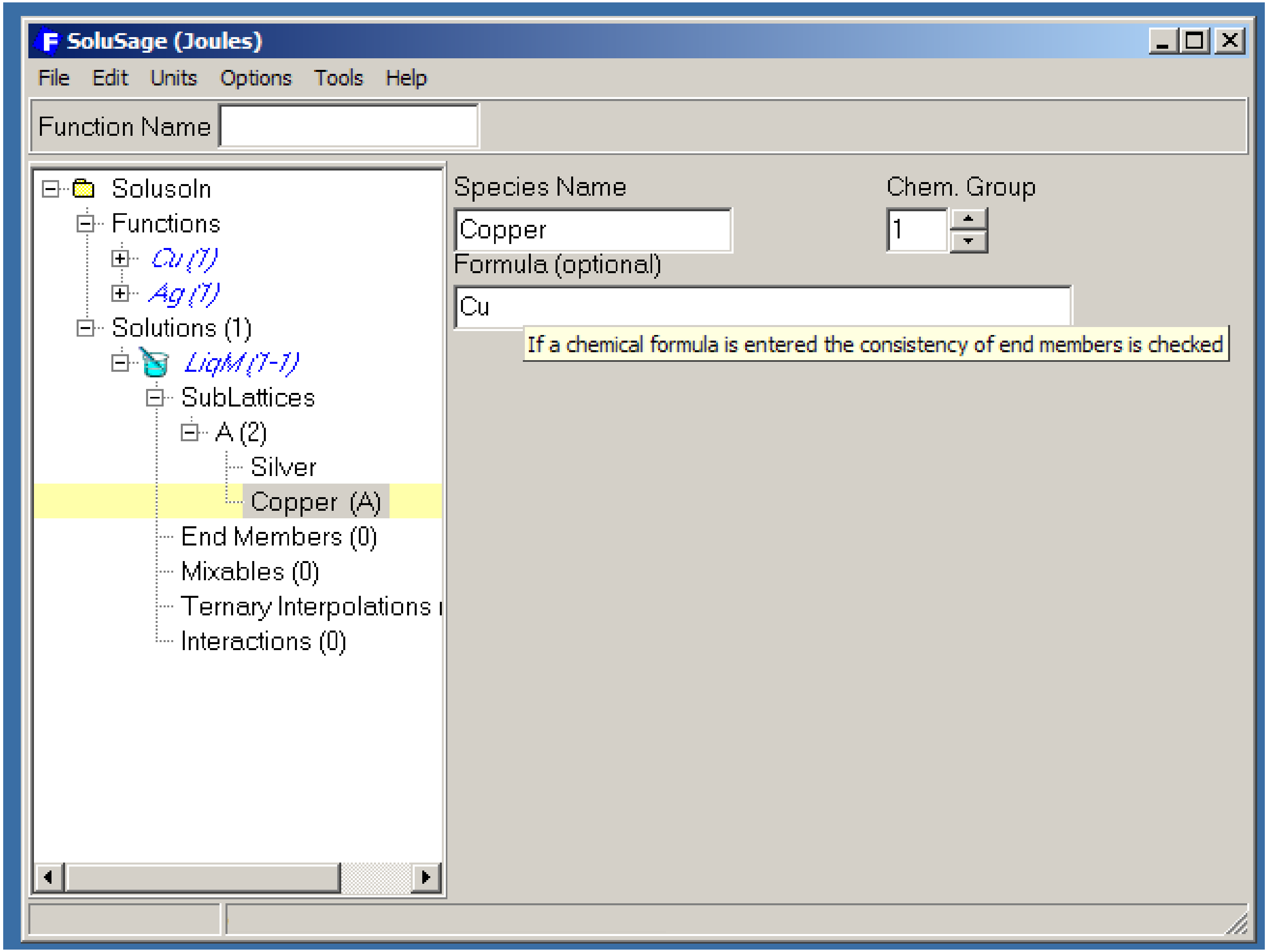


1. Click

3. Entry of a **formula** is **optional**, but if entered it **must** be the correct chemical formula in FactSage notation

(Note: Va is acceptable notation for a vacancy)

Identifying the second species (Cu)

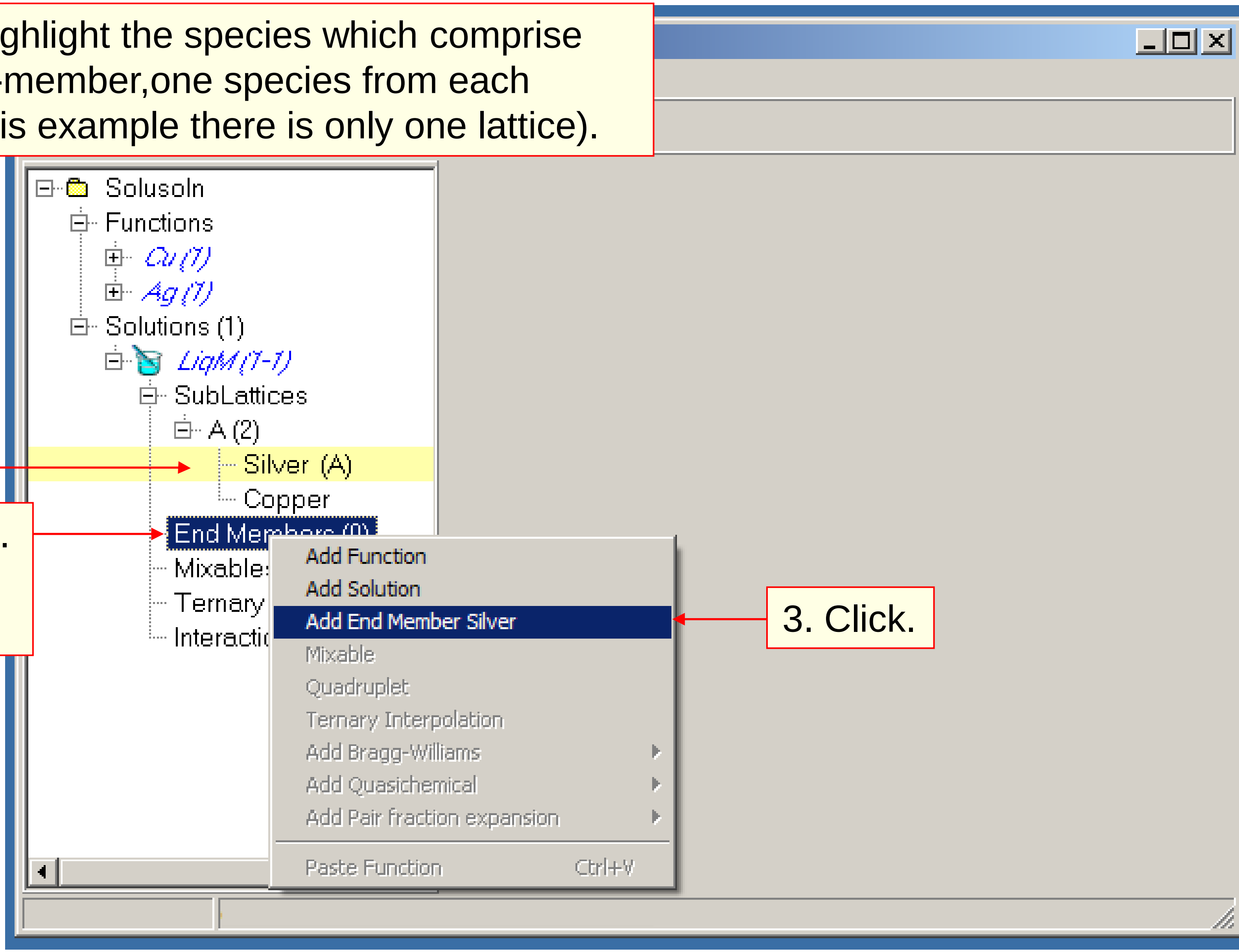


Entering the first end-member (pure liquid Ag)

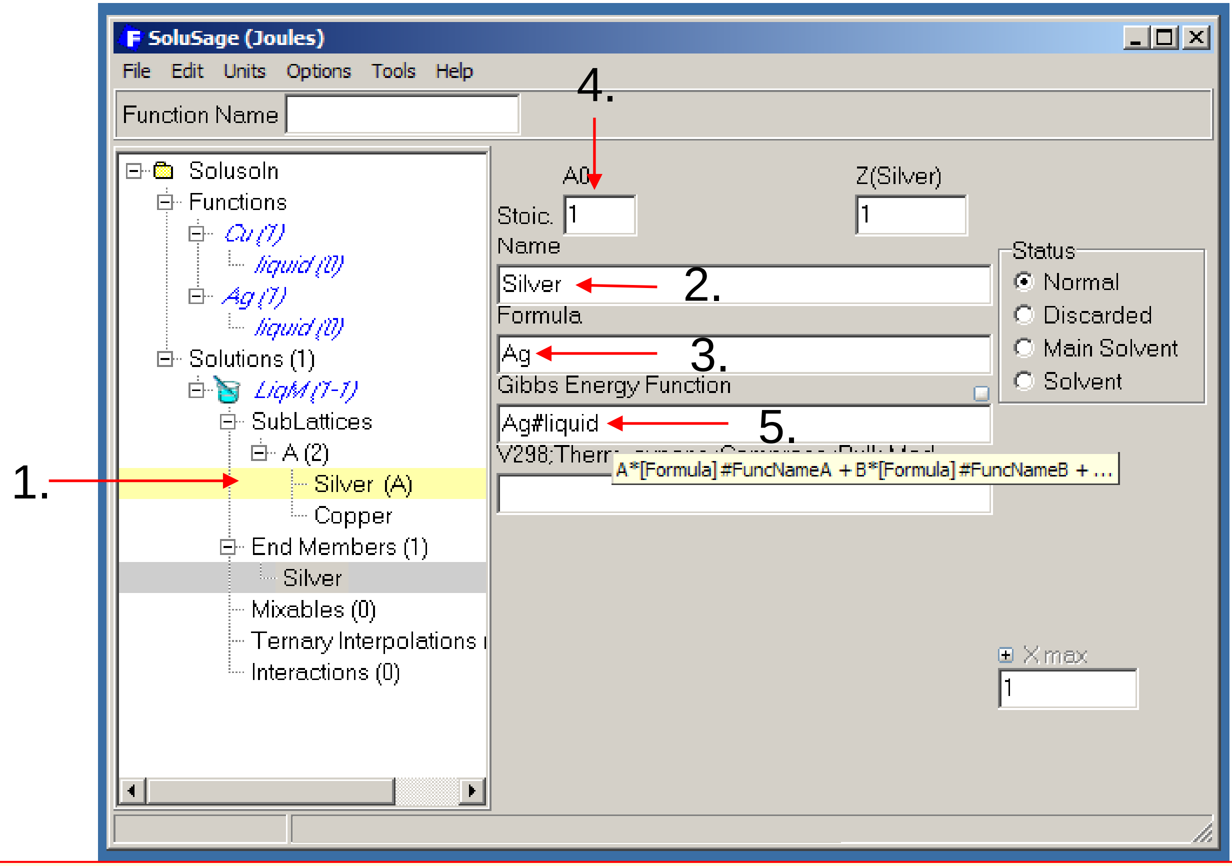
1. Click to highlight the species which comprise the first end-member,one species from each lattice. (In this example there is only one lattice).

2. Left click. Then right click.

3. Click.

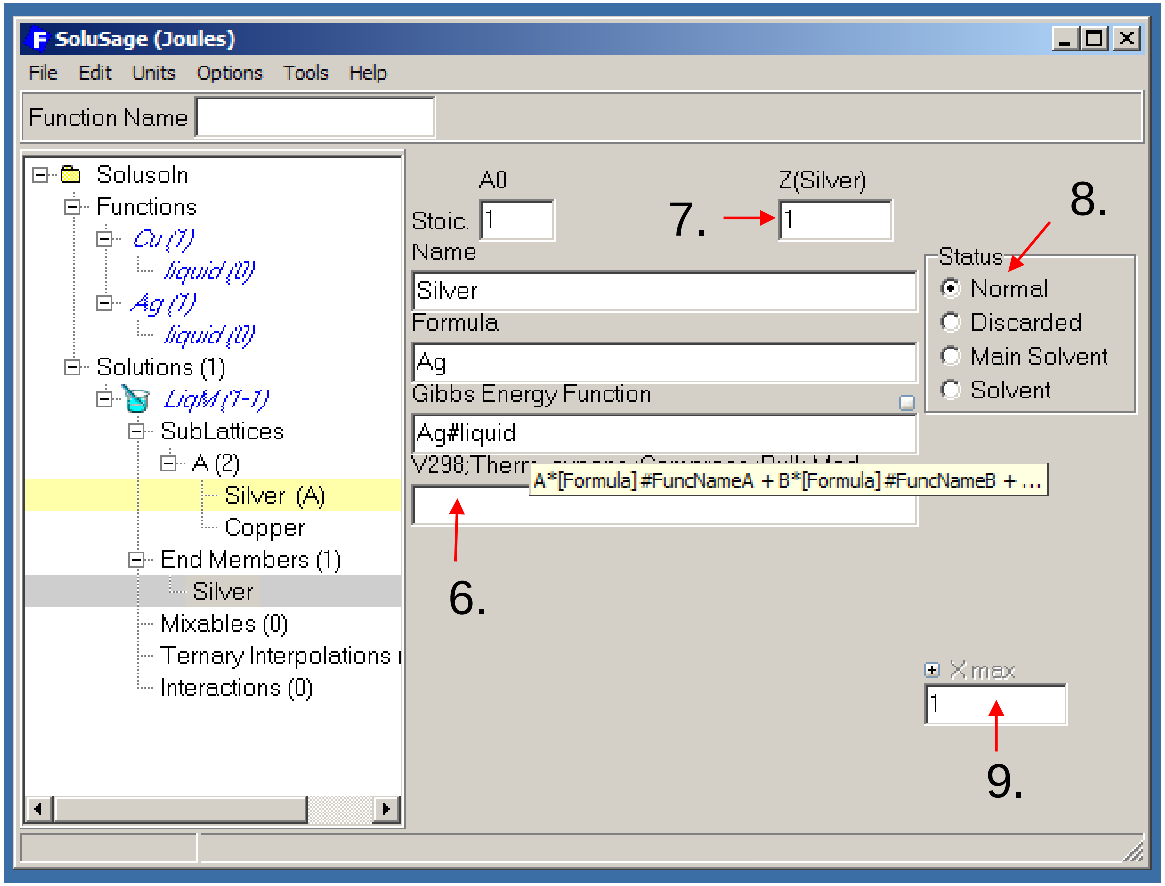


Entering data for first end-member



1. Click.
2. Any **name** is acceptable. This is not used in any calculation but will appear in FactSage outputs.
3. If a «formula» was entered for the species (slide…), then the **Formula** for the end-member is generated automatically. If not, enter it here.
4. This «stoichiometry» variable is the **number of moles of species per mole of end-member**. In most cases it is 1.0 (default). For exceptions, see Section 4.
5. The Gibbs energy for the end-member, per mole of **«Formula»,** as a linear sum of **functions.**

Entering data for first end-member (cont.)



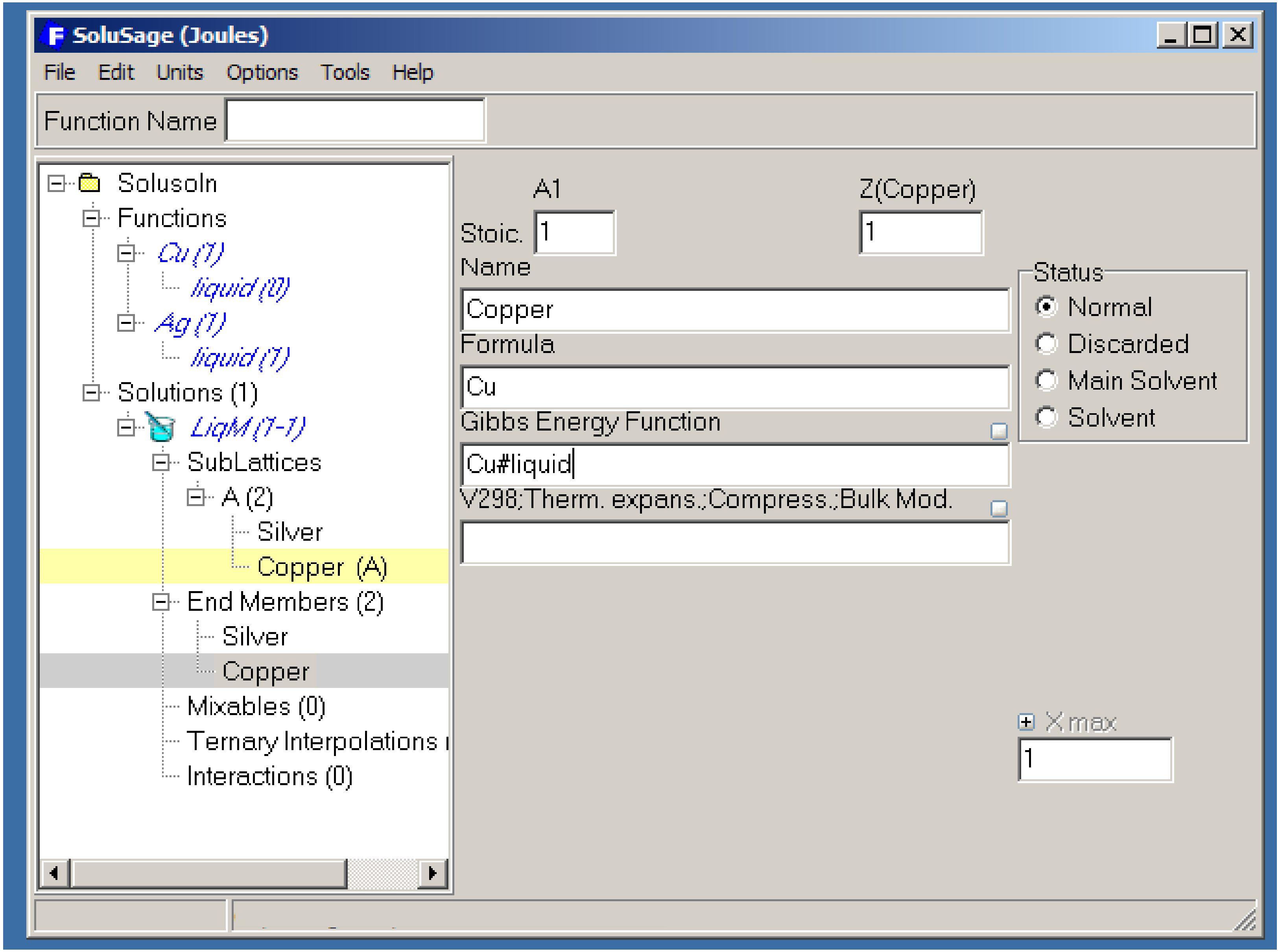
6. The volumetric properties may be entered as a linear sum of «functions». If nothing is entered, then V = 0 in calculations. See Section 13.

7. **<u>The «coordination number»</u>** Z of the silver species in the end-member. In the present one sub-lattice polynomial model set <u>Z = 1</u> (default) if g^E is written as an expansion in the mole fractions, as is usually the case. For exceptions, see Slide 1.19.

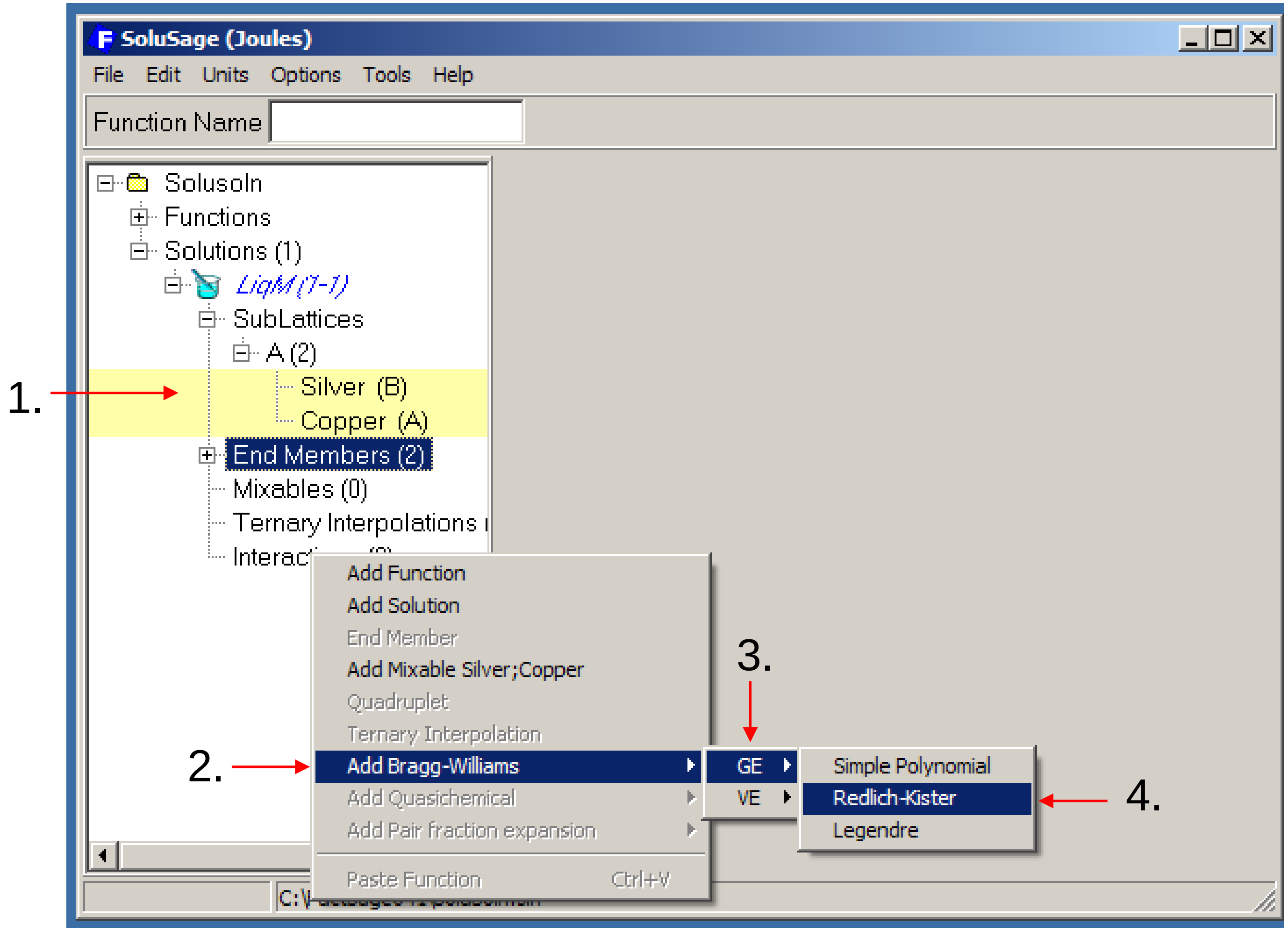
8. Select «normal» (default). See Section 16.

9. Select «X_{max}=1» (default). See Section 17.

Entering data for second end-member

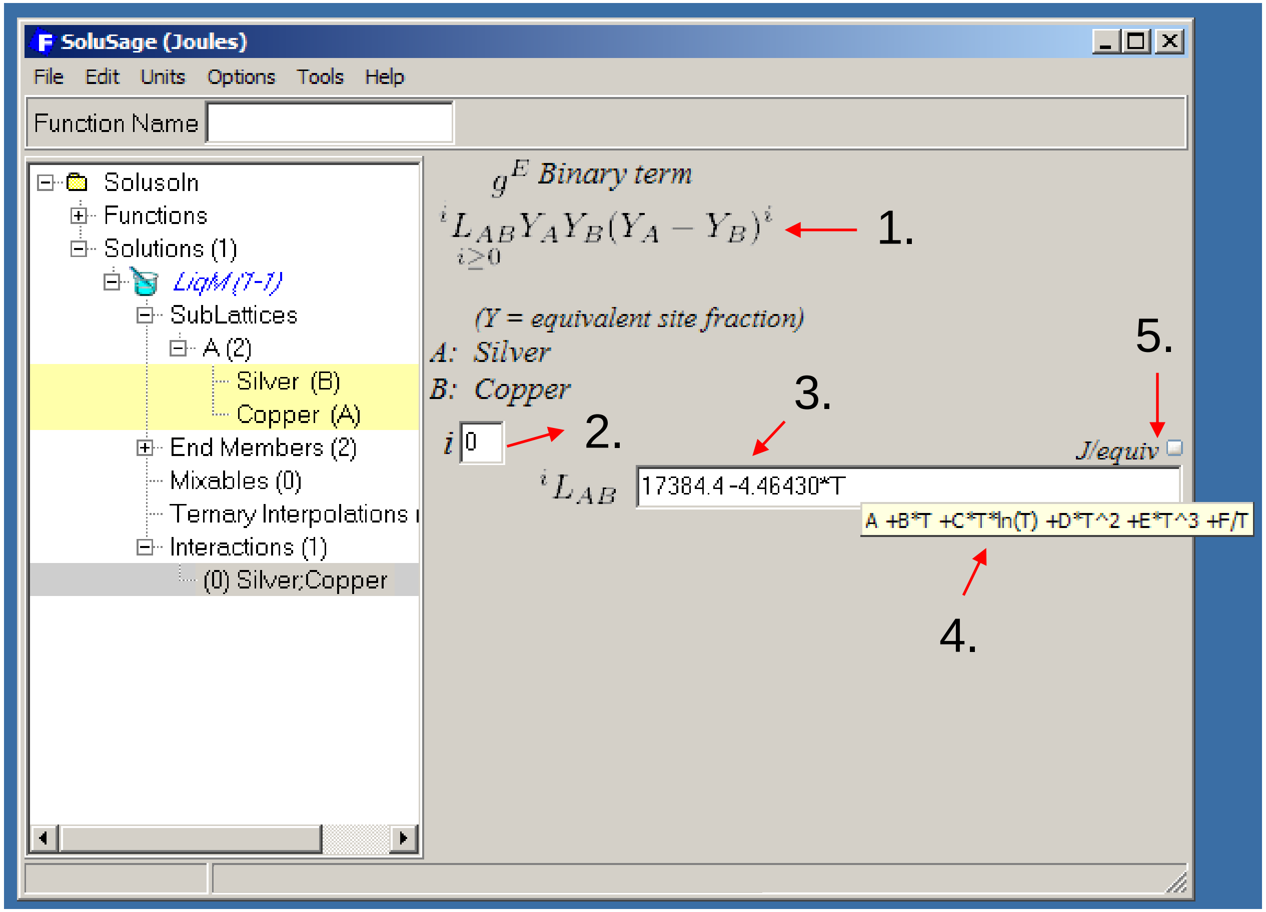


Entering the first excess Gibbs energy parameter (from Slide 1.1 Eq. [4])



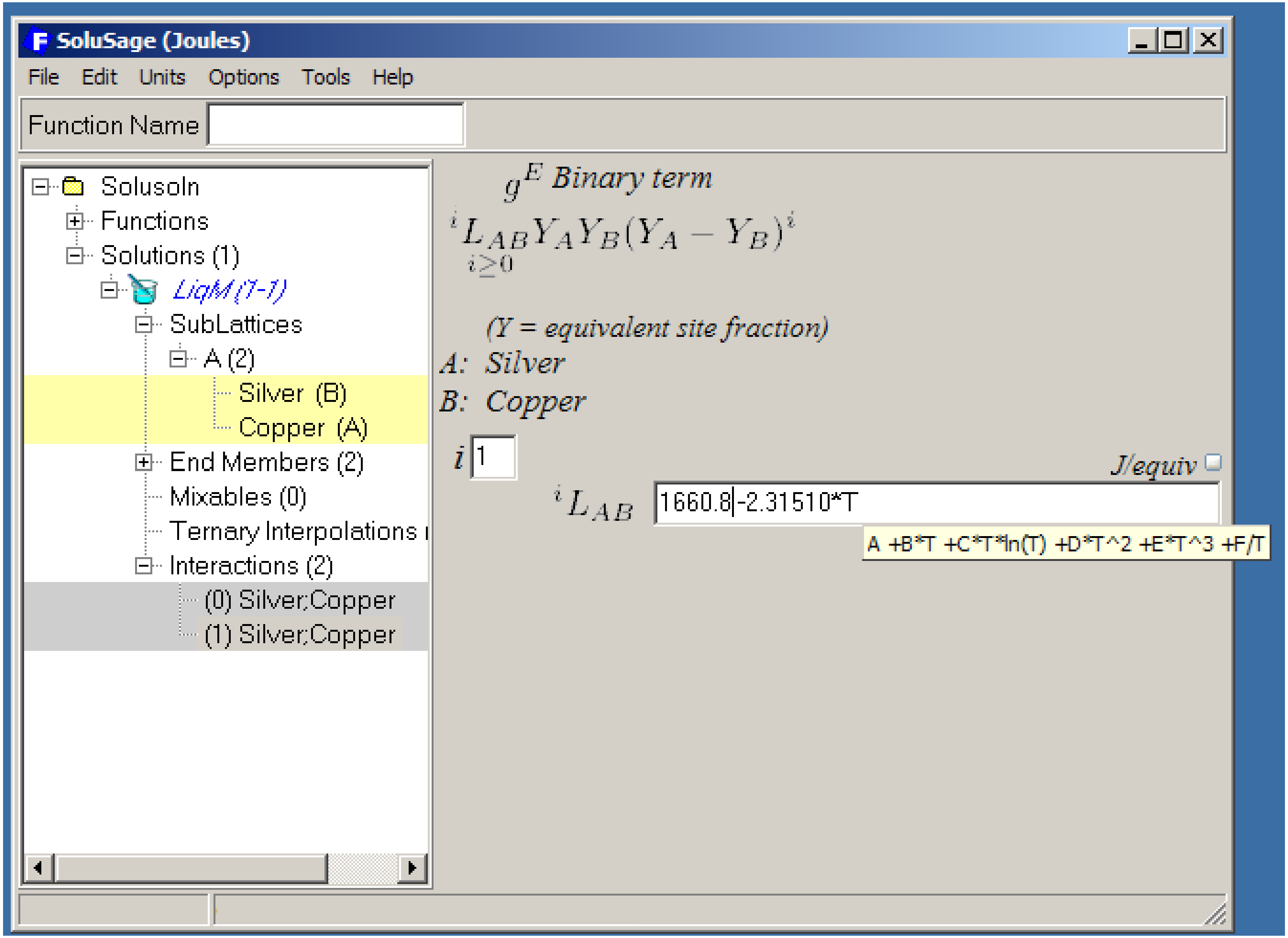
1. Holding down the Ctrl key, highlight the species involved in the interaction parameter, then right click.

2,3,4. Mouse over, then click on «Redlich-Kister».

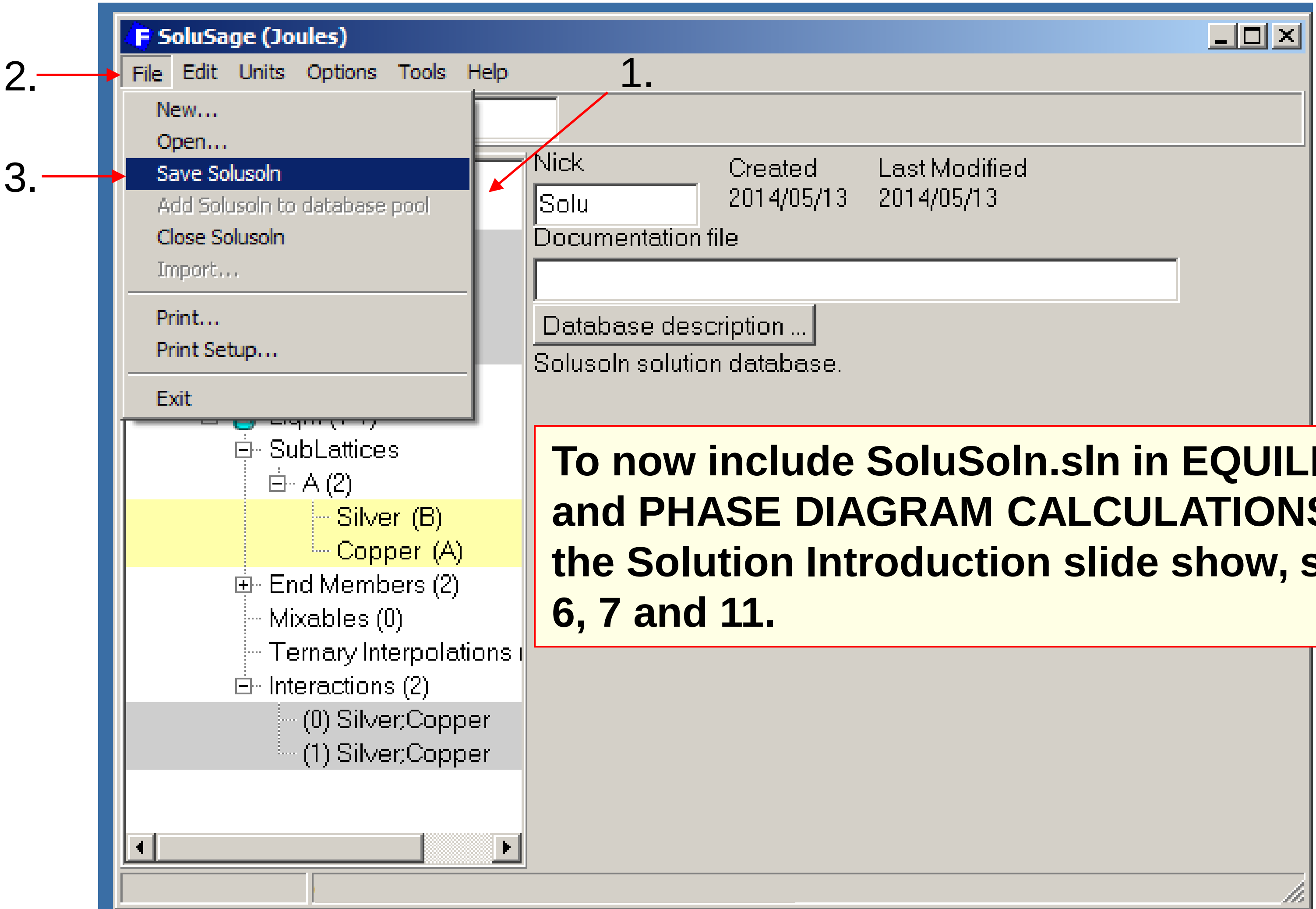


1. Y_A and Y_B are the «equivalent site fractions» of the species. Since, as is usually the case, we chose dafault values of $Z_{Ag} = Z_{Cu} = 1$ (Slides 1.13 and 1.14), these are equal to the molar site fractions X_A and X_B.
2. The power i in the Redlich-Kister expansion.
3. The first parameter in Eq. [4].
4. Terms must be entered exactly in this format. (Do not leave spaces where none are shown.) (T = Kelvins).
5. Click here to enter comments.

Entering the second g^E parameter (from Slide 1.1, Eq. [4])



Saving all entered data



To now include SoluSoln.sln in EQUILIB and PHASE DIAGRAM CALCULATIONS see the Solution Introduction slide show, slides 6, 7 and 11.

1. Click on the file name (SoluSoln).
2,3. Click on **«File → Save SoluSoln»**. All data will be now saved in the file SoluSoln.sln.

Excess parameters in terms of equivalent fractions

- On Slides 1.13 and 1.14 the "coordination numbers" Z_{Ag} and Z_{Cu} were set to 1.0 (default).
  In this case, the g^E expressions will be in terms of the site fractions as shown on Slide 1.1.
- In general, for a solution A-B with coordination numbers Z_A and Z_B:

$$g^E = (Z_A X_A + Z_B X_B) \sum {}^{i}L_{AB} Y_A Y_B (Y_A - Y_B)^i \qquad i \geq 0 \qquad [1]$$

or $$g^E = (Z_A X_A + Z_B X_B) \sum q_{AB}^{ij} Y_A^i Y_B^j \qquad i,j \geq 0 \qquad [2]$$

or $$g^E = (Z_A X_A + Z_B X_B) \sum q_{AB}^{i} Y_A Y_B P_i (Y_A - Y_B) \qquad i \geq 0 \qquad [3]$$

where Y_A and Y_B are **equivalent site fractions**:

$$Y_A = Z_A X_A/(Z_A X_A + Z_B X_B) \qquad Y_B = Z_B X_B/(Z_A X_A + Z_B X_B)$$

(The parameters ${}^{i}L_{AB}$, q_{AB}^{ij} or q_{AB}^{i} are thus expressed as **J/equivalent** where one mole of A or B consists of Z_A or Z_B **"equivalents"** respectively.)

- Hence in a "regular solution" (with only the quadratic term non-zero) $g^E = CY_AY_B$ where C = constant, and the extremum in g^E occurs at $Y_A = Y_B = 0.5$ rather than at $X_A = X_B = 0.5$
- This permits one to emulate a charge-asymmetric molten salt solution (See Section 7) or to approximate solutions with short-range-ordering (See Section 9).

2. (a) Interpolating binary interaction terms into a ternary solution phase

(Kohler/Toop/Muggianu "geometric" approximations (Refs: (2, 3)) and (b) Adding ternary interaction terms

In a ternary system A-B-C in the One-lattice polynomial model ("Model #1"):

$$g^E = X_A X_B \alpha_{AB} + X_B X_C \alpha_{BC} + X_C X_A \alpha_{CA} + \text{(ternary terms)} \qquad [1]$$

where the α_{ij} are binary interaction functions (as on Slide 1.1 Eqs. [1-3]).

In the ternary system, α_{ij} may be approximated as being constant along either:

(i) a line where X_i/X_j = constant (Kohler approx.)

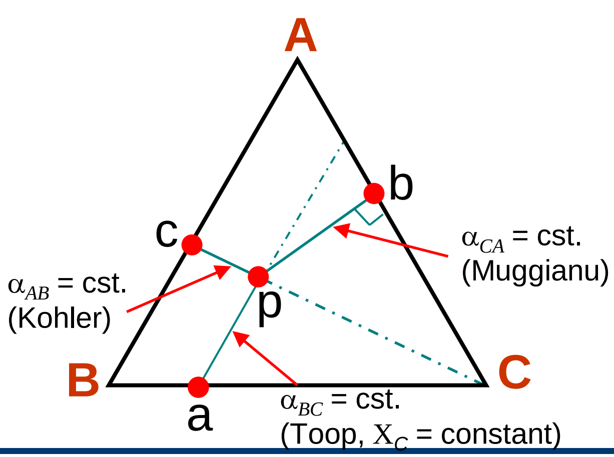
or (ii) a line where X_i = constant (Toop approx.)

or (iii) a line where X_j = constant (Toop approx.)

or (iv) a line perpendicular to the *i-j* edge of the Gibbs triangle (Muggianu approx.)

(Note: In the general case, replace X_i by "equivalent" fractions Y_i. See Slide 1.19)

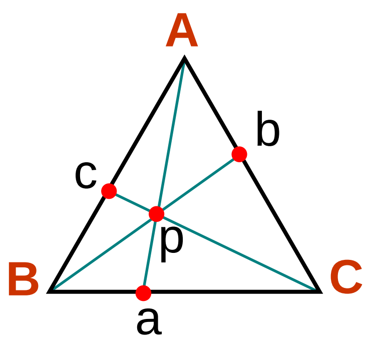
For example, in the following figure, α_{AB} is given by the Kohler approx., α_{BC} by the Toop (constant X_C) approx., and α_{CA} by the Muggianu approx. That is, g^E at point p is given in Eq. [1] by the values of α_{AB} , α_{BC} and α_{CA} at points c, a and b respectively.



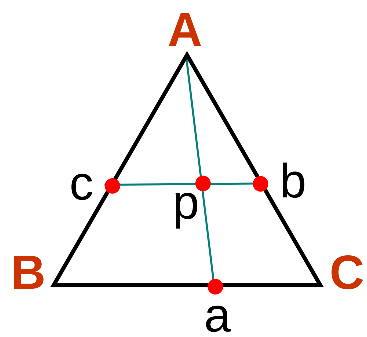
-For every ternary sub-system in an N-component solution, SoluSage allows you to specify the interpolation configuration. These are then carried over to the N-component system in a consistent manner (Refs. (2, 3)).

Default interpolations

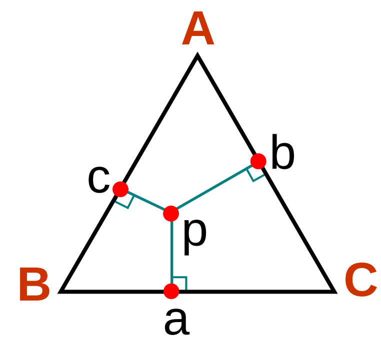
Three common ternary interpolation configurations are illustrated:



“All Kohler”



“Kohler/Toop (X_A = constant)”



“All Muggianu”

- Each component of a solution phase is assigned a **“chemical group number”** (1, 2, 3…). (Usually, components which are chemically similar are assigned the same group number.)
- If A, B and C are all members of the same group, or are members of three different groups, then the **“All Kohler”** configuration is the default.
- If B and C are in the same group while A is in a different group, then the **“Kohler/Toop (X_A = constant)”** configuration is the default.
- If one or more of A, B or C is in group “0”, then **“All Muggianu”** is the default configuration.
- However, for any ternary sub-system, the **default configuration can be over-written**.

Interpolating binary interaction terms

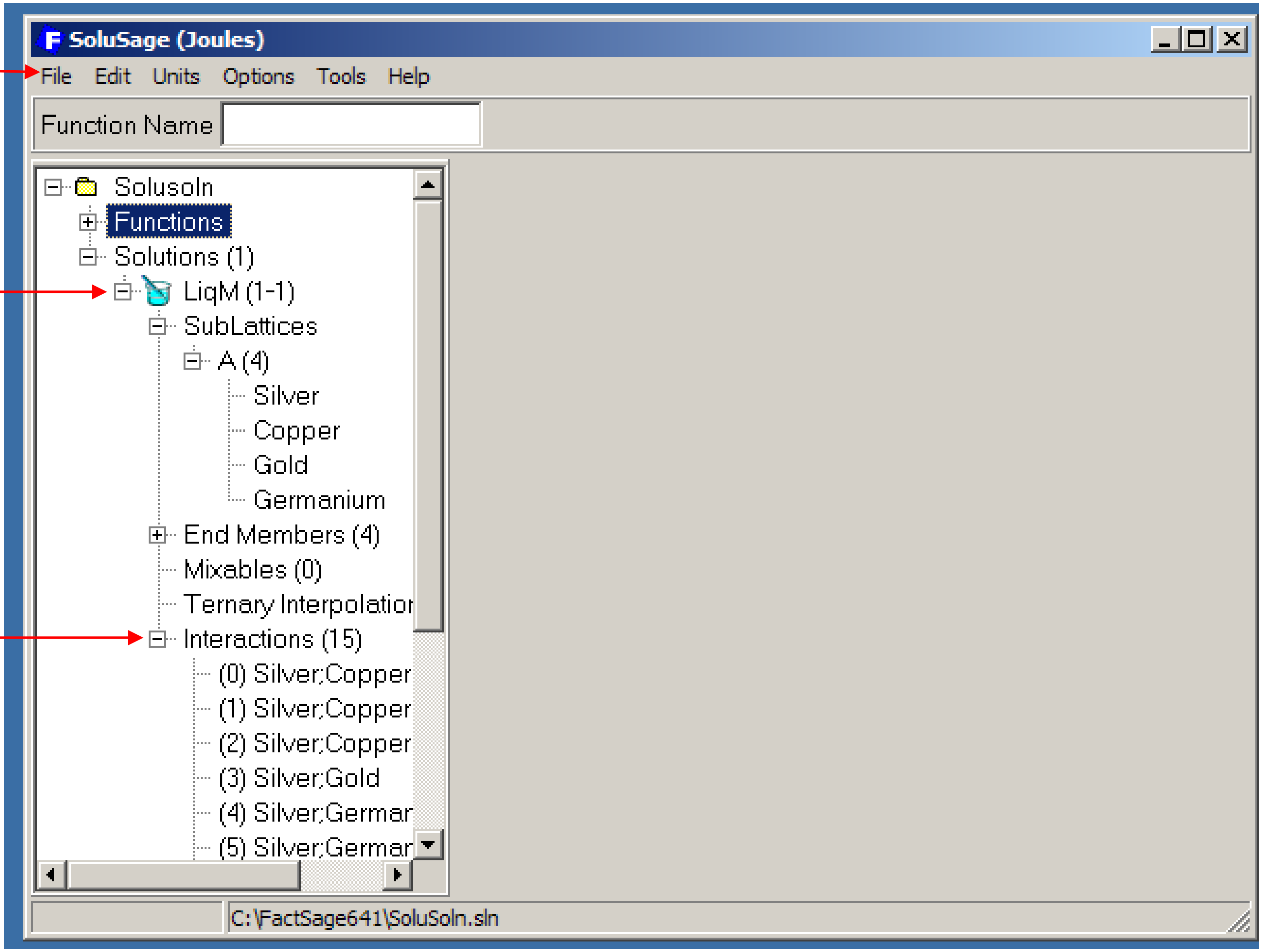
Example: Ag-Cu-Au-Ge quaternary liquid solution phase

The "LiqM" solution for liquid Ag-Cu alloys entered in Section… has been expanded to include Au and Ge and stored as a slide-show example.

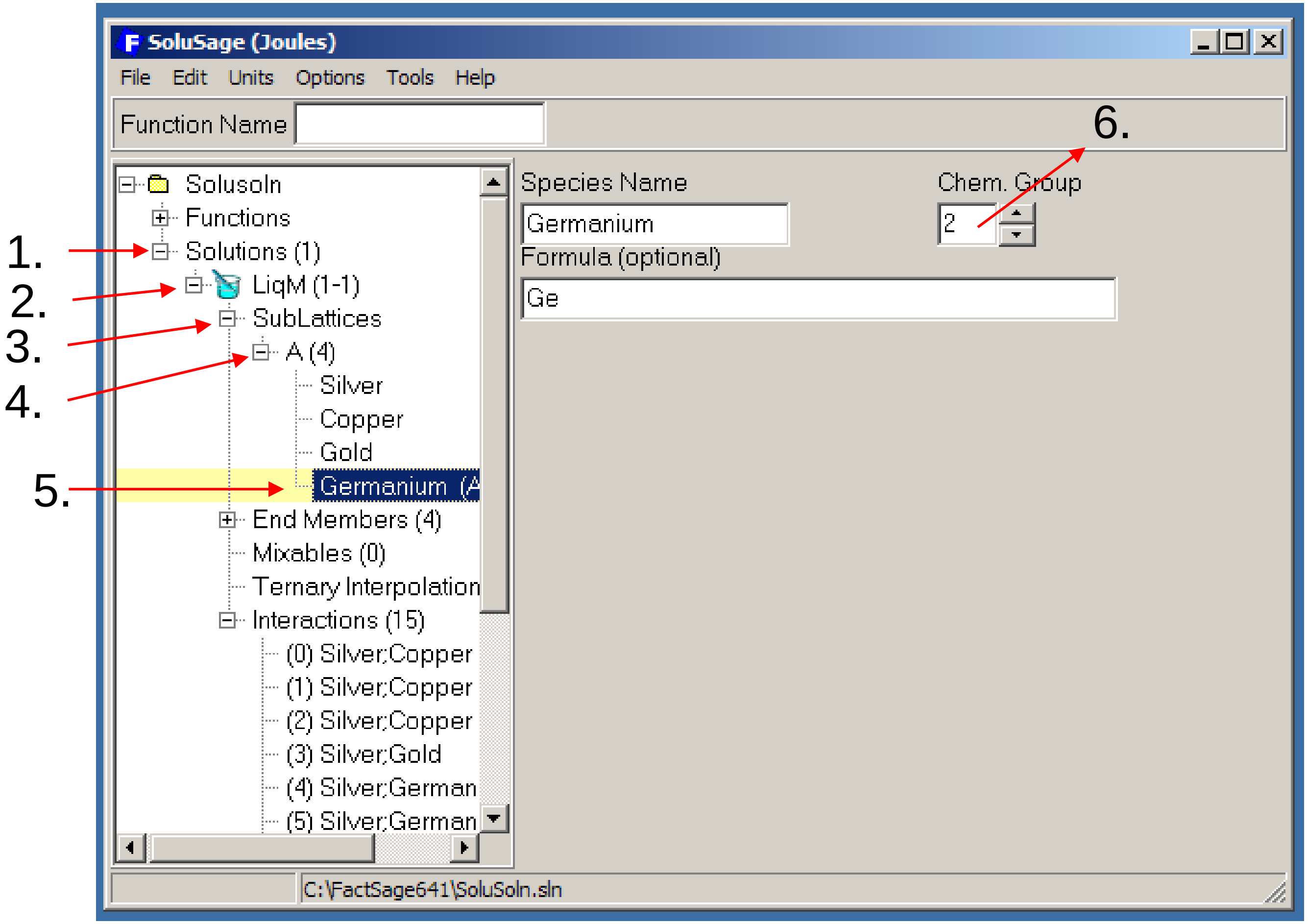
1. Click on «File→Open SoluSoln»

2. Click on «LiqM» and then expand the tree views

3. Binary interaction terms for all 6 binary sub-systems have been entered. You can view the parameters if you wish by clicking on them

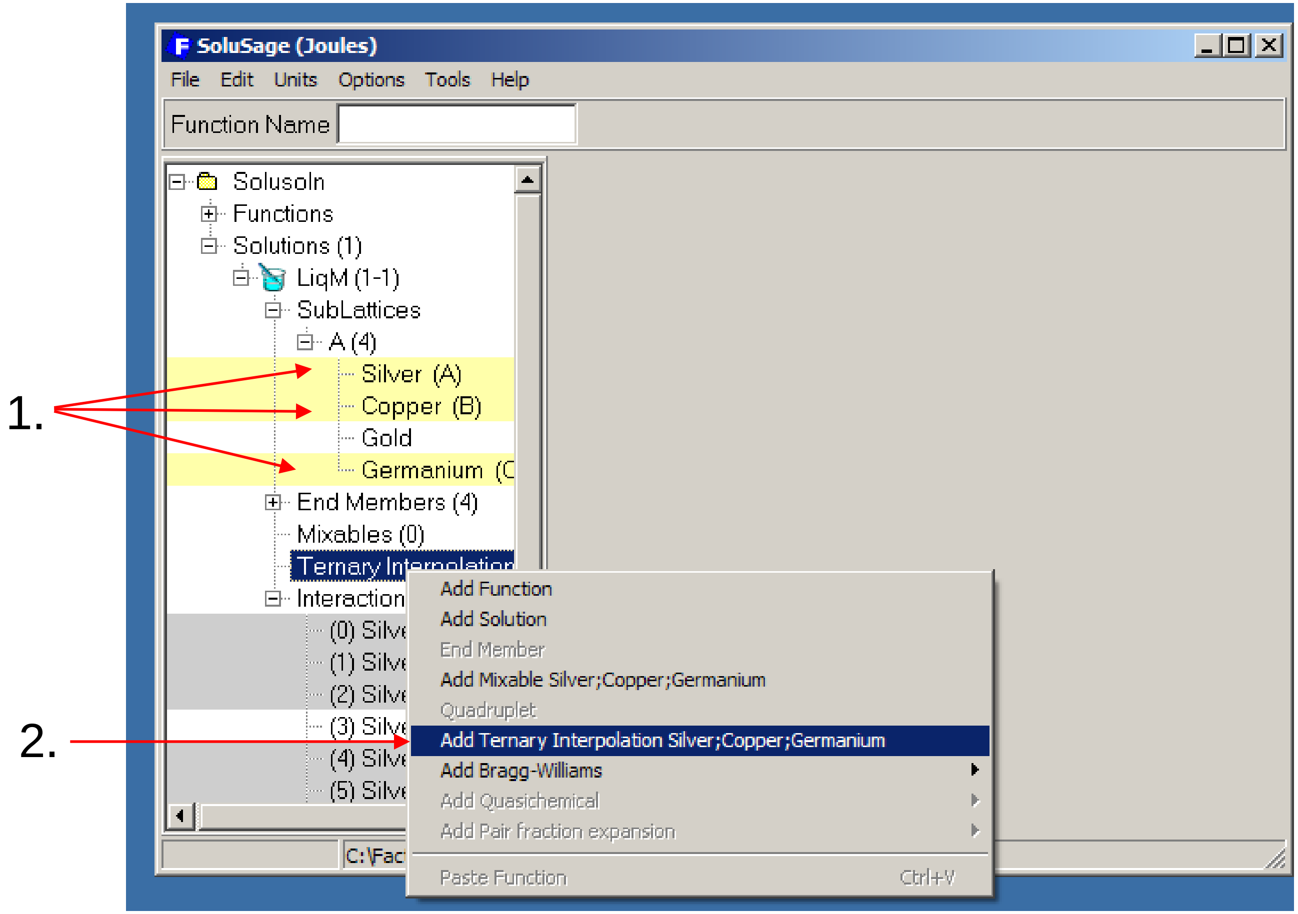


Entering the “chemical group”

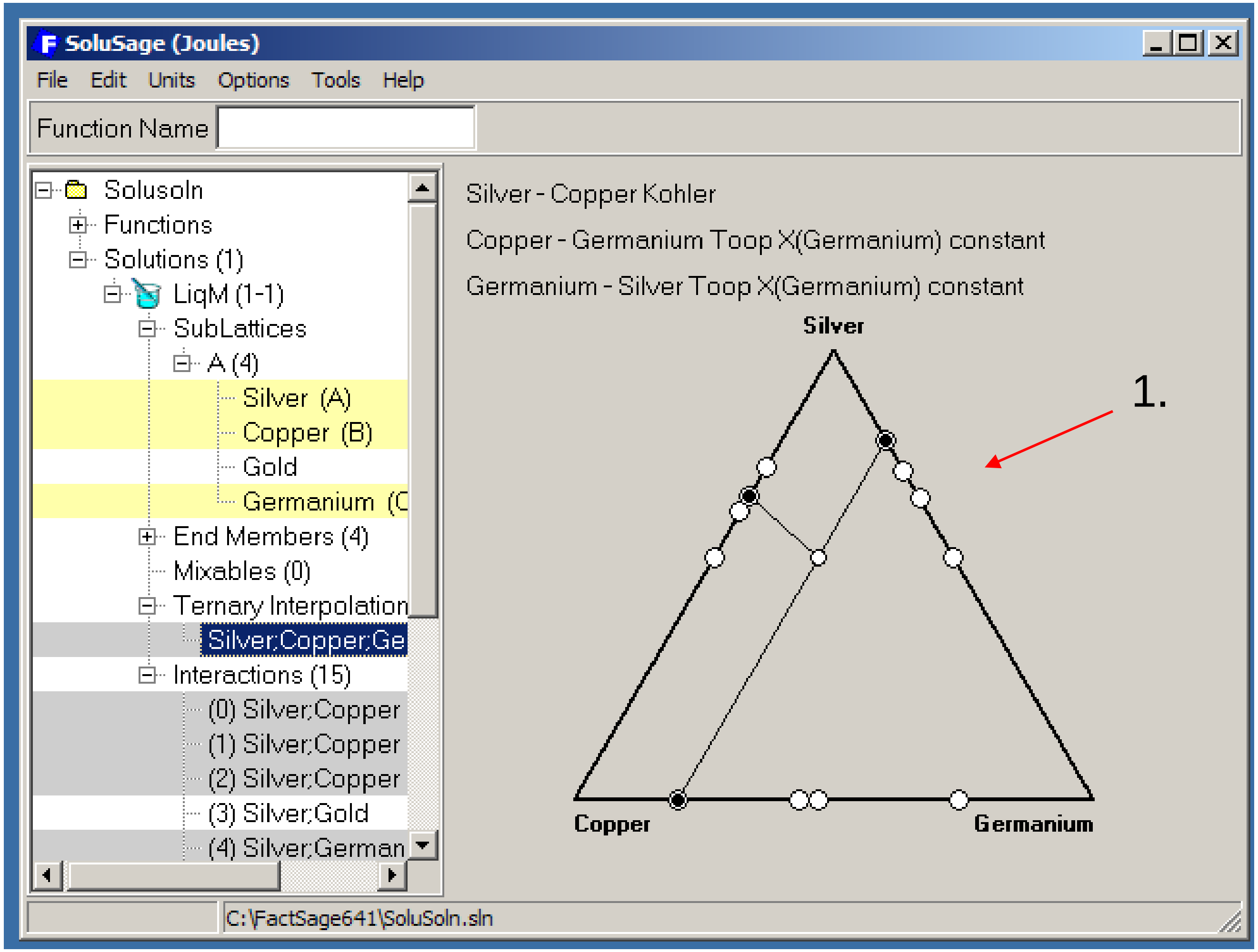


Click on 1, 2, 3, 4 to expand the tree view.
5. Click on the species Germanium.
6. Germanium has been assigned to **chemical group** «2». The other 3 species have been assigned to chemical group «1» (See slides…).

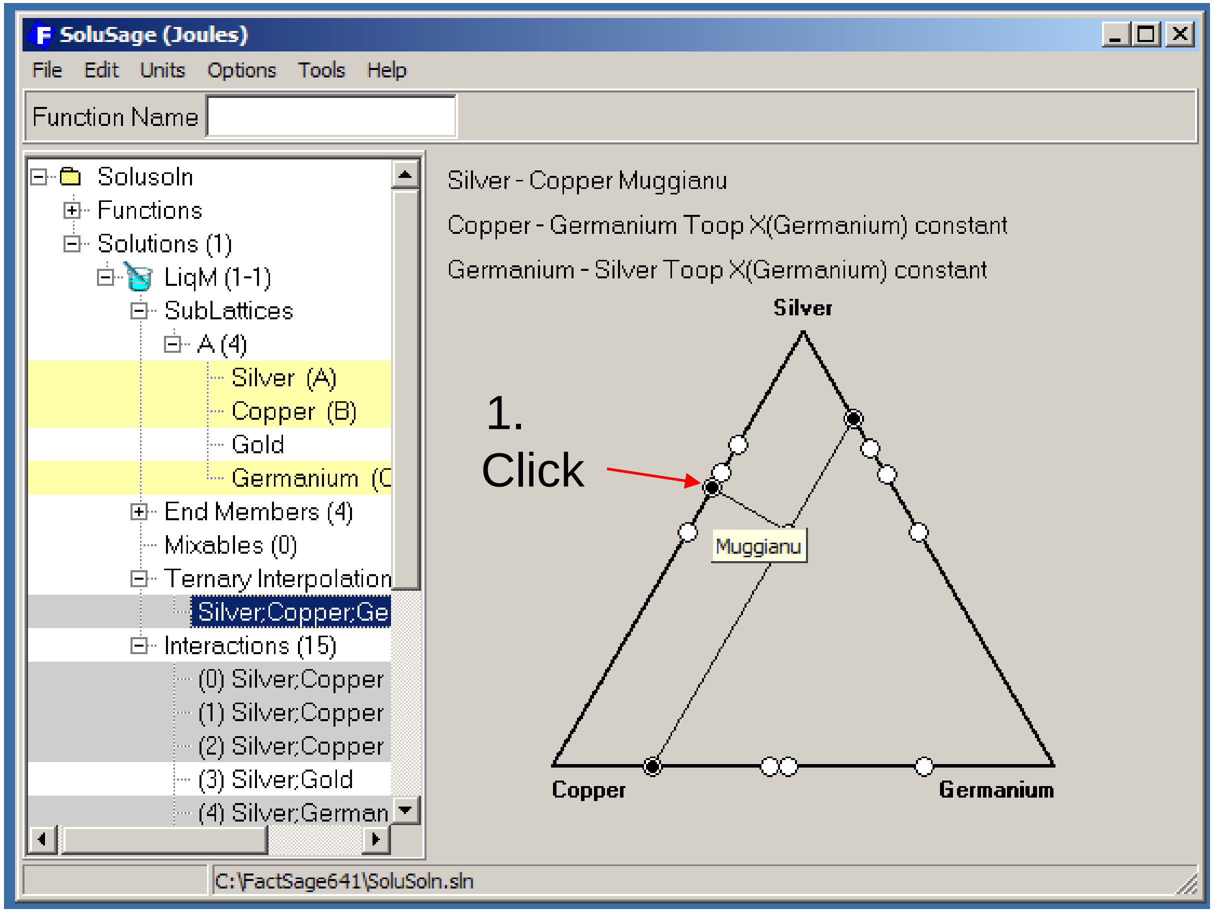
Selecting the ternary interpolation configuration for the Ag-Cu-Ge-ternary sub-system



1. Holding down the Ctrl Key, highlight three species (Ag, Cu, Ge), then right click.
2. Click.



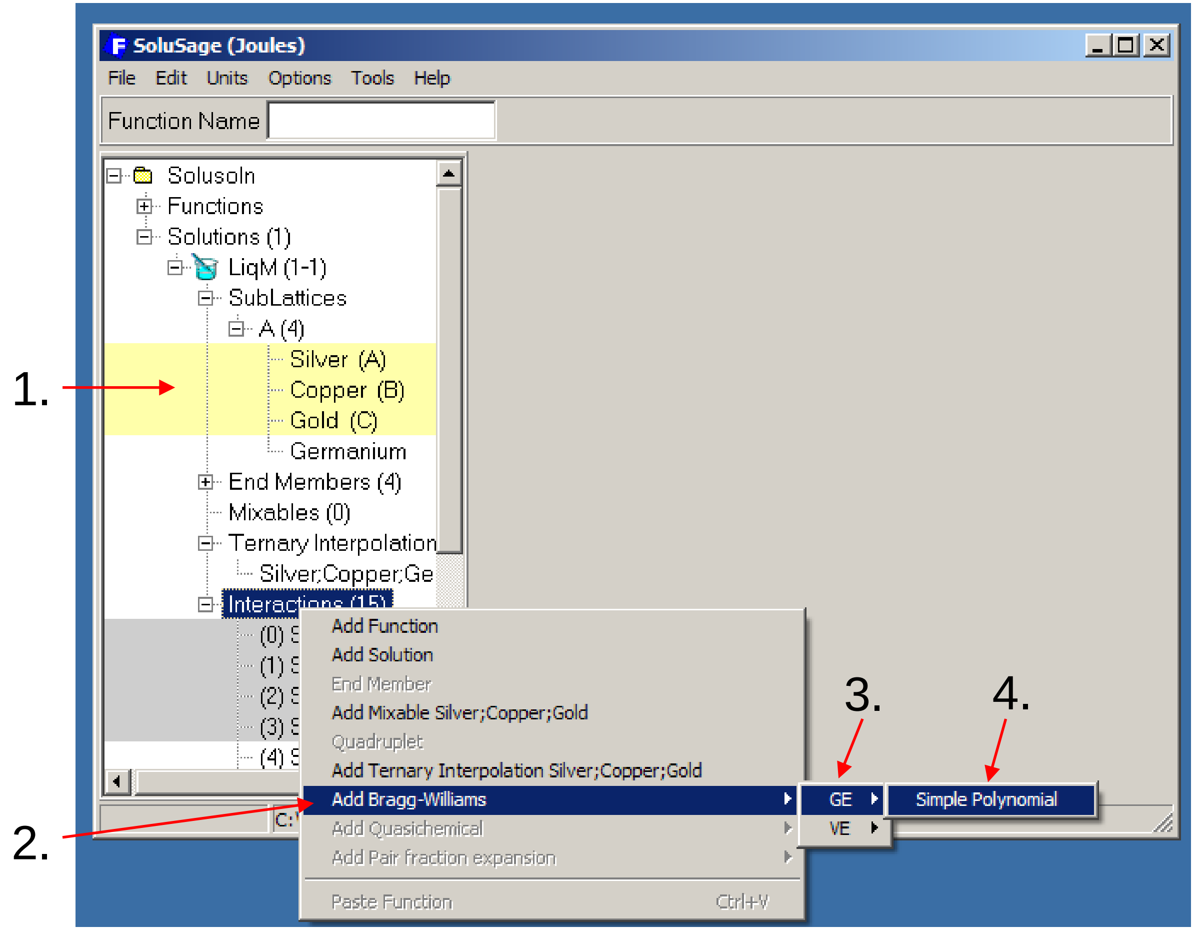
1. Since Ag and Cu are in chemical group «1» while Ge is in group «2», **Kohler/Toop (X_{Ge} constant)** is the **<u>default configuration</u>** as described in Slide 2.1. The diagram shows this.



1. The default configuration may be **over-written** by clicking on the small circles. In this case, by clicking on the circle as shown, the Ag-Cu binary parameters will now be interpolated into the ternary system by the Muggianu approximation.

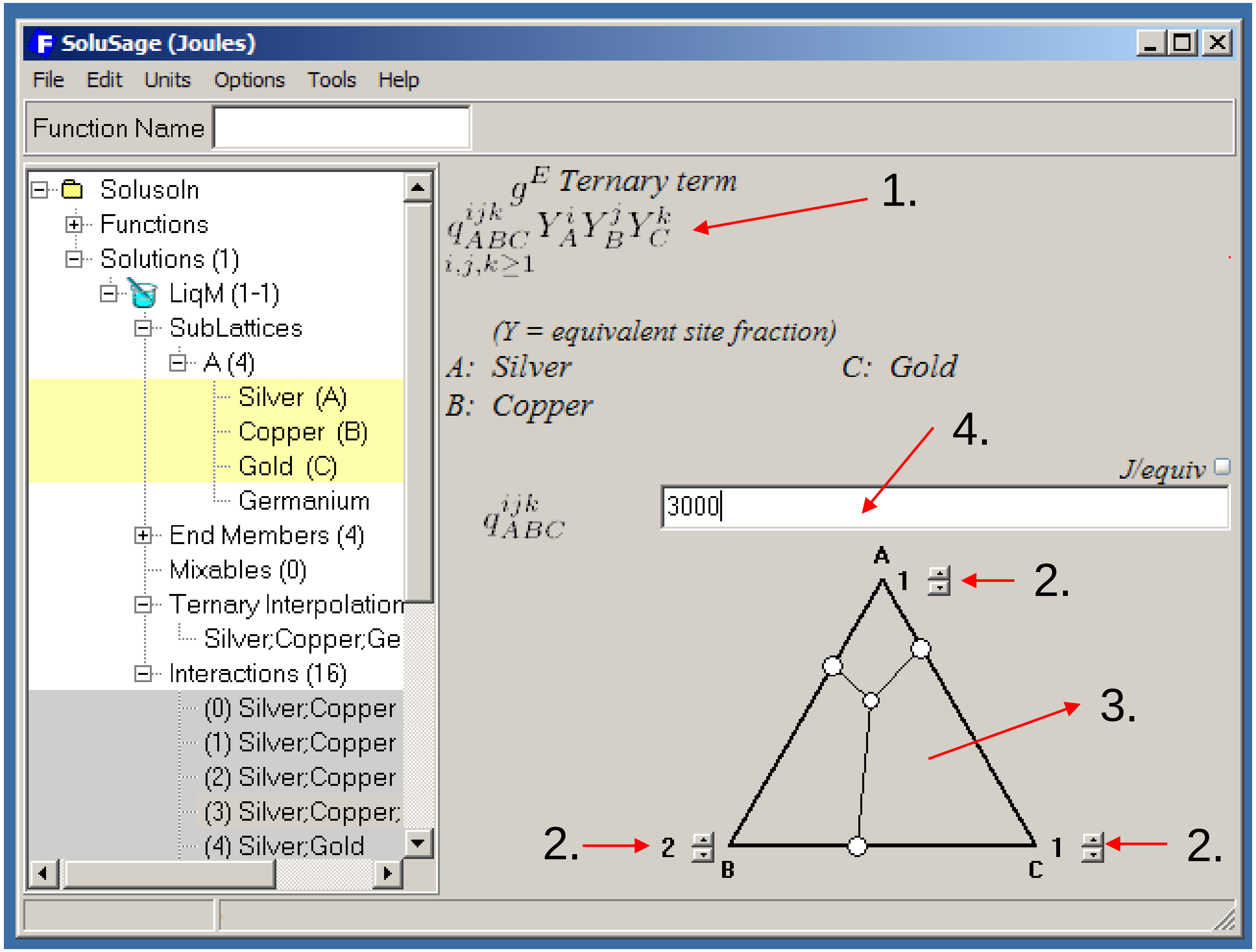
Adding ternary interaction parameters

Ternary terms may be added to the expression for g^E (Slide 1.1, Eq. [1])



1. Holding down the Ctrl Key, highlight the three species involved in the interaction, then right click.
2,3,4. Mouse over, then click.

Entering a ternary g^E term: 3000 $X_{Ag}^{2} X_{Cu}^{1} X_{Au}^{1}$ J/mol

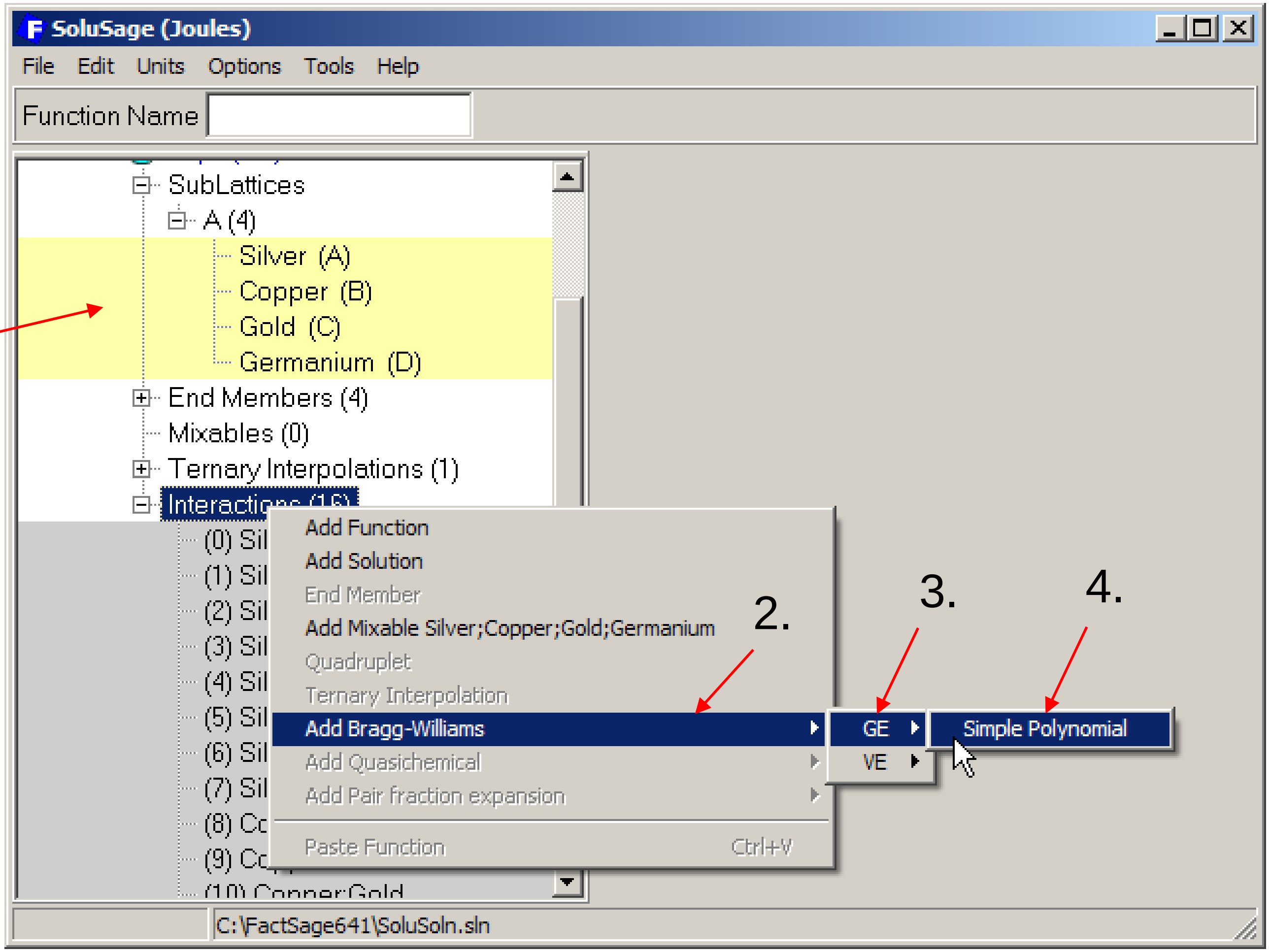


1. Since the LiqM solution is modeled with the single-sublattice polynomial model, ternary terms are of the form shown here.
2. The powers i, j, k are entered by clicking on the arrows.
3. The diagram reminds you of the interpolation configuration used for this system.
4. Enter the parameter (in general, as a function of T as for binary parameters).

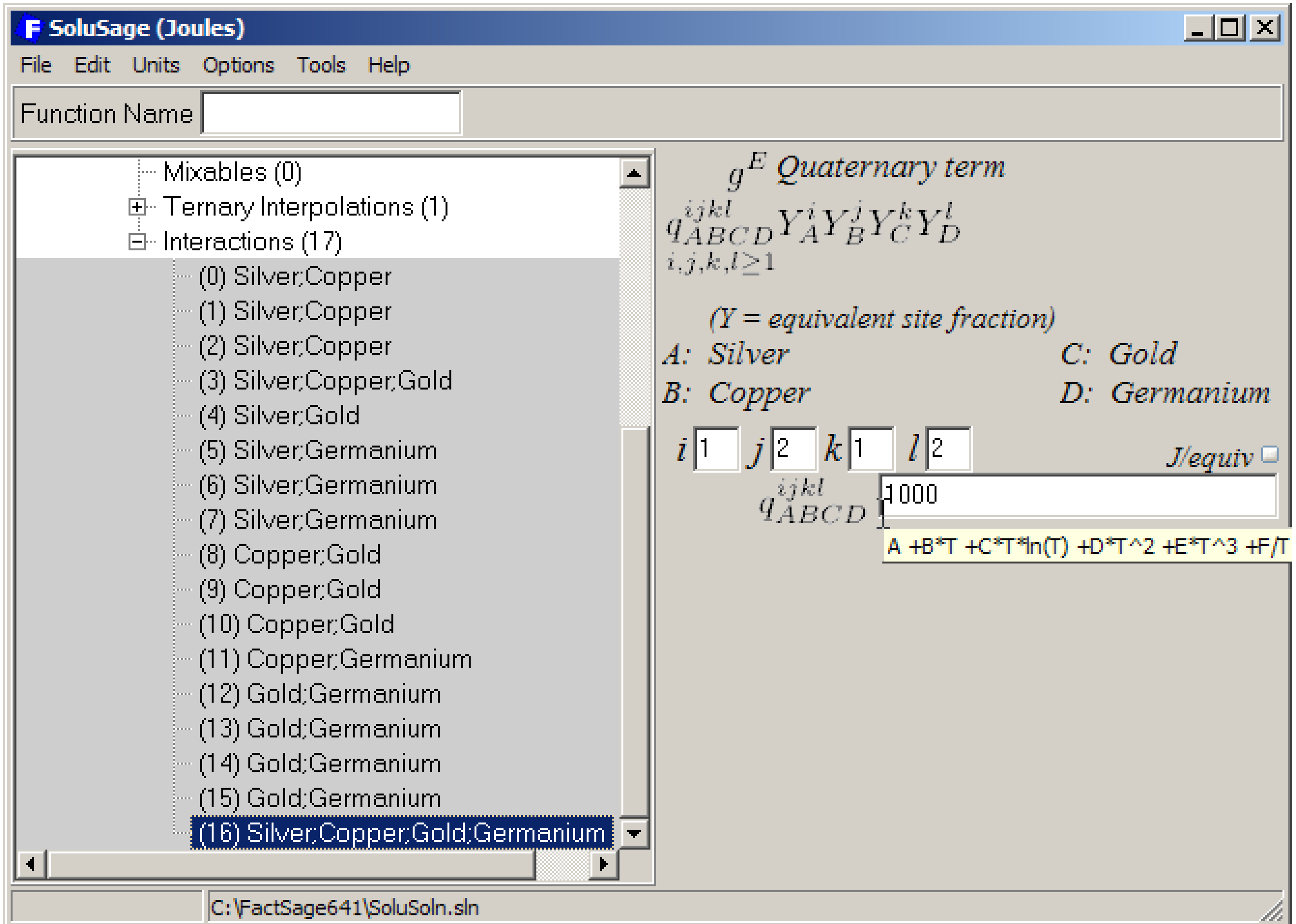
Quaternary Interaction Parameters

Quaternary terms may also be added to g^E.

1. Click, holding down the Ctrl key, then right click.



Adding the quaternary term 1000 $X_{Ag} X_{Cu}^2 X_{Au} X_{Ge}^2$ J/mol

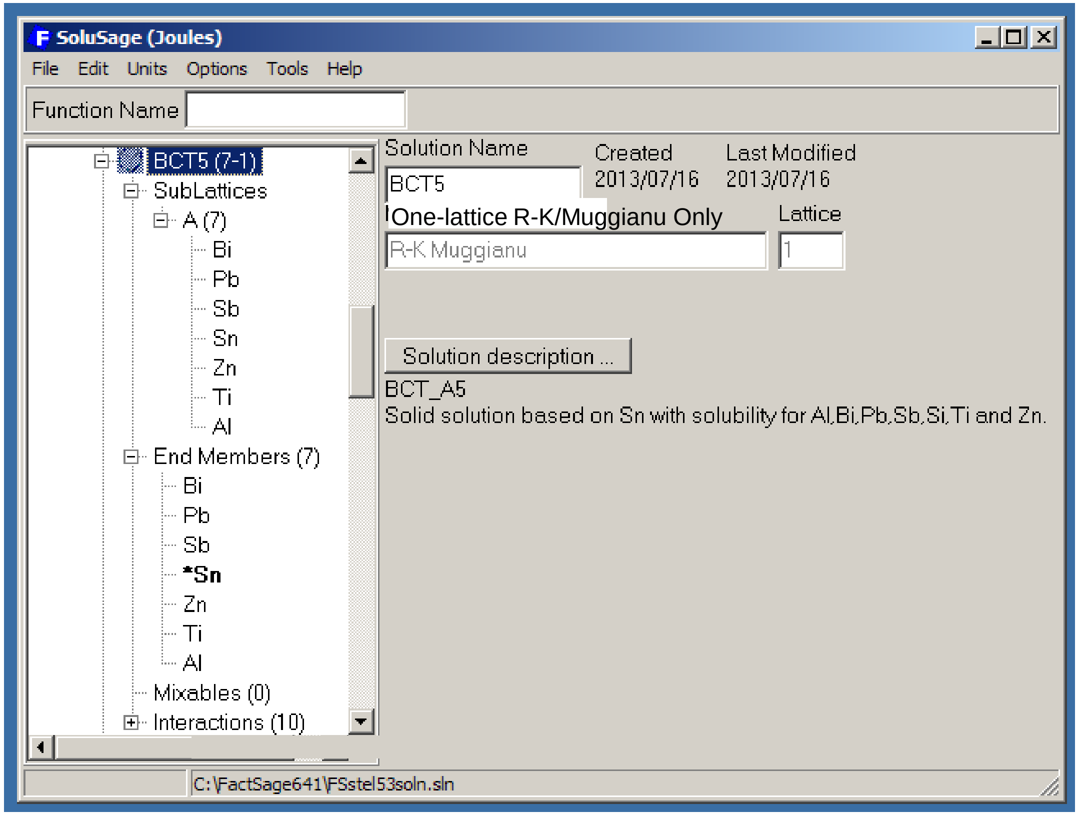


3. The “One-lattice Redlich-Kister Muggianu Only” Model (“Model 7”)

This model is a **restricted version** of the general One-lattice Polynomial Model (model #1) described in Section 1. The restrictions are:

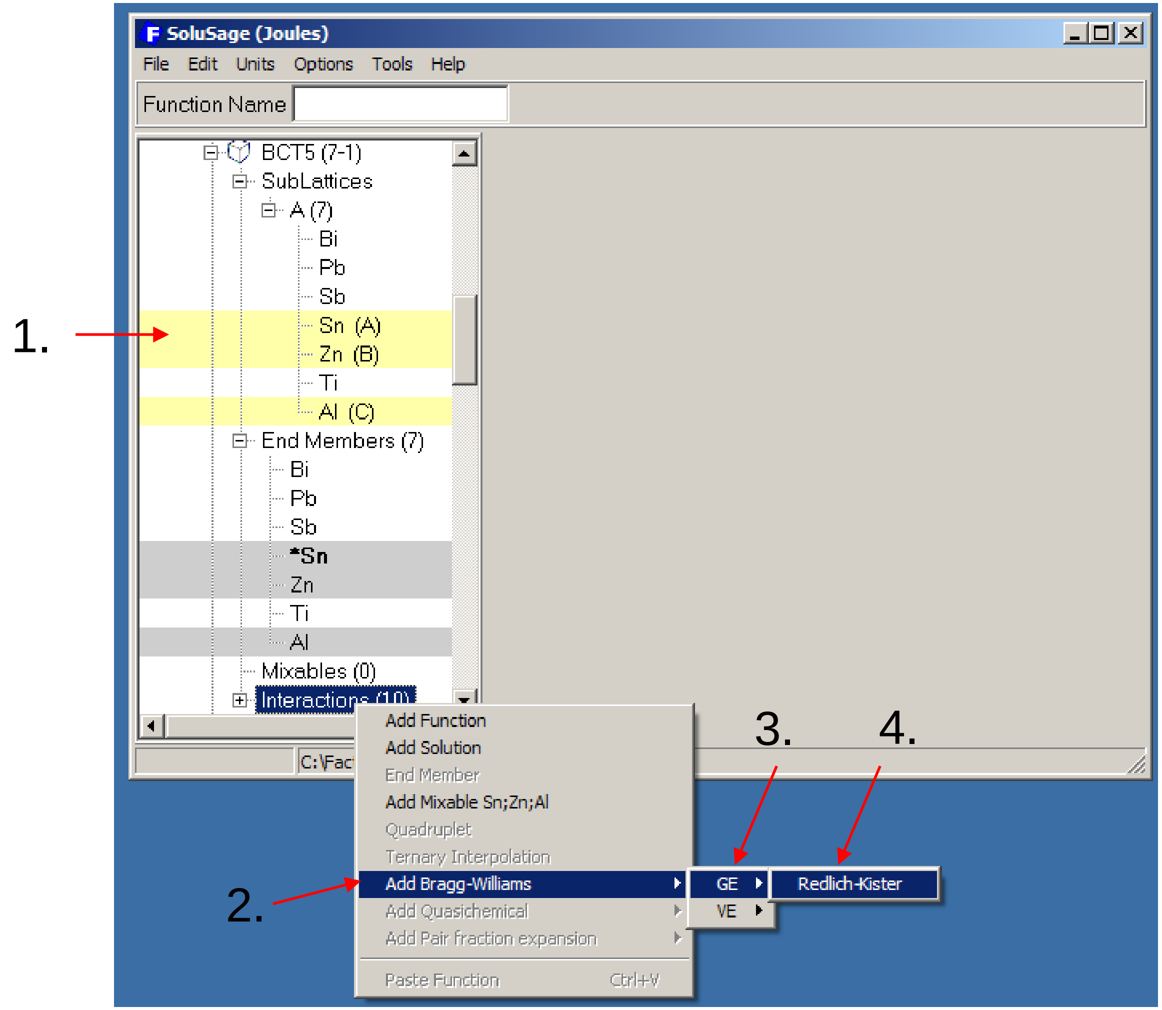
- Interaction terms expressed **only** as Redlich-Kister polynomials
- Excess terms expressed **only** as polynomials in molar site fractions (not equivalent site fractions).
- Binary terms interpolated into ternary systems **only** by the “All Muggianu” configuration (see Slide 2.1)

That is, this is a one-lattice version of the Compound Energy Formalism (see Section 5)

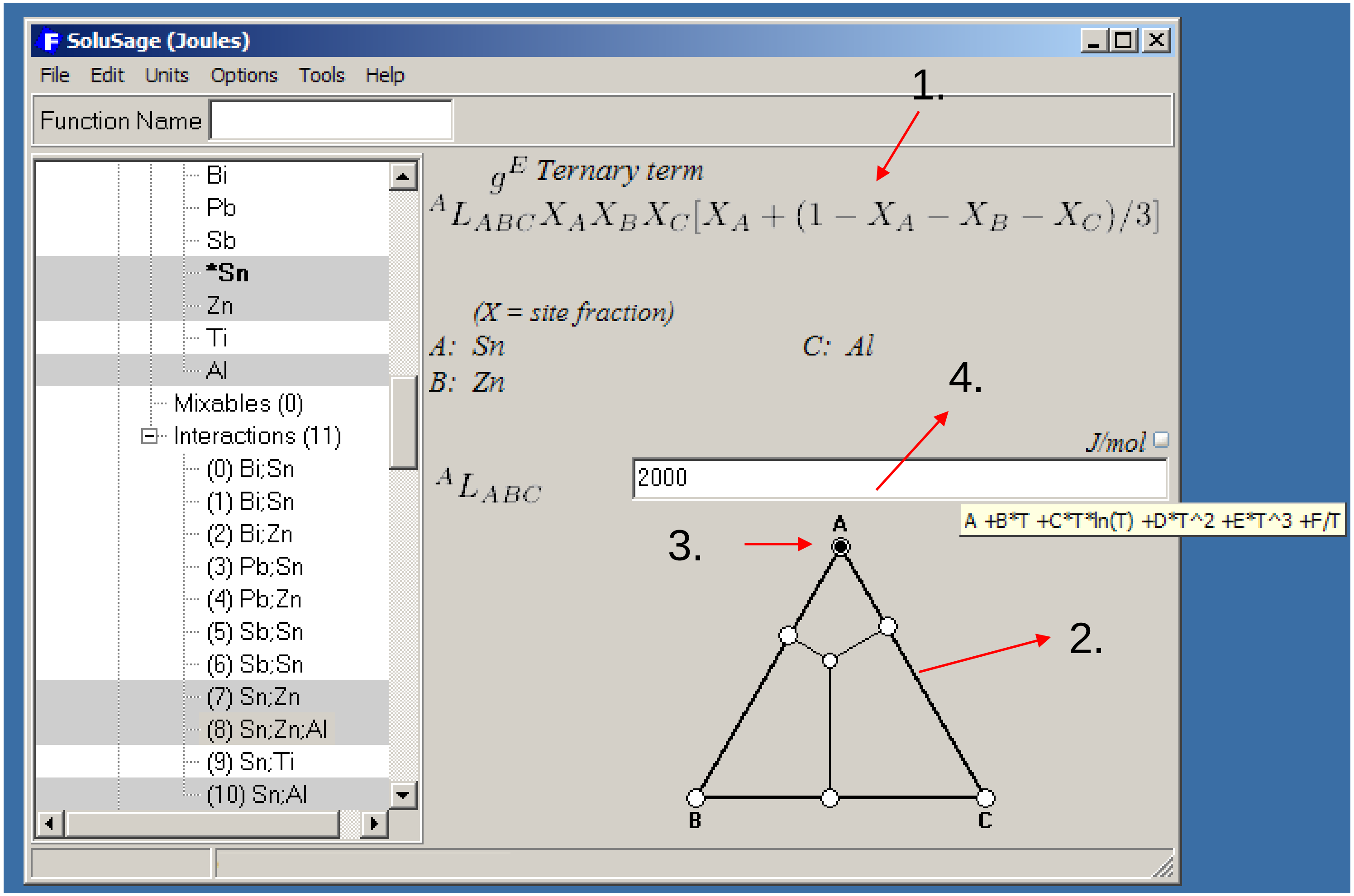


As an example, the BCT5 solution phase in the FSstel database is described with this model

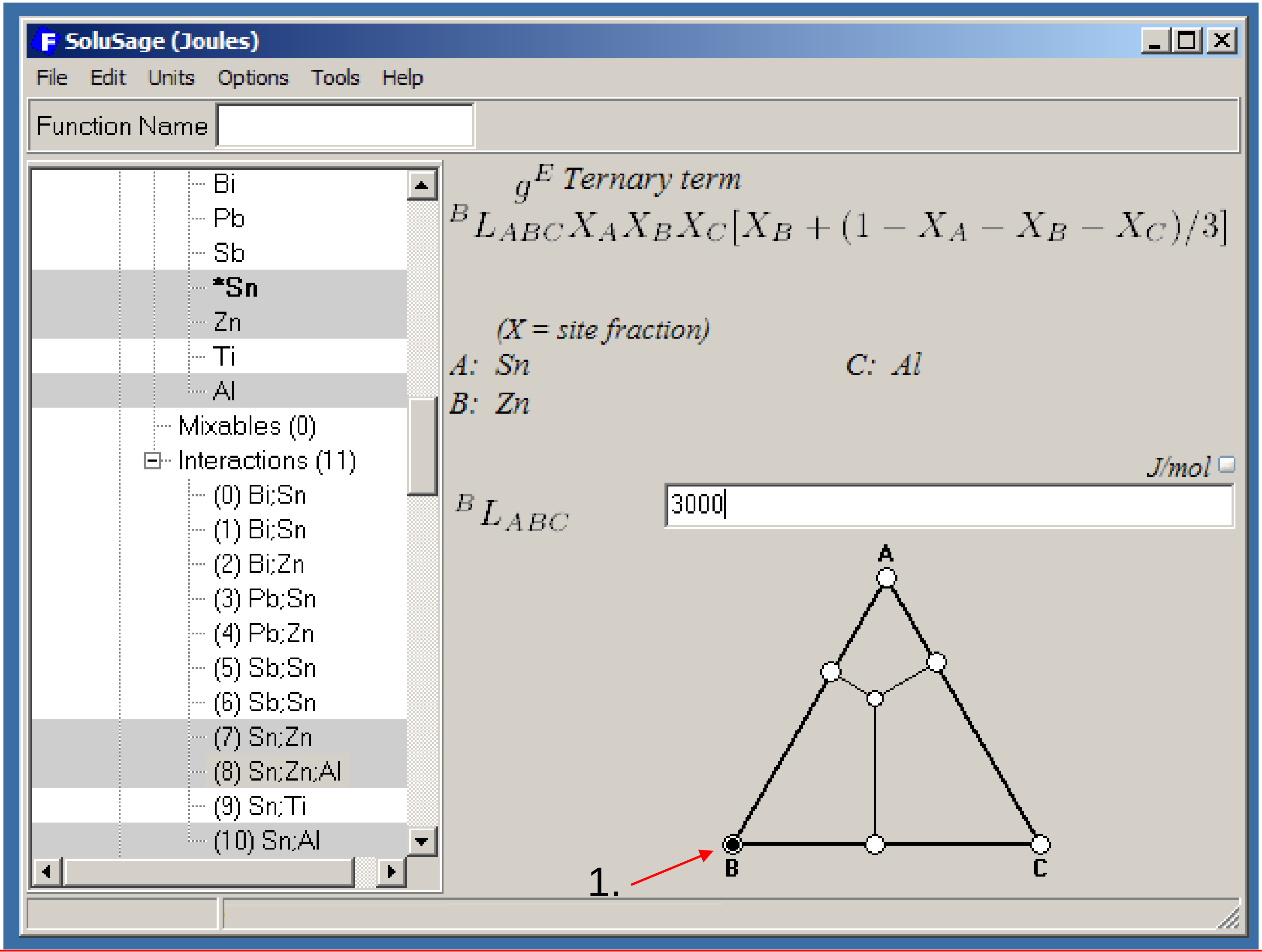
Ternary interaction terms in the One-sublattice R-K Muggianu Only Model



1. Holding down the Ctrl Key, highlight the three species involved in the ternary interaction (Sn, Zn, Al), then right click.
2,3,4. Mouse over then click.

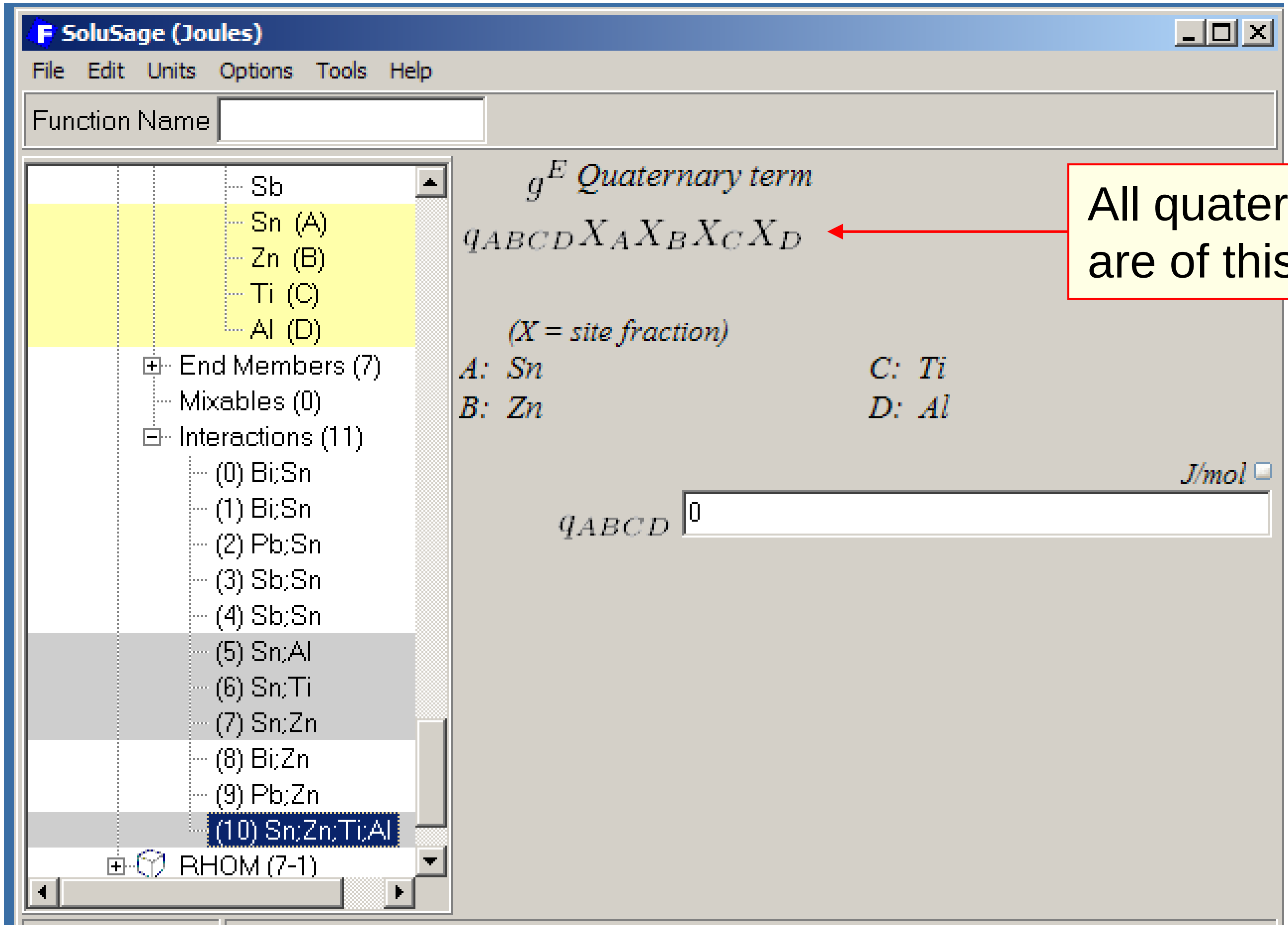


1. In this model, ternary parameters are expressed by the « Redlich-Kister » equation shown here.
2. The diagram reminds you that the «All Muggianu» configuration is used.
3. Click on the A-corner to enter the ${}^{A}L_{ABC}$ term as shown.
4. Enter the parameter (as a function of T in general).



1. To enter the $^B L_{ABC}$ parameter you must first repeat steps 2, 3, 4 of slide 3.1 (otherwise the data entered on slide 3.2 will be lost), then click on the B-corner of the triangle.

Quaternary interaction terms



All quaternary terms are of this form.

4. The Al_2O_3-Fe_2O_3 Corundum Solution

Illustrating: (1) Use of the "Stoichiometry" (Stoic) variable

(2) Using a one-lattice model when a second lattice contains only one species

- The Al_2O_3-Fe_2O_3 corundum solution in modeled assuming Al^{3+} and Fe^{3+} species mix randomly on a cation lattice while the anion lattice contains only O^{2-} ions.
- Since mixing occurs on only one lattice, a one-lattice model can be used.

$$g = (X_{Al} g^0_{Al_2O_3}/2 + X_{Fe} g^0_{Fe_2O_3}/2) + RT(X_{Al}\ln X_{Al} + X_{Fe}\ln X_{Fe}) + g^E \quad [1]$$

J/**mole of (Al + Fe) species**

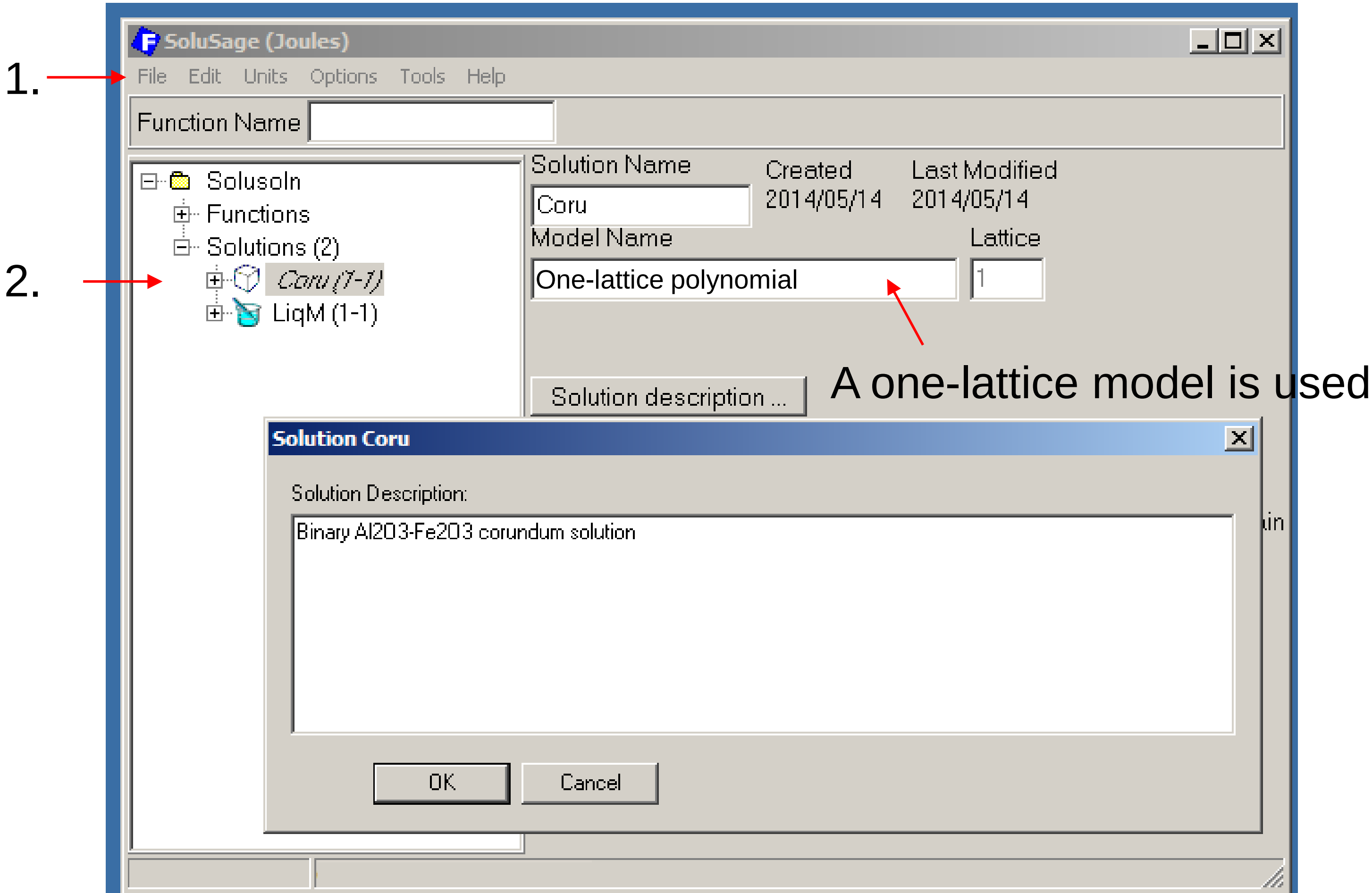
where: $$g^E = (9464.2 + 13.376T) X_{Al} X_{Fe} + 3970.6\ X^2_{Al} X_{Fe} \quad [2]$$

J/**mole of (Al + Fe) species**

where: X_{Al} and X_{Fe} are the molar site fractions

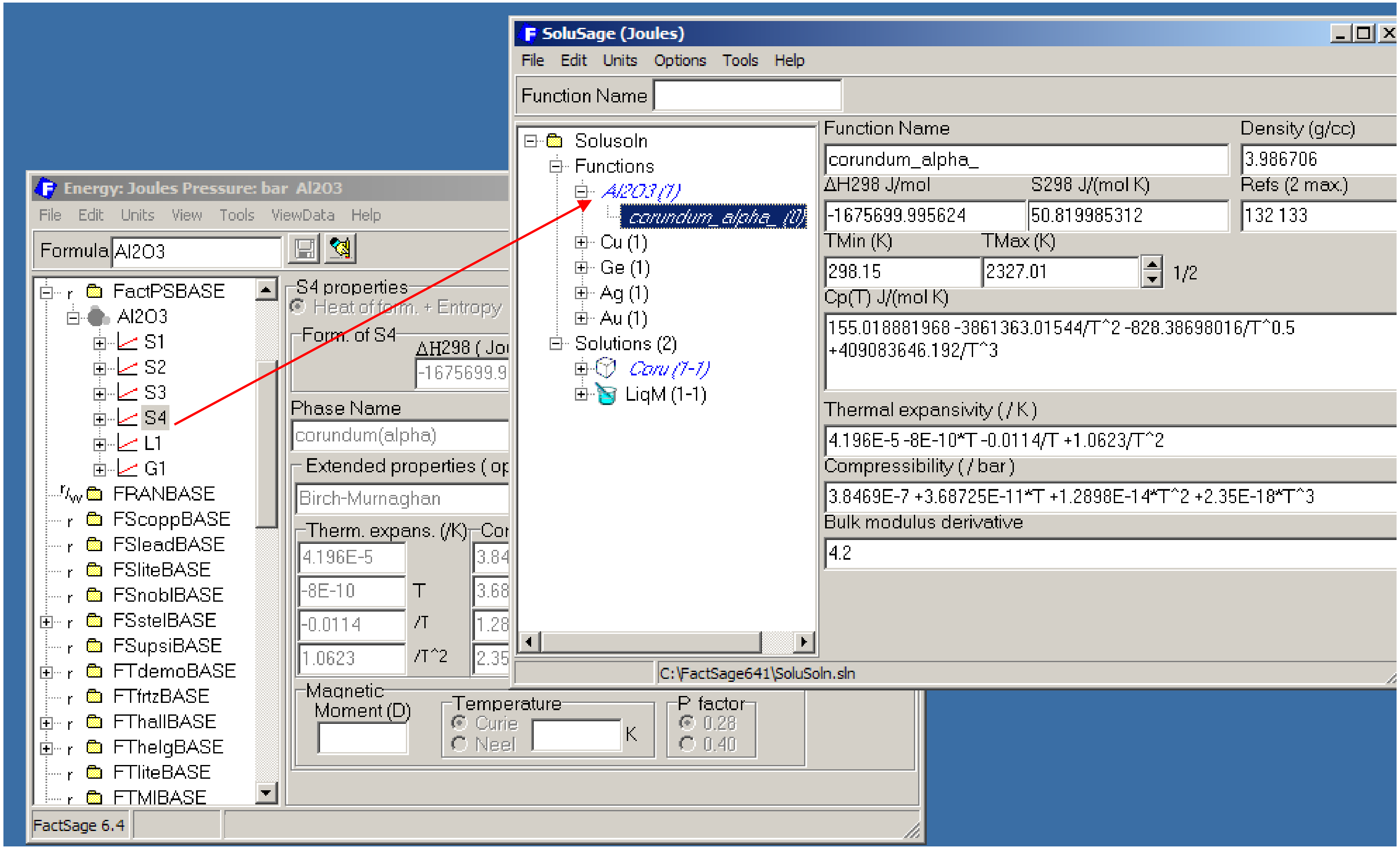
Note: g and g^E are expressed **per mole of species** (Al^{3+} + Fe^{3+})

$g^0_{Al_2O_3}$ and $g^0_{Fe_2O_3}$ are end-member Gibbs energies where **the end-member Al_2O_3 contains 2 moles of species Al^{3+}** and **the end-member Fe_2O_3 contains 2 moles of species Fe^{3+}**

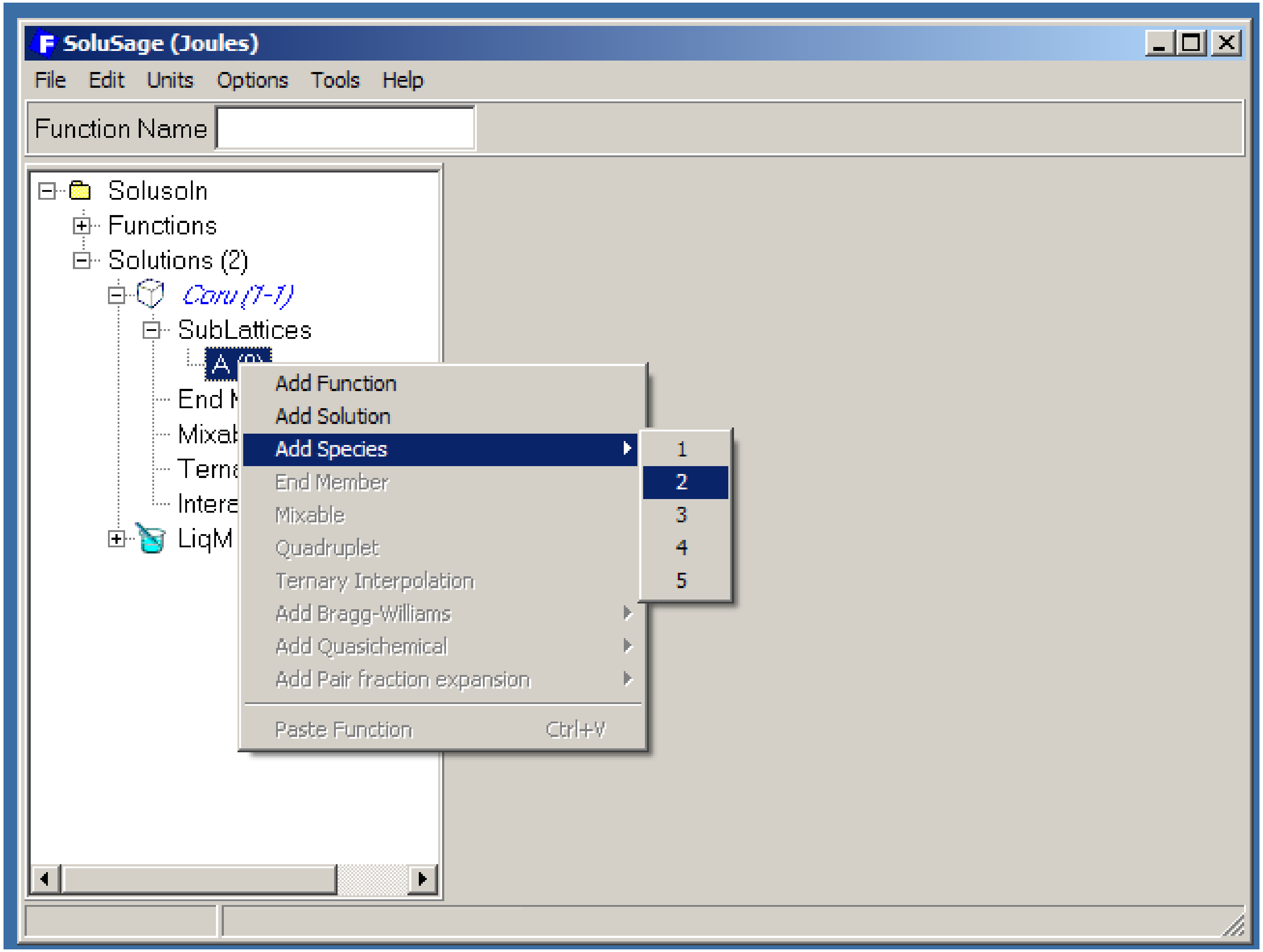


1. The data have been stored in SoluSoln.sln
   Click on «**File→Open SoluSoln**».
2. Click on the **Coru** solution phase.

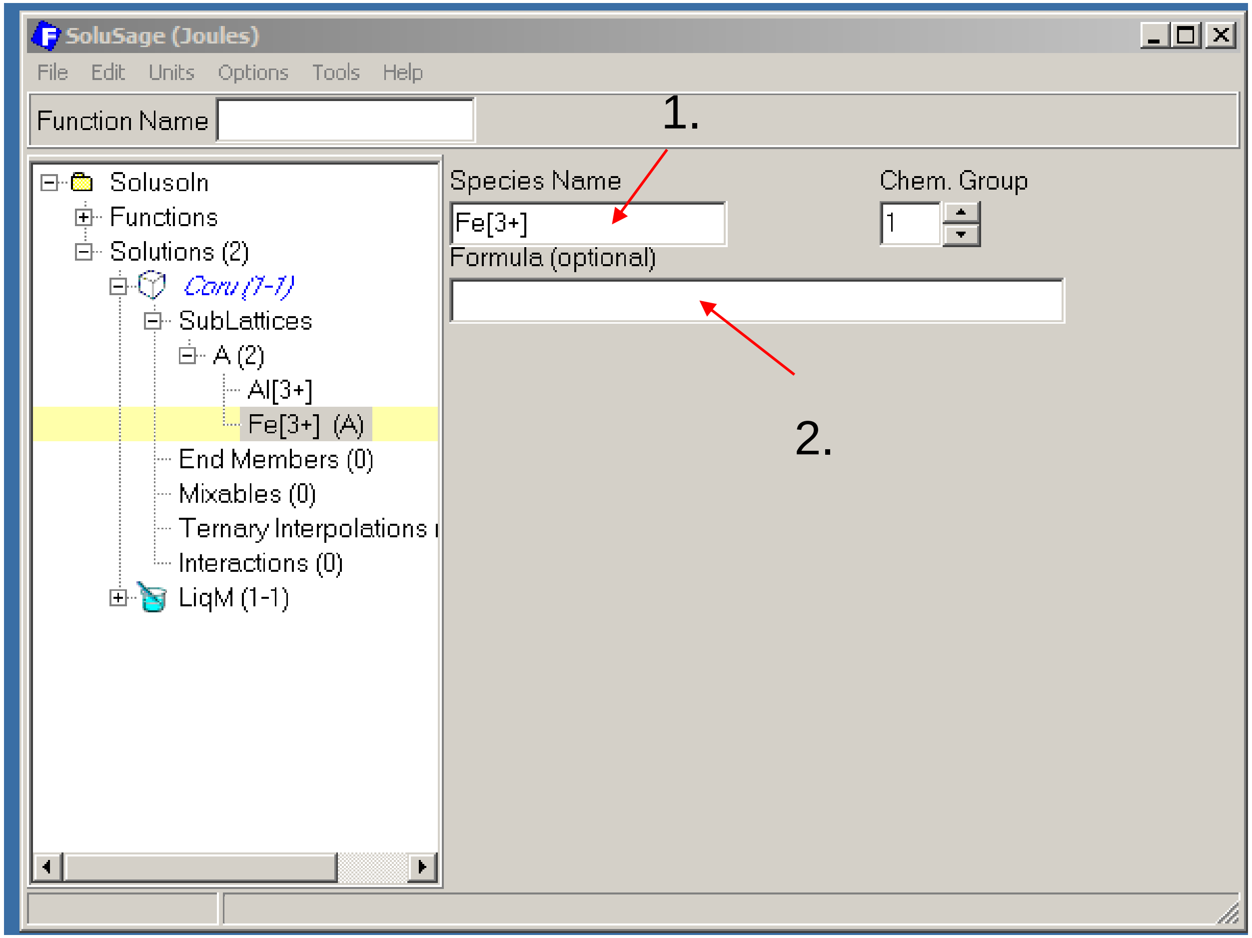
- The input follows closely that of the example in Section 1.



Drag and drop data for the S4 (corundum) phase from FactPS to create a «function» (see Slide 1.3). Do the same to create a function Fe2O3#hematite.

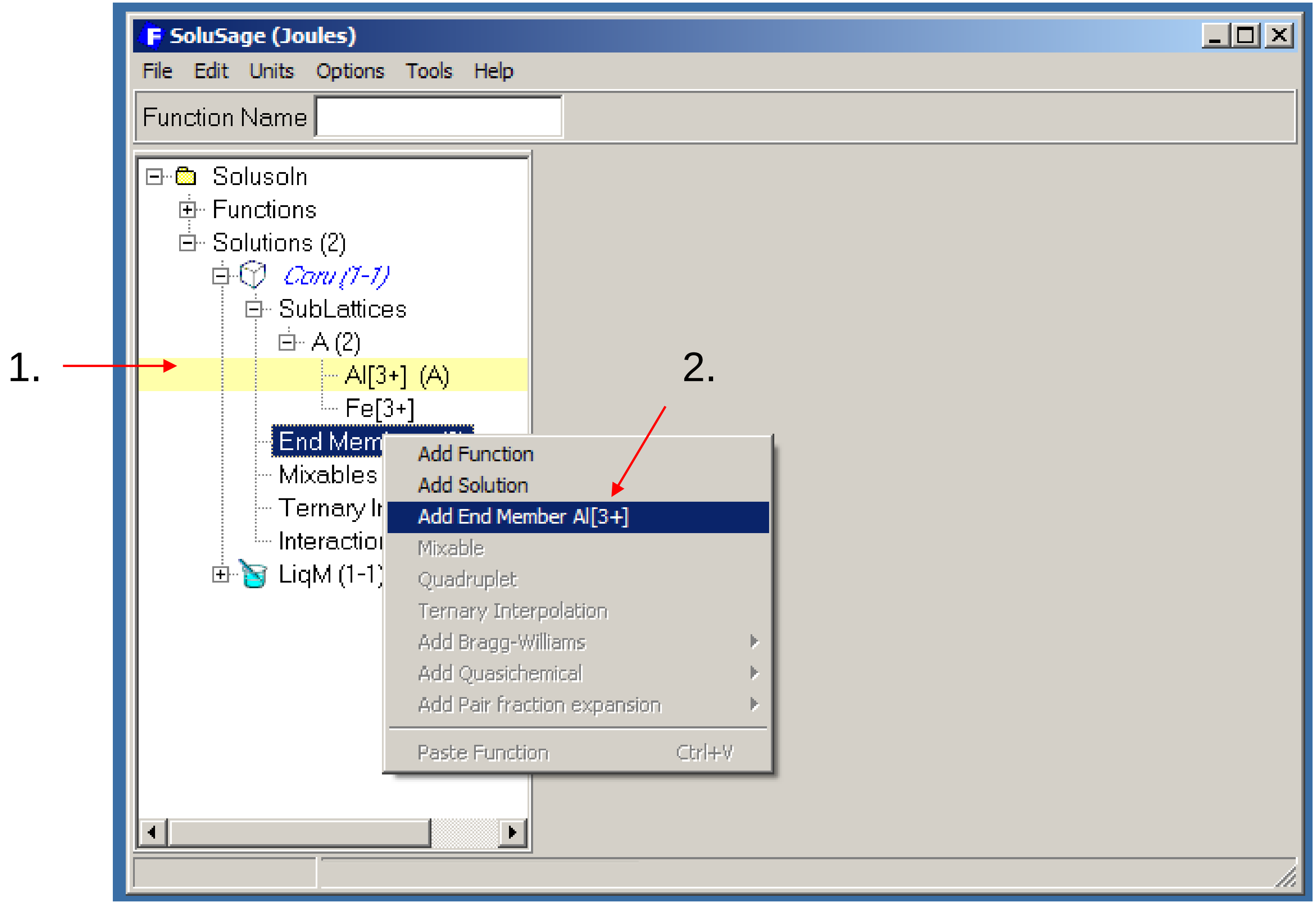


Create two species (see Slide 1.8)



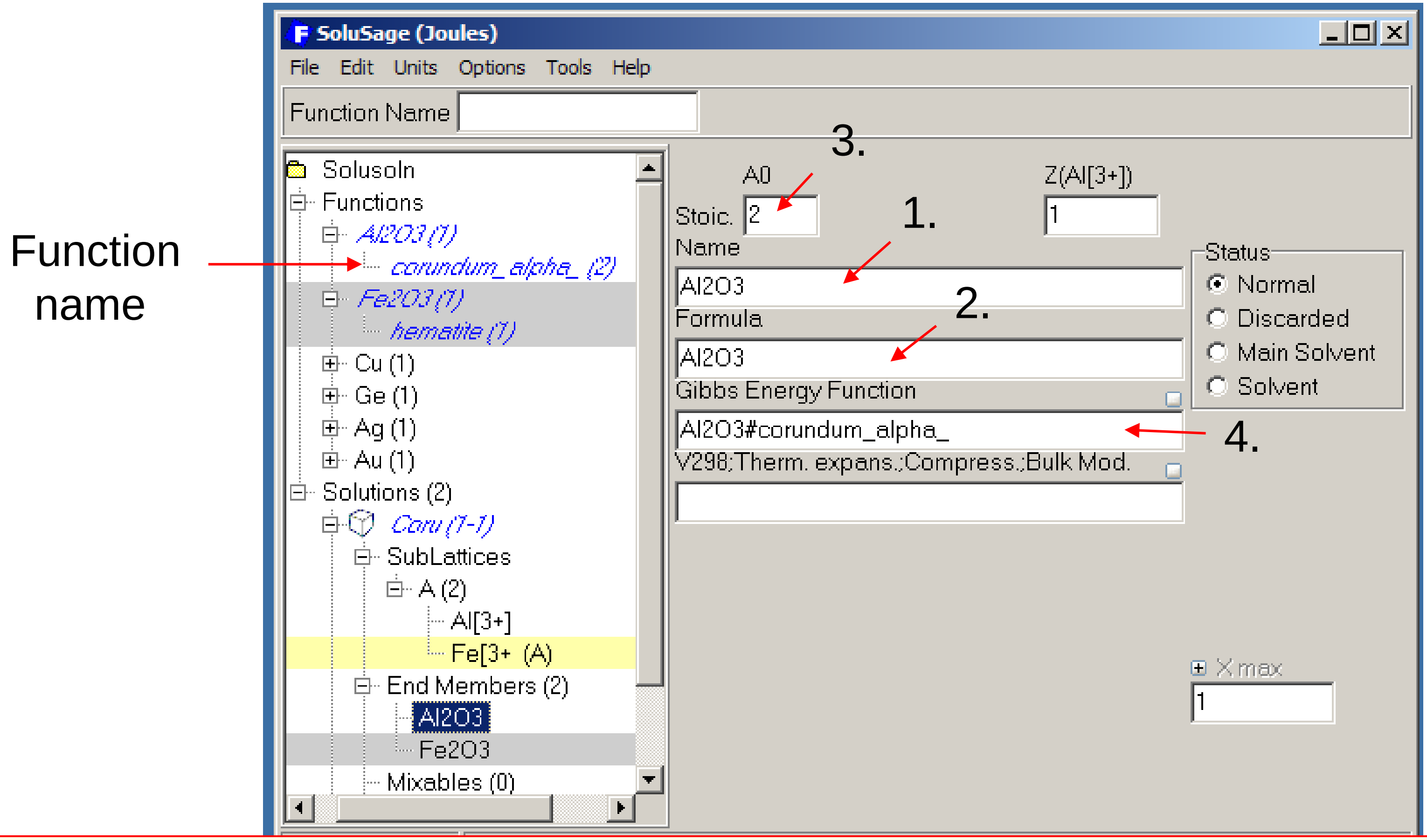
Assign a **name** to each species. (These **names** are not used in any calculations.)
IMPORTANT: Do **NOT** assign **formulae** for the species. (The species are Fe[3+] and Al[3+] which mix on the lattice.)

Entering the end-member Al_2O_3



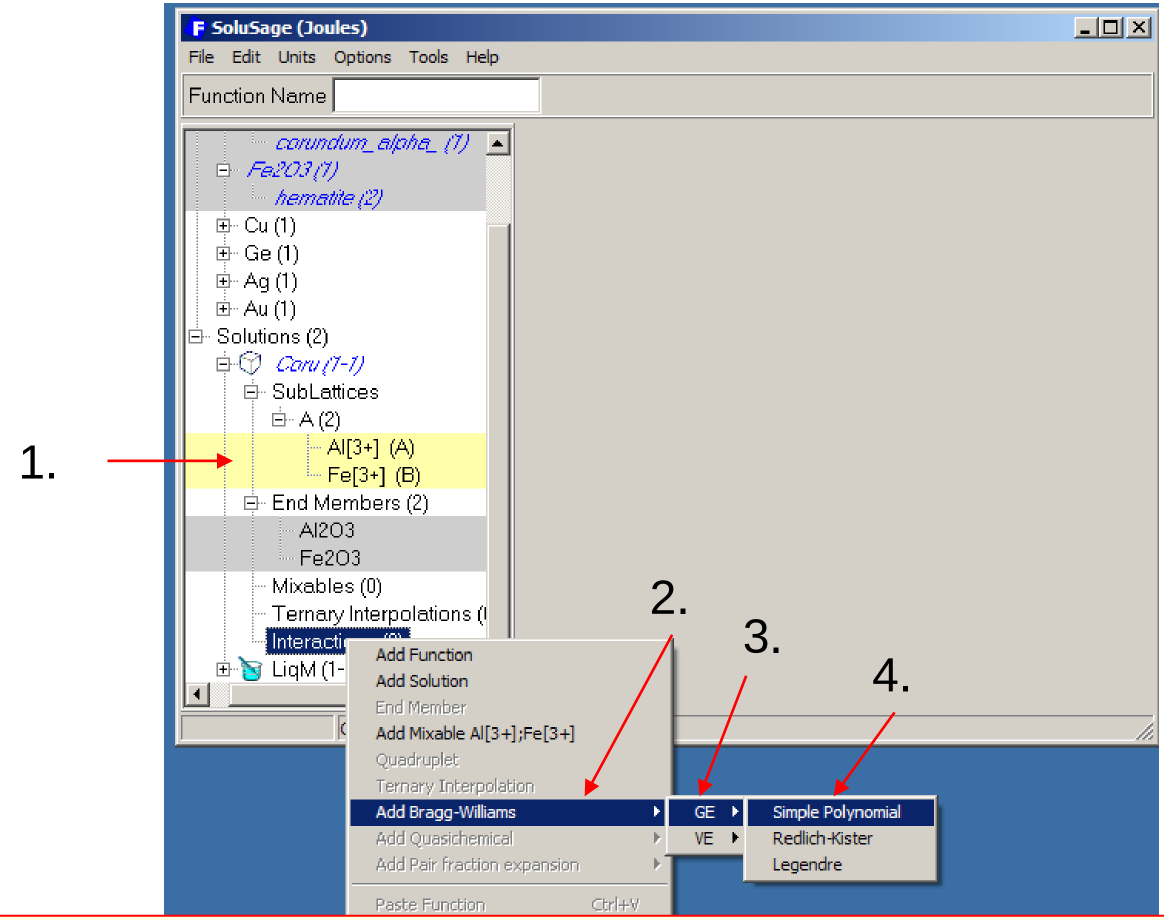
1. Highlight the species comprising the first end-member, then right click.
2. Click.

Entering the end-member Al_2O_3 (cont.)

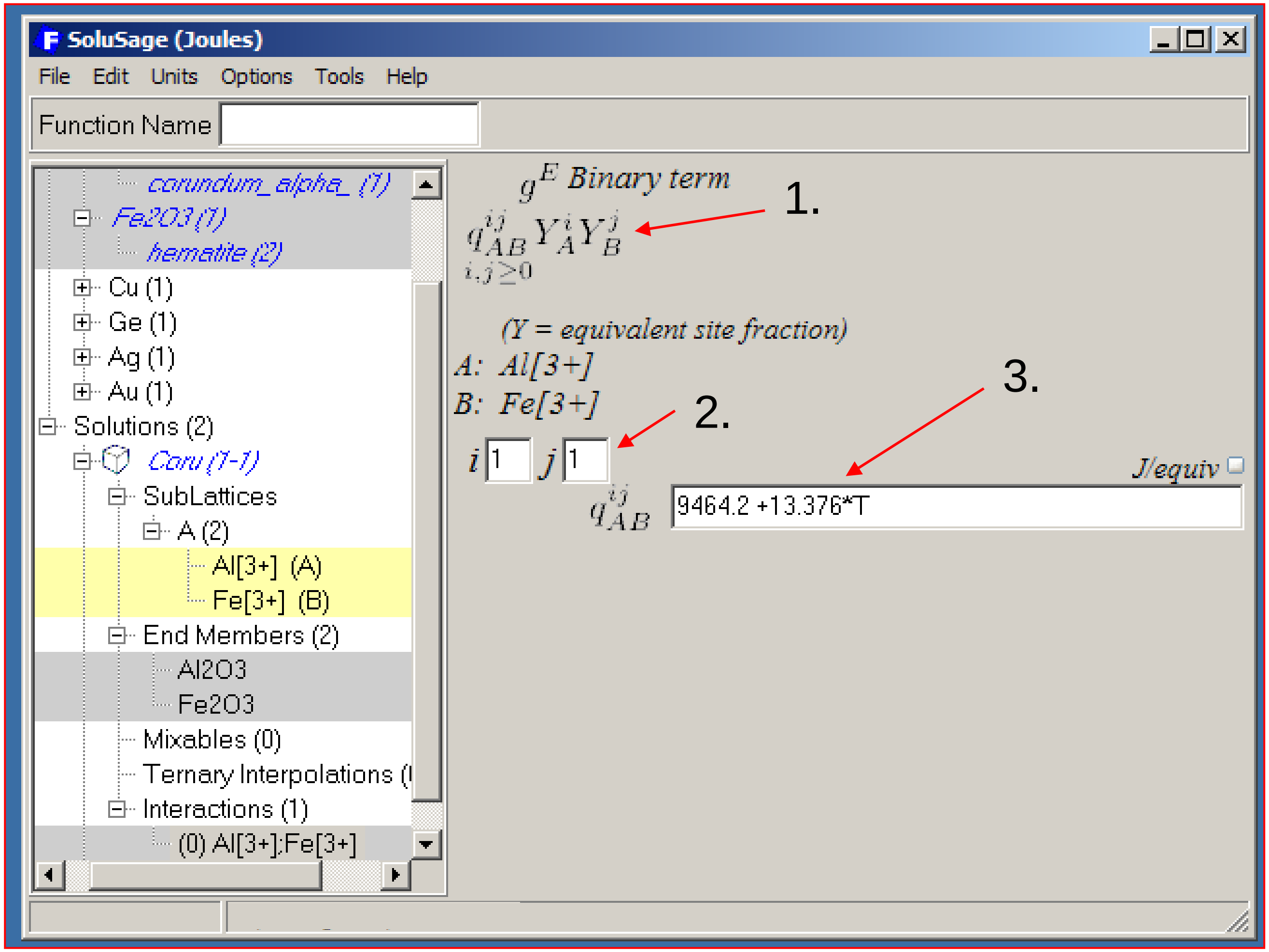


1. The **name** is not used in any calculations but will appear in FactSage outputs.
2. The **formula** of the end-member **is** used in the calculations.
3. One mole of **end-member** Al_2O_3 contains **2** moles of **species** Al^{3+}. This is entered as the **Stoic. variable**. (See factor «2» in Slide 4.0, Eq. [1]).
4. The Gibbs energy of the end-member as a sum of functions. Note that the **function name** (which was assigned automatically by the drag and drop (Slide 4.2)) must be reproduced exactly (including the underscores).

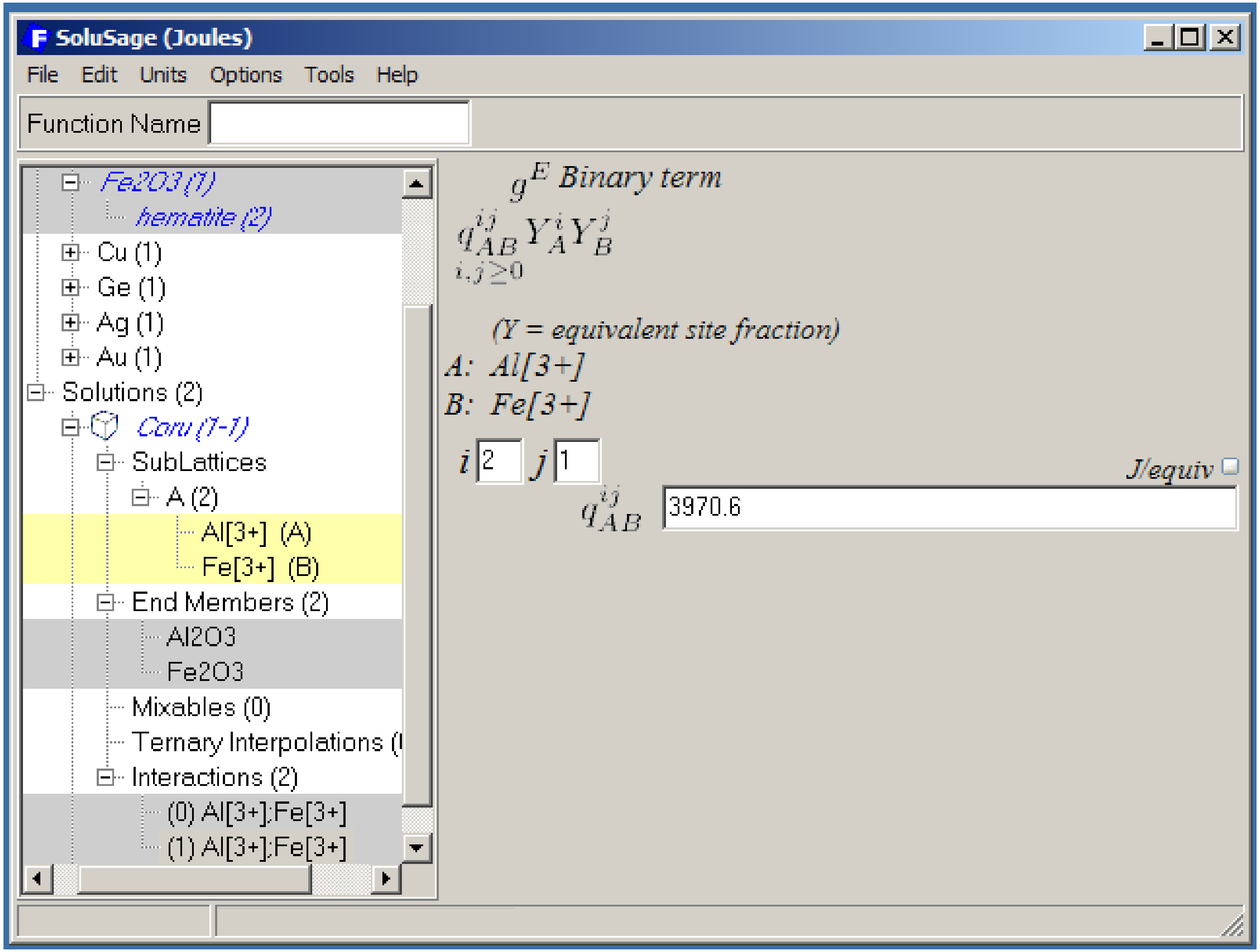
Entering interaction parameters



1. Highlight the species involved in the **interaction parameter,** then right click.
2,3. Mouse over then click.
4. The parameters (Slide 4.0, Eq. [2]) are in **simple polynomial form** (Slide 1.1 Eq. [2]).



1. **Simple polynomial form**.
2. Enter powers i and j.
3. Enter the first parameter from Slide 4.0, Eq. [2]. **PER MOLE OF SPECIES** (**<u>NOT</u>** per mole of end-members).



Entry of second interaction parameter from slide 4.0 Eq. [2].

5. The Compound Energy Formalism (CEF) (model # ”12/20”)

- The Compound Energy Formalism permits from 2 to 5 sublattices.

- Random mixing of species is assumed on each sublattice.

- Interaction parameters are expressed only in Redlich-Kister form (although Legendre expansions are also permitted for binary terms).

- Interpolation of binary parameters into ternary systems is performed only with the “All Muggianu” approximation (see Slide 2.1).

- The number of moles of sites on each sublattice is fixed, independent of composition.

- The CEF is the model used most commonly in tdb files.

Note: Before reading this Section, you should read Sections 1 to 4

Entry of data for the "$Al_{13}Fe_4$" solution phase with the Compound Energy Formalism (CEF) (model # "12/20")

Data for this phase have been stored in the file ..\FACTDATA\SolASoln.sln
The solution is modelled with **three sublattices** as **$(Al,Zn)_{32}(Fe,Mn)_{12}(Al,Si,Va)_7$** (where Va = vacancy)

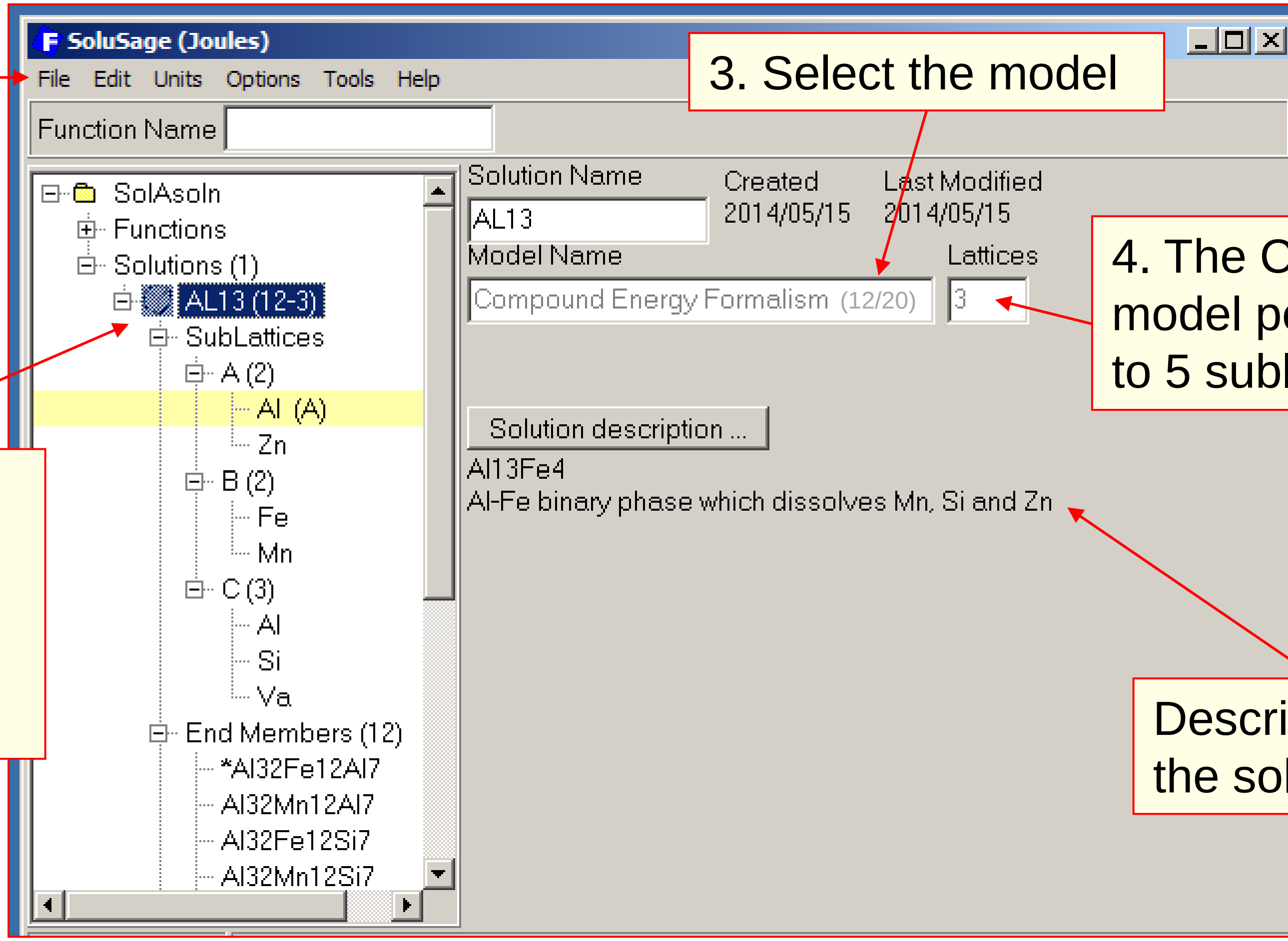
1. Click on «File → Open SolAsoln»

2. Click on the «AL13» nickname and expand the tree views

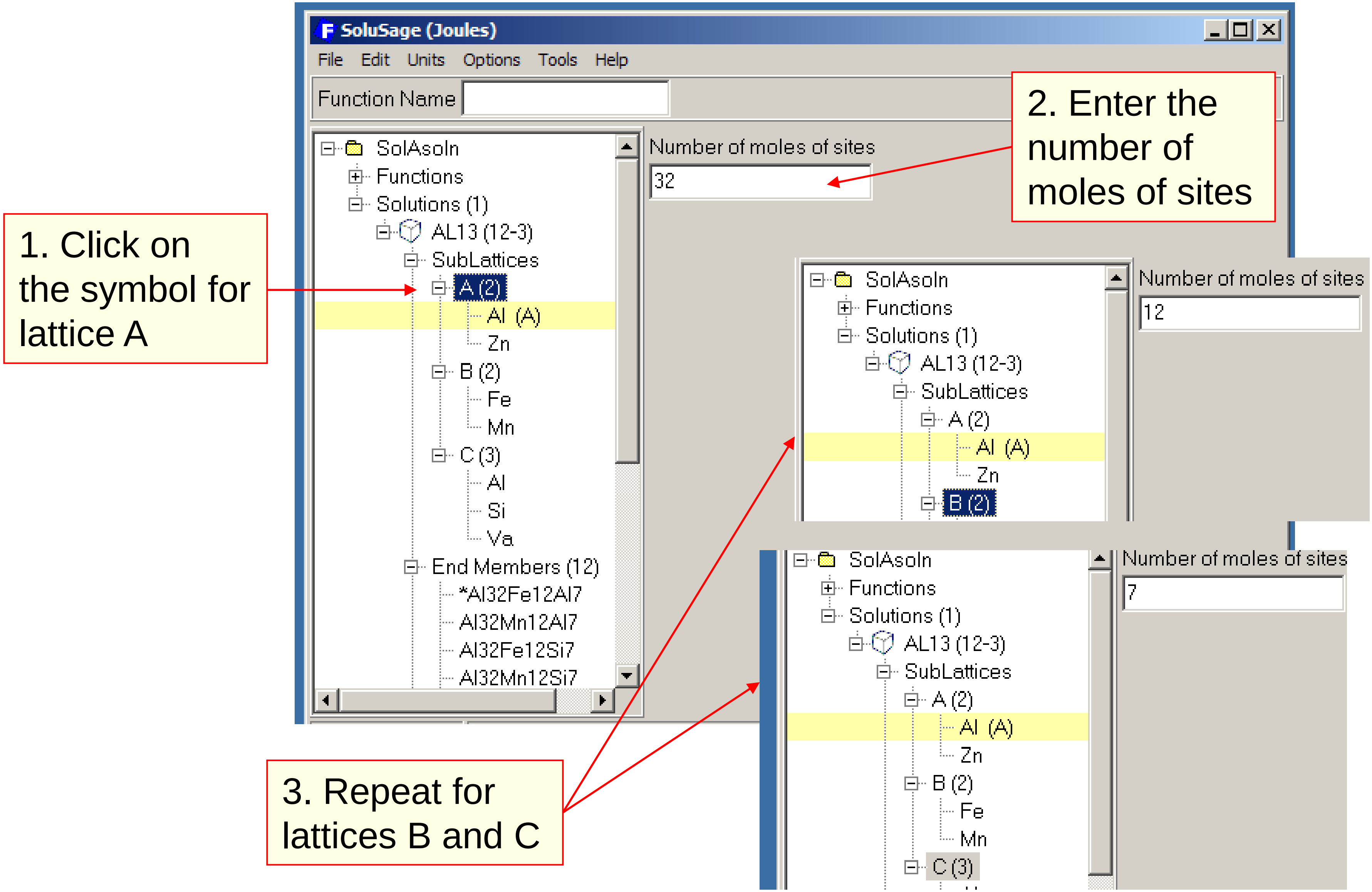
3. Select the model

4. The CEF model permits 2 to 5 sublattices

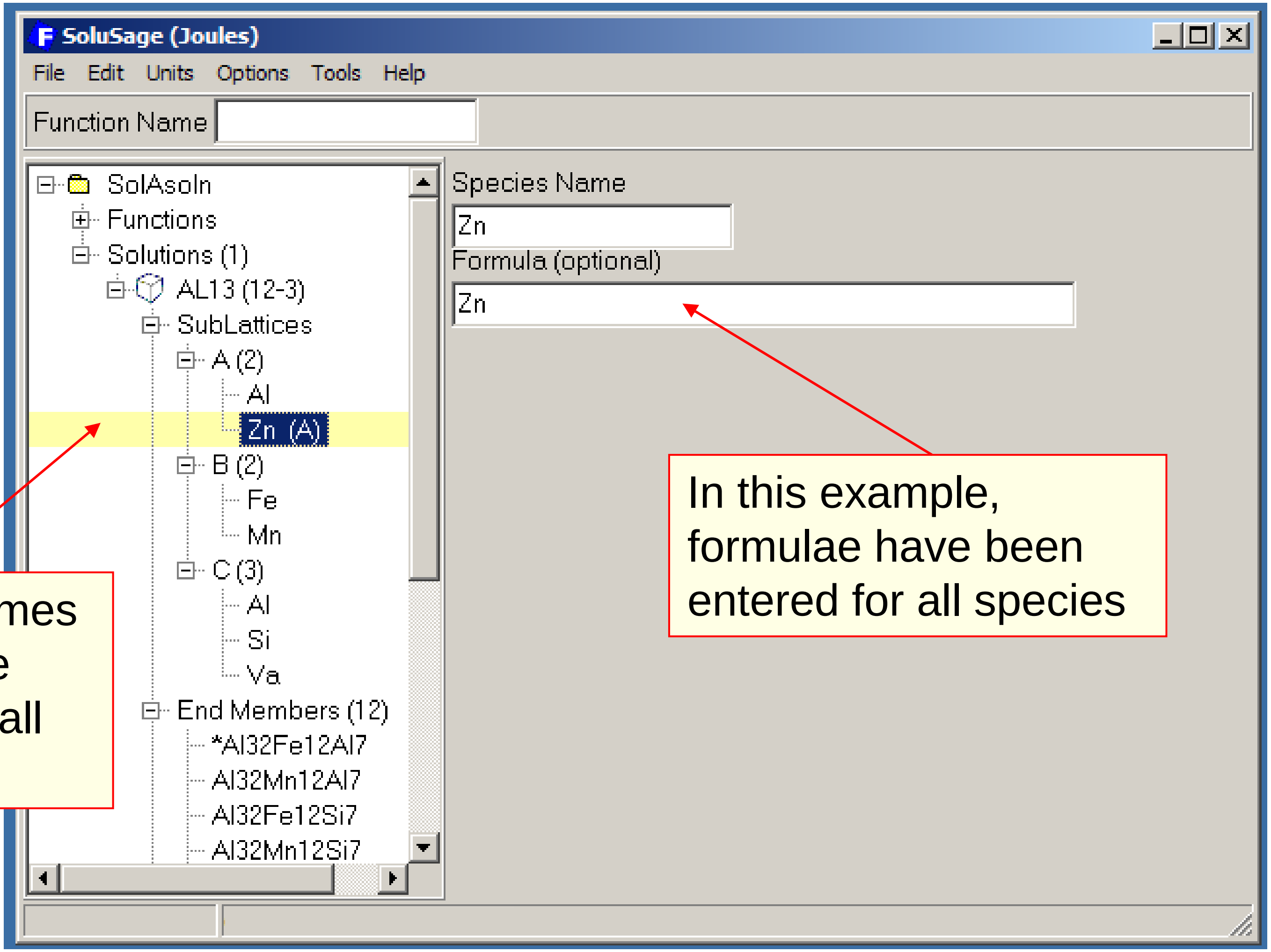
Description of the solution



Entering the number of moles of sites on each sublattice

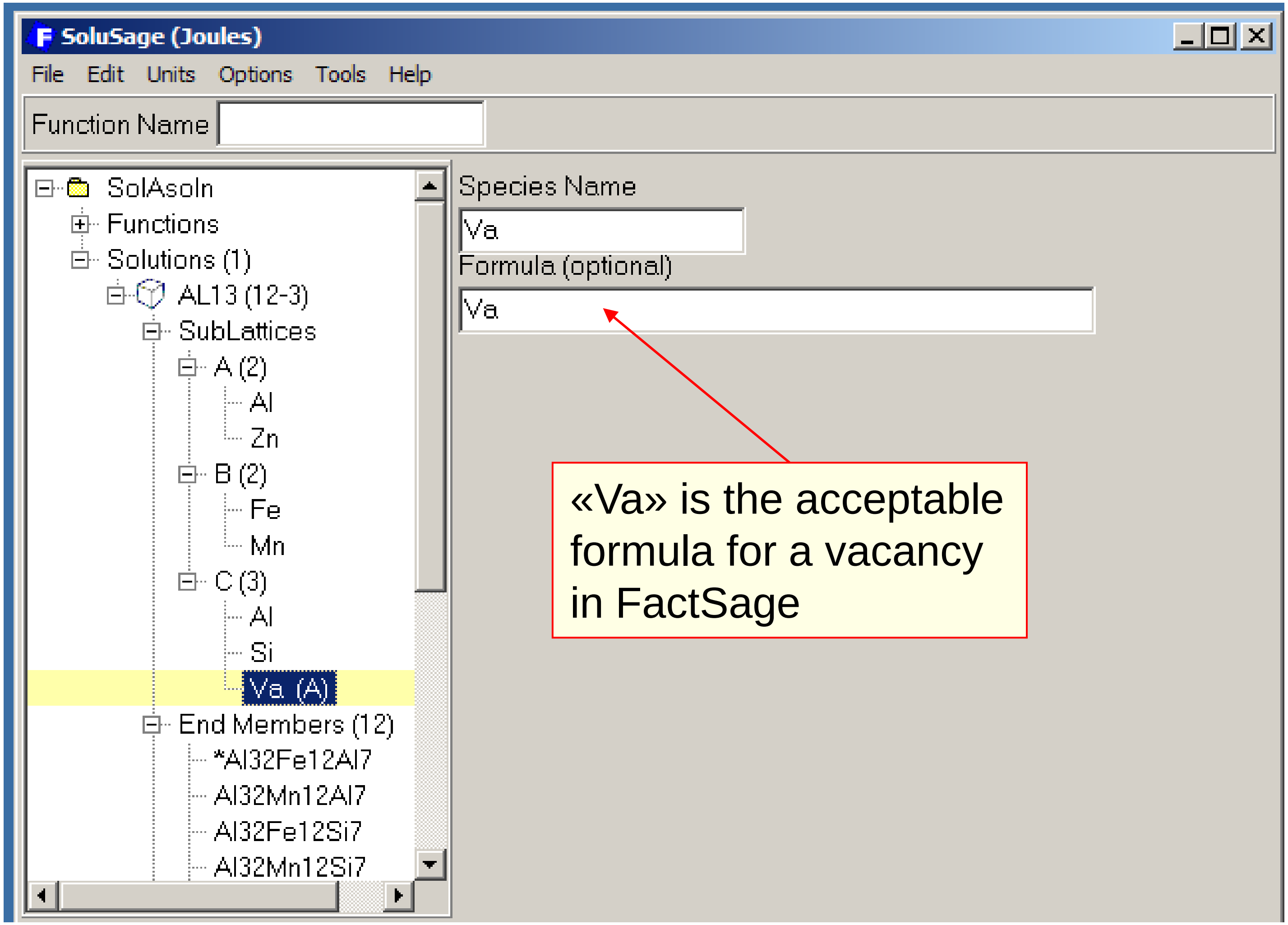


Entry of species



Enter the names and formulae (optional) of all species

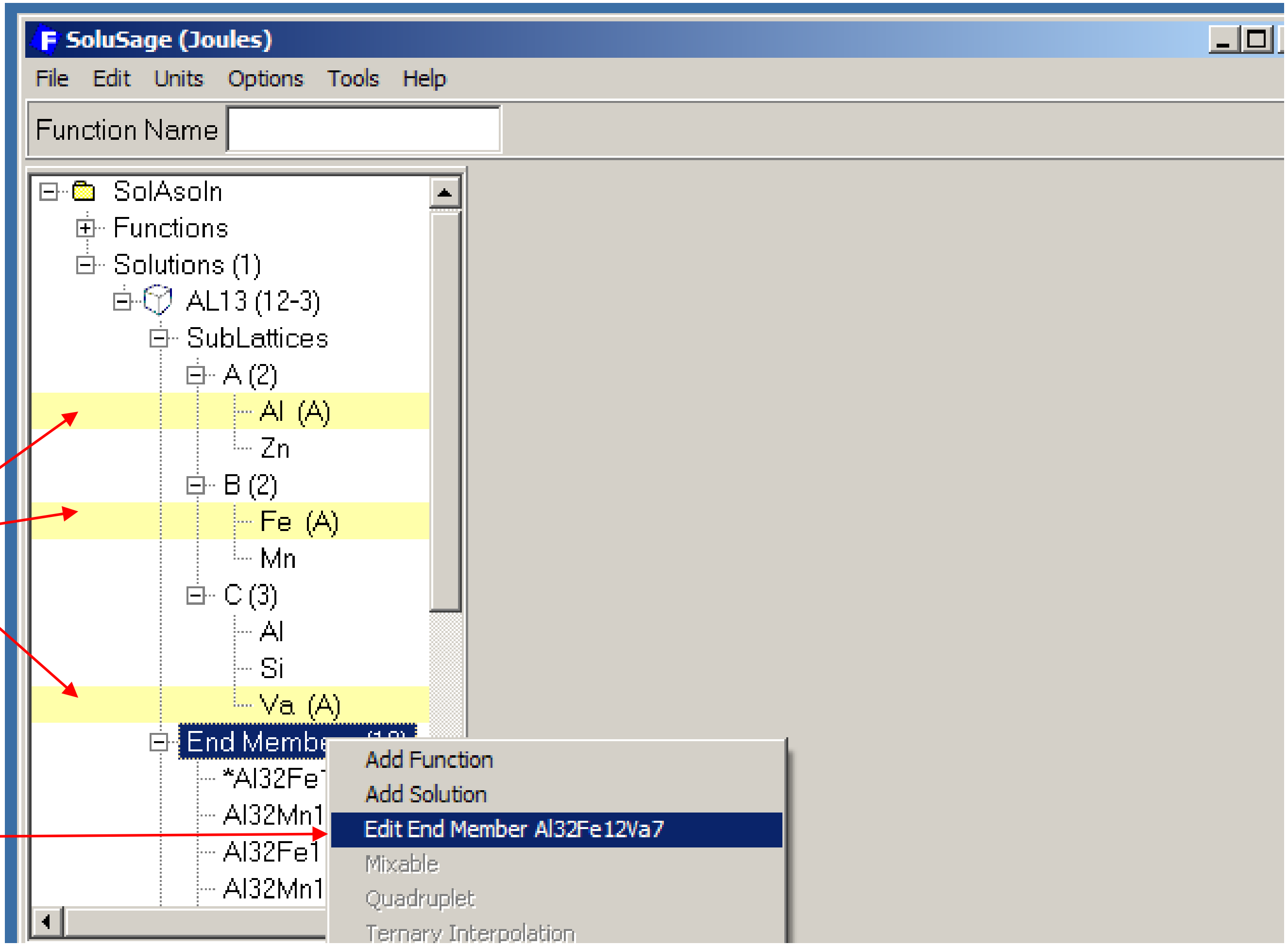
In this example, formulae have been entered for all species


SoluSage (Joules)
File Edit Units Options Tools Help
Function Name
SolAsoln
Functions
Solutions (1)
AL13 (12-3)
SubLattices
A (2)
Al
Zn
B (2)
Fe
Mn
C (3)
Al
Si
Va (A)
End Members (12)
*Al32Fe12Al7
Al32Mn12Al7
Al32Fe12Si7
Al32Mn12Si7
Species Name
Va
Formula (optional)
Va
«Va» is the acceptable formula for a vacancy in FactSage

Entry of end-members

1. Holding down the CTRL key, highlight one species from each lattice, then right click.

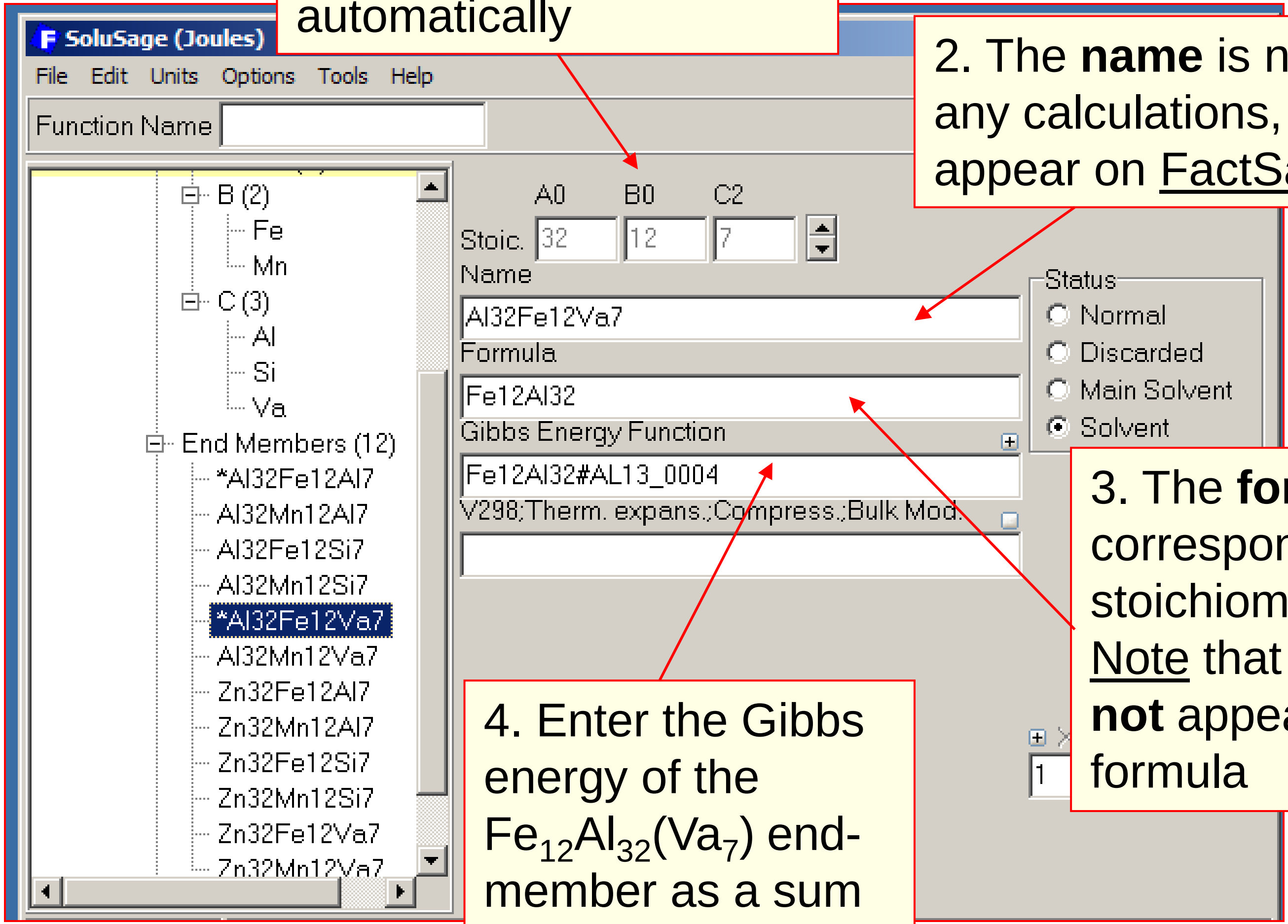
2. Click.



<u>All</u> (2x2x3) = 12 end-members **must** be entered, one for each combination of one species from each lattice

1. The **stoichiometry variables** are generated automatically

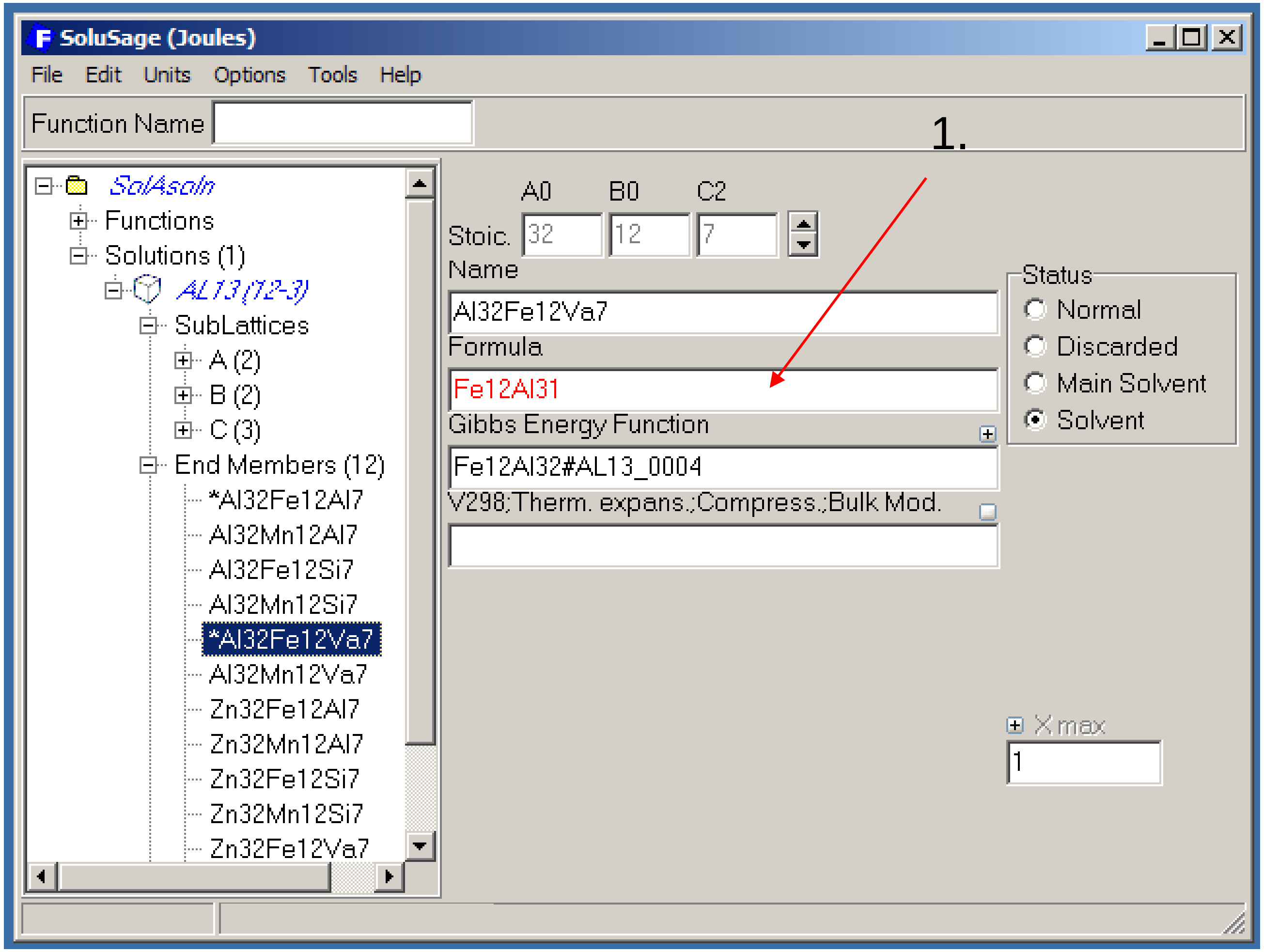
2. The **name** is not used in any calculations, but will appear on FactSage outputs



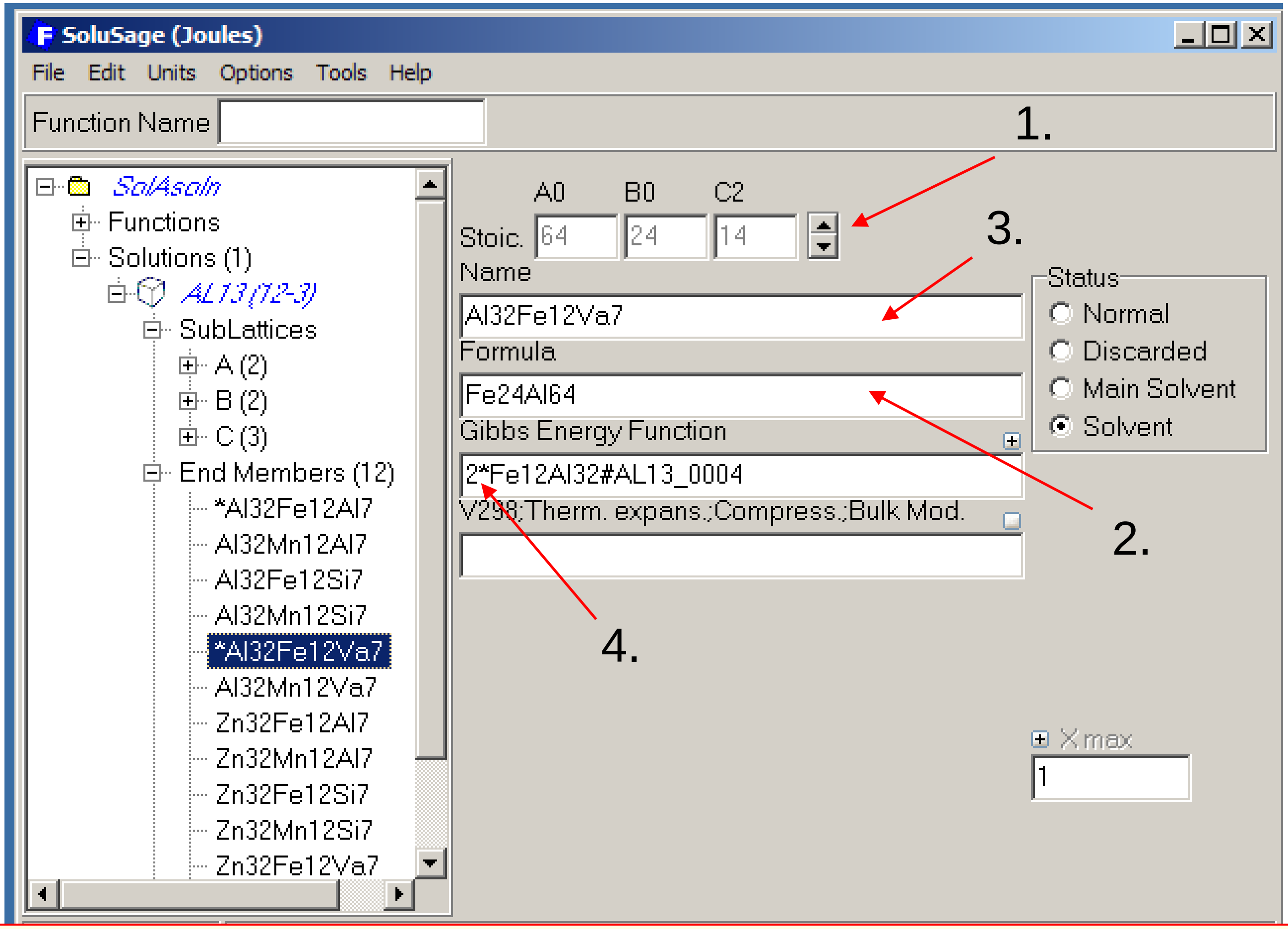
3. The **formula** must correspond to the stoichiometry $A_{32}B_{12}C_7$ Note that «Va» should **not** appear in the formula

4. Enter the Gibbs energy of the $Fe_{12}Al_{32}(Va_7)$ end-member as a sum of «functions»

Automatic entry and checking of end-member formulae



1. Since formulae were entered for all species (Slides…), the end-member formulae are automatically checked to be sure that they correspond to the proper stoichiometry. If incorrect, they appear in **red**.



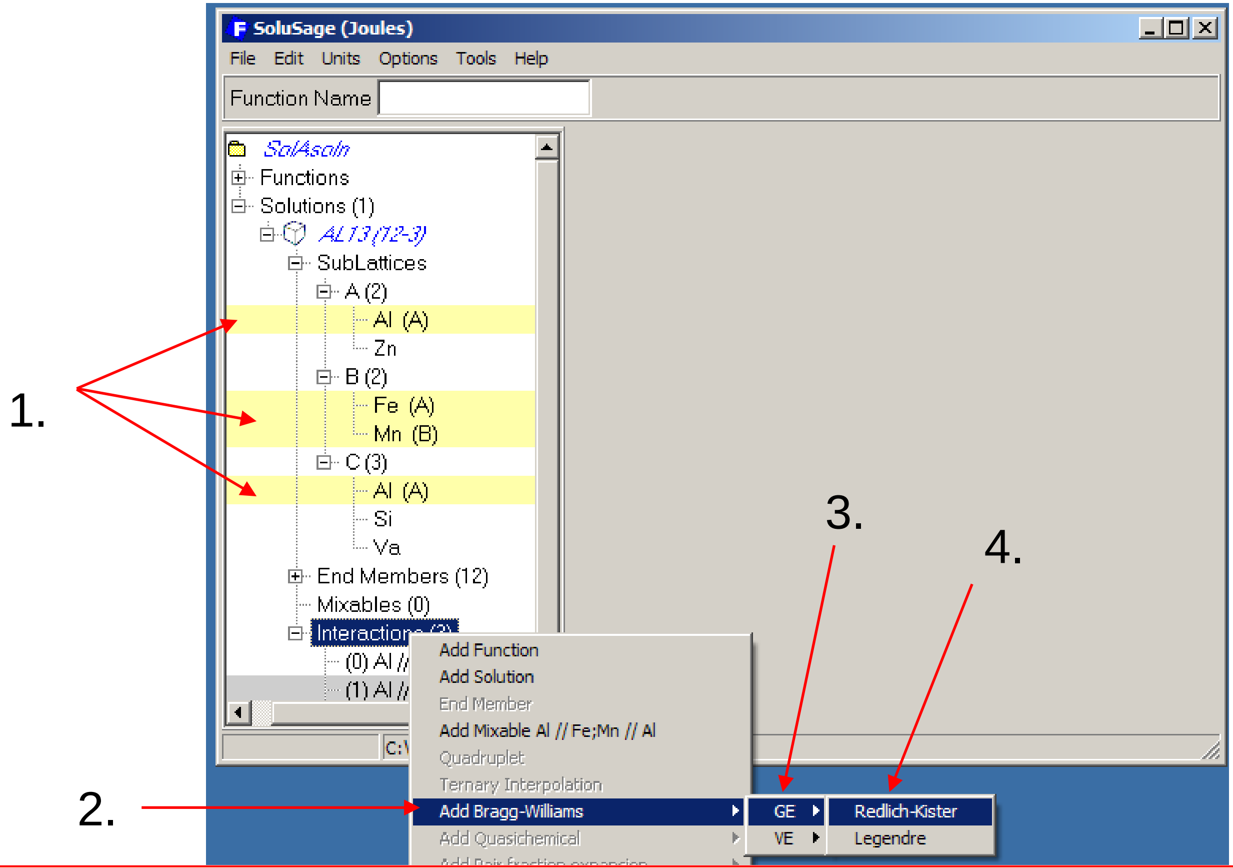
1. By clicking on the arrows, you can **change the stoichiometry of the end-member** by a factor of 2, 3, 4,…. Note that this has **no effect on the model** which is still based on one mole of $A_{32}B_{12}C_7$.
2. If formulae were entered for the species, the end-member formula is automatically changed. Otherwise it must be changed manually.
3. However, the **name** does not change unless you change it.
4. The Gibbs energy of $Fe_{24}Al_{64}$ is **2x** that in the function $Fe_{12}Al_{32}$#Al_{13}_0004

A note on “Vacanconium”

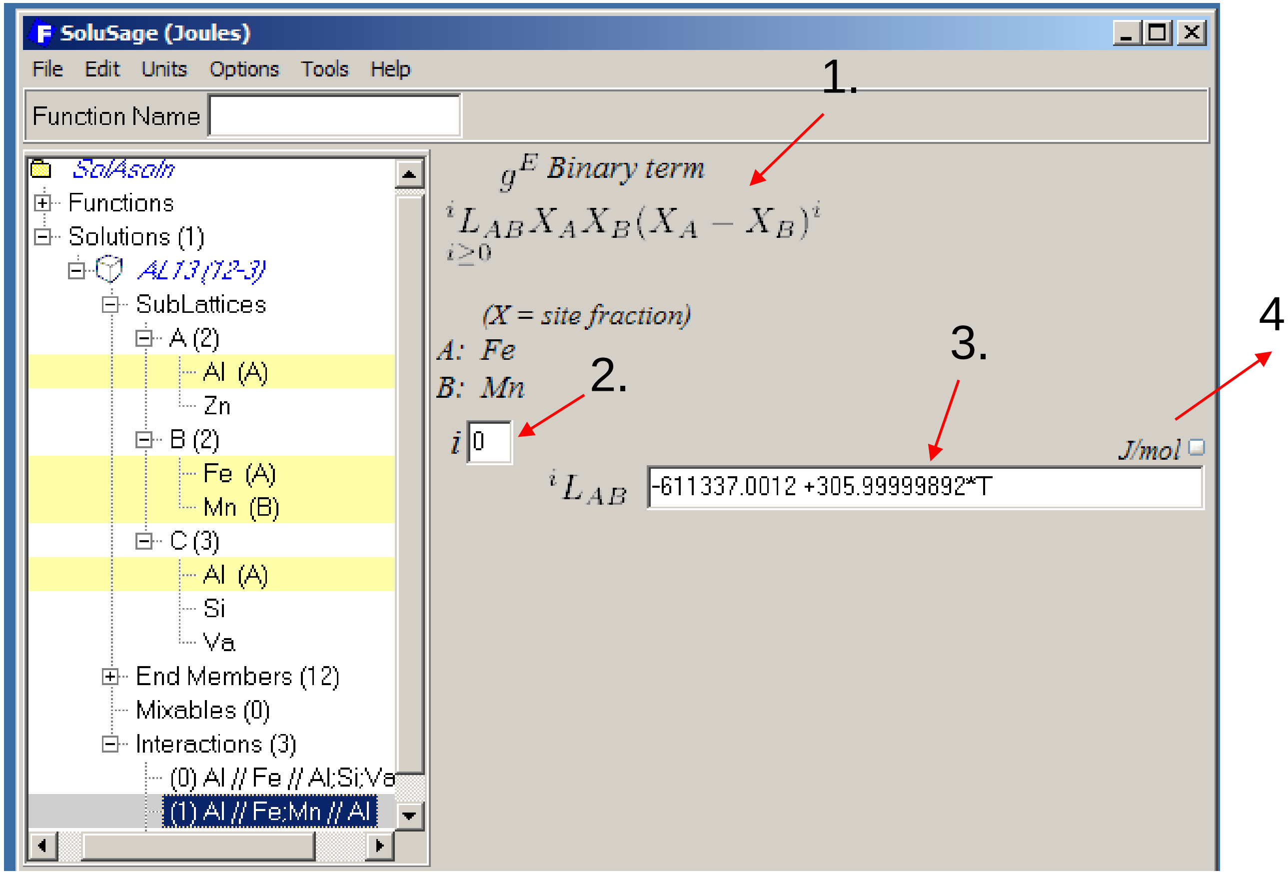
- If a vacancy is one of the species on **every** lattice, then an end-member consisting of vacancies on every lattice must be entered. In this case, enter **“Va”** as the **end-member formula**. This will be accepted as long as formulae have not been entered for the species.
(If the end-member has a net charge, then enter it as “Va [+]”, “Va [2-]”, etc.)

Entering a binary interaction parameter

In the CEF model, binary terms can only be in R-K or Legendre form



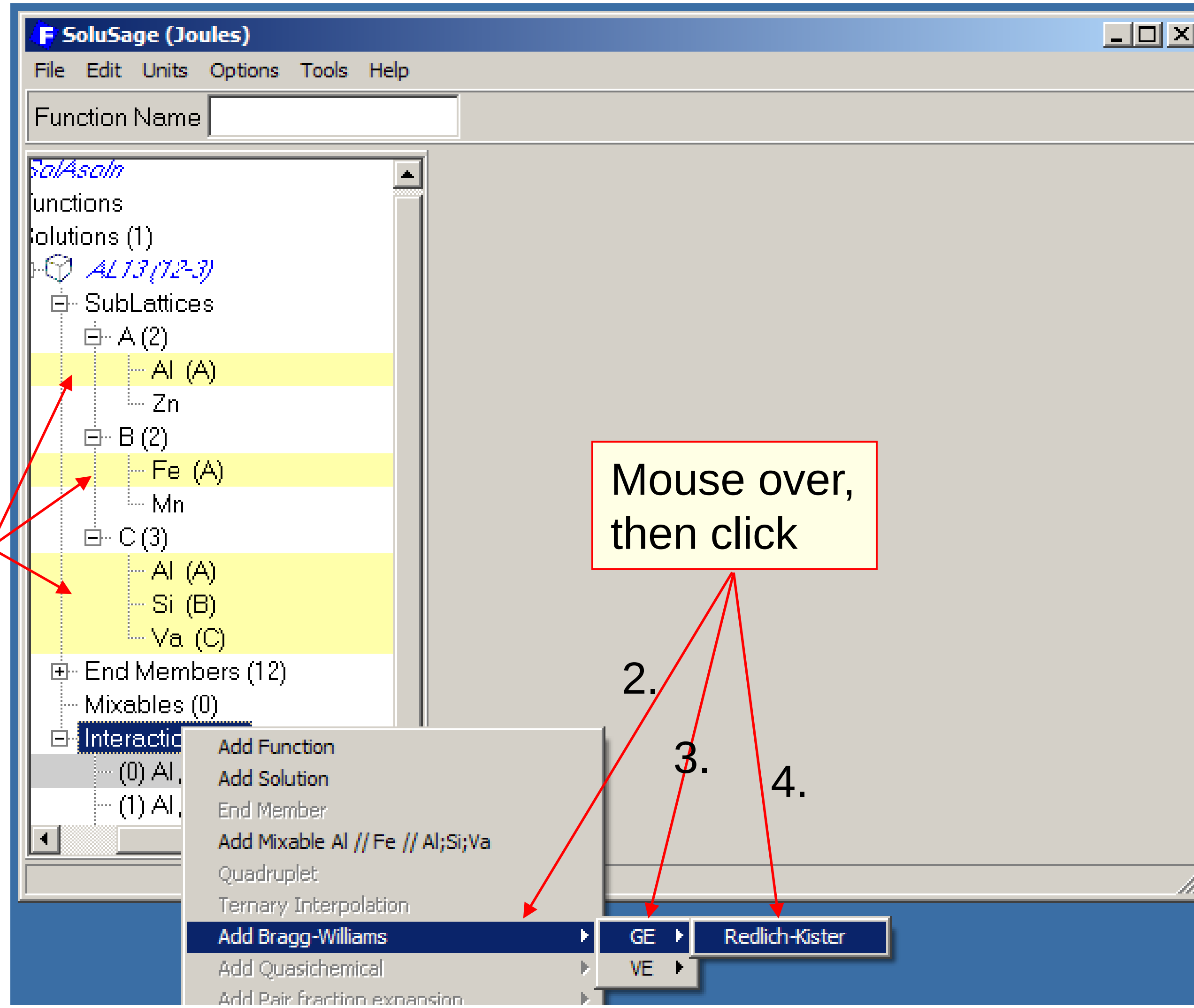
1. For a **binary** parameter, hold down the Ctrl key and highlight **two species on one lattice and one species on every other lattice**. This is the parameter for interactions between Fe and Mn on lattice B when lattices A and C are occupied exclusively by Al and Al respectively: $(Al)_{32}(Fe, Mn)_{12}(Al)_7$. Then right click.
2,3,4. Mouse over, then click.

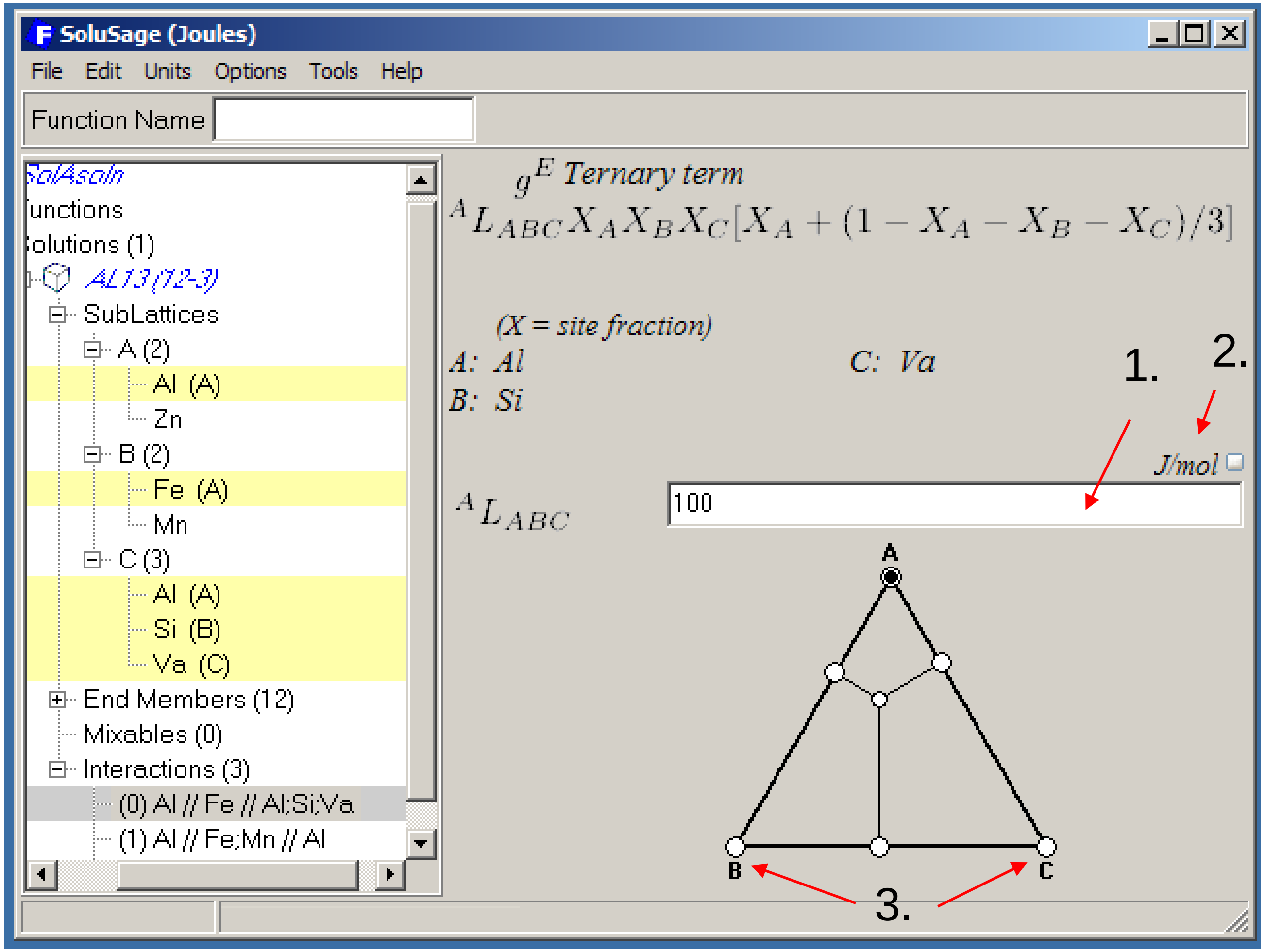


1. In the CEF model, the interaction parameters are always expressed in terms of site fractions («equivalent fractions» are not an option).
2. Enter the power i in the R-K expansion.
3. Enter the parameter.
4. **<u>Note</u>: This is the interaction parameter per mole of $(Al)_{32}(Fe, Mn)_{12}(Al)_7$**. That is, for **12 moles** of (Fe + Mn) mixing on the B lattice.

Entering a ternary interaction parameter

1. Highlight 3 species on one lattice and one on every other lattice. This is the ternary interaction $(Al)_{32}(Fe)_{12}(Al, Si, Va)_{7}$, then right click.

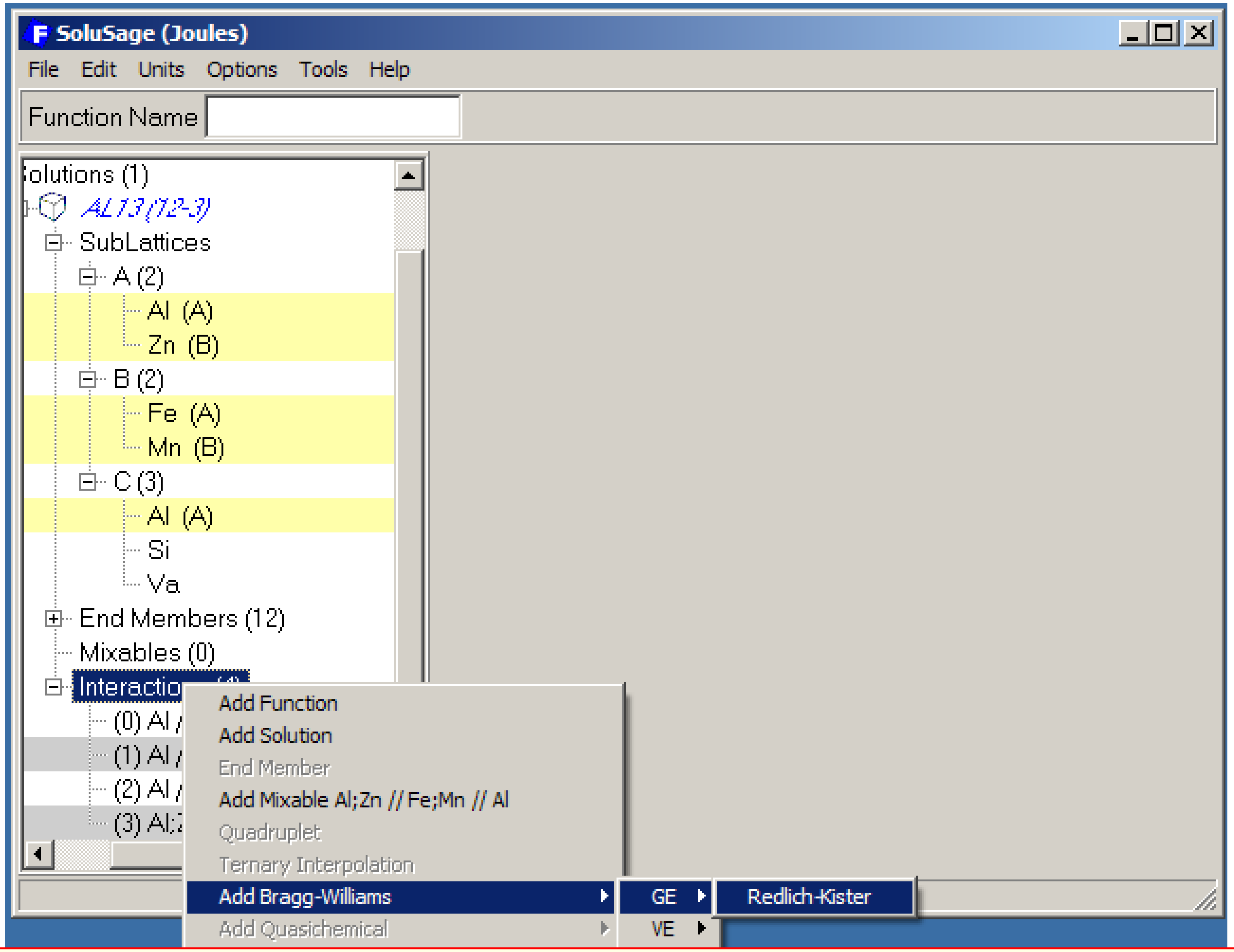




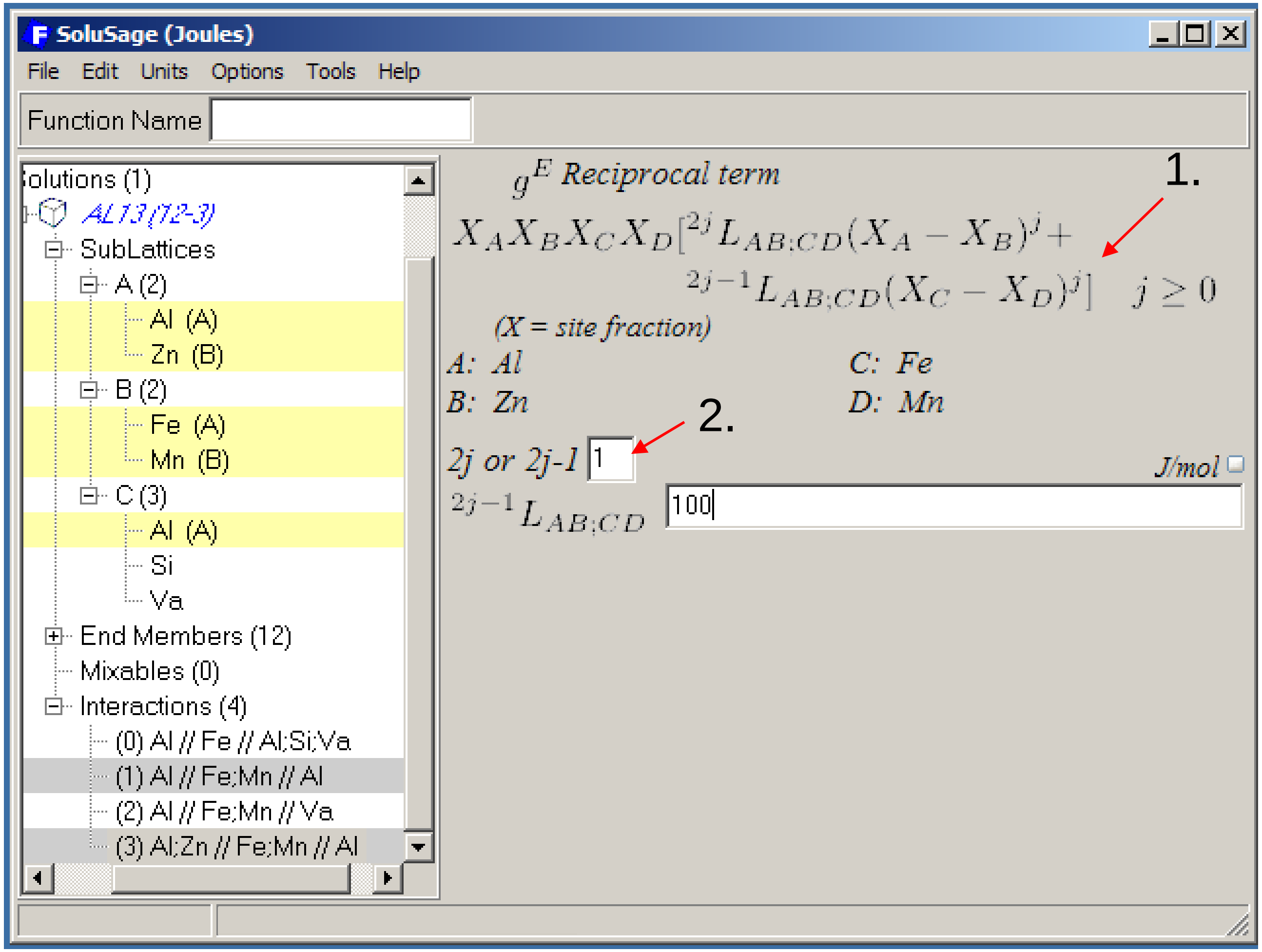
1. Enter the $^AL_{ABC}$ parameter. (See Slide 3.2).
2. Per mole of $(Al)_{32}(Fe)_{12}(Al, Si, Va)_7$.
3. Click to enter $^BL_{ABC}$ and $^CL_{ABC}$ parameters (**Important**: See Slide 3.3. You must first repeat steps 2, 3, 4 of slide 5.12, otherwise, entry of the $^AL_{ABC}$ parameter will be lost).

Entering a reciprocal interaction parameter (Ref. (4))

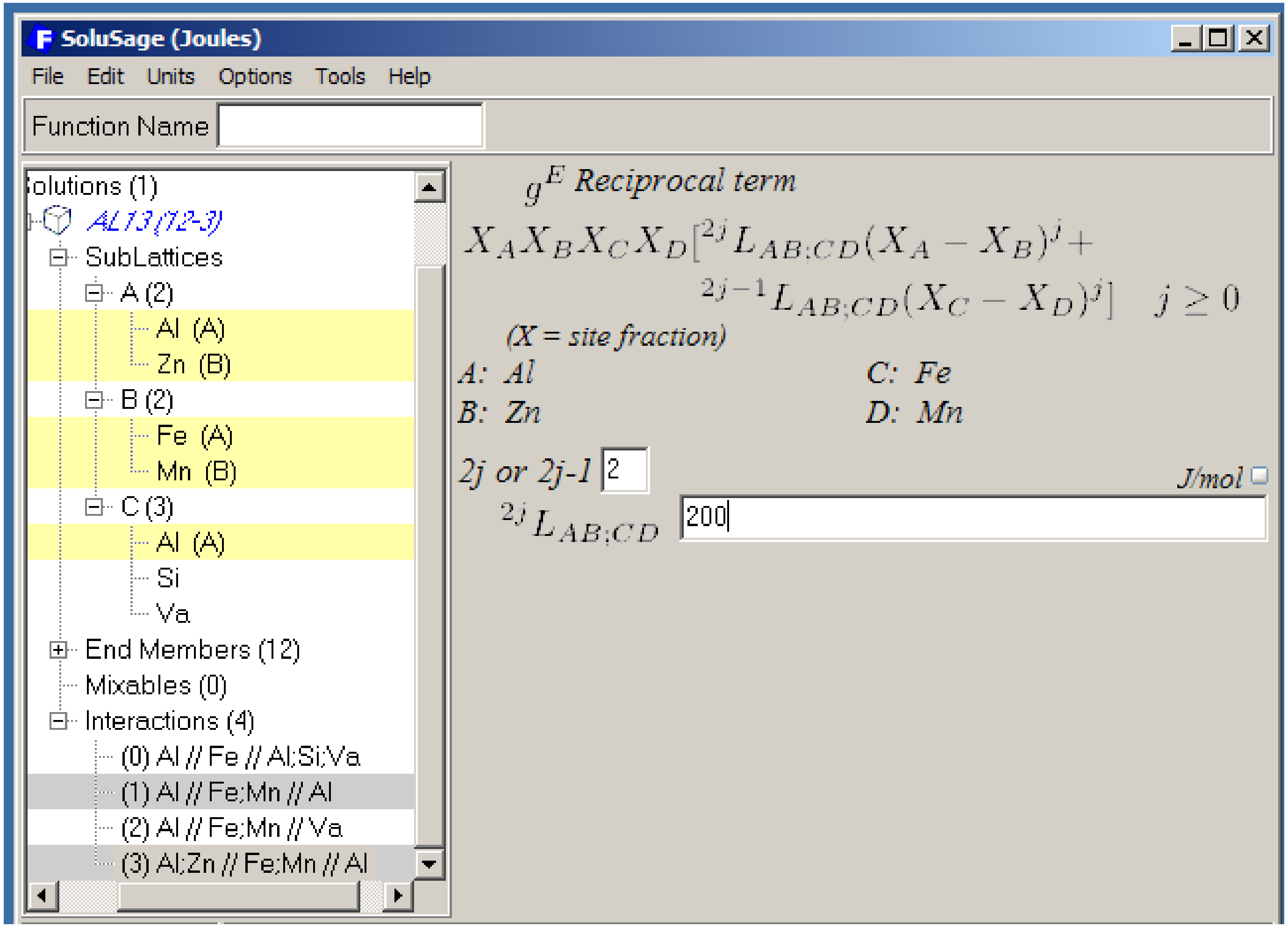
1. →



1. Highlight 2 species on one lattice, 2 species on another lattice, and one species on every other lattice. This is a reciprocal interaction (Al, $Zn)_{32}(Fe, Mn)_{12}(Al)_7$ among species on lattices A and B when lattice C is occupied exclusively by Al.



1. This is the form for reciprocal terms in the CEF (See Ref.(4)).
2. Enter a positive integer equal to either 2*j* or (2*j*-1). Even values specify an entry of a ^{2j}L parameter, while odd values specify entry of a $^{2j-1}$L parameter.



The parameters entered in this and the preceding slide together define the term $X_A X_B X_C X_D(200(X_A - X_B)^1 + 100(X_C - X_D)^1)$

- Quaternary interaction terms (4 species on one lattice and one on every other lattice) can also be entered in the CEF.

- These are of the form

$$q_{ABCD} X_A^1 X_B^1 X_C^1 X_D^1$$

6. More on Entering and Using "Functions"

- Entry of functions by copying from a COMPOUND database has been illustrated in Slides 1.3 and 1.4.

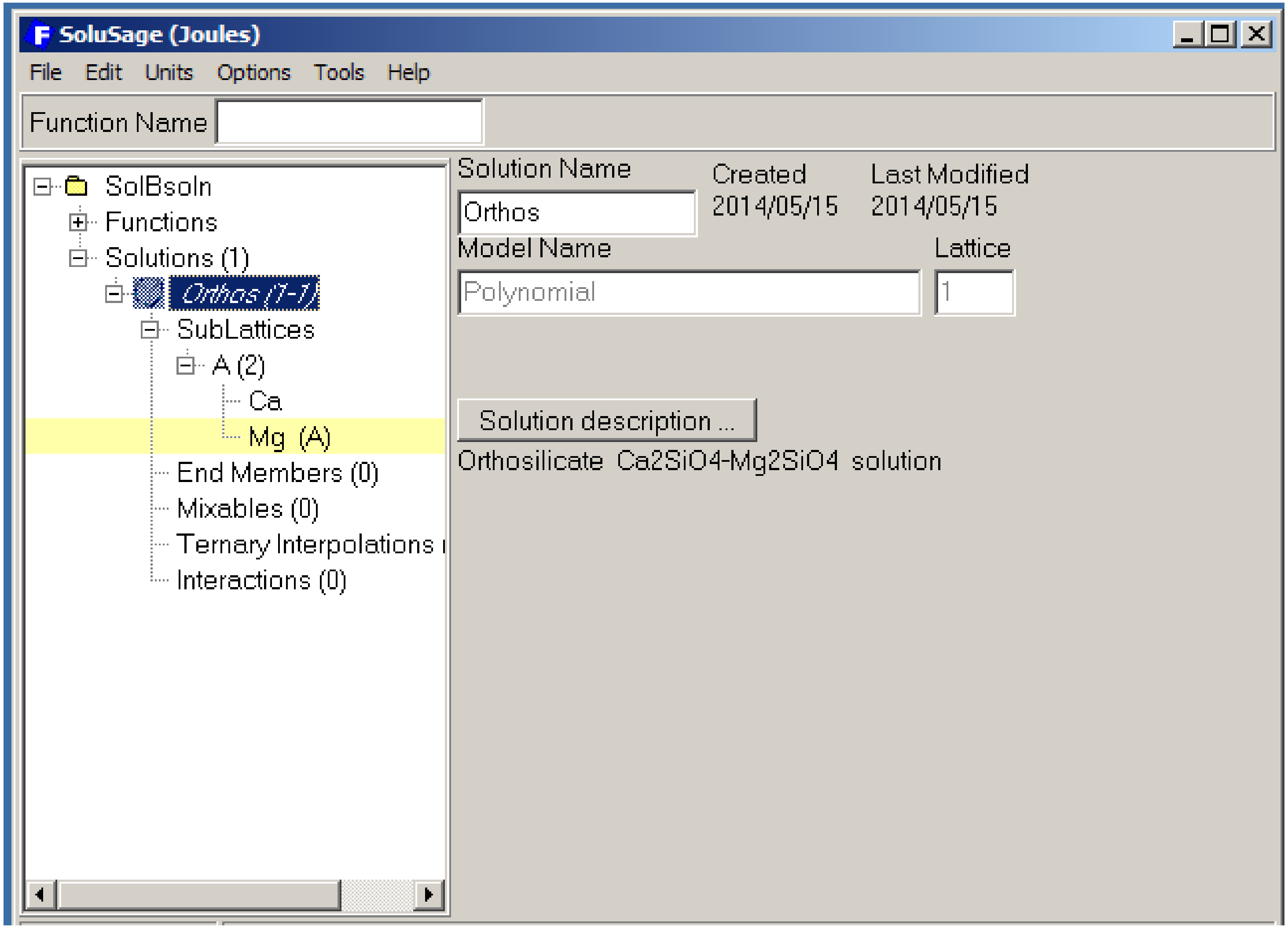
- In this Section we illustrate the direct entry of functions and the use of sums of functions in specifying the Gibbs energy of an end-member.

Example: In an orthosilicate solution Ca_2SiO_4-Mg_2SiO_4, we wish to specify the Gibbs energy of the end-member Ca_2SiO_4 as:

$$g^0_{Ca_2SiO_4} = 2g^0_{CaO} + g^0_{SiO_2} + \Delta g^0_{form} \qquad [1]$$

where: Δg^0_{form} = Gibbs energy of formation = -93000 - 30.0 T J/mol

This is illustrated in the following slides.

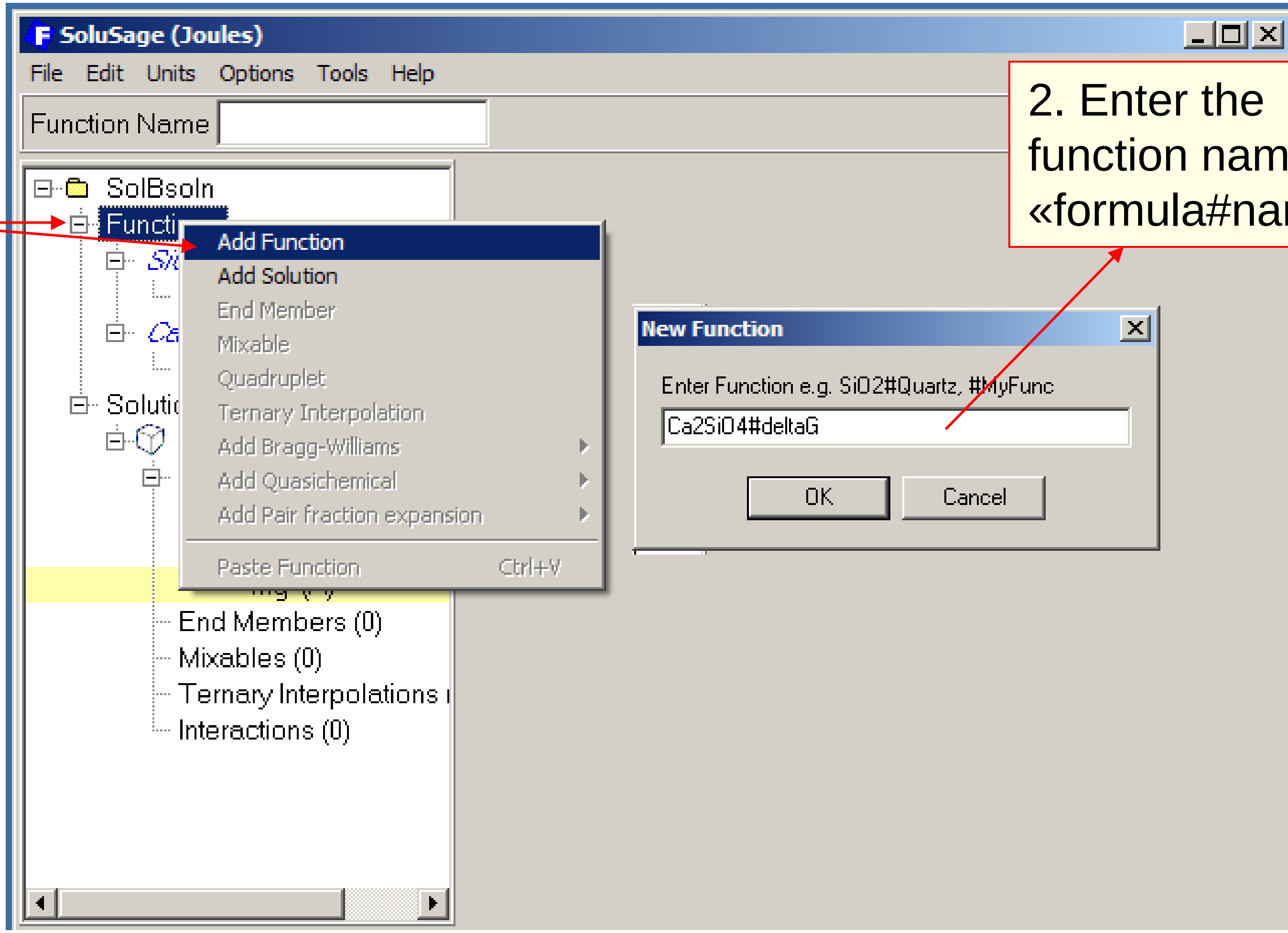


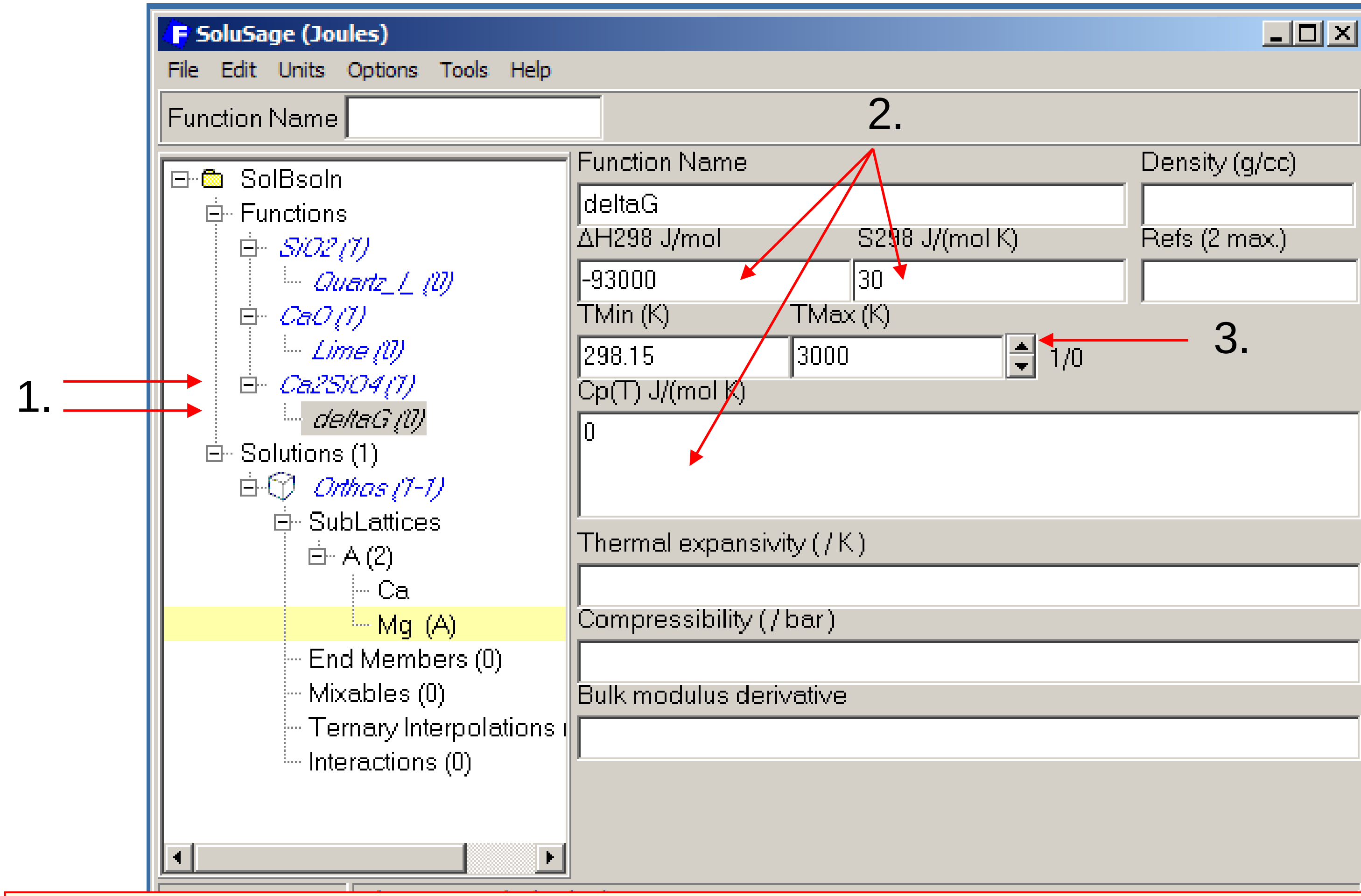
The solution and species are defined

Entering a new function Δg^{0}_{form}

1. Click

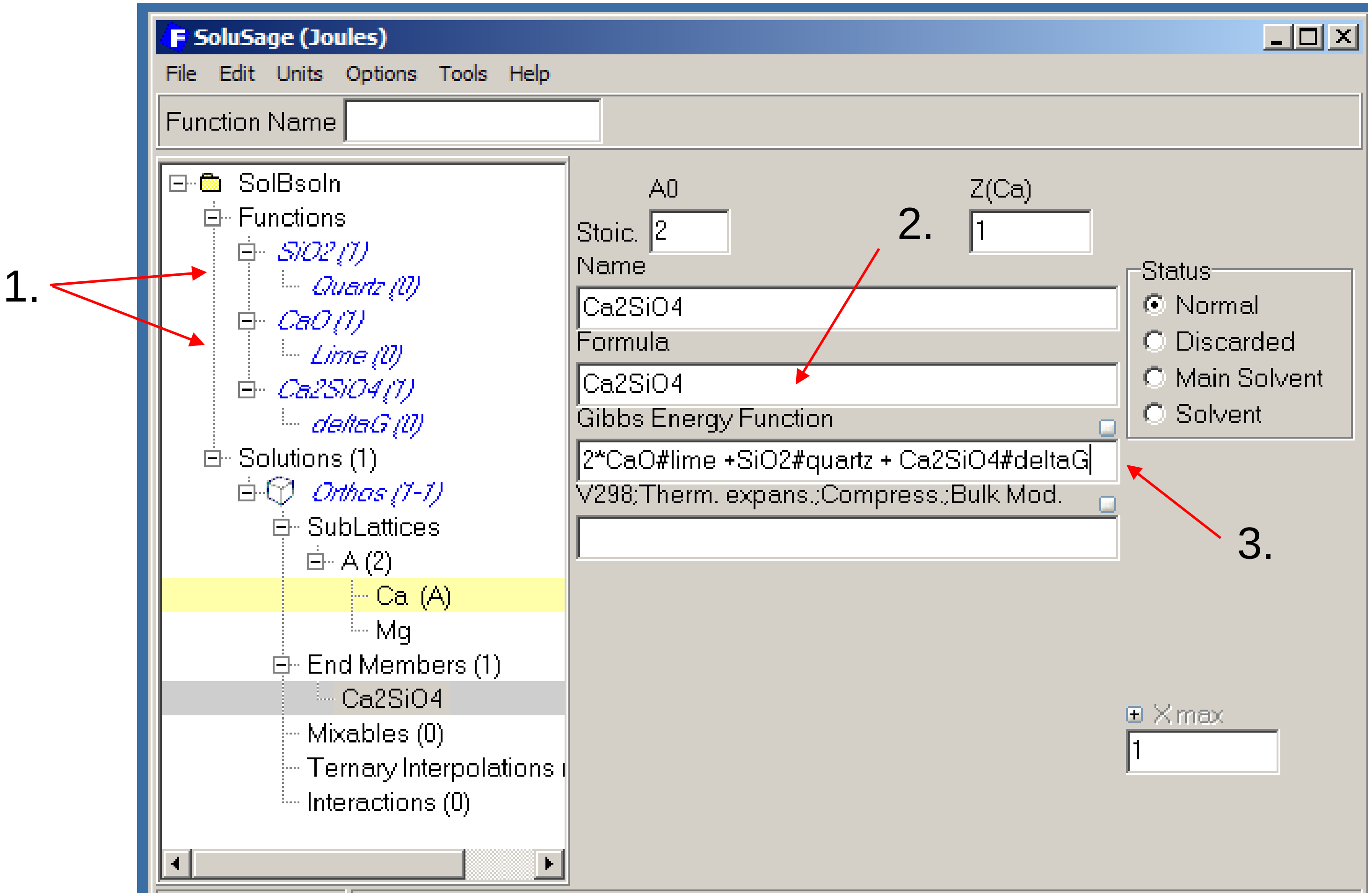
2. Enter the function name as «formula#name»





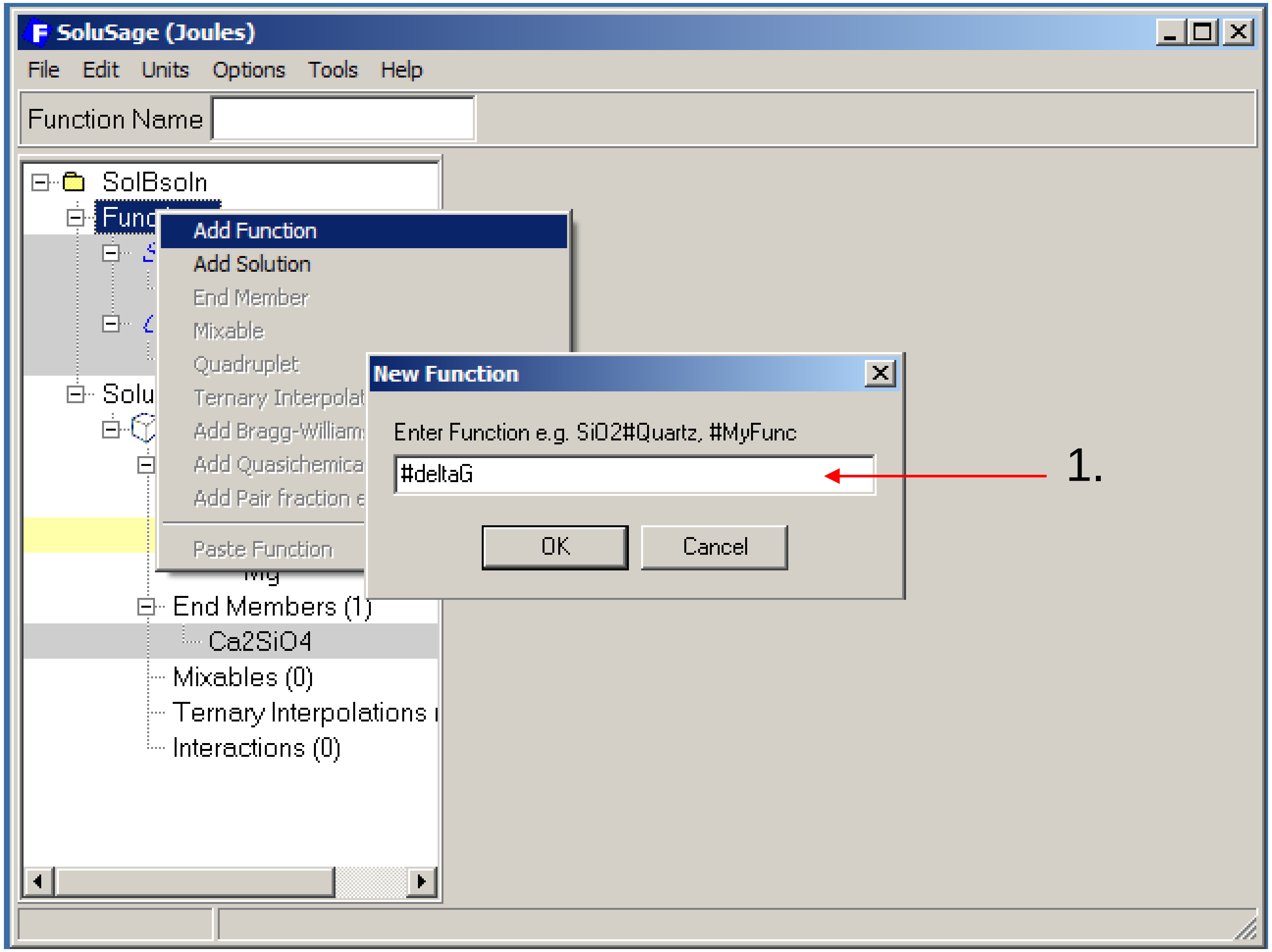
1. The formula appears as a main heading, and all names with the same formula as a sub-heading.
2. Enter ΔH_{298}, S_{298}, C_p for the function. In this case, $C_p = 0$.
3. Temperature ranges for C_p may be entered as in the COMPOUND program. (See COMPOUND slide show). (Density, expansivity, etc. can also be entered.)

Entering the end-member Ca_2SiO_4

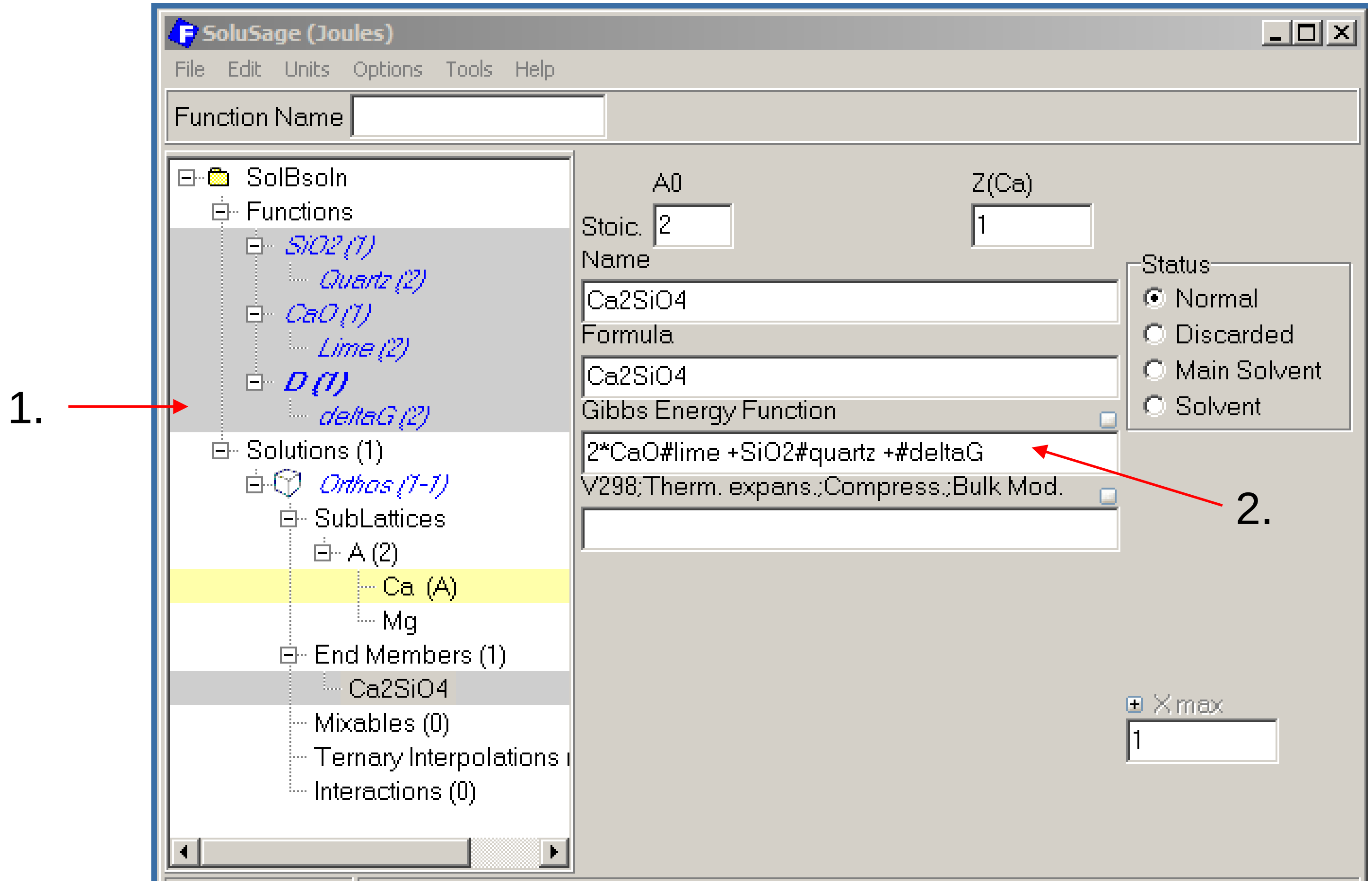


1. Functions for pure SiO_2 and pure CaO have been entered by dragging and dropping from the FactPS database.
2. The end-member is Ca_2SiO_4.
3. The Gibbs energy is given as a sum of functions as on Slide 6.0, Eq. [1].

Alternate method of naming a function



1. See slide 6.2. Alternatively, a function can be named «#name» without a chemical formula.



1. In this case, the main heading is not a chemical formula but rather it is the first letter of the name.
2. The function is called simply #deltaG

Entry of a function directly as an expression for G

- In slide 6.3 was illustrated the entry of a function by specifying values of ΔH_{298}, S_{298} and C_p.

- If you wish to enter an expression for G

  (G = a + bT + cTlnT + …) directly, this cannot be done at present in SOLUSAGE. You must first convert the expression to ΔH_{298}, S_{298} and C_p.

- However, you can avoid having to do this as follows:

  - See the COMPOUD slide show, Slides 6.1.
  - Create a private COMPOUND database.
  - Enter data for a "compound" phase using the "G edit" option. (Any formula can be used).
  - Drag and drop to create a function as in Slides 1.3 and 1.4.

7. Two-lattice polynomial model (“Model 4”) (Refs. (5 ,6)

- This is a Bragg-Williams model: - **Random mixing** of species on each lattice is assumed.

- It is an **extension of the one-lattice polynomial model** (Section 1).

- It is **specifically designed for ionic <u>liquid</u> solutions** in which the ratio R = (number of A lattice sites)/(number of B lattice sites) varies with composition. For example, in LiCl-Li_2SO_4 solutions, (Li)(Cl, SO_4), R varies from 1.0 in the end-member LiCl to 2.0 in the Li_2SO_4 end-member (i. e. the “Temkin model”.) (However, if R is the same for all end-members, then the model can also be used for solid solutions.).

- For each species, a **“valence” q_i** is assigned. For ionic salts this is the absolute charge, but in general the valence is defined as the **(number of “equivalents”) per mole**. For example, one mole of Li^+ ions or F^- ions are equal to one equivalent, while one mole of SO_4^{2-} ions equals two equivalents.

- We define **“charge equivalent site fractions” Y_i** for each lattice as:

$$Y_i = q_i X_i / \Sigma q_i X_i$$

where X_i = molar site fraction and the summation is over all species on the lattice.

For example, in (Li, Na, Ca)(F, SO_4) solutions:

$$Y_{Na} = X_{Na}/(X_{Li}+X_{Na}+2X_{Ca}),\ Y_{Ca} = 2X_{Ca}/(X_{Li}+X_{Na}+2X_{Ca}),\ Y_{Li} = X_{Li}/(X_{Li}+X_{Na}+2X_{Ca})$$

$$Y_F = X_F/(X_F+2X_{SO_4}),\ Y_{SO_4} = 2X_{SO_4}/(X_F+2X_{SO_4})$$

(Note that, by charge balance, $(X_{Li}+X_{Na}+2X_{Ca}) = (X_F+2X_{SO_4})$)

N. B. Excess properties are expressed as polynomials in the charge equivalent fractions in J/equivalent (see Slide 1.19)

- If R is the same for all end-members (i. e.: if all A lattice species have the same valence and all B lattice species have the same valence), then the model is very similar to the Compound Energy Formalism (Section 5), the main difference being that a choice of Kohler/Toop/Muggianu interpolation is available in the two-lattice polynomial model.

Note: before reading this Section you should read Sections 1, 2 and 4.

Entry of data for a liquid (Li, Na, K)(F, SO_4) solution

with the Two-lattice Polynomial Model ("Model #4")

Data for this phase have been stored in the file ..\FACTDATA\SolCsoln.sln

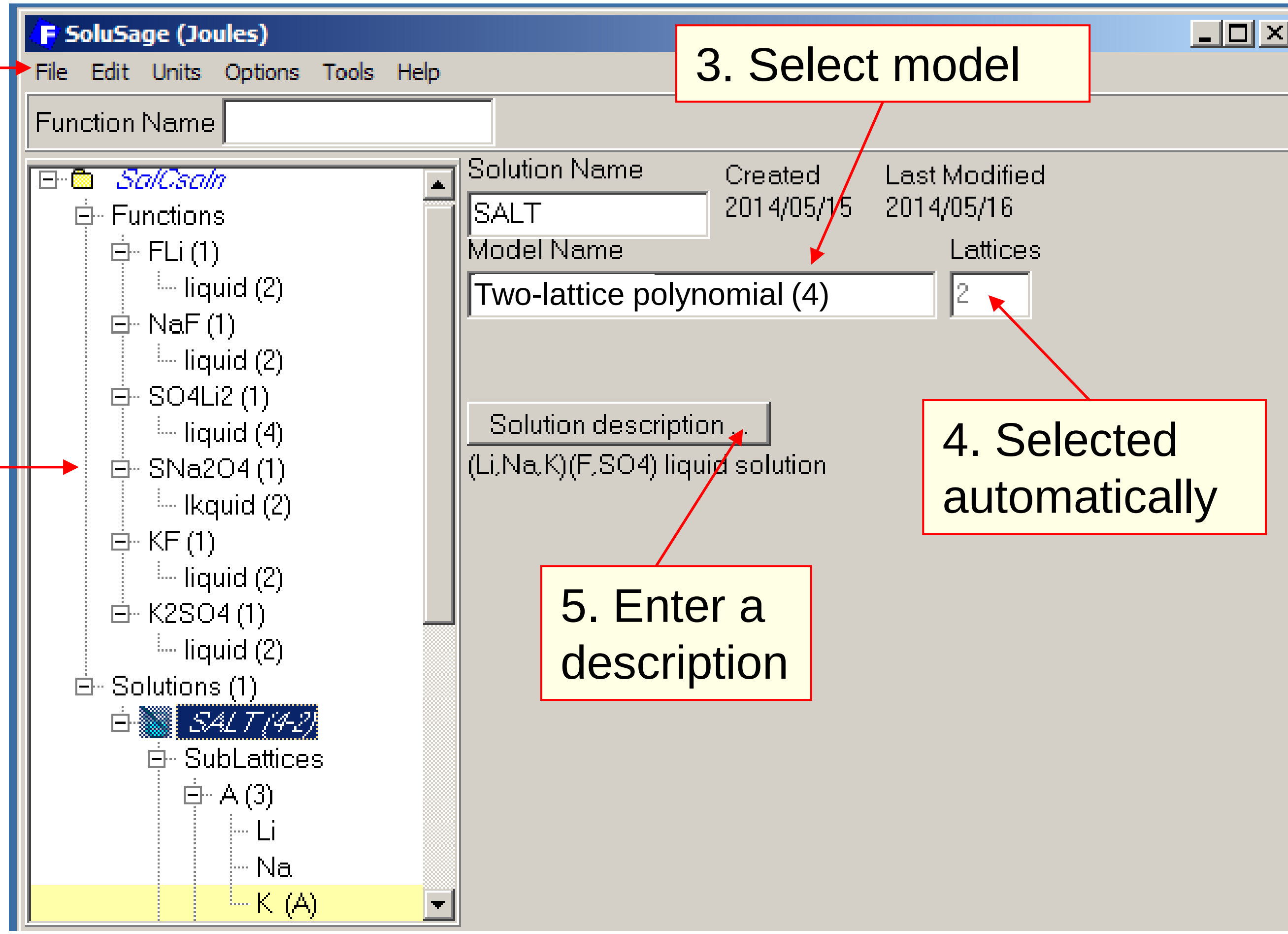
1. Click «File→ Open SolCsoln»

2. Functions for each end-member liquid have been copied from a COMPOUND database

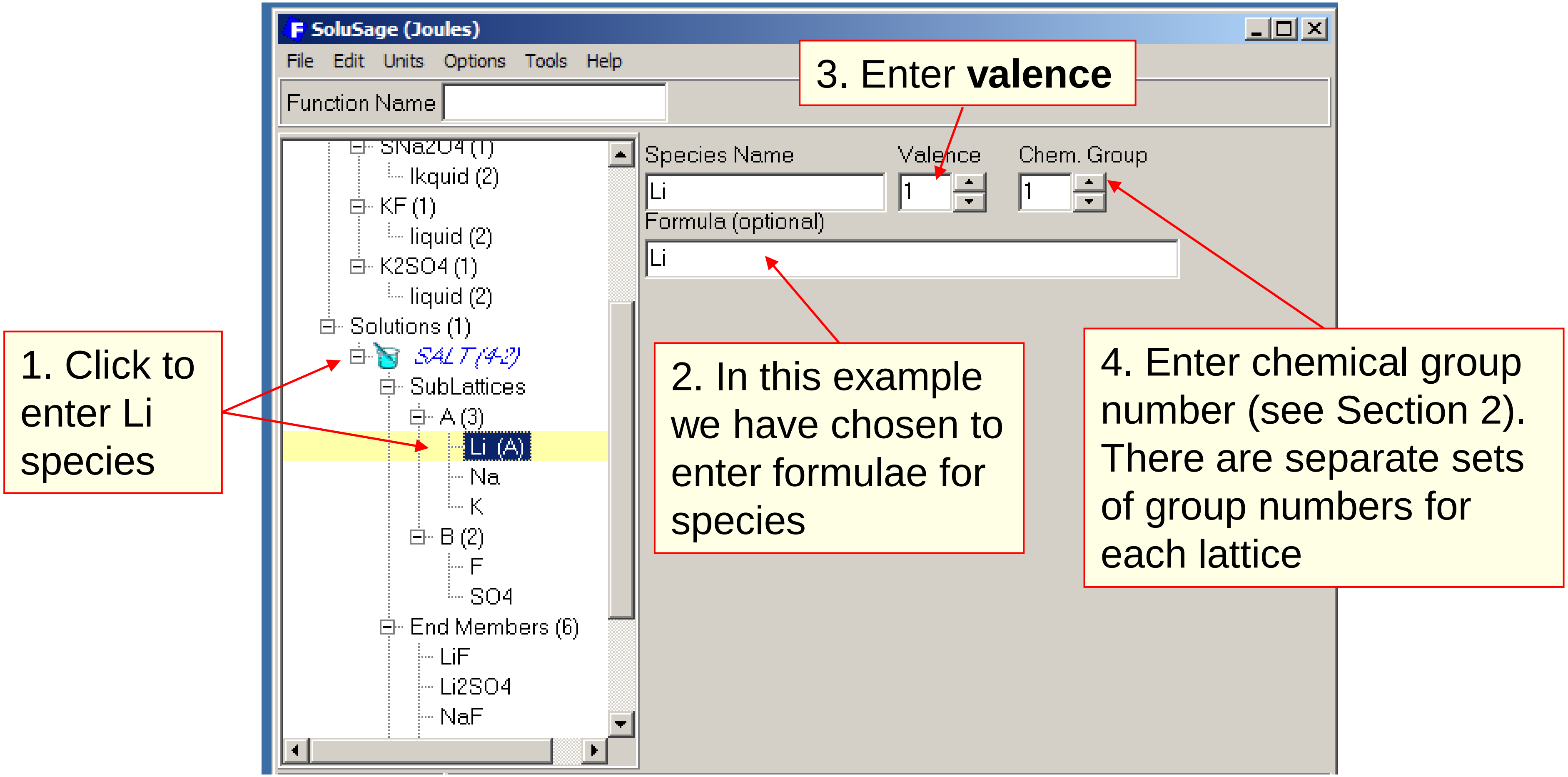
3. Select model

4. Selected automatically

5. Enter a description

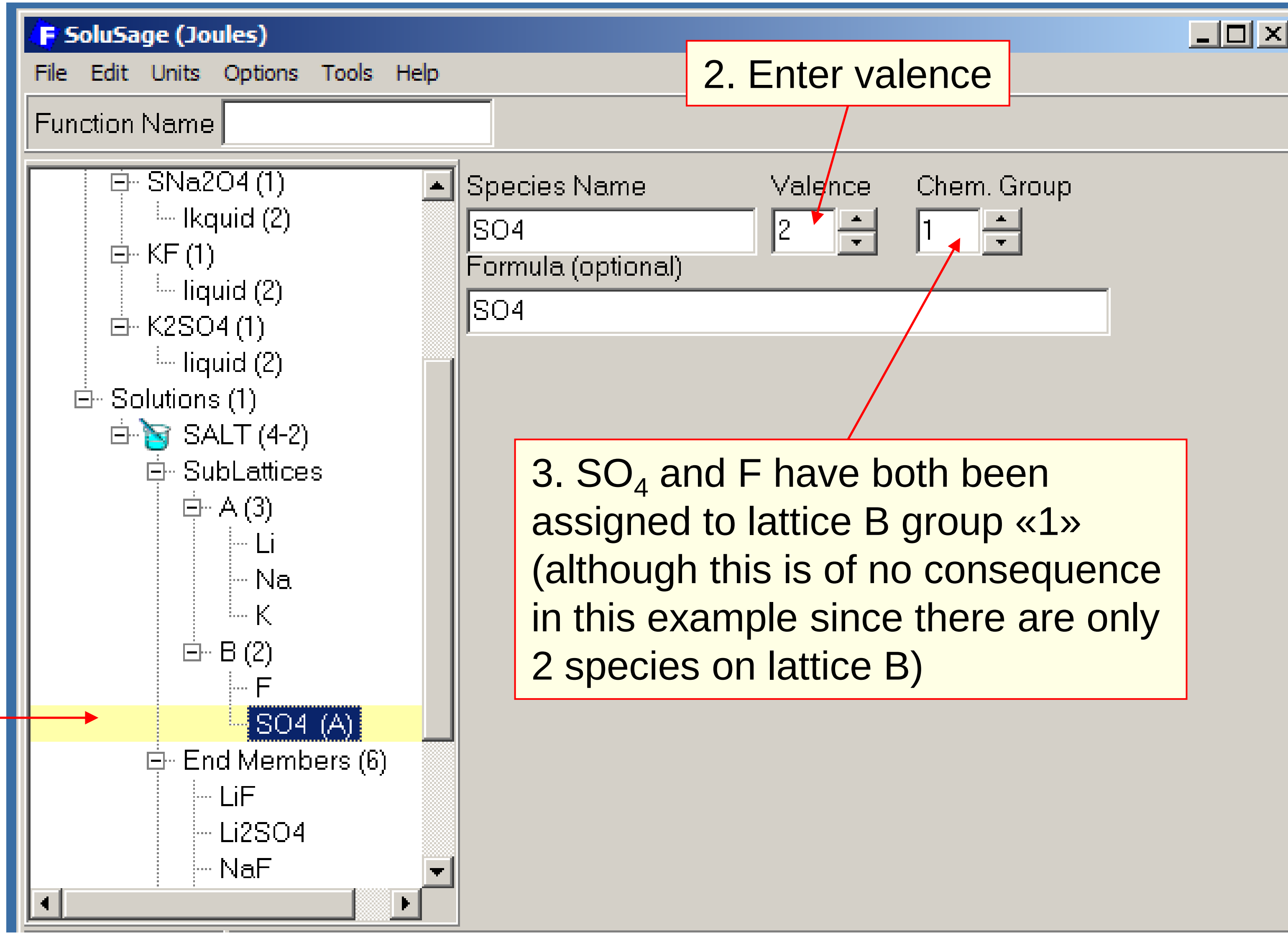


Entry of species



In this example, Li, Na and K are all assigned to group “1” (all-Kohler default) on lattice A

1. Click to enter SO_4 species



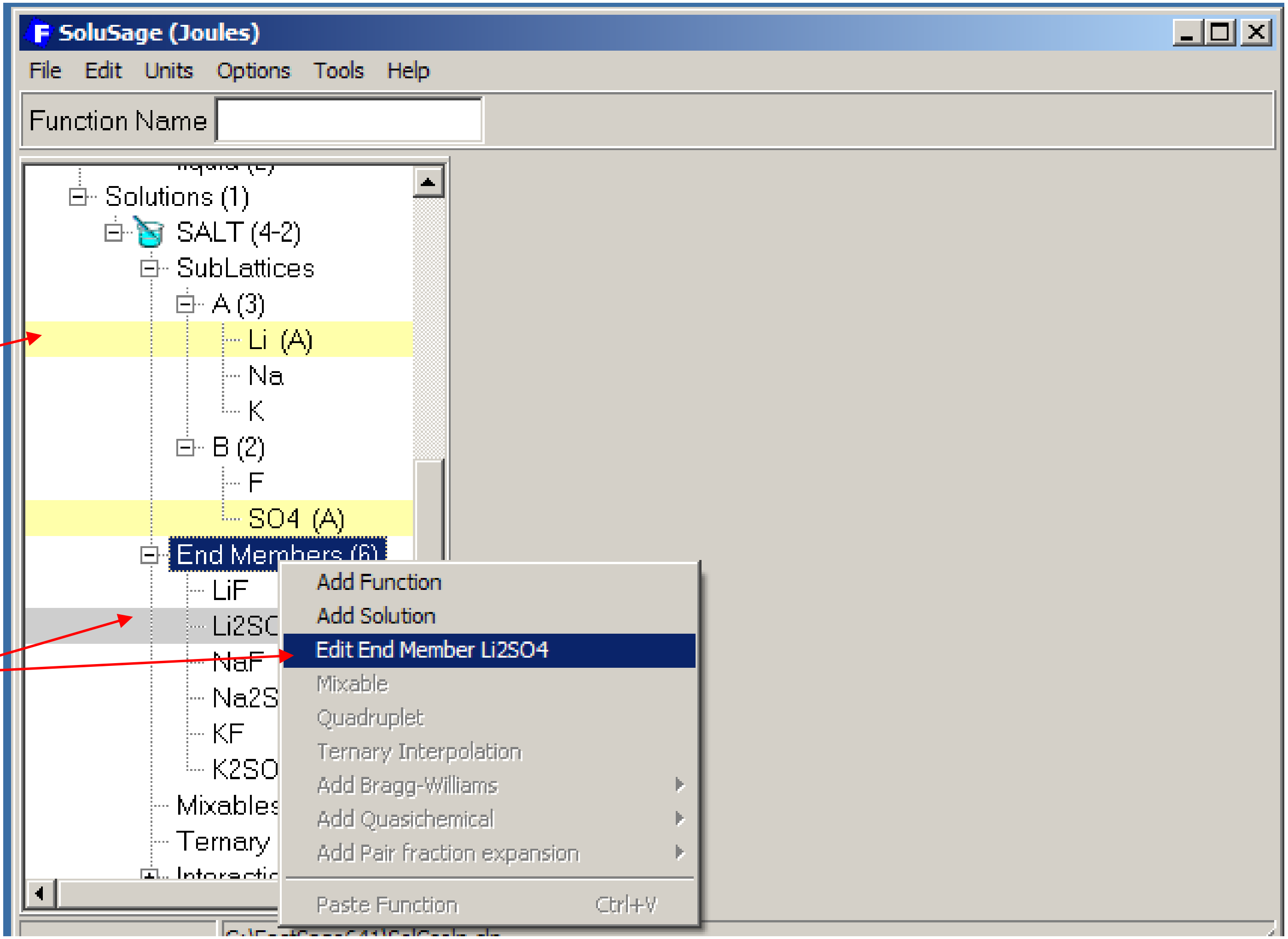
2. Enter valence

3. SO_4 and F have both been assigned to lattice B group «1» (although this is of no consequence in this example since there are only 2 species on lattice B)

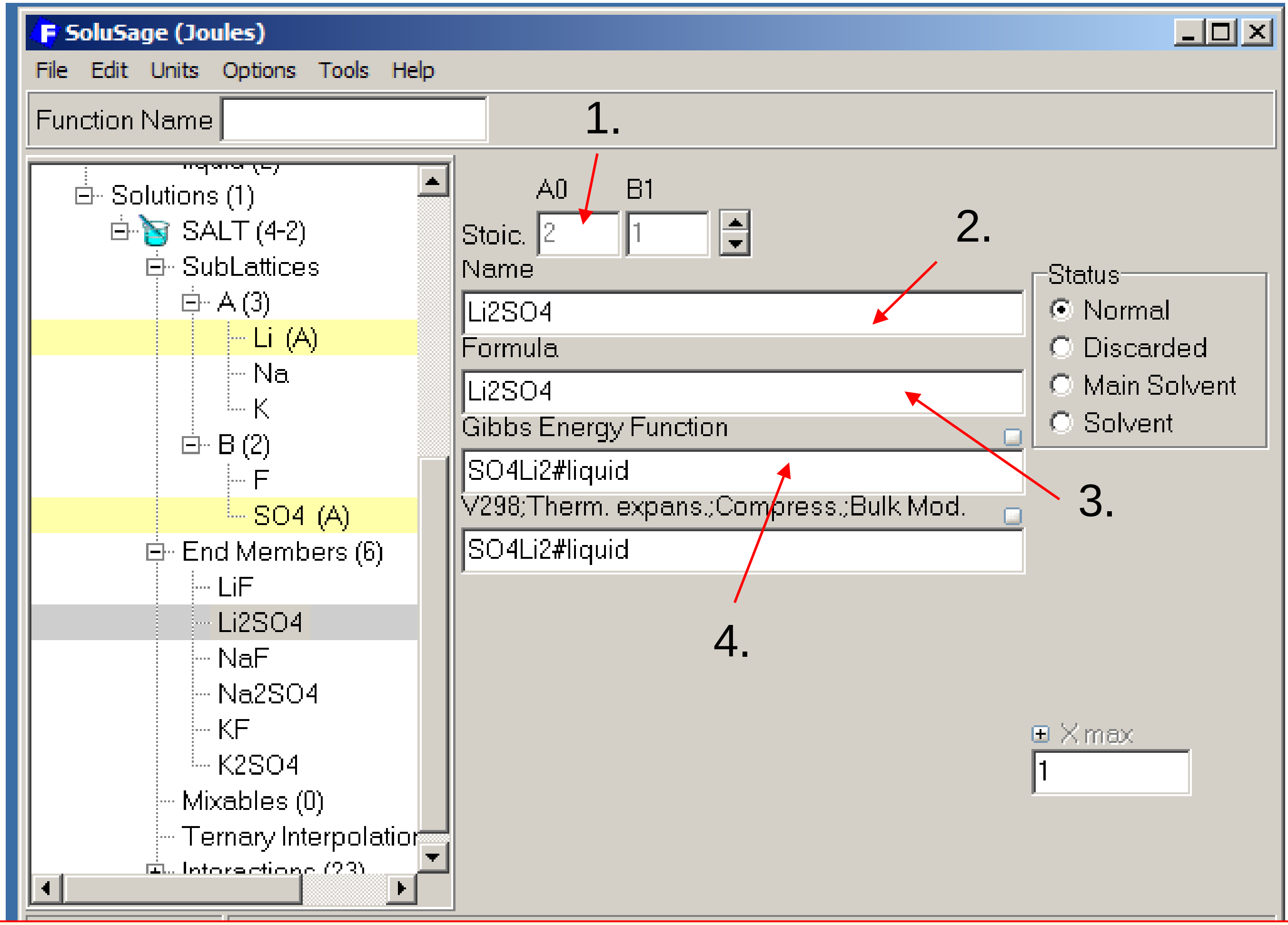
Entry of end-member Li_2SO_4

1. Highlight one species for each lattice, then right click.

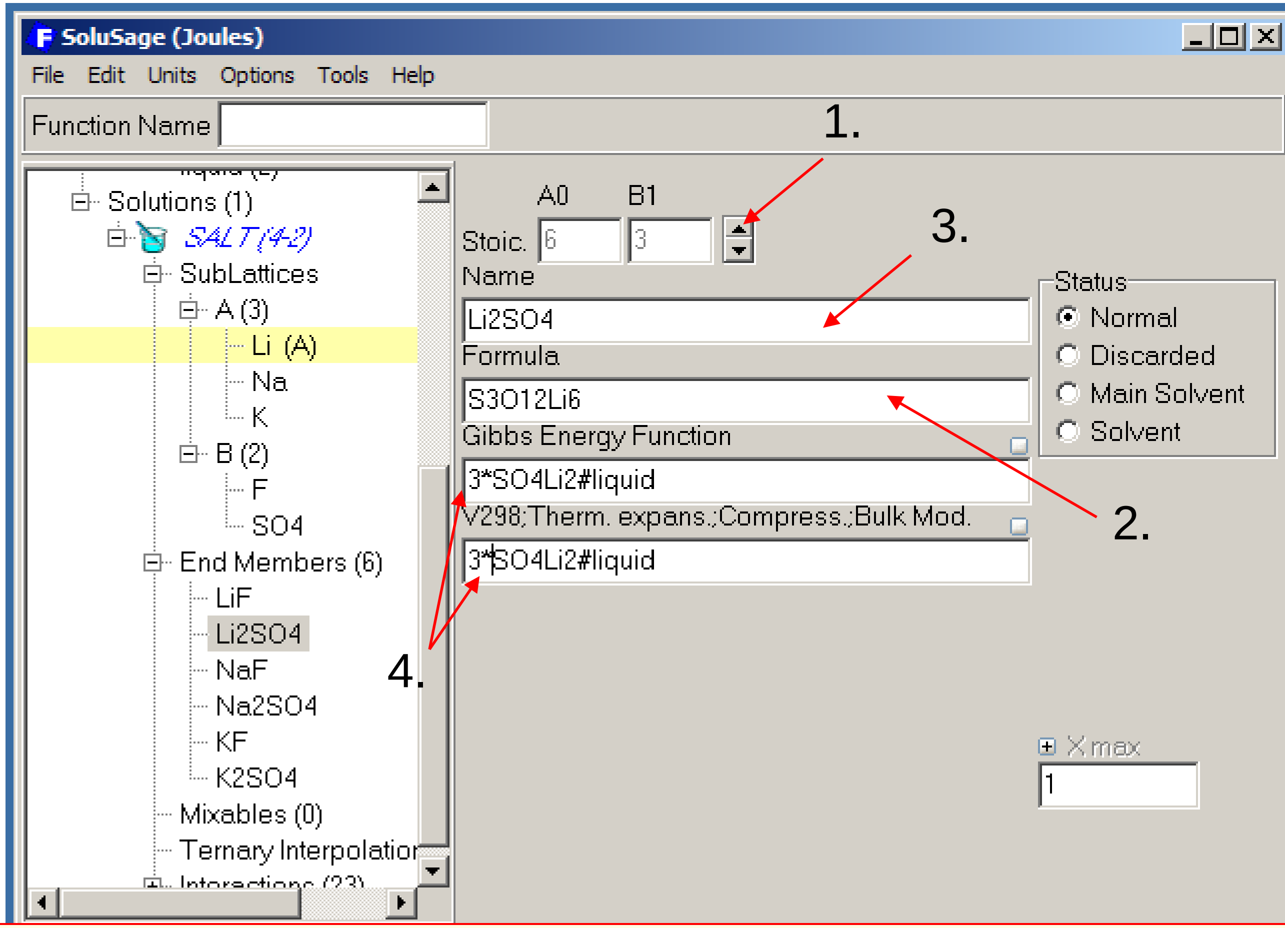
2,3.Click.



<u>Note</u>: All (2x3) = 6 end-members **must** be entered, one for each combination of one species from each lattice.



1. The **stoichiometry variables** are generated automatically from the entered valences.
2. The **name** is not used in any calculations but will appear on FactSage outputs.
3. The **formula** is entered automatically since formulae were enterd for the species.
4. Enter the Gibbs energy of end-member Li_2SO_4 as a sum of «functions».



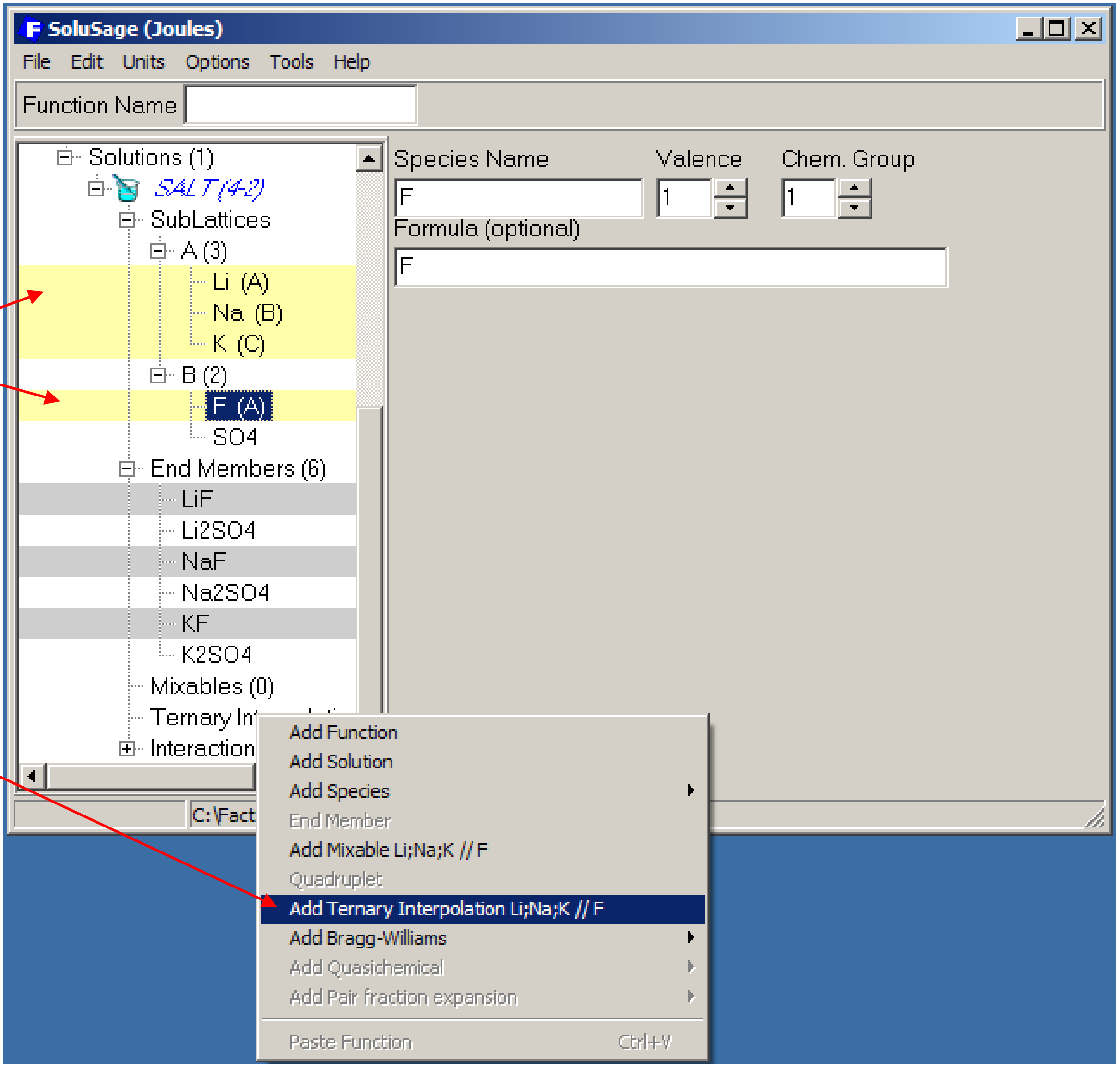
1. By clicking on the arrows **you can change the stoichiometry of the end-member** by a factor 2, 3, 4, …. Note that this does **not change the valences** of the species.
2. If formulae were entered for the species the end-member formula is changed automatically. Otherwise, it must be changed manually.
3. However, the **name** does not change unless you change it.
4. The Gibbs energy of $Li_6(SO_4)_3$ is **3x** that of the function SO4Li2#liquid.

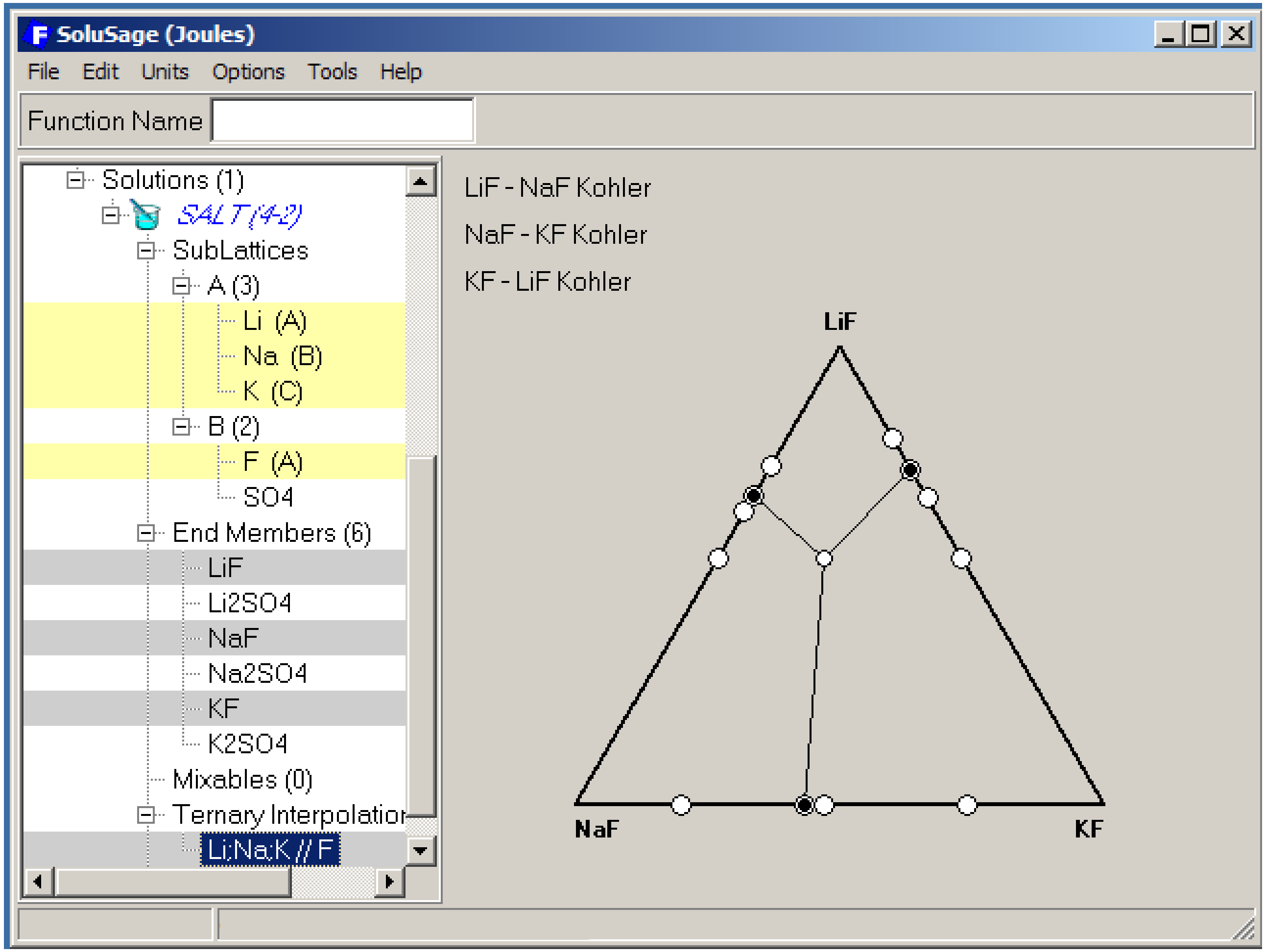
Editing ternary interpolation configuration for

the LiF-NaF-KF system

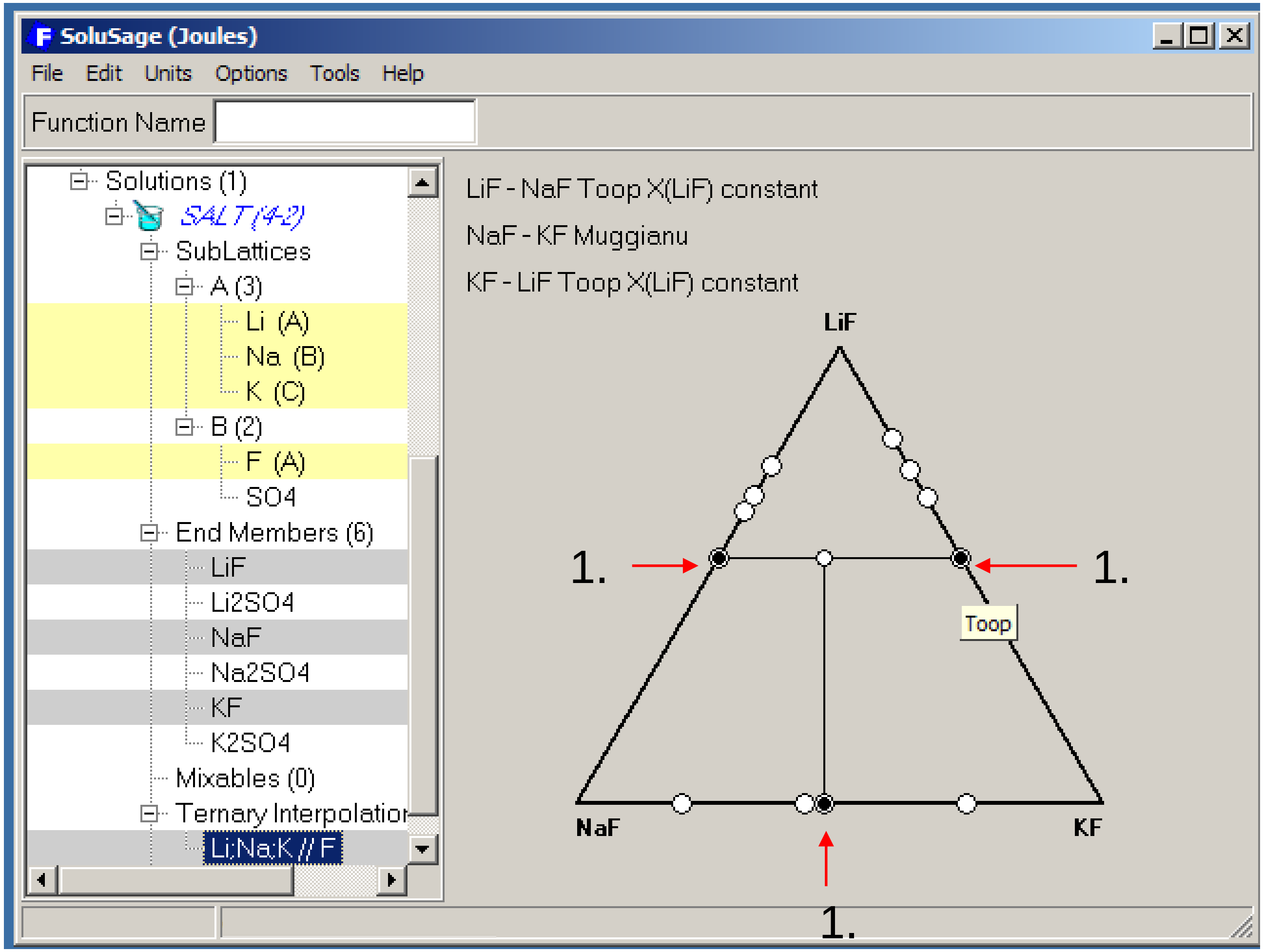
1. Holding down the Ctrl key, highlight three species from one lattice and one from the other, then right click.

2. Click.



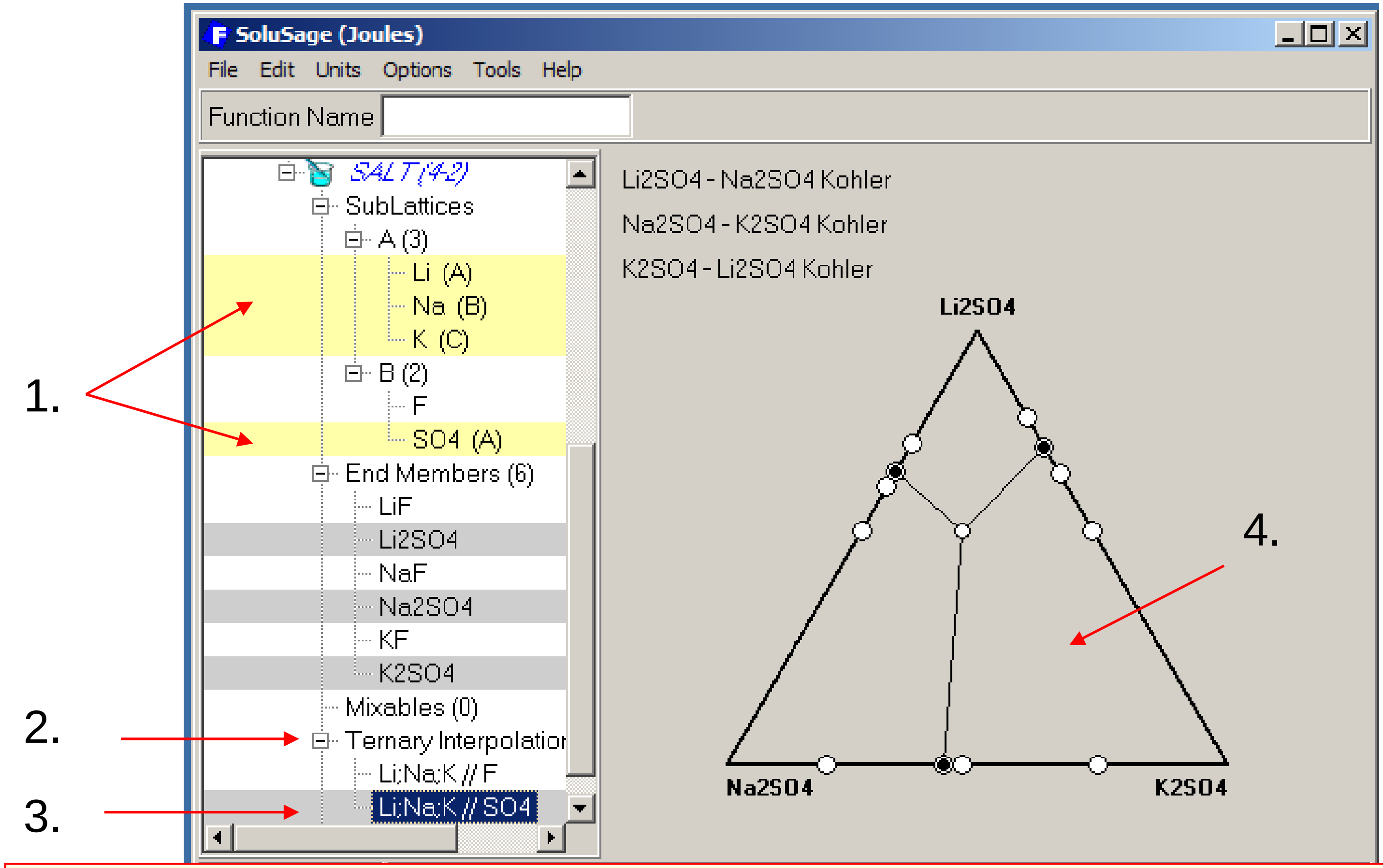


The default configuration is shown. Since Li, Na and K were all assigned to chemical group "1", the default is "All Kohler" in the LiF-NaF-KF system.



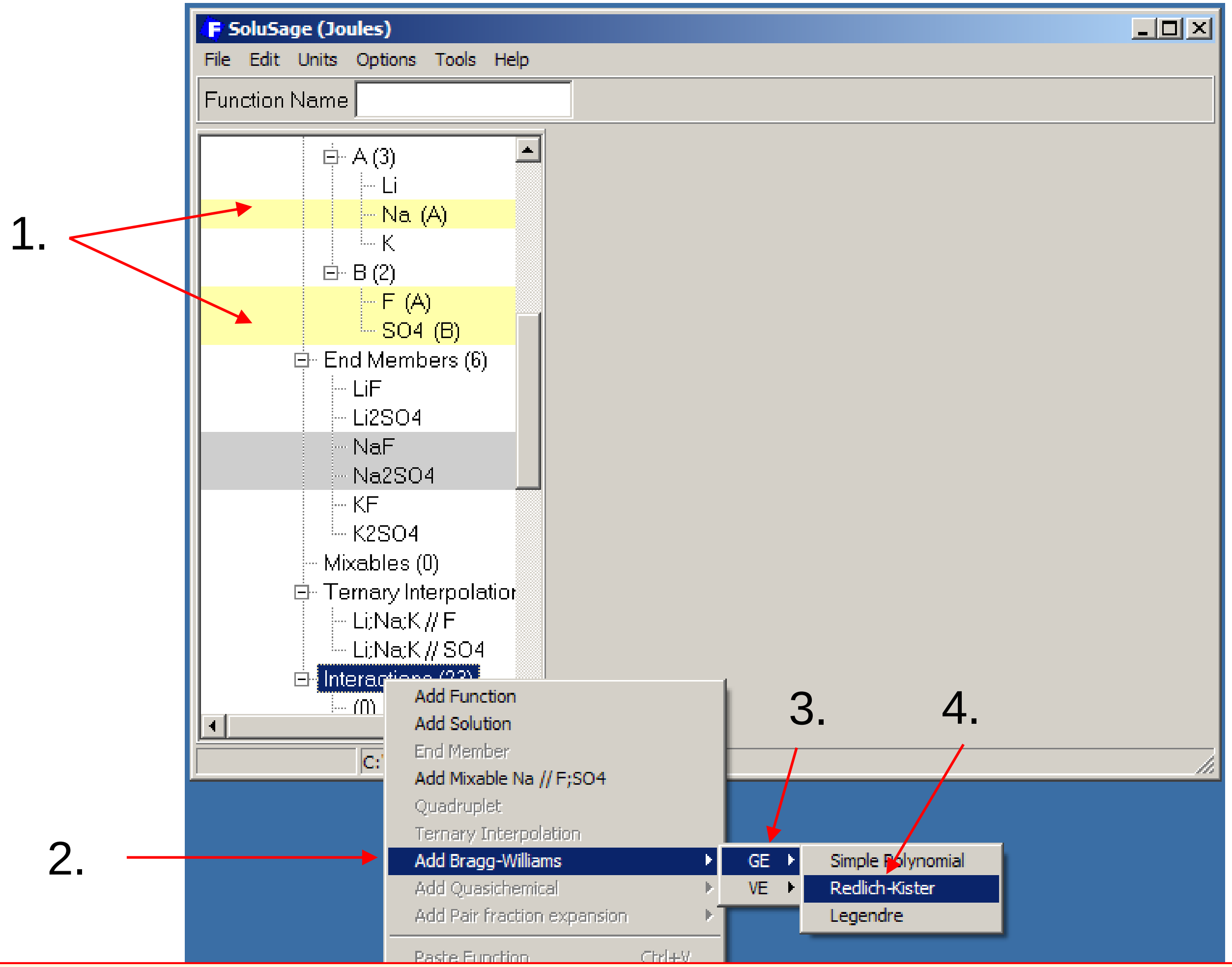
1. By clicking on the circles you can over-write the default, in this example to a Toop/Muggianu (X_{LiF} = constant) configuration.

Entering ternary interpolation configuration for the Li_2SO_4-Na_2SO_4-K_2SO_4 system



1,2,3. Clicks.
4. The default configuration is «All Kohler» because Li, Na and K have all been assigned to chemical group «1».
Note that changing the configuration for the (Li, Na, K)(F) system in the previous slide has not changed the configuration for the (Li, Na, K)(SO_4) system.

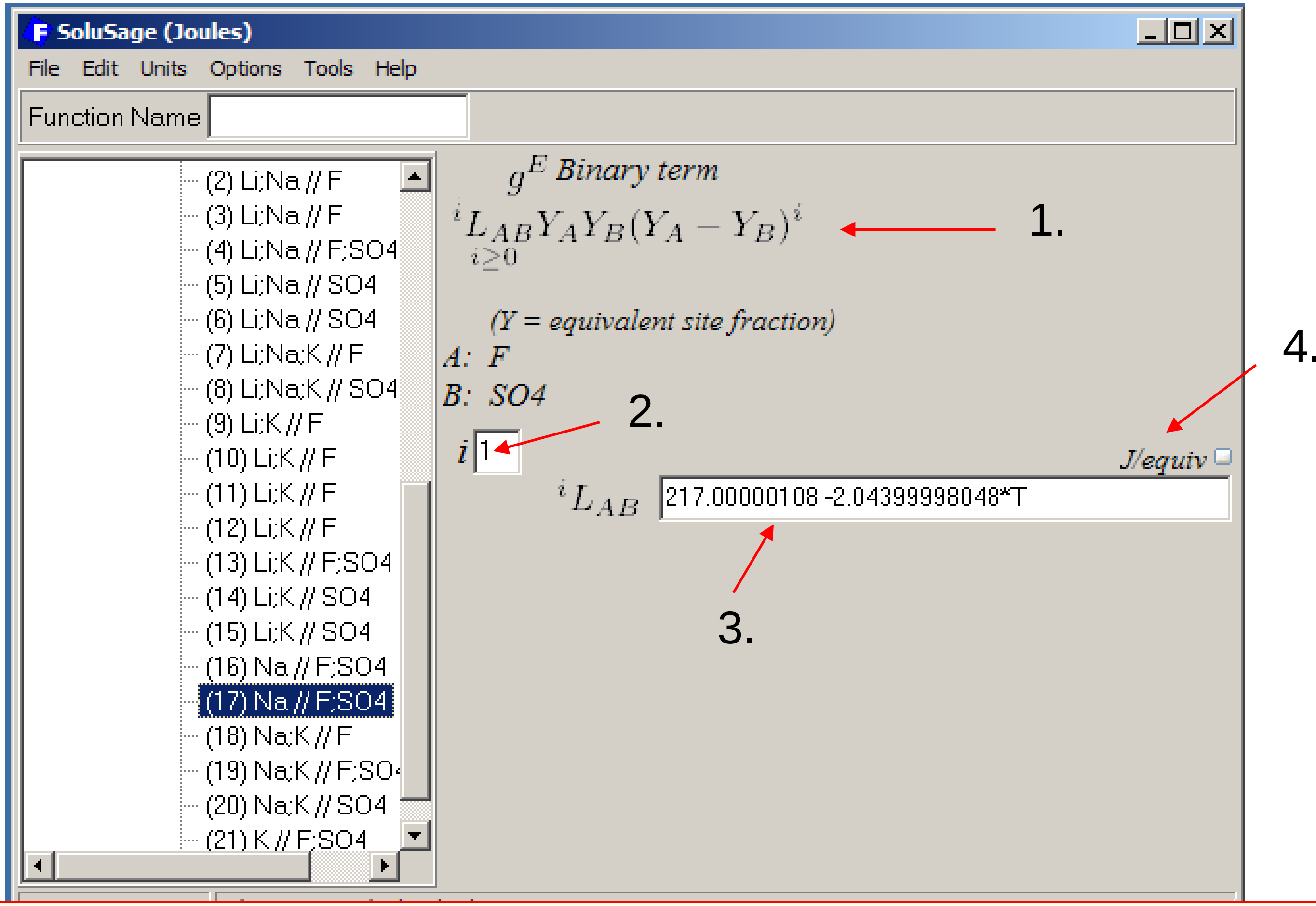
Entering binary interaction parameters



1. For a binary parameter, highlight two species on one lattice and one species on the other. This is a parameter for interaction between F and SO_4 on lattice B when lattice A is occupied solely by Na. Then right click.

2,3. Mouse over, then click.

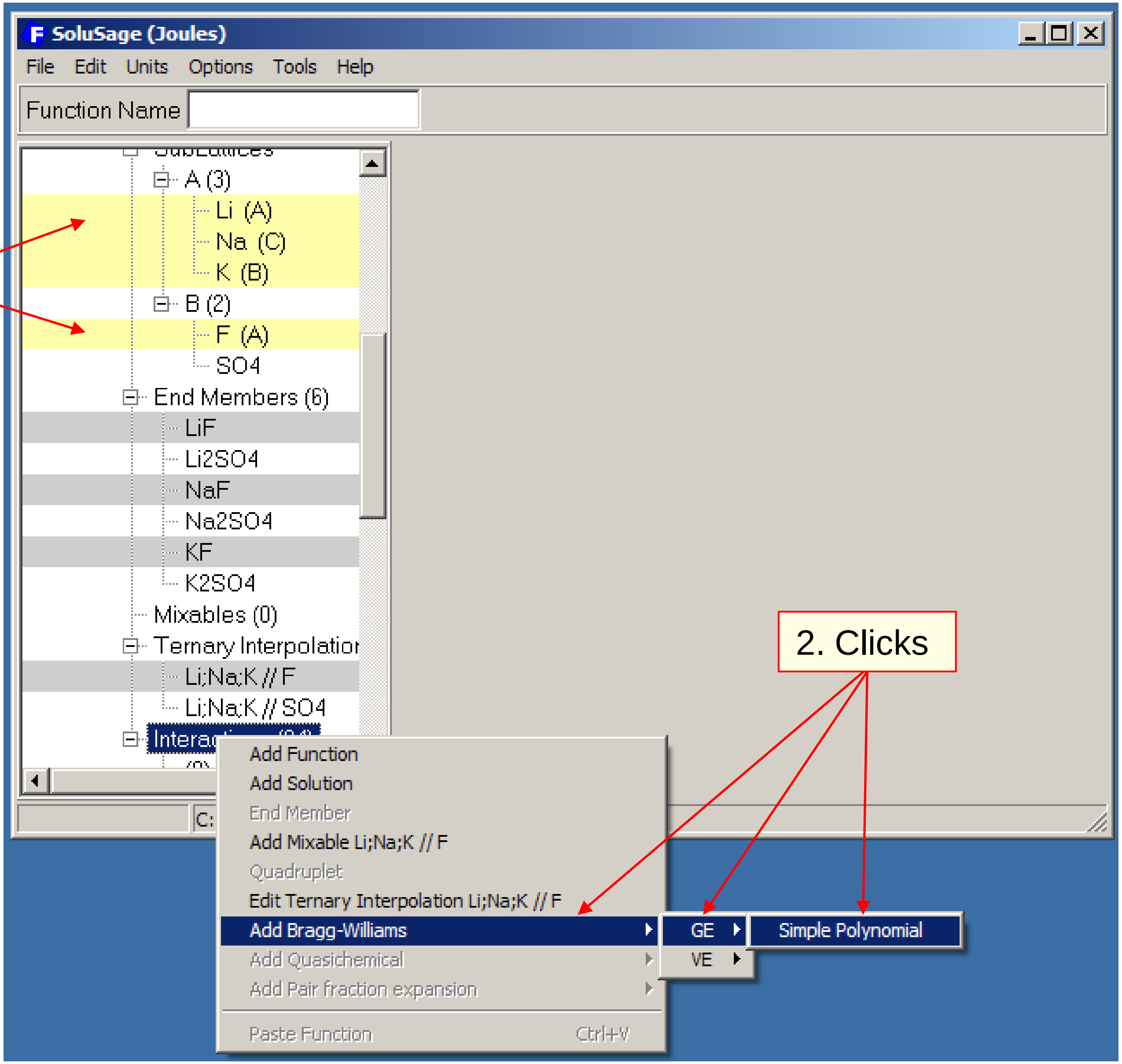
4. Choose the form of the polynomial (see Slides 1.1 and 1.19).



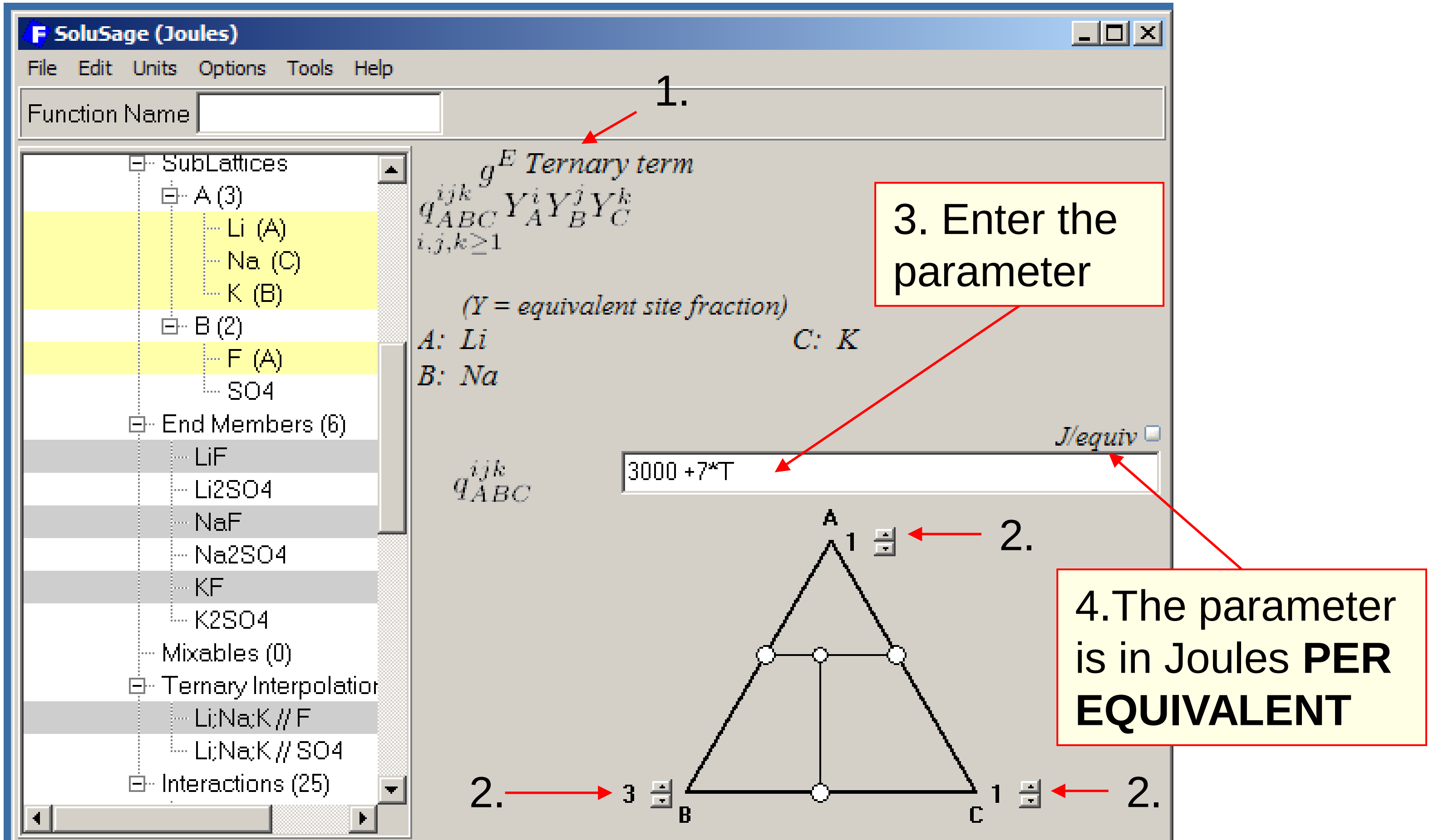
1. The excess terms are polynomials in the **equivalent fractions** (defined in Slide 7.0).
2. Enter the Redlich-Kister power.
3. Enter the excess parameter.
4. **<u>NOTE</u>:** The parameter is in Joules **PER CHARGE EQUIVALENT**, that is for a solution containing Y_F moles of **NaF** and Y_{SO_4} moles of **$Na(SO_4)_{1/2}$**.

Entry of a ternary interaction parameter

1. Highlight 3 species on one lattice and one species on the other lattice. This is the ternary interaction (Li, Na, K)(F). Then right click.



2. Clicks

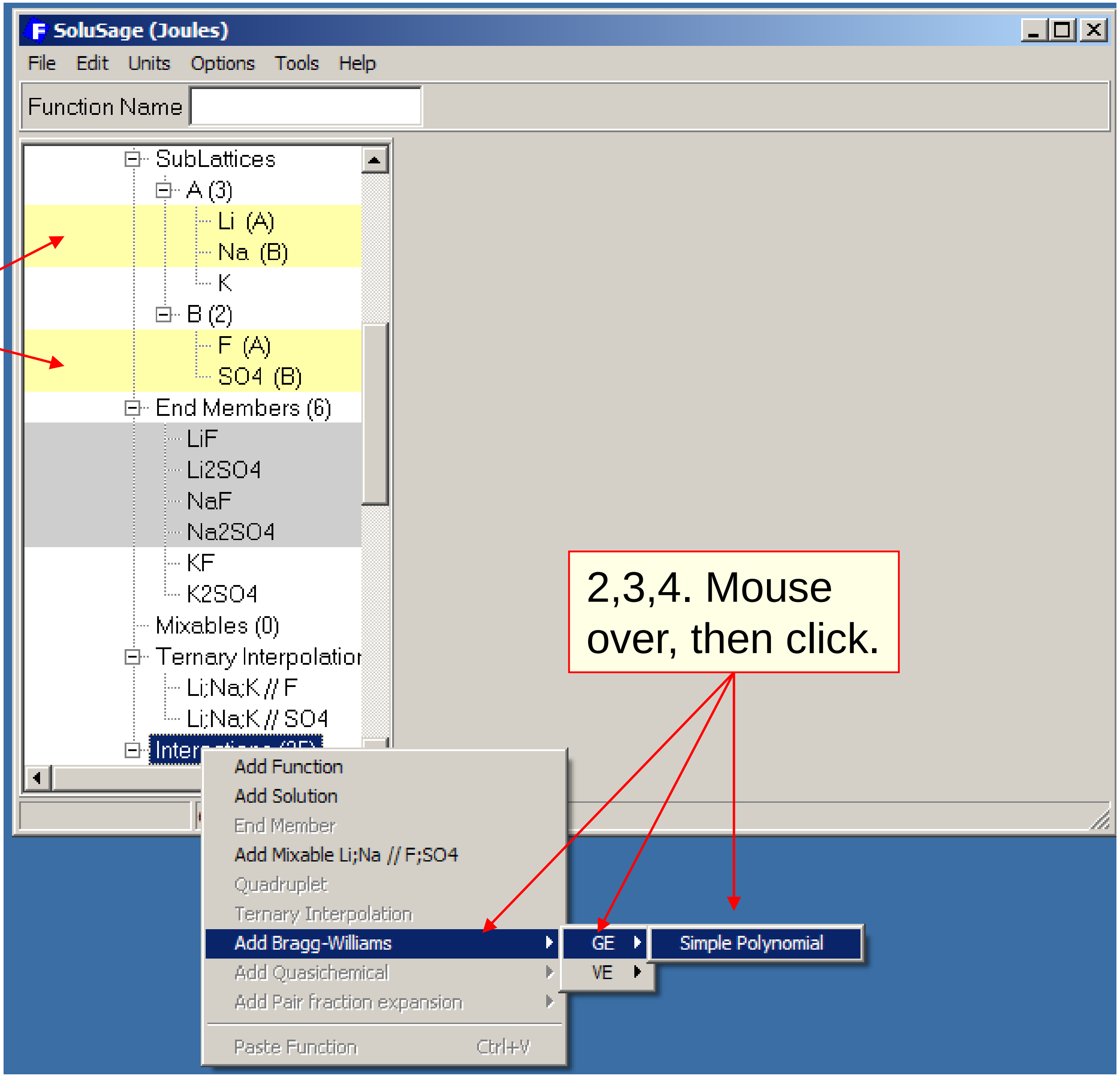


1. In this model, ternary terms are expressed in this form in terms of the **equivalent fractions**.
2. Choose the powers *i*, *j*, *k* by clicking on the arrows. This is the term

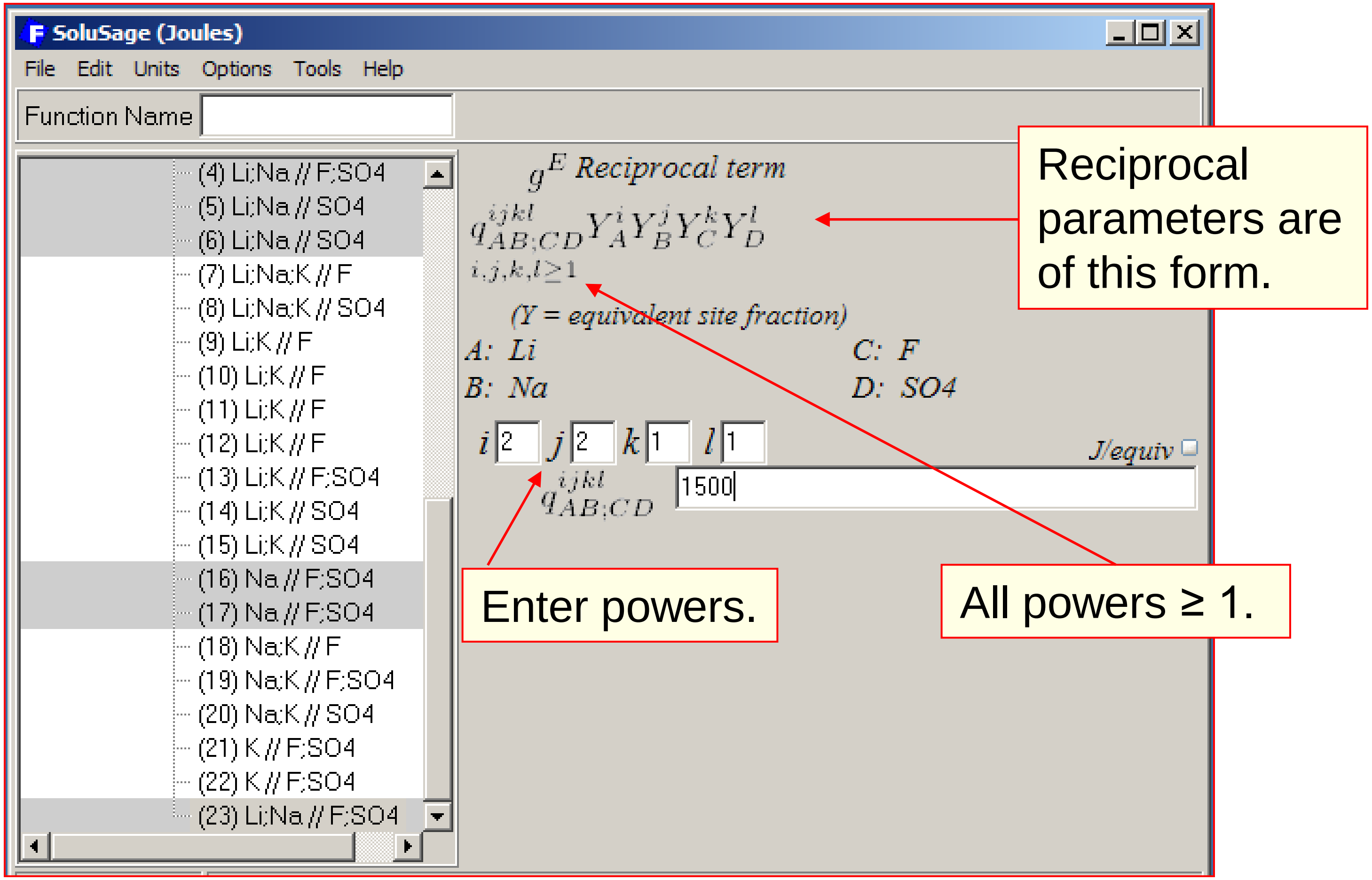
$$q^{132}_{ABC} \quad Y_A^{1} Y_B^{3} Y_C^{2}$$

Entry of a reciprocal interaction parameter

1. Highlight 2 species from each lattice.



2,3,4. Mouse over, then click.


SoluSage (Joules)
File Edit Units Options Tools Help
Function Name
(4) Li;Na // F;SO4
(5) Li;Na // SO4
(6) Li;Na // SO4
(7) Li;Na;K // F
(8) Li;Na;K // SO4
(9) Li;K // F
(10) Li;K // F
(11) Li;K // F
(12) Li;K // F
(13) Li;K // F;SO4
(14) Li;K // SO4
(15) Li;K // SO4
(16) Na // F;SO4
(17) Na // F;SO4
(18) Na;K // F
(19) Na;K // F;SO4
(20) Na;K // SO4
(21) K // F;SO4
(22) K // F;SO4
(23) Li;Na // F;SO4
g^E Reciprocal term
$q^{ijkl}_{AB:CD} Y^i_A Y^j_B Y^k_C Y^l_D$
$i,j,k,l \geq 1$
(Y = equivalent site fraction)
A: Li
C: F
B: Na
D: SO4
i 2 j 2 k 1 l 1
J/equiv
$q^{ijkl}_{AB:CD}$
1500
Reciprocal parameters are of this form.
Enter powers.
All powers ≥ 1.

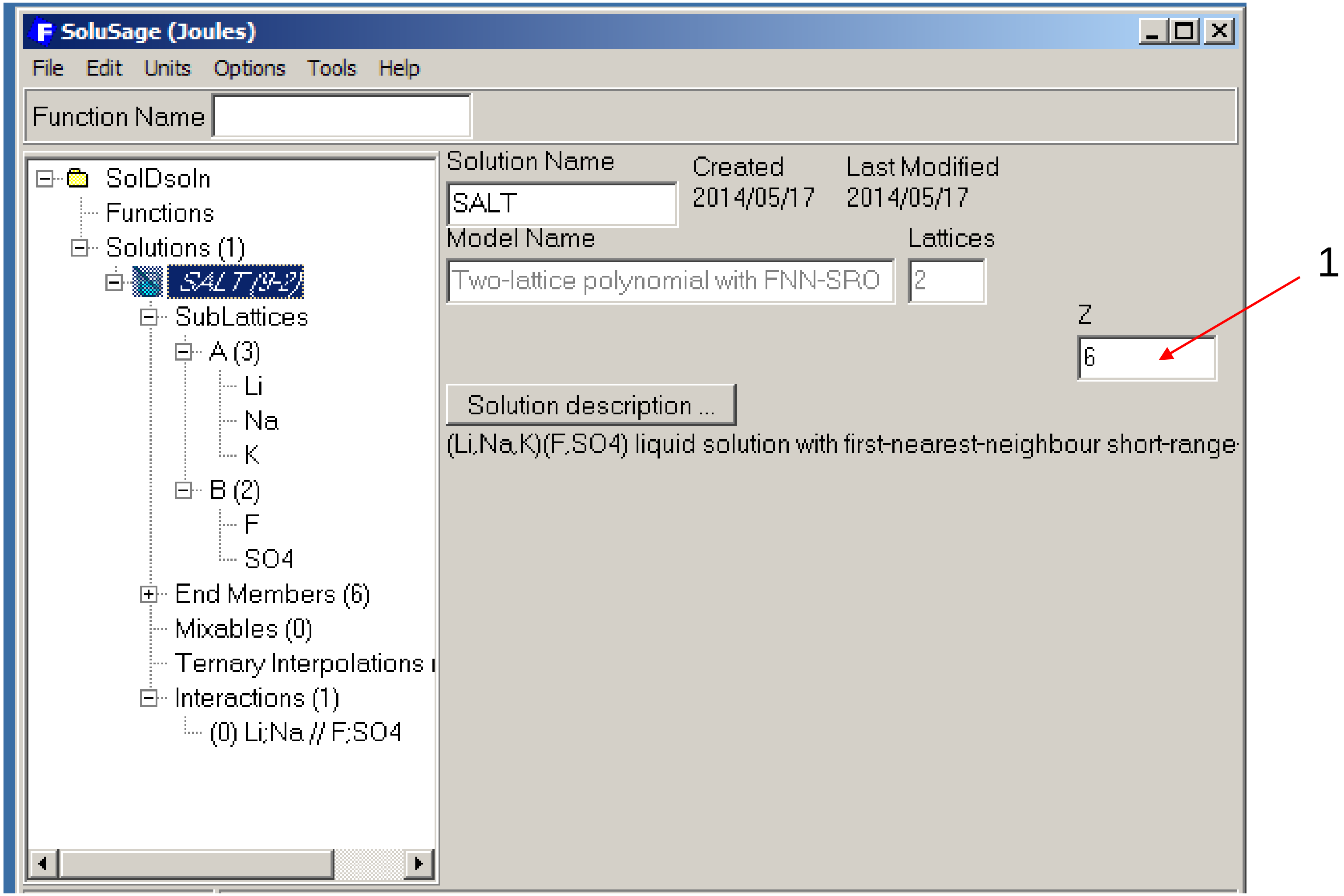
8. Two-Lattice Polynomial Model with FNN-SRO

(First-nearest-neighbour Short-range-ordering)("Model 9") (Refs. 7, 8)

- This model is the same as the Two-lattice Polynomial Model ("Model 4") described in Section 7, but taking account of short-range-ordering between first-nearest-neighbour pairs. In a solution (A, B)(X, Y) the model calculates the equilibrium numbers of nearest-neighbour A-X, A-Y, B-X and B-Y pairs which minimize the Gibbs energy

- **Input** is **identical** to that for the two-lattice polynomial model (**Section 7**) with **2 exceptions** described in the following slides.

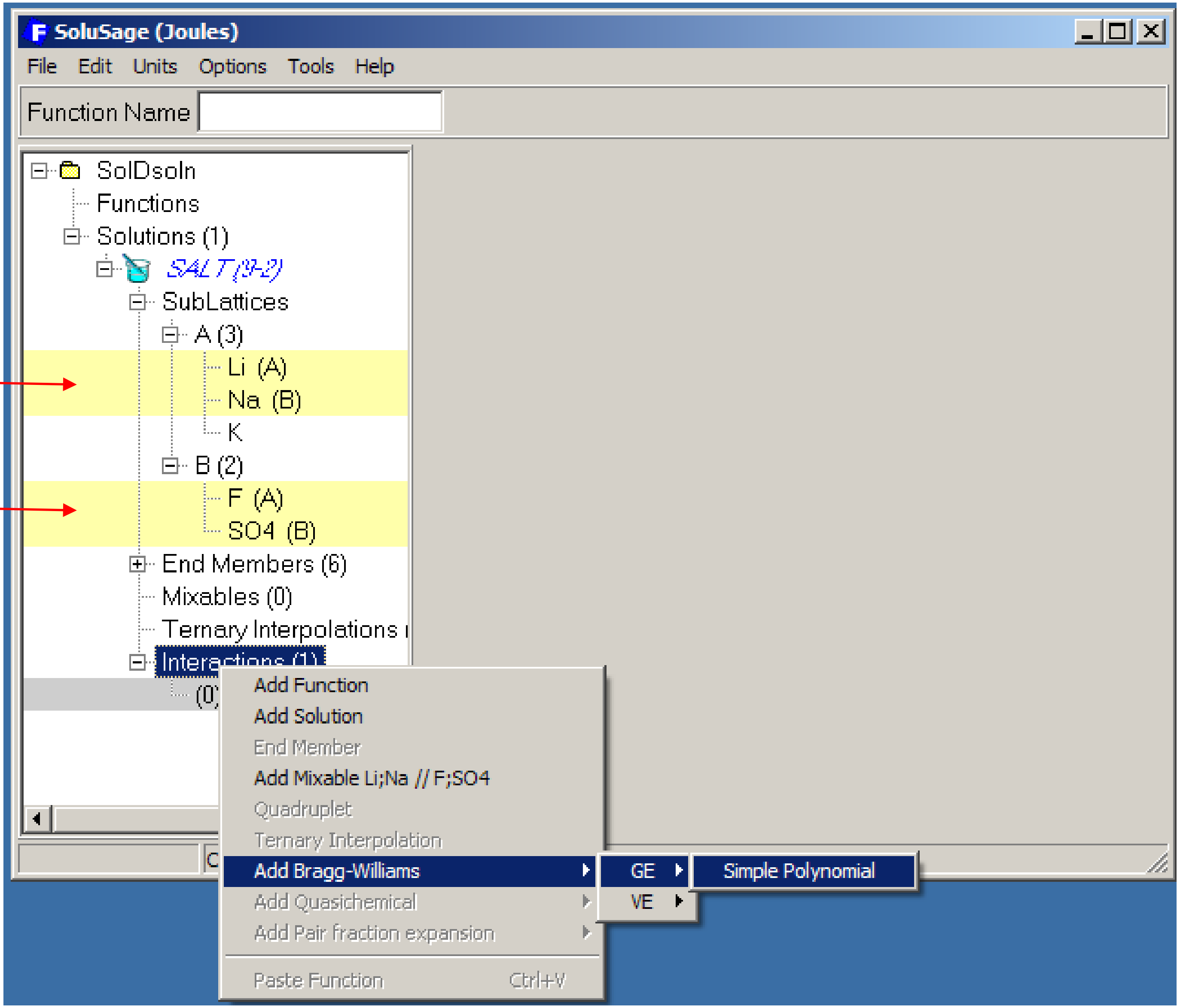
Entry of a nearest-neighbour coordination number

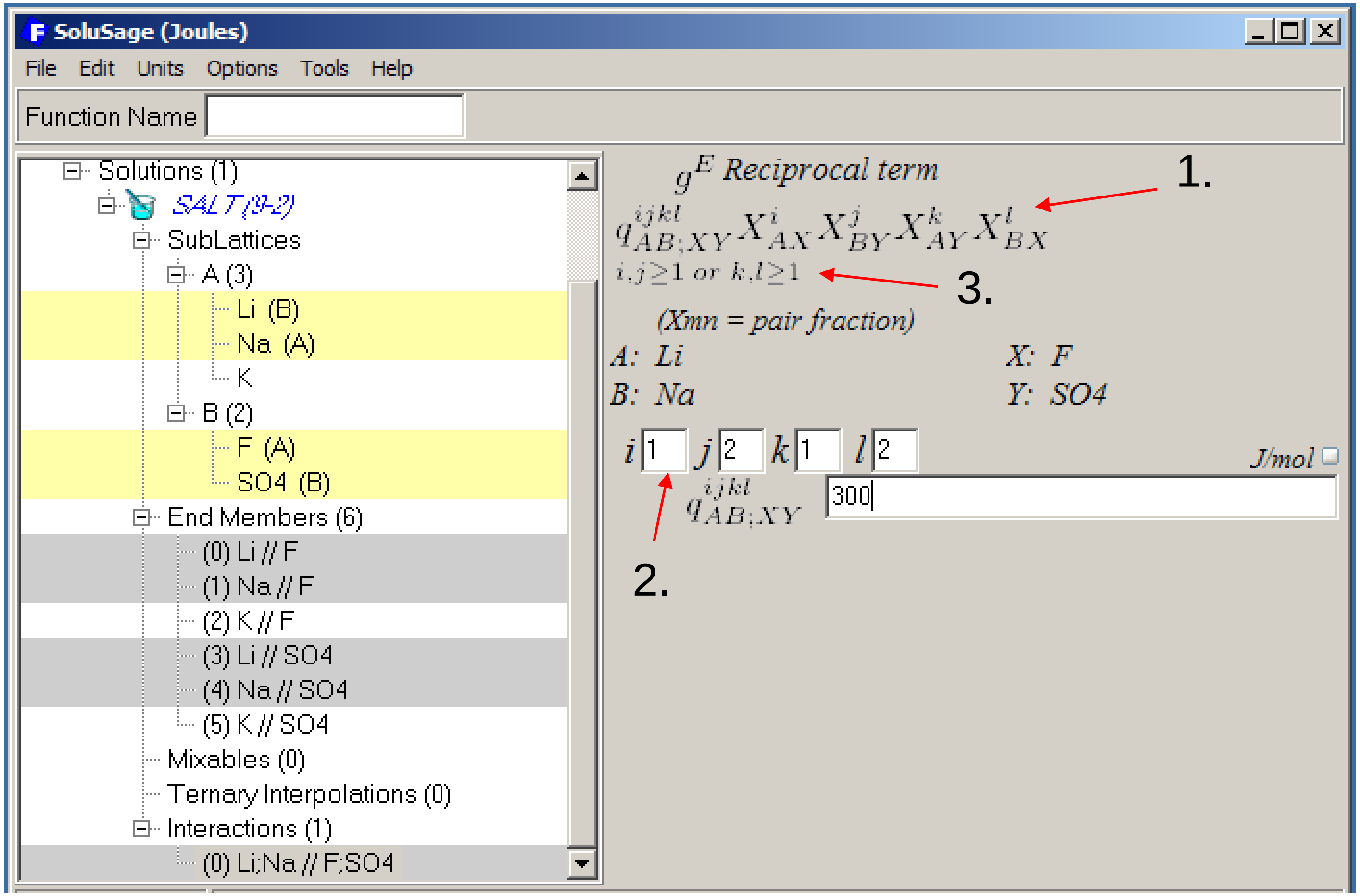


1. The model requires a FNN coordination number.

Entry of a reciprocal interaction parameter

1. A reciprocal interaction parameter is entered





1. Reciprocal parameters are in terms of the <u>pair fractions</u> X_{mn}.
2. Enter powers.
3. Note: i and j must both be ≥ 1 or k and l must both be ≥ 1.

9. The One-lattice Modified Quasichemical Model ("Model #3)

Refs. (9-12)

Short-range-ordering (SRO) is treated by calculating equilibrium among nearest-neighbour pairs. In a binary system A-B:

$$(\text{A-A})_{\text{pair}} + (\text{B-B})_{\text{pair}} = 2(\text{A-B})_{\text{pair}}; \qquad \Delta g_{AB} \qquad [1]$$

Δg_{AB} is the Gibbs energy of this pair-exchange reaction to form 2 moles of (A-B) pairs. (If Δg_{AB} = 0, the solution is ideal.)
In a binary system, Δg_{AB} is expressed as a polynomial in either:

(i) Redlich-Kister form: $\Delta g_{AB} = \sum {}^{i}L_{AB}(Y_A - Y_B)^i$ (i≥0) [2]

[or] (ii) Simple polynomial form: $\Delta g_{AB} = \sum q_{AB}^{ij} Y_A^i Y_B^j$ (i,j≥0) [3]

[or] (iii) Legendre polynomial form: $\Delta g_{AB} = \sum q_{AB}^{i} P_i (Y_A - Y_B)^i$ (i≥0) [4]

where: P_i is the Legendre polynomial of order i (Ref.(1))

(Note: the first terms in each of these series may also be called Δg_{AB}^{0})

where: Y_A and Y_B are coordination-equivalent site fractions:

$$Y_A = Z_A Y_A / (Z_A X_A + Z_B X_B) \qquad [5]$$

where Z_A and Z_B are "coordination numbers" of A and B and X_A and X_B are the site fractions.

- When Δg_{AB} is small, the model approaches the One-lattice Polynomial Model (Section 1) (random mixing) with

$$g^E \approx \left(\frac{X_A Z_A + X_B Z_B}{2} \right) Y_A Y_B \Delta g_{AB}$$

(cf. Slide 1.19, Eqs. [1-3])

(Note: Z_A and Z_B are model parameters which are not necessarily the actual physical coordination numbers

- In a solid solution, Z_A and Z_B must be equal. However, this is not necessary in a liquid solution.

If $\Delta g_{AB} << 0$, the solution is highly ordered, and the minimum in g^E will occur near the composition where the number of (A-B) pairs is a maximum, i. e. near $X_A/X_B = Z_B/Z_A$ (i. e. near $Y_A = Y_B = 0.5$).

Ternary Interpolations (cf. Section 2)

In a ternary system A-B-C, there are three binary functions: Δg_{AB}, Δg_{BC} and Δg_{CA}.

Δg_{ij} may be approximated as being constant along <u>either</u>:

(i) a line where Y_i/Y_j = constant (Kohler approx.)

(ii) a line where Y_i = constant (Toop approx.)

(iii) a line where Y_j = constant (Toop approx.)

(iv) a line perpendicular to the i-j edge of the Gibbs triangle (Muggianu approx.)

<u>Note</u>: Unlike Slide 2.0, it is the functions Δg_{ij} which are constant along these lines, not the binary α_{ij} functions.

- Input for this model is similar to that for the one-lattice Polynomial Model ("Model #1"), Section 1.

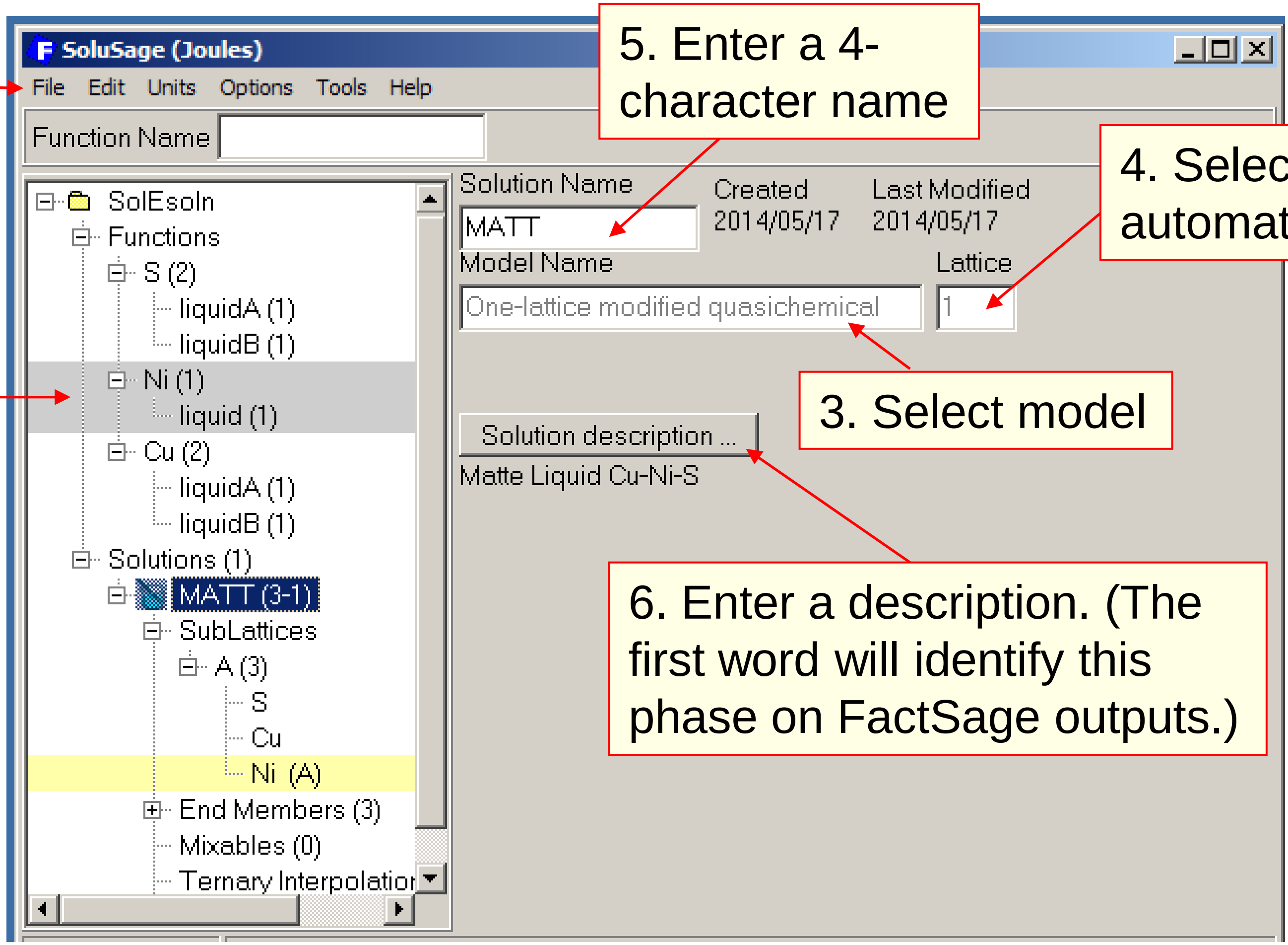
- Before reading this section, you should read Sections 1, 2, 4 and 6.

Entry of data for a liquid Cu-Ni-S solution with the One-lattice Modified Quasichemical Model (“Model #3) (Ref. (13))

Data have been stored in the file ..\FACTDATA\SolEsoln.sln

1. Click «File→Open SolEsoln»

2. Functions for each pure liquid end-member have been entered



5. Enter a 4-character name

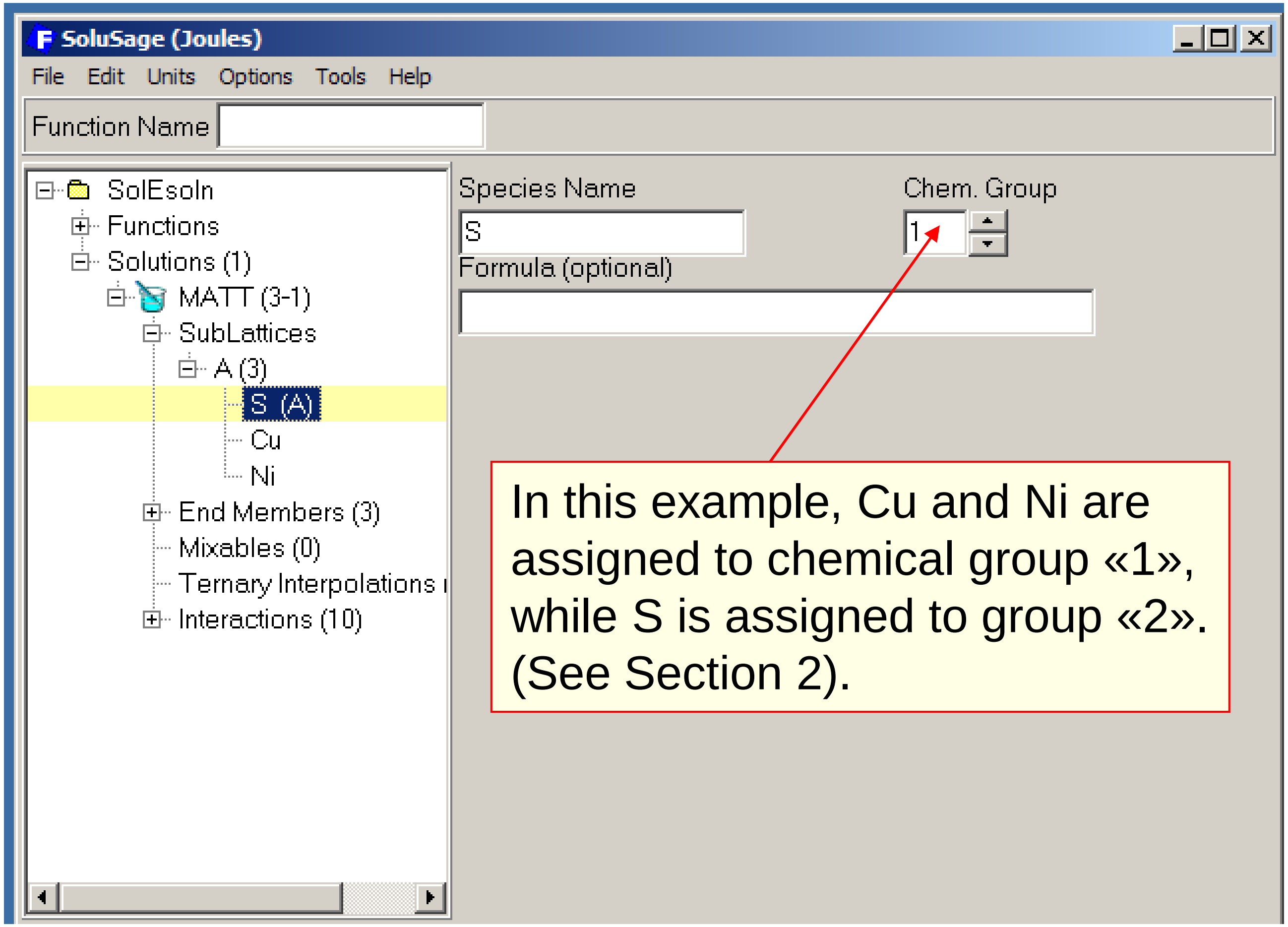
4. Selected automatically

3. Select model

6. Enter a description. (The first word will identify this phase on FactSage outputs.)

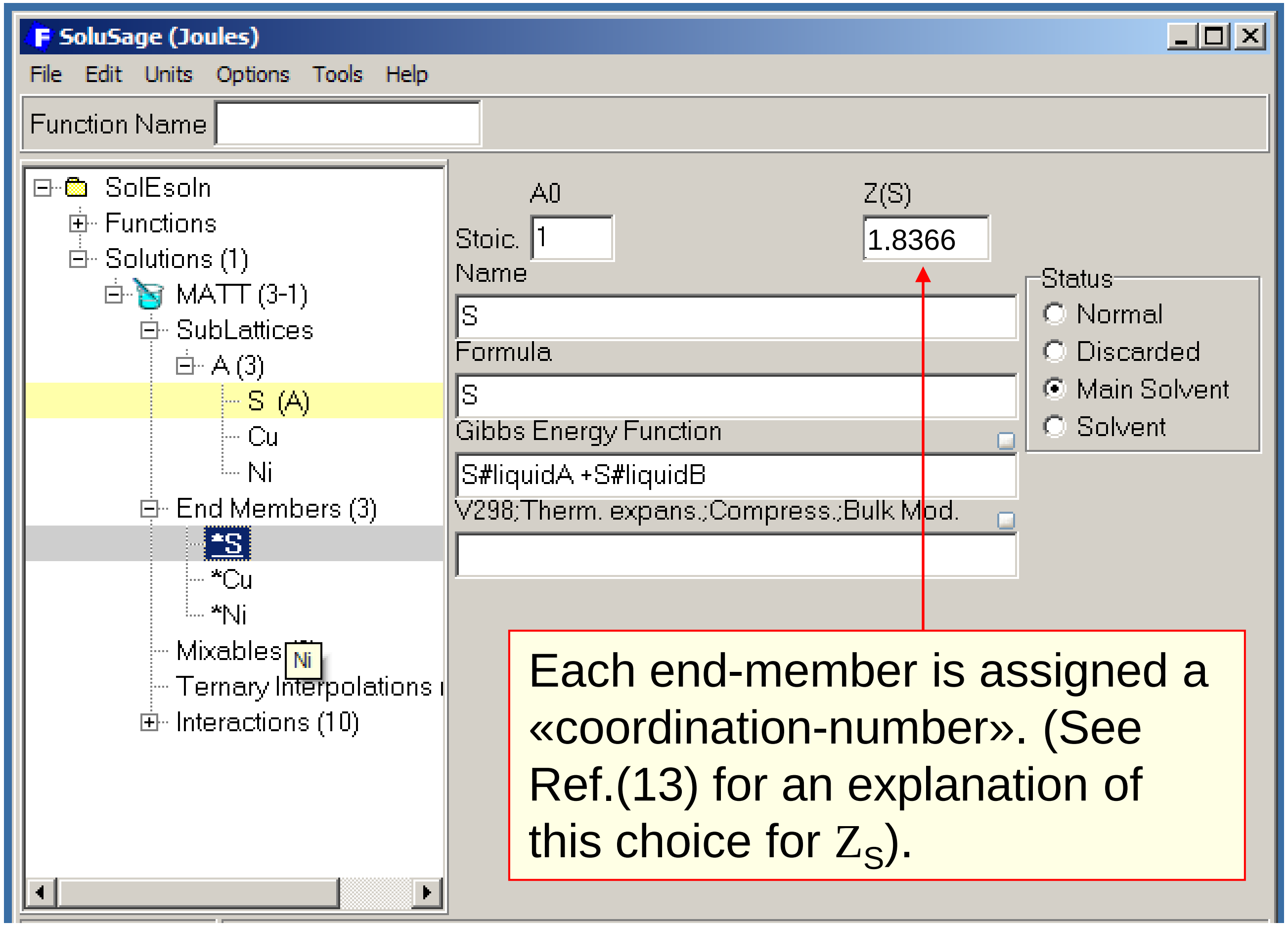
Entry of species

Enter species as described in Section 1.



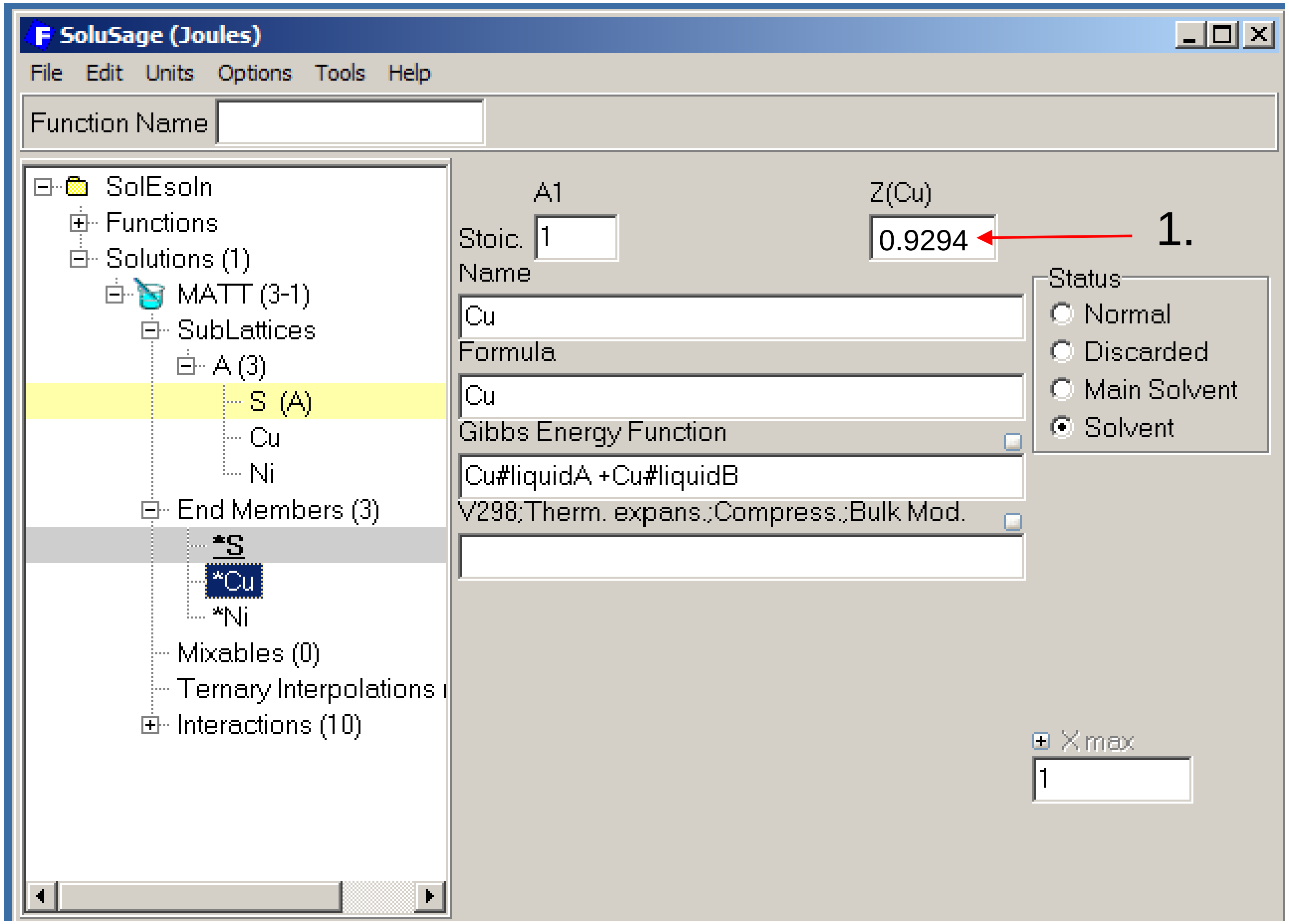
Entry of end-member S

Enter end-members as described in Section 1.



Each end-member is assigned a «coordination-number». (See Ref.(13) for an explanation of this choice for Z_S).

Entry of end-member Cu

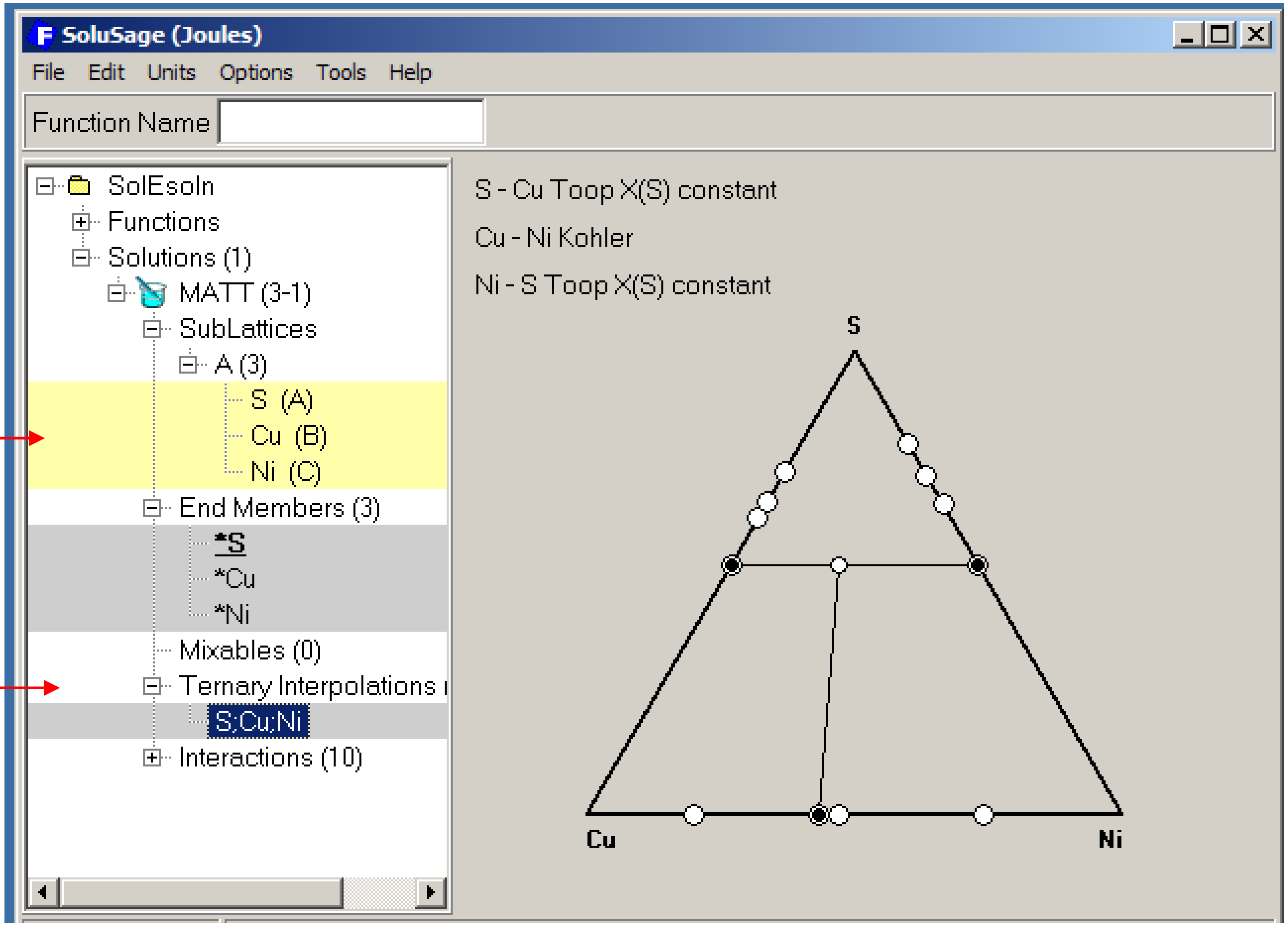


1. $Z_{Cu} \approx Z_S/2$ so that the composition of maximum SRO is close to the Cu_2S composition in the Cu-S binary solution.
2. Z_{Ni} (not shown) = Z_S so that the composition of maximum SRO is close to the NiS composition in the Ni-S binary solution.

Ternary interpolations

1. Highlight 3 species

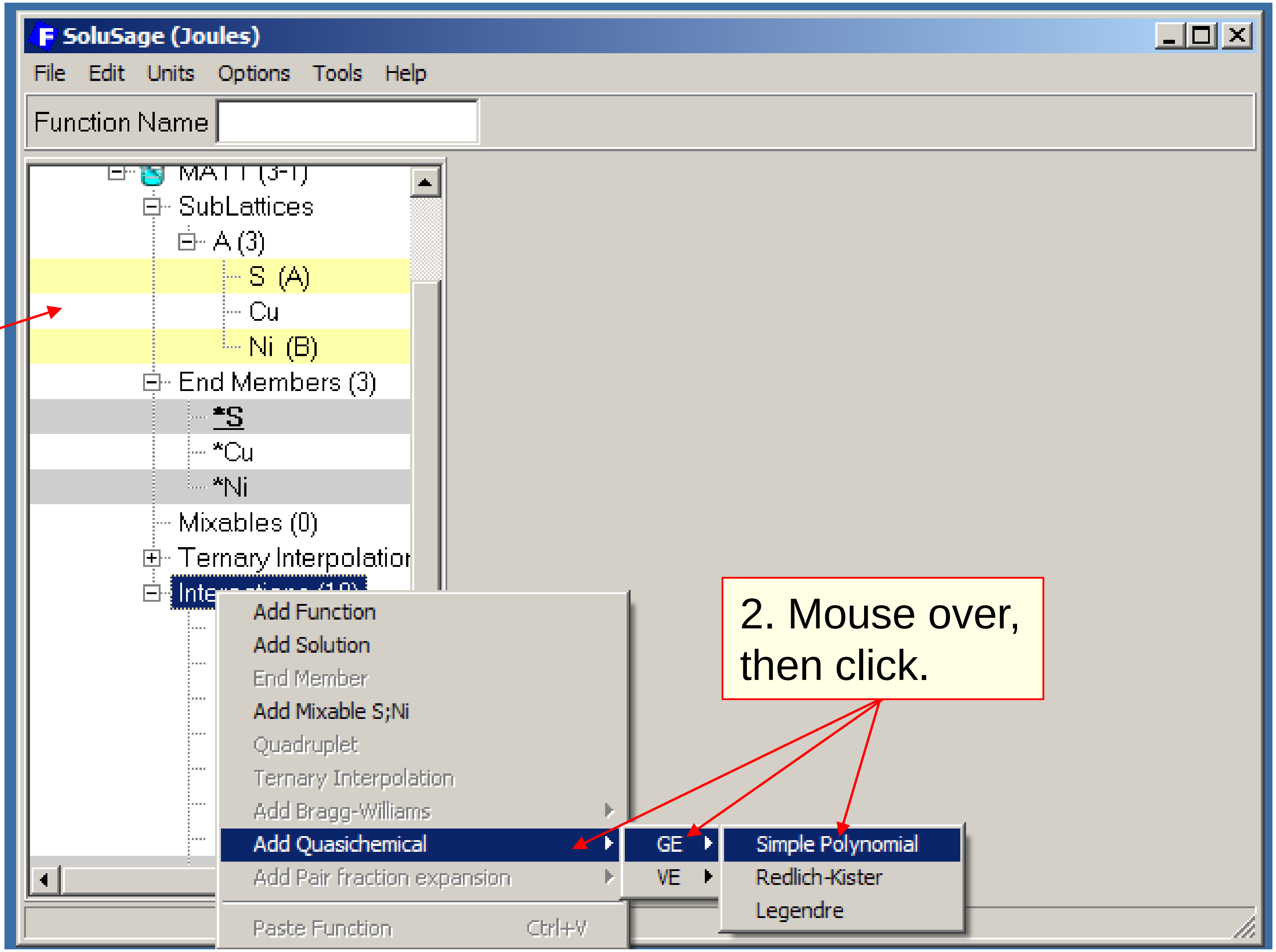
2. Click



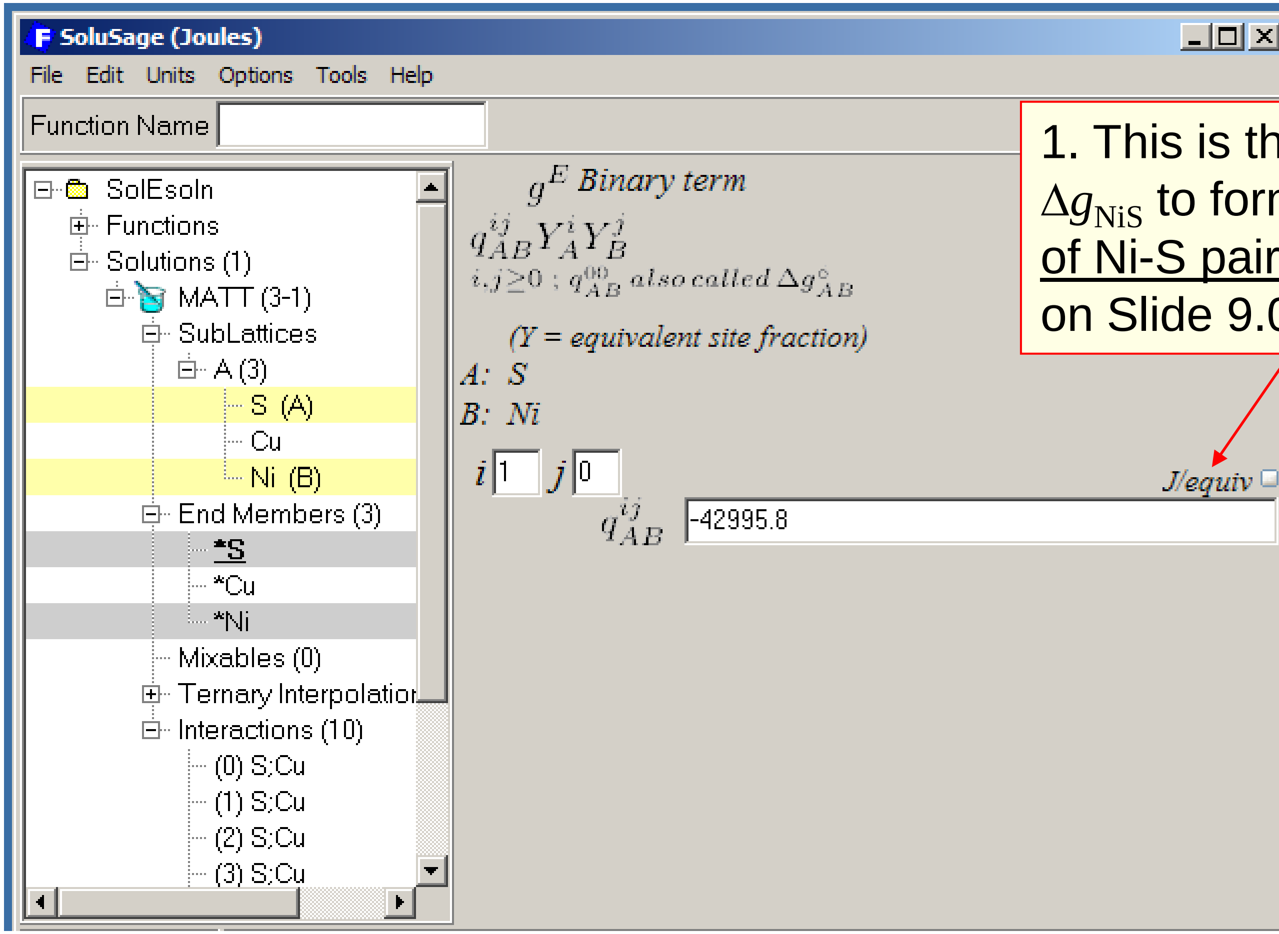
Since Cu and Ni are in chemical group “1” while S is in group “2” the default configuration is “Kohler/Toop (X_S = constant).” This may be over-written as described in Section 2.

Entry of a binary Ni-S interaction parameter

1. Highlight 2 species, then right click.



2. Mouse over, then click.



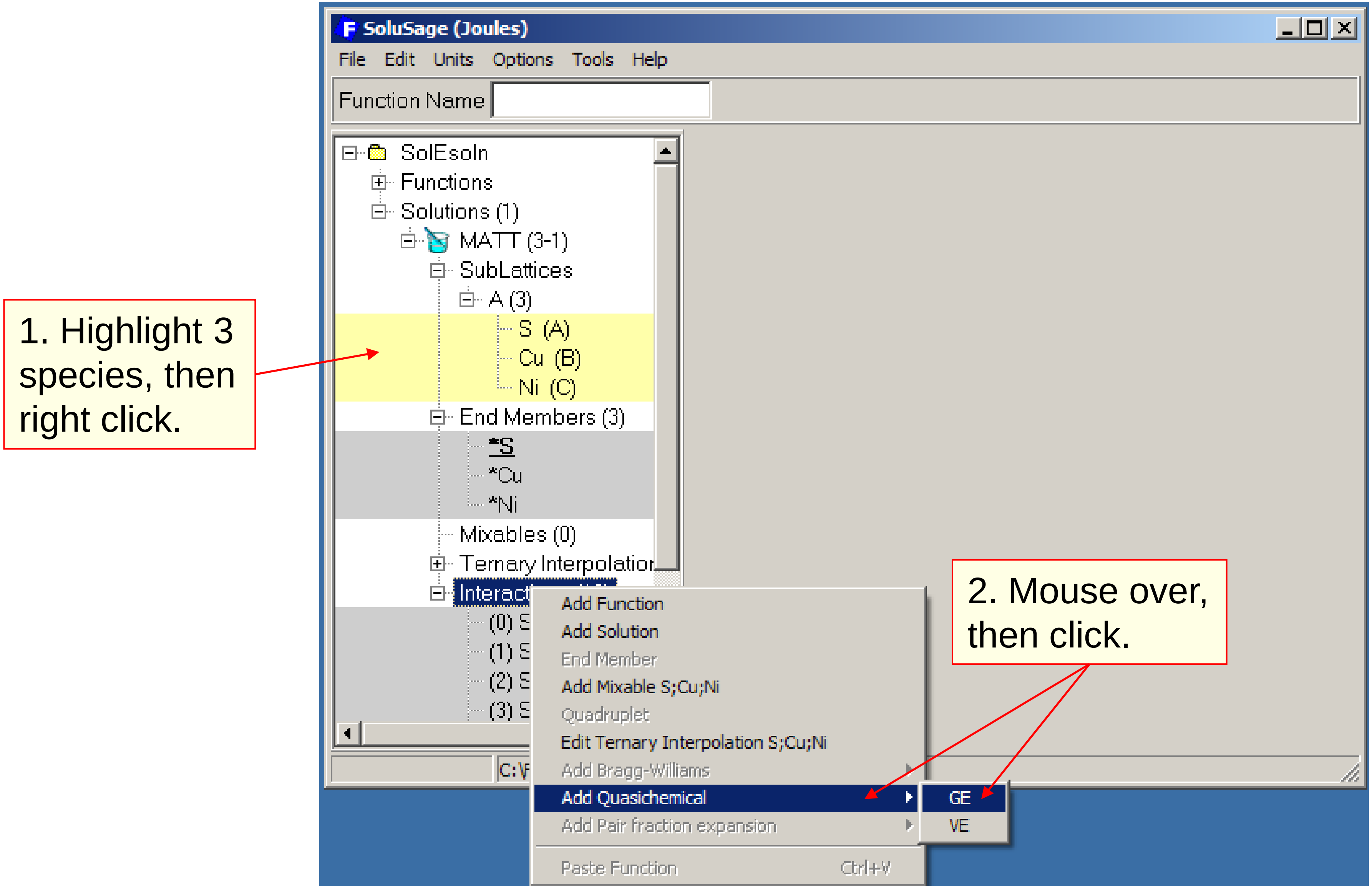
1. This is the energy Δg_{NiS} to form 2 moles of Ni-S pairs via Eq. [1] on Slide 9.0.

In the binary Ni-S solution (see Ref.(13)):

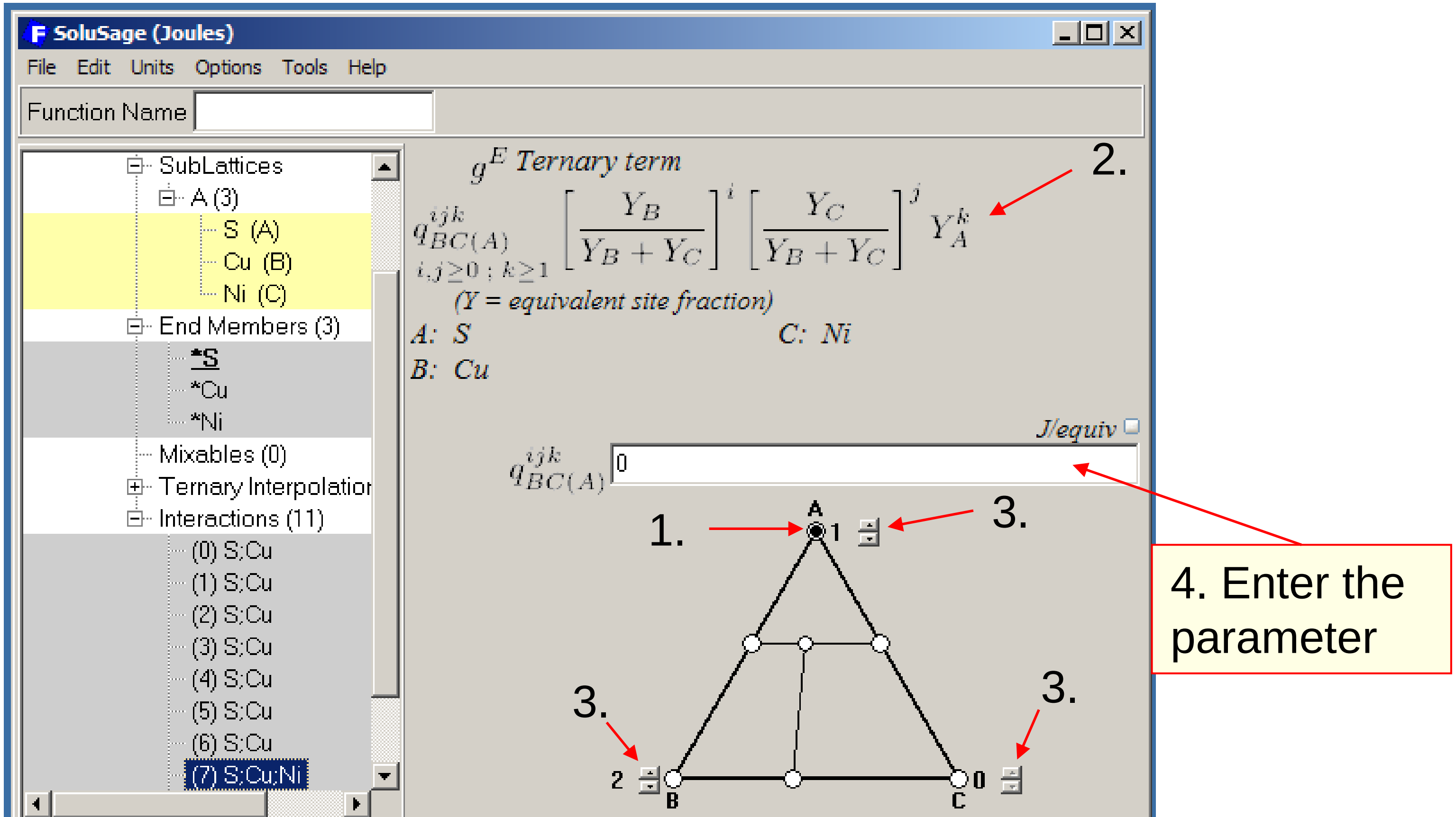
$$\Delta g_{NiS} = -96826.9 - 42995.8\ Y_S^1 Y_{Ni}^0 + 2411860.0\ Y_S^6 Y_{Ni}^0$$

In this slide we show the entry of the second term.

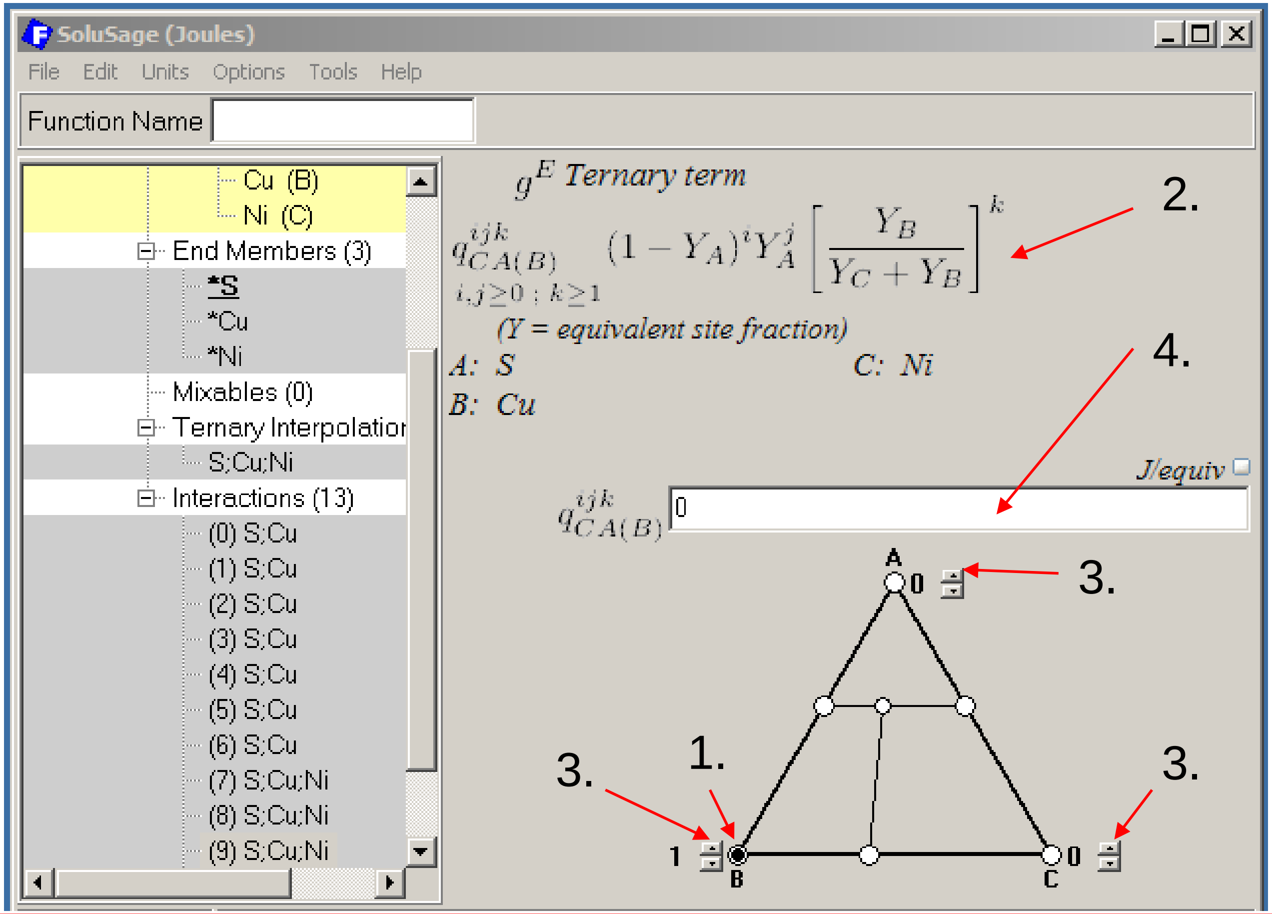
Entry of a ternary interaction parameter



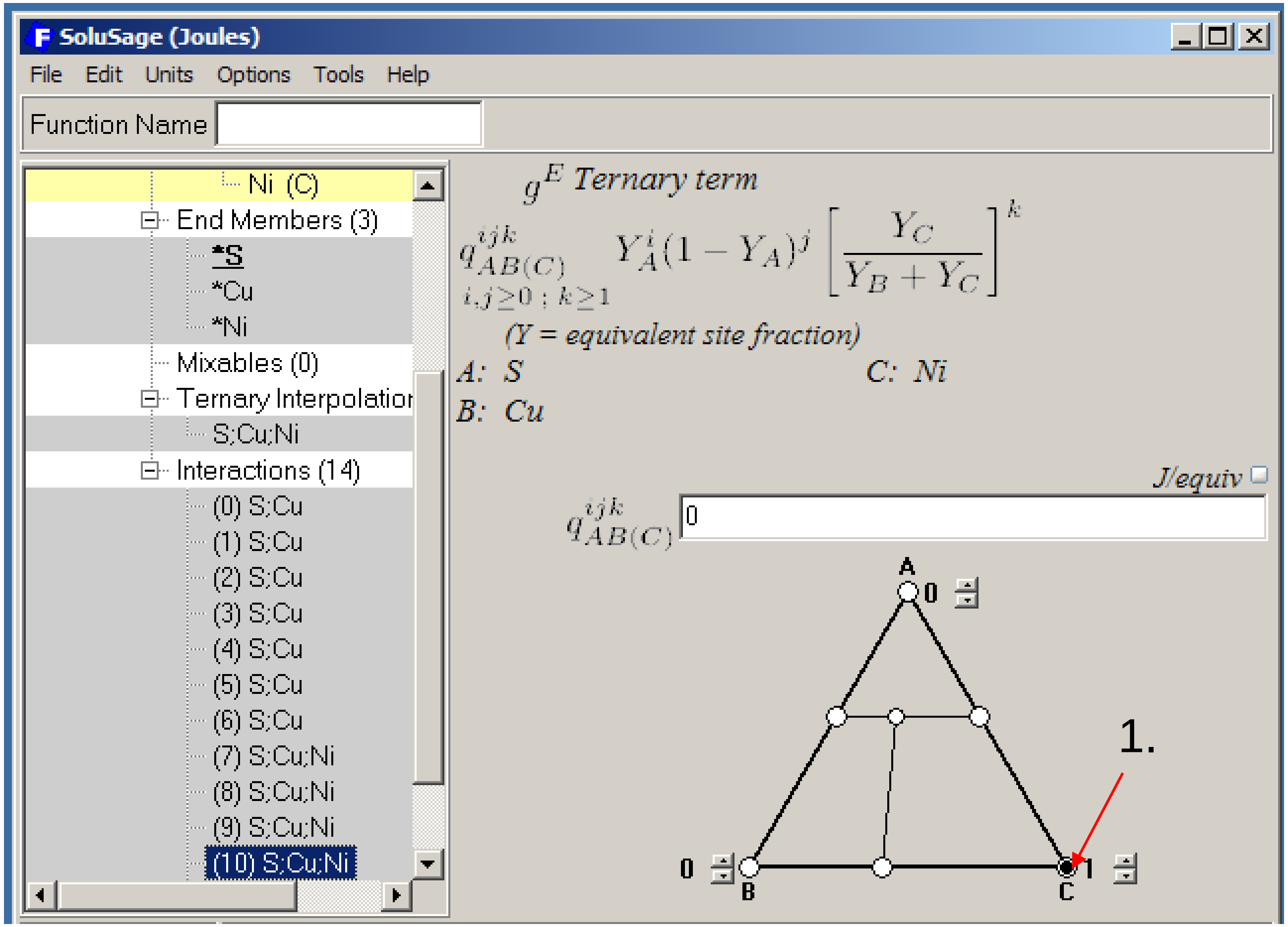
The diagram indicates the ternary interpolation configuration for this system



1. Click on the A-corner to indicate that the entered parameter gives the effect of component A on the Δg_{BC} function.
2. Since the binary Δg_{BC} terms are given by a Kohler approximation, this is the form of the ternary terms (Refs.(2, 3)).
3. Click on the arrows to select the powers i, j, k (1, 2, 0 respectively in this example).



1. Repeat step 2 of slide 9.10. Then click on the B-corner to indicate that the entered parameter gives the effect of component B on the Δg_{CA} function.
2. Since the binary Δg_{CA} terms are given by a Toop (X_A = constant) approximation, this is the form of the ternary terms (Refs.(2, 3)).
3. Click on the arrows to select the powers i, j,k.
4. Enter the parameter.



1. Repeat step 2 of slide 9.10. Then click on the C-corner to indicate that the entered parameter gives the effect of component C on the Δg_{AB} function. Continue as in previous slides.

Case where binary Δg_{AB} terms are given by a Muggianu approximation

In this case, ternary terms giving the effect of component C on the Δg_{AB} function are of the following form (Refs.(2, 3)):

$$q^{ijk}_{AB(C)}(1 + Y_A - Y_B)^i (1 - Y_A + Y_B)^j Y_C^k / 4 \qquad i, j \geq 0,\ k \geq 1$$

Refs. (11, 12, 14)

- This model accounts for short-range-ordering (SRO**) both within each lattice** (second-nearest-neighbour SRO) and **between lattices** (first-nearest neighbour SRO).

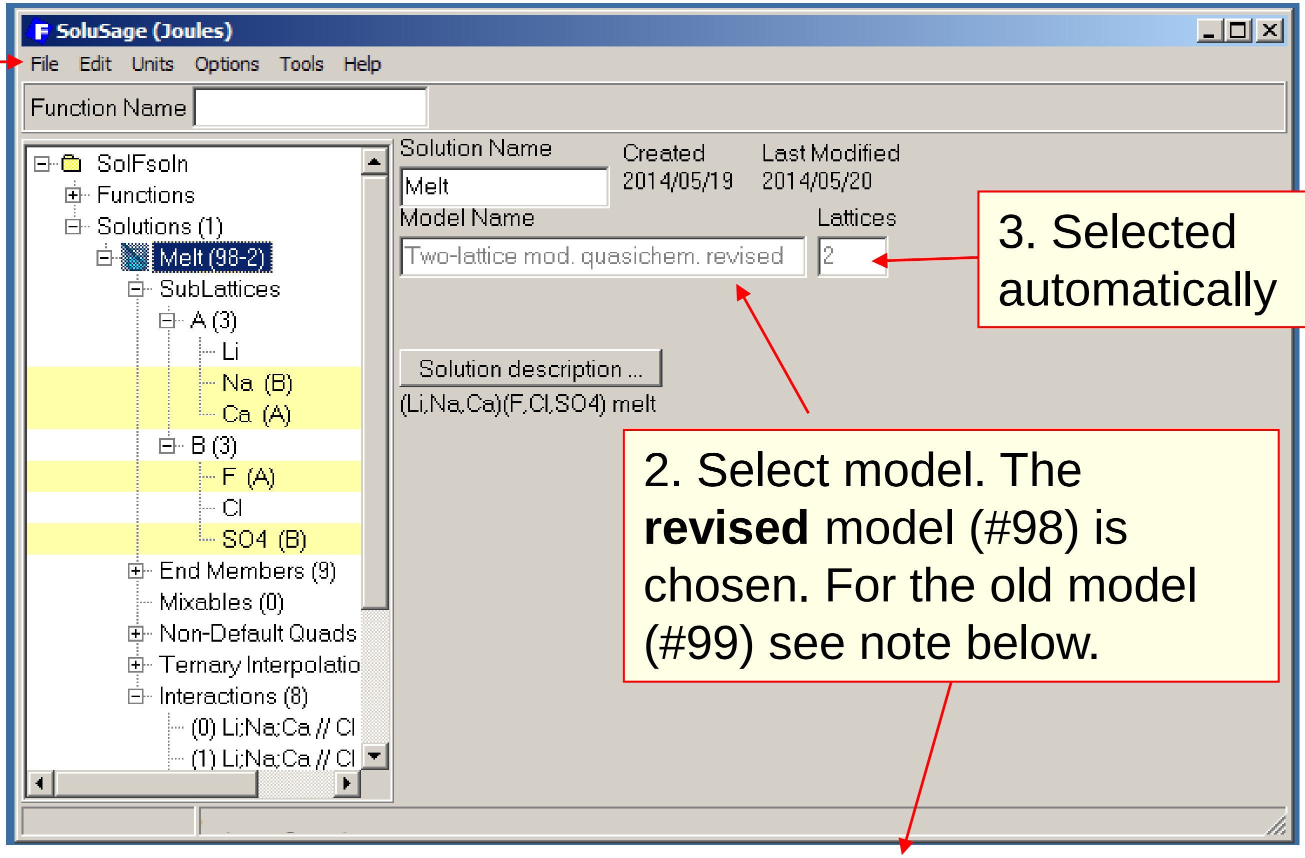
- The “Two-lattice Modified Quasichemical Model **revised**” (“Model #98”) (see Ref. (15)) incorporates 3 relatively minor improvements since the “Two-lattice Modified Quasichemical Model-**old**” (“Model #99”) was published. (See Ref.(14)). **Use the revised (#98) version** unless you are editing a file created previously with the old version.

- This model reduces exactly to the Two-lattice Polynomial model (#4), Section 7, if SRO is suppressed; or to the One-lattice Modified Quasichemical Model (#3), Section 9, if the second lattice is filled with vacancies and the coordination numbers of the species are constant, independent of composition; or to the One-lattice polynomial model (#1), Section 1, if the second lattice is filled with vacancies and SRO is suppressed.
- **Before reading this section, it essential to read Sections 1, 2, 4, 7 and 9 and to read Refs. (11, 12, 14).**

Entry of data for the Two-Lattice Modified Quasichemical Model

Data have been stored in the file ..\FACTDATA\SolFsoln.sln
(Note: no actual numerical values of the parameters have been stored.)

1. Click «File→ Open SolFsoln»

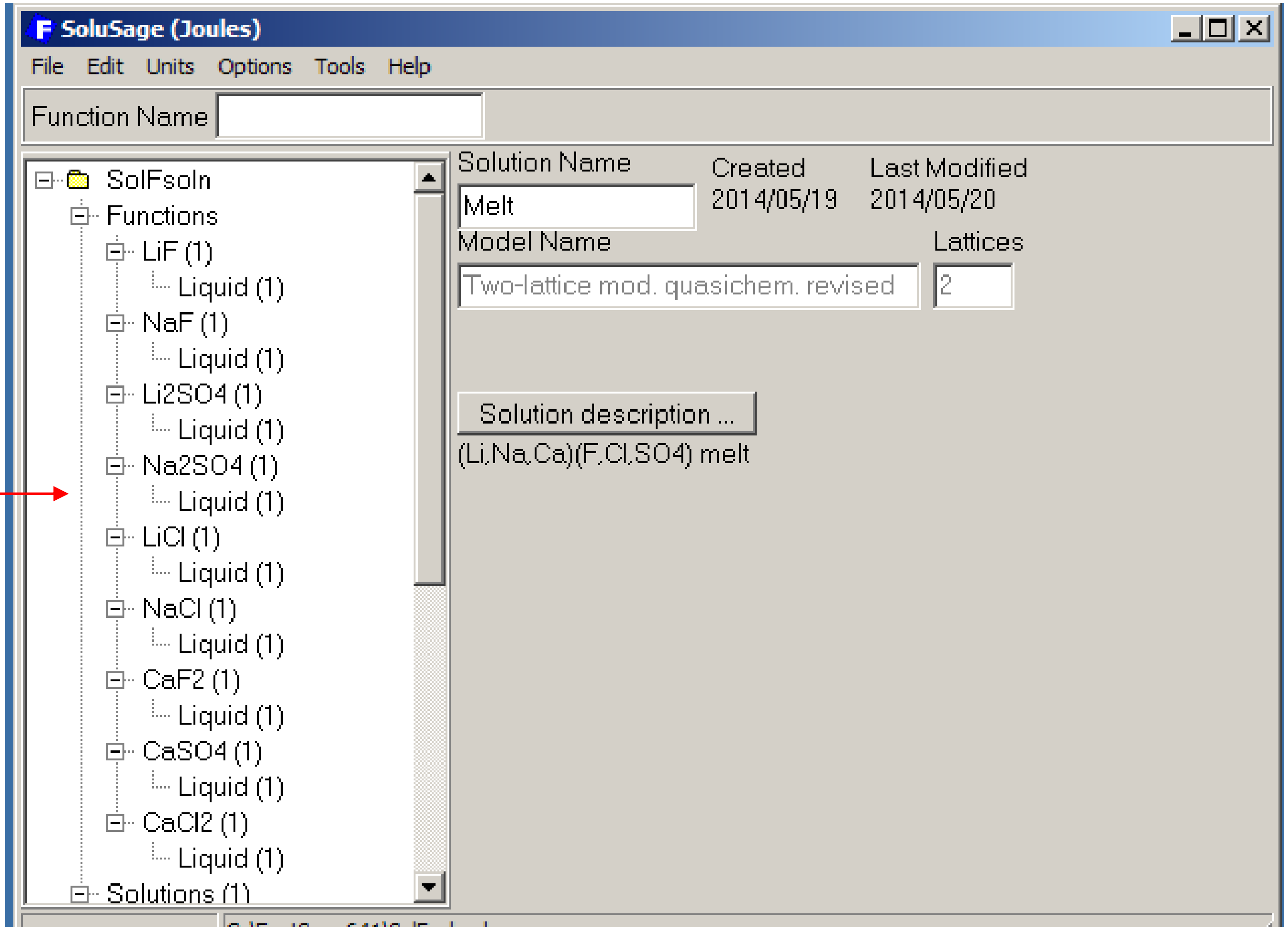


3. Selected automatically

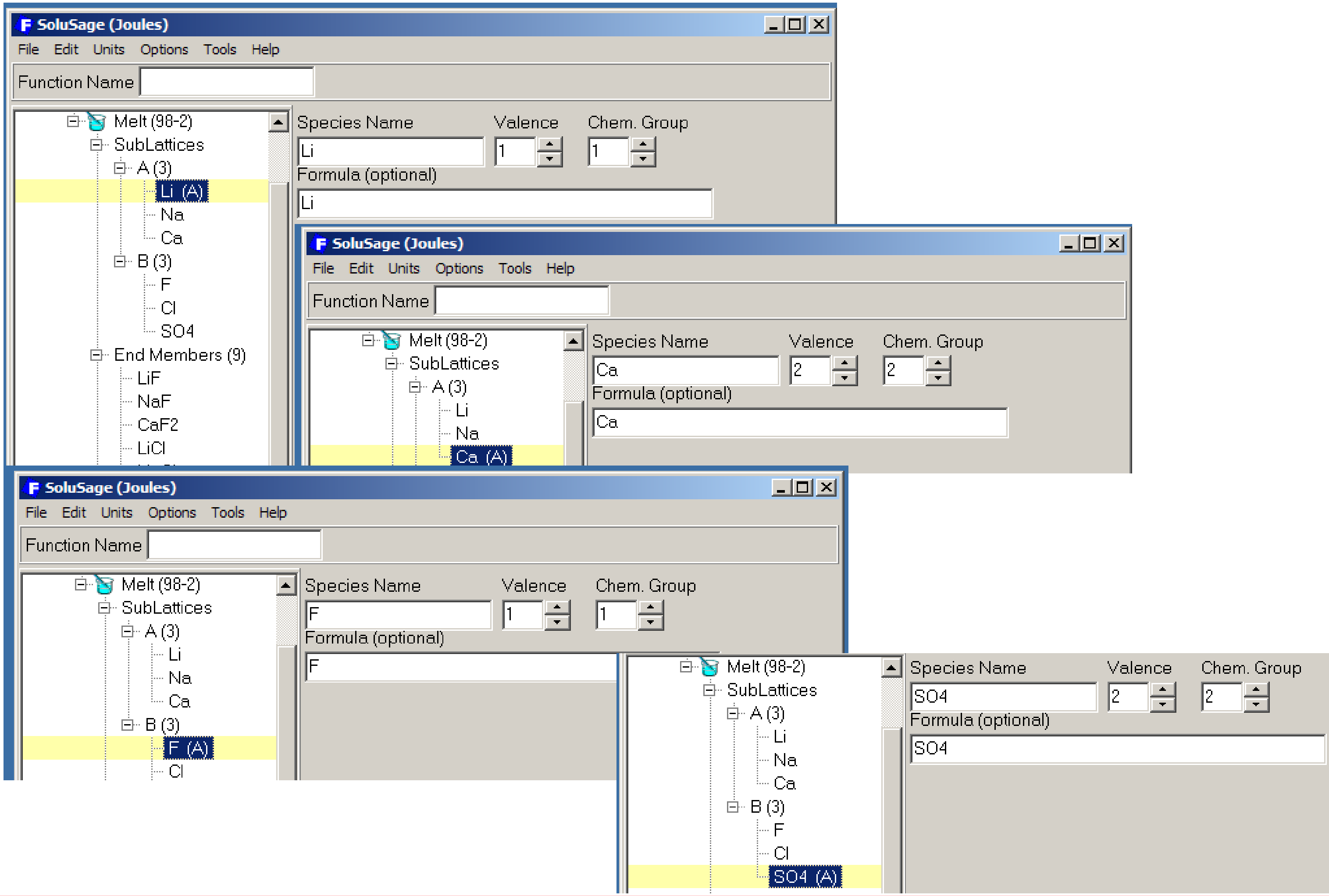
2. Select model. The **revised** model (#98) is chosen. For the old model (#99) see note below.

Note: in entry for the "Two-lattice Modified Quasichemical Model-**old** (Model #99), this window will also ask for entry of the parameter zeta (ζ) which applies for the entire solution (see Ref.(14)). Note that the value of zeta only affects the calculations when there are 2 or more species on each lattice.

Functions for pure liquid end-members have been dragged and dropped from the FactPS database

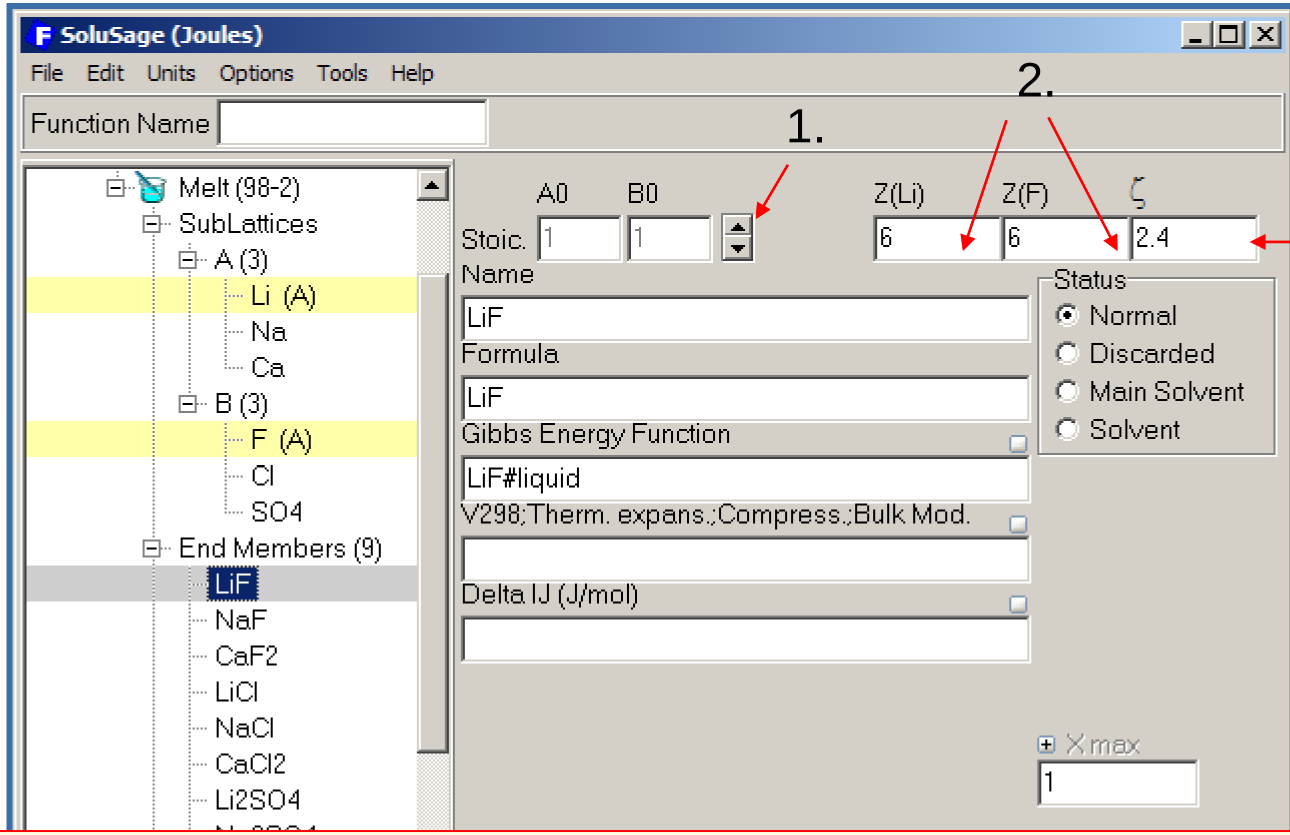


Entry of species



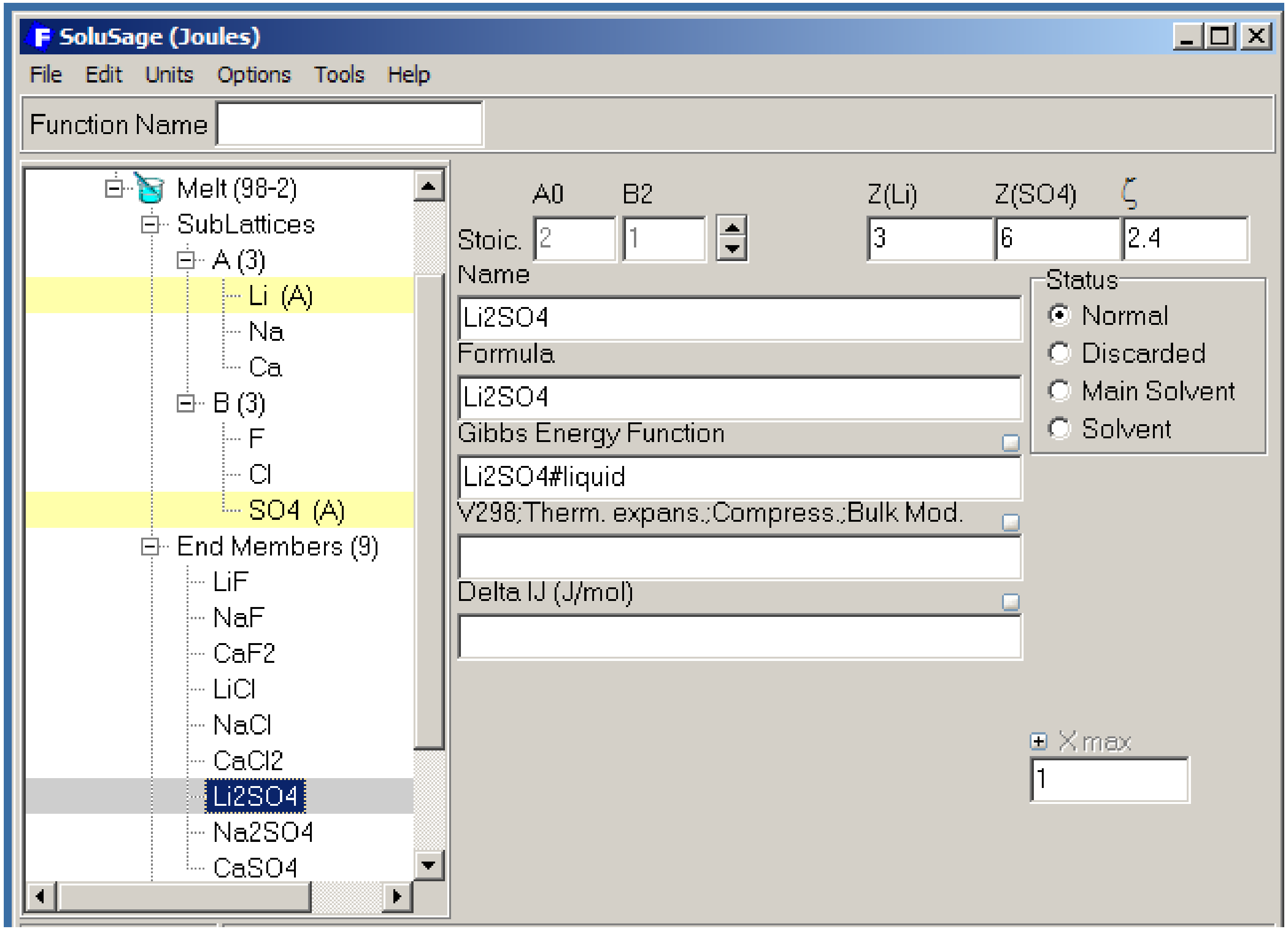
Each species is assigned a **«valence»** and a **«chemical group number».** (See Section 2.) There is a **separate set of group numbers for each lattice**. In this example, Li, Na, F, Cl have valence = 1 while Ca, SO_4 have valence = 2. Li and Na are members of lattice A group 1 while Ca is in lattice A group 2. F and Cl are in lattice B group 1 while SO_4 is in lattice B group 2.

Entry of end-member LiF



1. The **stoichiometry** of the end-member may be adjusted by clicking on the arrows. (See Slides 4.6 and 5.8).
2. There is a **second-nearest-neighbour «coordination number»** for **each** species in the pure end-member. In Ref. (14), these are the variables $Z^{Li}_{Li_2F_2}$ and $Z^{F}_{Li_2F_2}$.
3. In the «revised» model (#98), a value of ζ is assigned to **each** end-member (see Ref.15), while in the «old» model (#99) one value of ζ applies for all end-members (and would be entered on Slide 10.1). **This is the only difference in entry** between the «revised» and «old» models. Note that the values of zeta only affect the calculations when there are 2 or more species on each lattice.

Entry of end-member Li_2SO_4



Entry of "coordination numbers" for ABX_2 and A_2XY

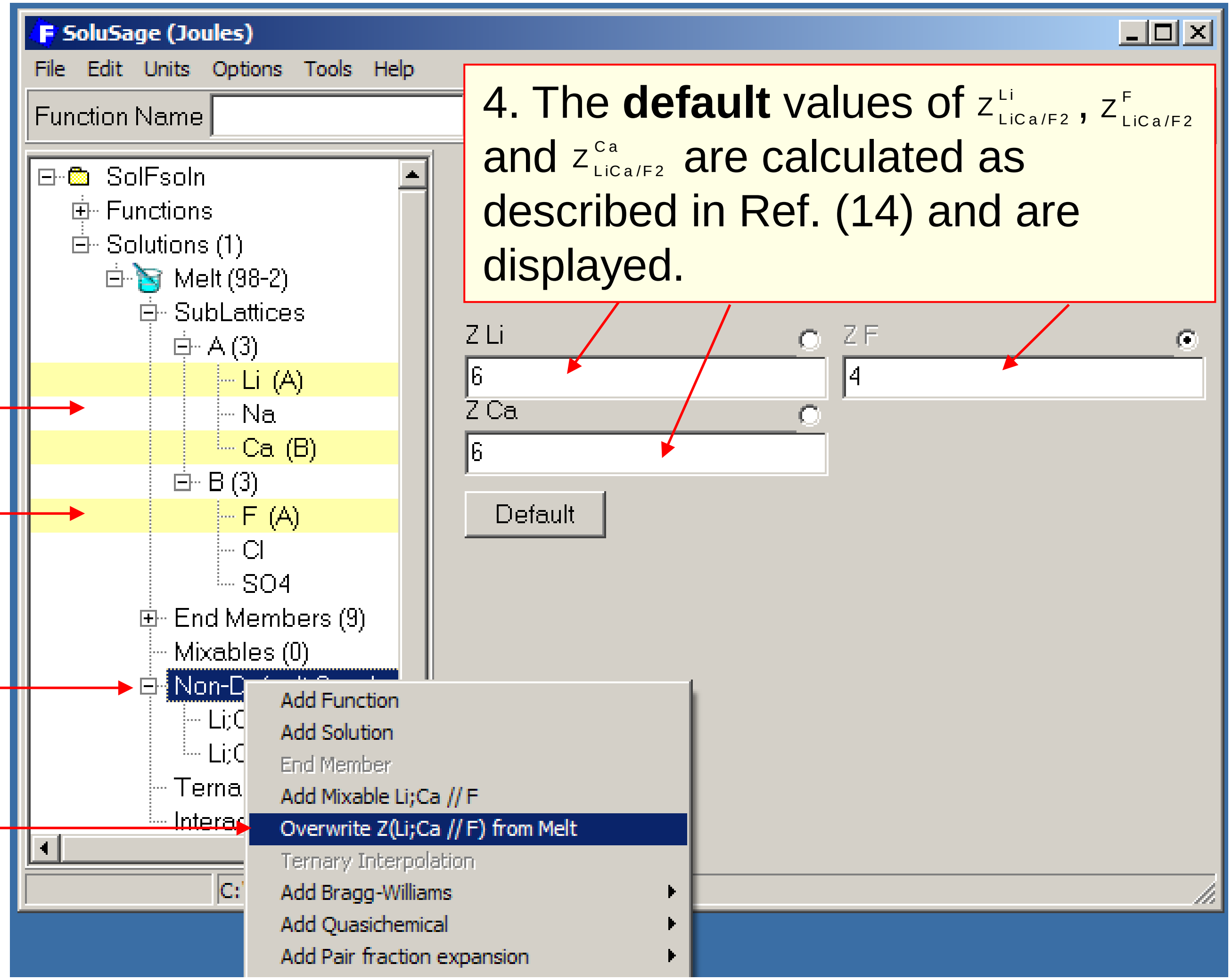
"binary quadruplets"

1. Select 2 species on one lattice and one species on the other

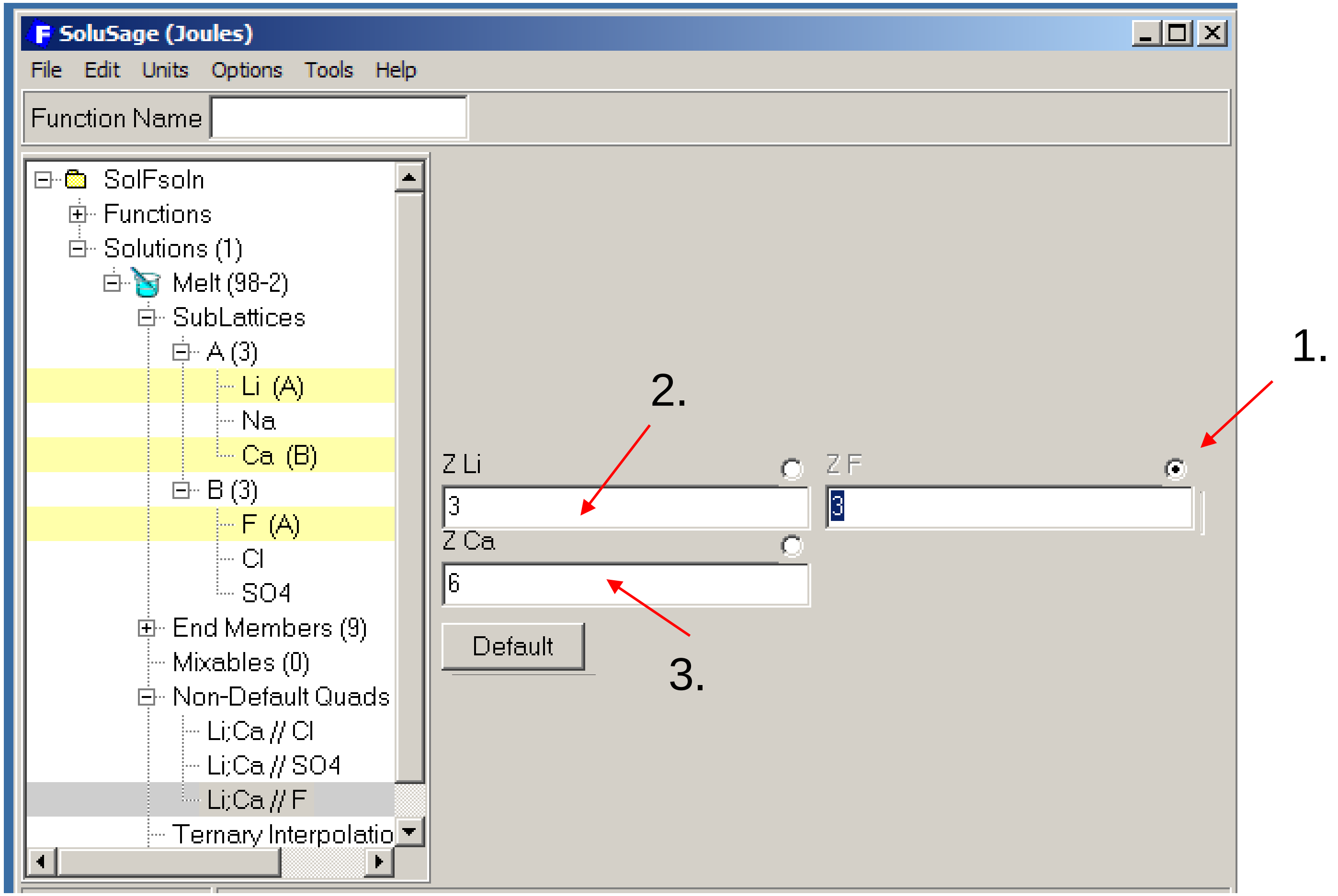
2. Click

3. Click

4. The **default** values of $Z^{Li}_{LiCa/F2}$, $Z^{F}_{LiCa/F2}$ and $Z^{Ca}_{LiCa/F2}$ are calculated as described in Ref. (14) and are displayed.

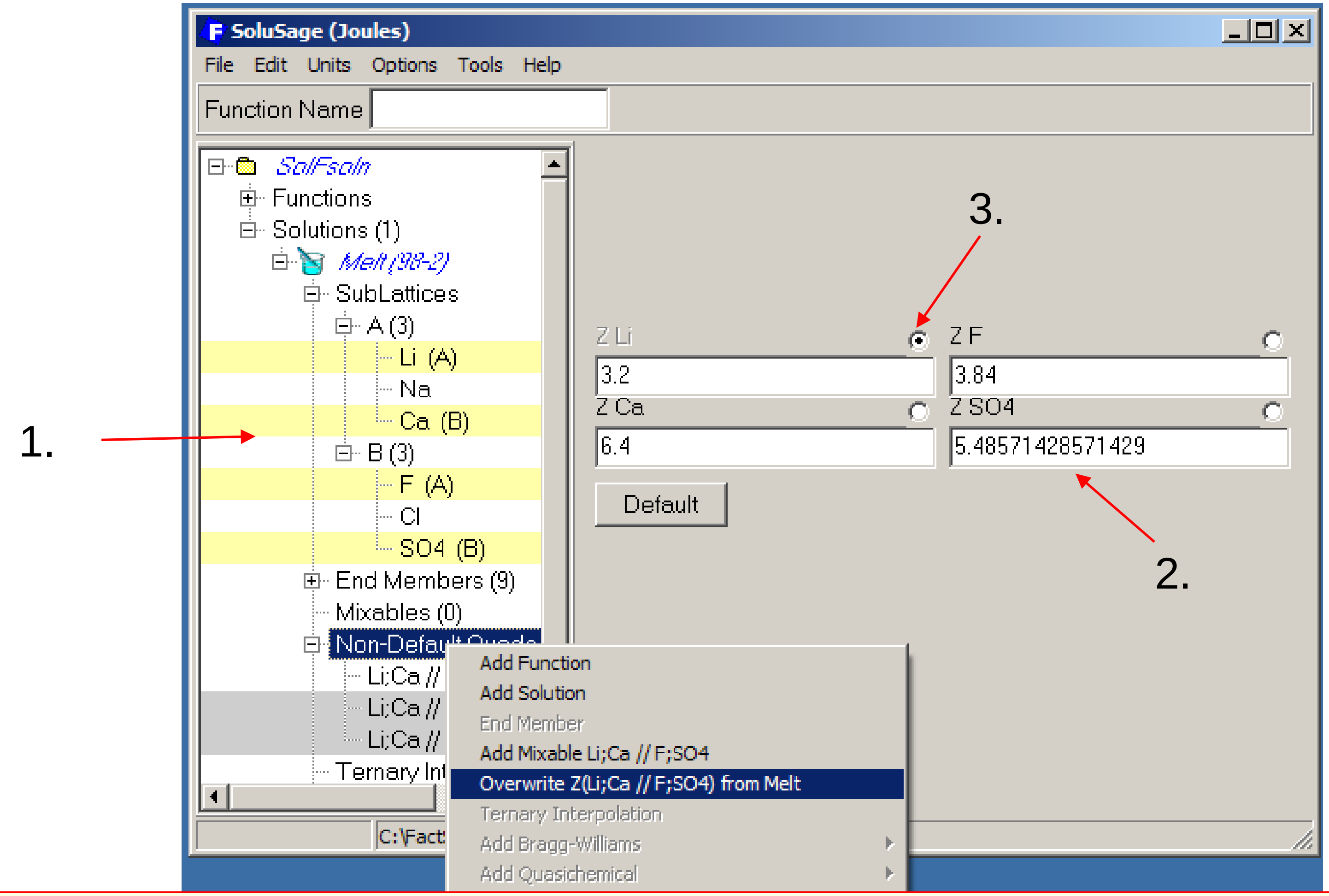


You may over-write two of the default values. The third will then be calculated as described in Ref. (14).



1. Click on the Z value which will be calculated (Z_F in this example).
2,3. Enter new values of the other two Z's (Z_{Li} and Z_{Ca}). Z_F will then be automatically re-calculated.

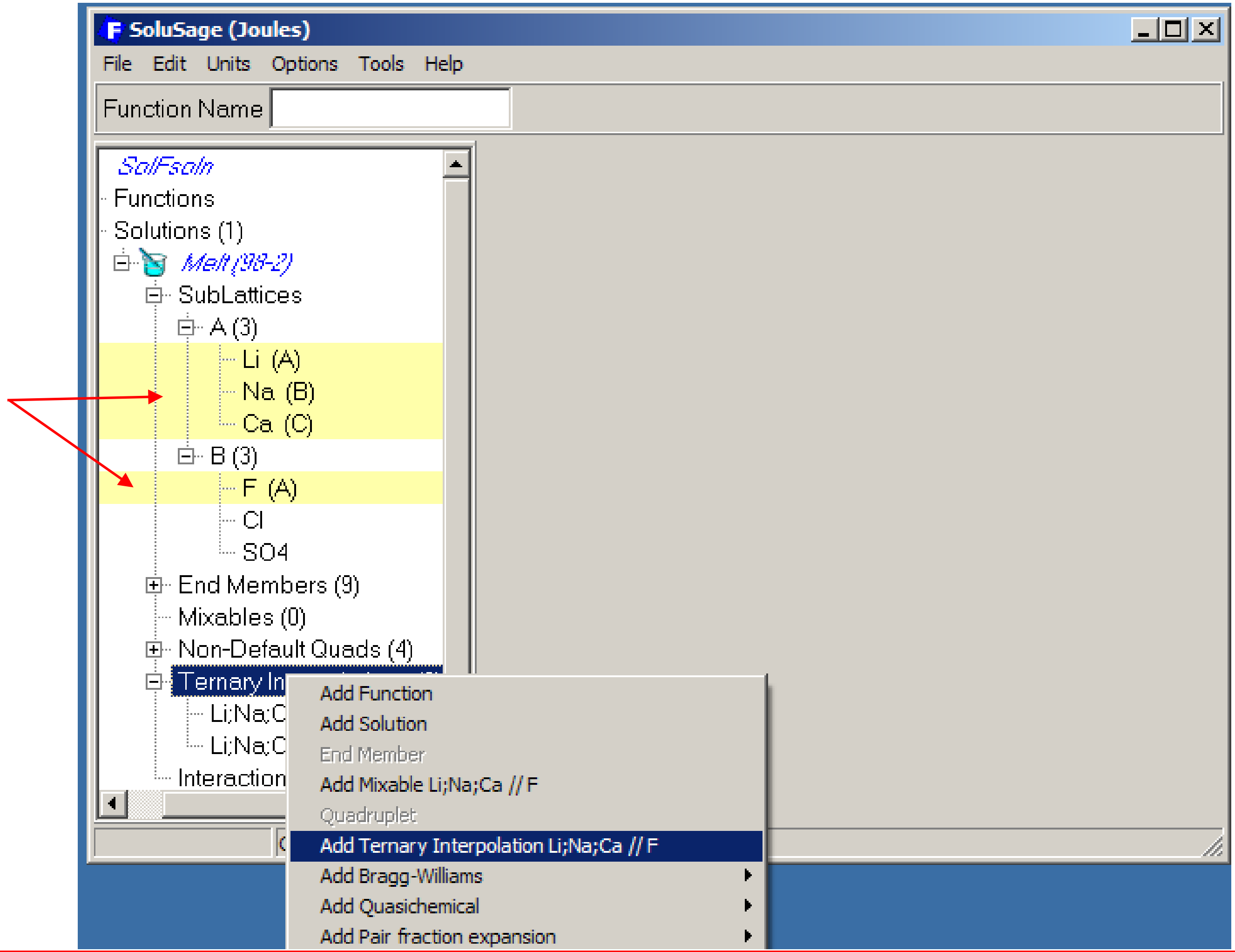
Entry of coordination numbers for "reciprocal quadruplets" $Z^{i}_{AB/XY}$



1. Select 2 species from each lattice.
2. The default values of the coordination numbers Z^{i}_{LiCa/SO_4} (i = Li, Ca, F, SO_4) are calculated and displayed.
3. To over-write, click on the value which is to be calculated automatically, and enter new values for the other three.

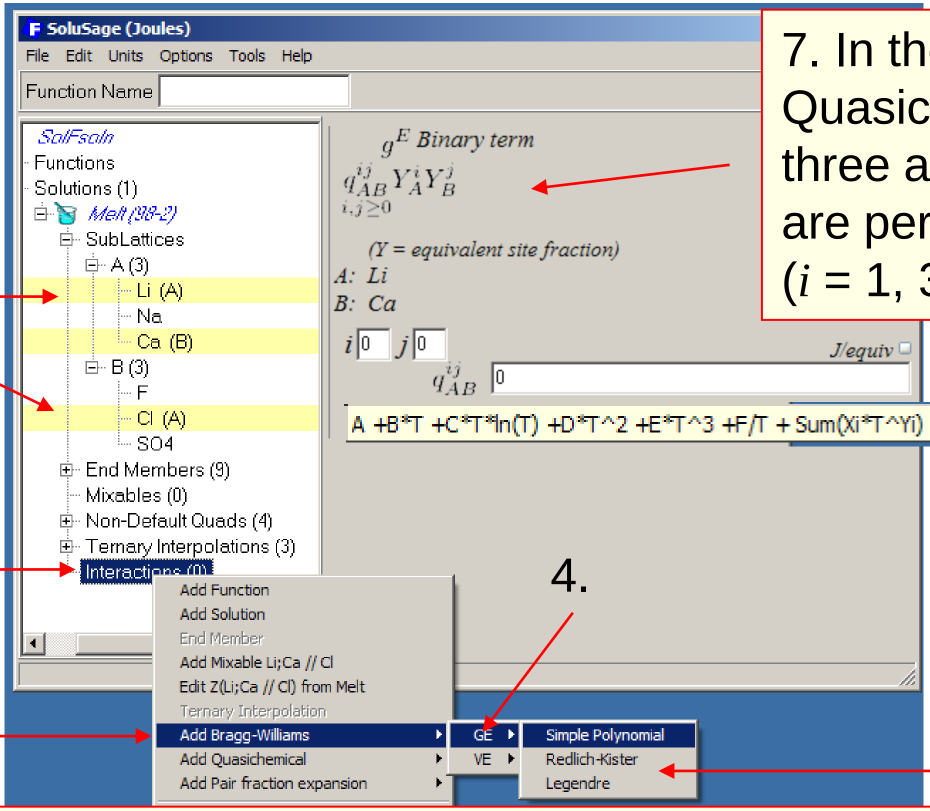
Ternary interpolation configurations

1.



1. As described previously, select 3 species from one lattice and 1 from the other. The default ternary interpolation for the (Li, Na, Ca)(F) system is shown (Kohler/Toop because Li and Na are in lattice A group 1 while Ca is in lattice A group 2). This may be over-written as described in Section 2.

Entering a "Bragg-Williams" binary interaction parameter



7. In the Modified Quasichemical Model (only) three additional terms X_i* T^{Y_i} are permitted where X_i and Y_i (i = 1, 3) are parameters.

1.

2.

3.

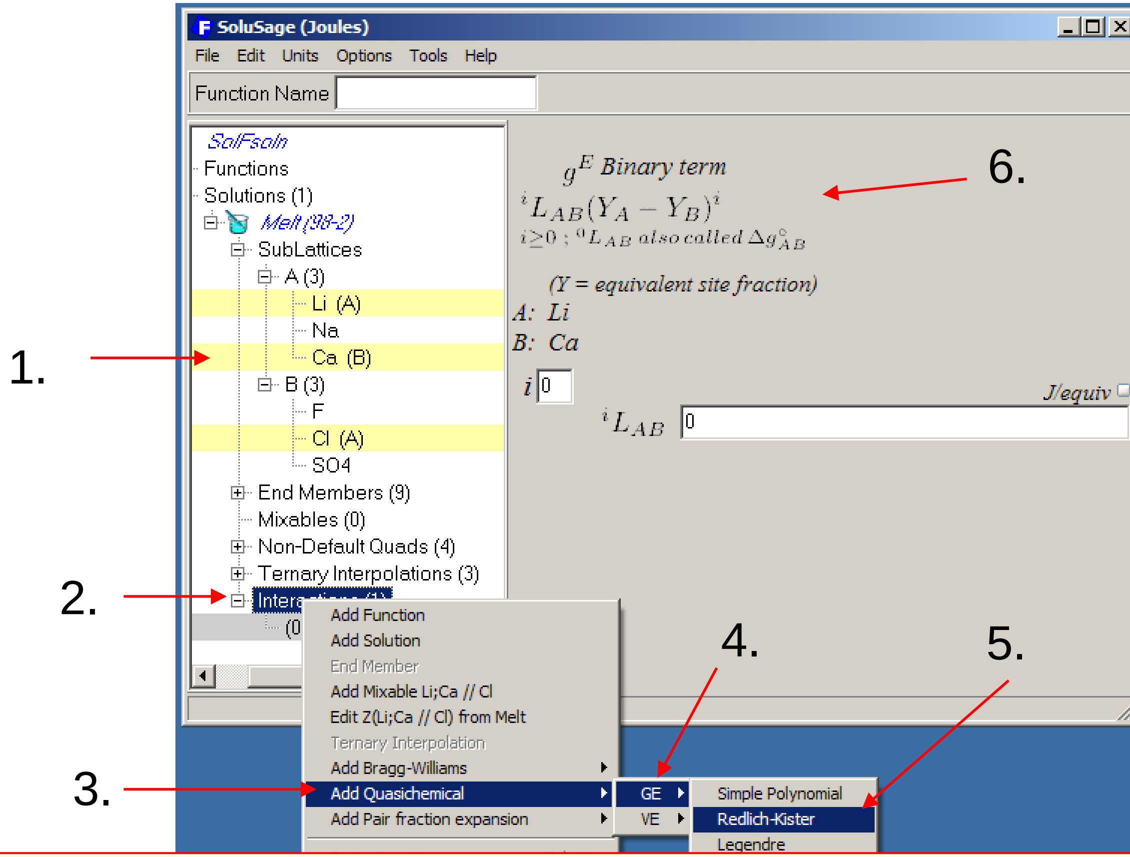
4.

5.

1. Select 2 species from one lattice and one from other.
2. Click.
3. Click. A **«Bragg-Williams g^E» term** will simply be added to the Gibbs energy of the solution. This will **NOT affect the quasichemical equilibrium**. That is, it will not affect the number of qudruplets at equilibrium.
4. Click.
5. The parameter may be entered in one of the 3 forms shown on Slide 1.19.
6. In this example, a polynomial form has been chosen.

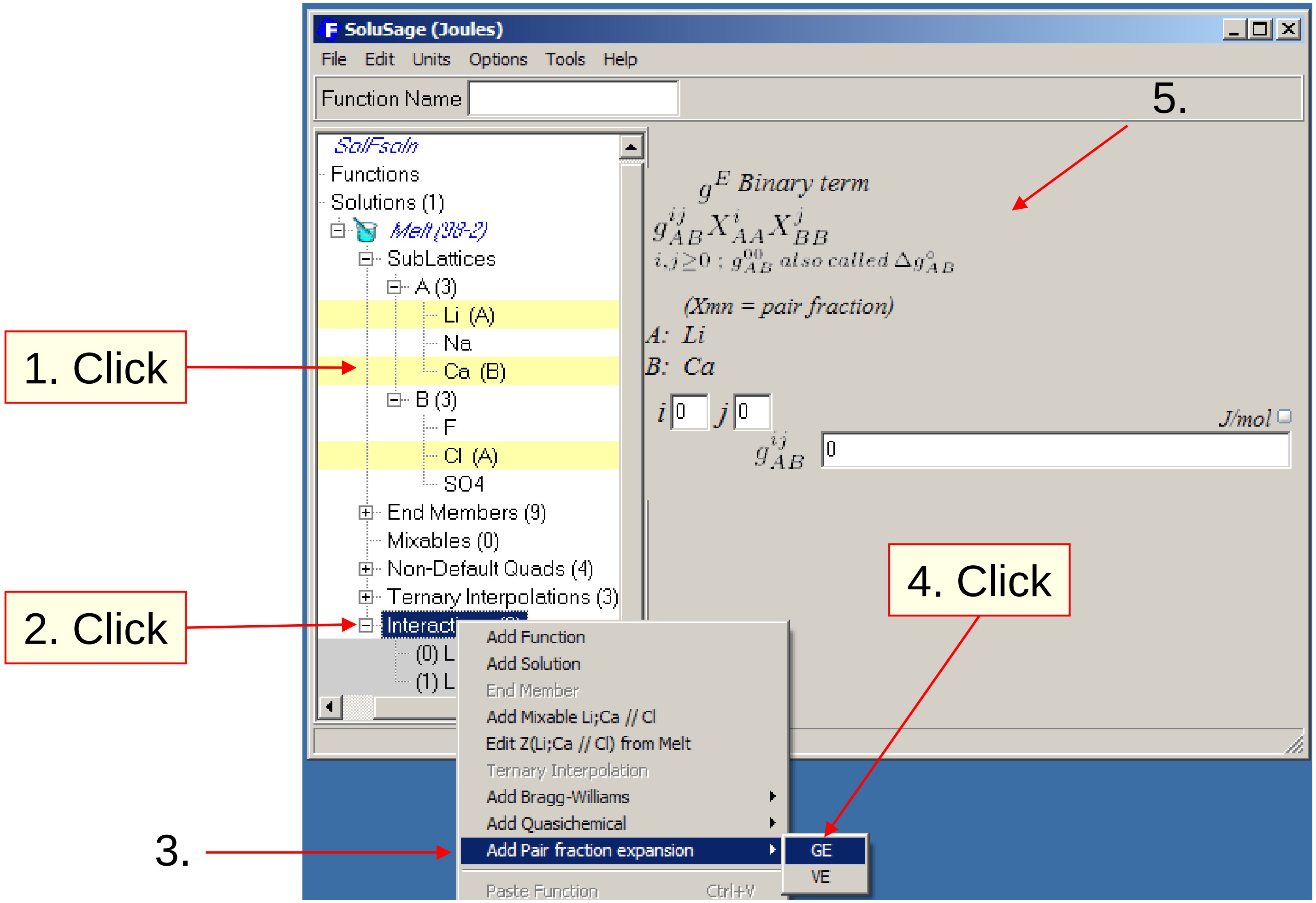
Note: If only Bragg-Williams interaction parameters are entered, the distribution on each sub-lattice will be random. That is there will be no SRO.

Entering a “quasichemical” binary interaction parameter



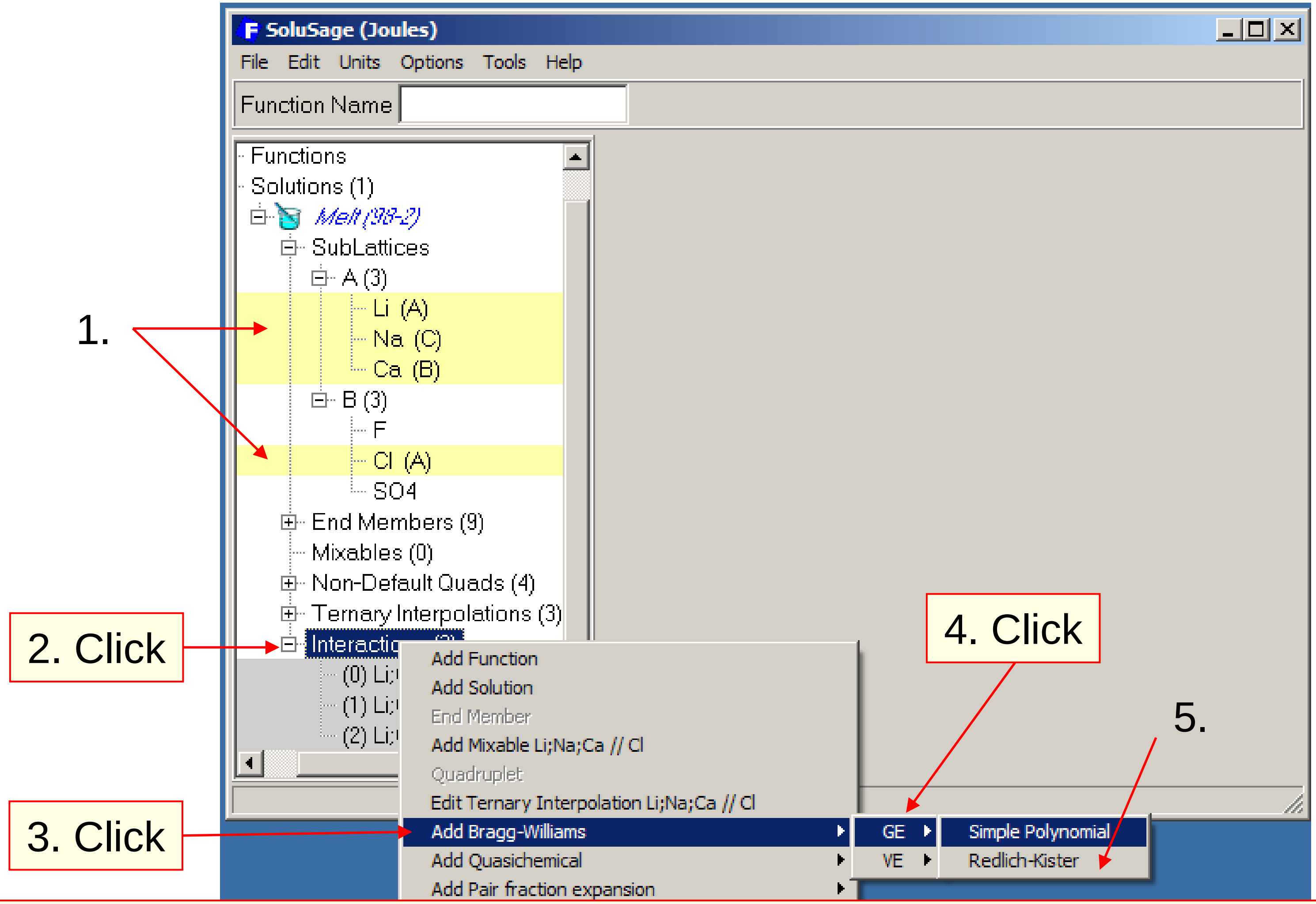
1. Click
2. Click.
3. A quasichemical term in the expansion for $\Delta g_{LiCa/Cl}$ as described in Refs. (11, 14) will be added for the pair formation reaction (Li-[Cl]-Li) + (Ca-[Cl]-Ca) = 2(Li-[Cl]-Ca) **as a function of the equivalent fractions Y_{Li} and Y_{Ca}**. This term **<u>DOES</u> affect the quasichemical equilibrium**.
4. Click.
5. The parameter may be entered in one of the 3 forms shown on Slide 9.0.
6. In this example, a Redlich-Kister form has been chosen.

Entering a "pair fraction" binary interaction parameter

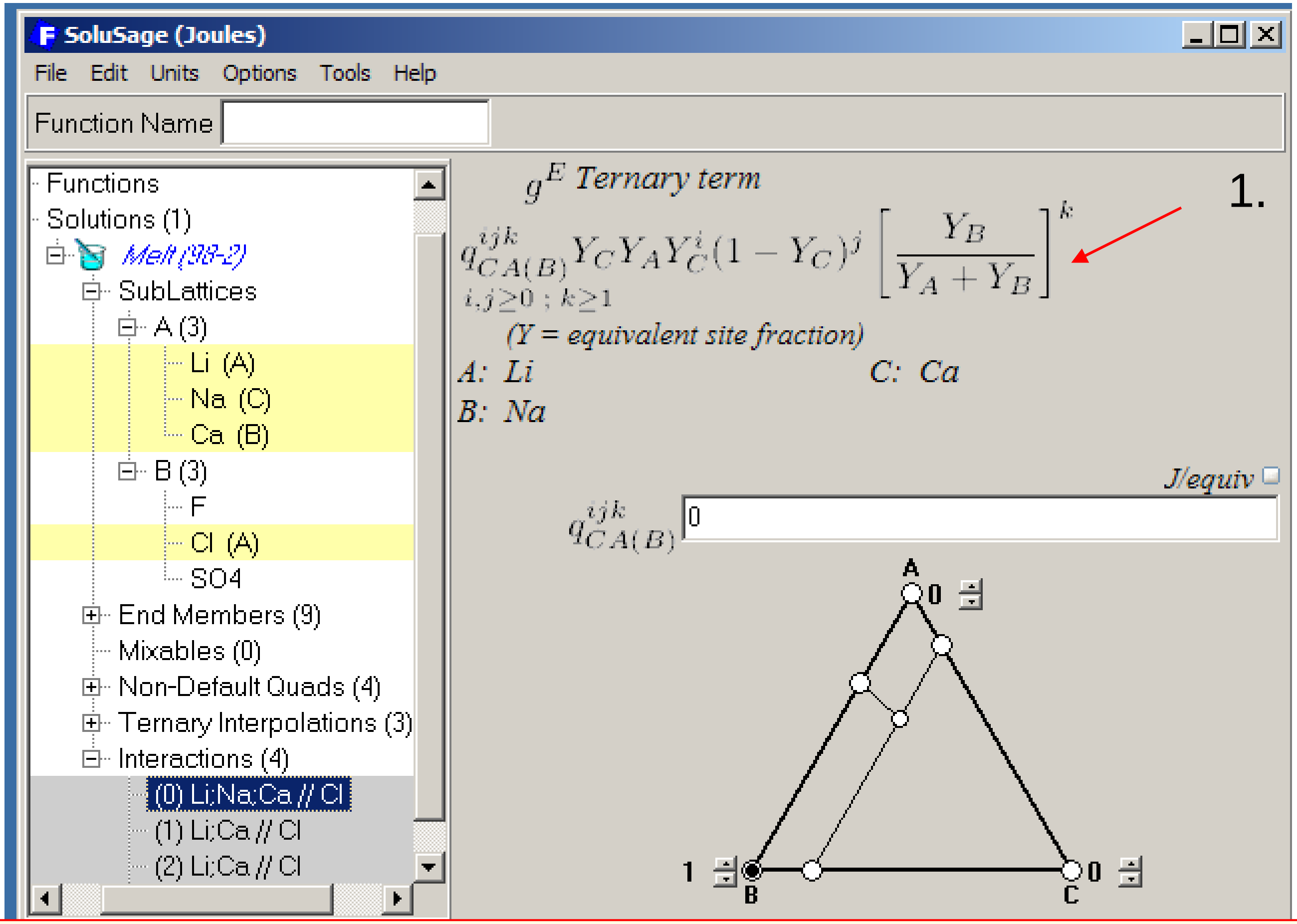


3. A term in the expansion for $\Delta g_{LiCa/Cl}$ as described in Ref. (14) will be added as **a function of the pair fractions X_{LiLi} and X_{CaCa}**. This **DOES** affect the quasichemical equilibrium.
5. This is the form of such a term. Note: Entry of this type of term is prohibited if the (Li, Ca)(Cl) binary terms are interpolated with the Muggianu approximation.

Entering a “Bragg-Williams” ternary interaction parameter



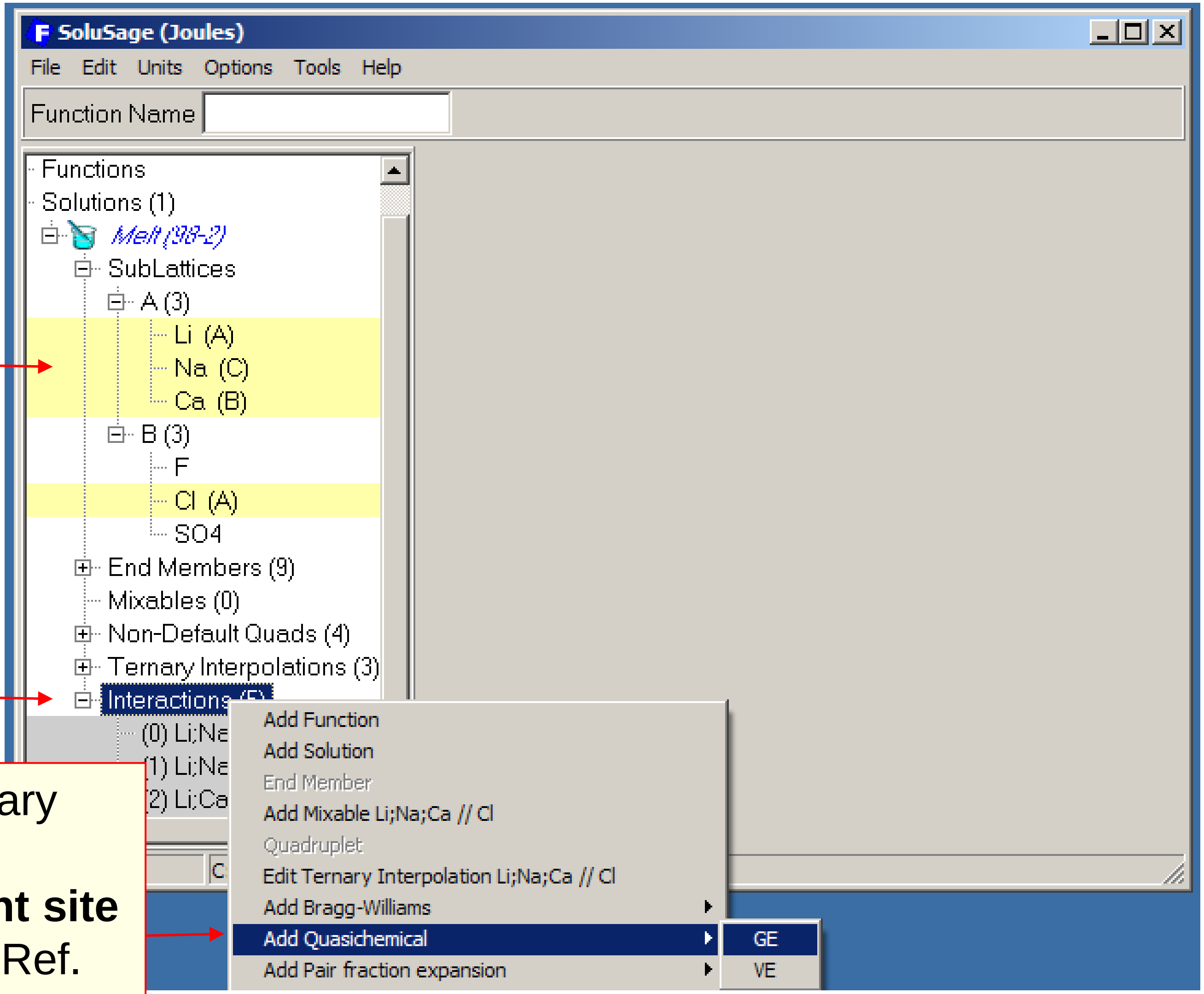
1. Select 3 species from one lattice and one from the other.
3. A ternary «Bragg-Williams» g^E term will simply be added to the Gibbs energy of the solution. This will NOT affect the quasichemical equilibrium.
5. The parameter may be entered in one of 2 forms.



1. This is the **simple polynomial form of a Bragg-Williams ternary term** giving the effect of component B upon the C-A binary interactions when the C-A binary terms are interpolated using the Toop (X_C = constant) approximation. (Similar to Slide 9.12.)

- If a Redlich-Kister term was chosen in the preceding slide, the form of the term would be similar to that in Slide 5.13.

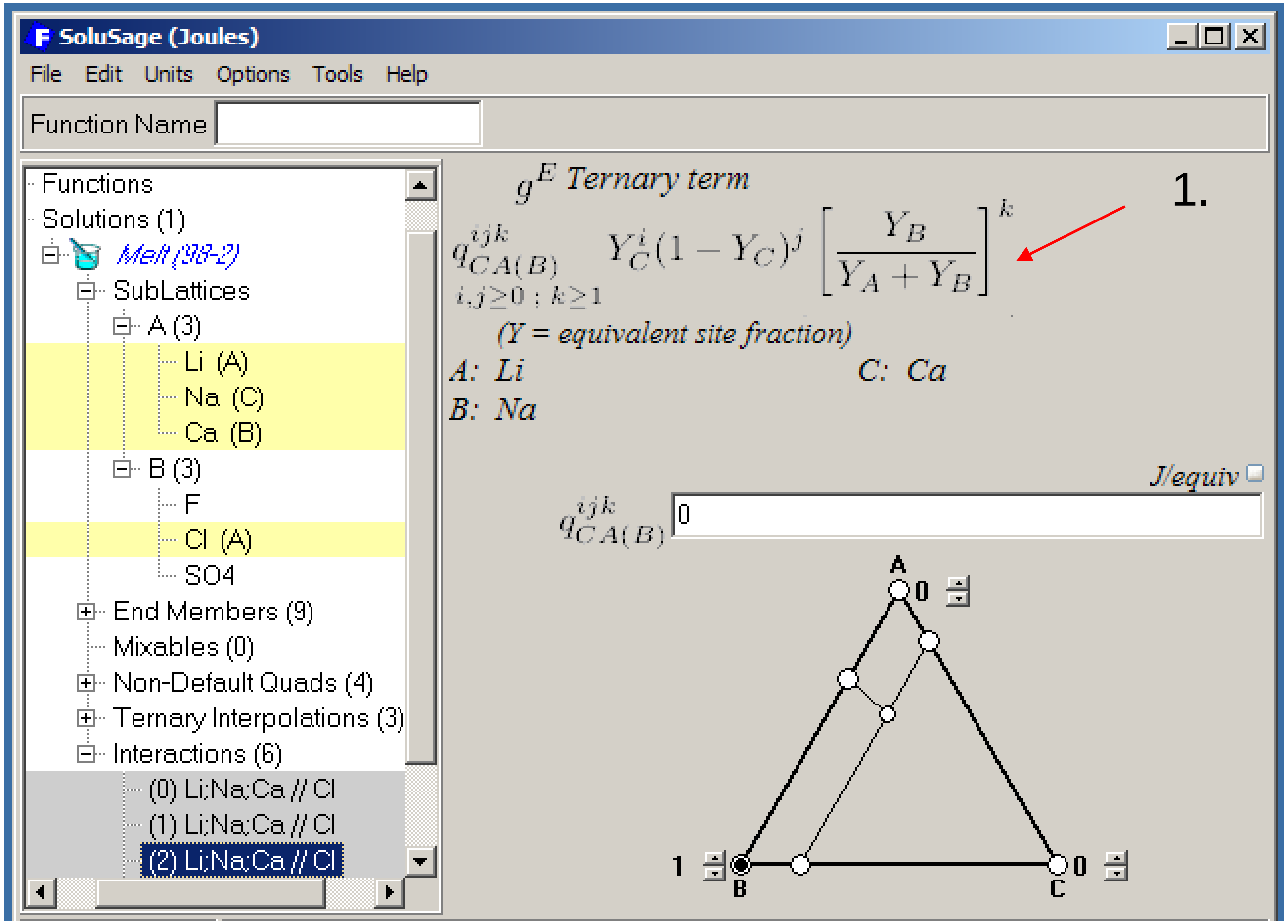
Entering a "quasichemical" ternary interaction parameter



1. Click

2. Click

3. A «quasichemical» ternary term will be entered **as a function of the equivalent site fractions** as described in Ref. (3). This term **DOES affect the quasichemical equilibrium**

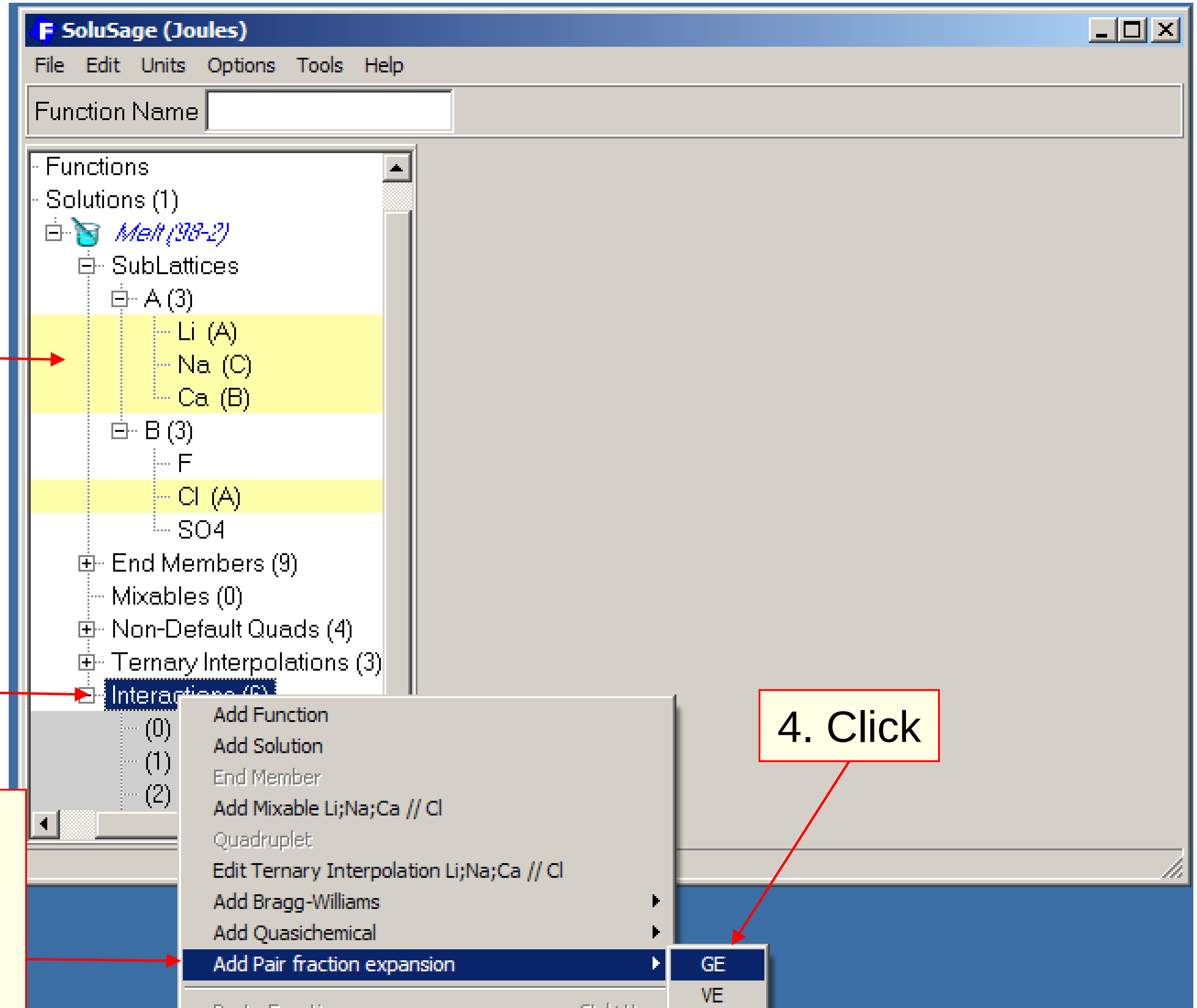


1. This is the form of a **«quasichemical» ternary term** giving the effect of component B upon the C-A binary interactions when the C-A binary terms are interpolated using the Toop (X_C = constant) approximation. See Section 9 for a complete description of the entry of such terms.

Entering a "pair fraction" ternary interaction parameter

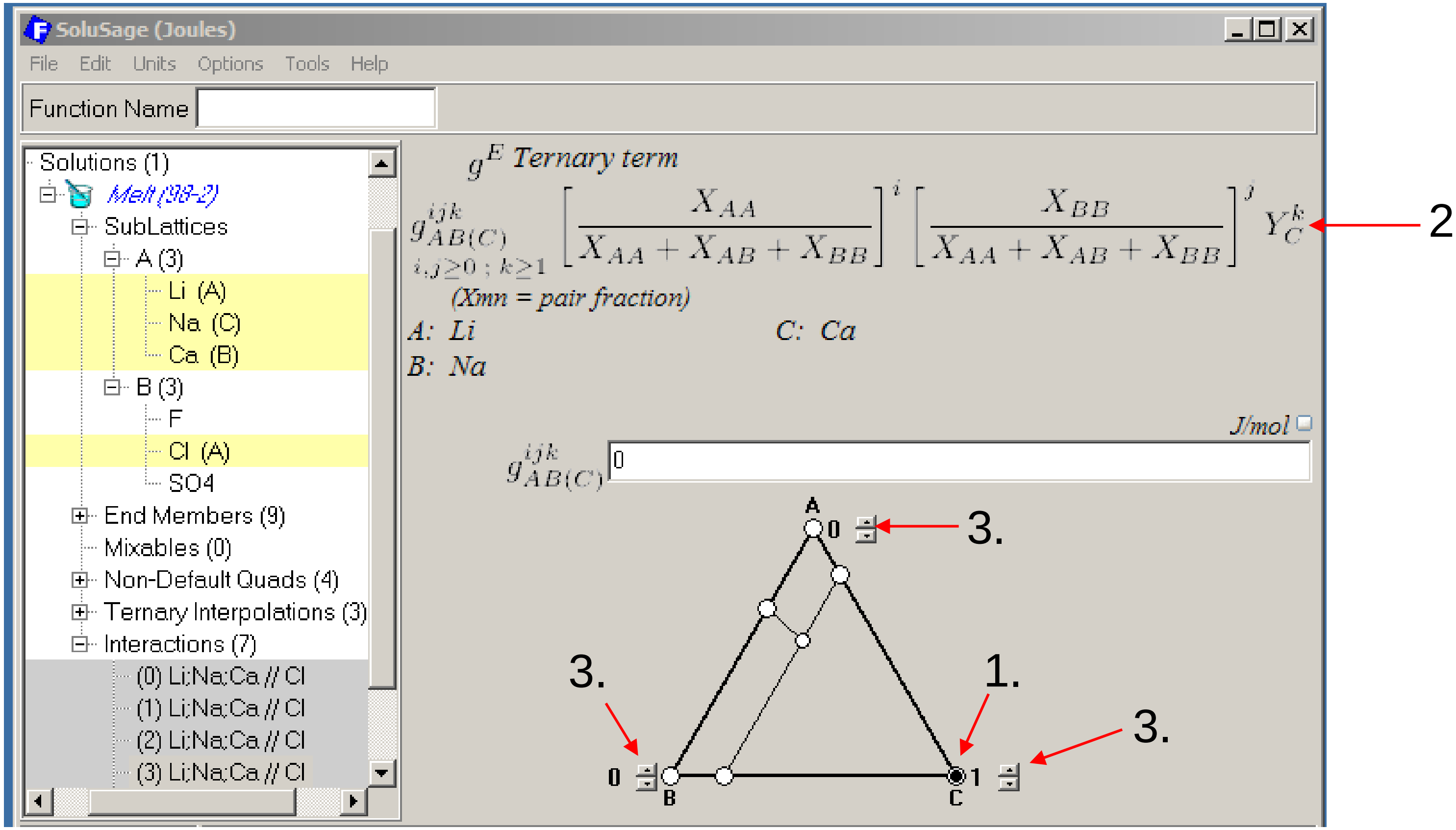
1. Click

2. Click



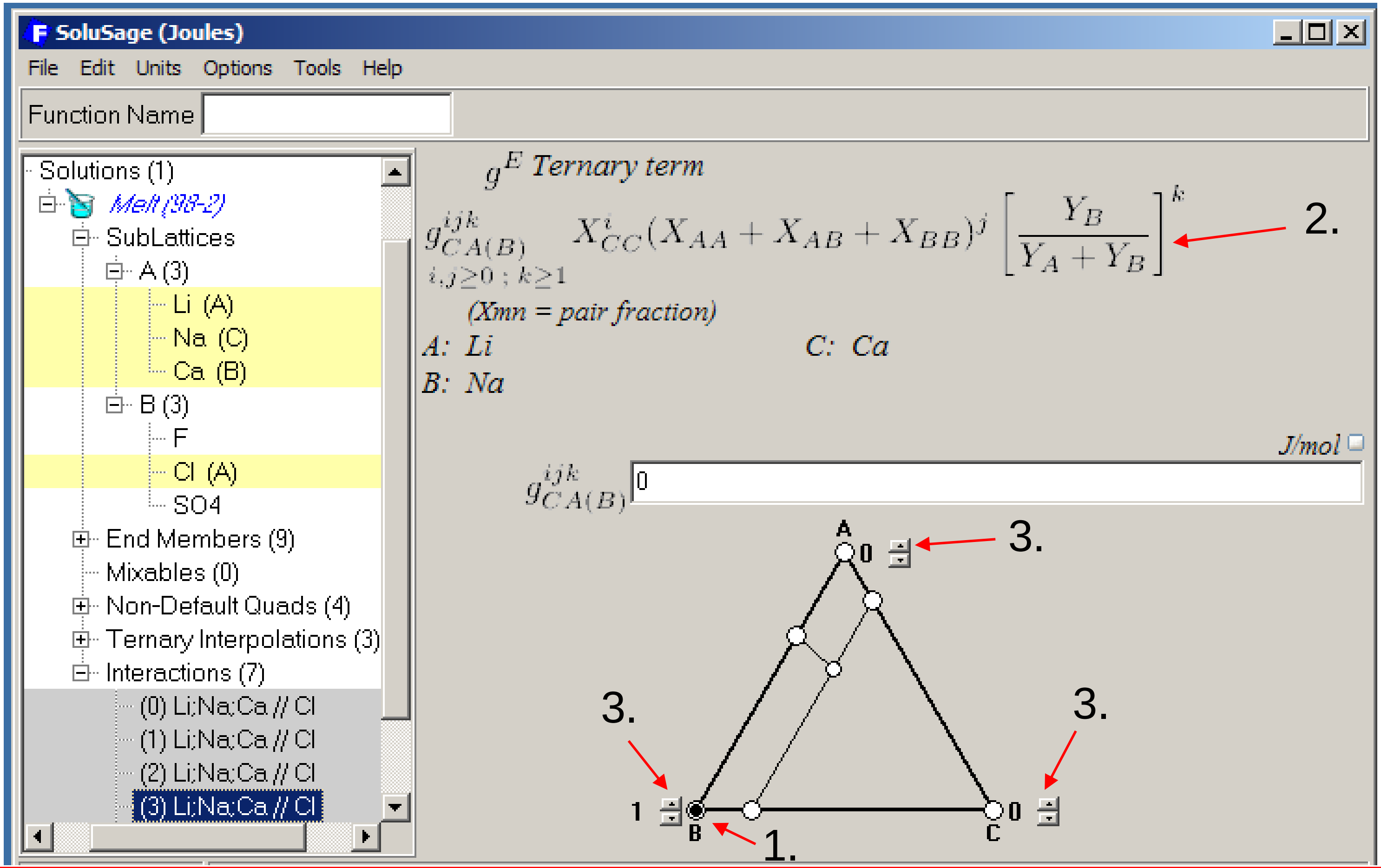
4. Click

3. A **ternary term** will be entered as **a function of pair fractions**. This term **DOES** affect the quasichemical equilibrium



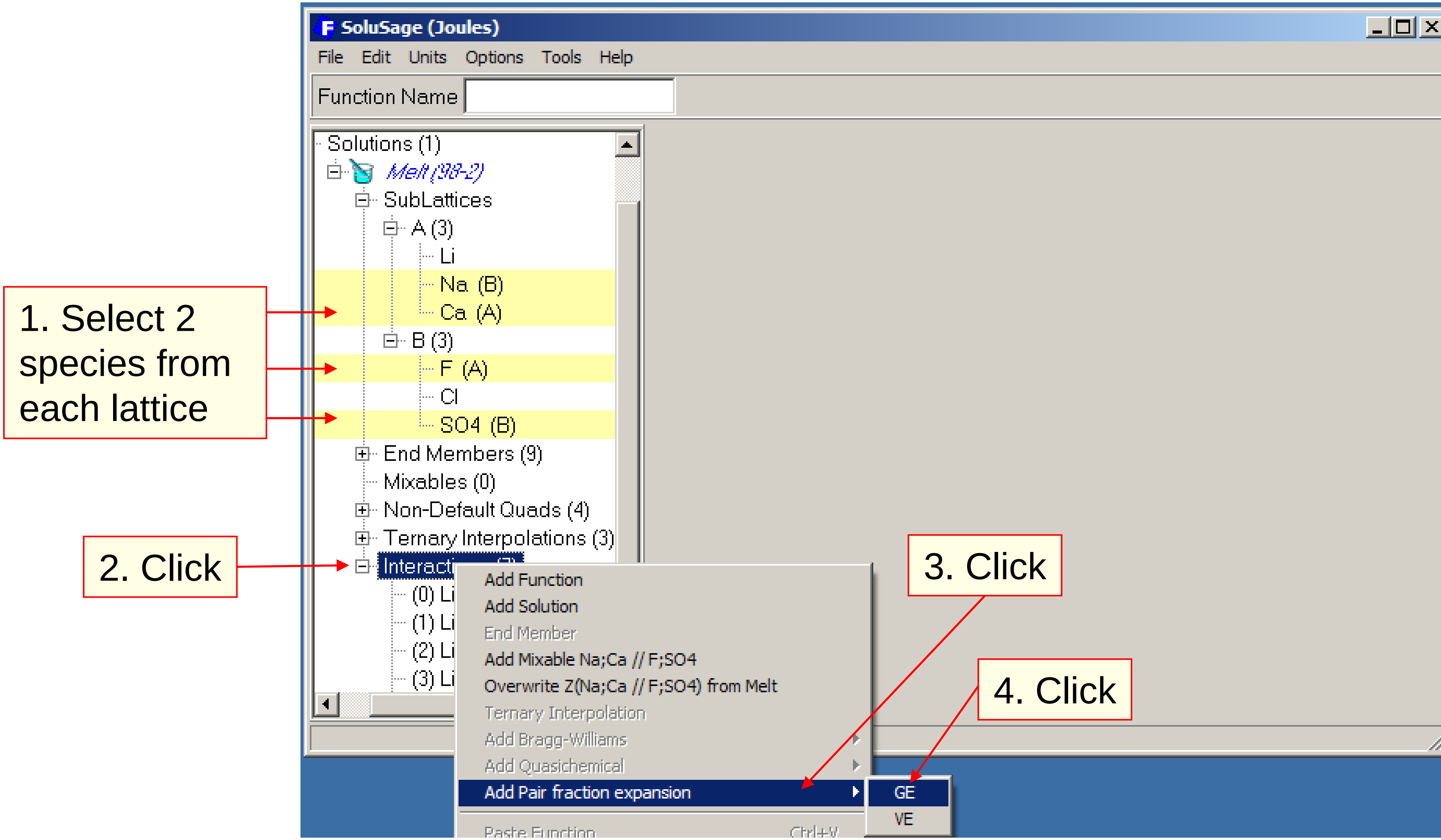
1. First repeat steps 2,3,4 of slide 10.15, then click here to indicate that this term gives the effect of species C (Ca) upon the interaction of species A and B (Li and Na) when the other lattice contains only Cl.
2. Since the A-B (LiCl-NaCl) binary terms are interpolated using the Kohler approximation, this is the form of the ternary term.
3. Click on the arrows to select the powers i, j and k.

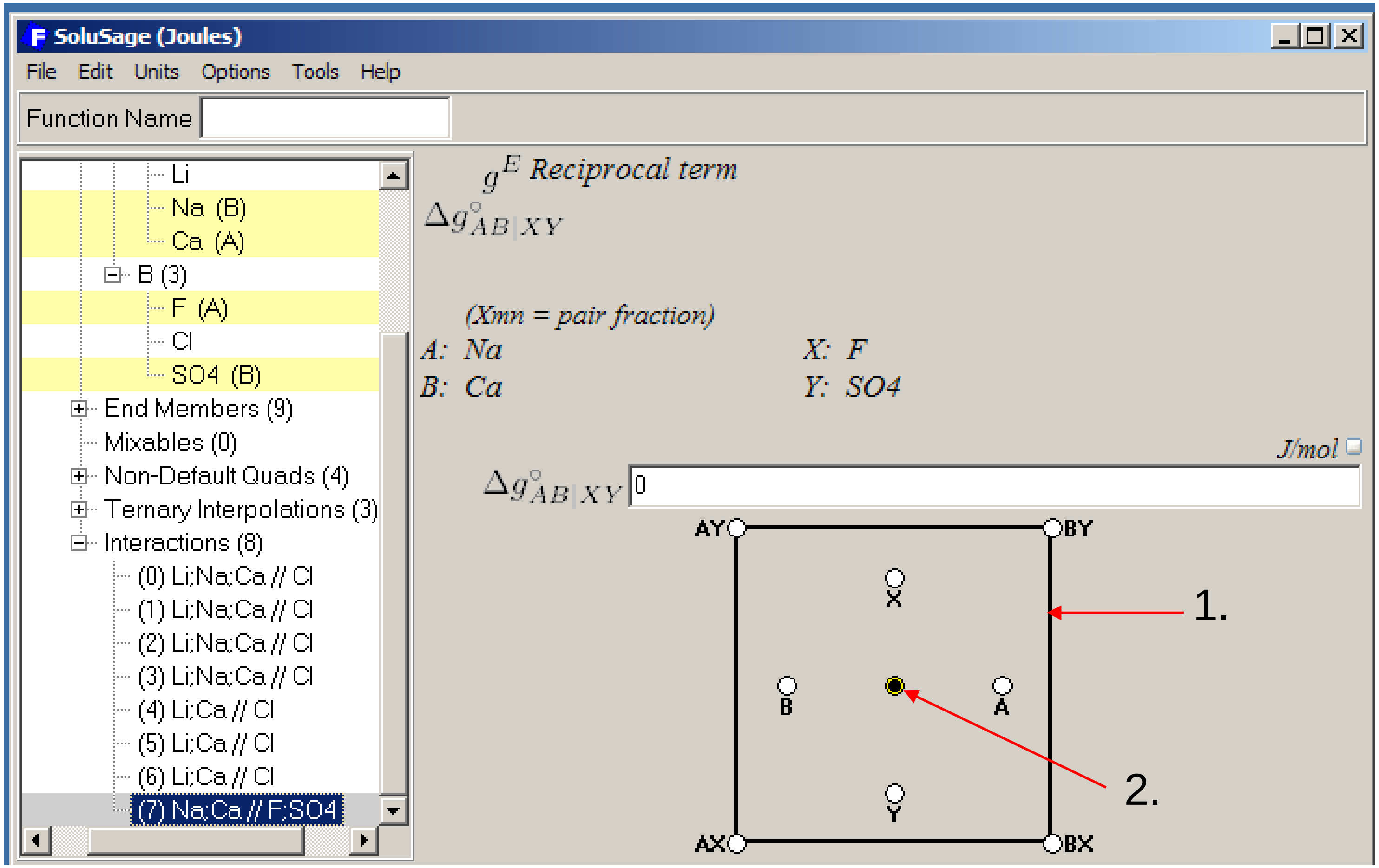
Note: Entry of this type of term is prohibited if the (Li, Na)(Cl) binary terms are interpolated using the Muggianu approximation.



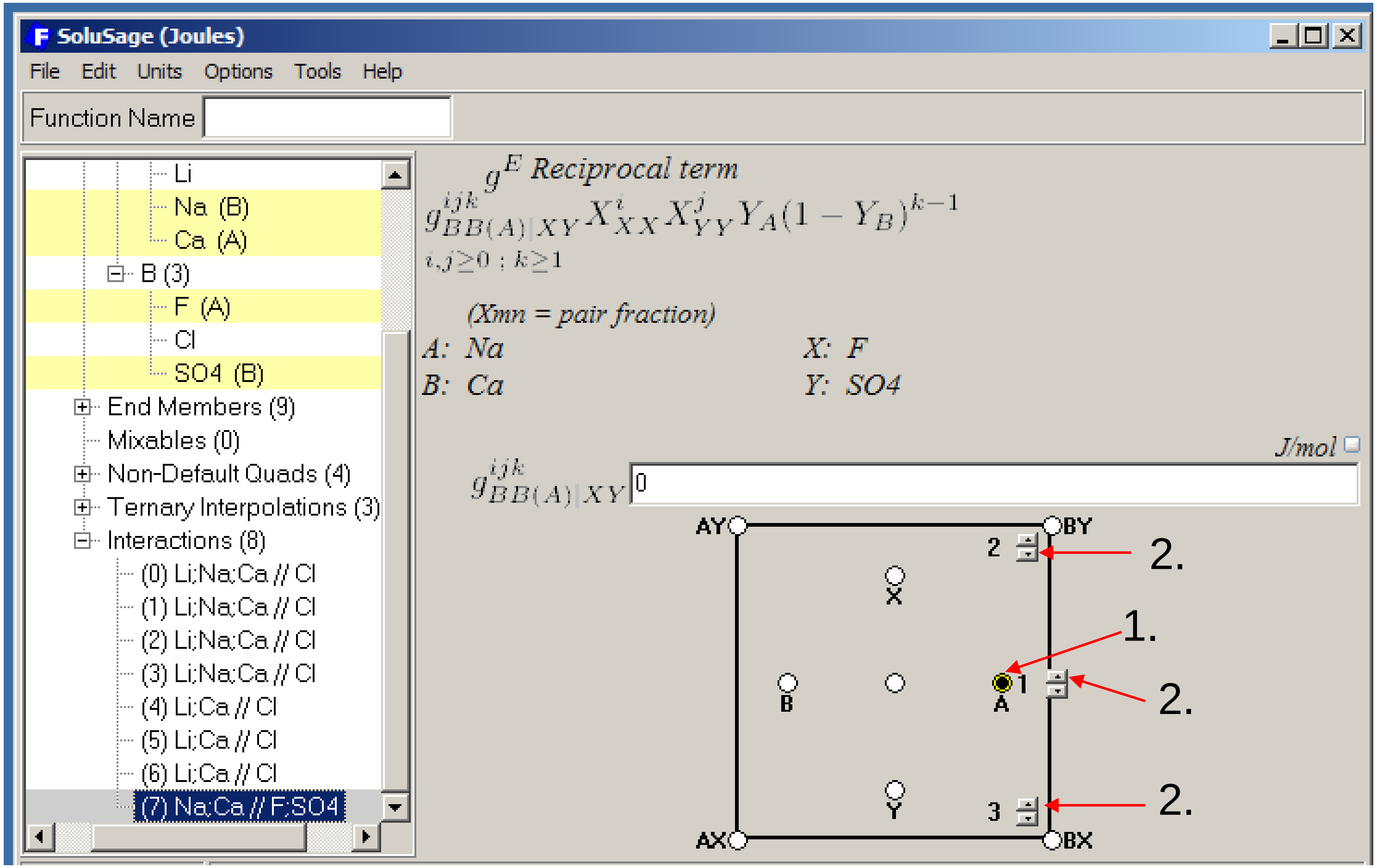
1. First repeat steps 2, 3, 4 of slide 10.15, then click here to indicate that this term gives the effect of species B (Na) upon the interaction of species C and A (Ca and Li) when the other lattice contains only Cl.
2. Since the C-A ($CaCl_2$-LiCl) binary terms are interpolated using the Toop (X_C = constant) approximation, this is the form of the ternary term.
3. Click on the arrows to select the powers i, j and k.

Entering a reciprocal interaction parameter

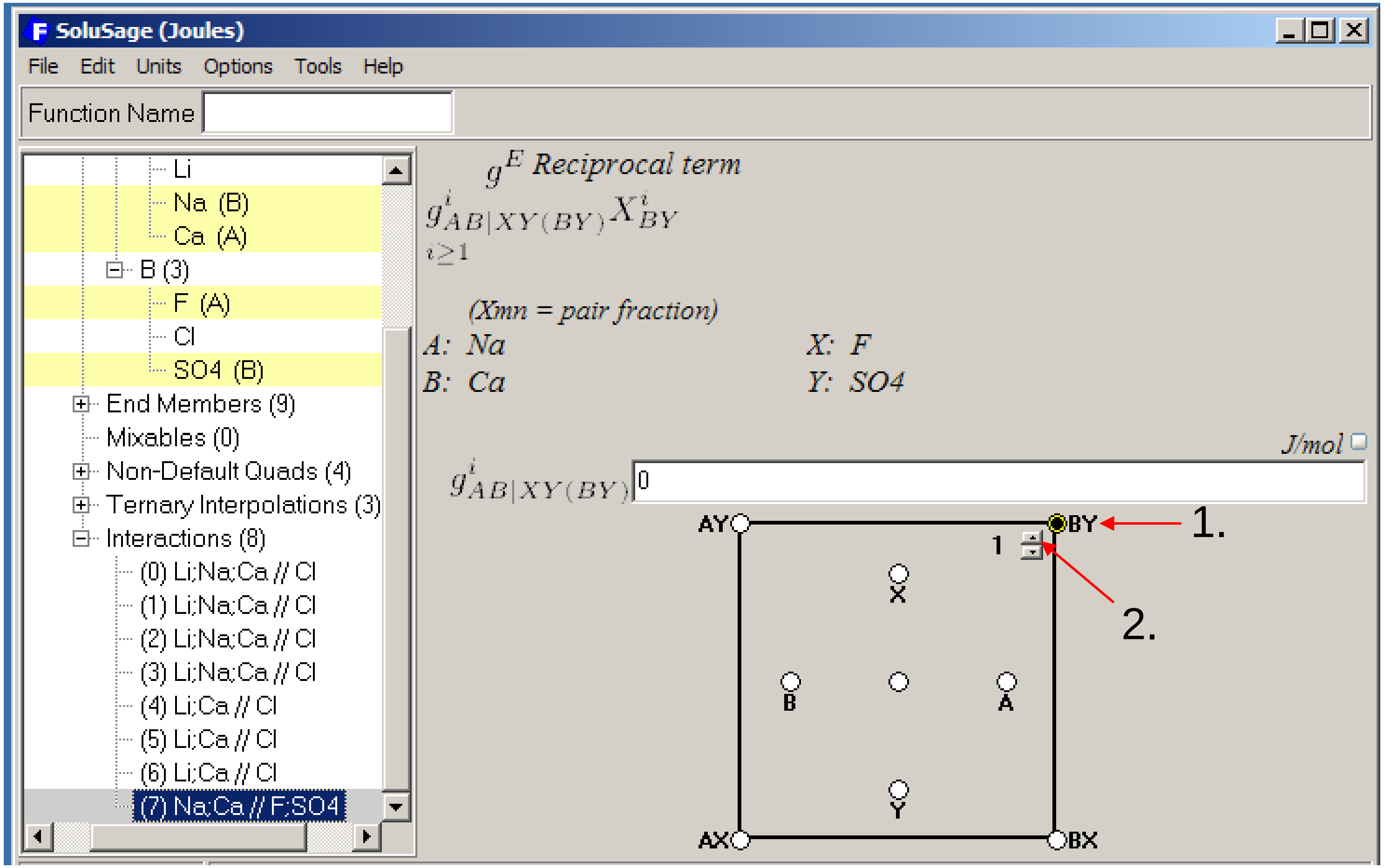




1. Nine different types of term may be entered. Click on one of the 9 circles.
2. Click here to enter the term $\Delta g^0_{AB/XY}$ defined in Ref. (14).



1. Repeat steps of slide 10.20, then click here to enter a reciprocal term of the form shown as defined in Ref. (14).
2. Click on the arrows to select the powers i, j and k.
- Click on the circles labelled B, X or Y to enter similar terms.

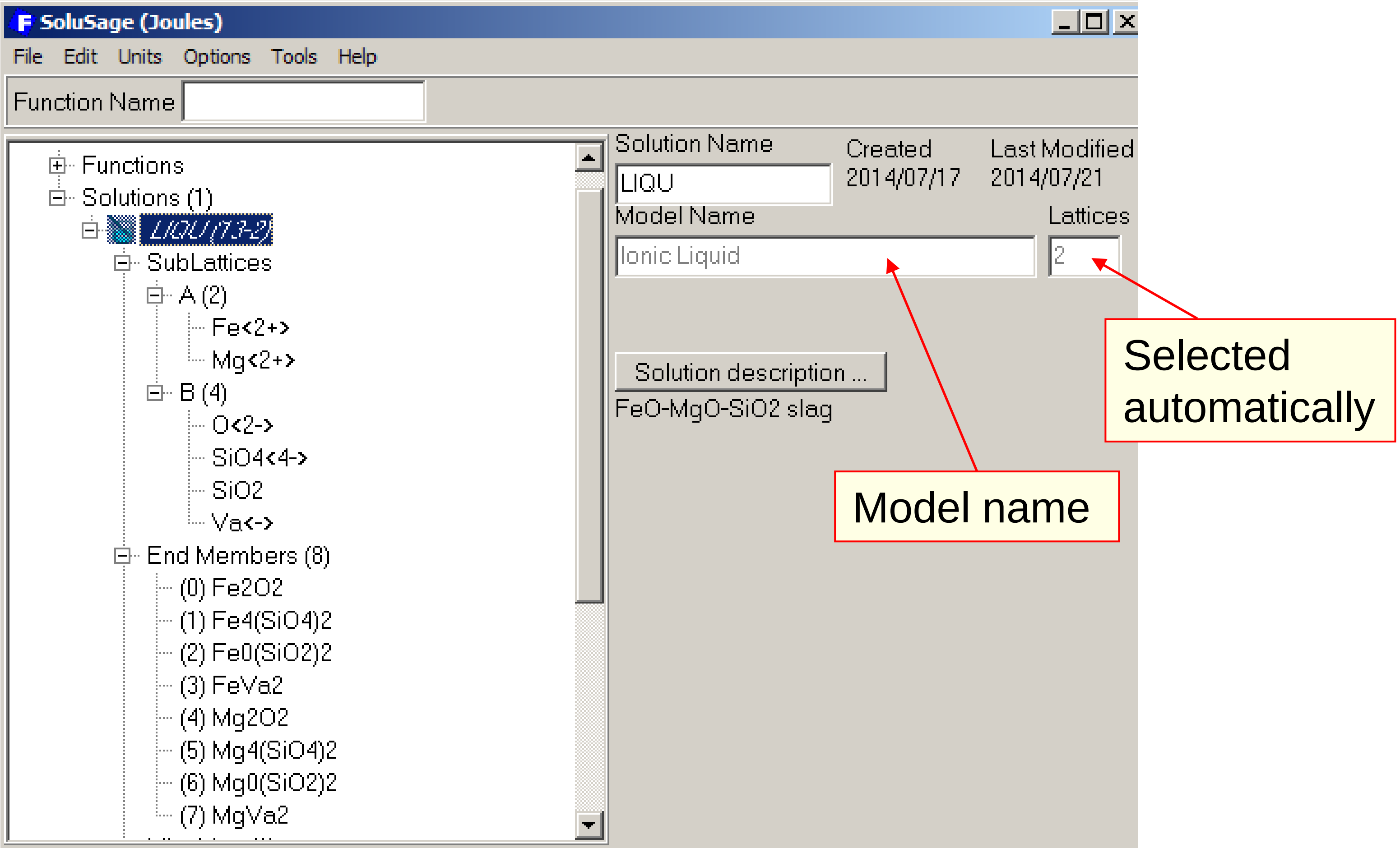


1. Repeat steps of slide 10.20, then click here to enter a reciprocal term of the form shown as defined in Ref. (14).
2. Click here to enter the power i.

- Click on the other corners of the square to enter similar terms.

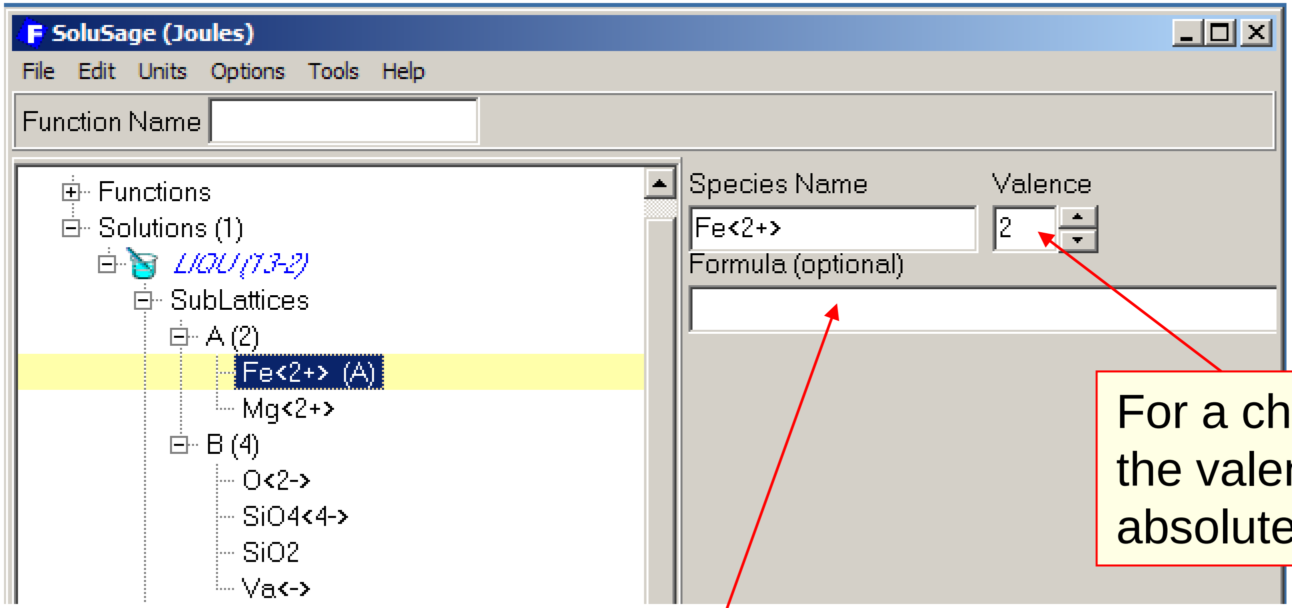
11. The Ionic Liquid Model (“model #13”)

- For a description of the model, see refs. (16, 17)
- Before reading this Section you should read Sections 1, 2 and 5.



In this example, an FeO-MgO-SiO_2 slag is modeled, with Fe^{2+} and Mg^{2+} cations on one sublattice and O^{2-}, SiO^{4-} anions, neutral SiO_2 species, and negatively charged vacancies on the other sublattice.

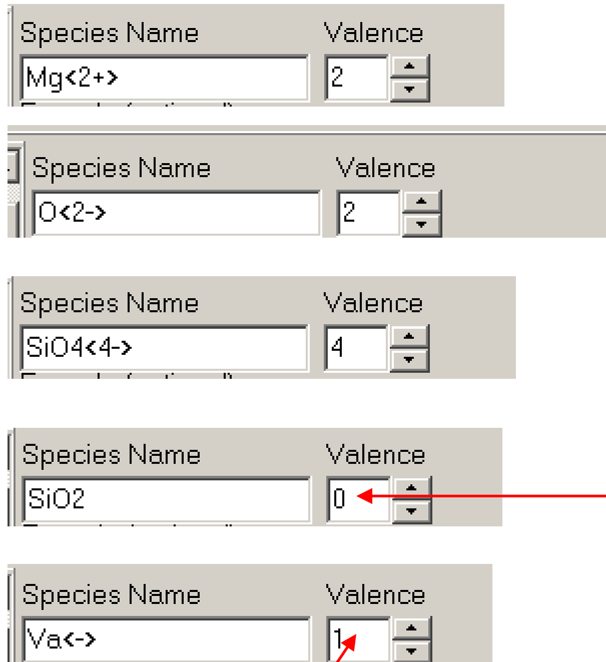
Entry of species



For a charged species, the valence is the absolute charge.

To avoid conflicts over charges and valences, it is recommended NOT to give formulae for the species.

Entry of species

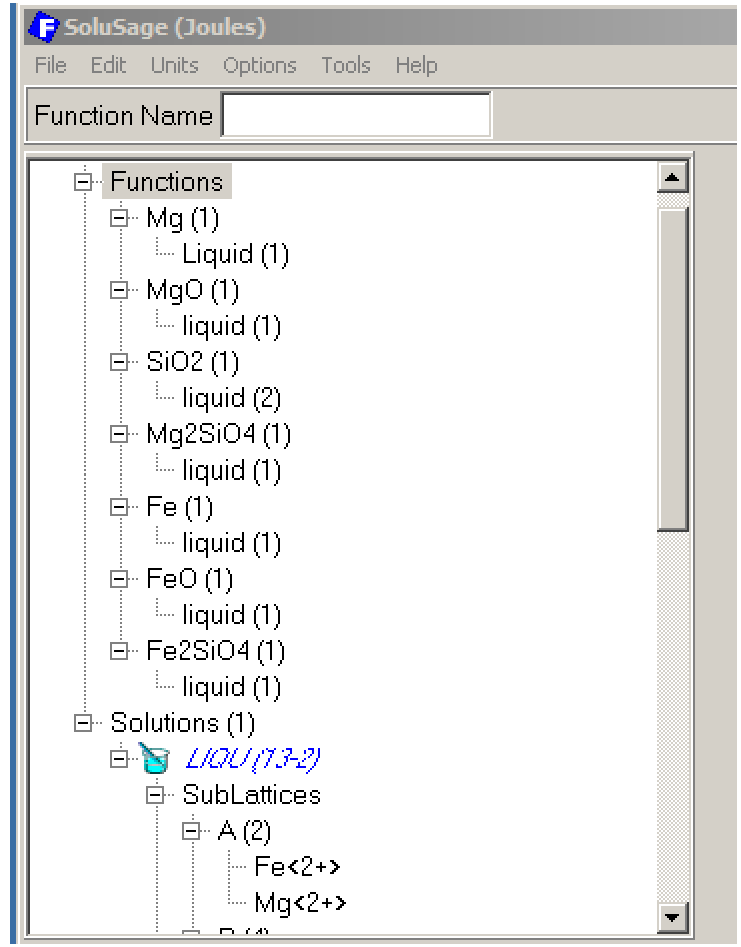


The valence of a neutral species is 0.

The vacancy has a charge of [-1].

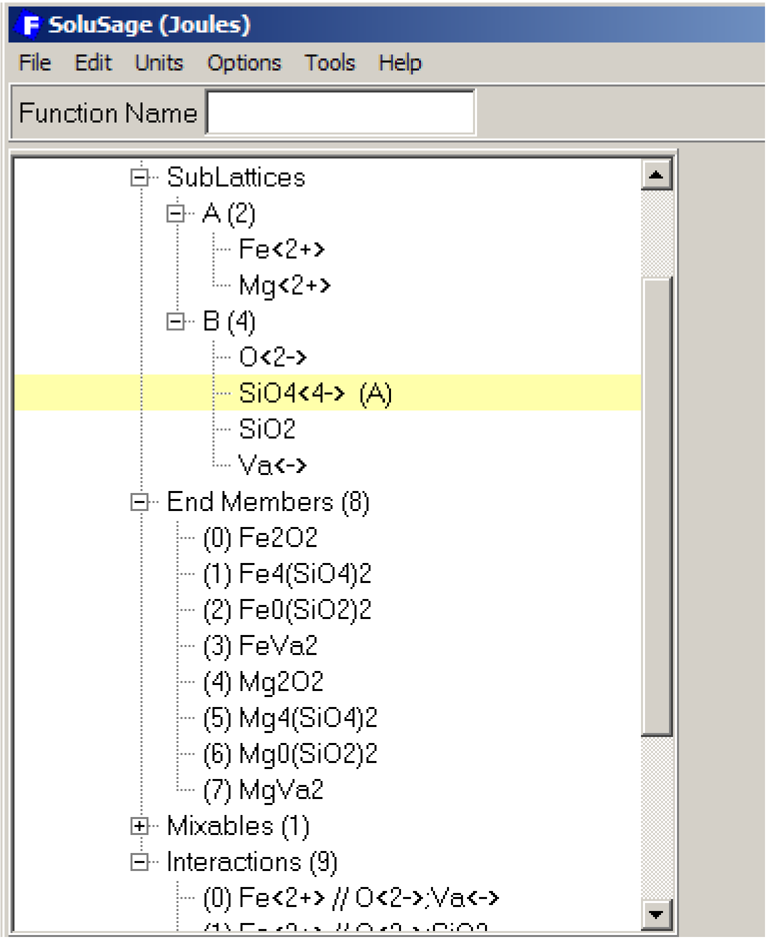
Functions

In this example, the functions contain the thermodynamic properties of one mole of the liquids shown. For example, the function Mg2SiO4#liquid is for one mole of liquid Mg_2SiO_4.



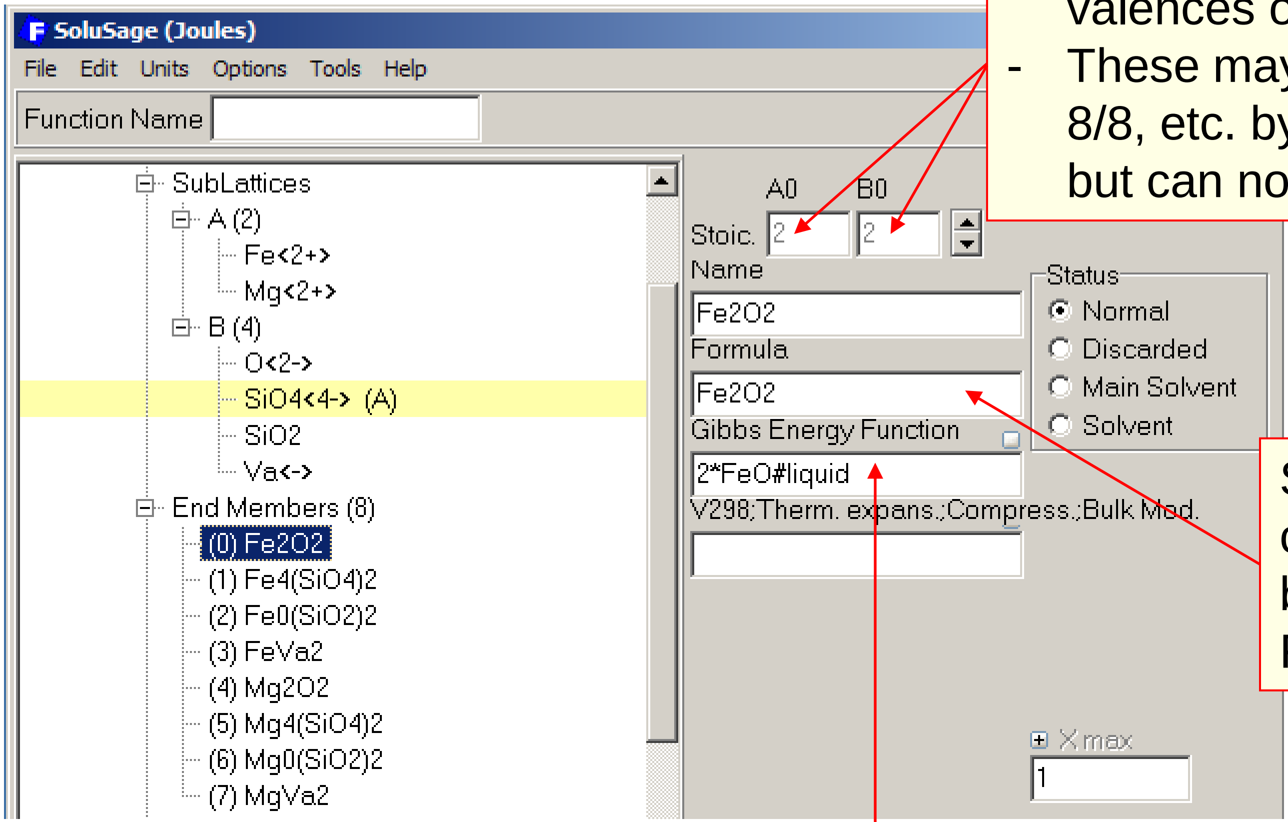
Entry of end-members

As in all models, an end-member consists of one species from each sublattice. In this example there are 8 end-members.



Entry of end-member Fe2O2

(consisting of species Fe<2+> and O<2->)



- Selected automatically from the valences of the species.
- These may be increased to 4/4, 6/6, 8/8, etc. by clicking on the arrows, but can not be decreased.

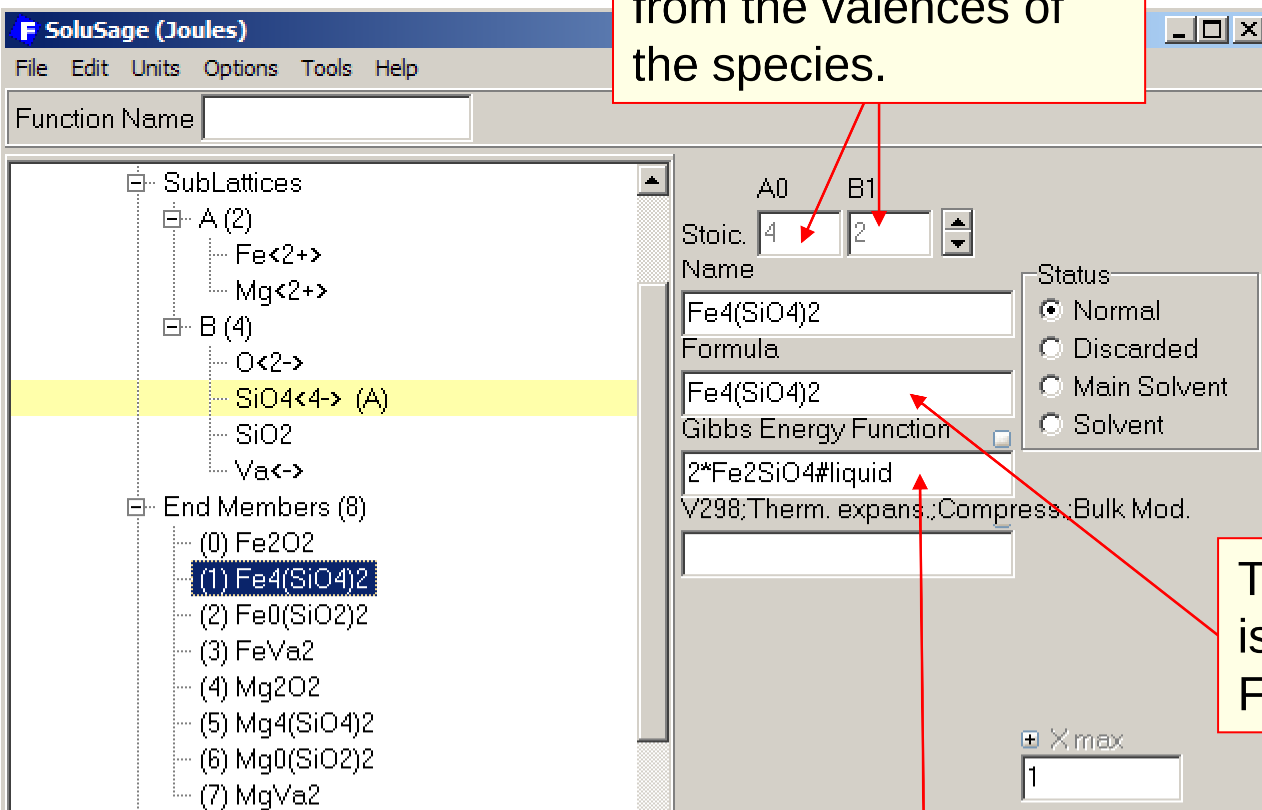
Since the stoichiometry can not be decreased below 2/2, the formula is Fe2O2.

The Gibbs energy of the end-member is then 2 times that of liquid FeO.

Entry of end-member Fe4(SiO4)2

(consisting of species Fe<2+> and SiO4<4->)

Selected automatically from the valences of the species.

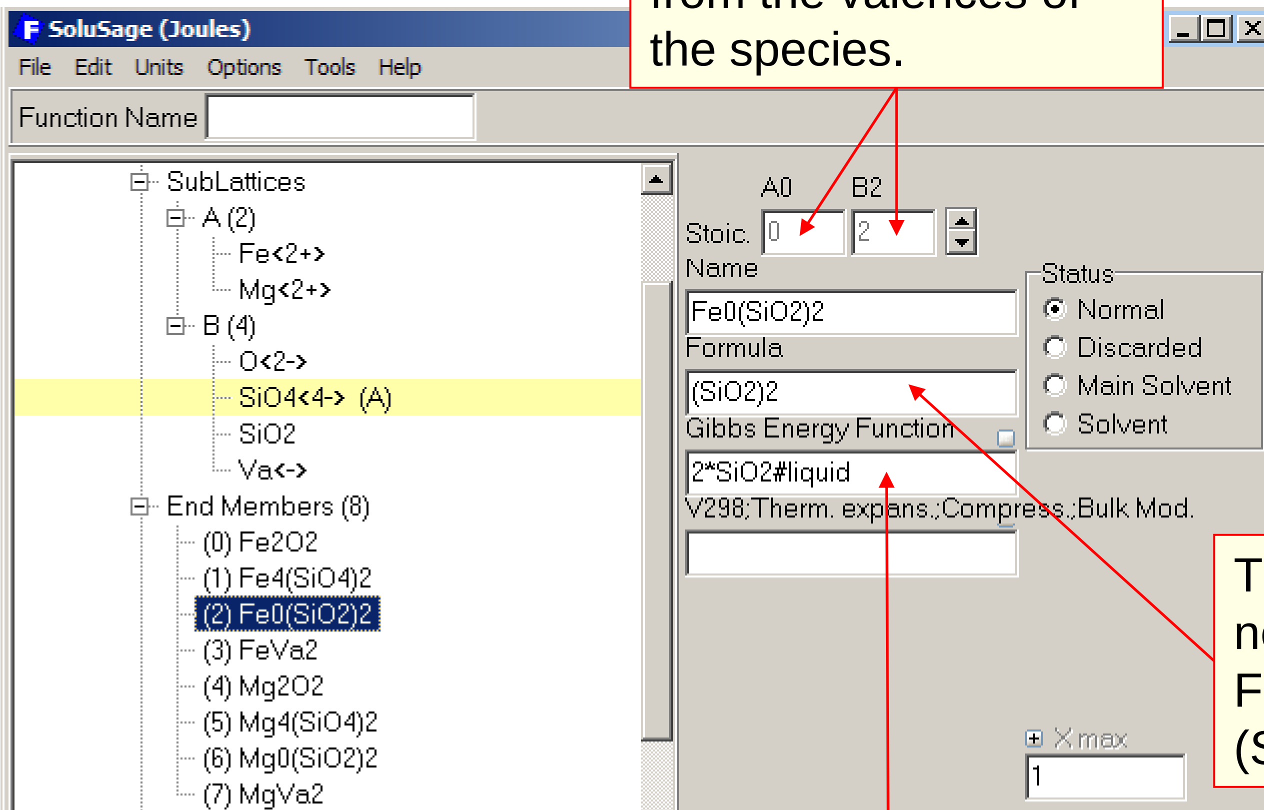


The formula is necessarily Fe4(SiO4)2.

The Gibbs energy is 2 times that of liquid $Fe_2(SiO_4)$.

Entry of end-member Fe0(SiO2)2

(consisting of species Fe<2+> and SiO_2)



Selected automatically from the valences of the species.

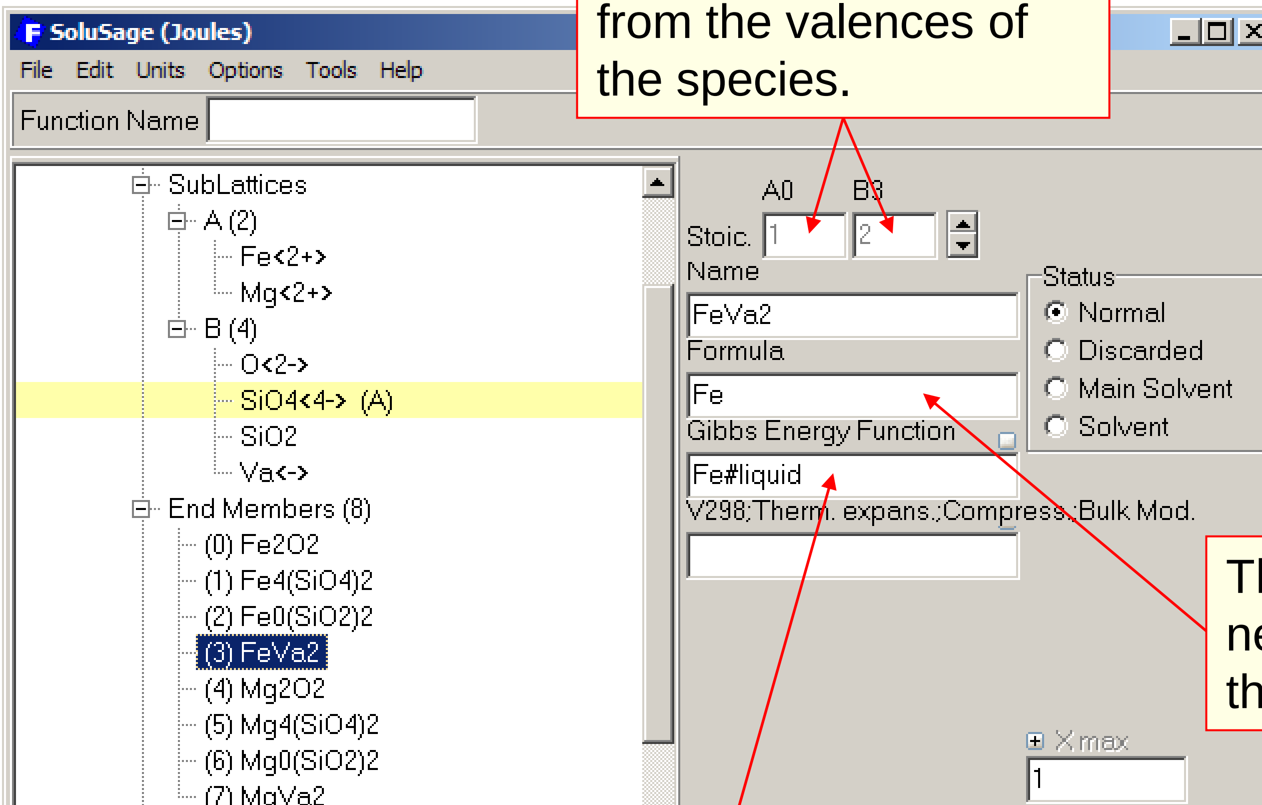
The formula is necessarily $Fe_0(SiO_2)_2$, that is: $(SiO_2)_2$.

The Gibbs energy is 2 times that of liquid SiO_2.

Entry of end-member FeVa2

(consisting of species Fe<2+> and Va<->)

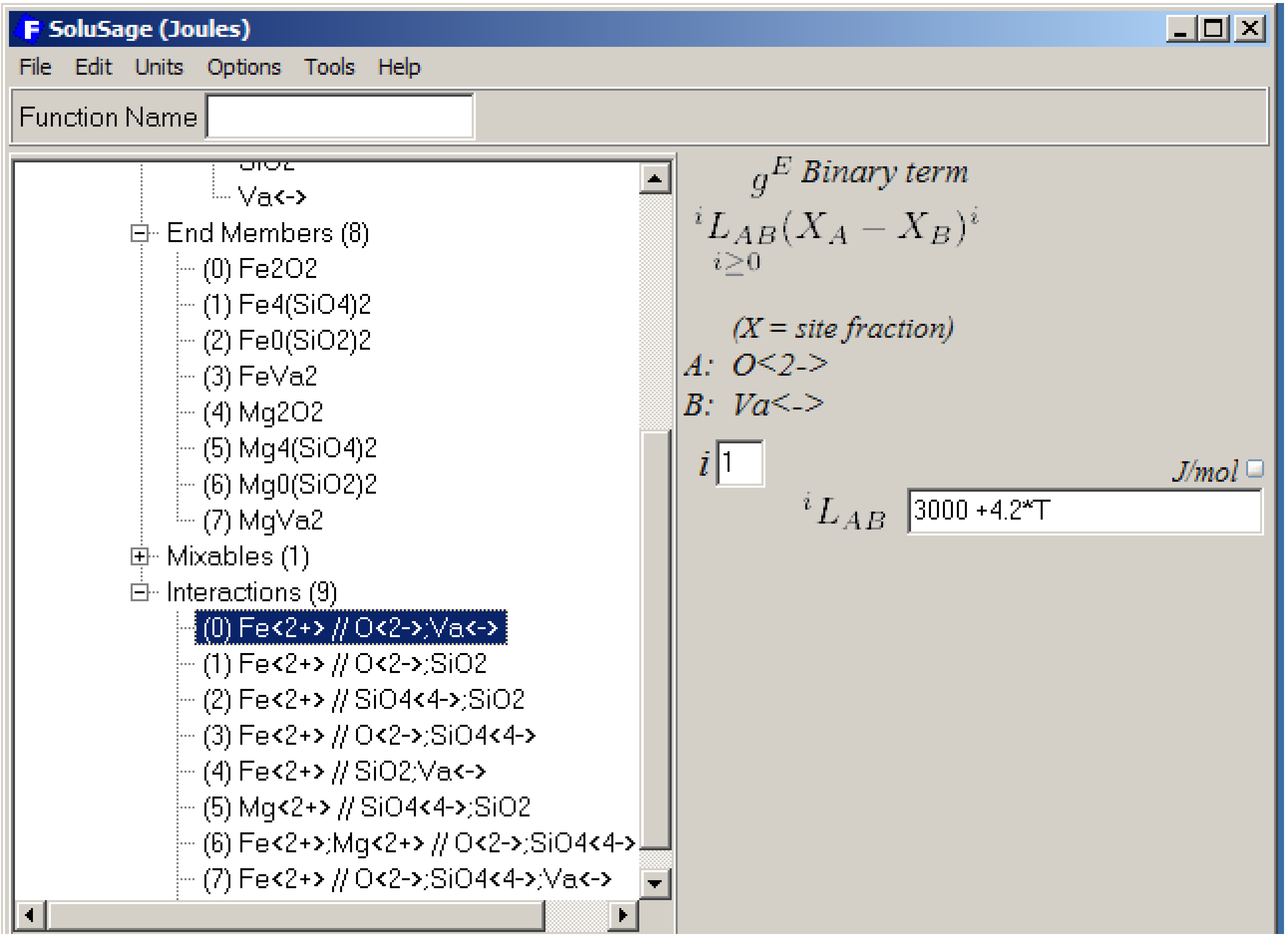
Selected automatically from the valences of the species.



The formula is necessarily $FeVa_2$, that is: Fe.

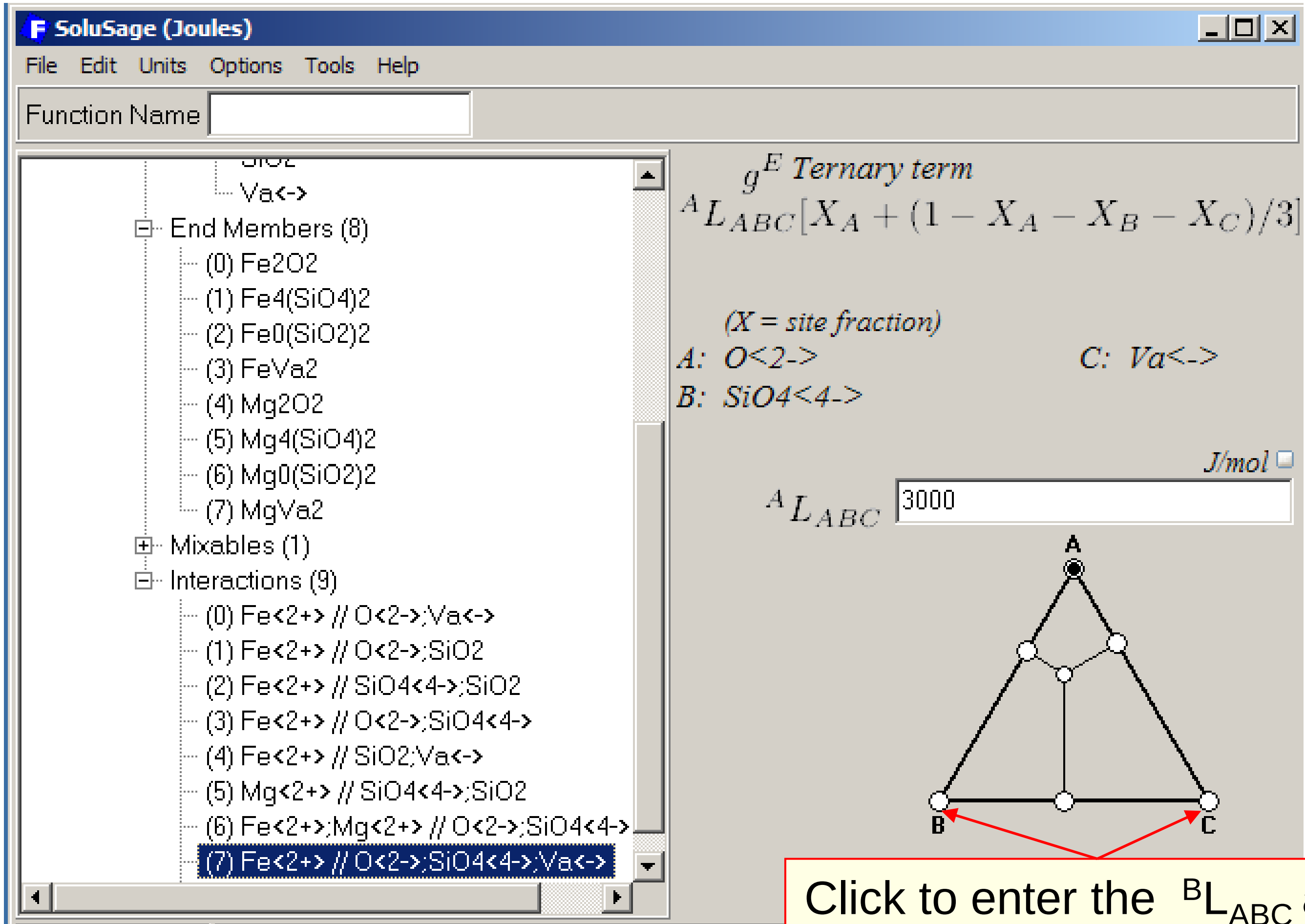
The Gibbs energy is that of liquid Fe.

Binary interaction parameters



Binary interaction parameters are expressed in Redlich-Kister form in terms of site fractions.

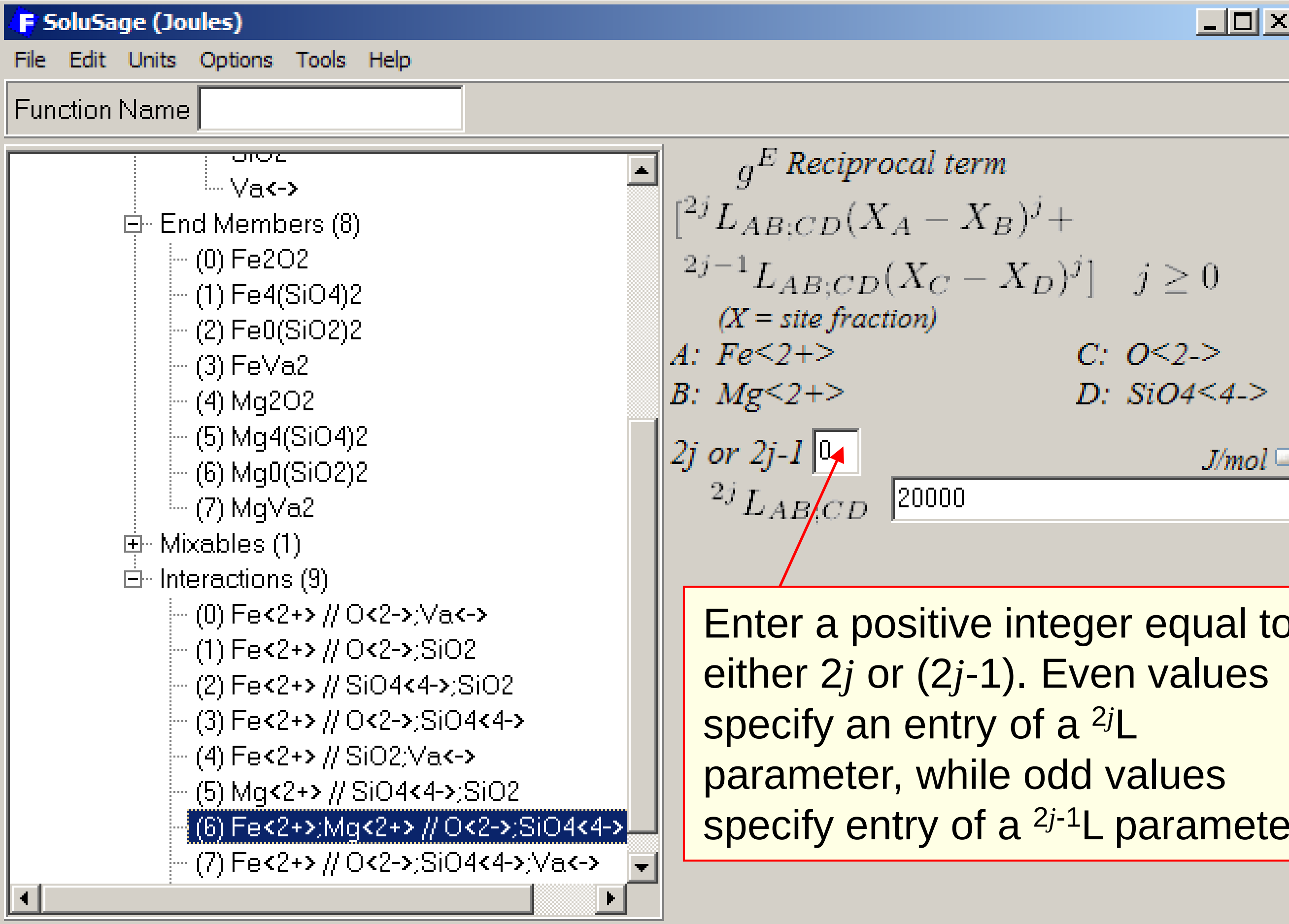
Ternary interaction parameters



Click to enter the $^{B}L_{ABC}$ and the $^{C}L_{ABC}$ parameters.

Ternary interaction parameters are expressed in Redlich-Kister form in terms of site fractions.

Reciprocal interaction parameters

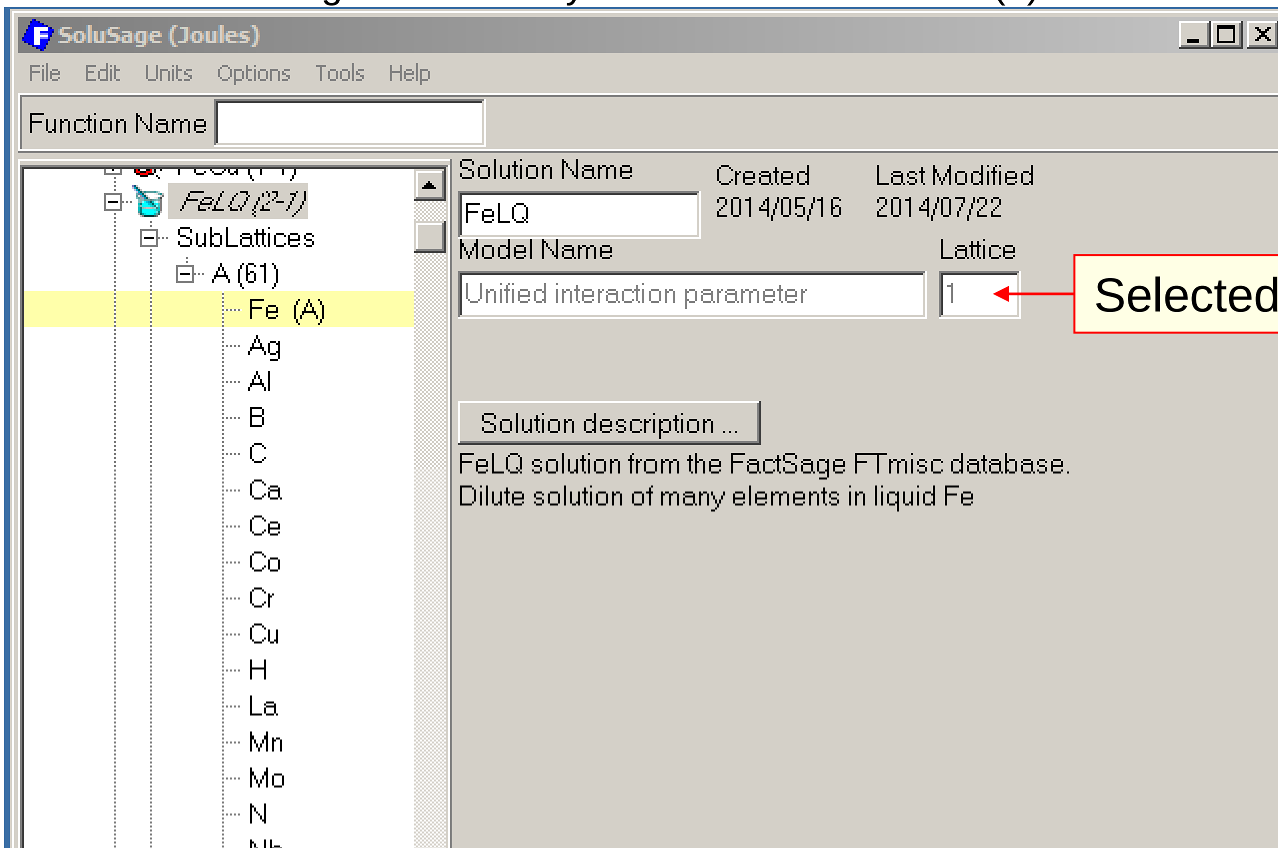


Enter a positive integer equal to either 2*j* or (2*j*-1). Even values specify an entry of a ^{2j}L parameter, while odd values specify entry of a $^{2j-1}$L parameter.

Reciprocal interaction parameters are entered in the form shown here.

12. The Unified Interaction Parameter Formalism ("model #2")

- For a description of the model, see refs. (18, 19).
- This is the Wagner Interaction Parameter Formalism for dilute solutions corrected to be consistent with the Gibbs-Duhem equation and other necessary thermodynamic relationships.
- Before reading this Section you should read Section (1).



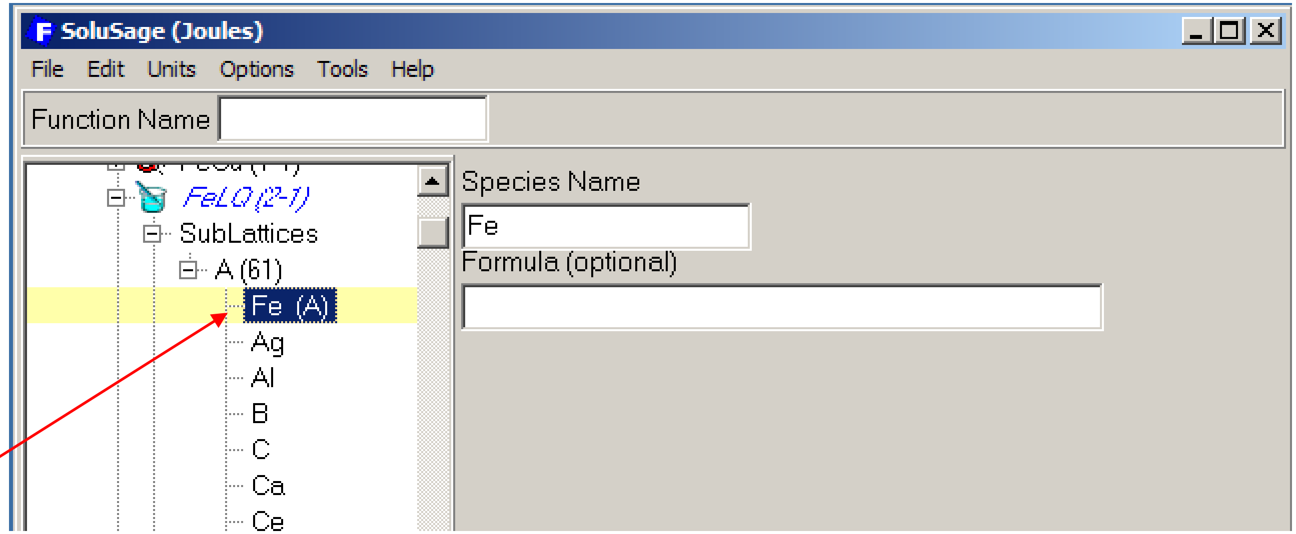
Selected automatically.

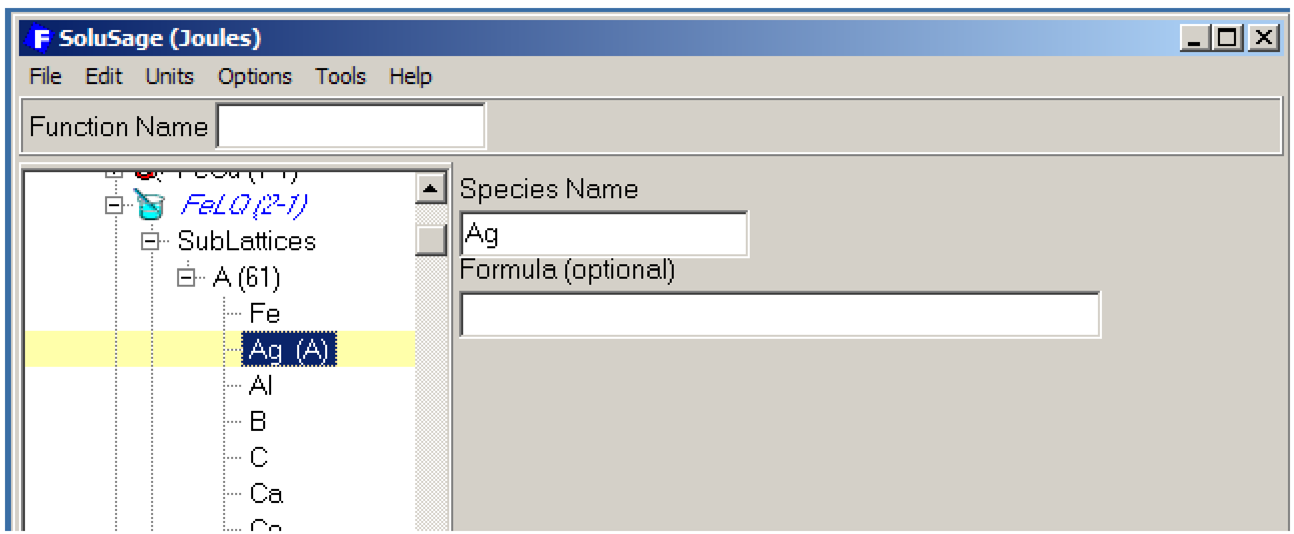
In this example, a solution of elements in liquid Fe is modeled.

Entry of species

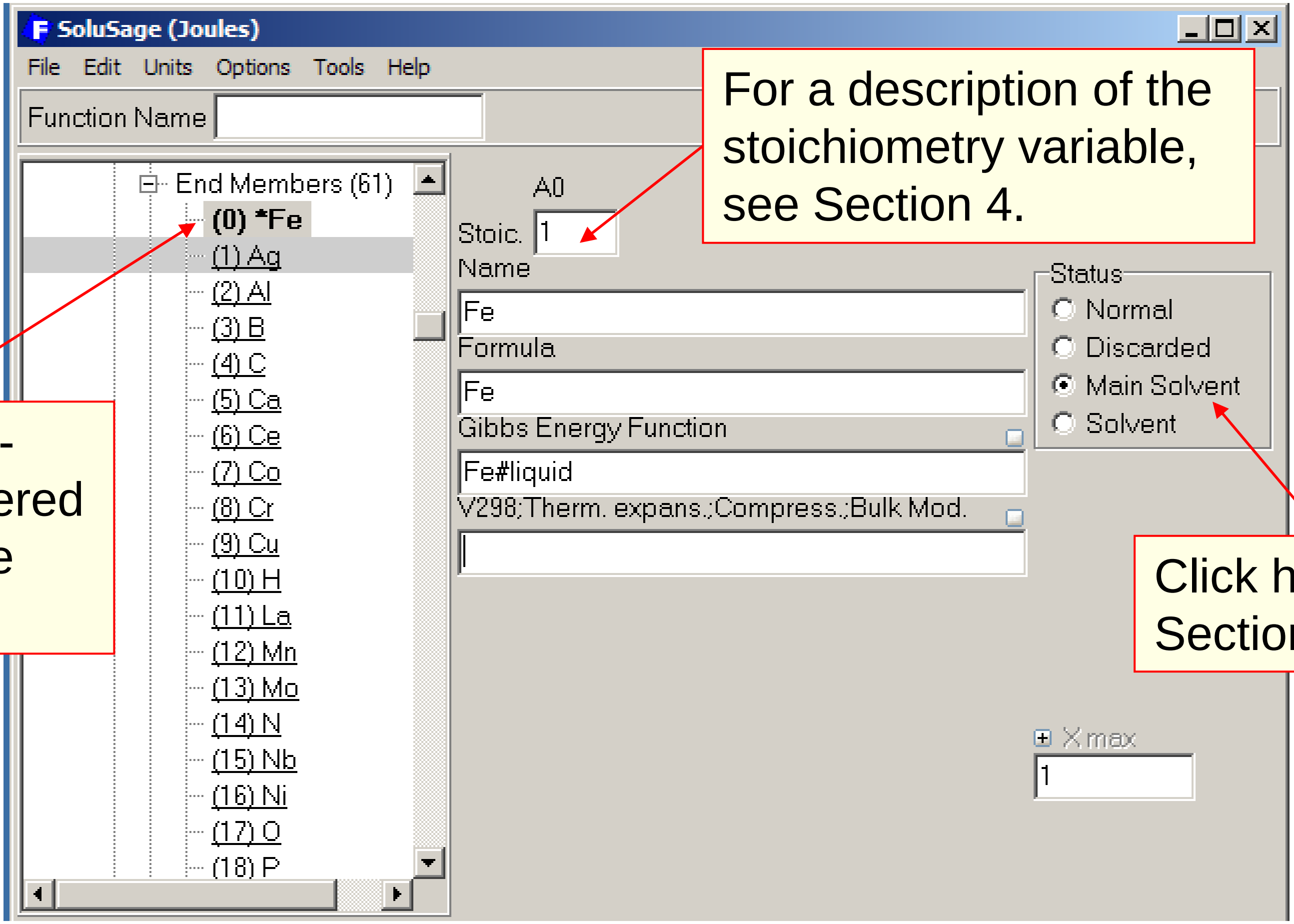
The species in this example are the elements.

One species (in this example, Fe) is the <u>solvent</u>. It **<u>MUST</u>** be entered first.





Entry of end-member Fe (the solvent)

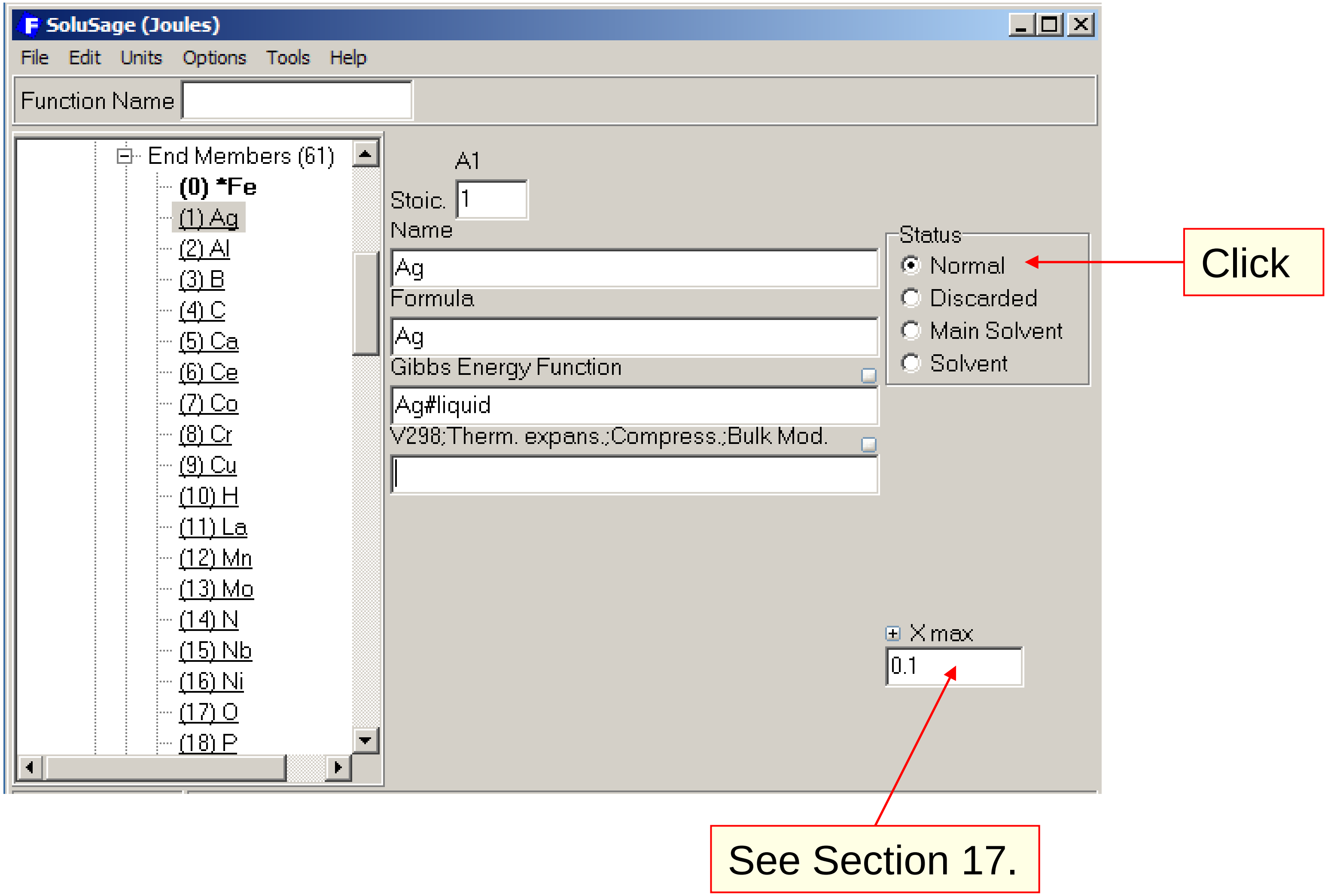


For a description of the stoichiometry variable, see Section 4.

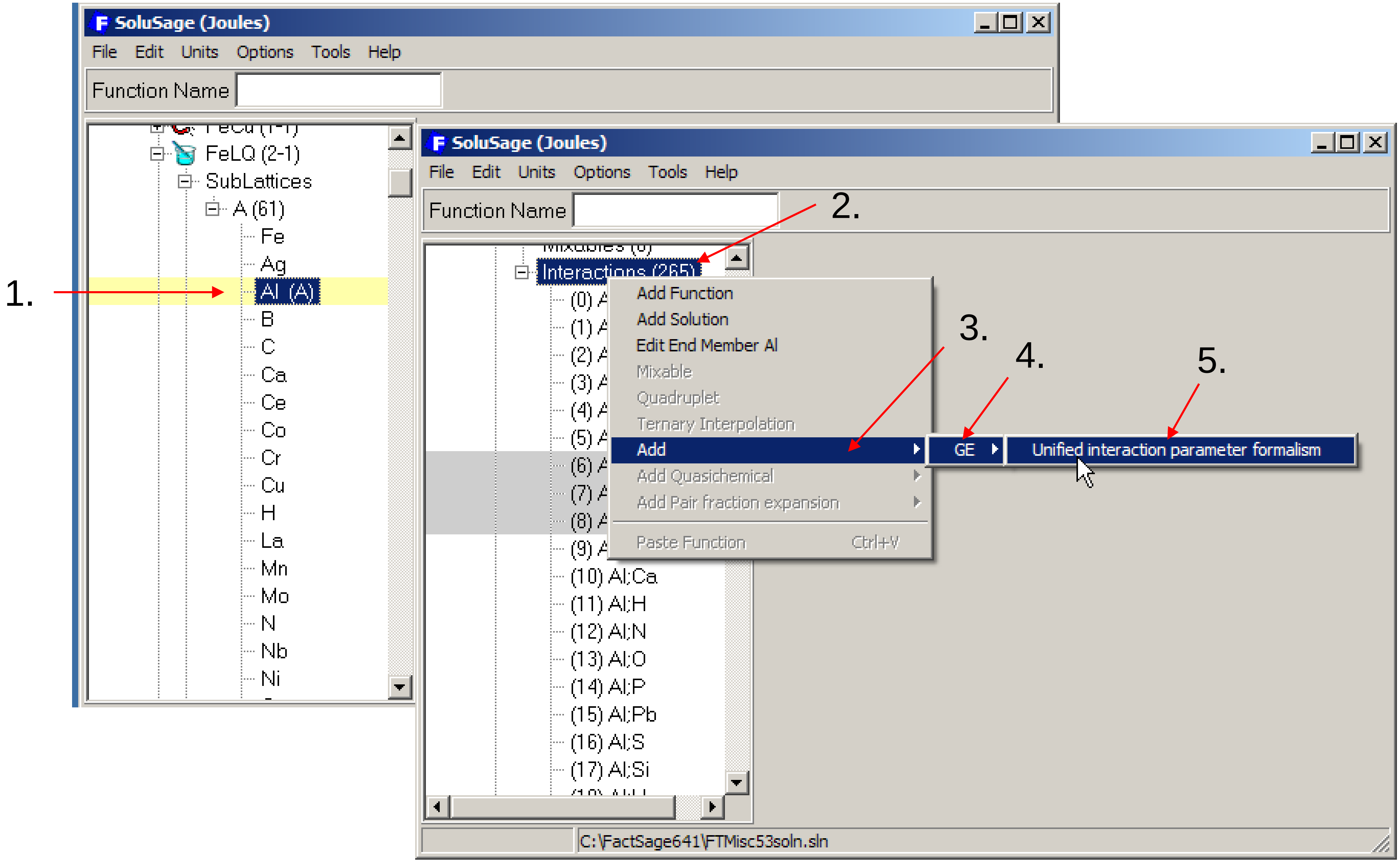
The first end-member entered MUST be the **solvent**.

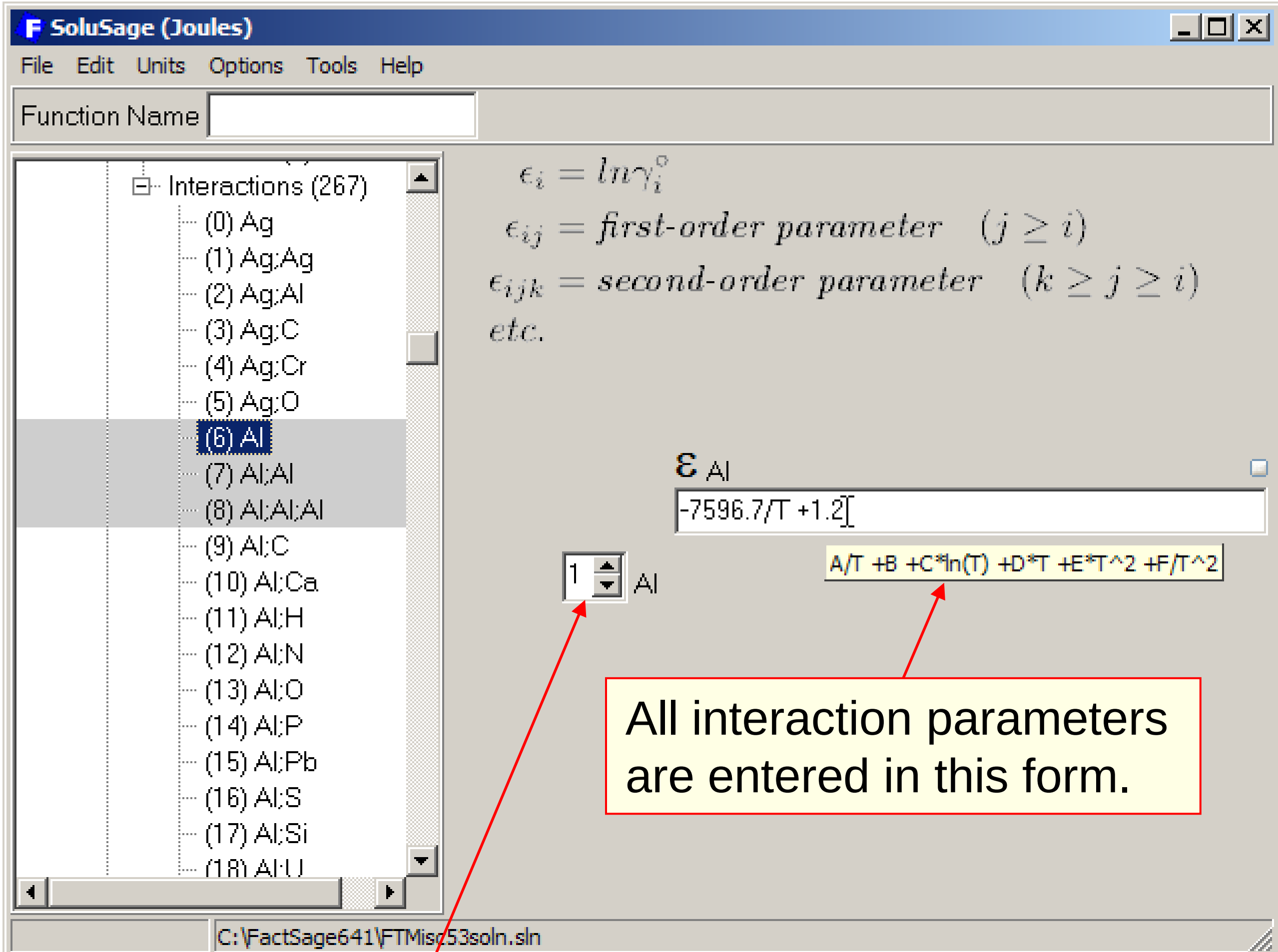
Click here. See Section 16.

Entry of other end-members (solutes)



Entry of self interaction parameters for Al

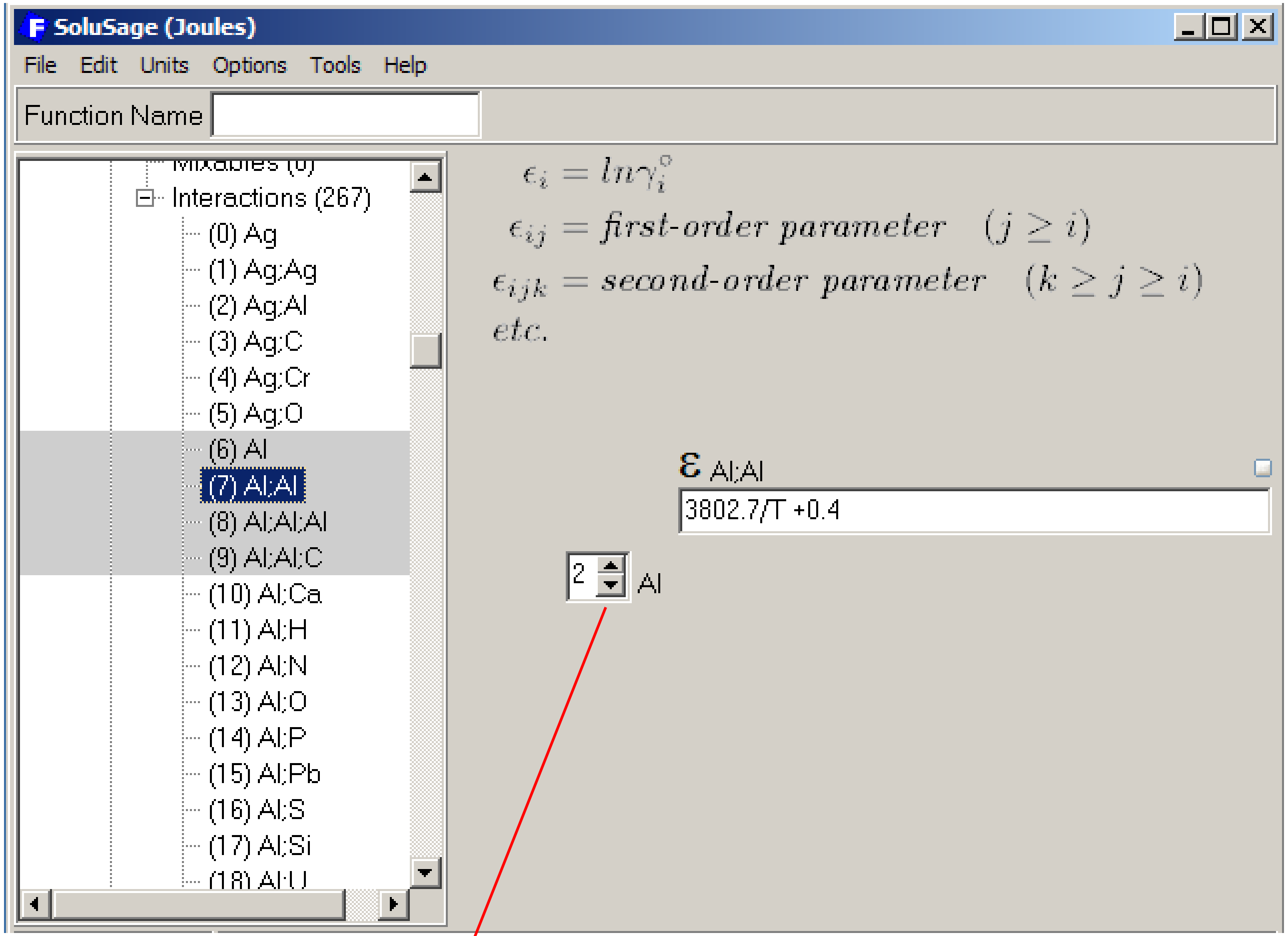




All interaction parameters are entered in this form.

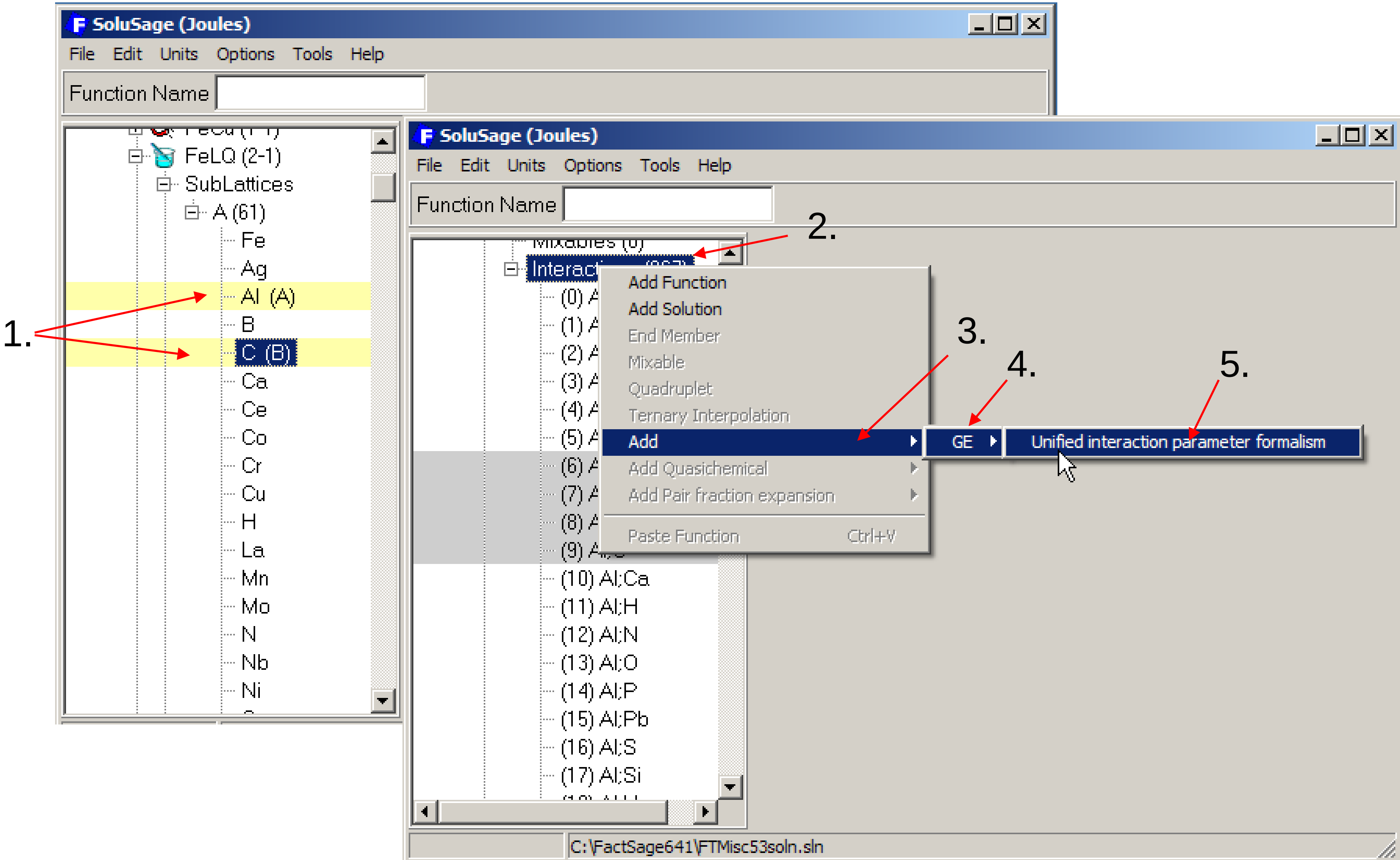
Enter “1” to indicate that this is the zeroth-order parameter ε_{Al} which is the Henrian activity coefficient of Al, $\ln \gamma^{0}_{Al}$ (See refs. (18, 19)).

Entry of first-order parameter $\varepsilon_{Al;Al}$

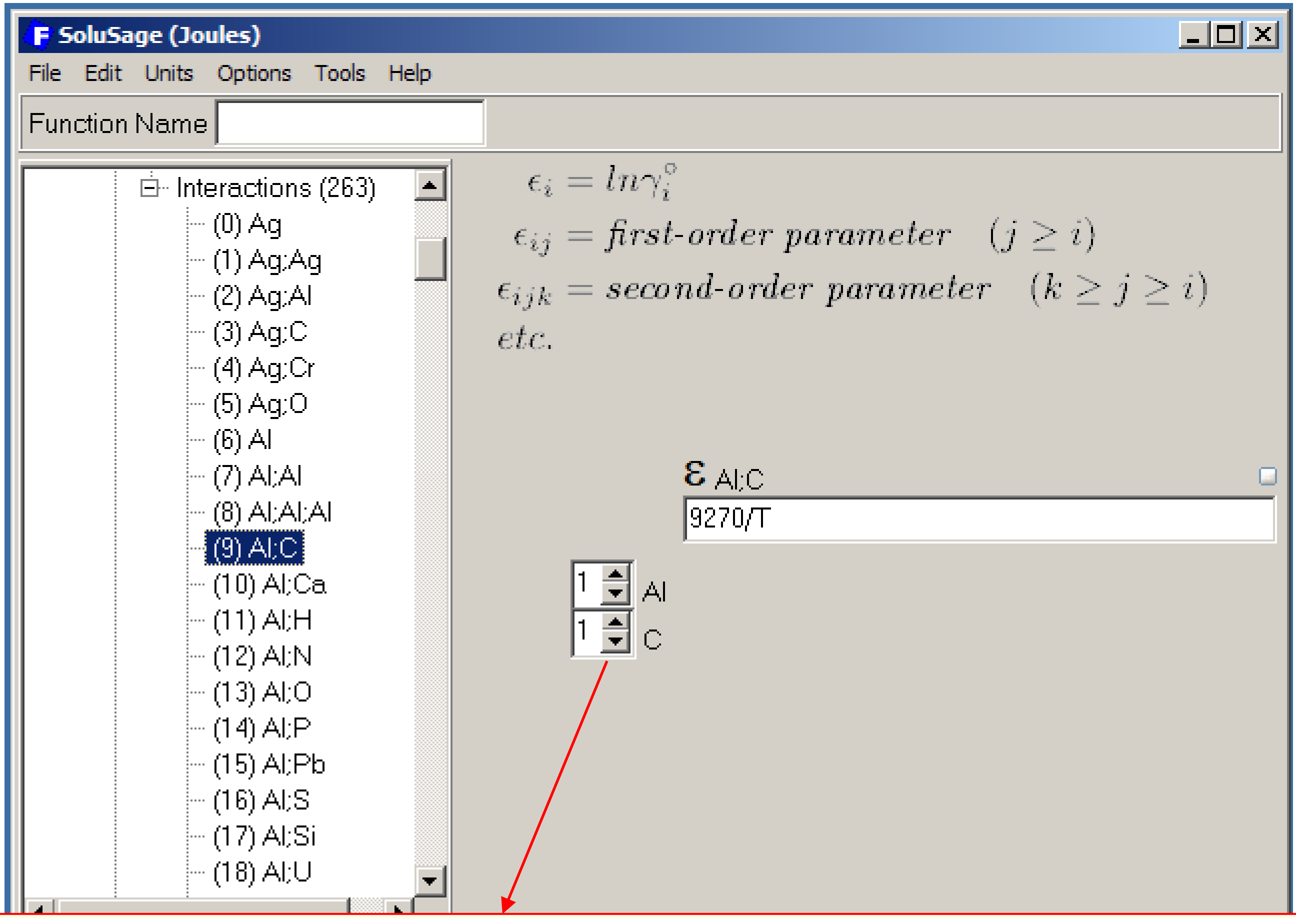


- Enter "2" to indicate that this is the first-order parameter $\varepsilon_{Al;Al}$.
- (Entering "3" would indicate the second-order parameter $\varepsilon_{Al;Al;Al}$, etc.)

Entry of cross-interaction parameters for Al and C

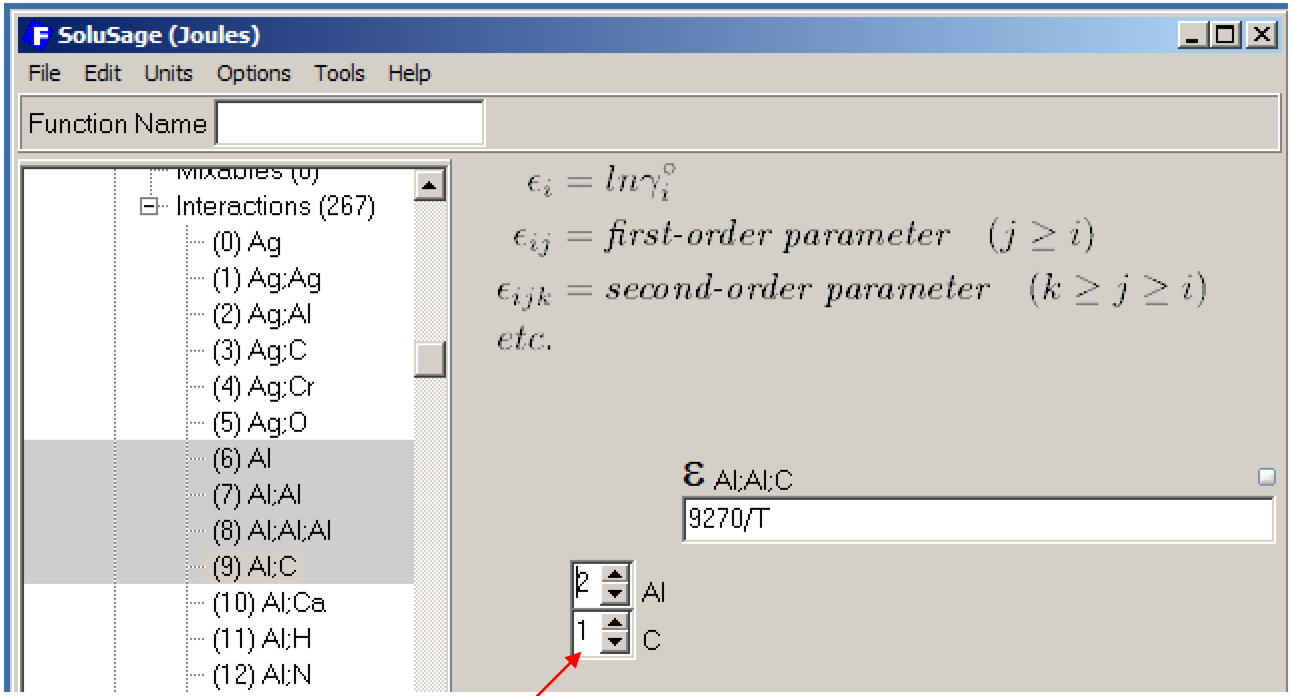


Entry of first-order parameter $\varepsilon_{Al;C}$



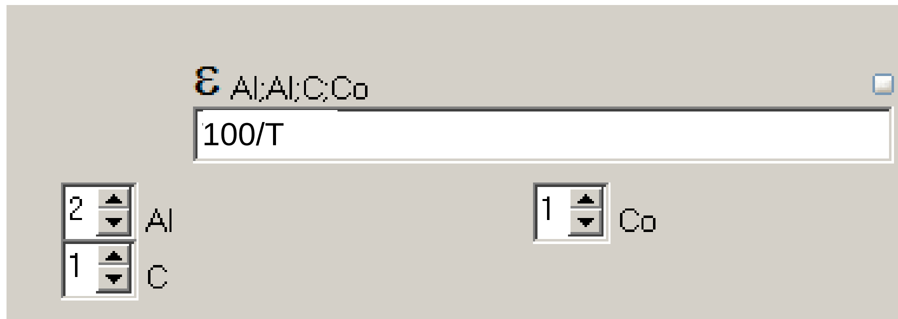
- Entry indicates that this is the first-order parameter $\varepsilon_{Al;C}$.
- <u>Note</u>: (See refs. (18, 19)) $\varepsilon_{Al;C} = \varepsilon_{C;Al}$. This single entry serves to enter both $\varepsilon_{Al;C}$ and $\varepsilon_{C;Al}$.

Entry of second-order parameter $\varepsilon_{Al;Al;C}$



- Entry indicates the second-order parameter $\varepsilon_{Al;Al;C}$.
- <u>Note</u>: $\varepsilon_{Al;Al;C} = \varepsilon_{Al;C;Al} = \varepsilon_{C;Al;Al}$. This single entry serves to enter all permutations.

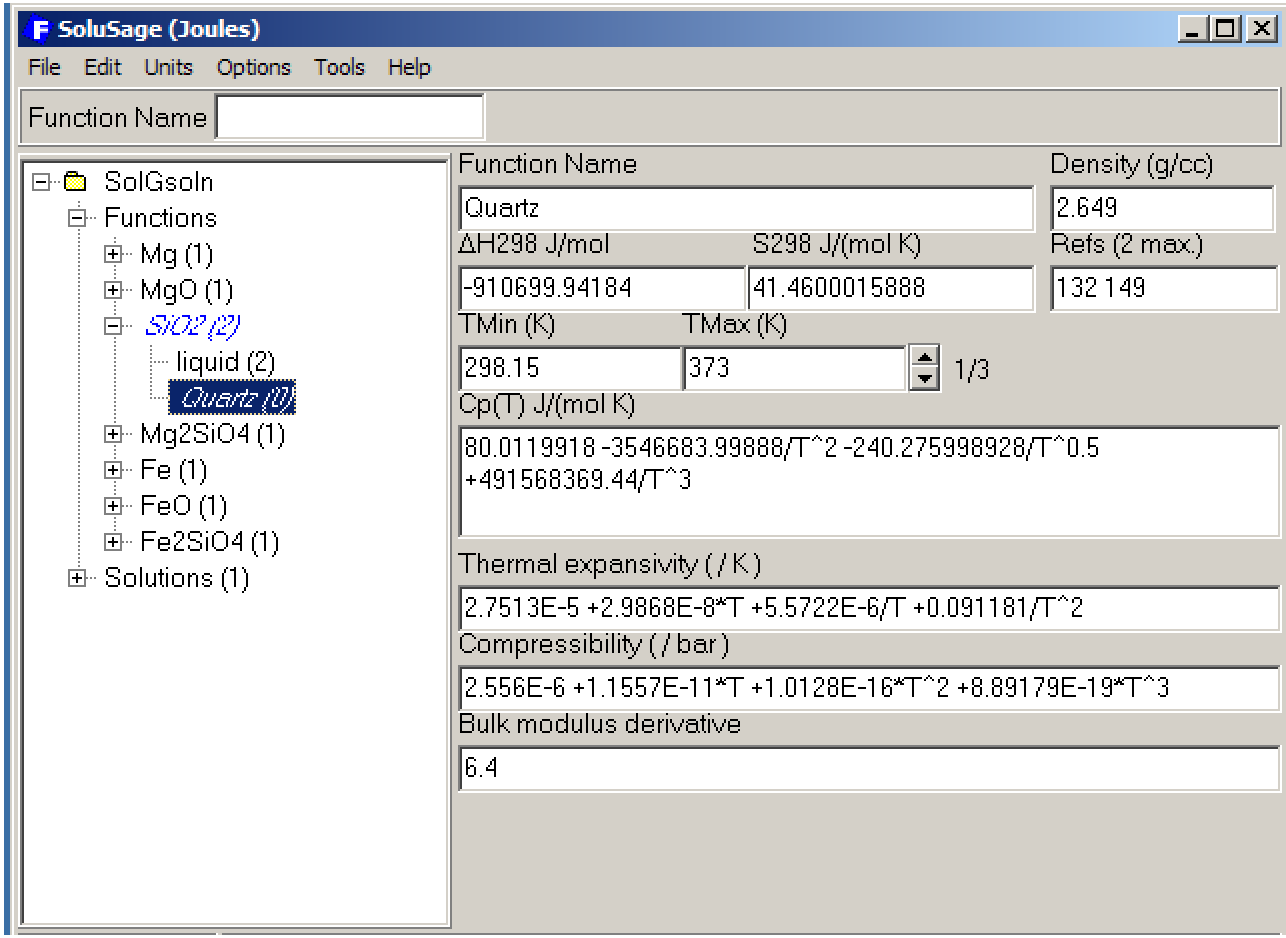
Entry of cross-interaction parameter $\varepsilon_{Al;Al;C;Co}$



$\varepsilon_{Al;Al;C;Co} = \varepsilon_{Al;C;Al;Co} = \varepsilon_{Co;C;Al;Al} = \ldots$ etc.
This single entry serves to enter all permutations.

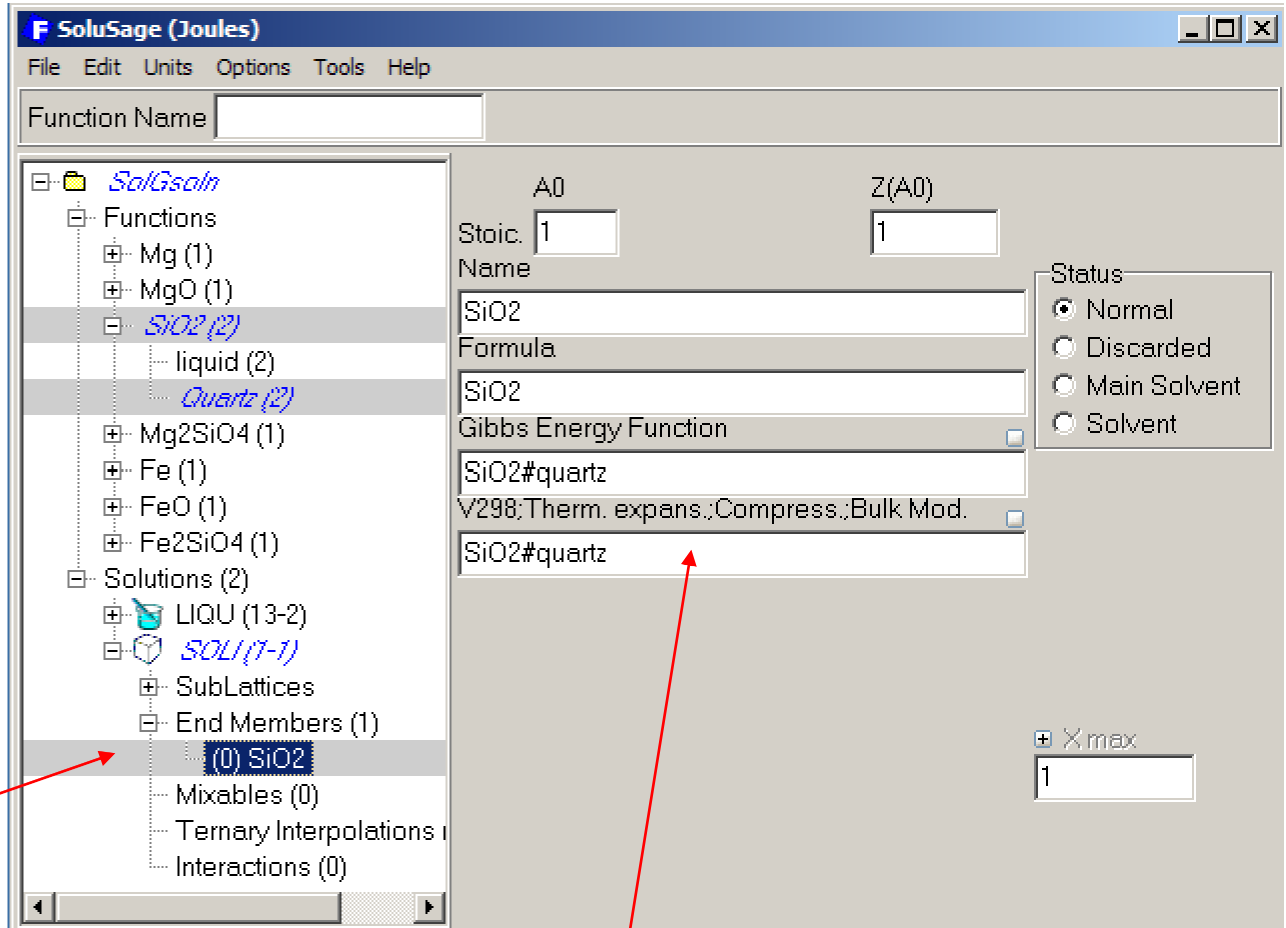
13. Entering Volumetric Data

- A <u>function</u> can contain volumetric data (density, thermal expansivity, compressibility, derivative of bulk modulus) as well as H, S and Cp.



- This is an example of a function SiO2#quartz copied (see Slide 1.3) from a compound database.

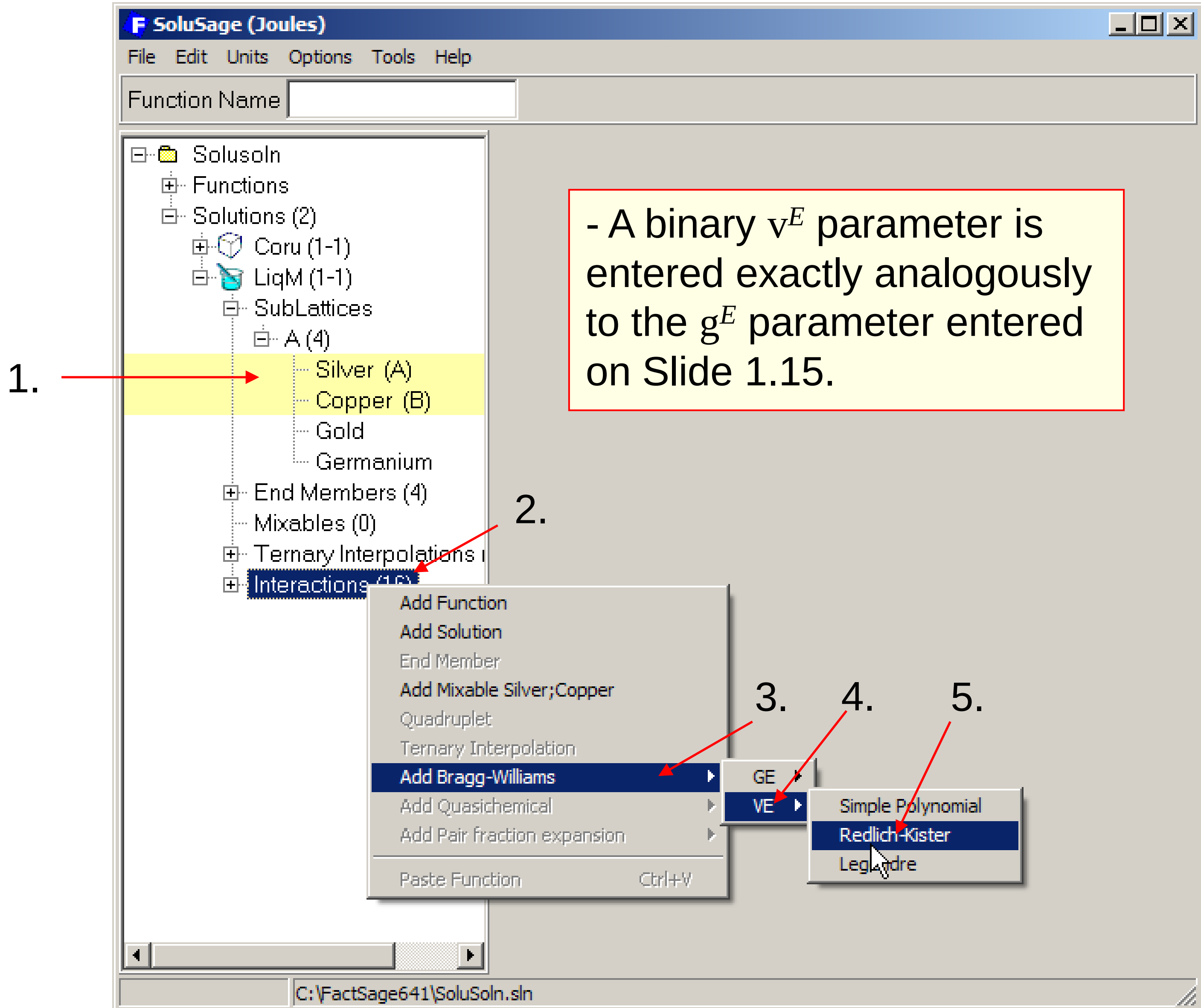
Specifying volumetric data for an end-member



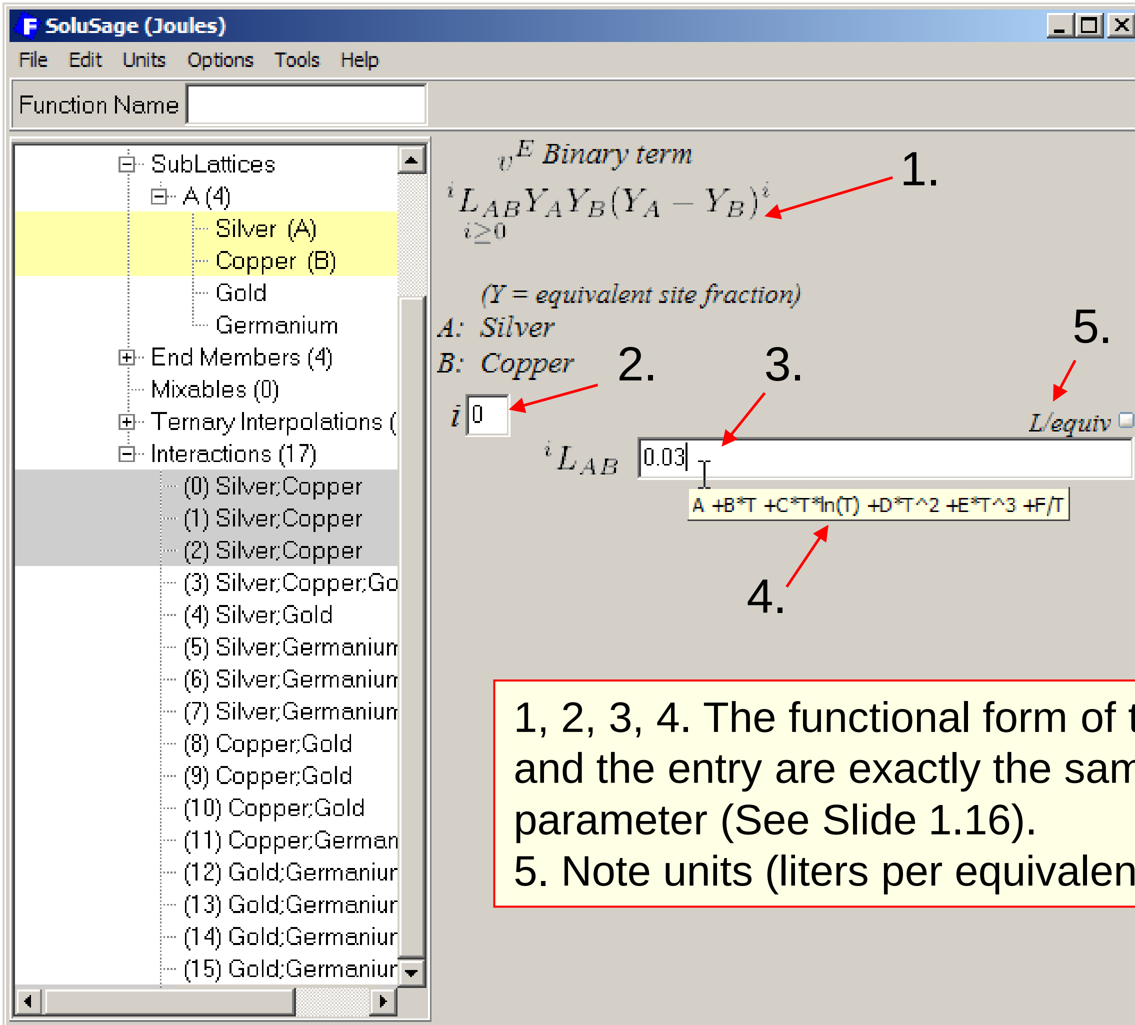
End-member

- By entering a function (or sum of functions) here, one specifies that the volumetric properties of the end-member are to be taken from this function (or sum of functions).
- It is not necessary to specify the same function(s) for the volumetric properties and the Gibbs energy.

Entering an excess molar volume parameter



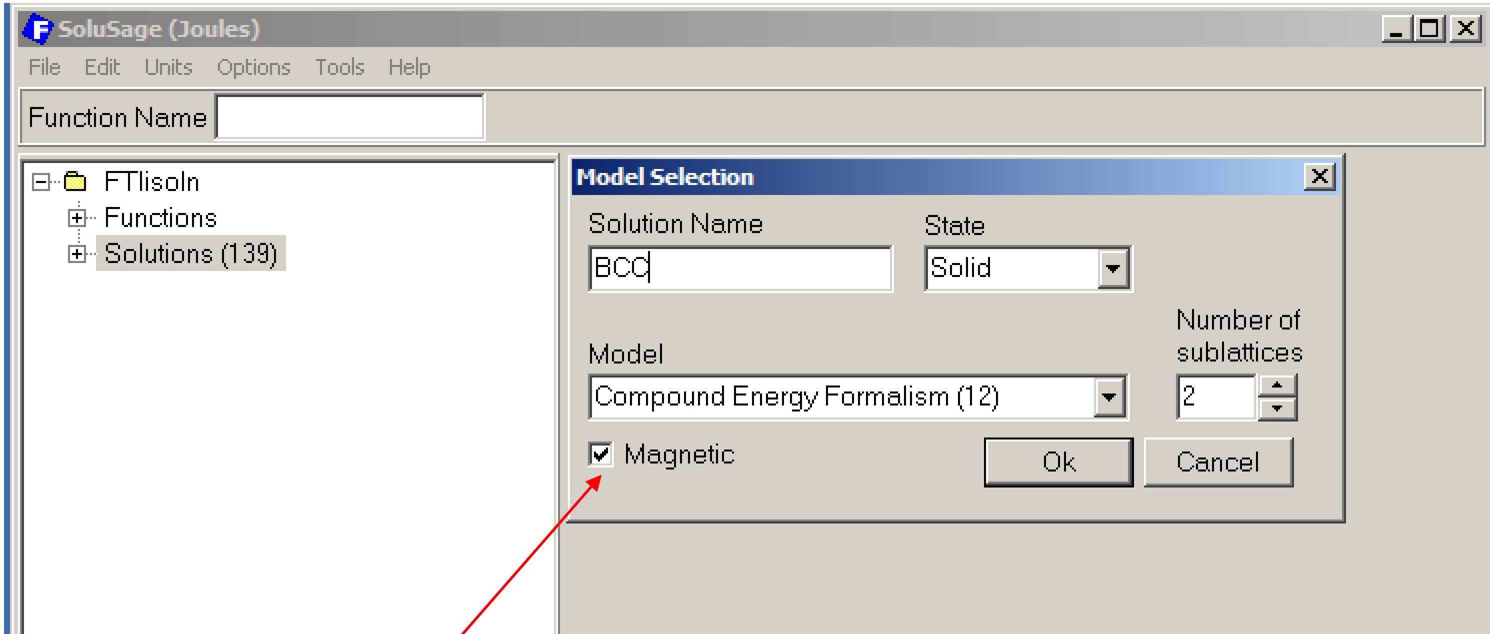
- A binary v^E parameter is entered exactly analogously to the g^E parameter entered on Slide 1.15.



1, 2, 3, 4. The functional form of the parameter and the entry are exactly the same as for the g^E parameter (See Slide 1.16).
5. Note units (liters per equivalent or per mole).

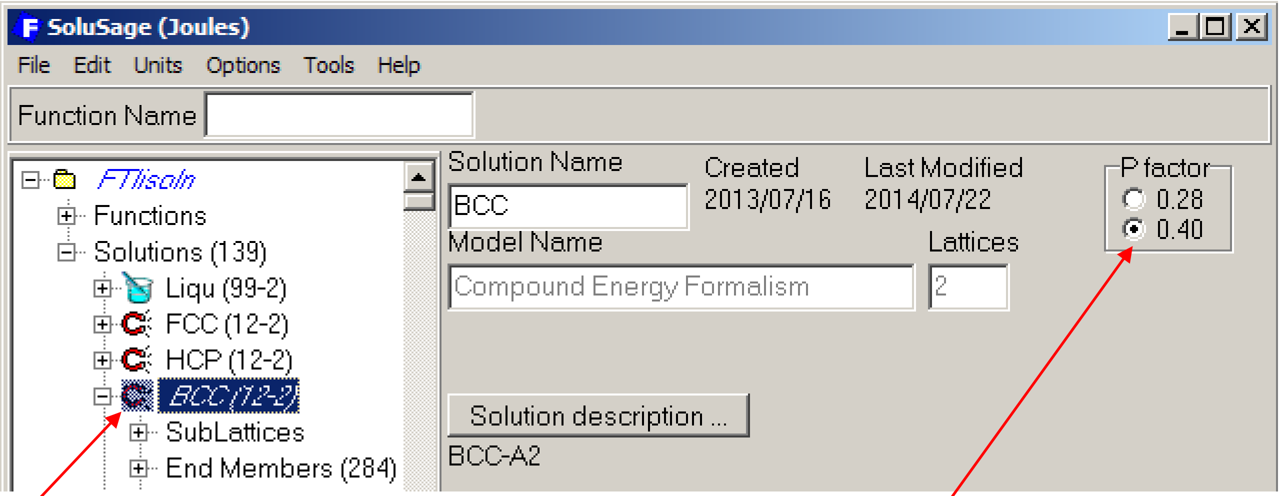
- For <u>all models</u>, the v^E parameters have the same functional forms as the g^E parameter except for the Unified Interaction Parameter Formalism (Section 12) where v^E terms are not accepted.

14. Magnetic Phases (See COMPOUND slide show, Slide 4.5)



When entering a new solution phase (see Slides 1.5-1.6) click here if the phase is magnetic.

- (If the "state" has been chosen as "Liquid", then magnetic terms will not be accepted.)
- (Magnetic terms are not accepted for the Ionic Liquid Model nor for the one-sublattice polynomial model.)

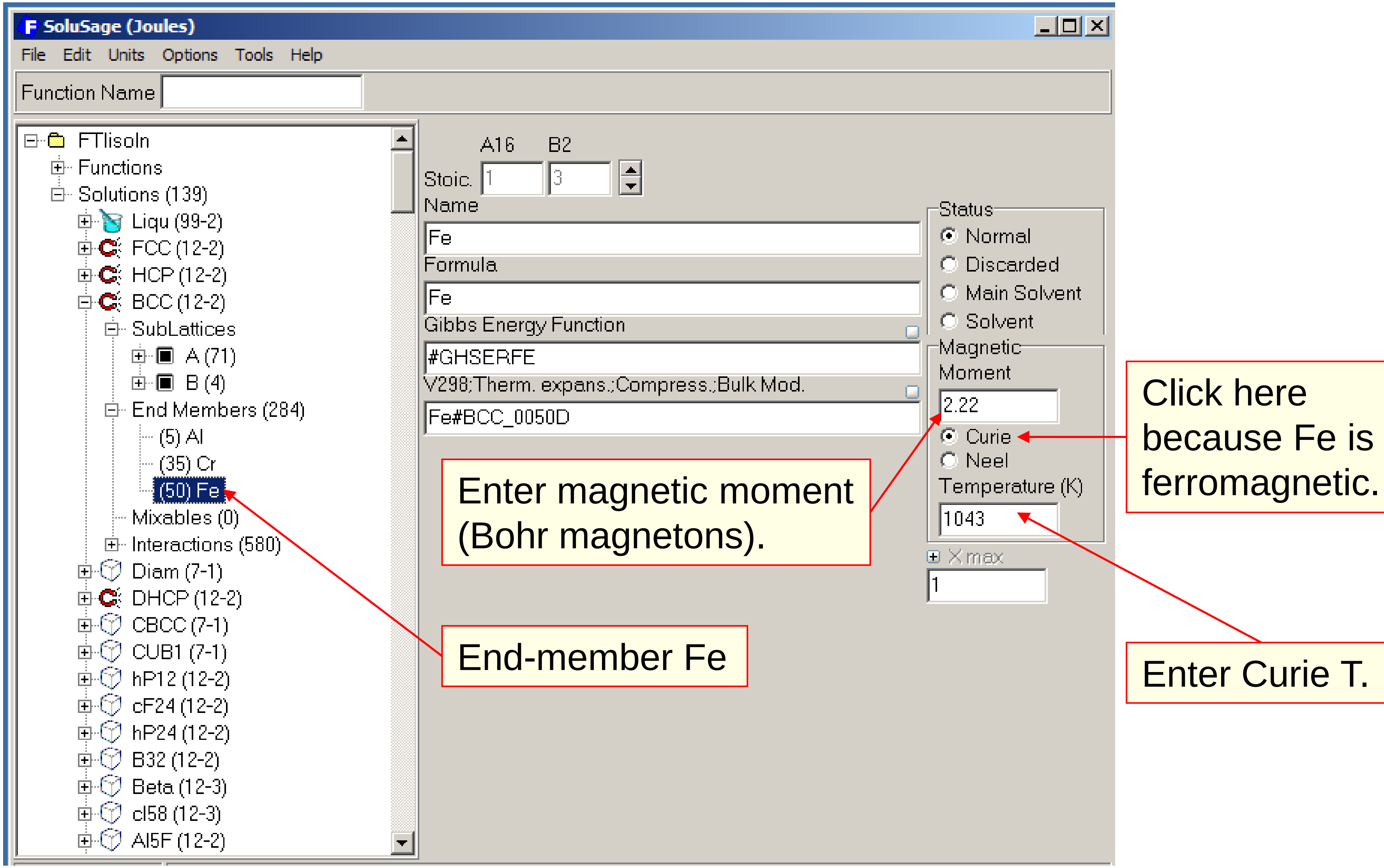


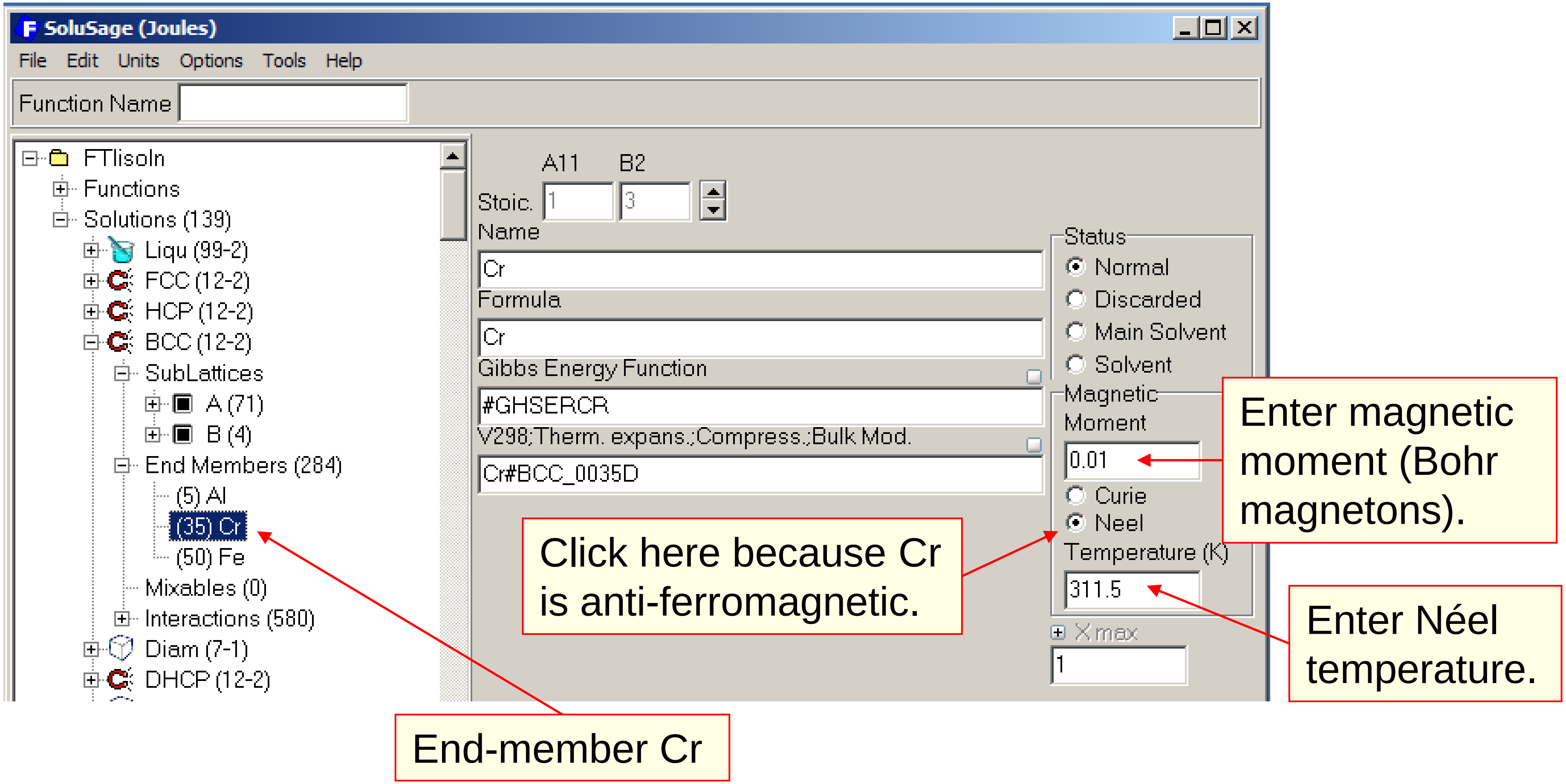
The magnet symbol indicates a magnetic phase.

- Enter the P factor for the phase (0.4 for bcc, 0.28 for fcc).

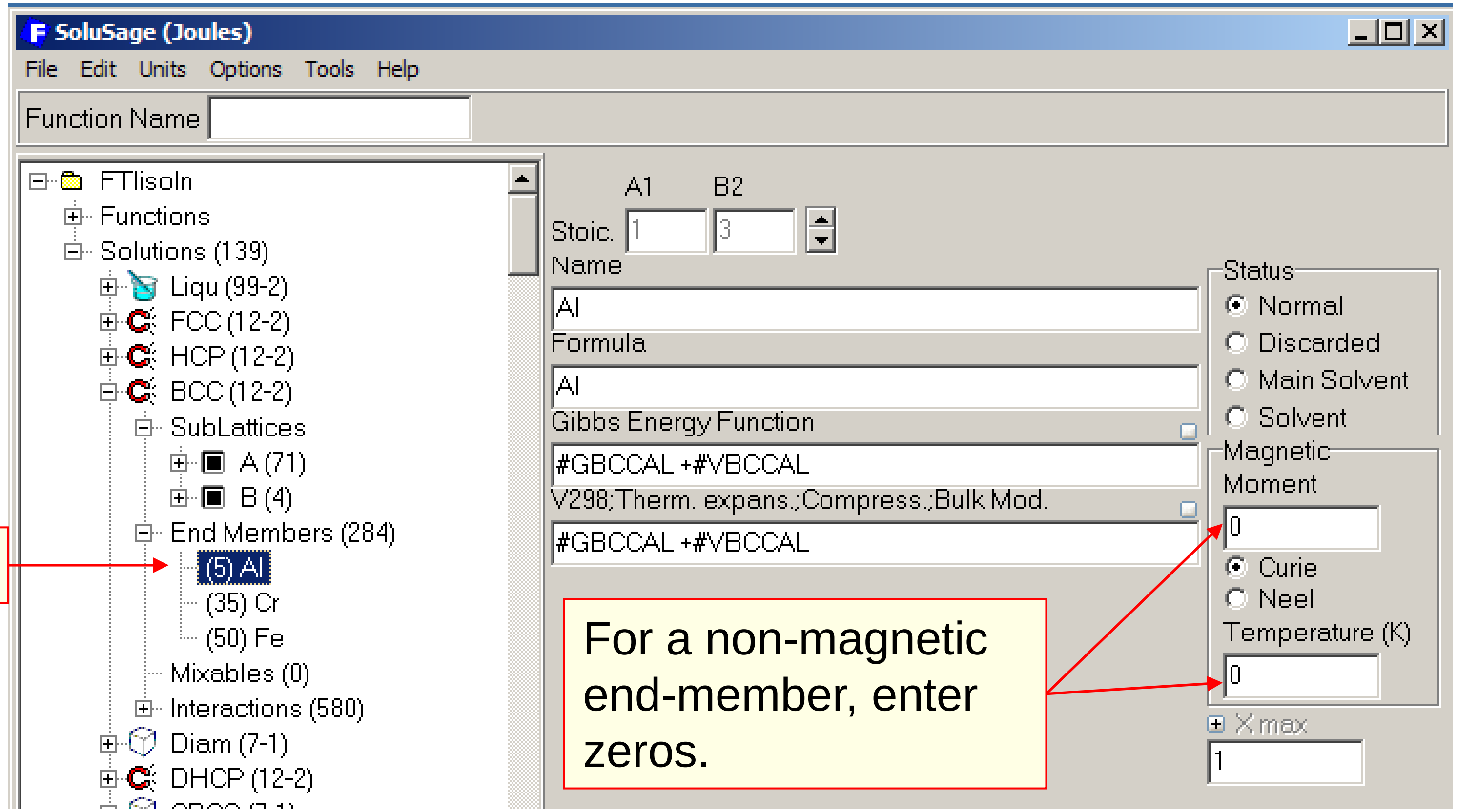
Entering magnetic properties of end-members

(Note: Magnetic properties are not included in functions)



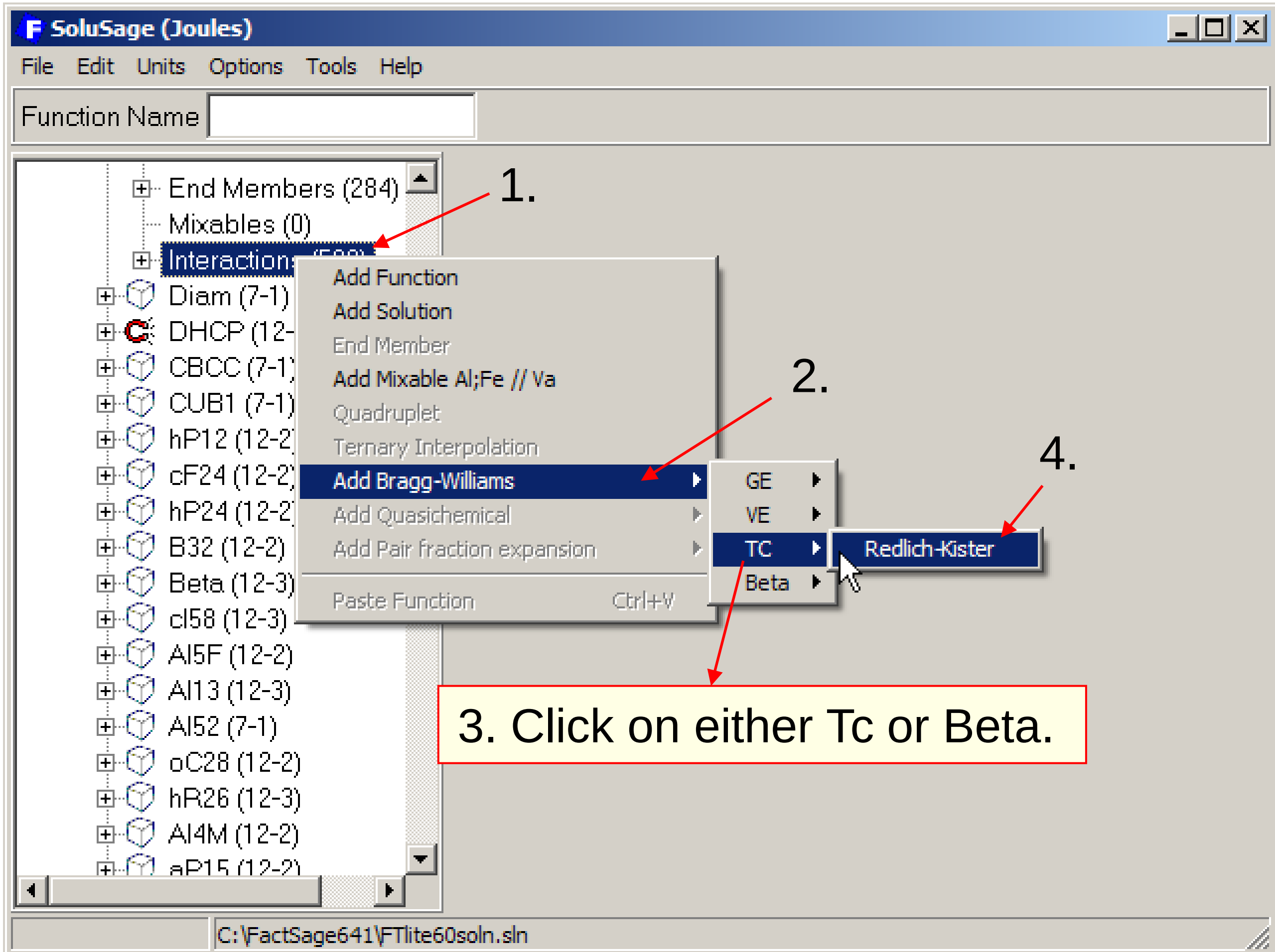

SoluSage (Joules)
File Edit Units Options Tools Help
Function Name
FTlisoln
Functions
Solutions (139)
Liqu (99-2)
FCC (12-2)
HCP (12-2)
BCC (12-2)
SubLattices
A (71)
B (4)
End Members (284)
(5) Al
(35) Cr
(50) Fe
Mixables (0)
Interactions (580)
Diam (7-1)
DHCP (12-2)
A11 B2
Stoic. 1 3
Name
Cr
Formula
Cr
Gibbs Energy Function
#GHSERCR
V298;Therm. expans.;Compress.;Bulk Mod.
Cr#BCC_0035D
Status
Normal
Discarded
Main Solvent
Solvent
Magnetic
Moment
0.01
Curie
Neel
Temperature (K)
311.5
X max
1
Enter magnetic moment (Bohr magnetons).
Click here because Cr is anti-ferromagnetic.
Enter Néel temperature.
End-member Cr

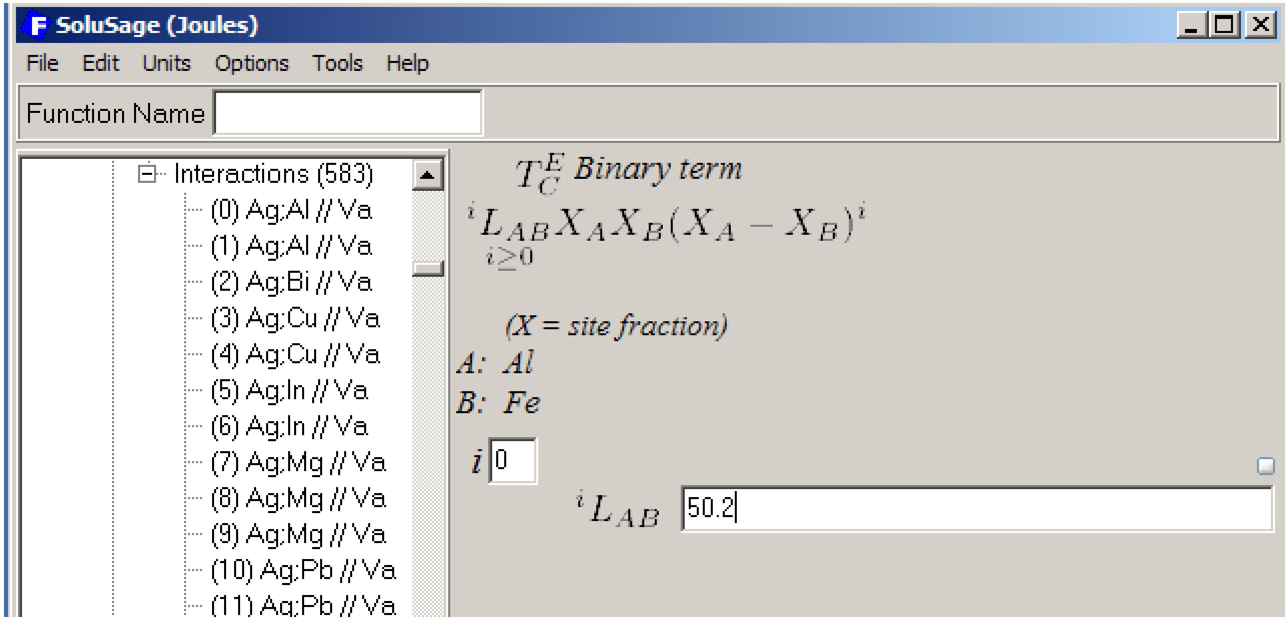
End-member Al



For a non-magnetic end-member, enter zeros.

Entering interaction parameters for excess critical temperature Tc and excess magnetic moment beta (β)





For <u>all</u> models, the Tc and β interaction parameters are always in Redlich-Kister form, are in terms of site fractions X*i* (never in terms of equivalent fractions Y*i*), and the ternary interpolations of the binary parameters are always via the Muggianu configuration.

15. Editing sub-groups of species

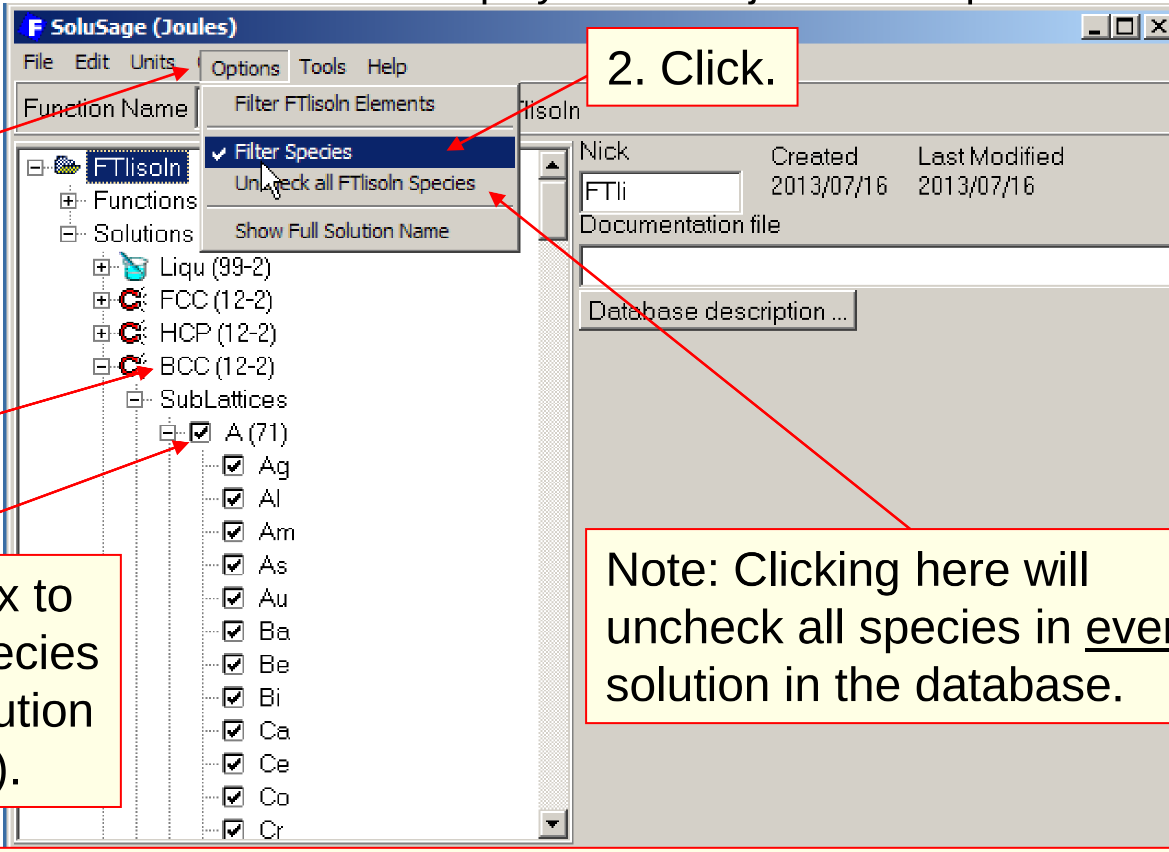
Editing a solution with a large number of species can be tedious if one is constantly obliged to hunt down relevant species, end-members and interactions from long lists. To relieve this tedium, provision is made to limit the displayed lists to just those species of interest for editing.

1. Click.

2. Click.

3. Click.

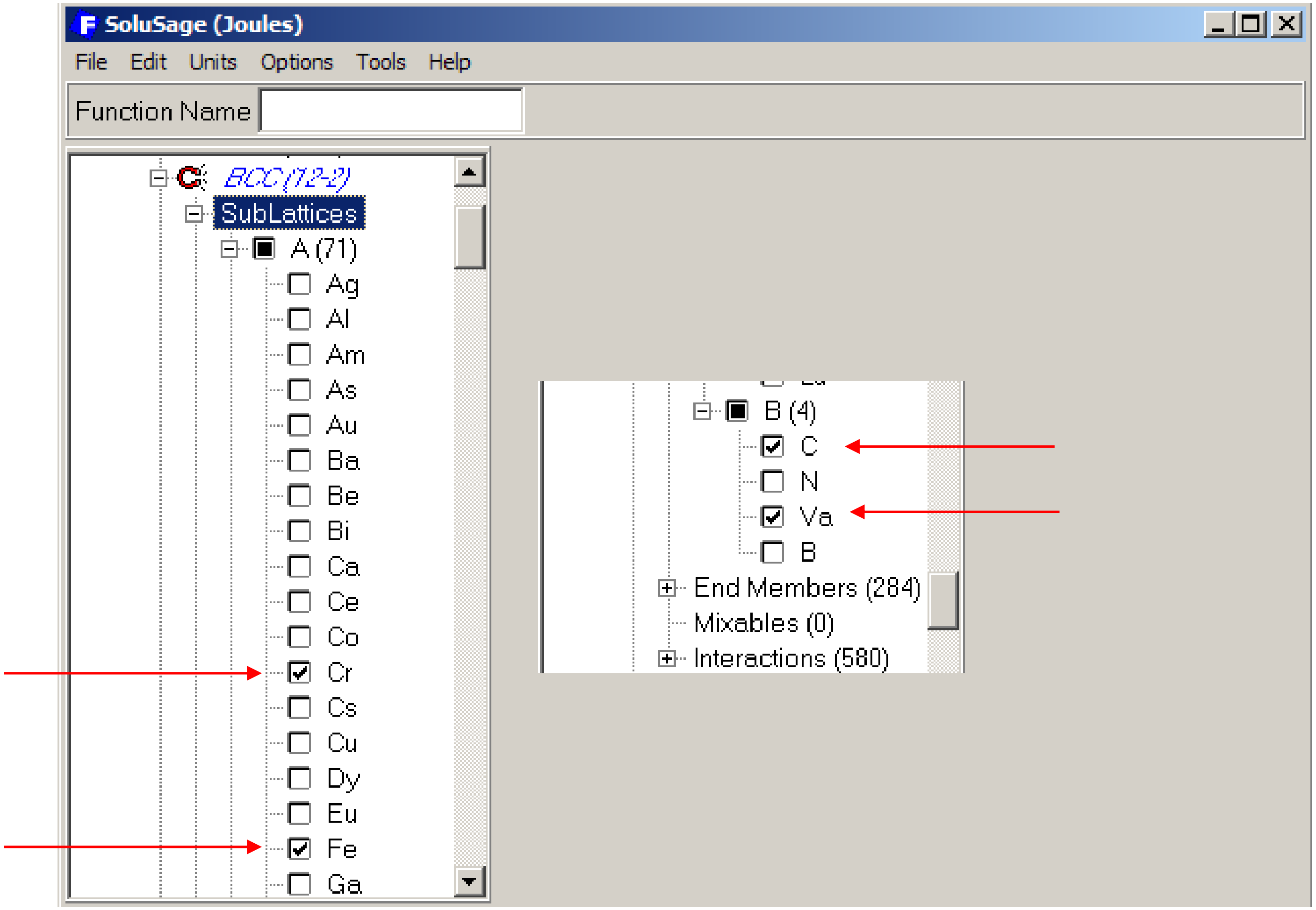
4. Click this box to <u>uncheck</u> all species in the BCC solution (see next slide).



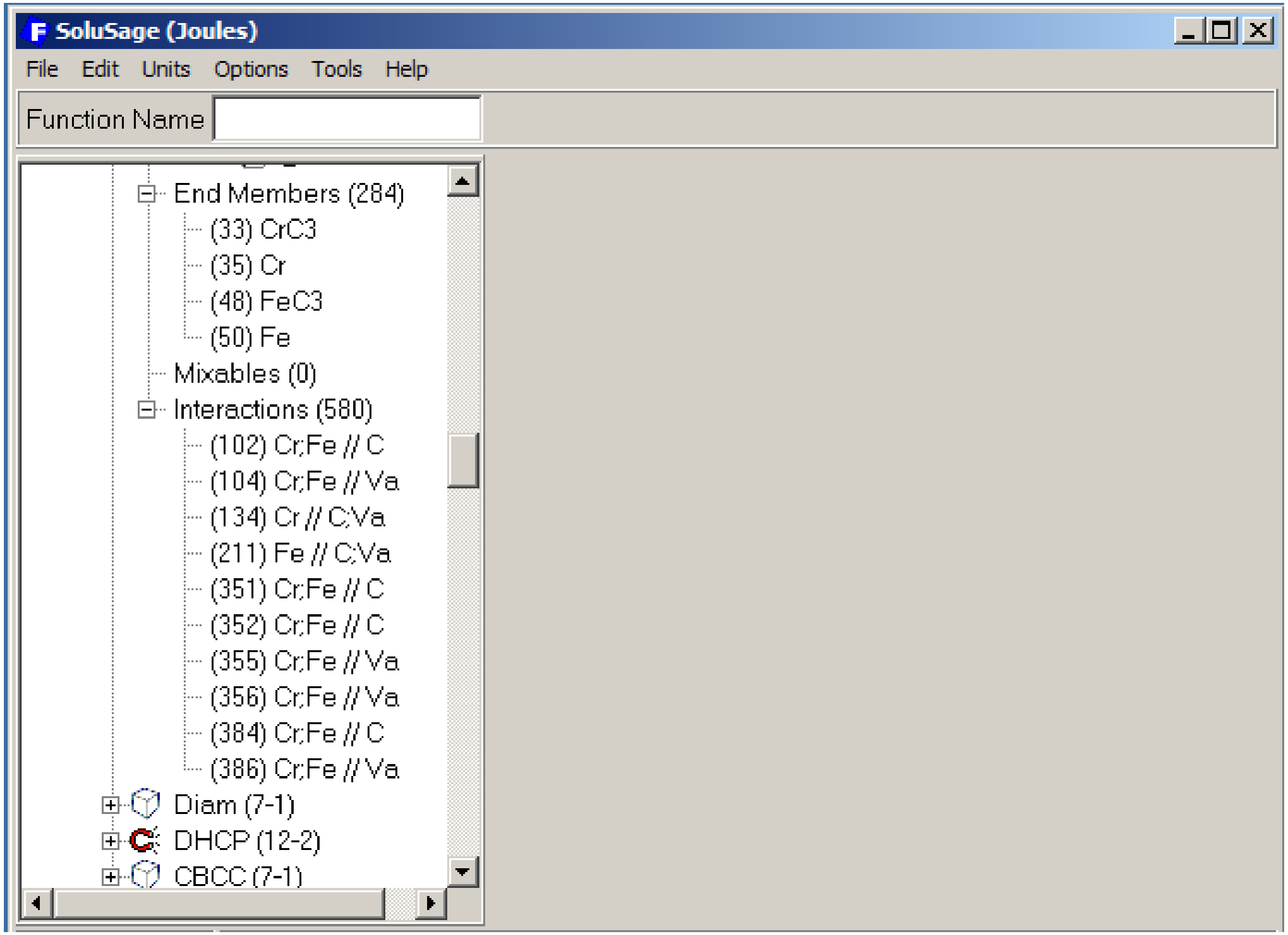
Note: Clicking here will uncheck all species in <u>every</u> solution in the database.

- In this example, one wishes to edit just those end-members and interactions in a bcc solution which contain Fe and Cr on one sublattice and Va and C on the other.
- Click 1,2,3,4.

Select the species of interest

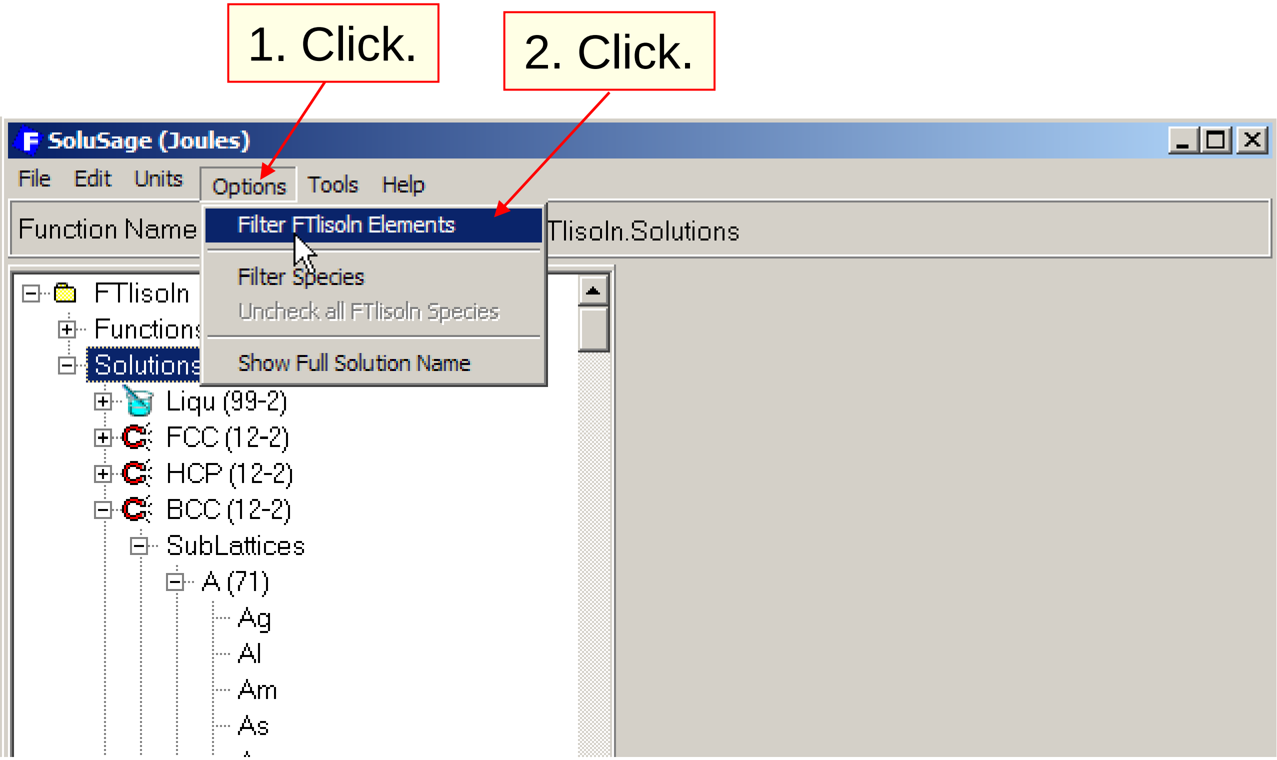


All species in the BCC solution have now been unchecked. Select just those of interest.



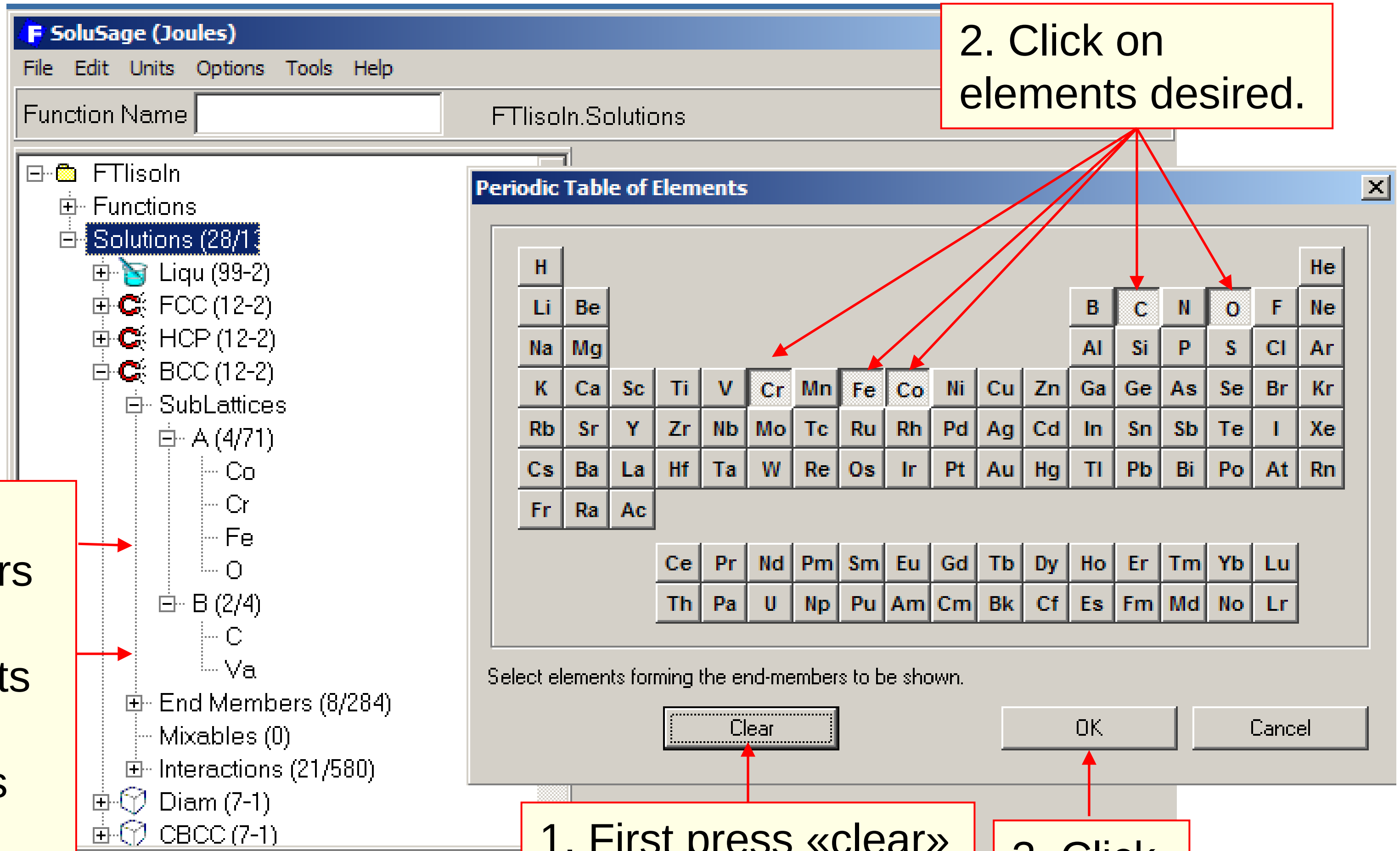
Only end-members and interactions involving the selected species are displayed.

It is also possible to filter by selecting only those elements of interest



Example: Selecting only those species, end-members, functions, etc. involving the elements Cr, Fe, Co, C and O

Note: This filtering will apply to all solutions in the database.



1. First press «clear» to de-select all elements.

2. Click on elements desired.

3. Click.

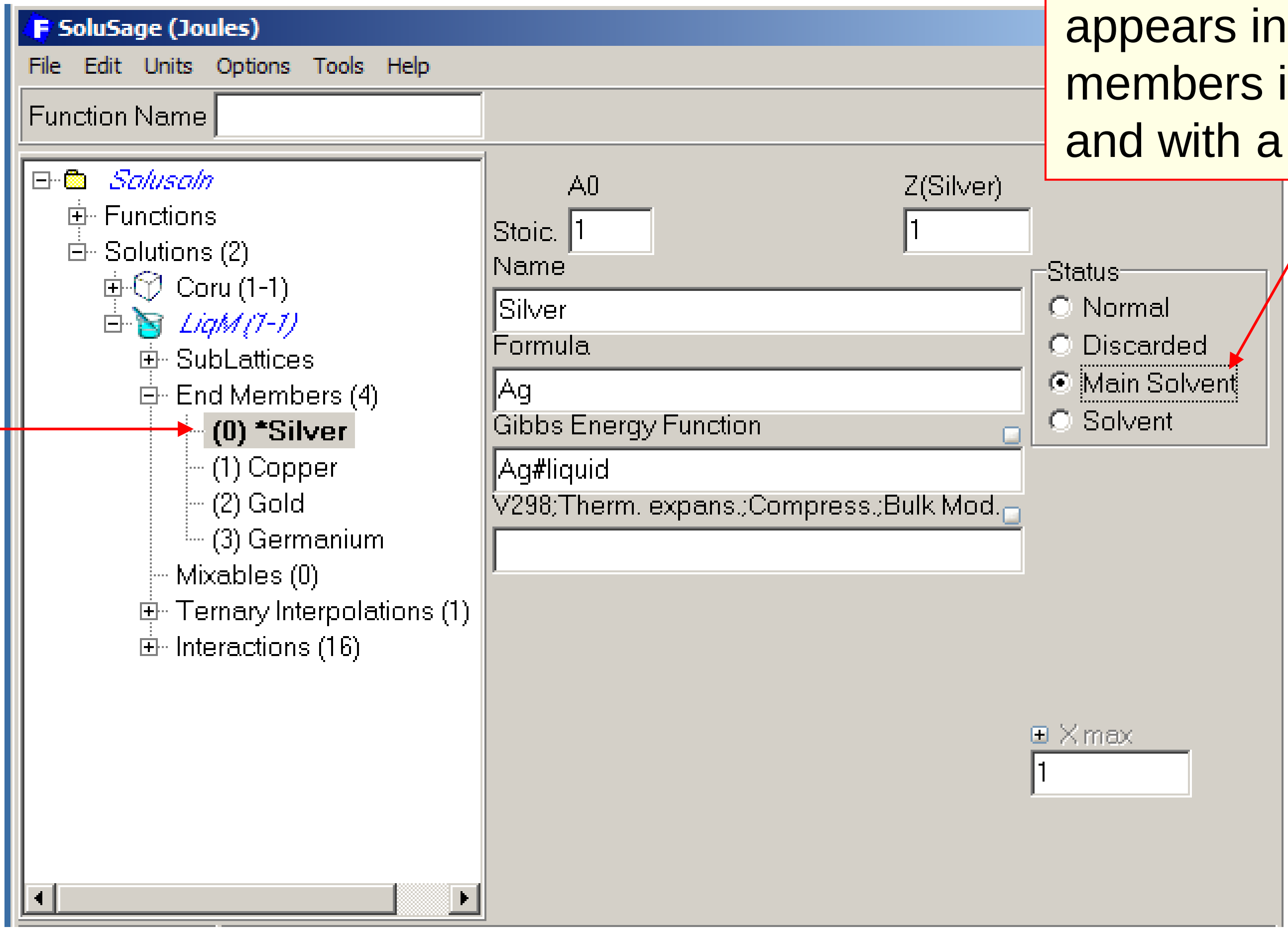
4. Only species and end-members involving the selected elements are displayed. (Note: Vacancies remain.)

16. The status options

Main solvent

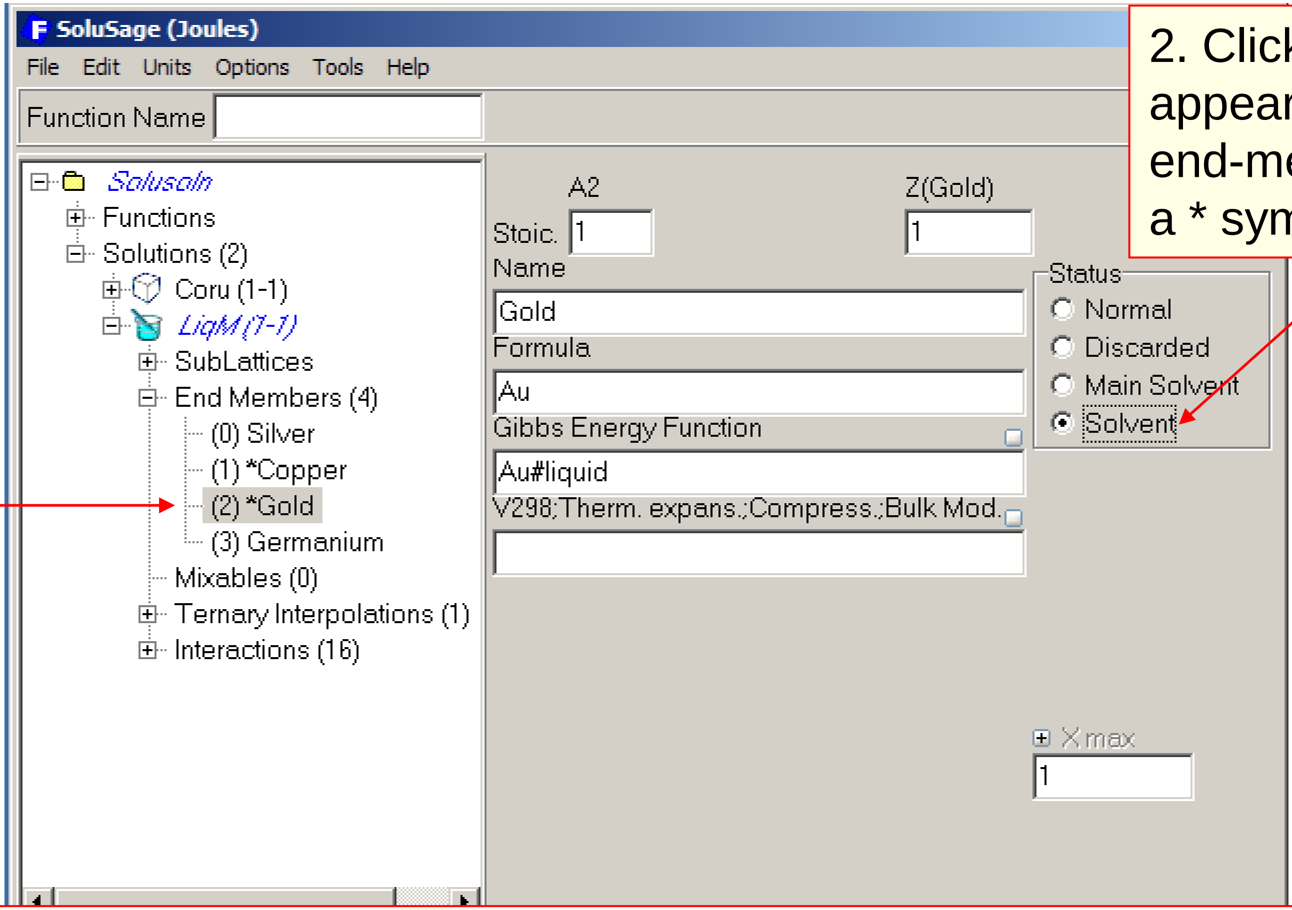
2. Click (Silver now appears in the list of end-members in bold type and with a * symbol).

1. Click.



In this example, Ag is selected as the «<u>Main solvent</u>» of the LiqM solution. When the EQUILIB or PHASE DIAGRAM programs are run, the LiqM solution will not appear as a possible output phase on the Menu window unless Ag is present.

The status option - solvent



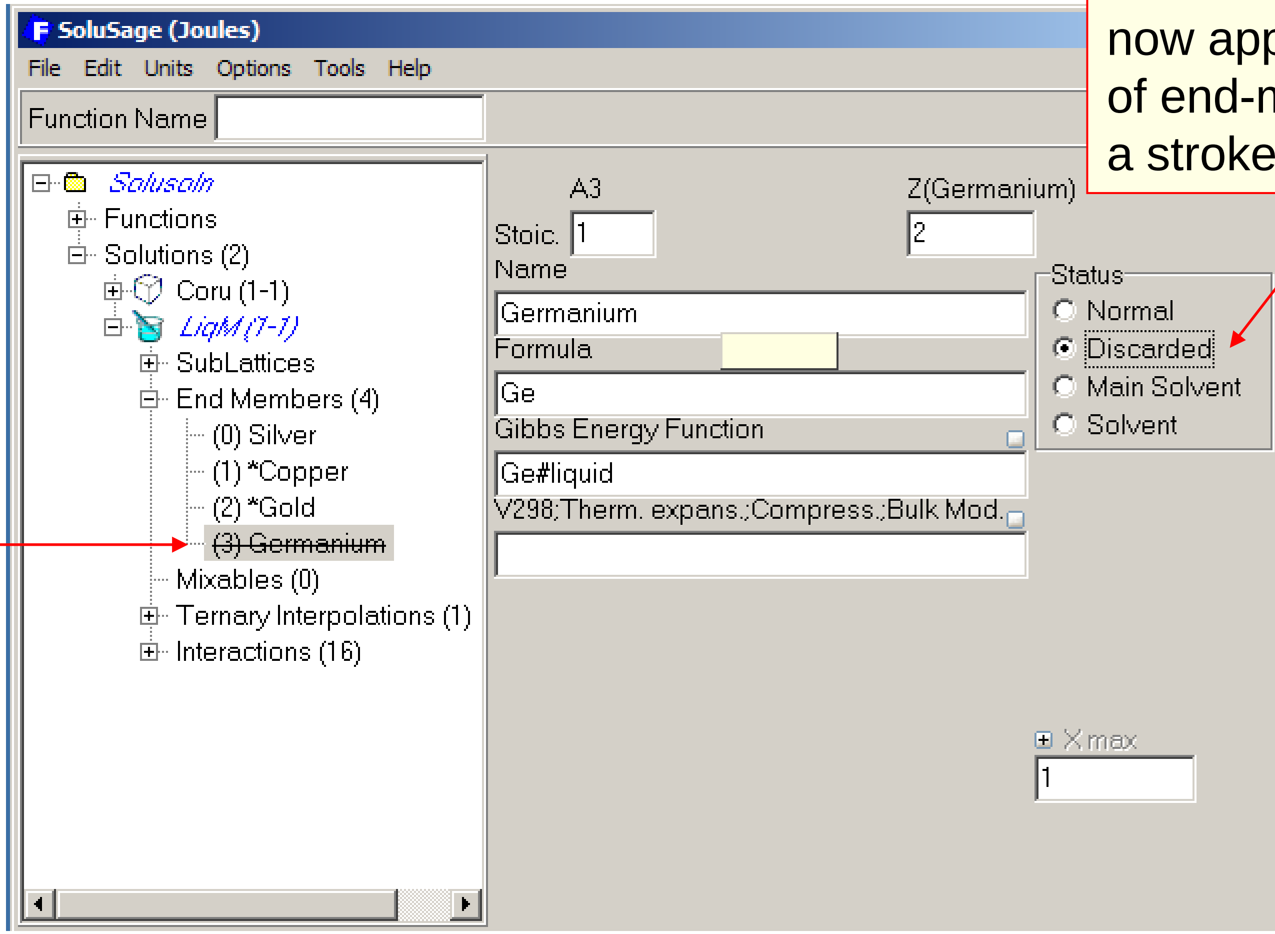
1. Click.

2. Click (Gold now appears in the list of end-members with a * symbol).

- Repeat steps 1. and 2. with the copper end-member.
- In this example, Au and Cu are selected as «solvents» of the LiqM solution. When the EQUILIB or PHASE DIAGRAM programs are run, the LiqM solution will not appear as a possible output phase on the Menu window unless at least one of Au and Cu is present.

The status option - Deleted

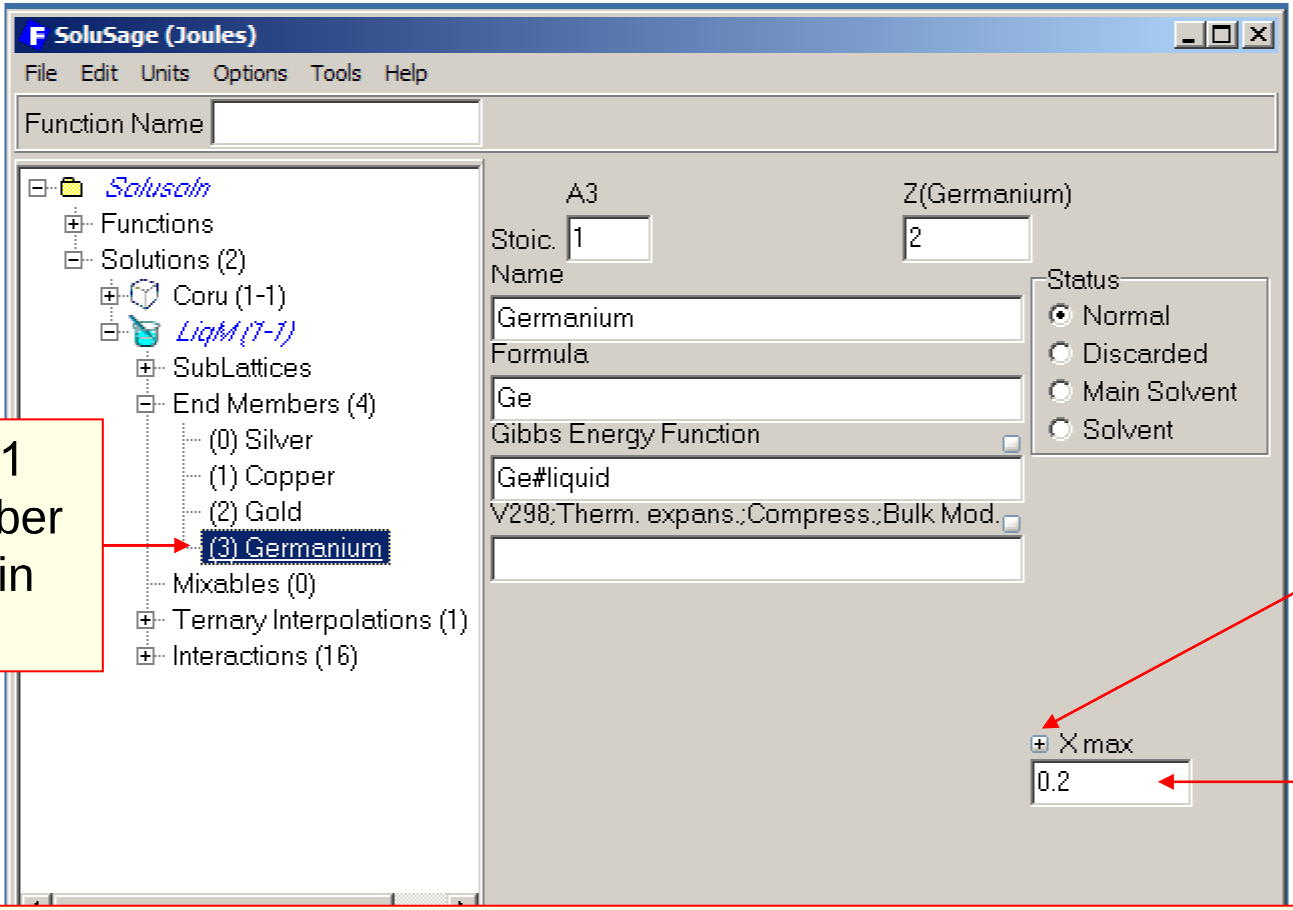
2. Click (Germanium now appears in the list of end-members with a stroke through it).



1. Click.

If you wish to remove germanium from the list of end-members but do not wish to delete it permanently, designate it as «discarded». Later, if you wish, you may reinstate it by simply changing its status back to normal.

17. Maximum and minimum compositions of end-members

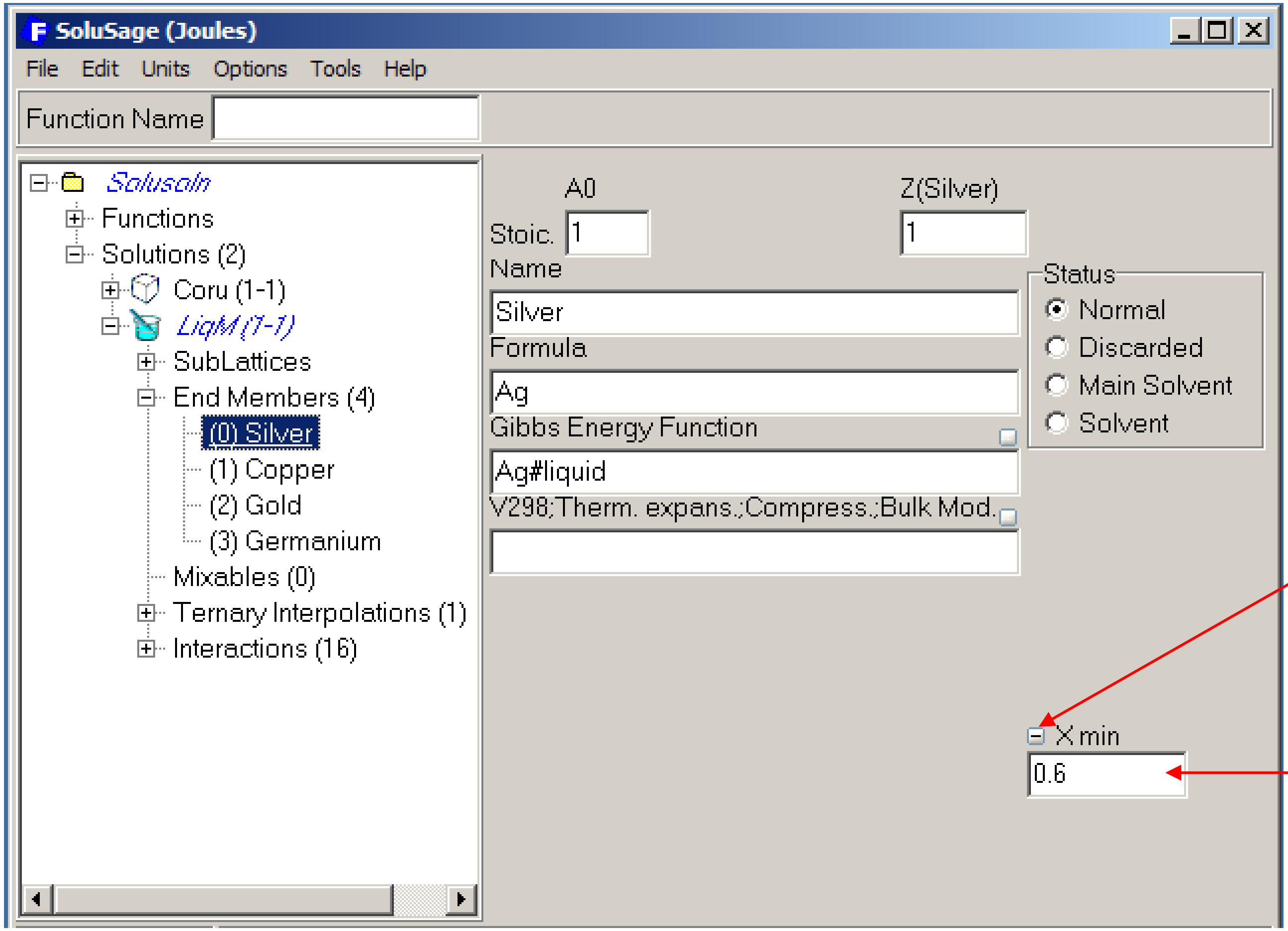


When $X_{max} \neq 1$ the end-member is underlined in the list.

1. Click.

2. Click.

- A maximum mole fraction for an end-member of a solution may be specified as shown in order to prevent the spurious appearence of the solution at compositions where the model equations extrapolate poorly. In this example, as the mole fraction of Ge exceeds 0.2, the Gibbs energy of the solution is forced to rise rapidly to a large positive value.



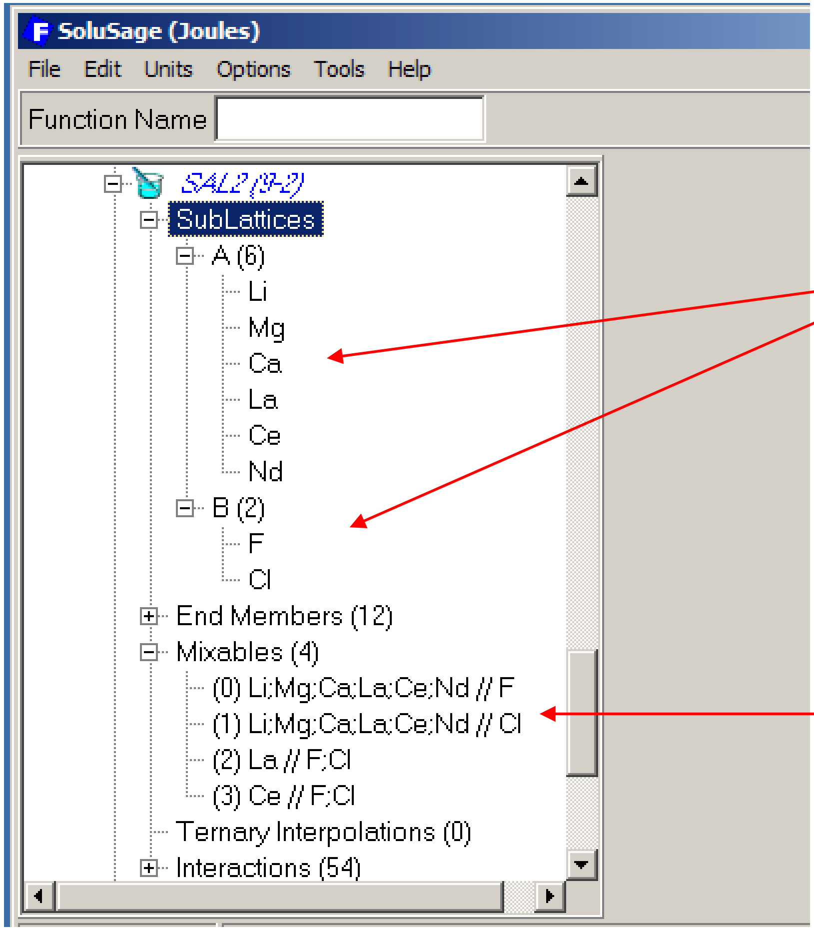
1. Click.

2. Click.

A minimum mole fraction for an end-member may also be specified.

18. Mixables

Before reading this section, go to the main FactSage window, click on Documentation → How to use the databases, and read sections 6.0 and 6.1.

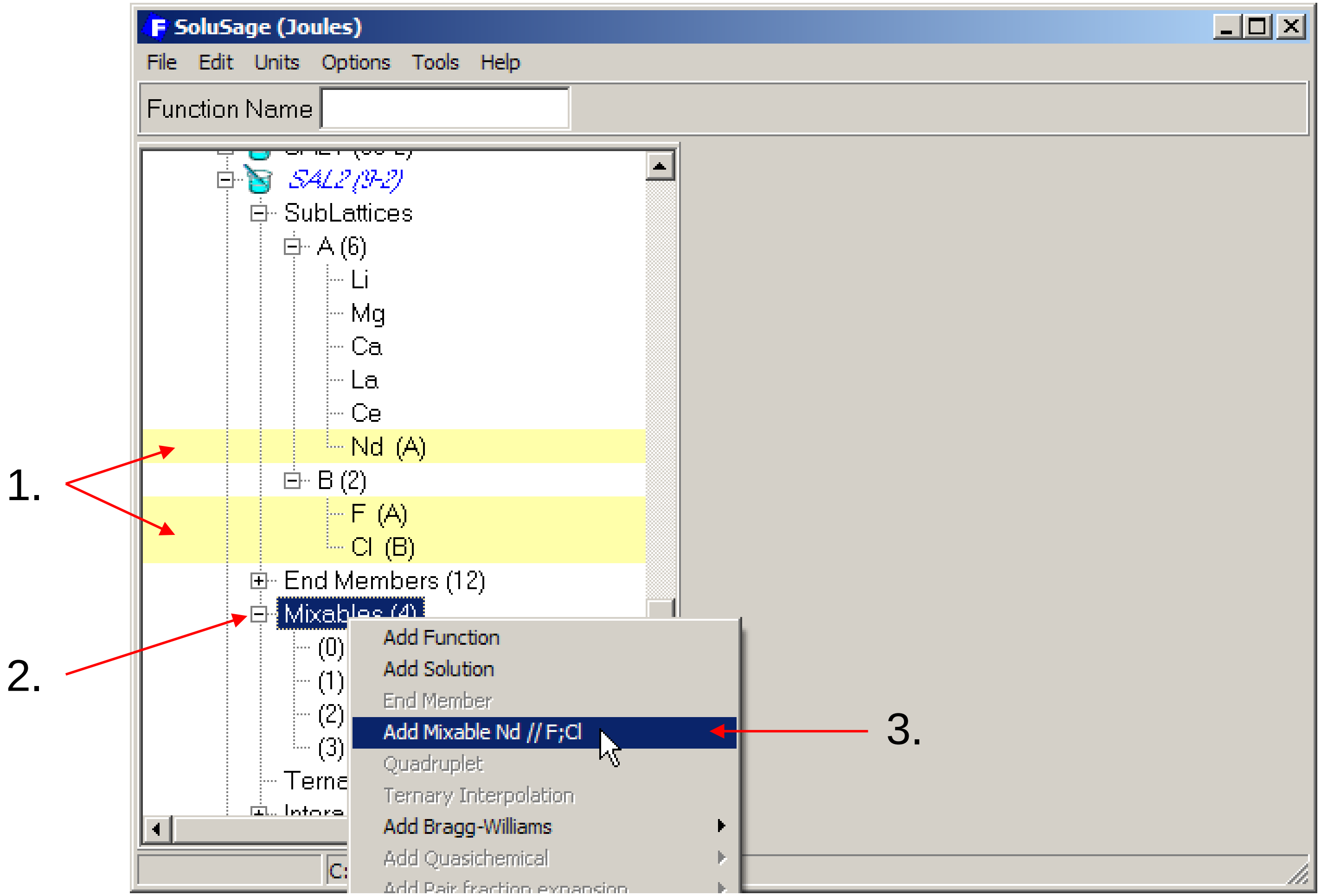


- The liquid solution SAL2 from the FTsalt database involves 6 cations and 2 anions on separate sublattice.

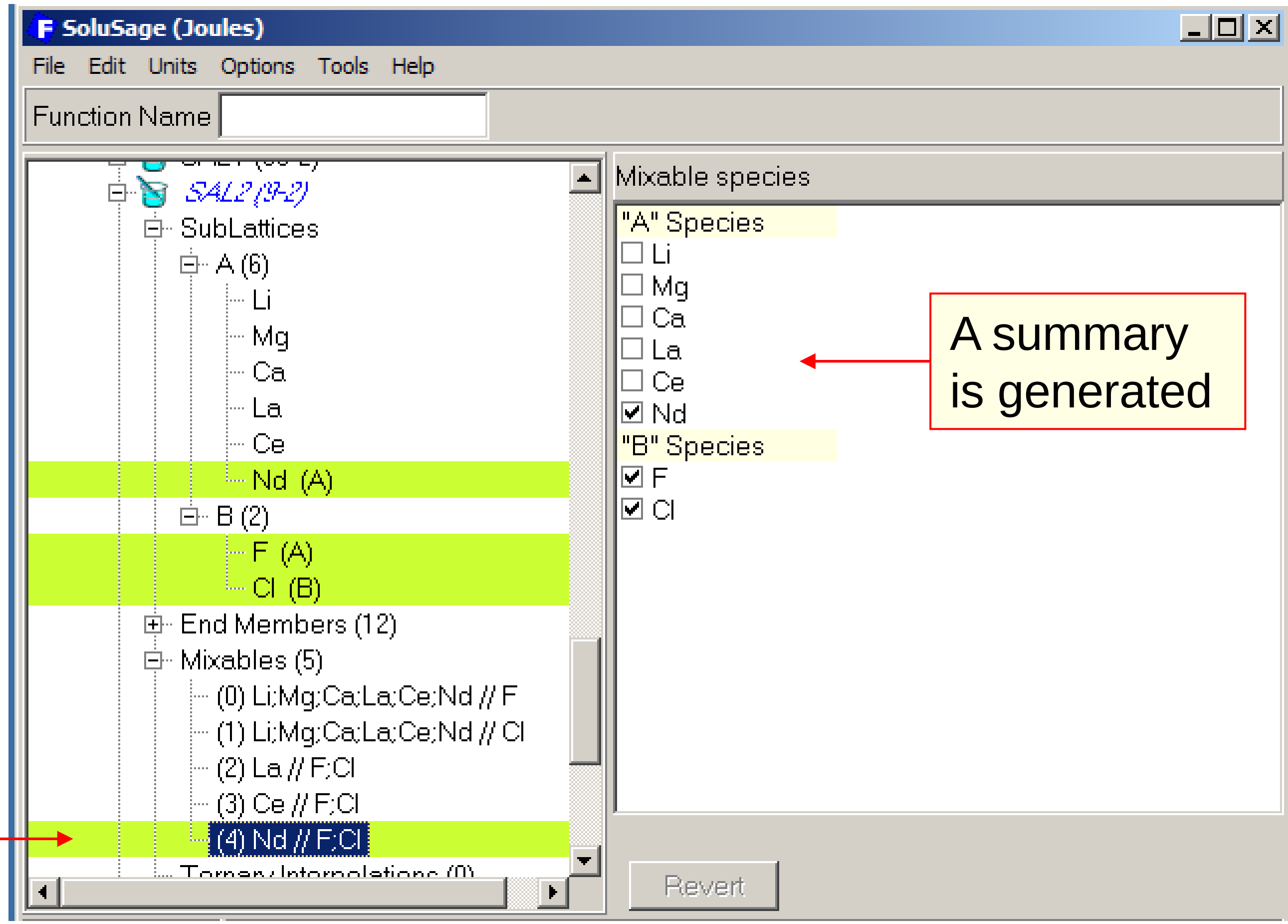
- These «mixables» are the species which will appear in the solutions FTsalt-SAL2A, FTsalt-SAL2B, FTsalt-SAL2C and FTsalt-SAL2D when the EQUILIB or PHASE DIAGRAM modules are run.

Note: If no mixables are specified, then this is equivalent to one mixable containing all species.

Adding a mixable Nd//F;Cl



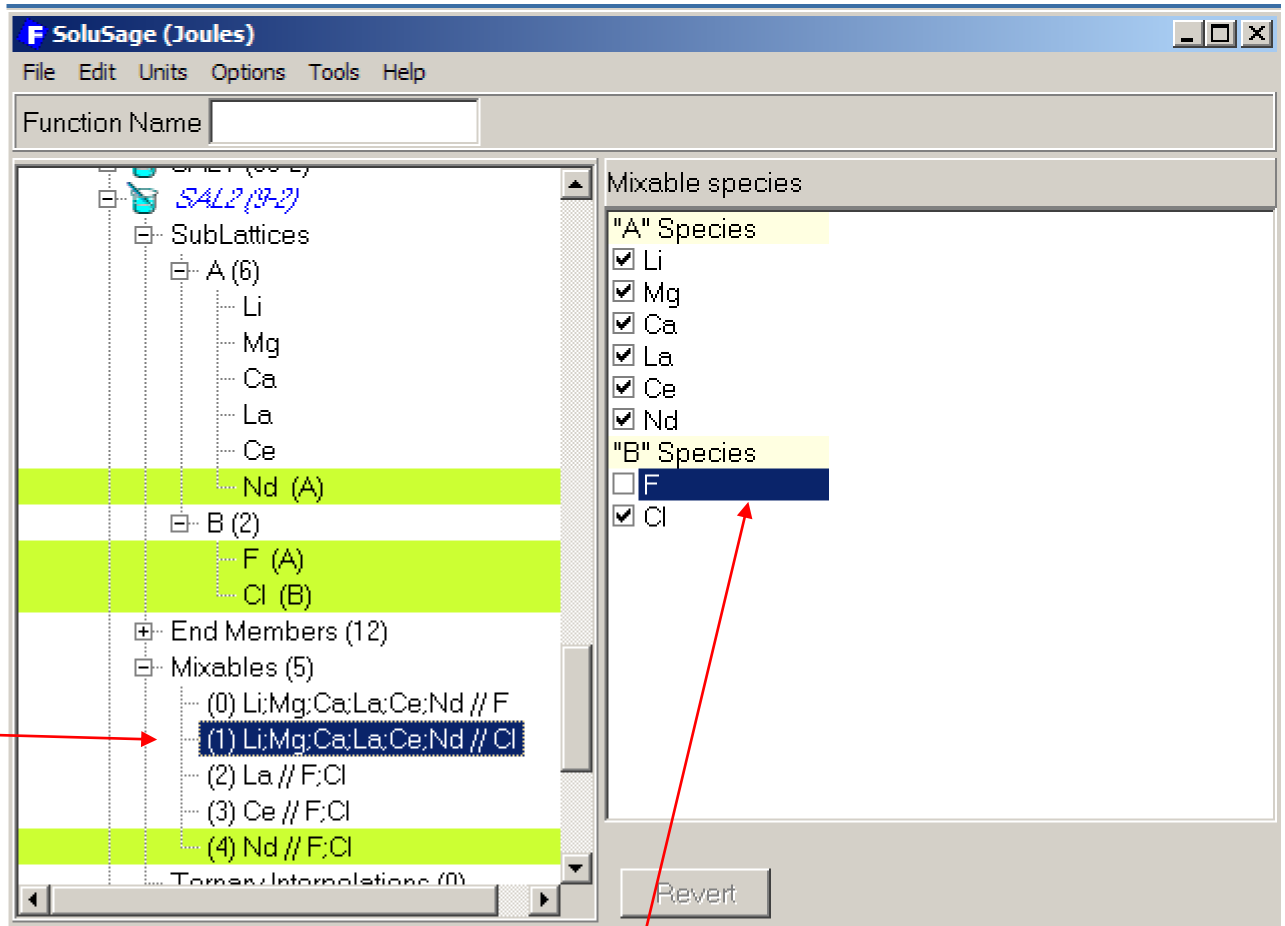
1. Holding down the Ctrl key, select the species.
2, 3. Click.



A summary is generated

A new mixable is added

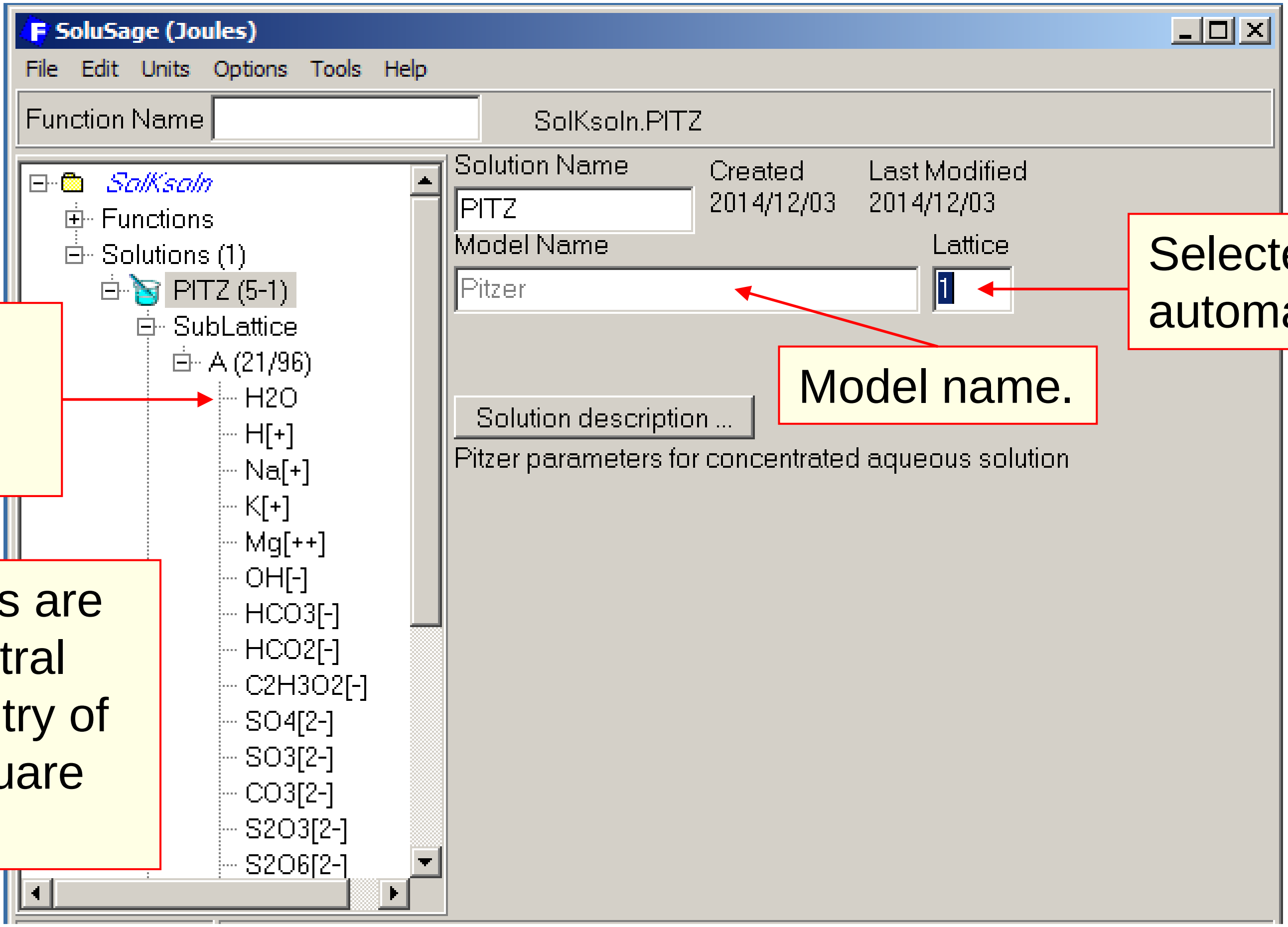
Editing a mixable



Click.

Simply click on the mixable to be edited. A summary is generated which may be edited.

PITZER Model ("Model #5") – Standard Pitzer model for relatively concentrated aqueous solutions. See refs. (20, 21)



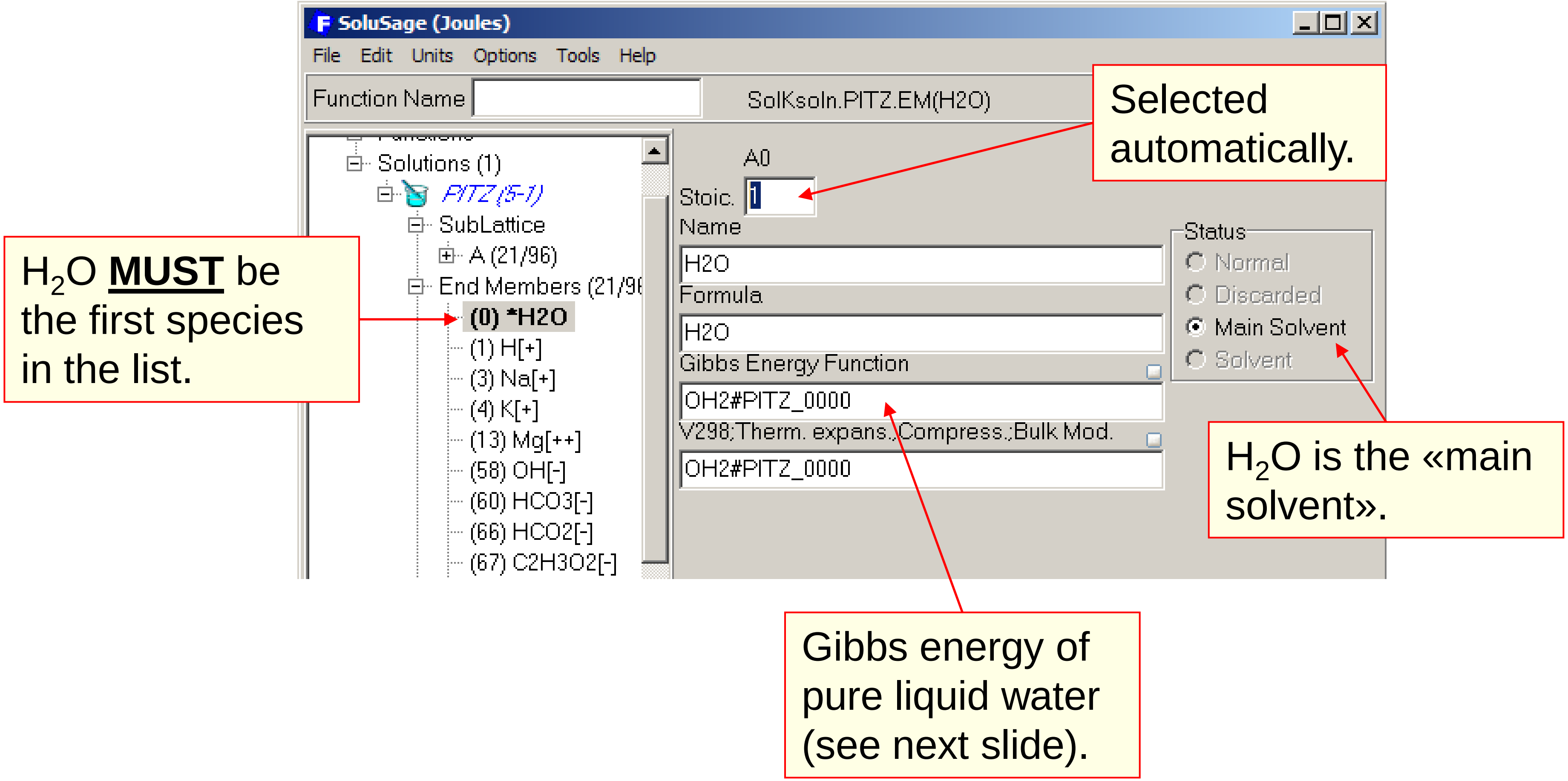
H_2O **MUST** be the first species in the list.

The other species are charged and neutral solutes. (Note entry of charge inside square parentheses.)

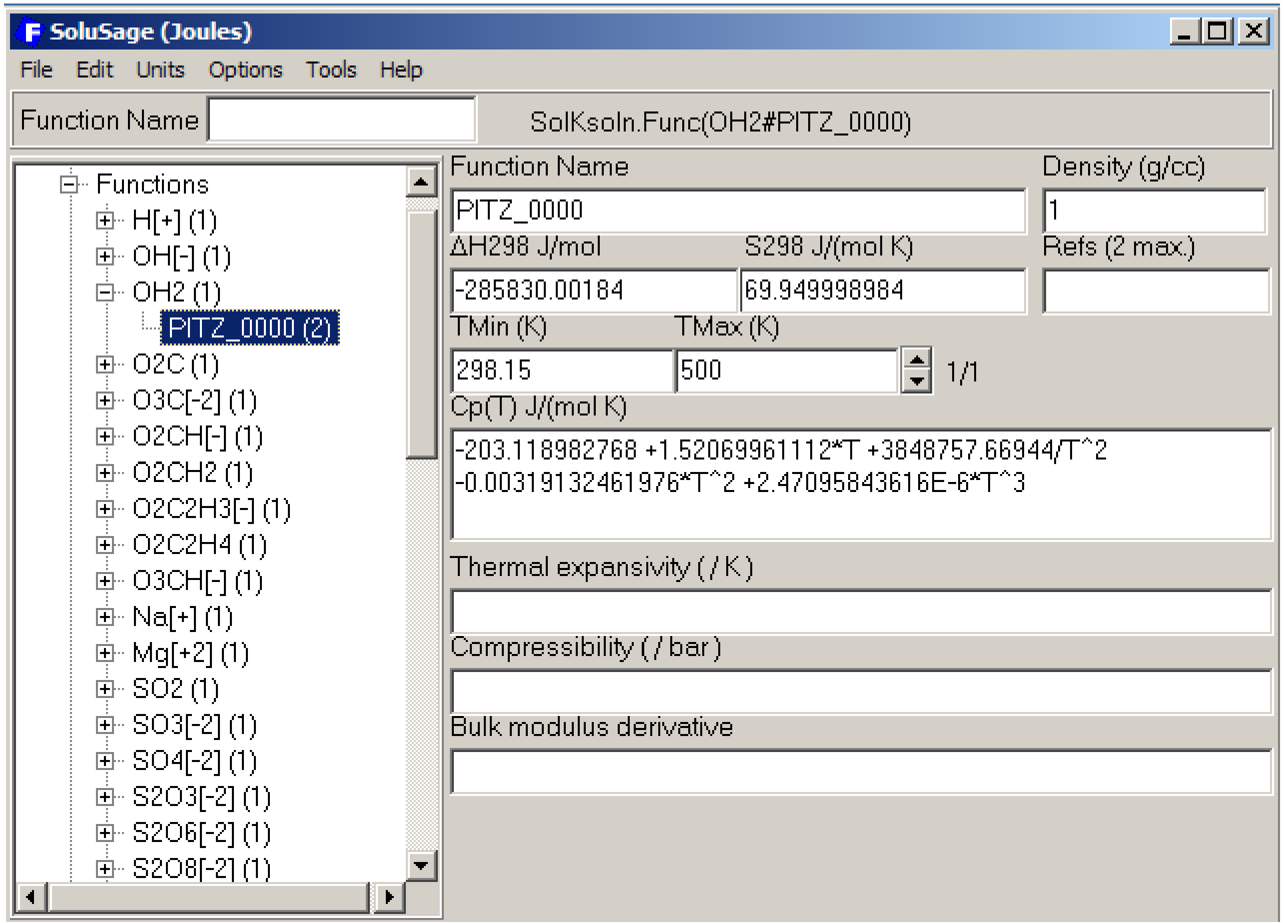
Model name.

Selected automatically.

Entry of end-members



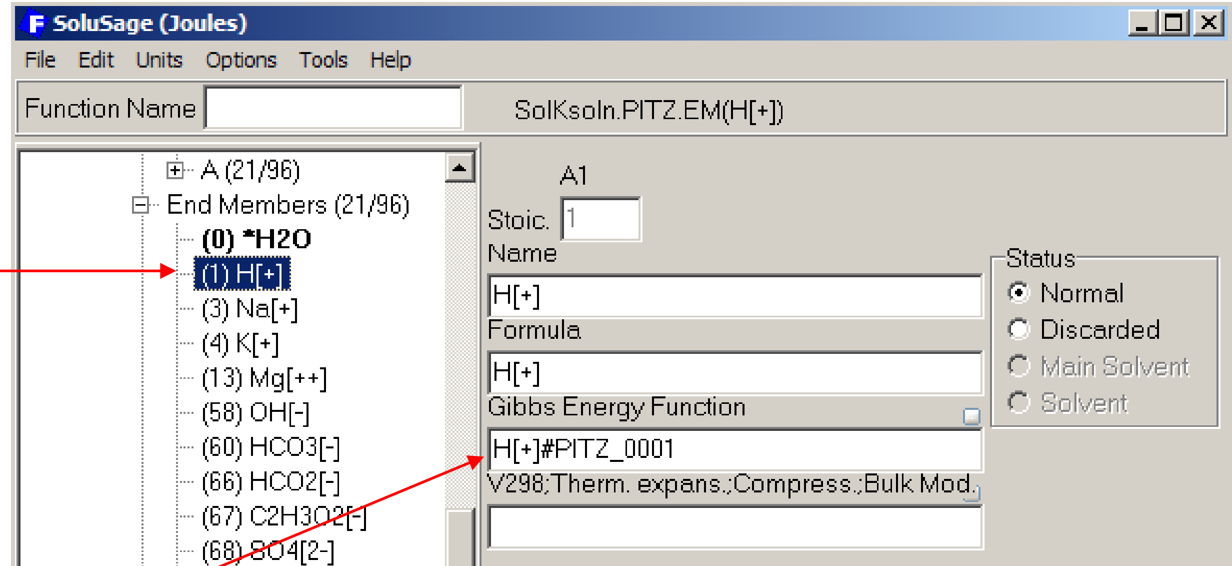
Function is the Gibbs energy of pure liquid H_2O



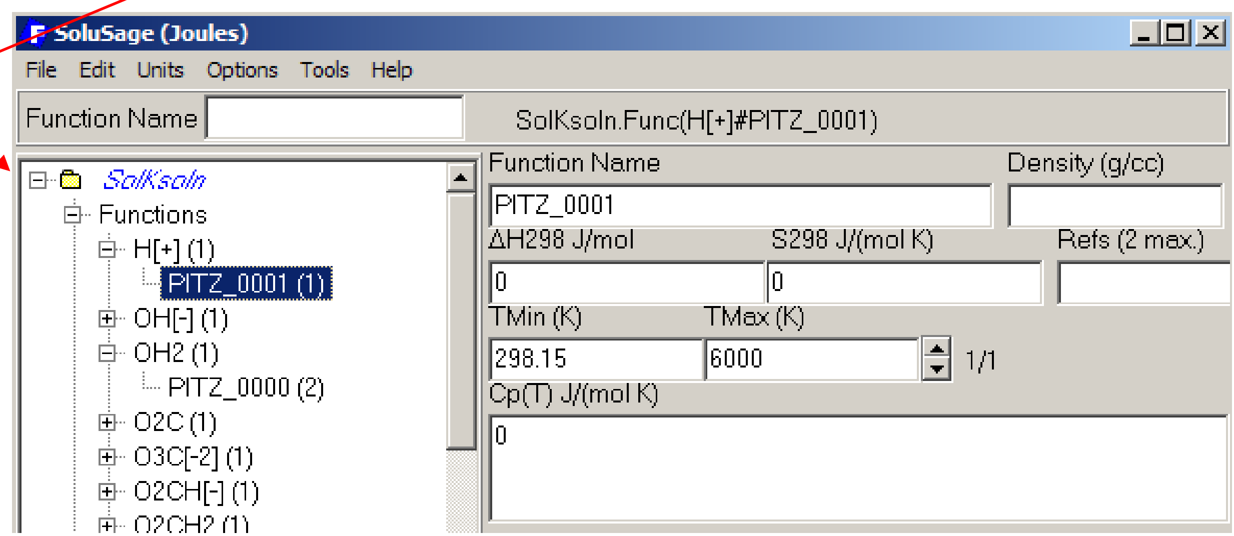
End-members each consist of one species

The Reference State is the H [+] ion

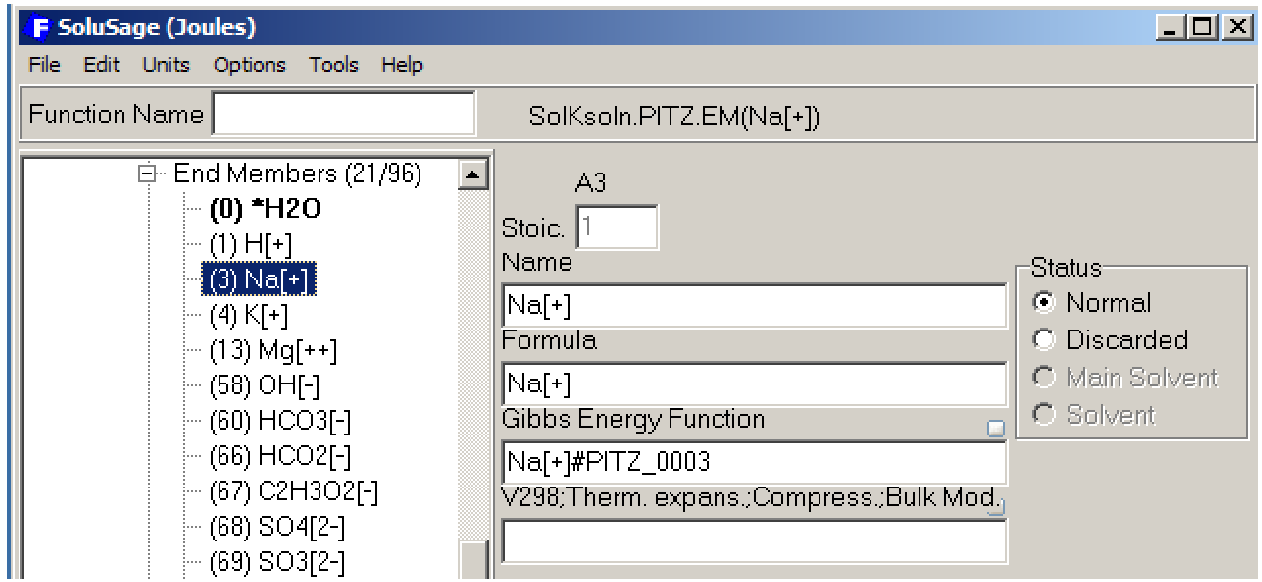
Hydrogen ion end-member.

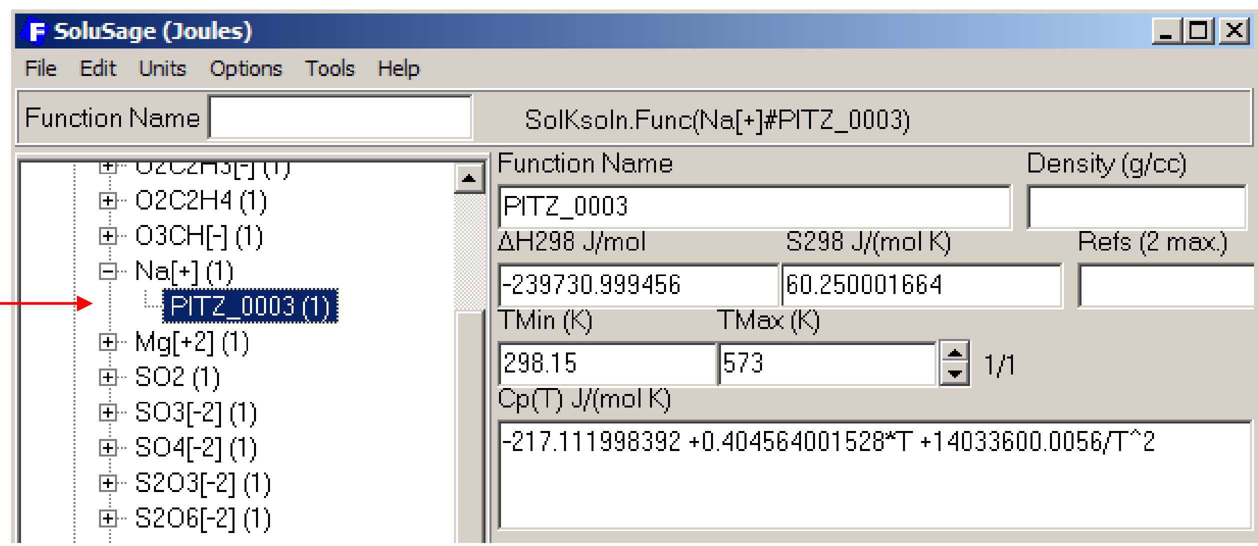


The reference state is the H [+] ion, 1.0 molal standard state, with G = 0.0 at all temperatures.



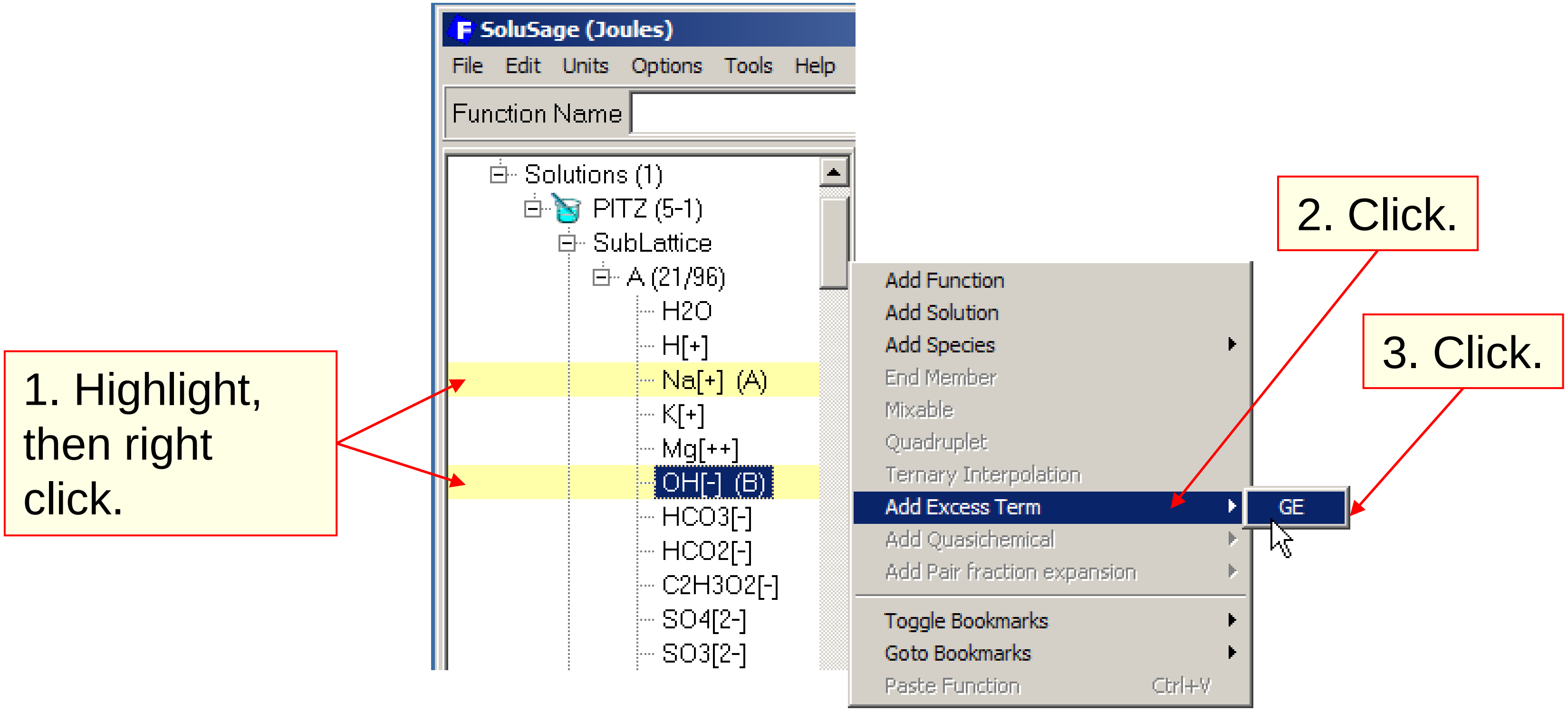
Gibbs energies of all species are for a 1.0 molal standard state (refered to the H [+] ion)

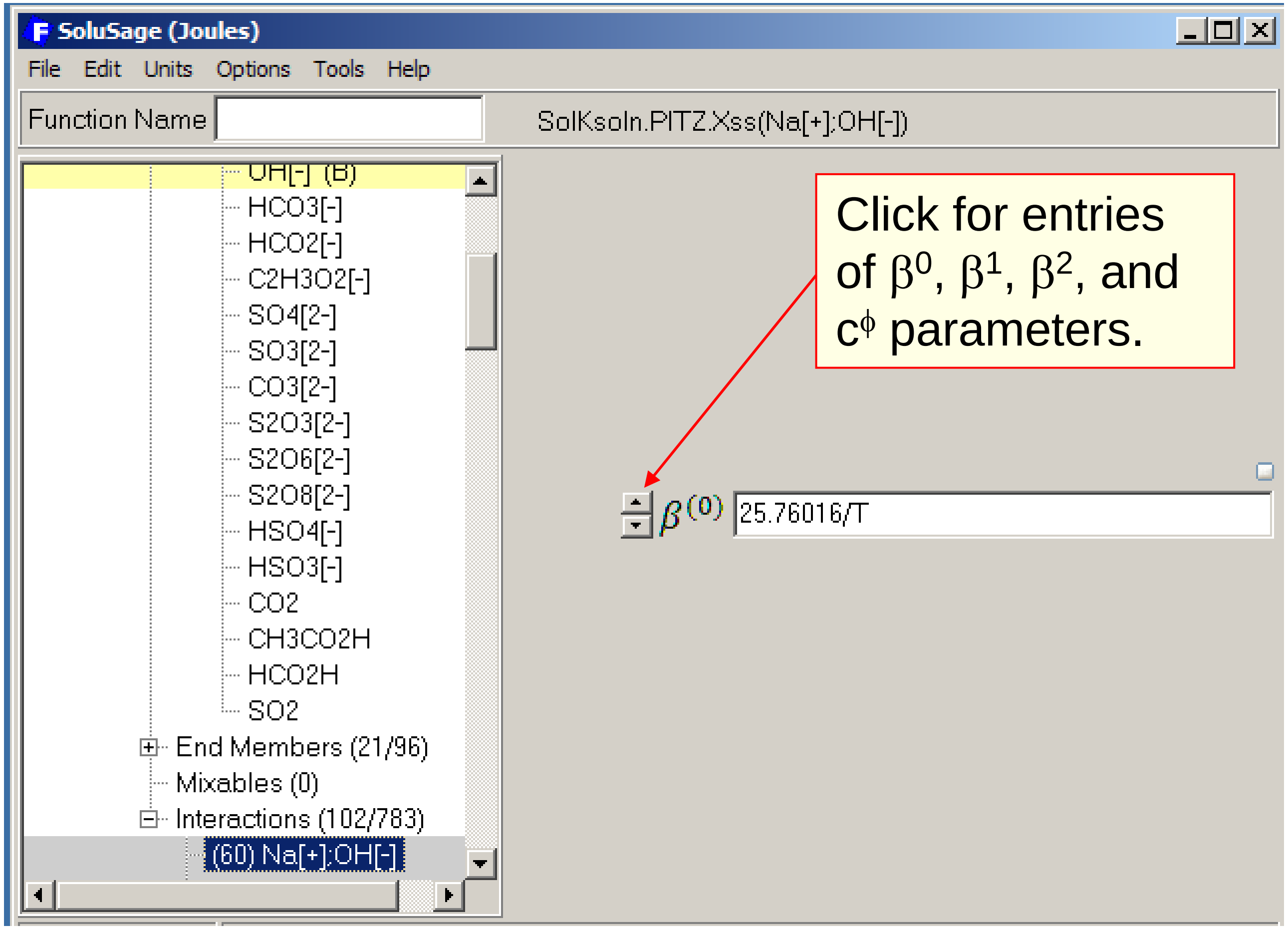




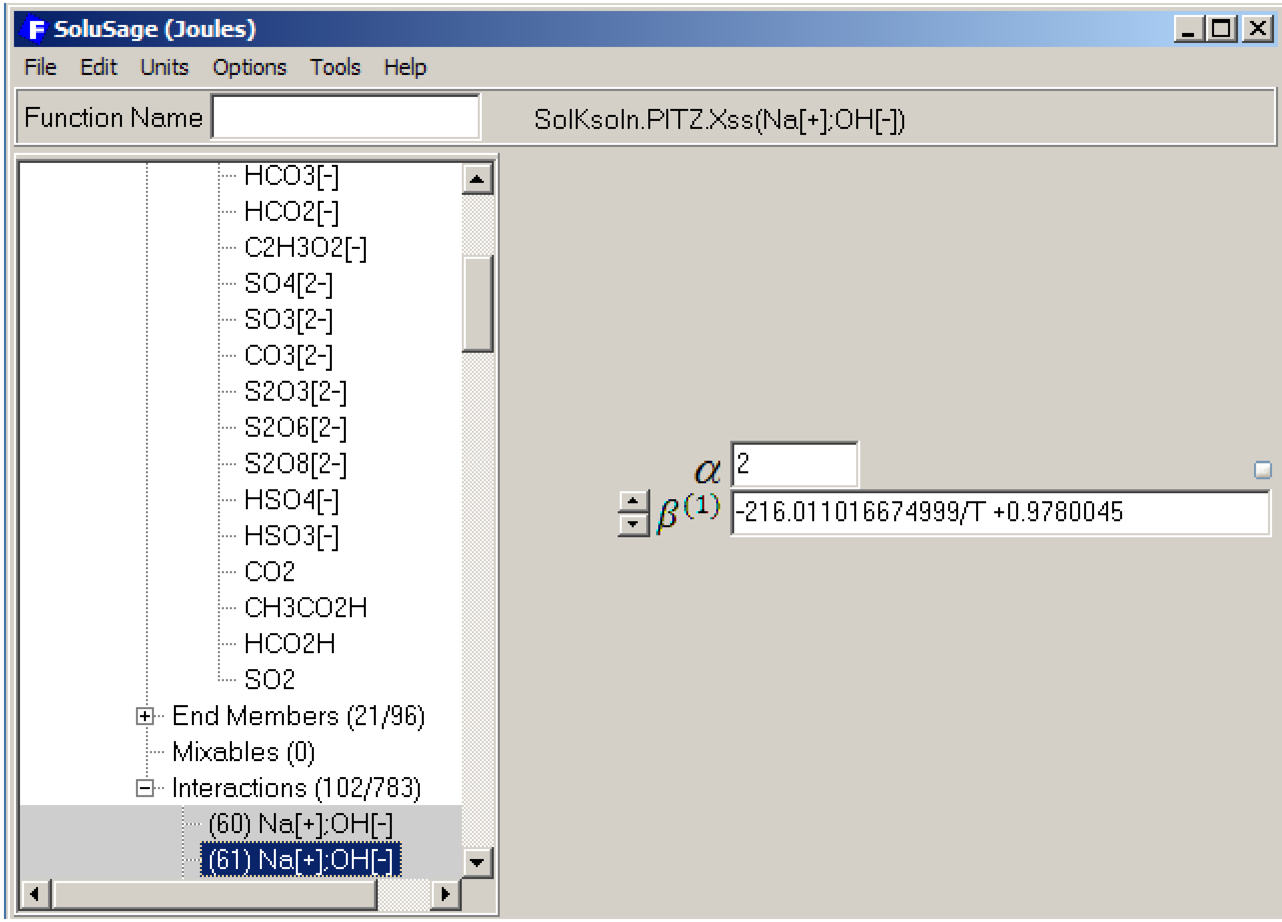
(Compare with the FactPS **AQ**ueous database).

Entry of a [cation-anion] interaction parameter

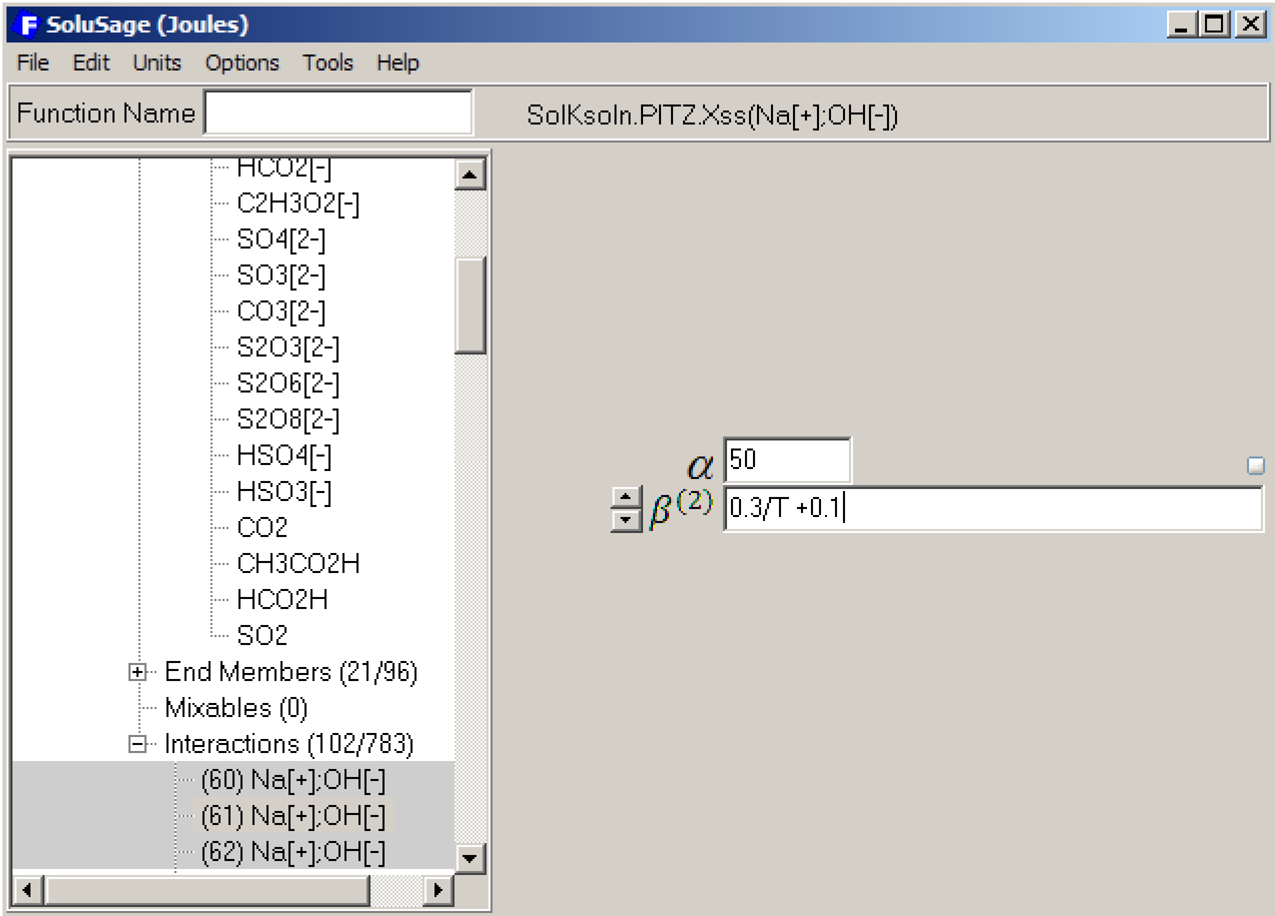




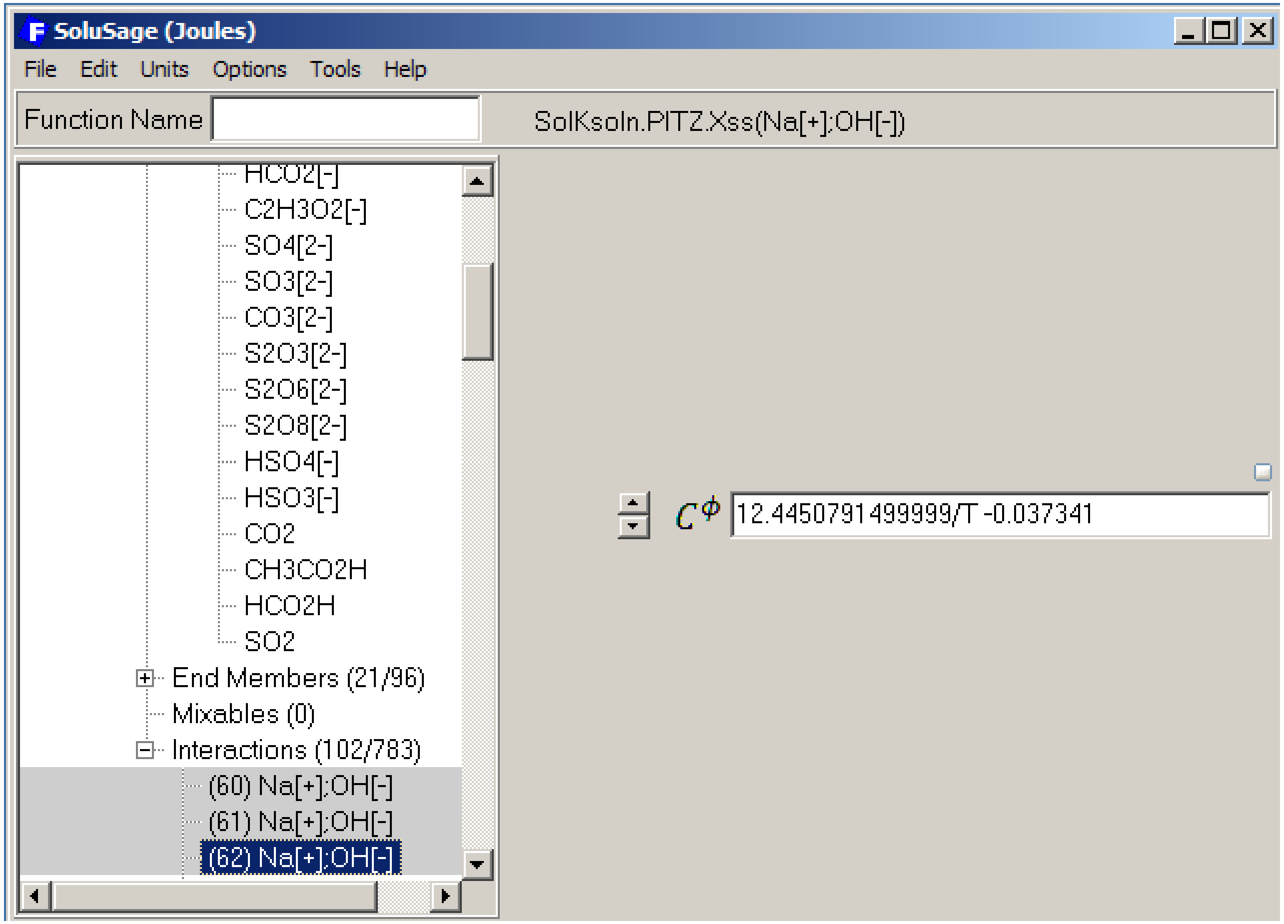
Entry of a [cation-anion] β^0 parameter (for all notations, see refs. (20, 21)).



Entry of [cation-anion] β^1 and α parameters (see refs. (20, 21)). If either or both ions are monovalent, the default value of α is 2.0; otherwise, the default value is 1.4 (see ref. (20)). Other values of α may be selected. (See ref. (21)).

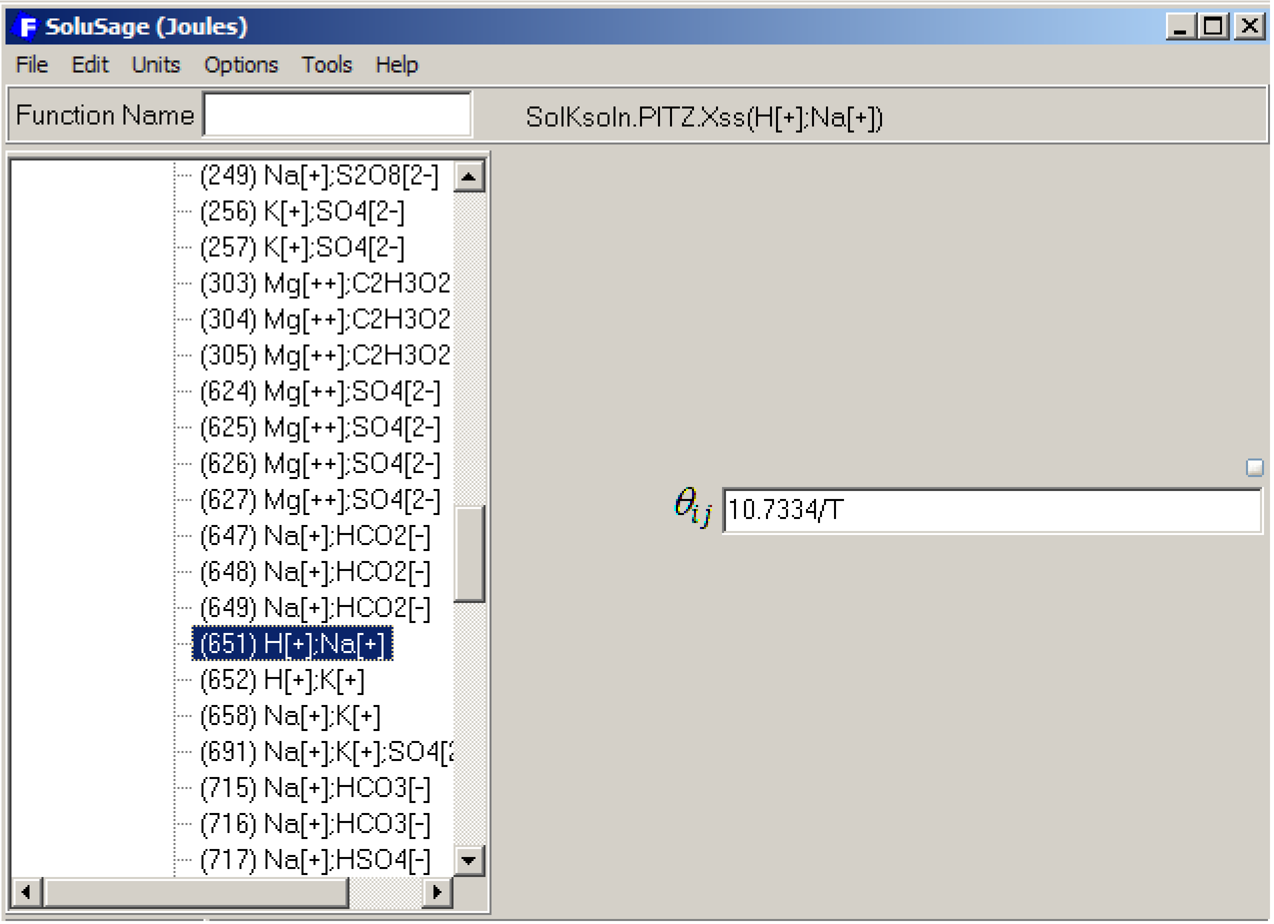


Entry of [cation-anion] β^2 and α parameters (see refs. (20, 21)). If either or both ions are monovalent, the default value of α is 50.0; otherwise, the default value is 12.0 (see ref. (20)). Other values of α may be selected. (See ref. (21)).



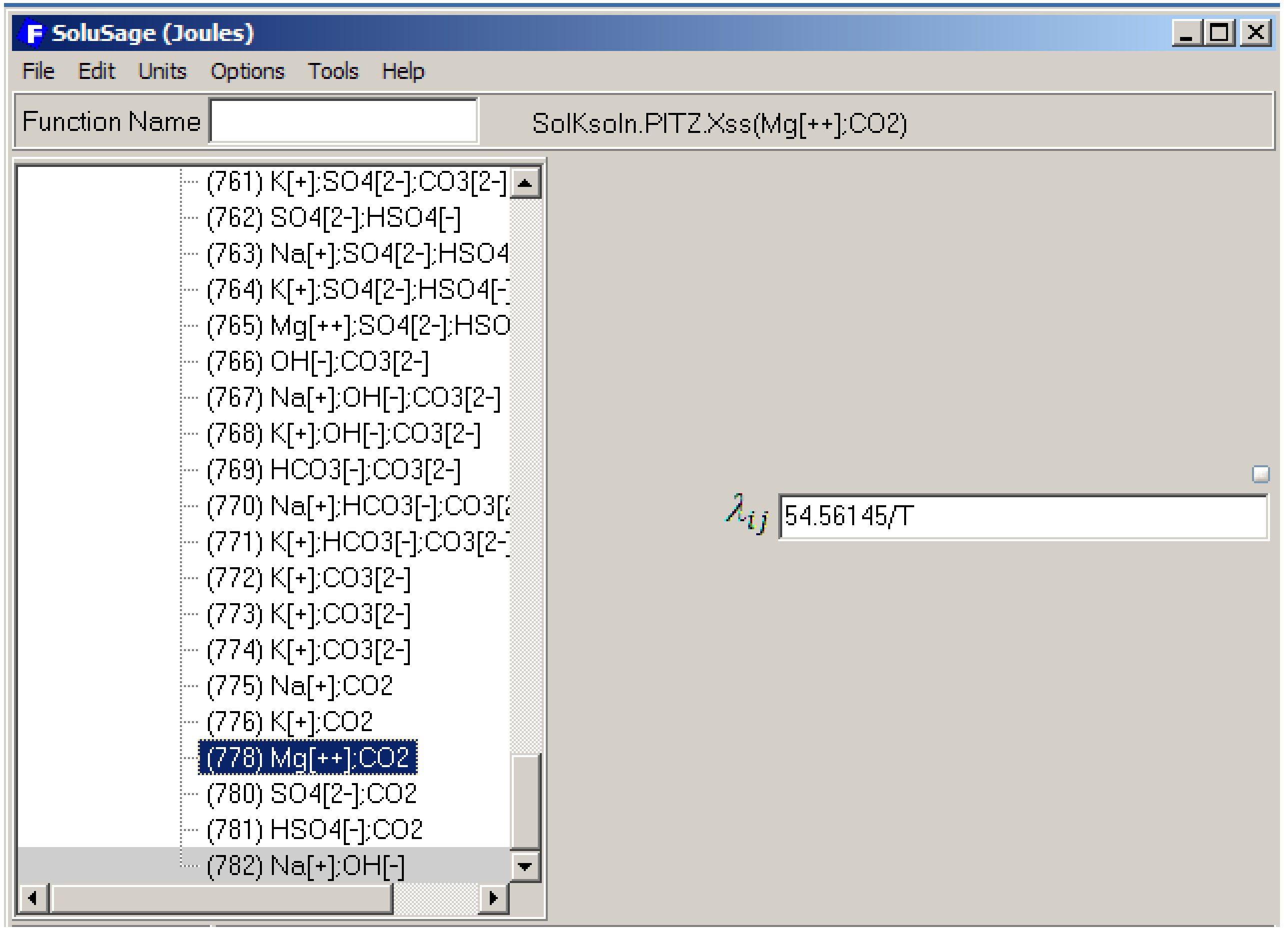
Entry of a [cation-anion] c^{ϕ} parameter (see ref. (20)).

Entry of [cation-anion] and [anion-anion] parameters



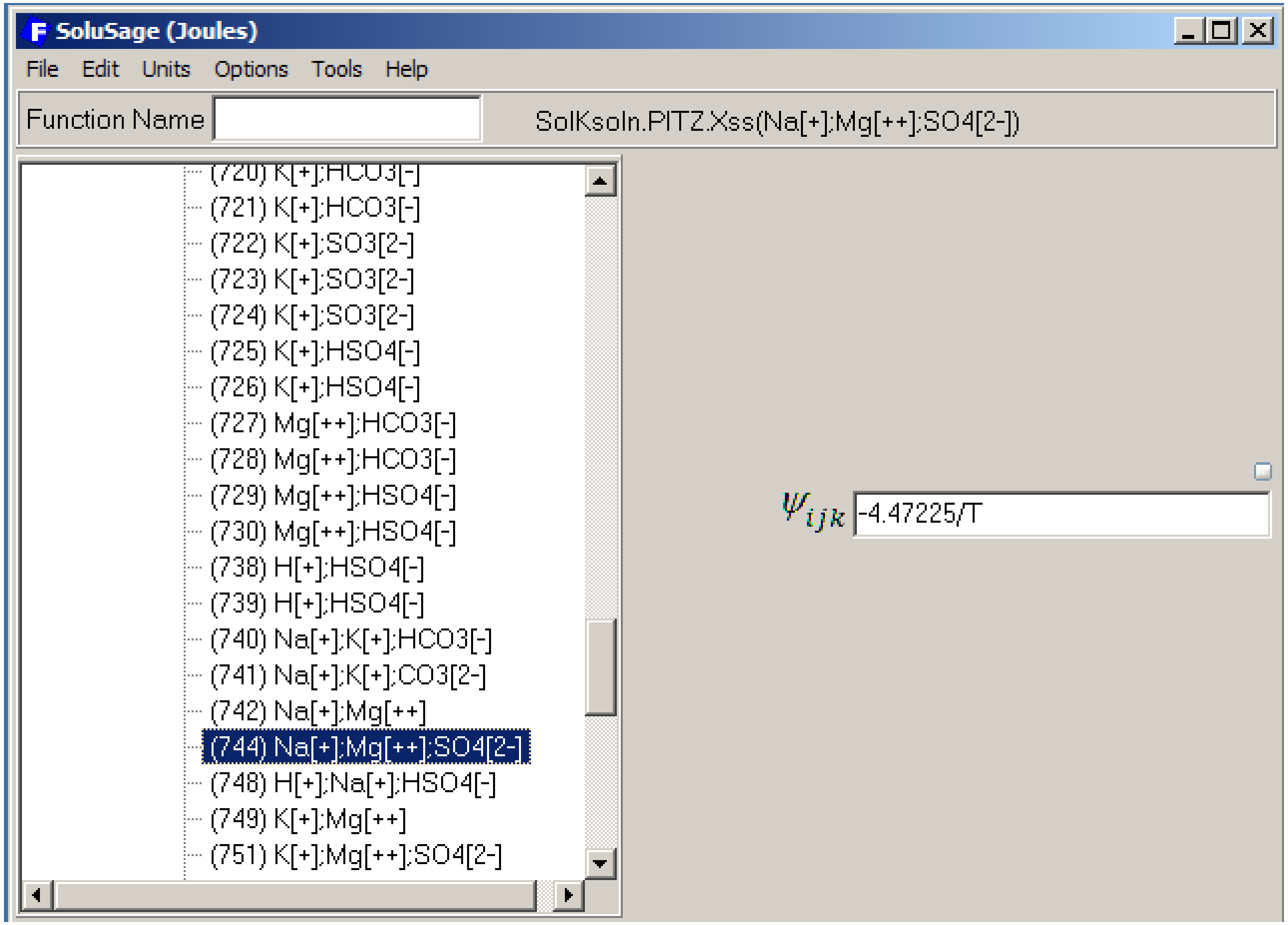
For notation, see ref. (20).

Entry of [cation-neutral species] and [anion-neutral species] parameters



For notation, see ref. (20).

Entry of [cation-cation-anion] and [anion-anion-cation] ternary parameters



For notation, see ref. (20).