

21. PHASE STABILITY DIAGRAMS

The phase stability diagrams show 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 6.0 can draw two types of phase stability diagrams. The new **Tpp Diagram** module calculates the diagrams on the basis of minimum Gibbs energy (area graphics) and the old **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 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 old Lpp module draws only diagrams with selected partial pressures on both axes. These both modules offer slightly different benefits and limitations; for example, the old Lpp module gives exact coordinates for the phase boundaries but the new Tpp module gives illustrative painted area diagrams and also a versatile T-p-axis option.

A common limitation for both the 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):

$$p_i = x_i * P \quad [1]$$

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

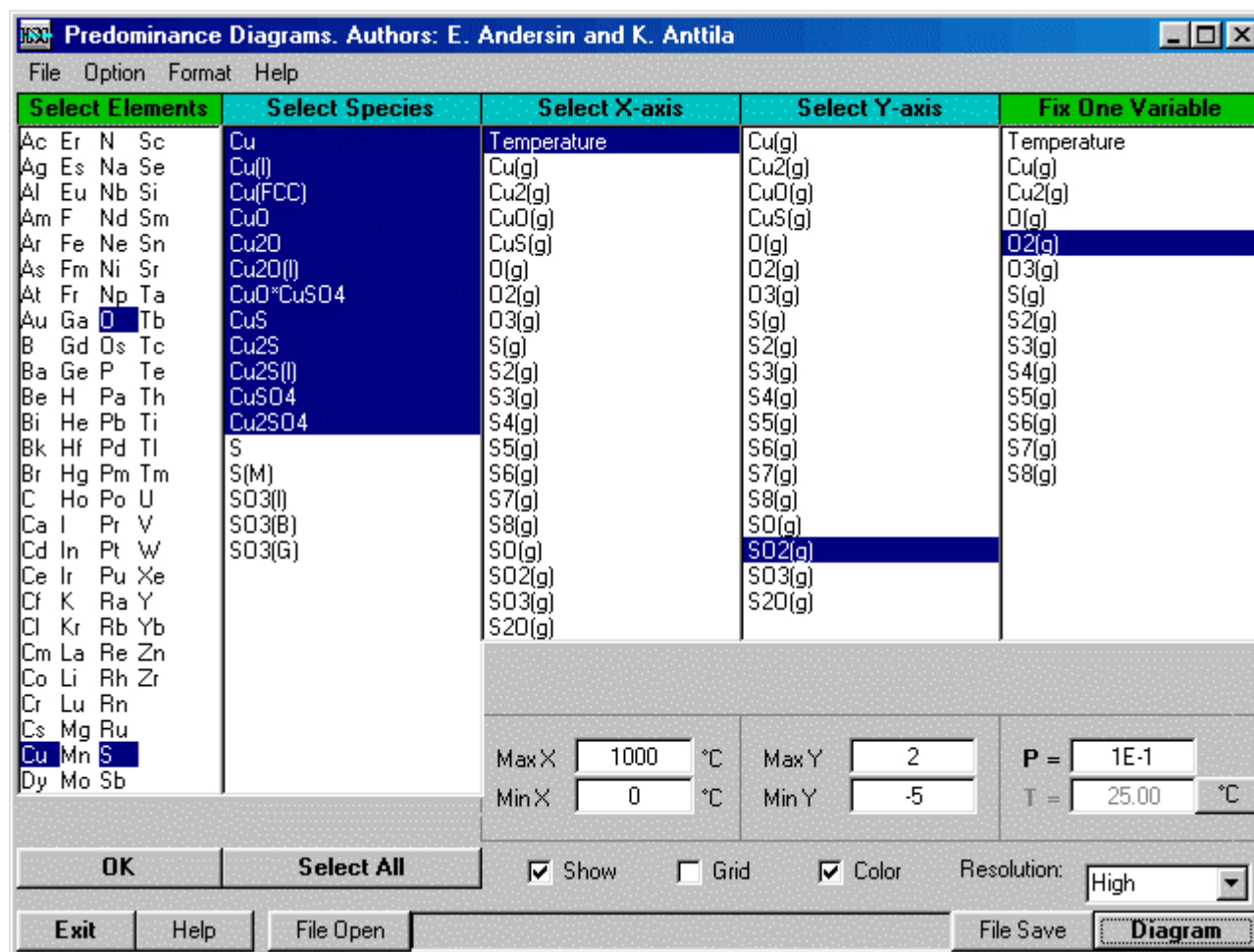


Fig. 1. Input data for Tpp phase stability diagrams.

The Tpp Diagram module calculates phase stability diagrams using partial pressures on both axis 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 a Cu-S-O-system. The diagram may be drawn using the following steps:

1. Select **three elements** from the element list and press **OK**.
2. Select the species to 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 lay-out options if needed:
 - **Show:** Show calculation progress.
 - **Grid:** Show grid on diagram
 - **Color:** Paint areas with colors
 - **Resolution:** Low -> coarse resolution diagram, fast calculations. High -> high resolution diagram, long calculation time. This setting sets the size of the smallest calculated detail. Each step into a higher resolution will halve the size of the smallest visible detail.
7. Press **Diagram**.

The system specifications can be saved using the **File Save TPP** selection for later use. These files can be read back to the Tpp module using **File Open TPP** selection.

The Tpp module uses different colors for each stability area if the **Color** option is selected. The user can modify the default color palette with the **Format Color Palette** selection. This will open the color palette dialog, see Fig. 2. The colors can be modified by double clicking the colors in the **Color** column or by typing the corresponding RGB values to the **Color Code** column.

This modified palette can be saved for later use by pressing **Save Palette**. The Tpp automatically loads the palette file, which is named PPTCOL.PAL, but you can also use other names. These palettes can be reloaded by the **File Load User Palette** selection.

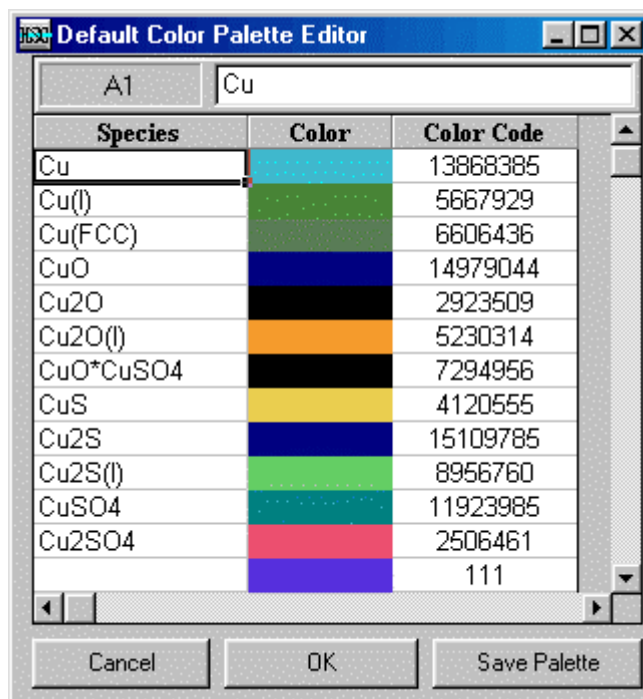


Fig. 2. The color palette dialog for the Tpp module.

21.2 Tpp Diagrams

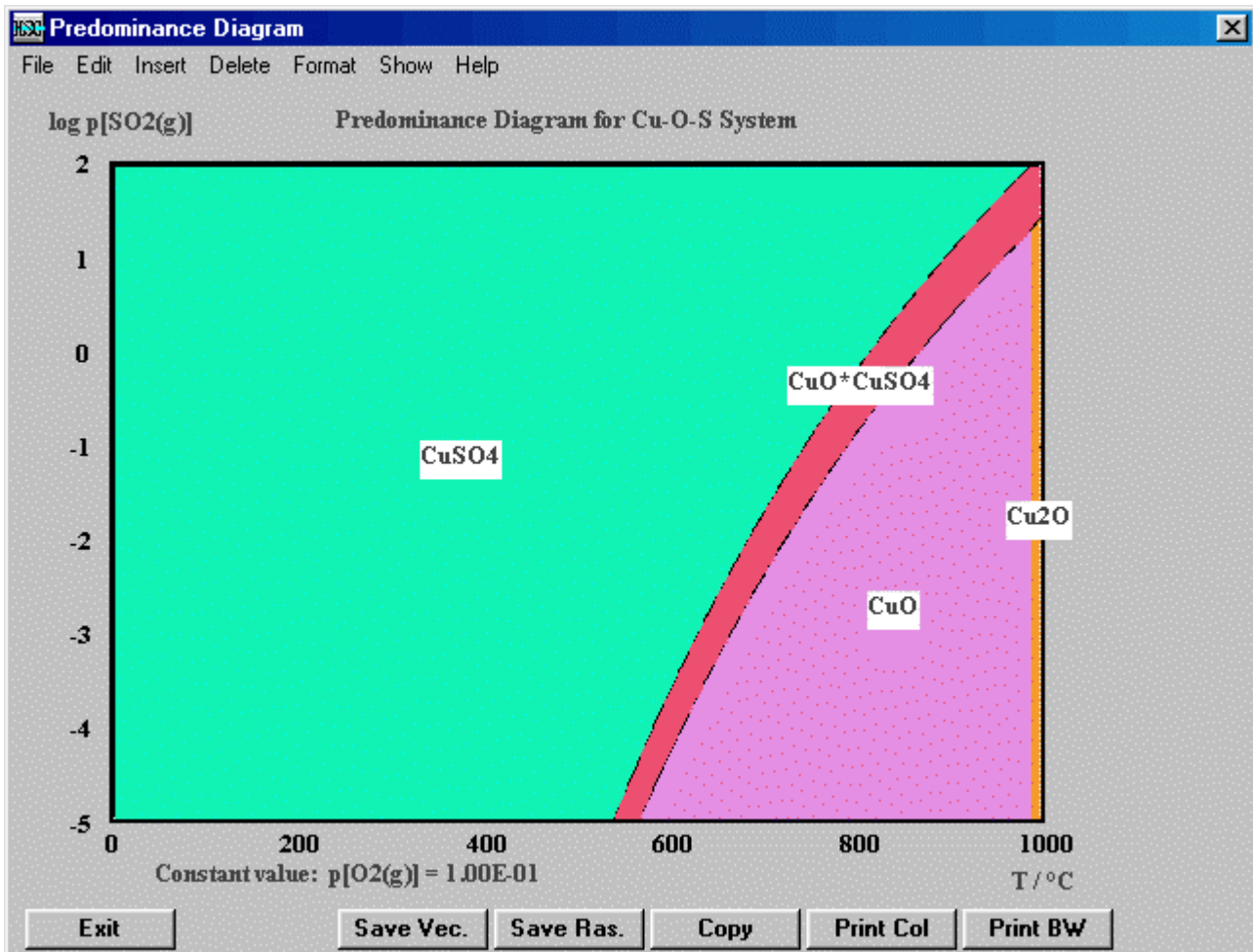


Fig. 3. Tpp phase stability diagrams based on data in Fig. 1.

The Tpp phase stability diagram is shown in Fig. 3, and the corresponding calculation system specifications are shown on the previous page. In this diagram we can see, for example, that copper oxide flue dust in a hot process gas tends to sulfatize, when the flue dust temperature decreases. It is also very easy to see that when the oxygen pressure decreases, the sulfates are reduced first into oxides and finally into metal form.

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 double 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. 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.

21.3 Lpp Diagram Module

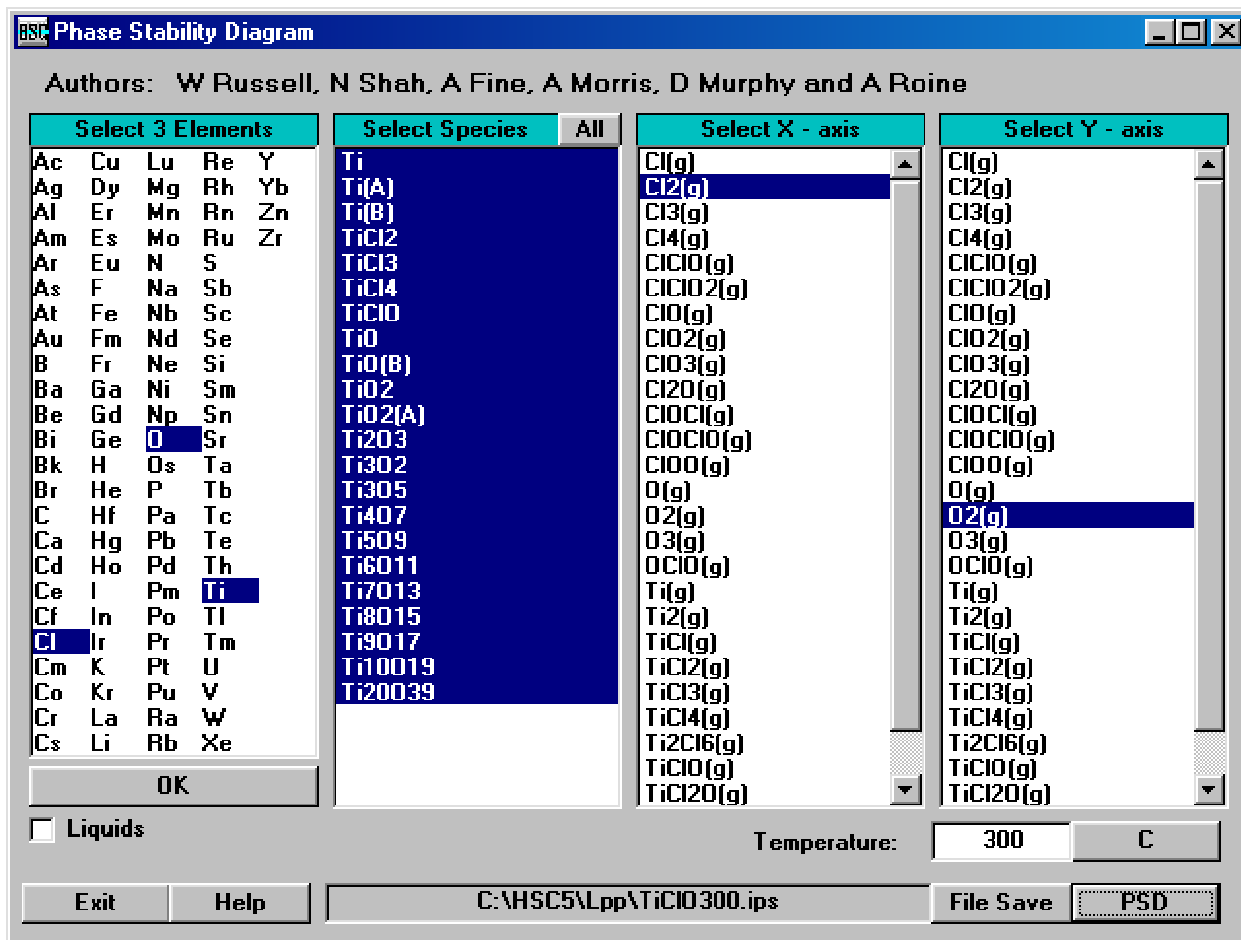


Fig. 4. Input data for phase stability diagrams.

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 Figs. 4-6, is a diagram of the Ti-Cl-O-system, which shows the stability areas of titanium containing substances as a function of Cl₂(g)- and O₂(g)-pressures in the atmosphere. Follow these steps to draw the diagram:

1. Select three elements with the mouse and press **OK**, in this case Ti, Cl and O.
2. Wait a while until 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 Cl₂(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 O₂(g). You may select any species for the y-axis except those which contain Ti.
5. Change the temperature if needed, in this example 300 C. You may choose between °C and K by pressing the button.
6. Press **File Save** and accept the name (TiClO700.IPS) for the input file. The PSD program draws the diagram on the basis of this file. It may be a good idea to save all *.IPS-files in a separate \HSC\PSD directory if available.

7. Press **PSD** and wait a minute to see the diagram. You can return to HSC by pressing **Exit**.
8. 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 $O_2(g)$, $S_2(g)$, $SO_2(g)$, $Cl_2(g)$, etc. These diagrams can be used, for example, to find the best conditions for oxidizing or sulfatizing reactions, etc.

Limitations:

Note that all 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. The user can make this selection himself in order to select exactly those substances which he wants to be taken into account.

21.4 Lpp Diagram Menu

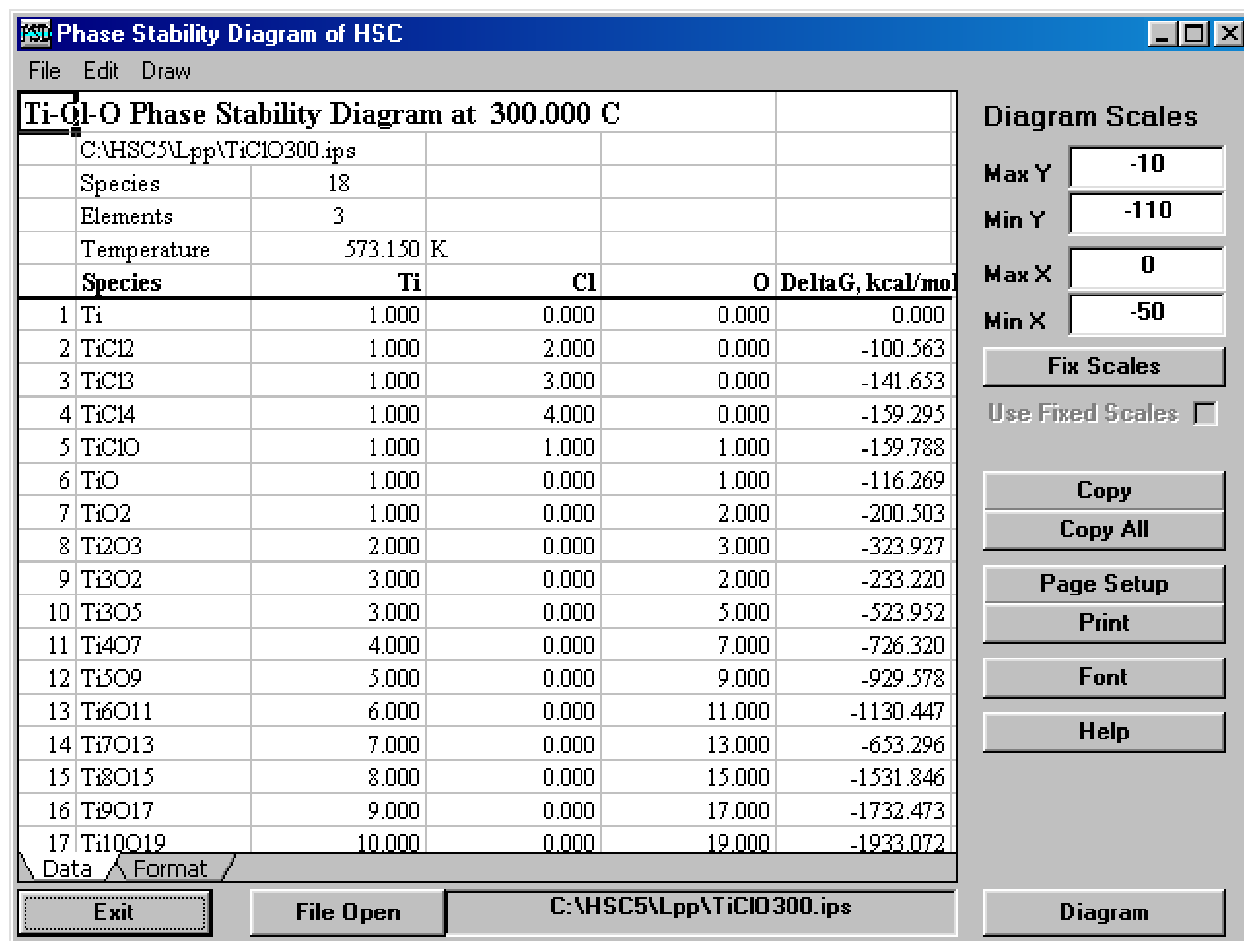


Fig. 5. Changing the default settings of the Phase Stability Diagram.

On the **Data** sheet of the PSD Menu you can see the calculated data of the PSD diagram in a 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 *.IPS 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. You will automatically get the diagram 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

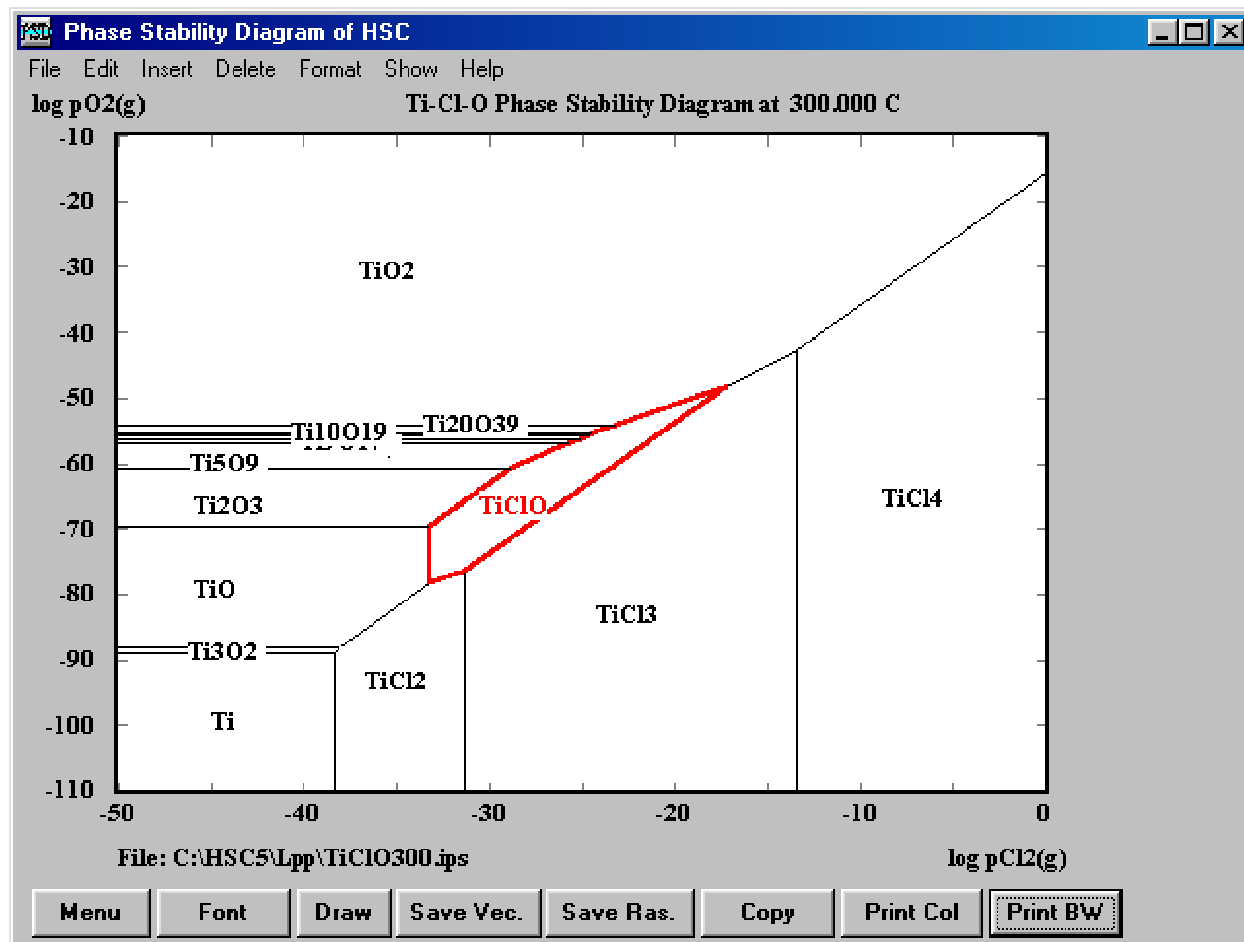


Fig. 6. Phase Stability Diagram of the Ti - Cl - O - system at 300 °C.

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. Press **Menu** to change the scales of the axes.
2. When you are satisfied with the scales, you can relocate all the **labels** by 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.
3. You can edit the text in the labels by simply clicking the text using the mouse and typing the new text. You can edit the format of the labels and lines by double-clicking the label, see Fig. 6.
4. The x- and y-scales can be changed by double clicking the axis numbers.
5. The first time you use HSC Chemistry it may be necessary to change the fonts by pressing **Font**, because the fonts available vary from one computer to another. Usually Times New Roman, bold, size 11 points is a good selection. The selection will be automatically saved in the HSC.INI-file.

6. When you are satisfied with the diagram you may print it by pressing **Print** at the best resolution of your printer.
7. Using **Copy** you may paste the diagram into other Windows programs using the Windows Metafile format.
8. Press **Menu** to return to HSC or to exit the PSD program.