

21. Phase Stability Diagrams Modules

The phase stability diagrams show the stability (*predominance*) areas of condensed phases in a ternary system as a function of temperature or in isothermal conditions, with the remaining constraints as the other axis. These diagrams are very useful when a fast estimation of the prevailing phases is needed. It is assumed that all phases are pure substances. Mixture phases are not taken into account in basic phase stability diagrams.

The new HSC Chemistry can draw two types of phase stability diagrams. The **Tpp Diagram** module calculates the diagrams on the basis of minimum Gibbs energy (area graphics) and the **Lpp Diagram** module calculates the phase stability boundaries as lines based on the reaction equations (vector graphics). These two modules have their own option buttons in the HSC main menu, i.e. **Tpp Diagrams** and **Lpp Diagram** buttons.

The Tpp diagram module draws temperature partial pressure diagrams (T-p diagrams) as well as p-p diagrams with partial pressures on both axes. The Lpp module only draws diagrams with selected partial pressures on both axes. Both these modules offer slightly different benefits and limitations; for example, the Lpp module gives exact coordinates for the phase boundaries, whereas the Tpp module gives illustrative painted area diagrams and also a versatile T-p axis option.

A common limitation for both diagram modules is that only three elements can be selected simultaneously in the calculation system. Another basic feature is that only two variables can be selected for the diagram, i.e.:

1. If partial pressures are selected for both axes, then the temperature must be fixed.
2. If the temperature is selected for the x-axis and partial pressure for the y-axis, then one partial pressure must be fixed. The partial pressure species may not contain more elements than the species selected for the y-axis.

The partial pressure p_i of gas i in a gas mixture is defined by Equation (1):

$$p_i = x_i \cdot P \quad (1)$$

where x_i is the mole fraction of i in the mixture and P is the total pressure. The HSC phase stability diagrams use logarithmic scales for partial pressures, which are expressed in bar units (1 bar = 100 kPa = 0.987 atm).

21.1. Tpp Diagram Module

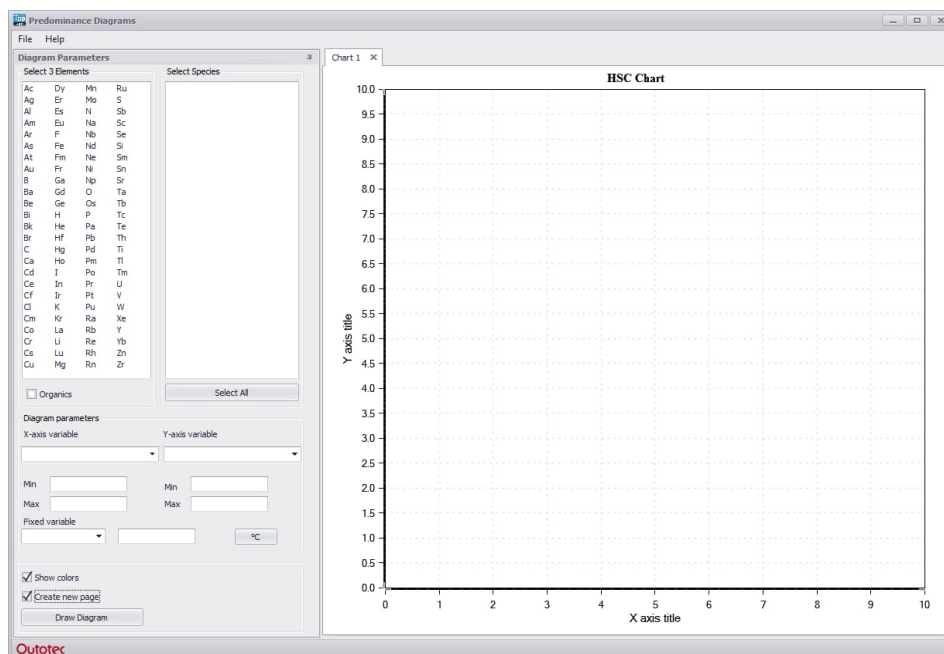


Fig. 1. Input data for Tpp phase stability diagrams.

The Tpp Diagram module calculates phase stability diagrams using partial pressures on both axes or temperature on the x-axis and partial pressure on the y-axis. This module calculates the diagram on the basis of minimum Gibbs energy. However, it does not check each x- and y-point in order to decrease calculation time. The calculation is made recursively using the preset resolution and a specific logout algorithm.

The user interface of the Tpp module is shown in **Fig. 1** with an example of the Cu-S-O system. The diagram may be drawn using the following steps:

1. Select **three elements** from the element list and include organic species if needed.
2. Select the species for the diagram one by one or by pressing **Select All**. Keep **the Ctrl key** down if you want to remove some species from the selection.
3. Select the x-axis species and the range for the x-axis. This selection will always reset the default x-range settings.
4. Select the y-axis species and the range for the y-axis. This selection will always reset the default y-range settings.
5. Set one variable, either temperature in p-p diagrams or one partial pressure in T-p diagrams. Please also remember to give a value for temperature or a selected partial pressure. The default value for partial pressure is 1E-20 and for temperature 25 °C. Both °C and K units can be used.
6. Make a selection for the diagram layout options as necessary:
 - **Gridlines:** Show grid on diagram
 - **Colors:** Paint areas with colors
 - **Create new page:** If you create new page you can look multiple calculation results easily clicking chart tabs.
7. Press **Diagram**.

21.2. Tpp Diagrams

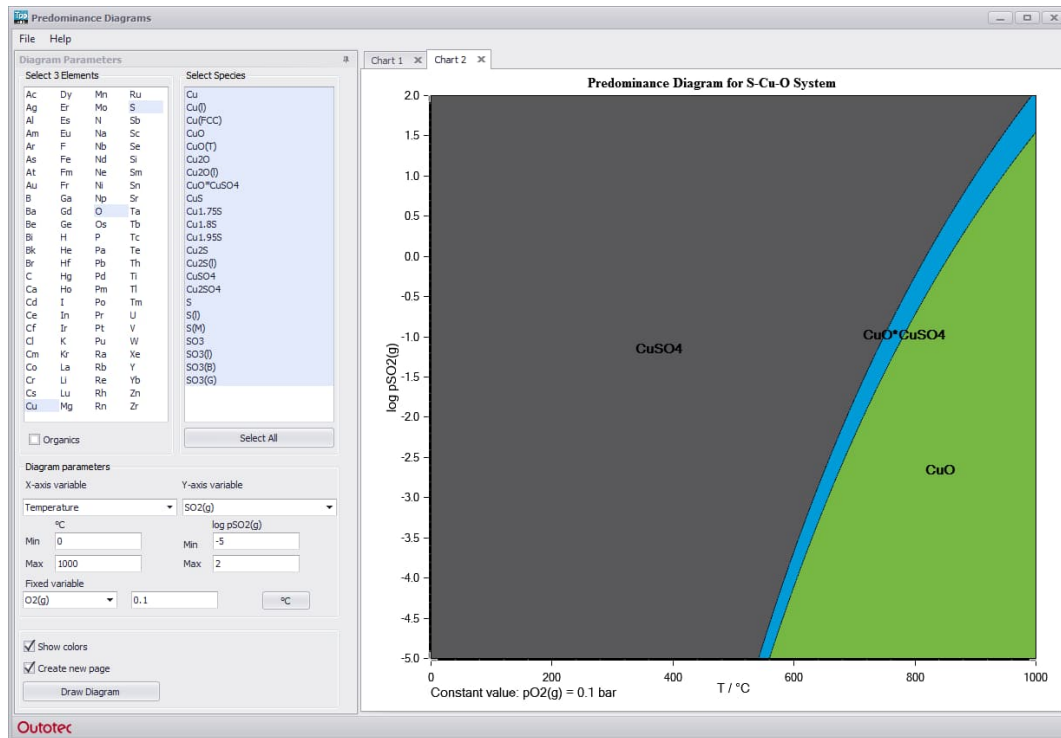


Fig. 2. Tpp phase stability diagrams based on data in **Fig. 1**.

The Tpp phase stability diagram is shown in **Fig. 2**, and the corresponding calculation system specifications are shown on the previous page. This diagram shows us, for example, that copper oxide flue dust in a hot process gas tends to sulfatize when the flue dust temperature decreases.

These diagrams can be modified in the same way as other HSC diagrams:

1. x- and y-axis scales and formats can be edited by clicking the axes with the mouse.
2. The labels and headings can be edited by double clicking the labels.
3. The diagrams can be copied to the Clipboard by pressing **Copy**.
4. The diagrams can also be cloned.
5. The diagram can also be zoomed using the mouse. After zooming, it is easy to use the redraw option to return to the diagram with the starting axis values.
6. Diagrams can be printed by pressing **Print**. The printing dialog gives several options for hard copies. The new resize option is very useful if there are several small stability areas in the diagram.

The system specifications can be saved using the **File Save TPP files** (*.tpp8 or *.tpp) selection for later use. These files can be read back to the Tpp module by selecting **File Open TPP files** (*.tpp8 or *.tpp).

21.3. Lpp Diagram Module

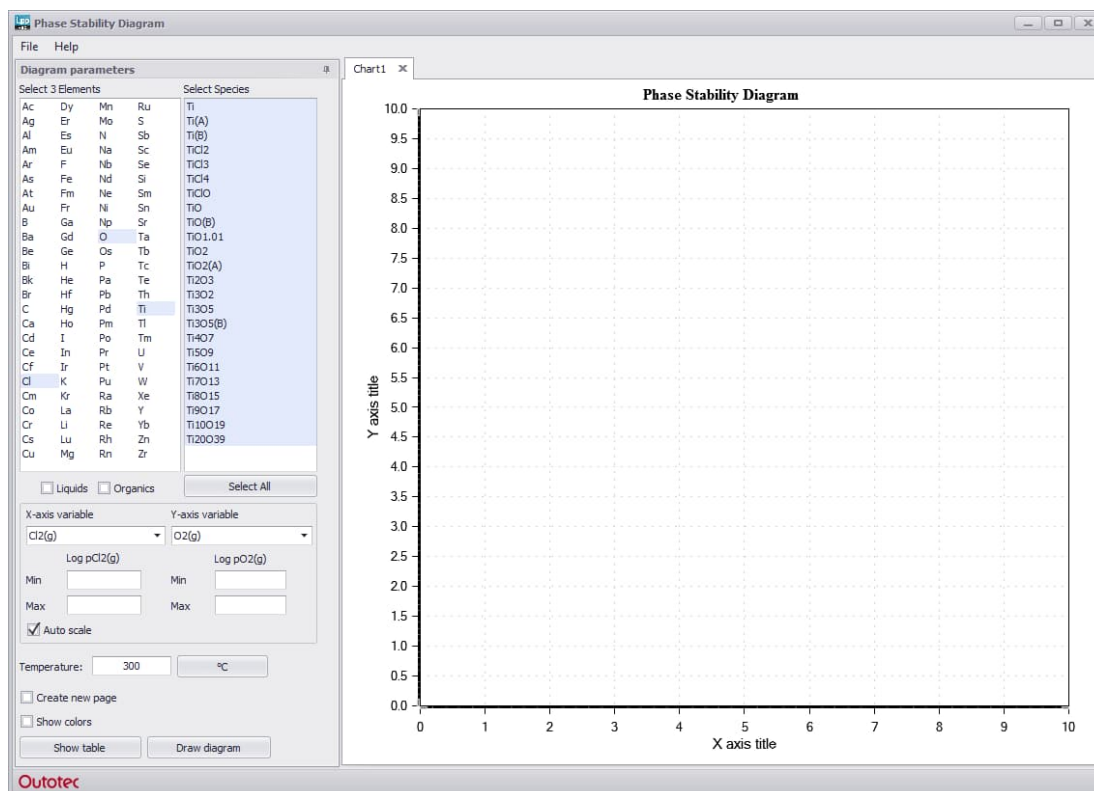


Fig. 3. Input data for phase stability diagrams.

The Lpp Diagram module draws isothermal phase stability diagrams of three element systems, also known as predominance area diagrams or Kellogg diagrams. An example, shown in **Fig. 3** and **Fig. 4**, is a diagram of the Ti-Cl-O system, which shows the stability areas of titanium-containing substances as a function of $\text{Cl}_2(\text{g})$ and $\text{O}_2(\text{g})$ pressures in the atmosphere. Follow these steps to draw the diagram:

1. Select three elements with the mouse, in this case Ti, Cl, and O.
2. HSC displays the substances from the databases. Press **All** or select at least three substances (species) for the diagram. Please select only Ti-containing substances.
3. Select one gas species for the x-axis, for example $\text{Cl}_2(\text{g})$. You may select any species for the x-axis except those which contain Ti.
4. Select one gas species for the y-axis, for example $\text{O}_2(\text{g})$. You may select any species for the y-axis except those which contain Ti.
5. Uncheck Auto scale if you want to change min and max values of the x- and y-axis.
6. Change the temperature if needed, in this example 300 °C. You may choose between °C and K by pressing the button.
7. Make a selection for the diagram layout options as necessary:
 - **Create new page:** If you create new page you can look multiple calculation results easily clicking chart tabs.
 - **Colors:** Paint areas with colors
8. Press **Draw diagram** and wait a minute to see the diagram. You can return to HSC by pressing **Exit**.

9. You can check the name and data of the species by double-clicking the list.

PSD diagrams offer an easy way to evaluate stabilities of different condensed substances as a function of gas pressures, typically $O_2(g)$, $S_2(g)$, $SO_2(g)$, $Cl_2(g)$. These diagrams can be used, for example, to find the best conditions for oxidizing or sulfatizing reactions, etc.

Limitations:

Remember that all the selected substances must contain the main element, for example Ti in the Ti-Cl-O system, but the species selected for the x- and y-axis should not contain this main element (Ti)!!!

If you have more than one substance with the same overall composition (stoichiometry) in the species list, for example NaS and Na_2S_2 , FeO and FeO(l), etc., please select only one such substance for the diagram. In any case, HSC will automatically omit substances with identical stoichiometry. Users can make this selection themselves in order to select exactly the substances that they want to be taken into account.

21.4. Lpp Diagram Menu

	A	B	C	D	E	F	G	H	I
1	Ti-Cl-O Phase Stability Diagram at 300 °C								
2									
3	Species		19						
4	Elements		3						
5	Liquids		FALSE						
6	Organics		FALSE						
7	Temperature		573.150 K						
8	Show Colors		FALSE						
9	Auto Scale		TRUE						
10	Log pCl2(g)	Min		-45.000	Max		-5.000		
11	Log pO2(g)	Min		-100.000	Max		-20.000		
12	Species	Ti	Cl	O		DeltaG, kcal/mol			
13	1	Ti	1.000	0.000	0.000	0.000	0.000		
14	2	TiCl2	1.000	2.000	0.000	0.000	-99.976		
15	3	TiCl3	1.000	3.000	0.000	0.000	-142.059		
16	4	TiCl4	1.000	4.000	0.000	0.000	-165.724		
17	5	TiClO	1.000	1.000	1.000	1.000	-159.788		
18	6	TiO	1.000	0.000	1.000	1.000	-116.269		
19	7	TiO1.01	1.000	0.000	1.010	1.010	-113.347		
20	8	TiO2	1.000	0.000	2.000	2.000	-200.503		
21	9	Ti2O3	2.000	0.000	3.000	3.000	-323.927		
22	10	Ti3O2	3.000	0.000	2.000	2.000	-233.220		
23	11	Ti3O5	3.000	0.000	5.000	5.000	-524.589		
24	12	Ti4O7	4.000	0.000	7.000	7.000	-726.359		
25	13	Ti5O9	5.000	0.000	9.000	9.000	-929.578		

Fig. 4. Changing the default settings of the Phase Stability Diagram (**Show table** button).

On the **Data** sheet of the PSD Menu, you can see the calculated data of the PSD diagram in tabular form. The **Format** sheet contains formatting settings of the diagram. It is not recommended to change these. HSC evaluates the default values automatically for Max Y, Min Y, Max X, and Min X for the axes.

You can calculate and display the diagram in the following way:

1. Select the *.lpp8 file for the diagram by pressing **File Open**, if not already selected. This file contains the DG values for the selected species at a given temperature.
2. The diagram will automatically be shown on the screen.

Change the default settings of the diagram in the following way:

1. You may change the minimum and maximum values for the x- and y-axis simply by clicking the value using the mouse and by starting to edit.
2. Press **Diagram** to display the diagram.
3. Press **Print** to get a paper copy of the tabular results. HSC will draw the diagram at the best resolution of any MS Windows-supported printer.
4. Press **Copy** to paste the data onto other Windows programs.
5. Press **Exit** to return to HSC or to exit the PSD program.

21.5. Lpp Module Diagram

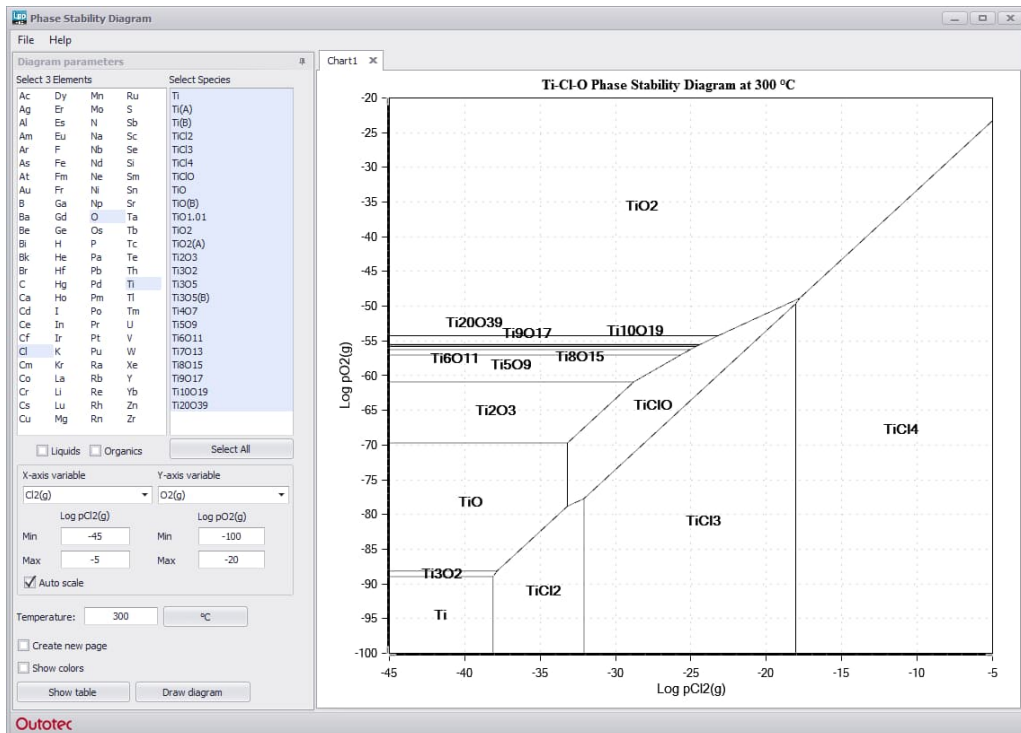


Fig. 5. Phase Stability Diagram of the Ti - Cl - O system at 300 °C with auto scale axis.

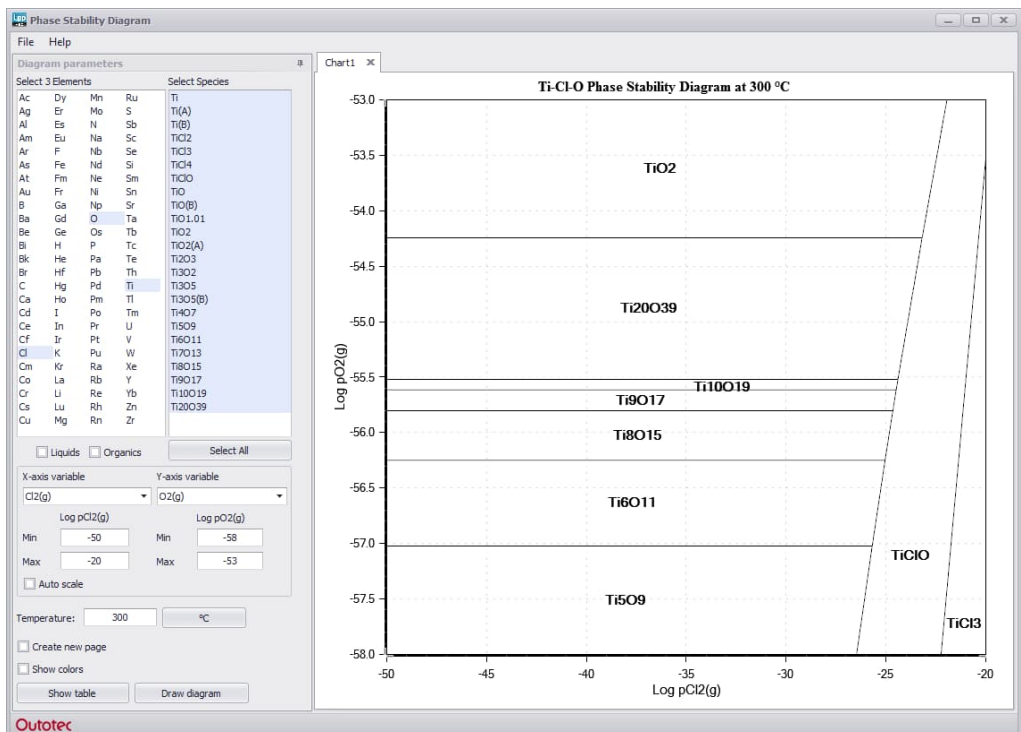


Fig. 6. Phase Stability Diagram of the Ti - Cl - O system at 300 °C with user-specified axis (zooming to the area of interest).

The phase stability diagram window shows the results of the PSD program in graphical form. In this diagram it is easy to see the stability areas of different pure substances under the prevailing conditions.

You can edit this diagram in the following ways:

1. You can relocate all the **labels** using the mouse with the drag and drop method. First select the label, keep the left mouse button down and drag the label to the right location, release the mouse button and the label will drop into the new location.
2. You can edit the format of the labels and lines by double-clicking the label, see **Fig. 5**.
3. The x- and y-scales can be changed by clicking the axis.
4. When you are satisfied with the diagram you can print it by pressing **Print** at the best resolution of your printer.
5. Using **Copy** you can paste the diagram into other Windows programs using the Windows Metafile format.
6. Press **Exit** to return to HSC or to exit the PSD program.