21. A Tour of Corrosion Analyzer

Overview

We will now take a brief tour of the Corrosion Analyzer. We will first study the stability diagram for iron in pure water and then the stability diagram for iron in the presence of hydrogen sulfide.

Iron in Water

Double-Click on the OLI Studio icon on the desktop or select it from the Programs menu.

After the splash screen displays you will see main screen for analyzers.

Click the **Add Stream** icon to begin.

Select the **Definition** tab of the newly created stream. This is the default view for all new streams. You can use the default name or use the **Description** tab to rename the stream.

- ***Click*** on the **Description** tab.
- Enter the name ***Generic Iron***.
- Enter the description ***Generic iron with H2S.***

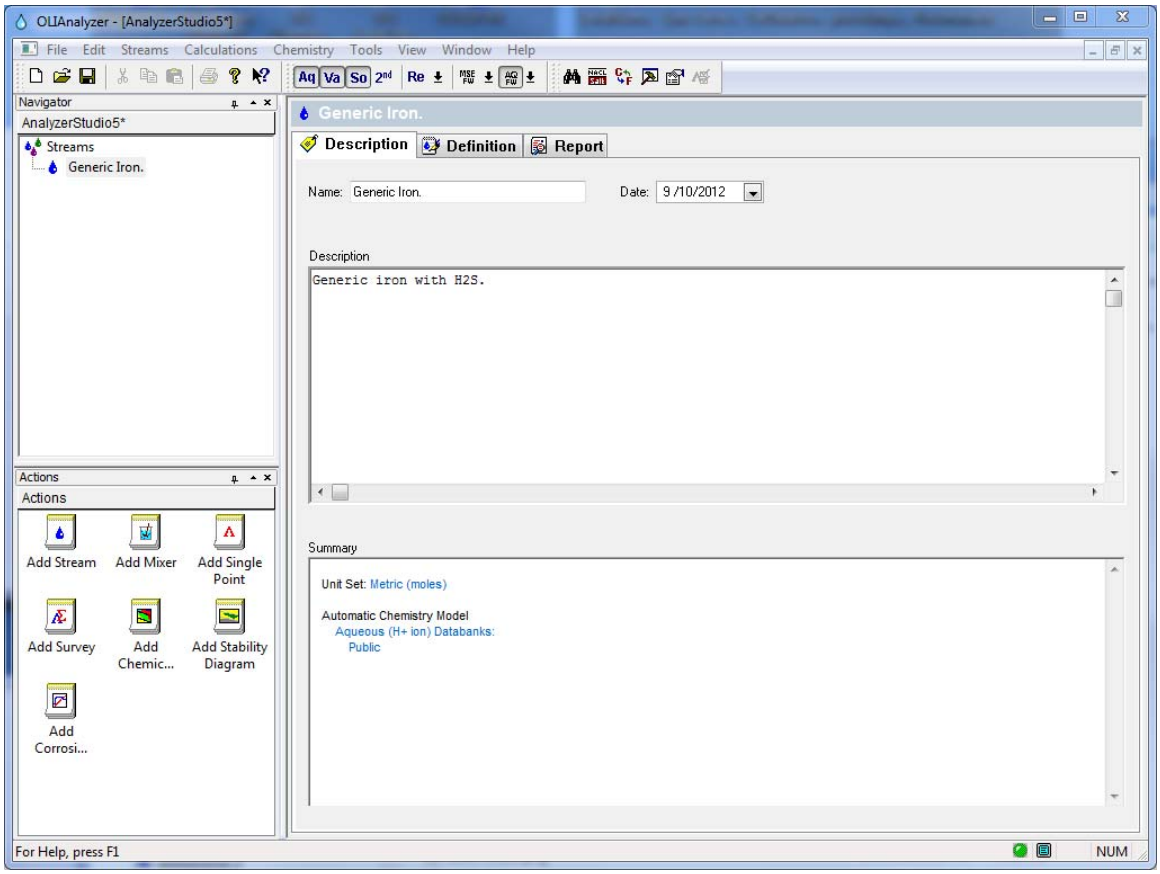


Figure 21-1 The Description tab.

As in other OLI Studio modules, you may perform single point and multiple point (survey) calculations. You may also study stability diagrams and perform rate calculations.

For this tour, we will first define the stream.

- Click on the **Definition** tab.

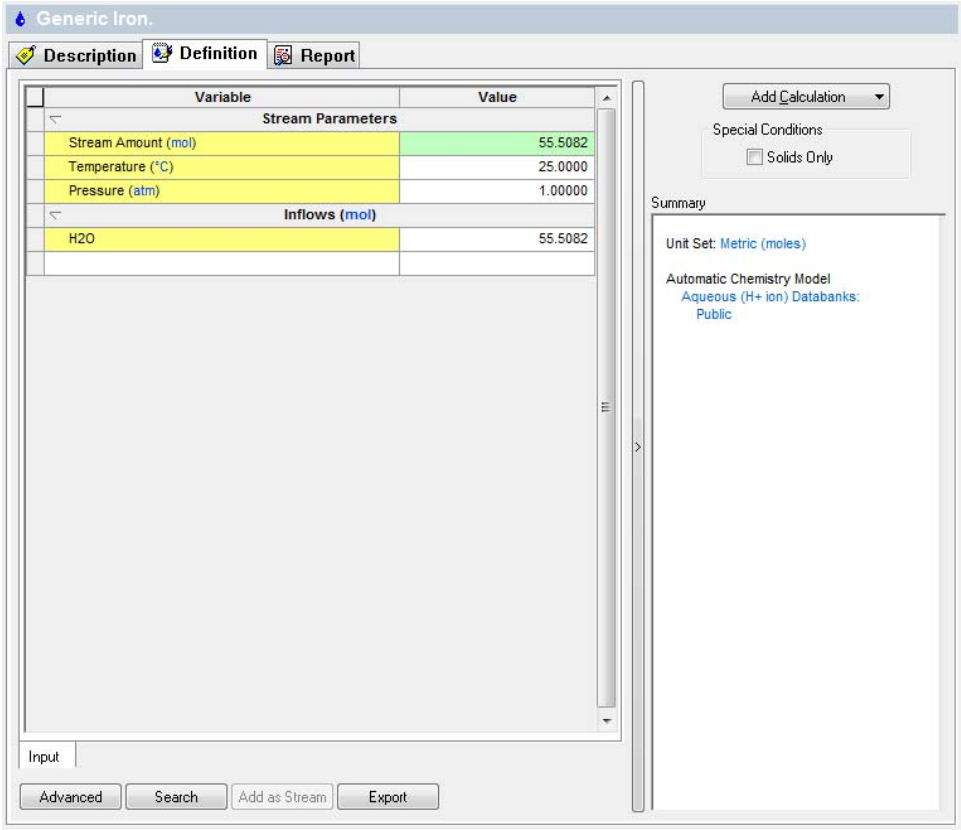


Figure 21-2 Default stream definition grid.

The units for this stream may not be in the set required for the tour.

- Click on the **Tools** menu item.

The **Tools** menu will be displayed. Select **Units Manager** the list.

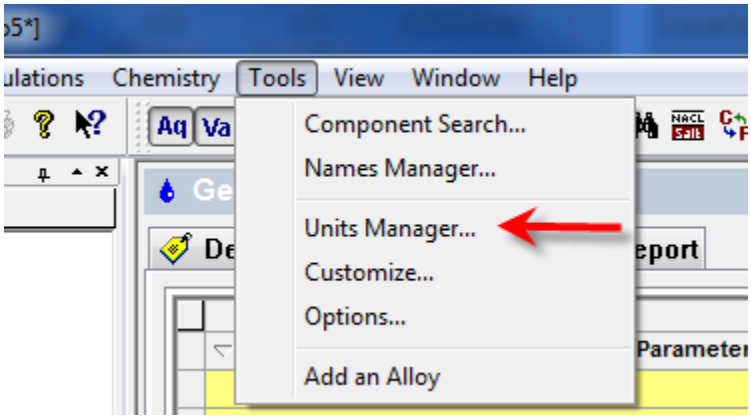


Figure 21-3 Tools Menu

We wish to use metric units. Click the down-arrow in the drop-down list box under the **Standard** radio button.

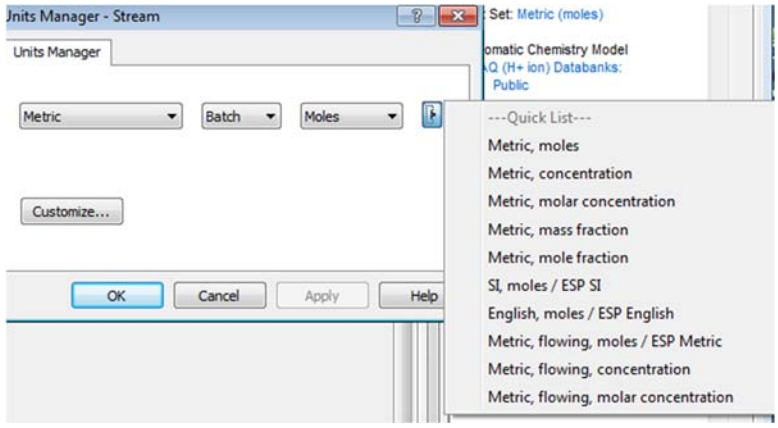


Figure 21-4 Default Units Manager

Scroll down and select **Metric, moles**.

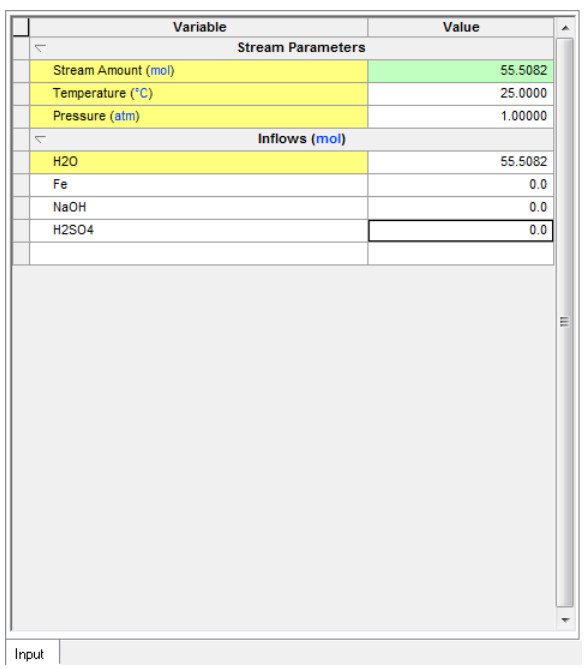
We now have the correct units for the tour. Enter the following species into the grid:

Fe

NaOH

H_2SO_4

Note: The display name may change these to a "Spelled out" display. You can use the **Names Manager** in the **Tools** menu to alter the display as you desire.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Fe	0.0
NaOH	0.0
H2SO4	0.0

Input

Figure 21-5 Stream definition in correct units.

Water is the default species and defaults to a value of 55.5082 moles.

Leave the remaining fields blank. Thus, we will simulate the behavior of iron in water at ambient conditions. Note that it is not necessary to include any Fe (i.e., iron) in the stream composition. Although it is permissible to include a corroding metal in the stream, it would not correspond to reality (e.g., a steel pipe is not a component of a stream) and would markedly increase the computation time.

We now need to verify that oxidation and reduction have been turned on in the chemistry model.

- Click on the **Chemistry** menu item and then select **Model Options…**

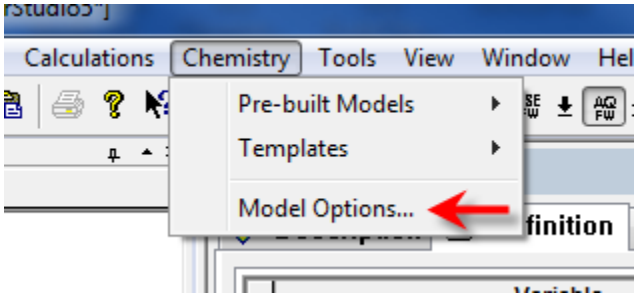


Figure 21-6 Chemistry Menu Items

This will display the model options.

- Click on the **Redox** tab.

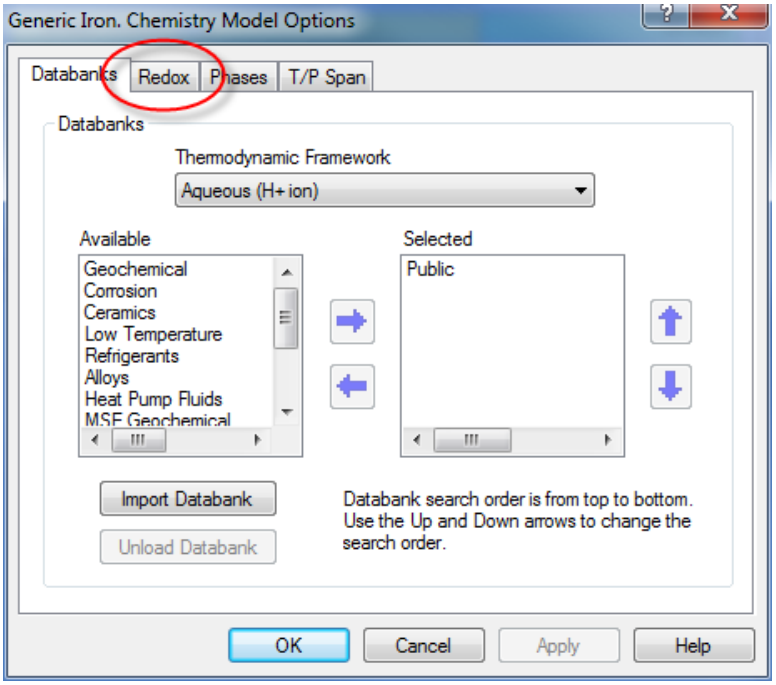


Figure 21-7 Model Options

We will now verify that the iron subsystems have been selected.

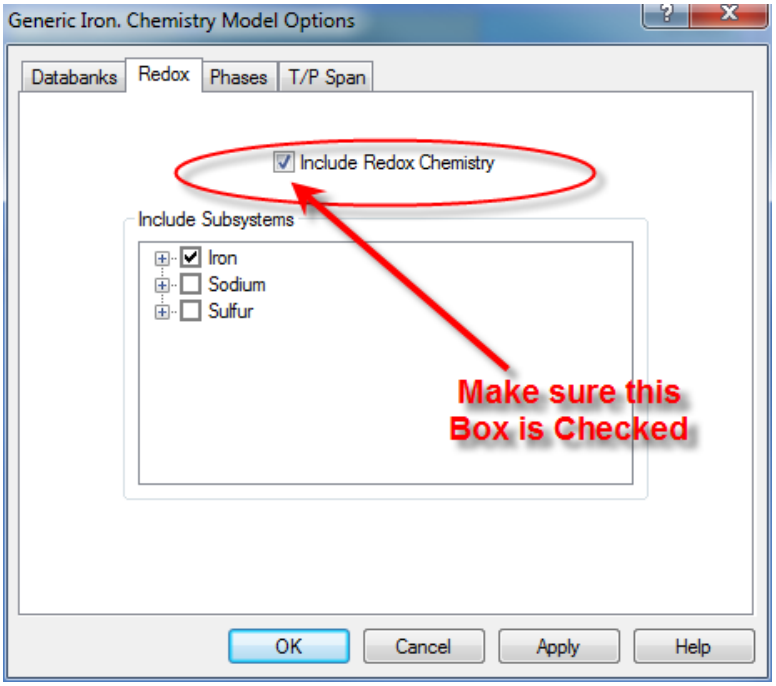


Figure 21-8 The selected redox subsystems.

Another way to make sure Redox is turned on is look at the top toolbar. Re button should be selected.

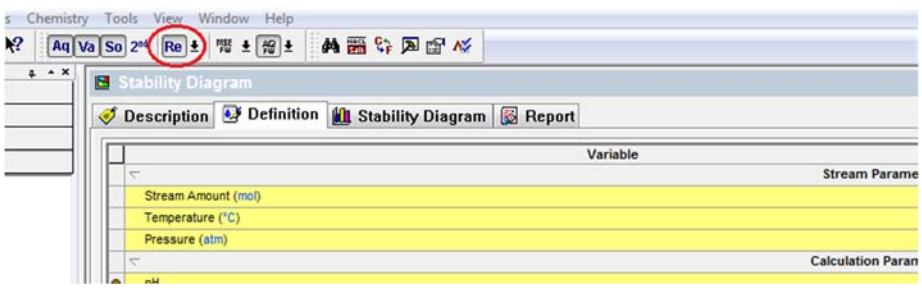


Figure 21-9 Shortcut to switch Redox On

You are free to choose all redox subsystems; this will usually result in longer computation times. It is advisable to choose the redox systems that are relevant to the studied corrosion processes.

In our example, we will choose the iron and sulfur systems. This means that the program will consider all redox states of iron (i.e., 0, +2 and +3) and those for sulfur (-2 to +6). You have the ability to turn individual redox elements on or off by expanding the element tag.

For the moment, leave the sulfur subsystem unchecked. We will eventually select sulfur when we add the hydrogen sulfide.

- Click on the **OK** button to return to the definition.

We have now defined the stream.

- Now click on the **Add Stability Diagram** Icon in the **Explorer**/**Actions** panel.

You can enter descriptive information if you want. Otherwise, click on the **Definition** tab.

Table 21-1Changing Conditions

Parameter	Value	Comment
Stream Amount (mol)	55.5082	Default value
Temperature (ºC)	25	
Pressure (atm)	1.0	
H2O (mol)	55.5082	Default Value
Contact Surface	Fe	

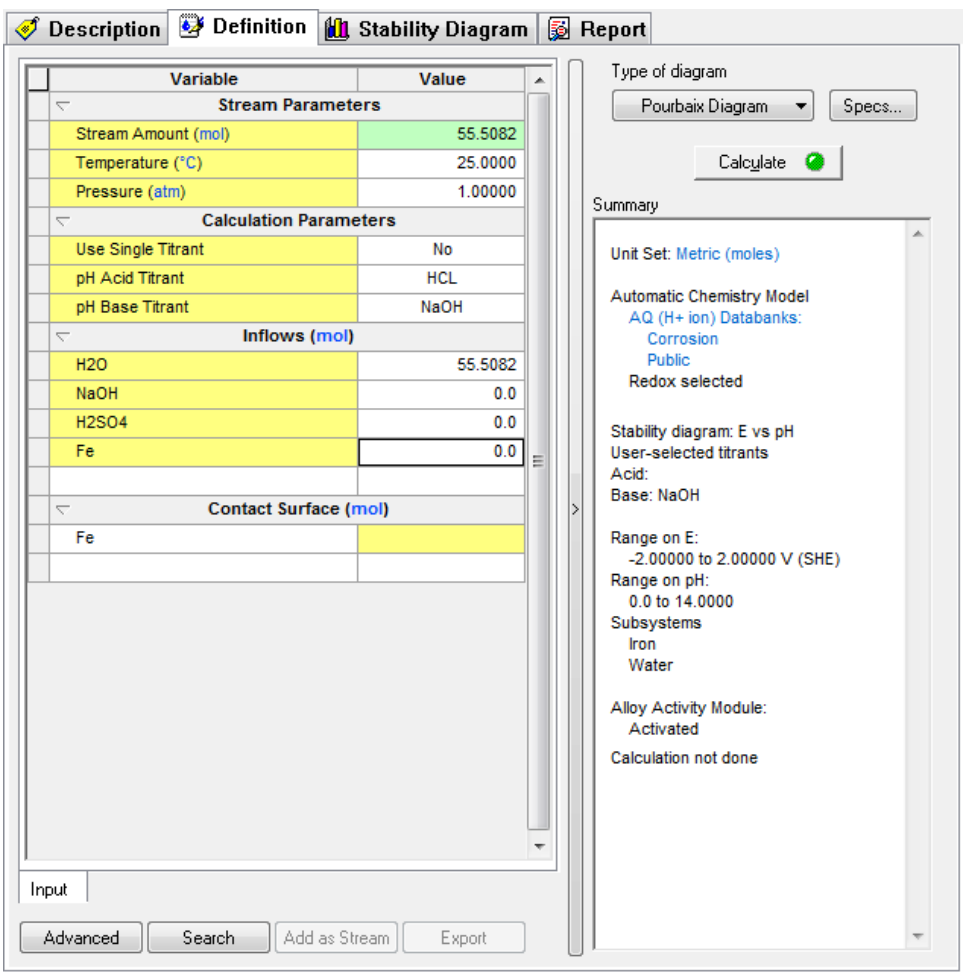


Figure 21-10 Diagram Definition

We now have some work to do to set up the calculation. Although the **Calculate** button is green we need additional information before we start calculating. We need to set some additional parameters for this tour.

We need to specify our surface metal. Frequently this will be Iron, as it is in this case, but we may use other metals. We also need to specify the titrants that will adjust the pH of the solution.

The summary box displays the current information about the calculation.

- Add the species **Fe** to the **Contact Surface** grid (if not already added)

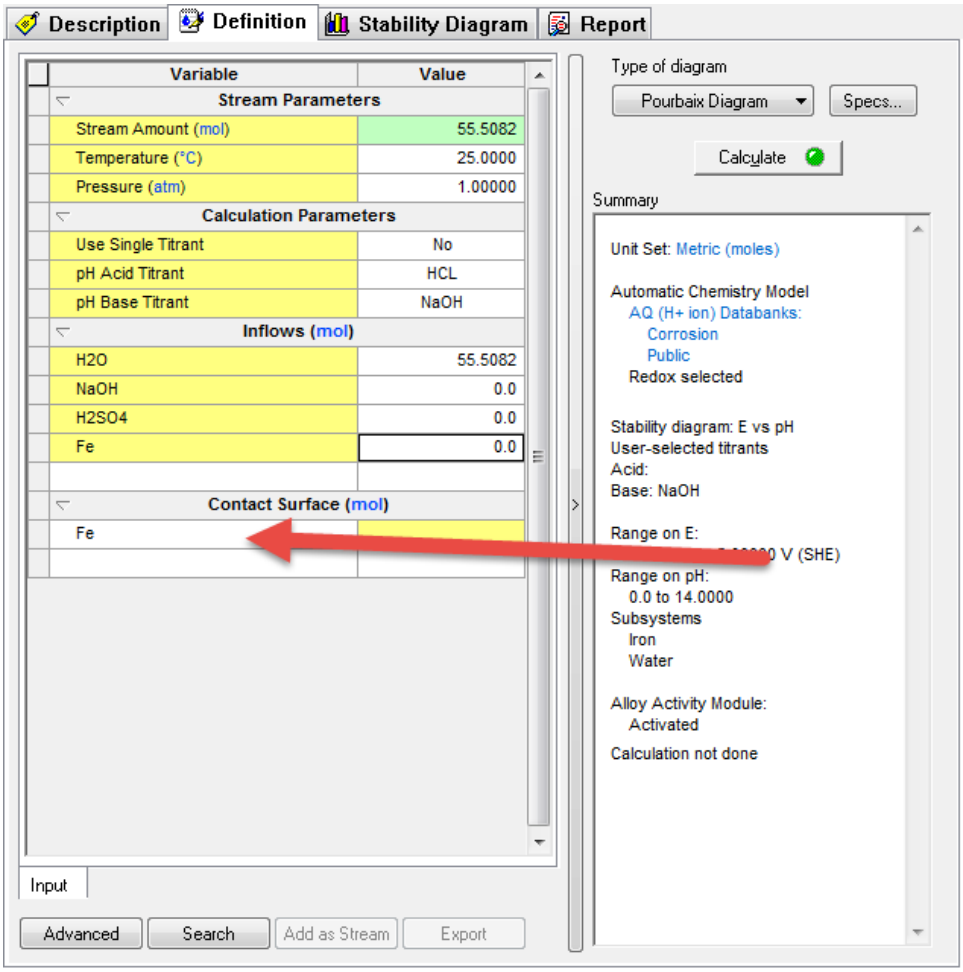


Figure 21-9 Adding Fe to the Contact Surface list.

Click on the **Specs…** button to fill out the remaining information.

- Click on the **Axes** category.

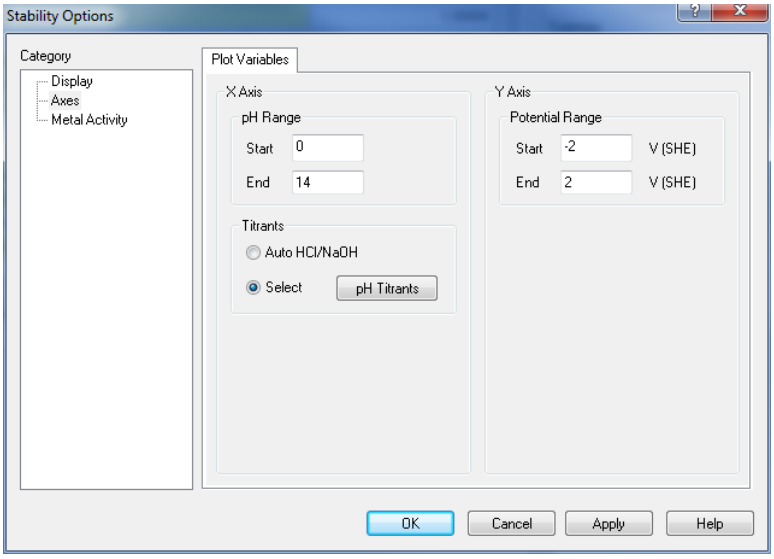


Figure 21-10 Select Titrants

Choose the **Select** radio button in the **Titrants** box. This will enable the **pH Titrants** button.

We now need to select an acid and a base. Select ***H_2SO_4*** as the acid (Sulfuric Acid) and ***NaOH*** as the base (sodium hydroxide).

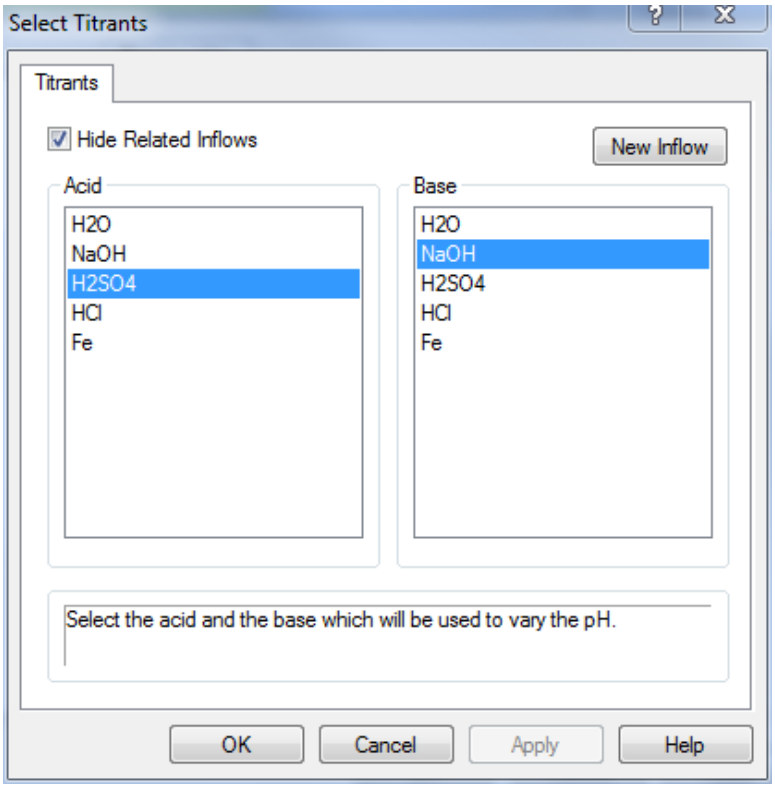


Figure 21-11 Choose an acid and base

- Click OK

The Y-Variable specifies voltage (E) as the variable; we wish to continue using it so will skip the category.

- Click on the **Display** category.

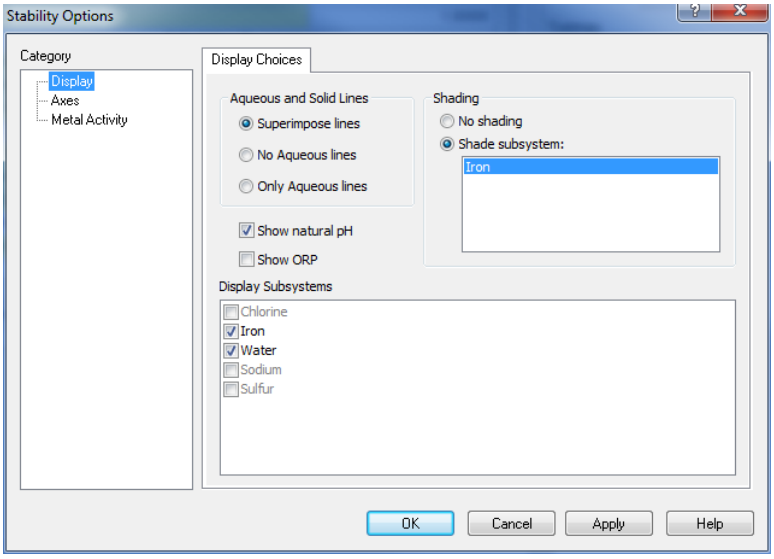


Figure 21-12 Make sure the Sulfur subsystem is unchecked.

Notice the **Display Subsystems** list. This tab will only display the selected subsystems. In this case only iron and water will be displayed. The subsystems are still calculated if they are not checked, merely not displayed.

Accept the default entries for the other options in this category.

- Click on the ***OK*** button.

We are now ready to calculate. Click the **Calculate** button and wait for the calculation to finish.

Once the calculation has finished, click on the **Stability Diagram** tab.

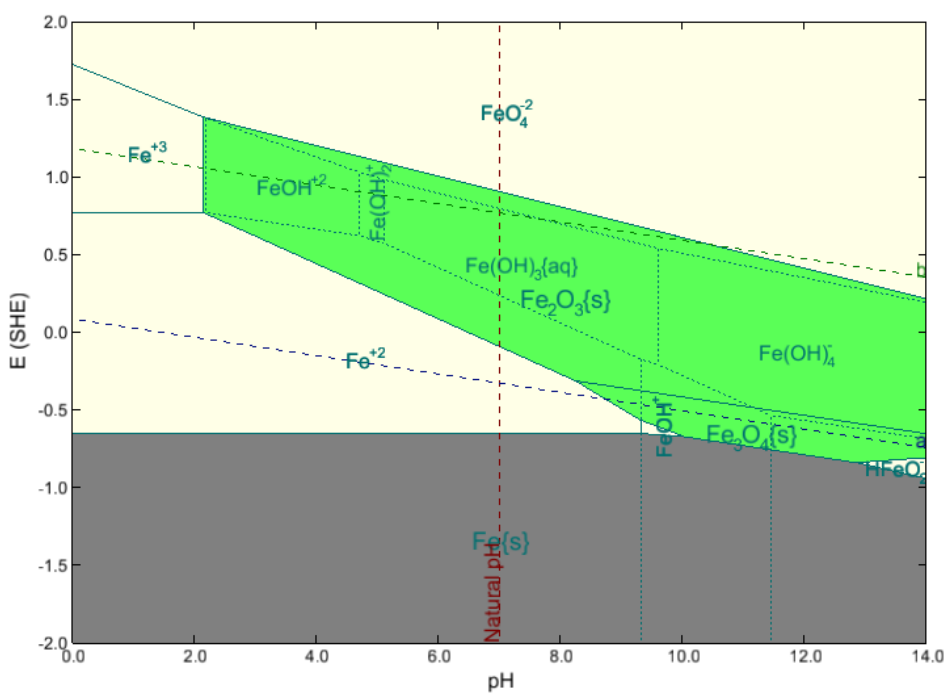


Figure 21-13 A Pourbaix diagram for iron

The obtained diagram is useful for assessing the corrosion behavior of iron. First, the equilibrium lines between elemental iron (i.e., Fe(s)) and other species can be found.

As shown in the diagram, elemental iron can be oxidized to the Fe^{2+} ions (i.e., FE+2) in acidic, neutral and weakly alkaline solutions (for pH below ca. 9.5) and to the $Fe(OH)_3^{-1}$ ions (i.e., FEIIOH3-1) in alkaline environments (for pH above ca. 11.5).

The oxidation of iron can be coupled with the reduction of the H^+ ions because the H^+/H_2^o equilibrium line (denoted by a) lies always above the lines that represent the oxidation of iron. Therefore, corrosion of iron can occur with the evolution of hydrogen and formation of soluble iron-containing ions (either Fe^{2+} or $Fe(OH)_3^-$).

Adding Hydrogen Sulfide

We will now **add 1.0 x 10^{-4} moles of H_2S** to the stream.

Click on the **Definition** tab.

In the grid, add hydrogen sulfide (H_2S) to the stream at a rate of 1.0000E-04 moles.

Click on the **Chemistry** menu item and select **Model Options…**

- Click on the **Redox** tab.

Select ***Sulfur*** from the list; ***Iron*** should also be checked.

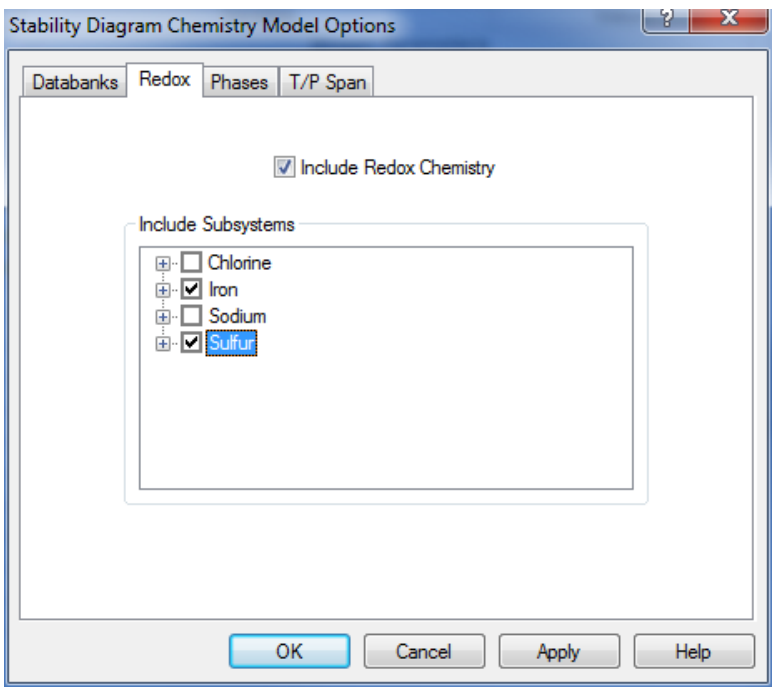
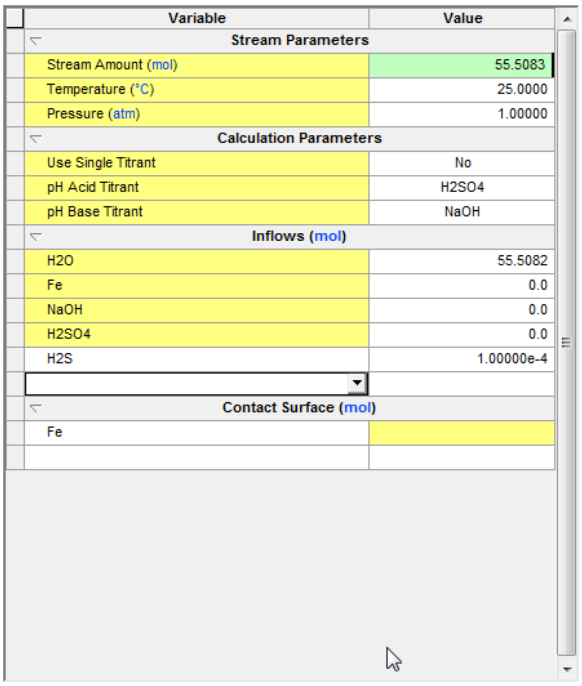


Figure 21-14 Enabling the sulfur redox subsystem.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5083
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	H2SO4
pH Base Titrant	NaOH
Inflows (mol)	
H2O	55.5082
Fe	0.0
NaOH	0.0
H2SO4	0.0
H2S	1.00000e-4
Contact Surface (mol)	
Fe	

Figure 21-15 Add Hydrogen Sulfide

Though calculation is set up, use the **Specs…** button to review the settings. The only change will be in the subsystems. Since we are now calculating the sulfur redox subsystems, we want to make sure that we are displaying them correctly.

Check the sulfur subsystems.

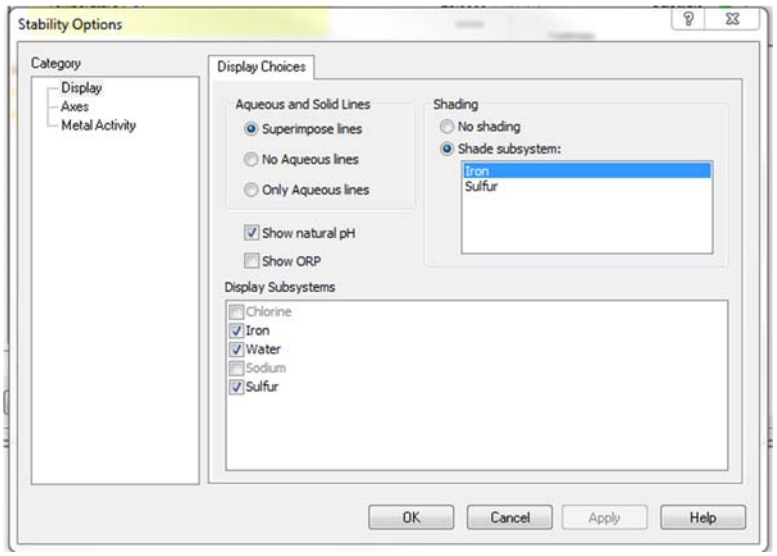


Figure 21-16 Turn on display on for Sulfur.

- Click the **OK** button

Click the Calculate button when you are ready. When the calculation finishes, click the ***Stability Diagram Tab***.

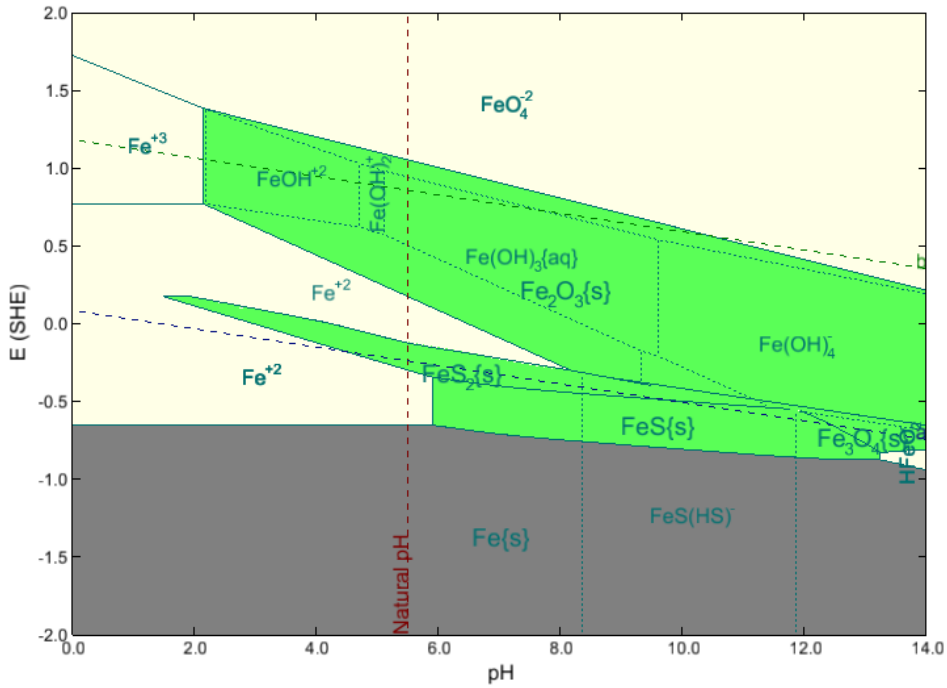


Figure 21-17 The stability diagram with Sulfur.

Inspection of the diagram reveals a profound effect of H_2S on the corrosion of iron. In addition to the species that were present in the first diagram, new stability fields of FeS and FeS_2 are observed. In particular, elemental Iron is found to be in equilibrium with FeS over for pH values ranging from ca. 6.0 to 12.5.

Since the Fe/FeS equilibrium line lies below the H^+ reduction line (**a**), a process consisting of the reduction of H^+ to H^0 and oxidation of Fe to FeS is likely in de-aerated environments. FeS forms a passive film and offers some protection against corrosion.

In fact, the protection due to the formation of FeS is possible over a much wider pH range than that due to the formation of Fe_3O_4 (magnetite) in the absence of H_2S. This has important implications for corrosion in refinery installations, where H_2S frequently occurs.

You can download a worked example for this chapter from the OLI Wiki Page