think simulation

getting the chemistry right

OLI Corrosion Modeling Basics

using OLI Studio: Corrosion Analyzer

August 10 and 12, 2020

Disclaimer

- The simulation results used for this presentation were obtained using OLI Studio V10
  - If you are using an older version, you may obtain slightly different results.

- This CMB course is open forum.
  - Feel free to share any information, but be aware that this session is being recorded and content may be shared with others outside this course.

Course Objectives

At the end of this course you will be able to:

1. Discuss general **OLI Studio: Stream Analyzer and Corrosion Analyzer** features

2. Choose appropriate thermodynamic models for your chemistry

3. Review major types of calculations
   - The different types of corrosion calculations
     - Corrosion rates
     - Propensity to localized corrosion
     - Pourbaix diagrams
   - How to enter your own data (stream or water analysis) – to accurately represent corrosive conditions
   - How to interpret your results

4. Formulate and build your own applications and interpret the data presented in reports and plots

Welcome to the Class!

- Training for **OLI Studio: Corrosion Analyzer**

- Two sessions:
  - Day 1 – 3 hours
  - Day 2 – 3 hours
- In each session:
  - Work 53-55 min and take a 5-7 min break
- If needed: Split your monitor to see presentation and work on the software at the same time.
  - Windows key + left or right

Materials

- **Software**
  - You should have received a trial Serial Number giving you access to the **Stream Analyzer** and **Corrosion Analyzer** Tools.
  - Is the OLI Software installed? Please let me know, so that we can help you.

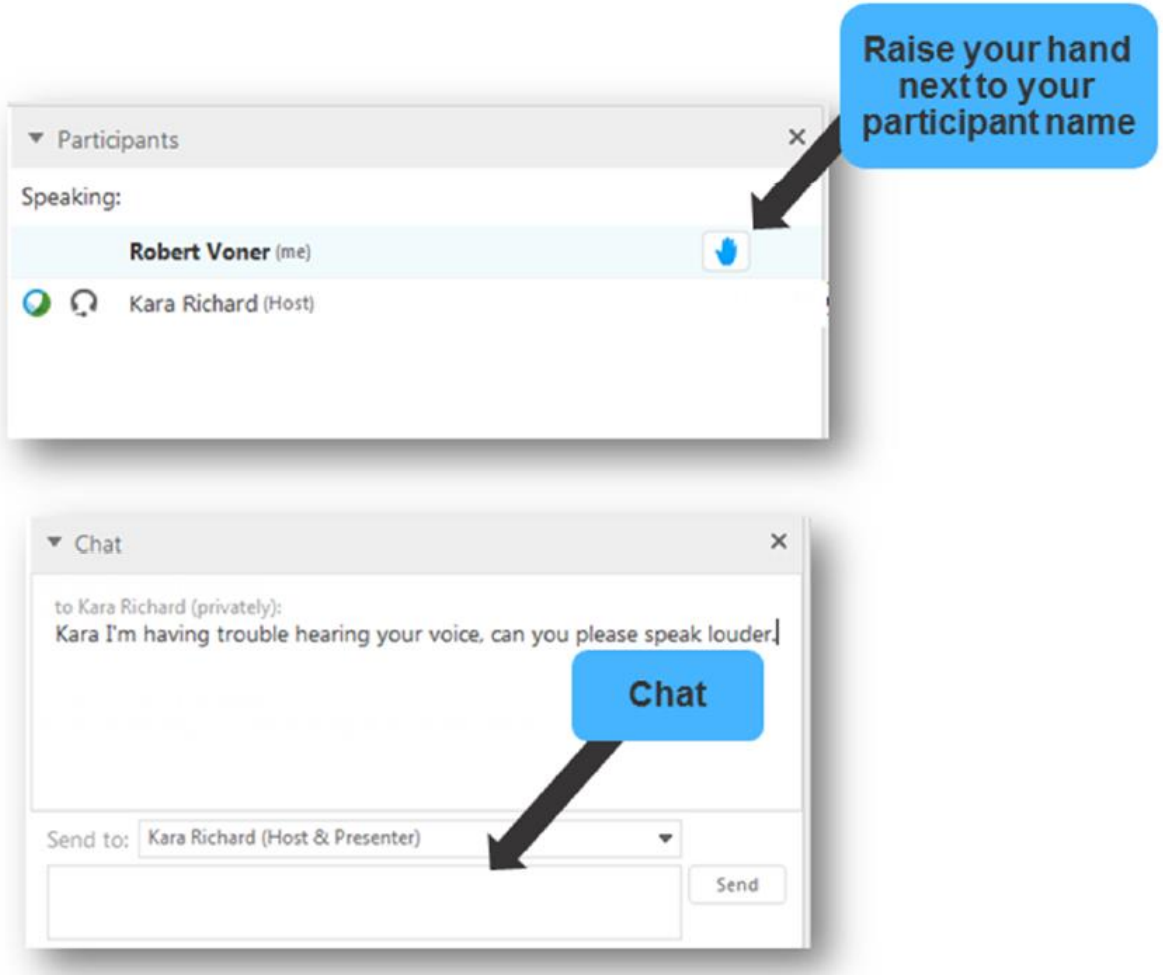
- **Manual**
  - During the training we will walk through the essence of the chapters.
  - You should have access to the manual, which will serve as a resource to study from.
  - The manual case files and the case files completed during the course will be provided.

Virtual Etiquette

- Inform the instructor if you:
  - Have technical issues
  - Leave the course for a moment
- Mute Mobile Devices 
- Actively participate
  - Feel free to interrupt if you have any questions

WebEx Tools

- Raise your hand next to your participant name
- Use your chat to ask any questions
- Unmute and ask your question



Certificate of Completion!

- Complete our course survey.

OLI Studio

Stream Analyzer

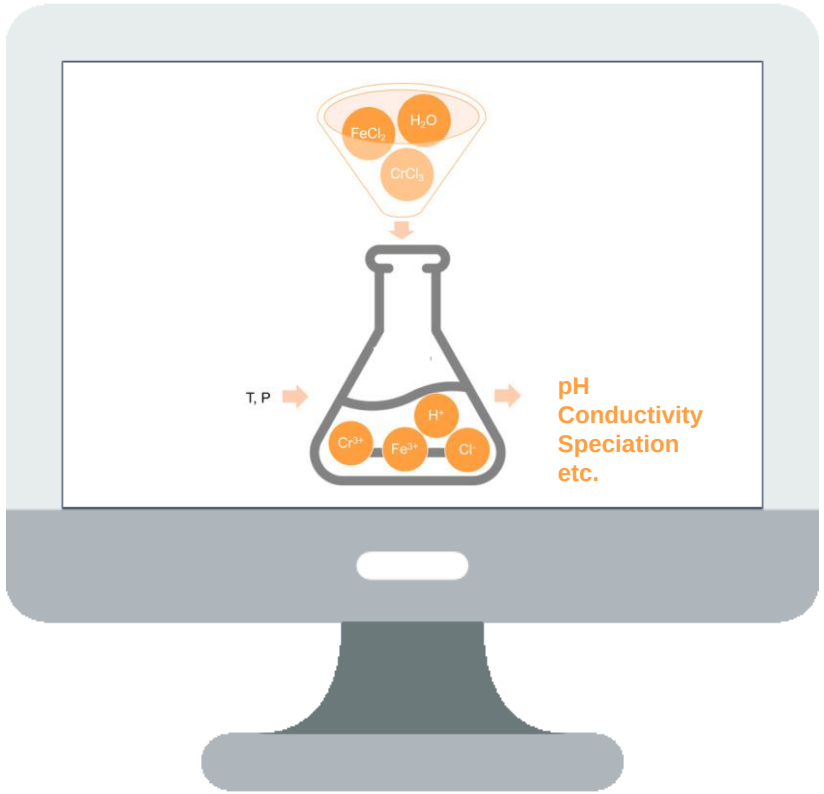
ScaleChem

Corrosion Analyzer

OLI Studio: Stream Analyzer Overview

Stream Analyzer is a comprehensive thermodynamic tool that calculates:

Speciation, Phase equilibria, Enthalpies, Heat capacities, Densities, etc., in mixed-solvent multicomponent systems



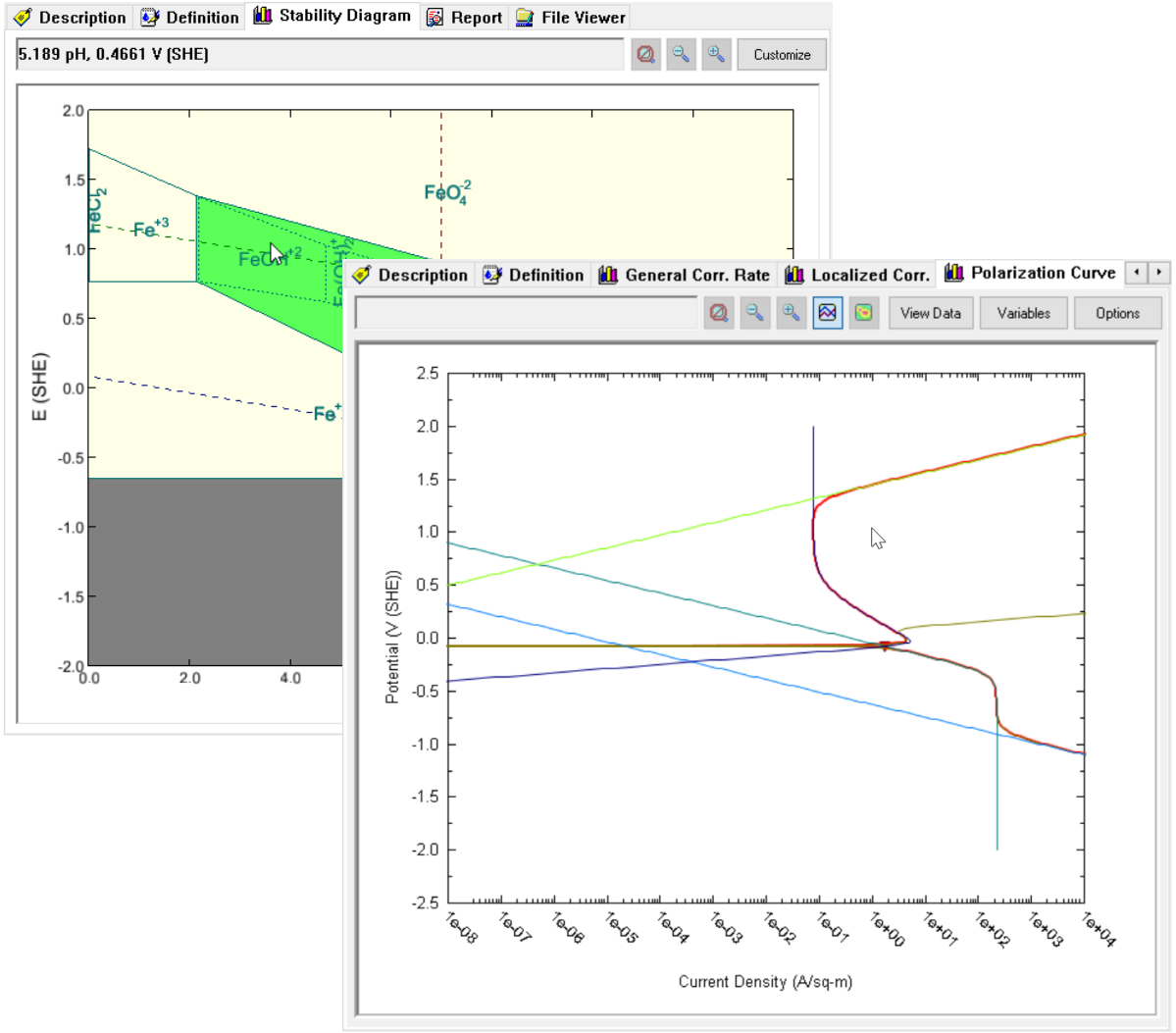
Capabilities and features of Stream Analyzer include:

- **Three different thermodynamic frameworks:**
  - Aqueous (AQ) model
  - Mixed Solvent Electrolyte (MSE) model
  - Mixed Solvent Electrolyte and Soave-Redlich-Kwong (MSE-SRK) model
- **Thermophysical properties:** Stream Analyzer has thermophysical models to predict surface tension, interfacial tension, viscosity, electrical conductivity, thermal conductivity, diffusivity, and osmotic pressure.
- **Molecular and ionic inflows:** Stream Analyzer accepts molecular inflows typical of a process stream; and ion inflows typical of a sample water analysis.

OLI Studio: Corrosion Analyzer Overview

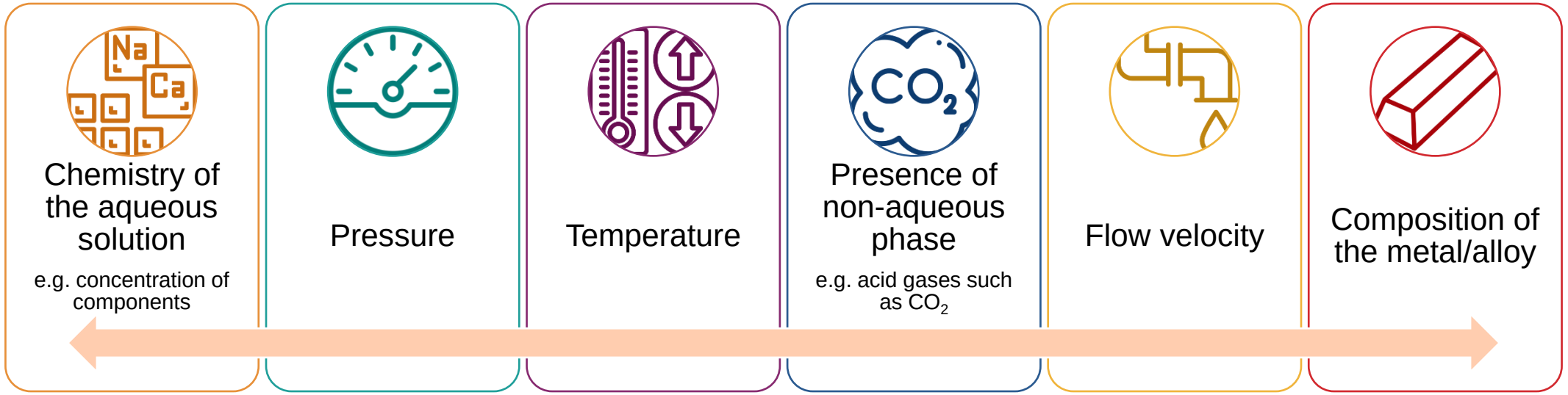
Capabilities and features of Corrosion Analyzer are:

- ✓ Calculation of **general corrosion** rates
- ✓ **Localized corrosion** susceptibility – *calculating the worst-case pitting rate*
- ✓ Generation of **polarization curves** plots
- ✓ Generation of **Pourbaix (E vs pH) diagrams**
- ✓ Heat treatment effect



Introduction to the OLI Corrosion Model

Corrosion rates in aqueous environments depend on multiple factors, such as:



To get an understanding of each one of these factors, or a combination of these factors, computational modeling is **advantageous**.

The strength of the OLI corrosion model is the ability to provide a realistic representation of **chemical equilibria** and **thermophysical properties** in the bulk solution, and at the same time, to account for the phenomena at the **metal-solution interface**.

Introduction to the OLI Corrosion Model

Thermophysical module

- Computes **the speciation** of species in aqueous solutions, e.g. $\boldsymbol{CO_2 + H_2O \rightarrow H^+ + HCO_3^-}$
- Calculates the **concentrations** and **activities** of ionic species and neutral species in aqueous solutions
- Calculates **transport properties** of individual species, such as viscosity and diffusivity, to predict mass-transfer effects

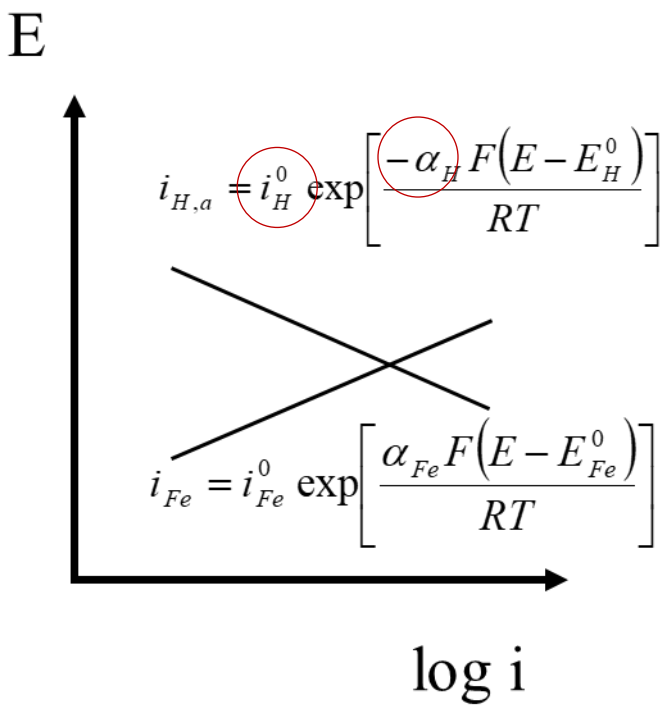
Thermodynamic Framework
Aqueous **(AQ)*** model

Electrochemical module

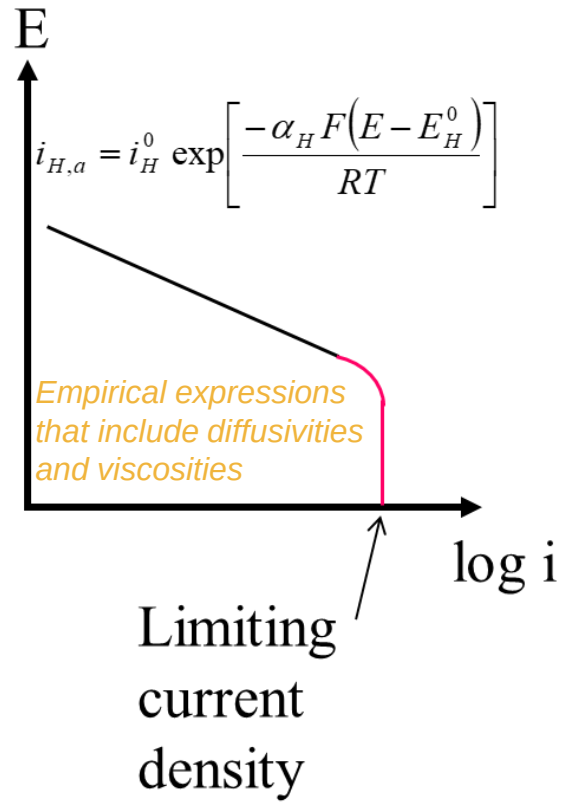
- Simulates partial **oxidation** and **reduction** processes on the surface of the metal
- Reproduce the **active-to-passive** transition and effect of solution species on passivity
- Reproduce **experimental corrosion rates** using parameters calibrated using experimental data
- The prediction of corrosion potential and corrosion rates involves 3 aspects of **Corrosion Kinetics**:
  - Chemical Kinetics – **Activation control model**
  - Mass Transfer – **Diffusion control model**
  - Passivity - **Fraction surface coverage model**

Prediction of corrosion rates

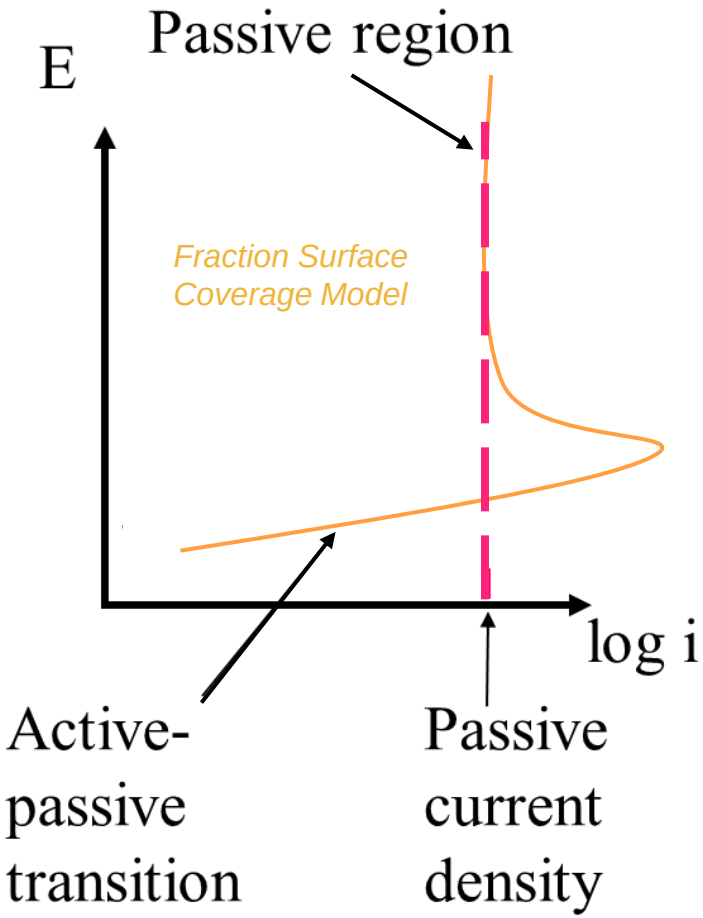
1. Activation Control



2. Diffusion Control

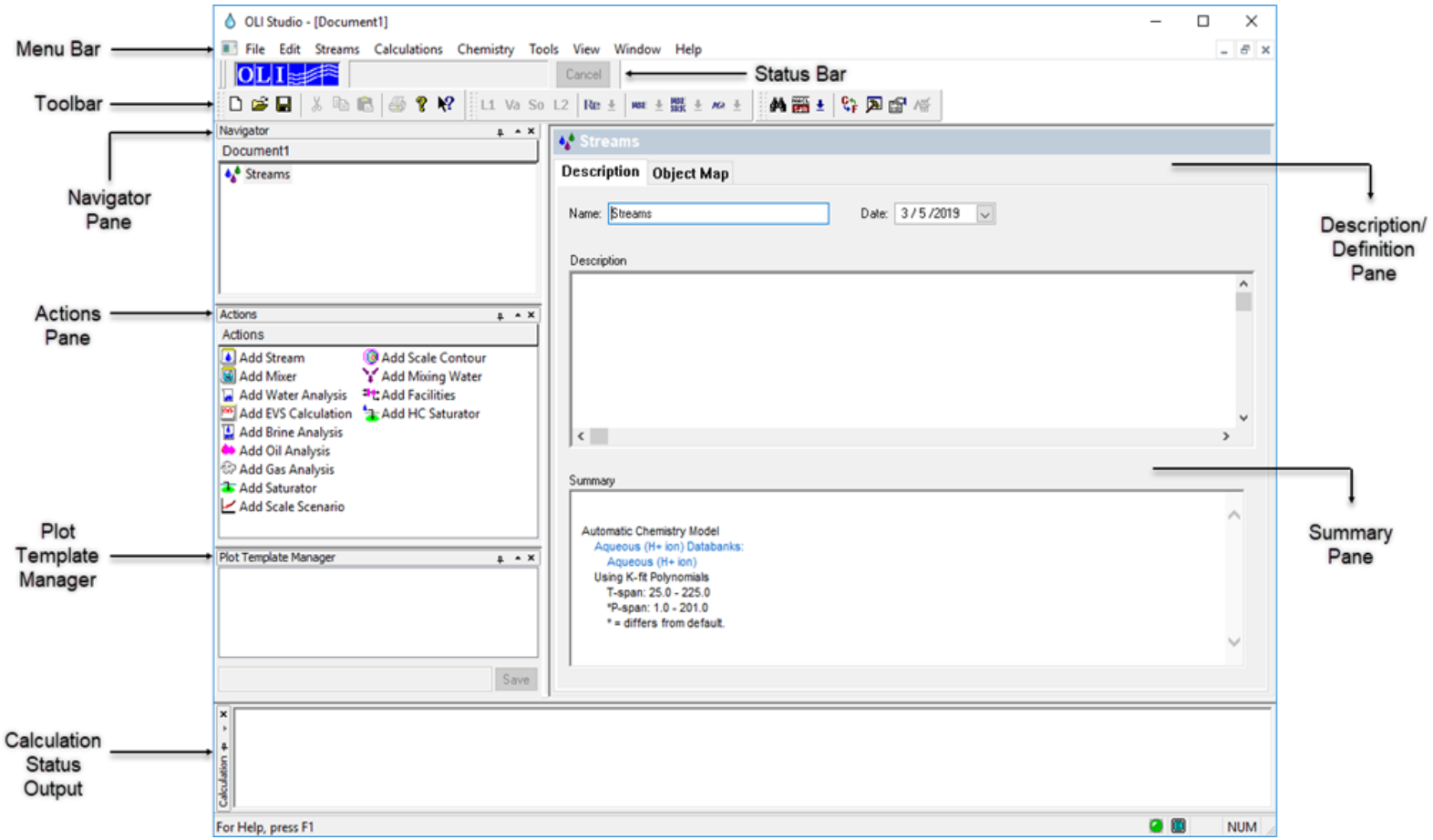


3. Passivity



User Interface

OLI Studio Desktop: User Interface



Navigator Panel

- Open files and add additional files
- Drag calculations from one document to another
- Add objects here from the Actions Panel

Actions Panel

- View objects present in the actions panel
- View objects that are installed with the software – depends on the add-ons that have been installed
- See different view options – use the view list to make it easier to find objects

Tool bar

- Quickly access different functions
- Select (or Turn ON) tools (they will be highlighted in blue when selected)

Plot template manager

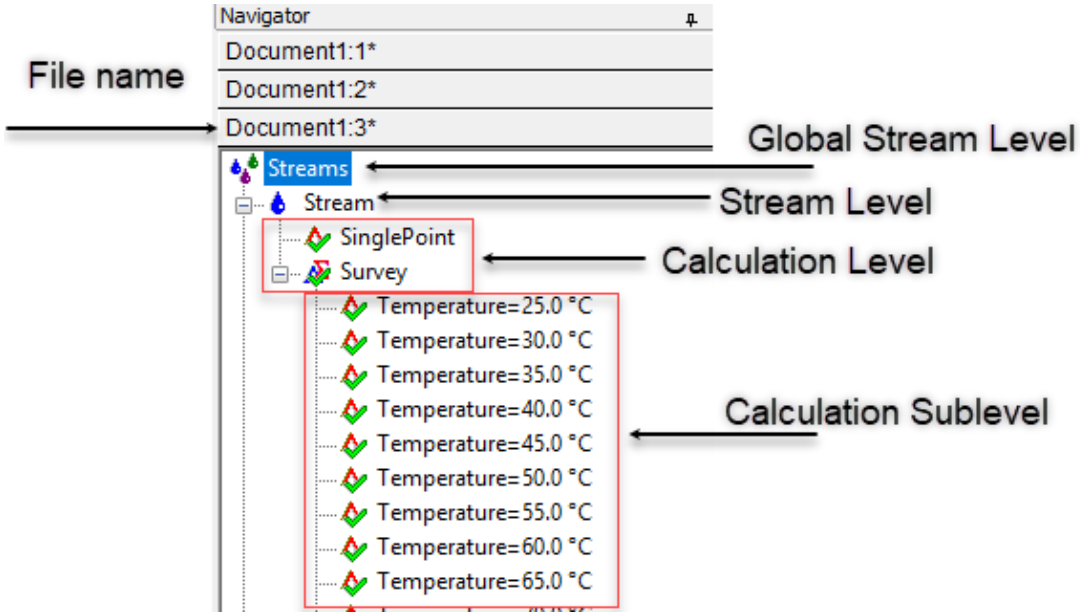
- Save commonly used plots

Calculation outputs

- Receive warnings or Calculation failures, including notice of the potential problem causing the calculation to fail
- Read and understand the cause of the error

Navigator Panel

- The Navigator Panel (or tree level) contains the list of streams and calculations that are active within a file.
- There are four levels:
  - **Global Stream Level:** Provides the broadest view of the navigator objects. At this level, the user can define default units, default component names, and general preferred calculation options.
  - **Stream Level:** Chemistry options such as phase selection, REDOX reactions, and thermodynamic databanks can be selected as this level.
  - **Calculation Level:** Calculation types such as Single point calculations, Survey calculations, etc., are subordinate to streams, and appear in this level.
  - **Calculation Sublevel:** Some calculations, such as Survey calculations, have their own calculation sublevels. They can be expanded or minimized using the small icon (+ or -) next to the calculation type.



Actions Pane

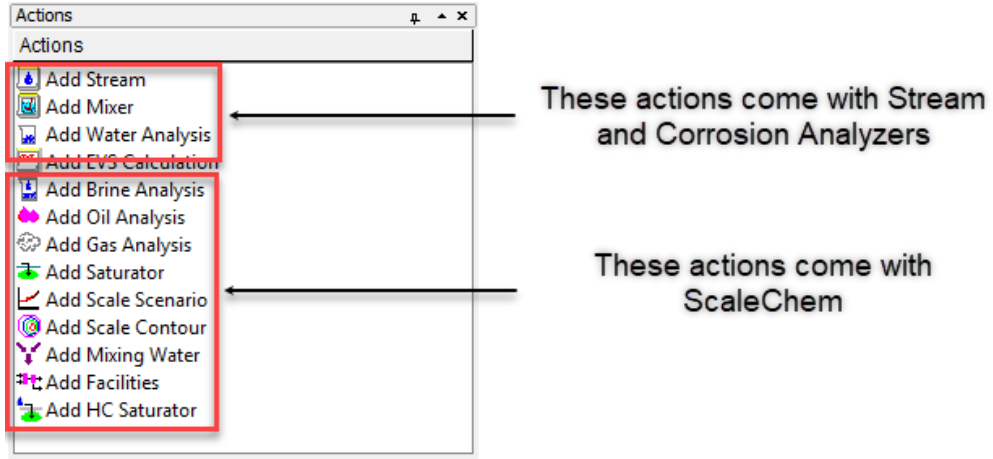
This view contains selectable action icons.

Each icon represents either a new stream input or new calculation.

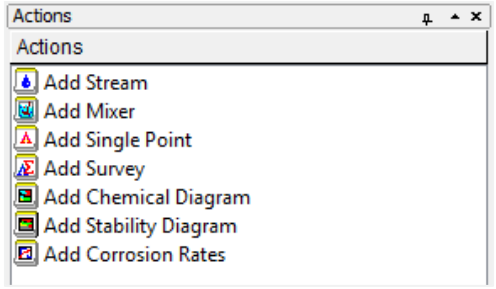
You can show the icons as a List, as Small Icons or as Large Icons.

To change the view: Right click on the white space > Select List

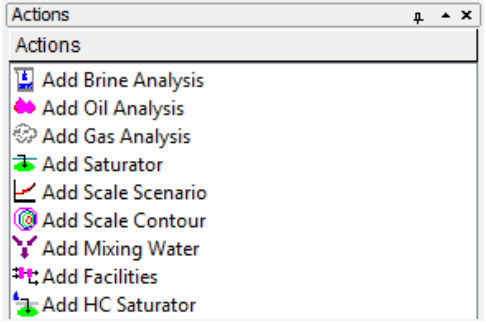
When located at the **Global Stream Level** the following action icons appear on the Actions Pane:



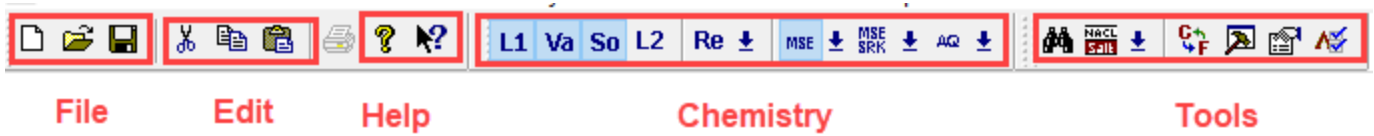
If you select an action item that belongs to Stream Analyzer, this action item will be located at the **Stream Level**, and only the following action icons appear on the Actions Pane:



If you select an action item that belongs to ScaleChem, this action item will be located at the **Stream Level**, and only the following action icons appear on the Actions pane:



Tool Bar



In the **Chemistry** quick access tool bar, you will find: Phases, Redox and Databanks.

Phases: Turns ON/OFF specific phases. Four different phases are available:

L1: Aqueous electrolyte rich phase, also referred to as Liquid 1 phase.

Va: Vapor phase

So: Solid phase

L2: Usually organic rich phase, also referred to as Liquid 2 phase.

Redox: Denoted as **Re**. Turns ON/OFF Reduction/Oxidation (REDOX) reactions.

Databanks: Turn ON/OFF a specific thermodynamic databank. There are three thermodynamic databanks available:

AQ: Aqueous databank

MSE: Mixed Solvent Electrolyte databank

MSE-SRK: Mixed Solvent Electrolyte and Soave-Redlich-Kwong databank

Component search
This tool helps you to look for a component using Formula, CAS number, or the periodic table.

Names manager
This tool allows to change the way component name will appear in tables and reports. The style options are: Display name, Formula and OLI Name.

Units manager
This tool allows you to select or change to preferred units for all calculations.

Customize toolbars
This tool allows you to remove or add preferred tools to the Tool Bar. For example, you can add or remove Chemistry from the Tool Bar.

General options
This tool allows you to adjust or change default software settings.

Calculation options
This tools allows you to include or exclude different types of properties in the calculations.

The Three Different Thermodynamic Frameworks

When to use which thermodynamic framework?

General rules:

- **AQ (Aqueous Framework):** ≥ 70% of the stream is aqueous (diluted solutions)

- **MSE (Mixed Solvent Electrolyte Framework):** There is no limit for the aqueous composition – preferred for most chemistries. Water does not need to be the dominant component.

- **MSE-SRK (Mixed Solvent Electrolyte and Soave Redlich Kwong Framework):** Upstream oil and gas applications containing light hydrocarbons and CO_2, that require high pressures (P> 80 atm)

Calculation types

Calculation types

For all calculations we will create one or more objects, referred to as a **Streams**, which are used to define a particular chemistry, temperature, and pressure.

Water Analysis allows you to enter ionic inflows, i.e. anions and cations, and offers reconciliation options.

There are four different types of calculations that can be carried out in **OLI Studio Stream Analyzer**:

Add Single Point	Single Point Calculations are used to find information (pH, volume, speciation, etc.) at one specific equilibrium state.
Add Survey	Survey Calculations are useful for plotting changes in stream parameters against temperature, pressure, or composition.

Add Mixer	Mixer Calculations are useful for mixing different streams, and offers four different mixing options, Single Point Mix, Multiplier, Ratio, and Volume.
Add Chemical Diagram	Chemical Diagram Calculations allow you to create a stability map for species based on concentration and other parameters such as pH.

There are two different types of calculations that can be carried out in **OLI Studio Corrosion Analyzer**:

Add Stability Diagram	Stability (Pourbaix) Diagrams allows you to map out the conditions of potential and pH where different redox species are stable.

Add Corrosion Rates	Corrosion rates allows you to calculate the rate at which any given metal deteriorates in a specific environment.

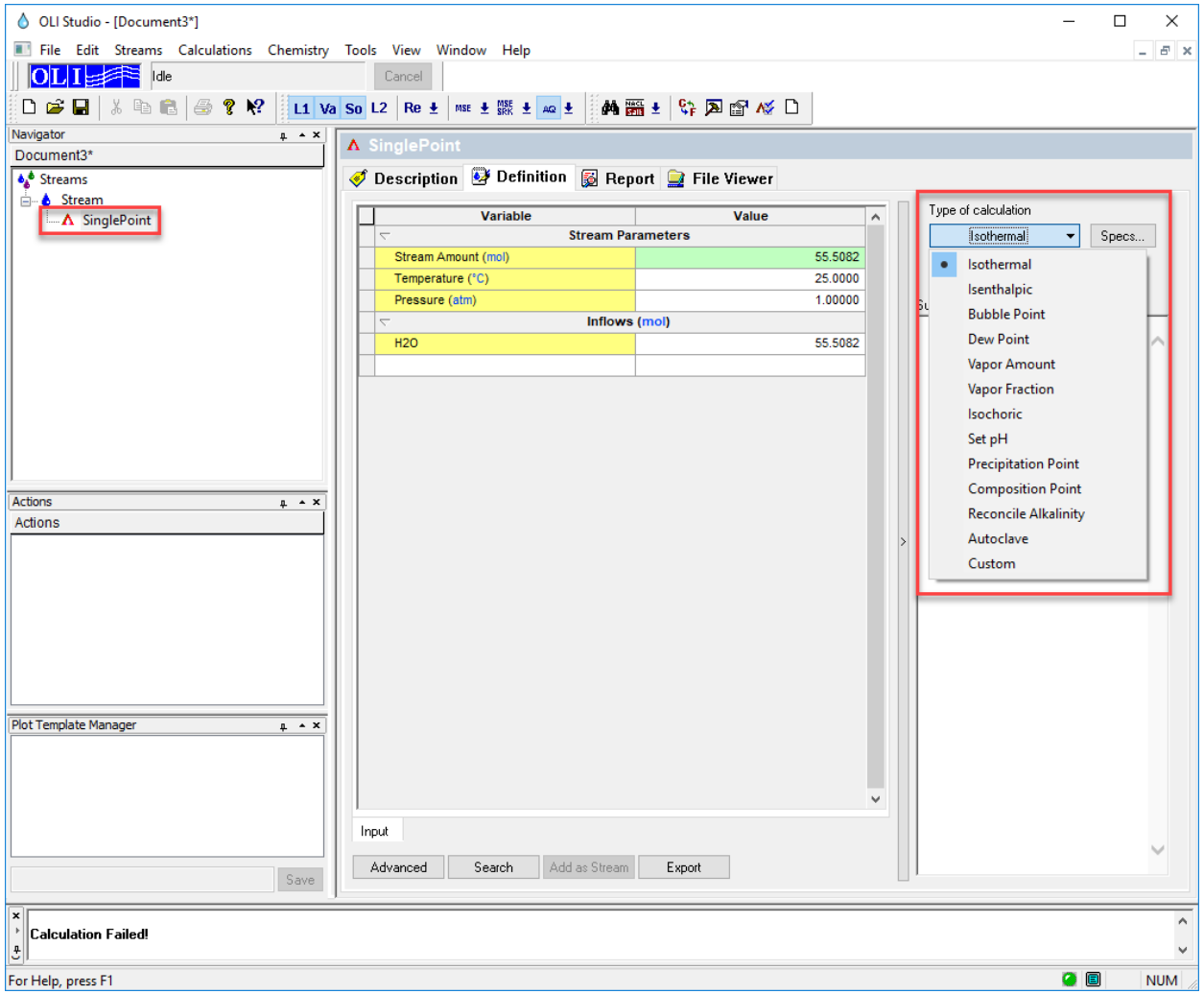
Single Point Calculations

Single Point Calculations

- Single point calculations are the simplest set of calculations in the software.

- There are 13 different single-point calculation types:

1. **Isothermal**
2. Bubble point
3. **Dew point**
4. Vapor Fraction
5. Precipitation Point
6. **Set pH**
7. Reconcile Alkalinity
8. **Autoclave**



Single Point Calculation Types – Definitions

For future reference

1. ***Isothermal***	The software computes solution properties based on a known composition, at a constant temperature and pressure.
2. ***Isenthalpic***	A constant heat loss/gain is applied to the calculation and temperature or pressure is adjusted to meet the heat content.
3. ***Bubble Point***	The temperature or pressure is adjusted to reach a condition where a small amount of vapor begins to appear.
4. ***Dew Point***	The temperature or pressure is adjusted to reach a condition where a small amount of aqueous liquid appears.
5. ***Vapor Amount***	The temperature or pressure is adjusted to produce a user-specified amount of vapor.
6. ***Vapor Fraction***	The temperature or pressure is adjusted to produce a user-specified amount of vapor as a fraction of the total quantity.
7. ***Isochoric***	The temperature or pressure is adjusted to produce the user-specified total volume.
8. ***Set pH***	The software adjusts the flowrate of an acid or basic titrant to maintain an aqueous solution at a user-specified pH.
9. ***Precipitation Point***	The software adjusts the flowrate of a species until a small amount of solid precipitates.
10. ***Composition Point***	The composition point calculation is used to fix a species value. The software adjusts the flowrate of a species until it reaches the user-specified/fixed species value.
11. ***Reconcile Alkalinity***	The software reconciles the alkalinity of a solution by adjusting the flowrate of species.
12. ***Autoclave***	The software uses an isochoric (constant volume) calculation in which mass, pressure and temperature are allowed to vary. This simulates a closed pressure vessel. You may have to enable this calculation from Tools | Options | Enable Features Under Development
13. ***Custom***	With the calculations stated so far, variables are predefined. For instance, we must select either temperature or pressure as a variable in the dew point calculation. With **Custom** single point calculations, we can manipulate a wider variety of variables.

Example – Isothermal Calculation

1 m Fe in water

- ✓ Add **Stream**
  - Click on the object **"Add stream"** icon
    - or go to the Menu bar Click **on Streams >Add Stream**
- ✓ Change the name to: **Isothermal**
  - Use **<F2>** key
    - or double click
    - or right click
    - or use the Description Tab
- ✓ Go to **Definition** Tab
  - Stream parameters
    - Stream amount – size of the stream
    - Temperature and Pressure
- ✓ **Inflows**
  - Moles are the default units for all calculations

  Before entering your chemistry make sure to set up **Units**, **Thermodynamic Framework**, and **Name Display** (optional).

- ✓ Entering your chemistry
  - Fe
    - Enter the value 1 (This will create a 1 m Fe in solution)

- ✓ Stream amount
  - 56.5082 moles (calculated)

  Note: Color code for cells

  Yellow cells: not editable

  White cells: editable

  Green cells: will be calculated automatically (but can be overwritten manually)

- ✓ Click on **Add Calculation** (or click on the icon in the action panel)
  - Select Single Point
  - By default the Isothermal calculation is selected
  - Notice the changes from stream to single point calculation

- ✓ Rename the new Single point as **1 m Fe**

- ✓ Click on the **Calculate** button

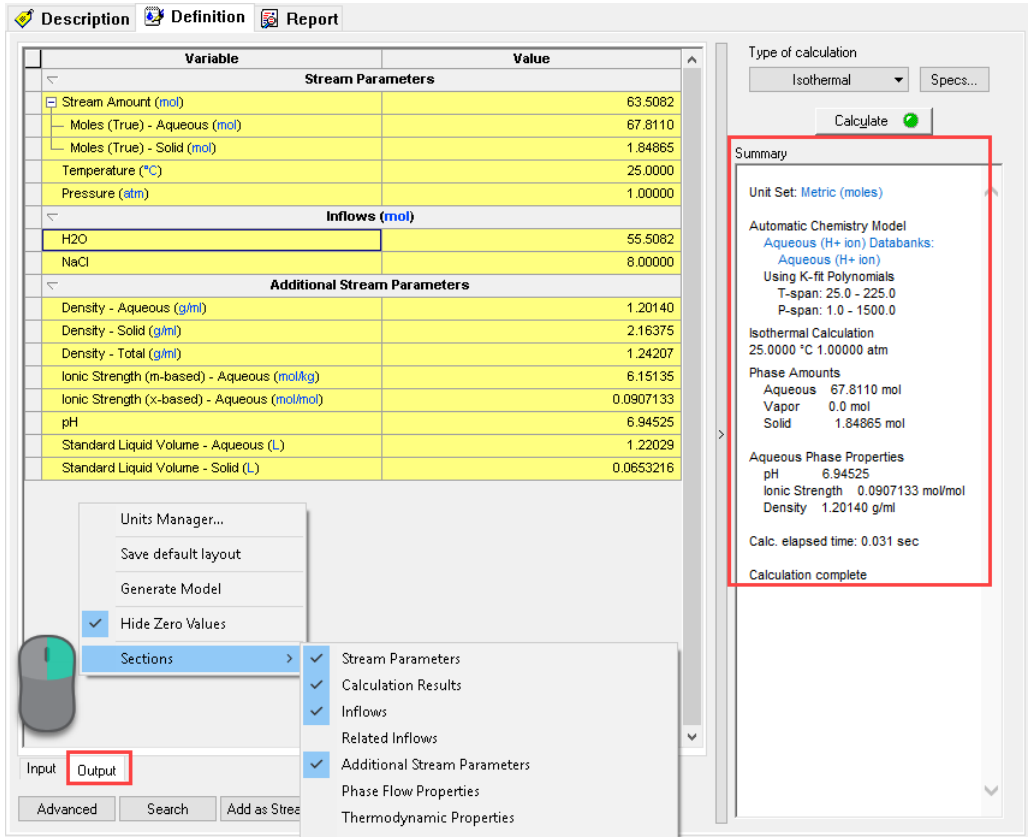
- ✓ Save your file (**File >Save as…)**

- ✓ Check the **Report** to understand the results

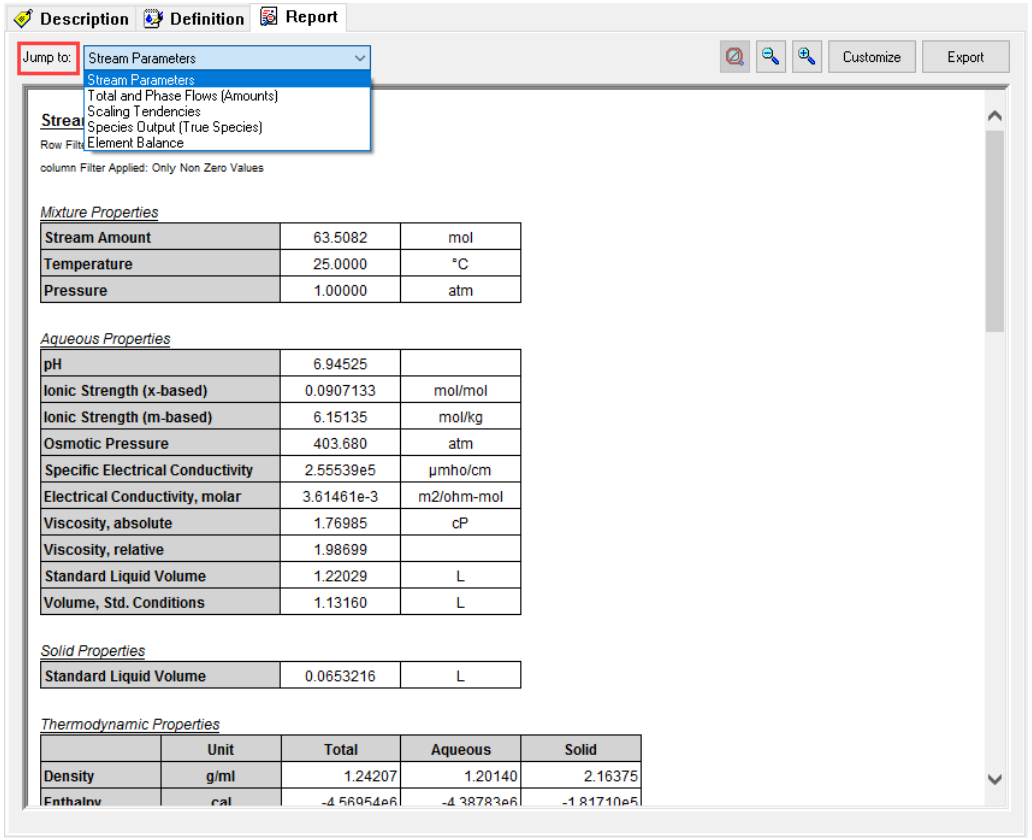
Example – Isothermal Calculation

1 m Fe in water

- Summary Box
- Output Tab
- Right click > Sections > Additional Stream Parameters



- **Report** tab
- Customize button: Add more tables that are not default



RedOx Reactions

Redox reactions

a.k.a. Half reactions

A **RedOx** (or reduction-oxidation) reaction is a type of chemical reaction that involves a transfer of electrons between two species (electrochemical reactions).

We can tell there has been a transfer of electrons if there is any change in the oxidation number between the reactants and the products.

Example: Fe in am oxygen-free environment:

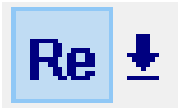
$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2\bar{e}$$

$$2H^{+}_{(aq)} + \overline{2e} \rightarrow H_{2(g)}$$

$$Fe_{(s)} + 2H^{+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)}$$

Oxidation: Al lost electrons
Reduction: H gained electrons

- In the software the RedOx reactions are turned OFF by default. The software assumes that there is not RedOx happening.
- To enable RedOx reactions we need to click on the **Re** button.



- **Note:** Only **transition metals** are turned ON.

Example – Redox

1 m Fe in water

1. Go to the **Add Calculation** button and select **Single Point** calculation

2. Select **Isothermal** Calculation
   - Rename it ***Fe Oxidation***

3. Turn on **Redox** (Re button)
   - Or Chemistry>Model Options > RedOx

4. Click **Calculate**

5. Go to the **Report** tab

Electrochemical Reaction

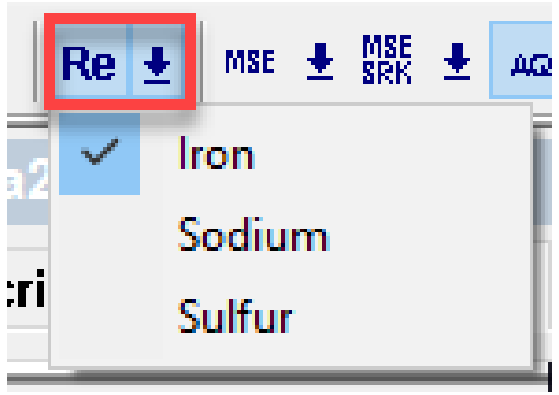
$$Fe_{(s)} + 2H^{+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)}$$

Hydrolysis and Precipitation Reactions

$$Fe^{2+}_{(aq)} + 2H_2O \rightarrow Fe(OH)_2 \downarrow + 2H^{+}$$

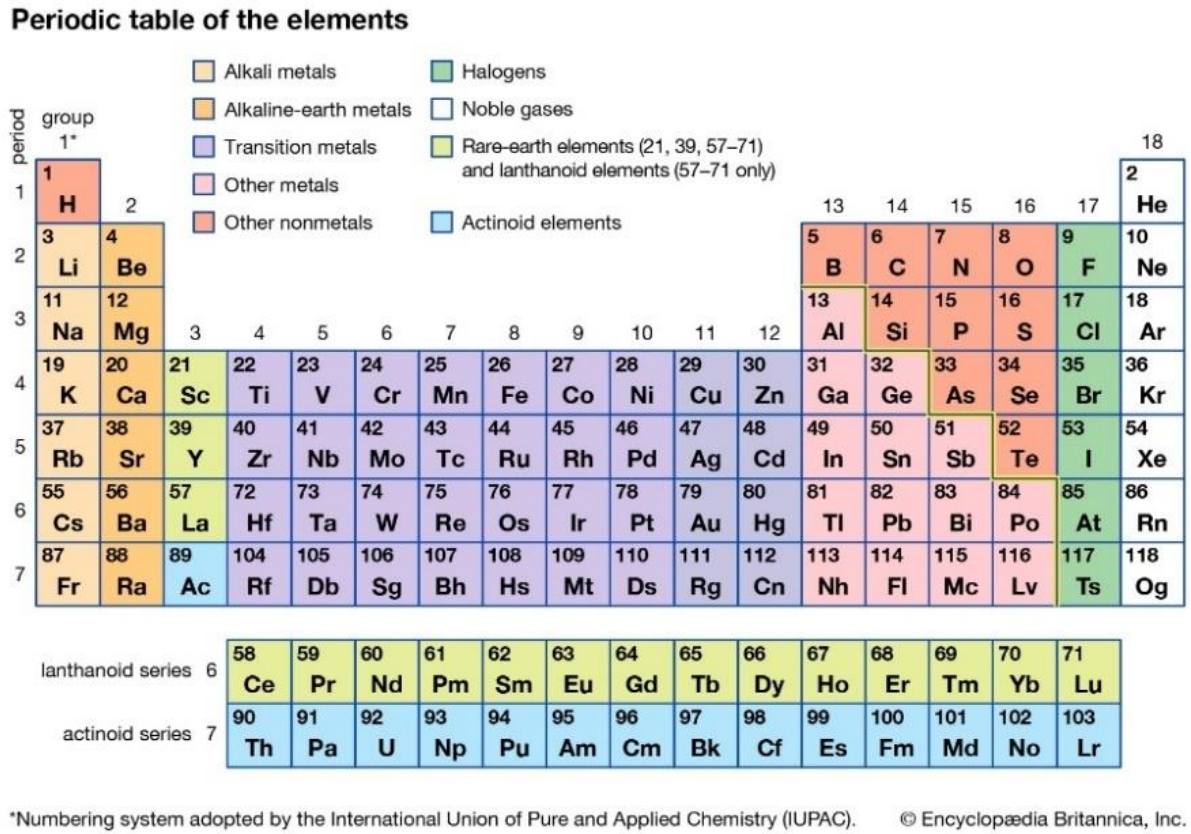
Example – Redox

Fe – Na_2S system [No Transition Metals]



Note: By default only the transition metals are turned ON.
Not all the oxidation states for RedOx reactions are allowed.

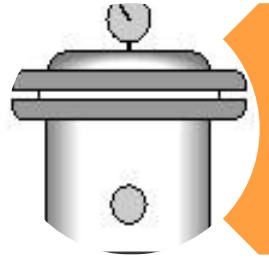
- Go to the **Add Calculation** button and select **Single Point** calculation
- Select **Isothermal** Calculation
  - Rename it ***Fe – Na2S***
- Add
  - Na2S – 0.1 moles
  - Turn on Redox Reactions and check the drop-down arrow
- Click **Calculate**
- Go to the **Report** tab
- Re-run the case with Redox ON for Sulfur (optional)



Some calculations

Dew point - Condensation

Set pH



Autoclave

Example – Dew Point

Sour Natural Gas

- ✓ Add a new **Stream**
- ✓ Rename it ***Dew Point***
- ✓ Select the **MSE** Framework
- ✓ Click on the **Units Manager** Icon
  - Select **Metric | Batch | Mole Frac.**
- ✓ Set
  - Stream Amount = **100 moles**
  - T = **120 C**
  - P = **1 atm**
- ✓ Add **Inflows**
  - H2O – (calculated)
  - CH4 - 94 mole %
  - CO2 – 3 mole %
  - H2S – 1 mole %
- ✓ Go to the **Add Calculation** button
  - Select **Single Point** calculation
- ✓ Select **Dew point** as Type of Calculation
  - Name it ***DPT***
- ✓ Click the **Calculate**, and see Results
- ✓ Repeat the same example to calculate the DPP
  - Copy and paste the previous single point calc.

Example – Set pH

Neutralizing Acetic Acid

- ✓ Add a new **Stream**
- ✓ Rename it ***Set pH***
- ✓ Select the **MSE** Framework
- ✓ Add Acetic Acid – 1 mol
  - The software will change it to CH3COOH, since Formula is the default display name style
- ✓ Go to the **Add Calculation** button and select **Single Point** calculation
- ✓ Select **Isothermal** as Type of Calculation
  - Name it ***Acetic Acid – Isothermal***
  - Check the pH
- ✓ Add another **Single Point** calculation
- ✓ Select **set pH** as Type of Calculation
  - Name it ***Acetic Acid – Neutralized***
- ✓ Target pH = 7.0
- ✓ Click the Calculate
- ✓ Results
  - 0.99 moles were needed to neutralized 1 mol of Acetic Acid.

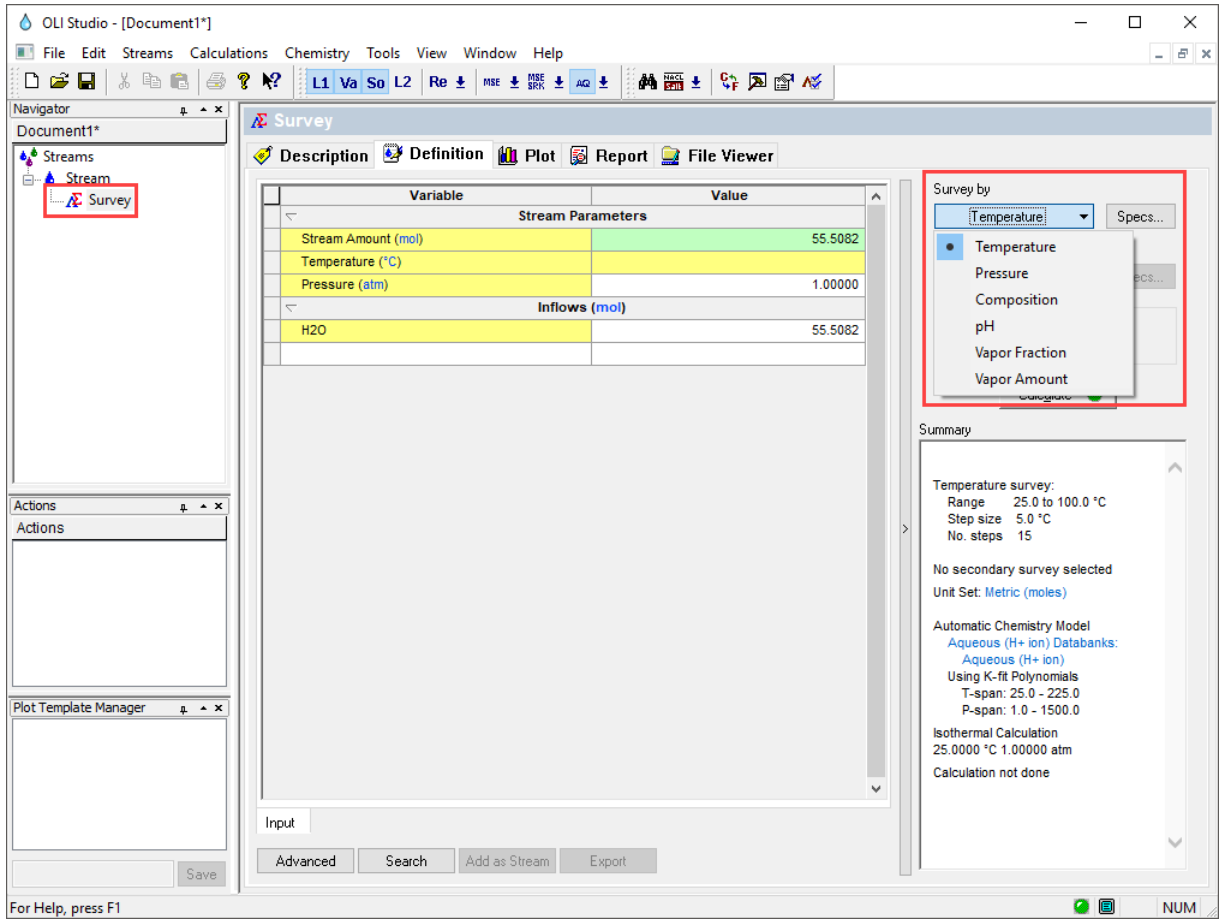
Survey Calculations

Survey Calculations

Survey calculations are single point calculations strung together in series. They are also referred to as multiple point calculations.

There are three different ways to set up surveys:

- **Single Survey:** These calculations allow the user to designate one independent variable.
    - The predefined single surveys are by: Temperature, Pressure, Composition, pH, Vapor Fraction, and Vapor Amount.
- **Dual Survey:** These calculations allow the user to designate two independent variables, e.g. Temperature and Pressure
- **Survey by changing the single point calculation type:** By default, the isothermal calculation is selected for survey calculations. If the user wants to study the solubility of a salt in solution, it is possible to change the survey from **Isothermal** to the **Precipitation Point** calculation type.

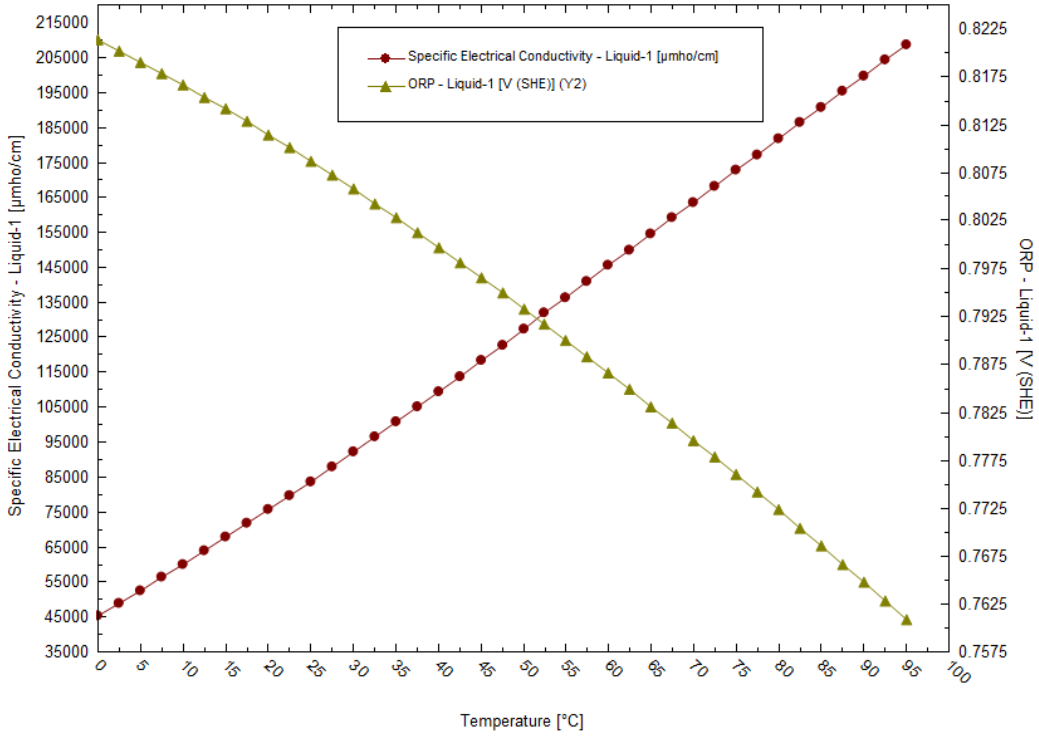


Example – Temperature Survey

Electrical Conductivity and the ORP* of a 1 m NaCl solution vs T

- ✓ Add a new **Stream**
- ✓ Rename it ***NaCl solution - Surveys***
- ✓ Select the **MSE** Framework
- ✓ **Units**: Metric-Batch-Conc.
- ✓ **Inflows**
  - H2O – Calculated
  - NaCl – 58500 mg/L
  - O2 – 8 mg/L
- ✓ Go to the **Add Calculation** button and select **Survey** calculation
- ✓ Select Survey by **Temperature**
  - Name it ***Elec. Conductivity and ORP vs T***
  - Select the **Re** button – this will enable to study the ORP
- ✓ Go to the **Specs…** button
  - Temperature Range: 0-95 ºC with increments of 2.5 ºC
- ✓ Click the **Calculate**, and see the **Plot** Tab

- ✓ Click on the **variables** button
  - **Thermodynamic Properties** > **Specific Electrical Conductivity** (Y1-Axis)
  - **Additional Stream Parameters** > **ORP** (Y2- Axis)

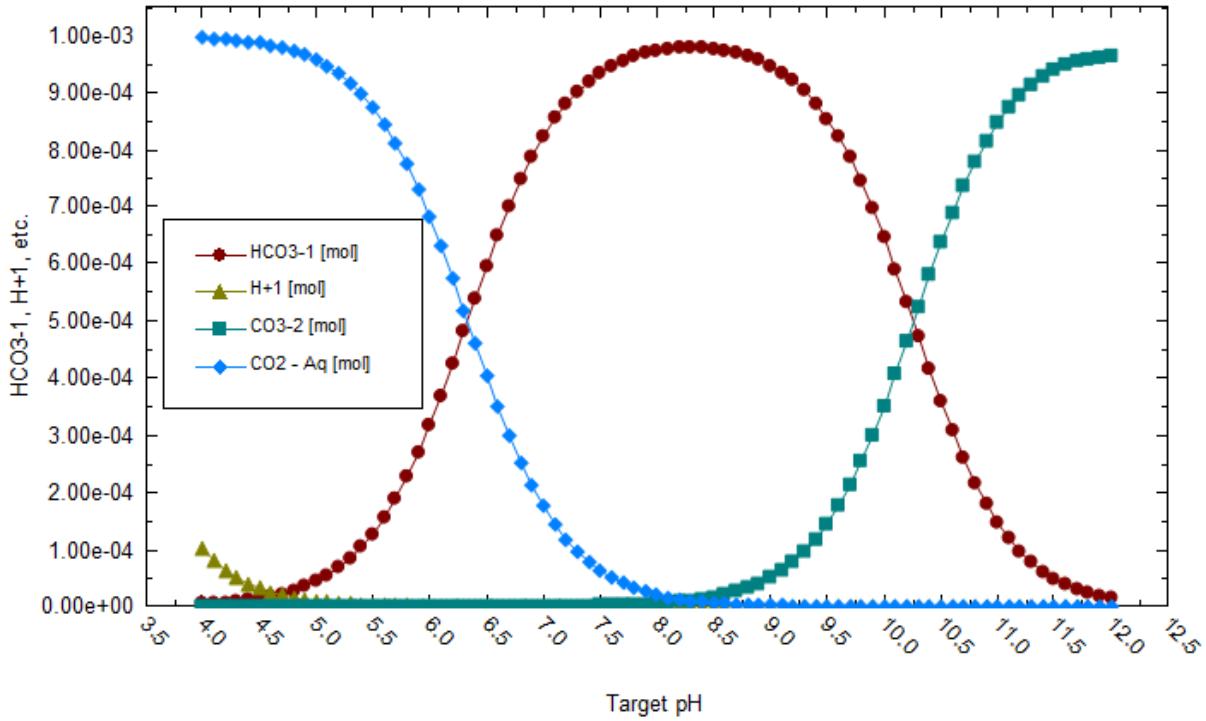


*ORP = Oxidation Reduction Potential of the solution

Example – pH Survey

The Carbonic system as a function of pH

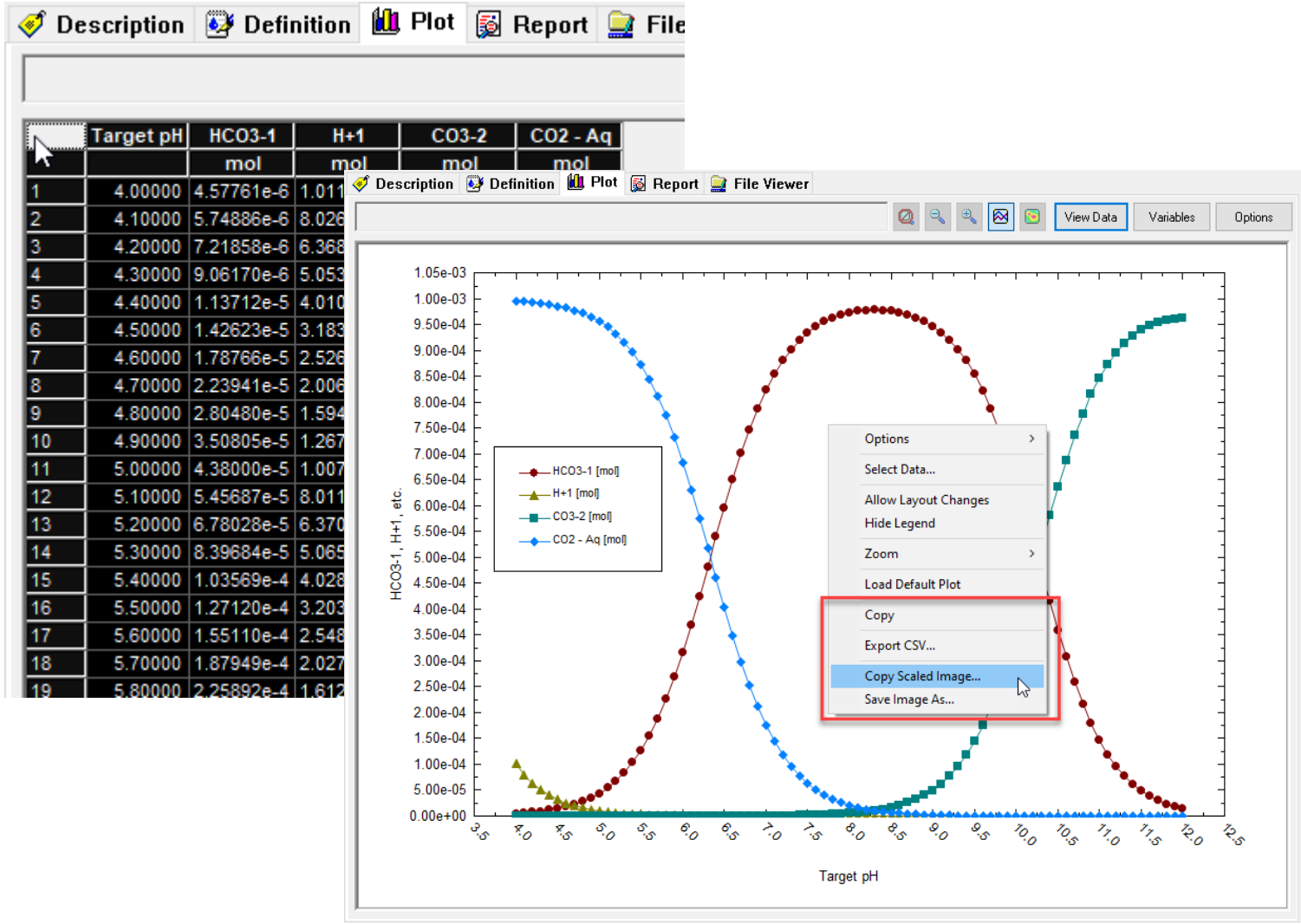
- ✓ Add a new **Stream**
- ✓ Rename it ***pH Survey***
- ✓ Select the **AQ** Framework
- ✓ Units: Metric-Batch-Moles
- ✓ Inflows
  - CO2 – 0.001 moles
- ✓ Go to the **Add Calculation** button and select **Survey** calculation
- ✓ Select Survey by **pH** as the Survey type
  - Change the name to **carbonic system**
- ✓ Go to the **Specs…** button
  - Default titrants are HCl and NaOH (leave defaults)
  - pH Range: 4-12 with increments of 0.1
- ✓ Click the **Calculate**, and see the **Plot** Tab
- ✓ Go to the **Variables** button
  - Species of Interest are: CO2-Aq, HCO3-1, CO3-2, and H+



Exporting Data and Image

✓ Exporting/Copying Data/Image options:

- **Ctrl+C** and **Crtl+V**
- Or Right-Click mouse and select **copy**
- Or Right-Click mouse and select **Export CSV**
- Or Click on the View Data button and then **Ctrl+C** and **Crtl+V**
- Right-Click mouse and select **Copy Scaled Image**



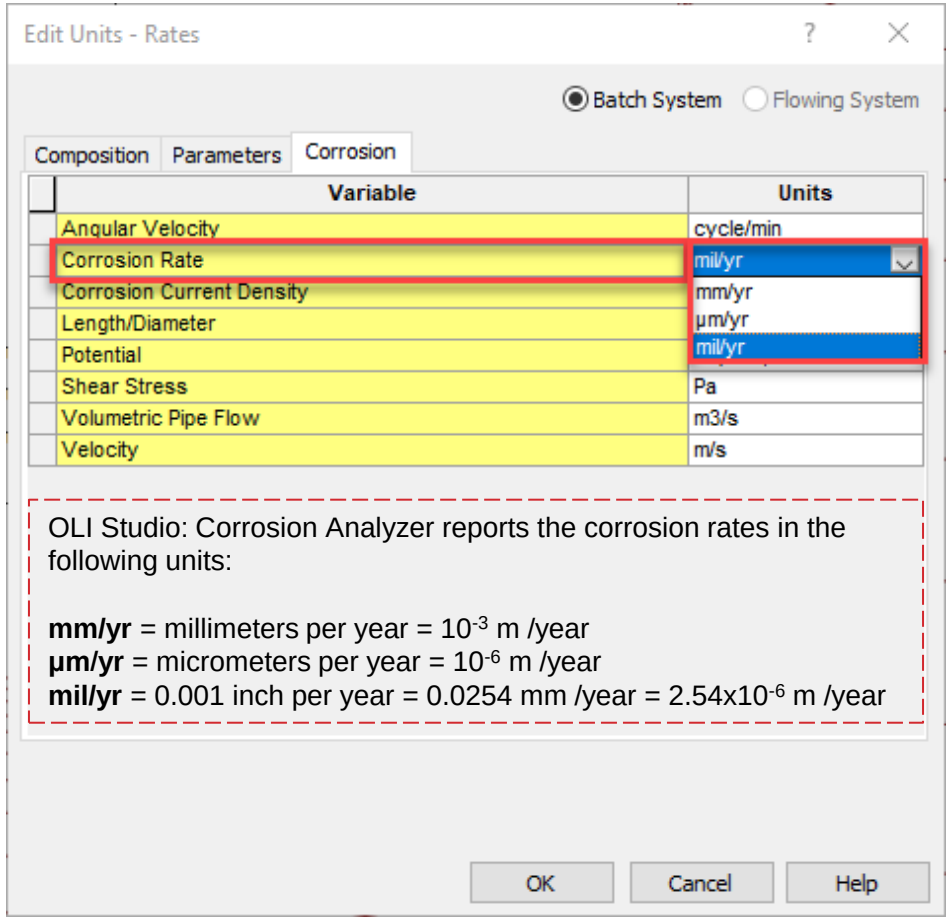
Corrosion Rate Calculations

AQ – framework only

Example – Corrosion Rates

Corrosion Rate of Carbon Steel 1018

- ✓ Add a new Stream
  - Rename it ***Corrosion Rates***
- ✓ Select the **AQ** Framework
- ✓ Change the **units** to Metric | Batch | Mass Frac.
  - Change the corrosion rate units to **mil/yr**
- ✓ Inflows
  - H2O – Calculated
  - NaCl – 3.5 wt%
  - O2 – 8e-4 wt%
- ✓ Go to the **Add Calculation** button and select **Corrosion Rates** Calculation – notice that the **Redox** button is turned ON
  - Select **Single Point Rate**
  - Rename it ***CS-1018***
- ✓ Select **Carbon Steel 1018** as the **contact surface**
- ✓ Click **Calculate** and Analyze the **Result**



Example – Corrosion Rates

Results - Overview

- **General corrosion rate**

	Temperature	Corrosion Rate	pH
	°C	mil/yr	
1	25.0000	5.04952	6.99032

- **Localized Corrosion**

	Temperature	Corrosion Potential	Repassivation Potential	Maximum Pit Current Density
	°C	V (SHE)	V (SHE)	A/sq-m
1	25.0000	-0.459350	-0.499125	0.0470029

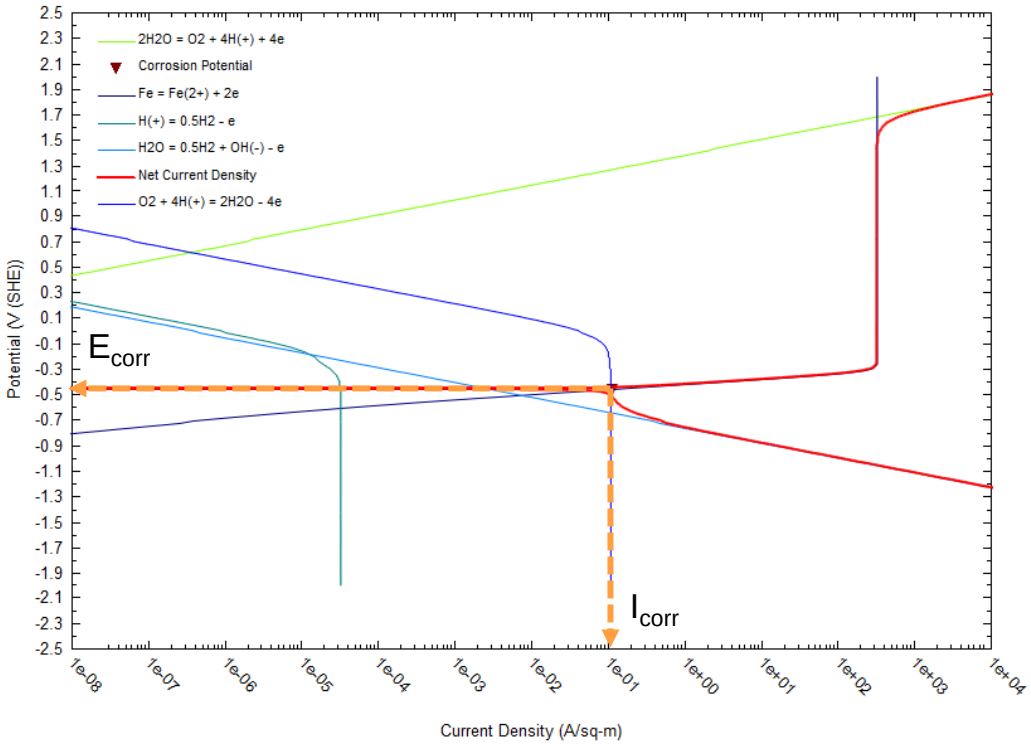
If **Ecorr > Erep** localized corrosion is predicted

Ecorr = Corrosion Potential

Erep = Repassivation Potential

Maximum Pit Current Density = The worst-case pitting rate

- **Polarization Curve**



Corrosion Rates and Polarization Curves

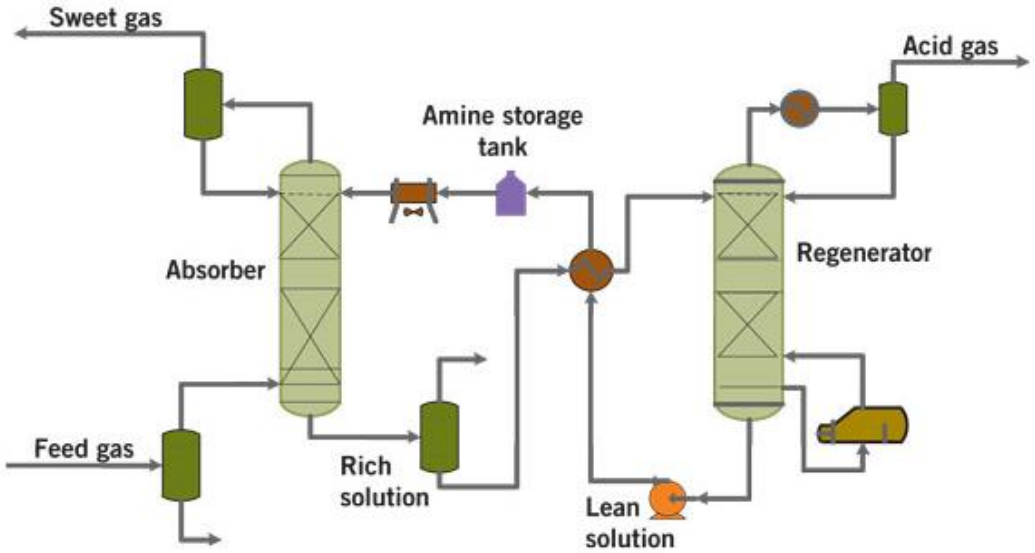
Gas Condensate Corrosion

Gas condensates from alkanolamine gas sweetening plants can be highly corrosive.

Diethanolamine is used to neutralize (sweeten) a natural gas stream. This removes carbon dioxide and hydrogen sulfide. The off gas (acid gas) from the regeneration is highly acidic and corrosive.

The **Corrosion Analyzer** will be used to:

- ✓ Determine the **dew point** of the acid gas
- ✓ Remove the condensed phase and perform corrosion rate calculations



Example – Corrosion Rates

Calculating the Dew Point Temperature

- ✓ Add a new **Stream**
  - Rename it ***Acid Gas***
- ✓ Select the **AQ** Framework
- ✓ Change the **units** to Metric | Batch | Mole Frac.
  - Change the corrosion rate units to **mil/year**
- ✓ Add the chemistry in the table to the right →
- ✓ Go to the **Add Calculation** button and select **Single Point** Calculation
  - Select **Isothermal,** rename it ***Isothermal_1***
  - Select **Dew Point,** rename it ***Dew Point T***
- ✓ Click **Calculate**
- ✓ Go to the **Report** tab

Conditions and composition of Acid Gas

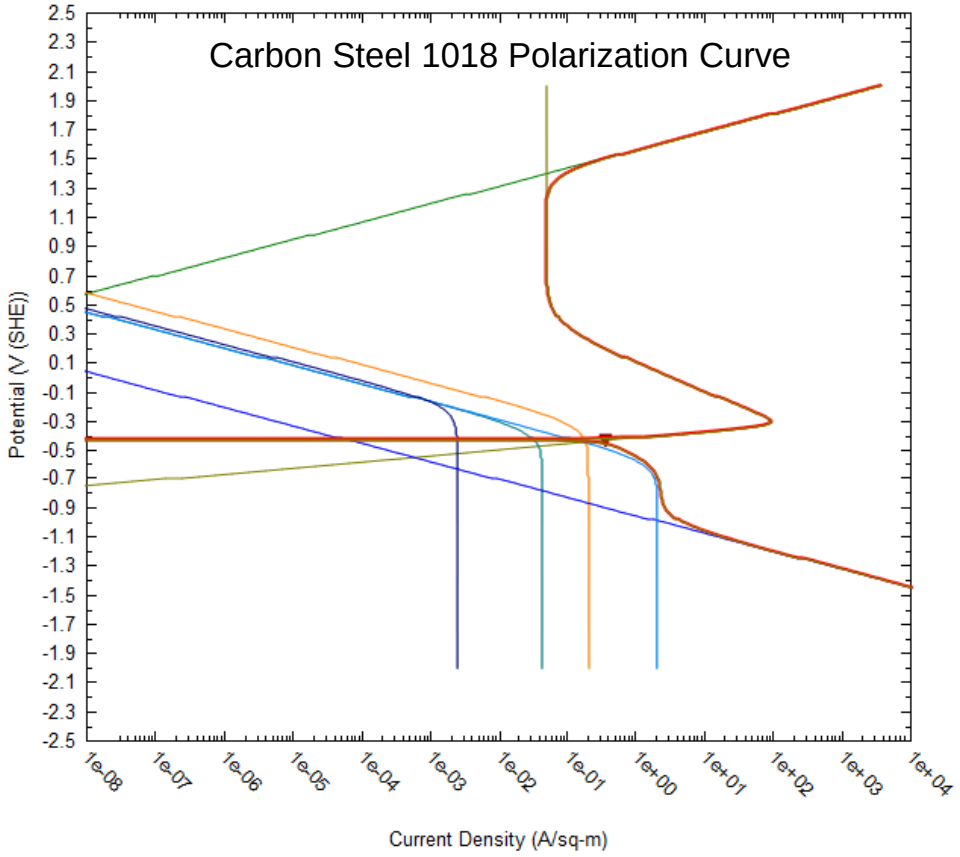
Temperature	38 °C
Pressure	1.2 atm

Species	Concentration (mole %)
H_2O	5.42 (Calculated)
CO_2	77.4
N_2	0.02
H_2S	16.6
CH4	0.50
C2H6	0.03
C3H8	0.03

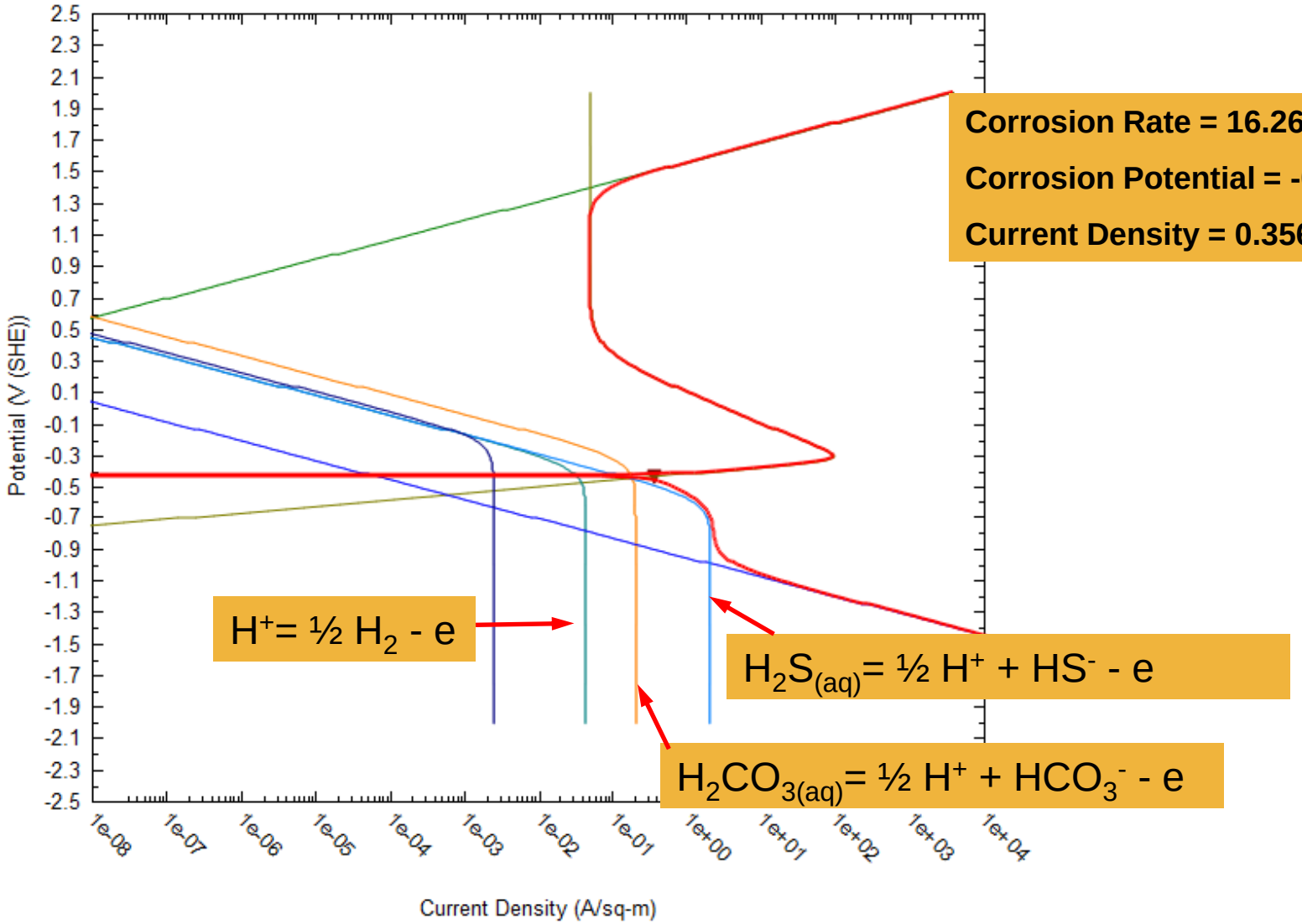
Example – Corrosion Rates

Calculating the Corrosion Rates of Carbon Steel 1018 and 13% Cr

- ✓ Select the **Dew Point T** Calculation
- ✓ Right click on it and **Add as Stream**
  - Name it: ***Gas Condensate***
  - Select the **aqueous** phase only
- ✓ Go to the **Add Calculation** button and select **Corrosion Rates**
  - Select **Single Point Rate**
  - Name it: ***CS 1018 - CR***
- ✓ Flow Type: **Static**
- ✓ Select **Carbon Steel 1018** as the **Contact Surface**
- ✓ Click **Calculate**
- ✓ Go to the **General Corrosion** tab and **Polarization Curve** tab
- ✓ Do the same for **13%Cr Stainless Steel**



Carbon Steel 1018 Corrosion @ Dew Point



Corrosion Rate = 16.26 mil/yr

Corrosion Potential = -0.437 V (SHE)

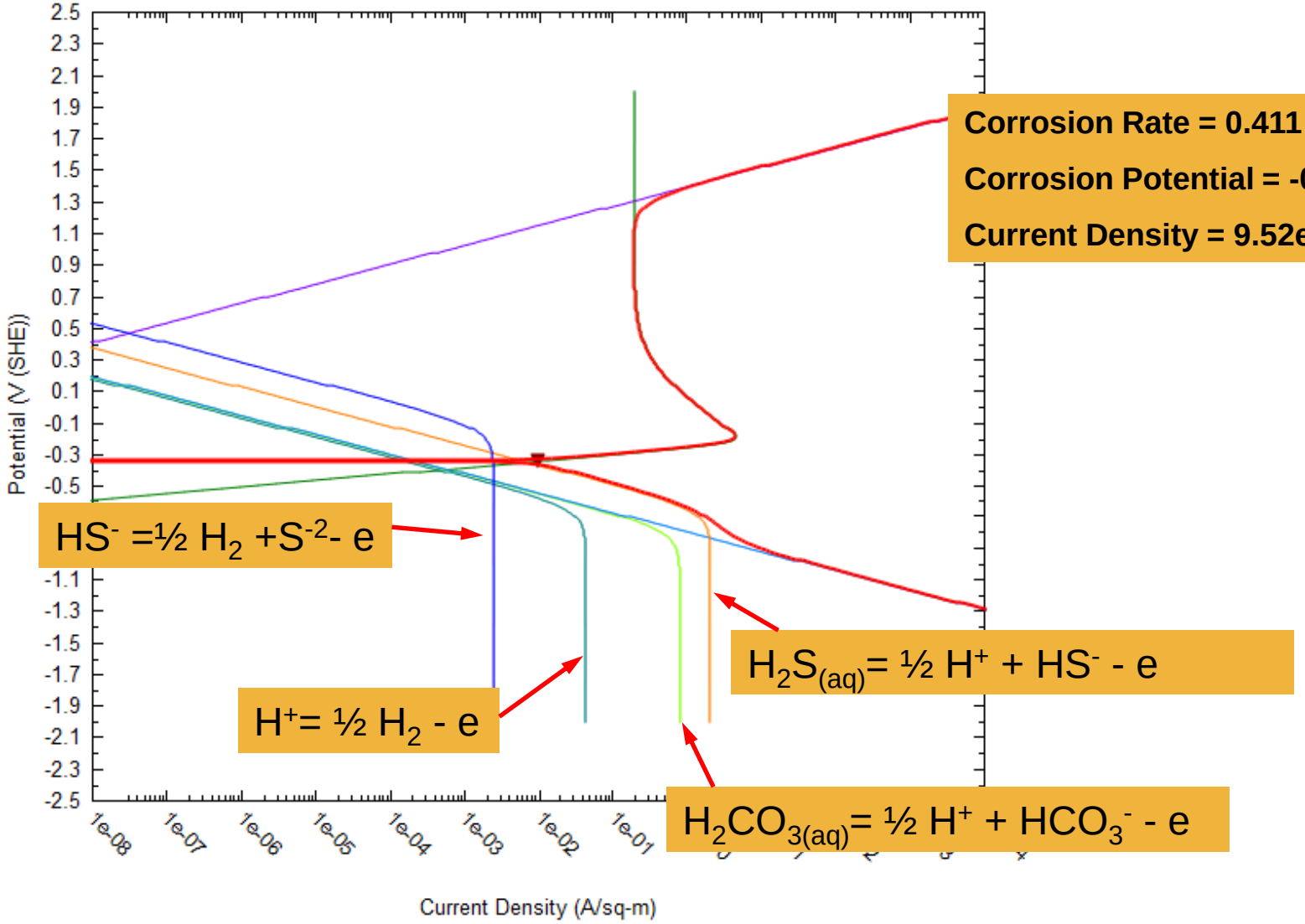
Current Density = 0.356 A/m²

$H^+ = ½ H_2 - e$

$H_2S_{(aq)} = ½ H^+ + HS^- - e$

$H_2CO_{3(aq)} = ½ H^+ + HCO_3^- - e$

13 % Cr Steel Corrosion @ Dew Point



Corrosion Rate = 0.411 mil/yr

Corrosion Potential = -0.346 V (SHE)

Current Density = 9.52e-3 A/m²

$HS^- = ½ H_2 + S^{-2} - e$

$H^+ = ½ H_2 - e$

$H_2S_{(aq)} = ½ H^+ + HS^- - e$

$H_2CO_{3(aq)} = ½ H^+ + HCO_3^- - e$

Example – Corrosion Rates

Neutralizing with an amine (DEA)

- ✓ Select the **Acid Gas** Stream
- ✓ Add a **Single point** calculation
  - ✓ Change it to **Set pH**
  - ✓ Rename it: ***Neutralizing with Amine***
- ✓ Add **DEA** under **inflows**
- ✓ Set the **target pH = 7.5**
- ✓ Select **DEA** as the pH Base Titrant
- ✓ Click **Calculate**

- ✓ Select the **Neutralizing with Amine** Calculation
- ✓ Right click on it and **Add as Stream**
  - Name it: ***Acid Gas Neutralized w\DEA***
  - Select the **aqueous** phase only
- ✓ Go to the **Add Calculation** button and select **Corrosion Rates**
  - Select **Single Point Rate**
  - Name it: ***CS 1018 – CR - neutralized***
- ✓ Flow Type: **Static**
- ✓ Select **Carbon Steel 1018** as the **Contact Surface**
- ✓ Click **Calculate**
- ✓ Go to the **General Corrosion** tab and **Polarization Curve** tab
- ✓ Do the same for **13%Cr Stainless Steel**

Corrosion Rates and Propensity to Localized Corrosion

Oilfield Produced Water on Corrosion

- **Oxygen** in **produced water** can attack the films that passivate the steels.

- The **Corrosion Analyzer** will be used to:

  - Enter ionic inputs
  - Model the effects of chlorides and oxygen on the rates of uniform corrosion, and the propensity of pitting (localized corrosion)

1. Adding a Water Analysis

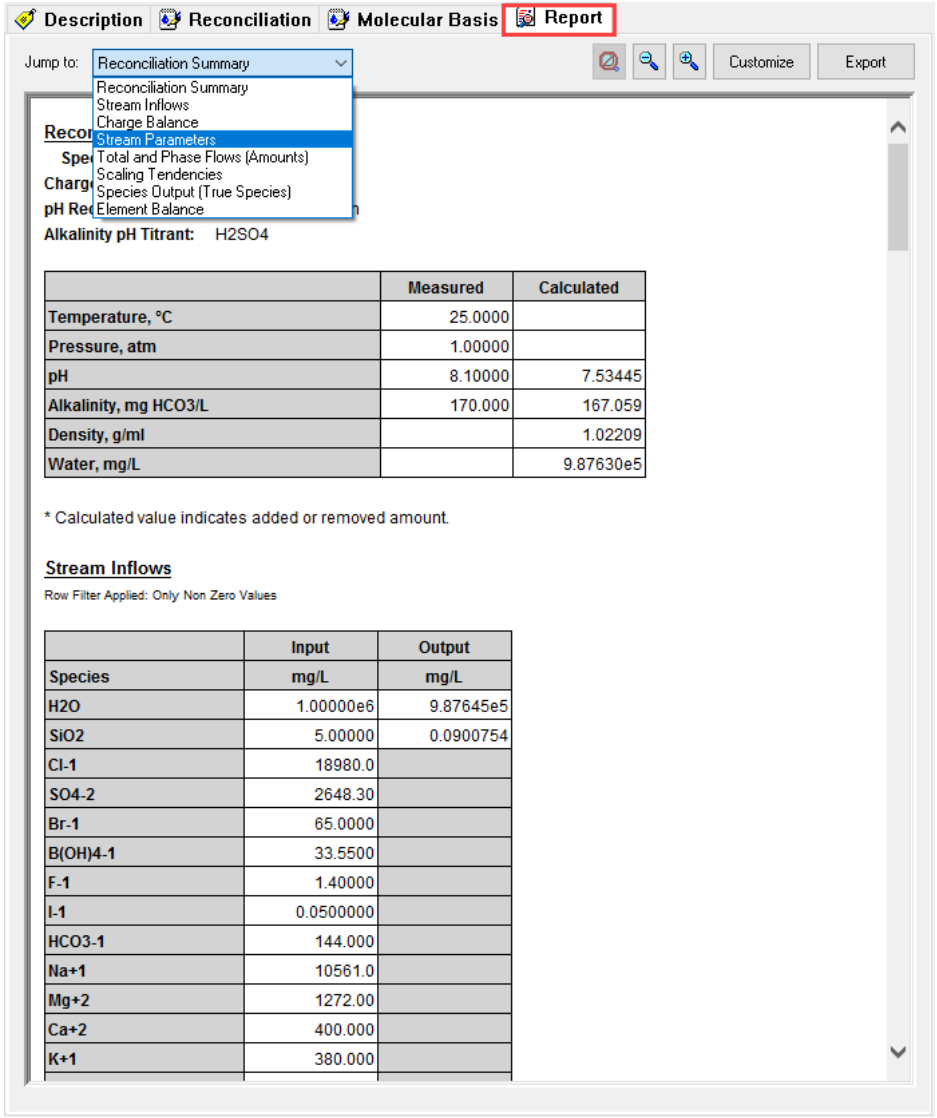
- Add a Water Analysis - 

  - Rename it *Produced Water*
- Select the **AQ** Framework
- **Enter** the data given in the table to the right →
- Go to the **Add Reconciliation** button
  - Rename it ***Deaerated Produced Water***
- Select **No Reconcile** option
- Click **Calculate**
- Go to the **Summary** section and **Report** tab

Produced Water Composition

Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	8.10000
Measured Alkalinity (mg HCO3/L)	0.0
Measured TIC (mol C/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (µmho/cm)	0.0
Neutrals (mg/L)	
H2O	
CO2	0.0
H2S	0.0
SiO2	51.0000
B(OH)3	33.0000
Total Ions (mg/L)	
P as PO4-3	0.0
Si as SiO2	0.0
B as B(OH)3	0.0
Cations (mg/L)	
Na+1	10550.0
K+1	380.000
Ca+2	400.000
Mg+2	1270.00
Sr+2	13.0000
Ba+2	0.0500000
Fe+2	0.0800000
Anions (mg/L)	
Cl-1	19150.0
SO4-2	2500.00
HCO3-1	144.000
HS-1	0.0
C2H3O2-1	0.0

Report Tab



- **Reconciliation Summary**

  Shows a comparison between the measured and calculated properties, in this case it shows the measured vs calculated pH

- **Stream Inflows**

  Summarizes all the species that were entered in the water analysis grid

- **Charge Balance**

  Contains the concentrations entered and the final balanced values

- **Scaling Tendencies**

  Shows the saturation ratios

Scaling Tendencies

The Scaling Tendency (ST) is the ratio of the Ion Activity Product (IAP) to the solubility product constant (K_{sp}).

$$Scale\ Tendency = S_{mineral} \cong \frac{C}{C_0} = \frac{IAP}{K_{sp}}$$

Where

C = measured concentration

C_0 = concentration at equilibrium

IAP = ion activity product

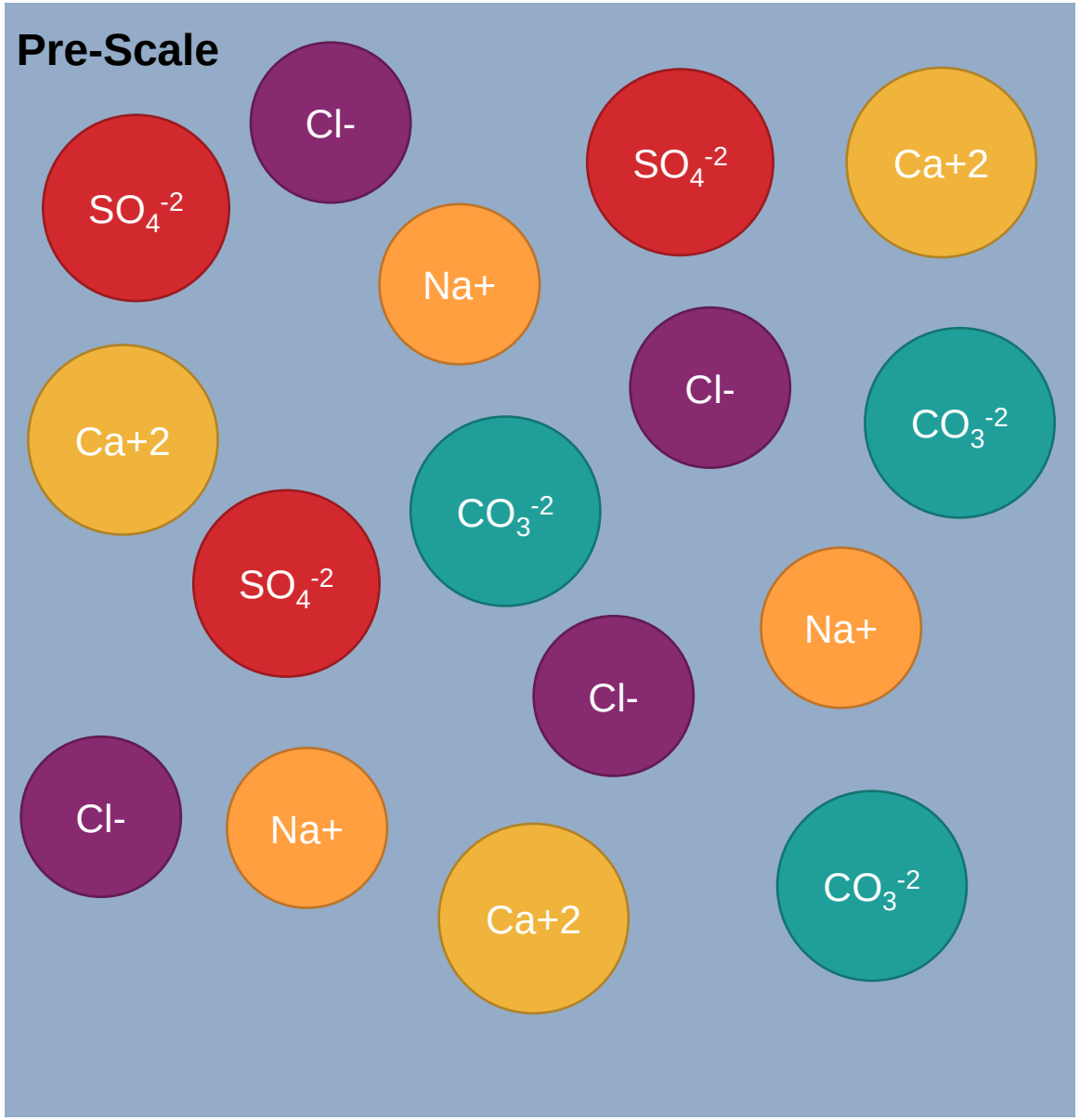
K_{sp} = Thermodynamic Solubility Product Constant

Thus,

- **ST < 1** Indicates sub-saturation, and the solid is not expected to form
- **ST = 1** Indicates saturation, and the solid is in equilibrium with water
- **ST > 1** Indicates supersaturation, and solids will form

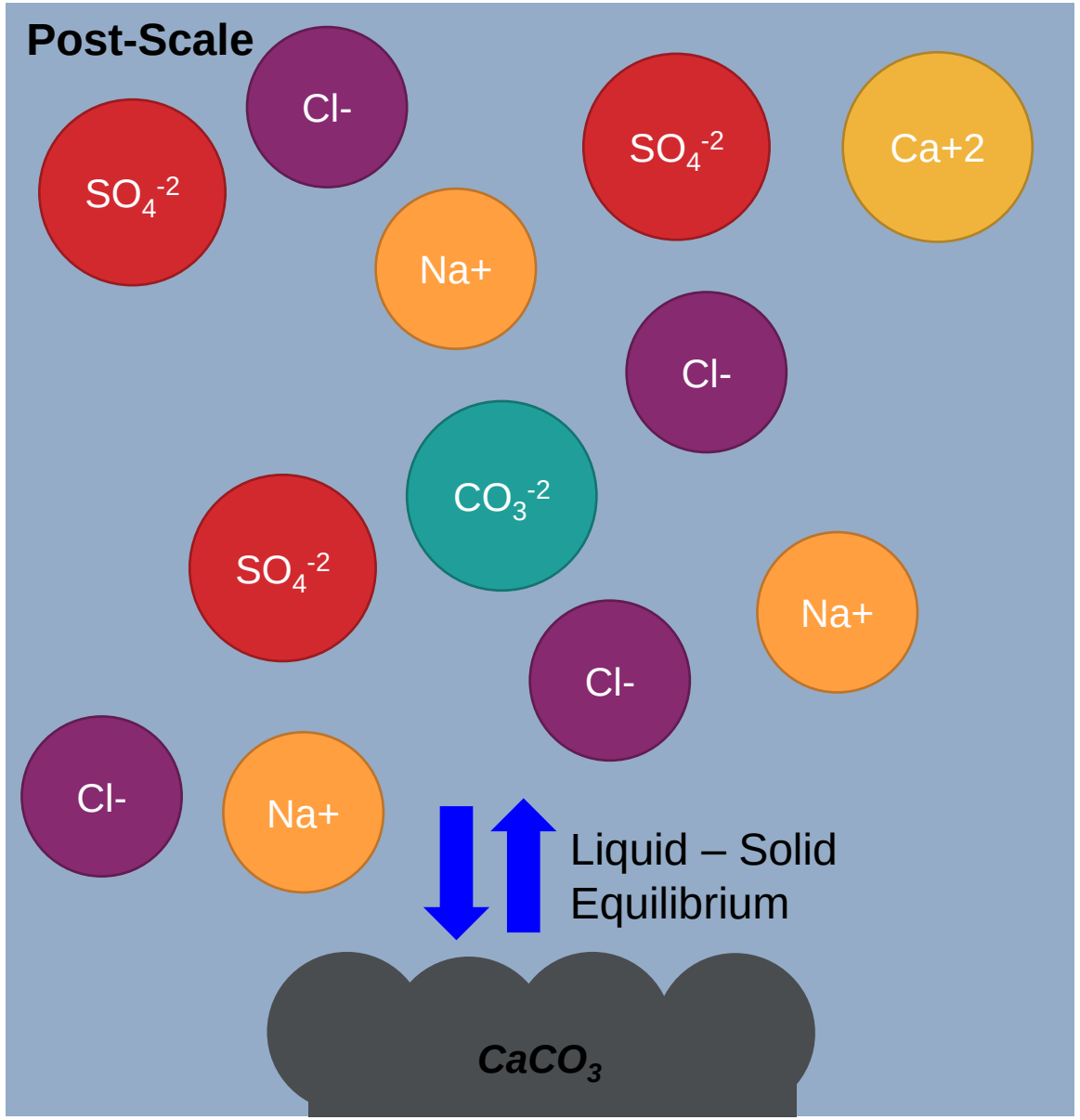
Pre-Scaling Tendency (before any solid forms)

Time = 0



Post-Scaling Tendency (after solids precipitate)

Time = ∞



Scaling Index

The Scale Index (SI) (aka: Saturation Index in the literature), is given by the following relationship:

$$SI = log_{10}\left(\frac{IAP}{K_{sp}}\right)$$

Note:

- The Scaling Index (SI) is reported in the software as SI, Index.

Thus,

- **SI < 0** Indicates sub-saturation, and the solid is not expected to form
- **SI = 0** Indicates saturation, and the solid is in equilibrium with water
- **SI> 0** Indicates supersaturation, and solids will form

2. Corrosion Rate Calculation

Corrosion of Carbon Steel in a **Deaerated** Produced Water Solution

- Select the **Molecular Deaerated Produced Water**
- Change voltage to **mV SCE,** and current density to **µA/cm²**
- Go to the **Add Calculation** button and select **Corrosion Rates**
  - Rename it *Carbon Steel*
- Flow Type: **Pipe flow**
  - Leave the default values for velocity and pipe diameter
- Select **Carbon Steel 1018** as the **Contact Surface**
  - A drop-down arrow will show the different alloys in the database
- Change to survey by **Temperature**
  - Range T = 25 - 50°C; steps = 15
- Click **Calculate**
- Repeat the same steps for **Stainless Steel 304**
- Go to the **General Corrosion** tab to analyze the corrosion rates

List of alloys	
Carbon Steel A212B	Ni
Carbon Steel A216	Alloy 600
Carbon Steel G10100	Alloy 690
Carbon Steel 1018	Alloy 825
Stainless Steel 304	Alloy 625
Stainless Steel 316	Alloy C-276
Alloy 254SMO	Alloy C-22
Duplex Stainless 2205	Alloy 28
Duplex Stainless 2207	Alloy 29
13%Cr Stainless Steel	Alloy 2335
Super13Cr Stainless Steel	Alloy 2550
Super15Cr Stainless Steel	Cu
Super17Cr Stainless Steel	CuNi 9010
Aluminum 1199	CuNi 7030
Aluminum 1100	

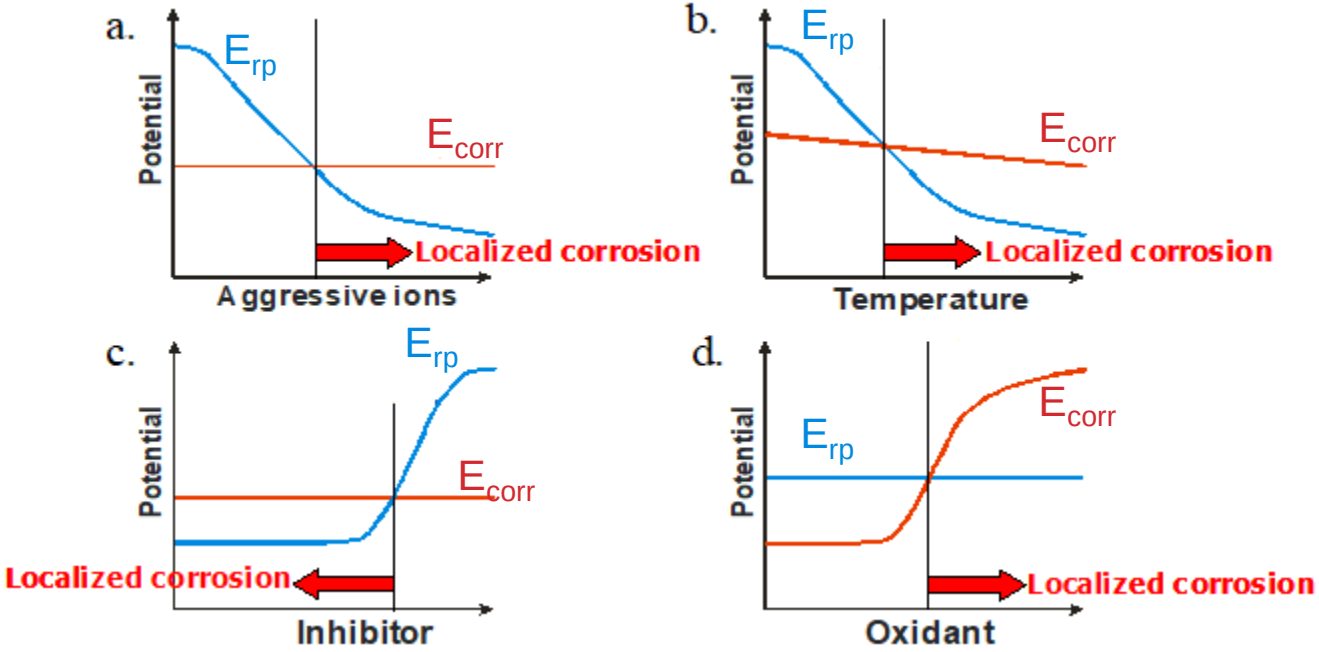
Predicting Localized Corrosion

- **Corrosion Potential (E_{corr}):** Also known as open-circuit potential or rest potential. It is the potential at which the rate of anodic dissolution of the electrode equals the rate of cathodic reactions and there is no net current flowing in or out of the electrode.

- **Repassivation Potential (E_{rp}):** The repassivation potential (also called protection potential) is the potential at which a stably growing pit or crevice corrosion will cease to grow. Thus, localized corrosion cannot occur at potentials below E_{rp}.

- The E_{rp} can be compared to the E_{corr} in the same environment to determine the alloy's susceptibility to localized corrosion.

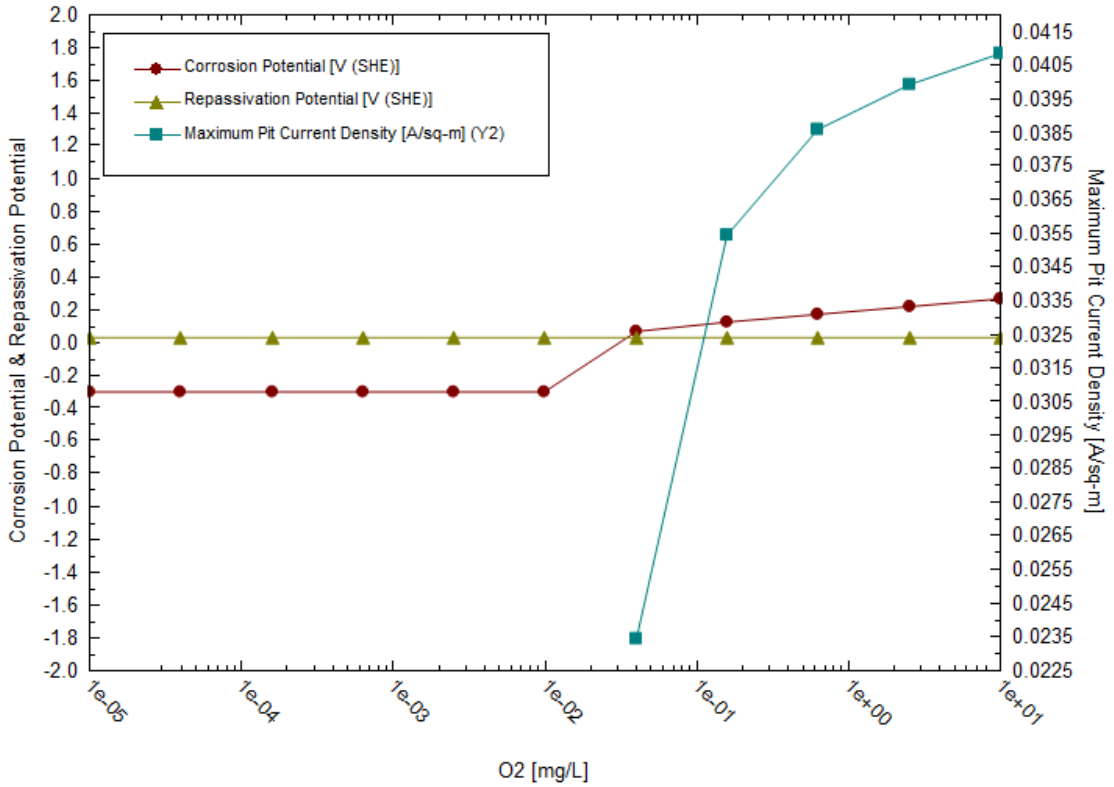
  - The arrow represents the region where $E_{corr} > E_{rp}$
  - The wider the E_{corr} - E_{rp} difference, the greater the propensity for localized corrosion



3. Corrosion Rate Calculation

Corrosion of Carbon Steel in an **Aerated** Produced Water Solution

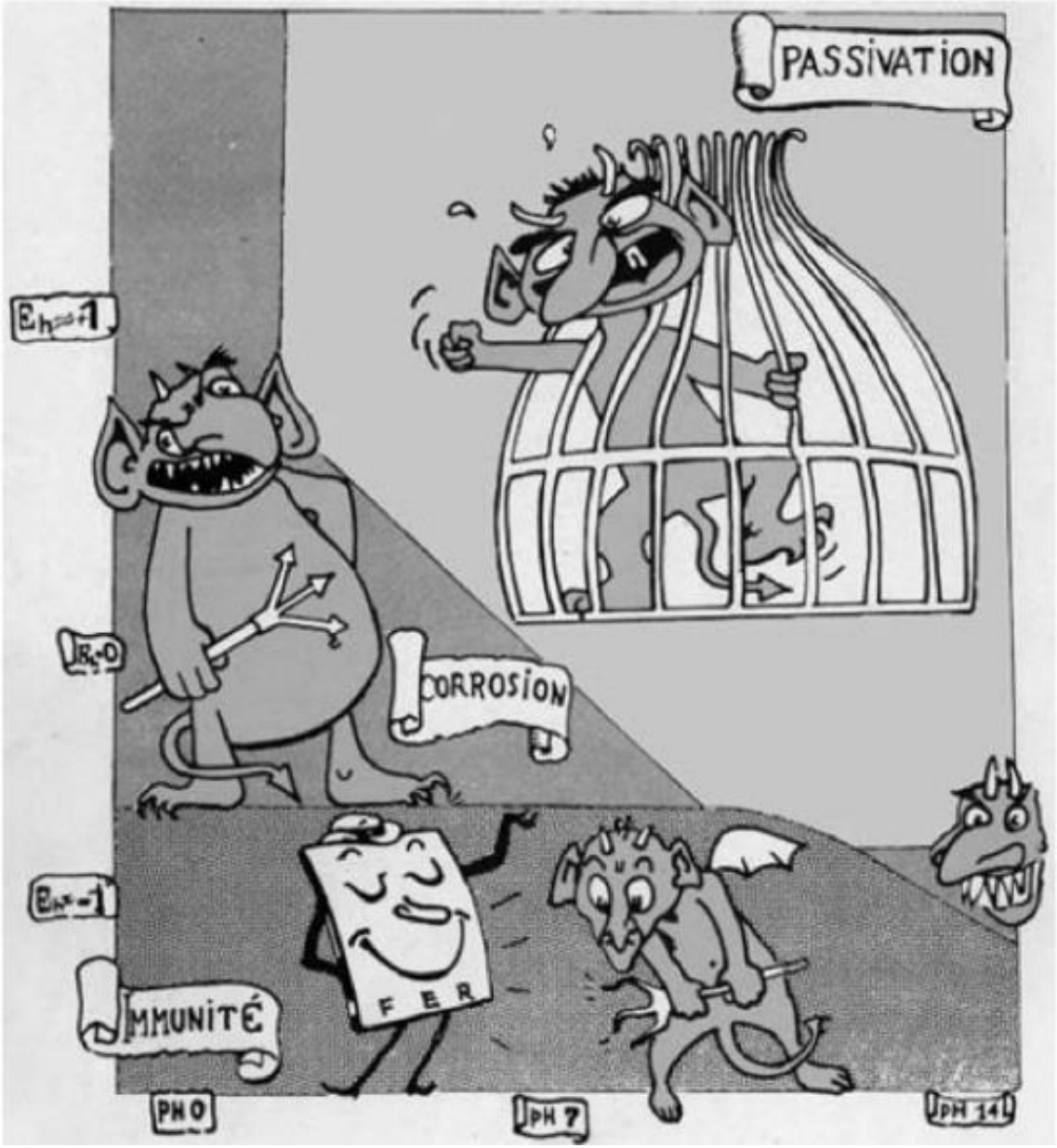
- Create a new the **Molecular Deaerated PW** stream
- Label it ***Molecular Aerated PW***
- Change the Temperature to 35°C
- Add **Oxygen** to the stream
- Change Units
  - Units manager **Metric | Batch | Conc.**
- Add a **corrosion rate** calculation and label it *Carbon Steel + O2*
- Select **Pipe Flow** and leave the default values
- Select the **Carbon Steel 1018** as the **contact surface**
- Change to survey by **Composition**
  - Click on the specs…button and select O2
  - Survey Range T = 1e-5 – 10 ppm by 10 steps; Select **log** scale
- Click **Calculate**
- Repeat the same steps for **Stainless Steel 304**
- Go to the **General Corrosion** tab and **localized corrosion** tab to see results



Pourbaix diagram

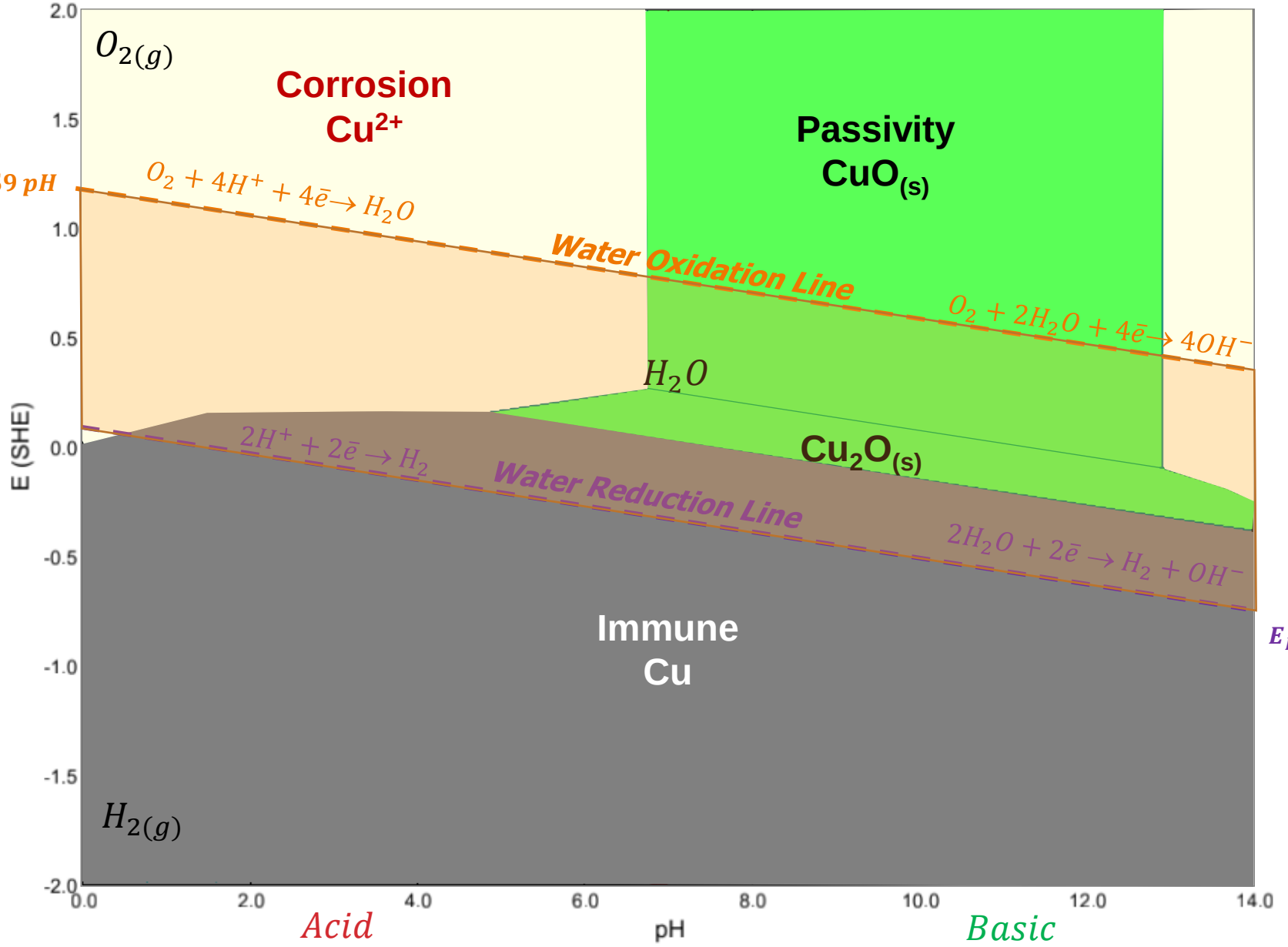
Real-solution Stability Diagrams

- Incorporates an accurate coefficient model for multicomponent systems (**AQ**, **MSE**, **MSE-SRK** thermodynamic models)
- Adds the ability to construct stability diagrams in wide range of T, P and concentrations of species
- Allows you to choose a solution component as an independent variable, so that the effect of any solution components can be studied explicitly
- Uses realistically modeled acids and bases to vary solution pH



Picture Courtesy: *Introduction to Corrosion Science by E. McCafferty*

Pourbaix Diagram of Cu in H_2O at 25 ºC and 1 atm



$$E_{O_2/H_2O} = E^0_{O_2/H_2O} - 0.059\,pH$$

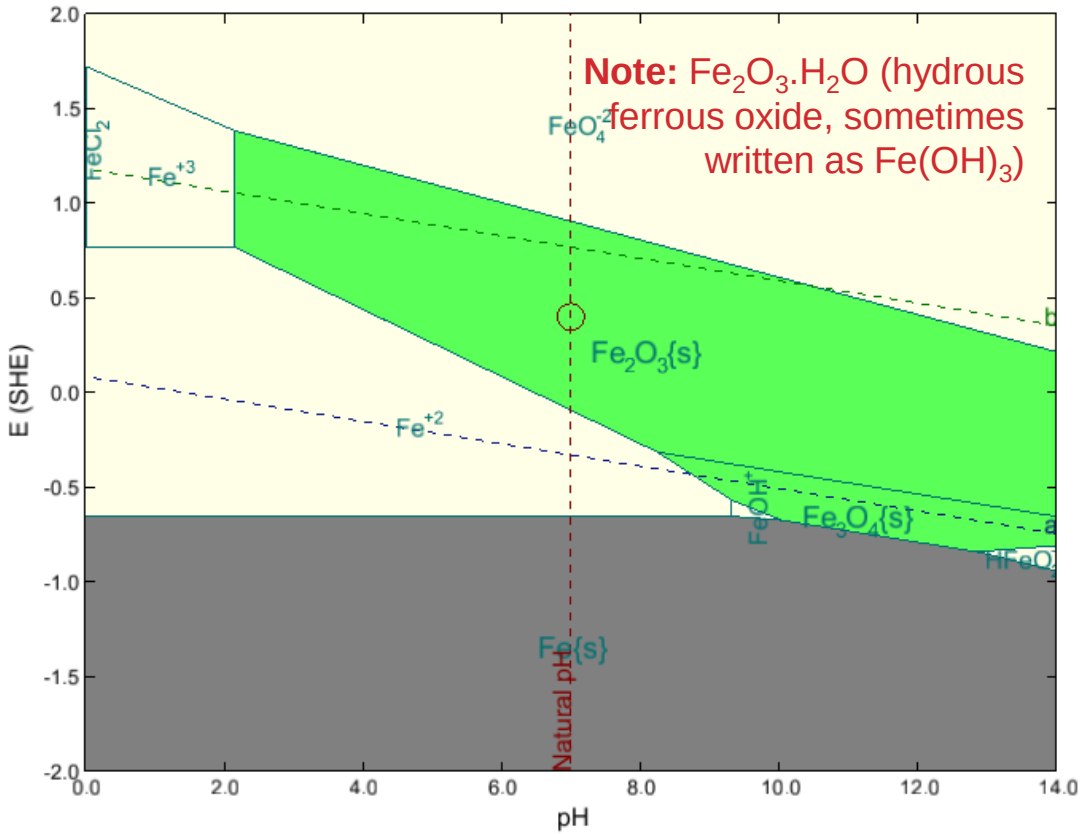
$$E_{H^+/H_2} = E^0_{H^+/H_2} - 0.059\,pH$$

Stability Diagram of Fe in Water

a.k.a. Pourbaix Diagram

- Add a new Stream
  - Rename it ***Fe Pourbaix Diagram***
- Select the **AQ** Framework
- Go to the **Add Calculation** button and select **Stability Diagram**
  - Or go to the **Actions** Panel and select the **Stability Diagram** icon
- Rename it ***Fe-H2O system***
- Add **Fe** as the **Contact Surface**
  - Show ORP and no Aqueous lines
- Click **Calculate**
- Go to the **Stability Diagram** tab

Fe-H2O system



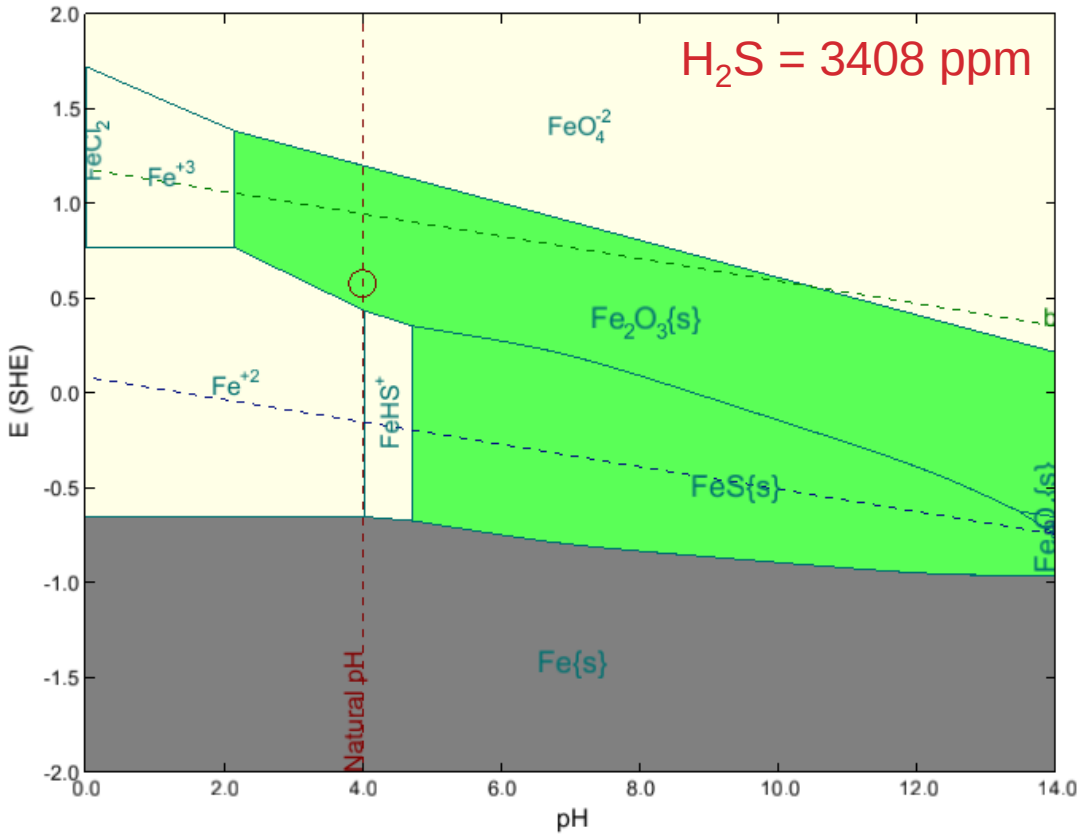
Note: The **Re** button is turned ON by default when selecting the Stability diagram calculation

Stability Diagram of Carbon Steel

Effect of H_2S

- Go to **Add Calculation** button and select **Stability Diagram**
- Rename it ***Fe-H2S-H2O system***
- Add Fe as the **Contact Surface**
- **Add** 1e-4 moles of H2S (3.4 ppm)
- Click **Calculate**
- Go to the **Stability Diagram** tab

Fe-H_2S-H_2O System

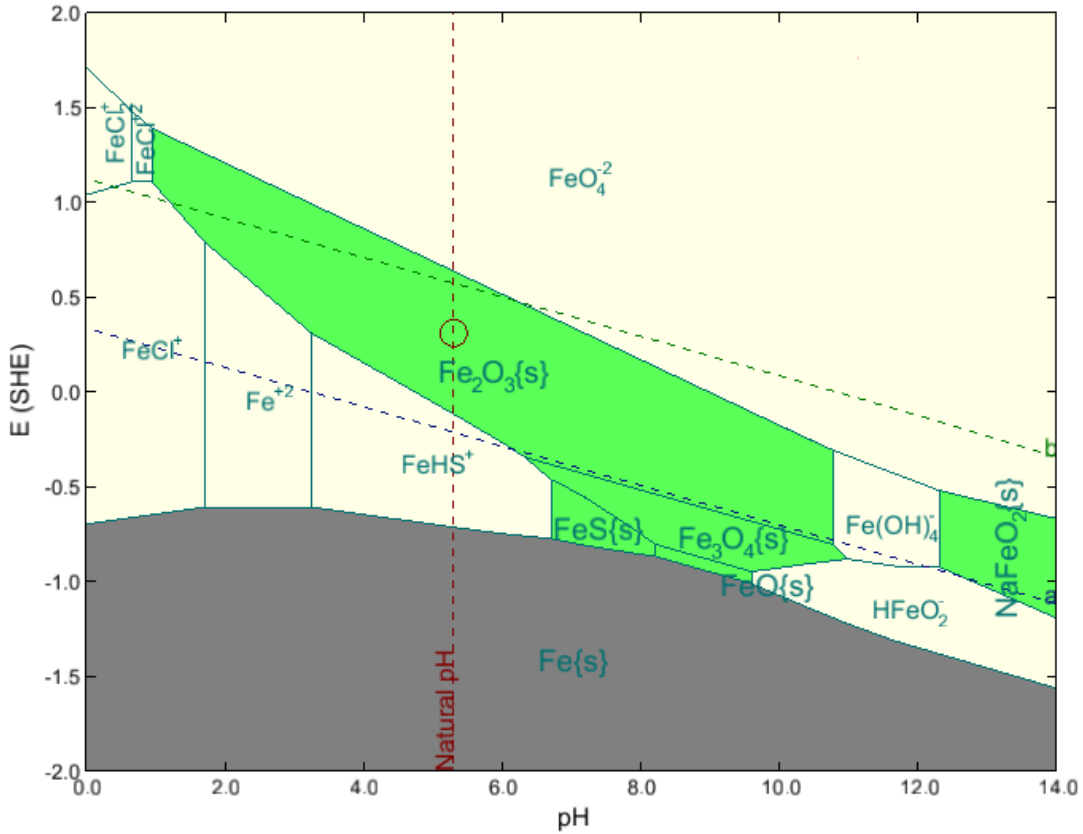


Stability Diagram of Carbon Steel

Effect of H_2S and Temperature

- Go to **Add Calculation** button and select **Stability Diagram**
- Rename it ***Fe-H2S-H2O vs T system***
- Add Fe as the **Contact Surface**
- **Add** 1e-4 moles of H2S
- **Temperature** and **Pressure** conditions
  - 25°C – 1 atm
  - 80°C – 1 atm
  - 250°C – 60 atm
- Click **Calculate**
- Go to the **Stability Diagram** tab

250°C, 60 atm

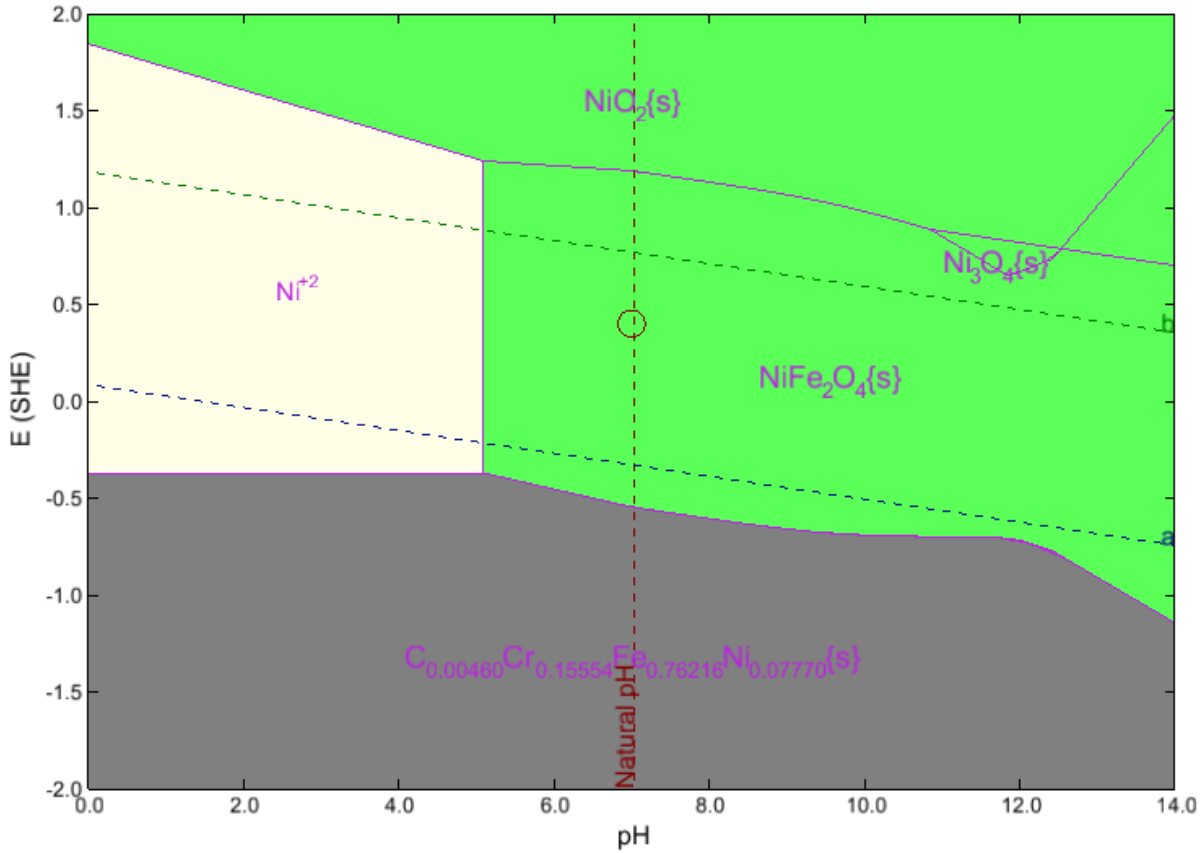


Stability Diagram of 304SS

Multiple Solvents

- Add a new Stream
  - Rename it ***Solvents***
- Select the **MSE** Framework – natural choice
- Add **Methanol**, **Ethanol**, and **1,2-Ethanediol** (Ethylene glycol)
- Set the **Water** value to **0**
- Go to the **Add Calculation** button and select **Stability Diagram**
- Rename it ***304SS-MeOH system***
- Set the **Methanol** inflow to **100 moles**
- Add **304** as the **Contact Surface**
- Click **Calculate**
- Go to the **Stability Diagram** tab

Repeat the same steps for **Ethanol** and **Ethylene glycol**



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