# 19. **Generating Stability Diagrams in Corrosion Analyzer**

## An Example

Before we go into detail on how the diagram is created and how to interpret the results, we will walk through a sample stability diagram calculation for metallic iron in pure water at 25 ºC and 1 atmosphere.

We begin by double-clicking the OLI Studio icon on the desktop or by using the Start menu.

- **Click** on the ***Add Stream*** icon.

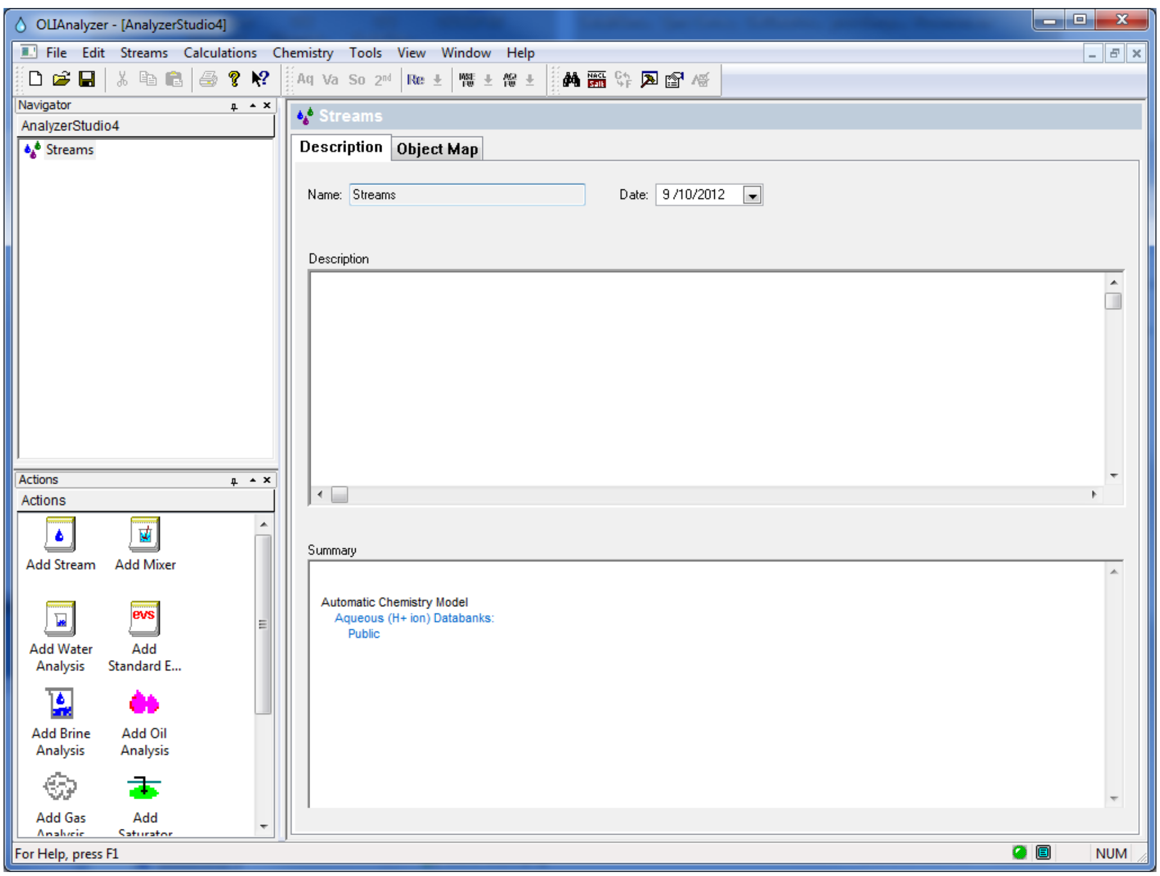


*Figure 19-1 The OLI Studio main window.*

- ***Click*** on the **Description** tab.

The **Description** tab is similar in functionality to other OLI software products. It is recommended that the user enter descriptive information to later identify the calculation and the streams.

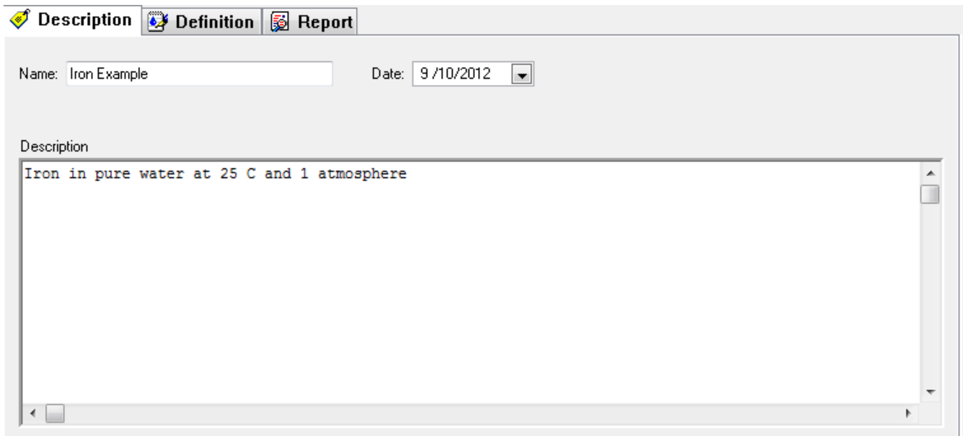


*Figure 19-2 The Description tab.*

- Enter some descriptive information.
- Click on the **Definition** tab.

You may use the **Tools->Names Manager** menu option to change the display of the species.

If the units are not in moles, centigrade and atmospheres, select **Tools->Units Manager** and then select the **Standard** radio button. Select **Metric, moles** from the drop down box.

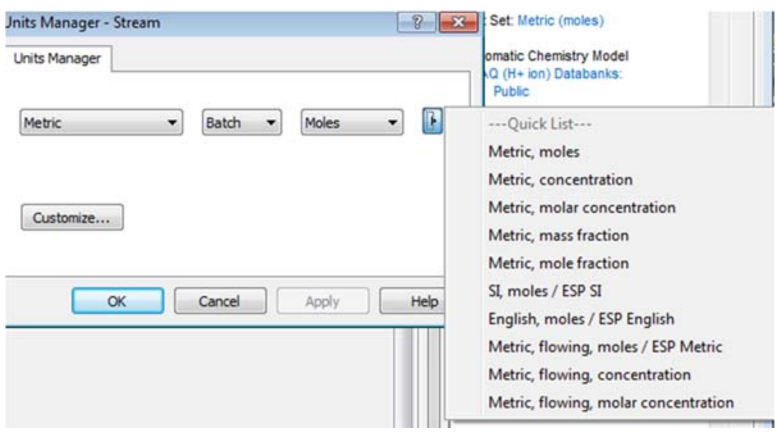


*Figure 19-3 Units Manager*

Enter ***Iron, Sodium Hydroxide*** and ***Sulfuric Acid*** to the grid as shown in Figure 19-4[41].

[41] Depending on the settings for names manager, the displayed names may be formulas or names.

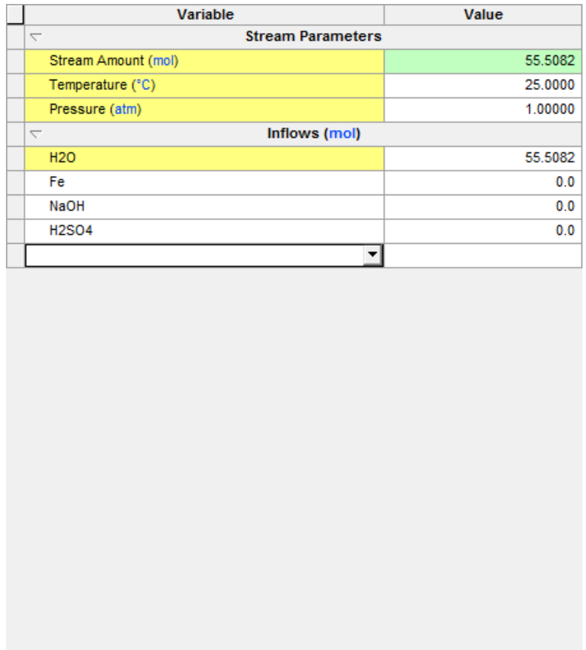


*Figure 19-4 The stream definition tab.*

We are now ready to add a stability diagram to the calculation.

***Click*** on the **<u>Add Stability Diagram</u>** icon in the Explorer/Actions panel.

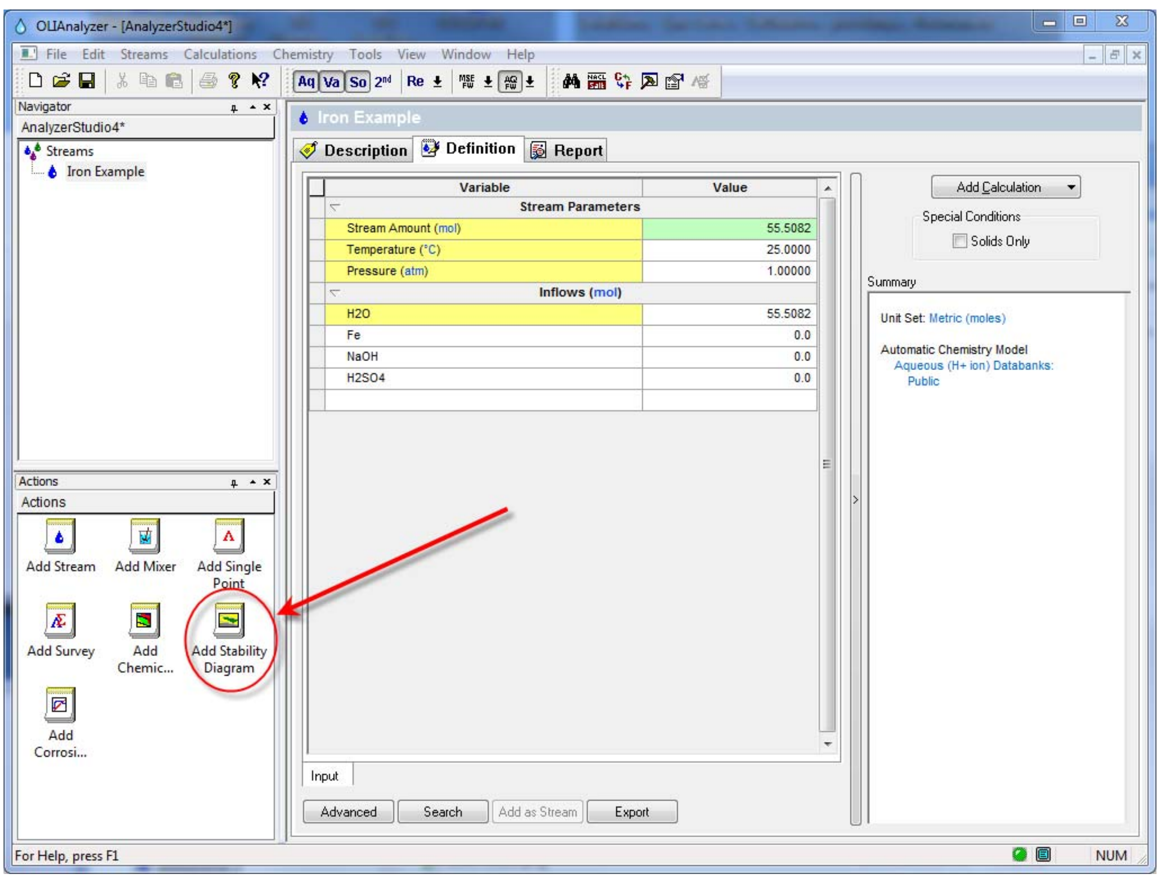


*Figure 19-5 Adding a stability diagram.*

Add a description if necessary by clicking on the **Description** tab. Otherwise, click on the **Definition** tab.

The diagram definition is not complete when you first enter the grid. The metal of interest (in this case iron) must be defined to the calculation as the surface metal. The pH titrants must also be defined (The defaults are HCl and NaOH)

Enter ***Fe*** as the **Contact Surface**

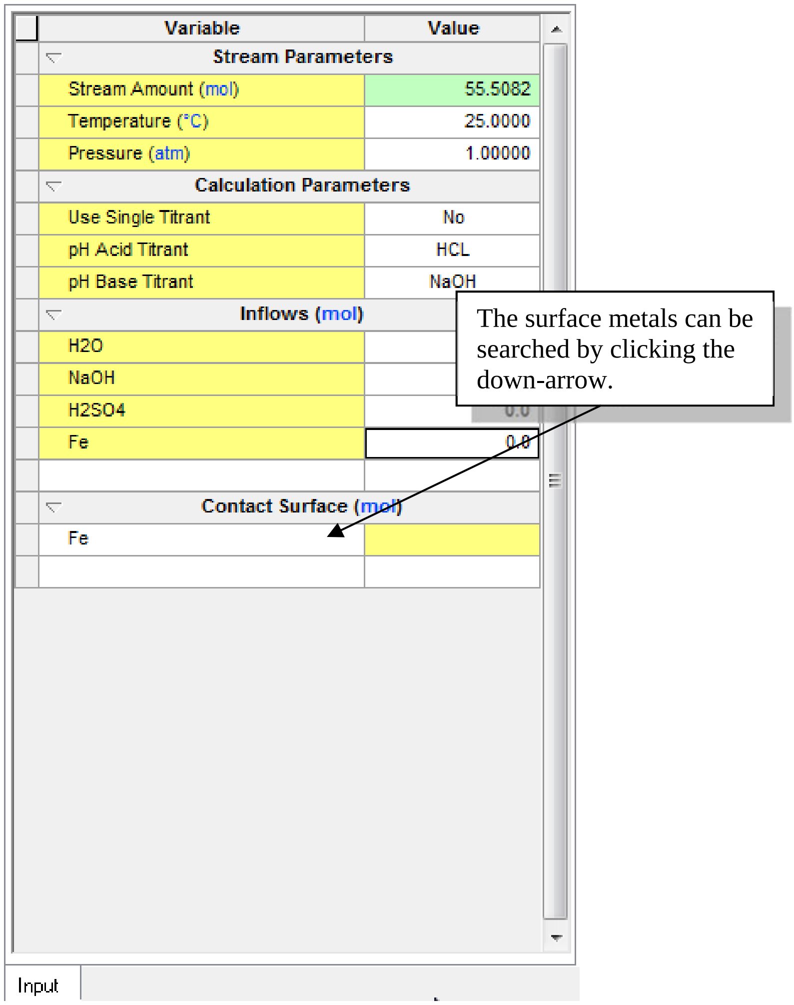


*Figure 19-6 The stability diagram Definition tab.*

Now we need to set up the titrants and ranges of calculations. We do not want to use HCl (hydrochloric acid) since the chloride ion complexes with both ferrous ($Fe^{2+}$) and ferric ($Fe^{3+}$) ions and will clutter our diagram.

Click on the **Specs…** button

The **Specs…** button has several tabs that should be reviewed.

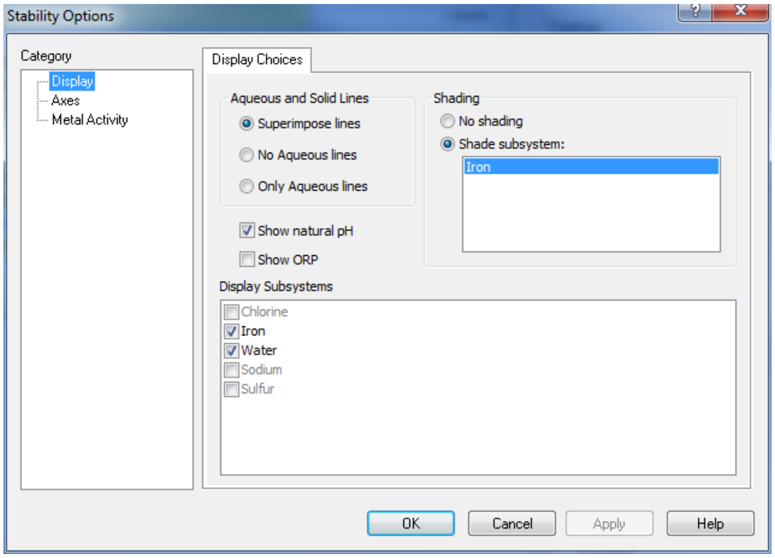


*Figure 19-7 The X-variable Tab*

Click on the **Axes** category. Choose the **Select** radio button in the **Titrants** section. This will enable the **pH Titrants** button.

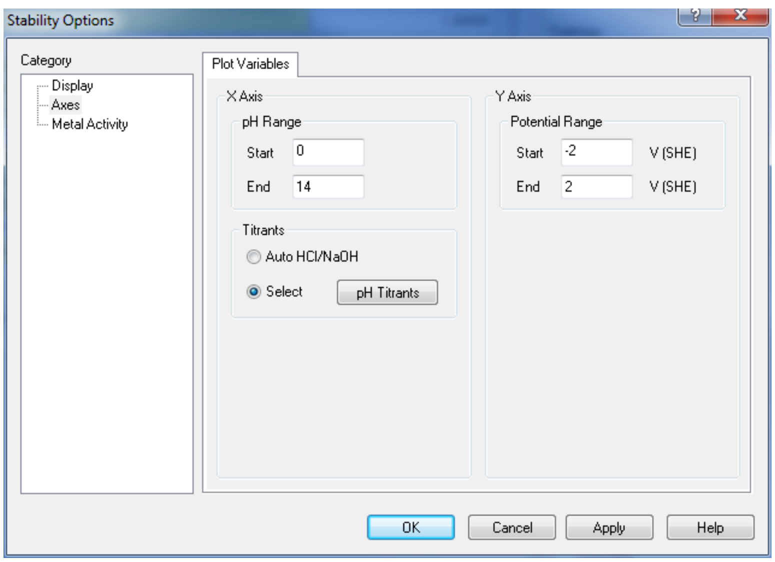


*Figure 19-8 enabling the titrants button.*

We wish to use sulfuric acid ($H_2SO_4$) and sodium hydroxide (NaOH) to adjust the pH.

Click on the **pH Titrants** button

As will other OLI applications, you can select an acid and a base.

Select **Sulfuric Acid ($H_2SO_4$)** as the acid titrant

Select **Sodium hydroxide (NaOH)** as the base titrant

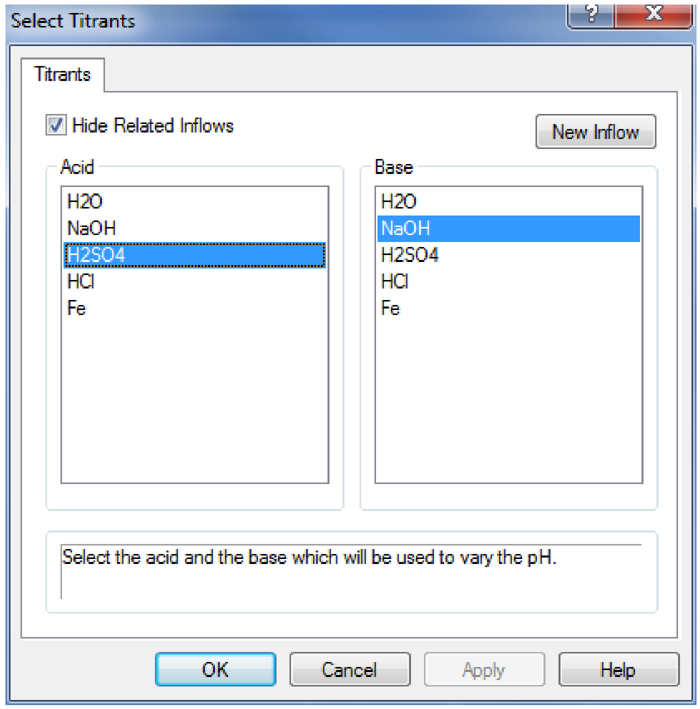


*Figure 19-9 Selecting sulfuric Acid and sodium hydroxide as titrants*

Click on the **OK** button

Click on the **Display** category. Look for the **Display Subsystems** section.

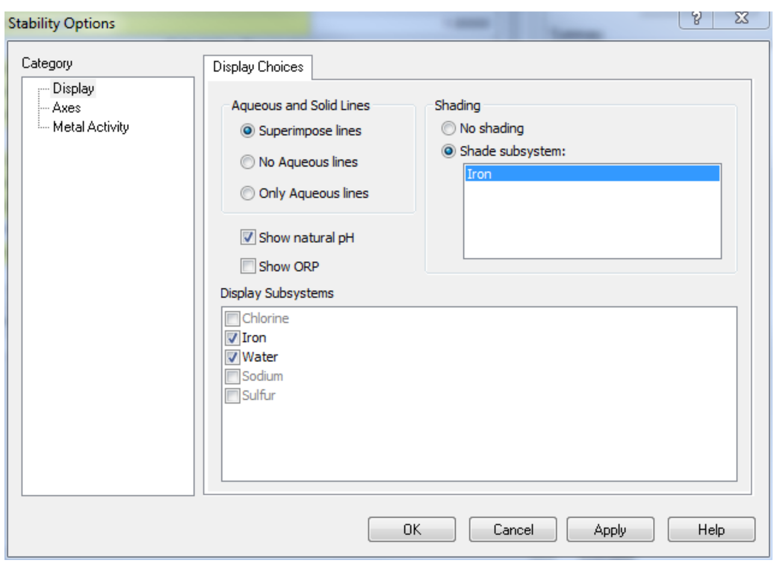


*Figure 19-10 Selecting displayed subsystems (using defaults)*

The display of particular oxidation and reduction species and be turned on and off with the subsystems options. We want to see the various oxidation states of iron.

Check ***Iron*** and ***Water.***

Look for the **Shading** section. Ensure that **Shade subsystems:** is selected.

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The user as some control over how the stability diagram will display. In this case we will accept the defaults.

Click **OK**

We are now returned to the **Definition**. The **Calculate** light should now be green.

Click **Calculate**

The program will run for several moments and finish.

Click on the **Stability Diagram** tab.

The following diagram is the stability diagram for Iron in pure water at 25 centigrade and 1 atmosphere. These diagrams are also referred to as Pourbaix diagrams.[42]

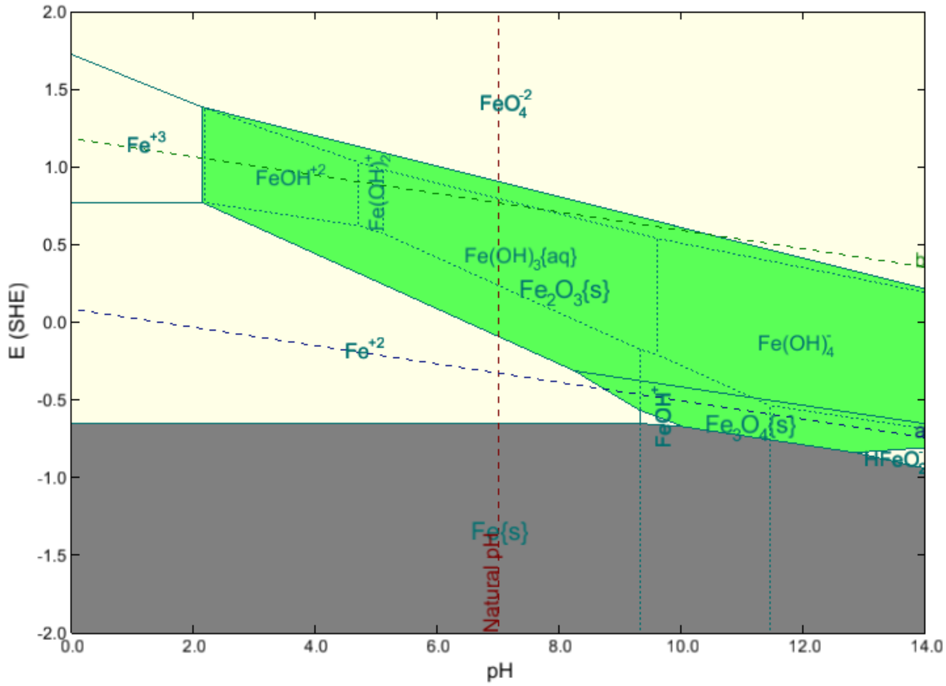


*Figure 19-11 The finished stability diagram*

# How to Use Stability Diagrams

## *What is a redox subsystem?*

- A set of species that contain a given element in all possible oxidation states.

Example: The iron subsystem consists of all species that contain $Fe^{o}$, $Fe^{2+}$ and $Fe^{3+}$.

## *What are the solid lines?*

- Boundaries between stability areas of a solid and an aqueous species or two aqueous species.
- Boundary between an aqueous and a solid species: A solid starts to precipitate or dissolve in an aqueous phase.
- Boundary between two aqueous species: The conditions for which the activities of the species are equal.

## *What are the dashed lines?*

- Boundaries between stability areas of two aqueous species that coexist with at least one solid phase.

[42] Marcel Pourbaix, “Atlas of Electrochemical Equilibria in Aqueous Solutions”. Translated from the French by James. A. Franklin. Pergamon Press, Oxford (1965).

- They are found only within the stability ranges of solids.

What are the areas delimited by the solid lines?

- Stability fields of solid or aqueous species.
- If the conditions are within the stability field of a solid, the solid is stable and usually coexists with an aqueous phase

If the conditions are within the stability field of an aqueous species, no solid can be stable and this species is predominant in the solution.

What are the areas delimited by dashed lines?

- Stability fields of predominant aqueous species that coexist with one or more solid phases.
- Dashed lines can be found only within the stability fields of solid species.

### *Names of aqueous species that are predominant only in the presence of a solid phase but not in a homogeneous solution are printed with small characters. What is the line denoted by a?*

- Equilibrium state between $H^+$ and $H_2^0$:
  - The oxidized form (i.e., $H^+$) is stable above this line;
  - The reduced form (i.e., $H_2^0$) is stable below it.

### *What is the line denoted by b?*

- Equilibrium state between $O_2^0$ and $O^{2-}$:
  - The oxidized form (i.e., $O_2^0$) is stable above this line;
  - The reduced form (i.e., $O^{2-}$) is stable below it.

Water (which is a combination of $H^+$ and $O^{2-}$) is stable between ***a*** and ***b***.

Why is it useful to view a superposition of diagrams for selected subsystems?

- Corrosion is observed when oxidation of the metal of interest leads to the formation of soluble metal species and can occur simultaneously with some reduction reaction.
- Similarly, passivation is observed when the oxidation of the metal leads to the formation of a protective layer of a sparingly soluble compound.
- A line that represents a reduction reaction (e.g., reduction of atmospheric oxygen to water) must lie above the line that represents an oxidation reaction (e.g., oxidation of a metal to aqueous ions or a potentially passivating oxide).
- The corrosion potential will establish itself somewhere between the equilibrium potentials for the oxidation and reduction reactions.

- Thus, it is possible to find out whether a certain species from one subsystem can be oxidized and, simultaneously, a certain species from the other system can be reduced.

What is the range of immunity to corrosion?

Stability field of elemental metal.

What is the range of corrosion?

Stability fields of dissolved (ionic or neutral) metal species in which neither the metal nor passivating solids are stable.

What is the range of possible passivation?

Stability field of a sparingly soluble compound (usually an oxide or hydroxide or salt).

- This compound will form a layer on the surface of the metal, which may protect the metal from corrosion.
- Having determined that a layer is formed, it is necessary to verify whether it is protective or not because this depends on the crystalline structure of the sparingly soluble compound.

How to determine whether corrosion in the absence of oxygen is possible?

- In the absence of oxygen, the most common reduction reaction is the reduction of the proton to elemental hydrogen (as shown by line a)•For a corrosion process to proceed, the line a must lie above a line that corresponds to an equilibrium between the metal and metal-containing ions.
- In oxygen-containing solutions, $O_2^0$ can be reduced to $H_2O$ (line ***b***)
- For a corrosion process to occur, the line b must lie above a line that corresponds to an equilibrium between the metal and metal-containing ions.
- Passivation is likely if ***b*** lies above a line that corresponds to an equilibrium between the metal and a sparingly soluble compound.

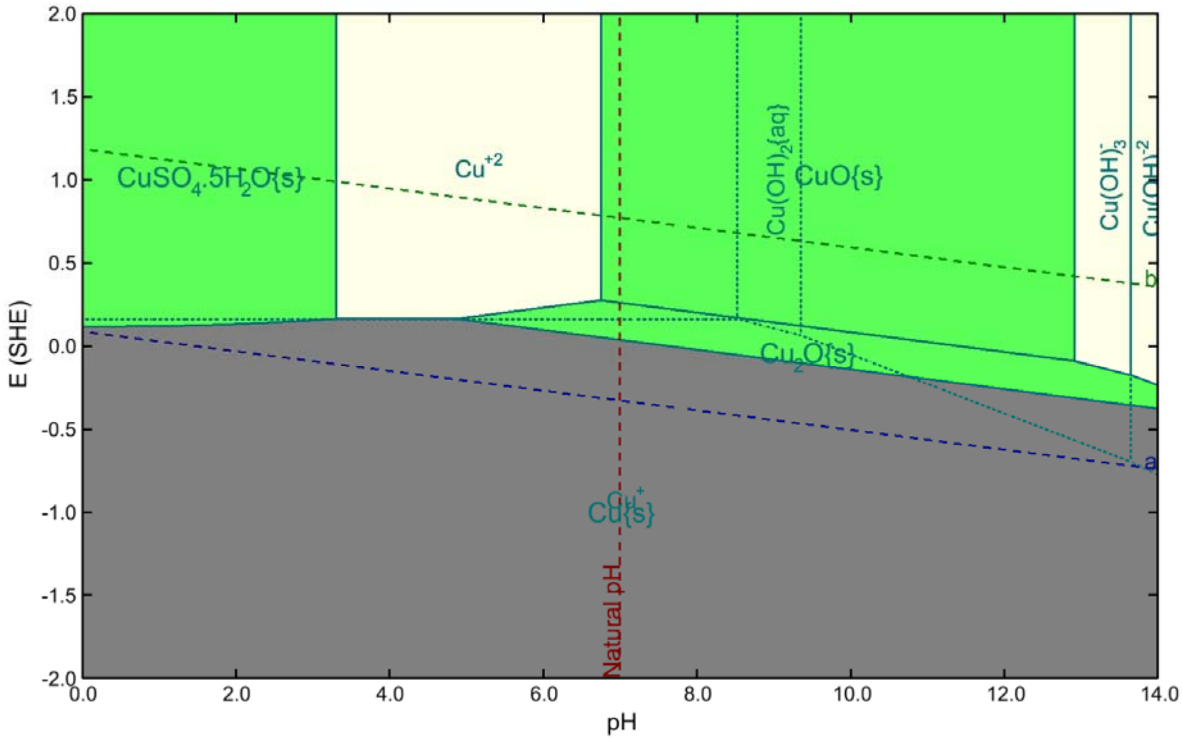


*Figure 19-12 Stability diagram for Copper*

*Some conclusion about the copper diagram to be inserted*

Features of real-solution stability diagrams

- Incorporation of solution non-ideality effects; there is no need to assume arbitrary values for the activities of species.
- Applicability to concentrated solutions.
- Applicability over wide temperature and pressure ranges.
- Usefulness for studying effects of various complexing, oxidizing and reducing agents because of OLI's comprehensive data bank.
- Facility to superimpose two or more stability diagrams to study interactions between different redox systems.
- Facility to screen various independent variables to find which one is really important.
- In contrast to the classical Pourbaix diagrams, pH variations result from adding realistic acids or bases.

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