26. Selective Oxidation and Reduction Chemistry

Overview

Occasionally the user may want to remove a particular oxidation state for an element in the simulation. There are a variety of reasons to perform such an activity, one being that a particular oxidation state may be kinetically unavailable for the reaction. Another case is that perhaps a user needs to compare and contrast two systems. That is what we have here in this example.

Creating the default oxidation case

In this example we will create a Stability diagram for iron in water at ambient conditions. See 21 for details on how to create this stream. In Figure 26-1 we have created the input for our standard Iron stability diagram.

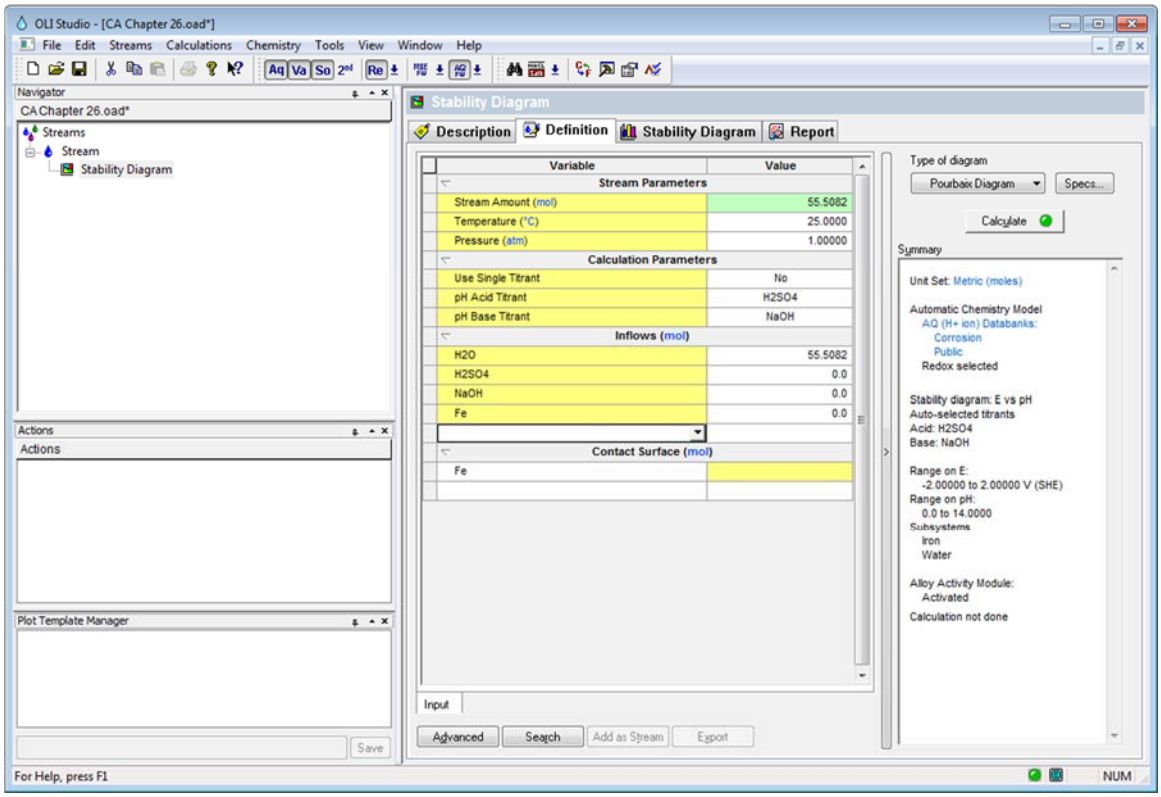

Figure 26-1 Generating a standard Stability Diagram for Iron

Calculate this diagram as you have done in previous examples. Figure 26-2 is the result of the standard diagram. This diagram is frequently referred to as a Pourbaix diagram[45].

[45] Named after Marcel Pourbaix, who in the 1960's created a series of such diagrams. The latest reference is: Pourbaix, M., Atlas of electrochemical equilibria in aqueous solutions. 2d English ed. 1974, Houston, Tex.: National Association of Corrosion Engineers

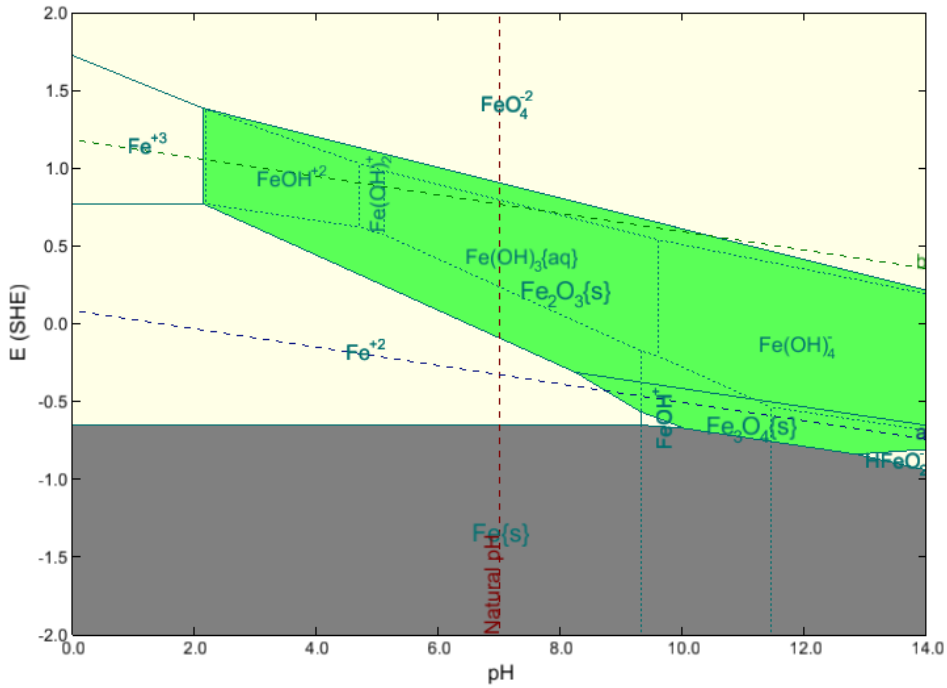

Figure 26-2 Standard OLI E-pH diagram for Iron

The issue here is that Pourbaix did not consider the FeO_4^{2-} ion in his work. This is iron in the +6 oxidation state for which there was little thermodynamic data available in the1960s. To reproduce his work we will need to remove the redox subsystem that pertains to Fe(+6).

Selective Redox, removing an undesired oxidation state.

To remove the undesired Fe(+6) oxidation state for this example we need to enter the model options for this diagram. To do that

Chemistry | Model Options…

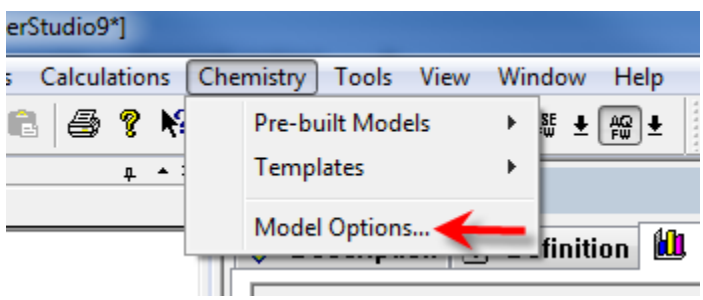

Figure 26-3 Selecting Chemistry | Model Options

Next select the **Redox** Tab.

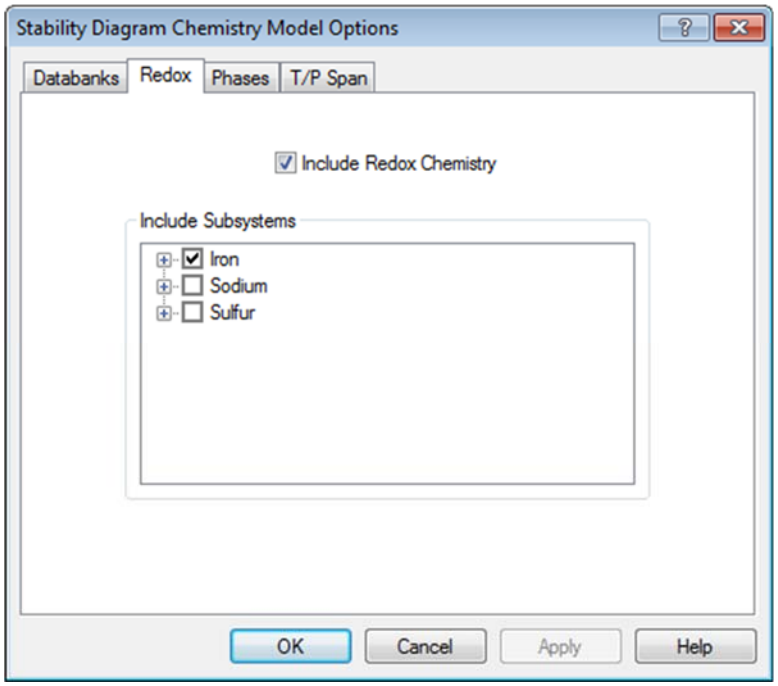

Figure 26-4 Selecting subsystems

Figure 26-4 shows the standard subsystems (collection of oxidation states) for each element. Please note that Hydrogen and Oxygen are automatically included and cannot be removed.

Expand the iron subsystem by clicking on the "+" next to the Iron subsystem.

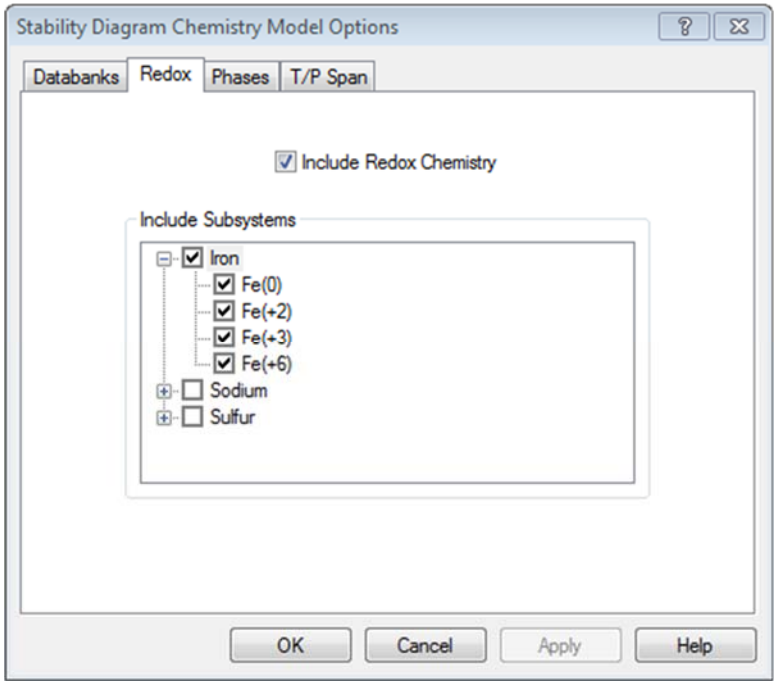

Figure 26-5 Expanding the individual oxidation states

This has expanded the iron subsystem. You can see in our example that we have all the oxidation states from Fe(0) to Fe (+6).

Uncheck the Fe(+6) oxidation state to remove it from consideration. Note that if you have an inflow component with this oxidation state it will remain in the calculation.

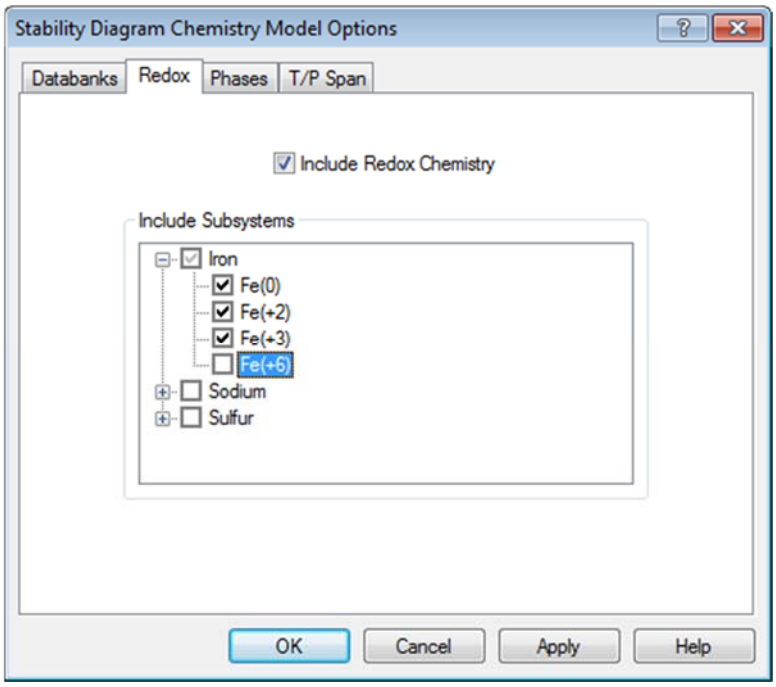

Figure 26-6 Unchecking the Fe(+6) oxidation state

Click the **OK** button to save your changes.

Rerun the calculation for the diagram. You can always press the **F9** key to calculate the object that you are currently viewing.

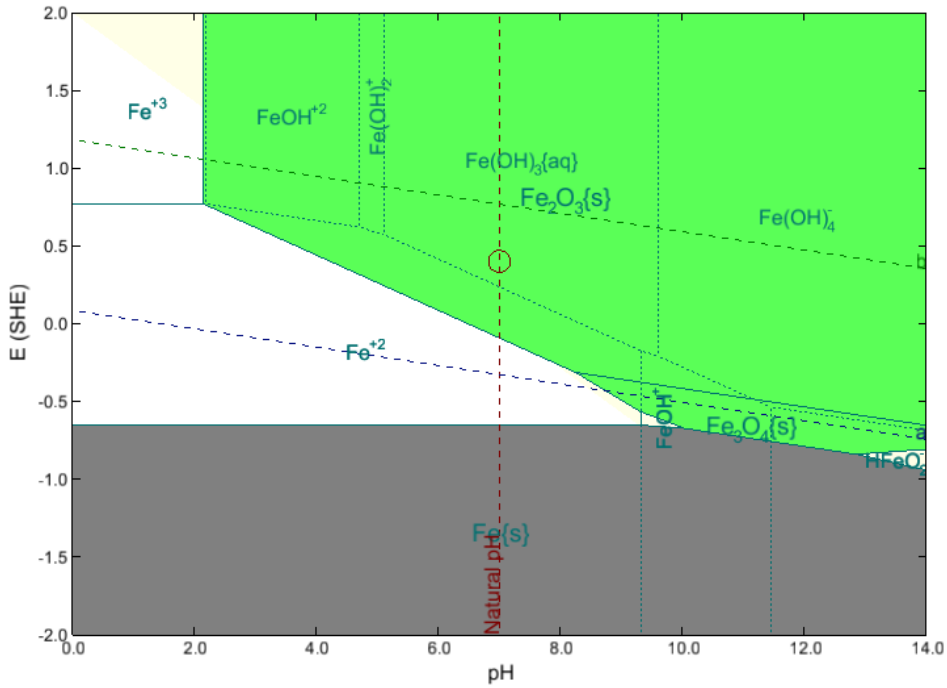

Figure 26-7 A more traditional Pourbaix diagram

Here you can see in Figure 26-7 that the region dominated by the FeO_4^{2-} ion is not present.

You can download a worked example of this chapter from the [OLI Wiki Page]