CaTCalcXE

Chemical and Thermodynamic Equilibrium Calculator

Expert Edition

User's Manual

Ver. 2.9

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Table of contents

Ⅰ. Overview

This software solves the equilibrium problem in chemical thermodynamics using the Gibbs Energy Minimization Method. A number of similar software programs have already been developed, but there still remain many problems to be aware of, especially in the case of ceramic systems. It is very easy to make mistakes unless the user is well versed in the software. This software has been developed mainly to improve this problem, with emphasis on reliability, quality and ease of use, which is necessary for a software tool used in various researches.

1. The software can automatically and correctly calculate not only metals, but also ceramics and intermetallic compounds. It is not necessary to select stable phases prior to the calculation. Phase separation and global minimization problem is automatically handled.
2. A highly reliable algorithm that considers the problems in numerical computations, such as rounding errors, loss of trailing digits, etc., is successfully developed. The algorithm is also strong in calculation in which trace elements are important.
3. Various standard thermodynamic solution models are supported.
4. Uniformity of operation.
5. Various calculation functions such as target calculation and solidification simulation, as well as the creation of phase diagrams, potential diagrams, and liquidus univariant-line projections of multicomponent systems.
6. Thermodynamic data assessment module is incorporated which is easy to use even for non-expert users.

Limitations of the Demo version

The number of elements that can be handled is limited to three.

Ⅱ. Installation

【Requirements】

1. Windows 10 or later. 64bit version only.

2. Display resolution is 1280*728 or higher. There may be a problem when a custom scale factor is set for Display setting in Windows. In such a case, please set it to 100%.

3. Required HD space: about 100M bytes or more.

4. Memory: 1G bytes or more, the more the better.

5. Spreadsheet software such as Excel, LibreOffice-Calc, etc.

【Installation procedure】

1. Use the installer.

2. A CaTCalcXE folder will be created in the Documents folder of the user folder. In this folder, folders are created for storing thermodynamic data, calculation results, etc. , which may or may not include the following:

   Data: The default folder where thermodynamic data files are stored. However, data from any other folder can also be used.

   Material: Files that define materials (mixtures) are stored

   Macro: Storing Macro Files

   Manual: Storing Database Manuals

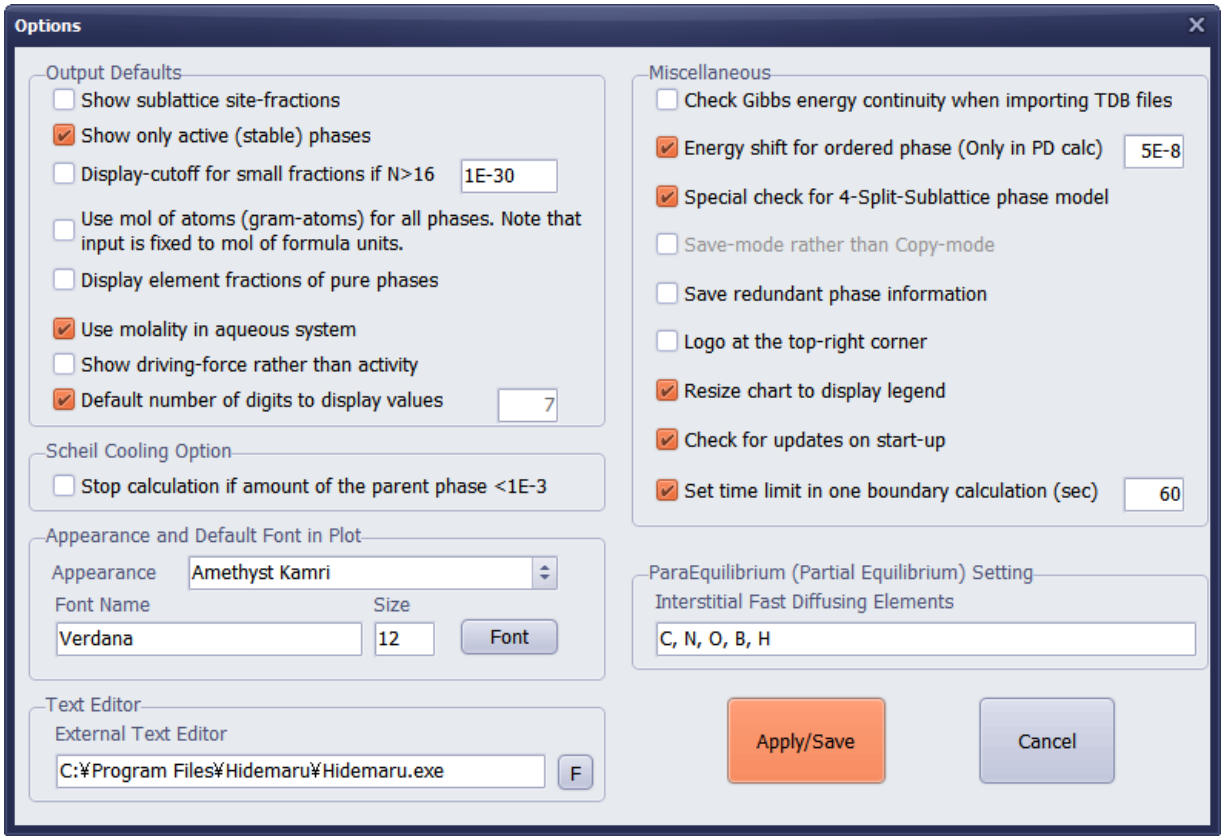
   Results: A standard folder for storing calculation results. However, it is recommended to create a dedicated folder for each subjects.

3. Shortcuts are registered to the desktop and start menu.

4. Software Activation: You need the license.dat file in the same folder as the program. Also, you need to install a USB-dongle.

Ⅲ. Preference setting

First of all, we recommend that you set up the appearance and font setting of the software. After starting the software, the setting screen will be opened by clicking [File]-[Preference] of the main screen menu. Select Appearance in particular according to your preference.



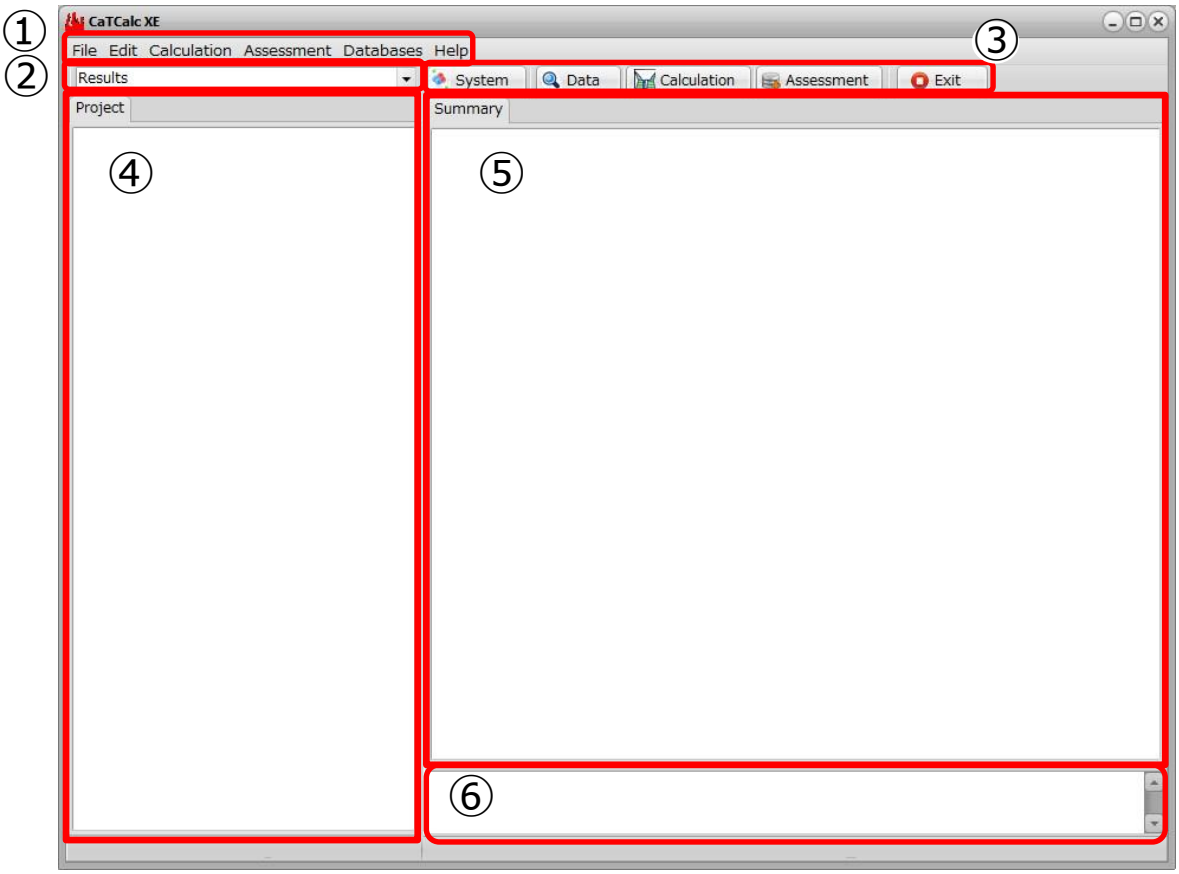
This software is designed in such a way that you do not need to refer to the manual when using it. If you are unsure of how to use the software, try the pop-up menu that appears when you press the mouse right button. Many functions are available.

For more information about the operation, please refer to the sample Project calculations. When you double-click on the calculation result to load it, the calculation conditions will be reset.

Ⅳ. Display screen and Menu

Ⅳ-1. Main Screen

Explanation of the main screen



① Menu bar

② List of Project folders

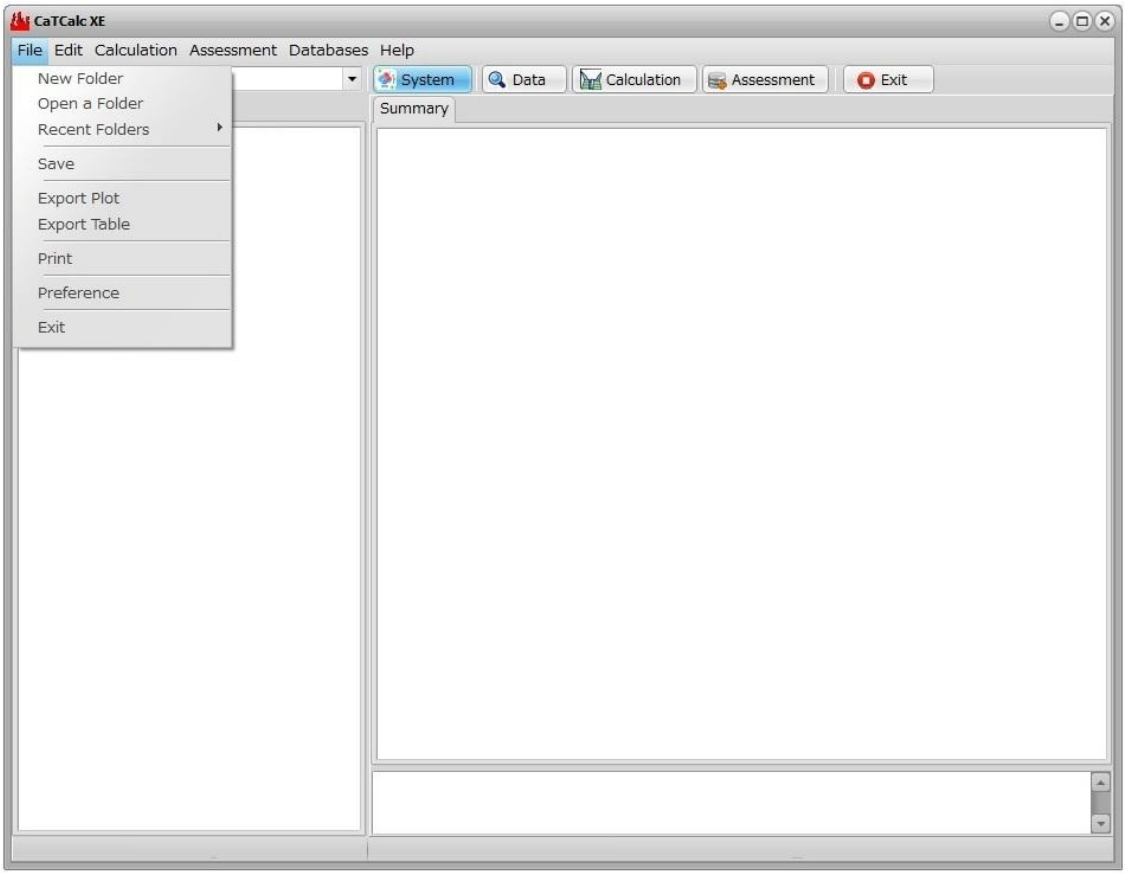
③ Application menu

④ Project panel: three different tabs are displayed depending on the situation.

⑤ Viewer Panel: Three different tabs are displayed depending on the situation.

⑥ Note panel: displays supplementary information and notes for calculations

① Menu bar



File

New Folder： Create a new folder (project folder) to save the calculation results

Open a Folder： Open an existing folder

Recent Folders： List of recently used folders

Save：The calculation results are automatically saved. This menu is used to explicitly save the results of editing, such as adding labels afterwards, though the edited result is usually saved automatically.

Export Plot： Export plot to JPEG, PNG, etc.

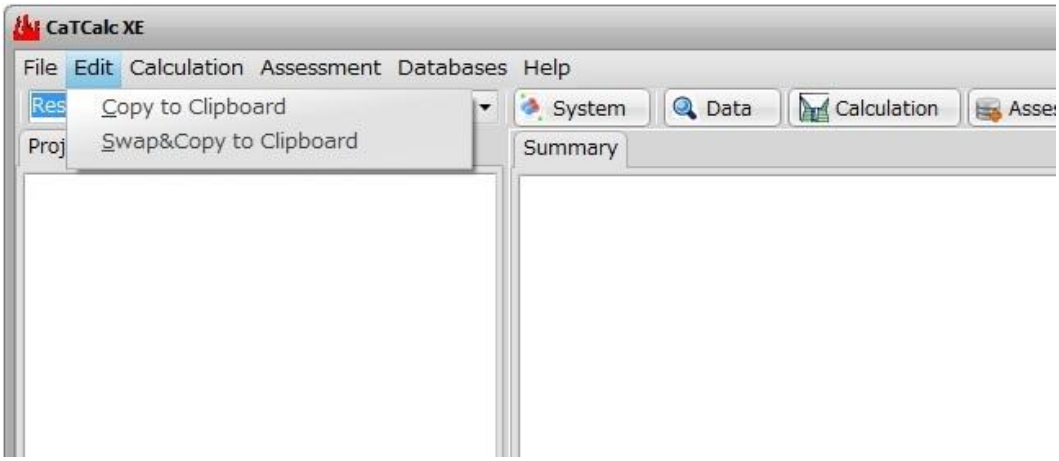
Export Table： Export the result table.

Print： Print

Preference： Various settings （Option）

Exit： Quit CaTCalc.

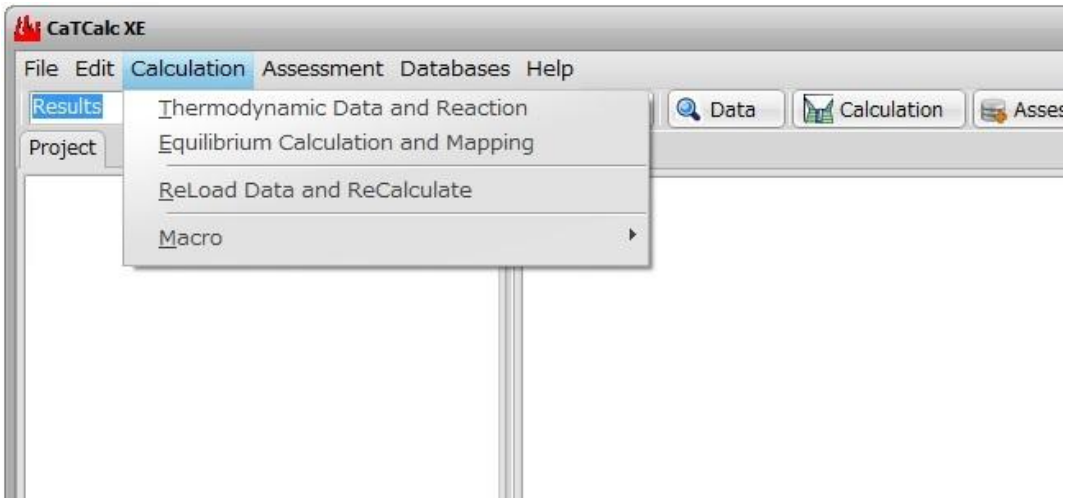
① Menu bar



Edit（＊Note： The Edit menu changes depending on the case of the plot view and the list view.）

Copy to Clipboard ：Copy result into the clipboard. In the plot view, the diagram is copied; in List view, the list is copied.

Swap&Copy to Clipboard ： In the case of list view, the rows and columns are swapped and copied into the clipboard.



Calculation

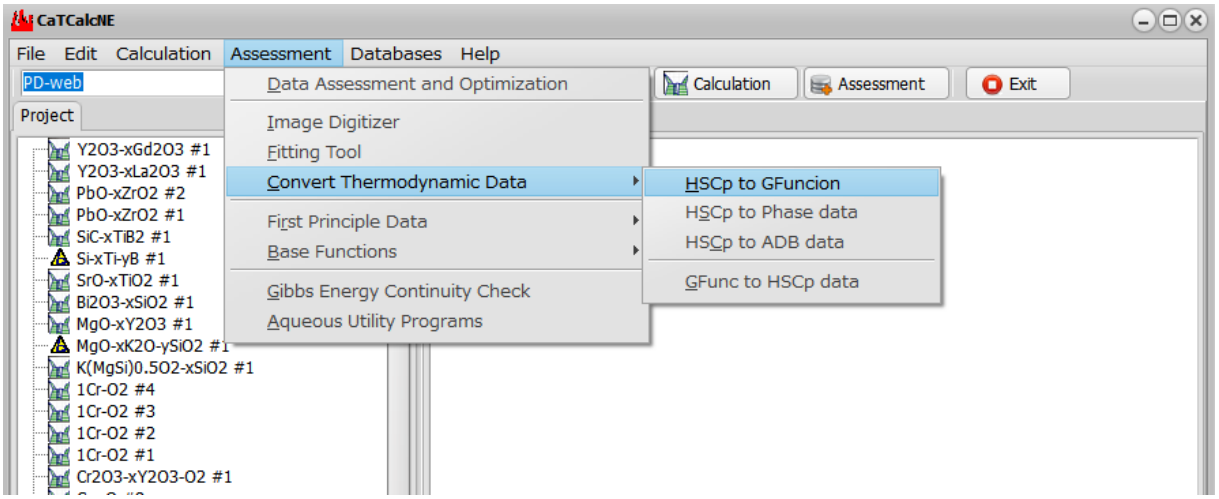
Thermodynamic Data and Reaction ： Same as the DATA button on the application bar.

Equilibrium Calculation and Mapping ： Same as the Calculation button on the application bar.

ReLoad Data and ReCalculate ： Recalculate under the same conditions. Maybe usable in database development.

Macro ： Macro menu

① Menu bar



Assessment

Data Assessment and Optimization：Same as the assessment button on the application bar.

Image Digitizer： A built-in digitizer for reading data from diagrams. Other digitizers can also be used. (See section Image Digitizer.)

Fitting Tool : A tool to make function approximation for X and Y data in the clipboard. Parameter optimization of various specific heat functions, the Redlich-Kister polynomial for excess Gibbs energy, the function for thermal expansion, and the EOS function for pressure dependence. (See section Fitting Tool.)

Convert Thermodynamic Data : Utility and inverse conversion utility to convert data of Enthalpy, Entropy, and Specific Heat polynomial parameters in the clipboard into Gibbs energy functions in the CDB format and parameter sets in the ADB format. (See section Convert Thermodynamic Data.)

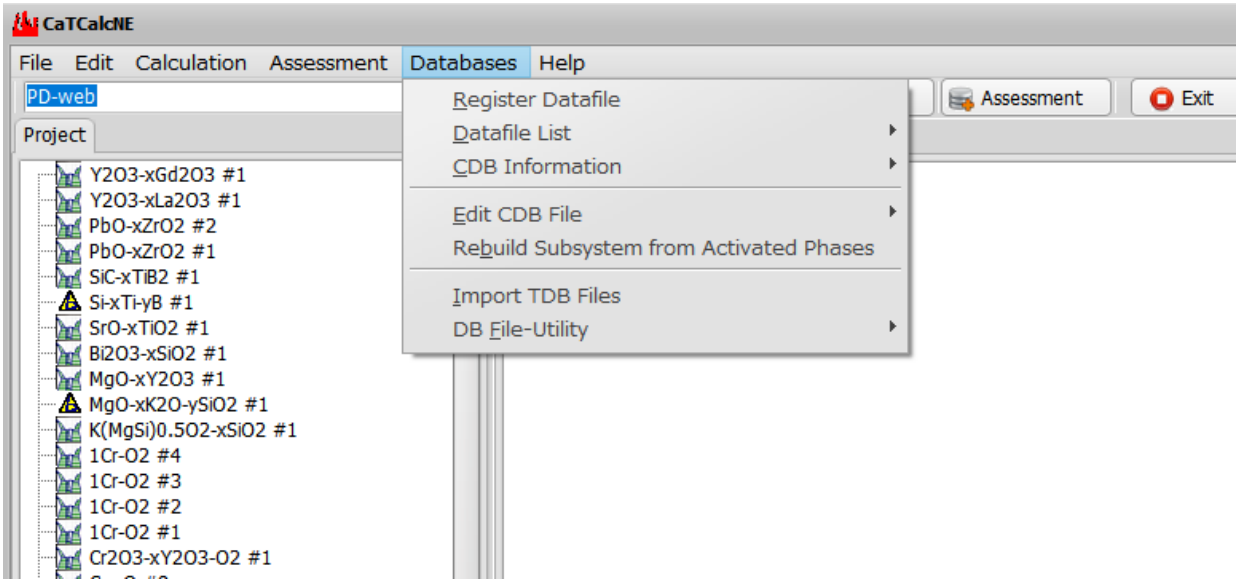
First Principle Data： A utility to convert data in units of eV/atom from ab initio calculations in the clipboard to kJ/mol_atom, and a utility to estimate specific heat and Entropy assuming the Debye function.

Base Functions： A utility that refers to a file that defines the basic Gibbs energy functions of the elements by SGTE, and a file that defines the Gibbs energy functions of some basic compounds.

Gibbs Energy Continuity Check：When Gibbs energy is temperature-split, check for sufficient connection accuracy at the split point. If the difference is too large, a warning message will be displayed, so it is necessary to correct it. The connection accuracy should be at least 10 significant digits.

Aqueous Utility Programs：Displays various thermophysical properties of H2O.

① Menu bar



Databases

Register Datafile：Register a database file. Registration is required to use the database file.

Datafile List：There are sub-menus such as updating registration information.

CDB Information： Display database Information.

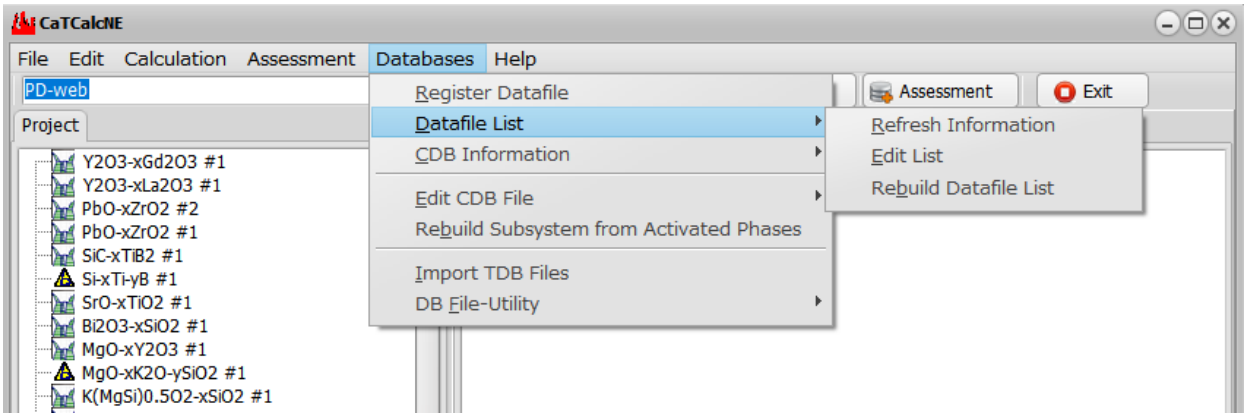
Edit CDB File：Database editing. Subset creation, etc.

Rebuild Subsystem with Activated Phases：A new subset of the database will be created with only the appeared/stabilized phases after calculation. Useful in the application-specific database development.

Import TDB Files： Importing files in the CALPHAD-standard TDB format.

DB File-Utility： Some utilities

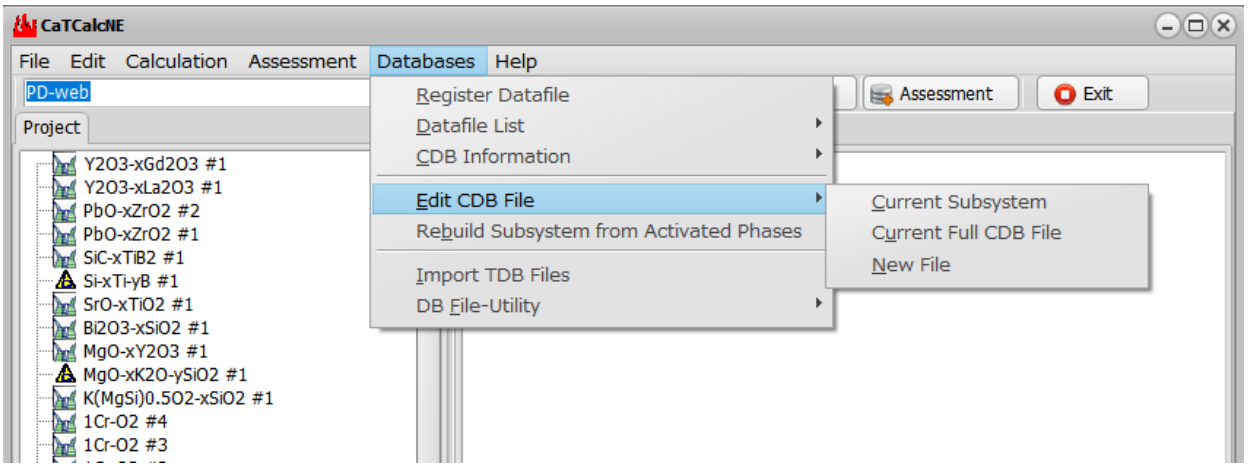
① Menu bar



Databases

Datafile List:

- Refresh Information: Update the information of the registered database file.
- Edit List: Edit the database list directly.
- Rebuild Datafile List: Regenerate the registration list.

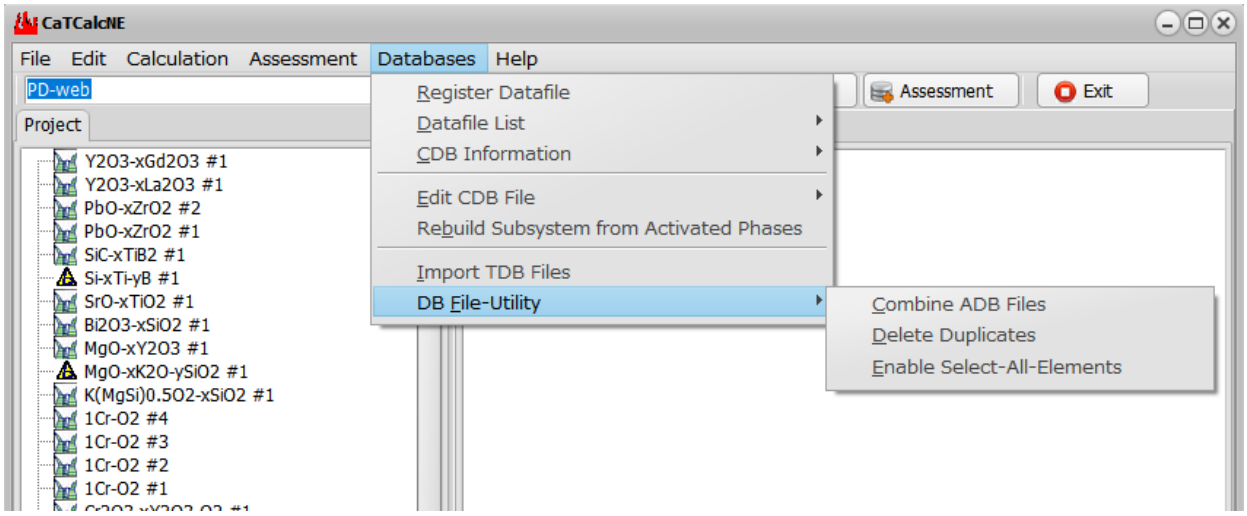


Databases

Edit CDB File： Editing the Database

- Current Subsystem： Create and edit a subset file for the currently selected element only.
- Current CDB File：Edit the selected CDB file.
- New File： New Edit.

① Menu bar

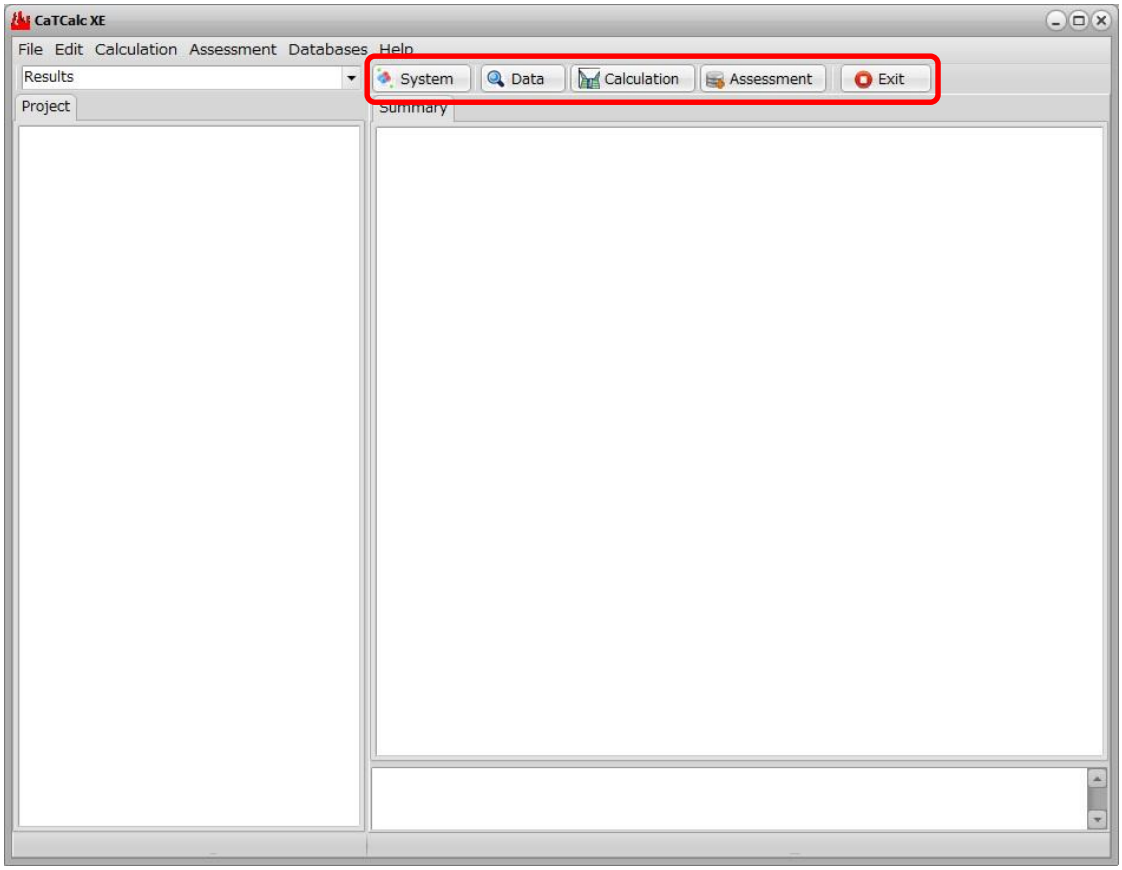


Databases

DB File-Utility

- Combine ADB Files：The integration of multiple ADB format data files.
- Delete Duplicates：Removal of duplicate data.
- Enable Select-All-Elements：This is a hidden command that allows you to batch select all elements in a large database file on the data file selection screen. A button appears in the screen.

Ⅳ-2. Application menu



① **System**： Specify elements and database files to load thermodynamic data.

② **Data**： Displays information on phases and species. If necessary, deselect each one.

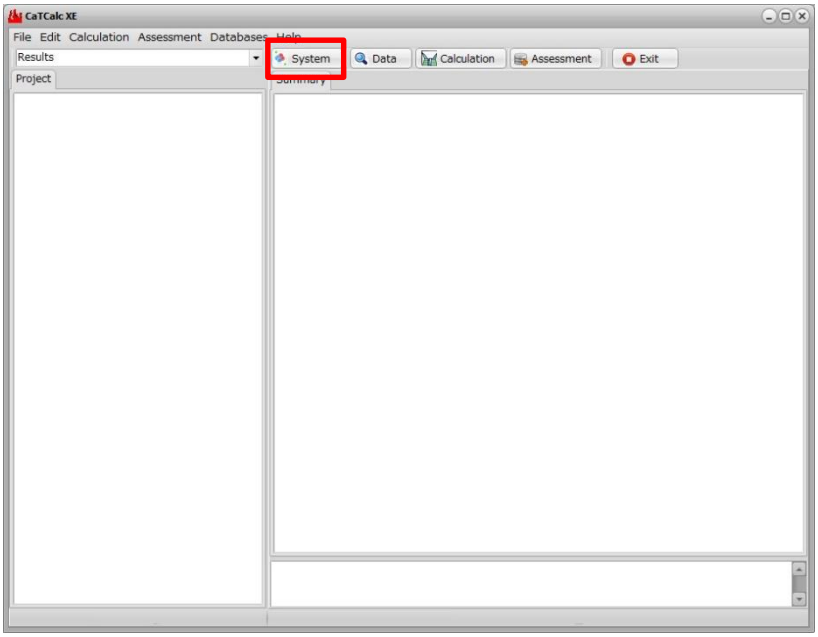
③ **Calculation**： Selects, sets conditions and executes various types of calculations.

④ **Assessment**： Database development.

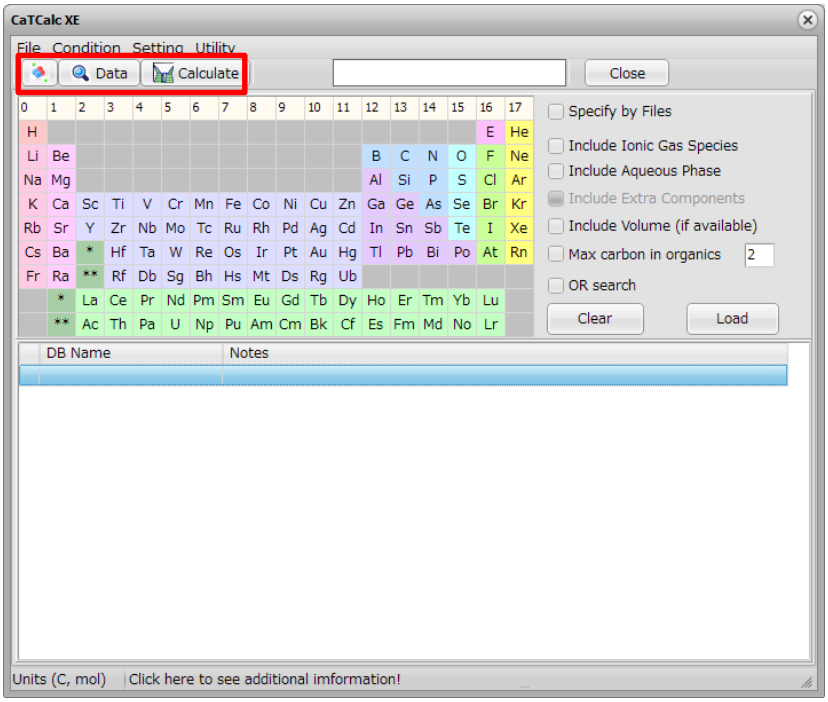
⑤ **Exit**： Quit CaTCalc.

① System screen

Main screen

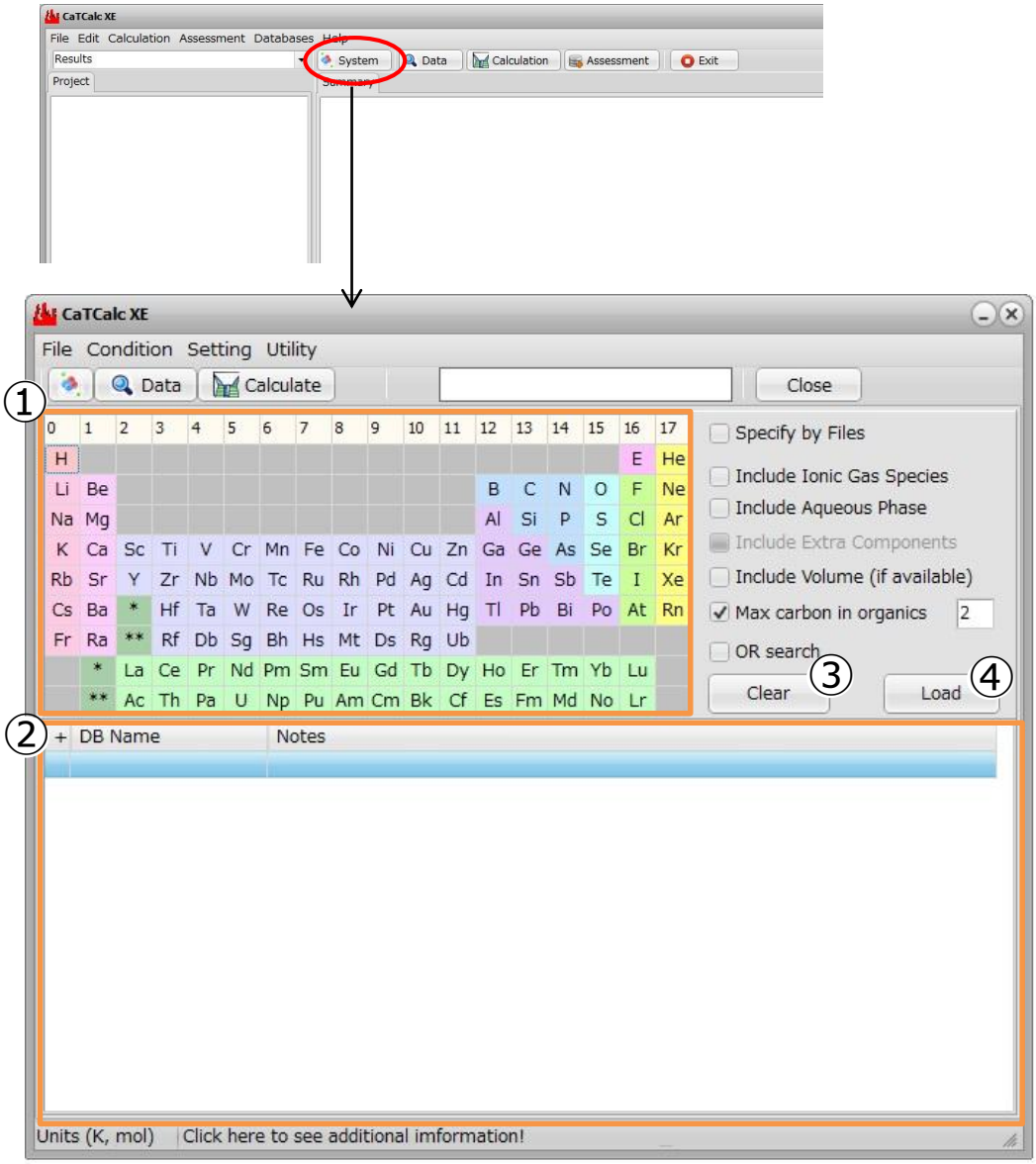


System screen：Select elements and database file(s) to be used.



*The "Application Menu" of the main screen is the same as the "Tab Menu" of the system screen.

① System screen



① **Periodic table**

The target elements are selected here with the mouse.

② **Data file area**

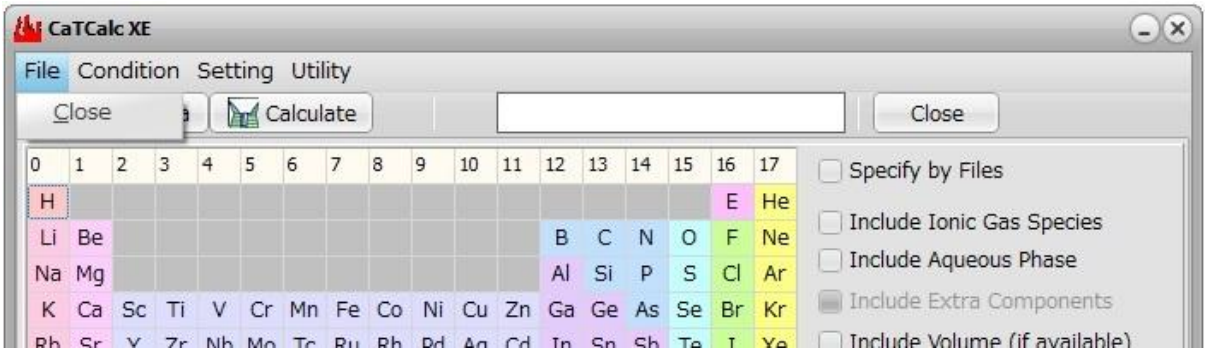
The thermodynamic data files containing the elements selected in the Periodic Table and their information are displayed.

③ **Clear Selection**

④ **Load**

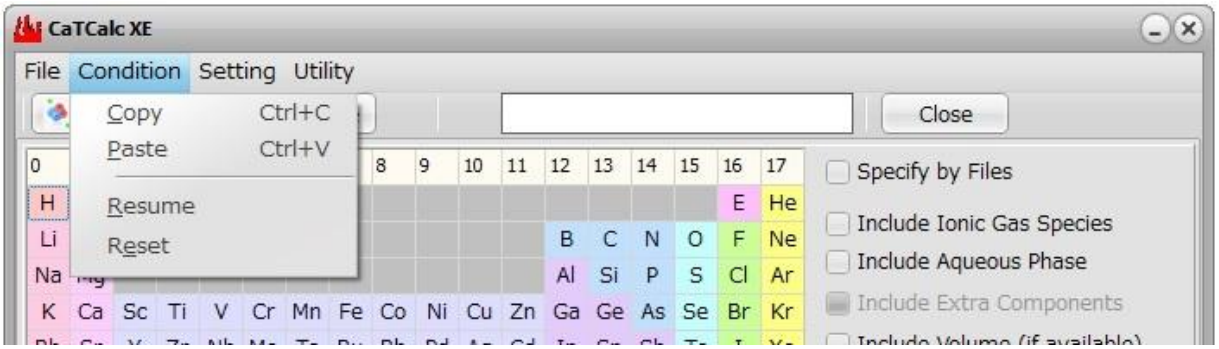
Load data from the selected thermodynamic data file.

① Menu bar of the System screen



File:

Close： Close the System screen.



Condition:

Copy： The calculation conditions are saved into the clipboard, so you can save them in Excel and so on.

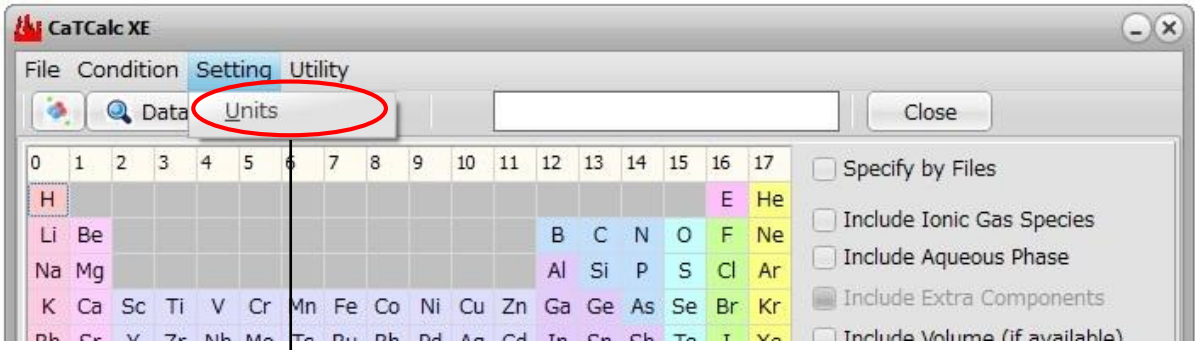
Paste： You can paste and reset the calculation conditions in the clipboard.

Resume： Set the previous calculation conditions. (Useful when recalculating after changing the database.)

Reset： Reset to default settings

① Menu bar of the System screen

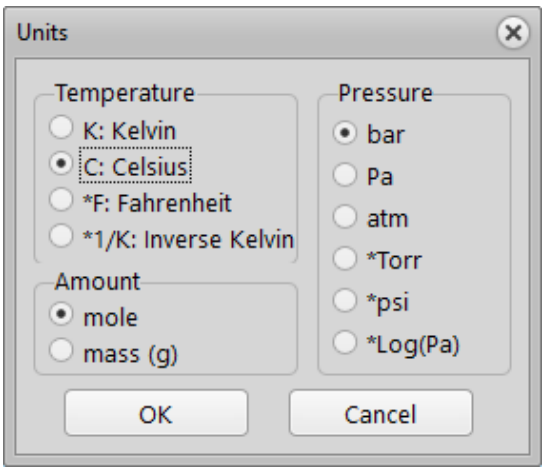
■ Unit setting



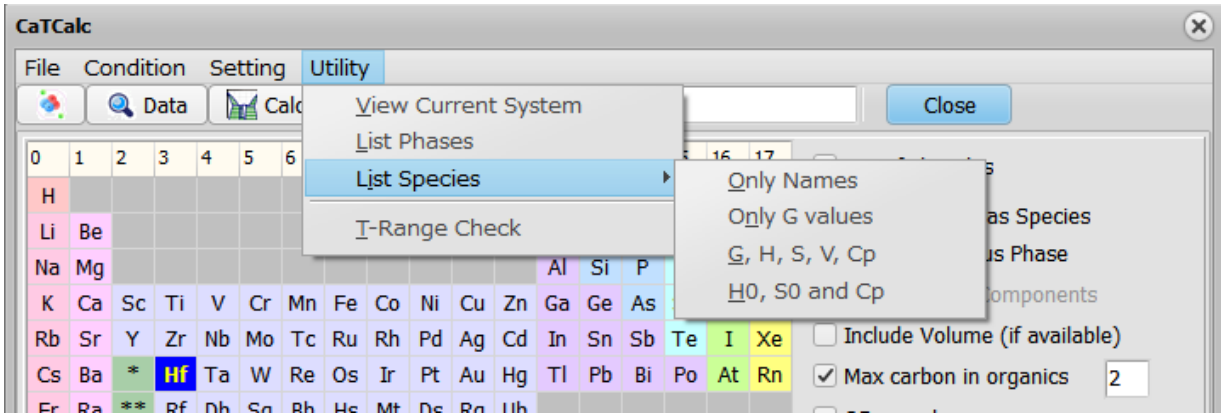
Setting:

Units: Allows you to change the units.

If there is no asterisk (*), it can be changed directly by double-clicking a label in each edit box on the Calculation screen.



① Menu bar of the System screen



Utility:

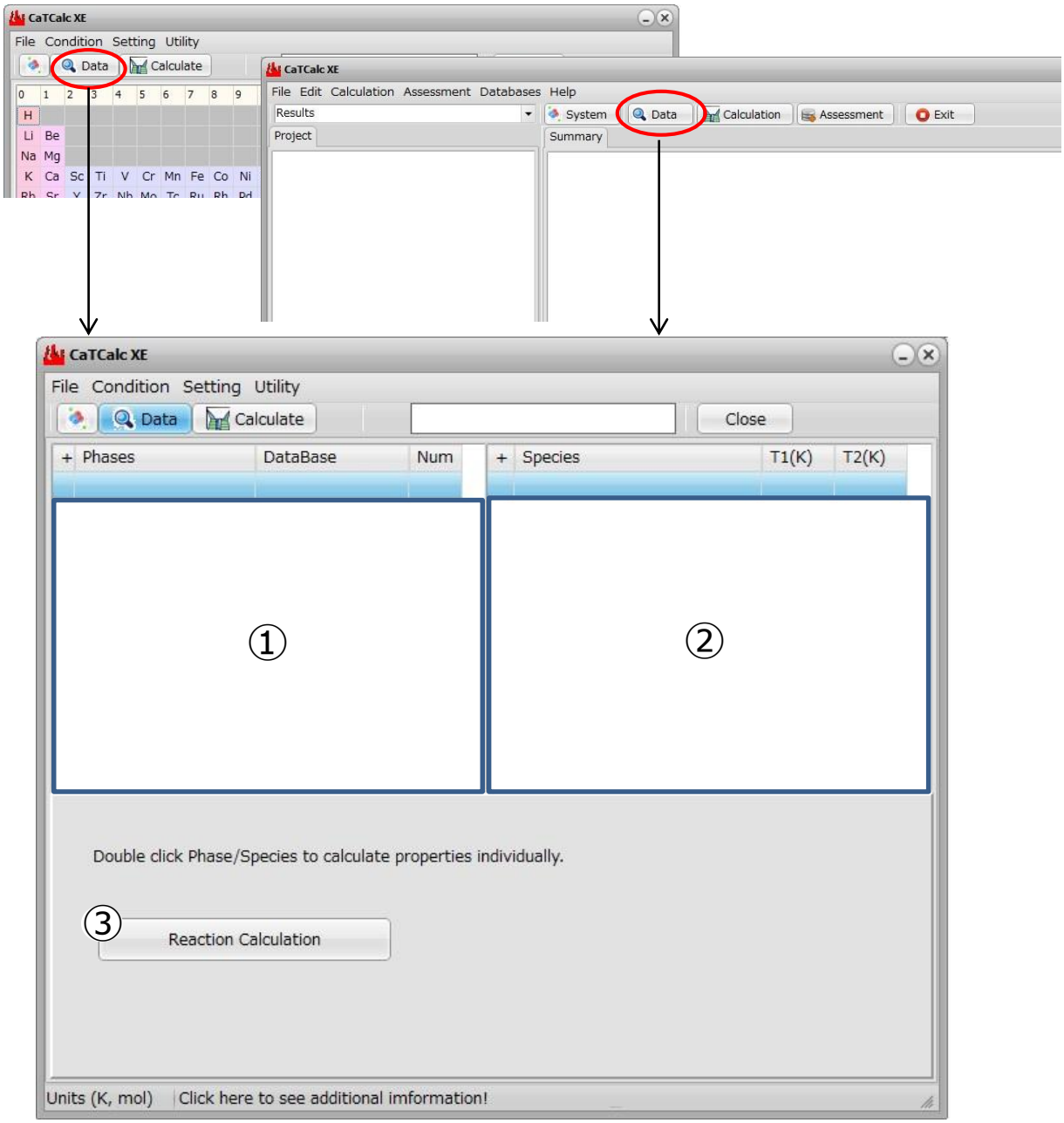
View Current System：Displays the thermodynamic database for the "current system" consisting of the currently loaded and selected phases.

List Phases：Displays information of the (selected) phases.

List Species：Calculates and displays information of the (selected) species of (selected) phases.

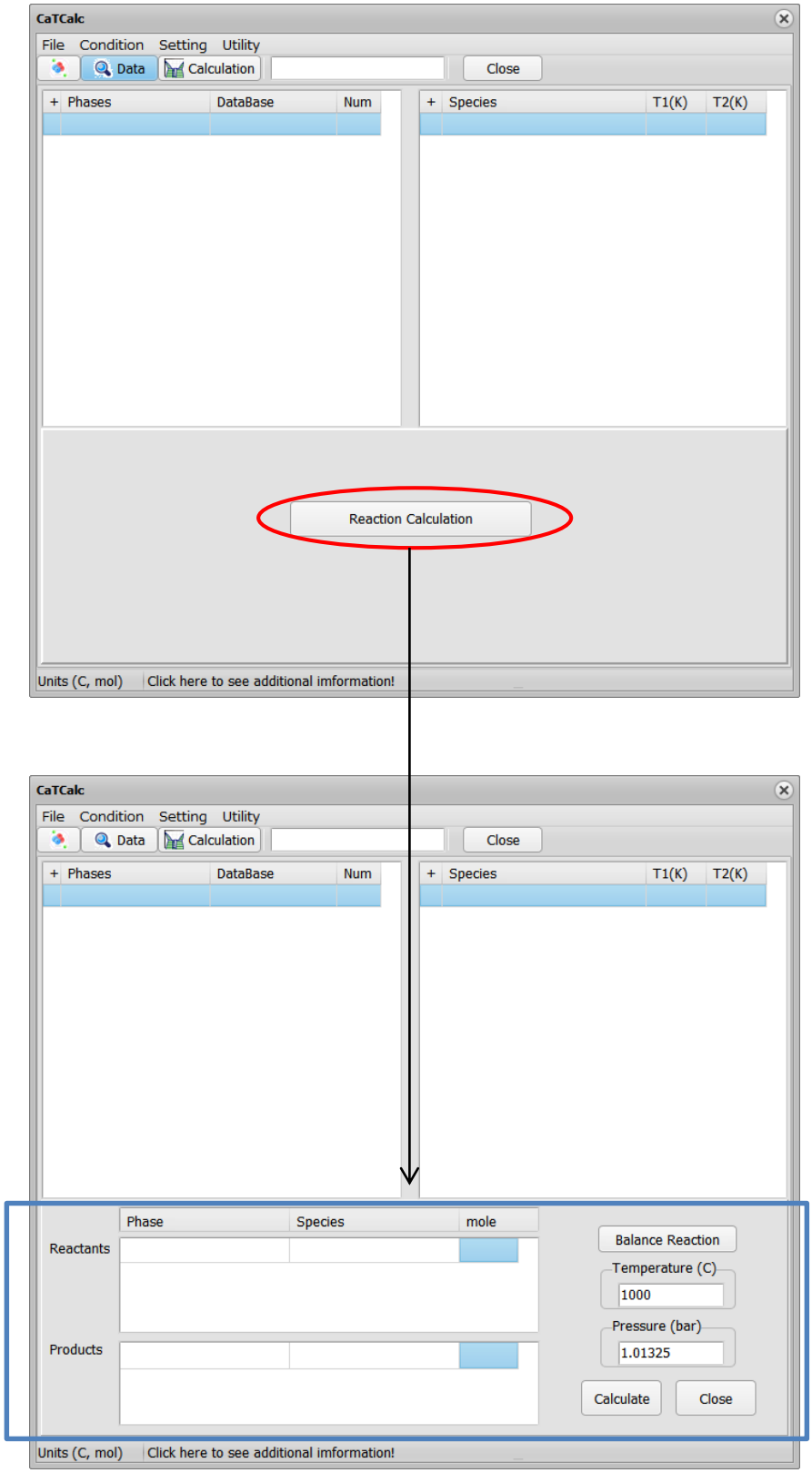
T-Range Check： For the current calculation conditions, select only the data that are within the guaranteed temperature range for each data in the database. (Use this only to identify which data may be problematic, if necessary.)

② Data screen



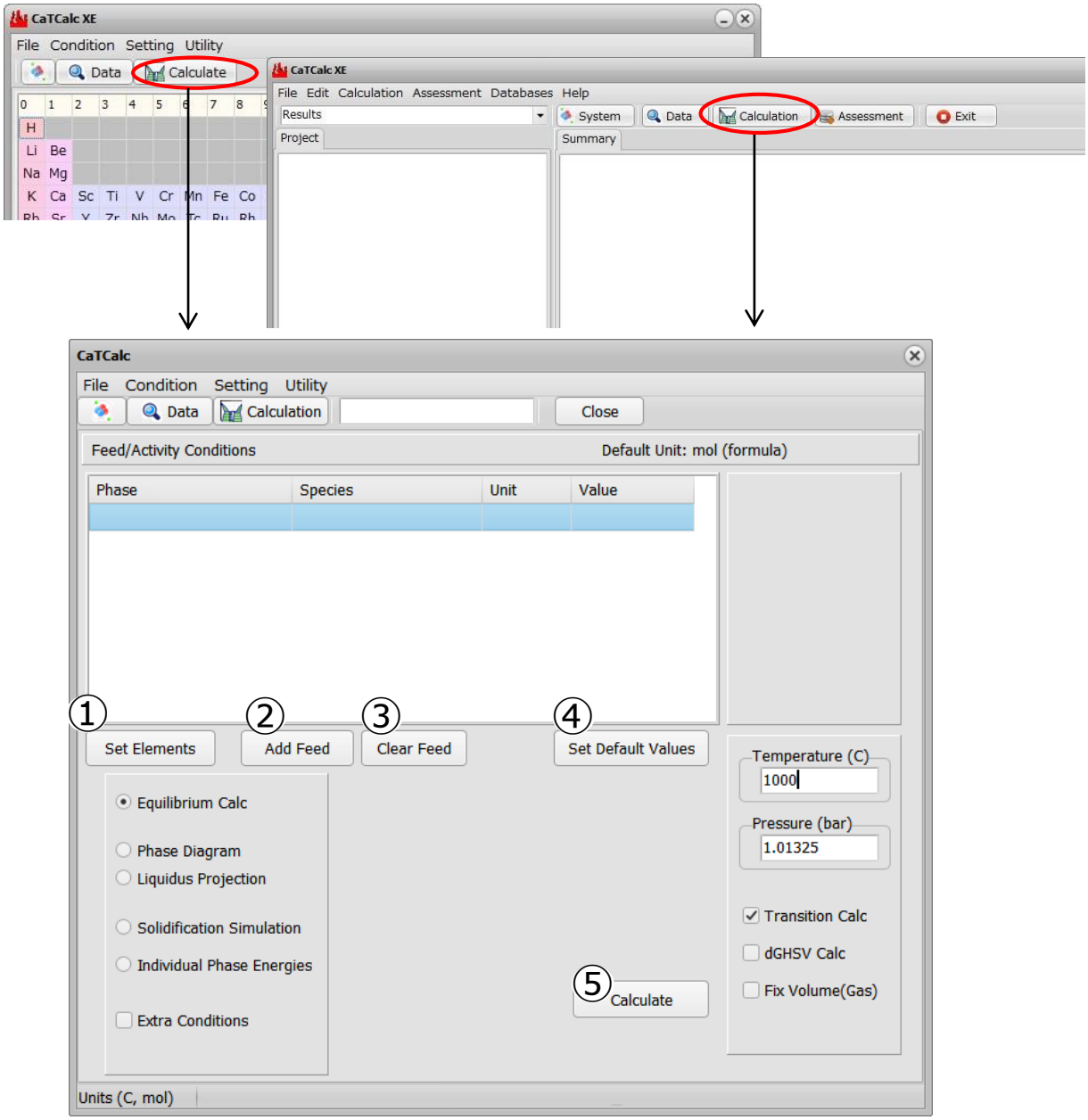
① **Phases list**: Display phases. The solid and liquid phases of pure substances are displayed together as PureSol and PureLiq.
② **Species list**: Lists the species that make up each phase. However, pure substances indicate a phase.
③ **Reaction Calculation**: This is a reaction calculation that uses individual chemical reaction schemes. Note that calculation that takes all possible reactions into account is performed by the equilibrium calculation in the Calculate screen.

② Data screen



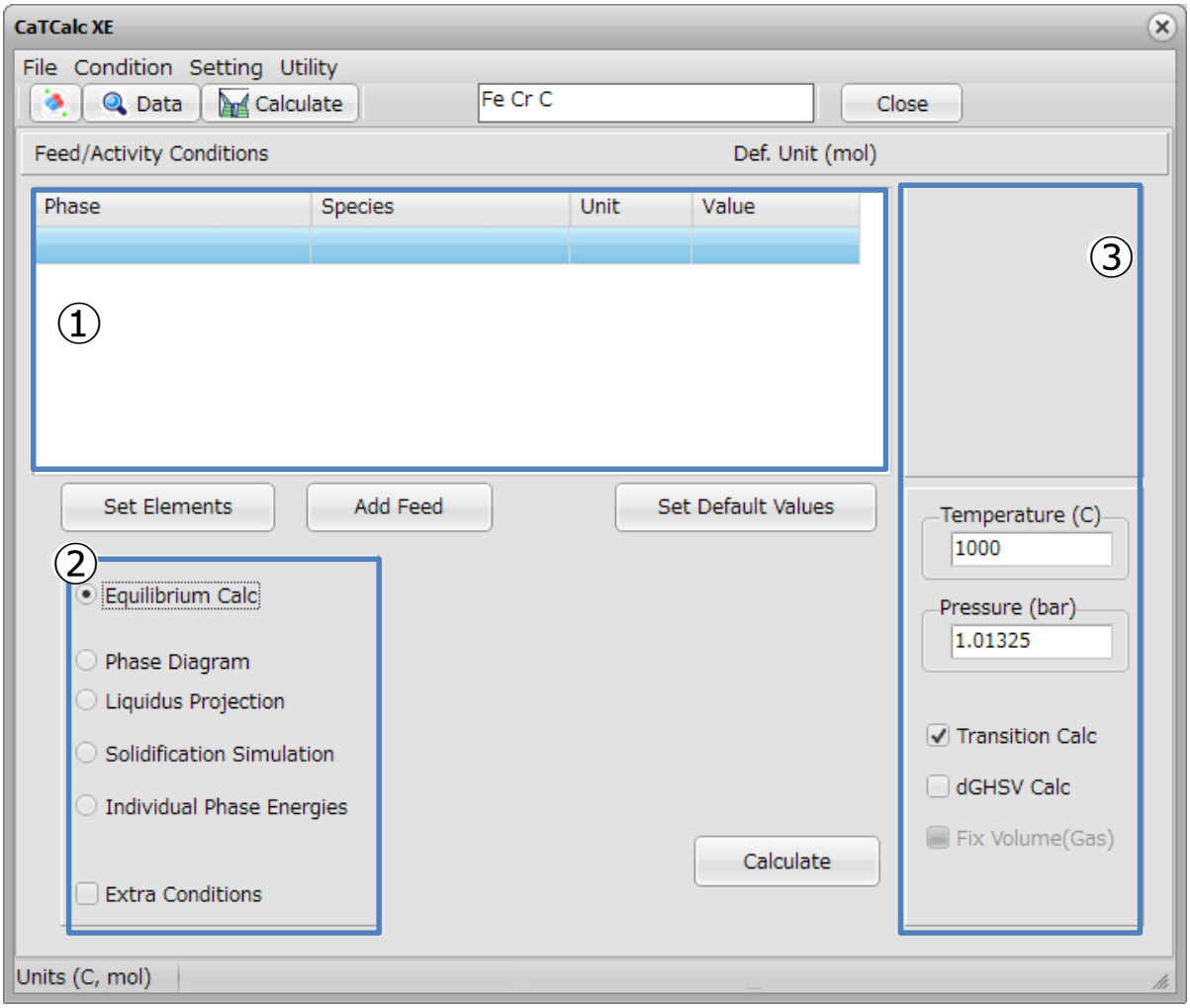
* See [Reaction Calculation] for details of the settings.

③ Calculation screen



① **Set Elements**：This button is used to set the element as a Feed (Reactant). It is useful for creating a normal phase diagram of metals.
② **Add Feed**： It is used for general equilibrium calculations and phase diagram calculations for ceramics and metal systems.
③ **Clear Feed**： Clear all the setting.
④ **Set Default Values**：Typical conditions for each type of calculation are set automatically. It is used after setting up Feed conditions and calculation type.
⑤ **Calculate**: The button to start the calculation.

③ Calculation screen

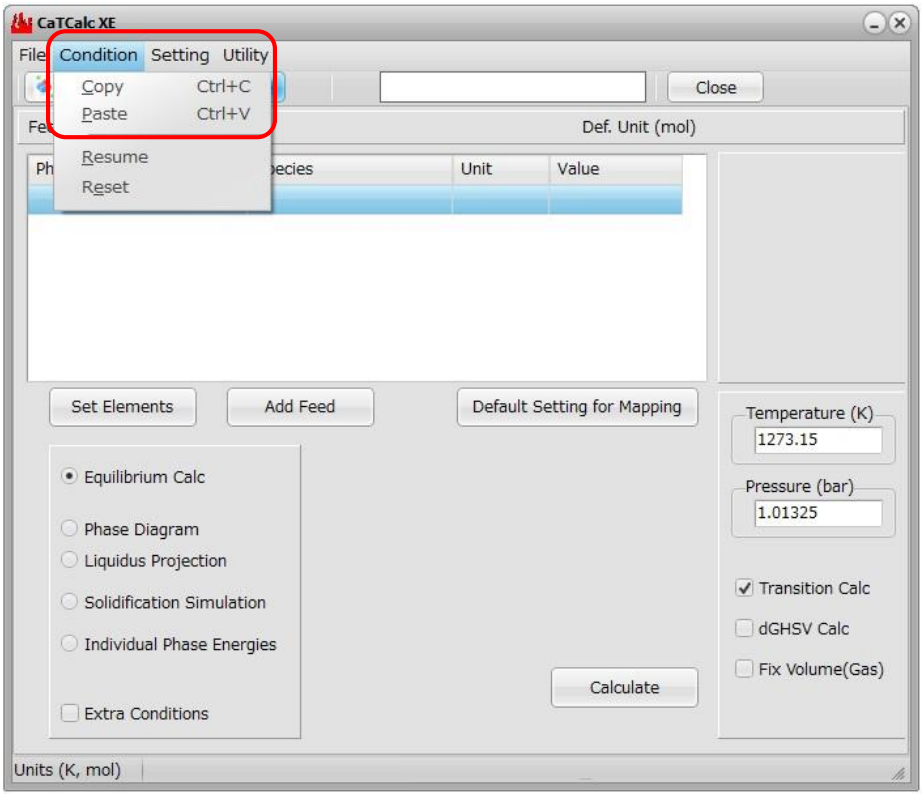


General procedure

① Set the Feed (reactant), select “unit" and enter "value".
② Select the type of calculation.
③ Set parameter values, temperature, pressure and other calculation conditions.

③ Calculation screen

■ Save/Reset Conditions

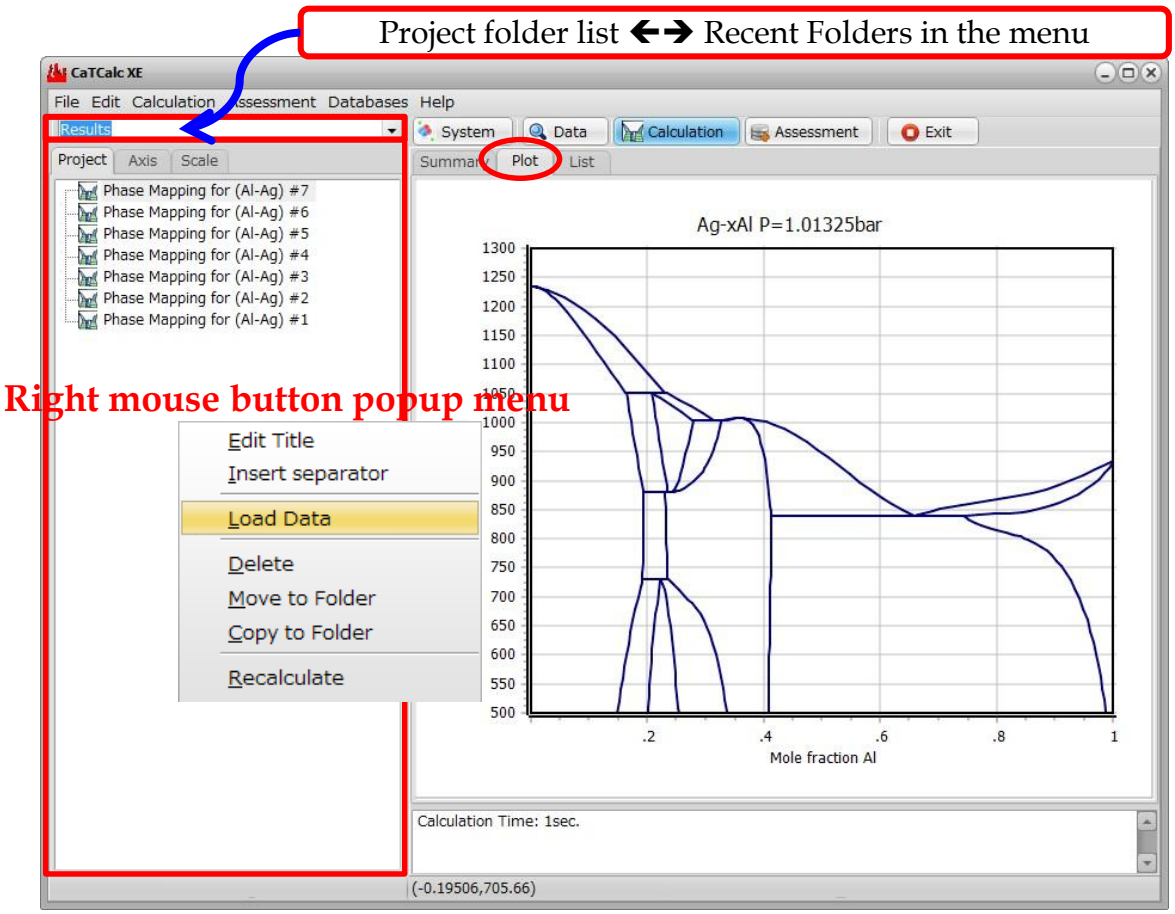


The calculation conditions can be copied into the clipboard by clicking the [**Condition**]–[**Copy**] menu. You may paste them in Excel or else to save. It is also possible to reset the calculation conditions by the [**Paste**] menu . [**Resume**] is to reset the calculation conditions of the previous calculation, which is useful when you try just the same calculation using different data file. Please make sure that the settings are correct.

Ⅳ-3. Viewing Projects and Calculations

① Project / Axis / Scale

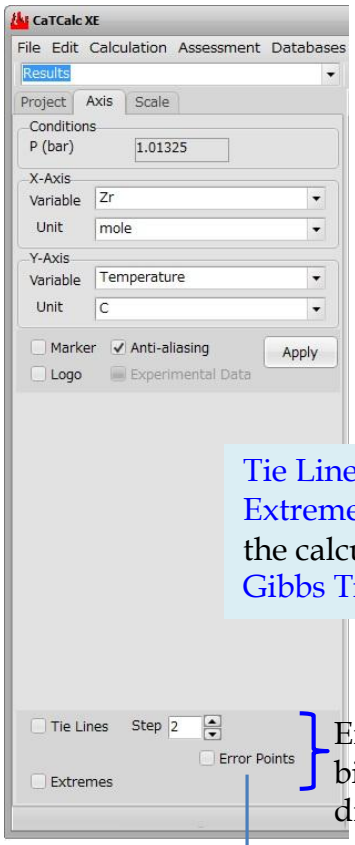
◆ Project： The results are automatically saved as a project



- For each calculation result displayed in the Project panel, you can use the pop-up menu displayed by pressing the right mouse button.
- When you click [**Load Data**], the calculation result is automatically loaded and displayed in the right viewer panel. Note that when the Plot tab appears to display a plot, the List tab also appears at the same time. In addition, the Axis and Scale tabs appear in the left Project panel.
- When the Plot tab does not appear, as in a single point calculation, only the List tab appears in the Viewer panel. In such a case, the Axis and Scale tabs of the Project panel will not appear.
- You can also reload the calculation results by double-clicking on the list of projects. Currently, the project list cannot be rearranged.
- The Project folder list corresponds to the Recent Folders list in the menu. To remove a folder from the list, use the right button pop-up menu in the Project folder list.

① Project / Axis / Scale

◆ Axis

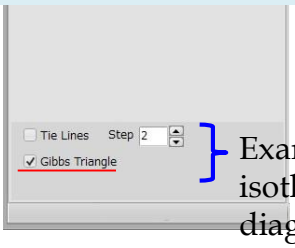


← The calculation conditions are displayed here.

← Select the variable for the axis.

Tie Line： Display tie-lines in the phase diagram, if present.
Extremes：Indication of temperature maxima and minima (only if the calculation is possible)
Gibbs Triangle： Gibbs Triangle for the ternary phase diagrams

Example for a binary phase diagram



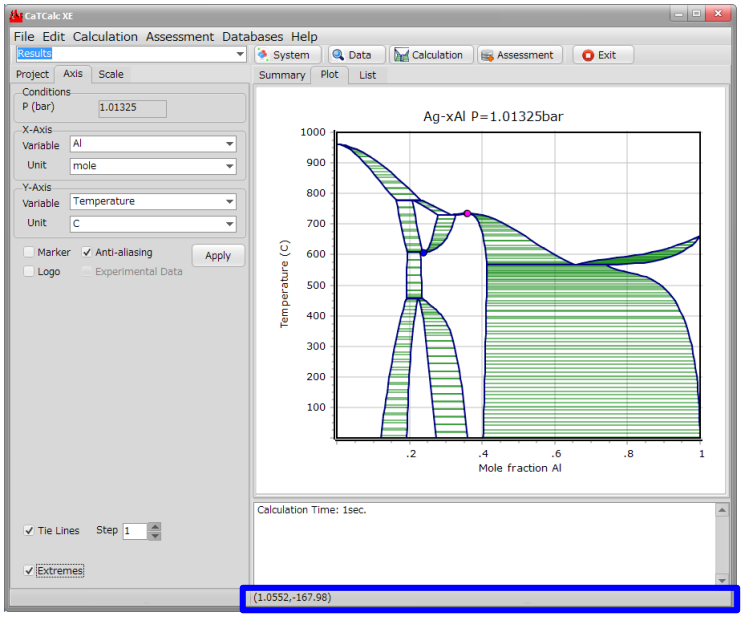
Example for a ternary isothermal phase diagram

Error Points： This checkbox appears when errors occurred during the calculation. Checking it will show up the point at which the error occurred. In most cases, you can ignore them because the system automatically tries recalculation if an error occurs. If the phase boundary calculation apparently failed, try a manual scan (see page 71).

① Project / Axis / Scale

◆ Axis

Tie-Lines and Extremes

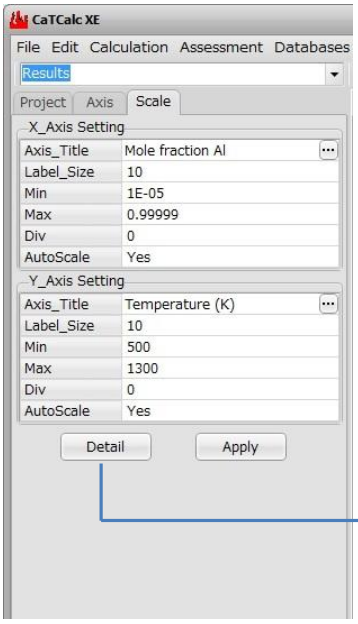


Status bar

The red and blue points for the Extremes indicate temperature maxima and minima, respectively.

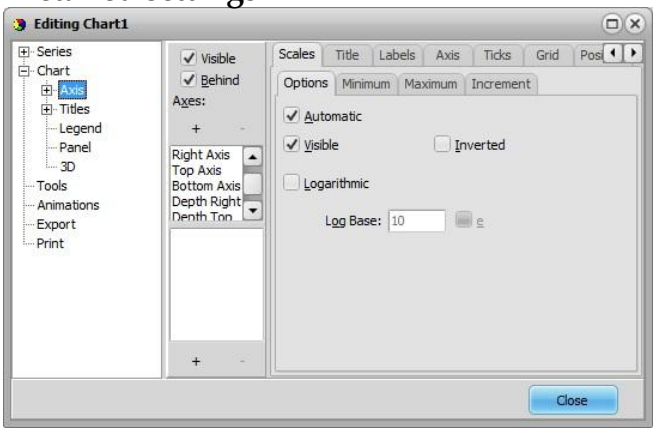
＊ Detailed information about each point will be shown in the Status bar when you hold down the Shift key and move the mouse cursor near the point.

◆ Scale： Setting the Display Scale of the Diagram



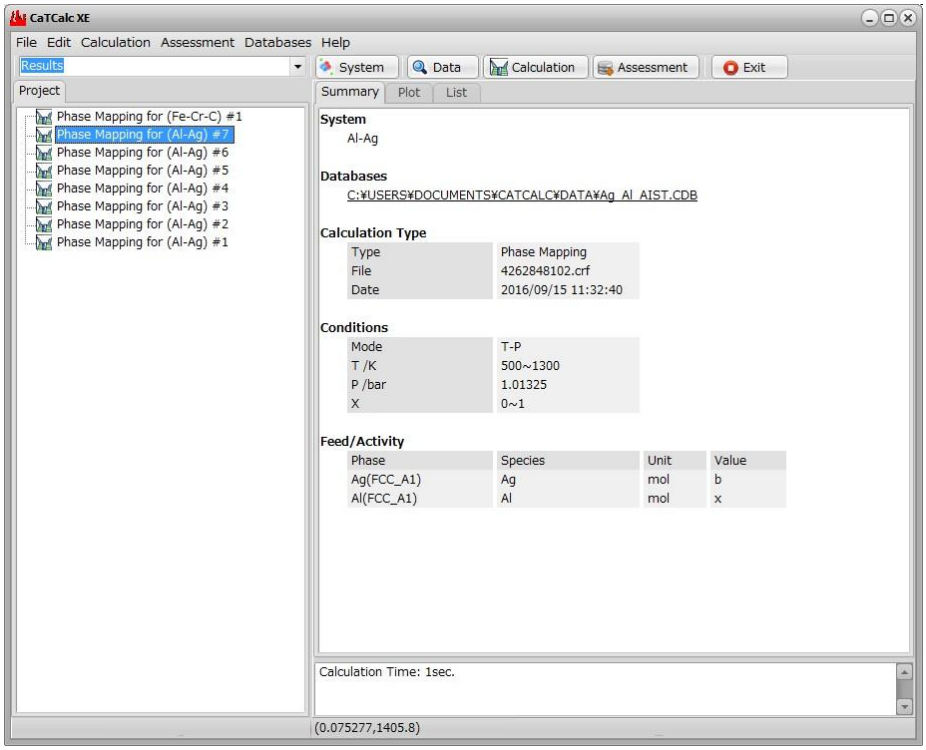
Press the Detail button to display the detailed setting menu, if necessary.

Detailed settings



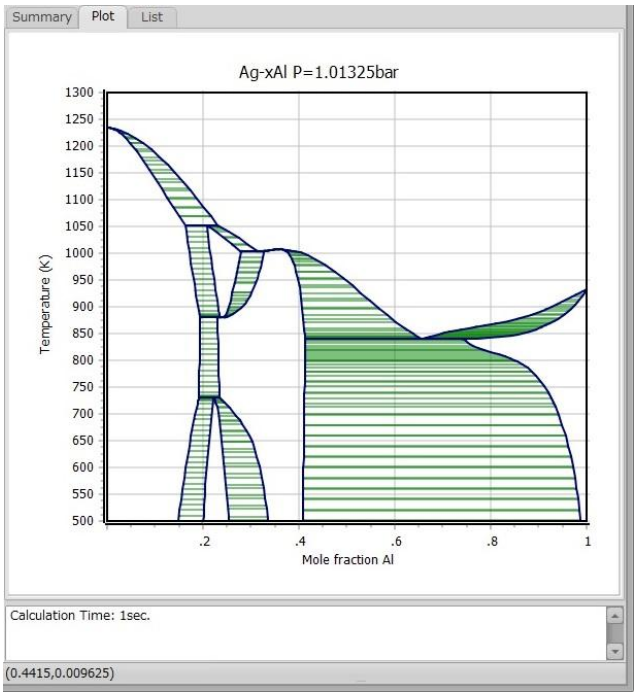
② Summary / Plot / List view

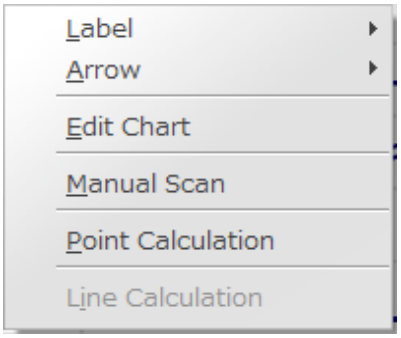
◆ Summary： The database and calculation conditions used for the calculation are displayed in one view.



② Summary / Plot / List view

◆ Plot panel: plot the results

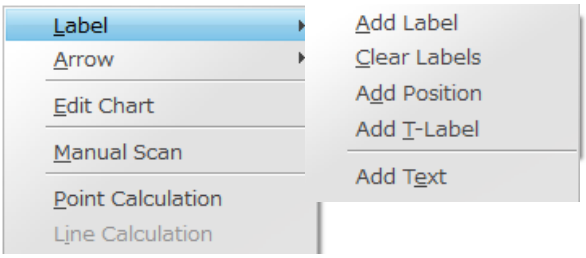


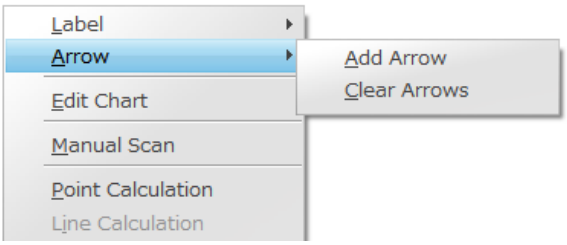


(Right click popup menu)

Right click on the plot area to bring up a pop-up menu. You can edit the details.

Labeling phase name : [Ctrl] + left mouse button click
Enlarge the graph: Left click and drag from top left to bottom right
Move the graph: [Ctrl] + right-click and drag
Return to the original graph: left-click and drag from bottom right to top left

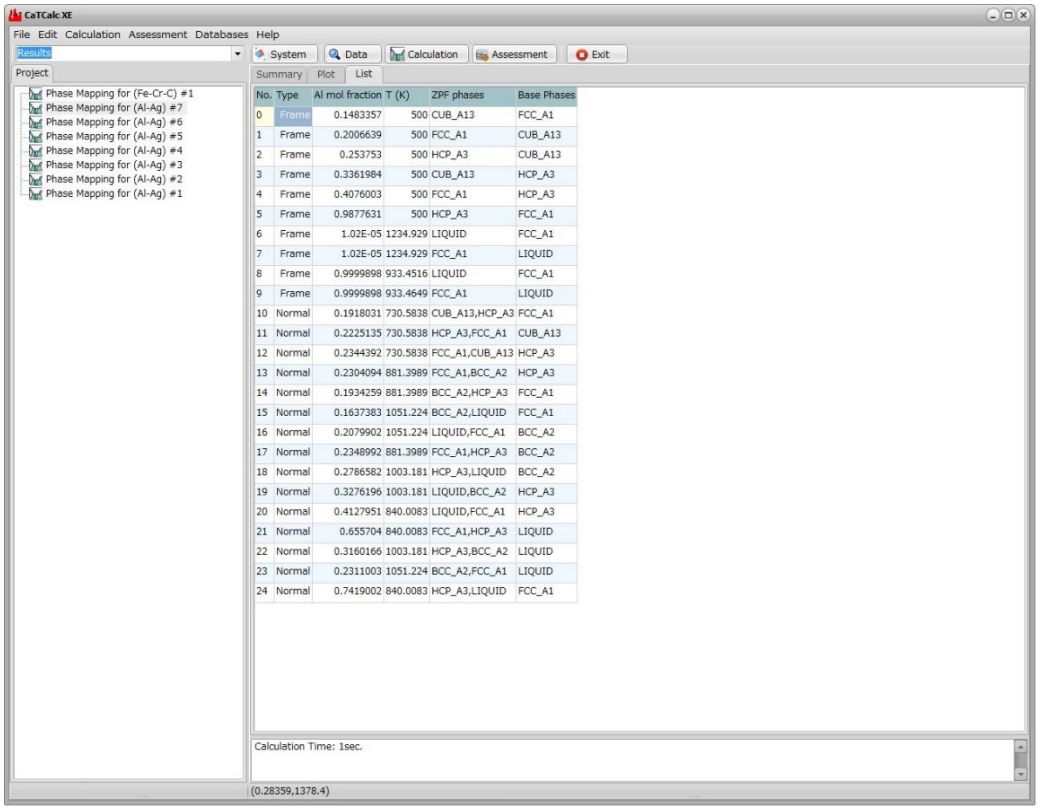




For example, eutectic temperature can be labeled as follows:
1. Move the mouse cursor to the vicinity of the eutectic point with pressing the [Shift] key and display the eutectic point information on the status bar.
2. Press the right mouse button and select [**Add T-Label**] from the menu. The position of the Label corresponds to the axis, and it automatically follows the scaling and movement of the figure. Therefore, the Label can only be placed within the plot area.
3. Use [**Add Text**] to place a label outside the axis frame.

② Summary / Plot / List view

◆ **List panel**: numerical values are listed.



No.	Type	Al mol fraction	T (K)	ZPF phases	Base Phases
0	Frame	0.1483357	500	CUB_A13	FCC_A1
1	Frame	0.2006639	500	FCC_A1	CUB_A13
2	Frame	0.253753	500	HCP_A3	CUB_A13
3	Frame	0.3361984	500	CUB_A13	HCP_A3
4	Frame	0.4076003	500	FCC_A1	HCP_A3
5	Frame	0.9877631	500	HCP_A3	FCC_A1
6	Frame	1.02E-05	1234.929	LIQUID	FCC_A1
7	Frame	1.02E-05	1234.929	FCC_A1	LIQUID
8	Frame	0.9999898	933.4516	LIQUID	FCC_A1
9	Frame	0.9999898	933.4649	FCC_A1	LIQUID
10	Normal	0.1918031	730.5838	CUB_A13,HCP_A3	FCC_A1
11	Normal	0.2225135	730.5838	HCP_A3,FCC_A1	CUB_A13
12	Normal	0.2344392	730.5838	FCC_A1,CUB_A13	HCP_A3
13	Normal	0.2304094	881.3989	FCC_A1,BCC_A2	HCP_A3
14	Normal	0.1934259	881.3989	BCC_A2,HCP_A3	FCC_A1
15	Normal	0.1637383	1051.224	BCC_A2,LIQUID	FCC_A1
16	Normal	0.2079902	1051.224	LIQUID,FCC_A1	BCC_A2
17	Normal	0.2348992	881.3989	FCC_A1,HCP_A3	BCC_A2
18	Normal	0.2786582	1003.181	HCP_A3,LIQUID	BCC_A2
19	Normal	0.3276196	1003.181	LIQUID,BCC_A2	HCP_A3
20	Normal	0.4127951	840.0083	LIQUID,FCC_A1	HCP_A3
21	Normal	0.655704	840.0083	FCC_A1,HCP_A3	LIQUID
22	Normal	0.3160166	1003.181	HCP_A3,BCC_A2	LIQUID
23	Normal	0.2311003	1051.224	BCC_A2,FCC_A1	LIQUID
24	Normal	0.7419002	840.0083	HCP_A3,LIQUID	FCC_A1

All calculation results are basically displayed.
Type of data to be displayed can be selected in "Select List" of "Edit Menu".

You can use other graphing software to create graphs as well, by copying data via the clipboard using the Edit menu.

Ⅴ. Various calculation methods

V-1. Single-point and series equilibrium calculation

V-2. Phase diagram calculation

V-3. Liquidus Projection calculation

V-4. Solidification Simulation

V-5. Adiabatic calculation

V-6. Calculation of Individual Phase Energy

V-7. Calculation of aqueous systems

V -1. Single-point and series equilibrium calculation

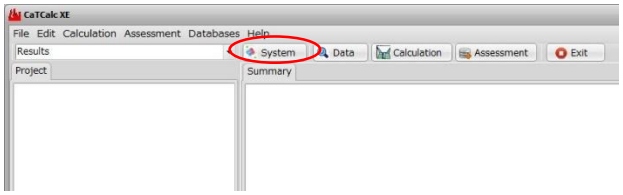
The general procedure for the calculation is as follows:

1) Specification of the elements of the system and selection of the thermodynamic data file to be used.
2) Select Phase and Species, if necessary.
3) Setting up the calculation conditions.
4) Calculation execution.
5) Display results as a plot and a list.

Examples are described in detail below.

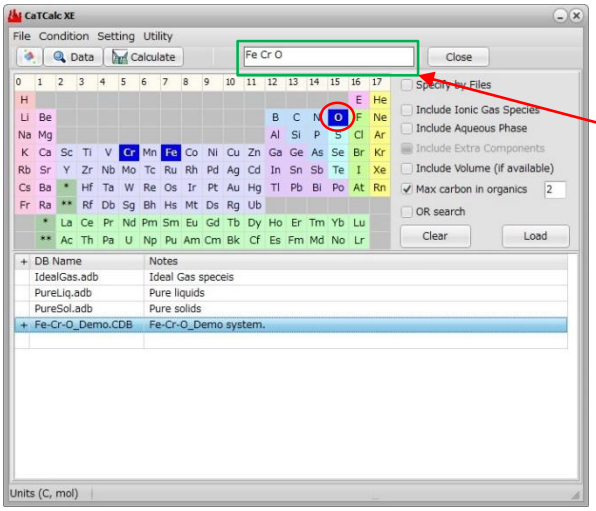
① Equilibrium Calculation

By double-clicking the shortcut key, CaTCalc is launched.



1. Press the System button.

The screen for selecting elements will appear.



2. Click directly on the element.

・ Alternatively, you can fill in the elements list directly and press enter. (separated by a space)

・Thermodynamic data files, that contain the elements, will be displayed in the data file area. The registered data files will be displayed. By default, the files stored in the CaTCalc/Data folder are registered automatically. (Files in other locations or newly added files must be registered manually).

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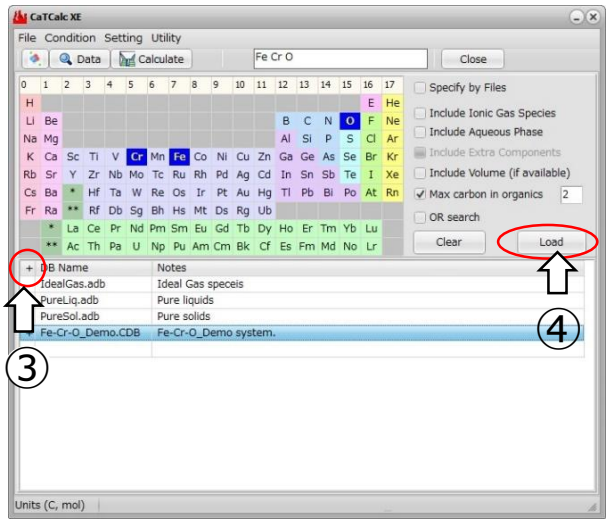
① Equilibrium Calculation



3. Select the data file.

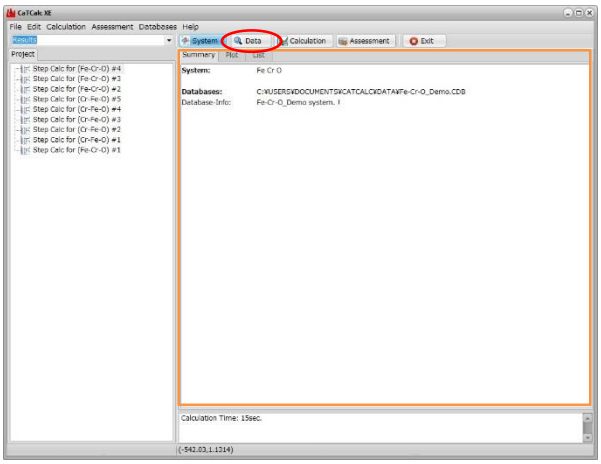
Check the cell next to the DB Name. Then "+" is displayed and selected.

If you need gas, select also "IdealGas.ADB“ in addition.

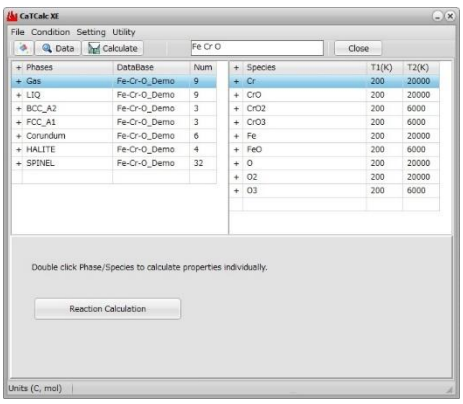
4. Click the [Load] button.

Reads the data in the selected data file.

You will see the information about the database file in the “Summary tab”.



[Data screen]



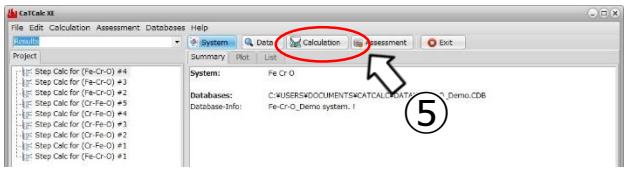
*By clicking the [Data] button, the loaded data will be displayed in the "Phase List" and "Species List“.

For pure stoichiometric phases, the Phase list shows solid and liquid phases as a group and the individual phases are listed in the Species list.

*The pure liquid phases are not selected by default because the liquid phase usually forms single solution phase.

Next page

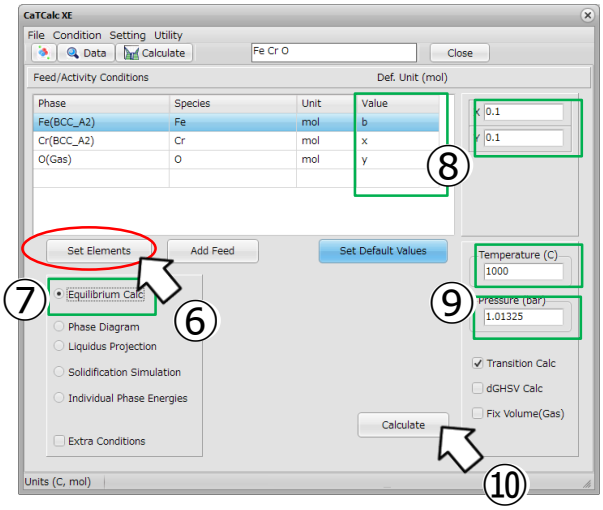
① Equilibrium Calculation



5. Press the "Calculation" button.
   - The "Calculations" screen appears.

6. Click the [Set Elements] button.
   - Each element is entered automatically.

7. Select "Equilibrium Calc".



＊At this point, the typical calculation conditions are set by clicking the [Set Default Values] button, and it is convenient to set the conditions by modifying them.

8. Enter the [Value] value.

・In general, Values can be entered as numeric values, parameters, a linear function of them, (e.g., 1+2x), or a special parameter, b. In the present case, it is set up as shown in the left figure.

＊There are 5 parameters available, “x”, “y”, “z”, “w”, and “a” (uppercase letters are also OK). b stands for balance, and is a dependent parameter that is automatically calculated so that the total amount of Feed is set to 1 (use "b100" if you want to calculate it as a percentage).

＊ After entering any of these parameters, the corresponding edit box will appear in the "Parameter Area" and you can specify their numerical values.

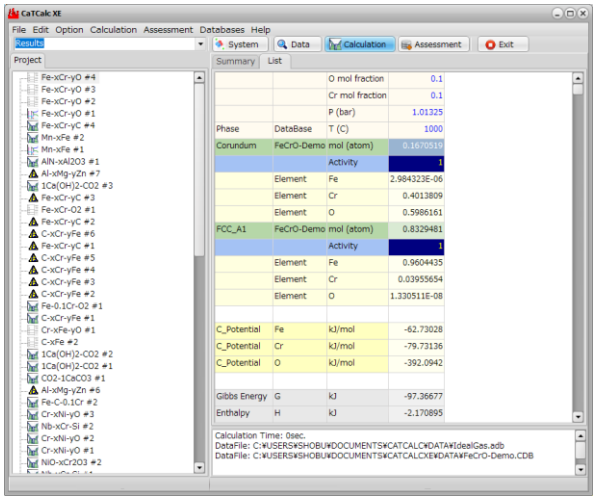
・Select [**Unit**] from the drop-down list that appears if you click the cell. You can also specify the activity in this list.

9. Set the values of "Temperature" and "Pressure".

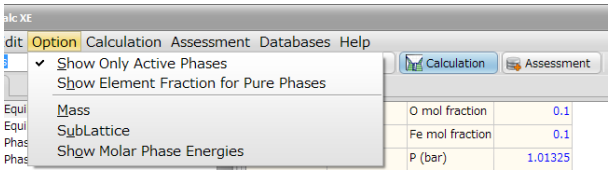
10. Use the [Calculate] button to start calculation.

Next page

① Equilibrium Calculation



The result of the calculation is automatically displayed as shown on the left.



You find the display options under [Option] in the menu.

		O mol fraction	0.1
		Cr mol fraction	0.1
		P (bar)	1.01325
Phase	DataBase	T (C)	1000
Corundum	FeCrO-Demo	mol (atom)	0.1670519
		Activity	1
	Element	Fe	2.984323E-06
	Element	Cr	0.4013809
	Element	O	0.5986161
FCC_A1	FeCrO-Demo	mol (atom)	0.8329481
		Activity	1
	Element	Fe	0.9604435
	Element	Cr	0.03955654
	Element	O	1.330511E-08
C_Potential	Fe	kJ/mol	-62.73028
C_Potential	Cr	kJ/mol	-79.73136
C_Potential	O	kJ/mol	-392.0942
Gibbs Energy	G	kJ	-97.36677
Enthalpy	H	kJ	-2.170895
Entropy	S	J/K	74.77193
Heat Capacity	C	J/K	33.58647
Volume	V	L	0
density	r	g/cm3	0
ErrorCode			0
Loop			33

Phase

Calculation conditions

Amount of the phase

Activity of the phase

Element fractions

Chemical potential of each element

The Gibbs energy of the entire system, etc. However, the volume and density are only for the gas phase if the database does not contain volume data for the solid or liquid phase.

(Note) mol amount

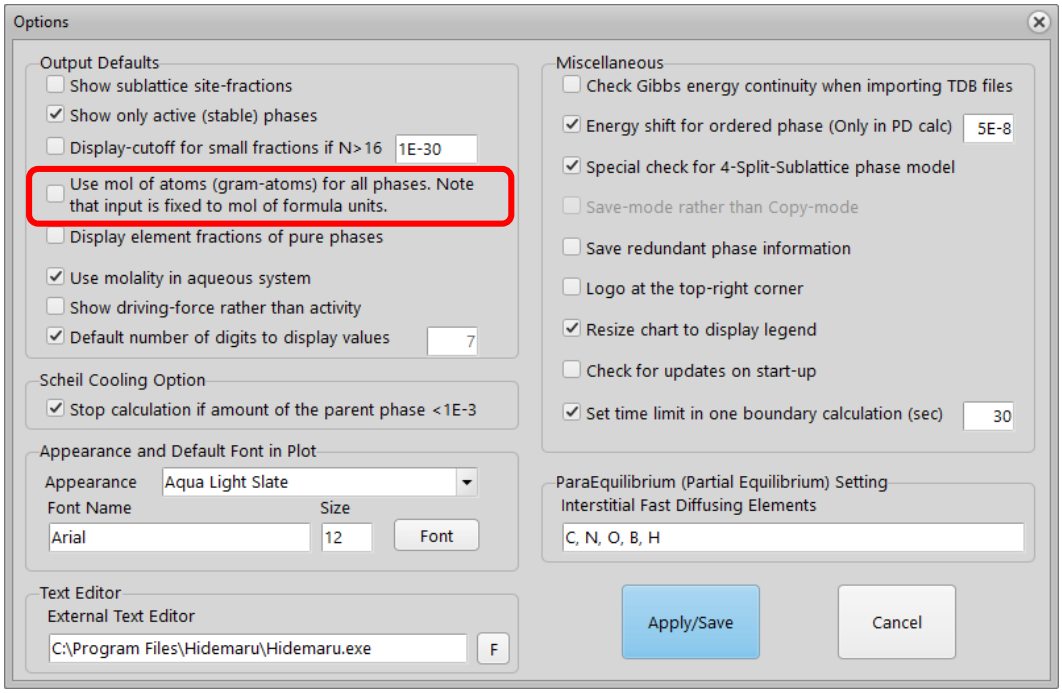
When displaying the amount of a phase in moles, it is important to note what the moles are of.

- For gases, water, etc.: Mole of molecules are natural as the molecules are real entities and important.
  - Examples: H2, O2, H2O, etc.
- For metals, moles of atoms are usually used since they are atomic units.
  - Example: BCC phase, etc.
- For pure inorganic compounds, moles of formula units are used.
  - Example: SiC, SiO2, etc.
- For solid solutions and melts, because amounts depend on the definition of the solution when moles of formula units are employed, moles of atoms are exclusively used in CaTCalc.
  - Example: SiO2-Al2O3 solid solution, mullite, etc.

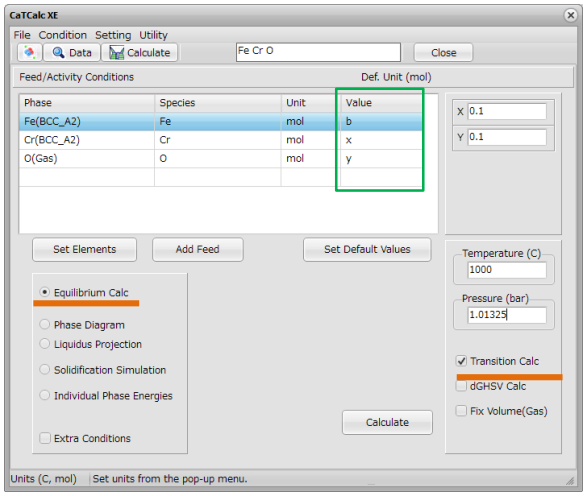
Accordingly, mol of atoms is usually used in computational thermodynamics for metallic systems, though mol of formula units is usually used in chemical reaction calculations.

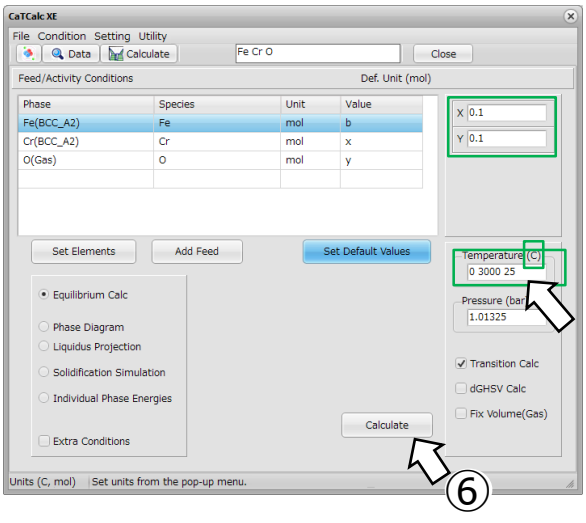
In the list display of the result in CaTCalc, the definition of the mole is clearly indicated, but in the graph plot, it is unclear, so care must be taken when comparing phase amounts. It is better to compare the amount of phases by mol of atoms or mass.

＊ The mol definition can be set in the menu [File]-[Preference]-[Output Defaults]. Note that the input of reactants (feed) is fixed to the mol of formula units.



② Series calculation with varying temperature





1. Set the calculation mode.

"Equilibrium Calc" should be checked. Make sure "Transition Calc" is checked to find transition points.

2. Set the [Value] value.

[Unit] can be switched individually from the list. You can also double click on the **Def. Unit** label to switch them all at once.

3. Set the value of "X", "Y".

4. Set the value of "Temperature".

Enter the initial value (start), the end value (end), and the interval value (step) in that order. Delimiter is a space or a comma.

You can switch between units by double-clicking on a unit label. Uncommon units can be chosen only in the unit selection dialog.

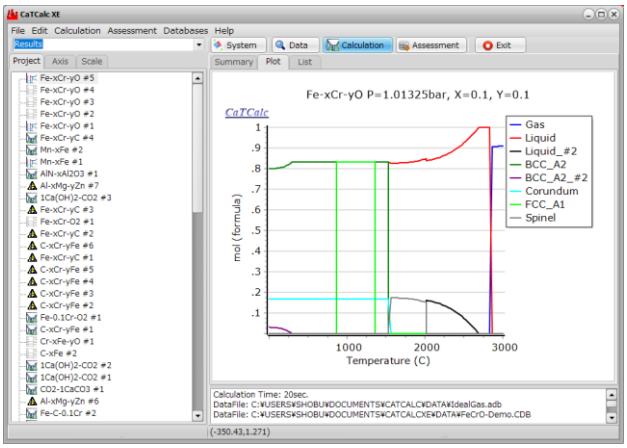
5. Set the value of "Pressure".

You can switch units by double-clicking on the unit. However, units such as Log(P) can only be set in the unit selection dialog.

6. Press the [**Calculate**] button to start calculation.

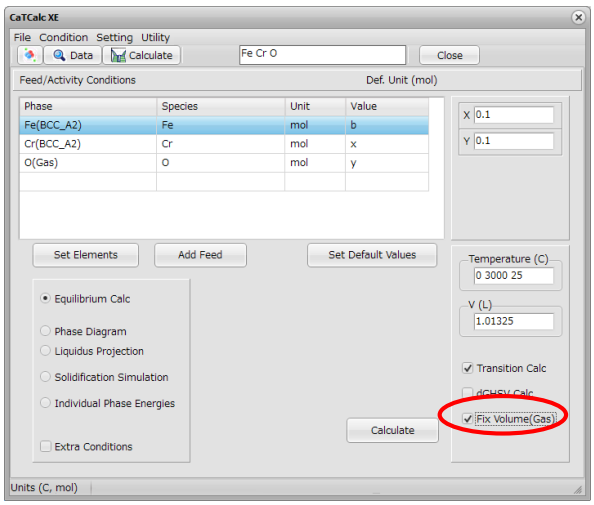
Next page

② Series calculation with varying temperature



The result of the equilibrium calculation is displayed as a graph.

<Fix Volume(Gas)>



The Pressure field changes to Volume. Note that currently only the volume of the gas is considered. If this field is gray, the gas phase is absent. Go back to the system setting and load the data for the gas phase.

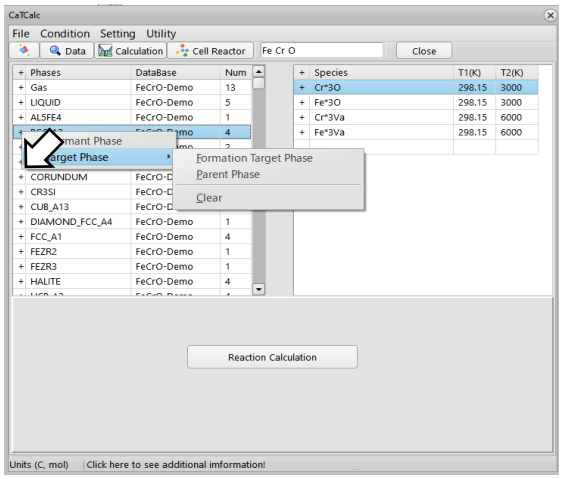
③ Target calculation

Two kinds of target calculation are supported.

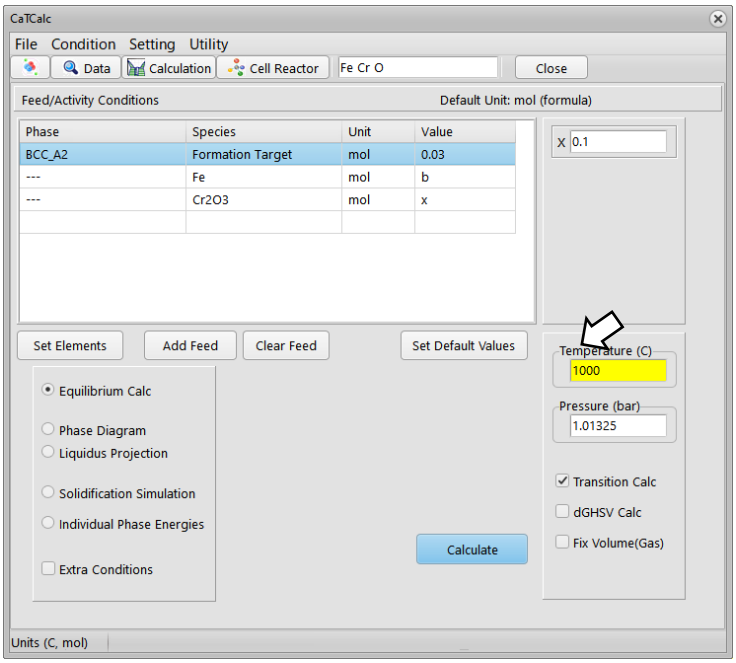
- Formation target
  - This determines the temperature or composition at which the target phase appears.
  - Calculations can also be made specifying the amount of the phase.
- Precipitation Target
  - This determines the temperature or composition at which other phases precipitate from the target phase.

In both cases, the Data screen is used to specify the phase of the Target, and the settings are also displayed on the Calculation screen.

[Data screen]



[Calculation screen]



(1) Right-click on the phase row to open the menu shown in the left figure, and specify the target phase.

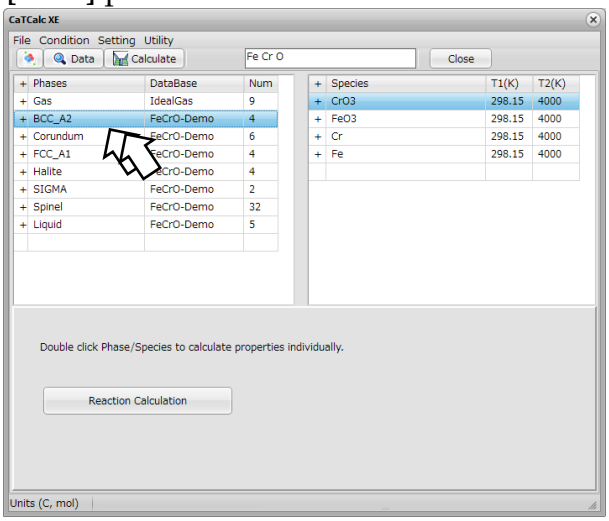
The “Parent Phase” specifies the phase of the precipitation target.
(The Dormant phase is a phase that is not included in the calculation but whose stability is evaluated.)
"F" or "P" will appear in the left column of the phase name.

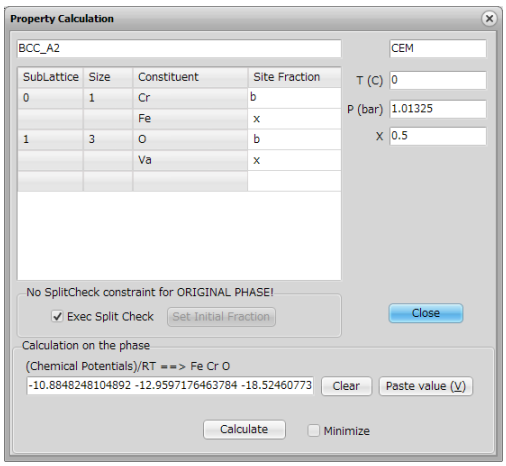
Then, back to the Calculation screen to set conditions.
1. Target calculation is performed in the equilibrium calculation mode.
2. The variable for the Target calculation is the quantity whose edit box is yellow. The variable can be changed by mouse-clicking on the label (upper right corner).

The phase amount can be specified, but since phase amounts often change discontinuously, we recommend that you first obtain an approximate value by series calculation and then refine it by Target calculation using that as the initial value.

④ Extended functions

[**Data**] panel





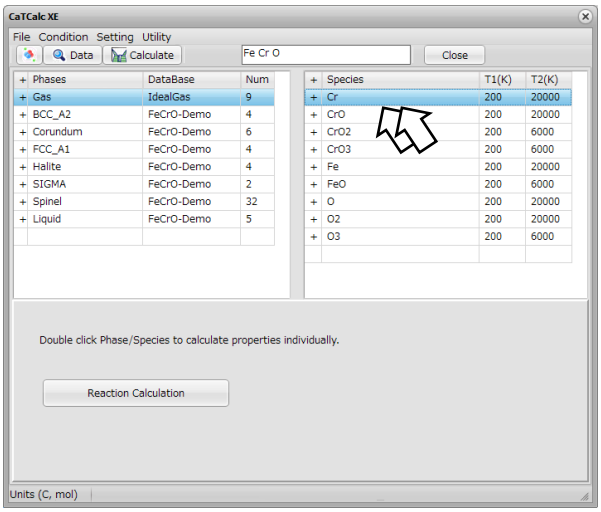
1) Double-click the Phase name.

The Property Calculation window appears.

In the Property Calculation window, the molar Gibbs Energy calculation and minimization calculation under for a set of specified chemical potentials can be performed. If you do not specify the [**Exec Split Check**] option, the initial value of Site Fraction is used as the initial value for the minimization calculation, and if you do, it will automatically try some of the initial values to find multiple minima of the Gibbs energy.

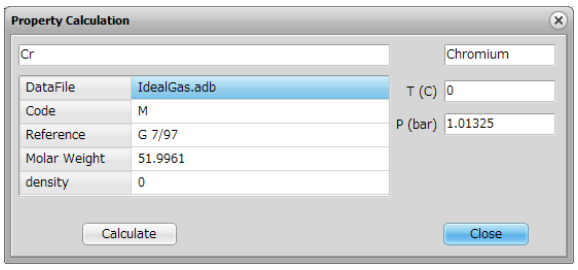
To calculate the Gibbs Energy of multiple phases at once, use the Individual phase energy calculation function in the [Calculation] panel.

④ Extended functions



2) Double-click the Species name.

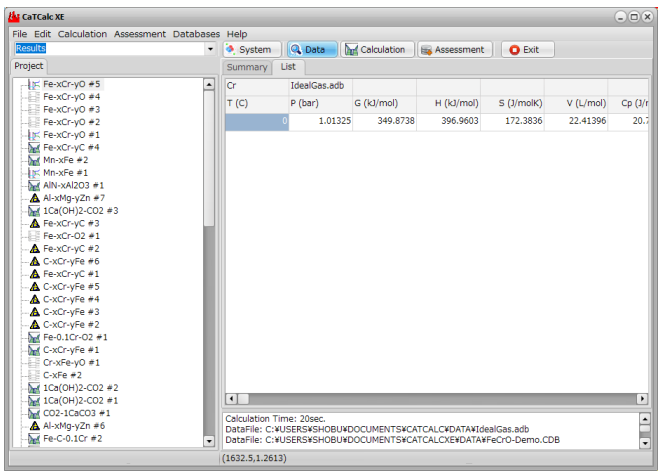
The <Properties> calculation dialog for the species appears.



3) Set the conditions and click the "Calculation" button.

You can calculate the individual G, H, etc. for each Species.

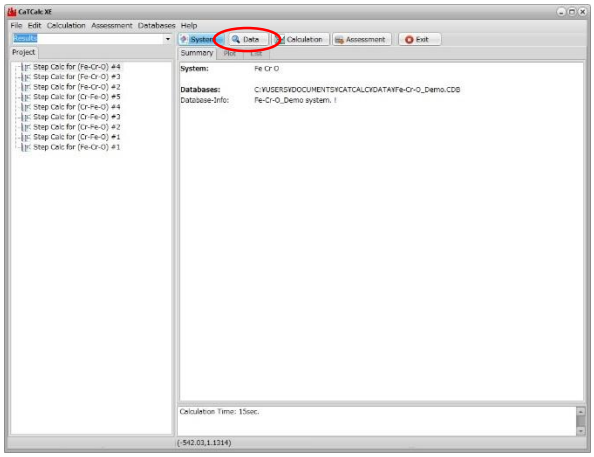
The [Utility]-[List Species] menu in the menu is useful when you want to calculate multiple species in a batch.



Display of calculation results

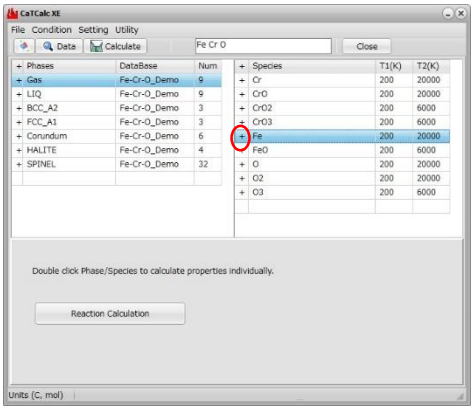
⑤ Notes on calculation conditions

Selection of phases and species to be included in calculations

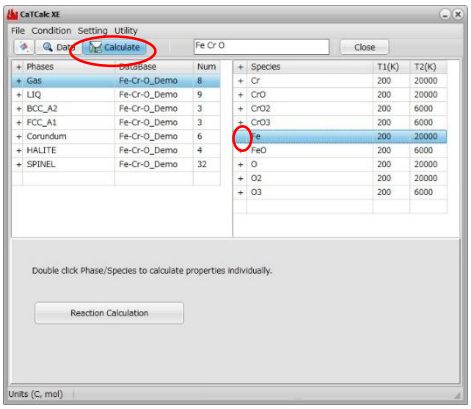


1. Click the [Data] button.

The Data panel will be displayed.



For example, if you select "Gas" in the <Phases> list and uncheck the "Fe" in the <Species> list, the calculation does not take “Fe” in the Gas phase into account.



2. After setting, click [Calculation].

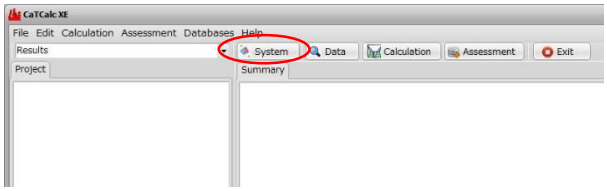
Go to the "Calculation" panel.

V-2. Phase diagram calculation

①Procedure to calculate phase diagrams

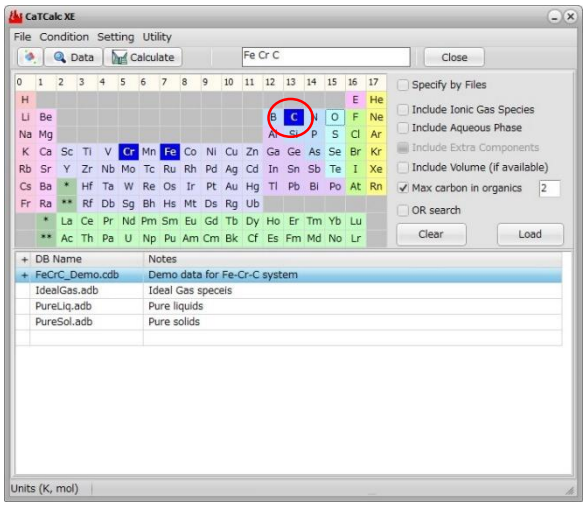
The calculation procedure is the same for both binary and ternary systems. The following is a detailed example of a ternary phase diagram calculation.

By double-clicking the shortcut key, CaTCalc is launched.



1. Press System button.

The "Element Selection" screen will appear.

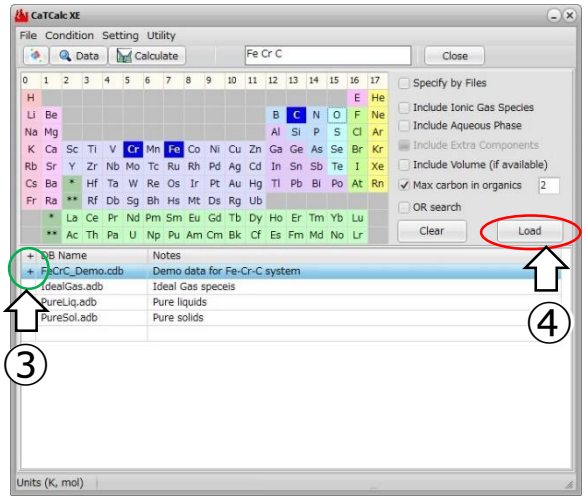


2. Click elements.

The thermodynamic data files containing the element will be listed in the data file area.

Next page

① Phase diagram calculation procedure



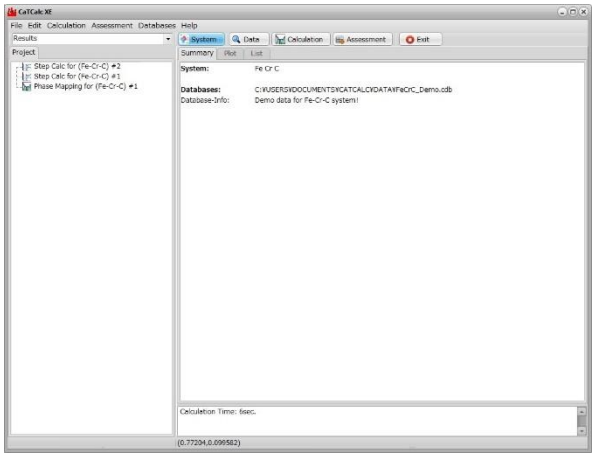
3. Select the data file.

Check the cell next to the DB Name to set "+".

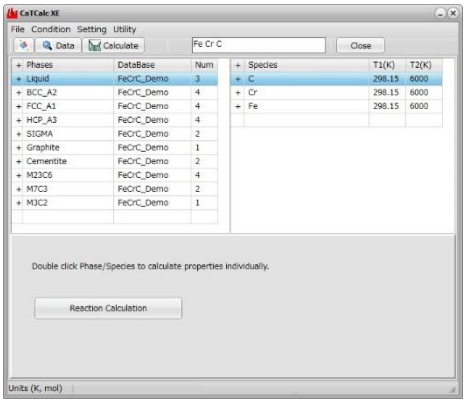
4. Click [**Load**] button.

You will see the information of the DB you selected in the "Summary" tab of the main screen.

Detailed information on the database will be displayed by clicking the [**Data**] button.

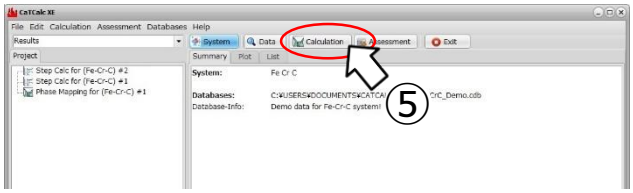


[Data] screen



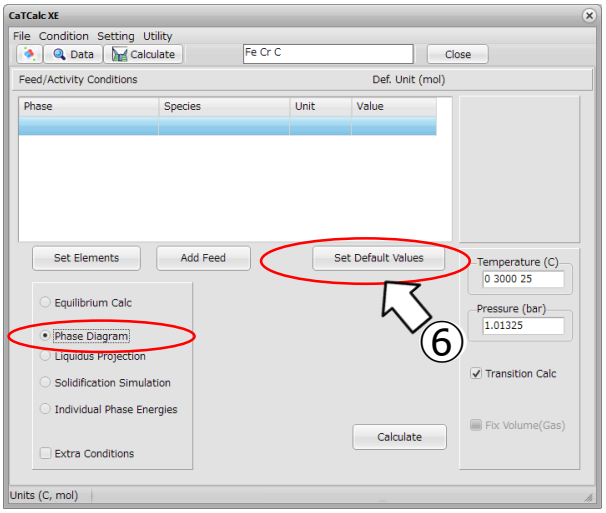
Next page

① Phase diagram calculation procedure



5. Click the [**Calculation**] button.

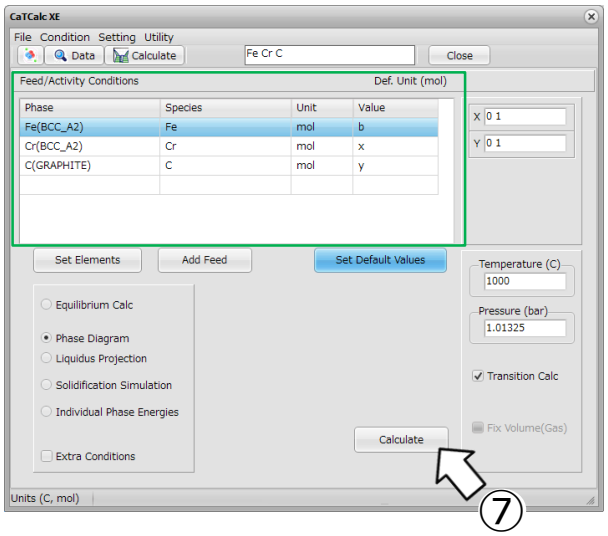
The Calculation screen is displayed.



The following shows how to use [**Set Default Values**] to set conditions. If you want to use [**Set Elements**] / [**Add Feed**], please refer to page 48 and 49.

Check that “Phase Diagram” is selected as the calculation type.

6. Click the [**Set Default Values**] button.



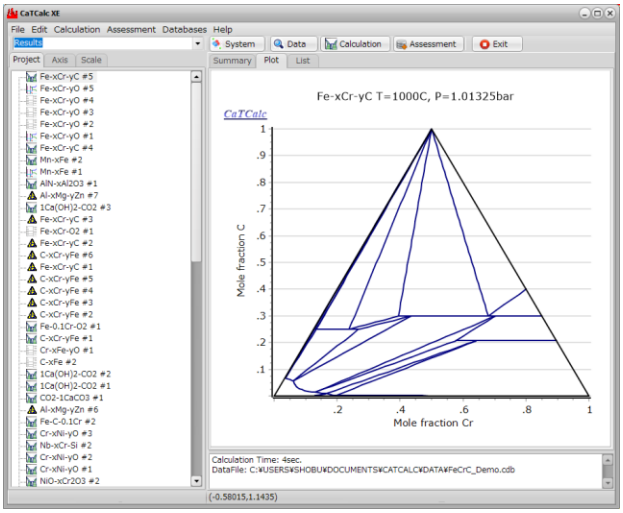
Typical values are set for the Feed/Activity Condition. For a ternary system, an isothermal phase diagram calculation is selected.

7. Press the [**Calculate**] button.

The phase diagram calculation starts.

Next page

① Phase diagram calculation procedure



The results will be displayed automatically.

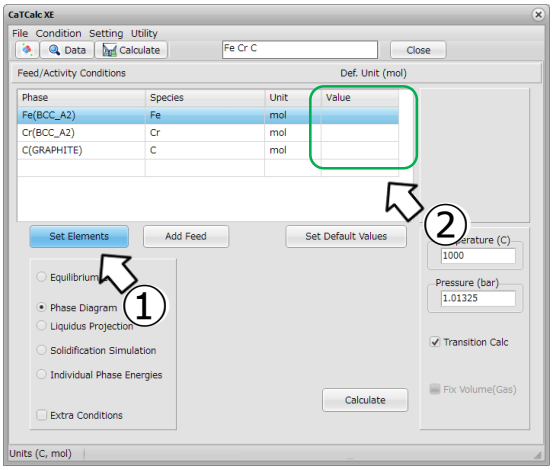
From the next page, following items will be explained:

- ◆ Changing the calculation conditions (p. 48)
- ◆ Edit the results (P.51)
- ◆ Use the [**Data**] screen (P.53)

② Changing the conditions for Feed

◆There are three ways to set up the Feed.
1. Use the [**Set Elements**] button
2. Use the [**Add Feed**] button
3. Specify in the Data screen

1. Use the [**Set Elements**] button

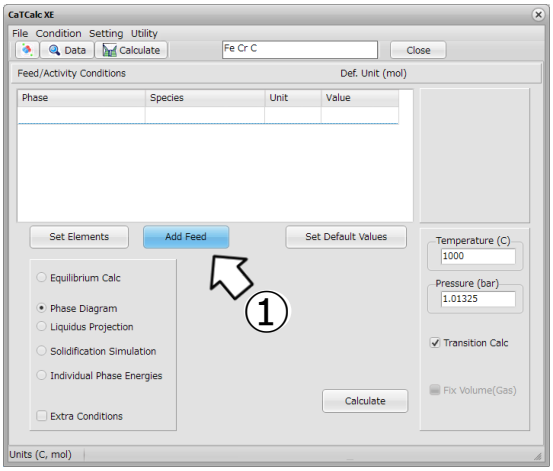


① Click the [**Set Elements**] button.

The elements in the standard state will be set in [Feed / Activity Conditions].

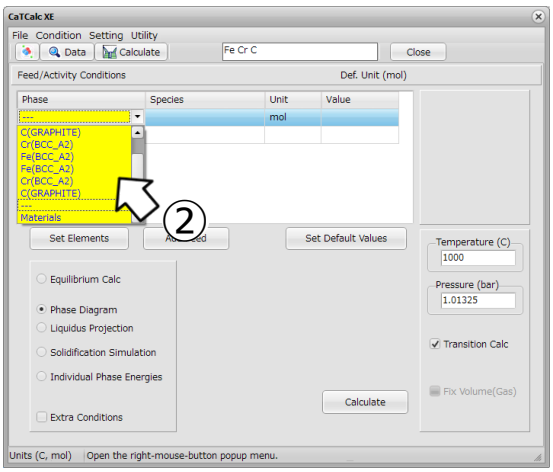
② The Value value can be entered manually, or by pressing [Set Default Values] button. In this case, you can also use b,x,y.

2. Use the [**Add Feed**] button. Feed can be of any composition.



① Click the [**Add Feed**] button.

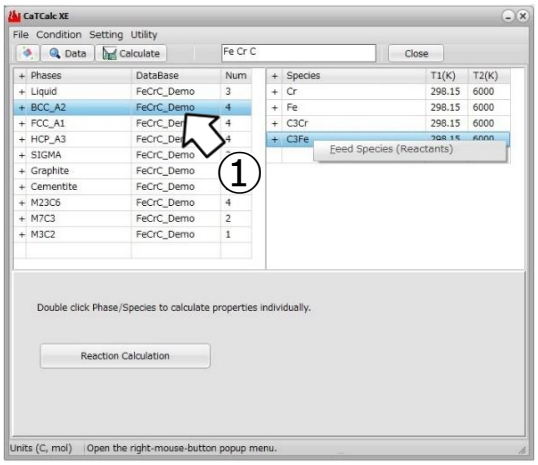
A single blank row will be inserted in the [Feed / Activity Conditions] list and if you leave Phase name as "---", you can manually enter a desired composition in the Species column.



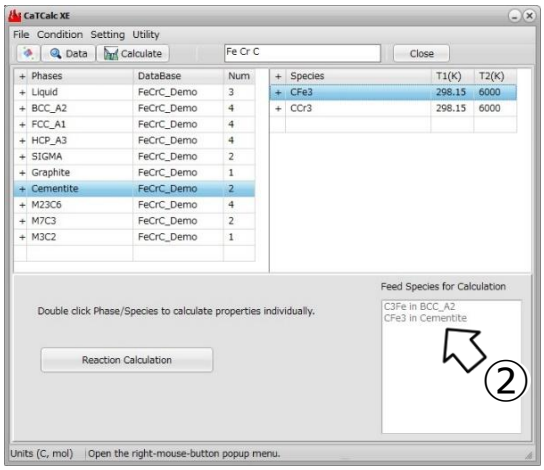
② If you click the [**Phase**] cell, you can choose from the list.
*Note: “Material” of mixed compositions is described in page 67.

② Changing the conditions for Feed

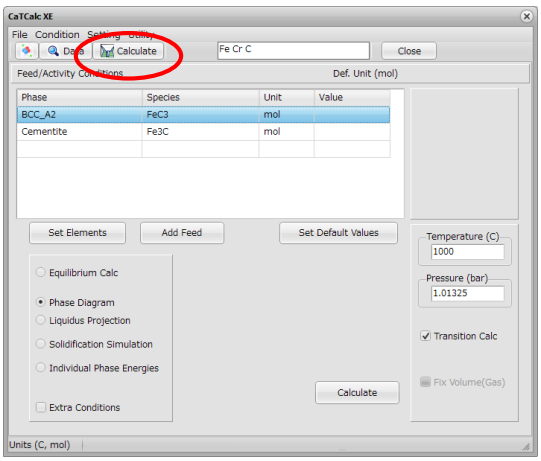
3. Set Feed in the [**Data**] screen.



① On the Data screen, select a Phase that includes a Species that you want to use as a feed, then select the Species from the list of Species and set it as a Feed Species in the pop-up menu that appears by right-clicking the mouse. Only species or pure stoichiometric phases can be set for Feed.



② The selected Feeds will be set in the Feed/Activity field of the Calculation screen, and will be displayed in a list as shown in the left figure, which can also be viewed on the Data screen (deletion from this list is not possible, so it will be done on the Calculation screen).



③ When you go to the Calculation screen, the Feed is set. This method is most useful for calculations of enthalpy changes associated with the reaction.

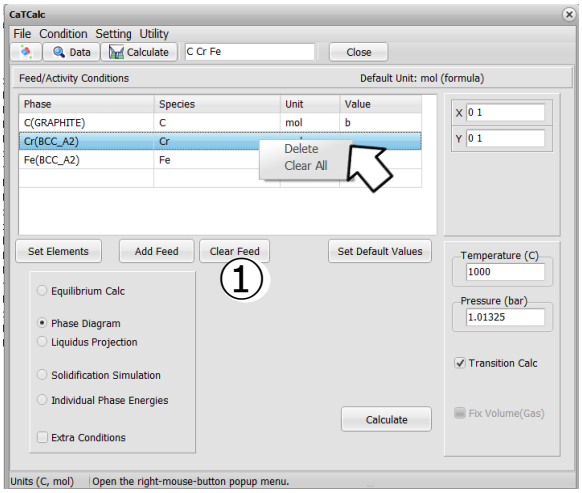
Recommendations

1. General reaction calculation: Use of the [**Data**] screen
2. Phase diagram calculation of metallic systems: [**Set Elements**]
3. Calculation of ceramics systems: [**Add Feed**] or the [**Data**] screen

Of course, combinations are possible.

② Changing the conditions for Feed

Removing Feed settings



① Press the [**Clear**] button to clear everything.
② You can delete the target line of the list by [Ctrl] + left mouse click. Alternatively, as shown in the left figure, you can use the pop-up menu with the right button (depending on where you click, the pop-up may not appear. Try a different position).

Notes on the formula of Feed

There are restrictions on the format that can be set for Feed, as shown in the following example:

①SiO2	OK
②2SiO2	OK
③2*SiO2	Not OK
④2(SiO2)	Not OK
⑤(SiO2)2	OK
⑥2SiO2*3Al2O3	OK

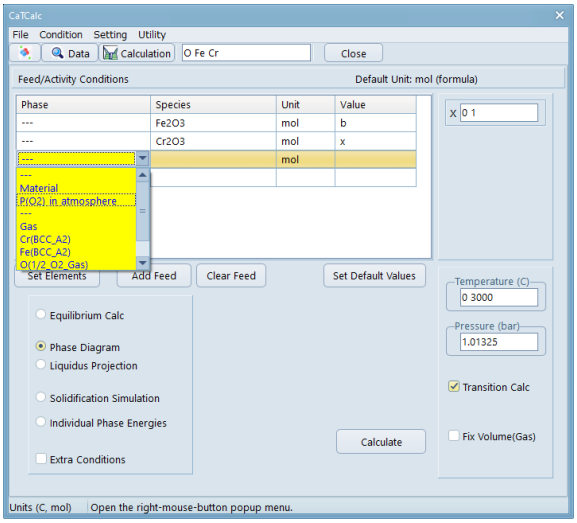
In general, when the last character of a chemical formula that ends with a right parenthesis, the part enclosed by the parenthesis is not recognized as a part of the formula, but as ancillary information. Ancillary information includes, for example, information that distinguishes the isomers of an organic substance.

Also note that **mol of Feed is always mole of formula units, and not mole of atoms**. You can set the mole of atoms as the standard output type in Preferences. If you want to set the mole of atoms in Feed, you should always use the "Elements" to specify Feeds.

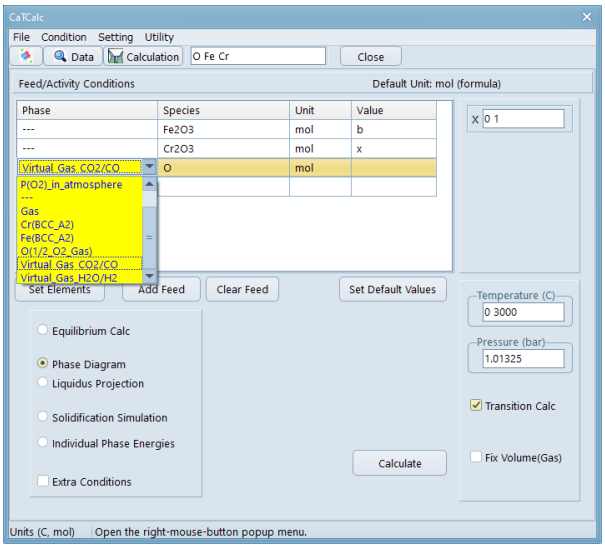
② Changing the conditions for Feed (gas pressure)

◆You can also specify the chemical potential or gas partial pressure as a feed.

Since calculations using the oxygen partial pressure (0.21 bar) as the atmospheric pressure at 1 atm are often performed, we have registered the condition in the dropdown menu so that it can be set easily. The default value is log(0.21)=-0.6777807 from the partial pressure of oxygen in the atmosphere, but it can be changed to any oxygen partial pressure.

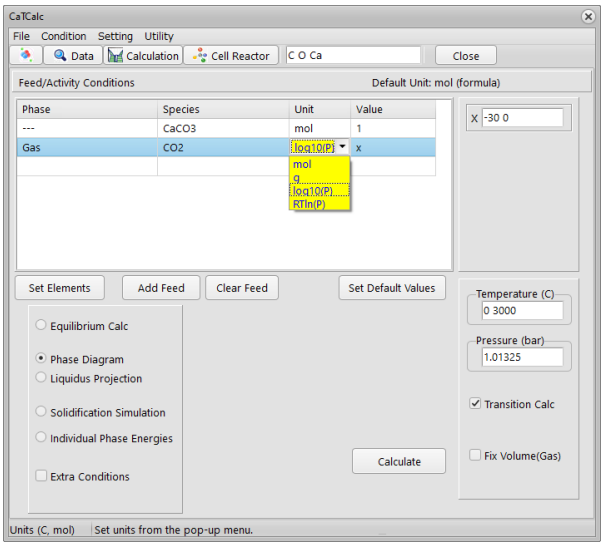


When controlling P(O2), the so-called buffered gas mixture method is sometimes used to control gas pressure ratios such as CO2-CO and H2O-H2. In this case, P(O2) varies depending on temperature, and Virtual_Gas is provided to perform calculations under such conditions. For example, by controlling P(CO2)/P(CO) ratio, P(O2) can be controlled as shown in the figure below. For now, the ratio is limited to less than 1. Choose log10(P) as the Unit and give the logarithm of the P(CO2)/P(CO) ratio in Value. Note that although only the P(O2) is considered in this method, in reality the chemical potential of carbon is also determined, so carburization, etc., may occur, and particular attention should be paid.

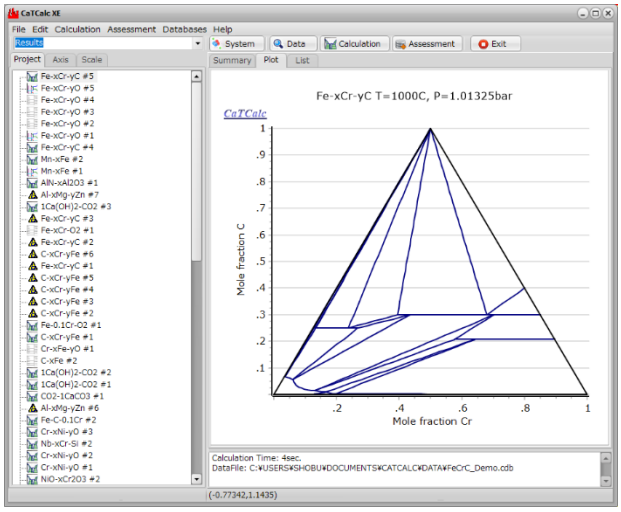


② Changing the conditions for Feed (gas pressure)

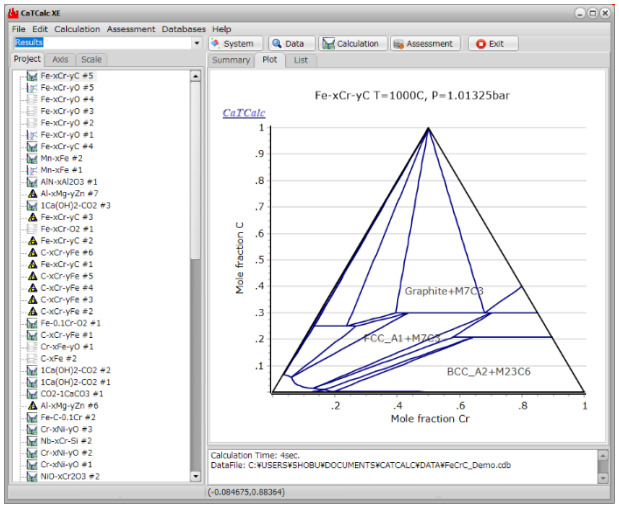
If you want to specify the partial pressure of other gases or the activity of other species, use the method of using the aforementioned data screen to select the component of the relevant phase as the Feed, and then click on the Unit column of Feed/Activity Conditions to select and set the activity specification.



③ Edit the diagram

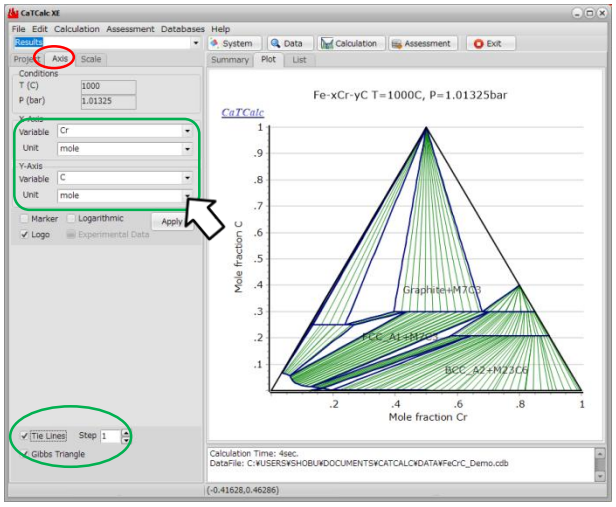


If the shape of the resultant figure is out of the equilateral triangle, please adjust the whole frame of CaTCalc. In addition, you can move the boundary between Plot area and Note area.



To add a label (phase name) to a phase region

Put your mouse over the area you want to name and click [Ctrl] + left mouse button. Then the phase name of the area will be displayed.



If you want to show the Tie Lines:

Select the [Axis] tab in the left pane.
If you check the "**Tie Lines**" box, they will appear in green, as shown in the figure.

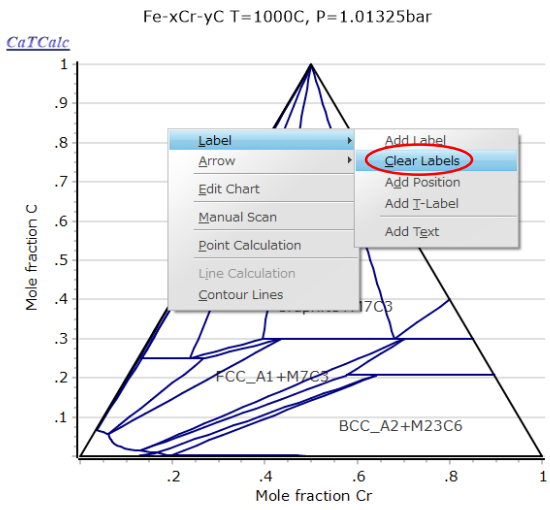
If you want to change the elements of X and Y:

Change the variables of "X-Axis" or "Y-Axis" and click the [Apply] button.

Tie-Line: a line connecting the points that indicate the compositions of two coexisting phases.

③ Edit the diagram

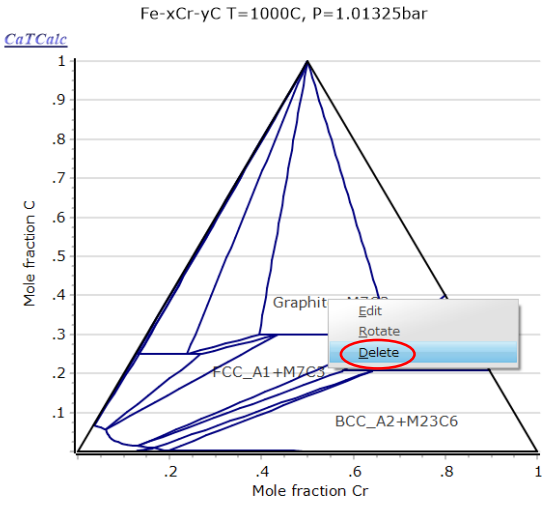
Remove all



To remove the label (phase name) of a phase region

Remove all: Right-click on the graph to display the pop-up menu. Delete all labels by [Label]-[Clear Labels].

Remove each label

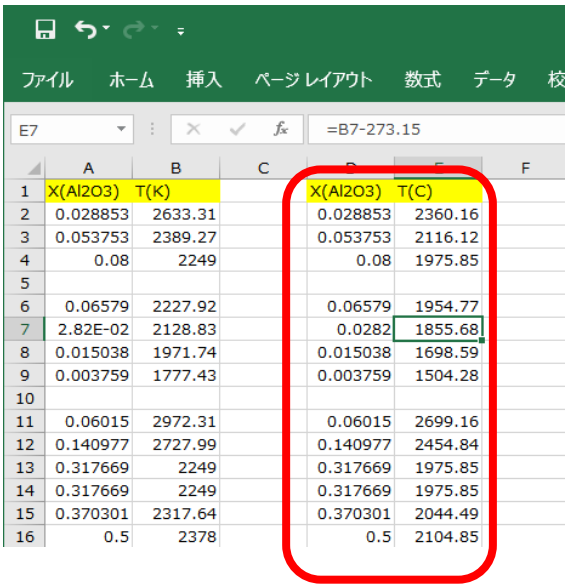


Remove a label: Select the phase label you want to delete by moving mouse cursor to the center of the label, and right click on the phase label and select [Delete] in the pop up menu.

You can use the [Edit Chart] pop-up menu, which appears when you right-click on the chart, to edit the chart in more detail.

For detailed editing of each line, please use the edit box that appears when left-double-clicking the line. You can also double-click each label to open the edit box.

④ Overlaying the experimental points

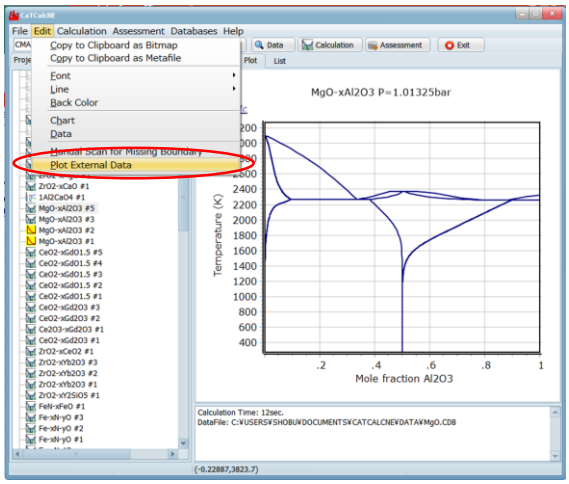


	A	B	C	D	E	F
1	X(Al2O3)	T(K)		X(Al2O3)	T(C)	
2	0.028853	2633.31		0.028853	2360.16	
3	0.053753	2389.27		0.053753	2116.12	
4	0.08	2249		0.08	1975.85	
5						
6	0.06579	2227.92		0.06579	1954.77	
7	2.82E-02	2128.83		0.0282	1855.68	
8	0.015038	1971.74		0.015038	1698.59	
9	0.003759	1777.43		0.003759	1504.28	
10						
11	0.06015	2972.31		0.06015	2699.16	
12	0.140977	2727.99		0.140977	2454.84	
13	0.317669	2249		0.317669	1975.85	
14	0.317669	2249		0.317669	1975.85	
15	0.370301	2317.64		0.370301	2044.49	
16	0.5	2378		0.5	2104.85	

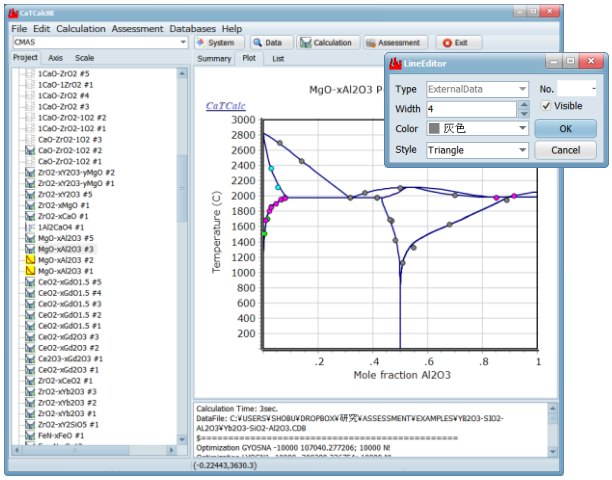
This section shows how to add experimental data to the calculation results.

Copy the experimental data to the clipboard as X-Y data with the titles. Pay attention to scales, such as temperature units.

Group the data by empty rows. Marker colors are automatically set for each group.



Click [**Edit**]-[**Plot External Data**] in the menu to plot the data.

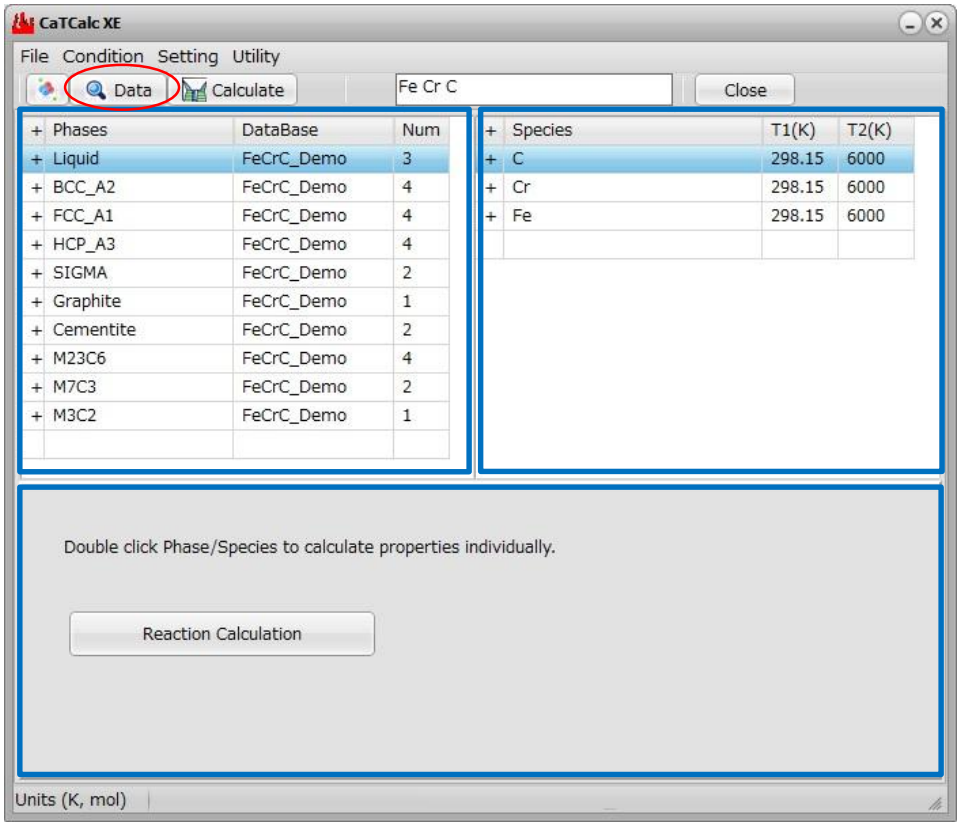


Edit Marker: Double-click on a marker and an edit box will appear.

Delete: select the marker and use the [Delete-Series] in the right mouse button pop-up menu.

④ Extended functions in the Data screen

Details of the data selected on the System screen are displayed.

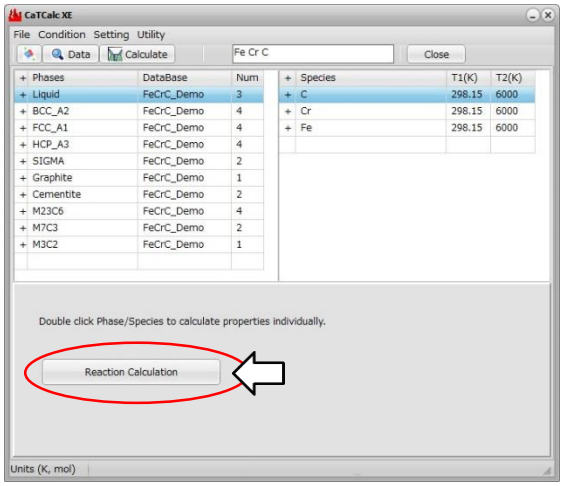


Phase: list of phases

Species: The list of species that comprise the selected phase

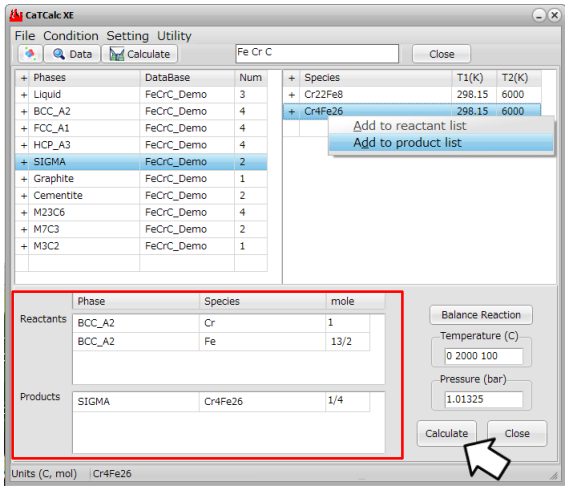
Reaction Calculation: Open a panel to calculate chemical reactions

④ Extended functions (Reaction Calculation)



[Reaction Calculation]

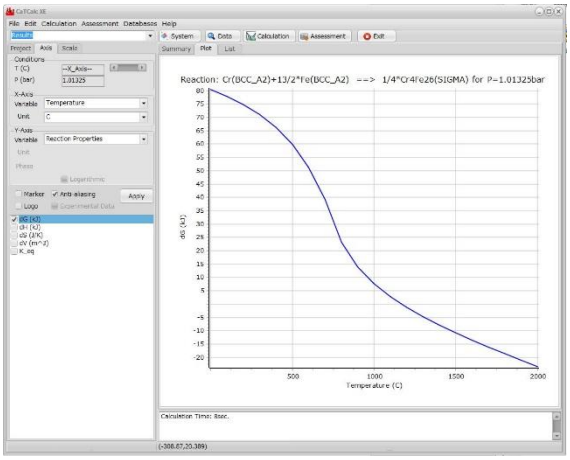
It performs individual chemical reaction calculations specifying reactants and products. The overall reaction, which takes into account all reactions, is calculated in the equilibrium calculation of the Calculation screen.



Reactants and products can be set up in the pop-up menu of the Species list after pressing the [**Reaction Calculation**] button, and opening Reactants and Products sheets.

You can automatically balance the reaction scheme by pressing the [**Balance Reaction**] button.

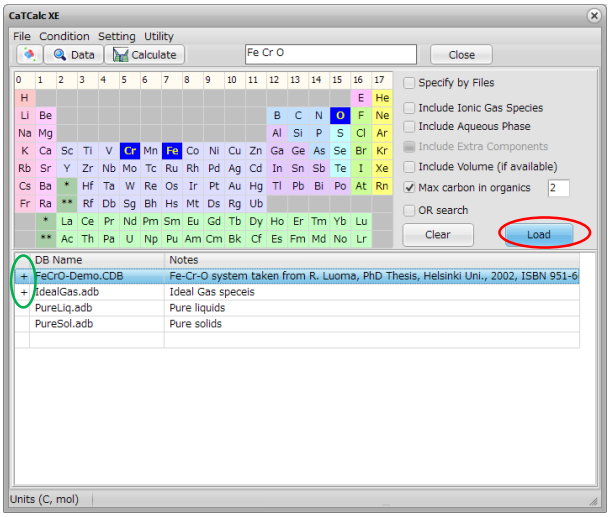
Set the temperature and pressure, and press [**Calculate**] button to start the reaction calculation.



The result will be displayed as a plot for the continuous calculation, or as a List for the one-point calculation. Note that the result of the reaction calculation is not saved automatically. If you want to save it, please use [**Edit**] in the menu and save it manually.

⑤ Potential diagram

Potential diagrams can be calculated in the same way as phase diagrams.



1. Select Fe, Cr, O on the System screen.
*Select FeCrO_Demo.cdb and IdealGas.adb here.

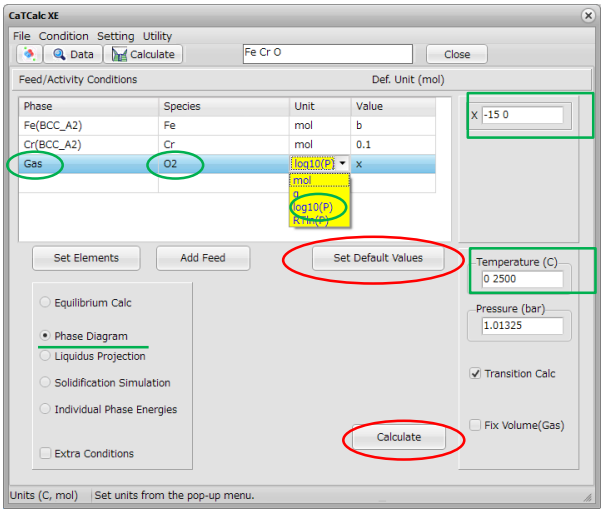
2. Click the [**Load**] button.

・Reads the thermodynamic data.

・Set the calculation conditions on the Calculation screen.

3. The type of calculation is “Phase Diagram”

4. Click on [**Set Default Values**].



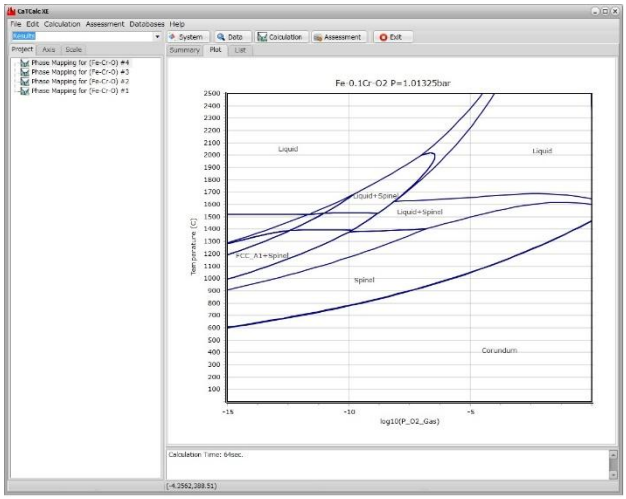
・Change the default value as follows:
Click on the "Phase" O (Gas) with your mouse to bring up the pull-down list and select "Gas". Do the same for "Species" and select "O2". Finally, change "Unit" to "log10(P)" (partial pressure).

・Set the Value of Fe and Cr to b and 0.1, respectively, and the Value of O2 to x.
・Specify the temperature and x-value as shown in the figure.

5. Click "Calculate".

Next page

⑤ Potential diagram

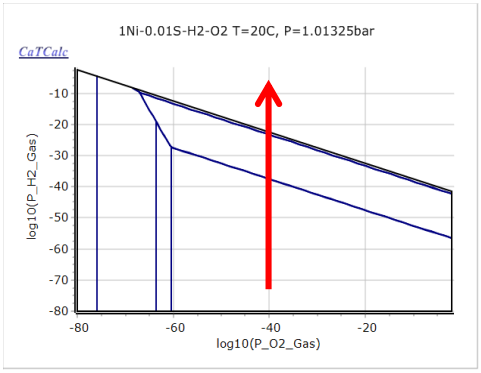


・The result of the calculation will be displayed.
Depending on the conditions, it may take some time to calculate, but please wait for a while.

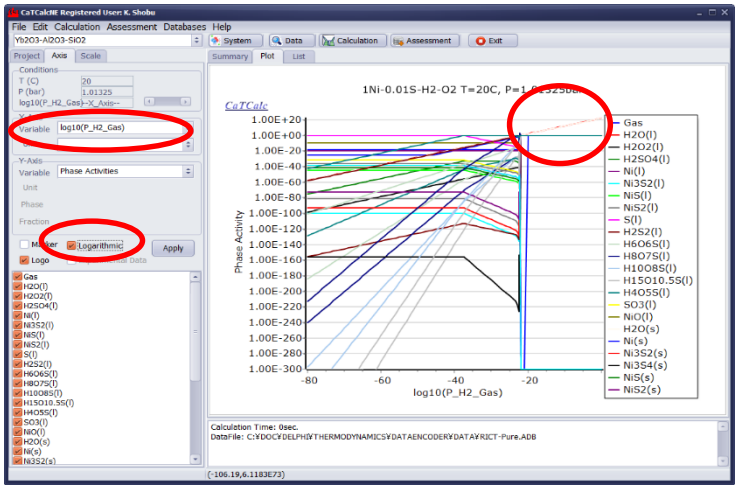
＊ In the left figure, [Cntl] + left click is used to label the phase names.

＊ Note: In this case, b = 1 - y. That is, the O2 amount, which is determined as a result of the activity specification calculation, is not included in the total amount: b.

＊ Unstable Regions in Potential diagrams



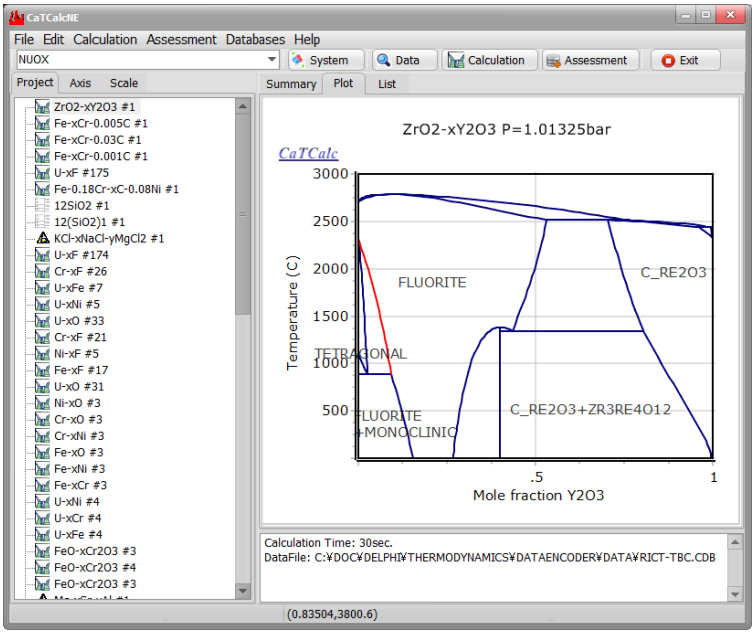
・ Sometimes labeling may show area that is labeled “Unstable” or “Error”. If this happens, use the equilibrium calculation to check the cause.
・The left figure shows the results of the equilibrium calculation along the red line as an example. If you display the phase activity, you will see that there are phases with activity greater than 1. Namely, the equilibrium state cannot be achieved under the condition.



・ You can find out the phase name by double-clicking the line to display the Editor.

⑥ T0-Line calculation

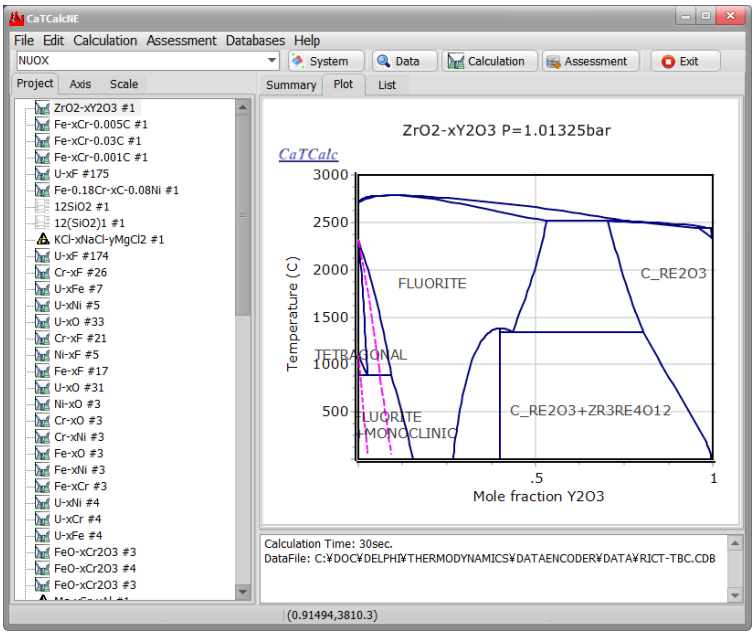
T0-temperature is the temperature at which two phases of the same composition have the same Gibbs energy. The T0-temperature is important in diffusionless transformations such as martensitic transformations.



・Here is an example of a T0 line calculation for martensitic transformation in the system ZrO2-Y2O3.

・ In this system, the martensitic transformation from the cubic Fluorite phase to the tetragonal phase occurs.

・Select the phase boundary line shown in red, and press [**T0-line Scan**] of the right button menu to automatically calculate the T0 temperature line.

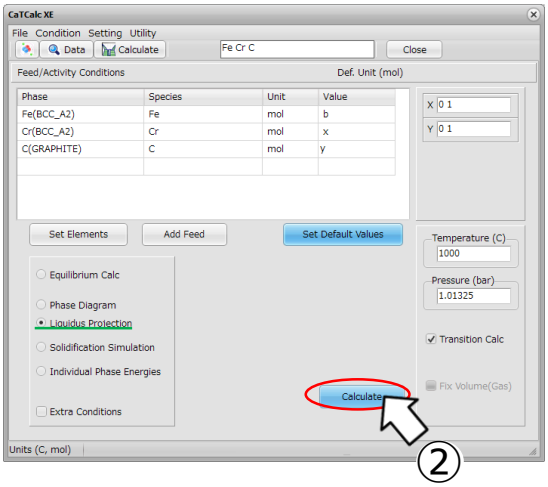


・The T0 line from Tetragonal to Monoclinic phase is also calculated, and the results are shown in the left figure.

V-3. Liquidus projection

① Liquidus projection calculation

The liquidus projection diagram is represented by Univariant Line and Isotherms (temperature contours). Calculate the Univariant Line first. Usually, the Univariant Line calculation is two dimensional (2D) in a 3-component system, but in a general case of multi-component system, the Univariant Line can be calculated from 1D to 6D.

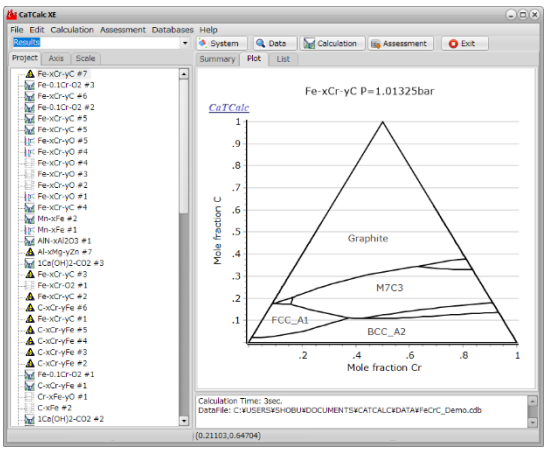


1. Use FeCrC_Demo.cdb to read the data of the Fe-Cr-C system.

2. Select "Liquidus Projection" as the type of calculation and click [**Set Default Values**].

3. Click the [**Calculate**] button.

・The calculation starts.



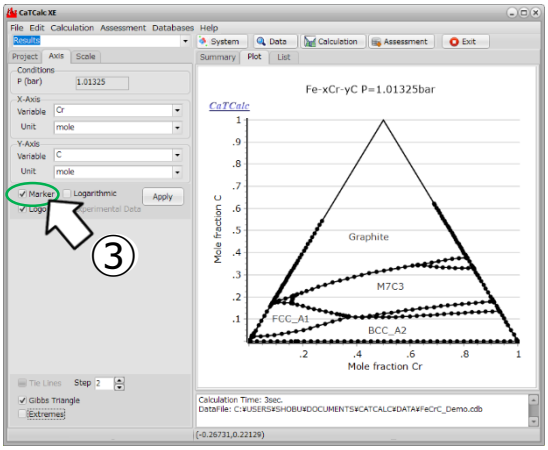
・The liquidus projection diagram will be displayed. Labeling is done as needed.

＊The phase label in the liquidus projection diagram is the phase name of the primary phase (the solid phase that first crystallizes out of the liquid phase as the temperature decreases).

*Note: The upper limit of liquidus temperature is set to 4000K.

① Liquidus projection calculation

Marker

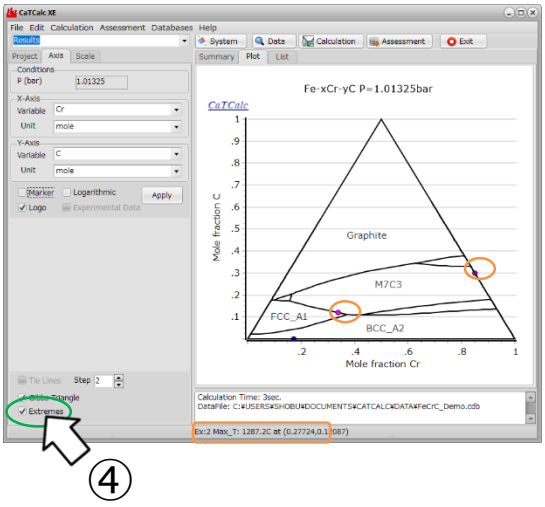


3. Check the "Marker" checkbox in the [Axis] tab.

・Marker indicates a calculation point. You can see the calculation point on the axis.

＊Note: The liquidus temperature calculation is made to an upper limit of 4000K.

Temperature extremes



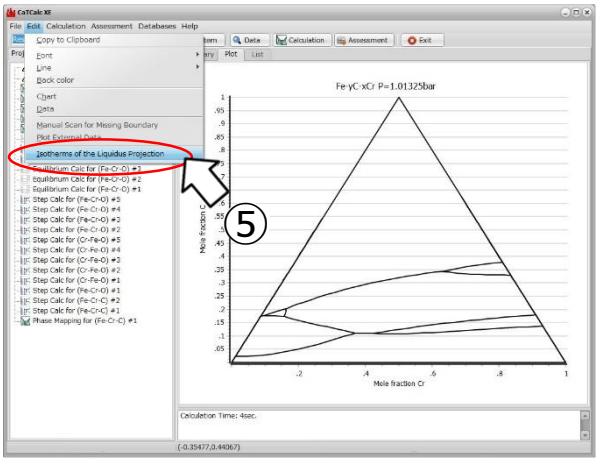
4. Check "Extremes" in the [**Axis**] tab.

＊ “Extremes” display temperature maxima (red) and minima (blue), e.g. on a Univeriant Line.

・ If you hold down the Shift key and move the mouse over these extreme points, the information will be briefly displayed in the Status bar at the bottom of the screen.

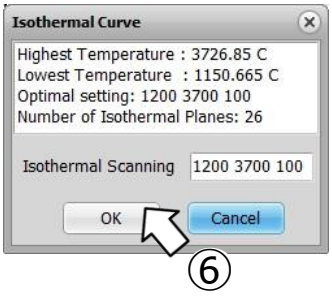
① Liquidus projection calculation

Calculation of isotherms



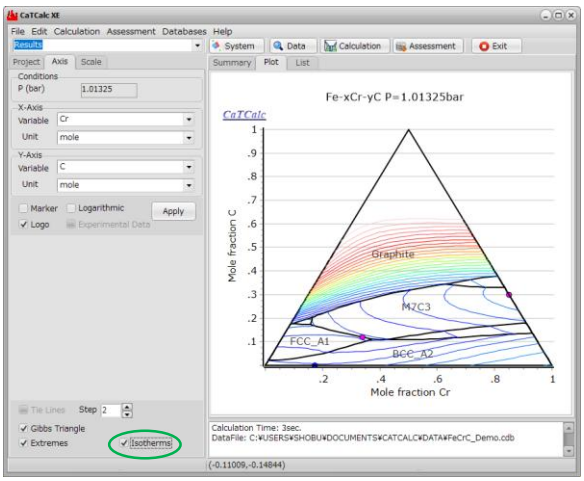
5. Select “Isotherms of the Liquids Projection" from the menu, or select "Isothermal Curve" of the pop-up menu in the Plot screen.

・The <Isothermal Curve> screen will be displayed, which will automatically calculate and display the best setting based on the information obtained from the Liquidus Projection calculation. You can change the settings (Start value, End value, and Step value) as necessary.



6. Click the OK button.

・Isothermal curve calculation starts.



＊ In the [**Axis**] tab, an "Isothermal" checkbox appears. The display of isotherms can be turned off or on here.

＊ [**Edit Chart**] in the pop-up menu allows you to make more detailed settings.

＊ The upper temperature limit for liquid phase line detection is internally set to 4000 K, and isotherms above this limit will not be calculated.

① Liquidus projection calculation

Taking the above 2D case as an example, the algorithm for a three-component liquidus projection calculation is as follows:

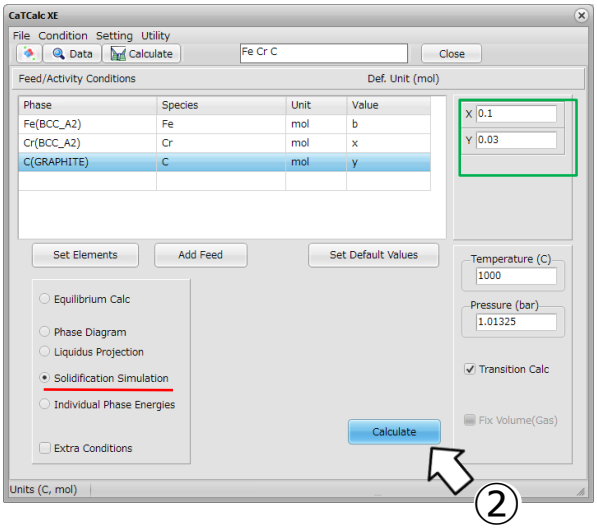
(1) The liquidus point is detected at each end-member composition of (X,Y) = (0,0), (0,1), and (1,0).
(2) Define the liquidus univariant lines of the three two-component systems with these liquidus points as the initial endpoints. Then the endpoints of the liquidus univariant lines of the three-component system are determined, and
(3) Finally, the Univariant-line of the three-component system is traced from these endpoints.

Therefore, in the case of three-component systems, detection of liquidus univariant lines would be perfect in most cases.

However, in a multi-component system of four-components and more, the procedure is simplified. That is, according to the order of the parameters (X,Y,Z,W,A), firstly, the liquidus point is detected with a single point composition (component for the balance) with all the other parameters as zero, then the liquidus univariant line of 2D for B-X, then the line of 3D for (B,X,Y), then the line of 4D for (B,X,Y,Z) and so on... to define the Univariant line of the multi-dimensional system. Therefore, it is necessary to calculate the ND univariant line by swapping the parameters. Note that the ND Extreme is only on the liquidus lines. The other phase than the liquid phase can be selected as the parent phase by specifying the target phase in the phase list (see VII).

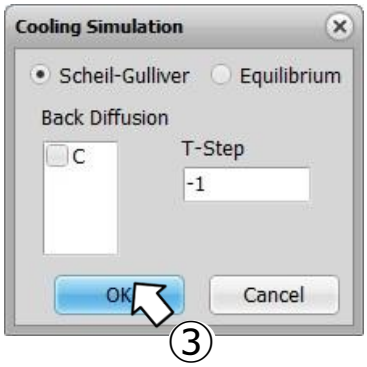
V-4. Solidification simulation

In the solidification simulation, all the calculation conditions are set to single fixed values.



1. Load thermodynamic data from the FeCrC_demo.CDB. Then, select “Solidification Simulation” as the calculation type, press "Set Default Values“, and modify the settings as shown in the left figure.

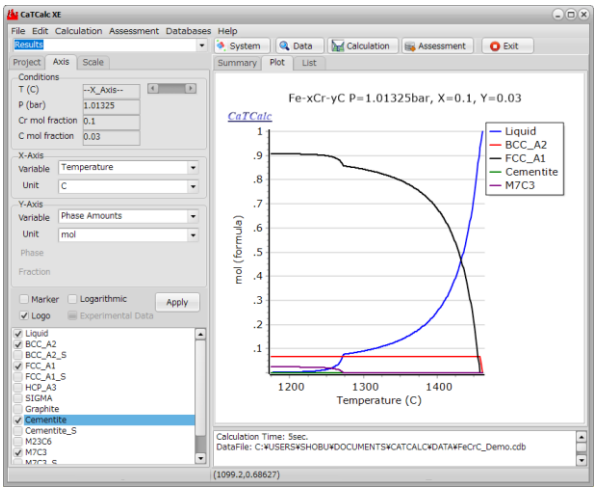
2. Click the [**Calculate**] button.



3. "Cooling Simulation" dialog appears.

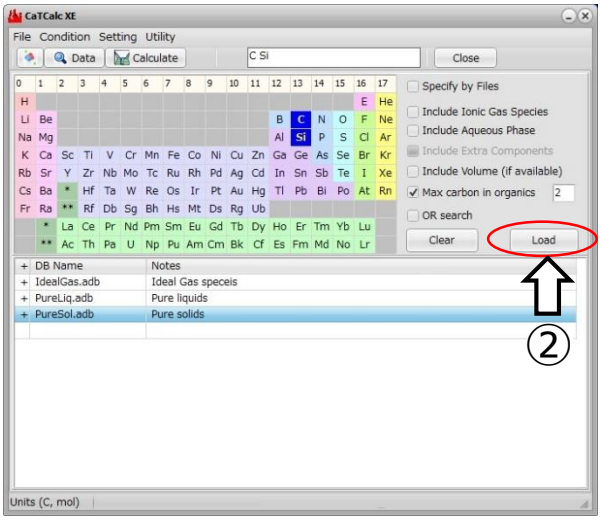
・Click the [**OK**] button without checking the box for “Back Diffusion“ in the present case.

＊The simulation that takes into account the diffusion of C is called a para-equilibrium calculation.



・After the calculation, the graph is automatically displayed. For more information on solidification simulation and the meaning of the results, please refer to books and/or literature.

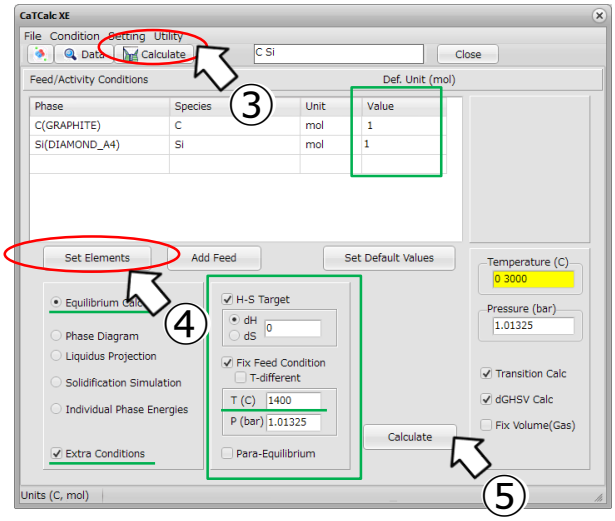
V-5. Adiabatic calculation



1. In the System screen, specify Si and C and select IdealGas.adb, PureLiq.adb and PureSol.adb.

2. Click the [**Load**] button.

- Load data from the selected DBs.



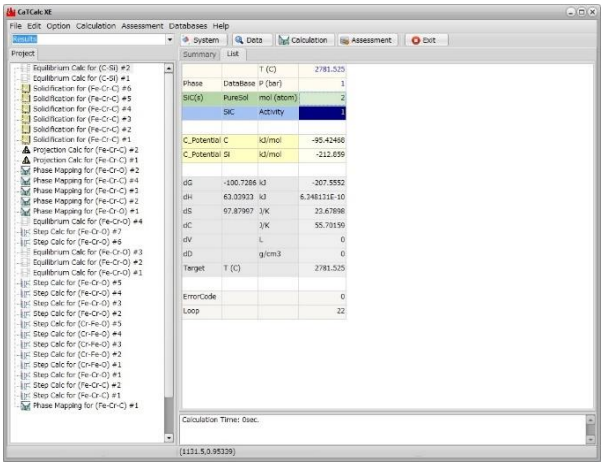
3. Click the [**Calculate**] button.

4. Click the [**Set Elements**] button.
- Set the value of Value to "1" for each.
- Check "Equilibrium Calc".
- Check the "Extra Conditions" and "H-S Target" boxes, and then select the "Fix Feed Condition". Set the temperature to 1400°C. This is because the reaction starts rapidly at this temperature.

The color of the "Temperature" edit box changes to yellow to indicate that the temperature is the target variable to be calculated.

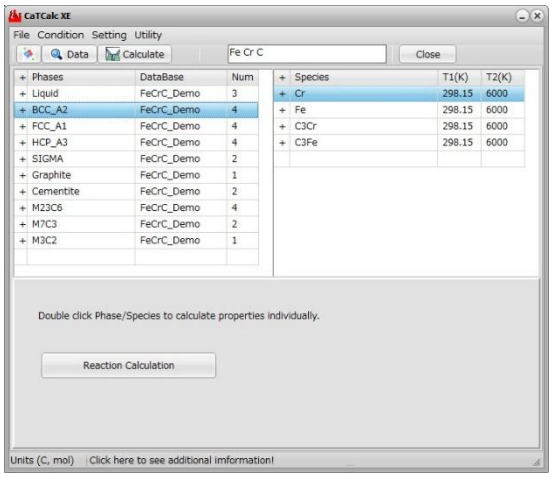
5. Click [**Calculate**] to perform the calculation.
- The result of the calculation will be displayed.

＊The adiabatic reaction temperature is close to 2800 °C, and the solid phase SiC is produced. This means that the temperature increased due to the heat of reaction between Si and C.

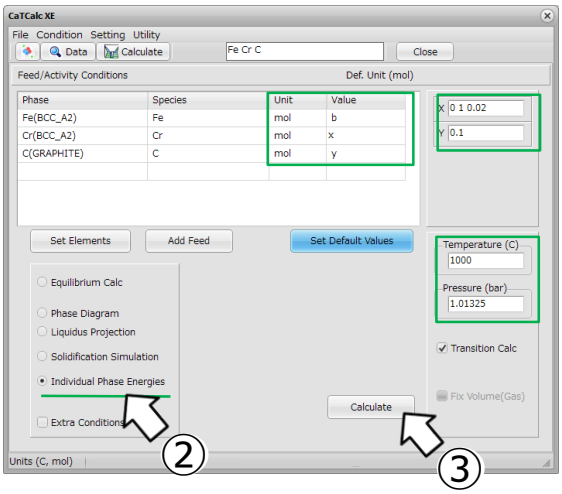


V-6. Individual Phase Energy

The energy calculations for individual phases are useful when comparing the behavior of the Gibbs energy of each phase at a time. It can also calculate the enthalpy and entropy of mixing of each phase, the change in phase composition, as well as the Curie temperature of a magnetic phase.



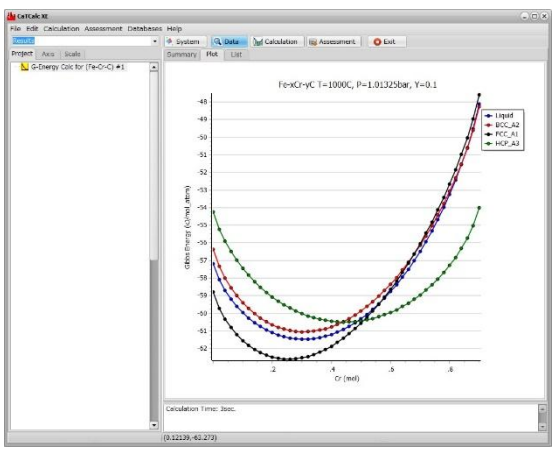
1. Select the target phases on the Data screen.



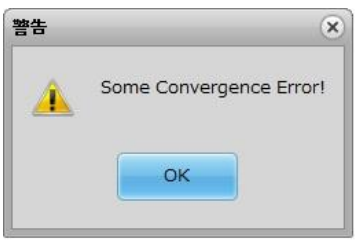
2. Set the calculation conditions on the Calculation screen.

・Check ”Individual Phase Energy”.
・Click the [**Set Default Values**] button.

3. Click the [**Calculate**] button.

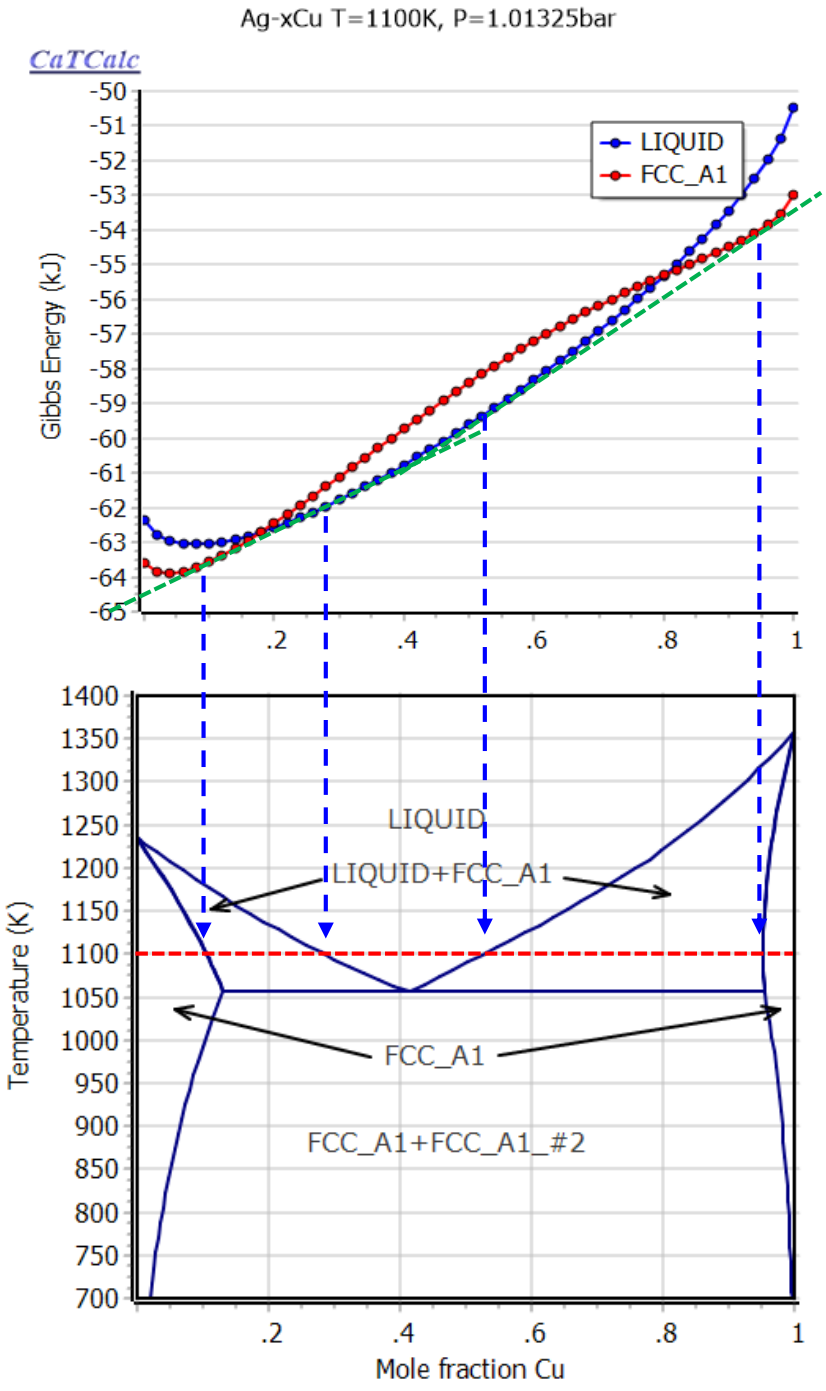


The result of the calculation is displayed.
＊ An error message will appear if the calculation includes pure substance phases of stoichiometric composition that cannot be calculated under the specified conditions. Ignore the message in such cases.



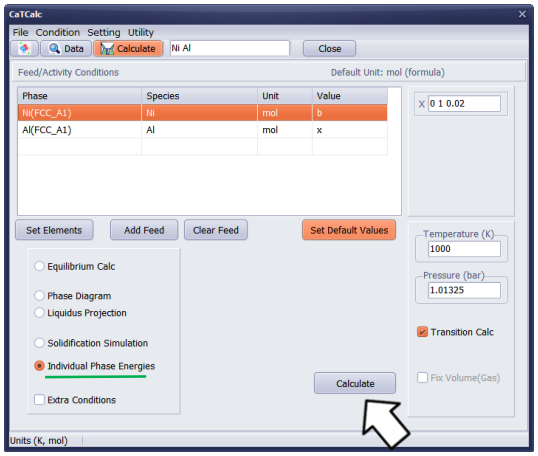
① Relationship between Gibbs energy of phases and phase diagram

The figure below shows the relationship between Gibbs energy of LIQUID phase and FCC_A1 phase of Ag-Cu system at 1100K and phase diagram. The phase or combination of phases that gives the lowest Gibbs energy of the whole system appears as the stable phase set.

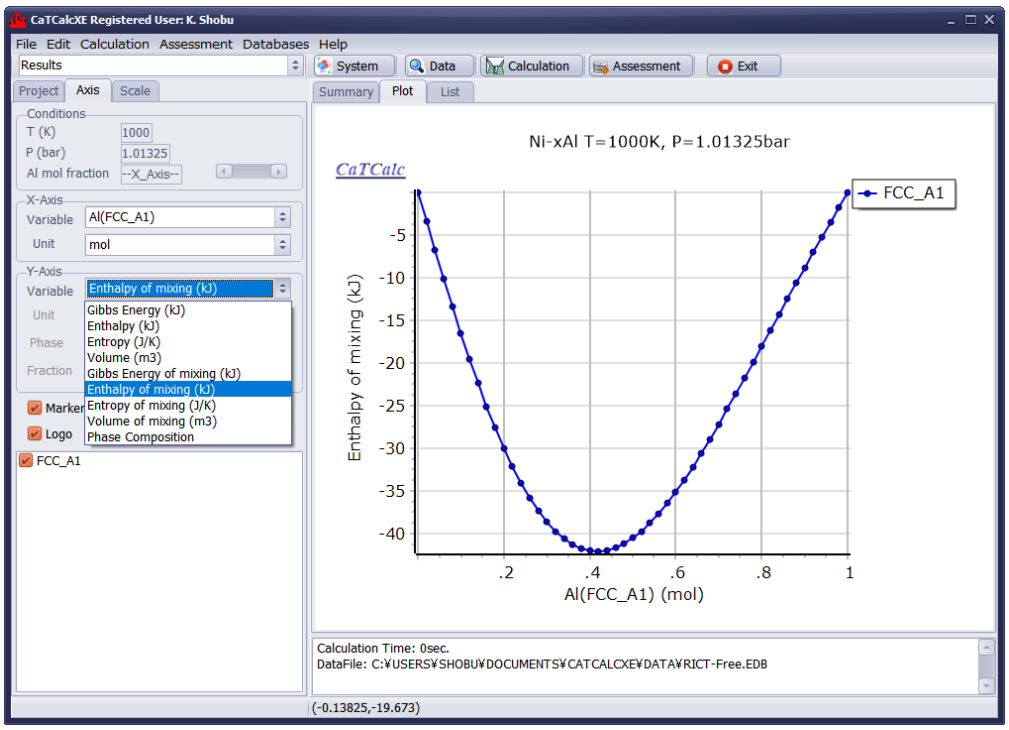


② Enthalpy of mixing, entropy of mixing and composition of phase

The calculation of enthalpy and entropy of mixing, and phase composition is shown using the FCC_A1 phase of the Ni-Al system as an example.

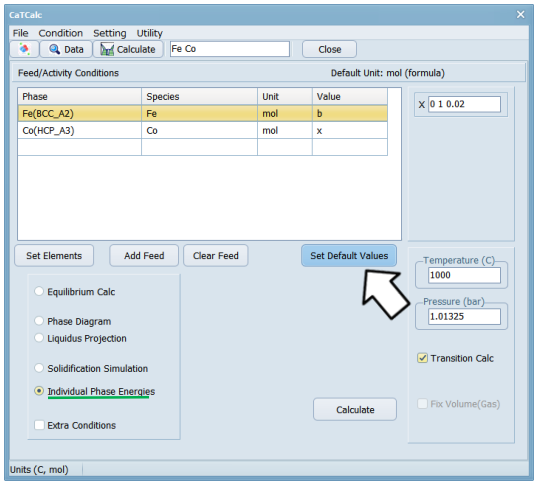


1. Load Ni-Al data from RICT-Free.EDB in the [System] screen. (Not shown.)
2. Select only FCC_A1 phase in the [Data] screen. (Not shown.)
3. In the [Calculation] screen, select "Individual Phase Energies" and click [Set Default Values].
4. Set the temperature, and click the [Calculate] button.
5. Select "Enthalpy of mixing" as the Variable for Y-Axis to see the result as shown in the figure below. You can also display the entropy of mixing and the composition of the phase.



③ Bohr magnetron and Curie temperature

The Inden-Hillert-Jarl model is used as a standard for magnetism, and the calculation method of the Bohr magneton and Curie temperature is shown using the Fe-Co FCC_A1 phase as an example.

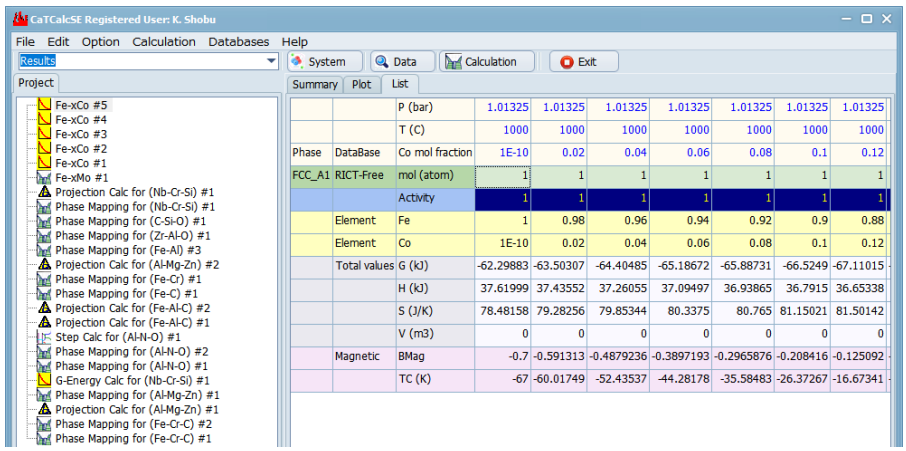


1. Load the data of the Fe-Co system using RICT-Free.EDB (not shown).

2. Select only FCC_A1 phase in the [Data] screen (not shown)

3. In the [Calculation] screen, select "Individual Phase Energies" and click [Set Default Values] as shown in the left figure, and click the [Calculate] button. (You can use any value for the calculation temperature.)

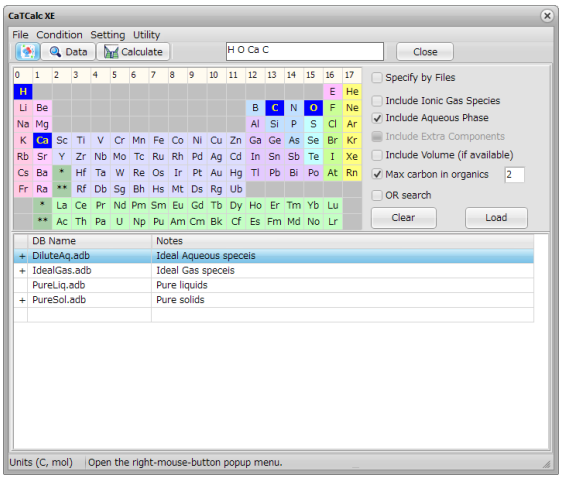
4. The result will be displayed in the list only. For a magnetic phase, the Bohr magneton and Curie temperature (or Néel temperature, if negative) are displayed in the bottom line. For graphing, use [User-defined Function] to draw them.



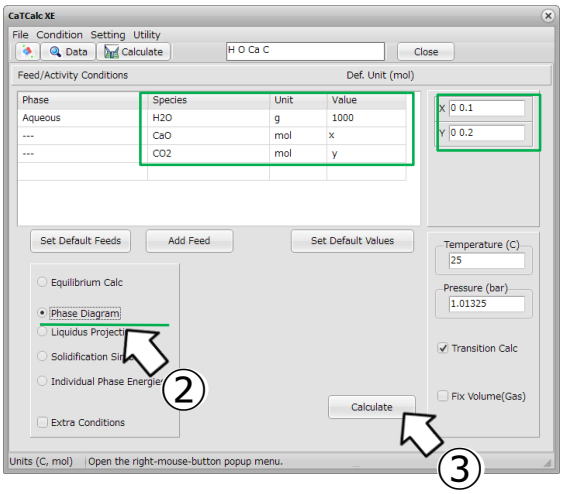
V-7. Aqueous system

① Phase diagram calculation

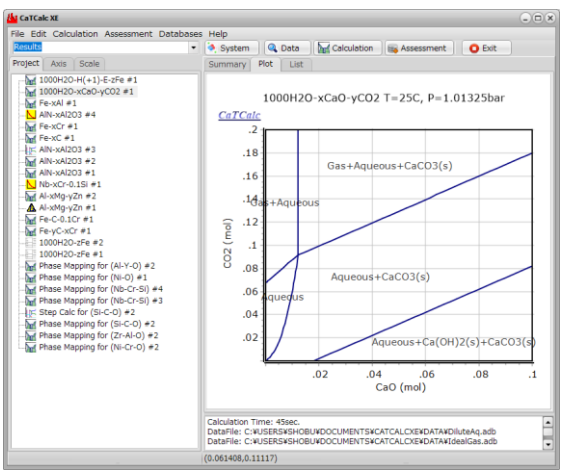
An aqueous solution phase can also be considered in combination with other phases.



1. In the System screen, check [Include Aqueous Phase], specify the elements as shown in the left figure, then select DiluteAq.adb, IdealGas.adb, and PureSol.adb to read the data. DiluteAq is a database of dilute aqueous solutions.



2. Set the calculation conditions on the Calculation screen.
- Check the ”Phase Diagram”
- Click the [**Set Default Values**] button.
- Modify the second and third lines as shown on the left.

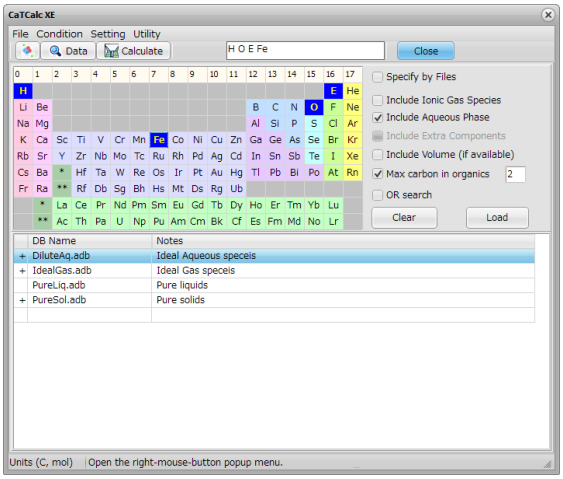


3.Click the [**Calculate**] button.

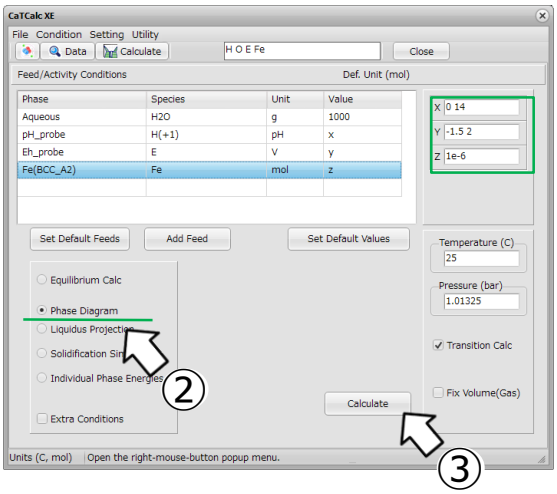
- The result will be displayed.

② Pourbaix Diagram

Since charge is required in the Pourbaix Diagram (E-pH diagram) calculation, we also select E as an element. The following is an example for Fe.



1. On the System screen, check [**Include Aqueous Phase**], specify elements as shown in the left figure, select DiluteAq.adb, IdealGas.adb, and PureSol.adb to read the data.



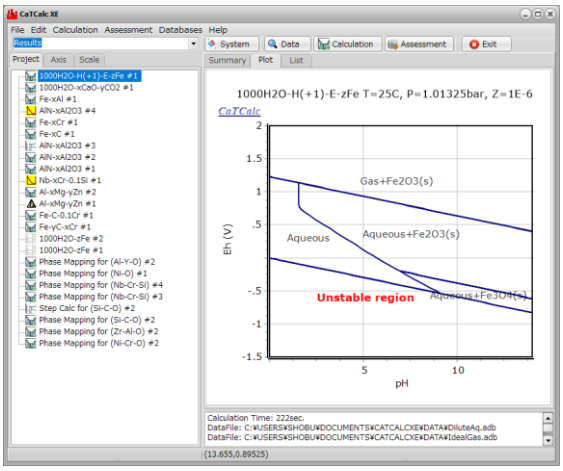
2. Set the calculation conditions on the Calculation screen.

・Select the "Phase Diagram"

・Click the [**Set Default Values**] button.

＊If E is included, pH and Eh are set at the same time by default. If you do not need, just delete it or both.

・Modify the parameter values as shown in the left figure



3. Click the [**Calculate**] button

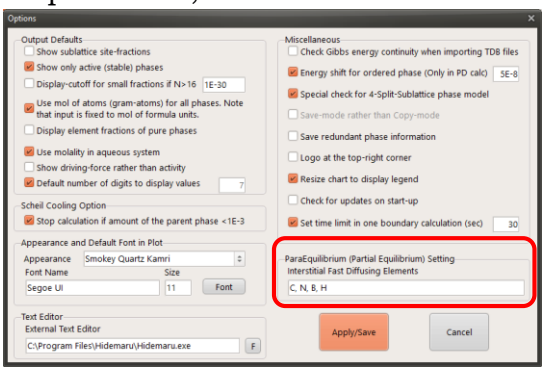
・The result of the calculation will be displayed.

(＊Important note)

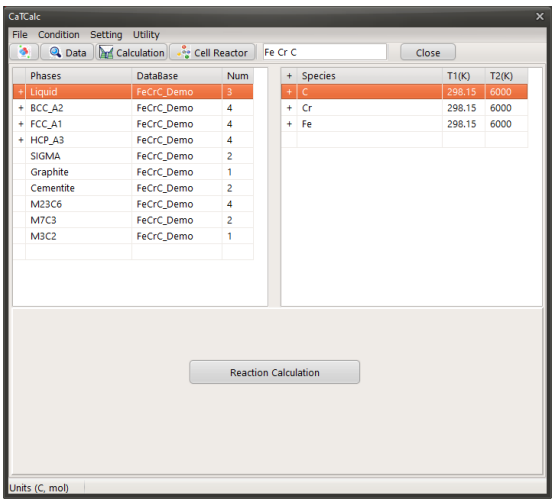
It is possible to include E explicitly in the usual calculation of aqueous systems under neutral conditions. In a multi-component system, calculation may be more stable.

V-8. Para-equilibrium calculation

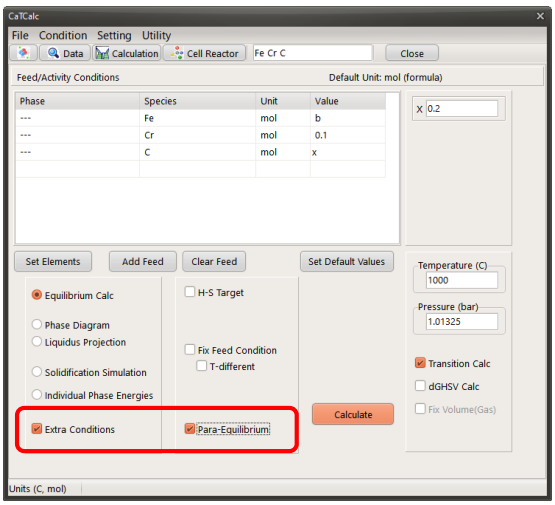
For example, in the case of solid solution of carbon in Fe-BCC phases, carbon is small and enter the interstitial site and diffuse very rapidly at high temperatures, so that equilibrium is quickly achieved. On the other hand, elements in substitutional solid solution with Fe may not diffuse well and remain in non-equilibrium state. Such a state is called para-equilibrium, and the calculation method is shown below.



1. Elements of fast diffusion are set by [Files]-[Preference] in the menu.



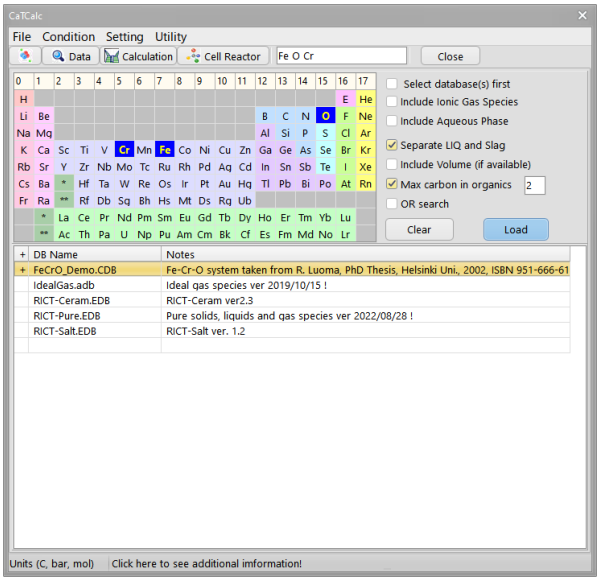
2. As an example, we show the para-equilibrium calculation of the Fe-Cr-C system. First, load the data of the Fe-Cr-C system from FeCrC_Demo.CDB. In para-equilibrium, the ratios of components other than C are fixed, so only phases containing all elemental components need to be considered. Also, since it will always be singular, a Gas phase is required. These settings are made on the data screen as shown in the left figure.

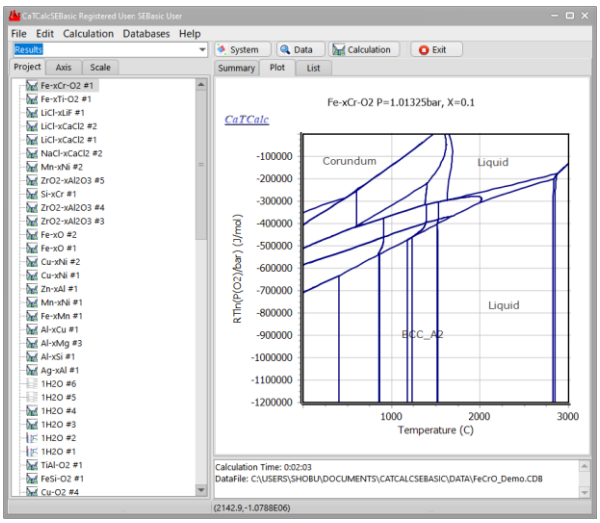


3. Next, refer to the left figure for the calculation conditions. The setting in the left figure is b=0.7, which means that the Cr/Fe ratio is 1/7, and confirm that the Cr/Fe ratio of each phase in the results is also 1/7.

V-9. Ellinghum diagram calculation

Ellingham diagrams can be calculated easily as one of the potential diagrams. However, to simplify the process of setting conditions, a dedicated calculation mode is provided. Currently limited to oxides, this mode can be easily modified to handle nitrides, sulfides, and other compounds as well. Calculations can be performed not only for pure substances but also for complex compounds and solid solutions.





Example: Reading data from the Fe-Cr-O_Demo.CDB solution database as shown in the left figure.

*When using RICT-Ceram, it is recommended to uncheck the [Separate LIQ and Slag] checkbox on the right.

Proceed to the Calculation Screen and Set Calculation Conditions

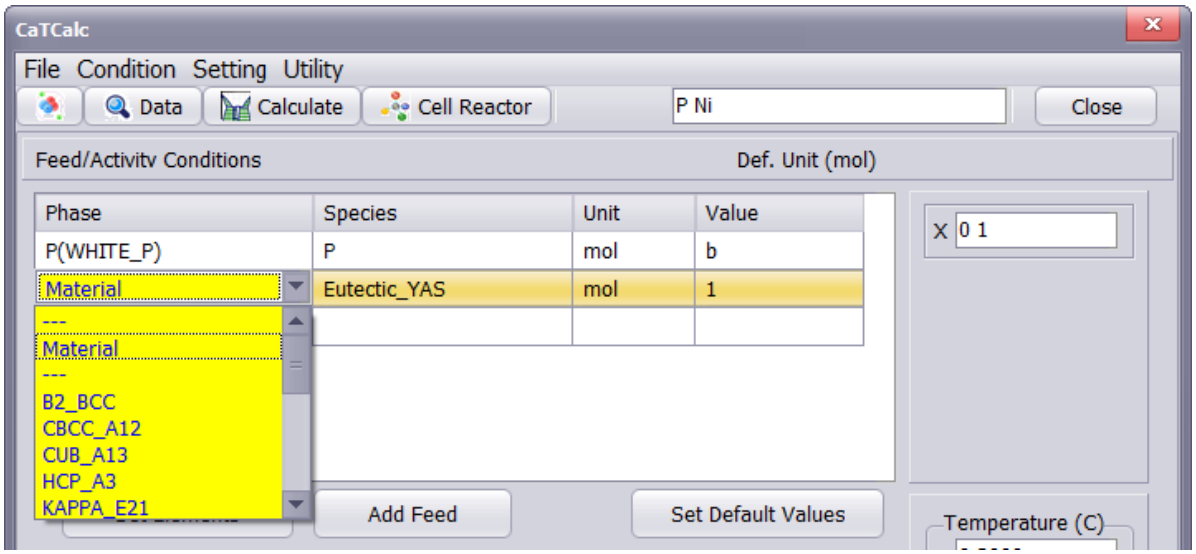
1. Add Feed Materials: Begin by clicking the "[Add Feed]" button twice to add iron (Fe) and chromium (Cr) as feed materials.
2. Select Calculation Mode: Choose "Ellingham Diagram" as the calculation mode.
3. Set Default Values: Click the "[Set Default Values]" button to establish default values for the calculation. The key point is to configure only non-oxygen-related parameters, as the oxygen potential and its range are automatically set.
4. Refine Calculation Parameters (Optional): If necessary, adjust other conditions, such as the x-axis variable, and initiate the calculation.
5. Analyze Results: The calculation outcome is an Ellingham diagram as shown in the left figure. The units of the y-axis can be switched between kJ/mol and eV using the "Axis" tab.

VI. Material(Mixture) and user-defined function

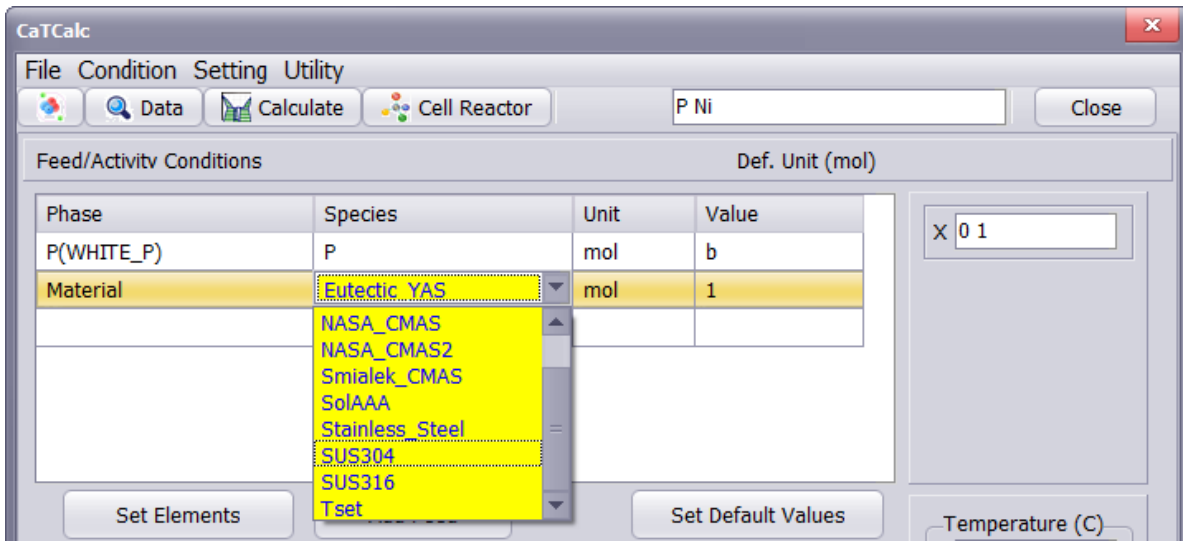
VI-1. Using Material

＊Material is a mixture and is defined by its elemental composition.
＊The definition file is a text file with an SMF extension and should be saved in the following folder: /User/Documents/CaTCalcXE/Materials

＊Material is used to set up calculation conditions. Click [**Add Feed**] button and select material from the drop down list.



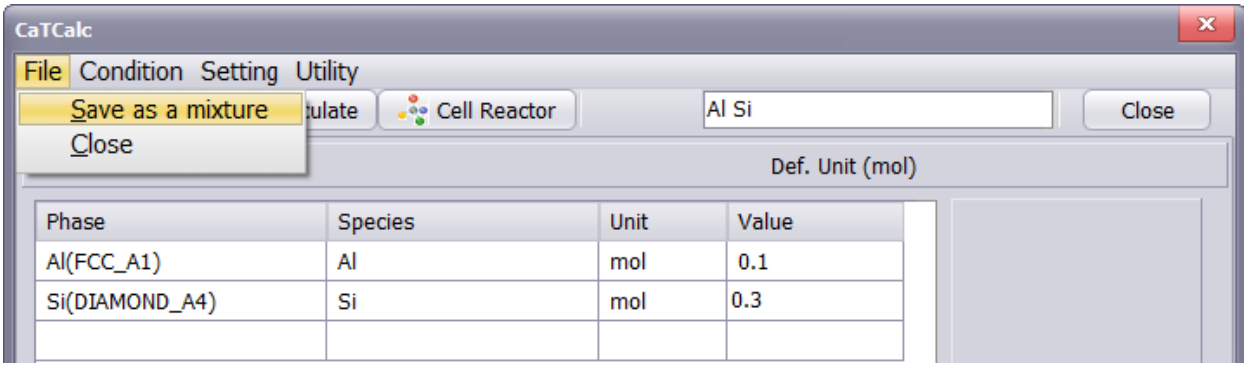
Next, click on the Species column and select your desired material from the drop-down list.



＊ If the thermodynamic data for the components defined in the material has not yet been loaded, a message will appear and you will be taken to the data loading screen automatically.

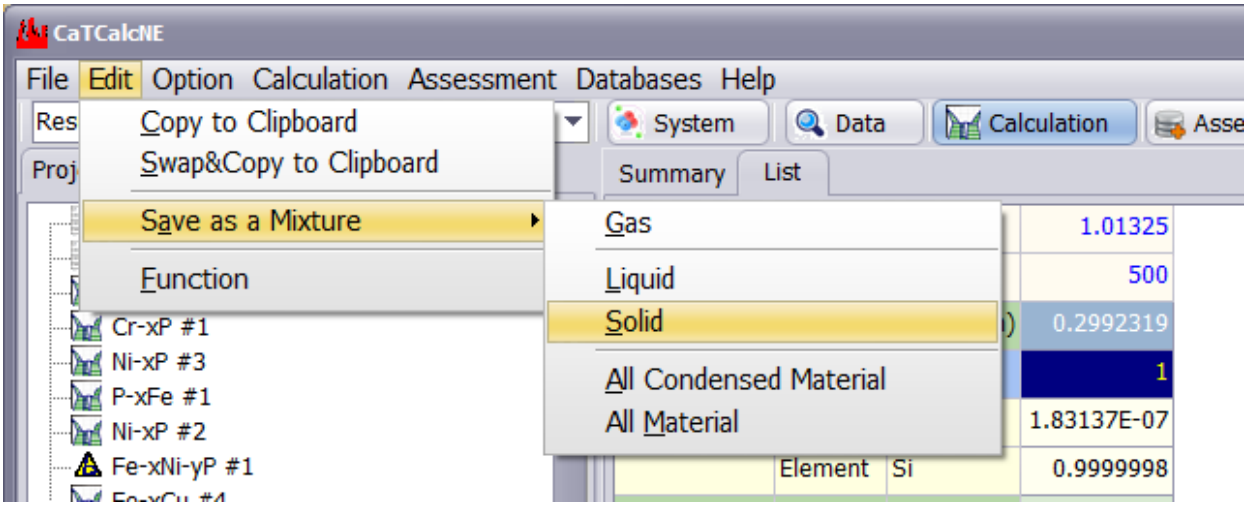
VI-2. Defining Material

∗ After setting the Feed, click [**File**]-[**Save as a mixture**] menu to save it.



In this case, only the elemental components are set.

∗ After the one-point equilibrium calculation, it is possible to save the data separately for the gas phase, liquid phase and solid phase. This is done using the menu on the main screen.

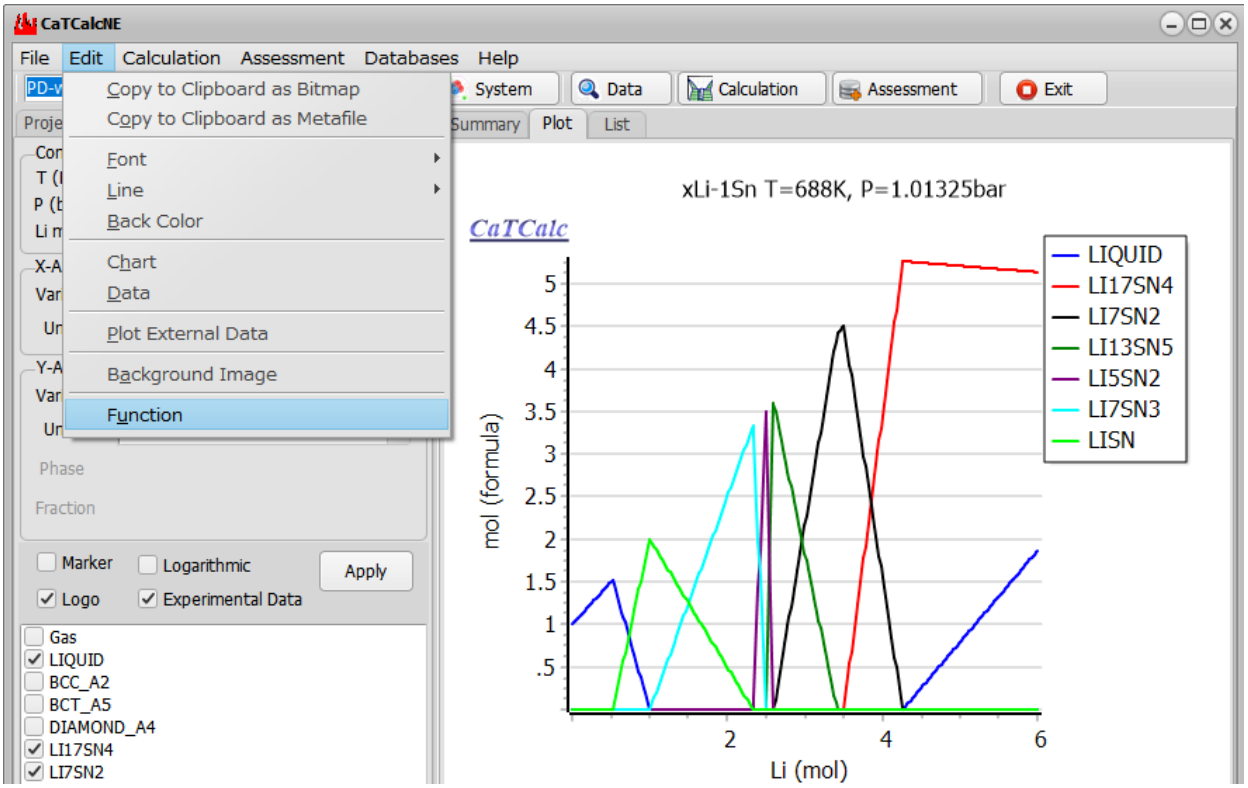


∗ Note

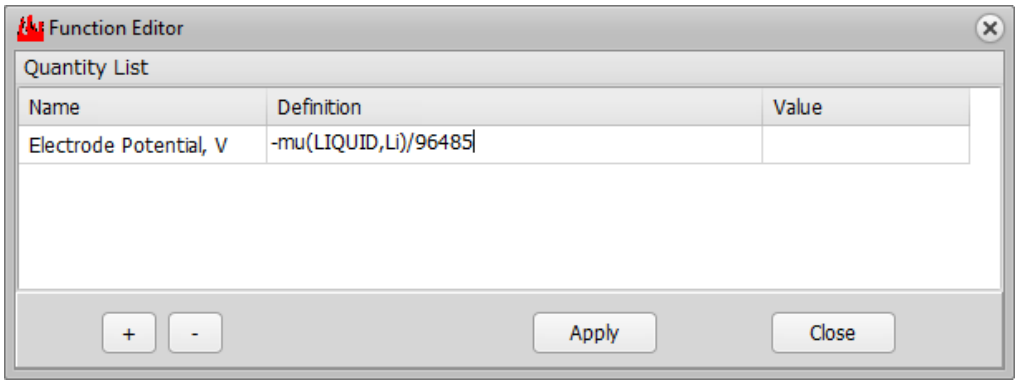
In the case of Material defined by weight percentages, the molar weight of each element used in the equilibrium calculation will be the value defined in the Elements.DBC file, which is one of the definition files of CaTCalc. The calculated values may differ slightly from those calculated using data defined in the CDB data file.

VI-3. User-defined function

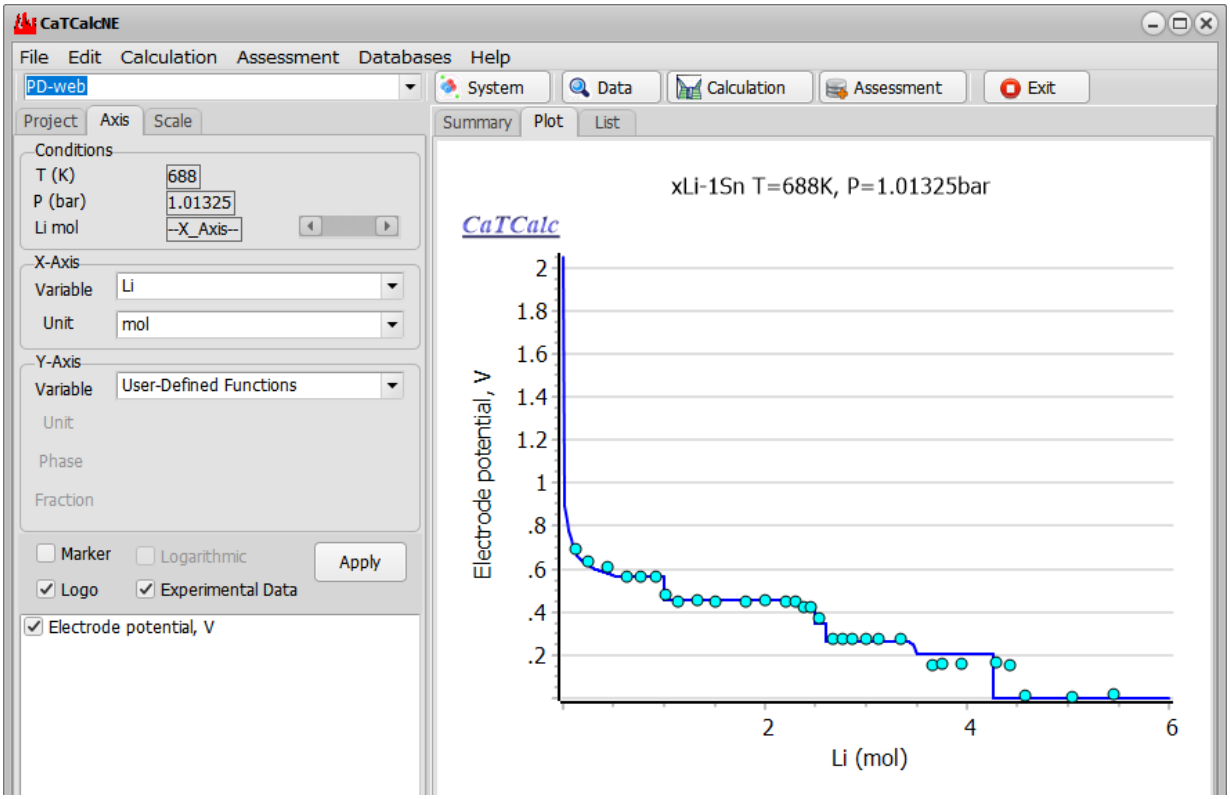
*Using the results of the equilibrium calculation, the user can define and calculate arbitrary quantities. After the equilibrium calculation, click [Edit]-[Function] in the menu to open the definition screen.



Function definition screen



The function name and its definition are defined in this screen, and Name will be used as the title of the vertical axis of the graph. The standard format for displaying units is a comma followed by the unit. In Definition, you can set up formulas that include physical quantities, though multiplying or dividing multiple physical quantities is not yet supported. Please refer to the "Quantity list" in the menu (see the next page) for the available quantities. After these settings are made, the result is automatically displayed by pressing the "Apply" button. The Value in the Function Editor shows the calculated value at the first point, which can be used for a simple verification of the calculation.



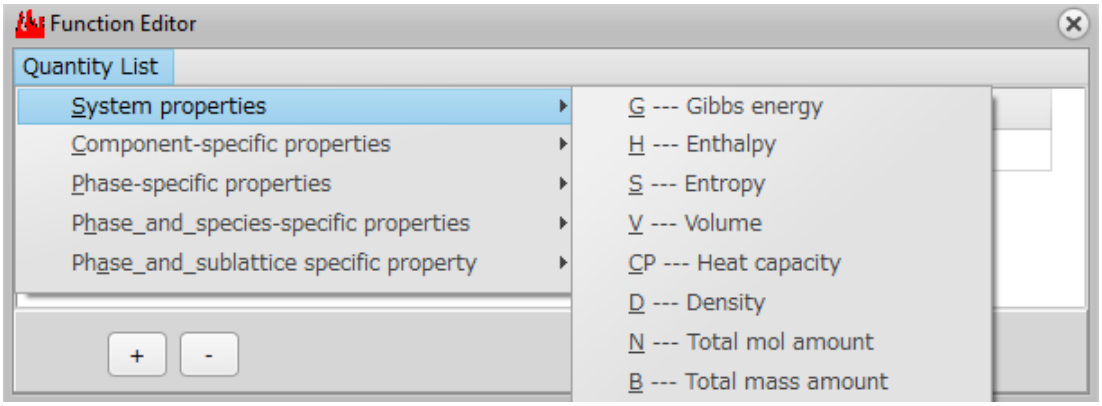
∗Example of electrode potential calculation. Note that the measured experimental data is also plotted.

Reference: https://doi.org/10.1016/j.pnsc.2019.05.007

As shown above, user-defined functions are automatically set to [User-Defined Functions] in the Y-axis selection menu in the Axis Tab. In the List view, they are listed in "Functions".

Physical quantities that can be referenced by Function

*The list of physical quantities that can be referenced is categorized into those related to systems, elemental components, phases, etc., as shown in the figure below. For example, [Phase-specific properties] are quantities related to phases, and the phase must be specified in parentheses. For example, G(BCC_A2) is used to calculate the molar Gibbs energy of the BCC_A2 phase. On the other hand, G alone is the total Gibbs energy itself.



[Note]
*Phase and component names are case-sensitive. The physical quantity itself can be in either upper or lower case.
*Function definitions support linear formulas, but not arbitrary formulas such as multiplication of physical quantities. Therefore, please verify thoroughly that the desired formula is calculated correctly. It is not possible (for now) to use function to define another Function.
*The function also supports [individual phase energy] calculations, so G and H calculations are possible. However, this individual phase calculation does not calculate Cp or CTE, so if necessary, please calculate them separately using the normal equilibrium calculation.
*Cp (specific heat) is obtained by the temperature derivative of Enthalpy. Therefore, if the composition of the solution phase changes with temperature, the effect is also taken into account in the value. Namely, the specific heat may be different even if the composition is the same.

VII. Macro Calculator and Console Mode

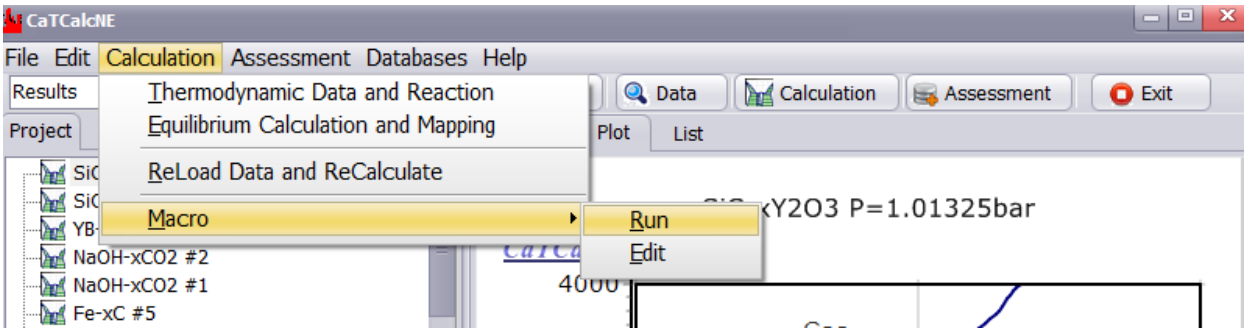
VII-1. Macro Calculator

The general procedure for macro calculations is as follows:

1. Creating and Editing Macro Files
 * By default, macros are stored in the Macro folder in the user's folder.
 /User/Documents/CaTCalcXE/Macro
 * The macro is a text file with the extension CMF, so you create and edit it with an appropriate editor. [**Calculation**]-[**Macro**]-[**Edit**] in the menu opens the editor specified in [**Preference**].
 * Each step of the macro is represented by a single line. The following commands are currently available; see the example in the Macro folder.

rc	: reset all conditions, DBs and elements
cf	: clear Feed/Activity conditions
sw DatabaseName	: switch (set) Database
def Fe Cr C	: define system elements
get	: get data from databases
rp GRAPHITE	: exclude phases from the calculation
ip GRAPHITE	: include phases in the calculation
lp	: list phases accounted in the calculation
su T=C,P=bar,A=g	: set-units
sc T=(100 300 10)	: set-condition of T
sc x(Fe)=b100	: set mol amount of Fe to be b100
sc w(Cr)=7	: set weight-amount of Cr to be 7(g)
sc x=(0 0.4 0.2)	: set parameter : x
st ATitle	: set title of the calculation
ce	: calculate equilibrium, save and plot
map	: map, save and plot

2. The saved macro file is executed by clicking [**Calculation**]-[**Macro**]-[**Run**] in the menu as shown below.



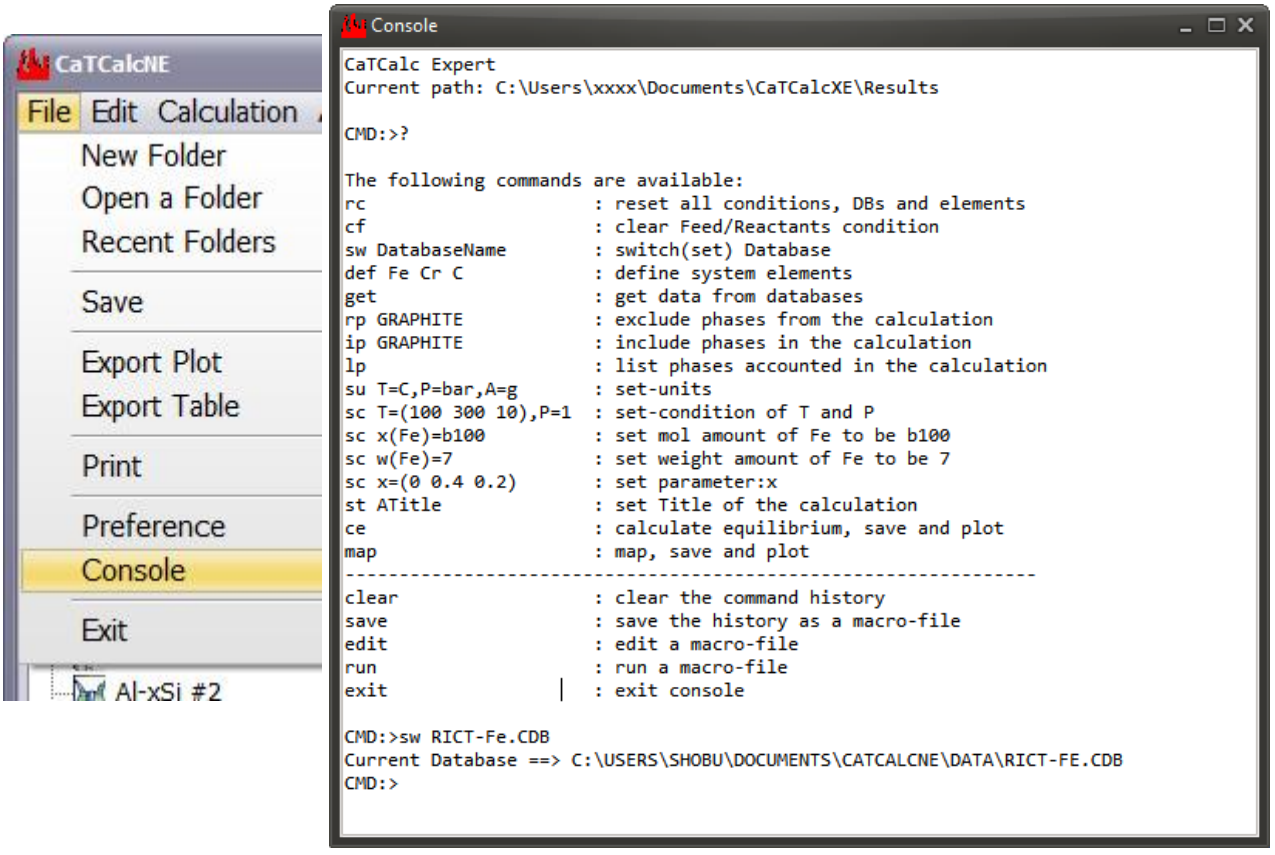
VII-2. Console mode

1. To open the console, click [**File**]-[**Console**] in the menu.
2. The following commands are available in addition to the ones described in the previous page

?	: list all available commands
clear	: clear the command history
save	: save the history as a macro-file
edit	: edit a macro-file
run	: run a macro-file
exit	: exit console-mode

3. Commands you enter will be automatically stored in a command history, but you can clear the command with the clear command.
4. After performing a calculation with the macro command, you can save it as a macro file with the save command.
5. In addition, you can edit a macro file by edit or run it, which is the same as the menu described on the previous page.
6. To exit console mode, use exit.

* The Calculation screen of CaTCalc can be displayed and edited in the console mode. Check conditions whenever necessary.



VIII. How to deal with errors

VIII-1. General errors

Thermodynamic equilibrium calculations are an optimization problem, but very small amounts of components may be critically important, or they may vary numerically discontinuously.

If a calculation error occurs, try adding a gas phase if one is not included. (It is usually added automatically, but not, for example, in phase name labeling calculations.) Note that it is sometimes advisable to add the gas phase even in metallic system calculations.

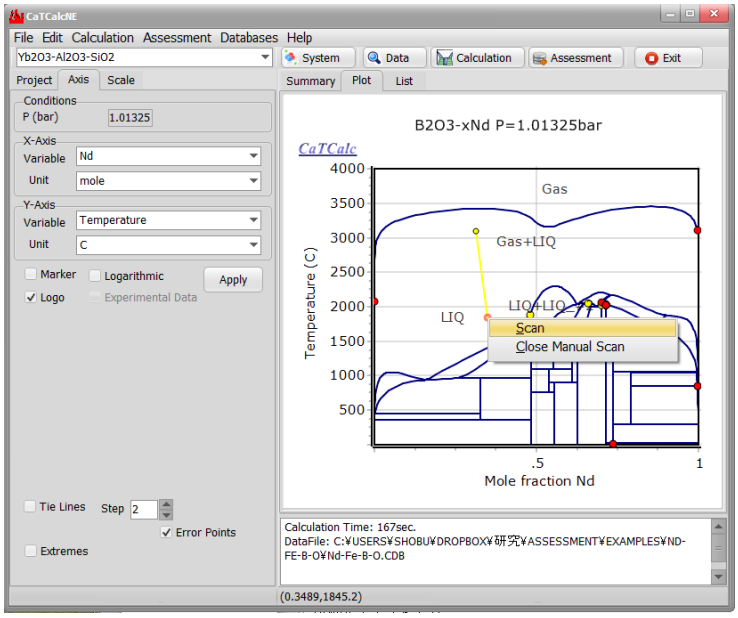
If multiple valences are possible, such as transition metal oxides, it is more stable to specify the oxygen partial pressure in the calculation.

Check the database for any other problems. For multi-component systems, there is a way to try recalculating the system with only the major components.

VIII-2. Phase diagram calculation

In the phase diagram calculation, the transition point is first found on the frame of the calculation area, and then the phase boundary is traced from there. It is possible that boundary tracing fails somewhere, or detection of the transition point fails due to errors in the numerical calculation. In such cases in the phase diagram calculation, try [**Manual scan**] of the right button menu. The function, however, is not supported in the liquidus projection calculation at present.

Using the Manual scan



Calculation of the phase boundary between LIQ and Gas+LIQ failed in the left figure. In this case, use the Manual scan mode of the right button popup menu to draw a line across the phase boundary as shown in the left figure, and then scan. Be sure to close this mode after completing the calculation.

IX. Thermodynamic data and database

IX-1. Phase model

The following phase models are supported by CaTCalc:

- Gas phase
  - Ideal gas
- Liquid phase
  - Ionic two-sublattice liquid model
  - Associate solution model
  - Modified QuasiChemical Model
- Solid phase (crystalline phase)
  - Compound energy formalism (Sublattice model)
- Magnetism
  - Inden-Hillert-Jarl model for magnetic contribution
- Order-disorder transition
  - Split-sublattice model for order-disorder transition
- Pressure dependence
  - Birch-Murnaghan EOS
  - Grover EOS
- Aueous phase
  - HKF Aqueous phase models
  - Extended UNIQUAC model

We plan to develop a non-ideal gas model and other models in future.

IX-2. Database format

There are two standard text formats, ADB and CDB. In both format, the Gibbs energies are expressed as functions of temperature and pressure.

1.ADB format

The former is a TAB-separated CSV format and is used for gaseous species and pure substances with stoichiometric composition, which represents Gibbs energy function, and is editable with spreadsheet software.
First Row: DB description; information displayed in the comment column of the List view.
Second row: Indicates the data storage format, where the number G represents the order: G(70), G(80), G(90), and G(99) represent sqrt(T), T*sqrt(T), ln(T), and T*ln(T), respectively. Density, thermal expansion coefficient, etc. will be supported in due course.
Third row and below: Data separated by TAB.

2.CDB format

It is a text format that conforms to SGTE's TDB format and can be edited with an appropriate editor. Please refer to the CDB Format Database Manual for details.

3.TDB files

ThermoCalc-TDB files in normal one-file format can be converted to CDB format using the Import conversion function. Select [Databases]-[Import TDB files] from the menu to open the file selection dialog.

IX-3. Databases

The following databases are available for CaTCalc.
1. RICT-Pure: Pure substance (solid and liquid phases) and gas phase species.
2. RICT-Fe: Database for iron-based alloys
3. RICT-Sol: General-purpose metal database
4. RICT-Ceram: Ceramic materials database
5. RICT-Cerm: Cermet and hard materials database
6. Various application-specific databases are available.

These are provided in encrypted form for a fee. Please contact us for more information.

X. References

1. “Development of New Equilibrium Calculation Software: CaTCalc”, K. Shobu and T. Tabaru, Mater. Trans., Vol. 46, No. 6, p. 1175 (2005). https://doi.org/10.2320/matertrans.46.1175
2. “CaTCalc : New thermodynamic equilibrium calculation software”, Kazuhisa Shobu, CALPHAD, 33 (2009), pp 279-287. https://doi.org/10.1016/j.calphad.2008.09.015
3. “Challenges in determining individual chemical potentials of system elements by Gibbs energy minimization”, K. Shobu, CALPHAD, 85 (2024) p102691. https://doi.org/10.1016/j.calphad.2024.102691

XI. Development of thermodynamic database

XI-1. How to use Image Digitizer

XI-2. Usage of Fitting Tool

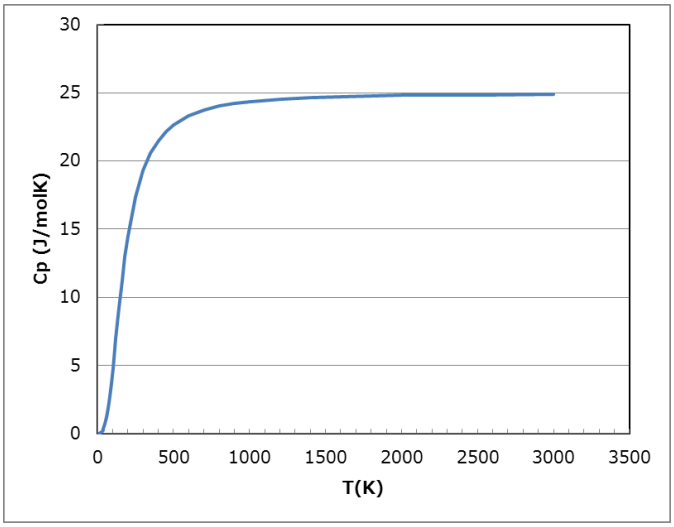
XI-3. Thermodynamic Data Conversion Methods

XI-4. Optimization of Thermodynamic Parameters

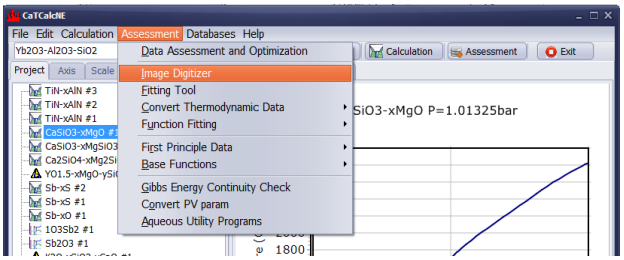
XI-5. How to Use First-Principles Calculation Data

XI-1. How to use Built-in Image Digitizer

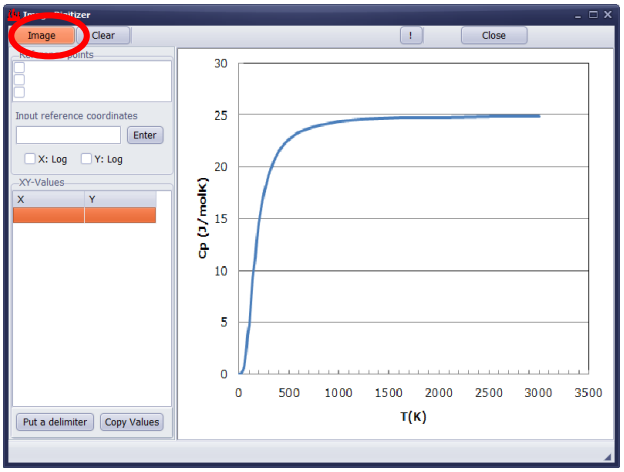
The following shows how to use the Digitizer, using specific heat diagram data as an example.



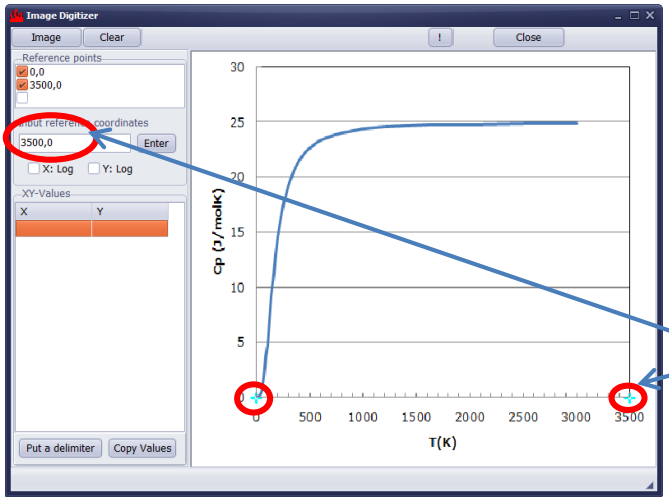
- Figure Example



- Launch the digitizer from the menu [Assessment]-[Image digitizer].

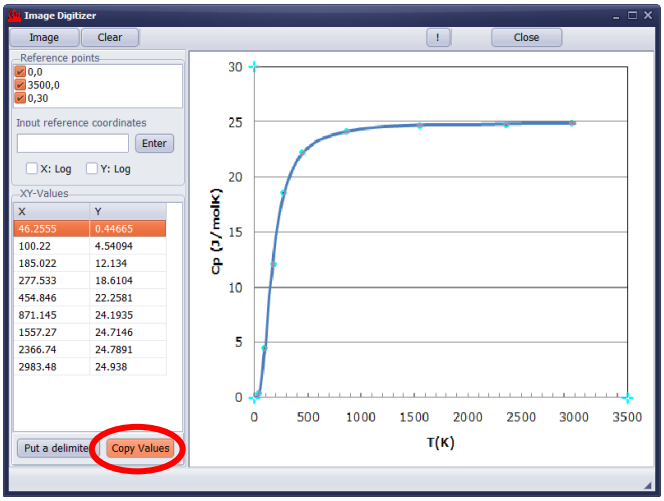


- Copy the figure to the clipboard and press the Image button to load the figure. Adjust the size of the figure using the whole frame.



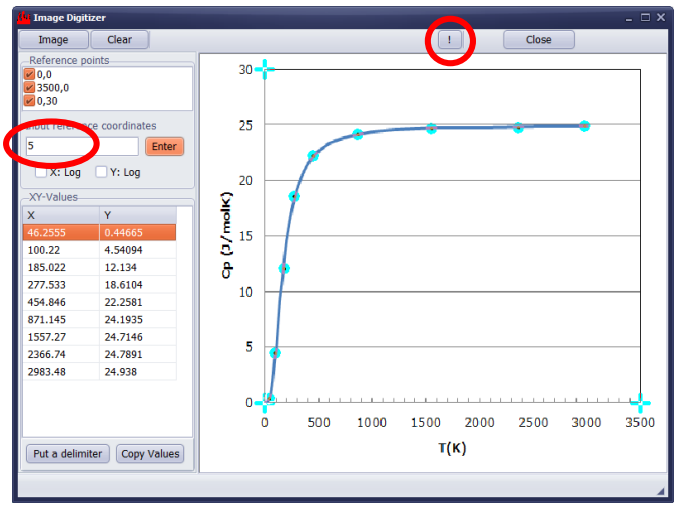
Setting Coordinates

- Set up three reference points. First, click on a suitable point as the origin and set its coordinates. In the same way, set a point on the X and Y axes. The left image shows a point on the X-axis.



- Click a point on the curve to convert and read the data. Move the cursor to the vicinity of the point to change the shape of the cursor and select that point, so you can modify the data. You can also click the right button to delete the data.

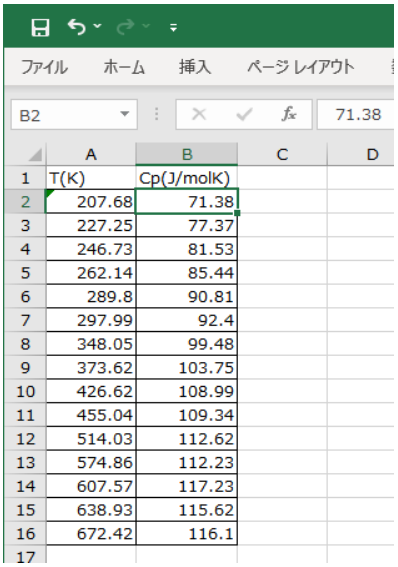
- Click [Copy Values] button at the bottom of the screen to copy the data to the clipboard, and then paste the data into an Excel file.



- By pressing the [i] button at the top, you can change the size of the drawing point.

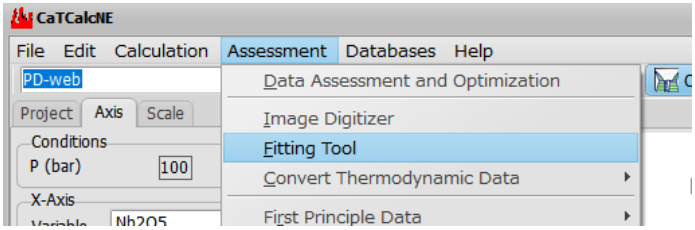
XI-2. How to use the Fitting Tool

The following shows how to use the built-in Fitting Tool, using specific heat data as an example.

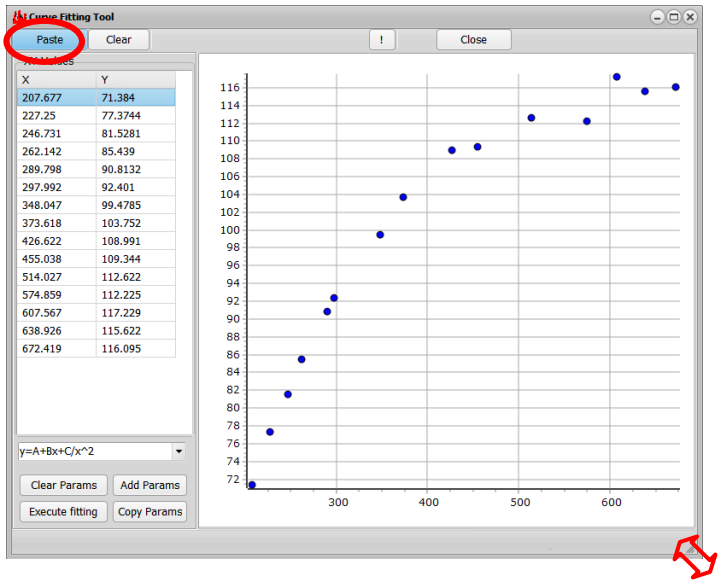


	A	B	C	D
1	T(K)	Cp(J/molK)		
2	207.68	71.38		
3	227.25	77.37		
4	246.73	81.53		
5	262.14	85.44		
6	289.8	90.81		
7	297.99	92.4		
8	348.05	99.48		
9	373.62	103.75		
10	426.62	108.99		
11	455.04	109.34		
12	514.03	112.62		
13	574.86	112.23		
14	607.57	117.23		
15	638.93	115.62		
16	672.42	116.1		
17				

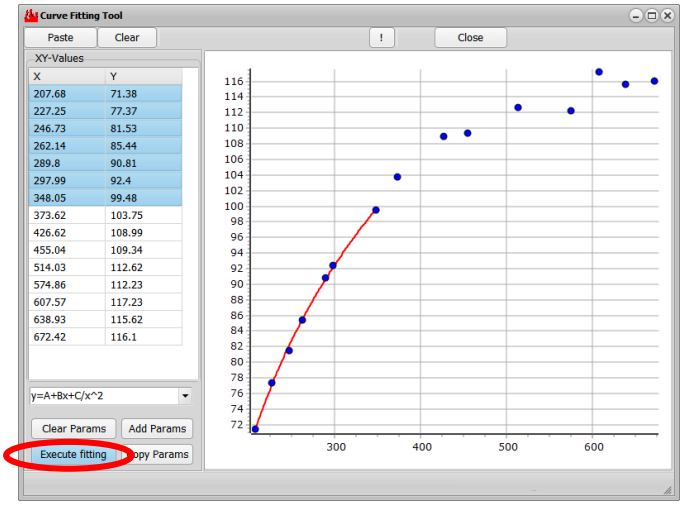
- Example of specific heat data. Copy this to the clipboard. The title line is not necessary but may be included.



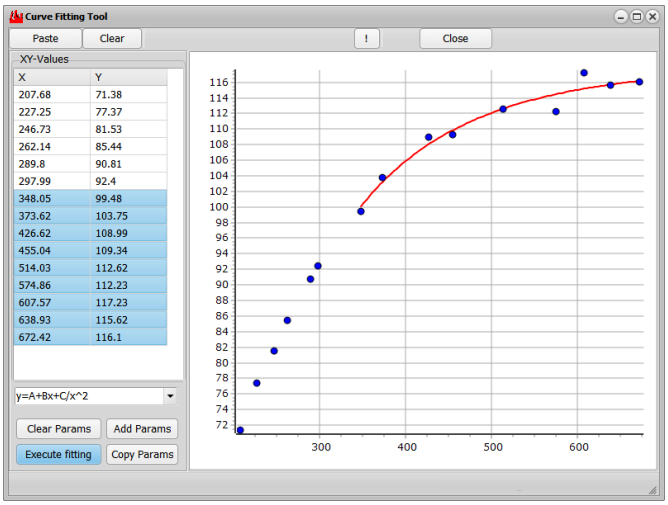
- Launch the Fitting Tool from the menu [Assessment]-[Fitting Tool].



- Paste the data in the clipboard by pressing the Paste button. The data will be plotted automatically, but its size should be adjusted using the overall frame.

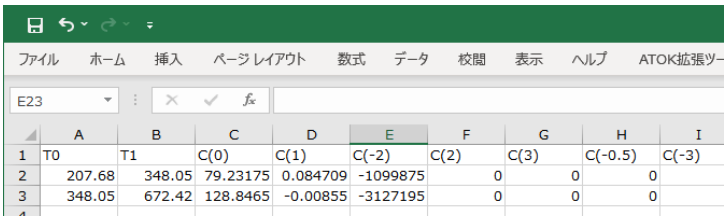


- In fitting, one usually tries several functions to find the best one, but here we use the default function and show how to divide the temperature range into two and approximate it. As shown in the left figure, the split point is selected at 348K, and the data from 207K to 348K is selected. Then, press [Execute fitting] to perform fitting, and the result is displayed as a red line in the plot.
- If the fitting is good, click [Add Params] to temporarily save the parameters for this temperature range.



- Next, select data of the rest of the temperature range and perform the fitting in the same way. If the fitting is good, save additional parameters with [Add Params]. (Note that small difference at the junction point would give negligible effect to the Gibbs energy, as the specific heat is the second derivative of the latter.)

- Then, copy the parameters to the clipboard using the [Copy Params] button and paste them into Excel or other application.



- The left figure shows an example of parameters, where T0 and T1 represent the lower and upper limits of the temperature range, and C(N) is the coefficient of the Nth order term of temperature in the polynomial equation of specific heat.
- See the next section, "Conversion Methods for Thermodynamic Data," for how to use this data to obtain the Gibbs energy function.

XI-3. Thermodynamic Data Conversion

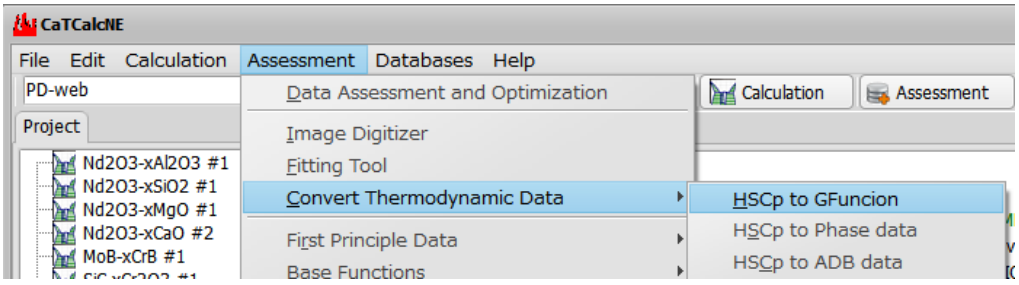
Below are the methods for converting H, S, and Cp data to Gibbs energy and vice versa.

(1) Using spreadsheet software

1. Conversion from Enthalpy, Entropy, and specific heat to Gibbs energy

	A	B	C	D	E	F	G	H	I	J	K
1	Phase	Formula	state	T0	T1	H0	S0	C(0)	C(1)	C(-2)	Ref
2	MxO	MxO	s	207.68	348.05	-1086000	84.83	79.23175	0.084709	-1099875	
3	MxO	MxO	s	348.05	672.42			128.8465	-0.00855	-3127195	
4											

- As shown in the figure above, create a table of temperature functions of specific heat with information on phase, formula, state, temperature range, standard Enthalpy and Entropy of formation at 298.15 K. (The function of specific heat obtained on the previous page is used as an example. Note that the Enthalpy and Entropy of formation were obtained separately from the literature.) The item name is required, and the state is s, l, or g for solid phase, liquid phase, and gas, respectively. Also, when using H and S at T0, use HT and ST instead of H0 and S0 at 298.15K in the item name.
- Copy the entire table to the clipboard, including the item names, and select [Assessment]-[Convert Thermodynamic Data]-[HSCp to GFunction] from the menu to convert the data in the clipboard to the Gibbs energy function.
- The result is saved in the clipboard and can be pasted into a data file. If you select [HSCp to Phase data], Phase information in CDB format is also added. [HSCp to ADB data] converts the data to ADB format for pure substances.



2. Conversion from Gibbs energy to Enthalpy, Entropy, and specific heat

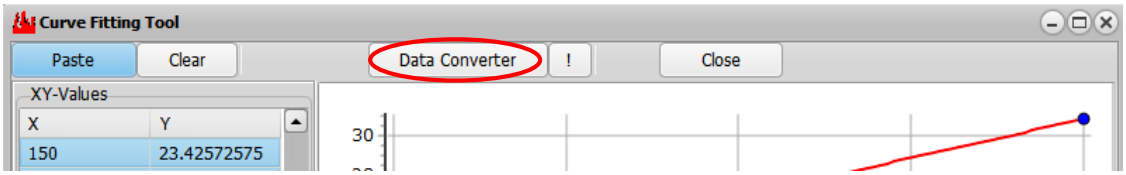
- As shown in the example below, copy the remaining part of the Gibbs energy function from the starting temperature to the clipboard and select [GFunc to HSCp data] from the menu. The converted result will be saved to the clipboard in the TAB-separated text format.

```
Function GCU2OSOL 298.15 -194216.99+344.07921*T-63.5877*T*LN(T)↓
      -0.00942505*T**2+289373.5*T**(-1); 6000 N !↓
```

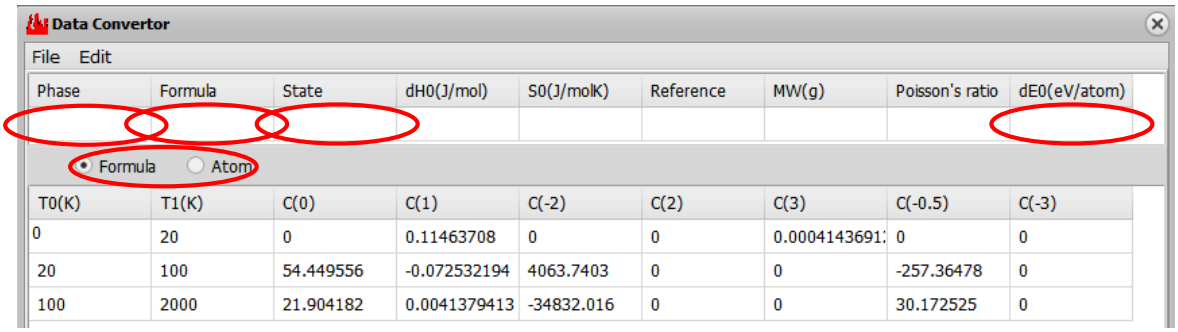
(2) Using the built-in conversion tool

Below we show how to use the built-in conversion tools. This may be useful when parameterizing data from measured specific heat or first-principles calculations.

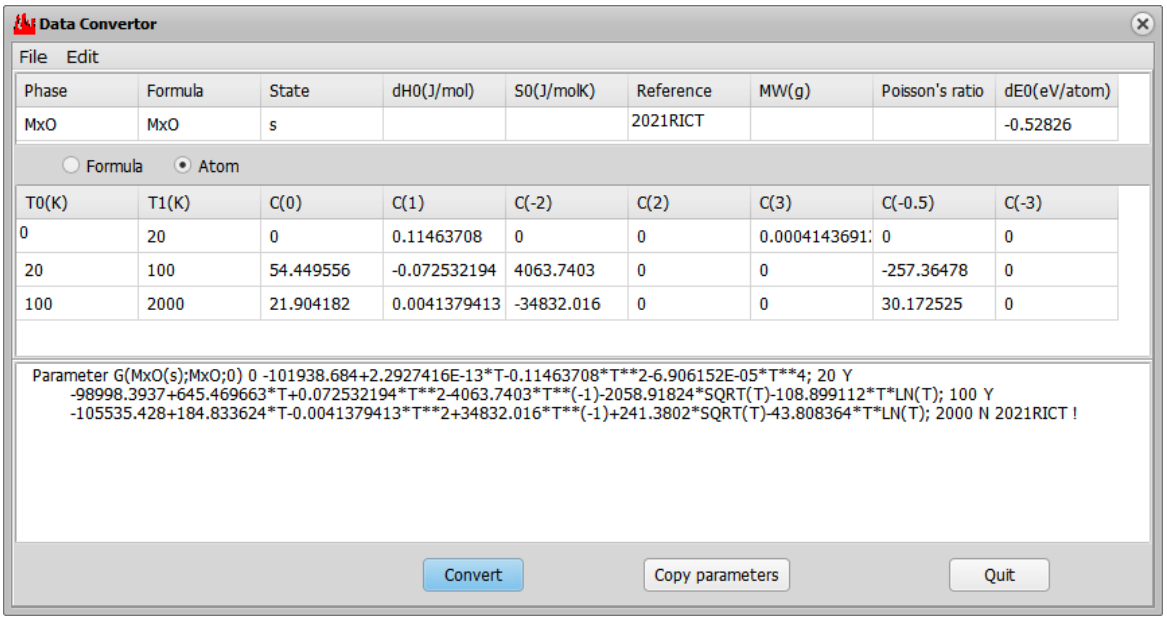
Fitting with the Fitting Tool



- After fitting using the Fitting Tool and saving the parameters with [Add Params], press the [Data Converter] button on the top of the Fitting Tool to start the conversion tool. The parameters are also transferred.



- Enter Phase, Formula and State, and dE0 if the data were obtained from first principles calculations. Also, check the box depending on whether the Cp is per formula or atom. Then press the [Convert] button at the bottom to obtain the Gibbs energy function.



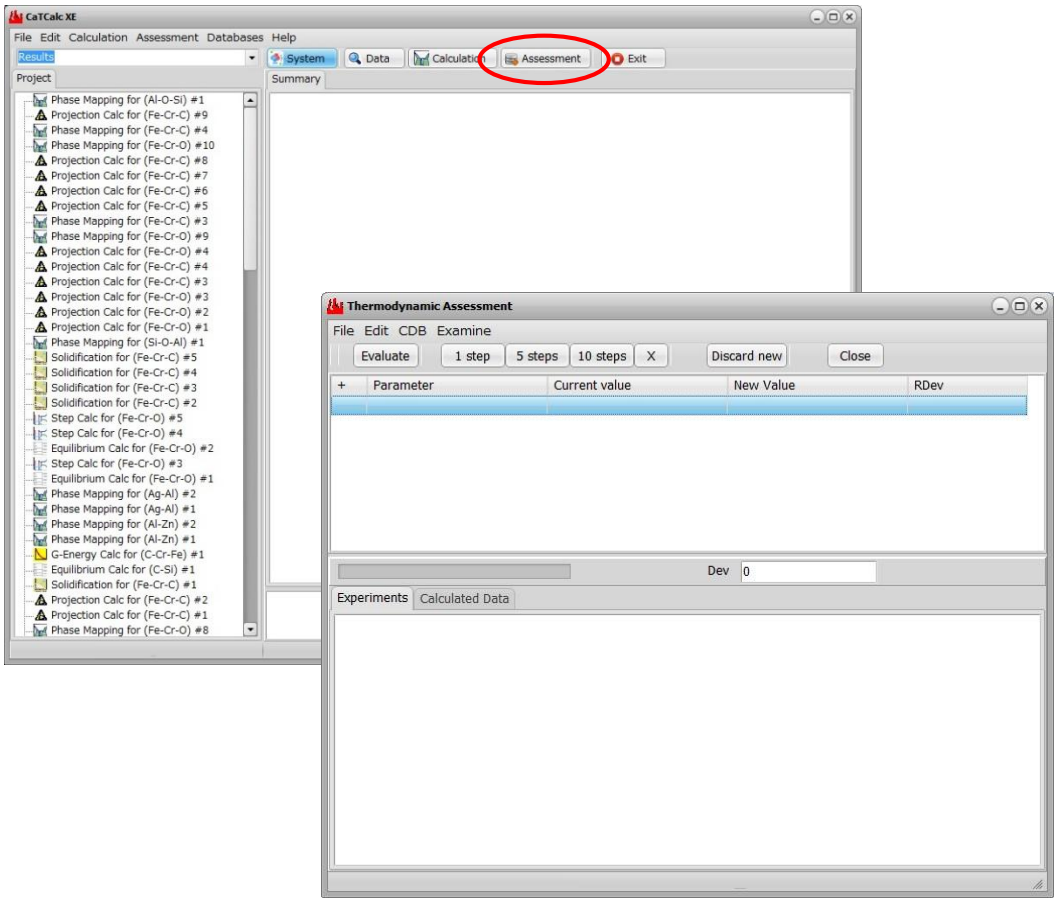
Optimization Steps

Usually, the following three steps are required:

1. Configuring Datafile
2. Summary of experimental data
3. Optimization through Assessment

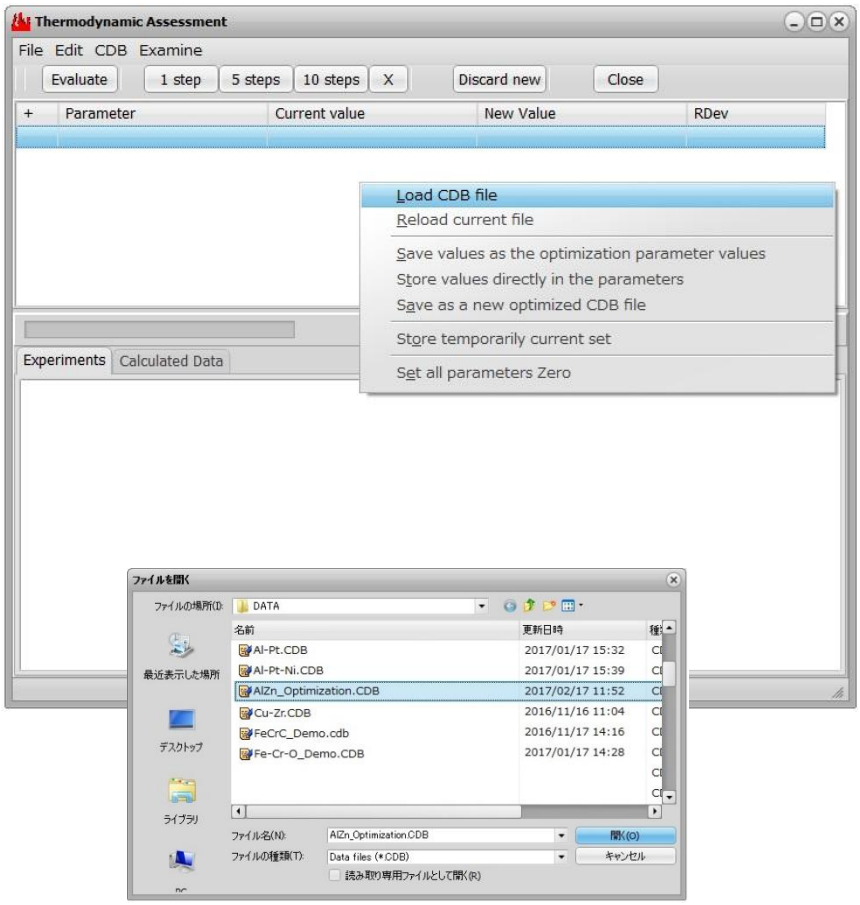
First, let's take an example of an Al-Zn system assessment.

Press the Assessment button in CaTCalc XE to open the Assessment module.



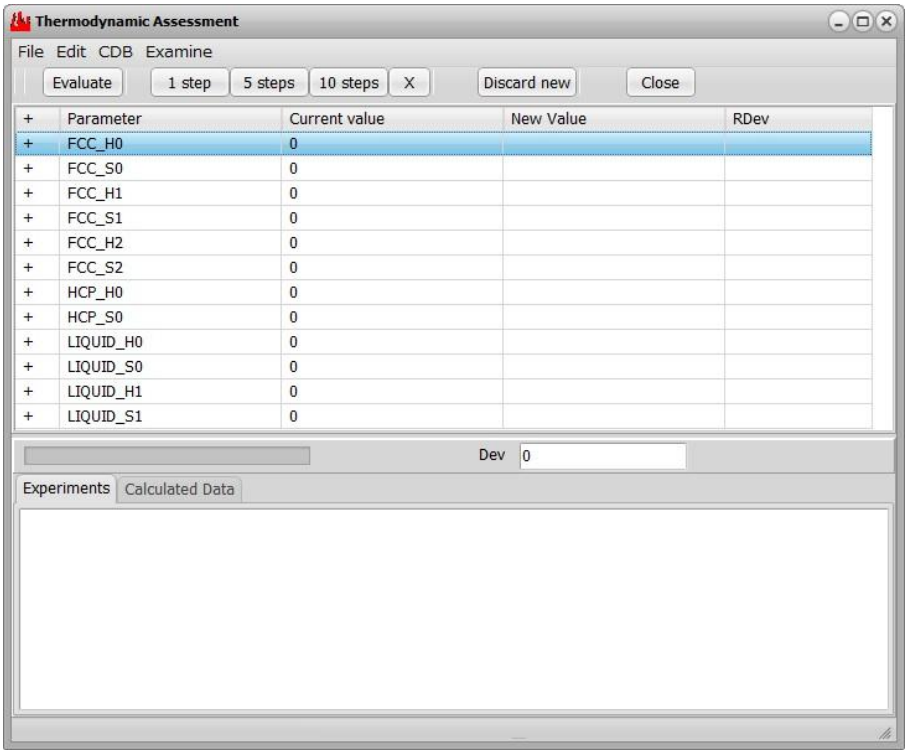
Loading Data

1. Press [Load CDB file] in the right button menu in the box above to bring up the File selection screen and load “AlZn_Optimization.CDB” in the data folder.



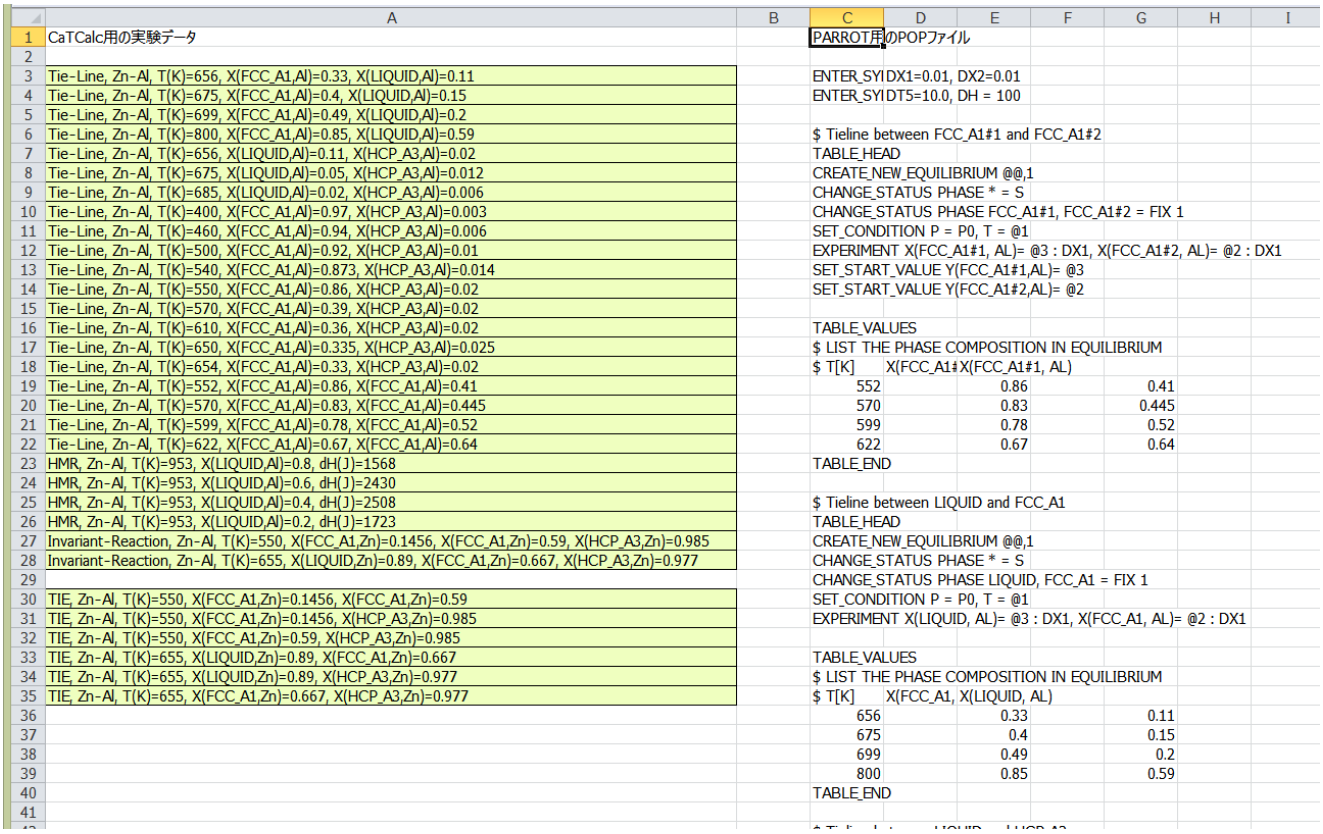
2. Select Al and Zn in the dialog that appears to select an element.

Reading DB files



- The data file is loaded and parameters to be optimized are displayed. Check the contents of the data file by pressing [CDB] in the menu.
- Next, open the file "AssessmentExample.xlsx" and open the Zn-Al sheet. This file is located in the data folder (/User/Documents/CaTCalcXE/DATA).

Editing experimental data

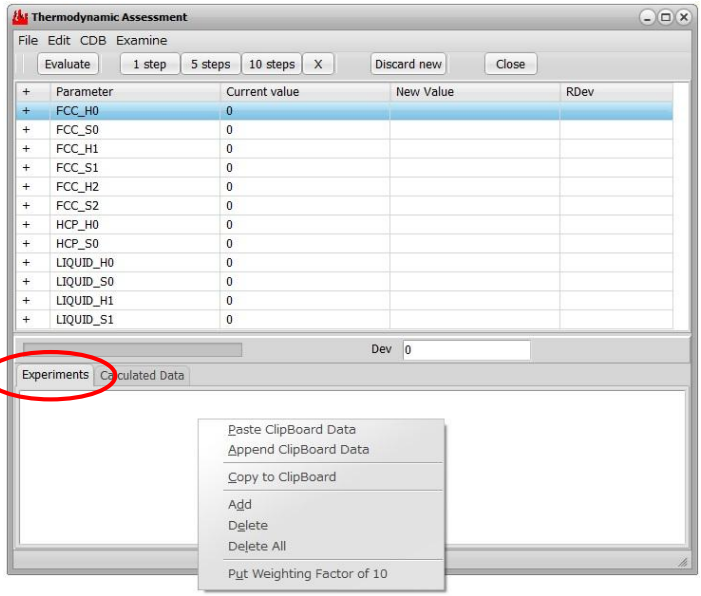


	A	B	C	D	E	F	G	H	I
1	CaTCalc用の実験データ		PARROT用のPOPファイル						
2									
3	Tie-Line, Zn-Al, T(K)=656, X(FCC_A1,Al)=0.33, X(LIQUID,Al)=0.11		ENTER_SYI DX1=0.01, DX2=0.01						
4	Tie-Line, Zn-Al, T(K)=675, X(FCC_A1,Al)=0.4, X(LIQUID,Al)=0.15		ENTER_SYI DT5=10.0, DH = 100						
5	Tie-Line, Zn-Al, T(K)=699, X(FCC_A1,Al)=0.49, X(LIQUID,Al)=0.2								
6	Tie-Line, Zn-Al, T(K)=800, X(FCC_A1,Al)=0.85, X(LIQUID,Al)=0.59		$ Tieline between FCC_A1#1 and FCC_A1#2						
7	Tie-Line, Zn-Al, T(K)=656, X(LIQUID,Al)=0.11, X(HCP_A3,Al)=0.02		TABLE_HEAD						
8	Tie-Line, Zn-Al, T(K)=675, X(LIQUID,Al)=0.05, X(HCP_A3,Al)=0.012		CREATE_NEW_EQUILIBRIUM @@,1						
9	Tie-Line, Zn-Al, T(K)=685, X(LIQUID,Al)=0.02, X(HCP_A3,Al)=0.006		CHANGE_STATUS PHASE * = S						
10	Tie-Line, Zn-Al, T(K)=400, X(FCC_A1,Al)=0.97, X(HCP_A3,Al)=0.003		CHANGE_STATUS PHASE FCC_A1#1, FCC_A1#2 = FIX 1						
11	Tie-Line, Zn-Al, T(K)=460, X(FCC_A1,Al)=0.94, X(HCP_A3,Al)=0.006		SET_CONDITION P = P0, T = @1						
12	Tie-Line, Zn-Al, T(K)=500, X(FCC_A1,Al)=0.92, X(HCP_A3,Al)=0.01		EXPERIMENT X(FCC_A1#1, AL)= @3 : DX1, X(FCC_A1#2, AL)= @2 : DX1						
13	Tie-Line, Zn-Al, T(K)=540, X(FCC_A1,Al)=0.873, X(HCP_A3,Al)=0.014		SET_START_VALUE Y(FCC_A1#1,AL)= @3						
14	Tie-Line, Zn-Al, T(K)=550, X(FCC_A1,Al)=0.86, X(HCP_A3,Al)=0.02		SET_START_VALUE Y(FCC_A1#2,AL)= @2						
15	Tie-Line, Zn-Al, T(K)=570, X(FCC_A1,Al)=0.39, X(HCP_A3,Al)=0.02								
16	Tie-Line, Zn-Al, T(K)=610, X(FCC_A1,Al)=0.36, X(HCP_A3,Al)=0.02		TABLE_VALUES						
17	Tie-Line, Zn-Al, T(K)=650, X(FCC_A1,Al)=0.335, X(HCP_A3,Al)=0.025		$ LIST THE PHASE COMPOSITION IN EQUILIBRIUM						
18	Tie-Line, Zn-Al, T(K)=654, X(FCC_A1,Al)=0.33, X(HCP_A3,Al)=0.02		$ T[K] X(FCC_A1#X(FCC_A1#1, AL)						
19	Tie-Line, Zn-Al, T(K)=552, X(FCC_A1,Al)=0.86, X(FCC_A1,Al)=0.41		552	0.86	0.41				
20	Tie-Line, Zn-Al, T(K)=570, X(FCC_A1,Al)=0.83, X(FCC_A1,Al)=0.445		570	0.83	0.445				
21	Tie-Line, Zn-Al, T(K)=599, X(FCC_A1,Al)=0.78, X(FCC_A1,Al)=0.52		599	0.78	0.52				
22	Tie-Line, Zn-Al, T(K)=622, X(FCC_A1,Al)=0.67, X(FCC_A1,Al)=0.64		622	0.67	0.64				
23	HMR, Zn-Al, T(K)=953, X(LIQUID,Al)=0.8, dH(J)=1568		TABLE_END						
24	HMR, Zn-Al, T(K)=953, X(LIQUID,Al)=0.6, dH(J)=2430								
25	HMR, Zn-Al, T(K)=953, X(LIQUID,Al)=0.4, dH(J)=2508		$ Tieline between LIQUID and FCC_A1						
26	HMR, Zn-Al, T(K)=953, X(LIQUID,Al)=0.2, dH(J)=1723		TABLE_HEAD						
27	Invariant-Reaction, Zn-Al, T(K)=550, X(FCC_A1,Zn)=0.1456, X(FCC_A1,Zn)=0.59, X(HCP_A3,Zn)=0.985		CREATE_NEW_EQUILIBRIUM @@,1						
28	Invariant-Reaction, Zn-Al, T(K)=655, X(LIQUID,Zn)=0.89, X(FCC_A1,Zn)=0.667, X(HCP_A3,Zn)=0.977		CHANGE_STATUS PHASE * = S						
29			CHANGE_STATUS PHASE LIQUID, FCC_A1 = FIX 1						
30	TIE, Zn-Al, T(K)=550, X(FCC_A1,Zn)=0.1456, X(FCC_A1,Zn)=0.59		SET_CONDITION P = P0, T = @1						
31	TIE, Zn-Al, T(K)=550, X(FCC_A1,Zn)=0.1456, X(HCP_A3,Zn)=0.985		EXPERIMENT X(LIQUID, AL)= @3 : DX1, X(FCC_A1, AL)= @2 : DX1						
32	TIE, Zn-Al, T(K)=550, X(FCC_A1,Zn)=0.59, X(HCP_A3,Zn)=0.985								
33	TIE, Zn-Al, T(K)=655, X(LIQUID,Zn)=0.89, X(FCC_A1,Zn)=0.667		TABLE_VALUES						
34	TIE, Zn-Al, T(K)=655, X(LIQUID,Zn)=0.89, X(HCP_A3,Zn)=0.977		$ LIST THE PHASE COMPOSITION IN EQUILIBRIUM						
35	TIE, Zn-Al, T(K)=655, X(FCC_A1,Zn)=0.667, X(HCP_A3,Zn)=0.977		$ T[K] X(FCC_A1, X(LIQUID, AL)						
36			656	0.33	0.11				
37			675	0.4	0.15				
38			699	0.49	0.2				
39			800	0.85	0.59				
40			TABLE_END						
41									

- The right-hand side of the figure above is a POP file of ThermoCalc-PARROT. Only the data in the POP file are extracted from the list, and this is the experimental data for CaTCalc. Select this part, and copy the data to the clipboard.

  - Spreadsheet software such as Excel is used to create and save the experimental data.

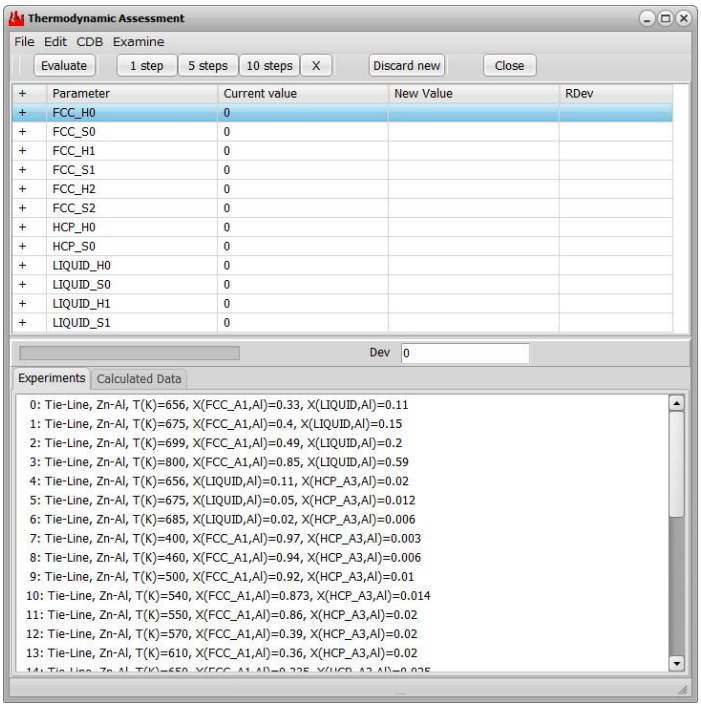
Loading experimental data



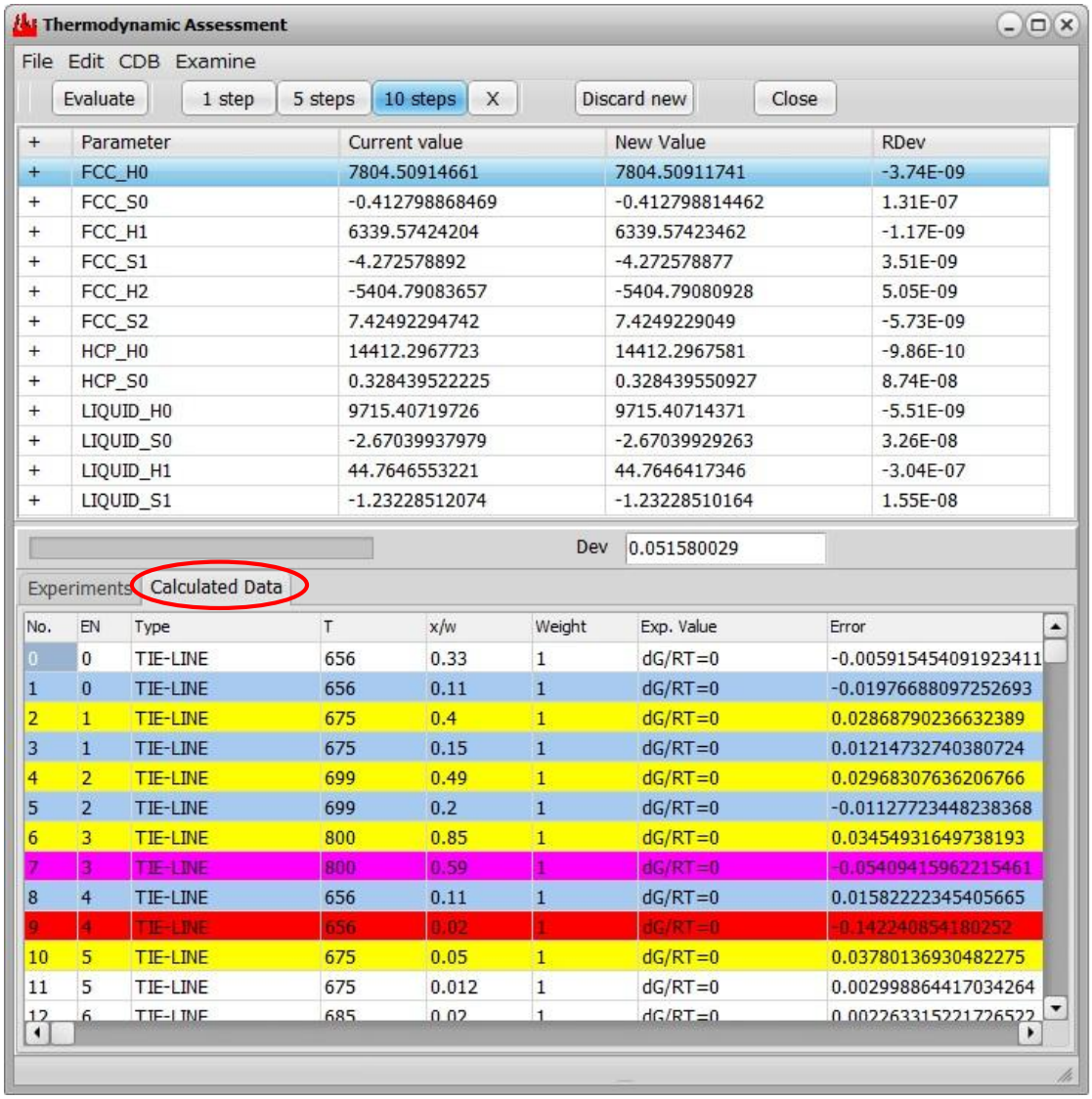
CaTCalc assessment module

1. Open the Experiments panel below and click on the menu that appears with the right mouse button
2. Paste Clipboard data with Paste.

That's all you need to know.



You can optimize parameters by pressing the 1step, 5steps, or 10steps button.



+	Parameter	Current value	New Value	RDev
+	FCC_H0	7804.50914661	7804.50911741	-3.74E-09
+	FCC_S0	-0.412798868469	-0.412798814462	1.31E-07
+	FCC_H1	6339.57424204	6339.57423462	-1.17E-09
+	FCC_S1	-4.272578892	-4.272578877	3.51E-09
+	FCC_H2	-5404.79083657	-5404.79080928	5.05E-09
+	FCC_S2	7.42492294742	7.4249229049	-5.73E-09
+	HCP_H0	14412.2967723	14412.2967581	-9.86E-10
+	HCP_S0	0.328439522225	0.328439550927	8.74E-08
+	LIQUID_H0	9715.40719726	9715.40714371	-5.51E-09
+	LIQUID_S0	-2.67039937979	-2.67039929263	3.26E-08
+	LIQUID_H1	44.7646553221	44.7646417346	-3.04E-07
+	LIQUID_S1	-1.23228512074	-1.23228510164	1.55E-08

No.	EN	Type	T	x/w	Weight	Exp. Value	Error
0	0	TIE-LINE	656	0.33	1	dG/RT=0	-0.005915454091923411
1	0	TIE-LINE	656	0.11	1	dG/RT=0	-0.01976688097252693
2	1	TIE-LINE	675	0.4	1	dG/RT=0	0.02868790236632389
3	1	TIE-LINE	675	0.15	1	dG/RT=0	0.01214732740380724
4	2	TIE-LINE	699	0.49	1	dG/RT=0	0.02968307636206766
5	2	TIE-LINE	699	0.2	1	dG/RT=0	-0.01127723448238368
6	3	TIE-LINE	800	0.85	1	dG/RT=0	0.03454931649738193
7	3	TIE-LINE	800	0.59	1	dG/RT=0	-0.05409415962215461
8	4	TIE-LINE	656	0.11	1	dG/RT=0	0.01582222345405665
9	4	TIE-LINE	656	0.02	1	dG/RT=0	-0.142240854180252
10	5	TIE-LINE	675	0.05	1	dG/RT=0	0.03780136930482275
11	5	TIE-LINE	675	0.012	1	dG/RT=0	0.002998864417034264
12	6	TIE-LINE	685	0.02	1	dG/RT=0	0.0022633152217265 22

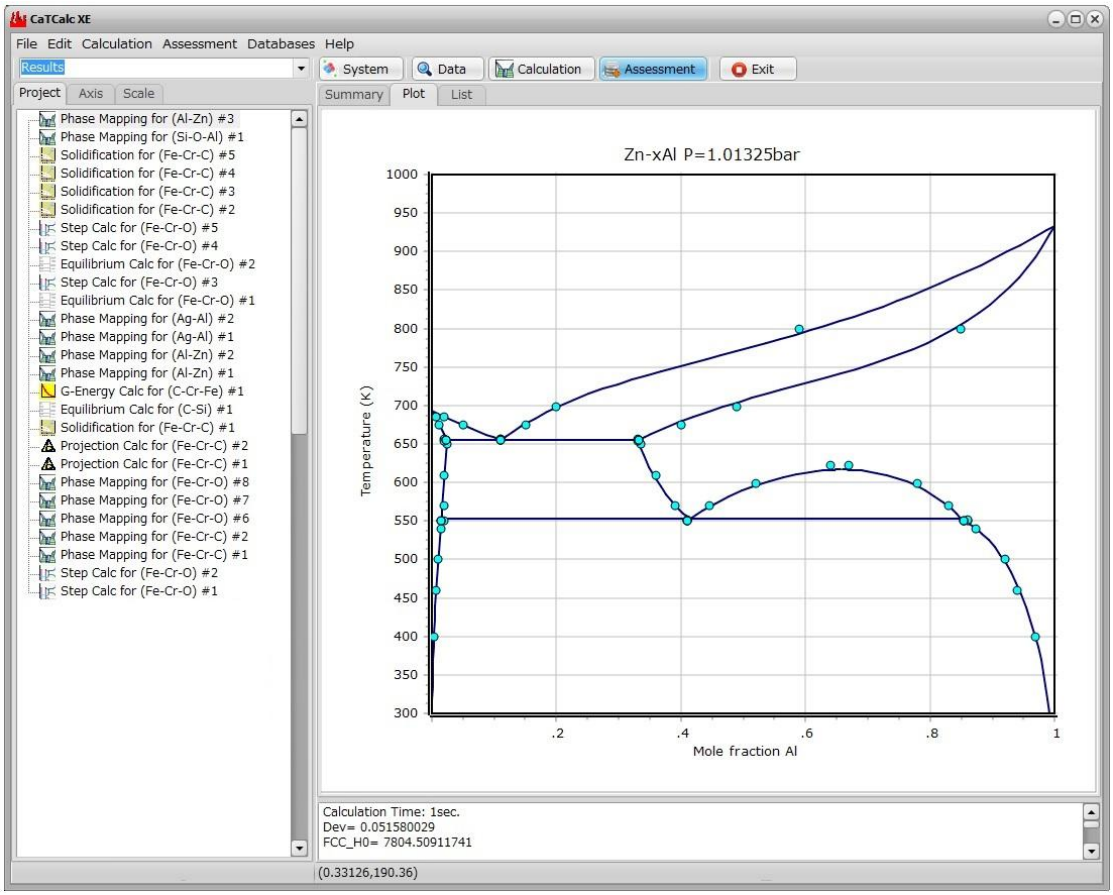
- The bottom panel switches to the list of Calculated Data, showing the differences between the experimental and calculated values. The experimental conditions T, x/w and weight can be edited.

In order of magnitude of error, they are colorized as colorless, blue, yellow, magenta and red. Colorless is the best, but if you have difficulty, some lines of yellow would be a good guide.

- Since experimental values are usually inconsistent, it may be better to adjust not only the weight, but also T and x/w (within the limits of experimental accuracy). Ideally, if there are a lot of data that are close to the average value, we can evaluate the data correctly, but it is not possible to obtain unbiased data that follow a Gaussian distribution. In the least-squares method, large deviations make a large contribution, which means that the data will have large errors. Therefore, it is better to correct the data. Of course, the correction must be within a reasonable range.

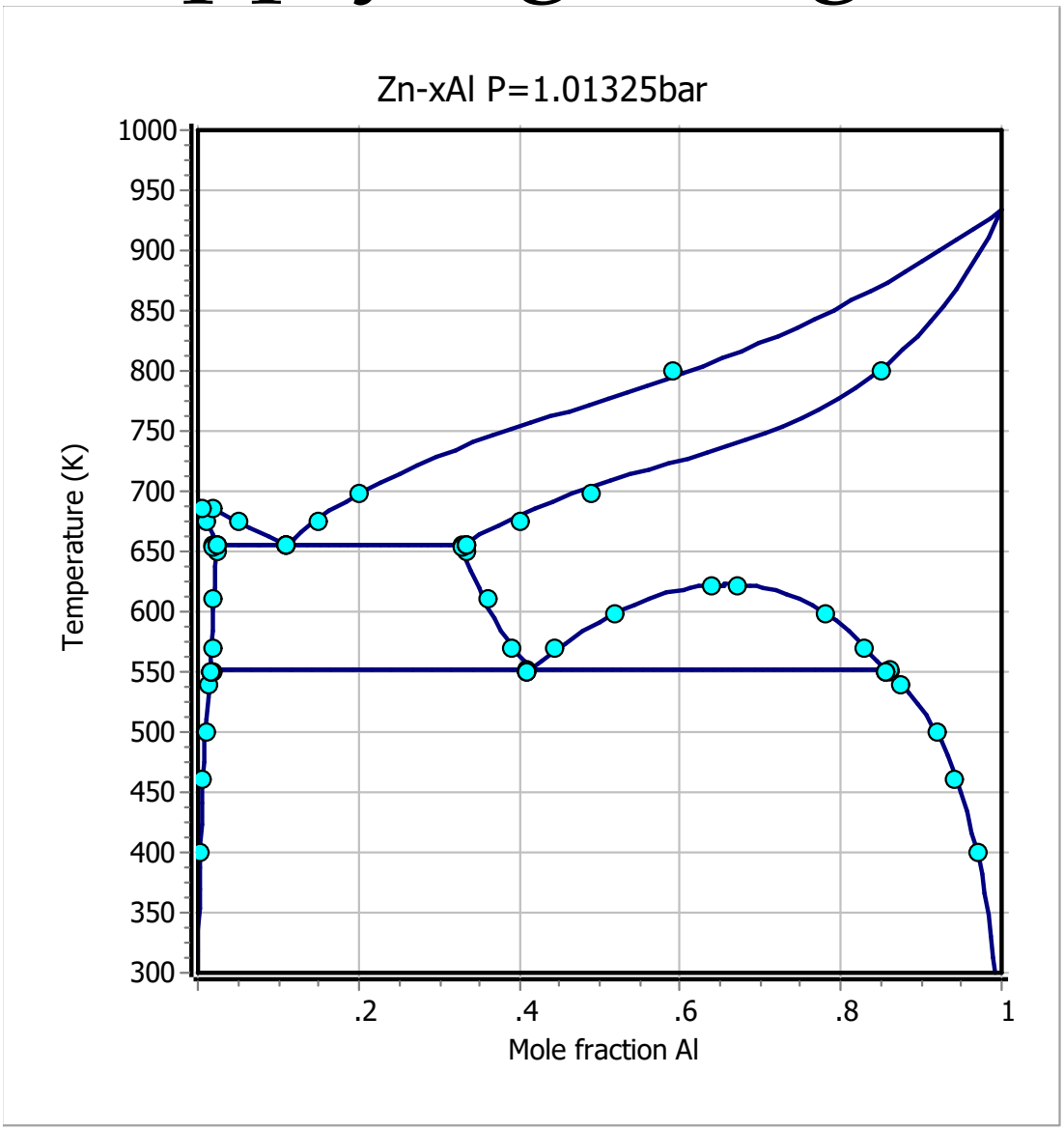
Confirmation of phase diagrams and other information

- Choose "Examine" menu and draw a phase diagram.



- In addition, the HMR and ACR should be checked.(If the calculations don't work, use normal equilibrium calculations.

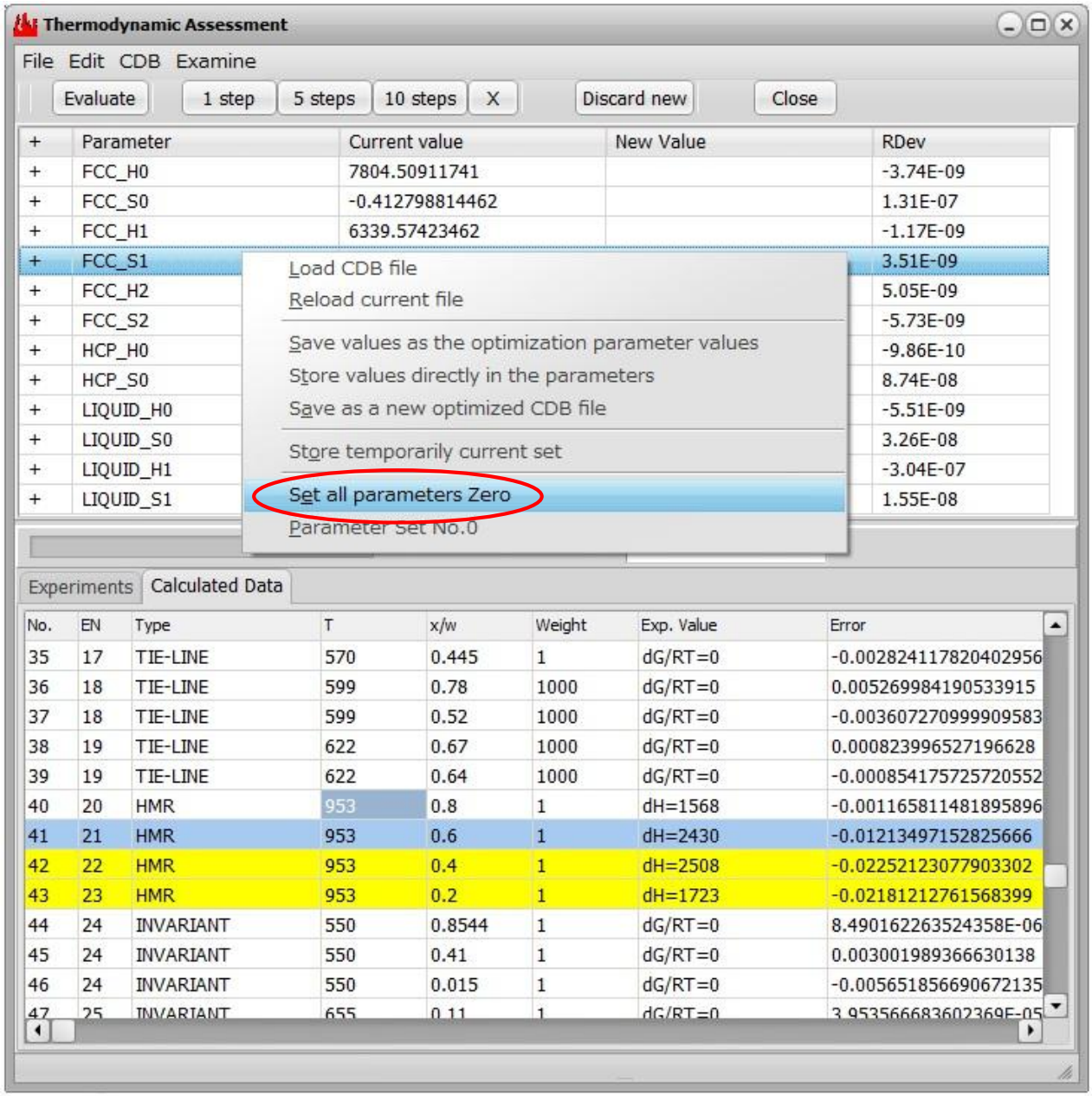
Applying Weight



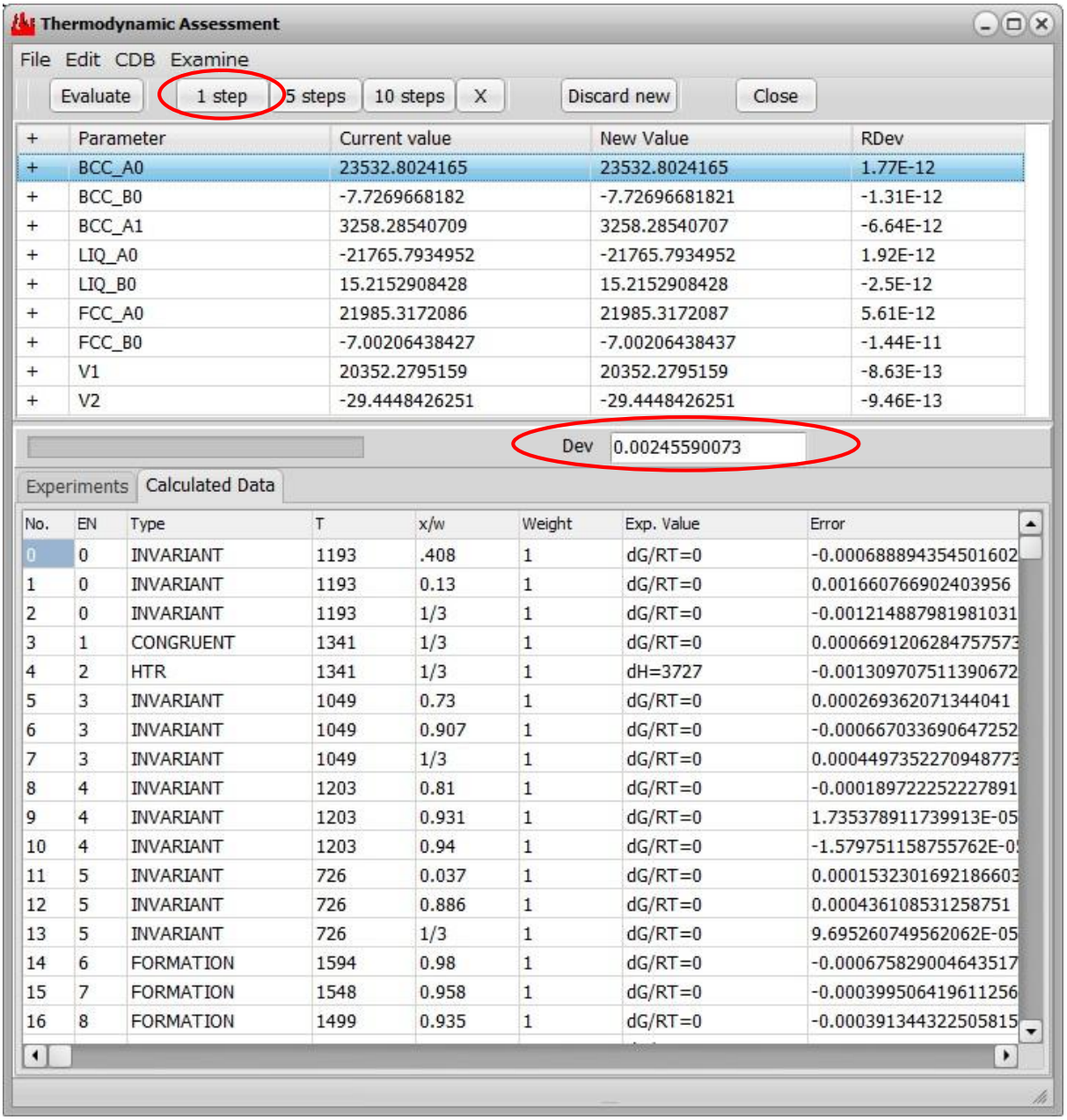
- In the list of Calculated data, if the Weights of No. 36~39 are set to 1000 each, the vertices of the miscibility gap match the experimental values almost perfectly. Thus, we need to carefully decide which data to focus on by referring to the original experimental conditions and experimental data.

Related functions

Initialization of Parameters



Optimization

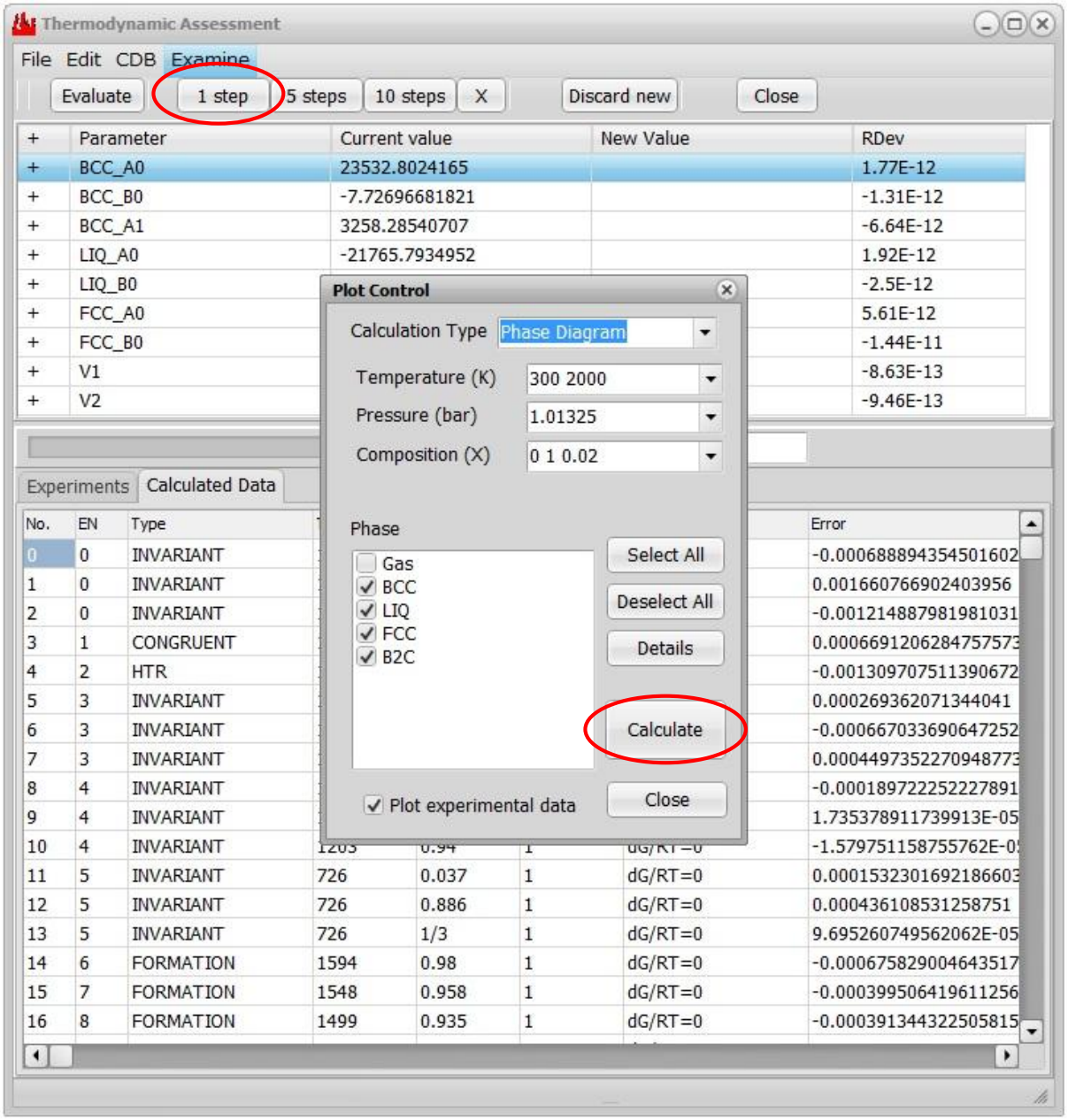


+	Parameter	Current value	New Value	RDev
+	BCC_A0	23532.8024165	23532.8024165	1.77E-12
+	BCC_B0	-7.7269668182	-7.72696681821	-1.31E-12
+	BCC_A1	3258.28540709	3258.28540707	-6.64E-12
+	LIQ_A0	-21765.7934952	-21765.7934952	1.92E-12
+	LIQ_B0	15.2152908428	15.2152908428	-2.5E-12
+	FCC_A0	21985.3172086	21985.3172087	5.61E-12
+	FCC_B0	-7.00206438427	-7.00206438437	-1.44E-11
+	V1	20352.2795159	20352.2795159	-8.63E-13
+	V2	-29.4448426251	-29.4448426251	-9.46E-13

No.	EN	Type	T	x/w	Weight	Exp. Value	Error
0	0	INVARIANT	1193	.408	1	dG/RT=0	-0.000688894354501602
1	0	INVARIANT	1193	0.13	1	dG/RT=0	0.001660766902403956
2	0	INVARIANT	1193	1/3	1	dG/RT=0	-0.001214887981981031
3	1	CONGRUENT	1341	1/3	1	dG/RT=0	0.0006691206284757573
4	2	HTR	1341	1/3	1	dH=3727	-0.001309707511390672
5	3	INVARIANT	1049	0.73	1	dG/RT=0	0.000269362071344041
6	3	INVARIANT	1049	0.907	1	dG/RT=0	-0.000667033690647252
7	3	INVARIANT	1049	1/3	1	dG/RT=0	0.000449735227094877
8	4	INVARIANT	1203	0.81	1	dG/RT=0	-0.000189722252227891
9	4	INVARIANT	1203	0.931	1	dG/RT=0	1.735378911739913E-05
10	4	INVARIANT	1203	0.94	1	dG/RT=0	-1.579751158755762E-0
11	5	INVARIANT	726	0.037	1	dG/RT=0	0.0001532301692186603
12	5	INVARIANT	726	0.886	1	dG/RT=0	0.000436108531258751
13	5	INVARIANT	726	1/3	1	dG/RT=0	9.695260749562062E-05
14	6	FORMATION	1594	0.98	1	dG/RT=0	-0.000675829004643517
15	7	FORMATION	1548	0.958	1	dG/RT=0	-0.000399506419611256
16	8	FORMATION	1499	0.935	1	dG/RT=0	-0.000391344322505815

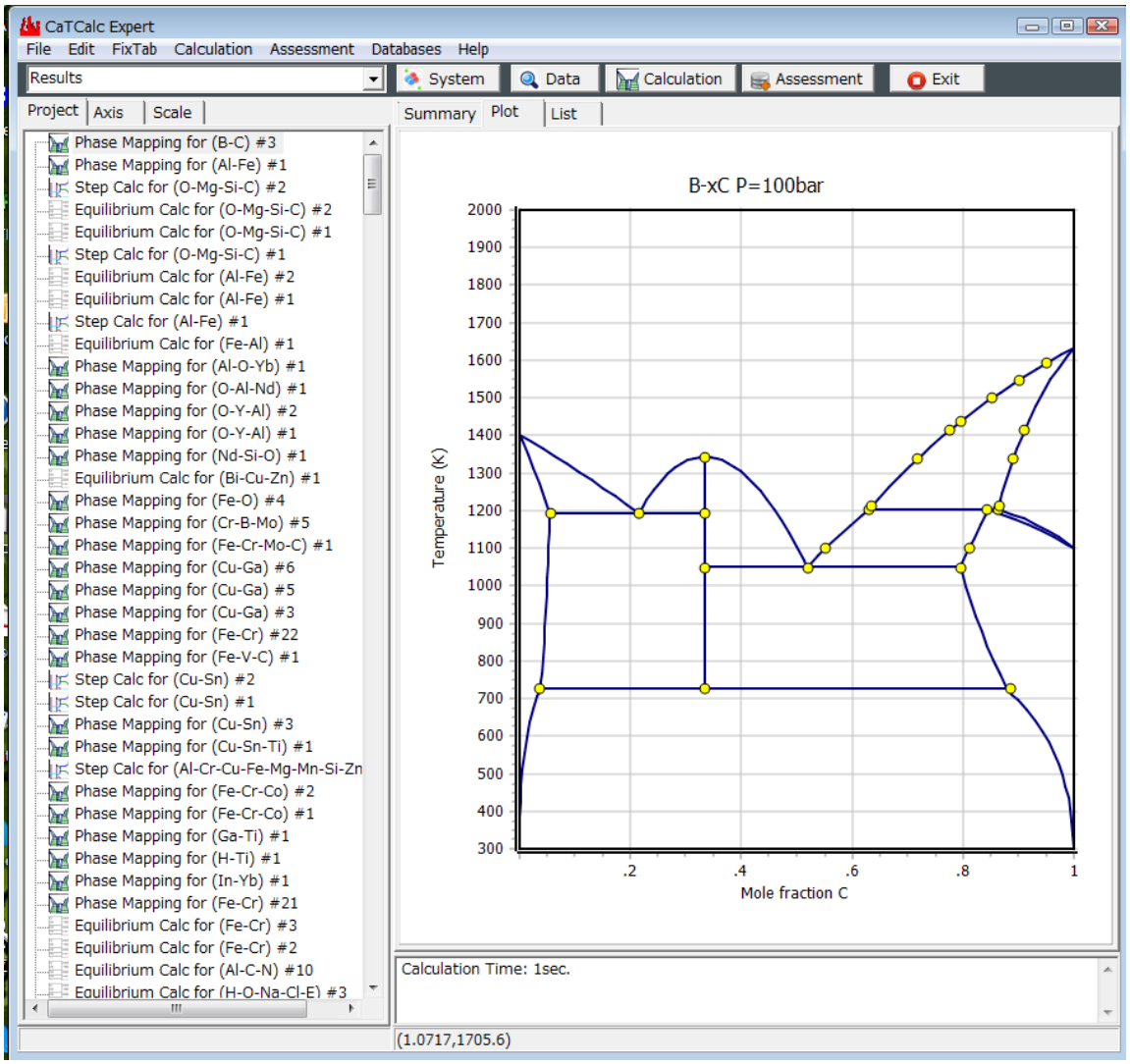
The data in the sheet of tcex36 in "AssesmentExample.xls" is loaded into the data file "tcex36.cdb", and the [1 Step] button is pressed 8 times. “RDev” in the parameter list indicates the amount of modification, which is almost converged, and "Dev" is the RMS of the error values in the experimental value list, which also converges when there is no change.

Phase diagram calculation



[Plot Control] appears as shown in the above figure when [Examine] of the menu is clicked.

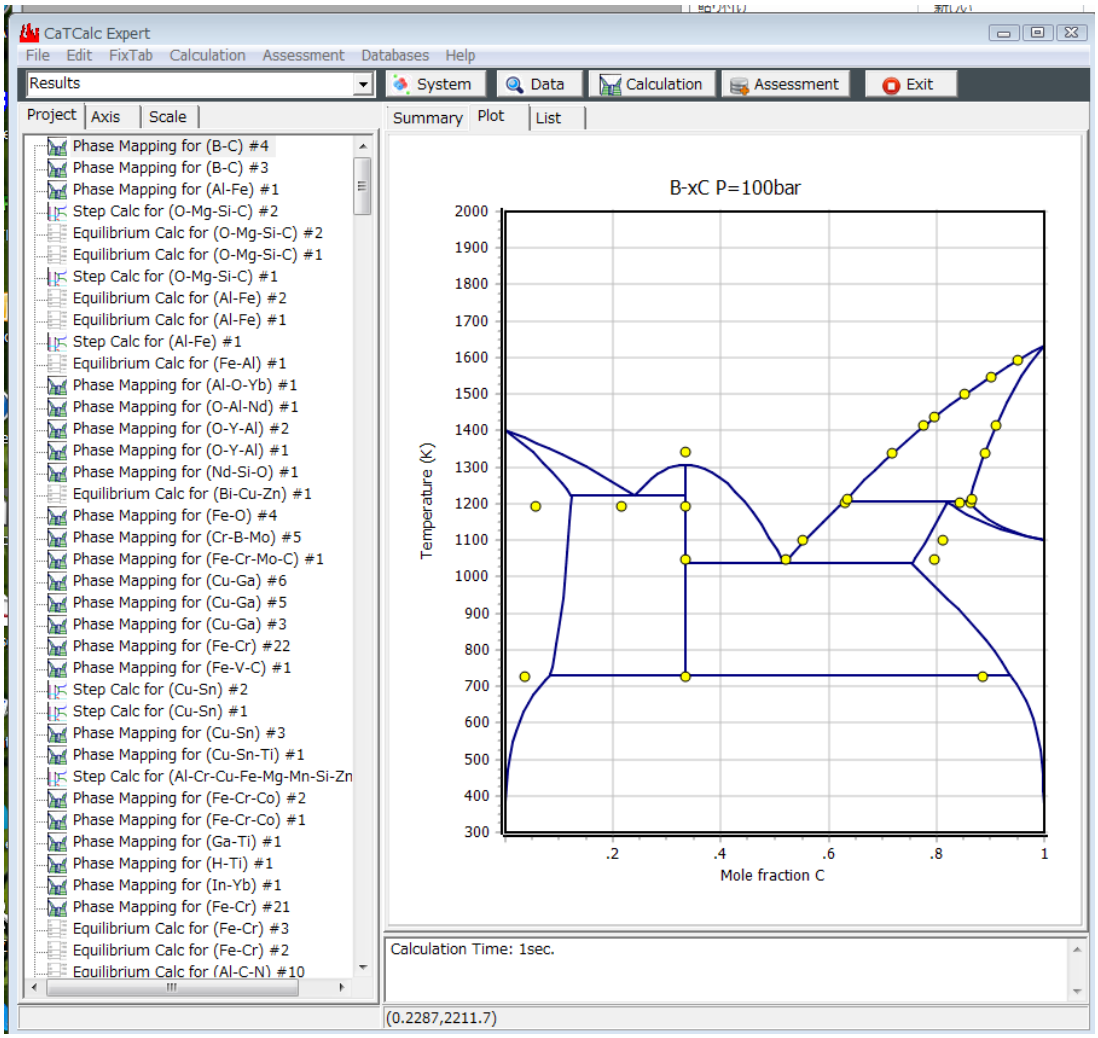
Display Results



Note: Since this system has a singularity problem, it is automatically recalculated including the gas phase. In this case, the pressure is automatically set to 100 bar, which is usually high enough to prevent the gas phase from being stabilized. If the gas phase appears, the pressure should be increased even higher. If the gas phase does not appear, the pressure may be reduced.

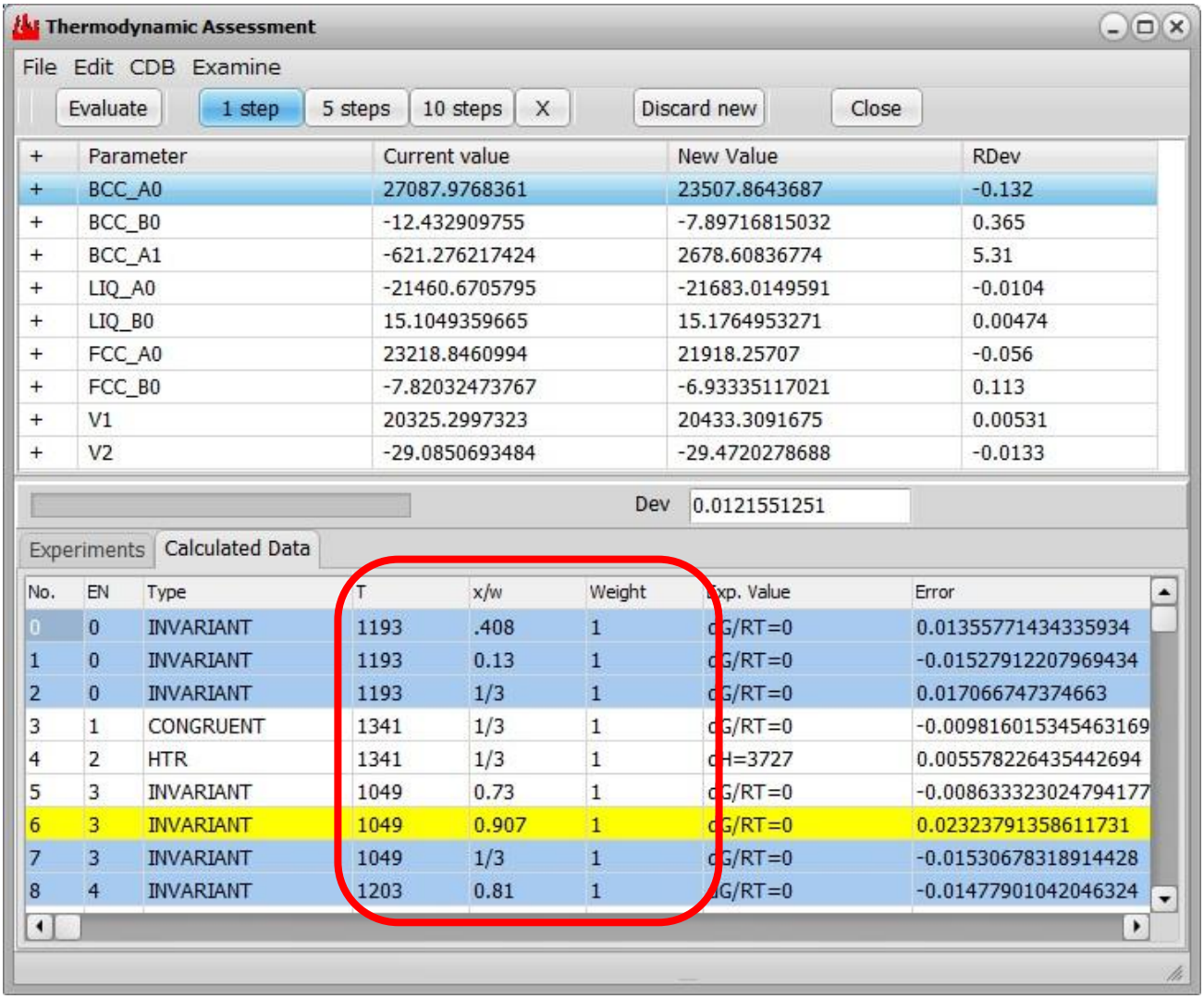
How to use the Weight Factor

Convergence to the Local Minimum



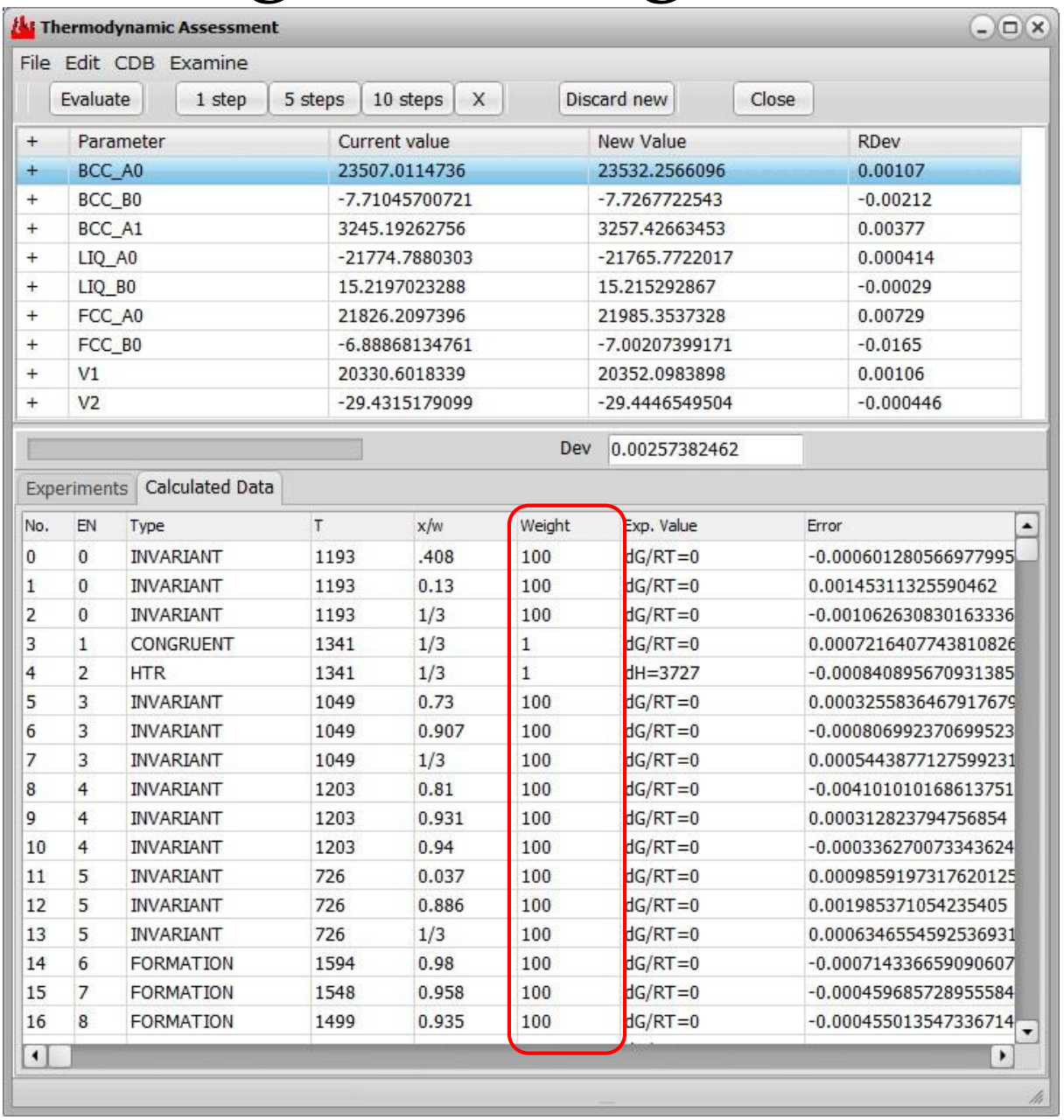
The above is a case where the values have converged to the local minimum. In such a case, it is effective to adjust the weight factor.

Manual Adjustment



In the list of calculated data, three columns of T, x/w and Weight are editable: T is the temperature, x/w is the molar percentage/weight percentage of components, and Weight is the weighting factor. In this optimization module, the comparison of these is made by that of the Gibbs energy. In this optimization method, better results are obtained when we give more weight to the phase diagram information. So we set the Weight of the data for Invariant, Formation and Tie-Line lines to 100.

Setting the Weight Factor



+	Parameter	Current value	New Value	RDev
+	BCC_A0	23507.0114736	23532.2566096	0.00107
+	BCC_B0	-7.71045700721	-7.7267722543	-0.00212
+	BCC_A1	3245.19262756	3257.42663453	0.00377
+	LIQ_A0	-21774.7880303	-21765.7722017	0.000414
+	LIQ_B0	15.2197023288	15.215292867	-0.00029
+	FCC_A0	21826.2097396	21985.3537328	0.00729
+	FCC_B0	-6.88868134761	-7.00207399171	-0.0165
+	V1	20330.6018339	20352.0983898	0.00106
+	V2	-29.4315179099	-29.4446549504	-0.000446

No.	EN	Type	T	x/w	Weight	Exp. Value	Error
0	0	INVARIANT	1193	.408	100	dG/RT=0	-0.000601280566977995
1	0	INVARIANT	1193	0.13	100	dG/RT=0	0.00145311325590462
2	0	INVARIANT	1193	1/3	100	dG/RT=0	-0.001062630830163336
3	1	CONGRUENT	1341	1/3	1	dG/RT=0	0.0007216407743810826
4	2	HTR	1341	1/3	1	dH=3727	-0.000840895670931385
5	3	INVARIANT	1049	0.73	100	dG/RT=0	0.0003255836467917679
6	3	INVARIANT	1049	0.907	100	dG/RT=0	-0.000806992370699523
7	3	INVARIANT	1049	1/3	100	dG/RT=0	0.0005443877127599231
8	4	INVARIANT	1203	0.81	100	dG/RT=0	-0.004101010168613751
9	4	INVARIANT	1203	0.931	100	dG/RT=0	0.000312823794756854
10	4	INVARIANT	1203	0.94	100	dG/RT=0	-0.000336270073343624
11	5	INVARIANT	726	0.037	100	dG/RT=0	0.0009859197317620125
12	5	INVARIANT	726	0.886	100	dG/RT=0	0.001985371054235405
13	5	INVARIANT	726	1/3	100	dG/RT=0	0.0006346554592536931
14	6	FORMATION	1594	0.98	100	dG/RT=0	-0.000714336659090607
15	7	FORMATION	1548	0.958	100	dG/RT=0	-0.000459685728955584
16	8	FORMATION	1499	0.935	100	dG/RT=0	-0.000455013547336714

Above figure shows the optimization. We can get the same optimization result as in page 78 by using Examine. Some parameters may give us an error in the equilibrium calculation, in this case, we should set the weight of the parameter to zero. When the parameters are somewhat better, the Weight is calculated back to the original value.

What to do when you're in trouble

(From Lukas et al. "Computational Thermodynamics")

- Selection and exclusion of experimental data
  - Initially, as few experimental data as possible are used for general matching. It is usually a good idea to start with an invariant-reaction or a metastable state diagram that excludes some phases. The important point is that inconsistent experimental values do not allow for convergence. Therefore, it is necessary to exclude such experimental data. It is important to select a minimum number of experimental data sets that are consistent with each other. Let's call this group of conditions critical-set.
  - If the calculation of the invariant reaction including the intermediate phase is not successful, the intermediate phase should be removed and only the liquid phase and the important solution phase should be optimized. If good results are obtained, then the excluded phases are introduced, but the parameters of the liquid and solution phases are fixed and the additional phases are optimized. One important aspect of the optimization is not to consider conflicting data at the same time. After all, if they are truly contradictory, then at least one of them is not correct. If such a contradiction is seen, then one of them and the rest of the data must be used to optimize at once. In other words, the experimental data must also be optimized.
  - Other notes Systematic errors must be corrected. For example, there is the adjustment of the temperature scale. If you want to optimize the liquid phase and the end components at both ends, except for the intermediate phase, you should calculate a metastable diagram of just these two phases. There should not be any strange kinks and turns in the metastable state diagram. Such a metastable state diagram may be useful for later optimization. Note that the values of the optimization parameters stay in a reasonable range. If they start to vary by many orders of magnitude, the experimental data may be incorrectly weighted, or there may be too many optimization parameters.

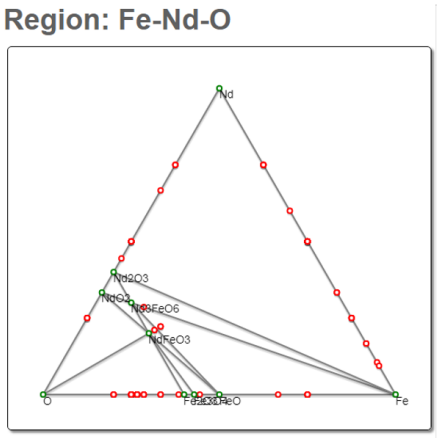
Optimization of Specific Heat

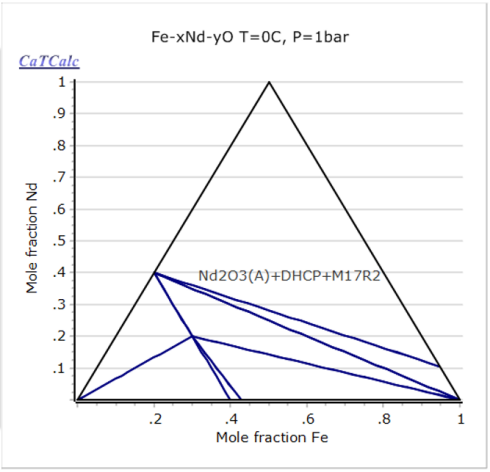
- The specific heat needs to be optimized separately, and since it is a second derivative of Gibbs Energy, it needs to be fixed before optimizing the others.
- A standard function for the specific heat is built into the fitting tool in the menu of the unit.

XII. How to use ab initio calculation data

* ab initio calculations and computational thermodynamics

Fe-Nd-O系低温断面図



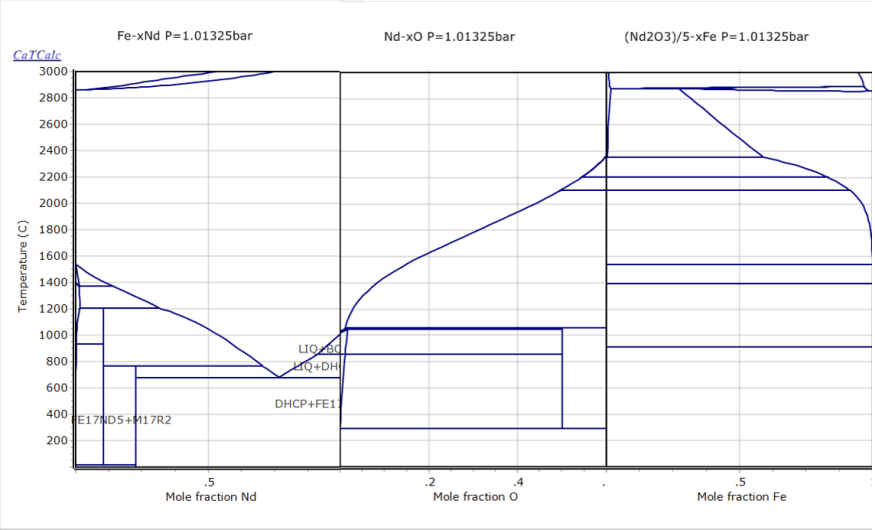


OQMD

Ab initio calculations: fundamental information at low temperatures

Practical information on room temperature and high temperature: Computational thermodynamics

Fe-Nd-O系縦断面図

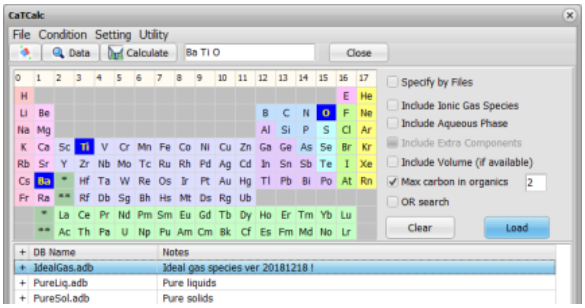


(Nd,Fe)2O3固溶体

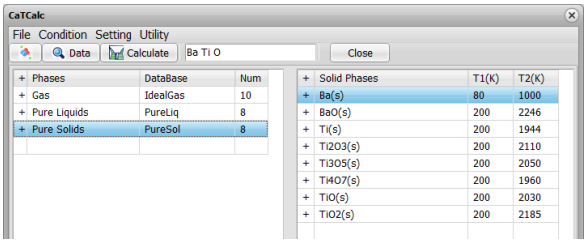
* Preparation for database creation

Taking BaTiO3 as an example, the Gibbs energy is obtained from the enthalpy of formation and the specific heat obtained by first-principles calculations, and the procedure for adding the data to the thermodynamic database is shown.

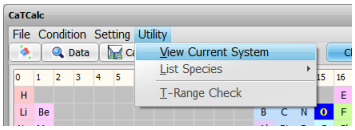
1. First, you need to prepare the database file to which you want to add data (not necessary if you want to add it to an existing file).



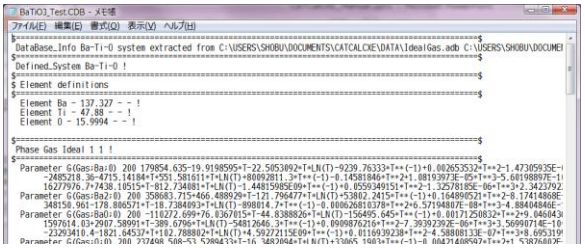
1. As shown in the left figure, the data of Ba-Ti-O is read from the pure material database in the System screen.



2. You can check the data on the Data screen.



3. Select [Utility]-[View Current System] in the menu, and you will be asked to save the current system information, so save it as a file. Save it as a file named "BaTiO3-Test.CDB" for your convenience.

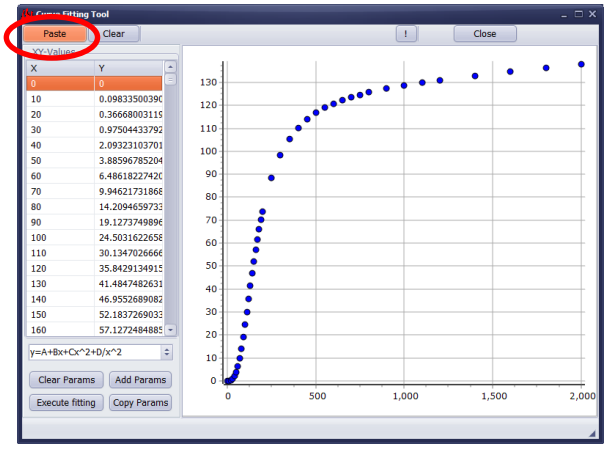


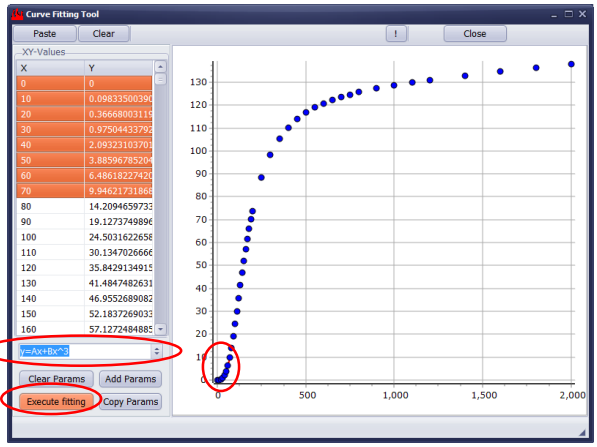
4. Editor will start up automatically. Add BaTiO3 data to this file afterwards.

① Parameterization of Specific Heat and Gibbs Energy Functions

2. The enthalpy of formation and specific heat data are prepared by first principles calculations. Here we use the data from the BaTiO3 sheet of AssessmentExample.xlsx as an example (this data is not correct, and is for illustration purposes only).

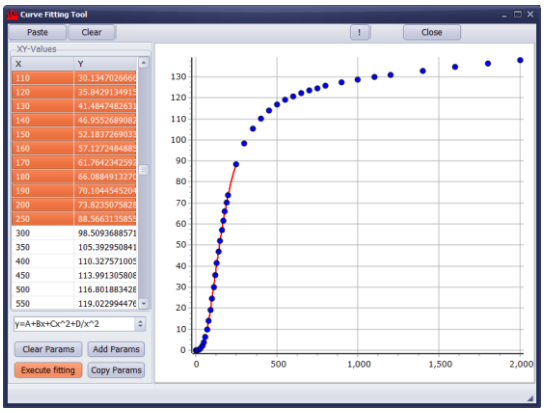
	A	B	C	D
1	変換係数	1 J/mol	1.04E-05	eV/atom
2				
3			①	
4	BaTiO3	P4mm	-3.504	eV/atom
5		H(T=0)	-3.38E+05	J/mol
6		S(T=0)	0	J/molK
7				
8	T(K)	Cp(J/molK)	②	
9	0	0		
10	10	0.098335		
11	20	0.36668		
12	30	0.975044		
13	40	2.093231		





1. ① in the figure on the left is the energy of formation, which can be converted to units of J/mol. Note that the value per atom is usually given in the first principle calculation, so do not forget to multiply by the number of atoms to get the value per Formula.
2. ② is the specific heat. This is also per Formula. Copy the values to the clipboard. (If you don't have specific heat data, you can use Kopp-Neumann method, which can be approximated by the sum of specific heat of the elements or compounds (BaO and TiO2 in the case of BaTiO3). (Usually, data above 298.15 K are sufficient.)
3. Open the Fitting Tool by clicking "Assessment" - "Fitting Tool" in the menu of CaTCalc, and paste the Cp data by clicking the "Paste" button.
4. Here, the approximate parameter is divided into three parts: 0~70K, 70~300K, and 300~2000K. (The best division method is usually determined by trial and error. First, select 0~70K as shown in the left figure. Next, choose Y=AX+BX^3 as the approximation function and click [Execute Fitting] button to find the approximation curve. A red curve is drawn in the right graph. If the approximation is good, click [Add Params] to save the parameters.

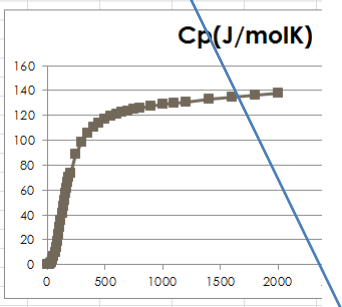
① Parameterization of Specific Heat and Gibbs Energy Functions



5. For the next 70~250K, fitting is done using Y=A+BX+CX^2+D/X^2 as an approximation function and the parameters are added and saved with [Add Params]. 250~2000K is similar.
6. Finally, copy the parameters to the clipboard with [Copy Params].

T0	T1	C(0)	C(1)	C(-2)	C(2)	C(3)	Ref
0	70	0	0.008846	0	0	2.73E-05	
70	250	-73.0147	1.06193	82822.23	-0.00168	0	
250	2000	118.458	0.014937	-2131983	-2.55E-06	0	

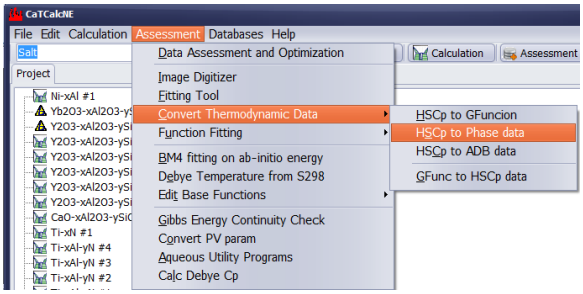
T	Cp_ex	Cp_calc
0	0	0
10	0.098335	0.11577
20	0.36668	0.395419
30	0.975044	1.002826
40	2.093231	2.101869
50	3.885968	3.856427
60	6.486182	6.430379
70	9.946217	9.987604
70	9.946217	9.966722
80	14.20947	14.09711
90	19.12737	19.13603
100	24.50316	24.61122
110	30.1347	30.25477
120	35.84291	35.90547
130	41.48475	41.46163
140	46.95527	46.85653
150	52.18373	52.04491
160	57.12725	56.99519
170	61.76423	61.68481
180	66.08849	66.09729
190	70.10445	70.22037
200	73.82351	74.04477
250	88.56631	88.48503
250	88.56631	87.92149



7. Open and paste Excel (see AssessmentExample.xlsx) and check that the difference between the original Cp data and the approximation function is about 0.1 J/molK, which is a sufficiently accurate approximation.
8. Next, the resulting parameters are used to create the parameter set shown below.

Phase	Formula	state	T0	T1	HT(J/mol)	ST(J/molK	C(0)	C(1)	C(-2)	C(2)	C(3)	Ref
BaTiO3	BaTiO3	s	0	70	-3.38E+05	0	0	0.008846	0	0	2.73E-05	
BaTiO3	BaTiO3	s	70	250	0	0	-73.0147	1.06193	82822.23	-0.00168	0	
BaTiO3	BaTiO3	s	250	2000	0	0	118.458	0.014937	-2131983	-2.55E-06	0	

9. Copy this whole thing to the clipboard. You'll also need a title line.

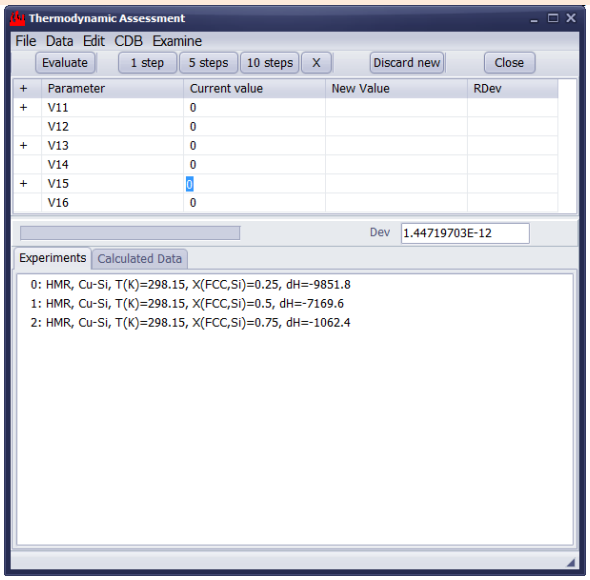


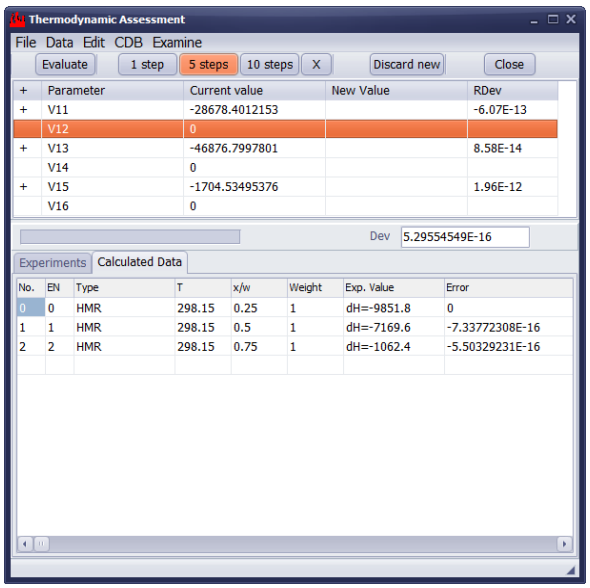
10. Click [Assessment]-[Convert Thermodynamic Data]-[HSCp to Phase data] in the menu to convert the data to Gibbs energy function. Paste the result into your first file, BaTiO3-Test.CDB and add the data. That's all.

② Gibbs energy of mixing

3. When the mixed enthalpies of the solid solution phase are obtained by SQS in the ab initio calculations, the method for determining the interaction coefficient is the same as the usual thermodynamic database assessment method. Here we use the data from the Cu-Si sheet of AssessmentExample.xlsx as an example.

HMR, Cu-Si, T(K)=298.15, X(FCC,Si)=0.25, dH=-9851.8
HMR, Cu-Si, T(K)=298.15, X(FCC,Si)=0.5, dH=-7169.6
HMR, Cu-Si, T(K)=298.15, X(FCC,Si)=0.75, dH=-1062.4





1. In this example, we will only focus on the FCC phase in the Cu-Si system; please use the Cu-Fe-FCC.CDB file. The left figure shows the mixed enthalpies of the FCC phase obtained by the SQS method in the experimental format used in the CaTCalc assessment. This is used to obtain the interaction coefficient.

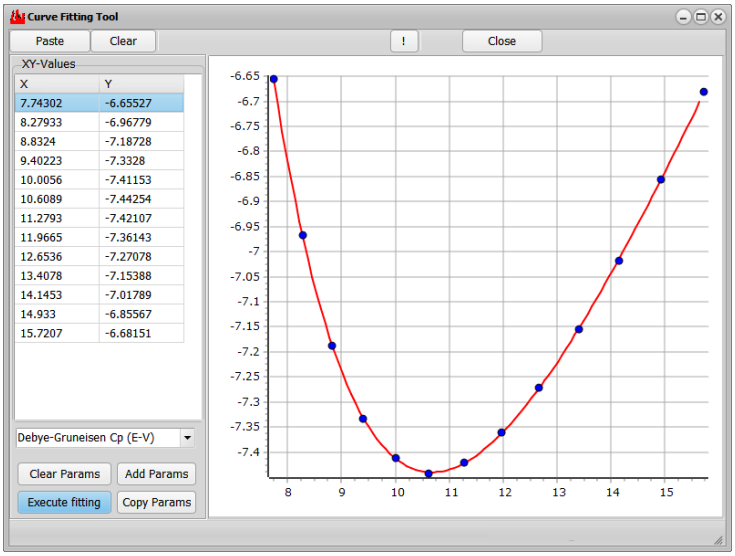
2. Open the assessment module of CaTCalc. Open Cu-Si-FCC.CDB as a CDB file to be optimized. Copy and paste the above experimental values into the Experiments panel of the assessment module.

3. Since there are only three experimental values, the maximum number of parameters that can be determined is three. Therefore, only V11, V13 and V15 are considered here.

4. Press the [5 steps] button, etc. to optimize the result. Save the result with the right button menu. For details, please refer to "XI. Development of thermodynamic database" in this manual.

③ Debye-Gruneisen model

CaTCalc incorporates thermodynamic parameter development capabilities based on the quasi-harmonic Debye-Gruneisen model of FP calculations. This method can be used to estimate temperature-dependent Cp, volume, elastic modulus, etc. Please refer to the EOS manual for more details. Below we show how to use it.



1. Numerical data of the volume dependence of Energy from FP calculations are loaded into the Fitting tool, as shown on the left. It is per atom.
2. Select Debye-Gruneisen Cp(E-V) as the fitting function, as shown on the left.
3. Execute fitting, and you will be asked for the effective mass, Poisson ratio, and the number of temperature divisions up to 3000 K. Enter the values as appropriate. Enter the number of temperature divisions as appropriate.
4. After pressing Add Params, use Copy Params to transfer the data to the clipboard and paste it into Excel, etc. to obtain the data shown in the figure below.

	A	B	C	D	E	F	G	H	I
1	E-mass(g)	Poisson's ra	Debye-T(K	Gruneisen Param					
2	19.44025	0.24	938.4114	1.419765					
3									
4	T(K)	ET(eV/ator	VT(m^3/m	VK(1/Pa)	VN	Cv(J/mol_a	VA(/K)	Cp(J/mol_atomK)	
5	10	-7.34506	6.49E-06	5.39E-12	3.842768	0.002457	2.90E-09	0.002457	
6	30	-7.34507	6.49E-06	5.39E-12	3.842788	0.066342	7.82E-08	0.066342	
7	60	-7.34509	6.49E-06	5.39E-12	3.843086	0.530448	6.25E-07	0.530476	
8	100	-7.34527	6.49E-06	5.39E-12	3.84471	2.350731	2.77E-06	2.351656	
9	150	-7.34607	6.49E-06	5.40E-12	3.84822	6.276822	7.41E-06	6.286731	
10	210	-7.34847	6.49E-06	5.42E-12	3.852152	11.12154	1.32E-05	11.16521	
11	280	-7.35376	6.50E-06	5.44E-12	3.855278	15.32095	1.82E-05	15.43186	
12	360	-7.3632	6.51E-06	5.48E-12	3.857606	18.37529	2.19E-05	18.58136	
13	450	-7.37789	6.53E-06	5.52E-12	3.859588	20.44197	2.45E-05	20.76245	
14	550	-7.39873	6.54E-06	5.56E-12	3.861595	21.81208	2.63E-05	22.26069	
15	660	-7.4265	6.56E-06	5.62E-12	3.86383	22.72381	2.76E-05	23.31191	
16	780	-7.46183	6.58E-06	5.68E-12	3.866386	23.33927	2.86E-05	24.07768	
17	910	-7.5053	6.61E-06	5.74E-12	3.869292	23.7624	2.93E-05	24.6623	
18	1050	-7.55743	6.64E-06	5.81E-12	3.872552	24.05895	2.99E-05	25.13229	
19	1200	-7.61867	6.67E-06	5.89E-12	3.876159	24.27072	3.05E-05	25.53033	
20	1360	-7.68945	6.70E-06	5.98E-12	3.880102	24.42461	3.10E-05	25.88435	

5. This is the temperature-dependent volume, elastic modulus, and specific heat estimated by the Debye-Gruneisen model, where VT, VK, and VN are, respectively, the volume parameter VT, the compressibility parameter VK, and the pressure derivative of the elastic modulus in the Birch-Murnaghan EOS. It corresponds to the parameter VN.

6. First, for Cp, the 0~298.15K part does not require an entropy value to be entered if the fitting is also done. For actual fitting and parameterization, please refer to the Fitting Tool and the Thermodynamic Data Conversion Method (2).

7. Next, parameters for VT, VK, and VN can be obtained by fitting with the VT function of the Fitting Tool. For practical use, for example, fitting data above 280 K should be sufficient. Since these are parameterized directly, they should be written in the data file as they are. However, it is necessary to edit the phase names and component formulas. For VK and VN, it is necessary to change the parameter names.