INTRODUCTION TO

OLI Analyzer

V11

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Introduction to OLI Analyzer

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Version: OLI Analyzer V11

Contact Information

Visit the Contact OLI Systems page at https://www.olisystems.com/techsupport to submit general inquiries, contact Technical Support, or search for an address and phone number.

If you need to contact Support, you can submit an online request via OLI Portal: https://portal.olisystems.com/

Other useful links and resources are:

- OLI Systems Portal – How to create and account: http://downloads.aqsim.com/Client%20Portal%20Instruction%20Manual.pdf
- Product Downloads: http://downloads.olisystems.com/
- OLI Systems YouTube Channel: https://www.youtube.com/OLISystems
- OLI Systems Wiki page: http://wiki.olisystems.com/wiki/Main_Page

Disclaimer

This manual was produced using the OLI Analyzer 11.0 build 1 (11.0.1). As time progresses, new data and refinements to existing data sets can result in values that you obtain being slightly different than what is presented in this manual. This is a natural progress and cannot be avoided. When large systematic changes to the software occur, this manual will be updated.

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About This Manual

This manual will provide an introductory guide for new OLI Analyzer Software users. OLI Analyzer is a software suite containing several modules including, Stream Analyzer, ScaleChem Analyzer and Corrosion Analyzer. A client's license determines which modules are enabled within the OLI Analyzer Software.

This introductory manual consists of one chapter showcasing the OLI Analyzer User Interface, and 4 main chapters showcasing the three main modules of OLI Analyzer: Stream Analyzer, Corrosion Analyzer, EVS Analyzer, and ScaleChem Analyzer.

If you have not yet installed the software, please install it following the instructions given in Installation and Security page in our Wikipage at: http://wiki.olisystems.com/wiki/Installation_and_security.

OLI Analyzer Components

Stream Analyzer

Stream Analyzer is standalone software, and it is the main interface of the OLI Analyzer. Stream Analyzer is a comprehensive thermodynamic tool that calculates speciation, phase equilibria, enthalpies, heat capacities and densities in mixed-solvent, multicomponent systems. Capabilities and features of Stream Analyzer are:

- 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.

Corrosion Analyzer

Corrosion Analyzer is a module within the OLI Analyzer. A separate license enables this module. Corrosion Analyzer is first-principles corrosion prediction tool. It is used to predict the corrosion rates of general corrosion, propensity of alloys to undergo localized corrosion, depletion profiles of heat-treated alloys, and thermodynamic stability of metals and alloys. It enables users to address the causes of aqueous corrosion by identifying its mechanistic reasons. As a result, users take informed action on how to mitigate or eliminate this risk.

Corrosion Analyzer calculates corrosion by quantifying the bulk chemistry, transport phenomena, and surface reactions through a thermophysical and electrochemical module.

- The thermophysical module calculates the aqueous solution speciation and obtains concentrations, activities and transport properties of the reacting species.

- The electrochemical module simulates partial oxidation and reduction process on the metal surface.

The tool reproduces the active-to-passive transition and the effects of solution species on passivity.

Effects of temperatures, pressure, pH, concentration, and velocity on corrosion are also included. Capabilities and features of Corrosion Analyzer are:

- Generation of Pourbaix (E vs pH) diagrams
- Calculation of general corrosion rates
- Localized corrosion susceptibility
- Heat treatment effect
- Generation of polarization curves plots

EVS Analyzer

Extreme value statistics (EVS) is one of the most powerful statistical techniques that have been used extensively to extrapolate damage (maximum pit depth) from small samples in the laboratory to larger area samples in the field.

ScaleChem Analyzer

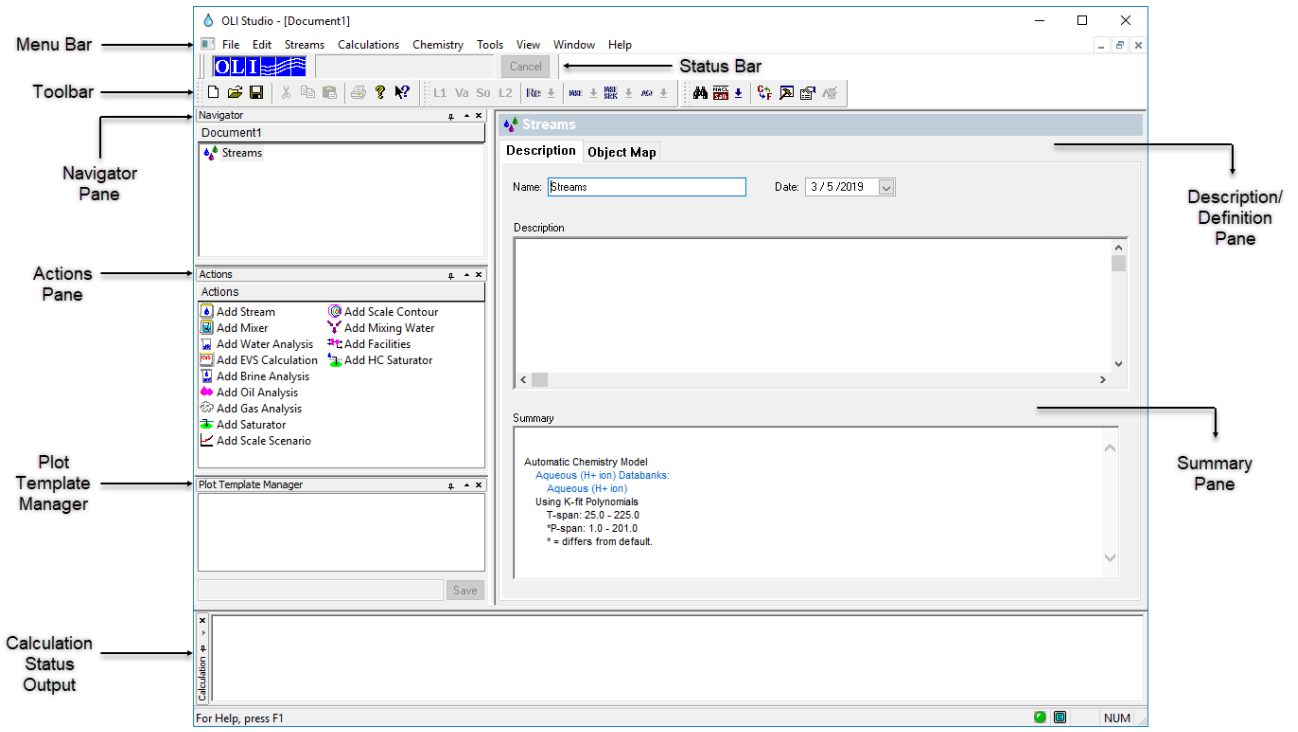
ScaleChem Analyzer is a simulation software tool that predicts scaling problems during oil and gas production. ScaleChem Analyzer simulates fluid production from the reservoir to the sales point, and computes the phase mass balance, scale tendencies, and scale mass of production fluid at each location in the production line. Capabilities and features of ScaleChem Analyzer are:

- Brine, gas and oil analysis
- Scaling scenarios
- Compatibility testing of brines using the stream mixing function
- Phase equilibrium calculation used to perform four-phase reservoir saturation, from which as whole fluid reservoir composition is determined
- Contour plots to study produced brine properties across a broad temperature and pressure range

Chapter I – The OLI Analyzer Software User Interface

General View of the User Interface

In the OLI Analyzer Software, the OLI Analyzer Desktop User Interface provides the environment to create, analyze and interpret the results of your application chemistry. In this manual, an overview of the different windows and tools that you will be using within the software, as well as how to navigate the OLI Analyzer User Interface, will be provided here.



The screenshot shown above is what you will see when you first start OLI Analyzer. You can customize the desktop to your own needs. The windows can be resized, moved, docked and detached.

Menu Bar

The Menu Bar gives access to the following options: File, Edit, Streams, Calculations, Chemistry, Tools, View, Window and Help.

File: Gives access to functionality such as New, Open, Close, and Save a file

Edit: Cut, Copy, Paste, Delete and Clear calculation results

Stream: The Streams menu contains actions that can also be performed using the Actions Pane

Calculations: The calculation menu contains all the calculations found in the Actions Pane

Chemistry: Advanced changes to the chemistry can be made here.

Tools: Gives access to tools such as component search, names manager, units manager and other customizations.

View: Gives the option to customize the view of the interface.

Window: Allows to arrange the different OLI Analyzer. documents in the window.

Help: Here you can have access to the Technical Support or any content that you may need related to OLI Software.

Tool Bar

The Tool Bar gives quick access to different functions and sits below the Menu Bar. Tools within this bar can be added, removed or repositioned. When a tool is selected (or turned ON) it is highlighted in light blue. When deselected (or turned OFF) comes back to gray.

They are laid out in the following order:

Quick access to **File:**

Quick access to **Edit:**

Quick access to **Help:**

Quick access to **Chemistry:**

Quick access to **Tools:**

Icons in the Chemistry section

In the quick access to **Chemistry** you find: Phases, Redox and Databanks.

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

L1: Liquid 1 or water-rich 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

Icons in the Tools section

A description of each icon in the Tools section is given below:

Component search:		This tool helps you to look for a component using Formula, CAS number, or via using the periodic table.
Names manager:		This tool shows you the name of components in different styles in tables and reports. The style options are: Display name, Formula or 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 into the calculations.

Navigator Pane

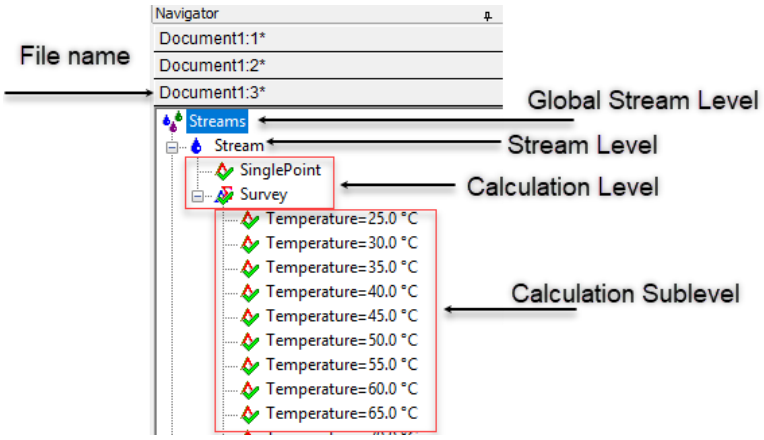
The Navigator Pane (or tree level) contains the list of streams and calculations that are active within a file. This view contains the icons and names of each action in a hierarchical tree. The Description/Definition pane changes depending on the level that is highlighted. A plus sign next to an object in the stream level indicates that that stream or object has sub-streams or branches. There are four levels: Global Stream Level, Stream Level, Calculation Level, and Calculation Sublevel.

Global Stream Level: Provides the broadest view of the navigator objects. At this level the user can define default units, default components name, and general preferred calculation options.

Stream Level: Chemistry options such as phase selection, REDOX reactions, and the 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. A more detailed explanation of calculation types can be found in Chapter II of this manual.

Calculation Sublevel: Some calculations, such as Survey calculations, have their own calculation sublevels. They can be expanded or maximized using the small icon (⊞ or ⊟) next to the calculation type.

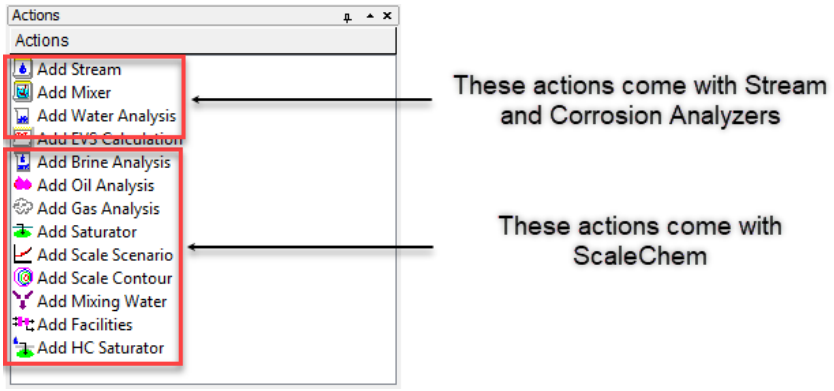


Note: A star (*) next to the file name indicates that the file has not been saved.

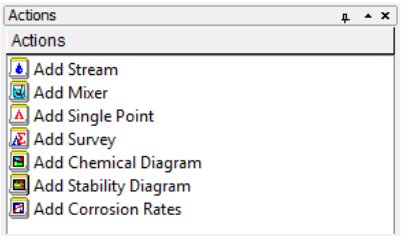
Actions Pane

This view contains selectable action icons. Each icon represents either a new stream input or new calculation. Additional actions will appear depending on what kind of stream we are working with. You can change the view of the actions pane by right clicking in the white area. You can show the icons as a List, Small Icons or Large Icons. In this case the List option was selected.

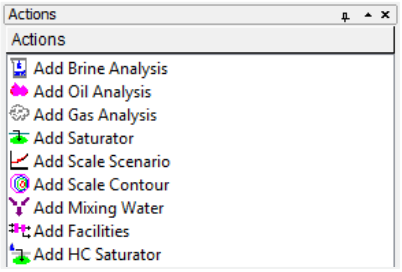
When located at the **Global Stream Level** the following action icons appear on the Actions Pane.



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

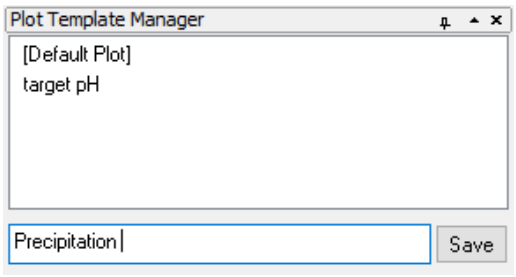


If you select an action item that belongs to ScaleChem Analyzer, this action item will be located at the **Stream Level**, and only the following action icons appear on the Actions pane.



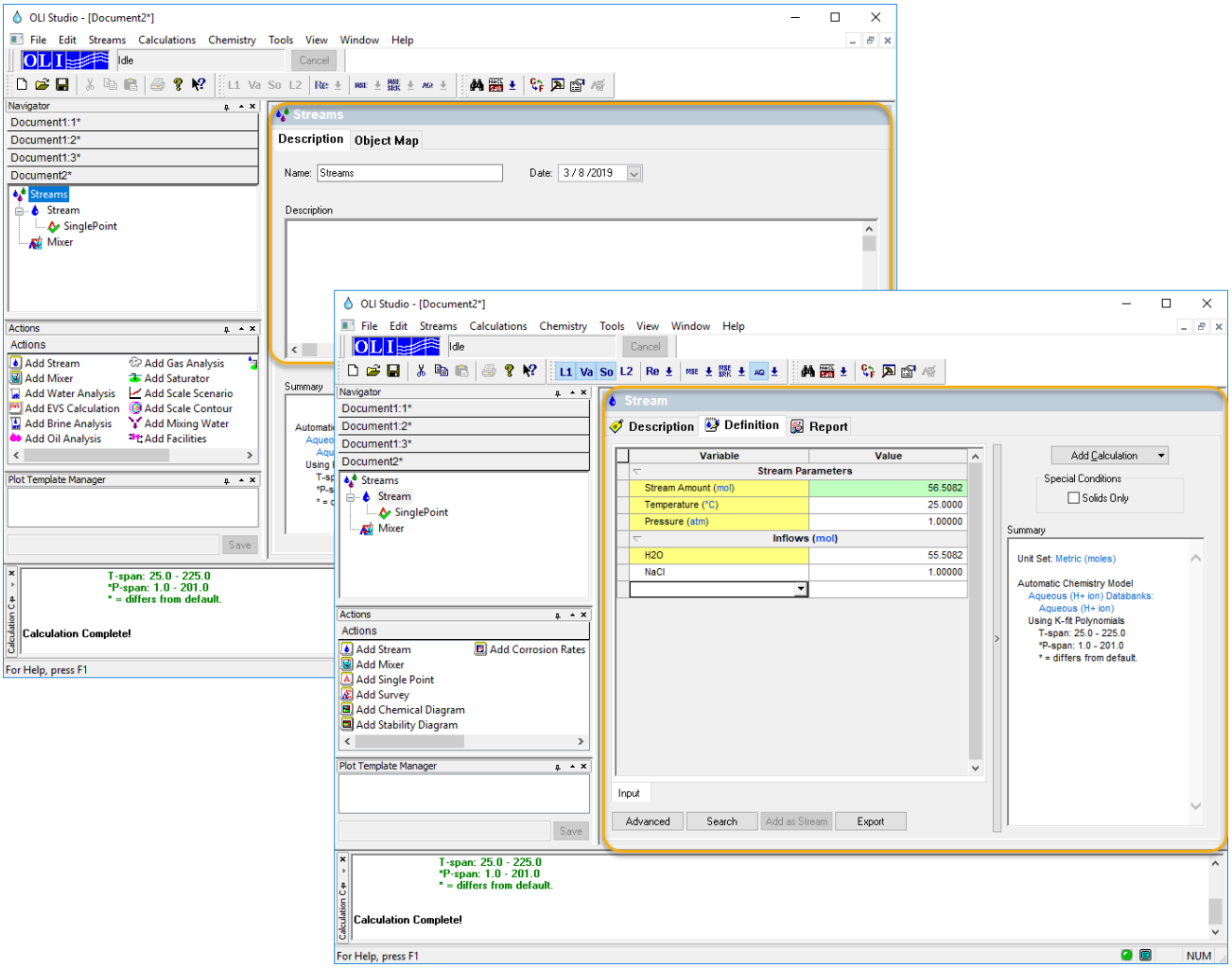
Plot Template Manager

The default location for the Plot Template Manager is in the lower left-hand corner of the main window. The Plot Template Manager is a tool that allows the user to create, save and use plot templates. This tool allows a fast plotting and analysis of the users results.



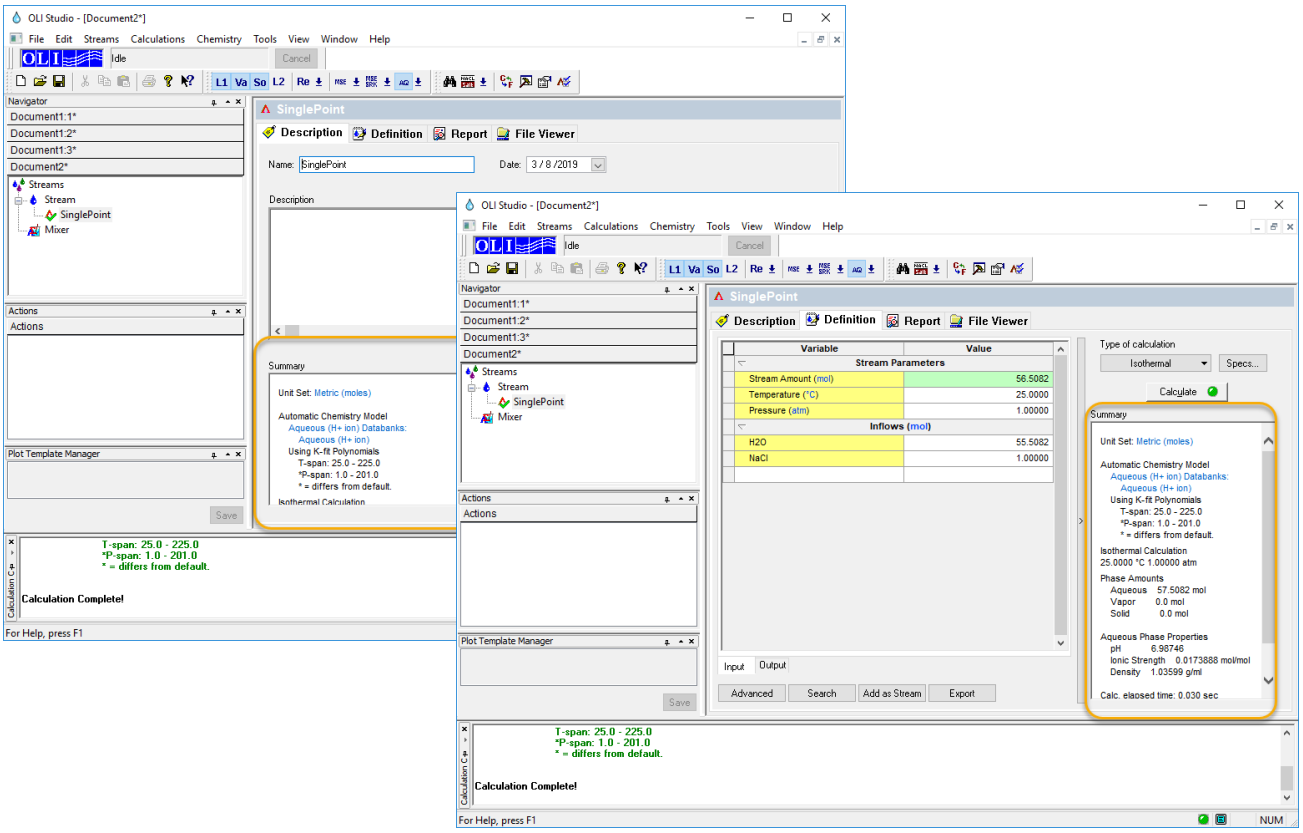
Description / Definition Pane

Users work most of the time on the Description / Definition area, which changes depending on which action object is being used.



Summary Pane

The Summary Pane can be viewed in both the Description and Definition Tabs. The Summary Pane shows inputs, calculation outputs, warnings, and has hyperlinks to the Units and Databank Managers. This window varies with object.



Calculation Status Output

The Calculation Status Output window shows progress, errors, warnings, temporary file locations, and other data.

Thermodynamic Frameworks and their Databases

You can access the databanks from the Menu Bar: **Chemistry > Model Options…** or via the quick access from the Tool Bar.

There are three main thermodynamic frameworks in OLI Analyzer. The user can pick the thermodynamic framework that is more suitable for their chemistry. These are the **AQ** (Aqueous), the **MSE** (Mixed Solvent Electrolyte), and the **MSE-SRK** (Mixed Solvent Electrolyte – Soave Redlich-Kwong) Thermodynamic Frameworks. A more detail description of each framework is given below:

Aqueous (AQ) Thermodynamic Framework

The OLI Aqueous (AQ) thermodynamic framework, is a mature electrolyte activity coefficient model that predicts the properties of solutions up to 30 molal ionic strength. Its accompanying database contains 6,000 species for 80+ elements (metals and non-metals) across multiple oxidation states.

This AQ framework is suitable for application involving electrolytes, gases and hydrocarbons dissolved in water.

The AQ framework utilizes the Bromley-Zemaitis activity model:

$$\log\gamma_{\pm} = -\frac{A|Z_+Z_-|\sqrt{I}}{1+\sqrt{I}} + \frac{(0.06+0.6B)|Z_+Z_-|\sqrt{I}}{\left(1+\frac{1.5}{|Z_+Z_-|}I\right)^2} + BI + CI^2 + DI^3$$

The model is capable of producing valid results in the following ranges:

Temperature	-50◦C to 300ºC
Pressure	0 – 1500 bar
Ionic Strength	0 – 30 molal

The AQ-framework selects the PUBLIC[1] database by default. Frequently there is more to the chemistry than what is covered in the PUBLIC database. The following is a partial list of additional databases available in the AQ framework:

1. Aqueous (H^+ ion) – Public Database and selected by default
2. Geochemical (AQ)
3. Ceramics (AQ)
4. Corrosion (AQ)
5. Low Temperature (AQ)
6. Alloys (AQ)
7. Ion Exchange (AQ)
8. Surface Complexation Double Layer Model (AQ)

[1] The PUBLIC database is the main OLI database, containing nearly 70 percent of the thermodynamic data available from OLI and 100 percent of the supporting information.

Mixed Solvent Electrolyte (MSE) Thermodynamic Framework

A system's thermodynamic properties are calculated from two sources; the first is from the Temperature and Pressure dependent standard-state Gibbs energies (i.e., $\overline{G_i}^0(T,P)$ of each species present. The second is from the temperature, pressure and composition dependent excess Gibbs energy $(i.e.,\gamma_i(m,T))$ for each species present. In the combined relationship, the partial molal Gibbs energy of the i^{th} species is, $\overline{G_i} = \overline{G_i^0} + RT\ln m_i\gamma_i$, where $\overline{G_i^0}$ is the standard-state partial Gibbs energy and γ_i is the activity coefficient. This activity coefficient γ_i, is computed using the MSE theory. A comprehensive explanation of the MSE theory is given in Wang et al. [7].

The MSE framework utilizes the MSE activity model which contains the extended Debye-Huckel term, that accounts for **long-range** interactions, an UNIQUAC term that accounts for **short-range** interactions, and a **middle-range** that includes the ionic interactions:

$$\log\gamma_i = \log\gamma_i^{SR} + \log\gamma_i^{MR} + \log\gamma_i^{LR}$$

The model is capable of producing results for the following ranges:

Temperature	-50ºC – to 90% T_{crit}
Pressure	0 – 1500 bar
Ionic Strength	no limit

The MSE framework contains the following databanks:

1. MSE (H_3O^+ ion) – Selected by default
2. Corrosion (MSE)
3. Geochemical (MSE)
4. Urea (MSE)
5. Surface Complexation Double Layer Model (MSE)

Mixed Solvent Electrolyte with Soave-Redlich-Kwong Equation of State (MSE-SRK) Thermodynamic Framework

The MSE-SRK model is based on the Mixed-Solvent Electrolyte (MSE) framework, which provides a very accurate representation of electrolyte systems in both aqueous and mixed-solvent (e.g., glycol-containing) environments. The MSE-SRK framework combines an equation of state for standard-state properties of individual species, an excess Gibbs energy model to account for solution non-ideality in the aqueous electrolyte phase, and the Soave-Redlich-Kwong equation of state (SRK EOS) to calculate the properties of the gas phase. The MSE-SRK framework, however, provides a different treatment of the non-electrolyte-rich second liquid phase for liquid-liquid equilibria. MSE-SRK assumes the second (usually organic-rich) liquid phase to be non-ionic, and reproduces its properties using the SRK EOS. This allows the MSE-SRK framework to more easily reproduce the critical behavior of nonelectrolyte systems.

In the MSE-SRK model, the electrolyte-containing (usually aqueous) liquid phase is represented by a combination of the Helgeson-Kirkham-Flowers (HKF) equation of state for standard-state properties and the MSE activity coefficient model for solution nonideality. Accordingly, the chemical potential of a species i in a liquid (electrolyte) phase is calculated as:

$$\mu_i^L = \mu_i^{L,0,x}(T,P) + RT\ln x_i\gamma_i^{x,*}(T,P,x) \quad (1)$$

where $\mu_i^{L,0,x}(T,P)$ is the standard-state chemical potential from the HKF theory [9], [10], x_i is the mole fraction, and $x_i\gamma_i^{x,*}(T,P,x)$ is the activity coefficient from the MSE theory of Wang et al. [7], which accounts for long-range electrostatic, specific ionic, and short-range intermolecular interactions.

The second liquid phase is assumed to be non-ionic and is modeled using the Soave-Redlich-Kwong equation of state (SRK-EOS) [11]. The chemical potential in the non-ionic liquid phase is then calculated as:

$$\mu_i^G = \mu_i^{G,0}(T) + RT\ln\frac{Py_i\varphi_i(T,P,y)}{P^0} \quad (2)$$

where $\mu_i^{G,0}(T)$ is the chemical potential of pure component i in the ideal gas state, y_i is the mole fraction, $\varphi_i(T,P,y)$ is the fugacity coefficient from the SRK-EOS, P is the total pressure, and $P^0 = 1\ atm$.

The properties of the gas phase are also obtained from the SRK equation according to Equation (2).

The MSE-SRK framework contains the following databanks:

1. MSE (H_3O^+ ion) – Selected by default
2. MSE-SRK (H_3O^+ ion) – Selected by default
3. Corrosion (MSE)
4. Geochemical (MSE)
5. Urea (MSE)
6. Surface Complexation Double Layer Model (MSE)

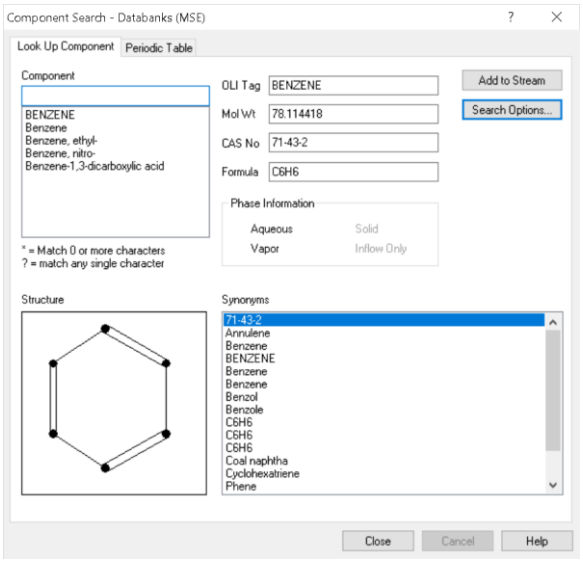
Component Search

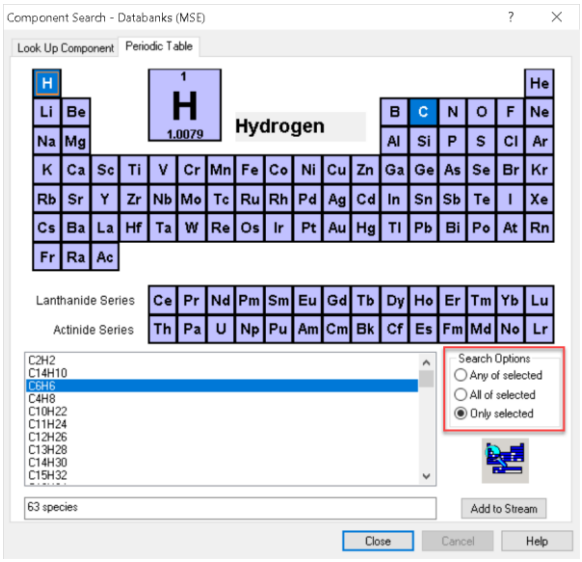
You can access the **Component Search** from the Menu Bar: **Tools > Component Search…** or via the quick access from the Tool Bar .

Note: When using the **Component Search** tool, you should be aware that the tool will only show components in the database that you have selected.

The **Component Search** option opens a new window where you can search for the component of interest by typing the component name or look up components using the Periodic Table option. In the periodic table option, you have 3 search options:

- Any of selected: Will show elements that you have selected
- All of selected
- Only selected





In any of the two options for component search, you can click on the **Add to Stream** button to add the component in your chemistry.

Names Manager

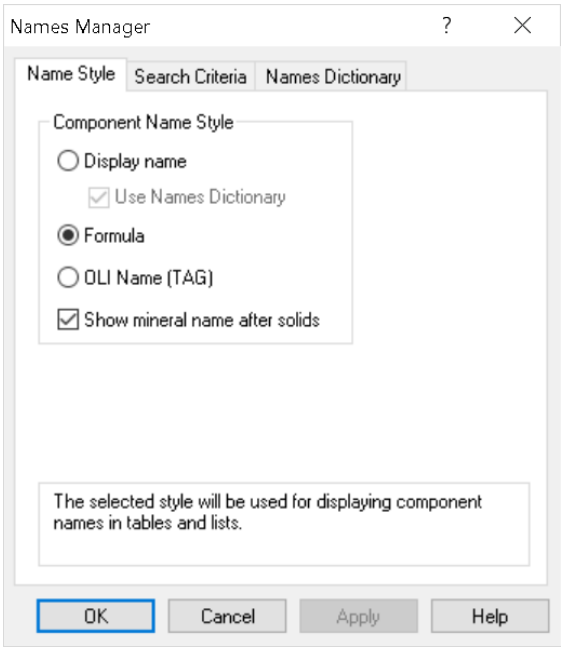
You can access the **Names Manager** from the Menu Bar: **Tools > Names Manager…** or via the quick access from the Tool Bar

.

The **Names Manager** option opens a new window where you can select the component name style. There are three different styles:

- **Display name**: This is the name that is commonly displayed when a species is entered. This is the default display. For example, Benzene, Cyclohexane, Sodium Chloride
- **Formula**: This is the chemical formula name. For example, C6H6, C6H12, NaCl
- **OLI Name (TAG):** This is the traditional name for the species stored internally in the OLI software. For example: BENZENE, CYCLOHEXAN, NACL (Note: These names are usually for OLI internal use).

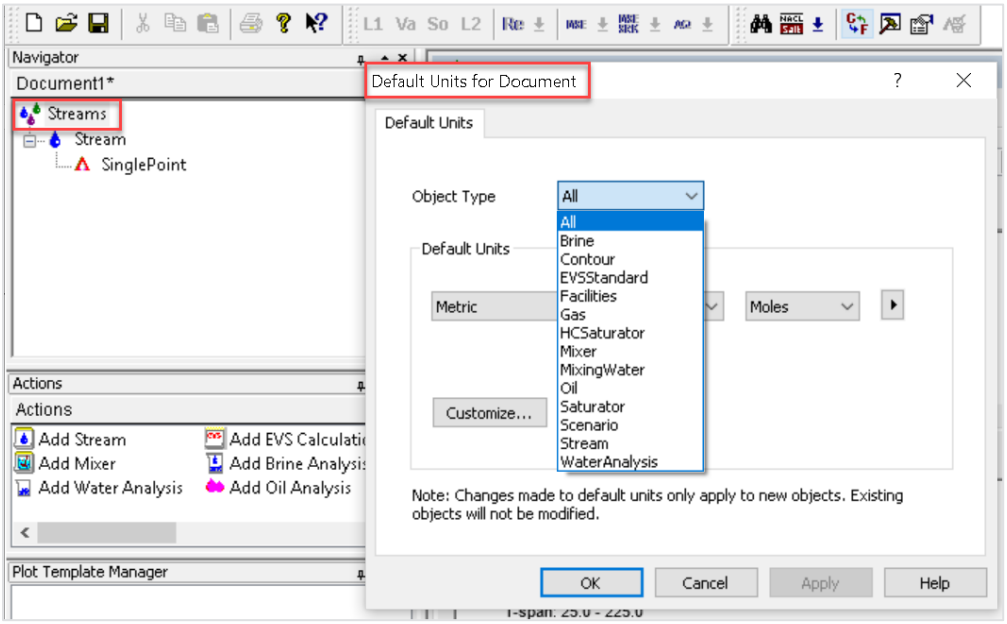
Additionally, you can select if you prefer the mineral name to appear after the solids. For example, NaCl (halite), KCl (sylvite), etc.



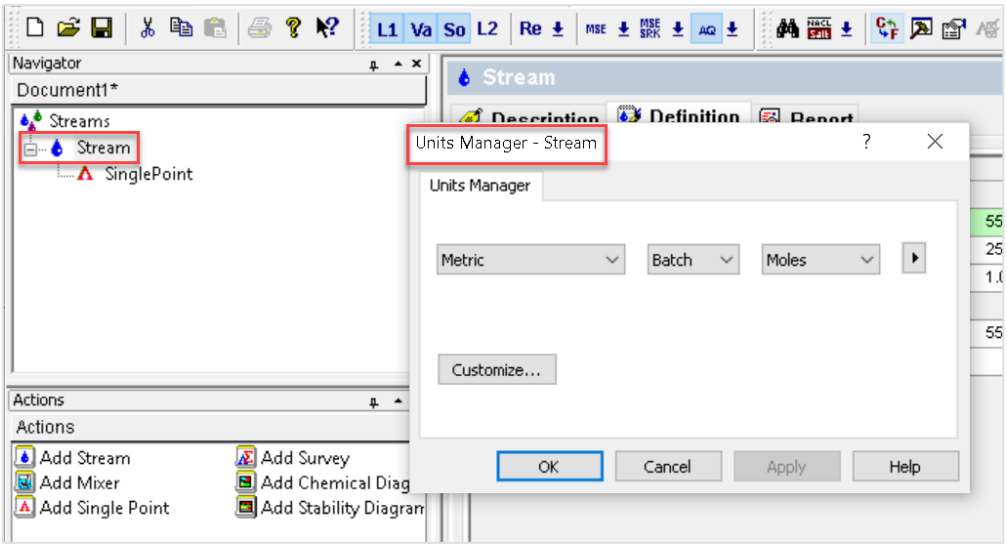
Units Manager

You can access the **Units Manager** from the Menu Bar: **Tools > Units Manager…** or via the quick access from the Tool Bar .

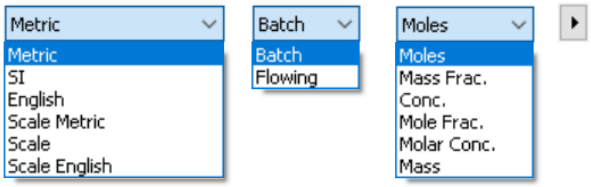
If you are changing units at the Global Stream Level, the **Units Manager** tool will open a new window where you can change the default units for the whole document. You can also select the default units of the different calculation objects.



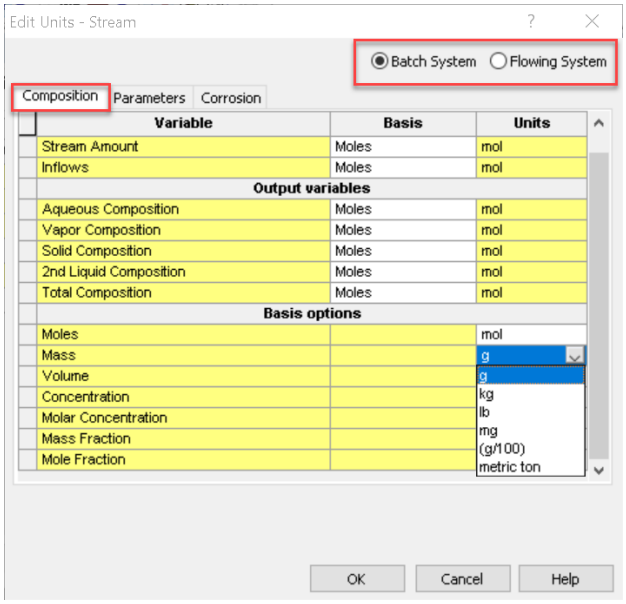
At the Stream Level, the Units Manager tool will open a slightly different window and will change the units only at the Stream Level and Calculation Level.

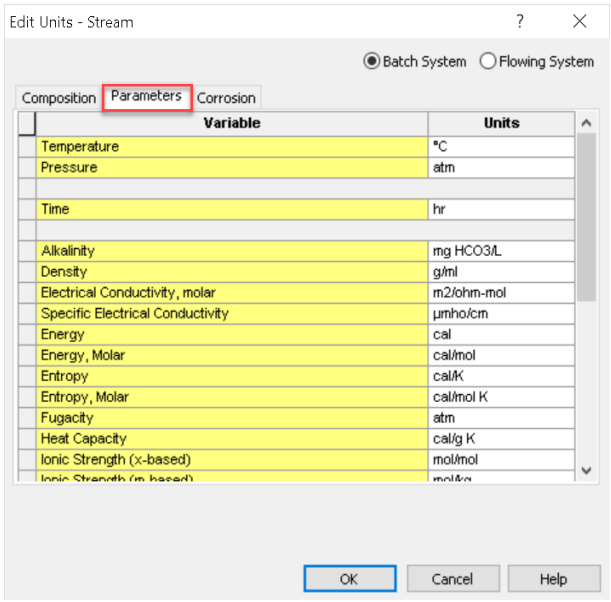


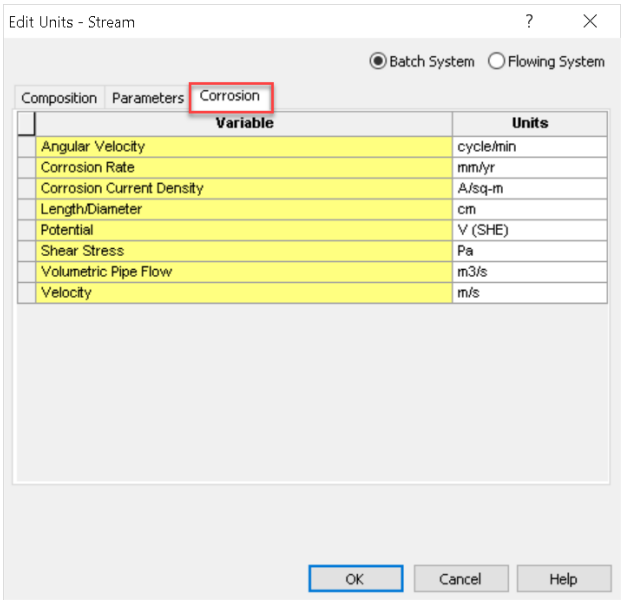
The default units are Metric, Batch and Moles, but you can change to any of the following default options:



You can customize specific units, by clicking on the **Customize…** button. This will open a new window where you can customize composition units, parameters units, and corrosion units. You can also select units for a Batch system or a flowing system.







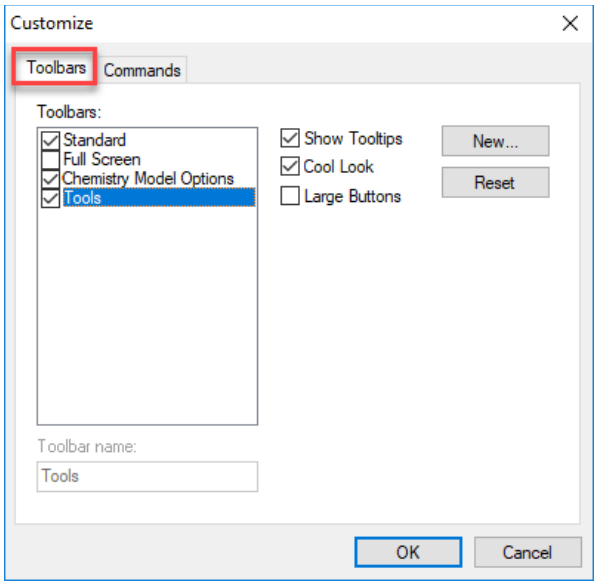
Another option to access the **Units Manager tool** is by clicking on the units highlighted in **blue**. This is a hyperlink to the Units Manager tool, and there you can make changes to the units.

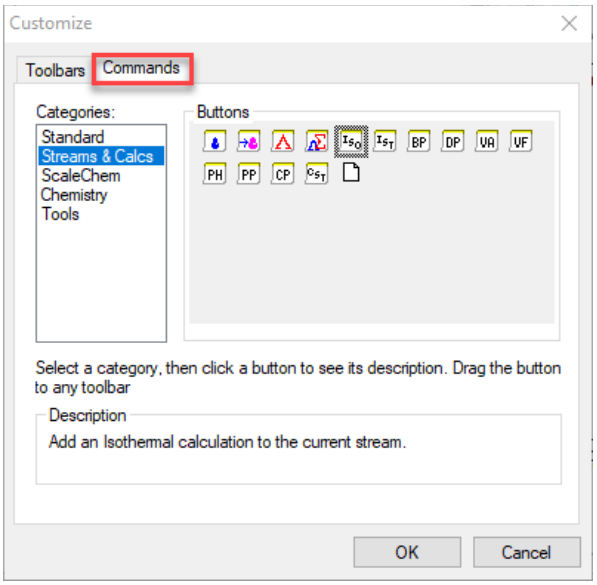
Stream Parameters	
Stream Amount (mol)	56.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
FeCl3	1.00000

Customize Toolbars

You can access the **Customize Toolbars** from the Menu Bar: **Tools > Customize…** or via the quick access from the Tool Bar . This will open a new window where you can disable or enable toolbars under **Toolbars** tab.

Under the **Commands** tab, you can also add your preferred buttons in the tool bar. If you click on any of them, it will give you a description of the actions the selected button will perform.

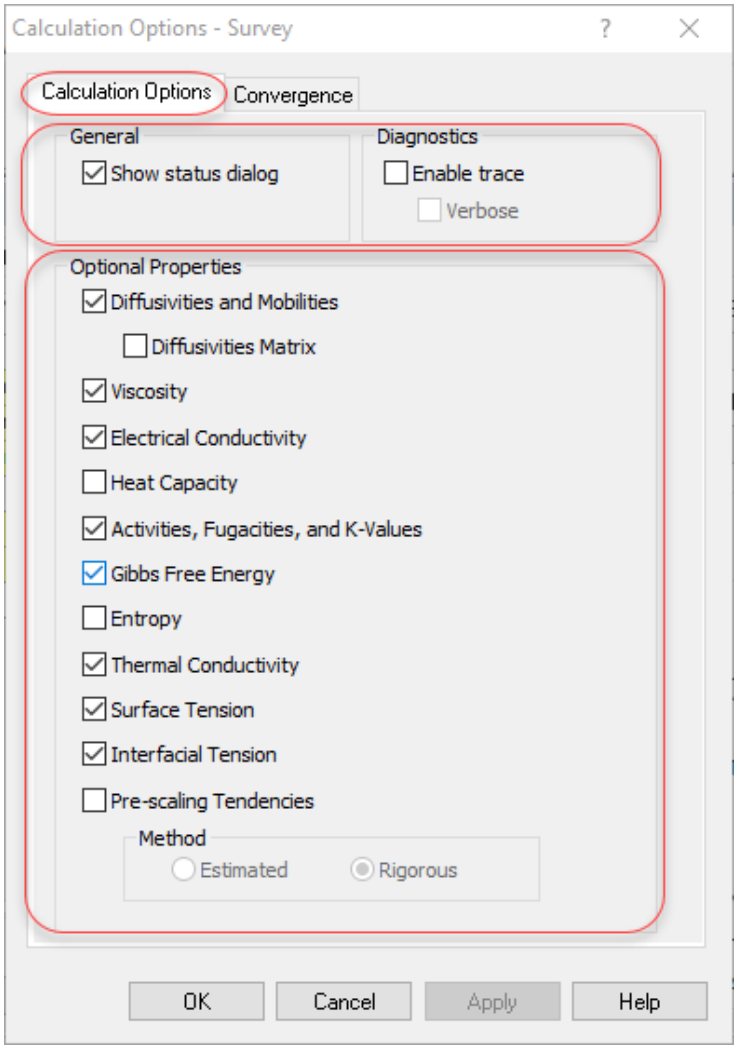




Calculation Options

You can access the **Calculation Options** from the Menu Bar: **Tools > Options…** or via the quick access from the Tool Bar . This will open a new window. Under the **Calculation Options** tab you can enable or disable the following options:

1. General
    a. Allows you to disable or enable
2. Diagnostics
    a. Enable trace
3. Optional Properties
    a. Diffusivities, electrical conductivity, heat capacity, activities, fugacities, and K-values, Gibbs free energy, entropy, thermal conductivity, surface tension, interfacial tension, and pre-scaling tendencies.

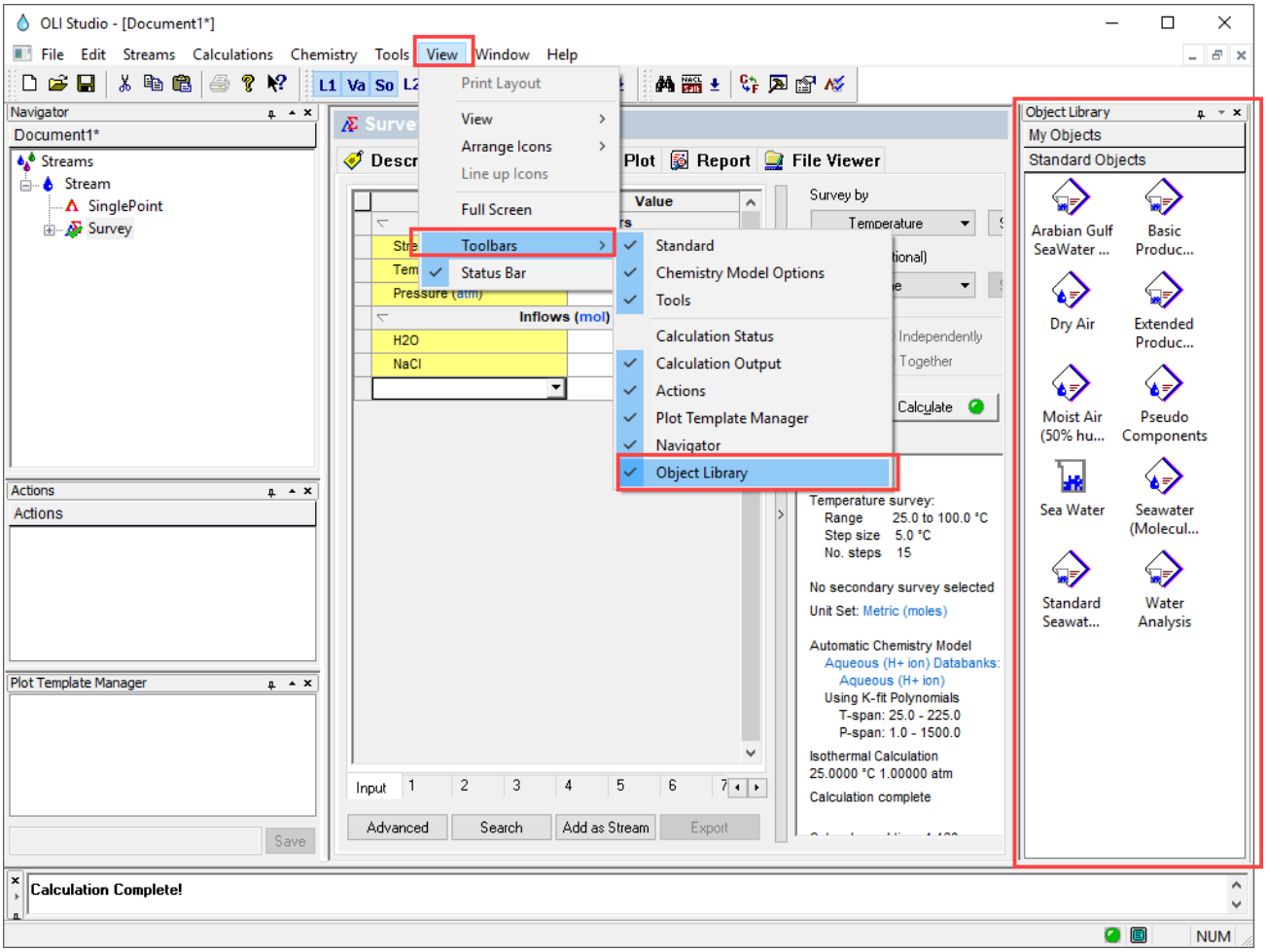


Object Library

You can access the **Object Library** from the Menu Bar: **View > Toolbars > Object Library**.

This option will create a new window (to the right). You can find commonly used objects like standard sea water, dry air, etc.

My Objects – save your own objects, such as a commonly used stream. You can drag an object and save it here for your future use.

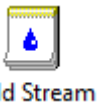


Tip: If by accident we lose a tool bar, we can go to **View > Toolbars >…** and select the toolbar that is missing.

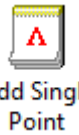
Chapter II – OLI Analyzer: Stream Analyzer

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.

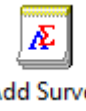
There are five different types of calculations that can be carried out in OLI Analyzer: Stream Analyzer: Single point, Survey (multiple point), Water Analysis, Mixer, and Chemical Diagram calculations. A brief definition of each type of calculation is given below.



Add Stream is used to add a **New Stream** as a molecular input and define a specific chemistry.



Single Point Calculations are used to find information (pH, volume, speciation, etc.) at one specific equilibrium state.



Survey Calculations are useful for plotting changes in stream parameters against temperature, pressure, or composition.

Water Analysis allows you to enter ionic inflows. i.e. allows you to enter anions and cations.

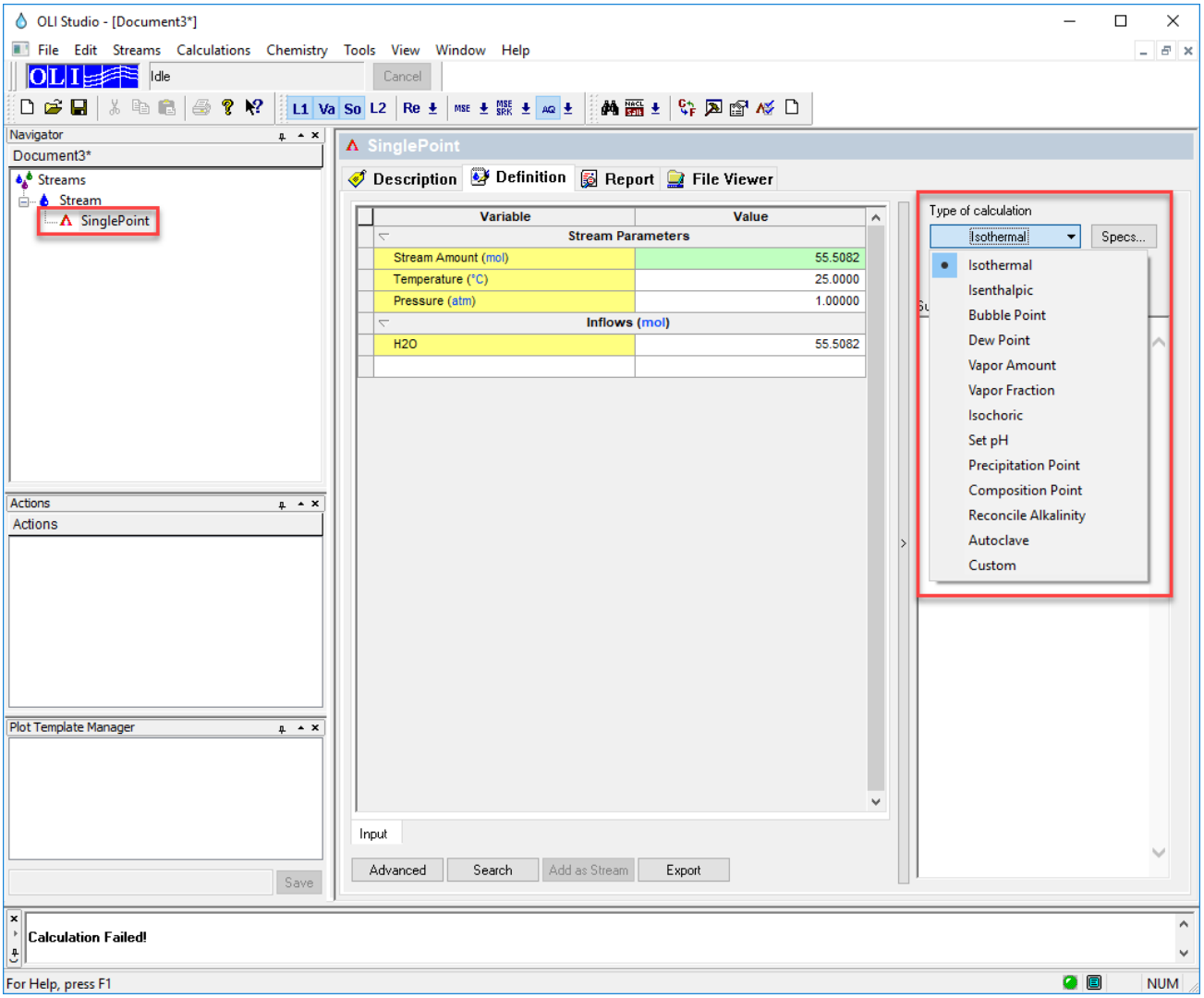
Mixer Calculations are useful for mixing different streams. You will familiarize yourselves with its four different mixing options, Single Point Mix, Multiplier, Ratio, and Volume.

Chemical Diagram Calculation allows you to create a stability map for species based on concentration and other parameters such as pH. A contour map is created showing the user where some solids are stable and where others are not.

In this chapter several examples will be provided to cover all of these calculation types.

Section 1. Single Point Calculations

Single point calculations are the simplest set of calculation in the software. There are 13 different single-point calculation types, and a brief explanation of each single point calculation is provided below.



1. ***Isothermal:*** The software computes solution properties based on a known chemical composition, at a constant temperature and pressure.
2. ***Isenthalpic:*** A constant heat change (loss/gain) is specified, and temperature or pressure is adjusted to meet the heat requirements.
3. ***Bubble Point:*** The temperature or pressure is adjusted to reach a condition where a small amount of vapor (bubble) begins to appear (a.k.a. boiling point).
4. ***Dew Point:*** The temperature or pressure is adjusted to reach a condition where a small amount of aqueous liquid (dew) appears.

5. ***Vapor Amount:*** The temperature or pressure is adjusted to produce a user-specified amount (in moles) of vapor in the system.
6. ***Vapor Fraction:*** The temperature or pressure is adjusted to produce a user-specified amount of vapor as a fraction of the total quantity of moles in the system.
7. ***Isochoric:*** The temperature or pressure is adjusted to produce the user-specified total volume (constant volume calculation).
8. ***Set pH:*** The software adjusts the flowrate of an acid or base 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 out. This can also be interpreted as the solubility.
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 calculates or reconciles the alkalinity of a solution. There are several reconciliation types within this option: Reconcile pH, Reconcile Alkalinity and pH, and Reconcile Alkalinity, pH and TIC.
12. ***Autoclave:*** The software simulates a constant volume vessel (autoclave) in which mass, pressure and temperature are allowed to vary in order to reach a user-specified mole fraction or partial pressure of key gases in the vapor phase.
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; for example, you can set up a custom calculation to determine the solubility of a gas in solution.

In this section, we will learn how to set up each one of these single point calculations, and will also introduce how to use custom units, the names manager, modify the report, and other useful tips to get the most out of your simulation results.

1.1. Isothermal

The default and most basic single point calculation is the **Isothermal calculation**. The software computes solution properties based on a known composition, pressure and temperature.

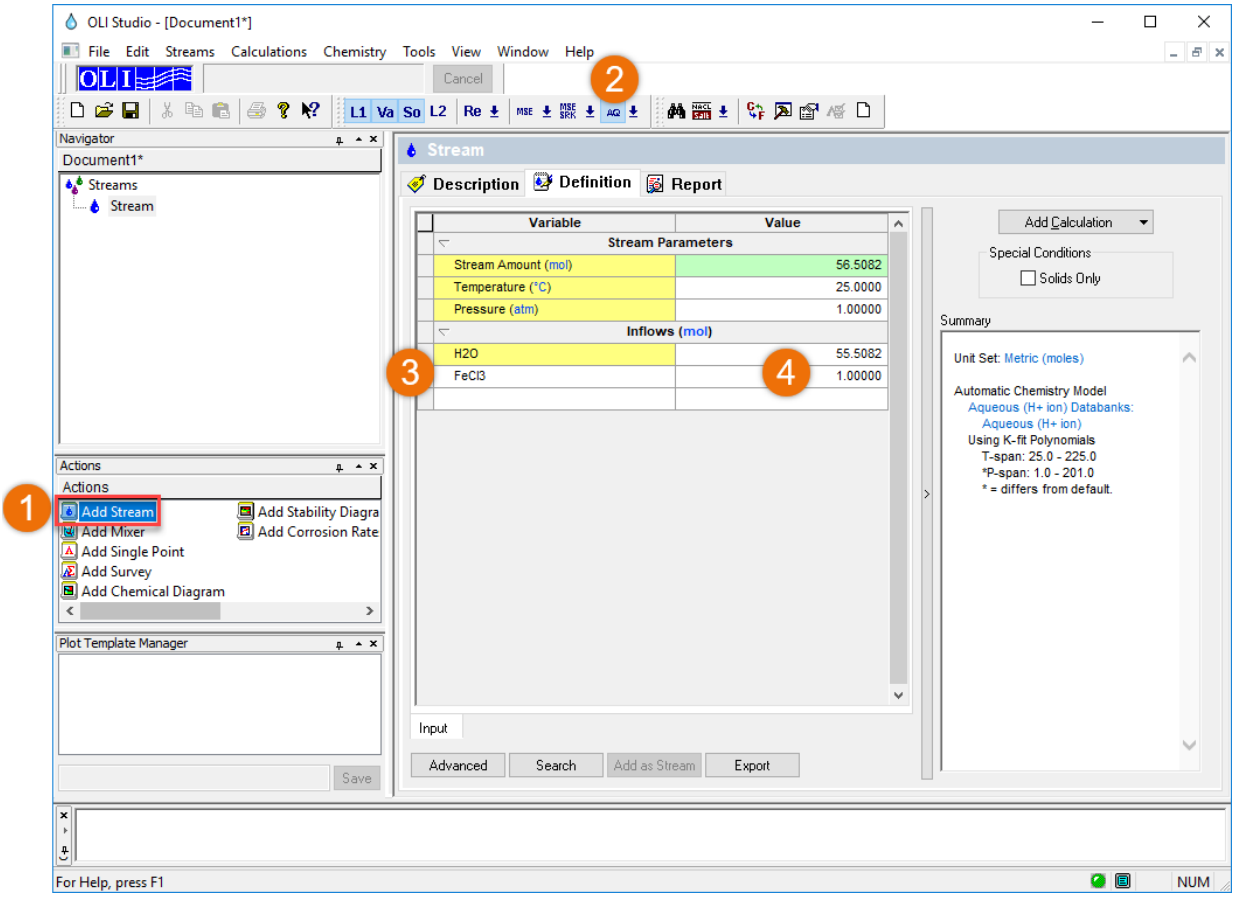
Example 1: Speciation and its importance for pH calculations

After completing this example, you will learn how to set up an **Isothermal calculation** and will also get a better understanding of the importance of full speciation on the calculation of pH. Let's calculate the pH of a 1 m $FeCl_3$ solution at 25 ºC and 1 atm.

Starting the Simulation

To start the software, double-click the OLI Analyzer icon on the desktop, which will take you to the OLI Analyzer interface where you can start creating your calculations.

1. Let's create a new stream. Click on the **Add Stream** located in the **Action Pane**. When a stream is created only H2O is present in the grid. Its cell is yellow because it cannot be removed, it is a permanent inflow.
2. For this example, we are going to use the **AQ-Databank** (The default databank)
3. Type **FeCl3** in the white cell below H2O inflows grid, and press **<Tab>** or **<Enter>**
4. Enter the value **1.0 mol** in the next cell.



Note: By default, the software populates the stream parameters table with 25ºC, 1 atm, and 55.5082 moles of water. This amount of water is 1 kg of water. All of OLI's internal aqueous concentrations are based on the molal concentration scale. You will see this value frequently throughout this manual. This effectively makes any component concentration a molal concentration.

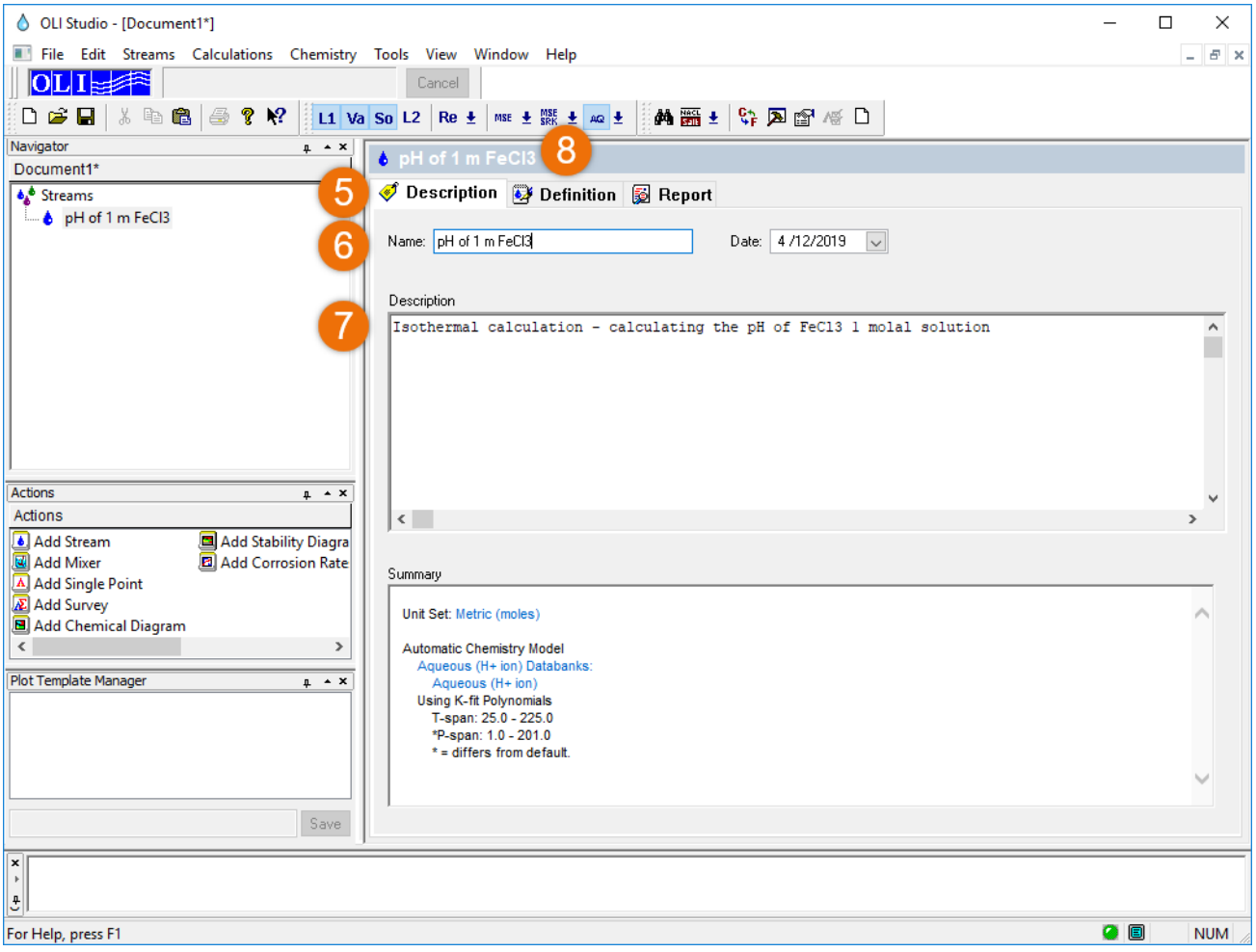
Also, notice that the stream amount will be automatically calculated from the sum of the component inflows. To indicate that the summation has occurred, the grid will highlight the stream amount cell in green.

5. Click the **Description** tab to change the name of the Stream. You can also change the name using the **<F2>** key or by **right-mouse click** on the object and selecting rename.

6. **Change** the generic name **Stream** to **pH of 1 m FeCl3**

7. **Add** the following **Description:** *Isothermal calculation - calculating the pH of FeCl3 1 molal solution*

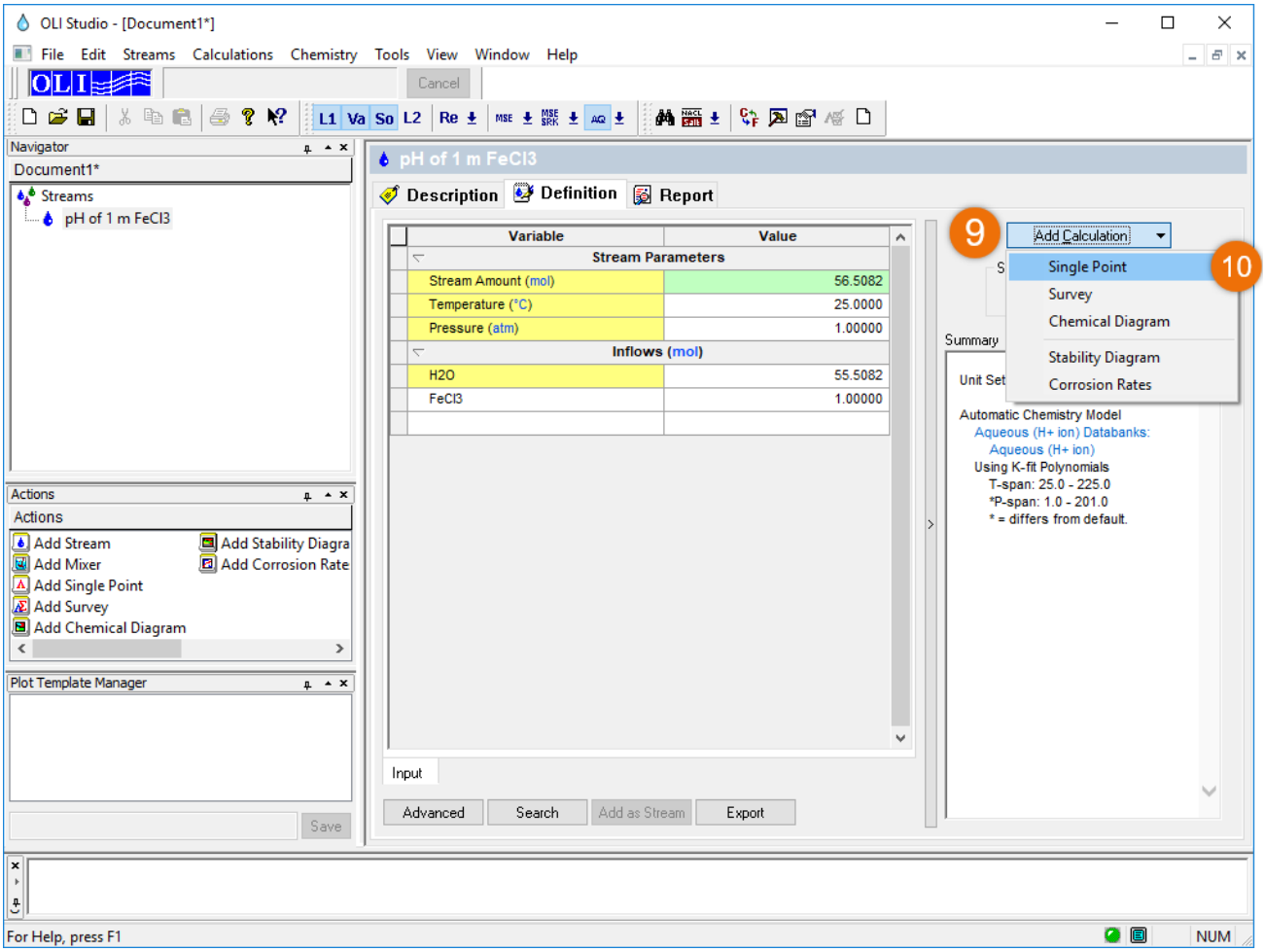
8. Go back to the **Definition** Tab



Now, we are ready to perform a calculation

9. Go to the **Add Calculation** button
10. Select **Single Point**

Note: By default, the software selects the **Isothermal** type of calculation



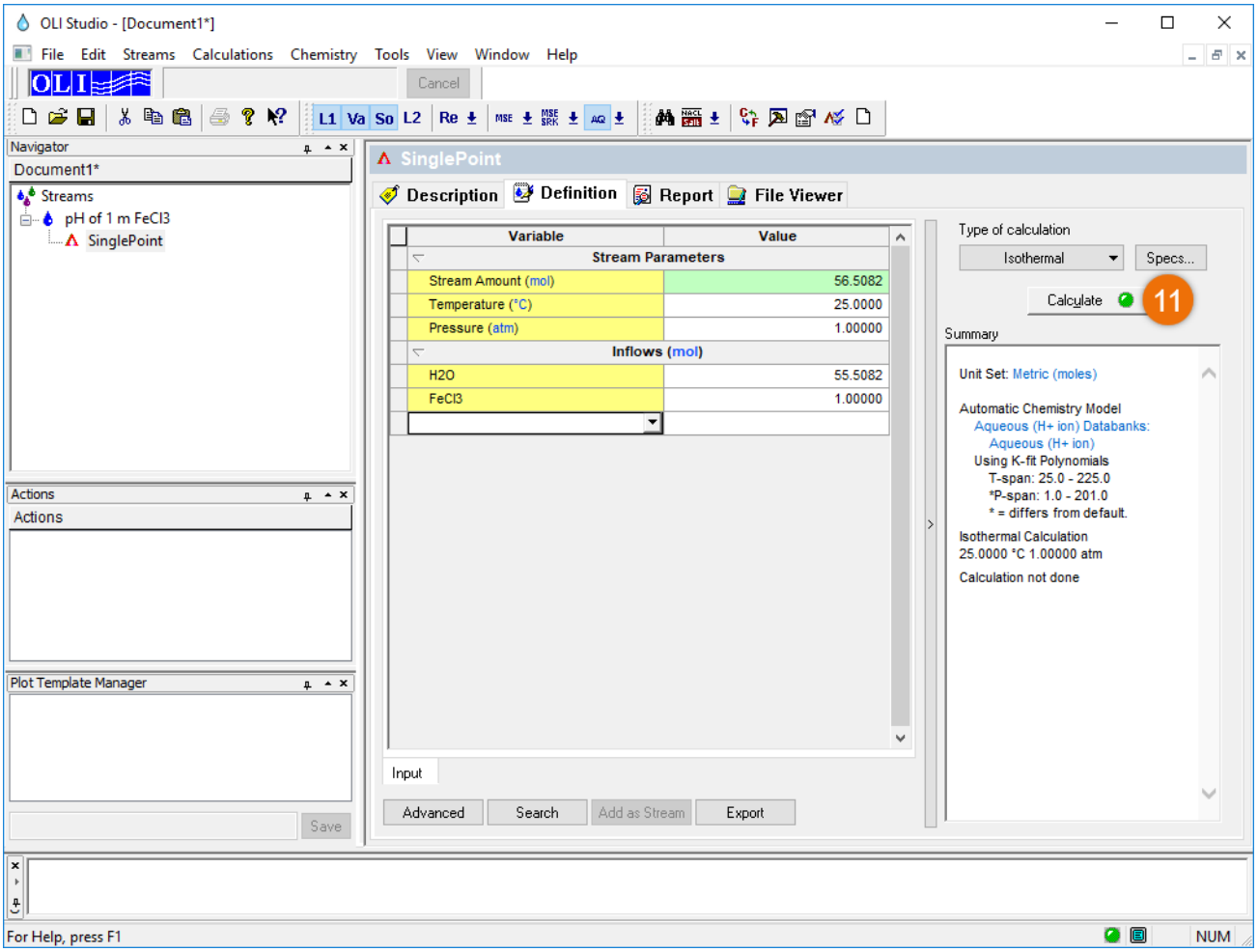
11. All the required variables have been entered, and the **Calculate** button has turned green. Click on the Calculate button. You can also press the **<F9>** key to run the calculation.

Note: The calculation button has three colors depending upon the specifications:

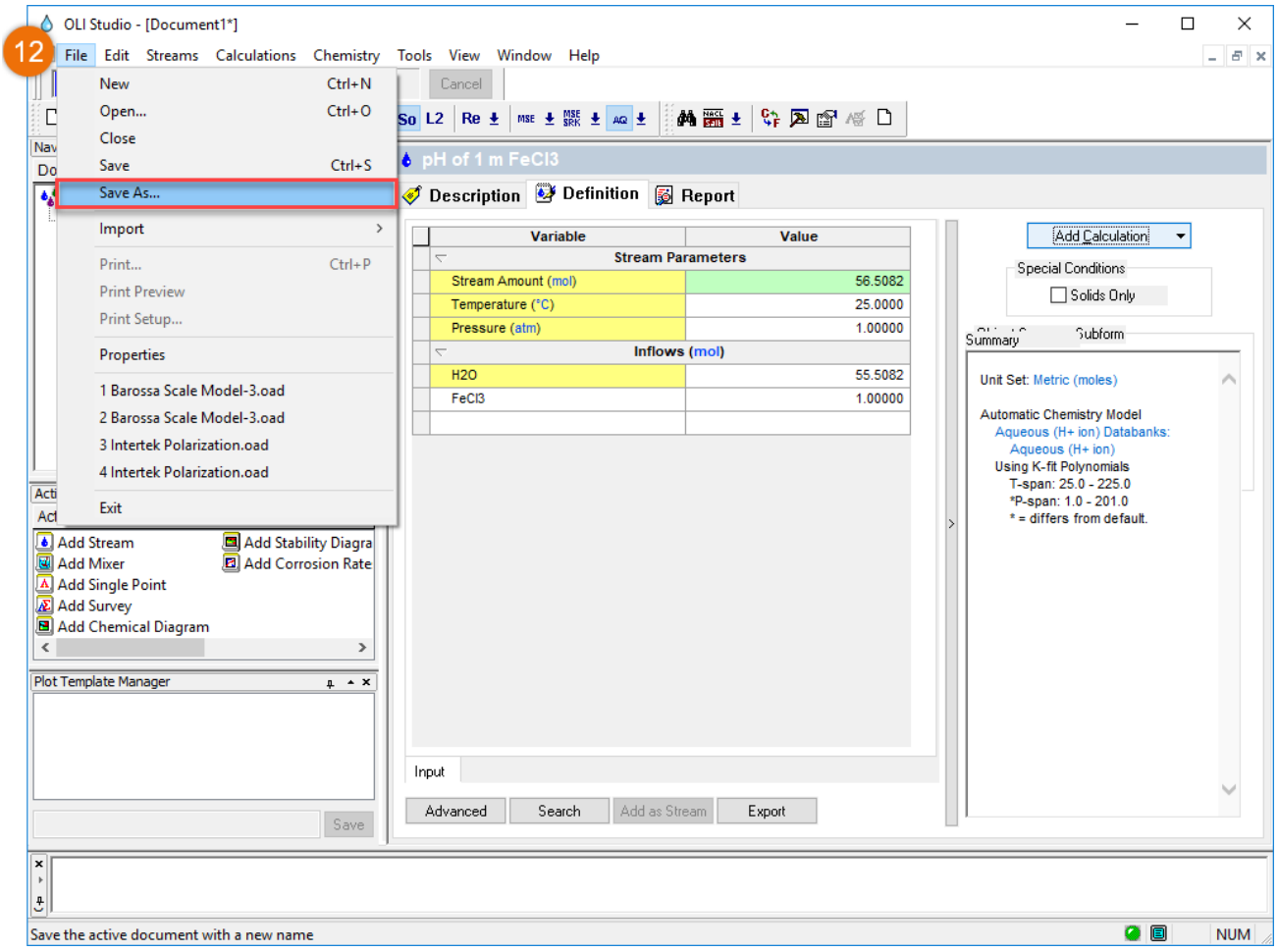
Red – Insufficient specifications for a calculation

Yellow – Incomplete specifications but calculation can continue

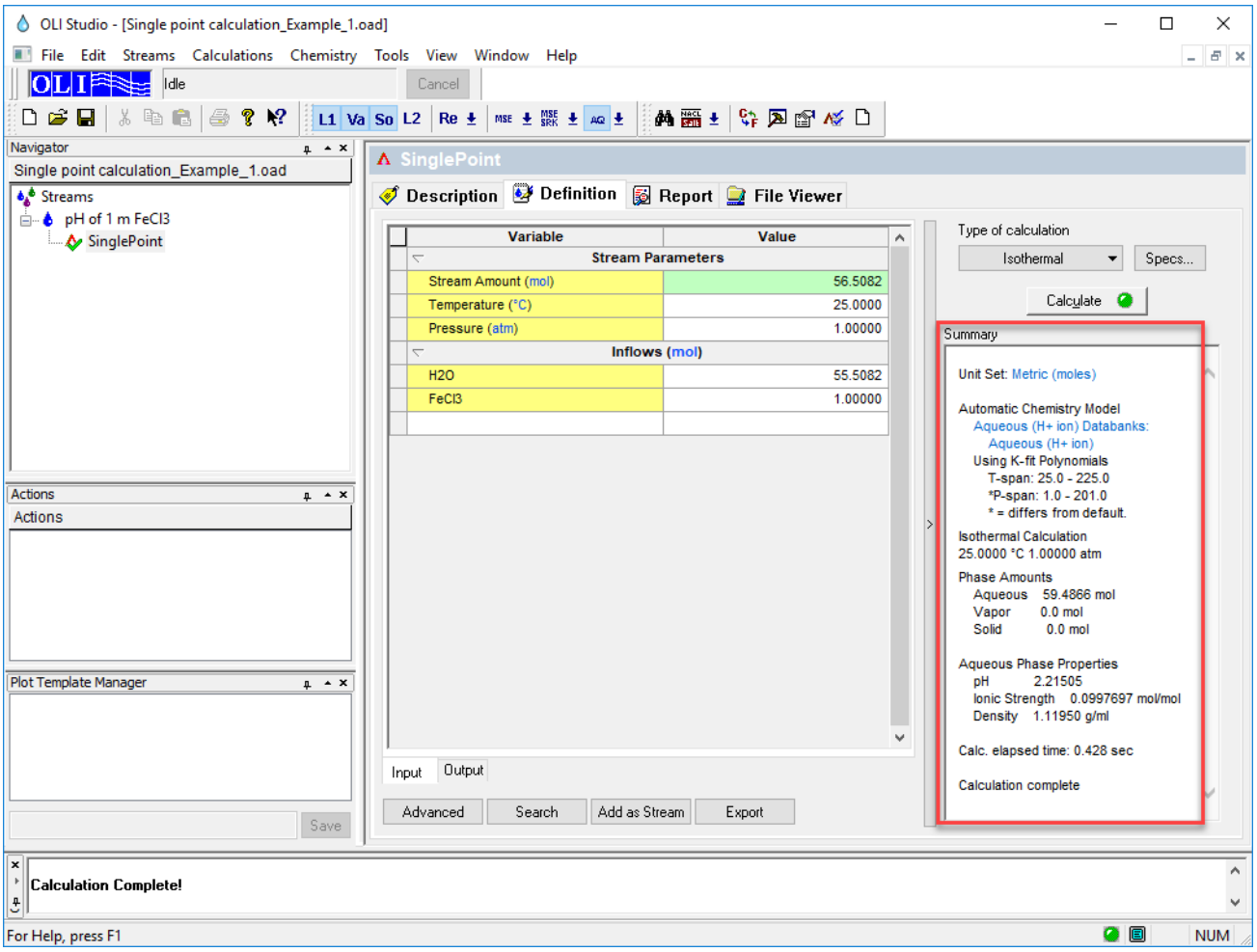
Green – Completed specifications, the calculation is ready



12. Please **save** the file (**File >Save as…)** and type an appropriate name, for example *Single Point Calculations*.



When the "**Calculation is complete**" a check mark appears on the calculation object . Now, let's analyze the results of the simulation.



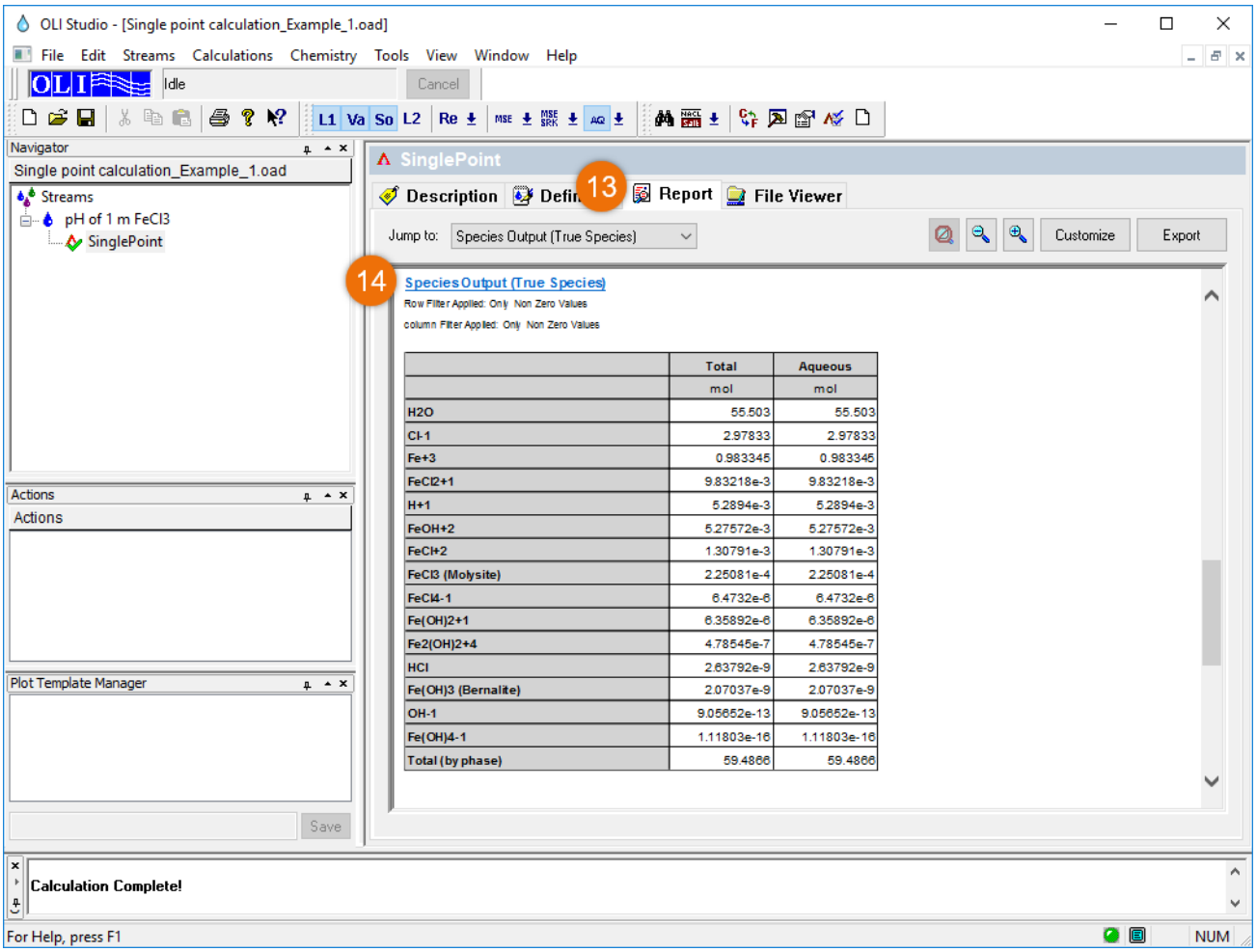
Anaylyzing the Results

The summary box displays a partial set of results including pH, density, and volume, as well as the total calculation time.

The **pH** is calculated to be approximately **2.2**

Let's analyze the simulation results in more detail

13. Click on the **Report** Tab
14. **Scroll down** and find **Species Output (True Species).** You will find a list of the all the different species present in the aqueous phase.



	Total	Aqueous
	mol	mol
H2O	55.503	55.503
Cl-1	2.97833	2.97833
Fe+3	0.983345	0.983345
FeCl2+1	9.83218e-3	9.83218e-3
H+1	5.2894e-3	5.2894e-3
FeOH+2	5.27572e-3	5.27572e-3
FeCl+2	1.30791e-3	1.30791e-3
FeCl3 (Molysite)	2.25081e-4	2.25081e-4
FeCl4-1	6.4732e-6	6.4732e-6
Fe(OH)2+1	6.35892e-6	6.35892e-6
Fe2(OH)2+4	4.78545e-7	4.78545e-7
HCl	2.63792e-9	2.63792e-9
Fe(OH)3 (Bernalite)	2.07037e-9	2.07037e-9
OH-1	9.05652e-13	9.05652e-13
Fe(OH)4-1	1.11803e-16	1.11803e-16
Total (by phase)	59.4866	59.4866

Why is the **pH** so low?

The aqueous iron species complexes the hydroxide ions. The water dissociation shifts in the direction to replenish the hydroxide ions[2].

This equilibrium is always present:

$$H_2O = H^+ + OH^-$$

[2] Le Châtelier's principle. P.W.Atkins. Physical Chemistry. W.H. Freeman and Company, San Francisco (1982) p 269.

Speciation Reactions

First iron (III) chloride dissociates:

$$FeCl_3 \rightarrow Fe^{3+} + 3Cl^-$$

Then the Fe^{3+} interacts with water; hydrolysis reaction:

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + 2H^+$$

Then another water molecule enters into the reaction:

$$FeOH^{2+} + H_2O \leftrightarrow Fe(OH)_2^+ + H^+$$

These last two reactions take up the **OH^-** from solution, and release **H^+** into the solution

More speciation reactions occur, but the reactions above where shown as an illustration. The following is a list of all the species that are formed in the aqueous phase:

Fe^{+3}	$FeCl_2^{+1}$	$Fe(OH)_3^0$	H_2O^0
$FeCl^{+2}$	$Fe(OH)_2^{+1}$	OH^{-1}	HCl^0
$FeOH^{+2}$	H^{+1}	$FeCl_4^{-1}$	$Fe_2(OH)_2^{+4}$
Cl^{-1}	$FeCl_3^0$	$Fe(OH)_4^{-1}$	

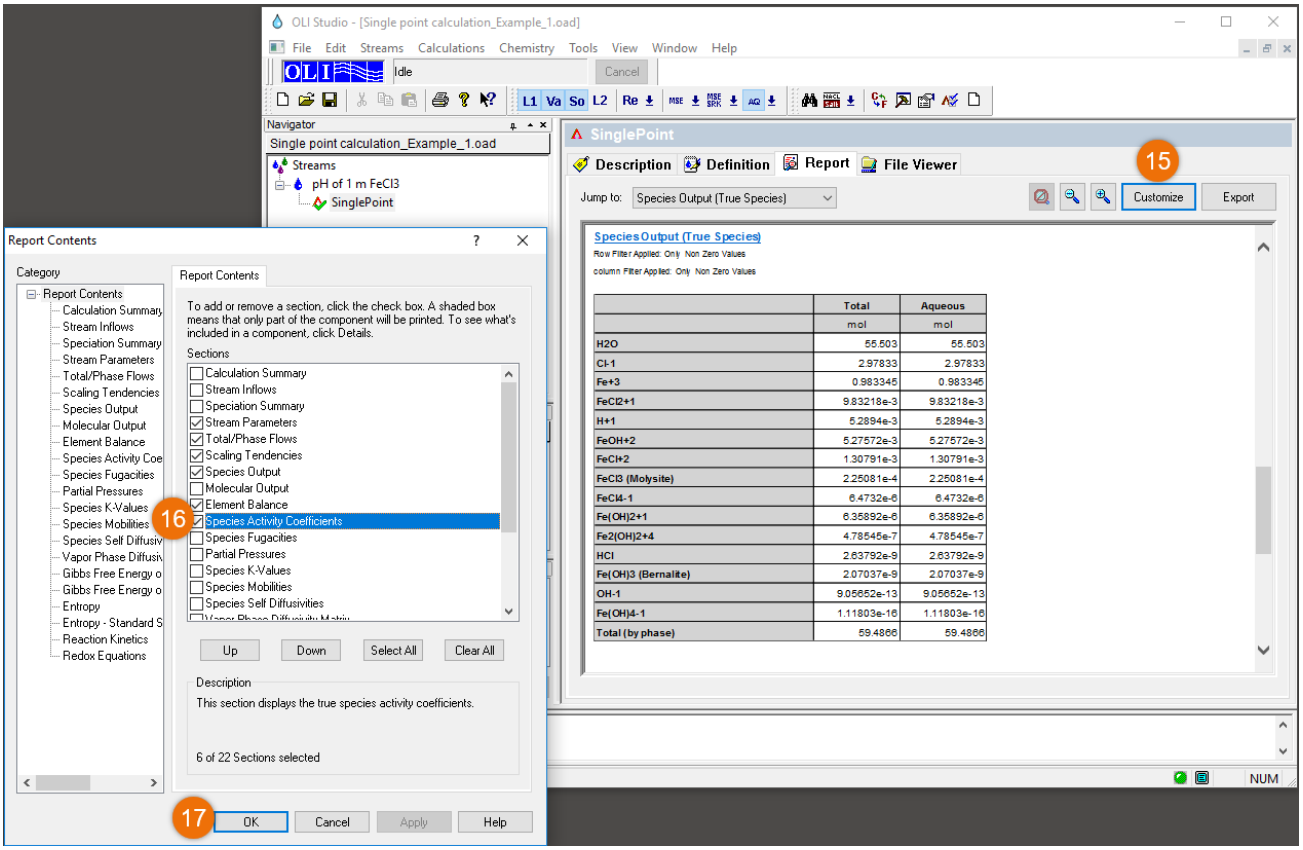
pH Calculation

The pH is calculating using the following formula:

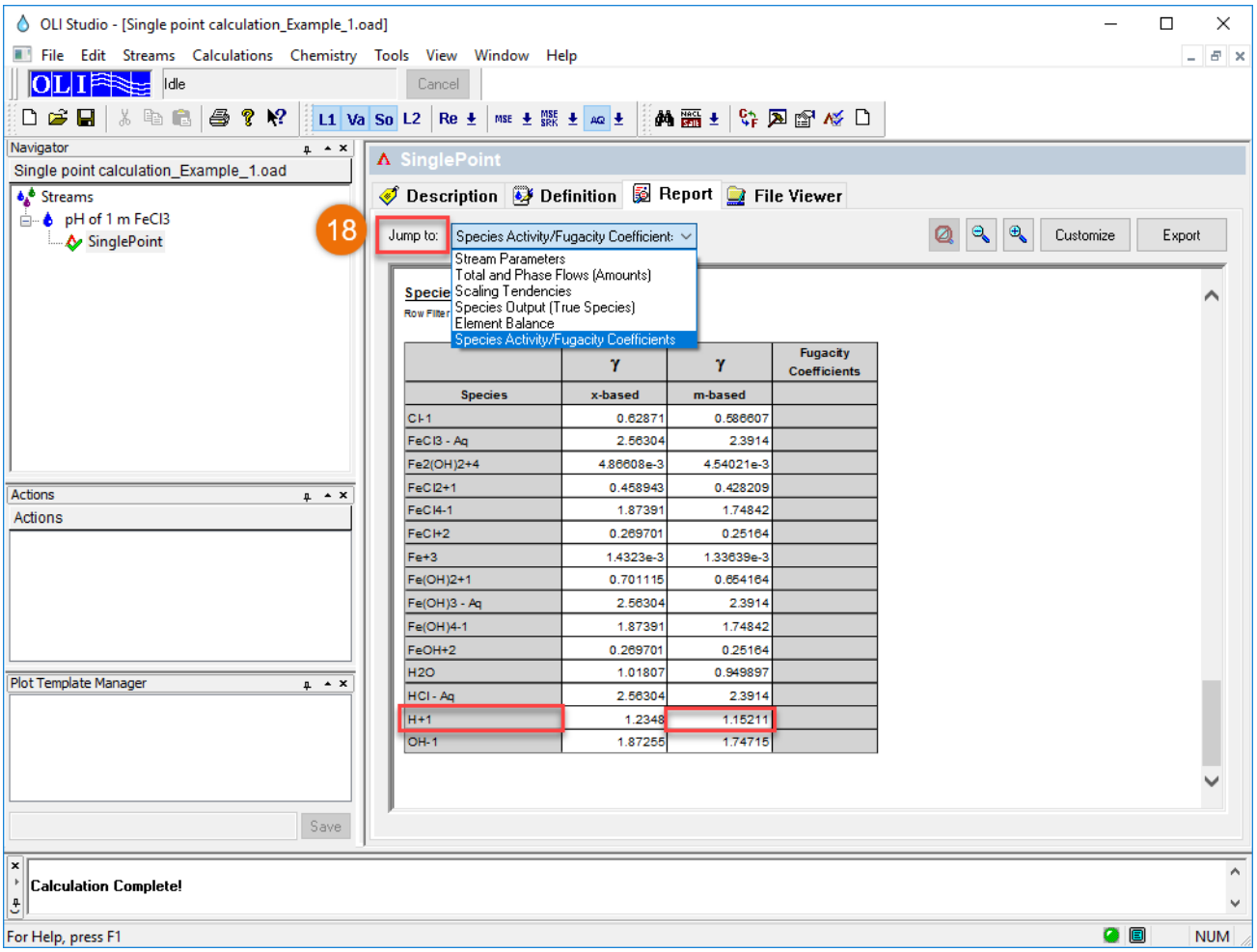
$$pH = -\log(m_{H^+}\gamma_{H^+})$$

For the pH calculation the molality and the activity coefficient of the H^+ species is needed. To reveal the activity coefficients calculated by software follow the steps below.

15. **Click** on the **Customize** Button
16. Select **Species Activity Coefficients**
17. **Click OK**



18. Go to the **Report** and **scroll down** or use the **Jump to** option and select **Species Activities/Fugacity Coefficients**.



Thus, the pH is:

$$pH = -\log(m_{H^+}\gamma_{H^+})$$

$$pH = -\log[(5.28940 \times 10^{-3})(1.15211)]$$

$$pH = -\log[6.094 \times 10^{-3}]$$

$$\boldsymbol{pH = 2.2151}$$

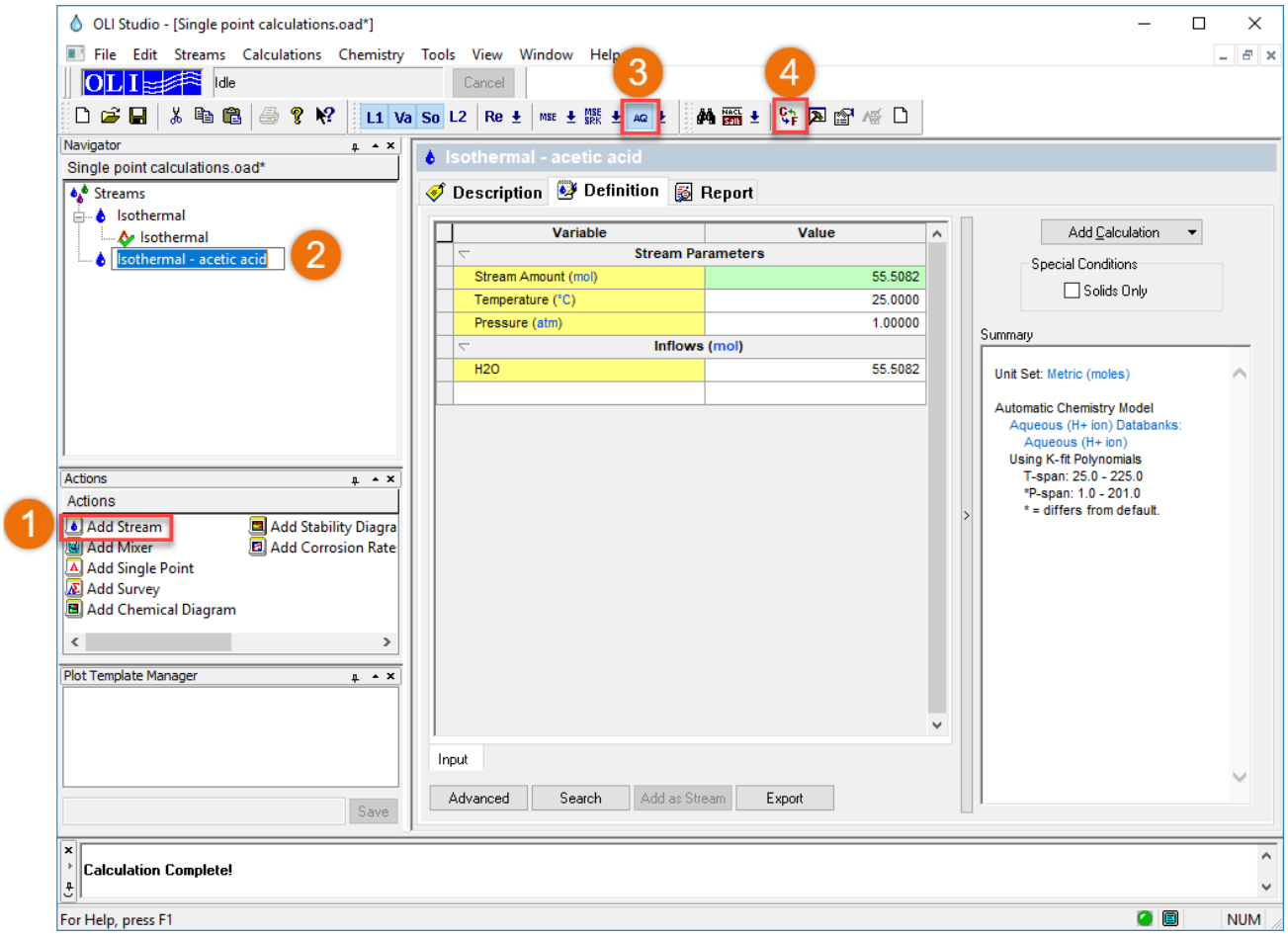
It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. We save this example initially as *Single Point Calculations*.

Example 2: Calculating the pH of an acetic acid solution

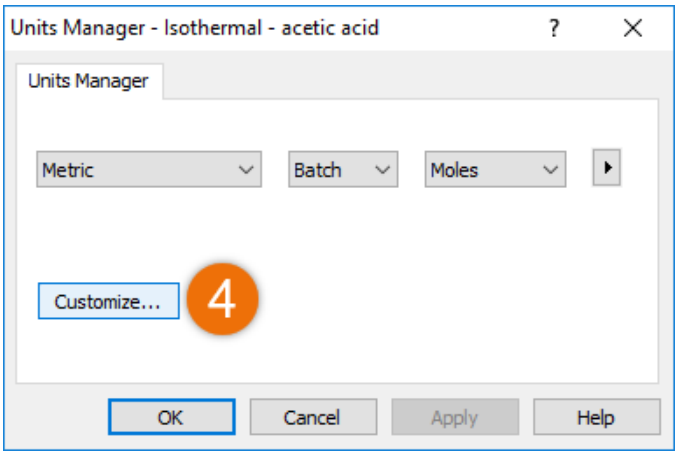
In this example, we will explore an isothermal calculation and how to set up the right units before you start your calculation. Let's calculate the pH of a 10 wt% acetic acid solution. The temperature and pressure will be 75°C and 1 atm, respectively.

Starting the Simulation

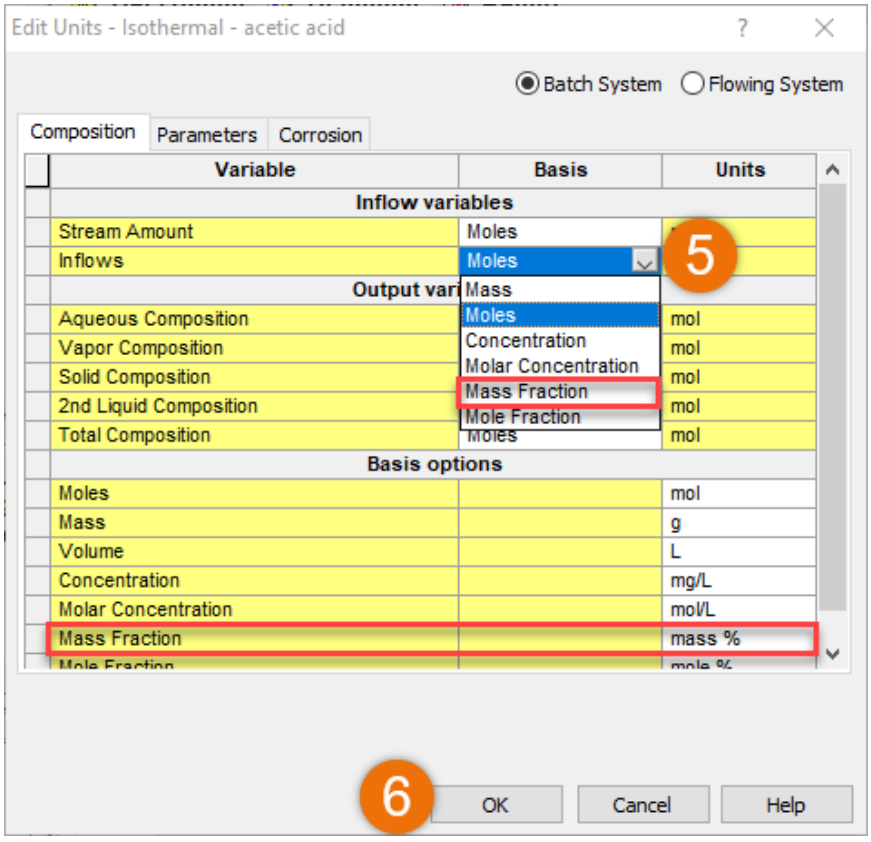
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Isothermal – acetic acid*
3. Select the AQ thermodynamic Framework (selected by default)
4. **Click** on the **Units Manager** Icon, and the Units Manger window opens



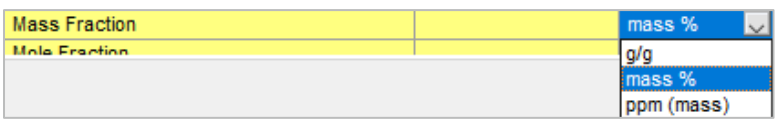
5. Click on the **Customize** Button



6. Let's change only the **Inflows** units. Click on the white box, **select** the drop-down arrow next to the unit, and **select Mass Fraction**. **Click OK**, to exit the Units Manager and go back to the **Definition** tab.



Note: The default unit is **mass%,** however you can change it to other to ppm (mass) or g/g.



We are now ready to enter the information to set up the single point calculation.

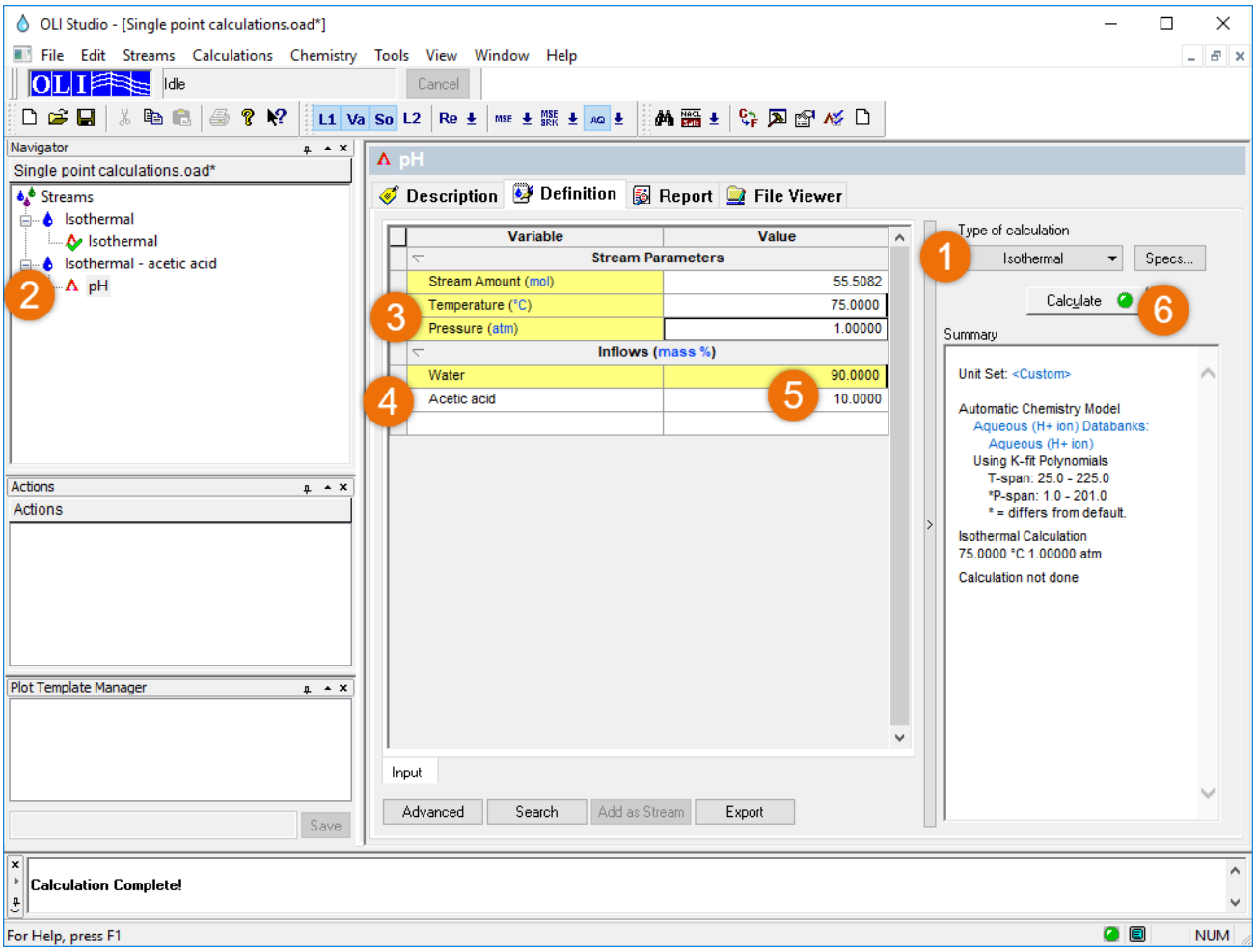
1. **Go** to the **Add Calculation** button and select **Single Point.** Select the default calculation type – **Isothermal**
2. **Change** the name to ***pH*** using the **<F2>** key or by **right-mouse click** on the object and selecting **rename**
3. **Change** the temperature to **75ºC** and pressure to **1 atm**
4. Type **Acetic Acid** in the white cell below H2O inflows grid, and press **<Tab>** or **<Enter>**

Note: If the name *Acetic Acid* changed to the formula type i.e. *CH3COOH*, or the OLI TAG name, i.e. *ACETACID*, you can change the name style to *Display Name* by clicking on the **Names Manager** icon

5. **Enter** the value 10 mass% in the next cell.

Note: When using mass-fraction units, it is assumed that the amount of water will be the difference of the components entered. In this case, the value field is highlighted in yellow to inform you that the value will be determined from the values of the other components.

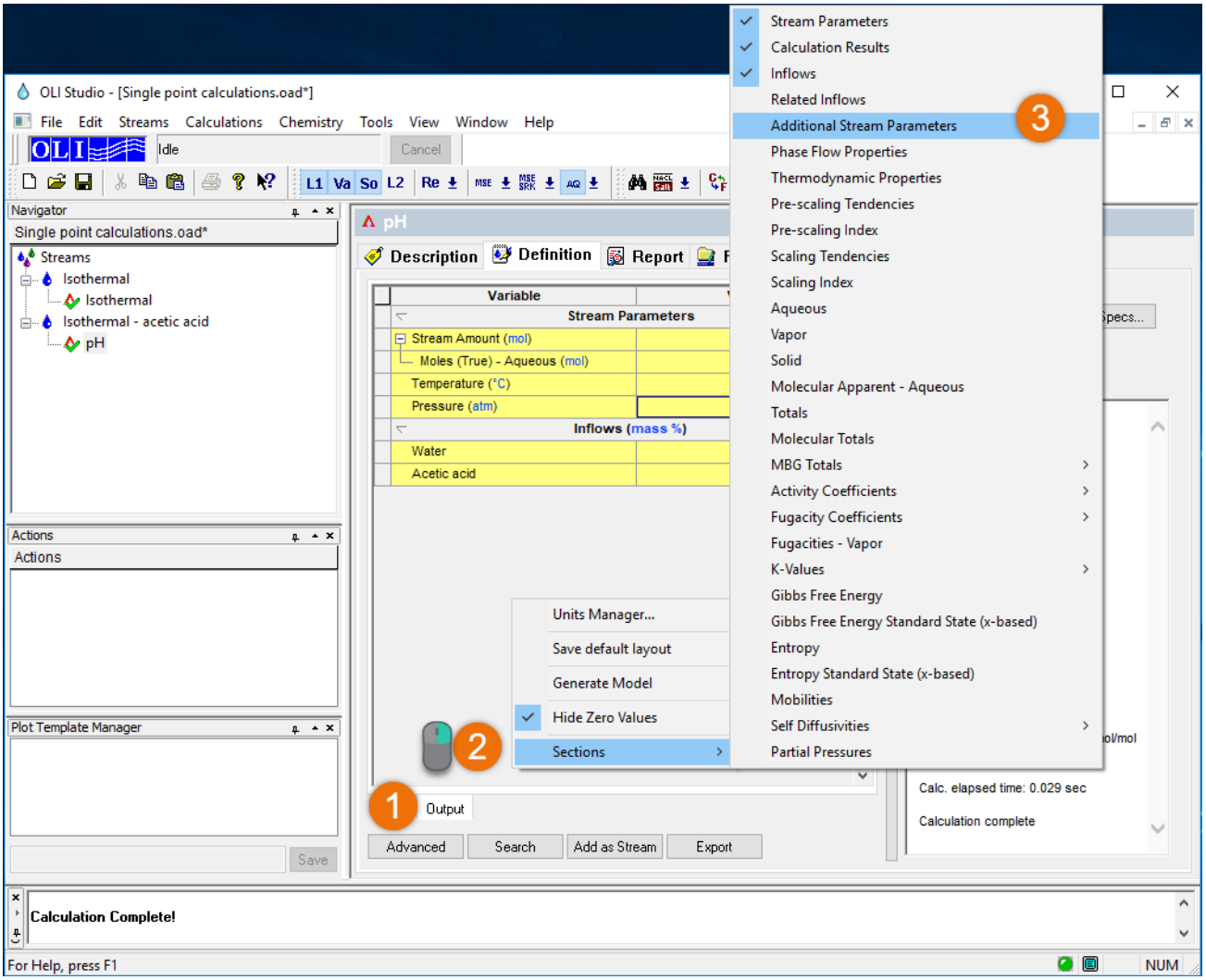
6. Click on the **Calculate** button



Anaylyzing the Results

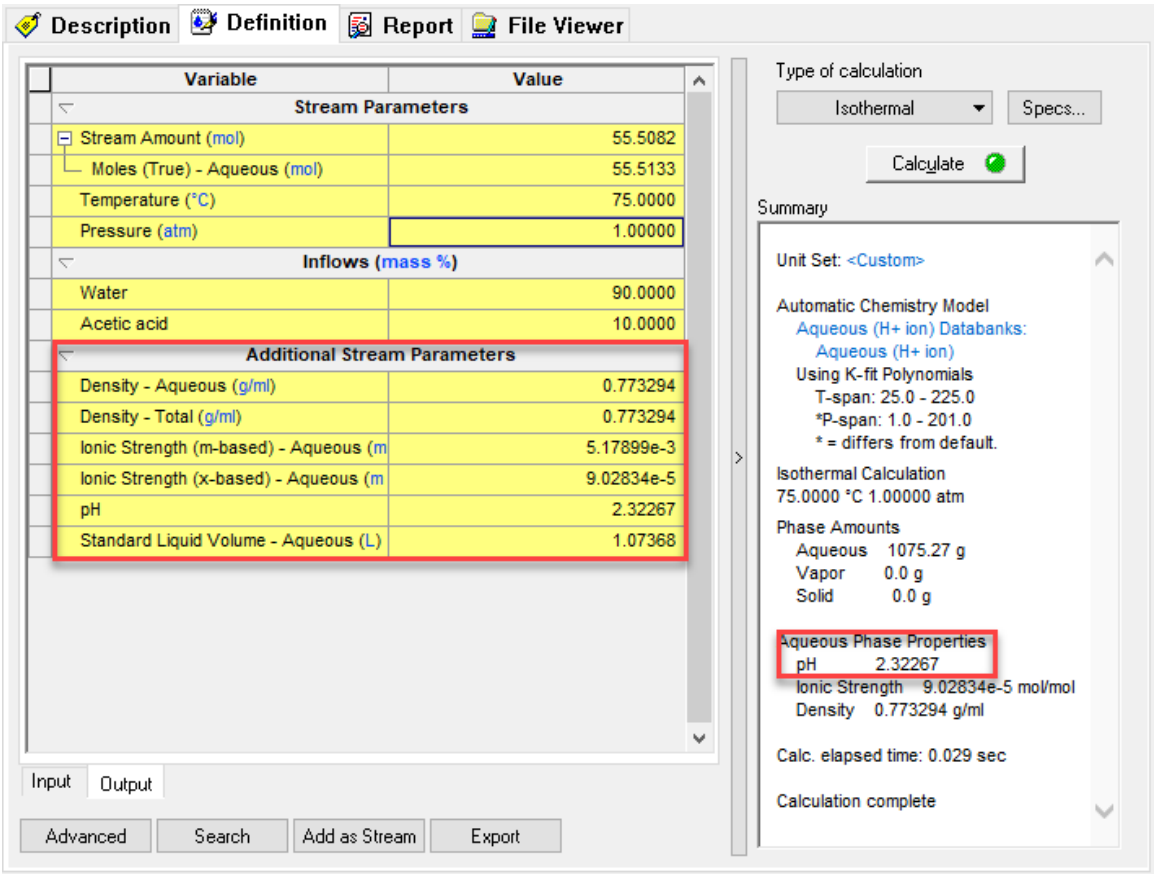
After the calculation is complete, another way of analyzing the results is using the **Output** mini-tab.

1. **Click** on the **Output** mini-tab
2. **Right-click** on the gray area and select **Sections**
3. Select **Additional Stream Parameters**



The Sections section offer more results such as Thermodynamic Properties, Scaling Tendencies, Equilibrium constants (K-values), etc., that you can further explore.

So, the calculated pH of this acetic acid solution is approximately 2.3.



It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created in Example 1 named as *Single Point Calculations*.

1.2. Bubble Point

Liquid boils when its vapor pressure exceeds its confining pressure. Boiling occurs by adding heat (isobaric boiling) or reducing confining pressure (isothermal boiling). Either way, the effect is the same: a vapor phase forms. Stream Analyzer calculates this phenomenon using a calculation type called **Bubble Point**. Since the OLI does not assume an air phase, the confining pressure acts like a plunger on a liquid's surface. The pressure the plunger exerts is the pressure specified in the software.

With the software, the temperature or pressure is adjusted such that a very small amount of vapor will form (i.e. 1×10^{-10} of the total stream amount in gmoles). This is another way of saying that the bubble point calculation is a determination of the boiling point. Usually we determine the temperature at which a solution will boil. If the pressure is set to 1 atm, then we calculate the **Normal Boiling Point**. If we set a constant temperature, then we determine the bubble point pressure.

Example 3: Calculating the Bubble Point of a 1 M Acetone Solution

In this example, we are going to compute the bubble point of a 1 M Acetone solution, by changing the temperature (isobaric) and then the pressure (isothermal). Additionally, you will learn how to change the **Inflows** units from moles to moles/L (M).

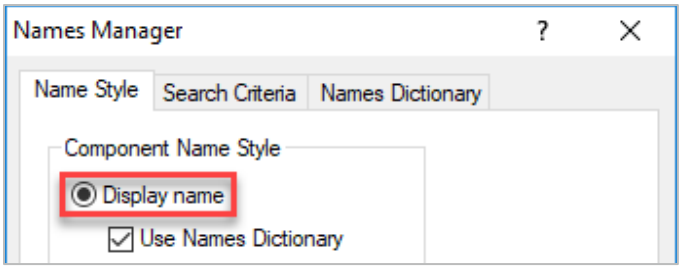
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

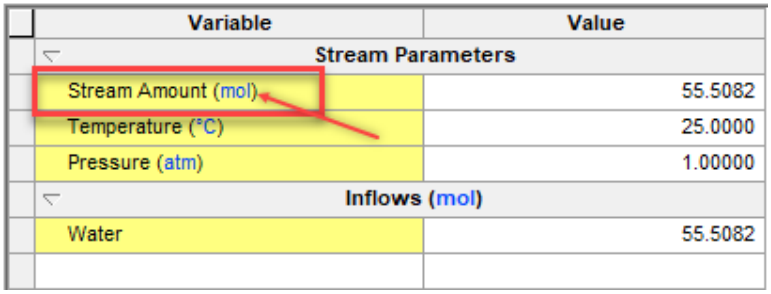
Bubble Point Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	1 L
Calculation Sub-type	Bubble Point	Temperature	25 ºC
Stream Name	Acetone Bubble Point	Pressure	1 atm
Name Style	Display Name	Water	Calculated
Unit Set	Custom	Acetone	1 mol/L
Framework	MSE		

Calculating the Bubble Point Temperature (Isobaric)

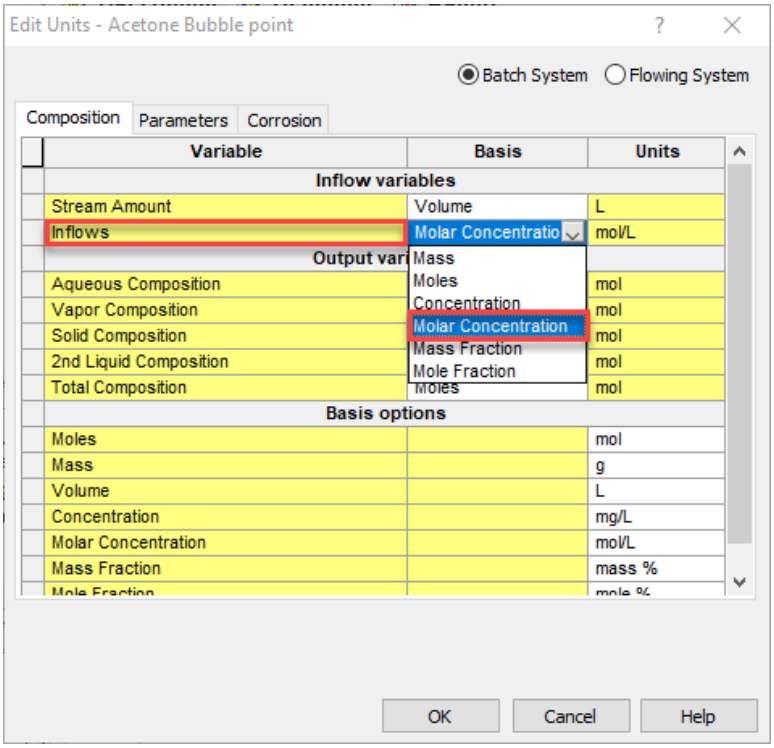
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Acetone Bubble Point*
3. Select the **MSE** thermodynamic Framework
4. **Click** on the **Names Manager** Icon, and select the ***Display Name*** option, and click **OK**



5. **Click** on the hyperlink **mol** next to **Stream Amount**



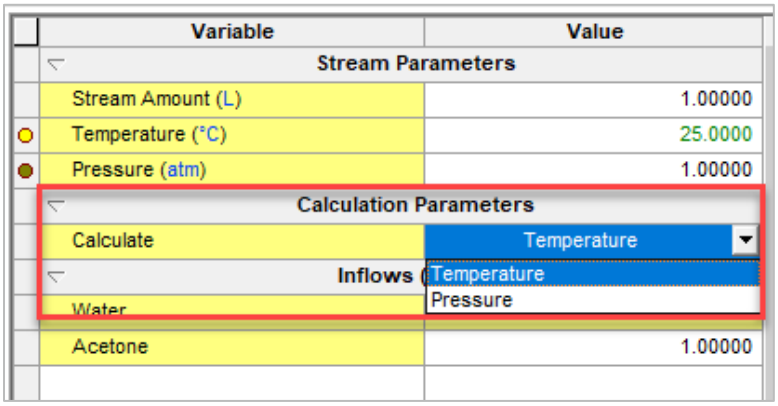
6. This will open the **Units Manager.** Under **Inflows**, select the option of **Molar Concentration**. It will automatically set the Stream amount as **Volume** in **Liters**. Then click **OK**.



7. Type **Acetone** in the white cell below H2O inflows grid, and press **<Tab>** or hit **<Enter>**, and then enter the value **1.0 mol/L** in the next cell.
8. Go to the **Add Calculation** button and select **Single Point** calculation

9. Select **Bubble point** as Type of Calculation.
10. Change the ***SinglePoint*** name to ***Bubble Point Temperature*** using the **<F2>** key
11. A new section appears in the grid, called **Calculation Parameters**. By default, the Temperature Bubble Point calculation is selected. For this calculation leave the default calculation: **Temperature**

Note: In the drop-down arrow you have the option to select Bubble Point **Temperature** or Bubble Point **Pressure**.



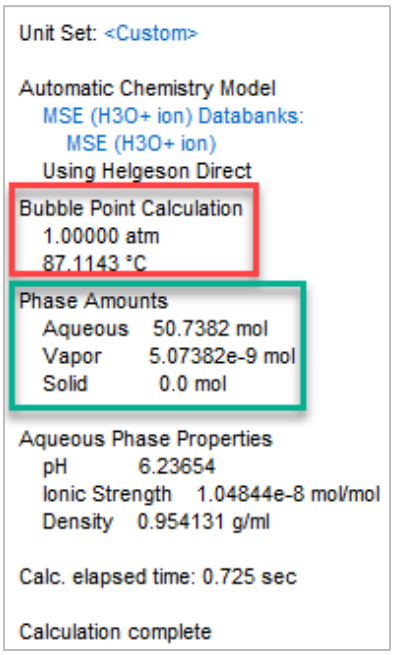
Note: There are also two dots to the left of the Temperature and Pressure rows. The yellow dot represents the **"dependent"** variable. The temperature value, 25.000 is colored green. This value is now an initial guess, since the final value will be computed. The brown dot adjacent to the Pressure variable indicates that this potentially dependent variable is **"fixed".**

12. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key.

13. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

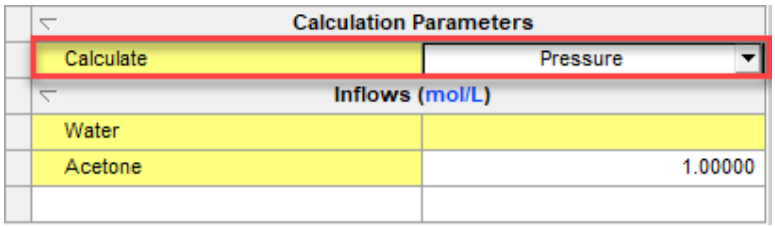
Review the Summary Box. The temperature at the bubble point is computed to be **87.11ºC** at 1 atm. Also notice that the **Vapor** amount is ≈ 5.074e-9 moles out of the total **Aqueous** amount of 50.74 moles. This is by design; the software sets the amount of vapor at 1/10th the moles of the stream amount.



Calculating the Bubble Point Pressure (Isothermal)

This next calculation computes the bubble point pressure for the same stream.

1. Select the Stream named **Acetone Bubble point**
2. Go to the **Add Calculation** button and select **Single Point** calculation
3. Select **Bubble point** as Type of Calculation.
4. Change the ***SinglePoint*** name to ***Bubble Point Pressure*** using the **<F2>** key
5. Change the Calculate-Temperature row to **Calculate-Pressure**

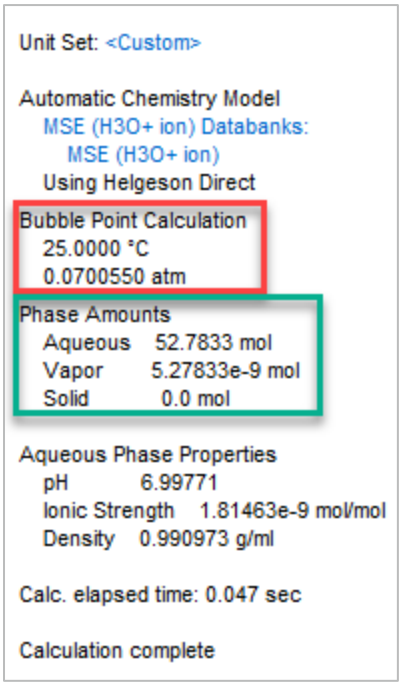


6. **Click** on the **Calculate** button or press the **<F9>** key.

7. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Anaylyzing the Results

Review the Summary Box. The bubble point pressure is computed to be **0.0700550** at 25 ºC. Also notice that the **Vapor** amount is ≈ 5.278e-9 moles out of the total **Aqueous** amount of 52.78 moles.



1.3. Dew Point

The **Dew Point** is defined as the temperature at which a condensable component of a gas, for example water vapor in the air, starts to condensate into a liquid. OLI Analyzer: Stream Analyzer calculates this phenomenon using a calculation type called Dew Point. With the software, the temperature or pressure is adjusted such that a very small amount of liquid will form.

It is frequently useful to determine the temperature or pressure at which a gas will condense. If the pressure is set constant, we calculate the dew point temperature; if the temperature is constant, then we determine the dew point pressure.

Example 4: Calculating the Dew Point of a Simple Sour Natural Gas

In this example, we are going to compute the dew point of a simple sour natural gas, by changing the temperature (isobaric) and then the pressure (isothermal).

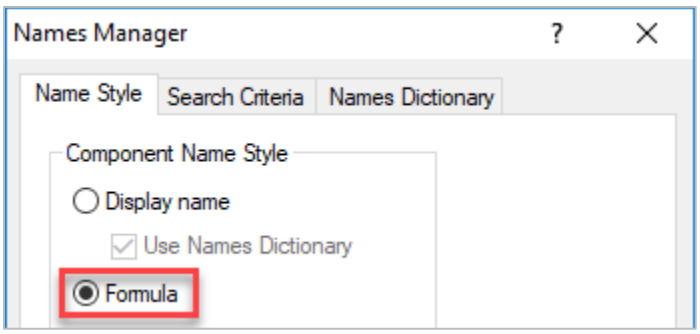
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

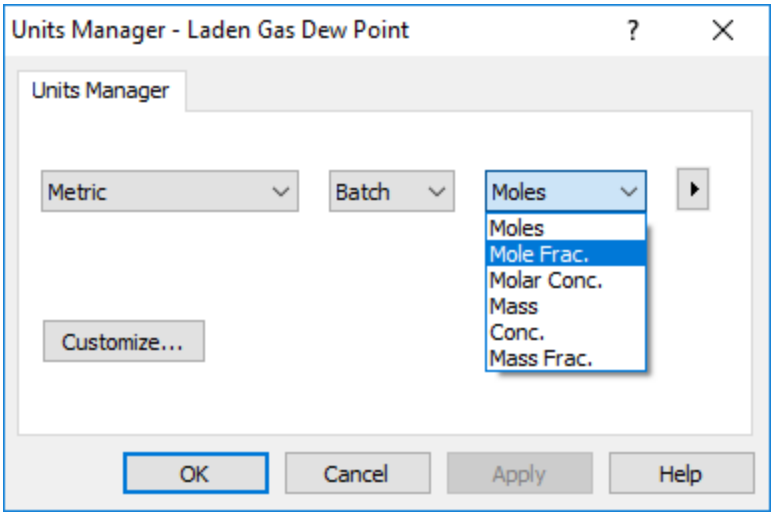
Dew Point Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Default – 55.5082 moles
Calculation Sub-type	Dew Point	Temperature	120 ºC
Stream Name	Sour Natural Gas Dew Point	Pressure	100 atm
Name Style	Display Formula	H2O	Calculated
Unit Set	Metric, Mole Fraction	CO2	1 mole %
Framework	MSE	CH_4	95 mole %
		H_2S	3 mole %

Calculating the Dew Point Temperature (Isobaric)

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Sour Natural Gas Dew Point*
3. Select the **MSE** thermodynamic Framework
4. **Click** on the **Names Manager** Icon, and select the **Formula** option, and click **OK**



5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Mole Frac. This will change all inflows to mole %.



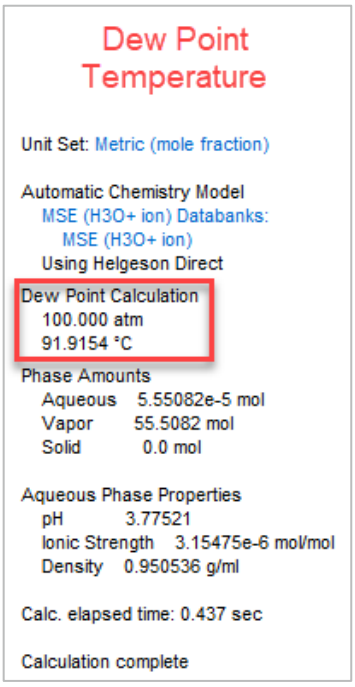
6. Enter the composition of the gas given in the table above
7. Go to the **Add Calculation** button and select **Single Point** calculation
8. Select **Dew point** as Type of Calculation
9. Change the ***SinglePoint*** name to ***Dew Point Temperature*** using the **<F2>** key
10. Keep the Calculate-**Temperature** option

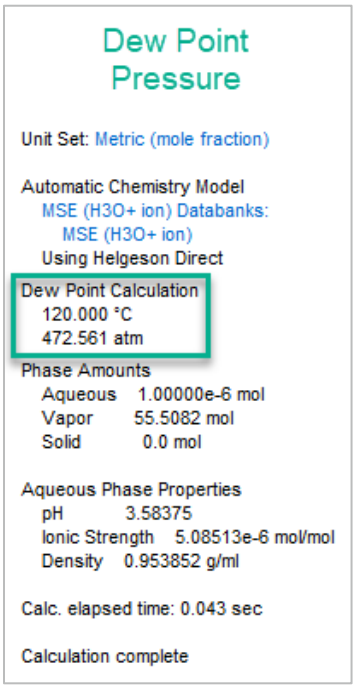
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	120.000
Pressure (atm)	100.000
Calculation Parameters	
Calculate	Temperature
Inflows (mole %)	
H2O	1.00000
CO2	1.00000
CH4	95.0000
H2S	3.00000

11. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
12. Create a **new *SinglePoint*** and name it ***Dew Point Pressure.*** Repeat the steps above, and select the Calculate-**Pressure** option
13. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

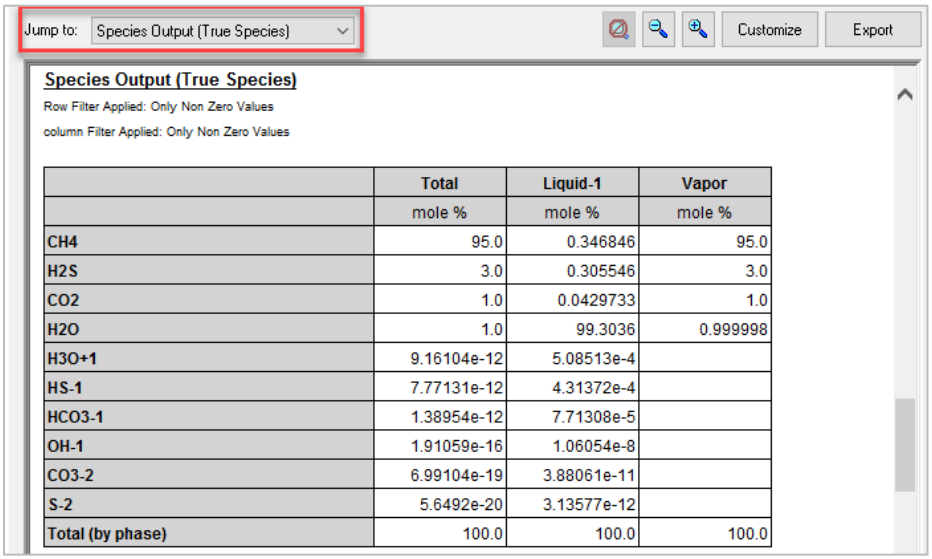
Review the Summary Box. The calculated dew point temperature is **113.5°C**. The calculated dew point pressure is **129.8 atm**.





Note: The software sets the amount of liquid to $1/10^6$ of the stream amount for the dew point calculation.

You can study the composition of the acid gases such as CO_2 and H_2S dissolved in the Aqueous phase. After you have calculated the Dew Point Pressure, click on the **Report** Tab. Scroll down or use the **Jump to** option to go to the **Species Output (True Species).**



	Total	Liquid-1	Vapor
	mole %	mole %	mole %
CH4	95.0	0.346846	95.0
H2S	3.0	0.305546	3.0
CO2	1.0	0.0429733	1.0
H2O	1.0	99.3036	0.999998
H3O+1	9.16104e-12	5.08513e-4	
HS-1	7.77131e-12	4.31372e-4	
HCO3-1	1.38954e-12	7.71308e-5	
OH-1	1.91059e-16	1.06054e-8	
CO3-2	6.99104e-19	3.88061e-11	
S-2	5.6492e-20	3.13577e-12	
Total (by phase)	100.0	100.0	100.0

The aqueous phase, also known as Liquid-1 in the MSE framework, is shown in the center column. The dissolved CH_4, H_2S, and CO_2 are 0.347, 0.305, and 0.043 mole % respectively.

1.4. Isochoric (constant volume)

The **Isochoric calculation** fixes the total system **volume** and adjusts the temperature or pressure. This can be understood in a gas-phase from the basis of the Ideal Gas Law:

$$PV = nRT$$

If temperature is the free variable, then the above equation becomes $T = \frac{PV}{nR}$, meaning that for a given volume, pressure, and gas moles, temperature can be obtained.

You will run a calculation, in which the system moles, temperature and volume are defined.

Example 5: Calculating the Total Pressure of a 10 L Vessel Containing Water and Air

In this example, you will add 1 kg water to a 10 L vessel and then fill the void (head space) with Air. The temperature is 25 ºC.

Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Autoclave Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Default – 55.5082
Calculation Sub-type	Isochoric	Ambient Temperature	25 ºC
Stream Name	Isochoric	H2O	Calculated
Name Style	Display Formula	N2	77 moles
Unit Set	Metric, Moles	O2	21 moles
Framework	AQ	CO2	1 mol
Calculate	Pressure	Ar	0.04 moles
Vessel Volume	10 L		

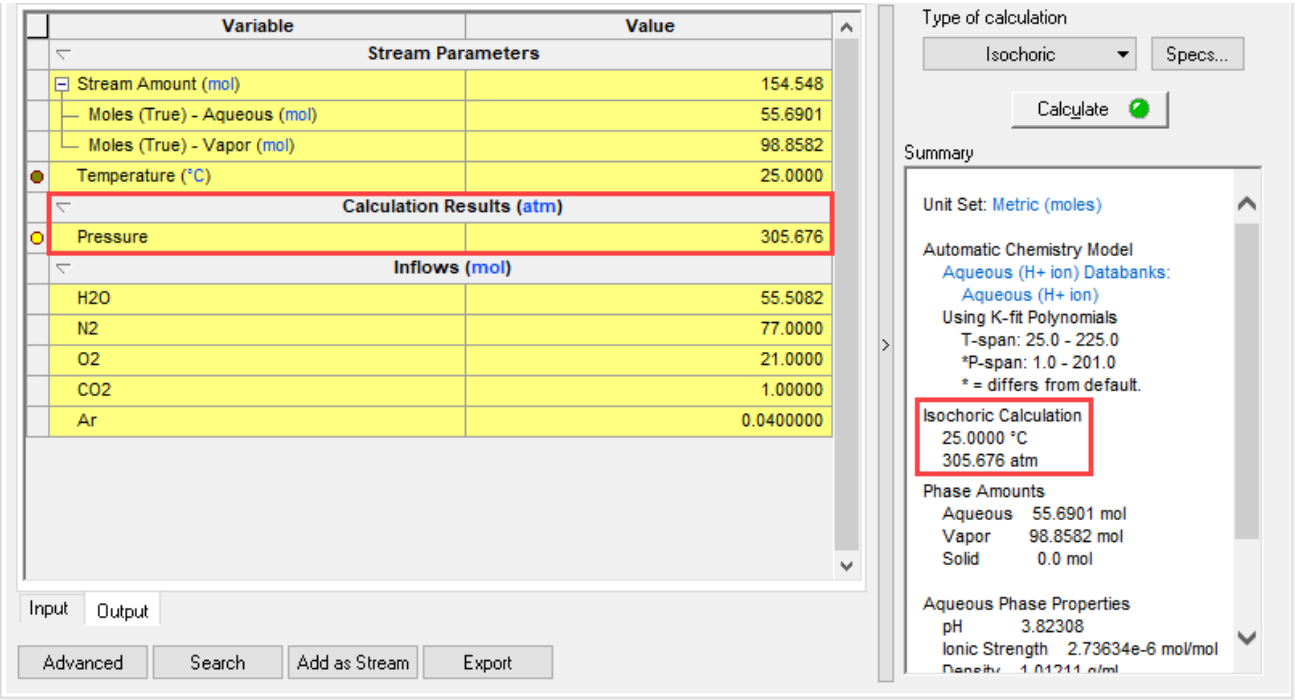
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Isochoric*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the **gas composition** in the table above
7. Go to the **Add Calculation** button and select **Single Point** calculation
8. Select **Isochoric** as Type of Calculation
9. Change the ***SinglePoint*** name to **10L Vessel** using the **<F2>** key
10. In the **Calculation Parameters** section set **Total Volume** to **10 L** and **Calculate Pressure**. (To select Pressure, click on the drop-down arrow).

Variable	Value
Stream Parameters	
Stream Amount (mol)	154.548
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Total Volume (L)	10.0000
Calculate	Pressure
Inflows (mol)	
H2O	55.5082
N2	77.0000
O2	21.0000
CO2	1.00000
Ar	0.0400000

11. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
12. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

Review the **Summary Box** or Click on the **Output-Minitab** to see the Results.



About **305.7 atm** of pressure are needed to compress the 154.55 moles of gas and liquid into a 10-L volume vessel at 25 ºC.

Go to the **Report** tab and view the **Total and Phase Flows (Amount)** table.

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mol	mol	mol
Mole (True)	154.548	55.6901	98.8582
Mole (App)	154.548	55.6901	98.8582
	g	g	g
Mass	3874.61	1006.11	2868.51
	L	L	L
Volume	10.0001	0.994072	9.00598

The system is 10 L as defined (within the $1/10^6$ tolerance). The water phase makes up slightly less than 1 L and the balance is vapor. At this pressure, about 0.1527 moles of water evaporates, and contributes to the total moles of vapor.

1.5. Vapor Amount and Vapor Fraction

The **vapor amount** and **vapor fraction** calculations are identical in nature to the Bubble Point calculation, except that instead of the software defining the vapor amount as 1×10^{-10} of the total stream amount, the user defines the vapor size in either mole fraction units (vapor fraction) or mole units (vapor amount). To create a specified amount of vapor (or vapor fraction) the software can adjust the temperature (or pressure).

Example 6: Evaporating a Brine

In this example, you will concentrate a brine via evaporation adjusting the temperature, until reaching a vapor fraction amount of 95 mole %.

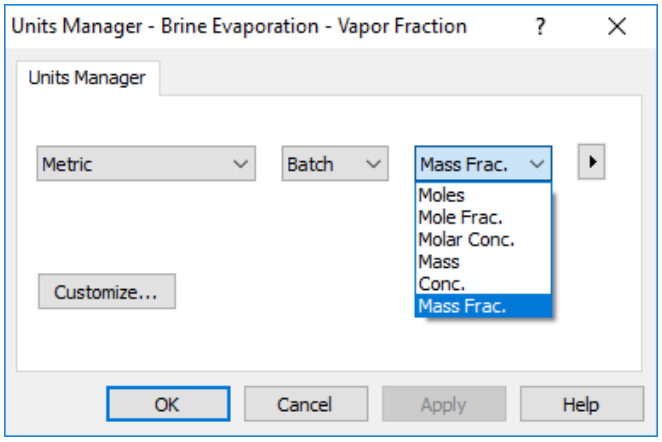
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Vapor Fraction / Vapor Amount Point Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Default - 1 kg
Calculation Sub-type	Vapor Fraction	Temperature	25 ºC
Stream Name	Brine Evaporation – Vapor Fraction	Pressure	1 atm
Name Style	Display Formula	H2O	Calculated
Unit Set	Metric, Mass Fraction	NaCl	9 mass %
Framework	MSE	$CaSO_4$	1 mass %

Calculating the Vapor Fraction Temperature (Isobaric)

13. Add a new **Stream**
14. **Click** on the new Stream and press **<F2>** to change the name to *Brine Evaporation – Vapor Fraction*
15. Select the **MSE** thermodynamic Framework
16. **Click** on the **Names Manager** Icon and select the **Formula** option
17. **Click** on the **Units Manager** Icon, and select Metric, Batch, Mass Frac. This will change all inflows to mass %.



18. Enter the gas composition given in the table above.
19. Go to the **Add Calculation** button and select **Single Point** calculation
20. Select **Vapor Fraction** as Type of Calculation
21. Change the ***SinglePoint*** name to ***Vapor Fraction Temperature*** using the **<F2>** key
22. Enter **95** as the **Vapor Fraction** amount.

    Note: The software will convert the 1 kg to mole units and will put 95% of this in the vapor phase.
23. Keep the Calculate-**Temperature** option

Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Vapor Fraction (Vapor/Inflow [mol]) (mole %)	95.0000
Calculate	Temperature
Inflows (mass %)	
H2O	90.0000
NaCl	9.00000
CaSO4	1.00000

24. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
25. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

Review the Summary Box. The calculated temperature to put 95% (mole based) of the total stream amount in the vapor phase is **~109°C**, however the results in the summary box are given in mass. Let's go to the **Report**.

Unit Set: Metric (mass fraction)

Automatic Chemistry Model
MSE (H3O+ ion) Databanks:
MSE (H3O+ ion)
Using Helgeson Direct

Vapor Fraction Calculation
1.00000 atm
108.805 °C

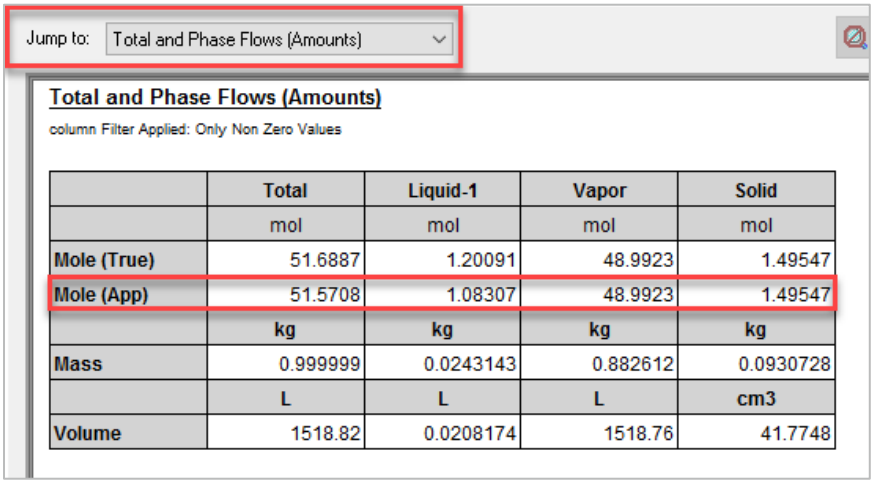
Phase Amounts
Aqueous 0.0243143 kg
Vapor 0.882612 kg
Solid 0.0930728 kg

Aqueous Phase Properties
pH 6.40682
Ionic Strength 0.0990622 mol/mol
Density 1.16798 g/ml

Calc. elapsed time: 0.131 sec

Calculation complete

1. Select the **Report** tab and scroll down to **Total and Phase Flow (Amounts)** Table.



Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor	Solid
	mol	mol	mol	mol
Mole (True)	51.6887	1.20091	48.9923	1.49547
Mole (App)	51.5708	1.08307	48.9923	1.49547
	kg	**kg**	**kg**	**kg**
Mass	0.999999	0.0243143	0.882612	0.0930728
	L	**L**	**L**	**cm3**
Volume	1518.82	0.0208174	1518.76	41.7748

The apparent moles (**Mole (App)**) are the molecular representation of the system. There is a total of 51.5708 moles in this system, and exactly 95% of this system is in the vapor phase with a total of 48.9923 moles.

1.6. Set pH

The **Set pH** calculation is a useful tool in analyzing or designing a process. It allows you to create a solution that conforms to a premeasured pH. Other applications include designing a system to meet an operational pH or testing the impact of adding an acid or base to a system.

Example 7: Neutralizing Acetic Acid

In this example, you will compute the amount of base titrant required to neutralize a 1 molal acetic acid solution. You will assume a neutral system at 7 pH and 25°C.

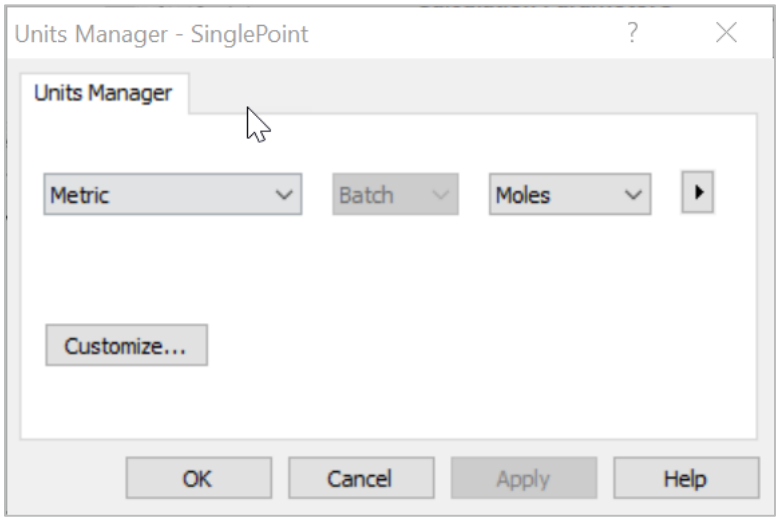
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Set pH Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Default
Calculation Sub-type	Set pH	Temperature	25 ºC
Stream Name	Neutralizing Acid	Pressure	1 atm
Name Style	Display Formula	H2O	Calculated
Unit Set	Metric, Moles	CH3COOH	1 mol
Framework	AQ		

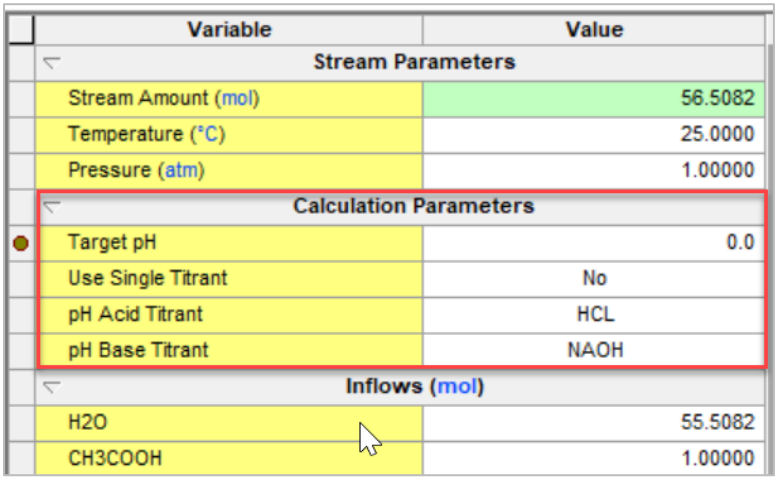
Setting the pH

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Neutralizing Acid*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles (default units). Click **OK.**

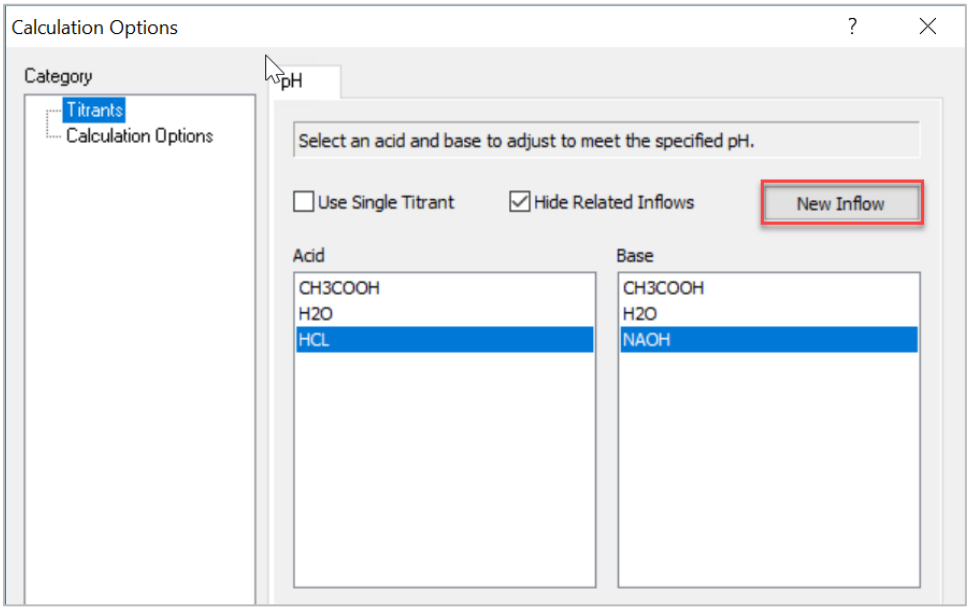


6. Enter **1 mol** of **CH3COOH** as an inflow
7. Go to the **Add Calculation** button and select **Single Point** calculation
8. Select **Set pH** as Type of Calculation
9. Change the ***SinglePoint*** name to ***Neutralizing acetic acid*** using the **<F2>** key

A new grid section named **Calculation Parameters** appears. In this grid the **Target pH** can be defined, as well as the **Acid** and **Basic** titrants. The default titrants are **HCl** and **NaOH** (common) and so no additional specifications are required except to set the pH.



Note: The default titrants can be changed by other acids or bases by adding the desired titrant as an inflow. The titrants in the **Set pH** calculation can be also set using the **Specs** button.



The default acid and base are already set, so no additional work is required If a different acid/base is desired, then the **New Inflow** button can be used to find additional components.

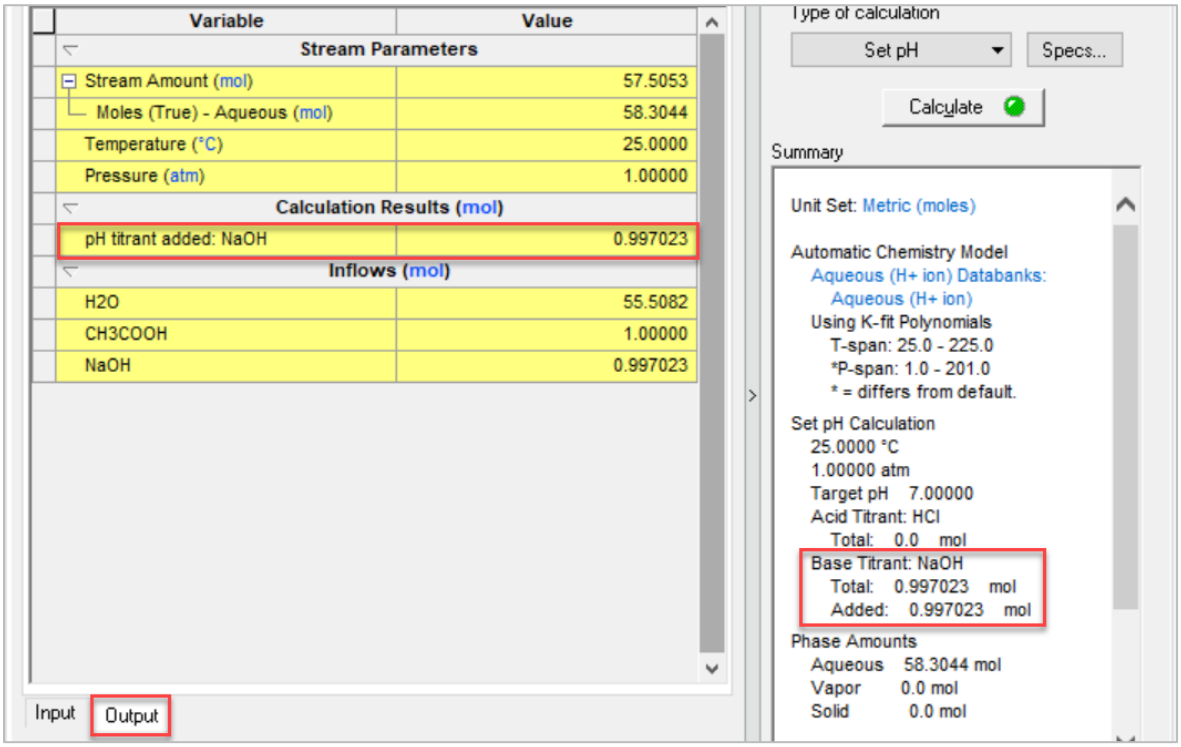
10. Enter **7** as the **Target pH** amount
11. Use the default titrants: **HCL** and **NAOH**

Variable	Value
Stream Parameters	
Stream Amount (mol)	56.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Target pH	7.00000
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Inflows (mol)	
H2O	55.5082
CH3COOH	1.00000

12. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
13. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

Review the **Summary Box** or Click on the **Output-Minitab** to see the Results. About **0.997 moles** of NaOH is needed to neutralize 1 mole of acetic acid.



1.7. Precipitation Point

The **precipitation point** calculation computes the amount of material held in solution at given conditions and forces a very small amount of solid to exist. This calculation could be also called a **solubility calculation**.

Example 8: Determining the Solubility of Calcite ($CaCO_3$)

Equilibrium based simulators suffer from a potential problem, that the most stable solid will tend to be included over less stable (meta-stable) solids. Such is the case of calcium carbonate. Calcium Carbonate ($CaCO_3$) is found in nature in many forms. Two common forms are the more thermodynamically stable solids, **Calcite** and the less stable form **Aragonite**.

In this example, we will compute the solubility of $CaCO_3$ as **Calcite** in a solution containing Ca^{+2}, Mg^{+2}, and Cl^- as well as dissolved CO_2.

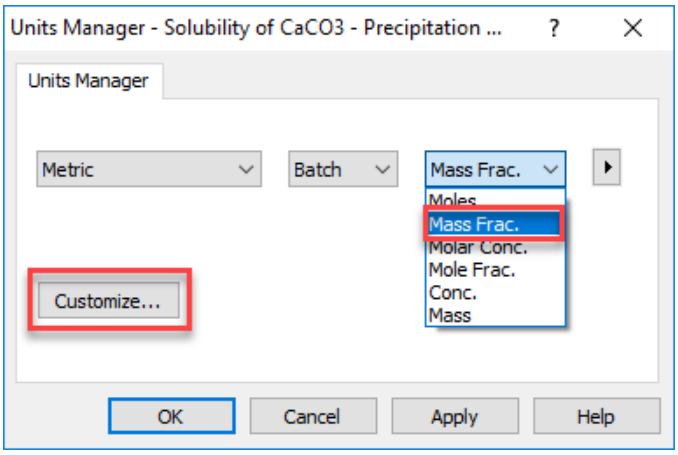
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

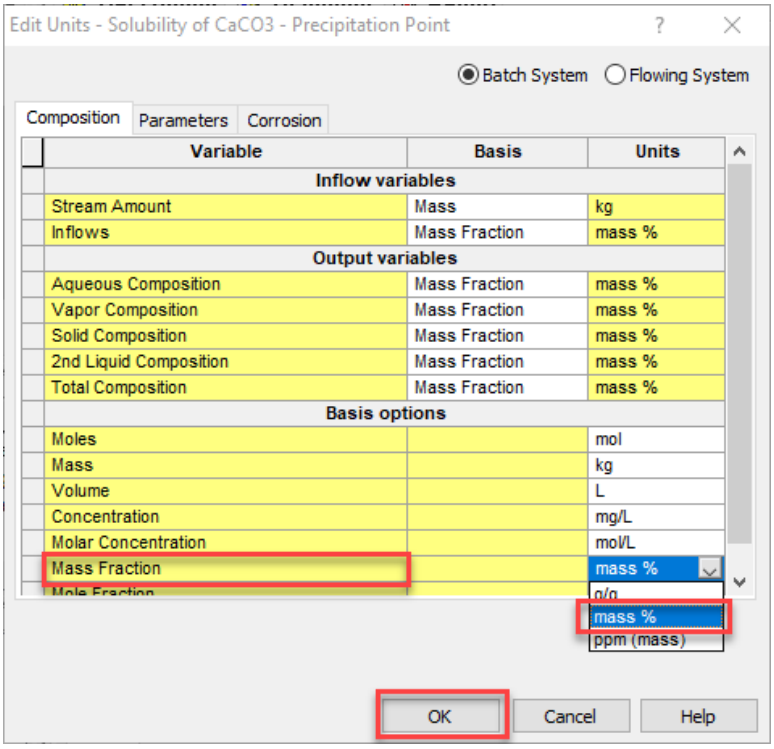
Precipitation Point Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Default - 1 kg
Calculation Sub-type	Precipitation Point	Temperature	25 ºC
Stream Name	Solubility of CaCO3 – Precipitation Point	Pressure	1 atm
Name Style	Display Formula	H2O	Calculated
Unit Set	Metric, Mass Fraction (ppm (mass))	CaCl2	10870 ppm (mass)
Framework	AQ	MgCl2	9325 ppm (mass)
		CO2	431 ppm (mass)
		CaCO3	0 ppm(mass)

Calculating the Precipitation of Calcite ($CaCO_3$)

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Solubility of CaCO3 – Precipitation Point*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Mass Frac. This will change all inflows to mass%. However, you need to change the units to ppm (mass), to do this **Click** on the **Customize button.**

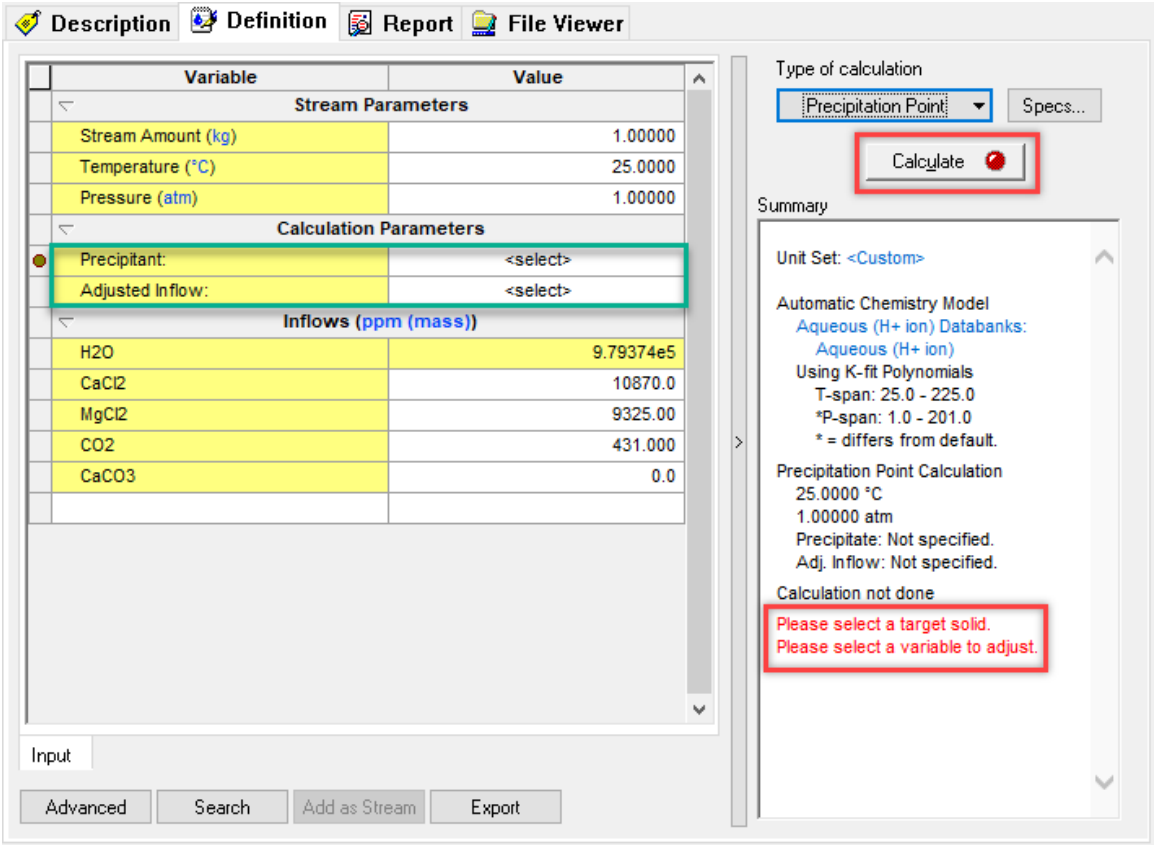


6. This will open the **Edit Units** window. **Change** the units from **mass%** to **ppm (mass).**



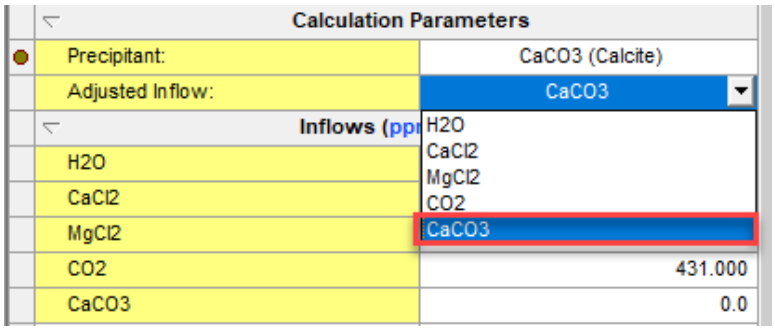
7. Enter the stream composition given in the table above.
8. Go to the **Add Calculation** button and select **Single Point** calculation
9. Select **Precipitation Point** as Type of Calculation
10. Change the ***SinglePoint*** name to ***Calcite Precipitation*** using the **<F2>** key

At this point you may have noticed that the Calculate button is red, and that there is a **red** text in the Summary Box with instruction that additional specs are needed. The specifications need to be defined in the **Calculation Parameters** grid section.



11. Select the **CaCO3 (Calcite)** as the **Precipitant**

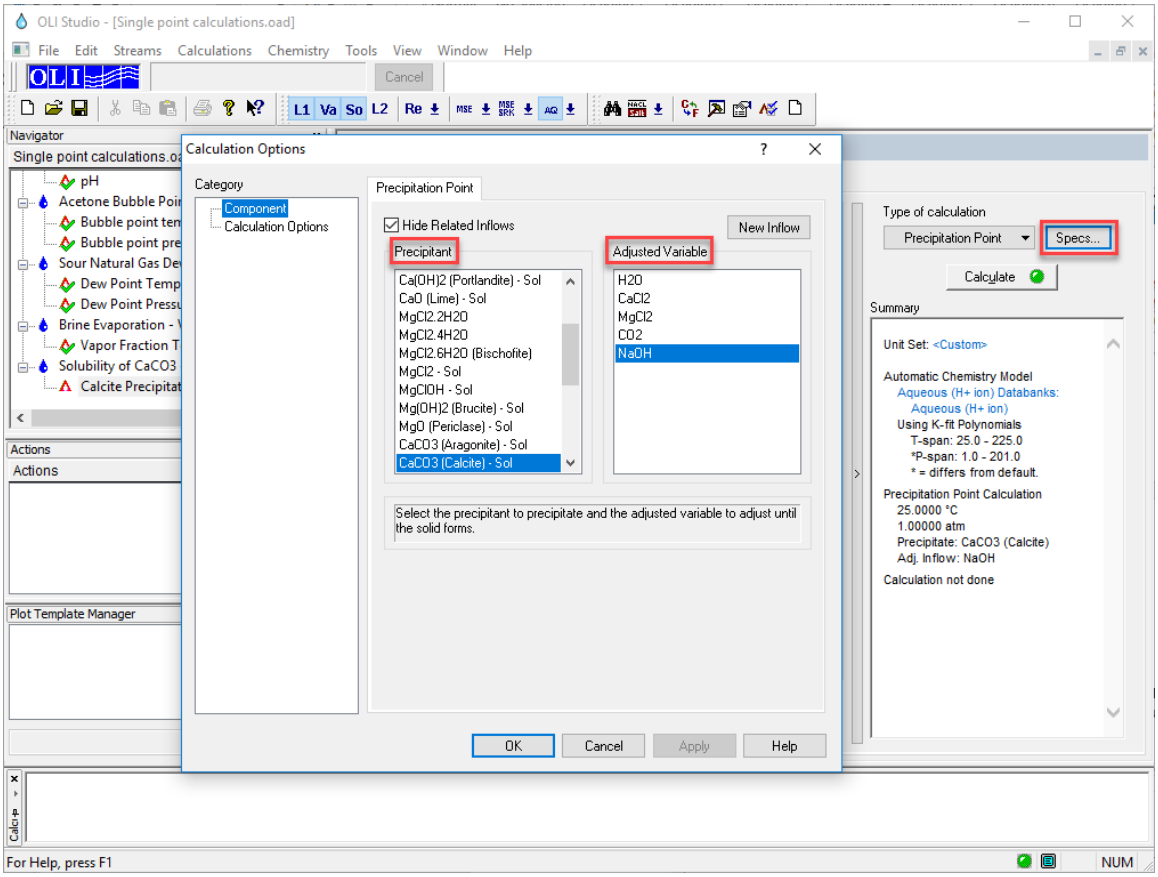
12. Select **CaCO3** as the **Adjusted Inflow**



The **Precipitant** refers to the independent variable – in this calculation, the solid phase selected will precipitate at amount of 1.0×10^{-10} times the stream amount.

The **Adjusted Variable** is the variable to be changed by the software until the solid target amount is achieved.

Note: The precipitation point parameters can be also set using the **Specs** button.

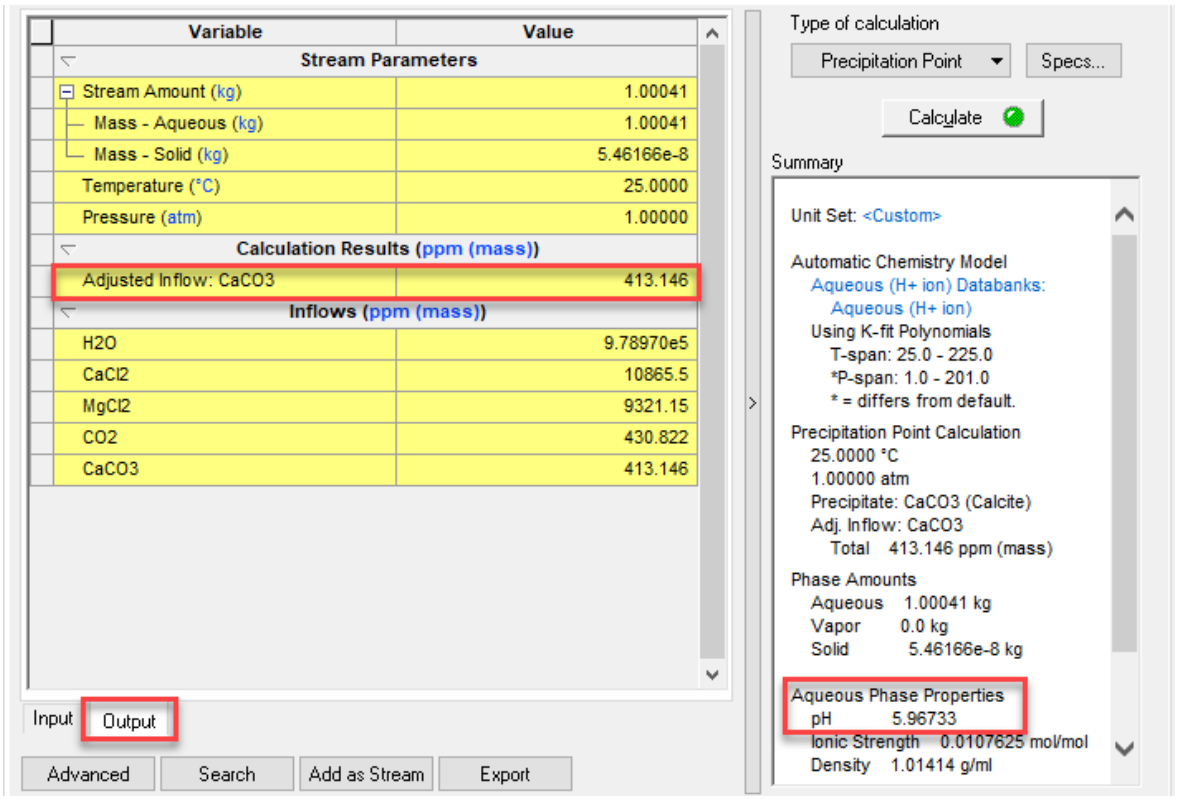


13. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
14. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

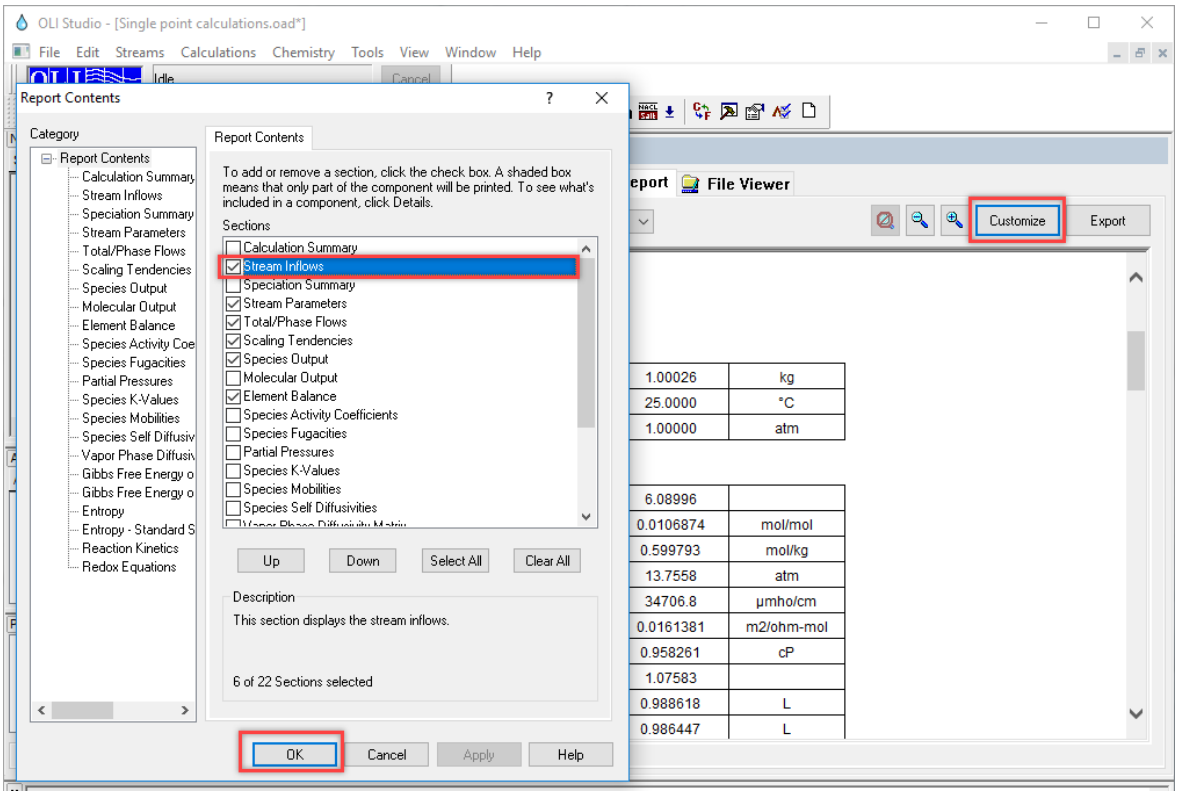
Anaylyzing the Results

Review the **Summary Box** or Click on the **Output-Minitab** to see the Results.

The software calculated that the solubility of $CaCO_3$ as Calcite in the solution under study is around **~431.15 ppm (mass)**. The pH of this solution is ~5.97.



You can also check the results in the **Report** Tab. Click the **Customize** button and Select **Stream Inflows**.



Notice that the concentrations have changed slightly. This is to accommodate the additional 413.15 ppm $CaCO_3$ needed to meet the calculation specifications.

Stream Inflows

Row Filter Applied: Only Non Zero Values

	Input	Output
Species	ppm (mass)	ppm (mass)
H2O	9.79374e5	9.78970e5
CaCl2	10870.0	10865.5
MgCl2	9325.00	9321.15
CO2	431.000	430.822
CaCO3	0.0	413.146

Example 9: Determining the Solubility of Aragonite ($CaCO_3$)

Calcite is the thermodynamically stable phase of calcium carbonate**. Aragonite,** calcite's orthorhombic polymorph, is about 1.5 times more soluble than calcite[3]. At surface conditions, aragonite spontaneously turns into calcite over geologic time, but at higher pressures aragonite, the denser of the two, is the preferred structure.

In this example, we wish to determine the solubility of the less thermodynamically stable solid, **Aragonite,** independently of the more stable solid **Calcite**. To do this, we need to modify the **solid phases** in the chemistry model and add a new **Databank**.

Starting the Simulation

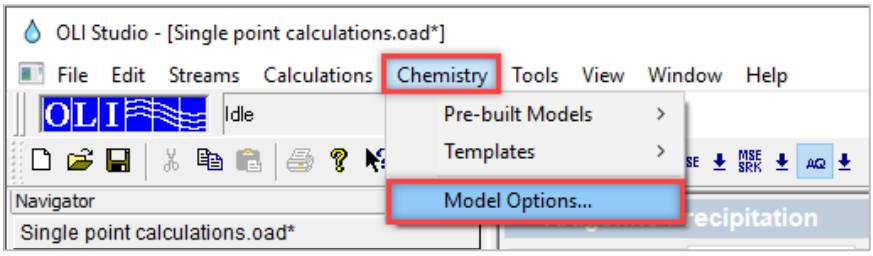
Calculating the Precipitation of Aragonite ($CaCO_3$)

1. Under the Stream *Solubility of CaCO3 – Precipitation Point*, **Add a Single Point** calculation
2. Select **Precipitation Point** as Type of Calculation
3. Change the ***SinglePoint*** name to ***Aragonite Precipitation*** using the **<F2>** key
4. Select the **CaCO3 (Calcite)** as the **Precipitant**
5. Select **NaOH** as the **Adjusted Inflow**

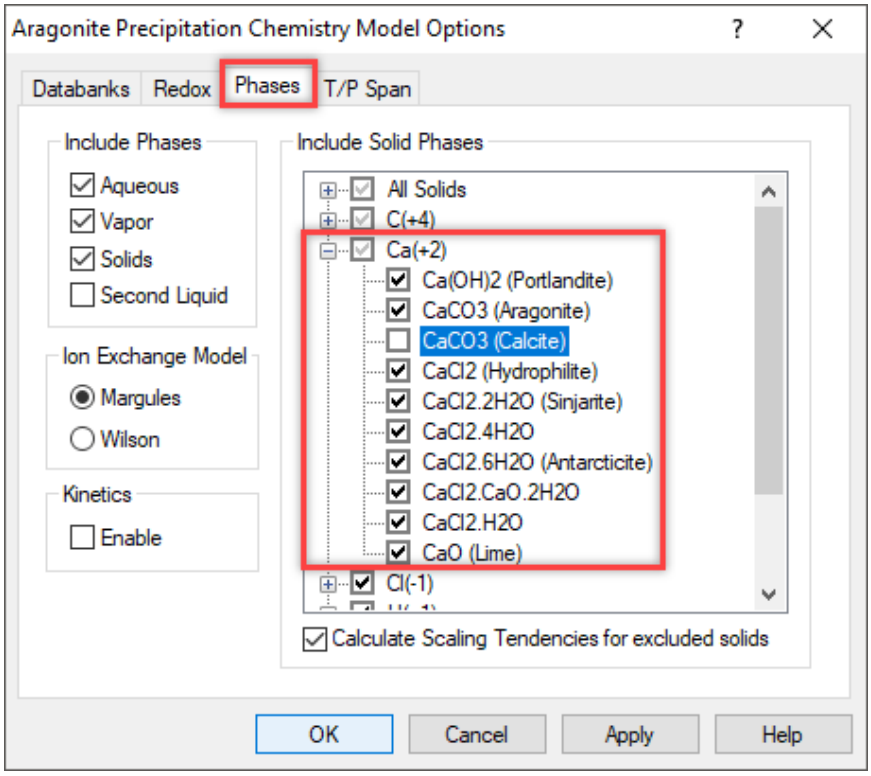
Calculation Parameters	
Precipitant:	CaCO3 (Aragonite)
Adjusted Inflow:	CaCO3

[3] https://www.sciencedirect.com/topics/earth-and-planetary-sciences/calcite

6. Click on **Chemistry** > **Model Options**



7. Select the **Phases** tab
8. **Click** on the **"+"** next to the Ca(+2) box to display all the calcium containing solids
9. Scroll down to find CaCO3 (Calcite) and **uncheck** this solid
10. Click **OK** continue.



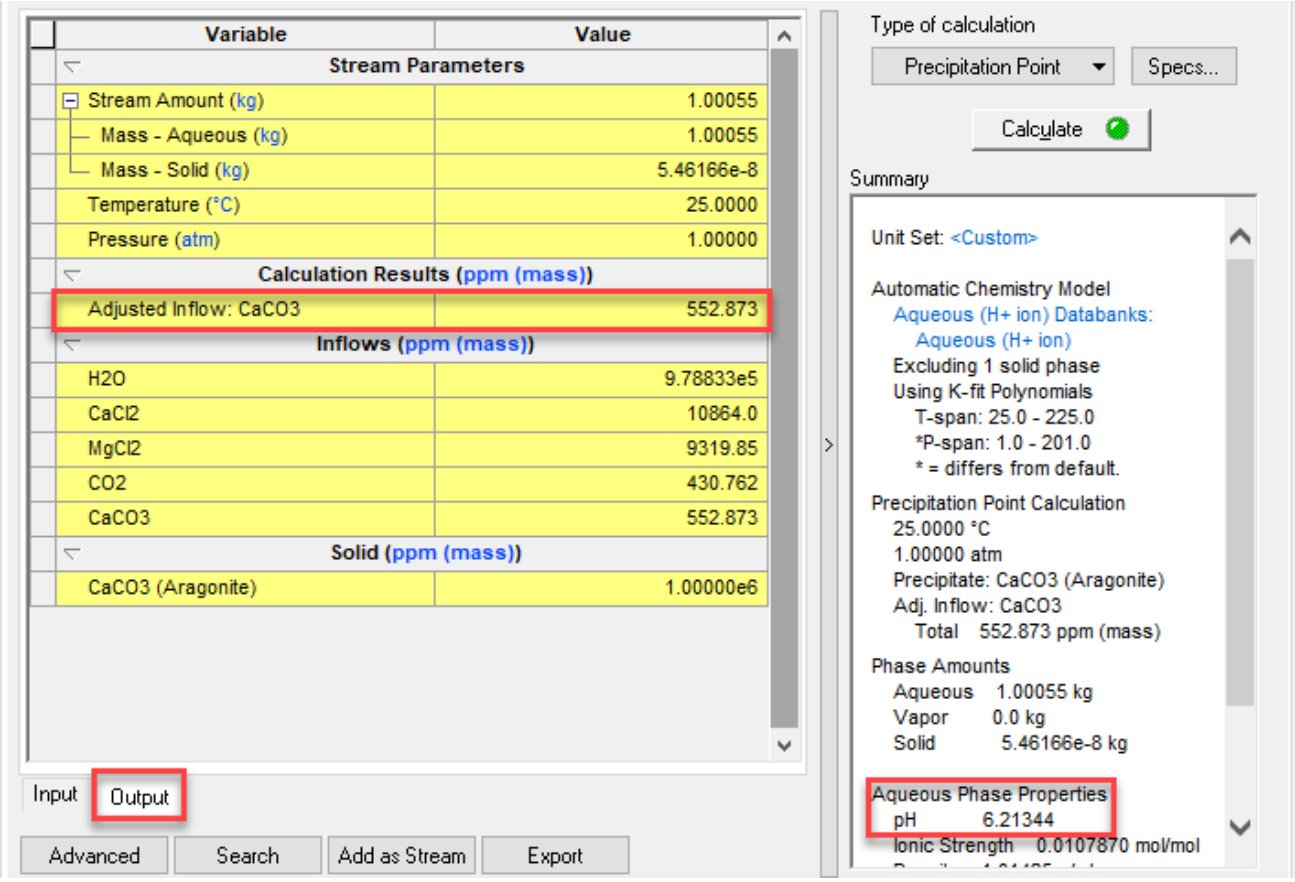
Note: The **Include Solid Phases box** lists the solids in the chemistry model. Unchecking these solids will mathematically eliminate the solid from consideration. The Scaling Tendency, however, will still be calculated.

11. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
12. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

Review the **Summary Box** or Click on the **Output-Minitab** to see the Results.

The software calculated that the solubility of $CaCO_3$ as Aragonite in the solution under study is around **~552.87 ppm (mass)**. The pH of this solution is ~6.21. You can see that the solubility of Aragonite is higher than the solubility of Calcite (~431.15 ppm (mass)).



Example 10: Determining the Solubility of Dolomite ($CaMg(CO_3)_2$)

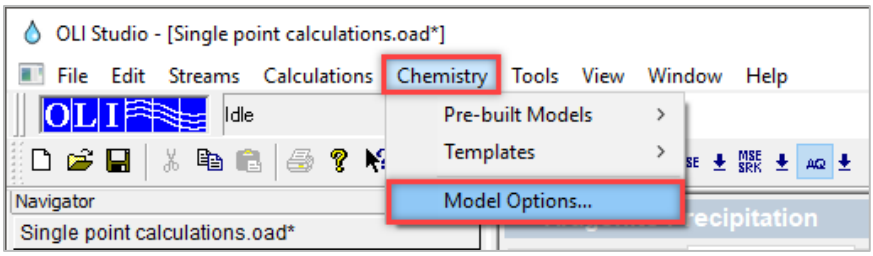
The third carbonate mineral to mention is **Dolomite**, which is something like calcite with a very high concentration of magnesium in it. Under some conditions there can be much more magnesium added in, and when the amount of magnesium becomes roughly the same as the calcium, the resulting mineral is called Dolomite with the following chemical formula: $CaMg(CO_3)_2$. The formation of Dolomite is believed to appear in geological time frames.

In the AQ Framework, the Public database does not include Dolomite. To add Dolomite into the Chemistry we need to add the **Geochemical Databank**.

Starting the Simulation

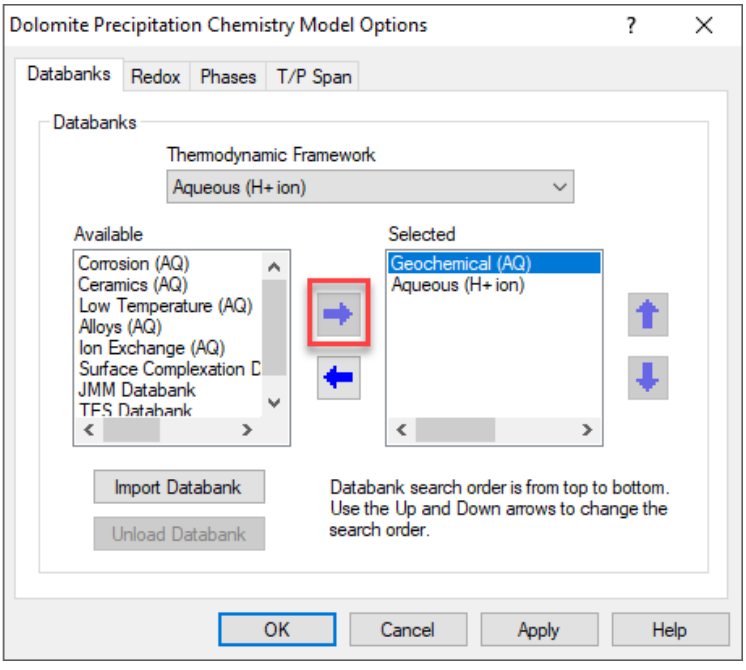
Calculating the Precipitation of Dolomite ($CaMg(CO_3)_2$)

1. Under the Stream *Solubility of CaCO3 – Precipitation Point*, **Add a Single Point** calculation
2. Select **Precipitation Point** as Type of Calculation
3. Change the ***SinglePoint*** name to ***Dolomite Precipitation*** using the **<F2>** key
4. Click on **Chemistry** > **Model Options**

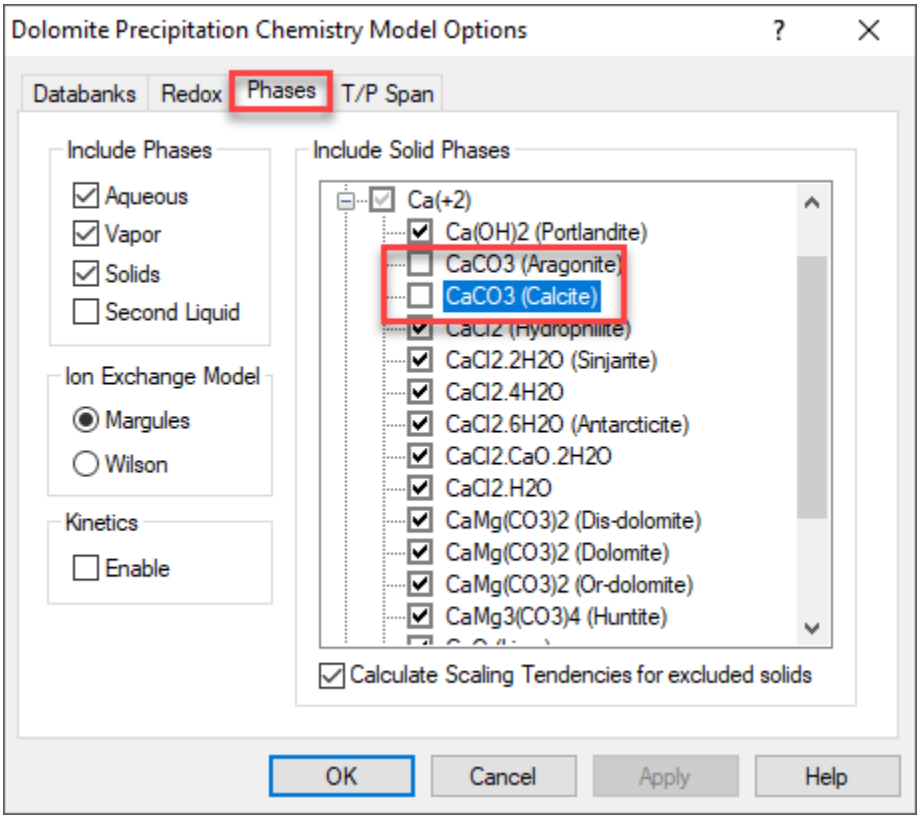


5. In the Databanks Tab, select the **Geochemical (AQ)** Databank. You can double click or use the right arrow to add the databank. Then Click **OK**.

You may have more or less databanks depending on previous installations and imported databanks



6. Select the **Phases** tab
7. **Click** on the **"+"** next to the Ca(+2) box to display all the calcium containing solids
8. Scroll down to find CaCO3 (Calcite) and CaCO3 (Aragonite) and **uncheck** these solids
9. Click **OK** continue.



Note: The **Include Solid Phases box** lists the solids in the chemistry model. Unchecking these solids will mathematically eliminate the solid from consideration. The Scaling Tendency, however, will still be calculated.

10. Select the **CaMg(CO3)2 (Dolomite)** as the **Precipitant**
11. Select **CaCO3** as the **Adjusted Inflow**

Calculation Parameters	
Precipitant:	CaMg(CO3)2 (Dolomite)
Adjusted Inflow:	CaCO3

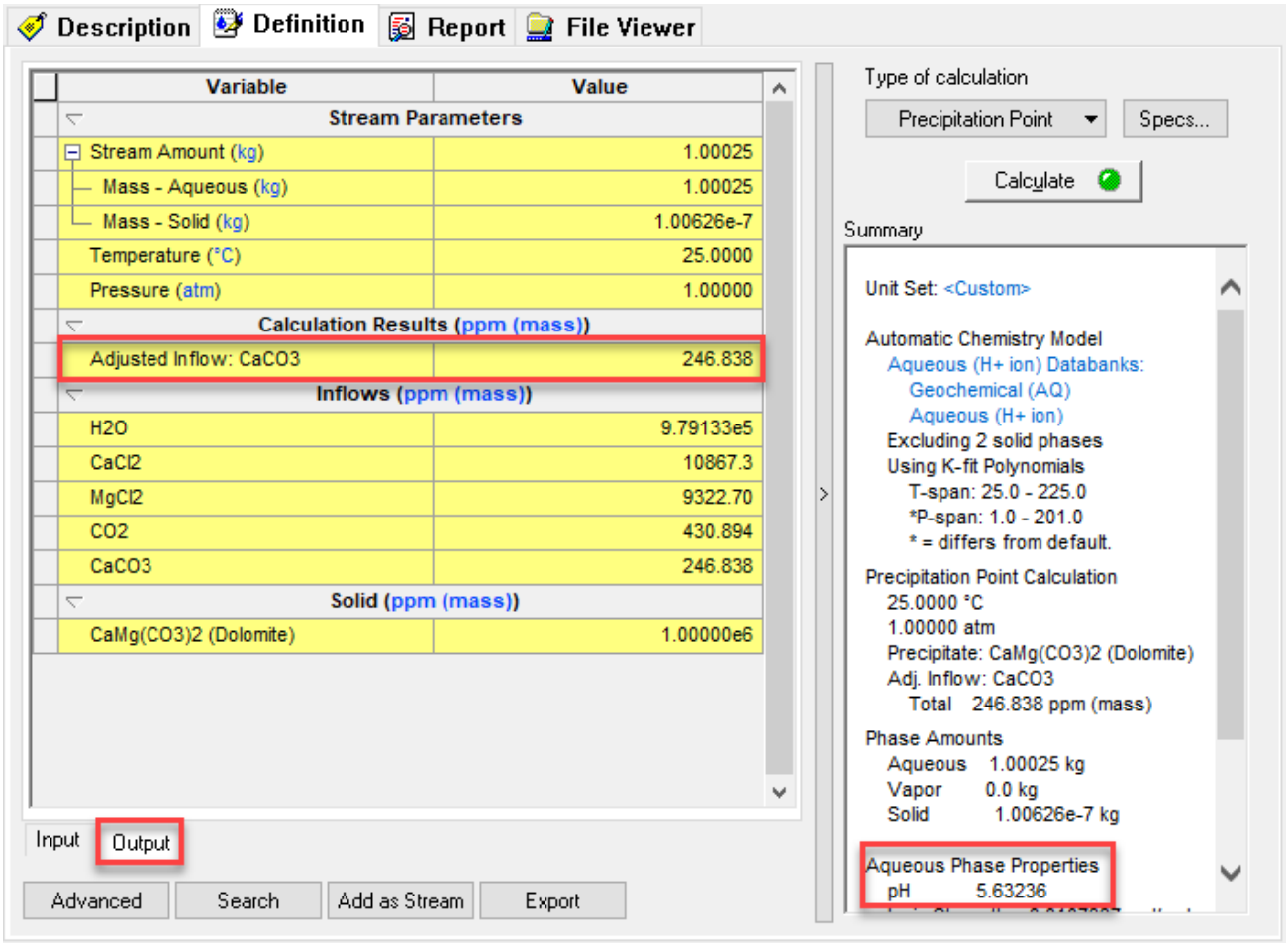
12. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
13. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

Review the **Summary Box** or Click on the **Output-Minitab** to see the Results.

The software calculated that the solubility of Dolomite in the solution under study is around **~246.84 ppm (mass)**. The pH of this solution is ~5.63.

So far, we know that the solubilities of Calcite, Aragonite, and Dolomite in a $MgCl_2$, $CaCl_2$ and CO_2 containing solution were 413.15, 552.87 and, 246.84 ppm (mass) respectively.



1.8. Composition Point

The **composition point** calculation is used to fix a species value. This calculation is useful when for example you want a target amount of a desired component or to fix an impurity or undesired component below a certain value.

Example 11: Targeting dissolved H_2S in water below 0.001 m

In this example, you will use the composition point calculation to target the amount of molecular H_2S dissolved in water below 0.001 m.

Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Composition Point Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Default – 55.5082
Calculation Sub-type	Composition Point	Temperature	25 ºC
Stream Name	Composition Point	Pressure	1 atm
Name Style	Display Formula	H2O	Calculated
Unit Set	Metric, Moles	H2S	0 moles
Framework	AQ	Target H2S-Aq value	0.001 moles

Calculating the Vapor Fraction Temperature (Isobaric)

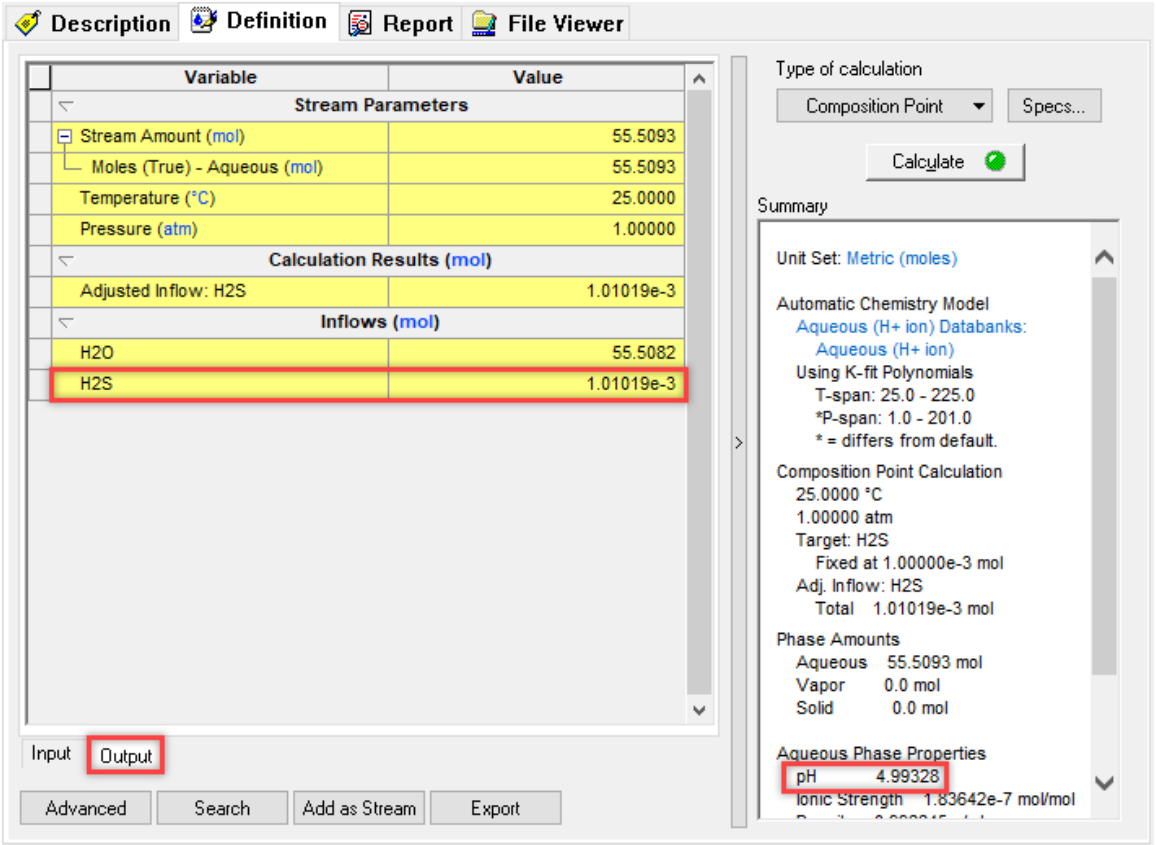
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Composition Point*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition of the gas given in the table above
7. Go to the **Add Calculation** button and select **Single Point** calculation
8. Select **Composition Point** as Type of Calculation
9. Change the ***SinglePoint*** name to ***H2S dissolved in water*** using the **<F2>** key
10. Set the **Target Species** to **H2S-Aq** (i.e. the molecular H_2S dissolved in the Aqueous phase)
11. Set the **Target H2S value** to **0.001** moles
12. Set the **Adjusted Inflow** to **H2S**

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Target Species:	H2S - Aq
Target H2S Value: (mol)	1.00000e-3
Adjusted Inflow:	H2S
Inflows (mol)	
H2O	55.5082
H2S	0.0

13. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
14. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

Review the Summary Box or Click on the Output-Minitab to see the results.



According to the calculation, ~0.00101 moles of H_2S were required to create a solution with 0.001 moles of H2S-aq. The pH of this solution is ~**5.0**.

You can also go to the **Report** to see the distribution of species under the **Species Output (True Species)** table.

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous
	mol	mol
H2O	55.5082	55.5082
H2S	1.0e-3	1.0e-3
H+1	1.01938e-5	1.01938e-5
HS-1	1.01928e-5	1.01928e-5
OH-1	1.00348e-9	1.00348e-9
S-2	1.391e-13	1.391e-13
Total (by phase)	55.5093	55.5093

You can see that the molecular H2S is the value that was specified as a target. Notice that the concentration of H^+ and HS^- are nearly identical. This is because the following reactions:

$$H_2S \leftrightarrow H^+ + HS^-$$

H^+ is slightly higher because a second reaction, the dissociation of water also contributes to the H^+ formation.

$$H_2O \leftrightarrow H^+ + OH^-$$

1.9. Autoclave

An **autoclave** is a high pressure, high temperature hydrometallurgy unit with carefully controlled conditions. From an OLI Software perspective, it is an **isochoric (constant volume) calculation** in which mass, pressure and temperature are allowed to vary.

Autoclave calculations are widely used in the upstream oil and gas applications. When performing corrosion testing, autoclave experiments are essential for simulating downstream conditions, i.e. conditions at high temperatures and pressures. Additionally, it is important to evaluate the corrosivity of production fluids by measuring solution properties, such as pH, and the concentration of aggressive species such as CO_2, H_2S, and chlorides. An autoclave, however, has a constant volume, so it is imperative to know how much material (NaCl solution, CO_2 and H_2S gases) is necessary to add at charging conditions (e.g. at room temperature) in order to reach the desired final specifications, such as partial pressure of CO_2 and H_2S gases.

We will use the Autoclave calculation to calculate partial pressures, fugacities and the final composition of key gases in the aqueous and vapor phases.

For the autoclave calculation 2 examples will be shown:

Using an Inert Gas

1. Calculating results at ambient conditions
2. Increasing the volume of the vessel and its implications
3. Increasing the final temperature and its implications
4. Increasing the final pressure and its implications

Using a Reactive Gas

1. Calculating results at final conditions
2. Using a Reactive Gas and a NaOH solution

Example 12: Using an Inert Gas

1. Calculating Results at Ambient Conditions

In this example, you will add 1 kg water to a 2 L autoclave and then fill the void (head space) with N_2. The ambient temperature is 25 ºC. The N_2 is presumed to be the gas that remains in the autoclave headspace after sparging (O_2 removal) is completed.

The amount of N_2 added is the combination of N_2 vapor filling the headspace, and N_2 that dissolves in the water (N_2 aqueous). Since N_2 has a low water solubility, this second amount is negligible. H_2O also evaporates, so the headspace will be a mixed gas, N_2 and H_2O.

We can use the ***Ideal Gas Law*** to estimate the amount of N_2 needed to fill the headspace:

$$PV = nRT$$

$$1\ atm \times 1\ L = n \times 0.082057 \frac{L - atm}{K - mol} \times 298.15\ K$$

$$n = 0.040874\ moles$$

Although this estimate does not consider the H_2O that is in the 1 L headspace or the amount of N_2 dissolved in water, it is still an easy approach to get a reasonable estimate.

You will review the results in greater detail here, because part of the goal of this first example it to show where the important variables and properties are.

Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

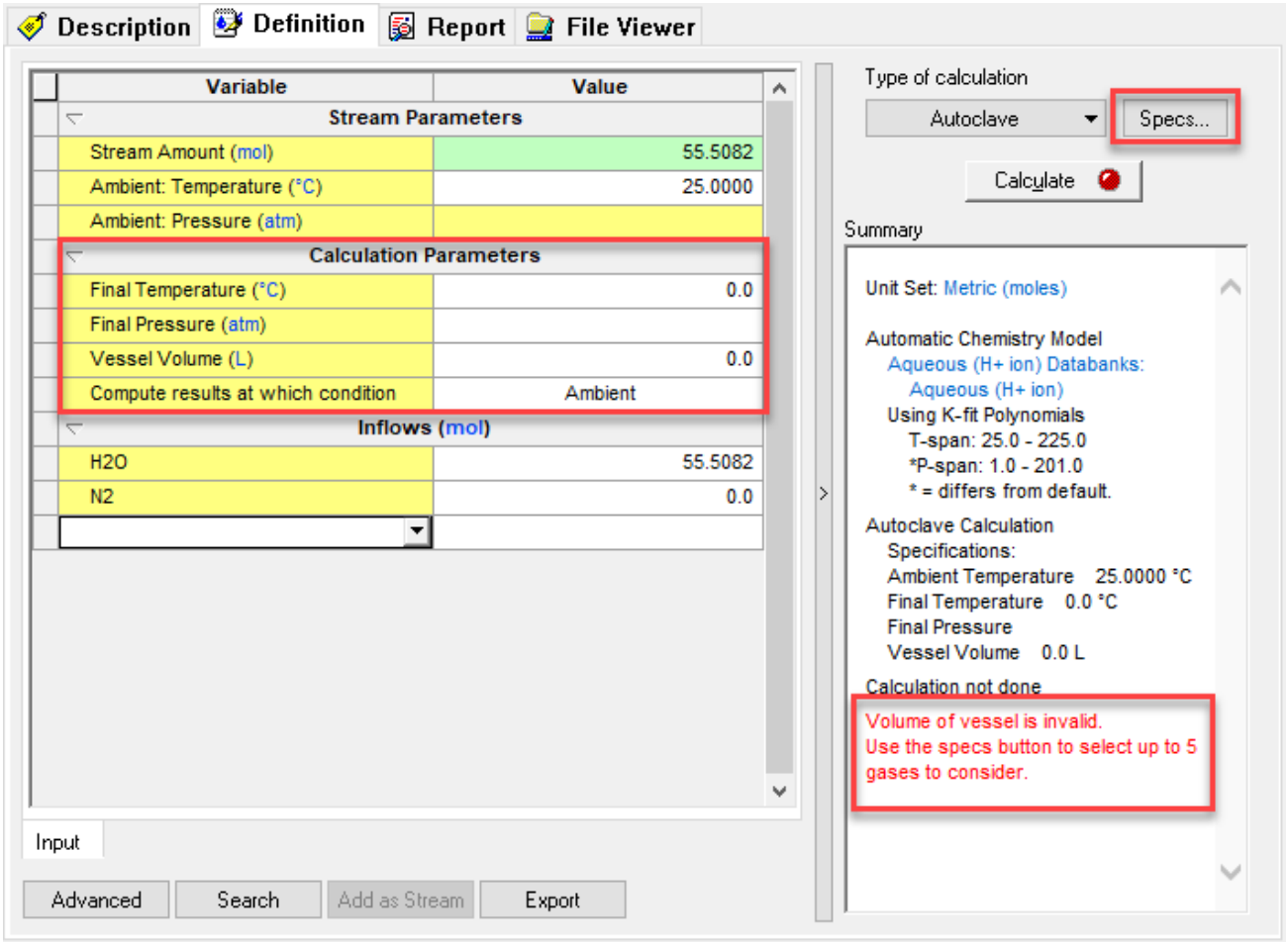
Autoclave Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Default – 55.5082
Calculation Sub-type	Autoclave	Ambient Temperature	25 ºC
Stream Name	Autoclave	Final Temperature	25 ºC
Name Style	Display Formula	Final Pressure	1 atm
Unit Set	Metric, Moles	Vessel Volume	2 L
Framework	MSE-SRK	H2O	Calculated
Results for	Ambient conditions	N2	0 moles

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Autoclave*
3. Select the **MSE-SRK** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the **N2** as an **inflow**
7. Go to the **Add Calculation** button and select **Single Point** calculation

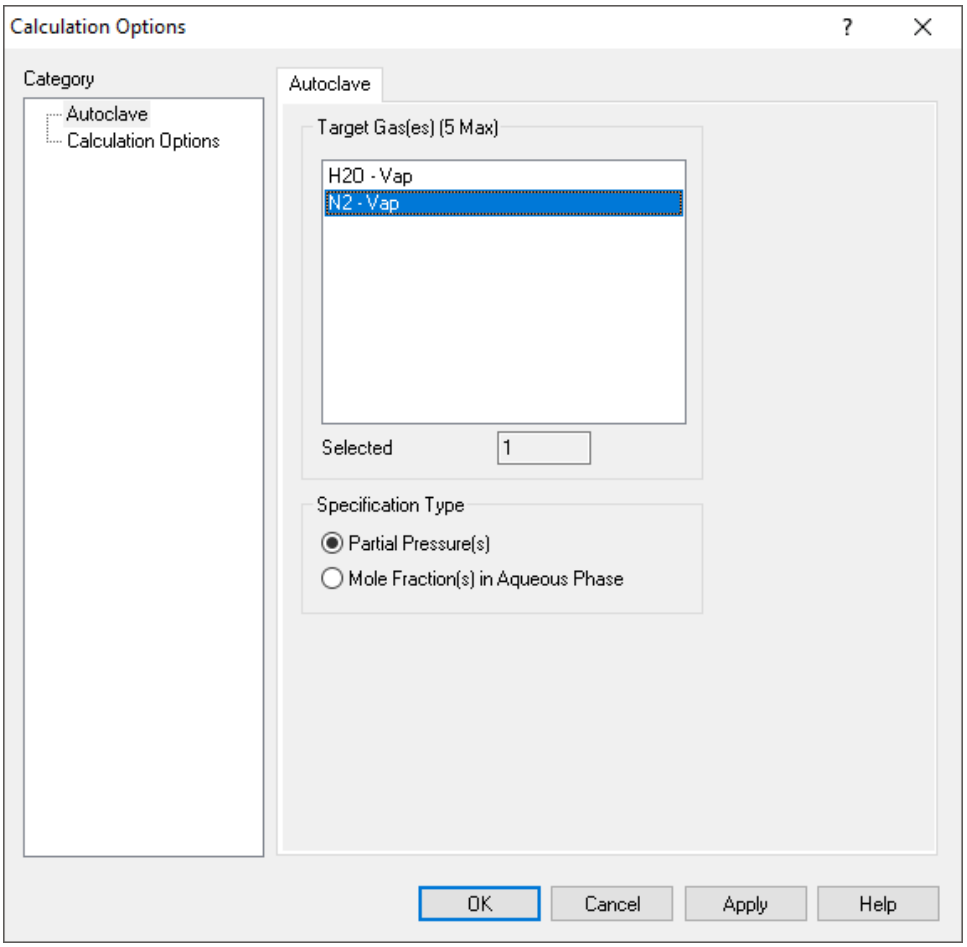
8. Select **Autoclave** as Type of Calculation
9. Change the ***SinglePoint*** name to **Autoclave – Inert Gas** using the **<F2>** key

Note: At this point you may have noticed that the Calculate button is red, and that there is a **red** text in the Summary Box with instruction that additional specs are needed. The specifications need to be defined in the **Calculation Parameters** grid section.

10. Click on the **Specs** button.



11. This will open the ***Calculation Options*** window to set up the target gas. Select **N2-Vap** and make sure to select the specification type **Partial Pressure** (default). Click **OK**.



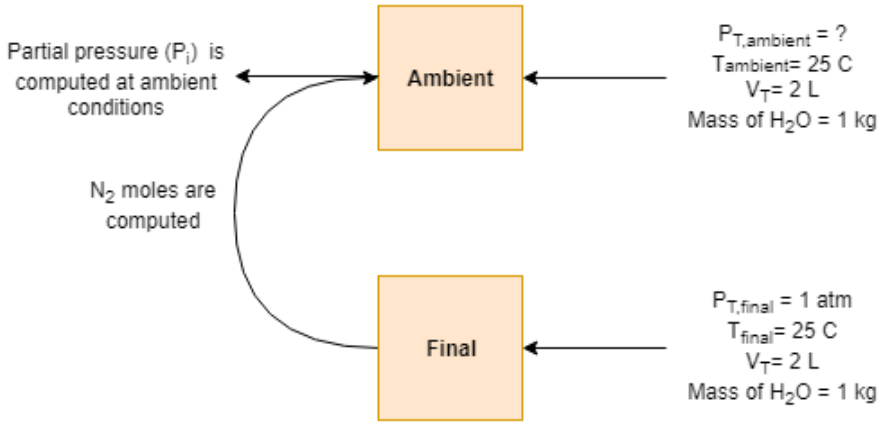
12. Set the **Final Temperature** to **25ºC,** the **Final Pressure** to **1 atm** and the **Vessel Volume** to **2 L**
13. Set the **compute results** at **Ambient** Conditions

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation Parameters	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	2.00000
Partial Pressure: N2 (atm)	
Compute results at which condition	Ambient

At this point the system is defined as 1 kg H_2O (55.5082 moles) at an ambient temperature of 25 ºC. The partial pressure of N_2 will be calculated at a final temperature, 25 ºC and pressure, 1 atm in a 2 L vessel.

Note: ***The Autoclave calculation pathway***

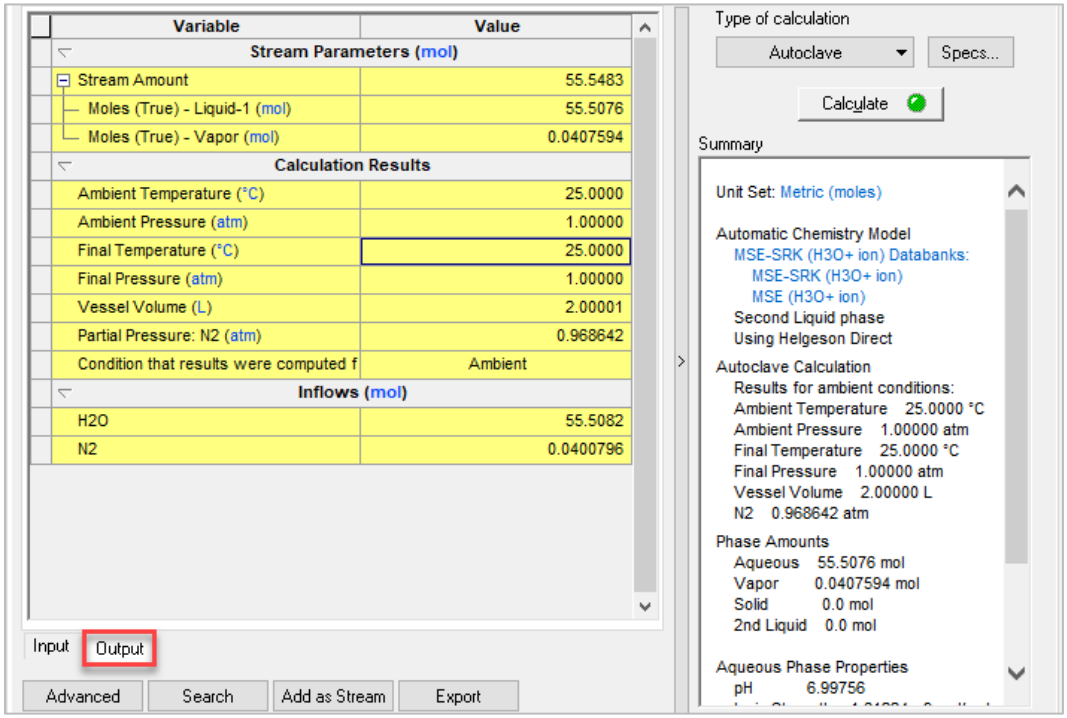
When performing an **autoclave calculation**, the software will perform two computations: First, at the final conditions, and the second one at ambient (initial) conditions. It will compute the amount (in moles) of N_2 needed to create a 1 atm pressure at final conditions. It will then use this N_2 to compute the pressure at ambient conditions. The calculation pathway is showed in the image below.



14. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
15. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

Review the Summary Box or Click on the Output-Minitab to see the results.



The calculated ambient pressure is 1 atm. It is identical to the final pressure, which is not surprising, since the ambient and final temperatures were defined at the same value, and by design, the autoclave calculation uses the identical inflows for ambient and final conditions.

The amount of N_2 added is 0.0400796 moles, which produces a ~0.9686 atm partial pressure. The computed N_2 inflow compares to the Ideal Gas value of 0.040874 moles, a ~2% deviation.

Let's review the distribution of N_2 in the liquid and vapor phase in the **Report** tab. Scroll down to the last table named **Element Distribution**.

The last row is N (which is representing the molecular nitrogen). The distribution is 98.5% in the vapor phase and 1.5% in the liquid phase. Also notice that around 0.0023% of the water has evaporated (see the H(+1) and O(-2) rows).

Element Distribution

	Total	Total	Liquid-1	Vapor
	mol	mole %	% of Total	% of Total
H(+1)	111.016	66.6346	99.9977	2.30264e-3
O(-2)	55.5082	33.3173	99.9977	2.30264e-3
N	0.0801591	0.0481133	1.49278	98.5072

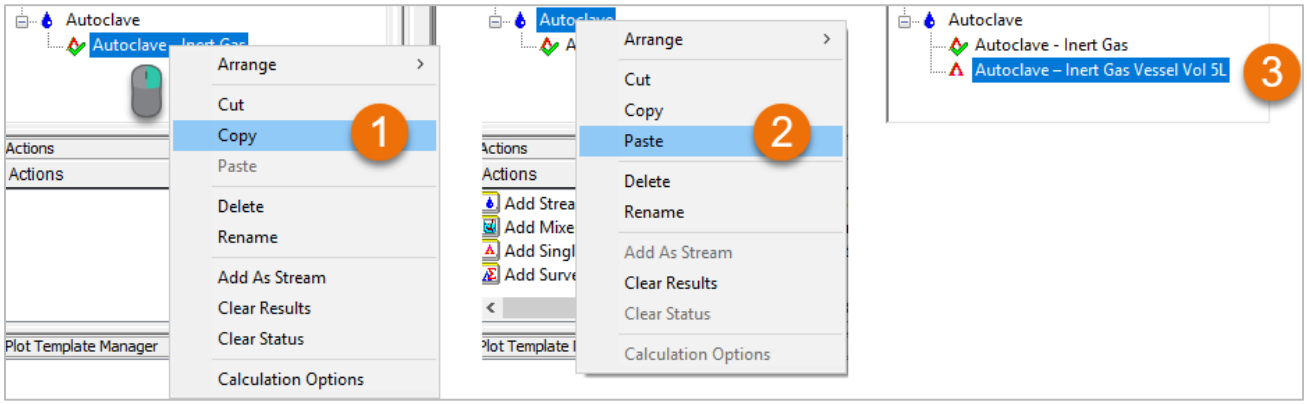
These results infer two effects:

1. As the final pressure (P_T) increases, additional N_2 will dissolve in the water, shifting the fraction of nitrogen to the liquid.
2. As the total autoclave volume (V_T) increases relative to the input liquid (which stays constant), additional water will evaporate, shifting the water to the vapor. This case will be shown next.

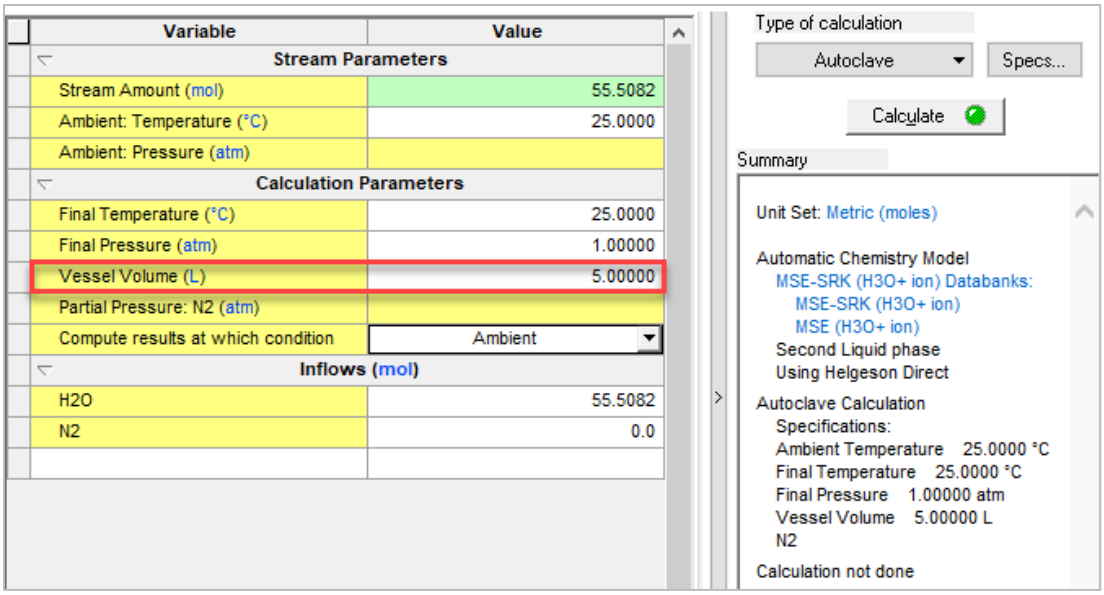
2. *Increasing the Vessel Volume to 5 L*

You are going to use the same case that you built up in the example above, with the only difference that you will change the **Vessel Volume**.

1. **Right click** on the *Autoclave – Inert Gas* single point calculation and select **copy**
2. Selecting the stream named **Autoclave**, right click on it and select **paste**
3. Select the copied stream and name it *Autoclave – Inert Gas Vessel Vol 5L*



Change the **Vessel Volume** to **5 L** and **Calculate** <F9>

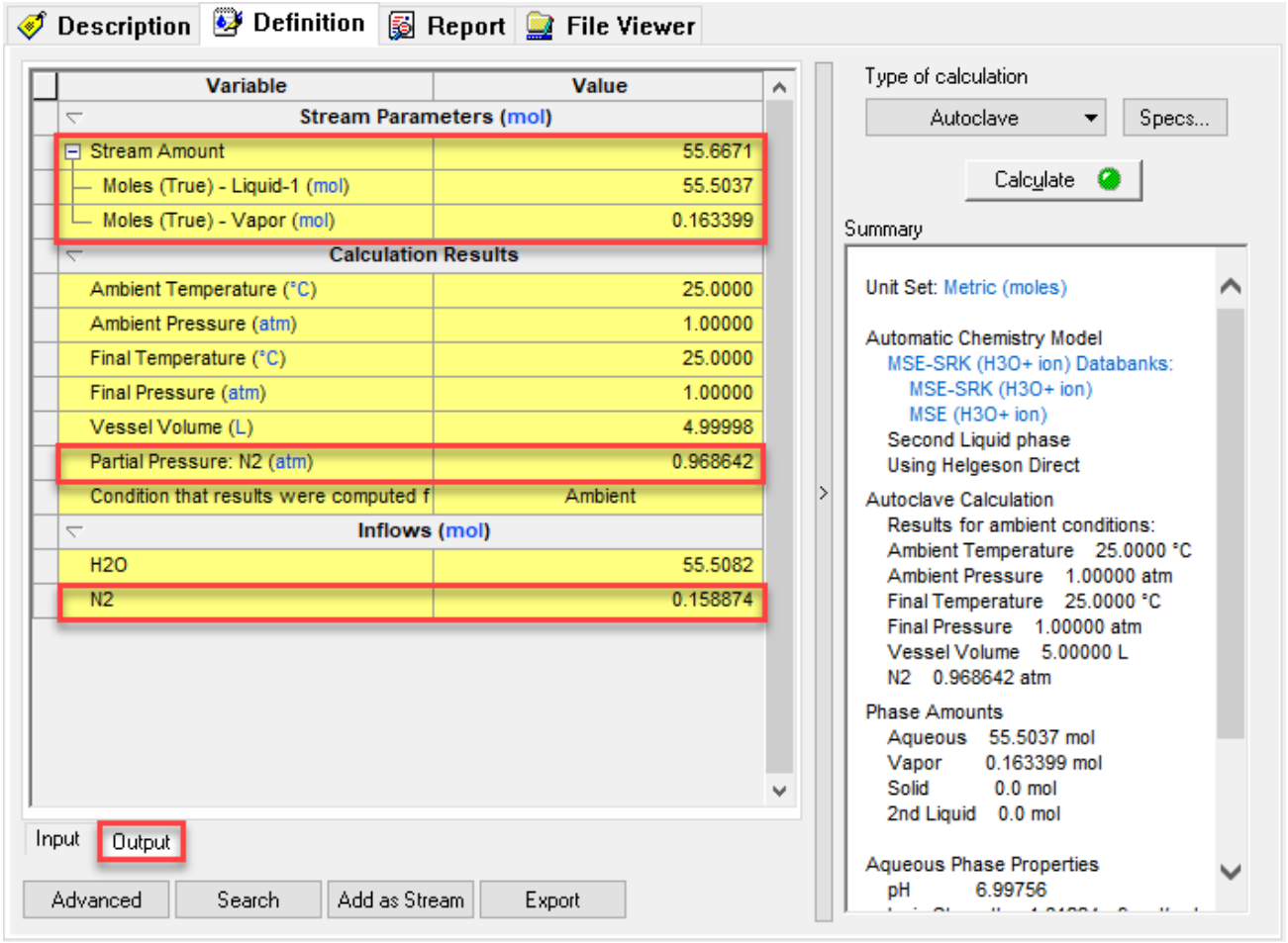


At this point the system is defined as 1 kg H_2O (55.5082 moles) at an ambient temperature of 25 ºC. The partial pressure of N_2 will be calculated at a final temperature, 25 ºC and pressure, 1 atm in a 5 L vessel.

It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Anaylyzing the Results

Review the Summary Box or Click on the Output-Minitab to see the results.



The moles of liquid are now 55.5037. The reduction of 0.0039 moles (compared to the case of 2 L which was 55.5076 moles) is because this amount of H_2O evaporated into the larger headspace. This phase distribution is important to modeling the autoclave system properly, especially at elevated conditions as will be seen in the next example.

The amount of N_2 required to fill the 4-L headspace is 0.1589 moles; this amount is ~4-times greater than the first case, which is expected for gas with a low water solubility.

3. Increasing the Final Temperature

In this example, you will add 1 kg water to a 5 L autoclave and then fill the void (head space) with N_2. The ambient temperature is 25 ºC, and the final conditions will be 1 atm and 100 ºC.

The purpose of this example is to raise the H_2O partial pressure relative to N_2. In the 5 L case above, the N_2 inflow is 0.1634 moles. As temperature increases, the H_2O vapor pressure increases, and the amount of N_2 required to fill the vapor void will decrease.

You are going to use the same case that you built up in the example above, with the only difference that you will change the **Final Temperature** to **25 ºC.**

1. **Copy** the *Autoclave – Inert Gas Vessel Vol 5L* single point calculation and **paste** under the **Autoclave** Stream.
2. **Name it** *Autoclave – Inert Gas Tf=100C*
3. Change the **Final Temperature** to **100ºC** and **Calculate** <F9>

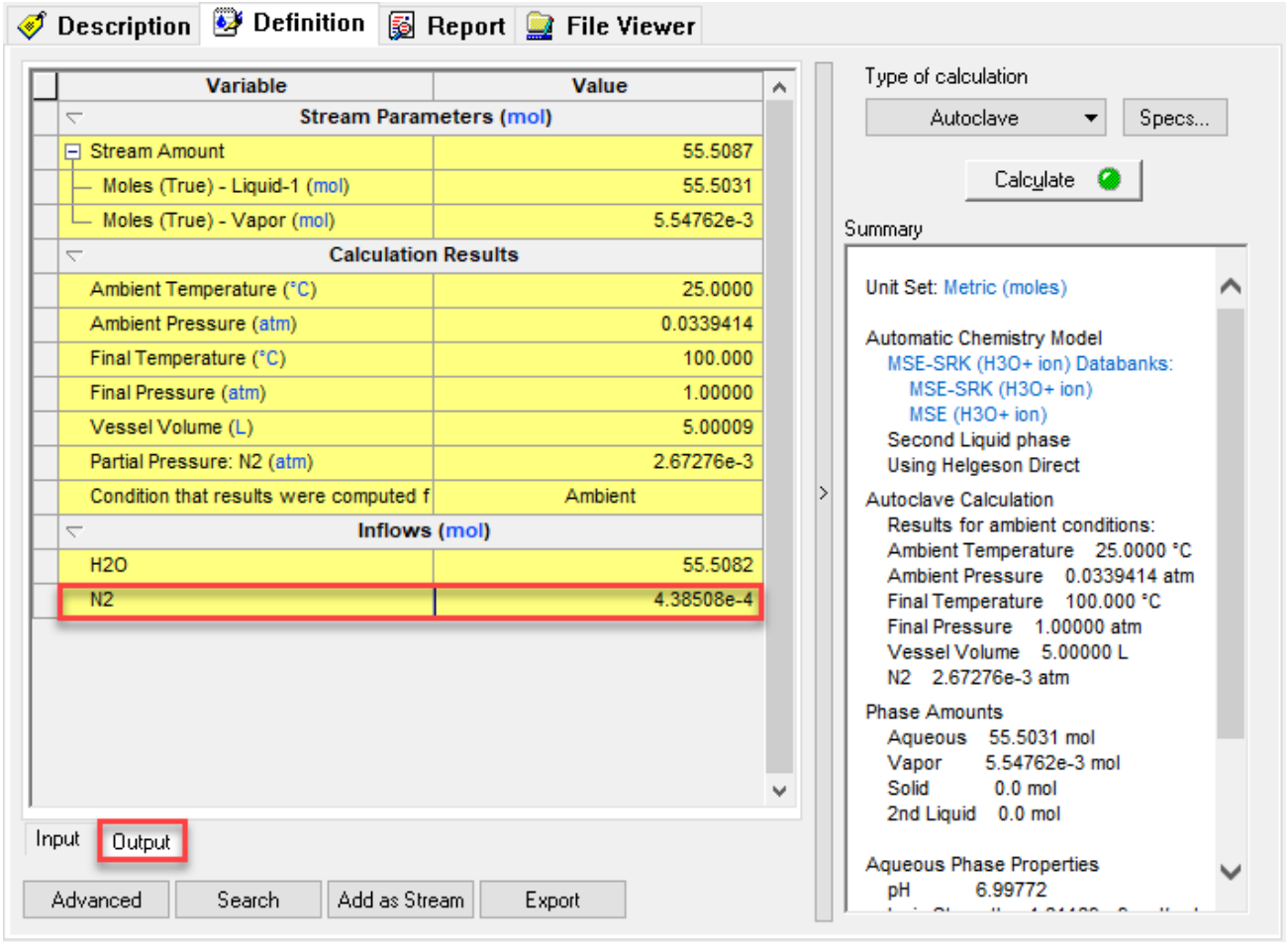
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation Parameters	
Final Temperature (°C)	100.000
Final Pressure (atm)	50.0000
Vessel Volume (L)	5.00000
Partial Pressure: N2 (atm)	
Compute results at which condition	Ambient
Inflows (mol)	
H2O	55.5082
N2	0.0

At this point the system is defined as 1 kg H_2O (55.5082 moles) at an ambient temperature of 25 ºC. The partial pressure of N_2 will be calculated at a final temperature, 100 ºC and pressure, 50 atm in a 5 L vessel.

It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Anaylyzing the Results

Review the Summary Box or Click on the Output-Minitab to see the results.

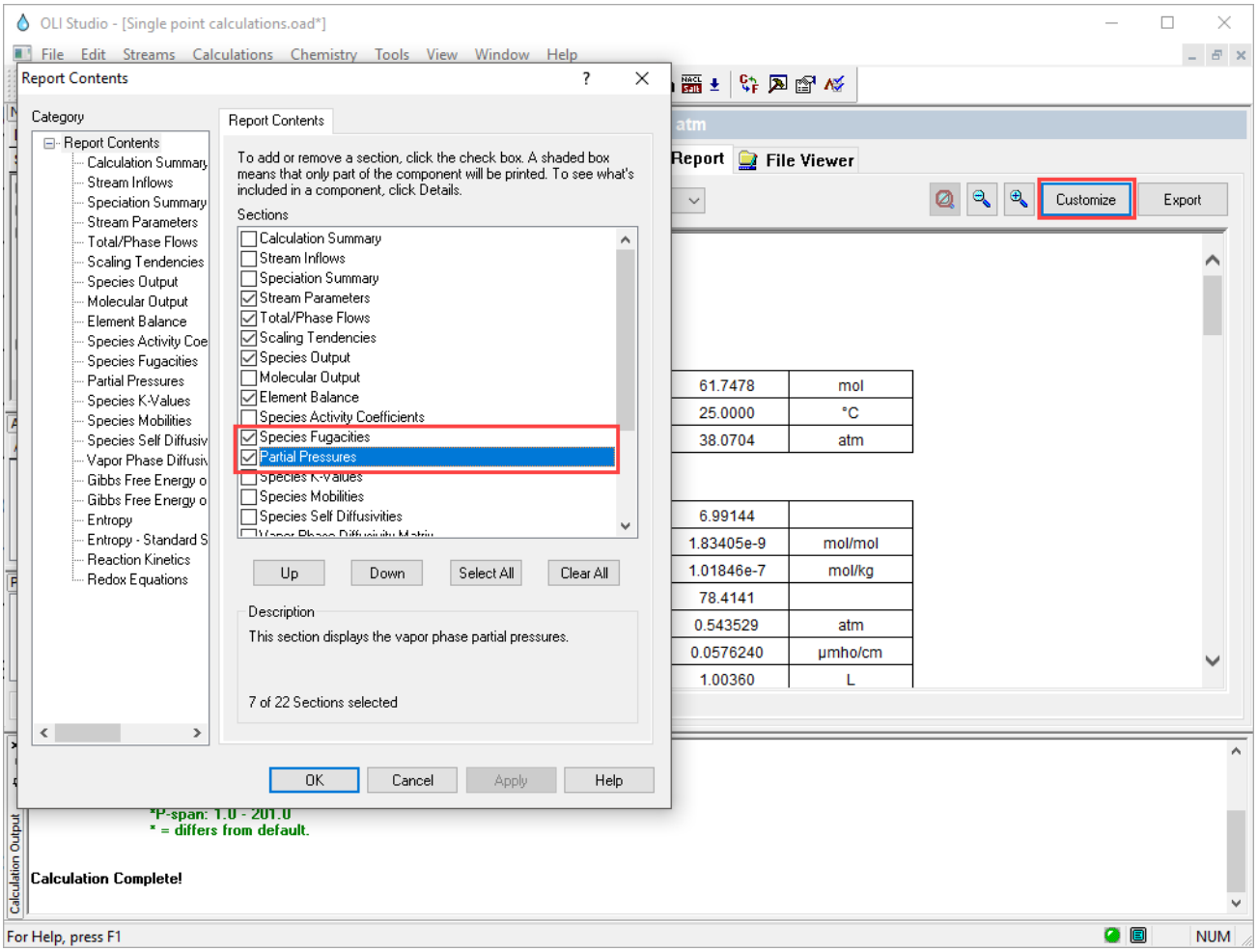


The amount of N_2 added is very small (~0.0004 moles). This is to be expected, because the vapor pressure of pure water at 100 ºC is 1 atm. Therefore, a negligible amount of N_2 is needed to raise the pressure. Notice also that the calculated ambient pressure is 0.0339 atm. The vapor pressure of pure water at 25º C is 0.0313.

The results above imply that the autoclave will have a vacuum pressure at the ambient temperature, and when heated to 100 ºC will reach atmospheric pressure.

In autoclave testing, it is also of utmost importance to study and understand the partial pressures and fugacities of key gases at the final conditions. You need to enable these properties to be shown in the **Report**.

Go to the **Customize** button and enable both the **Species Fugacities** and the **Partial Pressures** options, and then click **OK**.



Notice that the **Fugacity** and **Partial Pressure** of N_2 are nearly identical. This is expected since at low pressure the fugacity approaches its partial pressure.

Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.0312529
N2	2.67376e-3

Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.0312686
N2	2.67276e-3

4. Increasing the Final Pressure

In this example, you will add 1 kg water to a 5 L autoclave and then fill the void (head space) with N_2. The ambient temperature is 25 ºC, and the final conditions will be 100 atm and 100 ºC.

You are going to use the same case that you built up in the example above, with the only difference that you will change the **Final Pressure** to **100 atm.**

1. **Copy** the *Autoclave – Inert Gas Tf=100C* single point calculation and **paste** under the **Autoclave** Stream.
2. **Name it** *Autoclave – Inert Gas Pf=100 atm*
3. Change the **Final Pressure** to **100 atm** and **Calculate** <F9>

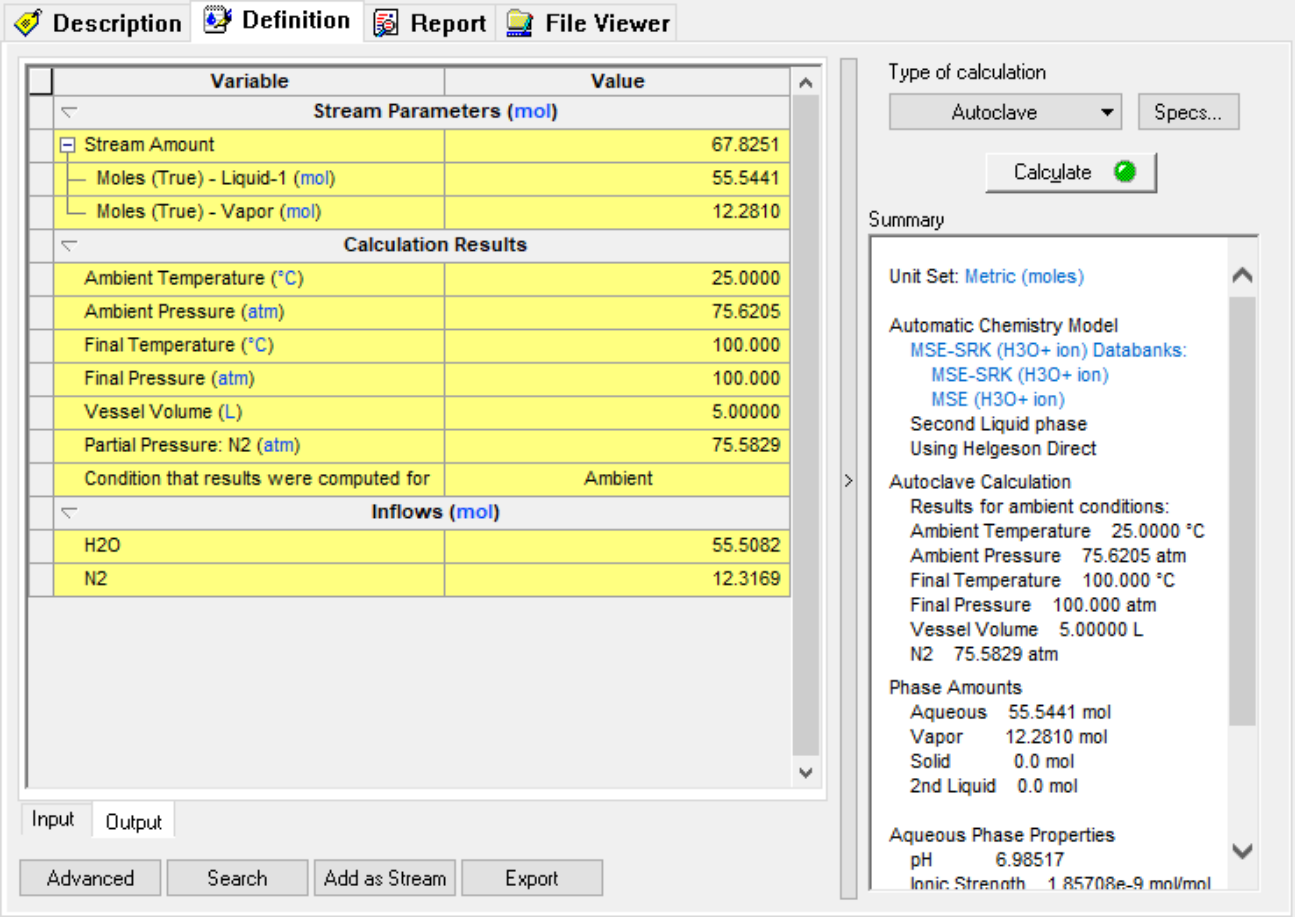
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation Parameters	
Final Temperature (°C)	100.000
Final Pressure (atm)	100.000
Vessel Volume (L)	5.00000
Partial Pressure: N2 (atm)	
Compute results at which condition	Ambient
Inflows (mol)	
H2O	55.5082
N2	0.0

At this point the system is defined as 1 kg H_2O (55.5082 moles) at an initial temperature of 25 ºC. The partial pressure of N_2 will be calculated at a final temperature of 100 ºC and a final pressure of 100 atm in a 5 L vessel.

It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Anaylyzing the Results

Review the Summary Box or Click on the Output-Minitab to see the results.



The computed ambient pressure $P_{T,A}$ is 75.6205 atm. Of this total, 75.5829 atm is N_2 (P_{N2}=75.5829 atm) and 0.0376 atm is H_2O (P_{H2O}=0.0376 atm). Thus, to create a 100 atm final pressure, the autoclave would need to be charged with N_2 at a regulator pressure of 75.6205 atm.

According to the calculation, the amount of N_2 in the autoclave is 12.3169 moles. This amount of N_2 plus the 55.5082 moles of H_2O produces a final pressure of 100 atm in a 5 L autoclave at 100 ºC.

Let's study the partial pressure and fugacity of N_2 at these final conditions. Remember, you need to enable these properties to be shown in the **Report**.

Go to the **Customize** button and enable both the **Species Fugacities** and the **Partial Pressures** options, and then click **OK**.

For comparison purposes, the **Species Fugacities** and the **Partial Pressures** for 100 ºC and 1 atm, and 100 ºC and 100 atm are shown.

100 °C and 1 atm

Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.0312529
N2	2.67376e-3

Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.0312686
N2	2.67276e-3

100 °C and 100 atm

Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.033019
N2	75.9152

Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.0376507
N2	75.5829

Notice that at low pressures, the partial pressures and fugacities values of both H_2O and N_2 are nearly identical. At the higher pressure, i.e. 100 atm, the partial pressures and fugacities of H_2O and N_2 start to differ.

The cause of this deviation is the *non-ideal effects of high pressures on gas molecules as they are forced closer together*. At low pressures, gas molecules are too far apart to interact. As pressure increases, the average distance between two molecules decrease, until at short range, intermolecular attractive forces begin to impact the molecular properties. The impact of this effect is quantified in the fugacity term. Notice that fugacity and partial pressure have the same units, atm.

Thus, when reviewing these two tables, the partial pressure can be seen as the idealized gas property at high pressures (which does not take into account intermolecular forces). The fugacity is the real gas property at this pressure. The non-ideal effect of pressure is therefore encapsulated in the following relationship:

$$\varphi = \frac{Fugacity}{Partial\ Pressure} = \frac{f}{p_i}$$

Where,
φ is the fugacity coefficient

At low pressures, a gas molecule fugacity (f) approaches its partial pressure (p_i), i.e. $f \to p_i$ or $\varphi = 1$.

Example 13: Using and Reactive Gas

1. Calculating Results at Final Conditions

In this example, you will add 1 kg water to a 2 L autoclave and then fill the void (head space) with CO_2. The ambient temperature is 25 ºC.

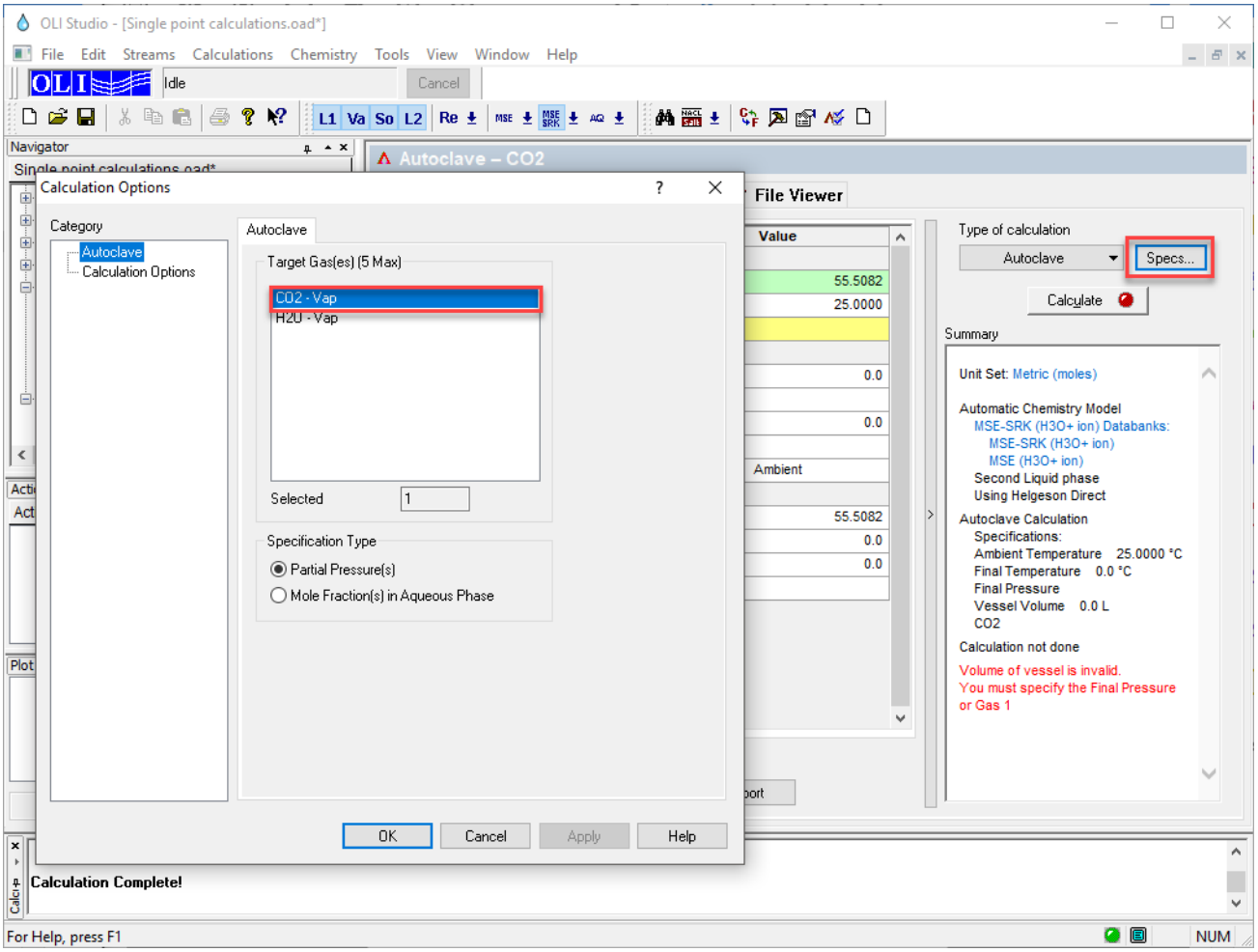
You will then modify the case further by adding NaOH so that additional CO_2 dissolves in water to form bicarbonate.

Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Autoclave Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Default – 55.5082
Calculation Sub-type	Autoclave	Ambient Temperature	25 ºC
Stream Name	Autoclave	Final Temperature	25 ºC
Name Style	Display Formula	Final Pressure	1 atm
Unit Set	Metric, Moles	Vessel Volume	2 L
Framework	MSE-SRK	H2O	Calculated
Results for	Final Conditions	CO2	0 moles
		NaOH	0 moles

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Autoclave Reactive Gas*
3. Select the **MSE-SRK** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the **CO2 and NaOH** as **inflows**
7. Go to the **Add Calculation** button and select **Single Point** calculation
8. Select **Autoclave** as Type of Calculation
9. Change the ***SinglePoint*** name to **Autoclave – CO2** using the **<F2>** key
10. Click on the **Specs** button. This will open the ***Calculation Options*** window to set up the target gas.
11. Select **CO2** and make sure to select the specification type **Partial Pressure** (default). Click **OK**.



12. Set the **Final Temperature** to **25ºC,** the **Final Pressure** to **1 atm** and the **Vessel Volume** to **2 L**
13. Set the **compute results** at **Final** Conditions. Click on the cell to enable the drop-down arrow.

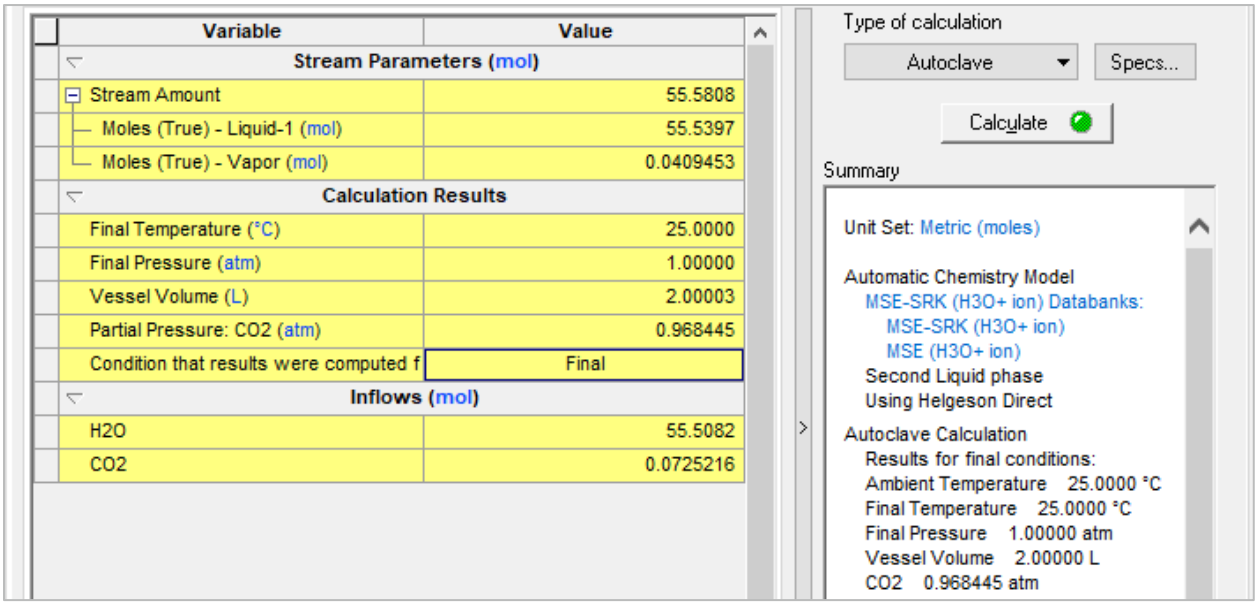
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation Parameters	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	2.00000
Partial Pressure: CO2 (atm)	
Compute results at which condition	Ambient
Inflows	Final
H2O	Ambient
CO2	0.0
NaOH	0.0

At this point the system is defined as 1 kg H_2O (55.508 moles) at an ambient temperature of 25 ºC. The partial pressure of CO_2 will be calculated at a final temperature, 25 ºC and pressure, 1 atm in a 2 L vessel.

14. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
15. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

Review the Summary Box or Click on the Output-Minitab to see the results.



A total amount of 0.0725 moles of CO_2 added was computed by the software to set the autoclave total pressure to 1 atm. For comparison, the same scenario in Example 12-1 Anaylyzing the Results required 0.04 moles of N_2. The difference is the amount of CO_2 that dissolved in the water. CO_2 is more soluble than N_2 in water.

To analyze the CO_2 distribution in more detail, go to the **Report** Tab, and Scroll down until you find the **Element Distribution** table.

Element Distribution

	Total	Total	Liquid-1	Vapor
	mol	mole %	% of Total	% of Total
H(+1)	111.016	66.5797	99.9977	2.32766e-3
O(-2)	55.6533	33.3768	99.8552	0.144823
C(+4)	0.0725216	0.0434932	45.3222	54.6778

The **Element Distribution** table contains three rows, H(+), O(-2), and C(+4). These are the elements of H_2O and CO_2. If you compare the C(+4) in the liquid and vapor phases, you will see that about 45.3% of the CO_2 dissolved in the water phase. By comparison, 1.5% of the added N_2 dissolved in water at the same condition (see Example 12-1).

2. Using a Reactive Gas and a NaOH solution

In this example, you will further modify the chemistry by adding NaOH so that additional CO_2 dissolves in water to form bicarbonate. This will increase the gas requirement.

Starting the Simulation

You are going to use the same case that you built up in the example above, with the only difference that you will add the **0.1 moles or NaOH.**

1. **Copy** the *Autoclave – CO2* single point calculation and **paste** under the **Autoclave** Stream.
2. **Name it** *Autoclave – CO2 – NaOH*
3. Change the **composition** of **NaOH** to **0.1 moles** and **Calculate** <F9>

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation Parameters	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	2.00000
Partial Pressure: CO2 (atm)	
Compute results at which condition	Final
Inflows (mol)	
H2O	55.5082
CO2	0.0
NaOH	0.100000

At this point the system is defined as 1 kg H_2O (55.508 moles) and 0.1 moles of NaOH at an ambient temperature of 25 ºC. The partial pressure of CO_2 will be calculated at a final temperature, 25 ºC and final pressure, 1 atm in a 2 L vessel.

4. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Anaylyzing the Results

Review the Summary Box or Click on the Output-Minitab to see the results.

Inflows (mol)	
H2O	55.5082
CO2	0.171600
NaOH	0.100000

The CO_2 inflow is calculated to be 0.1716 moles. This is exactly 0.1 moles more than the calculation with only CO_2 (Example 13-1) and results from the acid-base reaction with the 0.1 moles of NaOH.

To see the different species that have formed in solution go to the **Report** tab and select the **Species Output (True Species).**

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor
	mol	mol	mol
H2O	55.5083	55.507	1.28477e-3
Na+1	0.1	0.1	
HCO3-1	0.0998917	0.0998917	
CO2	0.0716542	0.0320887	0.0395654
CO3-2	5.42505e-5	5.42505e-5	
H3O+1	2.3994e-7	2.3994e-7	
OH-1	6.87229e-8	6.87229e-8	
NaOHCO3-2	2.76574e-14	2.76574e-14	
NaOH	3.90126e-15	3.90126e-15	
Total (by phase)	55.7799	55.7391	0.0408502

You can see that ~0.1 moles of bicarbonate (HCO_3^-) have been formed. This reaction is increasing the CO_2 gas requirement to reach a total final pressure of 1 atm.

1.10. Custom

In the calculations that we have seen so far, variables were predefined. For instance, we selected either temperature or pressure as a fixed value in order to find the dew point pressure or dew point temperature. With the **Custom** calculation, however, you have the option to choose which parameters to set at fixed values and which parameters to keep as variables, to calculate the desired information, such as, for example, to investigate the solubility of gases in solution.

Example 14: Solubility of Oxygen in Water

With a custom calculation, we are going to calculate the solubility of O_2 in water at 25°C and 1 atm.

Starting the Simulation

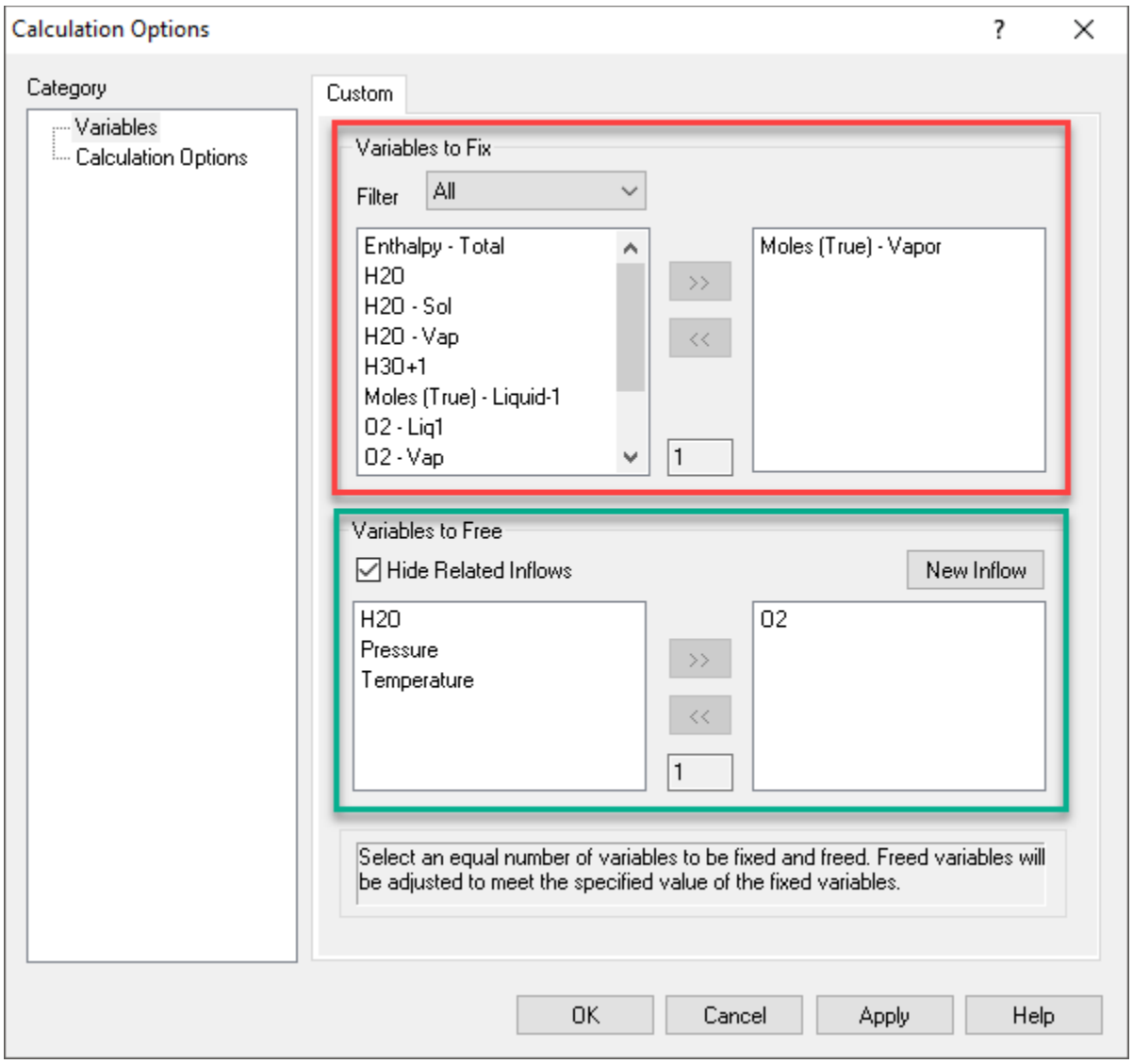
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Custom Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Default – 1kg
Calculation Sub-type	Custom	Temperature	30 ºC
Stream Name	Custom Calculation	Pressure	4 atm
Name Style	Display Formula	H2O	Calculated
Unit Set	Metric, Mass fraction – ppm (mass)	O2	0 mol
Framework	MSE		

Setting the pH

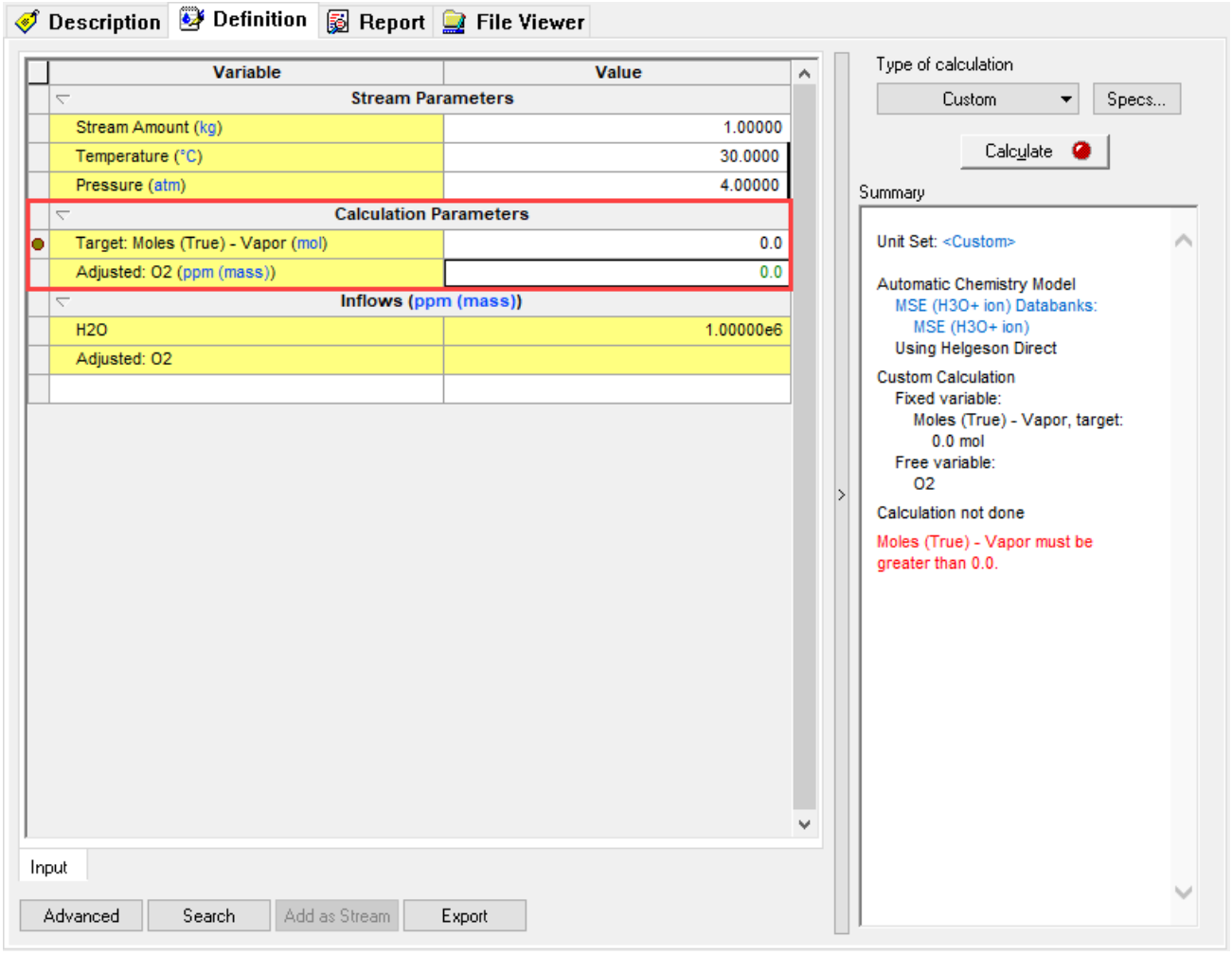
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Custom Calculation*
3. Select the **MSE** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Mass Frac. This will change all inflows to mass %.
6. **Click** on the **Customize button**. This opens the Edit Units window.
7. Under **Basis Options** change mass fraction from **mass %** to **ppm (mass)**
8. Enter **O2** as an inflow and **0** moles
9. Change the **T** to **30 ºC** and **P** to **4 atm**
10. Go to the **Add Calculation** button and select **Single Point** calculation
11. Select **Custom** as Type of Calculation
12. Change the ***SinglePoint*** name to ***Oxygen Solubility*** using the **<F2>** key
13. Select the **Specs** button. This will open the **Calculation Options window**

Note: In the Calculation Options window, you have the option to select the **Variables to Fix** and the **Variables to Free**. In this example, the Variable to Fix is the number of Moles (True) of Vapor which will be given a small value of $1 \times 10^{-7}\ moles$. You can interpret this as the first bubble of vapor formed, indicating that the aqueous phase is saturated. The Variable to Free is the inflow of oxygen, in order to achieve saturation.



14. In the **Variables to Fix** section, select **Moles (True) Vapor**, by double clicking or using the **>>** button.
15. In the **Variables to Free** section, select **O2** as the inflow. Then click OK.

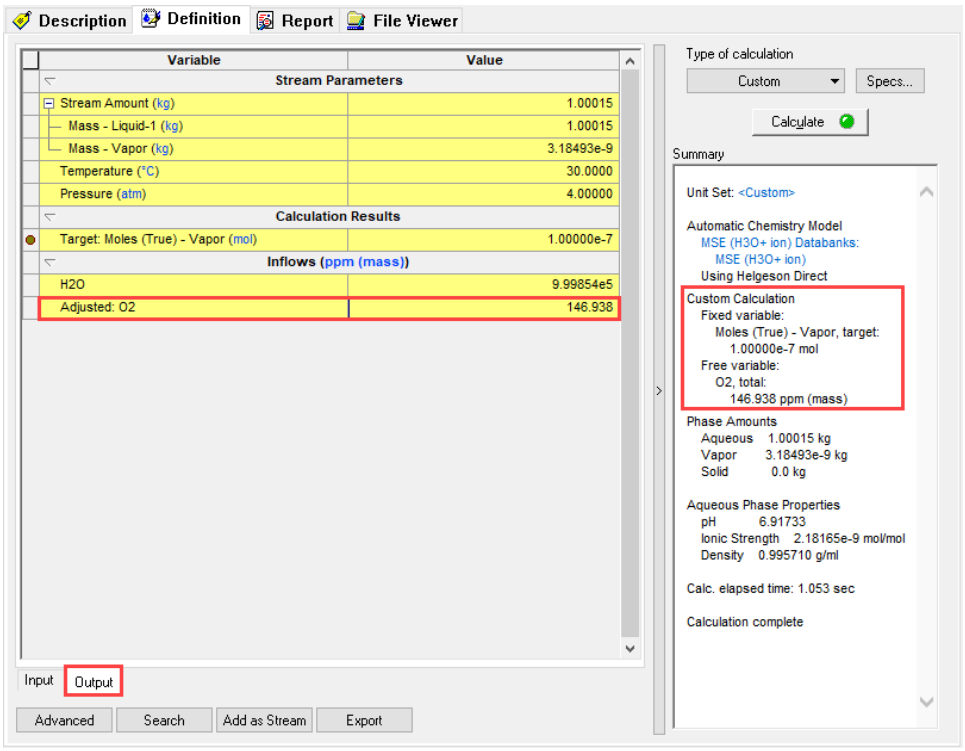
This will add a **Calculation Parameters** sections, were the Target (Variable to Fix) and the Adjusted Inflow (Variable to Free) are shown. The Target has a brown dot in front of it indicating that is fix value, and the Adjusted Inflow is in green indicating that the software will adjust this value.



16. Fix the Moles (True) Vapor to $1e^{-7}$
17. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
18. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

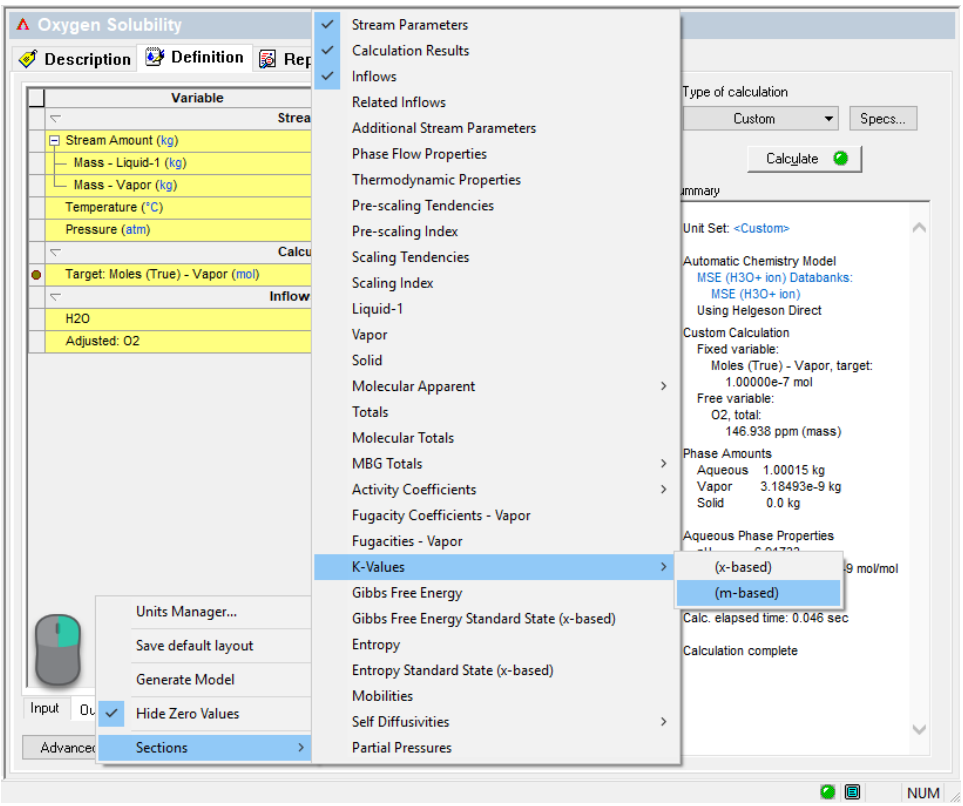
Review the Summary Box or Click on the Output-Minitab to see the results.



At 30ºC and 4 atm the solubility of O_2 in water is 146.94 ppm (mass)

To get an estimate of the Henry's constant, you can study the K-values reported by the software.

Right click on the gray area, go to **Sections**>**K-values**>**m-based**.



The reciprocal of KO2VAP: **O2VAP=O2AQ** will give you an estimate of the Henry's constant.

K-Values - (m-based)	
KH2O: 2H2O=H3OION+OHION	1.46564e-14
KH2OPPT: H2OPPT=H2O	1.32964
KH2OVAP: H2OVAP=H2O	23.8182
KO2VAP: O2VAP=O2AQ	1.15985e-3

1.11. Reaction Kinetics

Most of the chemistry and calculations that we have presented so far assumes equilibrium. However, chemical reactions vary in speed as they occur. Some can occur instantaneously, while others can take years to reach equilibrium. The speed of a chemical reaction is given by the **Reaction Rate**, which is a measure of the change in concentration of the reactants or the change in concentration of the products per unit time.

For the stoichiometric reaction below:

$$aA + bB + \cdots \rightarrow cC + dD + \cdots$$

The reaction rate is defined as:

$$rate = -\frac{1}{a}\left(\frac{d[A]}{dt}\right) = -\frac{1}{b}\left(\frac{d[B]}{dt}\right) = \frac{1}{C}\left(\frac{d[C]}{dt}\right) = \frac{1}{d}\left(\frac{d[D]}{dt}\right)$$

We can describe the kinetics of a chemical reaction by using a **Rate Law,** which is an expression that relates the concentration of each reactant raised to an exponent that reflects the reaction order (which is determined experimentally) and the **rate constant, k**, (a proportionality constate between reaction rate and concentration).

The general rate law is generally expressed as:

$$Rate = k\,[A]^s[B]^t$$

Where $s + t$ gives us the reaction order of the reaction. s and t are not the same as the stoichiometric coefficients a and b.

The reaction **rate constant** units are specific for the overall reaction order, since we always want the units of the rate to be concentration units per unit of time, e.g., M/s.

Reaction order	Units
0	M/s
1	1/s
2	1/(M•s)

The rate constant, k, is dependent on the temperature at which the reaction takes place. Its dependence with temperature can be studied using the Arrhenius Equation, as shown below.

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

where: k= Reaction rate constant $(units\ depend\ on\ reaction\ order)$
A = Arrhenius frequency factor $(has\ same\ units\ as\ k)$
E_a = Activation energy $\left(\frac{joule}{gmole}\right)$
R = Universal gas constant $\left(8.314\frac{joule}{gmole\ K}\right)$
T = Temperature (K)

There are two different ways to enter rate laws reaction kinetics in OLI Analyzer: Stream Analyzer

1. **Standard Rate Law** which uses the Arrhenius equation for the reaction rate constant k, referred to as STD type within the software.
2. **Non-Standard Rate Law**, referred to as SPEC type within the software.

In this section, we will show you how to set up both types of reaction kinetics.

The reaction kinetics is enabled Under the Chemistry menu > Model Options > Phases > Kinetics

1.11.1. Standard Rate Law

The Standard Rate Law (STD) considers both the forward and reverse reaction rates, the individual species reaction orders, and the forward and reverse reaction constants (determined using the Arrhenius Equation).

For the reaction below:

$$aA + bB + \cdots \leftrightarrow cC + dD + \cdots$$

where: $a, b, \ldots\ c, d$ are stoichiometric coefficients
$A, B, \ldots$ are reactant species
$C, D, \ldots$ are product species

The rate law is of the form:

$$Rate = \left(k_f a_A^{r1} a_B^{r2} \ldots - k_r a_C^{p1} a_D^{p2}\right)$$

where:

$Rate$	=	Reaction rate $\frac{mol}{h}$
k_f	=	Forward reaction rate constant $(units\ depend\ on\ reaction\ order)$
k_r	=	Reverse reaction rate constant $(units\ depend\ on\ reaction\ order)$
$a_A, a_B, \ldots$	=	Activities of reactant species $\left(\frac{mol}{m^3}\right)$
$r_1, r_2 \ldots$	=	Reaction order of individual reactant species $(normally\ from\ experimental\ data. Default\ is\ stoichiometric\ coefficients: a, b, \ldots)$
$a_C, a_D, \ldots$	=	Activities of product species $\left(\frac{mol}{m^3}\right)$
$p_1, p_2, \ldots$	=	Reaction order of individual product species $(normally\ from\ experimental\ data. Default\ is\ stoichiometric\ coefficients: c, d, \ldots)$

Within the software the naming of the constants defined above is the following:

OLI Keyword	Description
KF	Forward reaction rate constant
KR	Reverse reaction rate constant
AF	Forward reaction Arrhenius factor
AR	Reverse reaction Arrhenius factor
BF	Forward reaction activation energy divided by the universal gas constant (K)
BR	Reverse reaction activation energy divided by the universal gas constant (K)
ER_i	Reaction order of reactant species i
EP_i	Reaction order of product species i

Thus, when specifying a standard rate expression, the user must define one of the following: (1) The Arrhenius frequency factors (AF and AR), and reaction activation energies divided by the universal gas constant (BF and BR) or, (2) the reaction rate constants (KF and KR) directly. In addition, the user can specify the individual

species order coefficients for the forward and reverse reactions if these differ from the stoichiometric coefficients (which are the default).

When defining the reaction order for a species, the order in which the species appears in the reaction equation must be defined (i.e., subscript *i*) with a sequential number, for either the reactant or product species. Hence, the first reactant is identified with the number 1, the second, 2 and so on. Similarly, the product species are identified with the integers 1, 2, 3, etc.

If any of the keywords are not defined, the software assumes a default value for that variable. These default values are assumed to be zero for the reaction rate constants, Arrhenius factors, and activation energies (divided by the universal gas constant). For the species reaction order coefficients, the reaction stoichiometric values are assumed. To complete the standard rate expression definition, the reaction temperature and initial reactant molality are included in the process stream composition definition.

Example 15: Reaction of Ammonia and Carbon Dioxide

In this example, we are going to consider the reaction of ammonia and carbon dioxide to form urea and water, according to the following reaction:

$$2NH_{3(aq)} + CO_{2(aq)} \leftrightarrow NH_2CONH_{2(aq)} + H_2O$$

This reaction will take place in a plug flow reactor at 200ºC and 100 atm, with a total residence time of 100 hours.

Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Single Point Calculation with Reaction Kinetics Enabled			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Calculated
Calculation Sub-type	Isothermal	Temperature	200 ºC
Stream Name	Standard Rxn Kinetics	Pressure	100 atm
Single Point Name	Rxn Ammonia/CO2	Water	55.5082
Name Style	Display OLI Name (TAG)	CO2	2 moles
Unit Set	Metric, Moles	NH3	2 moles
Framework	AQ	UREA	0 moles
Kinetics	Enabled		
Kinetics Holdup Time	100 hours		
Number of Kinetic Steps	10		

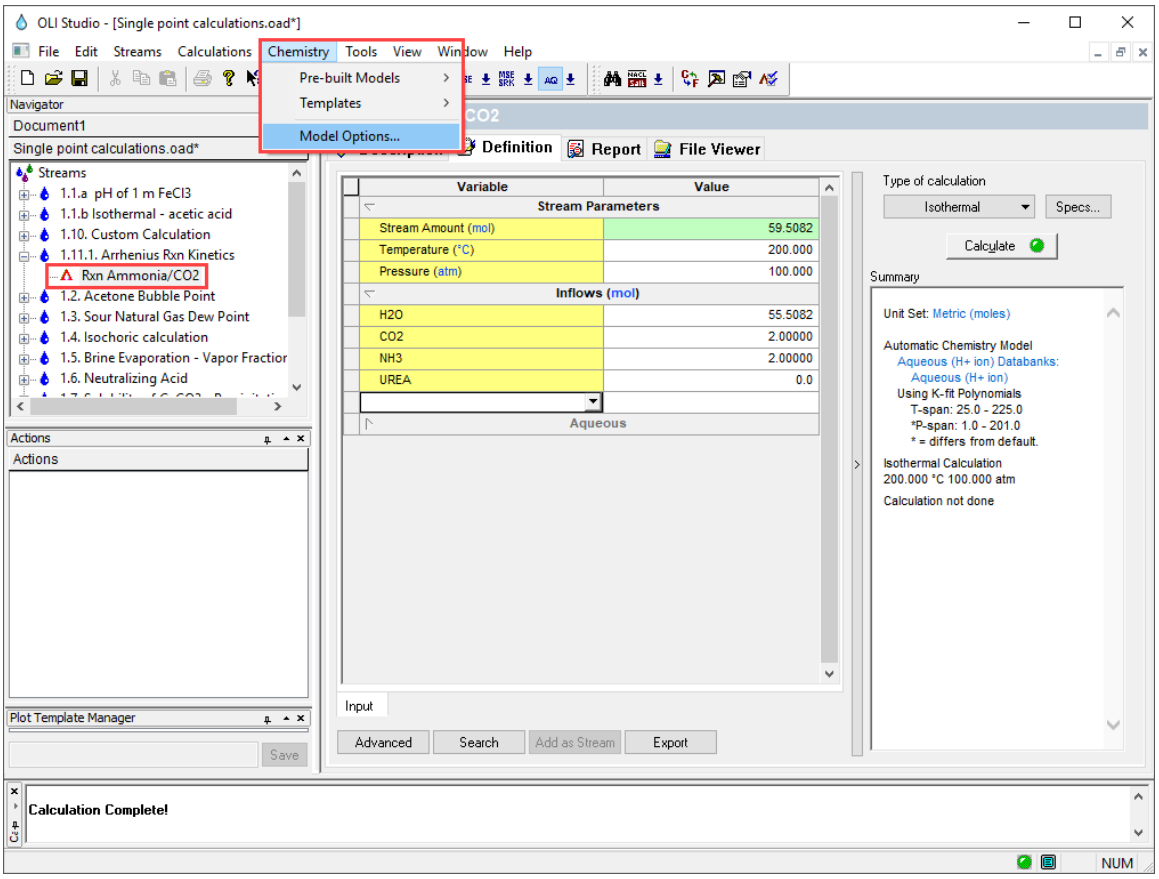
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Standard Rxn Kinetics*
3. Select the **AQ** thermodynamic Framework

4. **Click** on the **Names Manager** Icon, and select the ***OLI Name (TAG)*** option, and click **OK.**

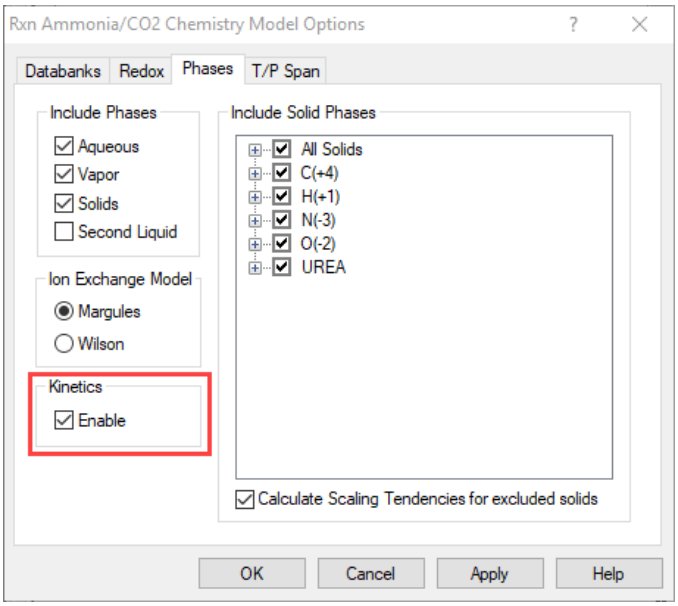
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles.
6. **Enter** the stream composition, temperature and pressure given in the table above.
7. Go to the **Add Calculation** button and select **Single Point** calculation
8. Select **Isothermal** (default) as Type of Calculation.
9. Change the ***SinglePoint*** name to ***Rxn Ammonia/CO2*** using the **<F2>** key

So far, we have created an Isothermal calculation. Now, we are going to enable the **Reaction Kinetics** option at the *Single Point Level*.

10. To enable reaction kinetics, make sure that you are at the *Single Point Level* by clicking on the Single Point Icon, and then go to **Chemistry menu** > **Model Options.** This will open the **Chemistry Model** window.

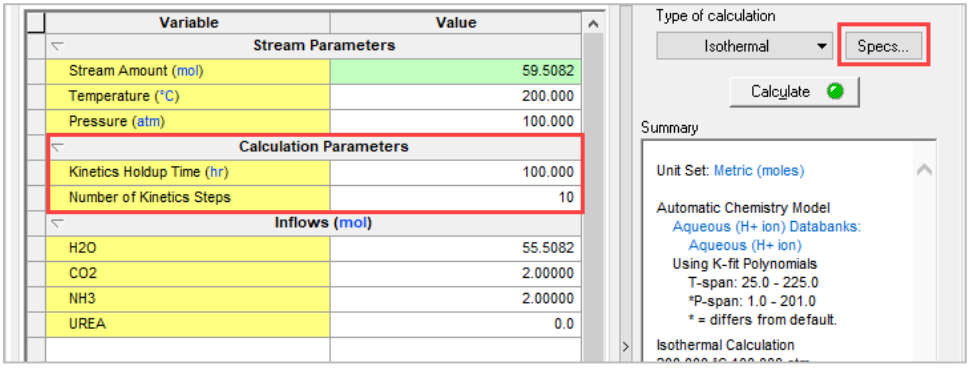


11. Select the **Phases** tab and check the **Kinetics** box. Then click **OK**.



A new grid section named **Calculation Parameters** appears. In this grid the **Kinetics Holdup Time,** and the **Number of Kinetic Steps** can be defined. The default values are 2 h and 2 steps respectively.

12. Change the **Kinetics Holdup Time** to **100** hours and the **Number of Kinetic Steps** to **10**.

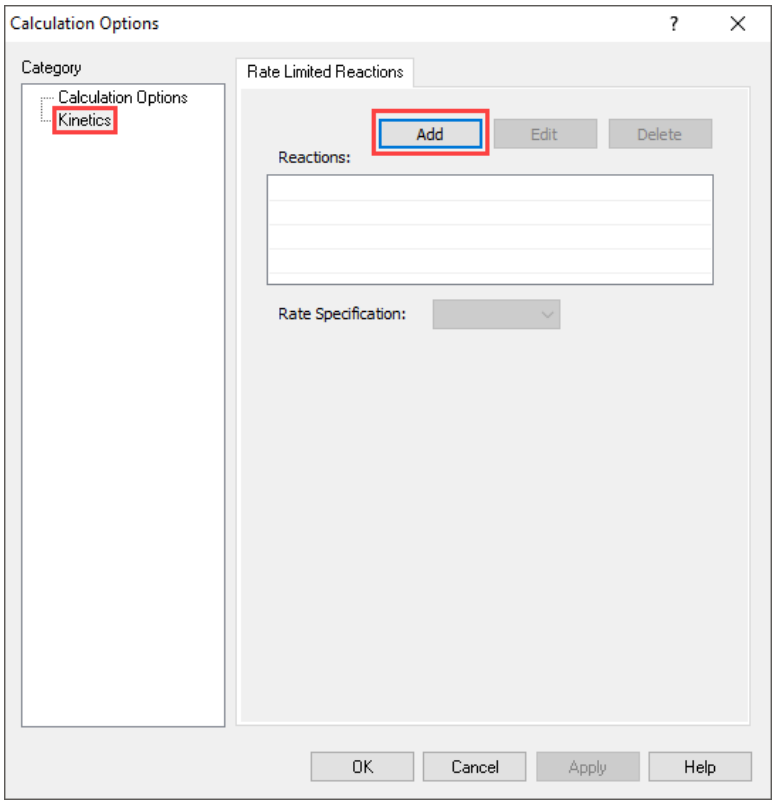


Kinetics Holdup time is equivalent to **Residence Time**. The **Number of Kinetic Steps** is equivalent to Δt, thus Kinetics Holdup time = ΣΔt.

Note: *Kinetics Holdup Time vs Number of Kinetic Steps*
For processes that have reaction kinetics, the software needs to know how the concentration of the reactants (or products) change over time during the reaction, which is given by the **rate law**. It is necessary to divide the total residence time into small steps. Adding more steps decreases the error; however, as you increase the number of stages, the computational time increases.

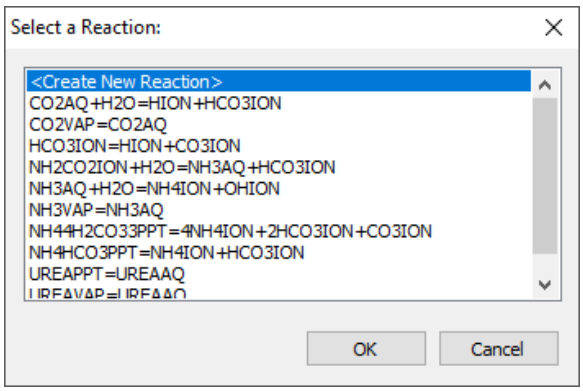
Now, our next step is to define the reaction kinetics.

13. Click on the **Specs** button. This will open the **Survey Options Window**.
14. Select **Kinetics** under the Category window
15. **Click** the **Add** button to add a new reaction. This will open the **Select a Reaction** Window.



You will be given a list of reactions which are already in the chemistry model. For our example, we need to create a new reaction.

16. Select the option **Create a New Reaction**, and then click **OK**.



This enables the option to enter a new reaction.

17. **Type** the following reaction: 2NH3AQ+CO2AQ=UREAAQ+H2O and then hit **Enter**. The window will update.

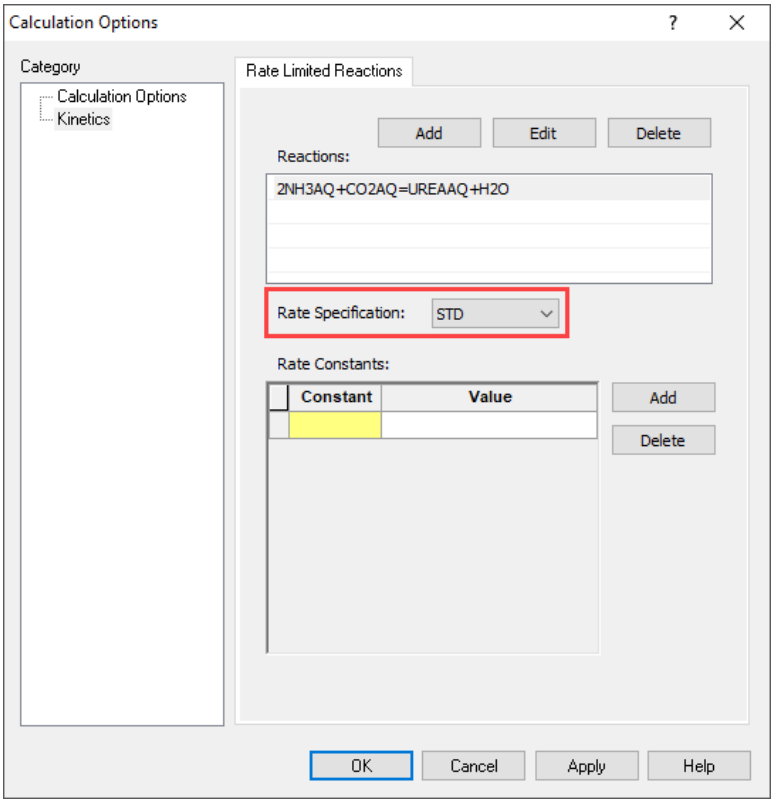
Note: You must use the OLI Tag Name for this step, and additionally specify the phase of the reactants and products. Water is a special case; it is written only as H2O.

As a general rule:

- For an aqueous phase: AQ
- For a vapor/gas phase: VAP
- For a solid phase: PPT
- For a hydrated solid: SOLIDNAME**.**nH2O, where n is the hydration number
- For an ion: ION

You can find the OLI TAG Name of your specific species using the Component Search Tool.

18. Select the STD (Standard Rate Reaction Kinetics) as the Rate Specification



Now, let's start entering the rate constants.

Remember, the forward and reverse reactions have the same format. The rate is the following:

$$R = k_f[NH_3]^2[CO_2] - kr[NH_2CONH_2]$$

For this example, the forward rate constant (KF) is a constant value equal to 2000.

And, the reverse rate constant (KR) is defined as follows:

$$KR = AR\, e^{\frac{-BR}{T}}$$

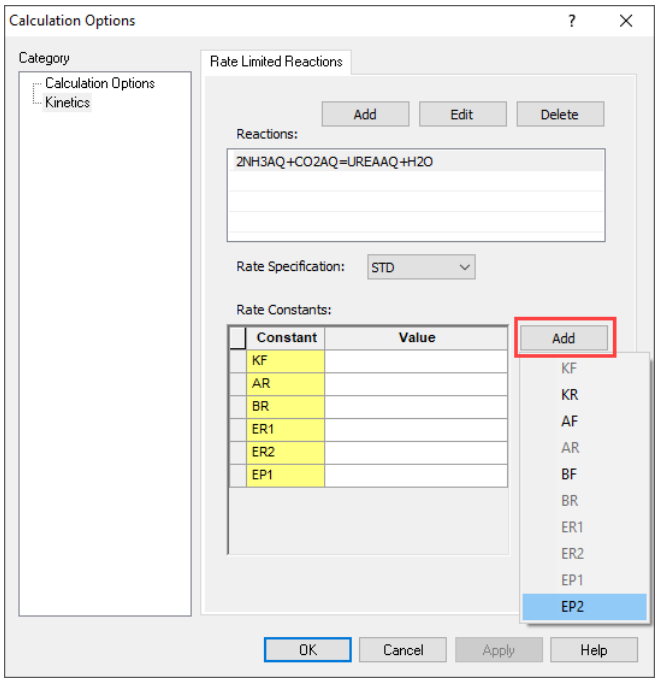
$$KR = 1.2 \times 10^{-10}\, e^{\frac{-3480.78}{T}}$$

A summary of the Reaction Rate Parameters is given in the table below (These parameters where created for illustration purposes, do not use them for any real design work).

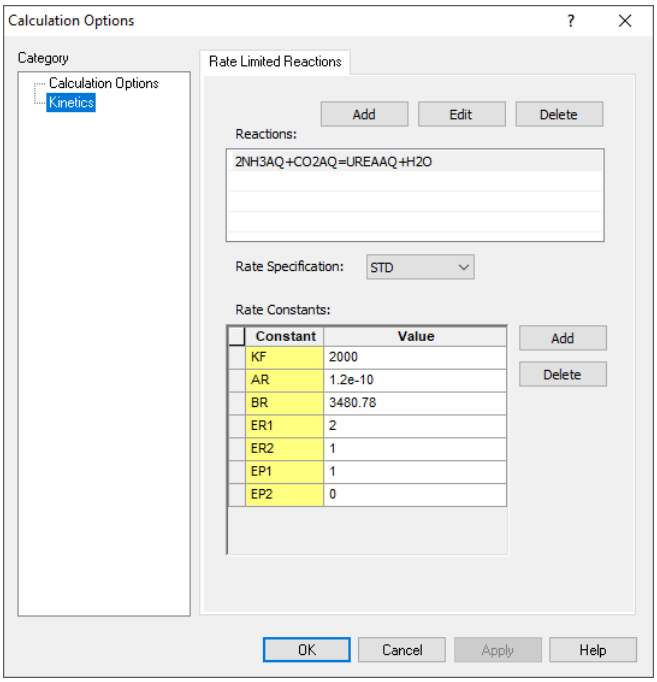
Parameters	Value	Comment
KF	2000	Forward Rate Constant
KR	Calculated	Reverse Rate Constant
AF		Not needed
AR		1.2×10^{-10}
BF		Not needed
BR	3480.78	Determined from $BR = \frac{E_a}{RT} = \frac{28939.9}{8.3142}$
ER1	2	This is the exponent of reactant 1 $[NH3]^2$
ER2	1	This is the exponent of reactant 2 [CO2]
EP1	1	This is the exponent of product 1 in the mechanism. In this case [NH2CONH2]
EP2	0	H2O does not participate in the reaction

Now that we have identified the parameters needed, we can add them.

19. Click on the **Add** button and select the parameters needed.



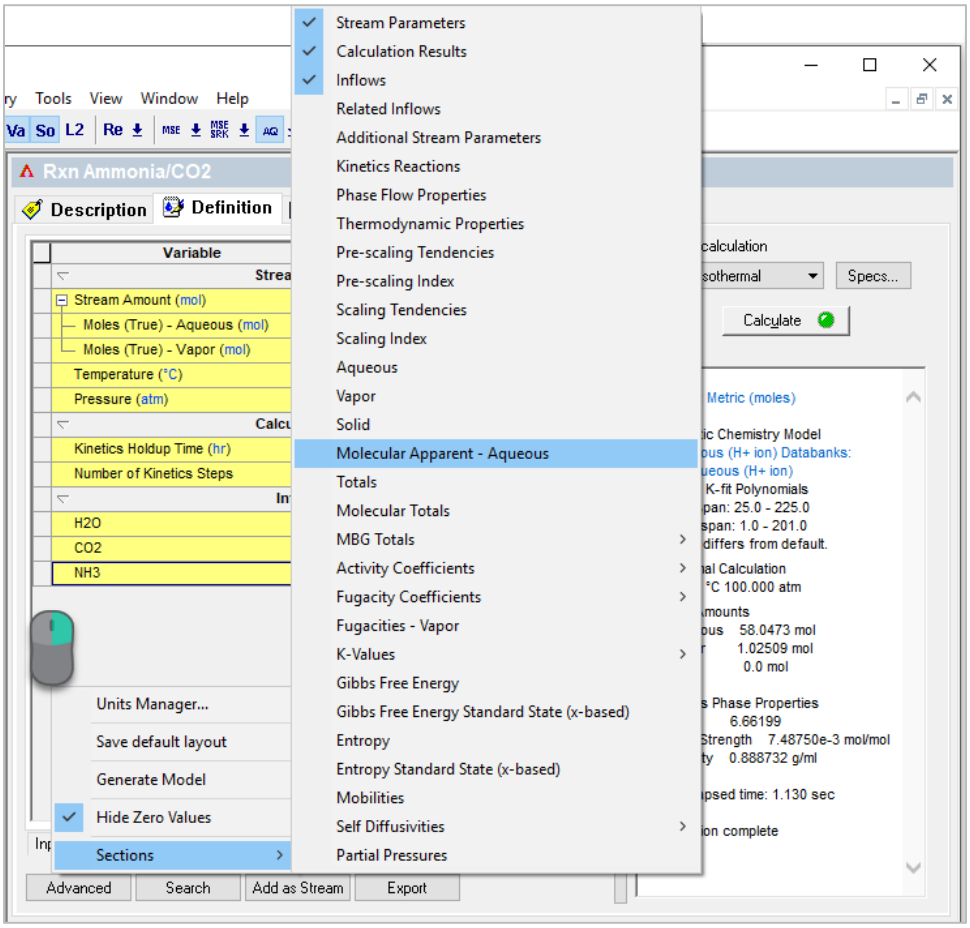
20. **Type** the constant values, and then click **OK**.



21. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key.
22. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

Anaylyzing the Results

1. Click on the **Output-Minitab** to see the Results.
2. Right click on the gray area and select **Sections**> **Molecular Apparent - Aqueous**



About **0.002 moles** of Urea had been formed with a total residence time of 100 hours.

Molecular Apparent - Aqueous (mol)	
H2O	55.2950
NH3	1.95686
CO2	1.22715
UREA	2.09657e-3

You can make changes on the residence time, reaction conditions or the rate of reaction to maximize the production of urea.

1.11.2. Non-standard Rate Law

Non-Standard Rate Law, also referred to as SPEC type within the software. These reactions do not follow the Arrhenius kinetics.

Example 16: Ammonia Hydrolysis

In this example we are using simpler chemistry. We are going to study the hydrolysis of ammonia.

$$NH_{3(aq)} + H_2O \rightleftharpoons NH_4^+ + OH^-$$

For this reaction we know the forward rate constant (k_f) but need to constrain the reverse reaction to the thermodynamic equilibrium constant. This implies that we are going to replace an existing equation within the software.

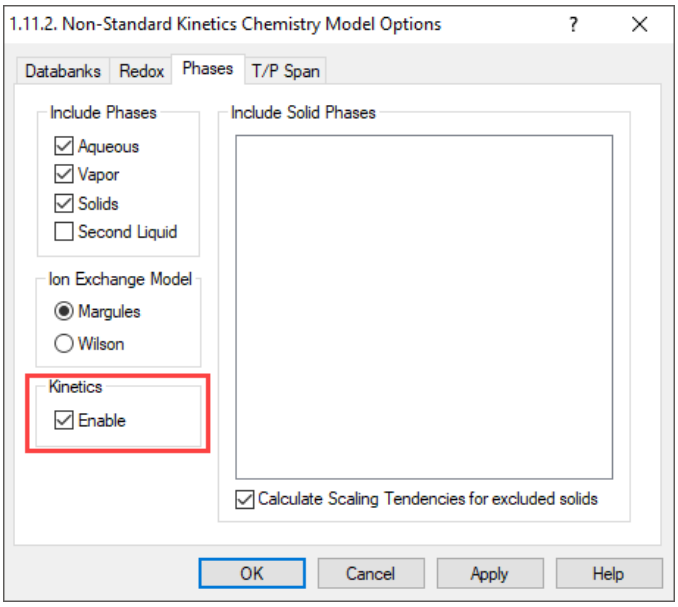
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Single Point Calculation with Reaction Kinetics Enabled			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Single Point Calculation	Stream Amount	Calculated
Calculation Sub-type	Isothermal	Temperature	25 ºC
Stream Name	Non-Standard Rxn Kinetics	Pressure	1 atm
Single Point Name	Ammonia Hydrolysis	Water	55.5082
Name Style	Display OLI Name (TAG)	NH3	0.1 moles
Unit Set	Metric, Moles		
Framework	AQ		
Kinetics	Enabled		

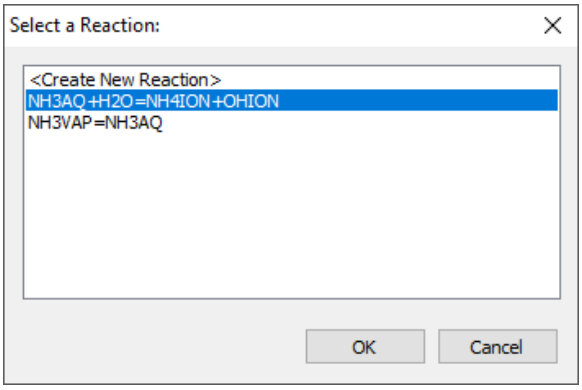
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Non-Standard Rxn Kinetics*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon, and select the ***OLI Name (TAG)*** option, and click **OK.**
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles.
6. **Enter** the stream composition, temperature and pressure given in the table above.
7. Go to the **Add Calculation** button and select **Single Point** calculation
8. Select **Isothermal** (default) as Type of Calculation.
9. Change the ***SinglePoint*** name to ***Ammonia Hydrolysis*** using the **<F2>** key

10. To enable reaction kinetics, make sure that you are at the *Single Point Level* by clicking on the Single Point Icon, and then go to **Chemistry menu** > **Model Options.** This will open the **Chemistry Model** window.
11. Select the **Phases** tab and check the **Kinetics** box. Then click **OK**.

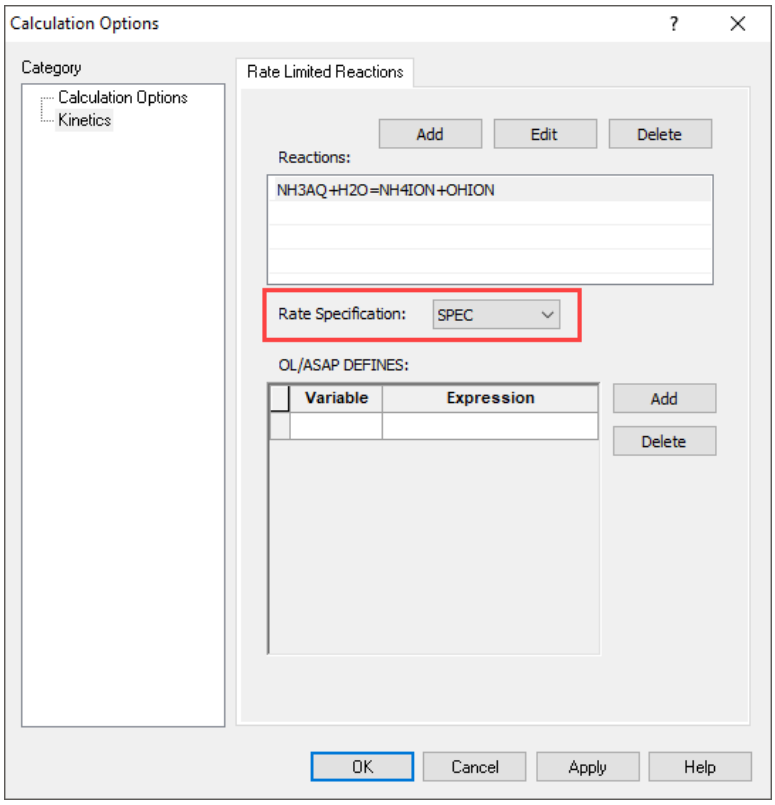


Now, our next step is to define the reaction kinetics.

12. Click on the **Specs** button. This will open the **Survey Options Window**.
13. Select **Kinetics** under the Category window
14. **Click** the **Add** button to add a new reaction. This will open the **Select a Reaction** Window.
15. **Select** the first reaction: NH3AQ+H2O=NH4ION+OHION, and then click **OK**.



16. Select the SPEC as the Rate Specification.



For this example, the forward and reverse reaction rates are the following:

$$Rate_f = k_f \cdot \gamma_{NH_{3,aq}}[NH_{3,aq}] \cdot \gamma_{H_2O}[H_2O] \qquad where\ \ k_f = 3$$

$$Rate_r = k_r \cdot \gamma_{NH_4^+}[NH_4^+] \cdot \gamma_{OH^-}[OH^-] \qquad where\ k_r = \frac{k_f}{K_{eq}}$$

Thus, the total rate is given by:

$$Rate = Rate_f - Rate_r$$

$$Rate = k_f \cdot \gamma_{NH_{3,aq}}[NH_{3,aq}] \cdot \gamma_{H_2O}[H_2O] - k_r \cdot \gamma_{NH_4^+}[NH_4^+] \cdot \gamma_{OH^-}[OH^-]$$

These is where things get difficult. You now need to speak “OLI”. We have some rules for SPEC type equations.

We now need to turn these values into "OLI" terms[4].

We can define any variable we want. We have some variables that you will need to use. Any concentration variable such as [NH_{3aq}] is defined as the natural log and is designated with the letter "L". So [NH_{3aq}] is used as LNH3AQ.

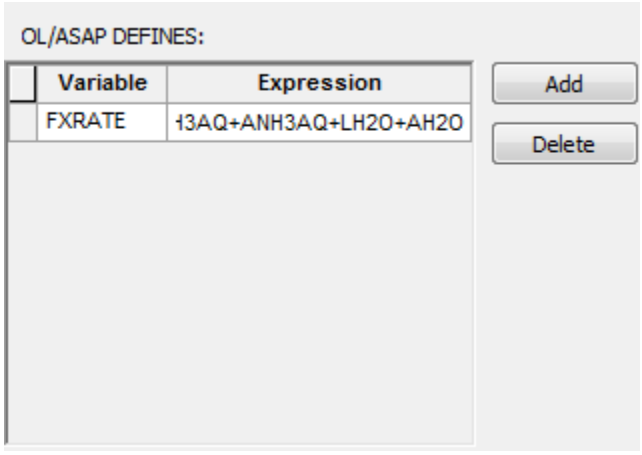
Similarly, activity coefficients γ are also taken as the natural log. So, γ_{OH^-} is written as $Log_e\ \gamma_{OH^-}$ = AOHION.

KEQ is the thermodynamic equilibrium constant for the equation. AH2O is special in the Aqueous thermodynamic framework in that it is the variable $Ln(a_{H_2O})$.

We now need to add these variables to the kinetics window[5]:

Variable	**Expression**
FXRATE	LNH3AQ+ANH3AQ+LH2O+AH2O
RXRATE	LNH4ION+ANH4ION+LOHION+AOHION
KF1	3
KR1	KF1/KEQ
RATE1	(KF1*EXP(FXRATE)-KR1*EXP(RXRATE))*VOLLIQ/1000

17. Change the **Kinetics Holdup Time** to **100** hours and the **Number of Kinetic Steps** to **10**.

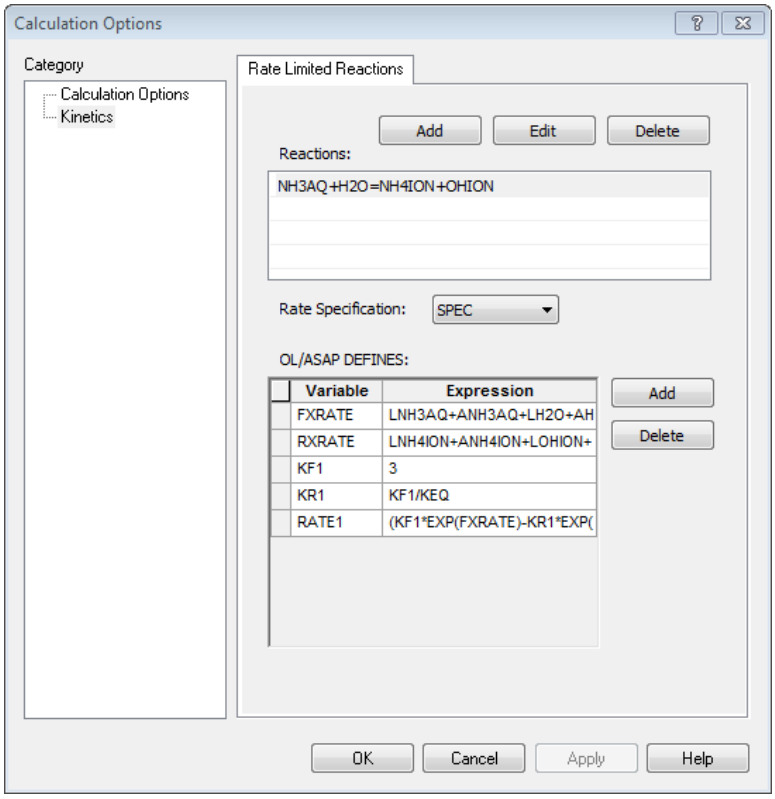


[4] Commonly referred to as ASAP variables.

[5] Copy and paste from this document can make this step easier

You will notice in the image above that we have scrolled to the end. That is ok. Click the **Add** button to continue with the equations. It is important that you keep the order correct. You see what we are using previously defined variables in subsequent equations.

Complete the remainder of the variables.



The completed equations

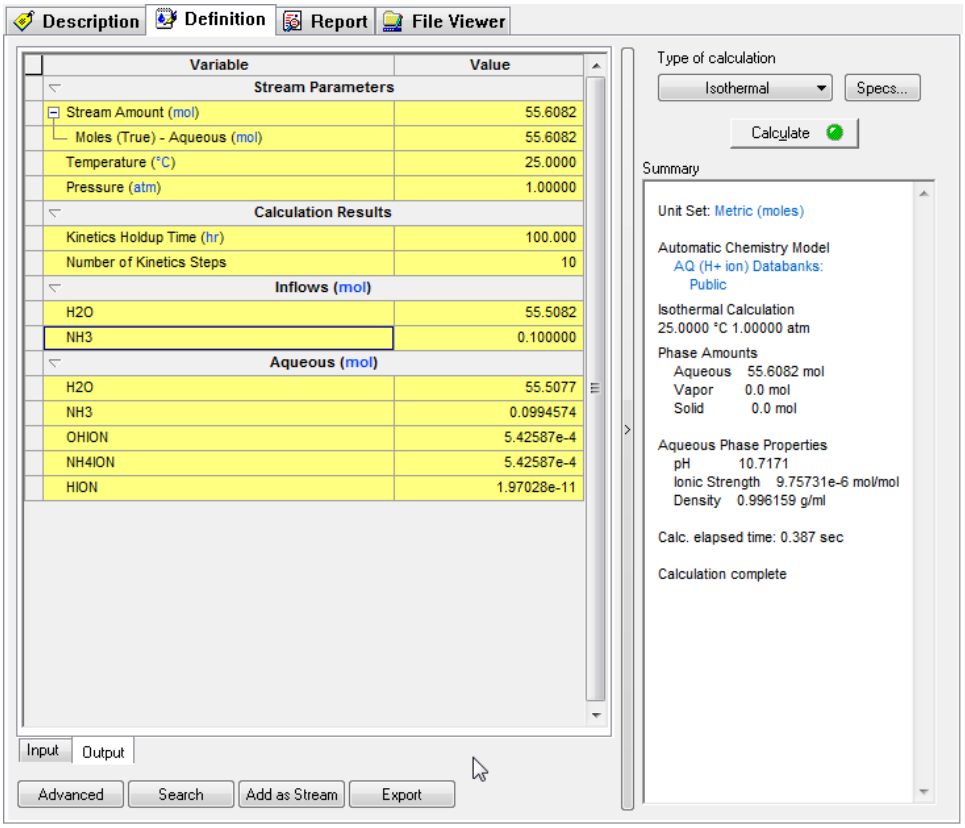
The variable VOLLIQ is the volume of the liquid phase in Liters. OLI requires the rate to be in mol/m^3 we need to divide by 1000.

Click the **OK** button.

Like the previous example, this is a plug-flow reactor with a holdup time of 100 hours and 10 steps.

Now **Calculate**

Once the calculation is complete you can click the **Output** mini tab and add the *Aqueous* section (not molecular aqueous):



You can see that some ammonium ion has been created. It is interesting to see what the equilibrium condition would be.

Create another single point isothermal calculation and run it without any reaction kinetics. Here are results below:

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Moles (True) - Aqueous (mol)	55.6082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
NH3	0.100000
Aqueous (mol)	
H2O	55.5069
NH3	0.0986221
OHION	1.37789e-3
NH4ION	1.37789e-3
HION	7.99755e-12

The reaction kinetics have forced the back reaction to be dominant. In the equilibrium case, approximately

1.3×10^{-3} moles of NH_4^+ have been created. By limiting the forward reactions, we allow the back reaction to take place and that only formed 5.4×10^{-4} moles of NH_4^+.

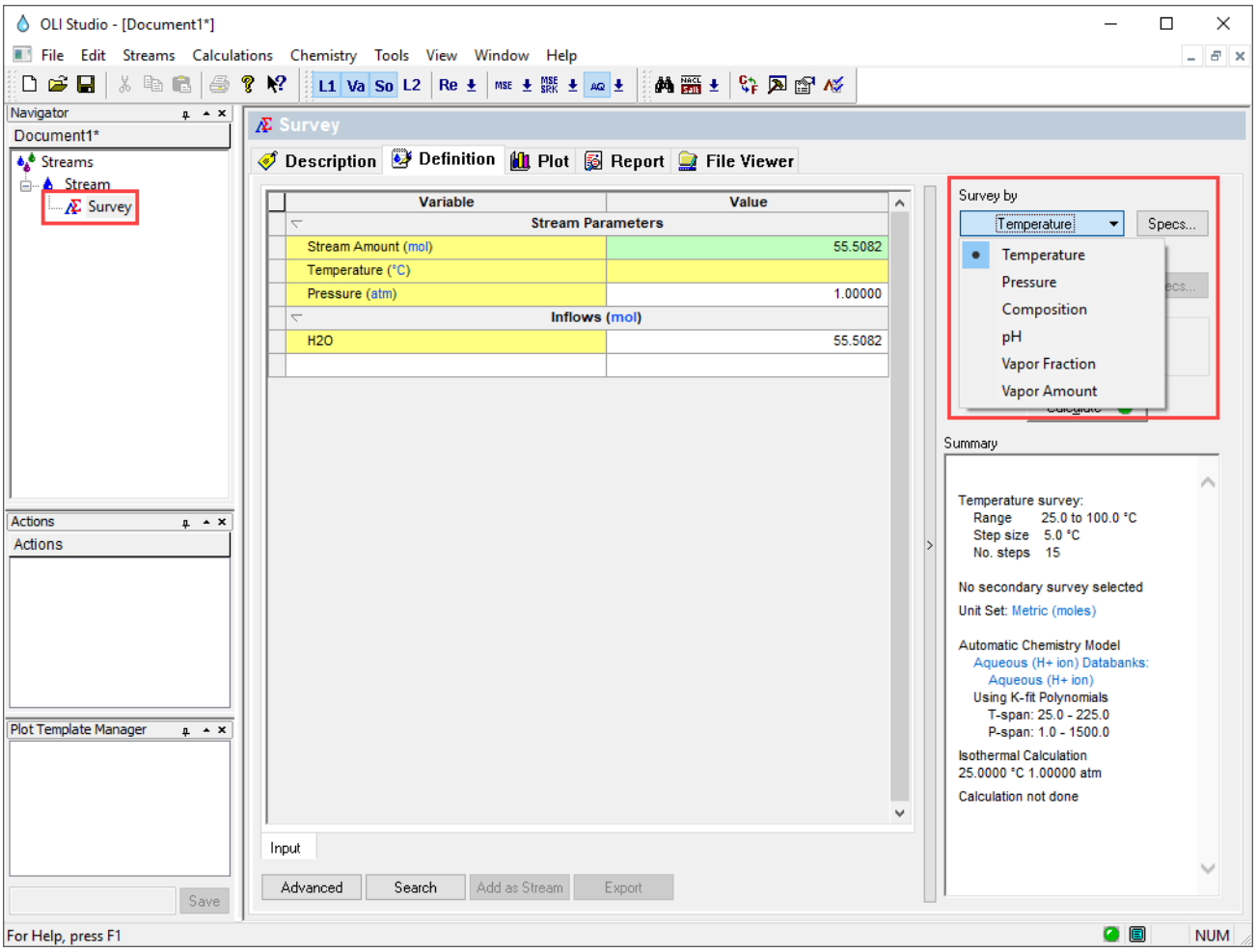
Section 2. Survey Calculations

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:

1. **Single Survey:** These calculations allow the user to designate one independent variable. The predefined single surveys include survey by Temperature, Pressure, Composition, pH, Vapor Fraction and Vapor Amount.
2. **Dual Survey:** These calculations allow the user to designate two independent variables.
3. **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.

In this section, you will learn how to set up **survey types** and introduce some additional features to get the most out of your simulation results.



2.1. Single Surveys

An introduction to single surveys is given here. We will illustrate, in detail, the steps necessary to conduct this type of calculation. The example below was designed to be used as a guide for future reference.

Example 17: Removal of Nickel from Wastewater

This case study is a typical wastewater treatment problem, the removal of a trace heavy metal ion (nickel) from a water stream in which the presence of another chemical (cyanide) significantly alters the treatment strategy. In this case, we are considering precipitation as an approach to removal of the nickel.

The wastewater in this case study contains nickel ions at a concentration of 0.002 m (or moles/ 1 kg H_2O). The existing treatment strategy is to precipitate the nickel ions as Nickel Hydroxide ($Ni(OH)_2$). The soluble nickel remaining after precipitation needs to be less than 1 ppm, which is the maximum contaminant level allowed.

During the course of the plant operation, some cyanide ion is inadvertently added to the waste stream. The soluble nickel is now more than 1ppm. Sulfide salts were then added to hopefully precipitate the nickel and once again achieve the design specification.

This example will be divided into three different scenarios:

1. Scenario 1: Wastewater without Additives
2. Scenario 2: Wastewater with Cyanide Content
3. Scenario 3: Wastewater with Sulfide Salts

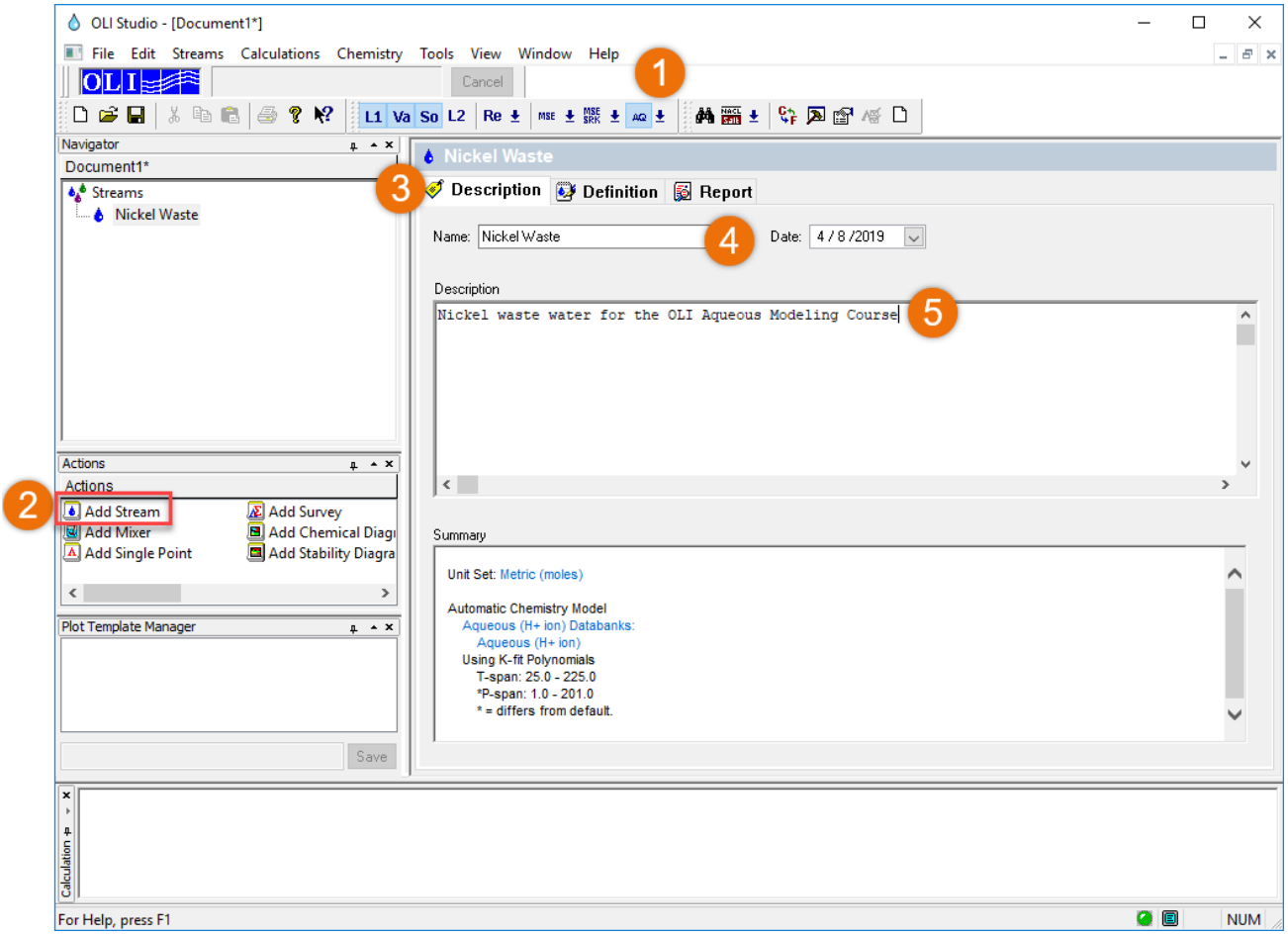
The power of the Stream Analyzer becomes apparent when we are seeking to study the chemistry of individual streams. For this specific example a Survey by **pH** will be used.

Scenario 1: Wastewater without Additives

We begin by starting the Stream Analyzer Program. This may be accomplished by ***clicking*** on the OLI Analyzer icon or by using the Start button and finding OLI Analyzer under *Programs*, which will take you to the New window where you start creating your calculations.

1. Select the **AQ-Databank** (The default databank)
2. Click on **Add Stream** icon (in the actions panel). This will display the **Definition** window. We should add some descriptive information about this stream, so we can later identify the stream
3. Click on the **Description** tab. This will display the description information
4. Replace the name ***Stream*** with the name ***Nickel Waste***. It is advisable to change the name of the stream from the default name. You may be entering many streams and will need to sort them out later
5. Add the following text to the **Description** box: "*Nickel waste water for the OLI Aqueous Modeling Course*"

Note: The summary box will contain additional information as the calculations proceed. This information maybe the name of additional databases or chemistry models imported from other OLI software packages. The filled-out window should look like the figure below.



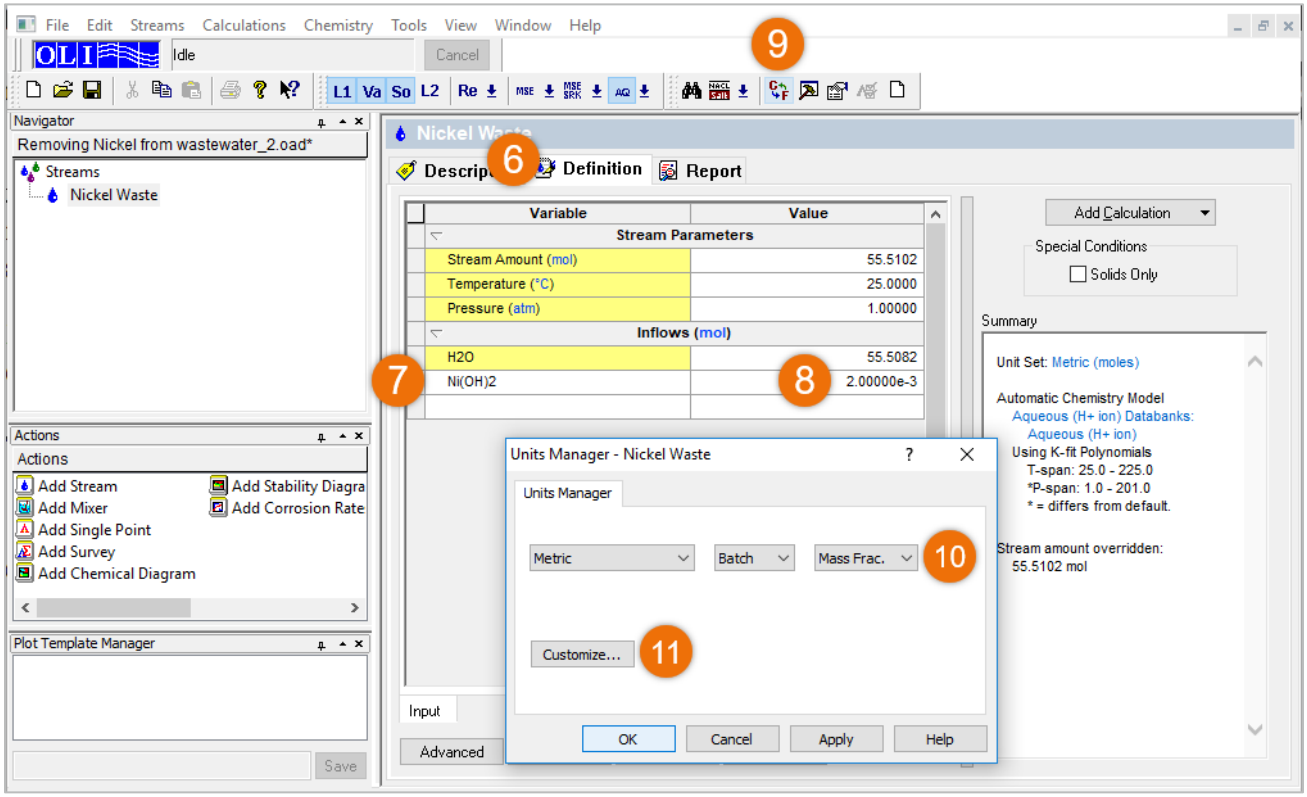
6. Click on the **Definition** tab to start defining the wastewater stream
7. Click in the white box in the grid below the **Inflows** line. Add the formula **$Ni(OH)_2$**
8. Click in the white box next to the species you just entered and enter the value **0.002**. Press **<Enter>** to update the list

   Note: Stream Analyzer will automatically change the name of the species to the selected display name. In this instance, the name you entered was **$Ni(OH)_2$** but it may have changed to a different form. If it changed you can specify which display name to use in the Names Manager icon

9. For the output results, we want output units in **ppm**. To change the output units, click on the Units Manager icon . This will open a new window.

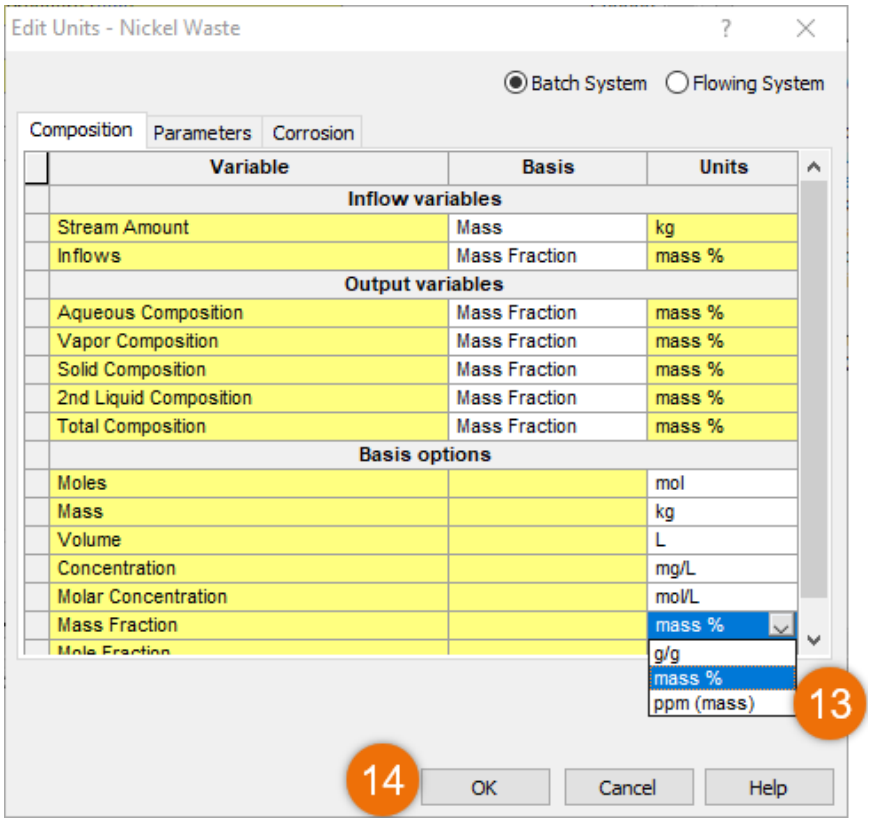
10. Change moles to Mass Frac. Using the drop-down arrow

11. Click on the **Customize** button. The **Units Manager** window will appear.



12. **Change the Mass Fraction Units to ppm (mass)**

13. **Click** OK

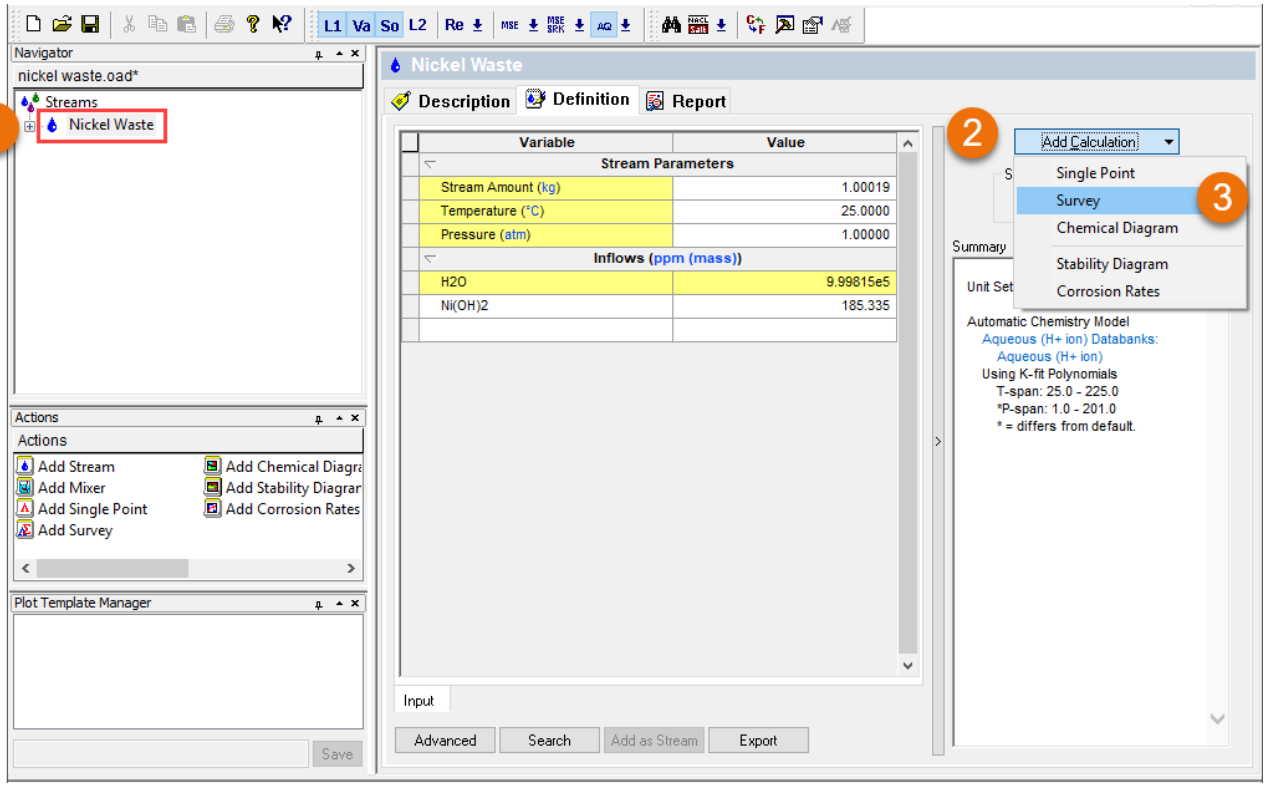


Our primary interest in this application is finding the optimum pH for nickel removal. To create a plot of Ni^{+2} as function of pH, we will need to run a pH survey.

Creating a pH Survey to find the optimum pH for nickel removal

Click on the **Nickel Waste** stream icon in the tree view on the left-hand side of the window. This will bring you back to the top of the series of calculations by displaying just the stream information.

1. Click on the **Add Calculation** button
2. Select **Survey**



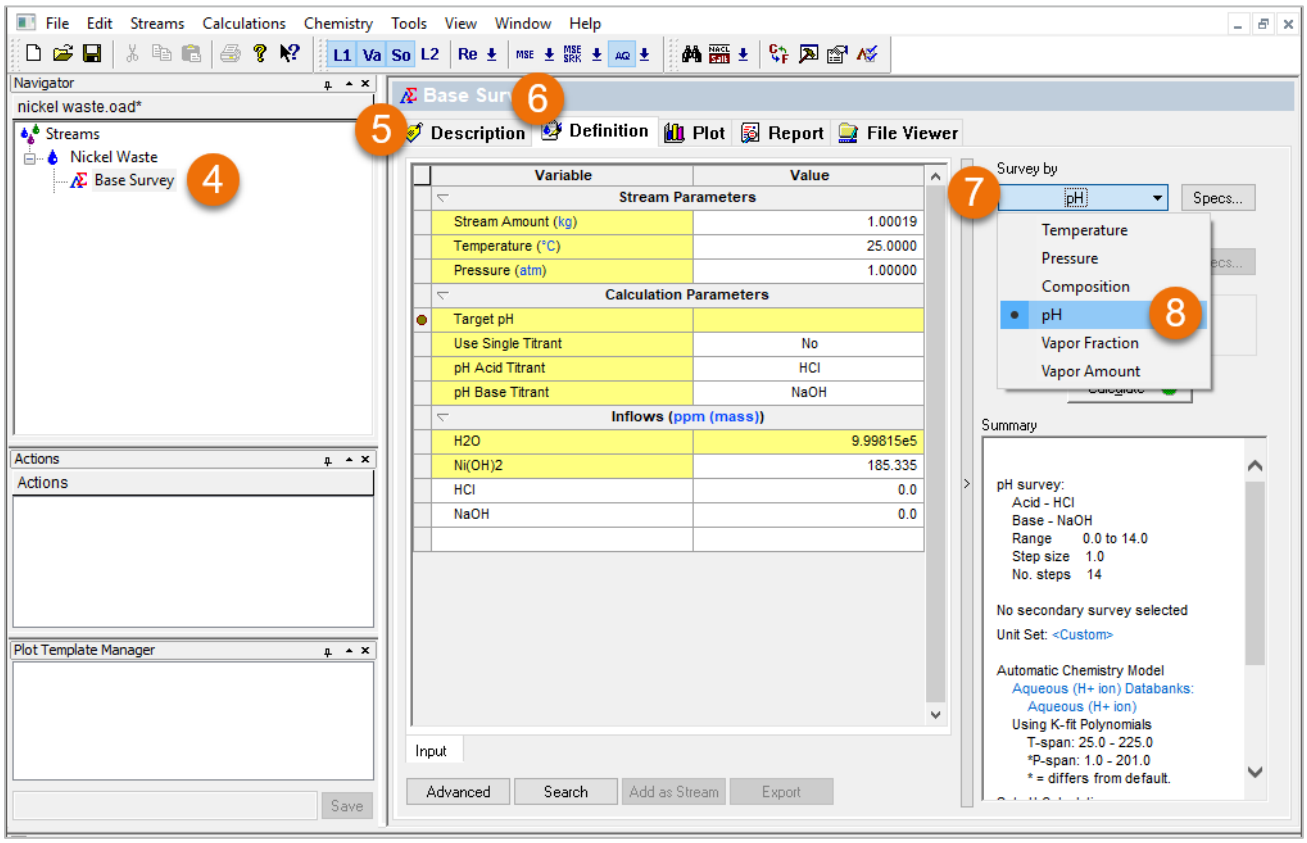
You can now add descriptive information about this calculation.

3. Enter a new **Survey name**: **Base Survey.** You can also double click on 'Survey' to change the name
4. Enter a **Description**: *Base pH survey without additives.*

Since we do not want a temperature survey which is the default, we will need to change the survey type.

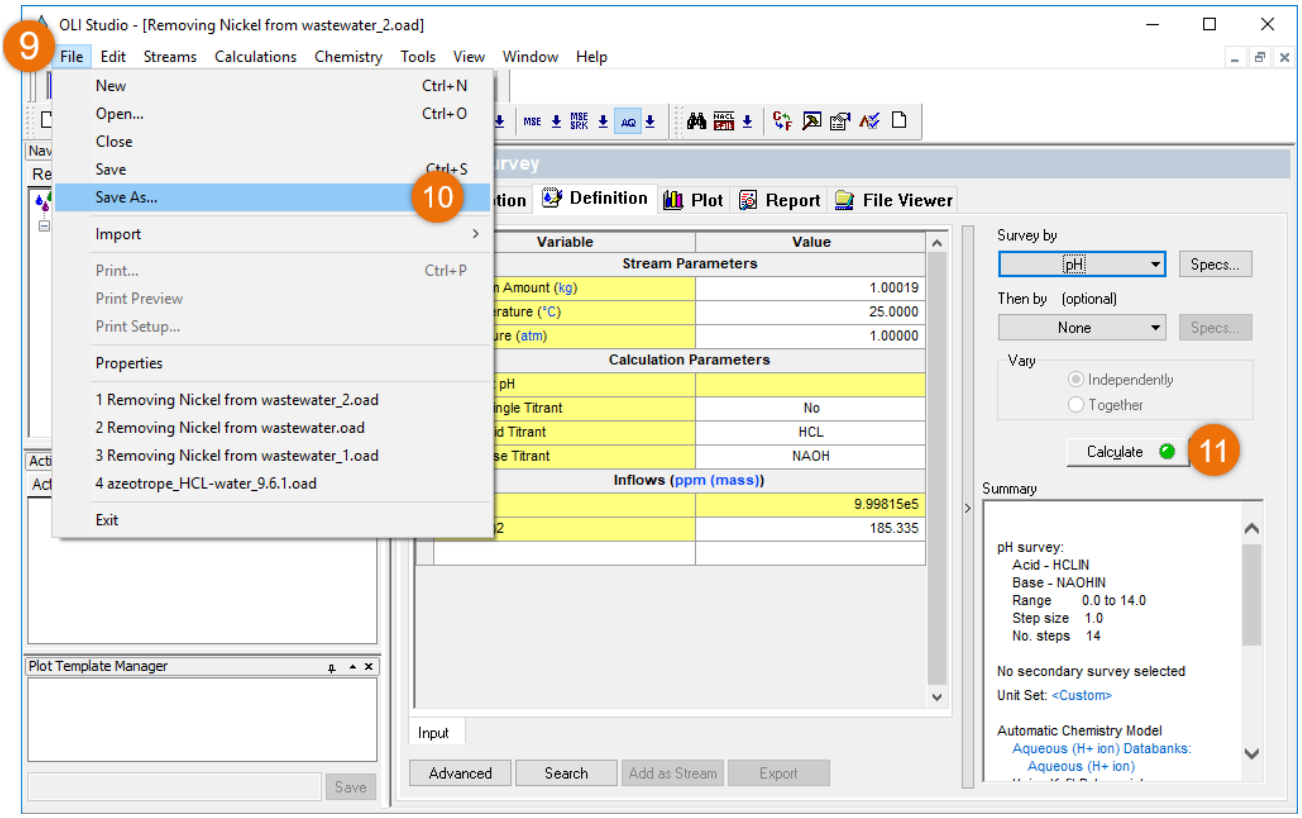
5. Click on the **Definition** tab to do the survey calculation.
6. Click on the **Survey by** button
7. Select **pH**

Note: The default acid titrant and the base titrant are already defined (HCl and NaOH). We are now ready to begin the calculations.

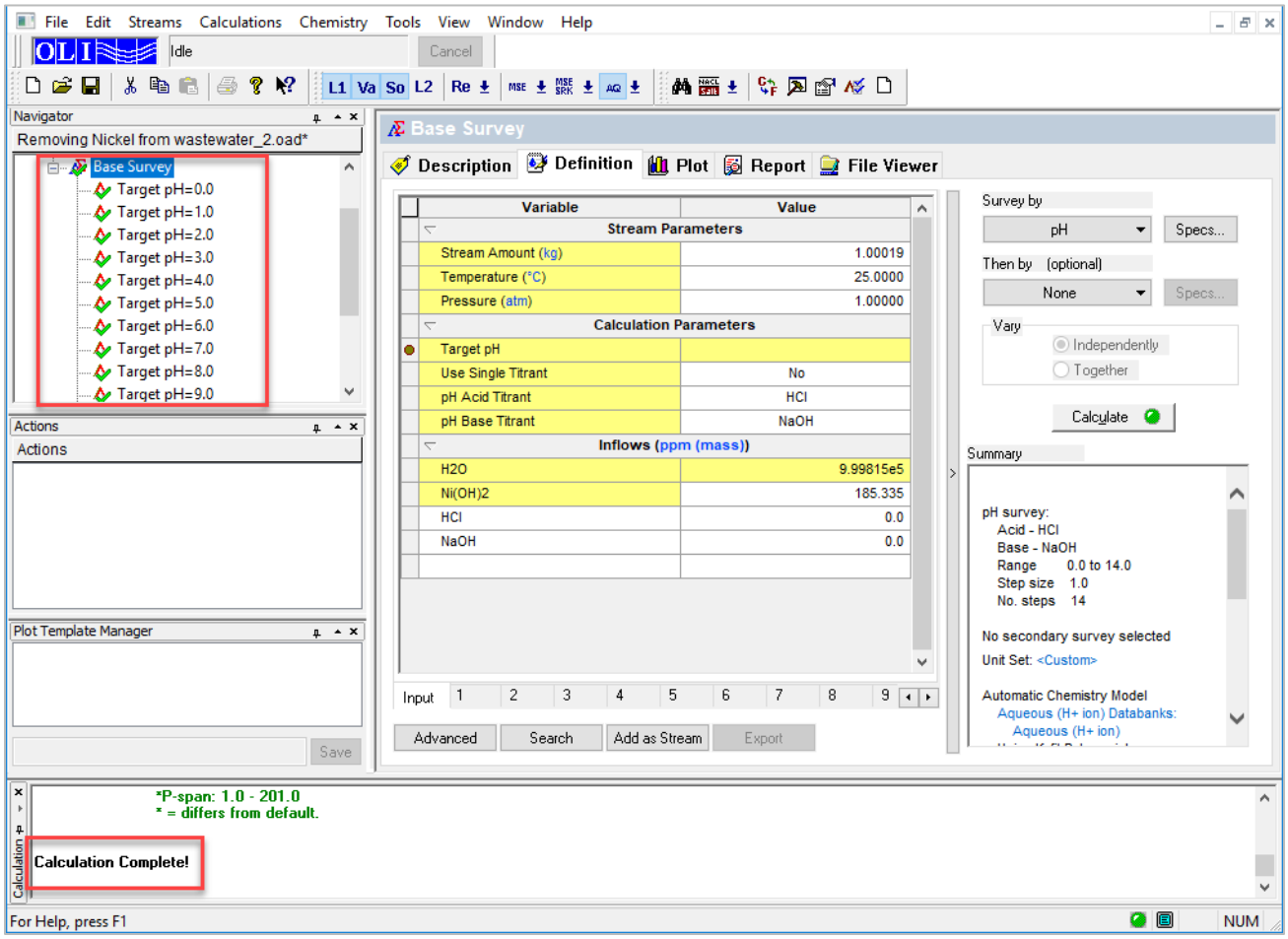


We should now save our work. It is very frustrating to work for a long period of time and forget to save our work. So please save.

8. Select **File**
9. Select **Save As** from the menu. Give the name *Removing nickel from wastewater*
10. Click on the **Calculate** button

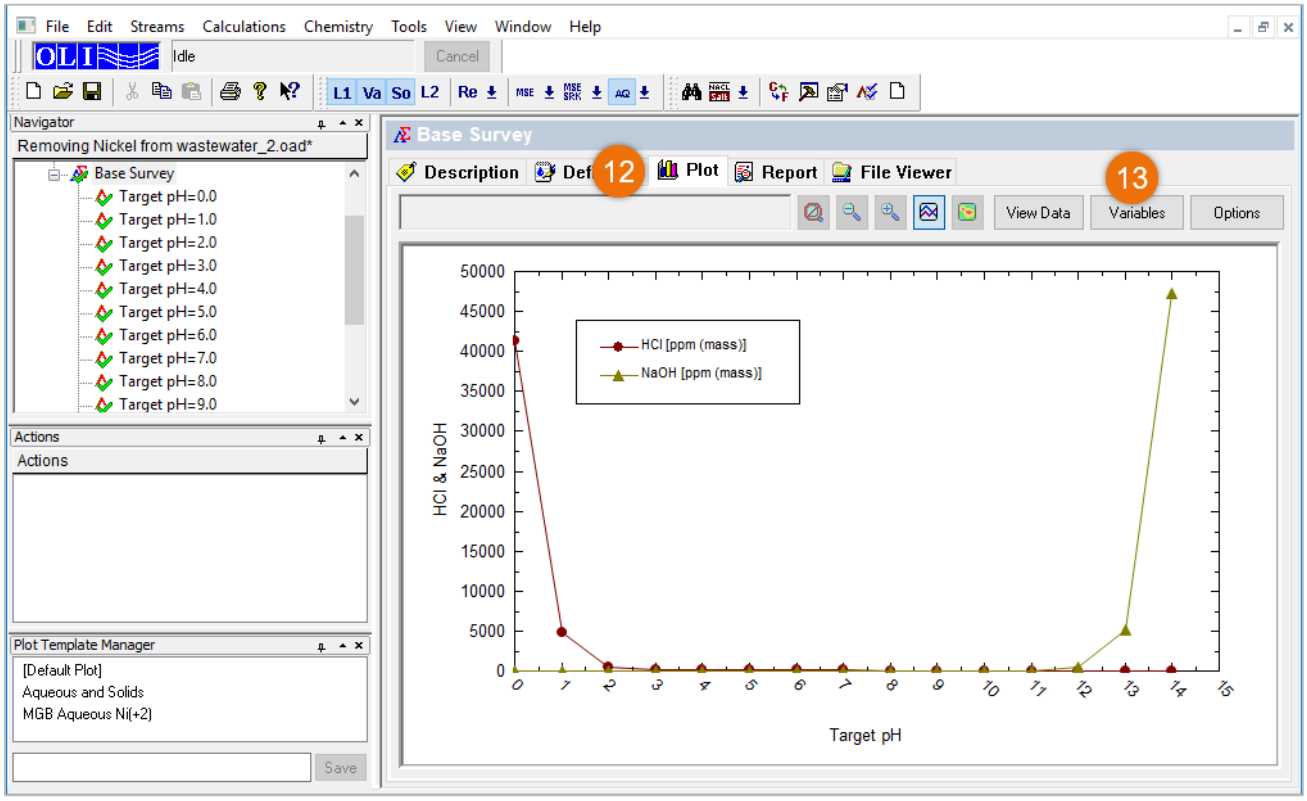


The program will run for a short time. When the orbit disappears, check the summary box to see if the calculation is complete. In the tree-view, you can expand the survey to see if all the points converged.



We can now obtain some graphical results.

11. Click on the **Plot** tab
12. Click on the **Variables** button

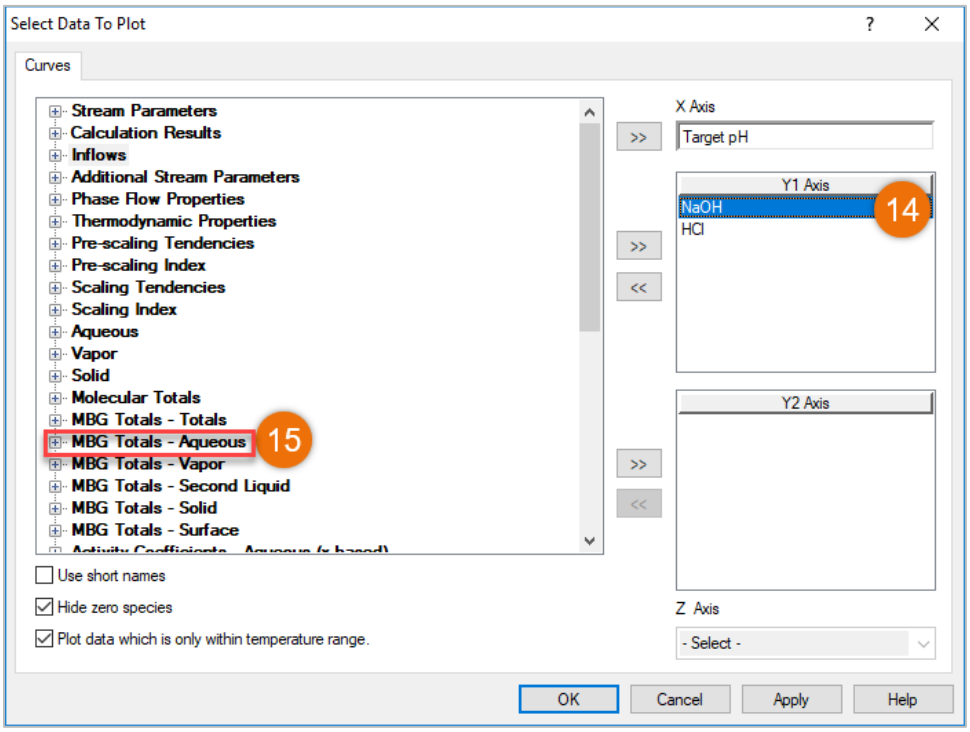


This will open a new window. The **NaOH** and **HCl** variables in the Y-Axis box should be displayed.

13. **Select** them and then **Click** on the left double-arrow **(<<)** button which will remove **NaOH** and **HCl** from the list. You can also select and double click to remove them.

14. Scroll down the left-hand window to find **MBG Totals - Aqueous** and expand the list by clicking the ⊞ box.

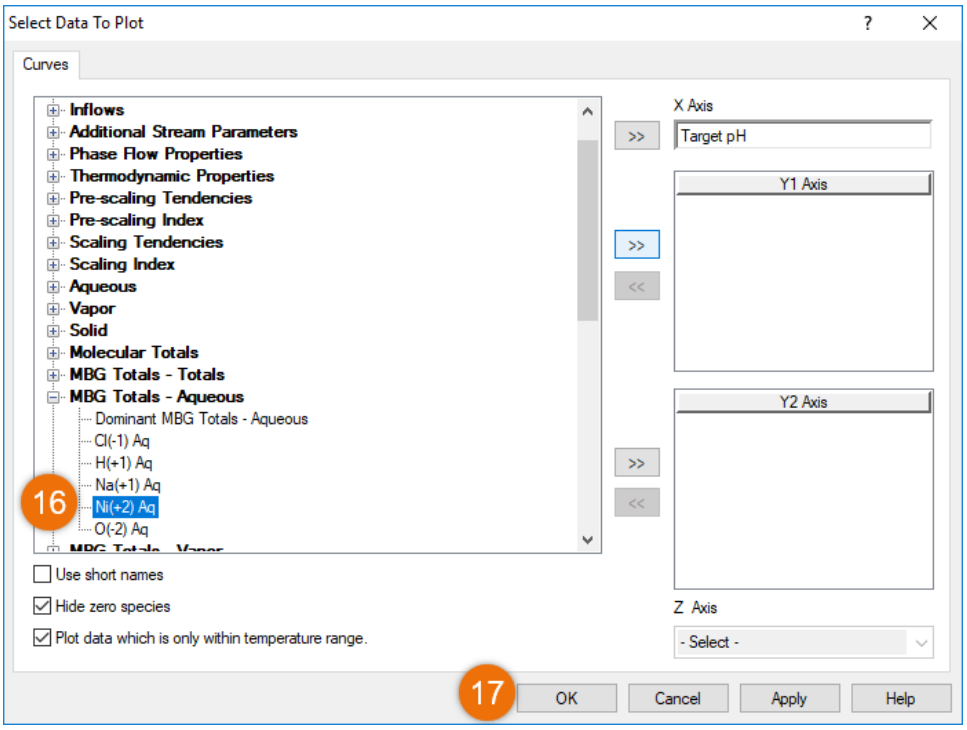
    Note: MGB is an abbreviation for Material Balance Groups. The **MGB** variable is a sum of all the species for that material in the phase requested.



The grid updates to show the **MGB** totals available to display. In this case we desire the Nickel(+2) species. in this case all the **Ni(+2) Aq** variable is a sum of all nickel containing ions in the aqueous phase in solution. Any solids are excluded from the summation.

15. **Double-Click** the **Ni(+2)** item or select it and use the **>>** button.

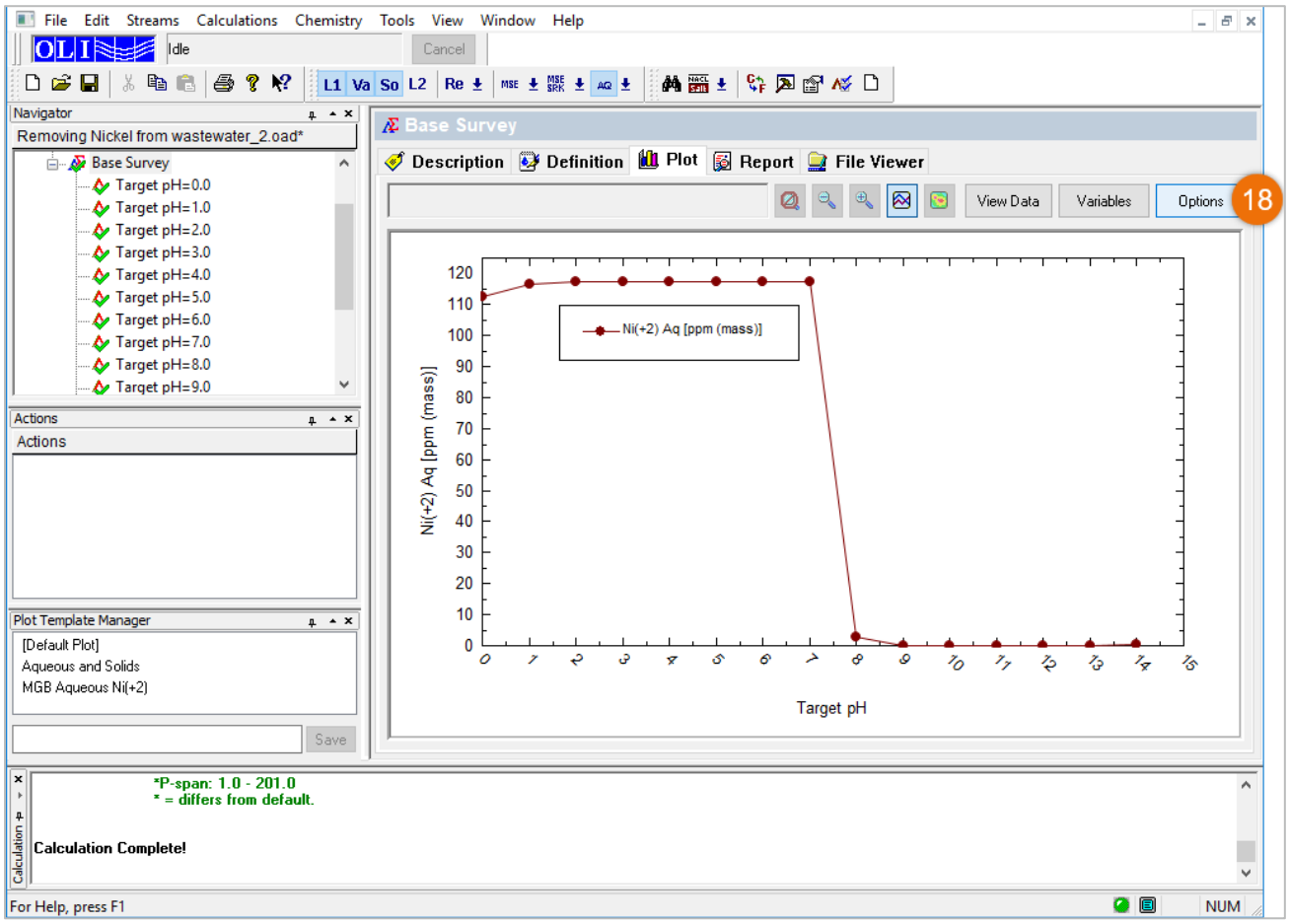
16. **Click** on the **OK** button.



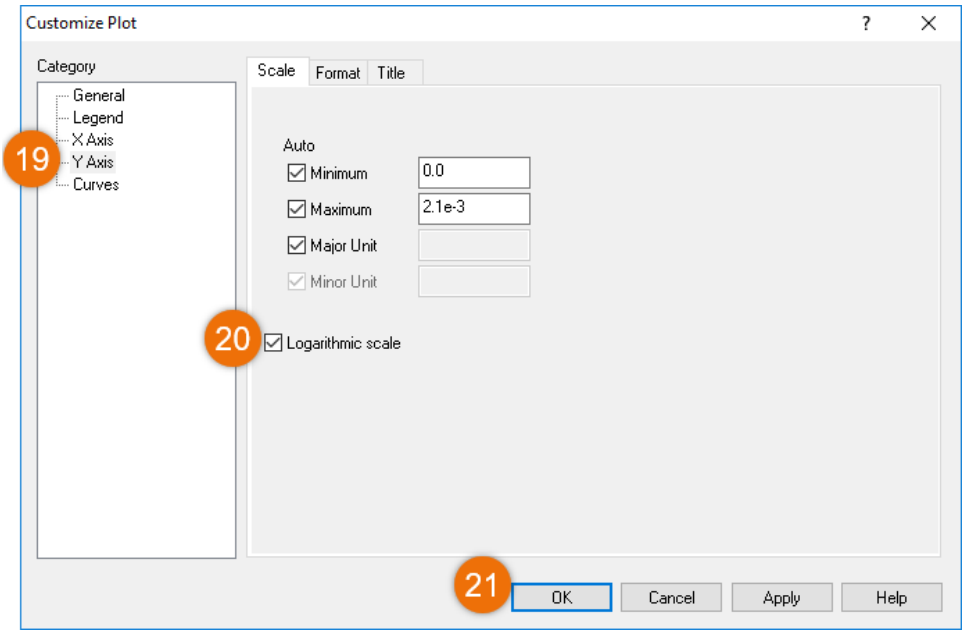
You will see the new plot.

For many calculations, the values on the plot extend over a very large range of numbers. The default linear axis may not capture all the details we require.

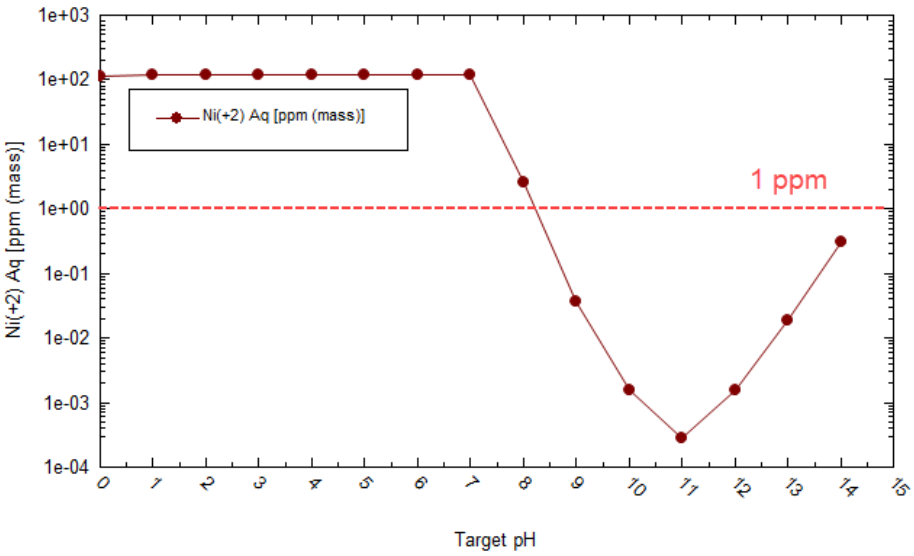
17. Above the plot window locate and select the **Options** button. This opens a new window.



18. Select **Y-Axis** from the Category List
19. **Check** the Logarithmic Scale Box
20. **Click** on the **OK** box



The modified plot is then displayed. The limit of 1 ppm for Ni^{+2} is approximately 2 x 10^{-5} moles. Above pH=9, we are several orders of magnitude below this limit. Additionally, you can see that a minimum amount of Ni^{2+} in the aqueous phase seems to occur in the pH=11 range. This is the result of nickel solids forming and leaving the aqueous phase.

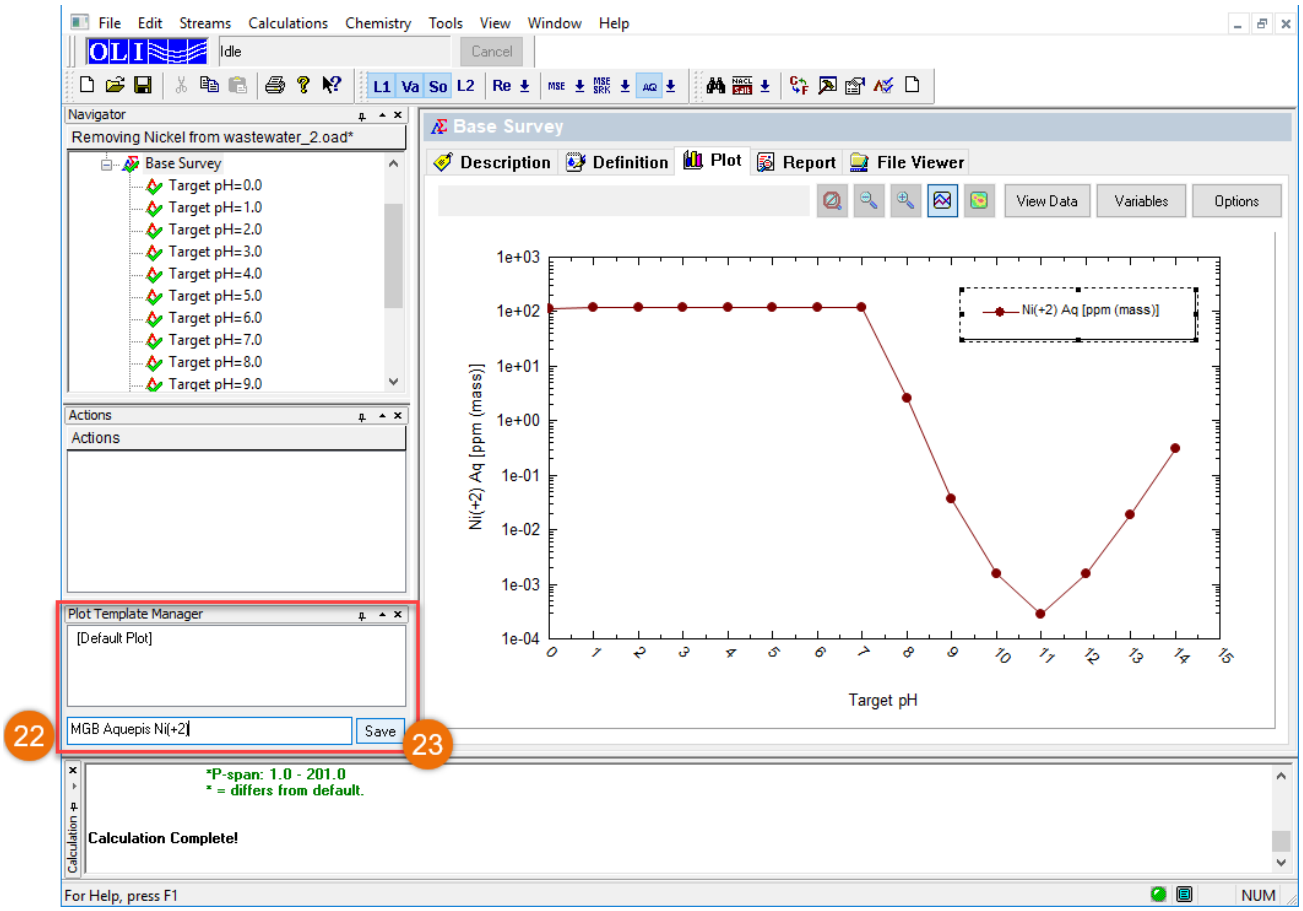


Note: The red line was put as a reference. it was not plot with the software.

Let's make the plot shown above the default plot. To do that we are going to use the Plot Template Manager Tool.

21. Save the description in the left-hand corner panel named **Plot Template Manager**. Type **MBG Aqueous Ni(+2)** as the name in this case.

22. Click **Save**



Now there will be two plots on that list now. First is default and second is **MBG Aqueous Ni(+2)**. You are now able to see these plot conditions for any other analyzer object in this case when you add survey for that object.

What else is important in this solution?

23. Click once more on the **Variables** button

24. **Add** the following **Aqueous** species to the plot. (you may need to scroll up or down to find all the species):

Ni(OH)2

NiOH+1

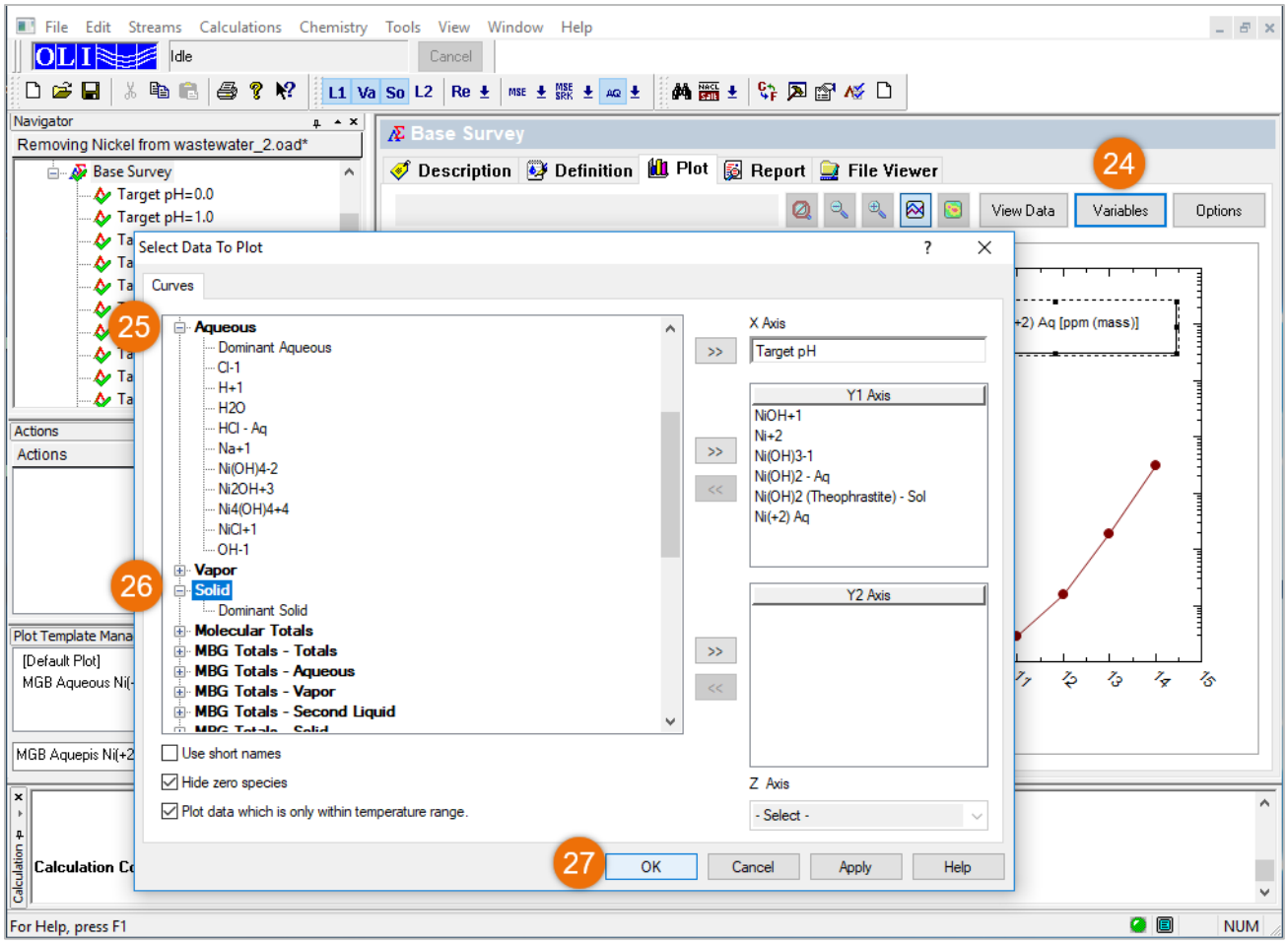
Ni+2

Ni(OH)3-1

25. **Add** the following **Solids** species to the plot:

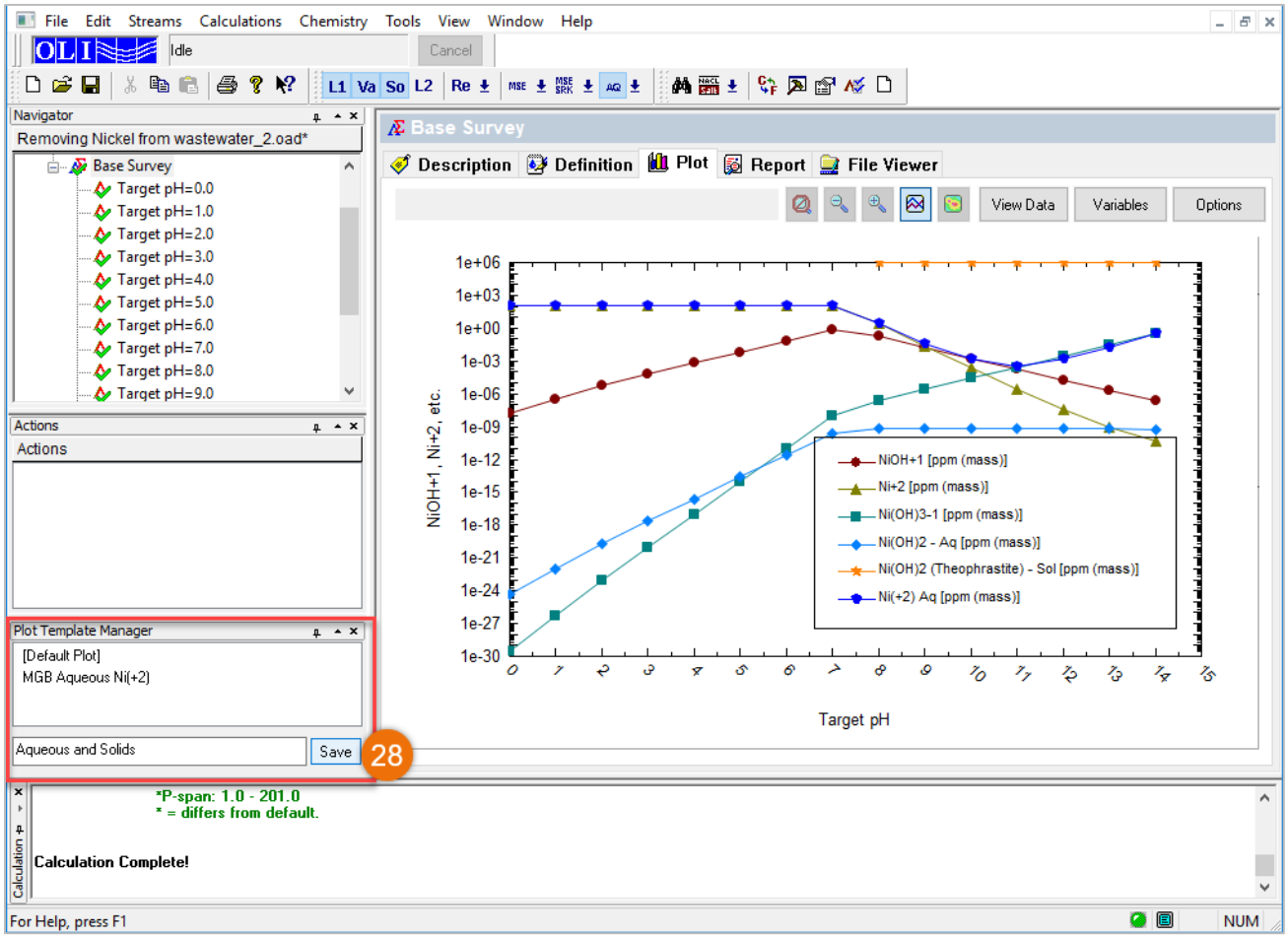
Ni(OH)2

26. **Click** on the **OK** button when done



You can see that the soluble nickel (**Ni(+2) Aq**) is a summation of the other species. The large drop in the value is because most of the nickel leaves the aqueous solution as Ni(OH)2-Solid at pH values greater than 7.0 with a maximum near pH=11.

27. Let's save this as a default plot as well in the Plot Template Manager as **Aqueous and Solids**



Scenario 2: Wastewater with Cyanide Content

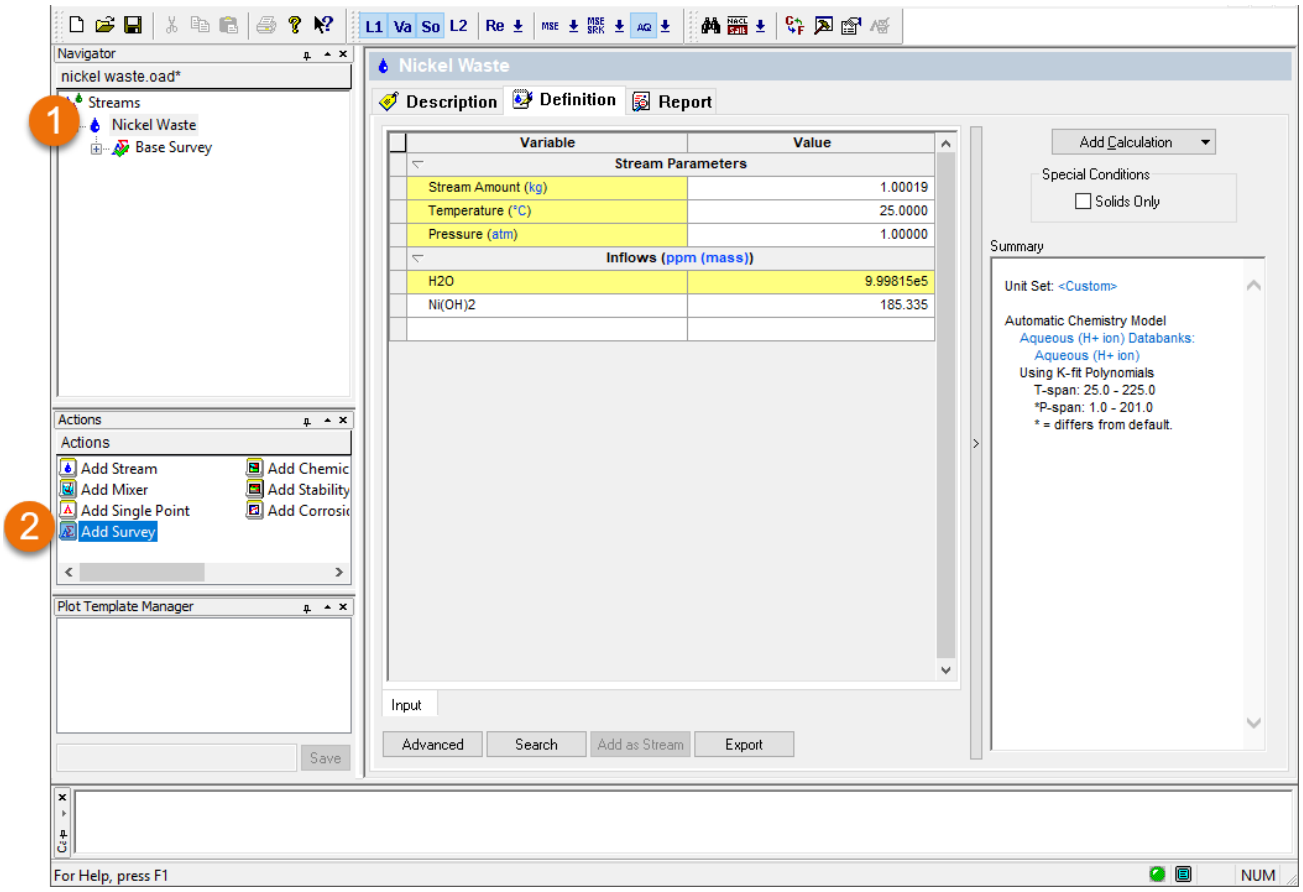
The real importance of aqueous speciation modeling of this treatment is only really appreciated if we introduce the cyanides, which brings us to the real waste treatment problem.

For this scenario, you will repeat many of the same steps as in Scenario 1. We recommend that you create new calculations below the **Nickel Waste** stream. This will keep the core composition the same without affecting the results of other calculations.

Please follow these steps for this scenario. Please note that we will only show the screens that are substantially different from those that you have already seen.

Creating a pH Survey to find the optimum pH for nickel removal

1. **Click** on the **Nickel Waste** stream in the tree view in the left-hand window
2. This will display the **Actions pane** in the bottom left corner of the Stream Analyzer window. **Click** on the **Add Survey** icon in the Actions pane



3. **Click** on the **Description** Tab, and **change** the *Name* and *Description* in the **Description** tab.

   Name: ***Waste Survey with CN***

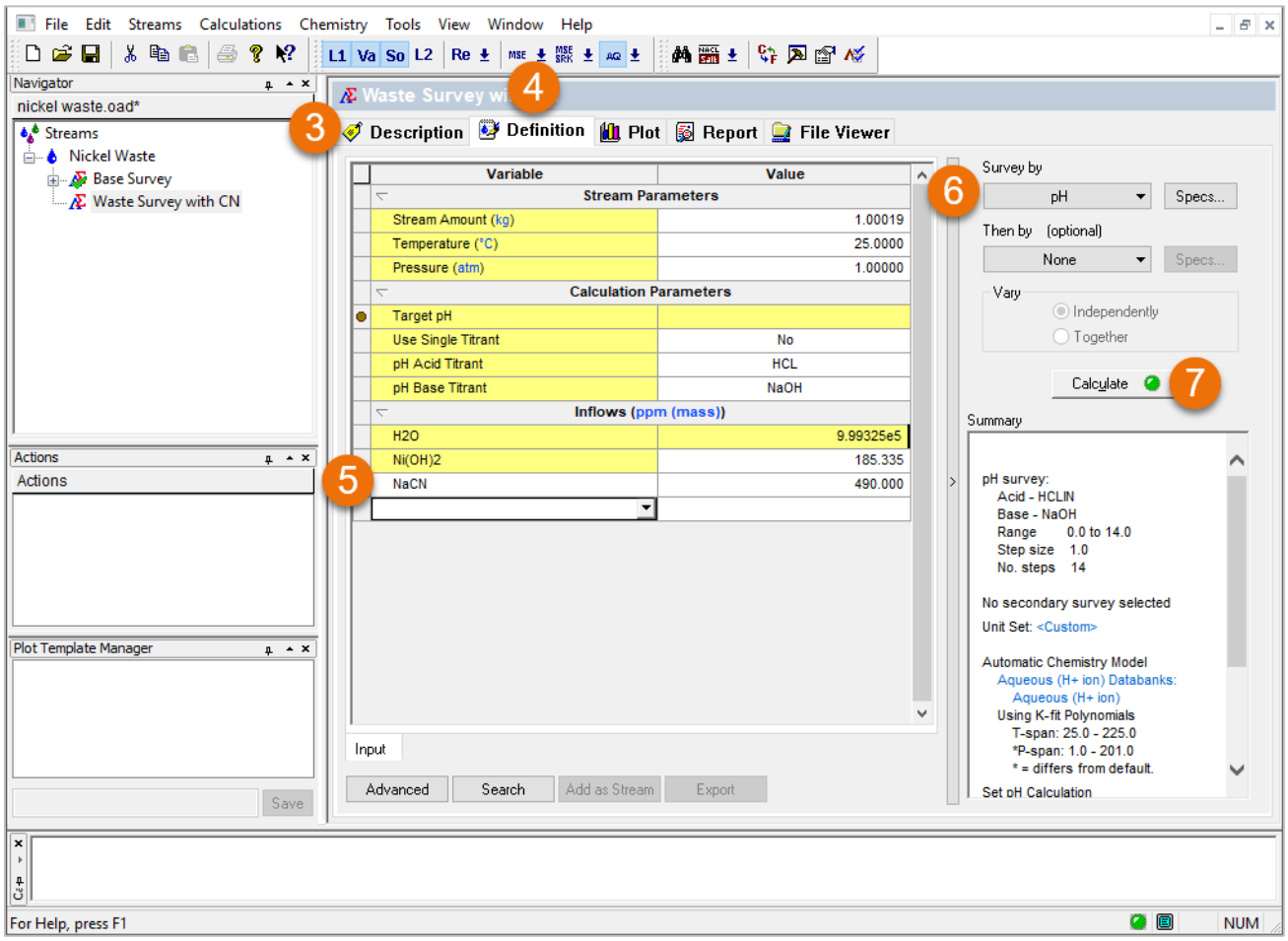
   Description: ***pH survey with both Nickel and CN***

4. **Click** on the **Definition** Tab

5. **Add NaCN** to the grid with a value of **490 ppm**

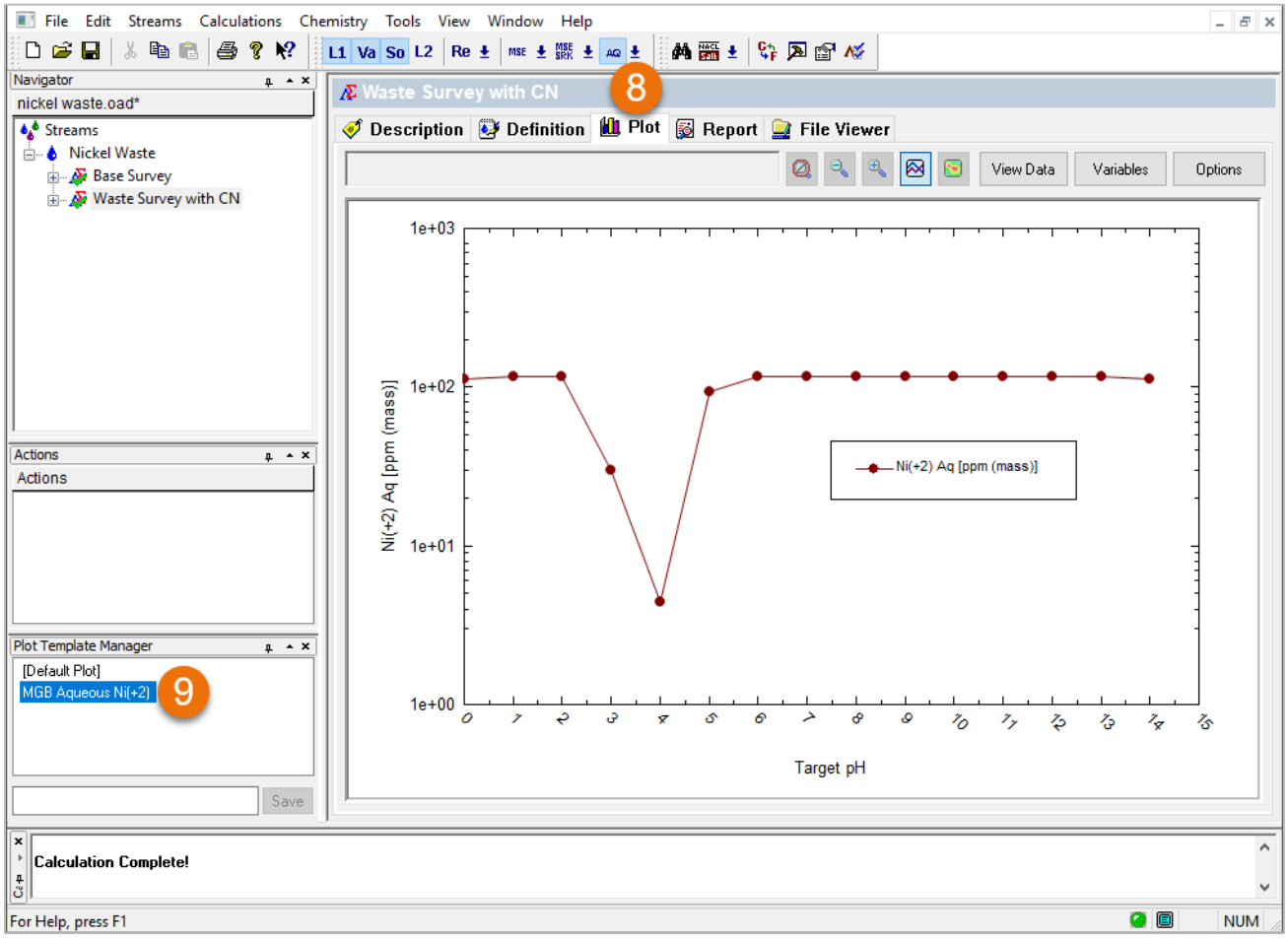
6. **Click** on the **Survey By** button and select **pH**. Note that HCl and NaOH are the default titrants and are automatically added

7. **Click** on the **Calculate** button.



Let's review the results.

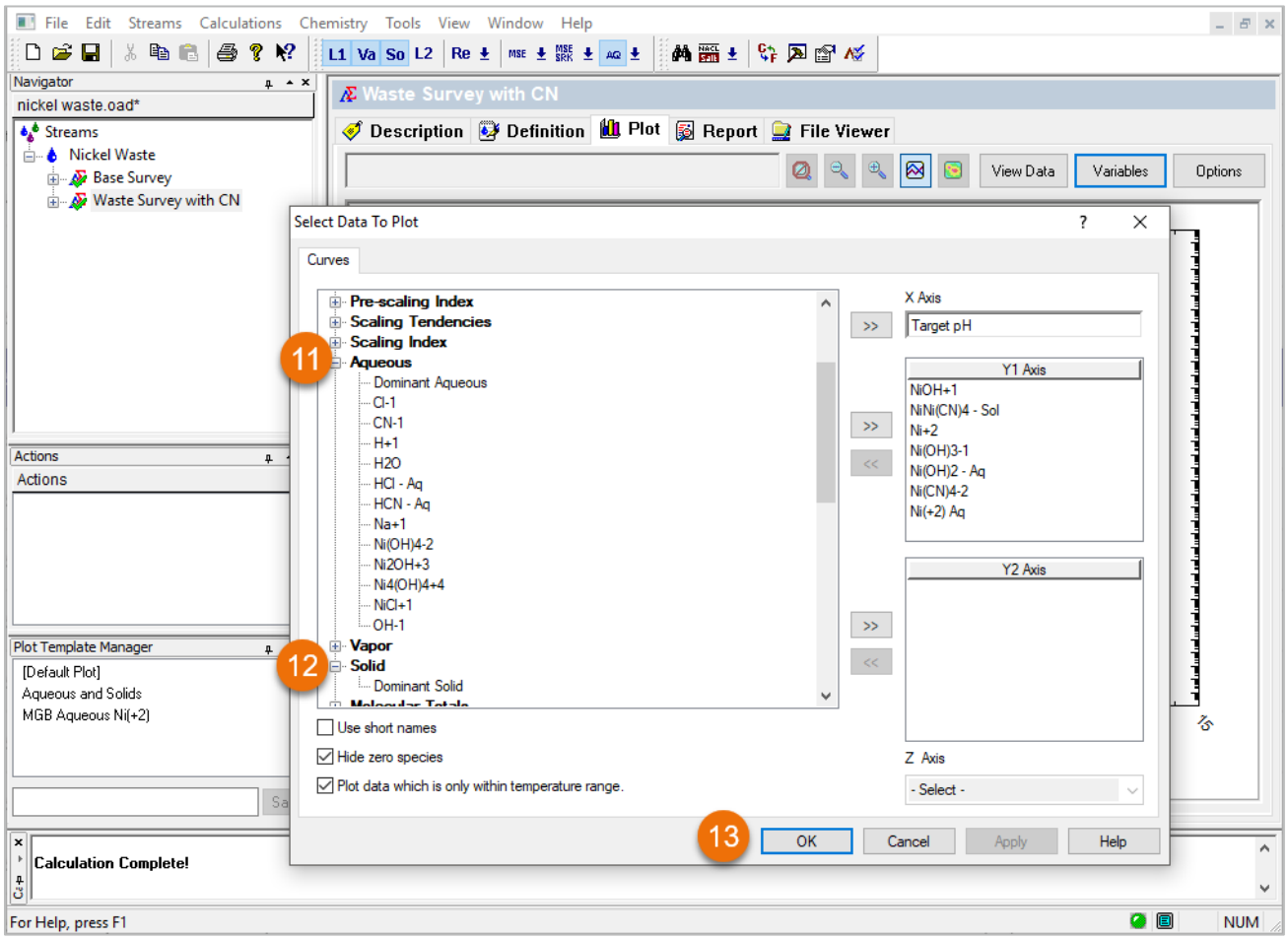
8. **Click** on the **Plot** tab
9. Go to the **Plot Template Manager** tool, and c**lick** on MGB Aqueous Ni(+2)



The results have changed very dramatically. The new optimum pH for Ni removal is around 4.0, rather than 11. However, the lowest total Ni remaining in solution is now around 4 ppm which is well over 1 ppm.

Let's analyze why this is happening. We can now modify the plot to display more variables. Select the **Aqueous and Solids** plot saved in the **Plot Template Manager**.

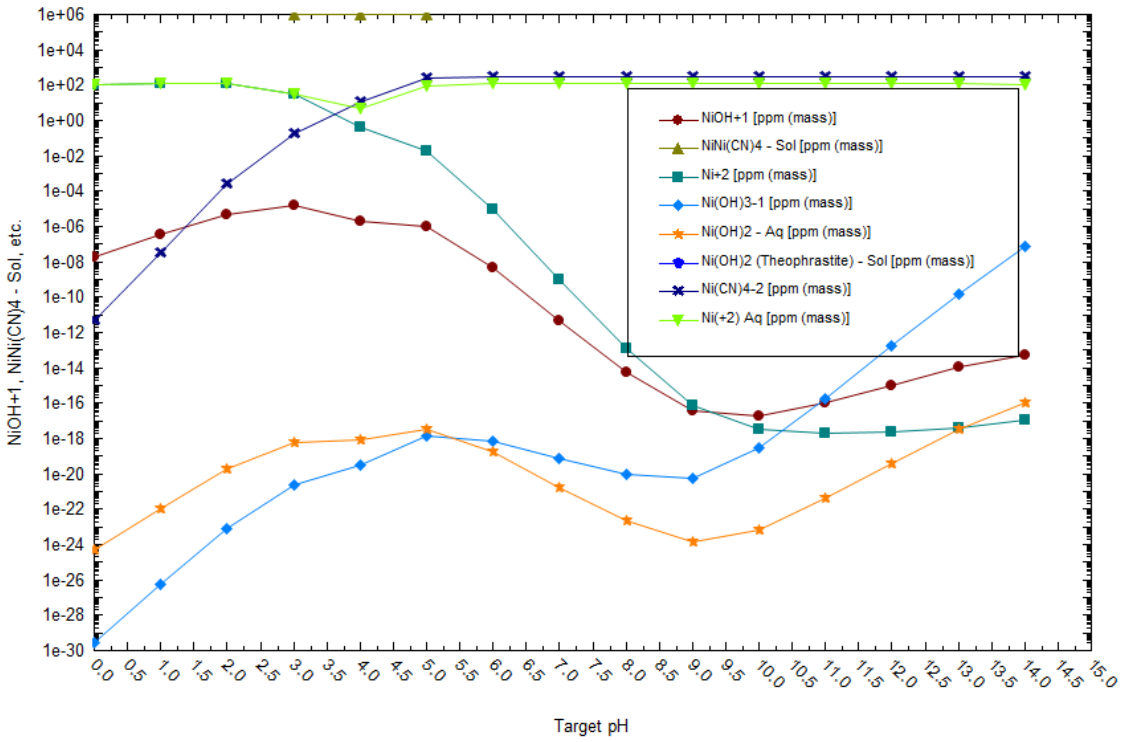
10. Click on **Variables**
11. **Add** the following new **Aqueous** species: Ni(CN)4-2
12. **Add** the following new **Solid** species: NiNi(CN)4-Solid
13. **Click OK**



Let's analyze the results.

The culprit is the $Ni(CN)_4^{-2}$ complex of nickel and cyanide. Basically, the plot of the total Ni in solution and the $Ni(CN)_4^{-2}$ complex overlap over the interval pH=5 to 12. This means that virtually all nickel in solution is in the form of this complex.

This complex thus holds the Ni in solution and does not allow the nickel hydroxide to even form. Instead, a much weaker precipitate, the $NiNi(CN)_4$ salt forms over a narrow range of pH with 4.0 being the optimum.



Scenario 3: Wastewater with Sulfide Salts

We can now try to influence nature by introducing a source of sulfide. We do this because nearly all metal sulfide salts are highly insoluble.

Create a new single point calculation and a survey as you did in the previous two scenarios.

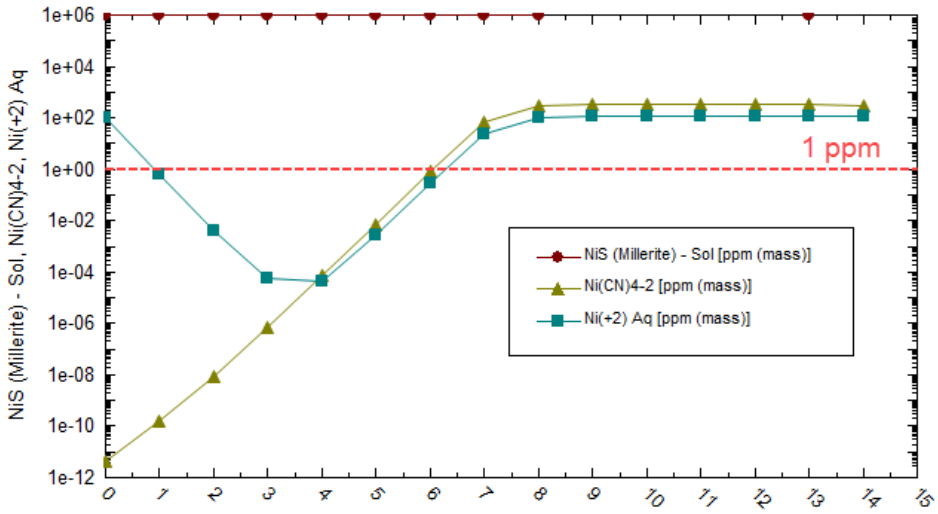
Add **490 ppm** of **NaCN**

Add **340 ppm** of **H2S**

For the survey case, use the plot template manager to start off with the MBG– Aqueous (Ni+2) and then add the following variables:

1. **Aqueous** Species: Ni(CN)4-2
2. **Aqueous** Species: Ni+2

3. **Solid** Species: NiS-Solid



The results reflect a "power struggle" between the $Ni(CN)^{-2}$ which is holding the nickel in solution and the NiS solid which clearly has a greater tendency to form than the $NiNi(CN)_4$ solid. As a result, our optimum pH is still around 4.0 and we are now around 10^{-5} ppm total nickel in solution which is a bit below 1 ppm.

This would be a good time to **save** your work. You may use the **File/Save As…** menu item or use the **Save icon** on the toolbar.

Final Thoughts…

Aqueous speciation modeling can teach us a great deal about complex chemical systems and the interactions of individual species.

The actual removal achieved with sulfide may not be quite enough to satisfy the regulations. This is useful information to have. In addition, with the power of OLI Analyzer: Stream Analyzer, one could now explore alternative treatment methods such as ion exchange.

Although such a simulation is beyond the scope of this demonstration, consider how vital it is to know that the dominant species to be exchanged (removed from solution) is an anion $Ni(CN)^{-2}$ and not the cation (Ni+2) as the conventional wisdom might dictate.

2.1.1. Temperature Survey

The default single survey calculation is the Survey by **Temperature.** The software computes solution properties based on a known composition and pressure at different temperatures.

Example 18: Studying a Four-phase mixture and its Partioning

The purpose of this first example is to present the basic Temperature survey. You will study how a four-phase mixture partitions as a function of temperature. The system composition will be basic, containing one primary phase component, H_2O (liquid), CH_4 (gas), Decane (organic), and NaCl (solid). Each component will partition each of the other three phases.

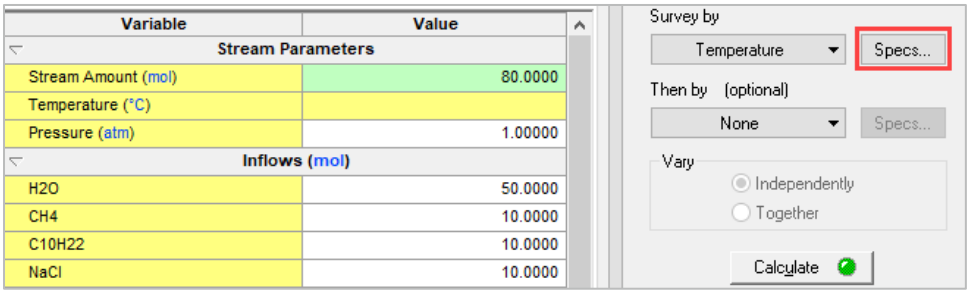
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

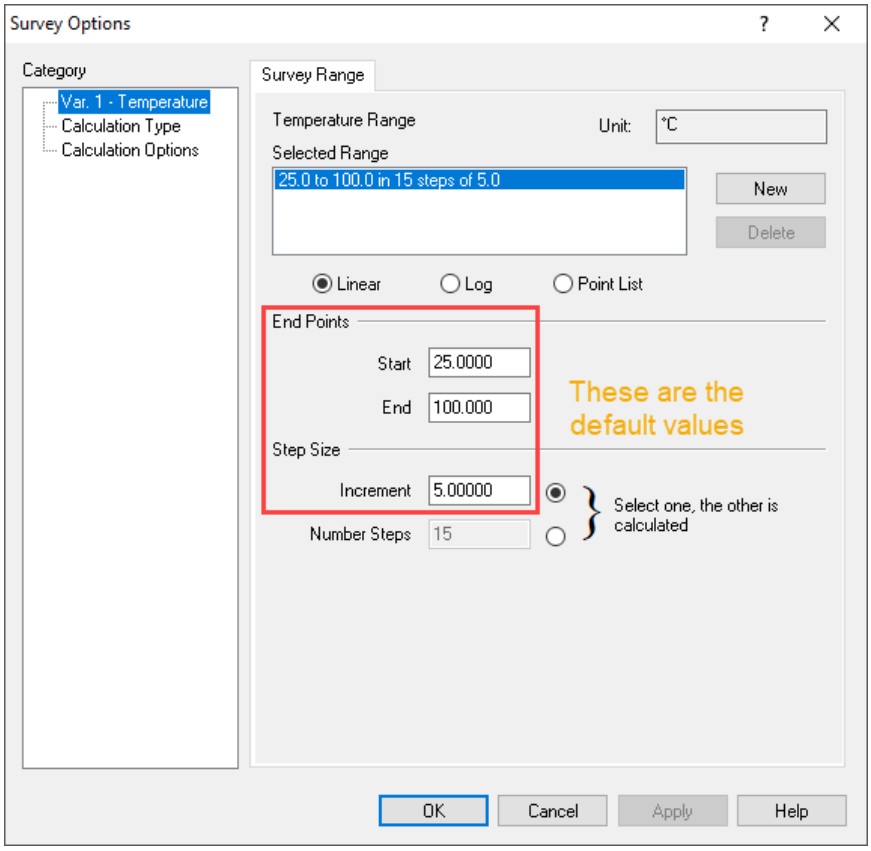
Temperature Survey Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Survey	Stream Amount	Calculated
Stream Name	Temperature Survey	Temperature Range	25-100 ºC
Survey Name	4-Phase Partioning	Step Size	Increment by 5 ºC
Name Style	Display Formula	Pressure	1 atm
Unit Set	Metric, Moles	H2O	50 moles
Framework	MSE-SRK	CH4	10 moles
		C10H22	10 moles
		NaCl	10 moles

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Temperature Survey*
3. Select the **MSE-SRK** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition of the stream given in the table above
7. Go to the **Add Calculation** button and select **Survey** calculation
8. Select **Temperature** as Type of Survey - Default
9. Change the ***Survey*** name to ***4-Phase Partioning*** using the **<F2>** key

10. Click on the **Specs** button. This will open the **Survey Options Window**



11. The Temperature Range is entered in the **End Point** section. The default values for the Temperature Range are 25ºC (Start) to 100ºC (End). Leave the default values.
12. The **Step Size** can be given as **Increments** or **Number of Steps**. By default, in the Temperature Survey the **Step Size** by **5** increments is selected. Leave the default values. Then click **OK**.



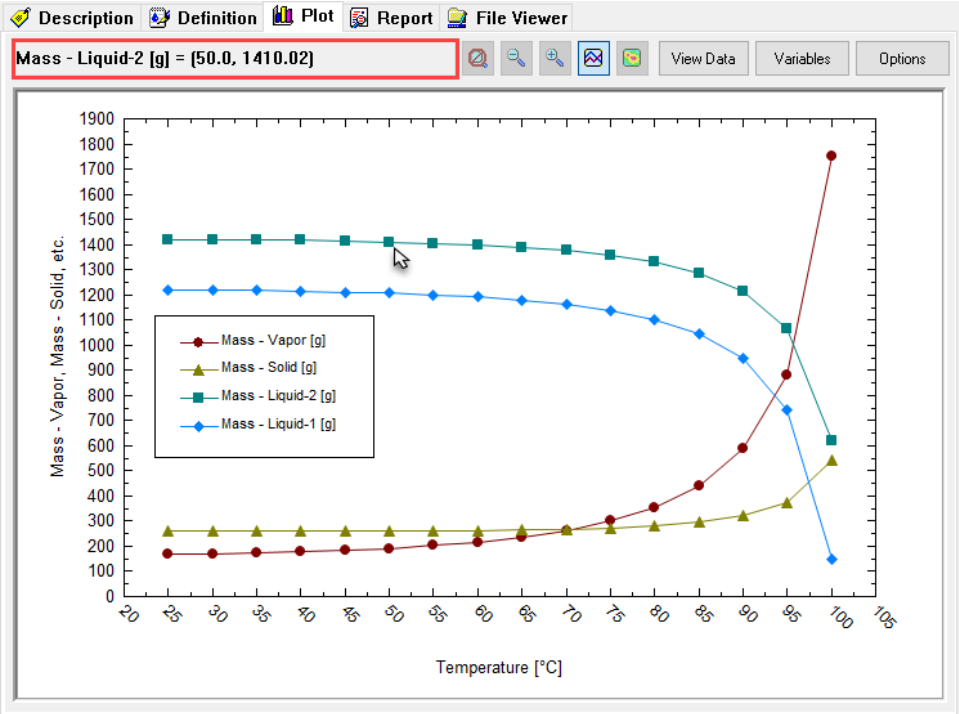
13. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
14. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

Anaylyzing the Results

Click on the **Plot** tab (Plot).

The default plot is the phase amounts in grams of Liquid-1 (Aqueous Phase), Liquid-2 (Organic Phase), Solid and Vapor.

The plot below, shows that as temperature increases, the mass of Liquid-1 and Liquid-2 (organic) decreases, as they evaporate, and hence the Vapor phase increases. The solid phase mass remains constant up to 80ºC, and then increases at higher temperatures.



Note: When the mouse-pointer is positioned over a point on one of the curves, the message box at the top of the plot indicates the variable and the coordinates of that point.

2.1.2. Pressure Survey

In the Survey by **Pressure, t**he software computes solution properties based on a known composition and temperature at different pressures.

Example 19: Dissolution of CO_2 in water as a Function of Pressure

Many thermodynamic properties are less dependent on pressure than they are on temperature. Vapor-Liquid-Equilibrium (VLE) is affected by pressure.

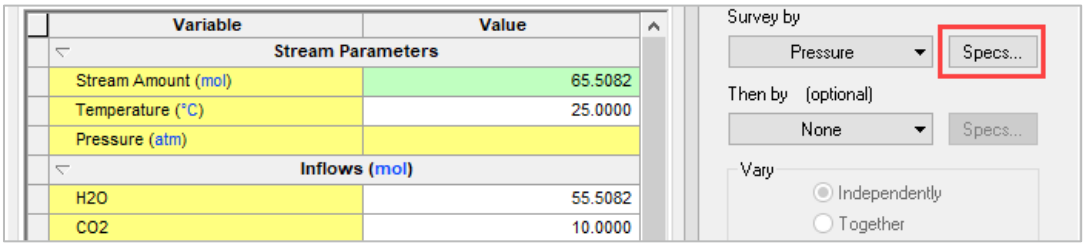
In this example, the dissolution of CO_2 in water (which is a direct reflect of VLE) will be studied as a function of pressure.

Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Pressure Survey Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Survey	Stream Amount	Calculated
Stream Name	Pressure Survey	Pressure Range	5-100 atm
Survey Name	CO2 dissolved in water	Step Size	Increment by 5 atm
Name Style	Display Formula	Temperature	25 ºC
Unit Set	Metric, Moles	H2O	55.5082 moles
Framework	MSE-SRK	CO2	10 moles

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Pressure Survey*
3. Select the **MSE-SRK** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition of the stream given in the table above
7. Go to the **Add Calculation** button and select **Survey** calculation
8. Select **Pressure** as Type of Survey
9. Change the ***Survey*** name to ***CO2 dissolved in water*** using the **<F2>** key
10. Click on the **Specs** button. This will open the **Survey Options Window**



11. The default pressure range is from 1-10 atm with an increment of 1 atm. Change the **Pressure Range** to 5-100 atm. Set the **Step Size** to **5 atm** increments. Then click **OK**.
12. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
13. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

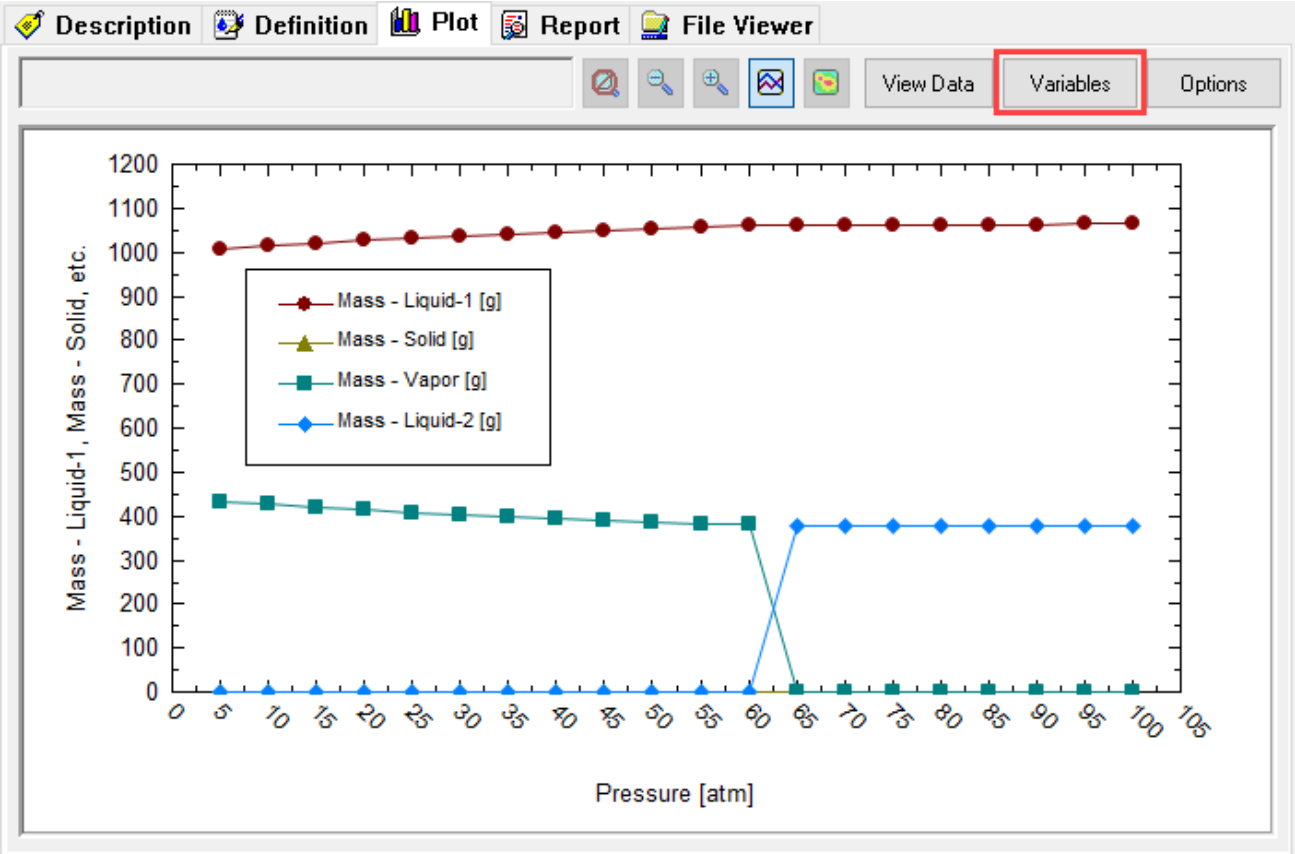
Anaylyzing the Results

Click on the **Plot** tab (Plot). The default plot is the phase amounts in grams of Liquid-1 (Aqueous Phase), Liquid-2 (Organic Phase), Solid and Vapor.

You can see that the Liquid-1 phase increases up to around 60 atm, and then it follows a constant trend as the pressure continues to increase. Regarding the Vapor phase, you can see that it shows a sudden decrease in mass from around 400 g at 60 atm to 0 g at 65 atm. The pressure of the system has increased in such a way that causes a phase change from vapor phase to Liquid-2 phase.

We are interested in the solubility of CO_2 in water, i.e. in the Liquid-1 phase. We can change the default plot to show the molecular CO2 dissolved in water (CO2-Liq1).

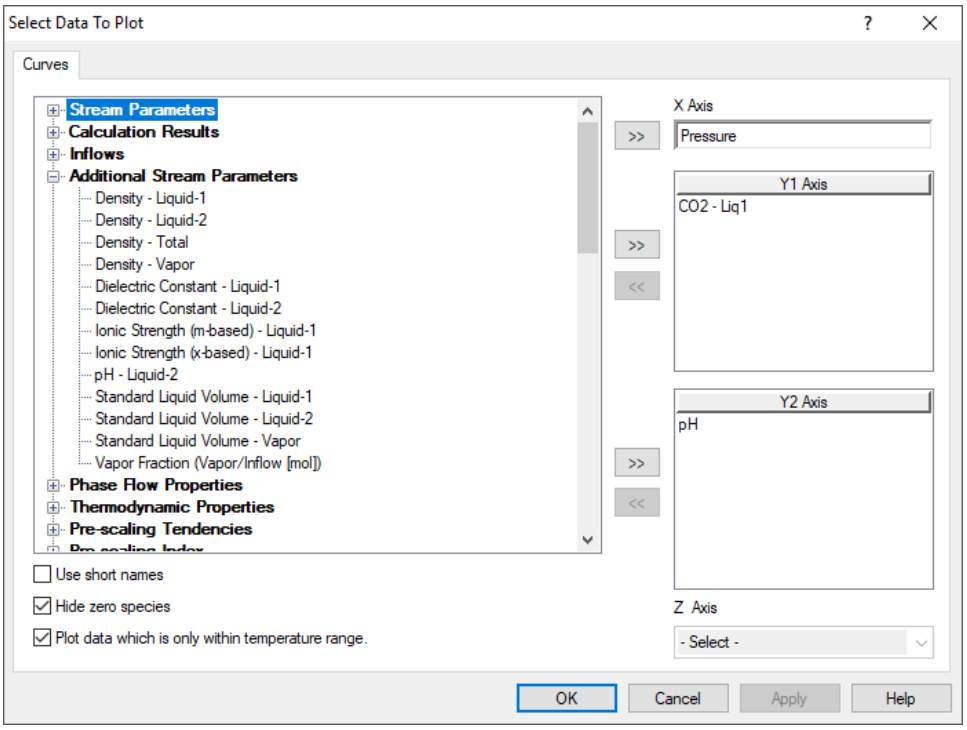
1. Click on the **Variables** button. This will open the **Select Data to Plot** window.



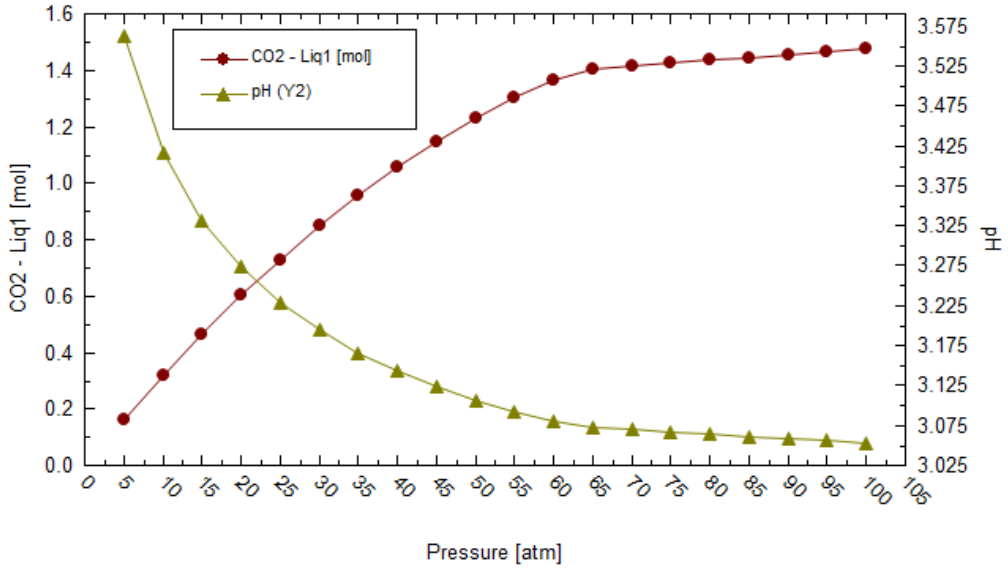
2. **Double click** or use the **<<** button to remove the **Phase Amount** variables.

3. Look for **Liquid-1** and click on the ⊞ box to show all the available variables. **Select** CO2-Liq1 and put it in the Y1 Axis using the **>>** button.

4. Look for **Additional Stream Parameters** section and click on the ⊞ box to show all the available variables. Select **pH** and put it in the Y2 Axis using the **>>** button. Then click **OK**.



The default plot now is showing the selected variables: The dissolved CO_2 in the water (Liquid-1 Phase) in the Y1 Axis, and the pH in the Y2 Axis. Both variables are presented as function of pressure.



The dissolved CO_2 in solution increases as the pressure increases. When the pressure goes above 65 atm, the dissolved CO_2 remains nearly constant.

A similar behavior is seen in the pH. As the pressure increases, a decrease in pH is observed. This is attributed to the following equilibria dissociation reactions:

$$CO_{2,vap} \leftrightarrow CO_{2,aq}$$

$$CO_{2,aq} + H_2O \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

Thus, as the amount of CO_2 in the aqueous phase increases, the dissociation reactions create more hydrogen ions (H^+) available in solution, subsequently decreasing the pH. As the pressure reaches values above 65 atm, the pH value remains constant. Hence, the pH is a direct reflection of the dissolved CO_2 in solution.

2.1.3. Composition Survey

In the Survey by **Composition, t**he software computes solution properties based on a given composition of species (or set of species) at a specific temperature and pressure.

Example 20: Dissolution of Calcite ($CaCO_3$) as a function of CO_2

Calcite is a scale that forms very easily in the production of oil. It has been found that the addition of CO_2 promotes the dissolution of Calcite scale. In this example, you are going to evaluate the effect of different CO_2 concentrations on the dissolution of Calcite.

Starting the Simulation

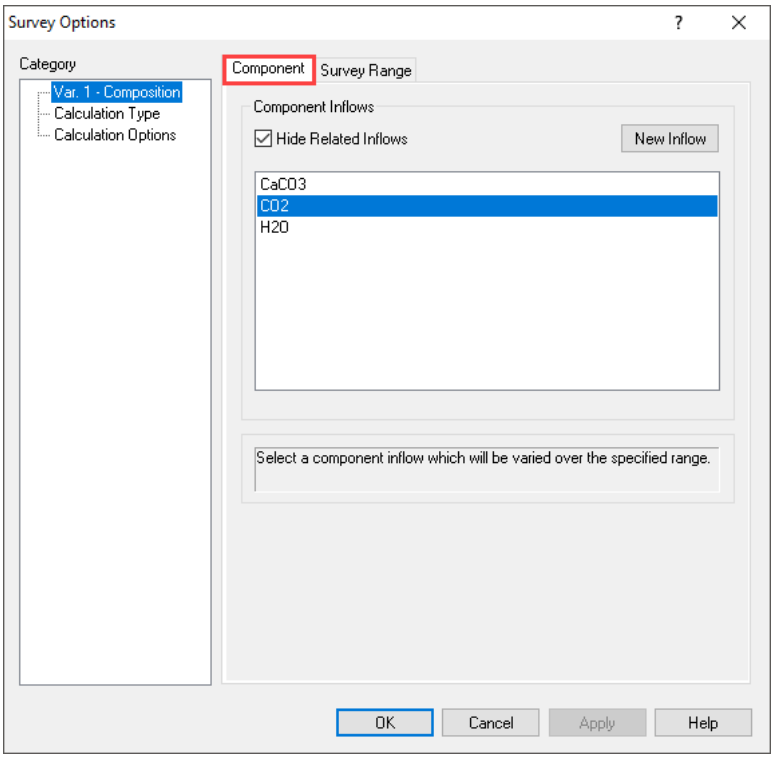
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Composition Survey Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Survey	Stream Amount	Calculated
Stream Name	Composition Survey	Temperature	25 ºC
Survey Name	Calcite Dissolution	Pressure	75 atm
Name Style	Display Formula	H2O	55.5082 moles
Unit Set	Metric, Moles	CaCO3	0.05 moles
Framework	MSE	CO2 concentration range	0 - 1 moles
		Step Size	Increment by 0.05 moles

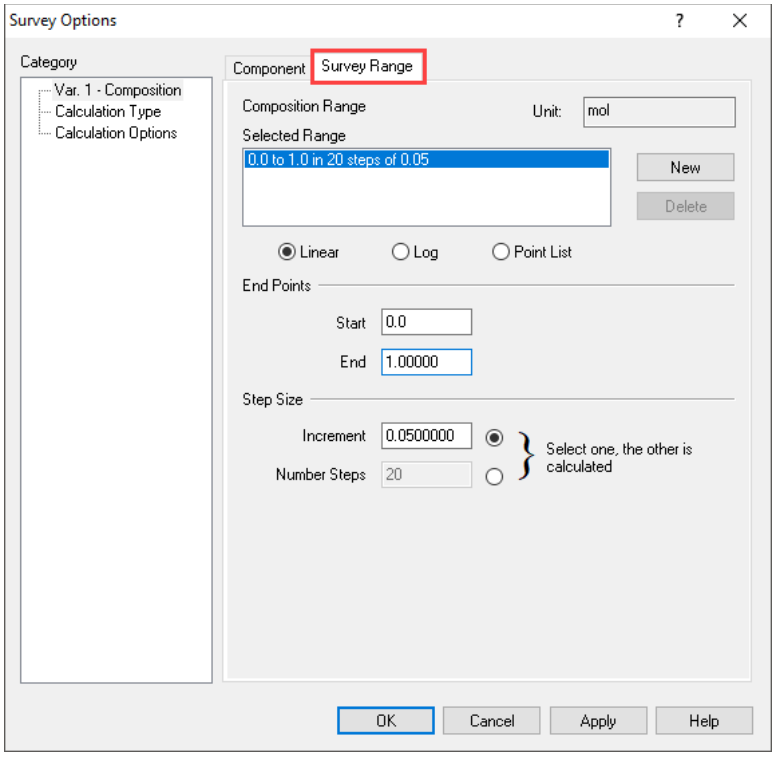
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Composition Survey*
3. Select the **MSE** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition of the stream given in the table above
7. Go to the **Add Calculation** button and select **Survey** calculation
8. Select **Composition** as Type of Survey.
9. Change the ***Survey*** name to ***Calcite Dissolution*** using the **<F2>** key

   Note: In the summary box a message in red appears: **'Component not selected for composition survey variable'.** This means that we need to select the component that we want to vary. In this example CO2.
10. To specify the component, click on the **Specs** button. This will open the **Survey Options Window.**

11. Under the **Component** tab, **select** CO2



12. Now, click on the **Survey Range** tab. Enter the CO2 composition range from 0 to 1 mol, by increments of 0.05 moles. Then click **OK**.



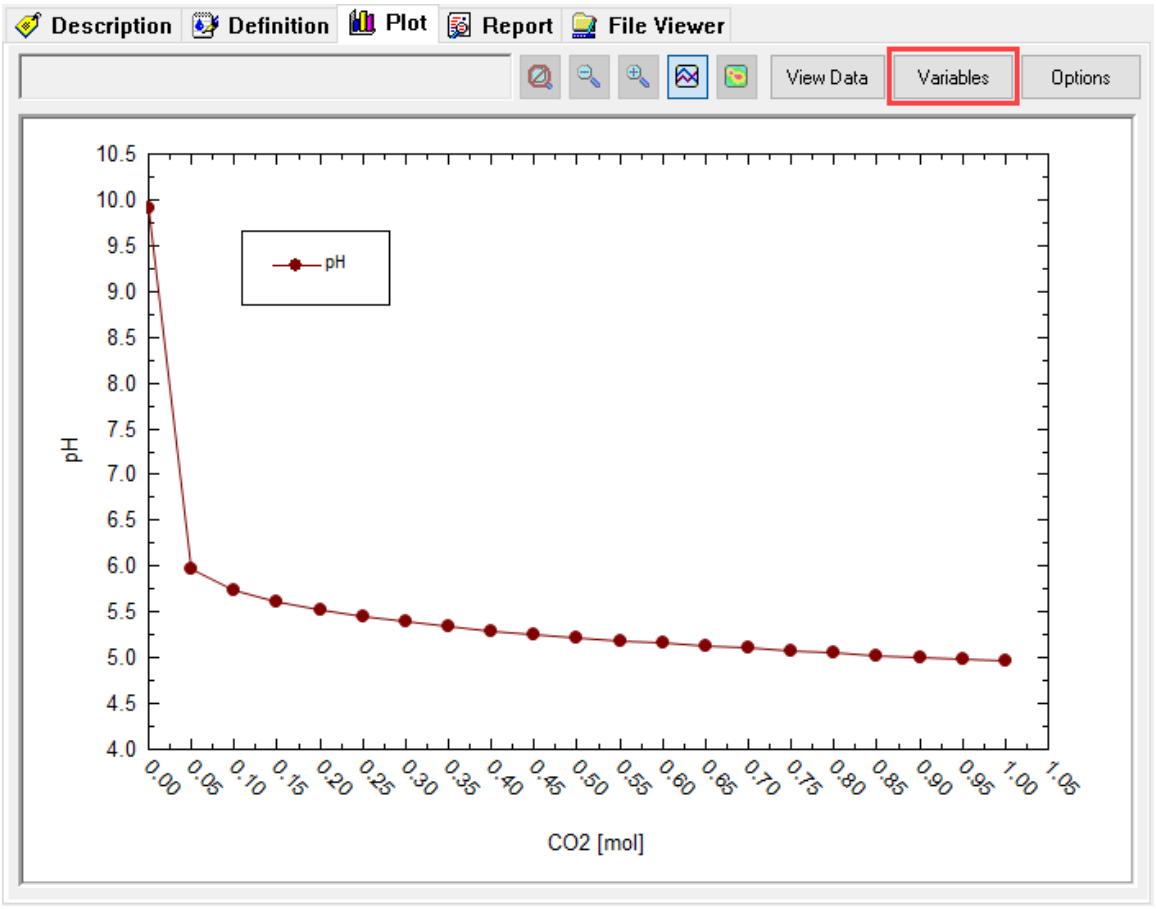
13. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
14. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

Anaylyzing the Results

Click on the **Plot** tab (Plot). The default plot is the pH as a function of total CO_2 in moles. As the concentration of CO2 increases, the pH decreases (as it was explained in the example above).

We are interested in understanding the dissolution of Calcite as a function of CO_2. To see these results, we need to study how the moles of solid calcite change as the concentration of CO_2 increases.

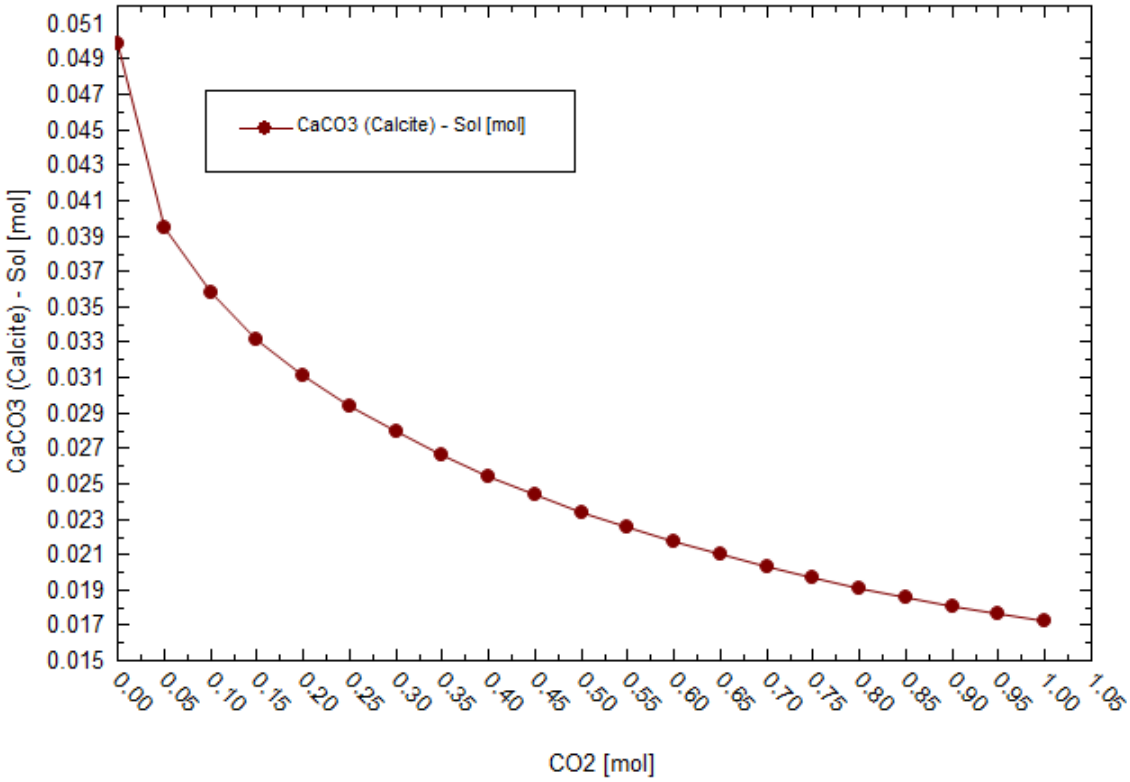
1. Click on the **Variables** button. This will open the **Select Data to Plot** window.



2. **Double click** or use the **<<** button to remove the **pH** variable

3. Look for **Solid** section and click on the ⊞ box to show all the available variables. **Select CaCO3 (Calcite) – Sol** and put it in the Y1 Axis using the **>>** button. Click **OK**.

The default plot now is showing the selected variable: CaCO3 (Calcite) – Sol as a function of CO_2.



As it was expected, the amount of $CaCO_3$ (Calcite) decreases with increasing CO_2. In an oil production setting, when there is a significant pressure drop, CO_2 will be lost. This will decrease the solubility of $CaCO_3$ and will increase the likelihood of scale formation.

2.1.4. pH Survey

In the Survey by **pH,** the software adjusts the flowrate of acid or basic titrants to at a predefined set of pH values and computes the solution properties of a solution based on a given composition of species (or set of species) at a specific temperature and pressure.

Example 21: A Speciation Diagram for the Carbonic Acid System as a Function of pH

In this survey calculation, a 1 molal CO_2 solution is titrated with HCl and NaOH. Instead of defining the amount of acid/base to add, the pH will be specified, and the software will compute the amounts of HCl and NaOH needed.

Starting the Simulation

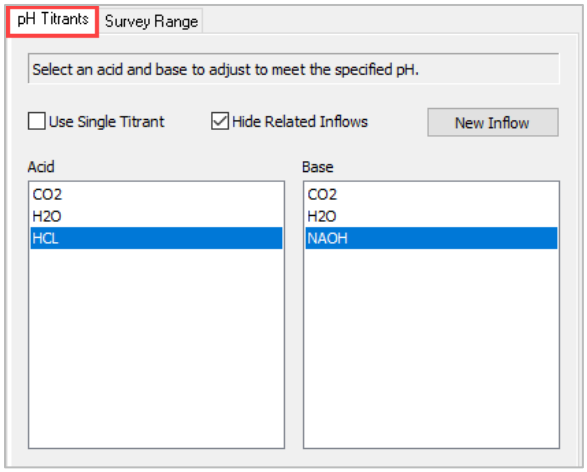
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

pH Survey Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Survey	Stream Amount	Calculated
Stream Name	pH Survey	Temperature	25 ºC
Survey Name	Carbonic Acid System	Pressure	1 atm
Name Style	Display Formula	H2O	55.5082 moles
Unit Set	Metric, Moles	CO2	0.001 moles
Framework	AQ	pH range	4-12
		Step Size	Increment by 0.1

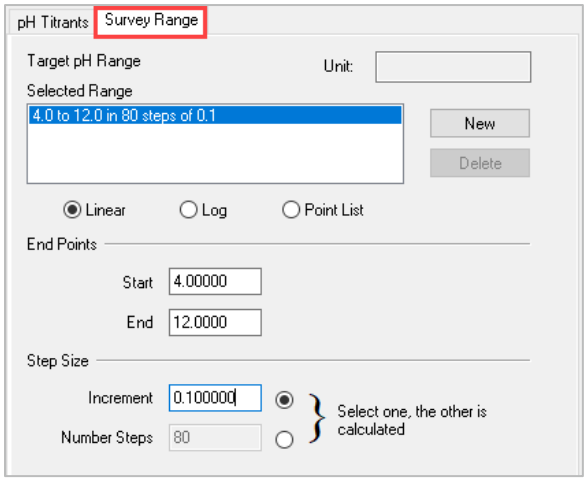
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *pH Survey*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. **Enter** the composition of the stream given in the table above
7. Go to the **Add Calculation** button and select **Survey** calculation
8. Select **pH** as Type of Survey
9. Change the ***Survey*** name to ***Carbonic Acid System*** using the **<F2>** key

The calculation can be run without modification. The default titrants are **HCl** and **NaOH**, and the default pH range is set from **0** to **14** with a step size of **1** increment. However, this pH range is too broad for the carbonate system, in which most of the speciation occurs between pH=4 and 12. Additionally, it is ideal to specify finer increments to see a smoother curve.

10. Click on the **Specs** button. This will open the **Survey Options Window**
11. In the **pH Titrants** tab, leave the default pH Titrants: **HCl** and **NaOH**



12. Now, click on the **Survey Range** tab. Enter the pH range from 4 to 12, with increments of 0.1. Then click **OK**.

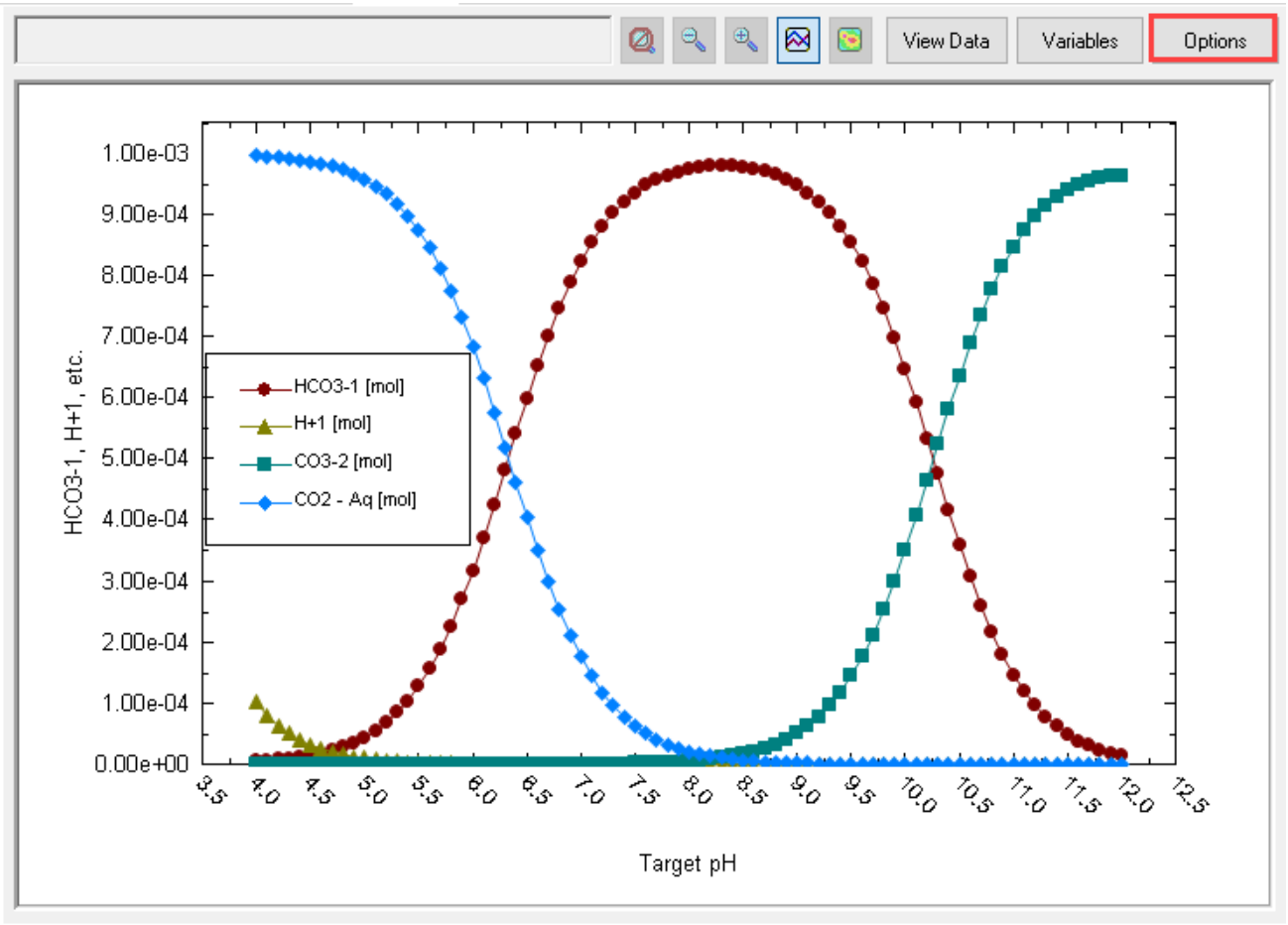


13. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
14. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

Anaylyzing the Results

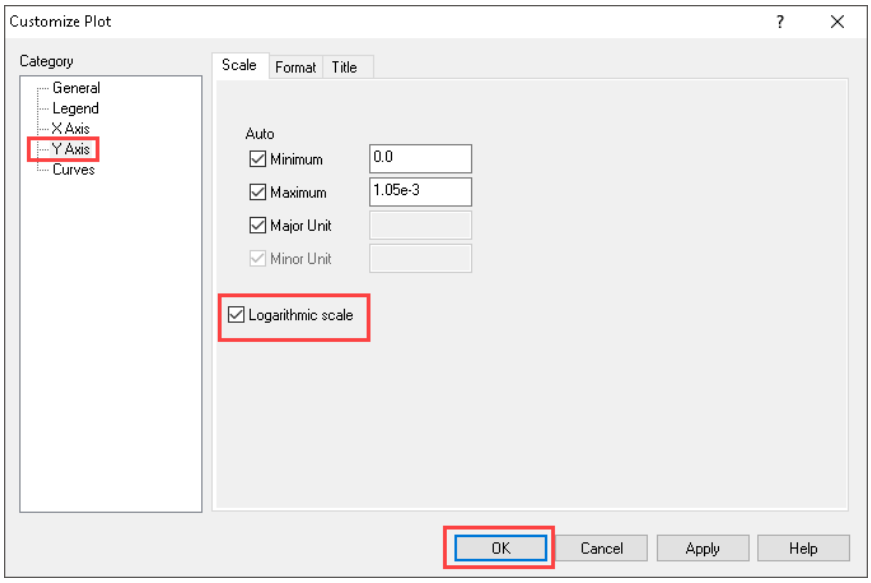
Click on the **Plot** tab (Plot). The default plot is the moles of added HCl and NaOH vs Target pH. This is not the target variable and you will change it to display the carbonate-containing species.

1. Click on the **Variables** button
2. Remove the **NaOH** and **HCl** from the Y1 axis (double click or use the **<<** button)
3. Look for **Aqueous** section and click on the ⊞ box to show all the available species. **Select** the following species: CO2-Aq, HCO3-1, CO3-2, and H+ and put them in the Y1 Axis using the **>>** button or by double clicking. When you are done, click **OK**.



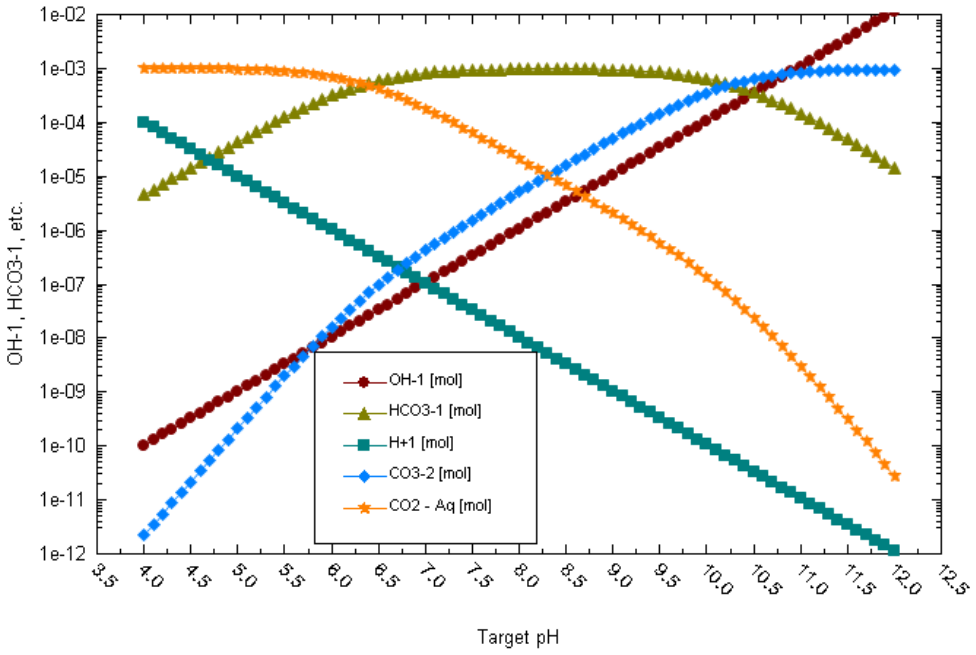
You can also present this plot on a semi-log scale.

4. Click on the **Options** button. This will bring the **Customize Plot** window
5. Select **Y Axis** in the Category window
6. **Check** the Logarithmic scale box, and then click **OK**.



Before analyzing the plot, let's add the OH- species.

7. Click on the **Variables** button, look for OH-1 in the **Aqueous** section, add it to the Y1 Axis, and then click **OK**. Now we are ready to analyze the plot.



At lower pH, CO2-Aq dominates the system, and notice how the HCO3-1 slope is 1 and the CO3-2 slope is 2. Likewise, in the pH region where CO3-2 dominates (high pH), the HCO3-1 slope is -1 and the CO2-Aq slope is -2. These $\frac{mole}{pH}$ slopes are based on the number of H+ ions added or removed in the chemical reactions. See reactions below.

$$CO_{2,aq} + H_2O \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

Note the pH where the CO2-Aq and HCO3-1 lines intersect (pH~6.3), and where the HCO3-1 and CO3-2 lines intersect (pH~10.3). These pH values are the same as the pKa values (the equilibrium equations the specific equilibrium reactions).

As NaOH is added to convert HCO3- to CO3-2, a portion of the NaOH remains as free base, OH-1. This fraction increases at higher pH values, and its concentration is reflected in the calculated pH. A similar pattern is seen at pH below ~3 for HCl and H+.

2.1.5. Vapor Fraction / Vapor Amount Survey

The purpose of the **Vapor Fraction/Vapor Amount Survey** calculation is to set a specific fraction of the stream to the vapor phase, and compute the temperature or pressure required to achieve the specified Vapor Fraction/Vapor amount.

Example 22: Seawater Evaporation

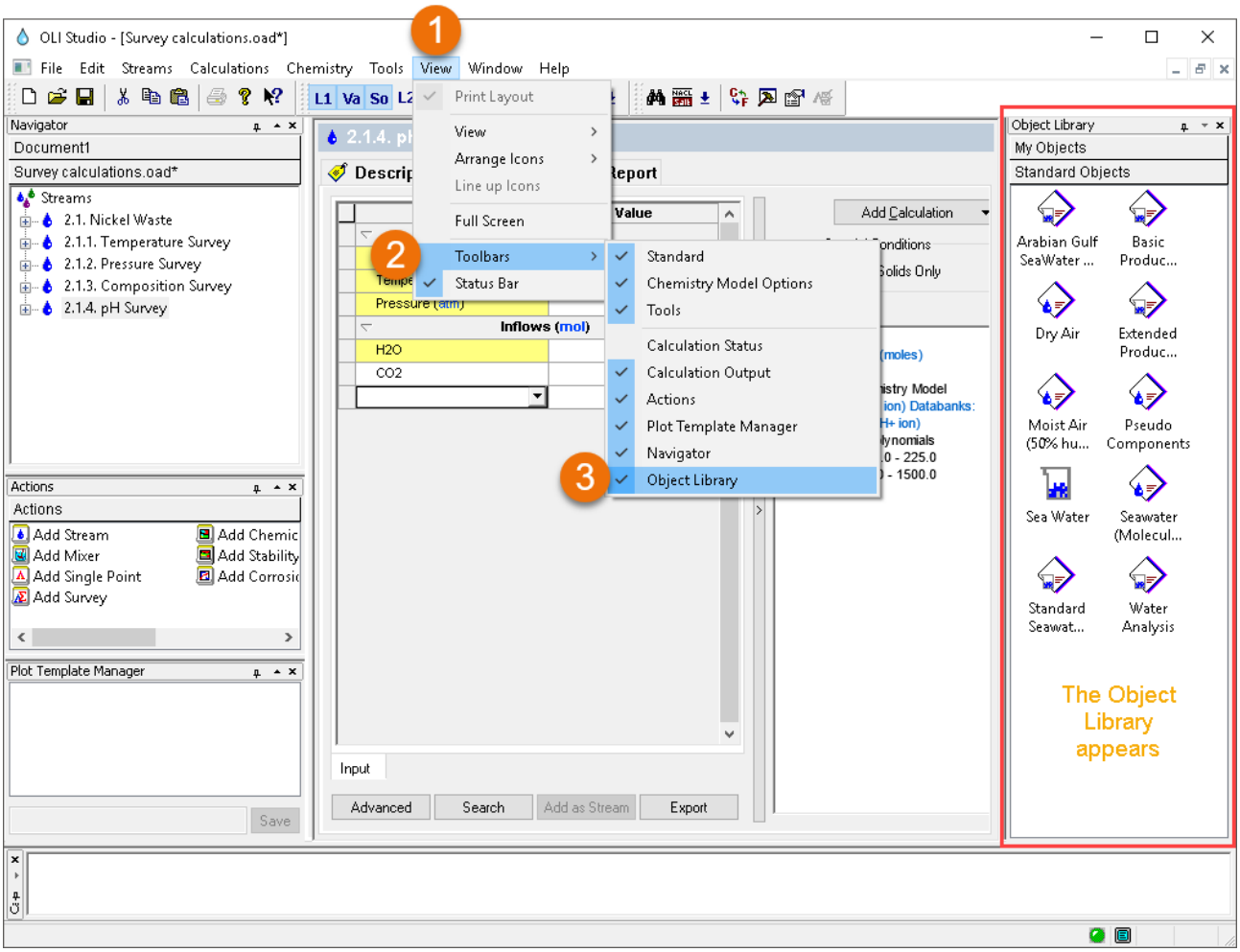
Seawater contains a variety of salts, and when seawater evaporates, these solids are left behind. The most abundant salt in seawater is sodium chloride (NaCl) which is also technically referred to as halite.

You will evaporate seawater to dryness and look at the solids that form. What is interesting is the number of phases that can be produced when seawater evaporates, giving you a sense of how certain natural systems build up sediment of a particular nature.

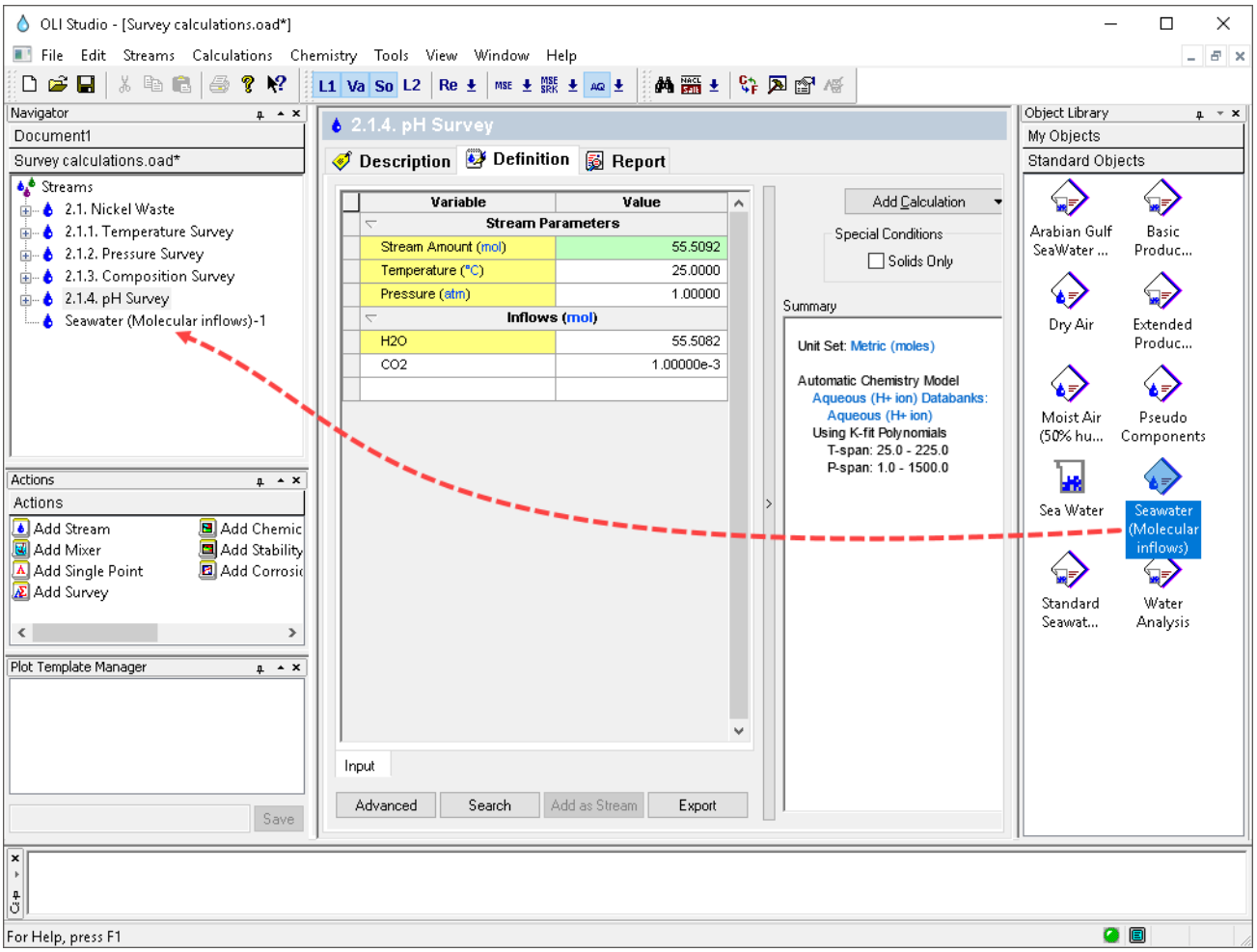
In this example we will also introduce the **Object Library** tool.

Starting the Simulation

1. Open the **Object Library** window – from the menu, View > Toolbar > Object Library. The Object Library appears in the right-hand side of the window.



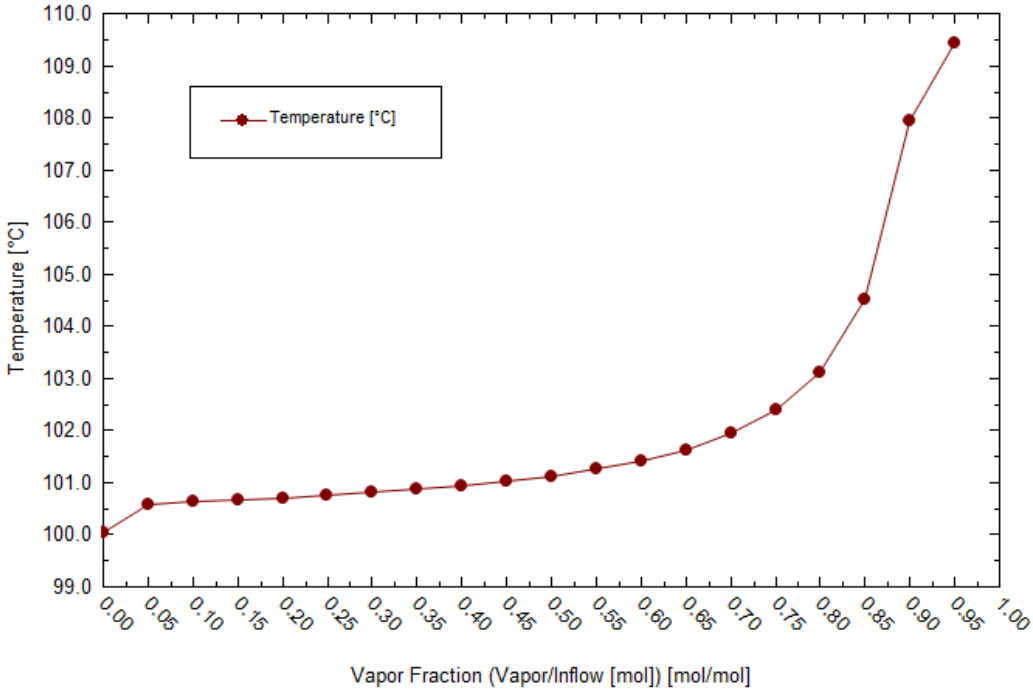
2. Drag the **Seawater (Molecular inflows)** stream to the navigation panel (in the white-space below the other streams and calculation objects)



The inputs and parameters are automatically populated when selecting the Seawater (molecular inflows) form the Object Library.

3. **Click** on the new Stream and press **<F2>** to change the name to *Vapor Fraction Survey*
4. Go to the **Add Calculation** button and select **Survey** calculation
5. Select **Vapor Fraction** as Type of Survey
6. Change the ***Survey*** name to ***Seawater Evaporation*** using the **<F2>** key
7. Click on the **Specs** button. This will open the **Survey Options Window**
8. The default Vapor Fraction range is from 0-1 with an increment of 0.1. Change the **Vapor Fraction Range** to **Survey End** to 0.95. Set the **Step Size** to **0.05** increments. Then click **OK**.
9. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
10. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

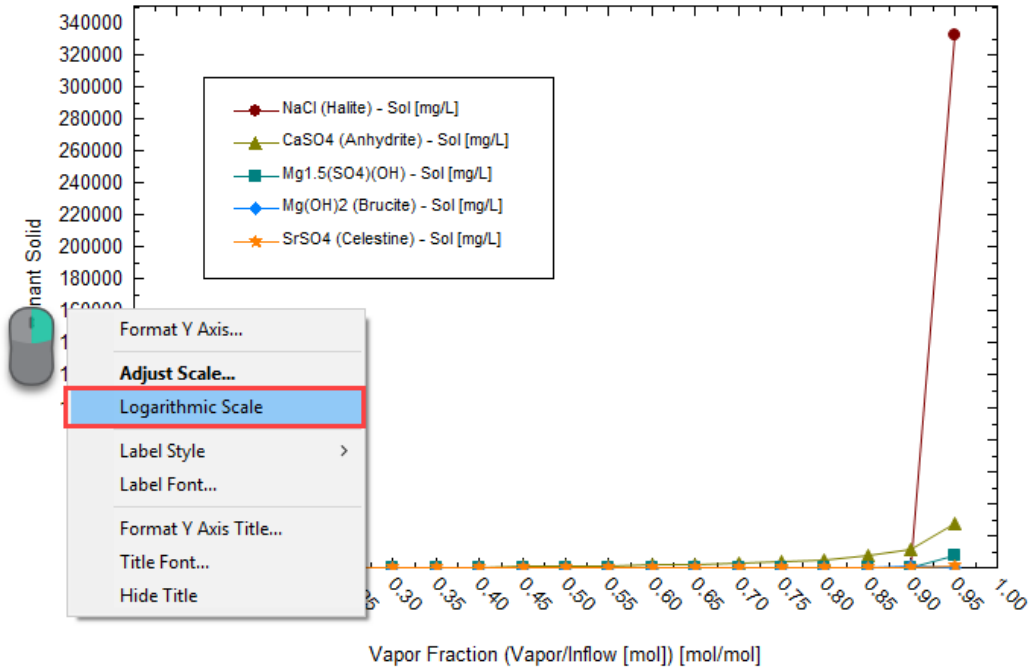
Click on the **Plot** tab (Plot). The default plot is the Vapor Fraction plot (as the dependent variable) vs Temperature. It shows that seawater boils initially at 100ºC, and at near complete evaporation (95%) the temperature is 109.4ºC.



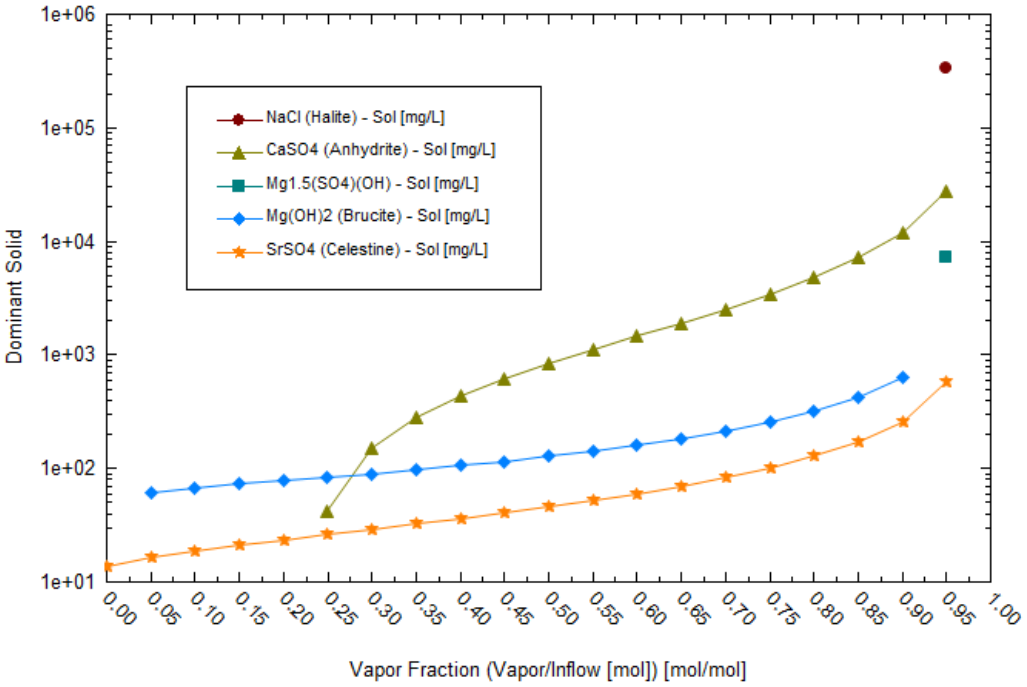
We are also interested to know which solid phases precipitate as the water evaporates.

1. Click on the **Variables** button
2. Remove **Temperature** from the Y1 axis (double click or use the **<<** button)
3. Look for **Solid** section and click on the ⊞ box to show all the available species. **Select** the option **Dominant Solids** and put it in the Y1 Axis using the **>>** button or by double clicking. When you are done, click **OK**.

4. The default plot is not very easy to read. To see the plot more clearly, **right click** on any number in the Y axis, and select the **Logarithmic Scale** option.



Plot in semilogarithmic scale



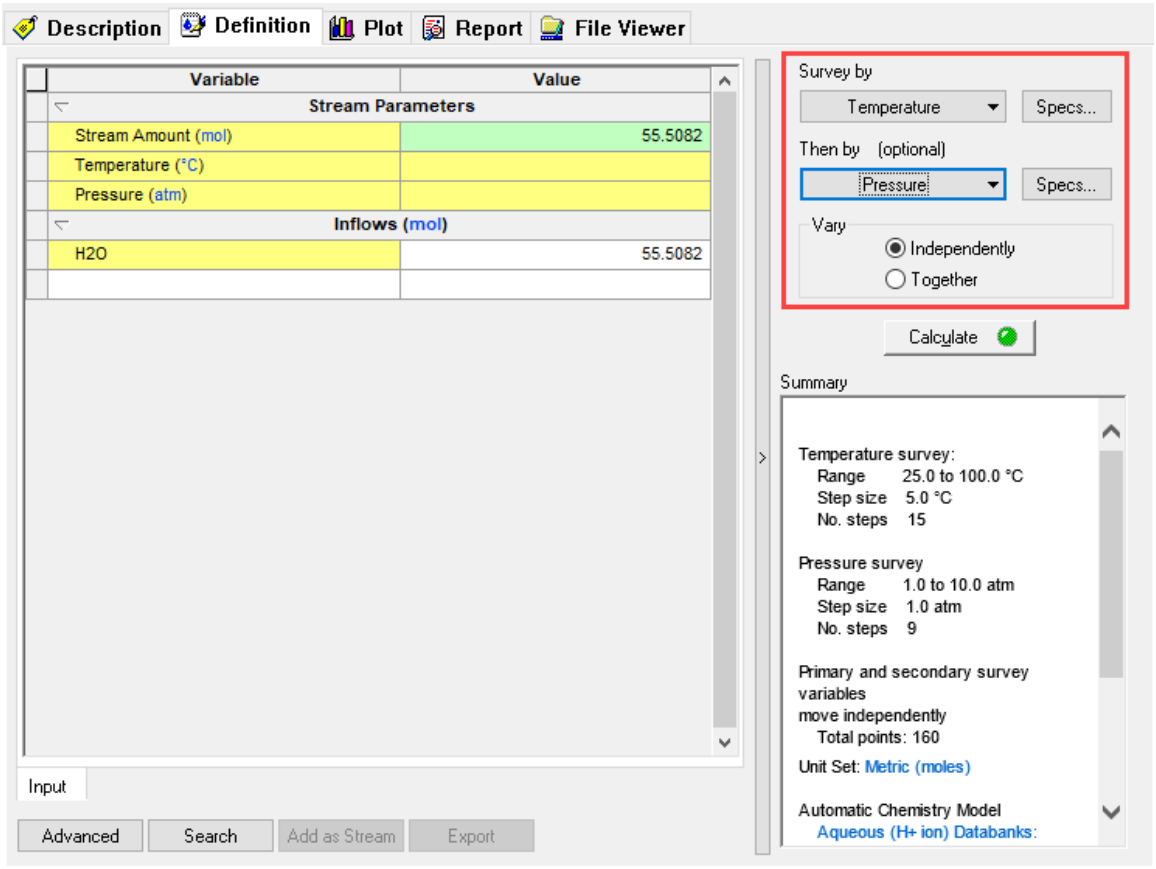
As the water evaporates $CaSO_4$, $Mg(OH)_2$ and $SrSO_4$ salts precipitate at all temperatures. NaCl and a Mg/SO4 double salt start to precipitate at 95% vapor fraction.

2.2. Dual Surveys

Dual Surveys allow you to study the effect of two independent variables on your system under study.

The option for the dual survey is highlighted in red box highlighted in the image below. There are three options available, survey by Temperature, Pressure and Composition.

Additionally, you have the option of varying the selected variables independently or together. We will explore this in more detail in the upcoming examples.



Temperature and Pressure Survey

In this type of survey two variables are adjusted simultaneously, temperature and pressure. This type of survey creates a matrix of results, which can then be interpreted using the plot function in different ways.

Example 23: Dissolution of CO_2 in water as a Function of Temperature and Pressure

In Example 19, the dissolution of CO_2 in water was studied only as a function of pressure. In this case, we are going to study the effect of both temperature and pressure on the CO_2 dissolution.

In this example the Contour Plot will be used to analyze the results.

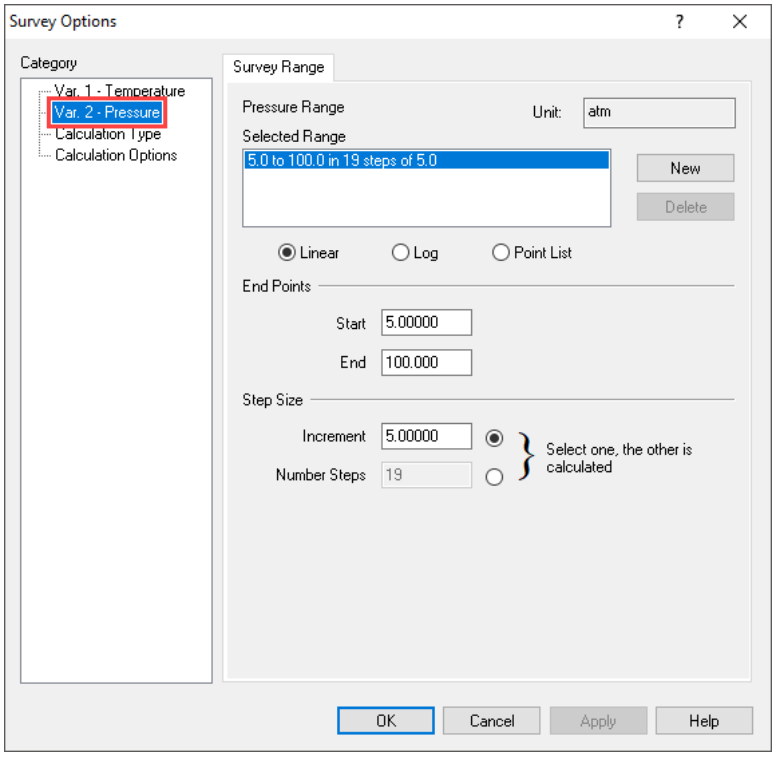
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

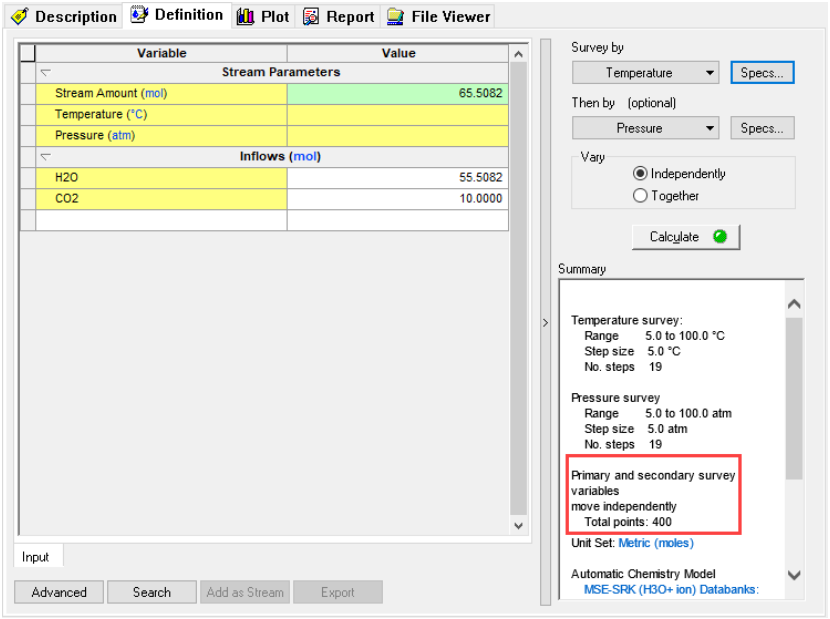
Temperature and Pressure Survey Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Survey	Stream Amount	Calculated
Stream Name	T/P Survey	Pressure Range	5-100 atm
Survey Name	CO2 dissolution – T/P	Step Size	Increment by 5 atm
Name Style	Display Formula	Temperature Range	5-100 ºC
Unit Set	Metric, Moles	Step Size	Increment by 5 ºC
Framework	MSE-SRK	Vary	Independently
		H2O	55.5082 moles
		CO2	10 moles

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *T/P Survey*
3. Select the **MSE-SRK** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition of the stream given in the table above
7. Go to the **Add Calculation** button and select **Survey** calculation
8. Select **Temperature** and then by **Pressure**
9. Change the ***Survey*** name to ***CO2 dissolution T/P*** using the **<F2>** key
10. Click on the **Temperature Specs** button. This will open the **Survey Options Window**

11. Change the **Temperature Range** to 5-100 ºC. Set the **Step Size** to **5** ºC increments.
12. Click on **Var. 2 – Pressure**, in the Category Window to define the Pressure Range.
13. Change the **Pressure Range** to 5-100 atm. Set the **Step Size** to **5 atm** increments. Then click **OK**.



14. In the summary box, notice that a total of 400 points will be calculated. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key



15. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

Anaylyzing the Results

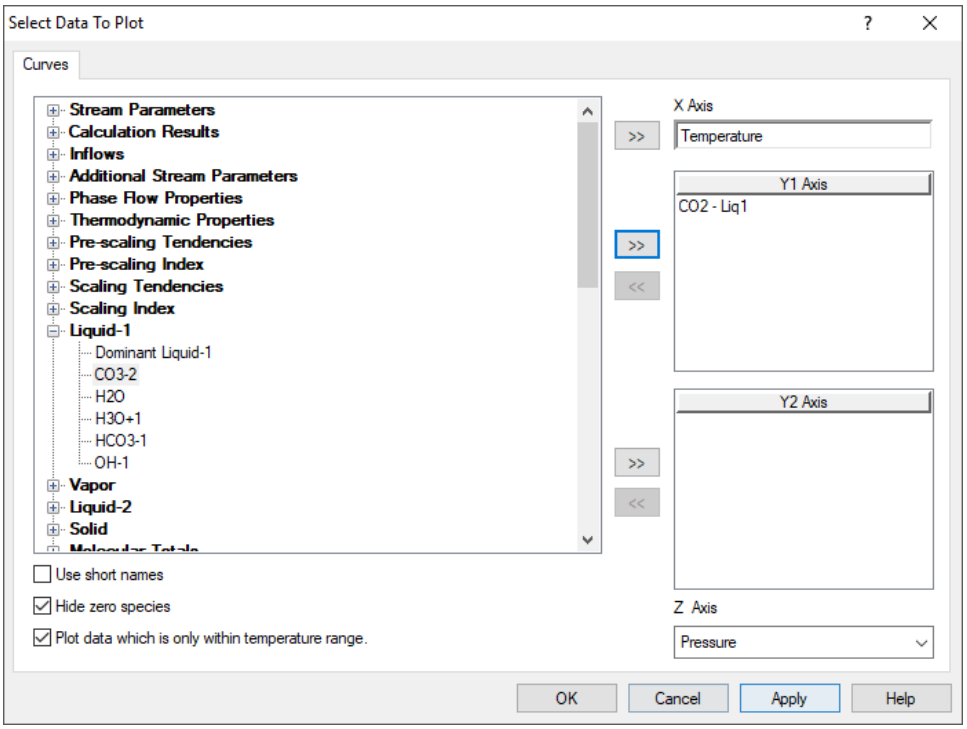
Click on the **Plot** tab (Plot). The default plot is the phase amounts in grams of Liquid-1 (Aqueous Phase), Liquid-2 (Organic Phase), Solid and Vapor.

We are interested in the solubility of CO_2 in water, i.e. in the Liquid-1 phase. We can change the default plot to show the molecular CO2 dissolved in water (CO2-Liq1).

1. Click on the **Variables** button. This will open the **Select Data to Plot** window.

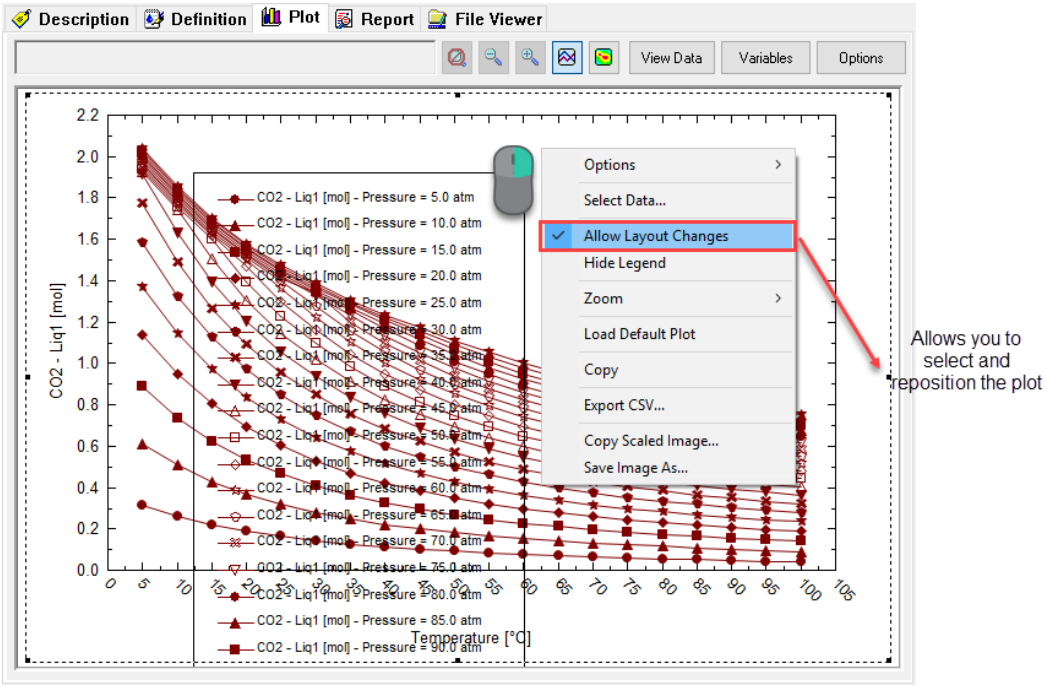
2. **Double click** or use the **<<** button to remove the **Phase Amount** variables.

3. Look for **Liquid-1** and click on the ⊞ box to show all the available variables. **Select** CO2-Liq1 and put it in the Y1 Axis using the **>>** button. Then click **OK**.

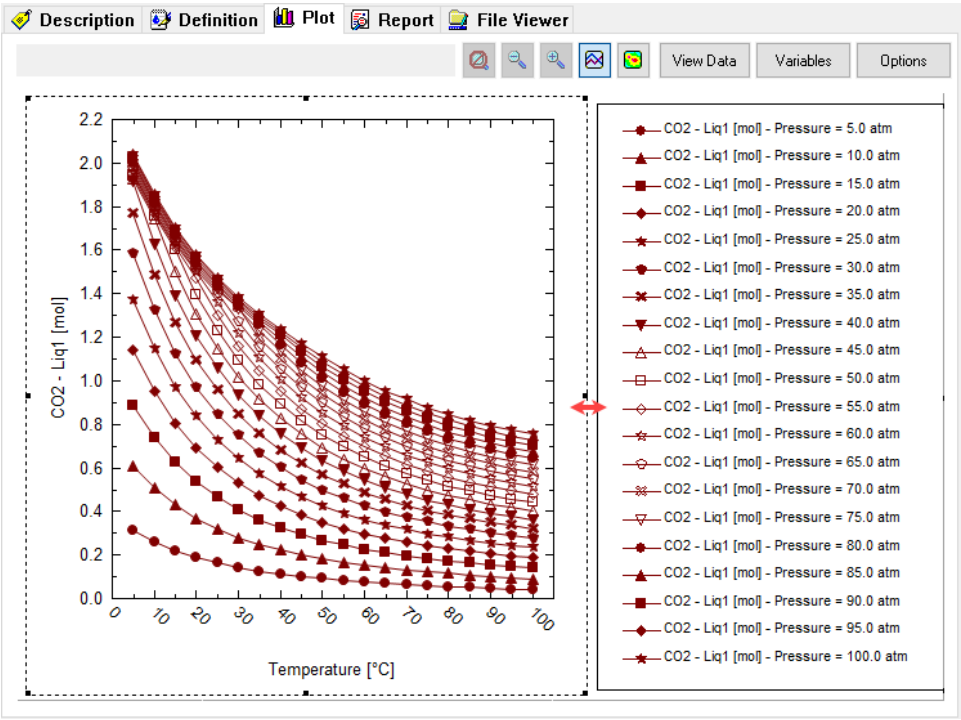


The default plot now is showing the dissolved CO_2 in the water (Liquid-1 Phase) in the Y1 Axis as function of pressure. Unfortunately, the legend is covering the plot.

4. To move the legend to the side without interfering with the results, right click on any white space within the plot and **Allow Layout Changes**. This option allows you to select and reposition the plot.



5. **Resize** the plot to make it smaller and create space for the legend. Drag the legend to the right.

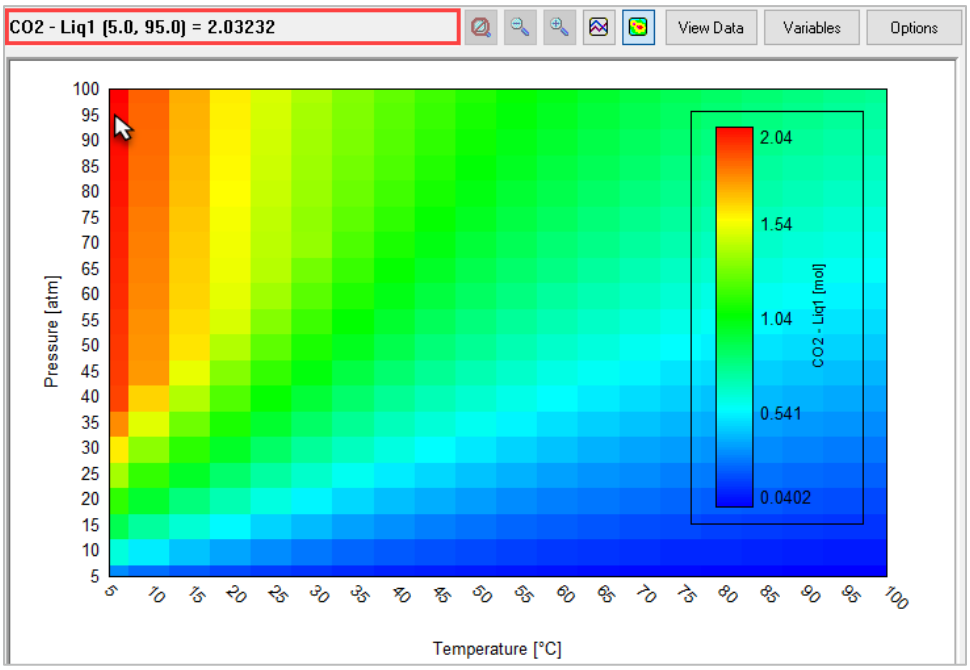


As the temperature increases (at a fixed pressure) the solubility of CO_2. This is to be expected since at higher temperatures it is easy to overcome the vapor pressure and CO_2 is released as gas. As the pressure increases (at a fixed temperature) the solubility of CO_2 in solution increases.

The plot above can be represented better using a **Contour Plot**. To convert the results into a contour plot view, simply click on the contour plot icon ( ).

The resulting plot is now a pixilated color plot showing the moles of molecular CO2 dissolved in the Liquid-1 (Aqueous) phase, at each T and P value.

The number of moles of CO_2 is characterized by a different color that is shown in the legend (maximum value is given in red, and minimum value is given in blue). You can mouse over any location in the plot and the moles of CO2 dissolved in the Liquid-1 phase at each T and P value will be shown in the left corner box.

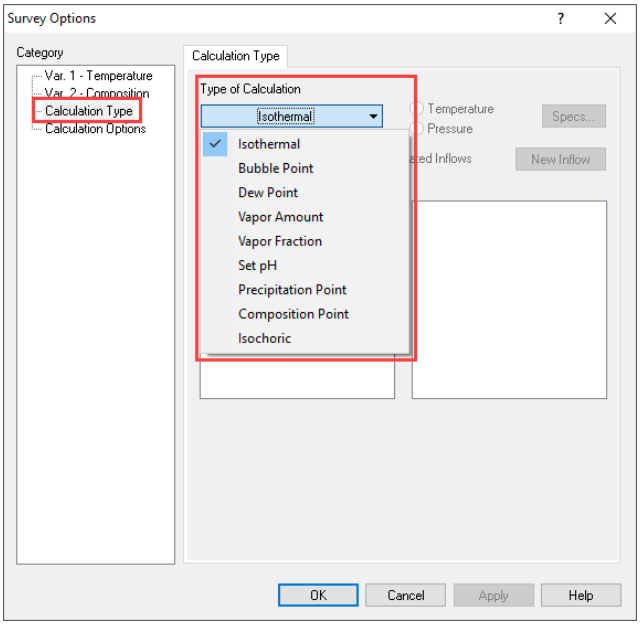


Note: The legend scale can also be optimized by either right-mouse-clicking on the Legend and selecting **Options>Plot Options>Contour** or clicking on the **Options** button in the upper right and selecting **Contour**. Both open to the Contour options window, where the color and range can be modified.

In the contour plot, you can see the effect of both Temperature (x-axis) and Pressure (y-axis) on the solubility of CO_2 in water. Higher solubilities are obtained at high pressures and low temperatures, while lower solubilities are obtained at high temperatures and low pressures.

Survey by changing the single point calculation type

The sections presented so far have presented single and dual surveys. In addition to adjusting these survey variables, you can select one of several single point calculations embedded within the survey. The embedded single point calculations include: Isothermal (default), bubble point, dew point, vapor amount, vapor fraction, set pH, precipitation point, composition point, and isochoric.



Temperature Survey with a Precipitation Point Calculation

In this **Temperature Survey**, the Calculation Type will be changed from Isothermal Calculation to **Precipitation Point**. This will allow us to model the solid solubility vs temperature.

Example 24: Solubility of Halite as a Function of Temperature

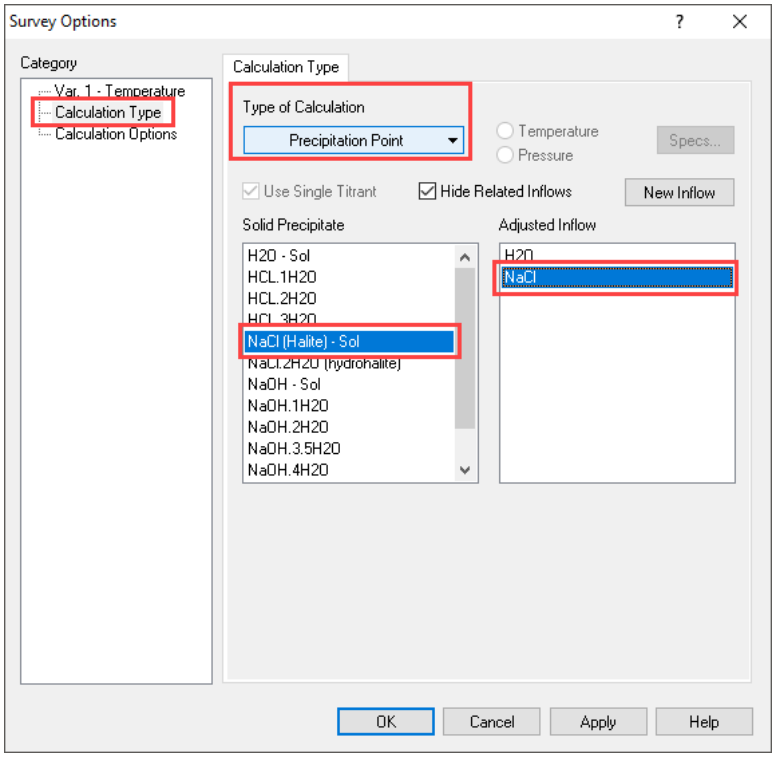
In this example, we are going to study the solubility of NaCl (halite) as a function of temperature.

Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Temperature Survey with a Precipitation Point Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Survey	Stream Amount	Calculated
Stream Name	Solubility vs T	Pressure	1 atm
Survey Name	Halite Solubility vs T	Temperature Range	5-100 ºC
Calculation Type	Precipitation Point	Step Size	Increment by 5 ºC
Name Style	Display Formula	H2O	55.5082 moles
Unit Set	Metric, Moles	NaCl	0 moles
Framework	MSE		

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Halite Solubility vs T and P*
3. Select the **MSE** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition of the stream given in the table above
7. Go to the **Add Calculation** button and select **Survey** calculation
8. Select **Temperature** as the type of survey
9. Change the ***Survey*** name to ***Halite Solubility vs T*** using the **<F2>** key
10. Click on the **Temperature Specs** button. This will open the **Survey Options Window**
11. Change the **Temperature Range** to 0-100 ºC. Set the **Step Size** to **5** ºC increments.
12. Click on **Calculation Type**, in the Category Window to define the Type of Calculation
13. Under Type of Calculation Change the Default Isothermal to **Precipitation Point** (use the drop-down arrow)
14. Select **NaCl (Halite)-Sol** as the **Solid Precipitate** and **NaC**l as the **Adjusted Inflow**. Then click **OK**.



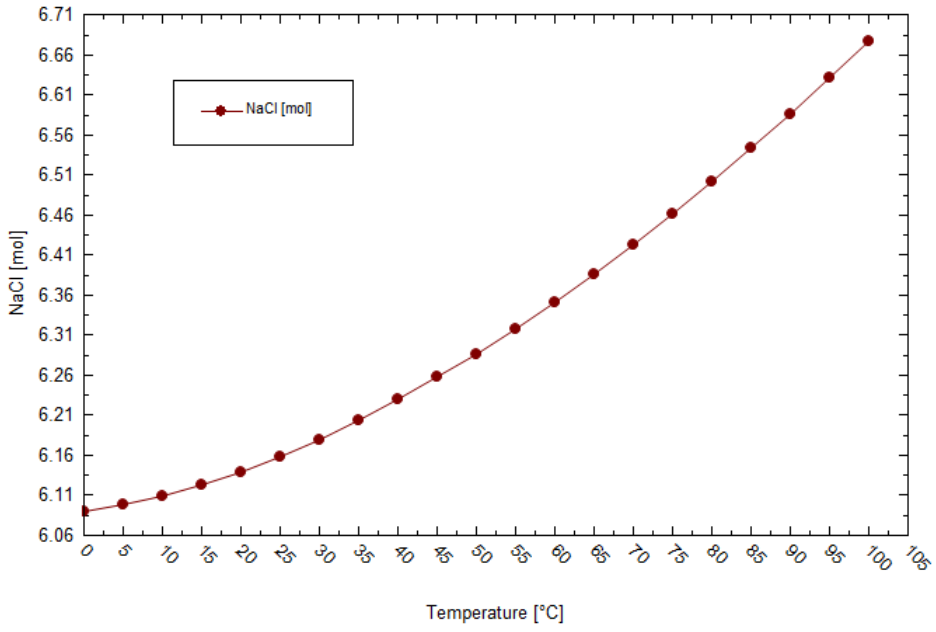
The **Calculation Parameters** section is now shown in the Definition Tab, highlighting the Precipitant (NaCl (Halite)) and the Adjusted Inflow (NaCl).

Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	
Pressure (atm)	1.00000
Calculation Parameters	
Precipitant:	NaCl (Halite)
Adjusted Inflow:	NaCl
Inflows (mol)	
H2O	55.5082
NaCl	0.0

15. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
16. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

Anaylyzing the Results

Click on the **Plot** tab (Plot). The default plot is the amount of NaCl in moles added to 1 kg of water before Halite precipitates as a function of Temperature.



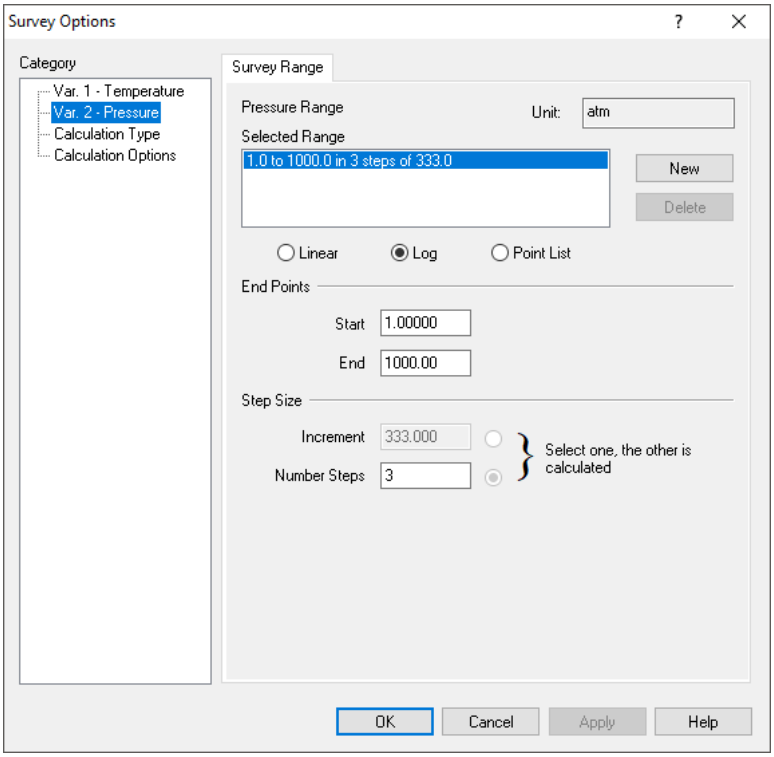
Halite solubility increases slightly with temperature, from 6.16 moles/1kg H_2O at 25ºC to 6.68 moles/1kg H_2O at 100ºC.

Example 25: Solubility of Halite as a Function of Temperature and Pressure

The effects of pressure on mineral solubility is generally less important than temperature. There is still an effect that can be observed. The same stream created on Example 24 will be used.

Starting the Simulation

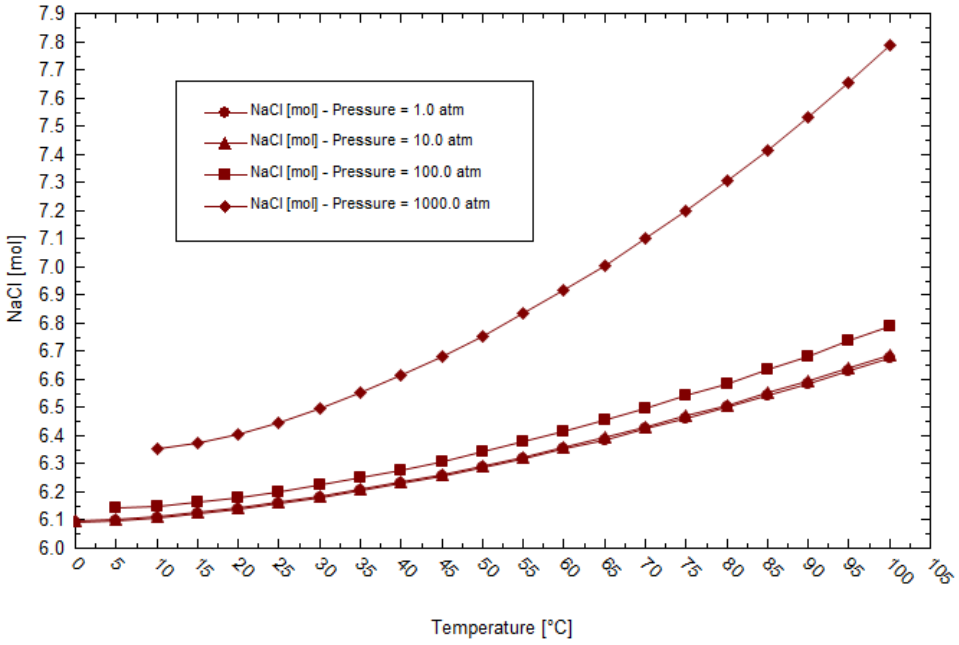
1. Under the **Solubility vs T** stream add a new Survey (see Stream information in Example 24)
2. Change the ***Survey*** name to ***Halite Solubility vs T and P*** using the **<F2>** key
3. Select Survey by **Temperature** and then by **Pressure** (This is a dual survey)
4. Click on the **Temperature Specs** button. This will open the **Survey Options Window**
5. Change the **Temperature Range** to 0-100 ºC. Set the **Step Size** to **5** ºC increments.
6. Click on **Var. 2 – Pressure**, in the Category Window to define the Pressure Range.
7. Change the Scale to **Log**, change the **Pressure Range** from 1 to 1000 atm, and set the N**umber of Steps** to **3** (i.e. it will plot the following pressures: 1, 10, 100 and 1000 atm). Then click **OK**.



8. Click on **Calculation Type**, in the Category Window to define the Type of Calculation
9. Under Type of Calculation Change the Default Isothermal to **Precipitation Point** (use the drop-down arrow)
10. Select **NaCl (Halite)-Sol** as the **Solid Precipitate** and **NaC**l as the **Adjusted Inflow**. Then click **OK**.
11. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key.
12. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

Anaylyzing the Results

Click on the **Plot** tab (Plot). The default plot is the amount of NaCl in moles added to 1 kg of water before Halite precipitates as a function of Temperature.



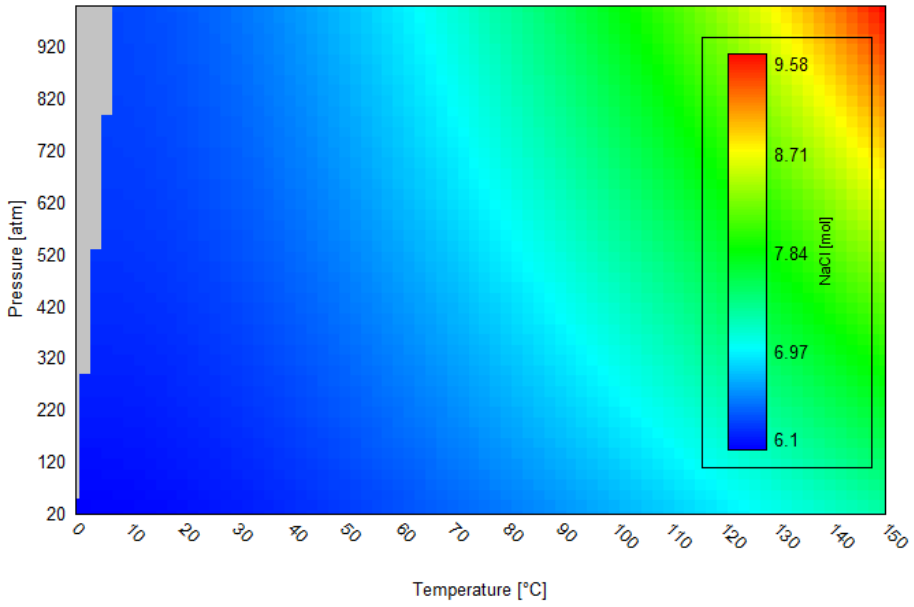
The effect of pressure is significant between 100 and 1000 atm relative to the effects between 1 and 100 atm.

We can also present the Halite Solubility using a Contour Diagram. It would be ideal to define a finer range of temperature and pressure.

1. Return to the **Definition Tab**
2. Click on the **Temperature Specs** button.
3. Change the **Temperature Range** to 0-150 ºC. Set the **Step Size** to **2** ºC increments.
4. Click on **Var. 2 – Pressure**, in the Category Window to define the Pressure Range.
5. Change the survey to **Linear** scale, change the **Pressure Range** from 20 to 1000 atm, and set the **Step Size** to **20 atm** increments. Then click **OK**.

Note: In the Summary box we can see that survey creates a matrix of 75 steps x 49 steps for a total of 76 temperature and 50 pressure points, or 3800 points in total.

6. Click the **Calculate** button. This calculation will take a few minutes to compute.
7. Click on the **Plot** tab and change the Plot to contour ( ).



The solubility is shown to increase as temperature and pressure increase. The increase is up to 50% from the low values. A few of the points failed to converge at the low temperature and high-pressure conditions (shown in gray).

Composition Survey with a Bubble and Dew Point Calculation

In this **Composition Survey**, the Calculation Type will be changed from Isothermal Calculation to **Bubble and Dew Point calculations**. This will allow us to model the vapor liquid equilibria (VLE) of mixtures.

Example 26: Ethanol-Water Azeotrope

In this example, you are going to calculate both the bubble point and dew points as a function of Ethanol-Water composition.

The two data sets will then be transferred to a spreadsheet where the curves will be plotted together to locate the azeotrope. You will need a spreadsheet/plotting software to complete this case.

Starting the Simulation

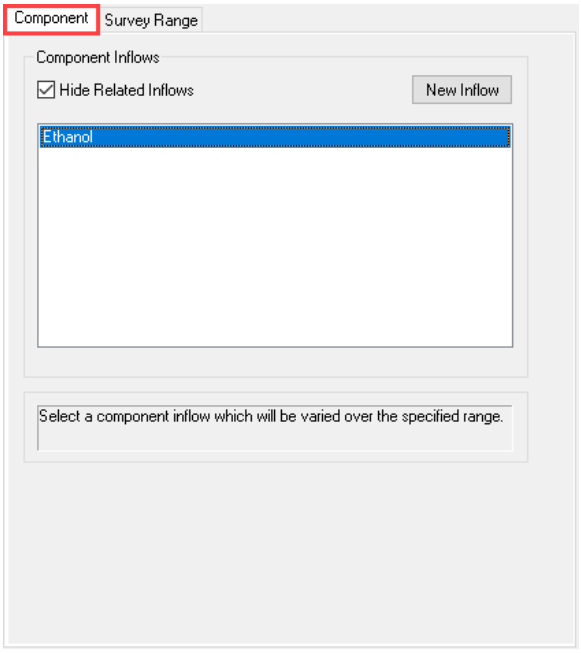
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

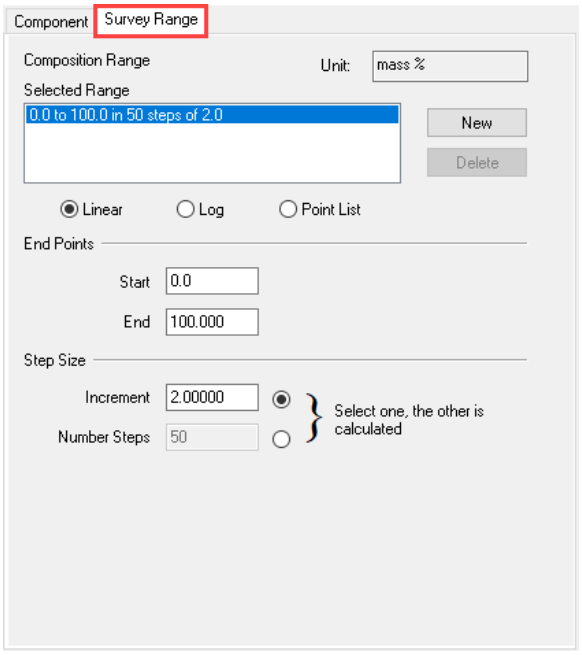
Composition Survey with a Bubble and Dew Point Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Calculation Type	Survey	Stream Amount	Default – 1kg
Stream Name	Composition survey - Azeotrope	Pressure	1 atm
Survey Name	Ethanol-Water Azeotrope	Temperature	It will be calculated
Calculation(s) Type	Bubble Point / Dew Point	H2O	100 mass % - default
Name Style	Display Name	Ethanol	0 mass%
Unit Set	Metric, Mass Frac.	Composition Range	0 -100 mass%
Framework	MSE	Step Size	Increment by 2 mass%

Calculating the Bubble Point

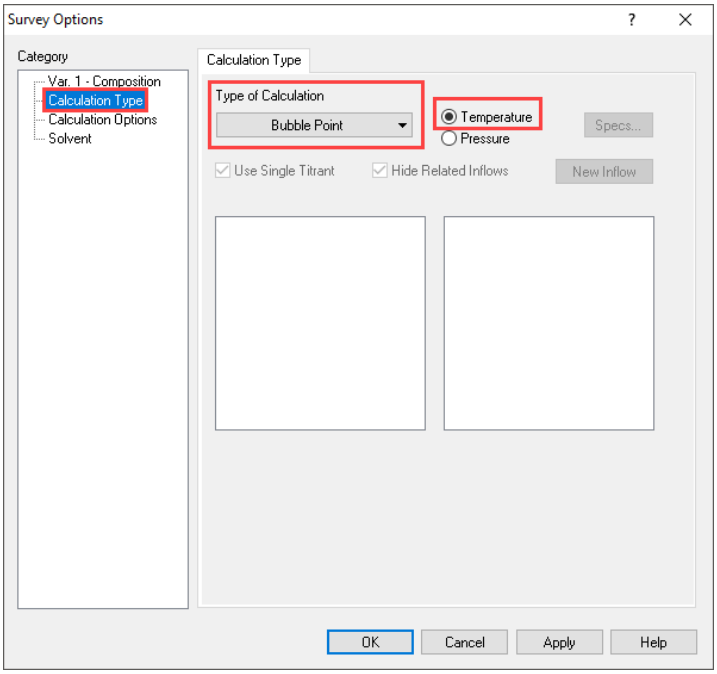
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Composition survey - Azeotrope*
3. Select the **MSE** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Display Name** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Mass Frac.
6. Enter the composition of the stream given in the table above
7. Go to the **Add Calculation** button and select **Survey** calculation
8. Select **Composition** as the type of survey
9. Change the ***Survey*** name to ***Ethanol-Water Azeotrope*** using the **<F2>** key
10. Click on the **Composition Specs** button. This will open the **Survey Options Window**

11. Under the **Component tab**, select **Ethanol**
12. Click on the **Survey Range tab.** Change the **Composition Range** to 0-100 mass%. Set the **Step Size** to **2** mass% increments.





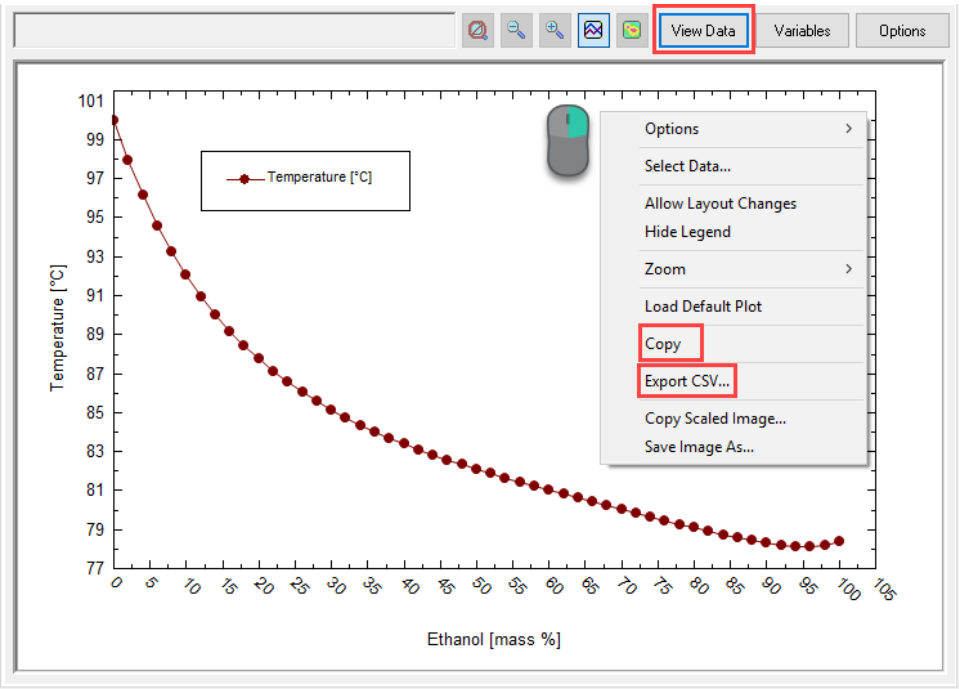
13. Click on **Calculation Type**, in the Category Window to define the Type of Calculation
14. Under Type of Calculation Change the Default Isothermal to **Bubble Point** (use the drop-down arrow). Then click **OK**.



15. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key.
16. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

Anaylyzing the Results

Click on the **Plot** tab (Plot). The default plot is the bubble point temperature vs the mass fraction ethanol. As the mass% of ethanol increases the bubble point temperature decreases.



You have 3 different options to retrieve this data to use it in your preferred plotting software.

Option 1: Right-click on the white region of the plot to open the drop-down menu and select **Copy.**

Option 2: Right-click on the white region of the plot to open the drop-down menu and select **Export CSV**.

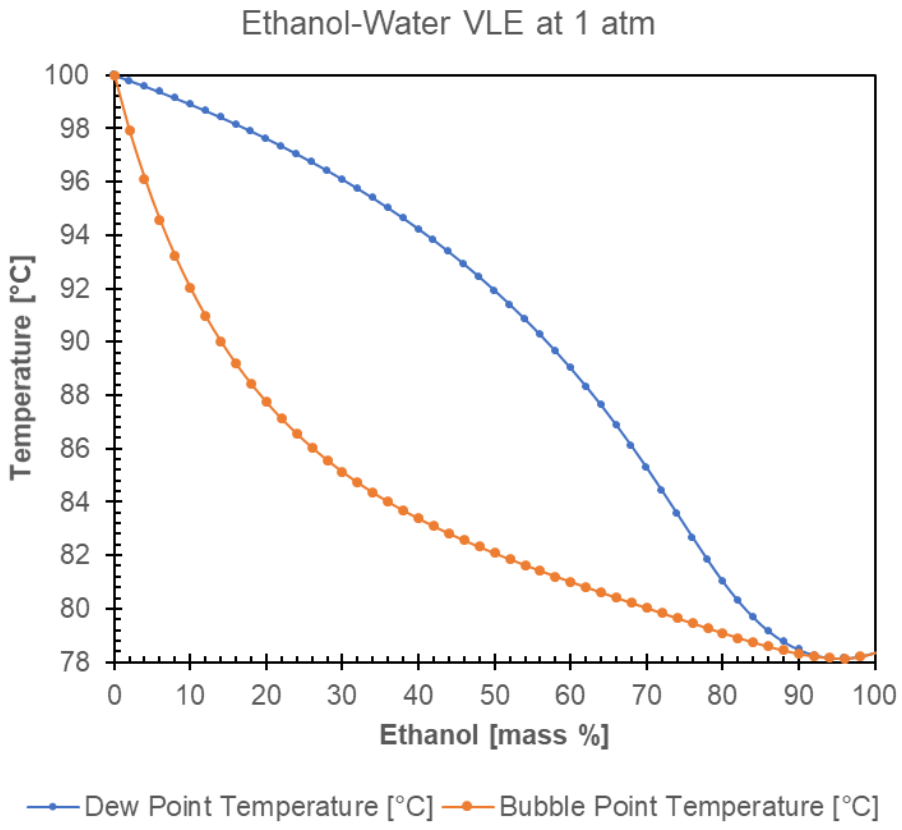
Option 3: Click on the **View Data** button, select all data by clicking on the upper left corner of the table, and copy the data using **Ctrl+C.**

	Ethanol	Temperature
	mass %	°C
1	0.0	99.9976
2	2.00000	97.9141
3	4.00000	96.1248
4	6.00000	94.5734
5	8.00000	93.2174
6	10.0000	92.0237
7	12.0000	90.9664
8	14.0000	90.0246
9	16.0000	89.1815

In this case let's use **Option 1**. Right click and **Copy** the data, then open your preferred plotting tool and **Paste** the data.

Calculating the Dew Point

1. Return to the **Definition tab**
2. Click on the **Composition Specs** button. This will open the **Survey Options Window**
3. Click on **Calculation Type**, in the Category Window to define the Type of Calculation
4. Change the calculation type to **Dew Point** (use the drop-down arrow). Then click **OK**.
5. **Recalculate,** and click on the **Plot tab**
6. Right click and **Copy** the data, then open your preferred plotting tool and **Paste** the data
7. **Plot** the two temperature curves vs mass% of ethanol and format as needed

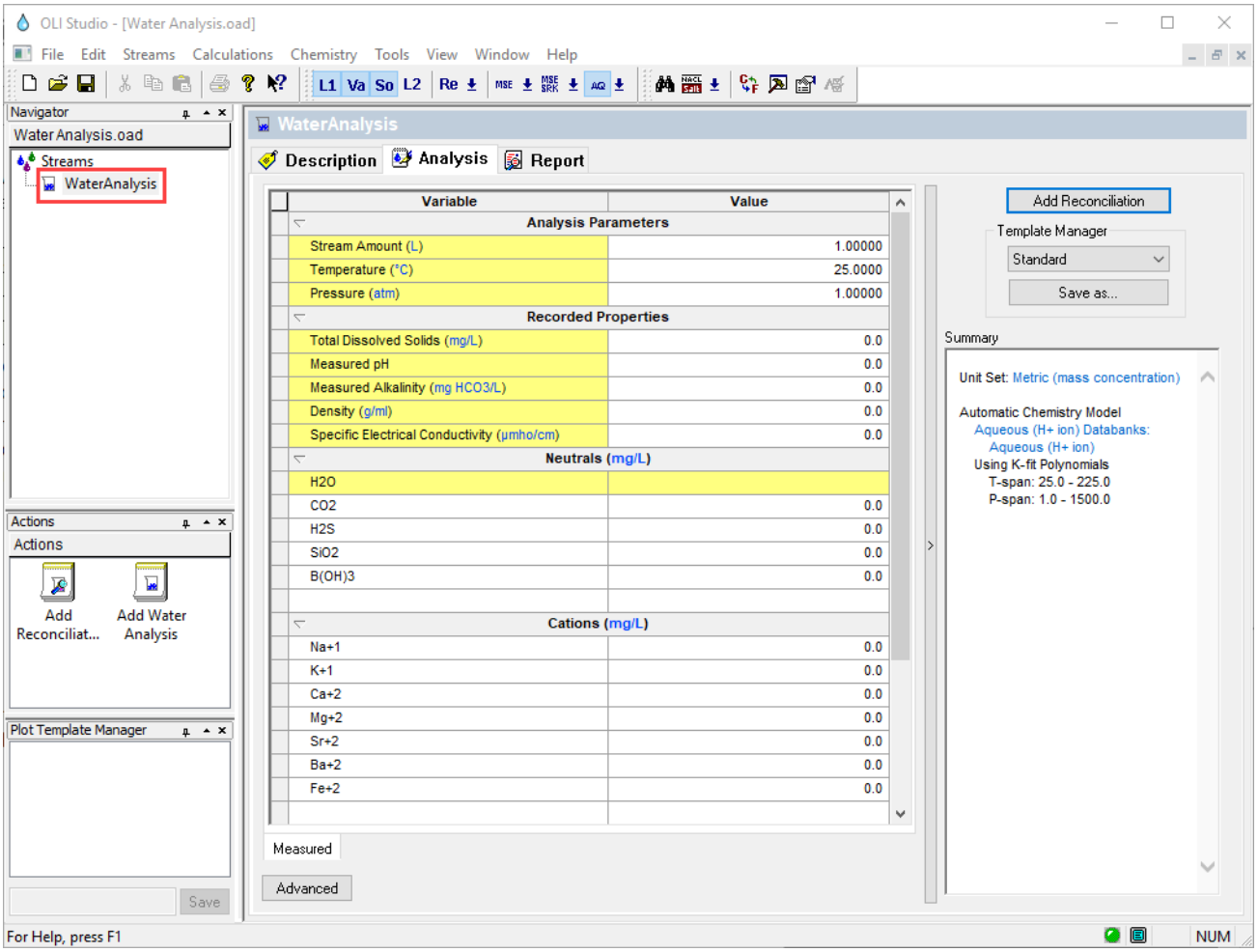


The azeotrope occurs at about 95% ethanol where the two curves intersect, at 78.15 ºC.

Section 3. Water Analysis (Ionic Inputs)

OLI Analyzer: Stream Analyzer can accept two input types: molecular inflows and ionic inflows.

Sections 2 and 3 focused on molecular inflows. In this section, we will focus on **ionic inflows**, and we will learn how to enter cations and anions using the object called **Water Analysis**. Additionally, we will show how the reconciled sample can be converted into a molecular representation.



3.1. Basic Terminology

When reviewing laboratory analysis of water samples, it is quite common for the positive ions (cations) and the negatively charged ions (anions) in solution to not balance. This may be due to the precision limits of the various experimental procedures used to measure the ions - i.e. some ions may not have been analyzed. These solutions must have a neutral charge. Stream Analyzer will adjust/modify inflows in order to balance the charges and make the solution neutral. This adjusting procedure is referred to as **Reconciliation**.

The pH and the alkalinity of the solution are frequently measured. However, since the analysis is experimental and subject to errors, the pH and alkalinity values that are calculated by the Water Analysis tool may be different from what is measured experimentally. Stream Analyzer can also reconcile this difference.

Scaling

Scaling is the deposition of a mineral salt on processing equipment. Scaling is a result of supersaturation of mineral ions in the process fluid. Through changes in temperature, or solvent evaporation or degasification, the concentration of salts may exceed the saturation, leading to a precipitation of solids (usually crystals). The saturation level of a salt in water is a good indicator of the potential for scaling.

The potential for scaling is calculated using the solubility product constant (K_{sp}) and Ion Activity Product (IAP) definitions.

Solubility Product Constant, K_{sp}

The solubility of ionic compounds of salts and minerals in water are governed by a solubility equilibrium expression and a solubility product constant known as K_{sp}. It is important to note that the solubility product, K_{sp} is a function of both temperature and pressure. Consider the general dissolution reaction below (in aqueous solutions):

$$aA_{(s)} \rightleftharpoons bB_{(aq)} + dD_{(aq)}$$

With equilibrium constant K_{sp} defined as:

$$K_{sp} = (a_B)^b \cdot (a_D)^d$$

Where, a_B and a_D are the activities of the aqueous species. The activity of any species i is defined as the product of its concentration in molality by its corresponding activity coefficient:

$$a_i = m_i \gamma_i$$

Ion Activity Product, IAP

A real solution may not be in the state of equilibrium. This non-equilibrium state is described by the ion activity product (IAP). It has the same form as the equilibrium constant K_{sp}, but involves the actual activities of the species in solution.

$$IAP = (a_B)^b_{actual} \cdot (a_D)^d_{actual}$$

Scaling Tendency and Scale Index

The Scaling Tendency (ST) is defined as the ratio of the Ion Activity Product (IAP) divided by the equilibrium constant (K_{sp}).

$$ST = \frac{IAP}{K_{sp}} \qquad Equation\ (1)$$

Scaling tendencies are essentially saturation ratios. Thus, if

$ST < 1$ 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

Note: The Scaling Tendency (ST) is reported in the software as Post-Scale.

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

$$SI = \log_{10}\left(\frac{IAP}{K_{sp}}\right) \qquad Equation\ (2)$$

Thus, if

$SI < 0$ 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

Note: The Scaling Index (SI) is reported in the software as SI, Index under the Post-Scale name.

Pre-scaling Tendency and Scale Index

Pre-Scaling tendency is defined as the scaling tendency before any solids are formed (this can be seen as all the species suspended in solution). The same equations (Equations 1 and 2) are used for calculating ST and SI.

The Pre-Scaling tendency is reported in the software as Pre-Scale, with its respective SI, index.

Difference between Post-scale and Pre-scale

Pre-Scale: The saturation ratio before solids precipitate.

Post-Scale: The saturation ratio **after** solids precipitate (if solids are selected).

Another way to interpret these two definitions is:

Pre-Scale represents the condition before any solids are allowed to form. This is a non-equilibrium condition and can be viewed as the condition where $time = 0$.

Post-Scale Tendency is the saturation ratio after all potential solids come to equilibrium with water. This is the true equilibrium condition $(time = \infty)$.

Example 27: Calculation the Scaling Tendency and the Scale Index of $CaSO_4 \cdot 2H_2O$

Let's calculate the Scaling Tendency and the Scale Index of 0.01 moles of gypsum $(CaSO_4 \cdot 2H_2O)$ dissolved in 1 kg of water at 25ºC and 1 atm.

The equilibrium expression for the dissolution reaction is:

$$CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O$$

Where, $K_{sp} = 3.2 \times 10^{-5}$

The molal concentration and the activity coefficients for each one of the species are:

$[Ca^{+2}] = 0.0093\ m$ $\quad$ $\gamma_{Ca^{+2}} = 0.4663$

$[SO_4^{-2}] = 0.0093\ m$ $\quad$ $\gamma_{SO_4^{-2}} = 0.4663$

$a_{H_2O} = 0.9997$

Calculating the IAP

With the information given above, we can calculate the IAP as follows:

$$IAP = a_{Ca^{+2}} \cdot a_{SO_4^{-2}} \cdot \left(a_{H_2O}\right)^2$$

$$IAP = \left(m_{Ca^{+2}}\, \gamma_{Ca^{+2}}\right) \cdot \left(m_{SO_4^{-2}}\, \gamma_{SO_4^{-2}}\right) \cdot \left(a_{H_2O}\right)^2$$

$$IAP = (0.0093 \times 0.4663) \cdot (0.0093 \times 0.4663) \cdot (0.9997)^2$$

$$IAP = 1.879 \times 10^{-5}$$

Calculating the Scaling Tendency

$$ST = \frac{1.879 \times 10^{-5}}{3.2 \times 10^{-5}}$$

$$ST \approx 0.587$$

This result indicates that the solution is under-saturated with respect to calcium sulfate.

Calculating the Scaling Index

$$SI = \log_{10} \frac{IAP}{K_{sp}} = \log_{10} ST$$

$$SI = \log_{10}(0.587)$$

$$SI \approx -0.231$$

3.2. Entering Data for Water Analysis

The grid for water analysis has 5 different grids where we need to enter information: Analysis Parameters, Recorded Properties, and Neutrals, Cations and Anions concentration in solution.

The **Analysis Parameters** grid is where you enter the conditions at which the sample properties were measured. The default values are 1 L, 25°C and 1 atm.

Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000

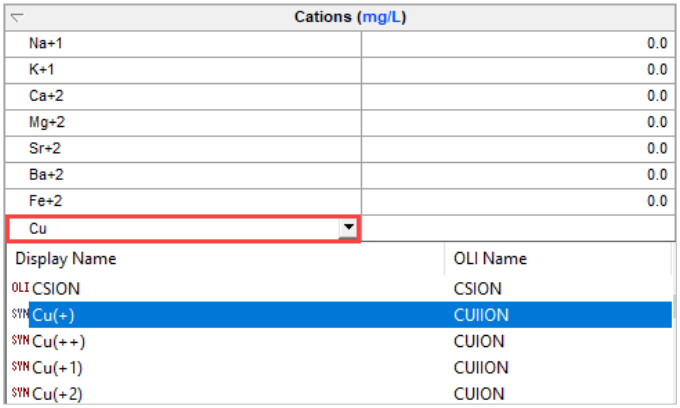
The **Recorded Properties** grid is where you enter the laboratory measured properties of the solution. These are: Total Dissolved Solids (TDS), Measured pH, Measured Alkalinity, Density, and Specific Electrical Conductivity. You can always change the units of these properties by clicking on the units highlighted in blue. This action will open the Units Manager Window.

Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	0.0
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (µmho/cm)	0.0

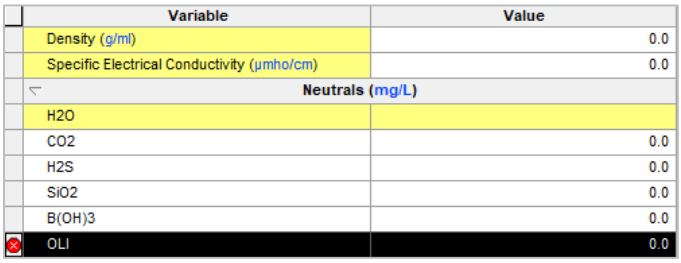
The concentration of Neutrals, Cations and Anions is entered in the section. The Water Analysis grid comes already prepopulated with some of the most common cations, anions, and neutrals species found in laboratory water analyses. If your species is not present in the prepopulated grid, simply click on the white grid and type the ion or neutral of interest. If it is a **cation**, type the element followed by a plus (+) sign and the corresponding oxidation state, e.g. Cu+2. If it is an **anion**, type the element followed by a minus (-) sign and the corresponding oxidation state, e.g. Br-1. If it is a **neutral**, simple type the species either using the formula name or its name, as has been shown in the previous sections.

Neutrals (mg/L)	
H2O	
CO2	0.0
H2S	0.0
SiO2	0.0
B(OH)3	0.0
Cations (mg/L)	
Na+1	0.0
K+1	0.0
Ca+2	0.0
Mg+2	0.0
Sr+2	0.0
Ba+2	0.0
Fe+2	0.0
Anions (mg/L)	
Cl-1	0.0
SO4-2	0.0
HCO3-1	0.0
HS-1	0.0
C2H3O2-1	0.0

The Water Analysis grid also contains search aids to find a specific cation or anion. The first search aid is the drop list located in each the cation, anion, and neutral grid sections. The list is alphabetic and is activated using the drop-down arrow within the cell, after the first few letters of the ion is typed.



If a name is misspelled or if the text is unrecognized, then a red 'X' appears to the left of the name. This name needs to be corrected or the row deleted before proceeding. To delete the row, simply select the wrong entry (which will turn black) and hit the key **<Delete>**.



3.3. Water Analyses - Reported Elements

Water analysis data obtained from ICP measurements will contain concentrations for B, P, S, and Si. These elements do not exist in the water, rather they exist as dissolved ions. If they are part of your analysis, then you should convert them to the following before entering them into the Water Analyses object.

Table 1. Converting element concentration to species for Brine or Water Analysis

ICP data	Aqueous Species	Formula to enter	Formula weight multiplier
B, boron	Boric Acid	H3BO3	B (mg/l) × 5.72 = H3BO3 (mg/l)
Si, Silicon	Silica	SiO2	Si (mg/l) × 2.14 = SiO2 (mg/l)
P, Phosphorus	Dihydrogen Phosphate	H2PO4-1	P (mg/l) × 3.13 = H2PO4 (mg/l)
S, Sulfur	Sulfate or Sulfide	HS-1 or SO4-2 (cannot tell from total S only)	S (mg/l) × 1.03 for HS-1 (mg/l) or S (mg/l) × 3.0 for SO4-2 (mg/l)

3.4. A Basic Water Analysis

A brief introduction to the water analysis tool will be shown in the example below. As we go through the example, the basic definitions, functionalities and reporting for the *Water Analysis tool* will be introduced.

Example 28: Ground Water Analysis

Will calculate the **pH** and **density** of a Ground Water sample based upon its measured composition at 1 atm and 25 ºC. Then we will create a molecular stream based on the ionic inflows.

Starting the Simulation

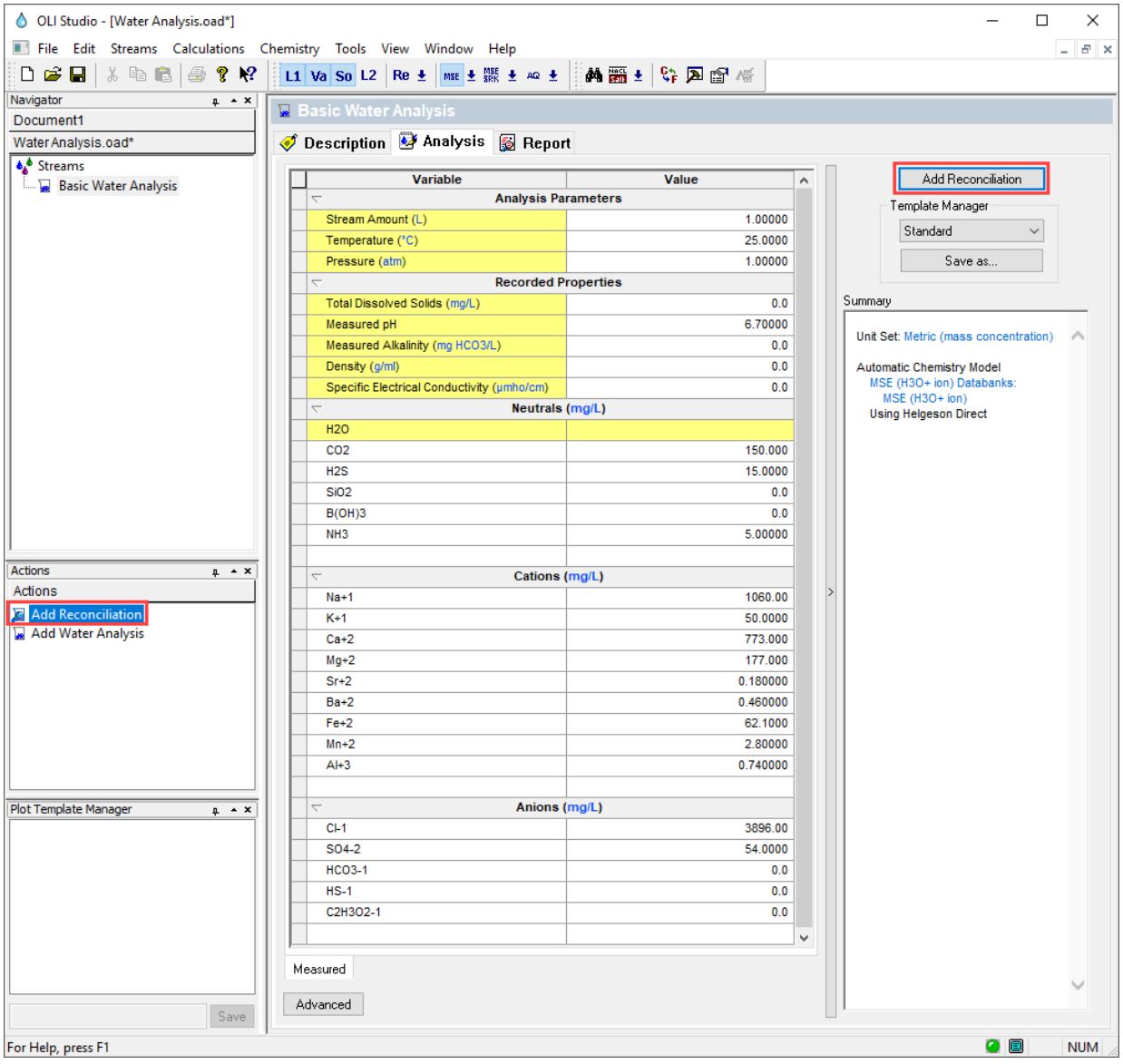
Use the inputs and parameters from the table below to create the water analysis. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Ground Water Analysis					
Analysis Parameters/Settings			**Recorded Properties**		
Stream Amount	1 L (Default)		Total Dissolved Solids	Not recorded	
Temperature	25 ºC		Measured pH	6.7	
Pressure	1 atm		Measured Alkalinity	Not recorded	
Name Style	Display Formula		Density	Not recorded	
Unit Set	Metric, Batch, Concentration		Specific Electrical Conductivity	Not recorded	
Framework	MSE				
Calculation Type	Water Analysis				
Stream Name	Basic Water Analysis				
Composition					
Neutrals (mg/L)		**Cations (mg/L)**		**Anions (mg/L)**	
CO2	150	Na+1	1060	Cl-1	3896
H2S	15	K+1	50	SO4-2	54
NH3	5	Ca+2	773		
		Mg+2	177		
		Sr+2	0.18		
		Ba+2	0.46		
		Fe+2	62.1		
		Mn+2	2.80		
		Al+3	0.74		

Setting the Water Analysis

1. Add a **Water Analysis**
2. **Click** on the new WaterAnalysis and press **<F2>** to change the name to *Basic Water Analysis*
3. Select the **MSE** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Concentration (it may be defined by default)

6. Under the **Analysis** Tab, enter the Analysis Parameters, Recorded properties, and composition of the water given in the table above.
7. Go to the **Add Reconciliation** button of the top right corner or select **Add Reconciliation** from the Actions Panel.



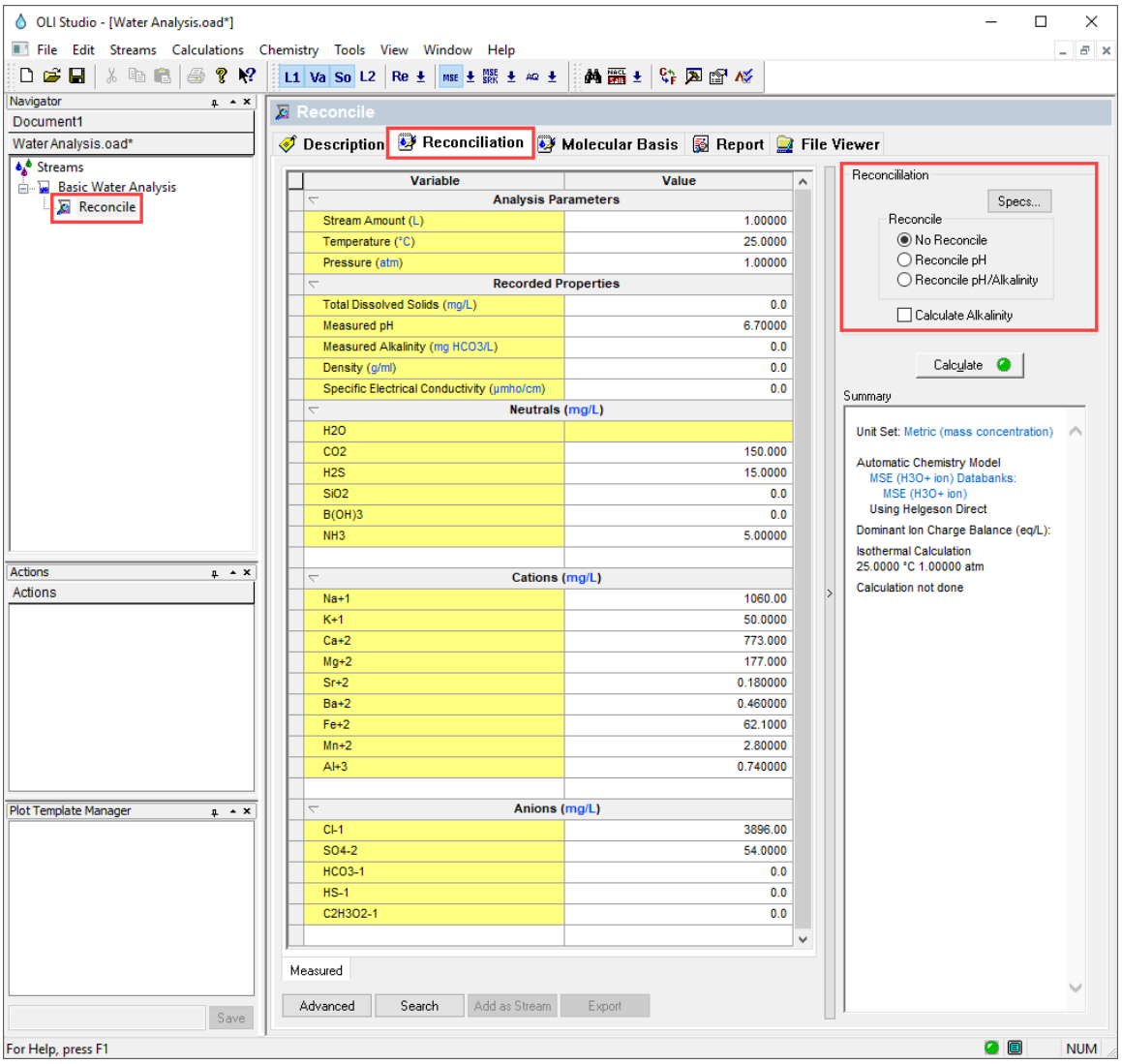
Note: You may notice that after selecting **Add Reconciliation** option, the navigator panel displays a sub-stream called **Reconcile**, and this **Reconcile** sub-stream opens a new tab named **Reconciliation**. The Reconcile sub-stream copies the original inputs entered in the *Water Analysis*. Any changes made in the sub-stream will not change the original Water Analysis.

Additionally, three different types of reconciliation are enabled in the upper right corner of the window: (1) No Reconcile, (2) Reconcile pH and (3) Reconcile pH/Alkalinity. These types of reconciliation will be described in more detail later in the next section.

The selected default calculation is **No Reconcile**. This option means that the software will compute the water properties based on the current concentration of neutral, cations, and anions species. The calculation will not use the measured pH, or the measured alkalinity entered (if any).

The Calculate Alkalinity box (☐ Calculate Alkalinity) allows you to compute the alkalinity, also based on the concentration entered.

8. Select the **No Reconcile** option

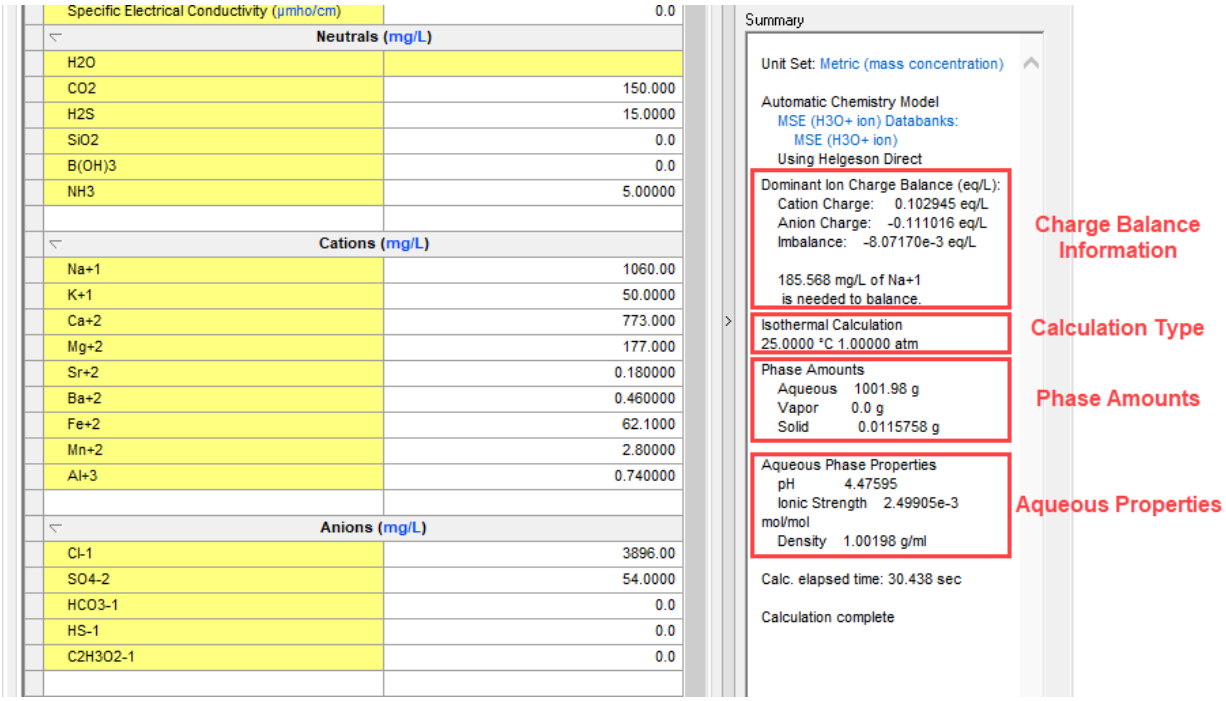


9. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
10. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Create a new file and name it: *Water Analysis Calculations.*

Analyzing the Results

Viewing the Summary Box

Review the Summary Box. Let's analyze it in detail since it contains several pieces of important information, as shown in the image below.



The top section contains the **charge balance information** showing the total equivalent charge (positive and negative), and the charge imbalance. This example has a negative imbalance of -8.072×10^{-3} eq/L, indicating that more cations are needed in solution in order to reach electroneutrality. The software calculates that 185.568 mg/L of Na+ are needed to balance the solution. The software adds this amount of Na+ to the solution. This information can be further confirmed in the **Report Tab** in the Charge Balance table.

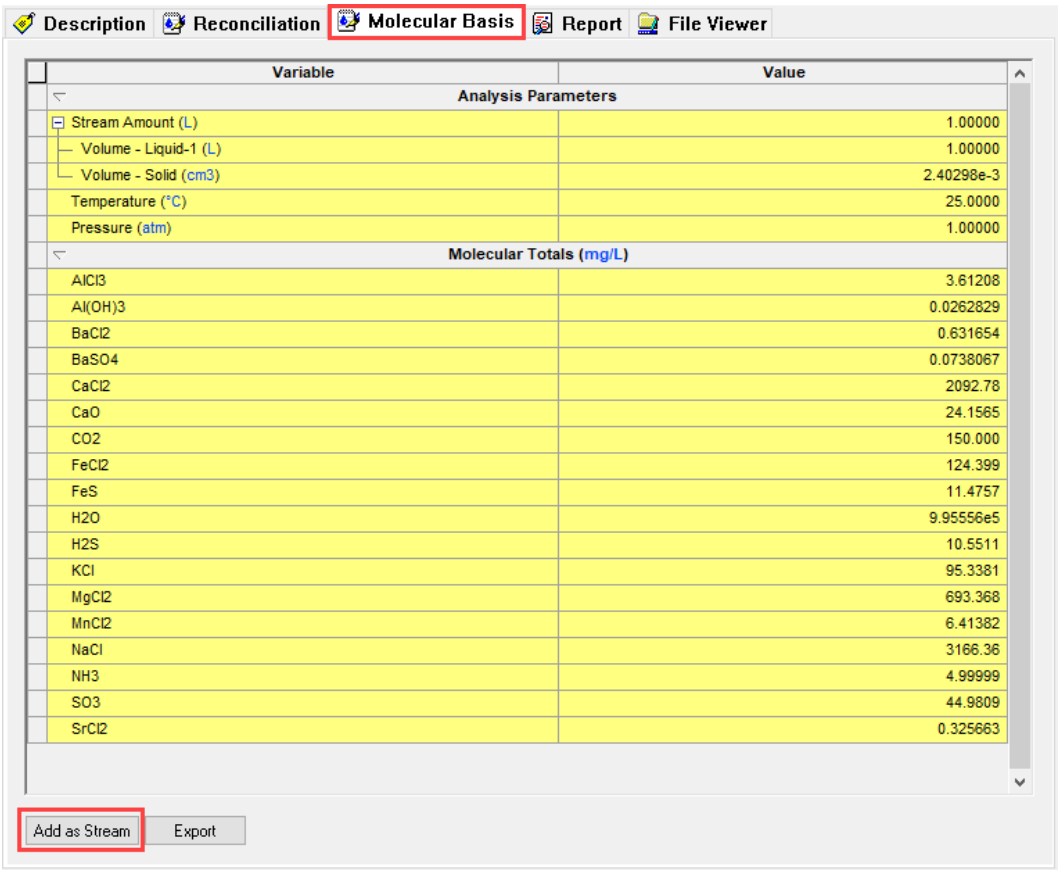
The **calculation type information** shows the calculation type the software used. In this example, the software performed a default isothermal calculation at 25 ºC and 1 atm. If we selected other calculation specifications, they would appear here.

The **phase amounts information** shows the distribution of species in the different phases. This analysis contains two phases: aqueous and solid.

The **aqueous properties information** shows the computed pH, ionic strength, and density of the solution. It is important to note here that the measured pH is 6.70 and the computed pH is 4.47. The density of this solution is 1.00198 g/ml. Remember, for this example the software used only the concentration of neutrals, cations and anions in solution to do a reconciliation.

Viewing the Molecular Basis Tab

Let's review the **Molecular Basis** Tab. The Molecular Basis tab is one of several tabs of the Reconciliation object. The information contained in this tab is the molecular composition of the solution after it has been reconciliated. In other words, the software has converted the **ionic inflows** into a **molecular stream**.



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Volume - Liquid-1 (L)	1.00000
Volume - Solid (cm3)	2.40298e-3
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Molecular Totals (mg/L)	
AlCl3	3.61208
Al(OH)3	0.0262829
BaCl2	0.631654
BaSO4	0.0738067
CaCl2	2092.78
CaO	24.1565
CO2	150.000
FeCl2	124.399
FeS	11.4757
H2O	9.95556e5
H2S	10.5511
KCl	95.3381
MgCl2	693.368
MnCl2	6.41382
NaCl	3166.36
NH3	4.99999
SO3	44.9809
SrCl2	0.325663

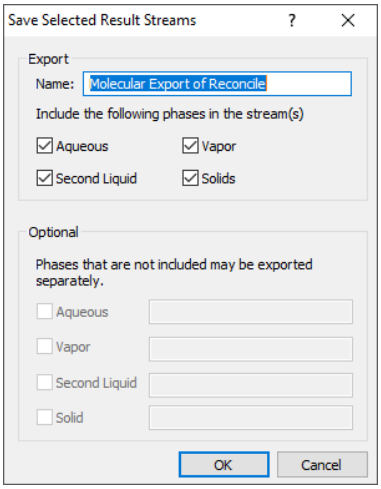
Note: The software generates molecular concentrations based on two priorities. The first priority is to create the least number of molecular inflows. This example contains eighteen inflows (plus H2O not shown). The second priority is to create the least number of total moles. Moles are not shown here, since the units are mg/l. The moles are shown in the Report tab.

You can use this molecular form as a new Stream in OLI Analyzer, by using the **Add as Stream** button, or it can be exported to a separate software like ESP FS, Aspen Plus, UniSim Design, or other simulators.

Converting the Ionic Inflows into a Molecular Stream

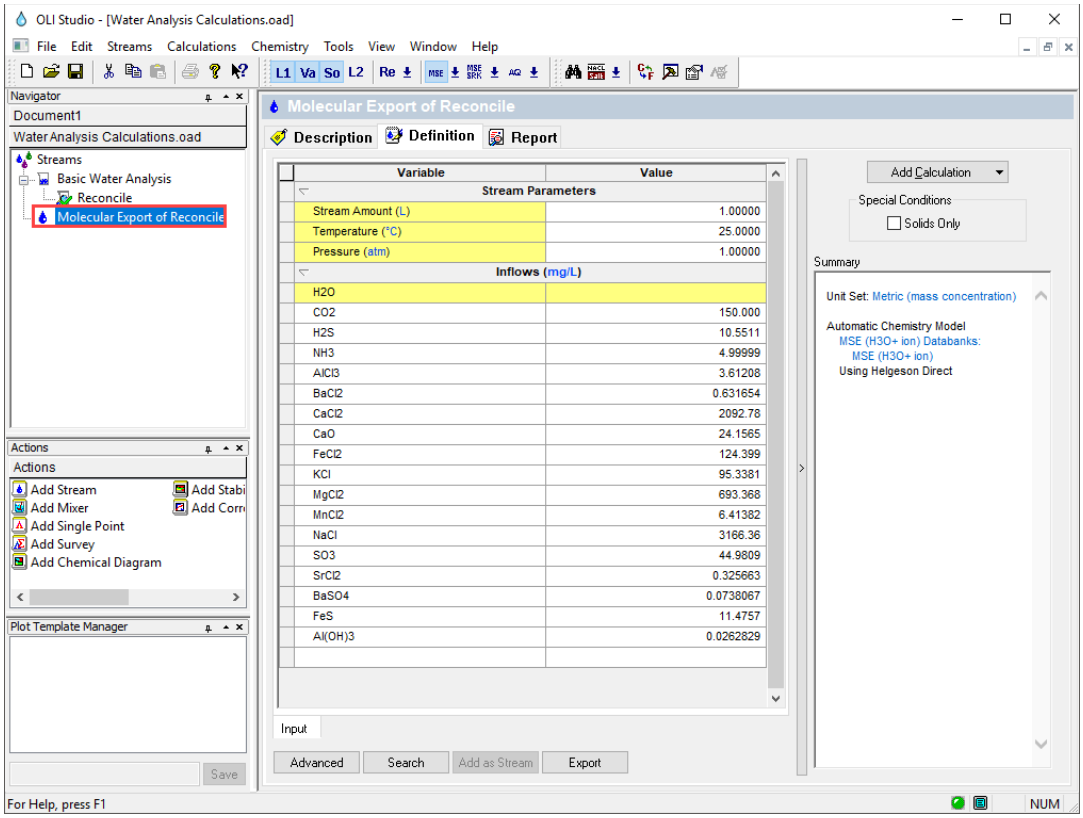
For practice, let's add this Molecular Basis as a Stream into the Navigator Panel.

1. Click on the **Add as Stream** button. This will open a new window



Note: By default, the name of the stream is **Molecular Export of Reconcile**. You can change the name if you prefer. Additionally, you can include or exclude the phases that you want to export into your stream by checking or unchecking the corresponding boxes.

2. Leave the defaults and click **OK.** The program automatically adds a new stream in the navigation panel.



Viewing the Report Tab

The **Report** tab is slightly different from the Single Point report described in Section 1. This Report contains three additional tables, all of which are located at the top. These tables are the Reconciliation Summary, Stream Inflows, and Charge Balance.

The **Reconciliation Summary** table confirms the specifications for the reconciliation such as the charge balance method and the reconciliation type (these concepts will be discussed in more detail later in the manual). Additionally, shows the conditions at which the calculation was run, in this case 25ºC and 1 atm. And finally, shows a comparison between the measured and calculated properties, in this case it shows the measured vs calculated pH.

Reconciliation Summary

Specification

Charge Balance Method Dominant Ion

pH Reconciliation Type No reconciliation

	Measured	Calculated
Temperature, °C	25.0000	
Pressure, atm	1.00000	
pH	6.70000	4.47595
Density, g/ml		1.00198
Water, mg/L		9.95554e5

The **Stream Inflows** table summarizes all the species that were entered in the water analysis grid.

Stream Inflows

Row Filter Applied: Only Non Zero Values

	Input	Output
Species	mg/L	mg/L
H2O	1.00000e6	9.95554e5
Na+1	1060.00	
K+1	50.0000	
Ca+2	773.000	
Mg+2	177.000	
Sr+2	0.180000	
Ba+2	0.460000	
Fe+2	62.1000	
Mn+2	2.80000	
Al+3	0.740000	
CO2	150.000	150.000
H2S	15.0000	15.0000
Cl-1	3896.00	
SO4-2	54.0000	
NH3	5.00000	4.99999

The **Charge Balance** table contains the concentrations entered and the final balanced values. In this case only the sodium (Na+1) concentration was changed.

Charge Balance

Cation Charge:	0.102945 eq/L
Anion Charge:	-0.111016 eq/L
Imbalance:	-8.07170e-3 eq/L
Adjusted Species:	Na+1

Charged Species	Input	Balanced	Difference
	mg/L	mg/L	%
Na+1	1060.00	1245.57	17.51
K+1	50.0000	50.0000	
Ca+2	773.000	773.000	
Mg+2	177.000	177.000	
Sr+2	0.180000	0.180000	
Ba+2	0.460000	0.460000	
Fe+2	62.1000	62.1000	
Mn+2	2.80000	2.80000	
Al+3	0.740000	0.740000	
Cl-1	3896.00	3896.00	
SO4-2	54.0000	54.0000	
HCO3-1	0.0	0.0	
HS-1	0.0	0.0	
C2H3O2-1	0.0	0.0	

3.5. Exploring Reconciliation Options

When reconciling a Water Analysis, there are three options for reconciliation:

1. **No Reconcile:** The software will run an electroneutrality reconciliation only, and then compute the water properties such as pH, density, etc., based on the entered concentration of neutral, cations, and anions species. In the **No Reconcile** option you may allow the program to pick the species to adjust for **electroneutrality** or you may manually choose the species to perform the adjustment. (See electroneutrality options).

2. **Reconcile pH:** The software will run both an electroneutrality and pH reconciliation. This type of reconciliation will match your recorded pH. Additionally, the software will compute the water properties such as, density, electrical conductivity, etc. The **pH** of the solution is automatically **adjusted** by the software by **adding** either **HCl** or **NaOH**, or you may select your preferred acids and bases to adjust the pH.

3. **Reconcile pH/Alkalinity:** The software will run an electroneutrality, pH and alkalinity reconciliation. This type of reconciliation will match your recorded pH and alkalinity values. Additionally, the software will compute the water properties such as density, electrical conductivity, etc. The pH of the solution is automatically adjusted by the software by adding either HCl or NaOH or you may select your preferred acids and bases to adjust the pH. The **Alkalinity** is automatically adjusted by the software, using **CO_2** as the **alkalinity titrant**, **H_2SO_4** as the **alkalinity pH** titrant and **4.5** as the **alkalinity end point pH**.

4. **Reconcile pH/Alkalinity:** The software will run an electroneutrality, pH, alkalinity and Total Inorganic Carbon (TIC) reconciliation. This type of reconciliation will match your recorded pH, alkalinity and TIC values. Additionally, the software will compute the water properties such as density, electrical conductivity, etc. The **TIC** is automatically calculated by the software, using **CO_2** as the titrant, **H_2SO_4** as the alkalinity pH titrant and 4.5 as the end point pH. The (total) Alkalinity is adjusted by the software by adjusting the acetate concentration (organic acids) to match the target Alkalinity. The Alkalinity is adjusted by adding or removing **acetic acid**. In this calculation, you cannot change the CO_2 or Acetic Acid for the alkalinity adjustment, these are fixed by the software.

Additionally, there is the option to Calculate Alkalinity: ☐ Calculate Alkalinity. It is important to note, that this is only an alkalinity calculation based on the concentration entered, it is not an alkalinity reconciliation.

We will explore the different types of reconciliation and introduce the different specification options according to the reconciliation type.

In this section we will create a new file. We will run a basic water analysis, from which the various reconciliation options will be explored.

Example 29: Water Analysis – No Reconcile Option

In this example we will calculate the **pH** and different properties of a Produced Water sample based upon its measured composition at 1 atm and 25 ºC.

Starting the Simulation

Use the inputs and parameters from the table below to create the water analysis. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

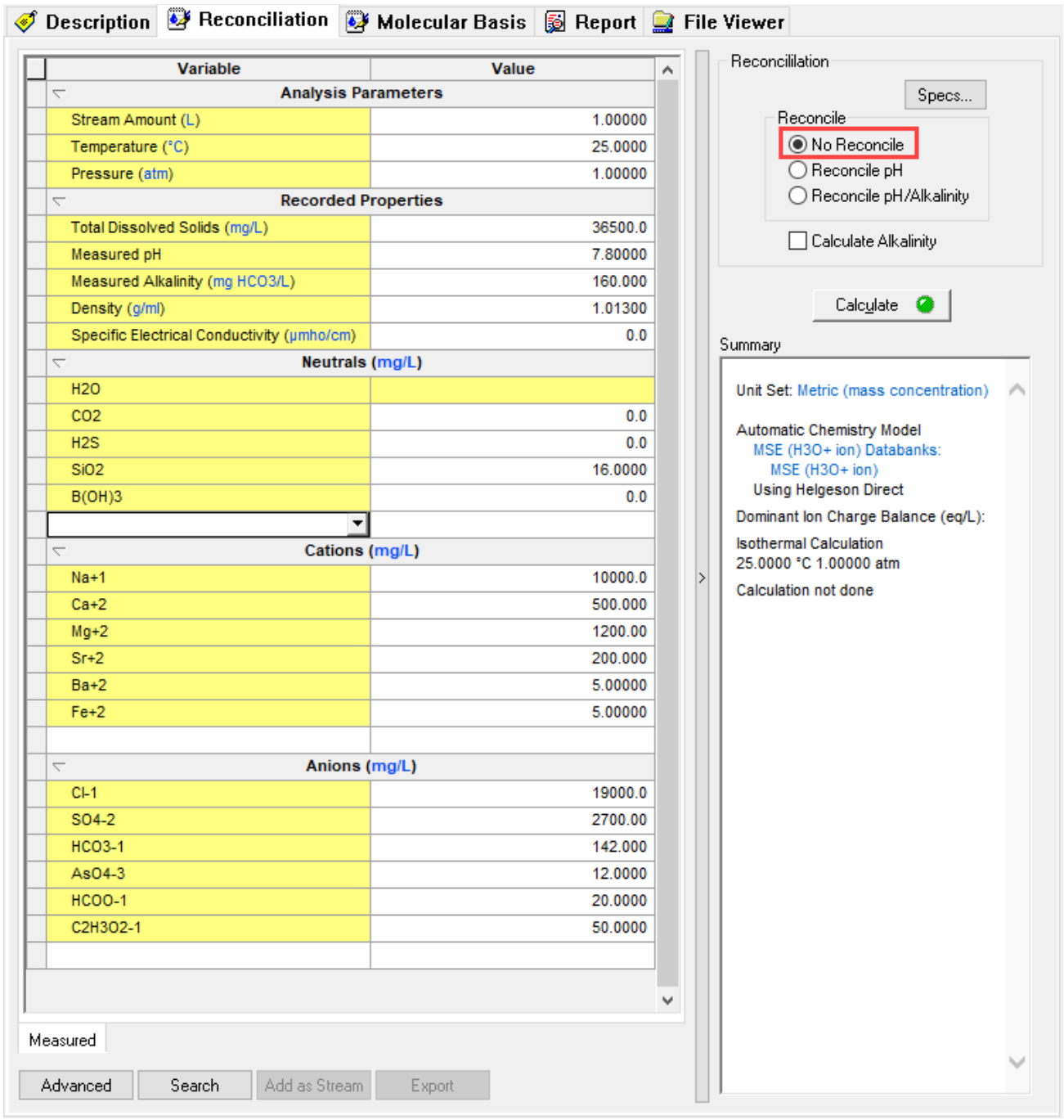
Water Analysis – Reconcile Options					
Analysis Parameters/Settings			**Recorded Properties**		
Stream Amount	1 L (Default)		Total Dissolved Solids	36500 mg/L	
Temperature	25 ºC		Measured pH	7.8	
Pressure	1 atm		Measured Alkalinity	160 mg HCO3/L	
Name Style	Display Formula		Density	1.013	
Unit Set	Metric, Batch, Concentration		Specific Electrical Conductivity	Not recorded	
Framework	MSE				
Calculation Type	Water Analysis				
Stream Name	Water Analysis – Reconcile Options				
Composition					
Neutrals (mg/L)		**Cations (mg/L)**		**Anions (mg/L)**	
SiO2	16	Na+1	10000	Cl-1	19000
		Ca+2	500	SO4-2	2700
		Mg+2	1200	HCO3-1	142
		Sr+2	200	AsO4-3	12
		Ba+2	5	CHO2-1	20
		Fe+2	5	C2H3O2-1	50

Calculating the pH

Setting the Water Analysis

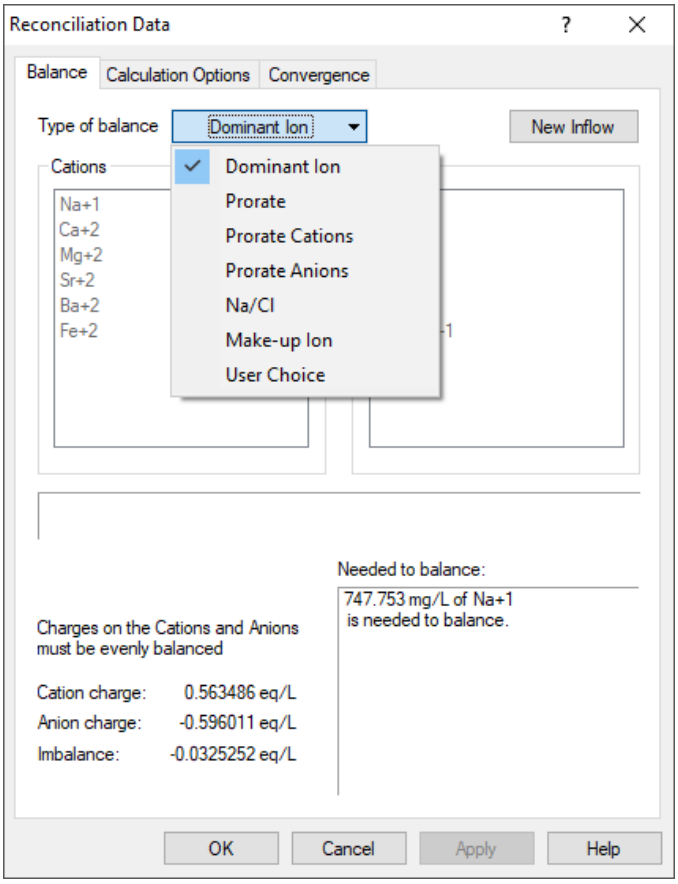
1. Add a **Water Analysis**
2. **Click** on the new WaterAnalysis and press **<F2>** to change the name to *Water Analysis – Reconcile Options*
3. Select the **MSE** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Concentration (it may be defined by default)
6. Under the **Analysis** Tab, enter the Analysis Parameters, Recorded properties, and Composition of the water given in the table above.

7. Go to the **Add Reconciliation** button of the top right corner or select **Add Reconciliation** from the Actions Panel, and name it **No Reconcile**.
8. Select the **No Reconcile** option (selected by default)



Note: In the **No reconcile** option, the software runs an electroneutrality reconciliation. The **type of balance** for reconciling electroneutrality is the **Dominant Ion** method. You can select different types of balance for electroneutrality by clicking on the **Specs** button.

9. Click on the **Specs** button. This will open a new window.



There are 7 different Types of Balance:

1. **Dominant Ion**: This is the default method. The largest counter ion is used to adjust the electroneutrality. In our example,747.753 mg/L of Na+1 are added since there is an excess of negative charge (see the above image).

2. **Prorate**: This option keeps the relative amount of the counter ions (for this example, the cations) the same and are adjusted up or down equally until reaching electroneutrality.

3. **Prorate Cations**: All cations are adjusted up or down equally

4. **Prorate Anions**: All anions are adjusted up or down equally

5. **Na+/Cl-**: Sodium is added when there is an excess of negative charge. Chloride is added when there is an excess of positive charge.

6. **Make-up Ion**: This option allows for a single ion species to be adjusted. User selects an ion to increase or decrease.

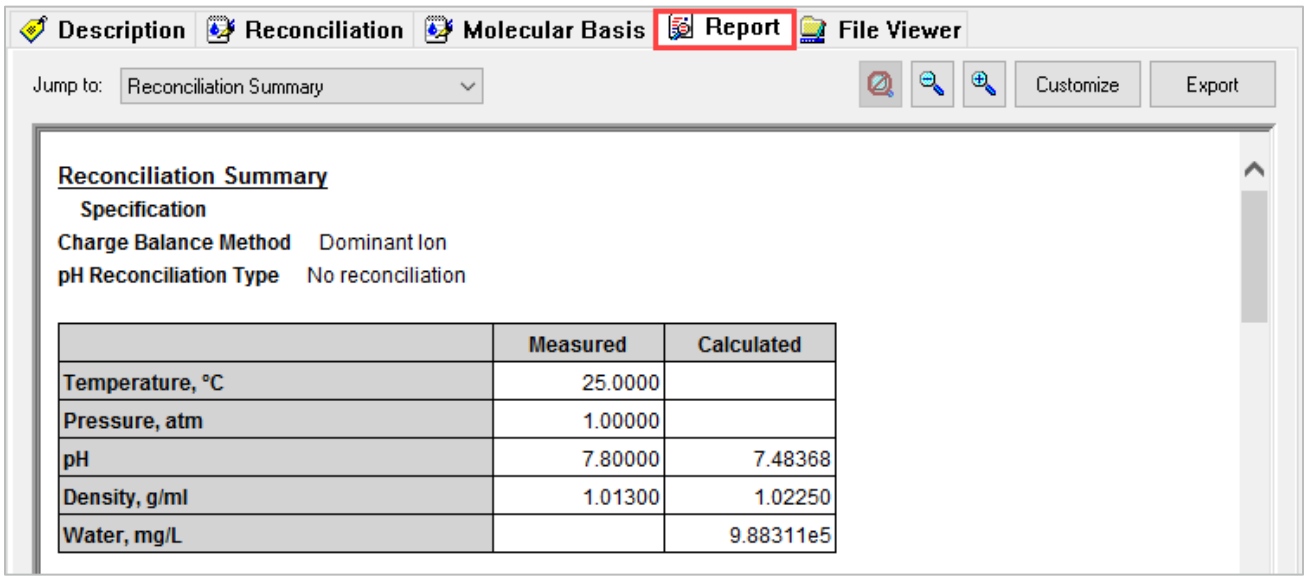
7. **User Choice**: The software determines if an anion or cation is needed to balance the solution and the user choses the specific ion.

10. Keep the default option, **Dominant Ion**, as the balance type then press **OK**
11. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
12. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named *Water Analysis Calculations*.

Analyzing the Results

Once you run the simulation there are two options to analyze the results: The summary box and the Report

1. Go to the **Report** Tab and look at the **Reconciliation Summary** Table.



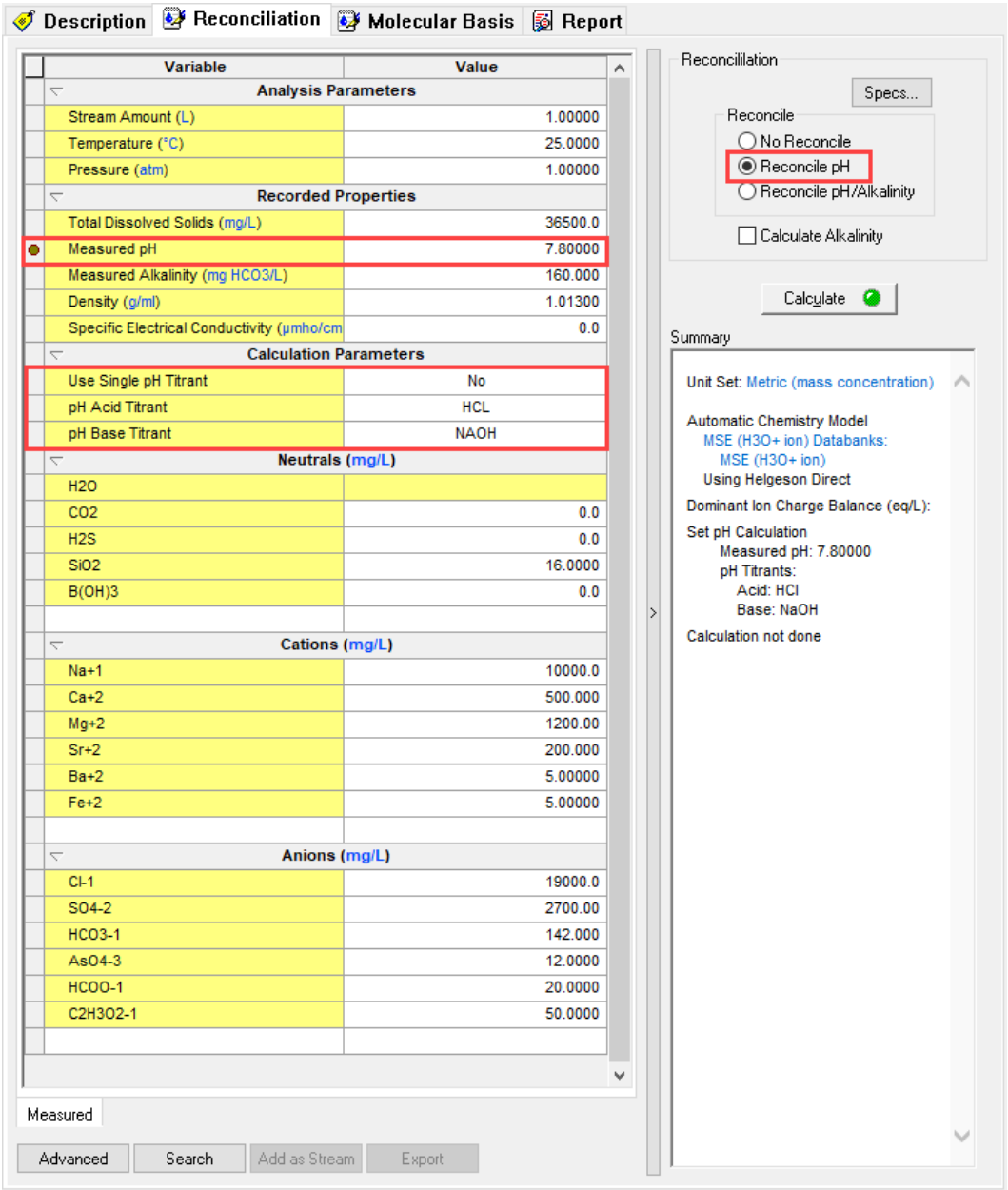
The calculated pH and density are different to the measured values. The software only used the concentration data to calculate these properties.

Example 30: Water Analysis – pH Reconcile Option

In this example we will reconcile the sample by **pH** and also calculate the **alkalinity** of the same Produced Water sample used in the previous Example 29: Water Analysis – No Reconcile Option.

Starting the Simulation

1. Under the *Water Analysis – Reconcile Options* Stream go to the **Add Reconciliation** button
2. **Click** on the new Reconcile-1 icon and press **<F2>** to change the name to *Reconcile pH*
3. The default units, names and framework have been previously defined
4. Select the **Reconcile pH** option

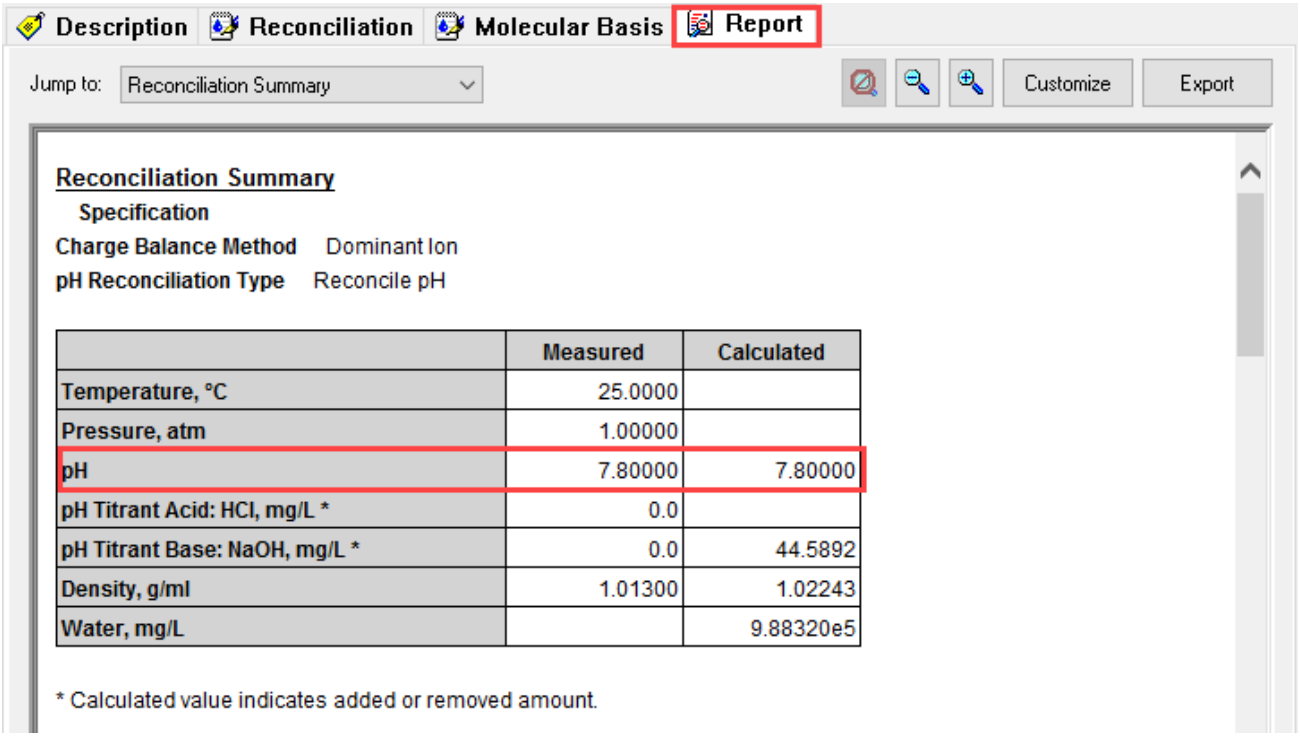


Note that by selecting the *Reconcile pH* option, now the measured pH is a fixed value (and brown dot appears in front of this cell). To match the measured pH, the software added a Calculation Parameters section which indicates the acid and basic pH titrants to adjust the pH. By default, HCl and NaOH are selected by the software. This is similar to the set pH single point calculation.

5. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
6. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named *Water Analysis Calculations*.

Analyzing the Results

1. Go to the **Report** Tab and look at the **Reconciliation Summary** Table.



The measured and calculated pH are the same. The software added 44.5892 mg/L of NaOH to match the experimentally measured pH.

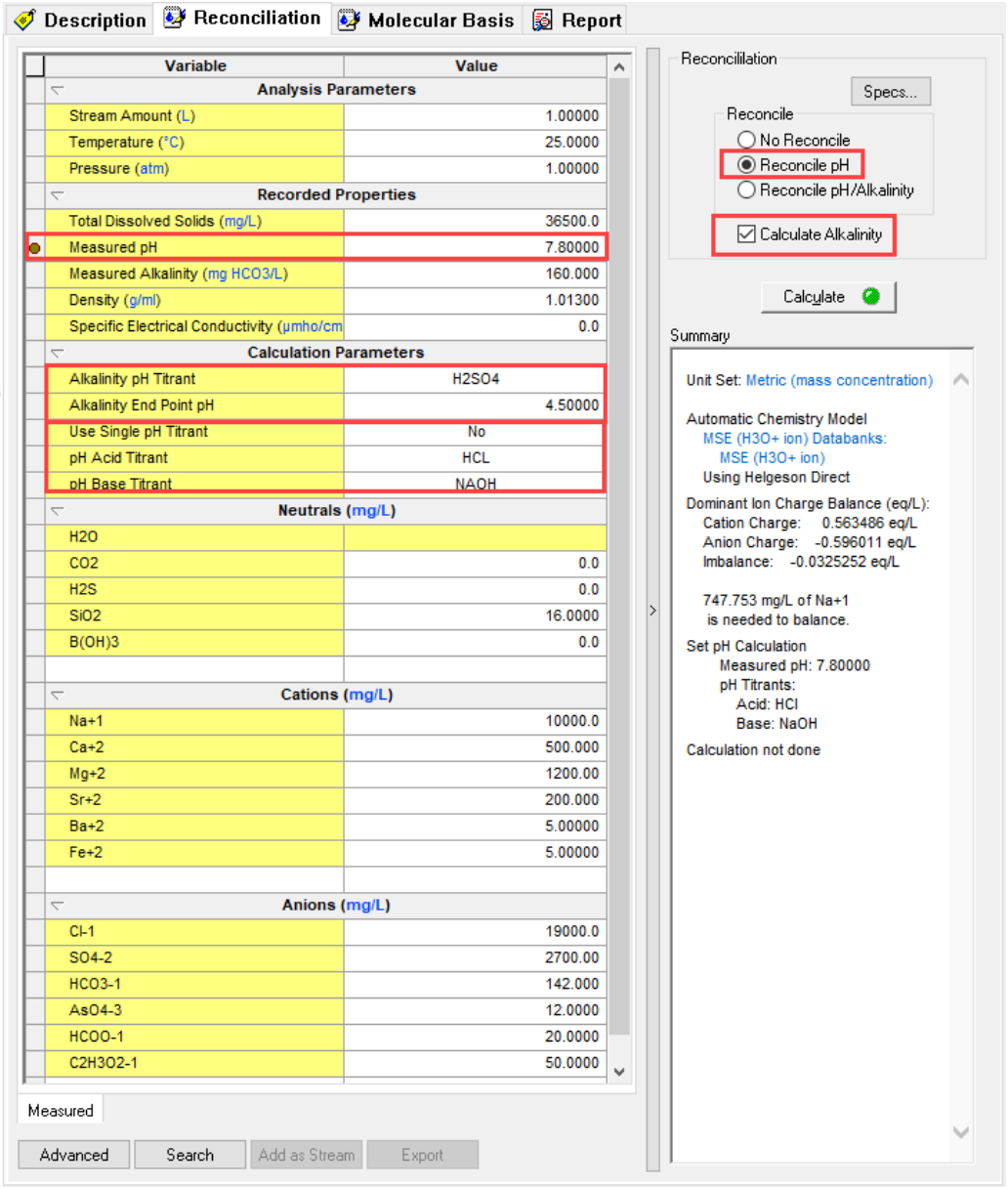
Calculating Alkalinity

Now we will instruct the software to calculate Alkalinity.

1. Go back to the **Reconciliation Tab** and check the **Calculate Alkalinity** box.

Alkalinity titrants

pH titrants

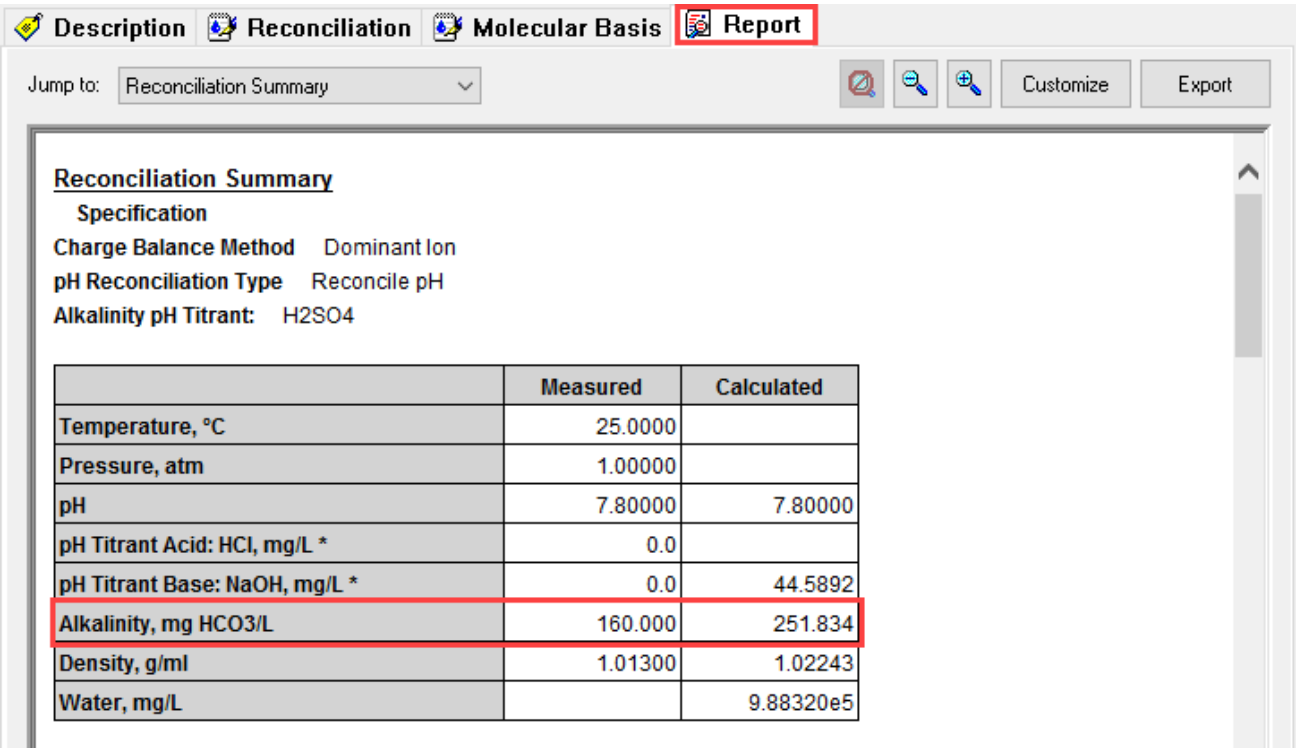


Notice that by selecting the Calculate Alkalinity box two more rows were added to the Calculation Parameters section: Alkalinity pH Titrant and Alkalinity End Point pH, besides the pH titrants rows. These two new rows indicate that the software will add H_2SO_4 (selected by default) until the pH reduces to 4.5. The software then converts the amount of additional H_2SO_4 into the alkalinity value.

2. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key.
3. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Analyzing the Results

1. Go to the **Report** Tab and look at the **Reconciliation Summary** Table.



	Measured	Calculated
Temperature, °C	25.0000	
Pressure, atm	1.00000	
pH	7.80000	7.80000
pH Titrant Acid: HCl, mg/L *	0.0	
pH Titrant Base: NaOH, mg/L *	0.0	44.5892
Alkalinity, mg HCO3/L	160.000	251.834
Density, g/ml	1.01300	1.02243
Water, mg/L		9.88320e5

The calculated alkalinity value is different to the measured value. This is because the software is not doing an alkalinity reconciliation, rather the software is using only the concentration data to calculate alkalinity. You can see this as single point alkalinity calculation.

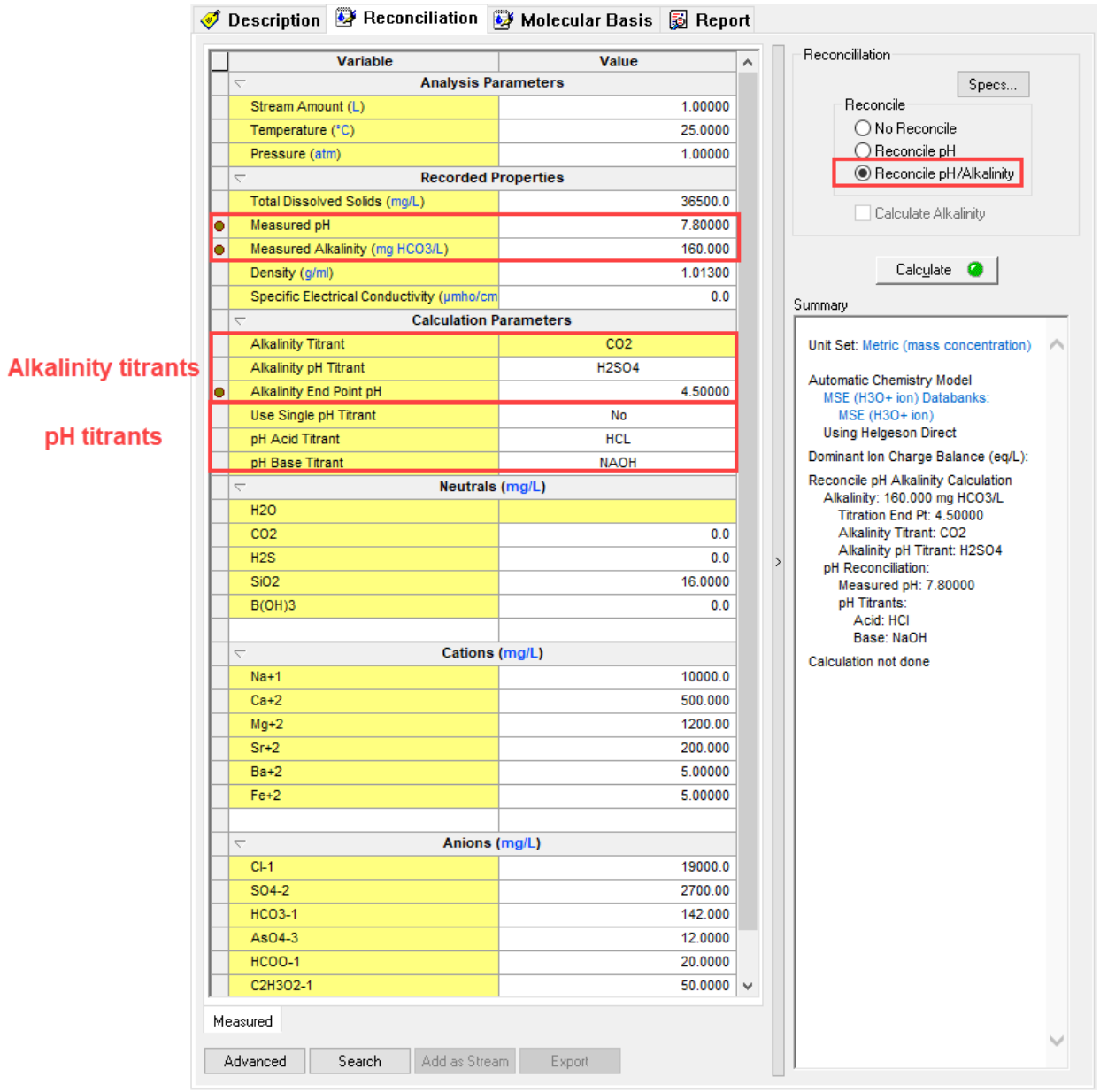
Note that in this example, the alkalinity being reported because we checked the **Calculate Alkalinity** box; if the box wasn't checked we would not see the calculated value in the Reconciliation Summary table.

Example 31: Water Analysis – Reconcile pH/Alkalinity Option

In this example we will reconcile the sample by **pH and alkalinity** and also calculate the **pre-scaling tendencies** of the same Produced Water sample used in the previous Example 29: Water Analysis – No Reconcile Option.

Starting the Simulation

1. Under the *Water Analysis – Reconcile Options* Stream go to the **Add Reconciliation** button
2. **Click** on the new Reconcile-1 icon and press **<F2>** to change the name to *Reconcile pH*
3. The default units, names and framework have been previously defined
4. Select the **Reconcile pH/Alkalinity** option



Note that by selecting the *Reconcile pH/Alkalinity* option, now both the measured pH and alkalinity values are fixed values (and brown dot appears in front of this cell).

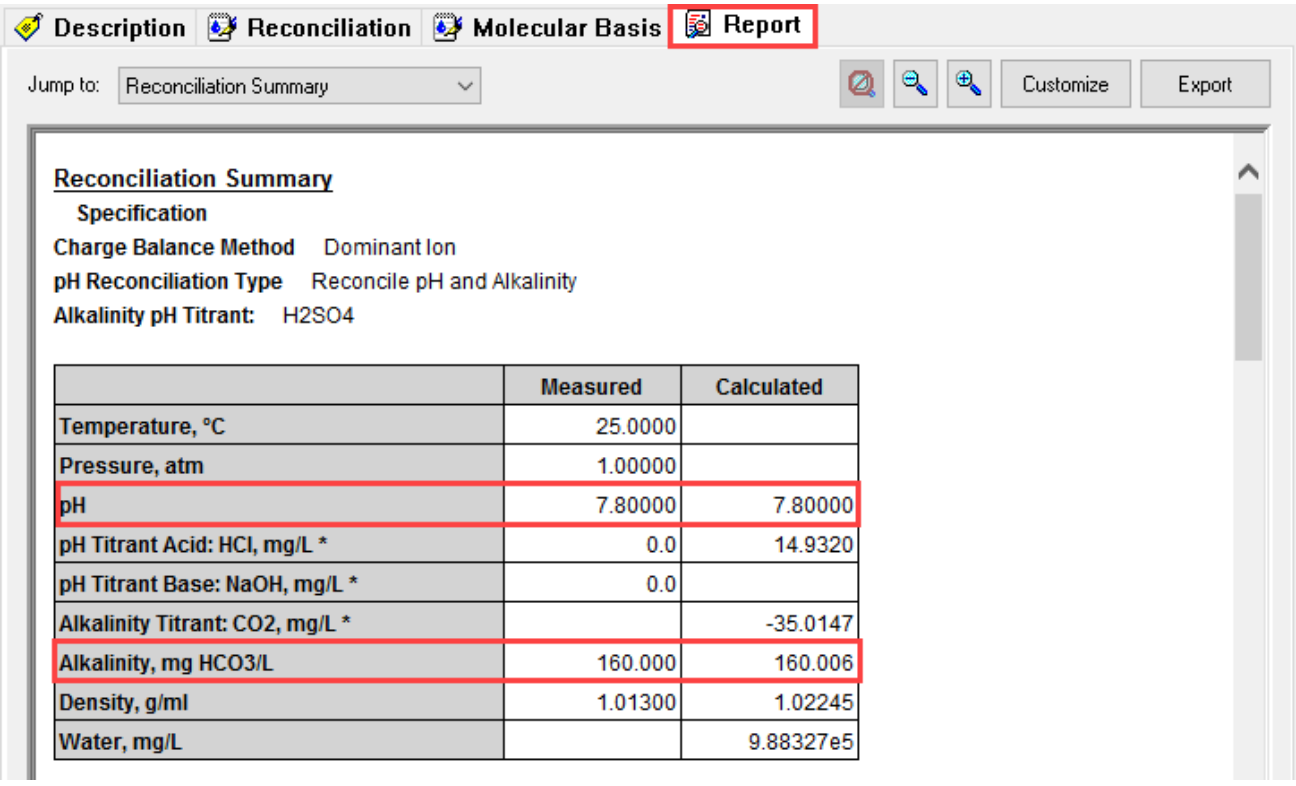
To match the measured alkalinity value, the software added a **Calculation Parameters** section which indicates the alkalinity titrant and the pH titrant used to adjust the alkalinity. CO2 is used by default as the alkalinity titrant. This is similar to an *alkalinity* single point calculation.

To match the measured pH, the software also added a **Calculation Parameters** section which indicates the acid and basic pH titrants to adjust the pH. By default, HCl and NaOH are selected by the software. This is similar to the *set pH* single point calculation. Also notice that the alkalinity box is grayed out. This is because we have asked the software to match the measured alkalinity value. This means that calculated alkalinity value is no longer needed.

7. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
8. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named *Water Analysis Calculations*.

Analyzing the Results

1. Go to the **Report** Tab and look at the **Reconciliation Summary** Table.



Reconciliation Summary

Specification

Charge Balance Method Dominant Ion
pH Reconciliation Type Reconcile pH and Alkalinity
Alkalinity pH Titrant: H2SO4

	Measured	Calculated
Temperature, °C	25.0000	
Pressure, atm	1.00000	
pH	7.80000	7.80000
pH Titrant Acid: HCl, mg/L *	0.0	14.9320
pH Titrant Base: NaOH, mg/L *	0.0	
Alkalinity Titrant: CO2, mg/L *		-35.0147
Alkalinity, mg HCO3/L	160.000	160.006
Density, g/ml	1.01300	1.02245
Water, mg/L		9.88327e5

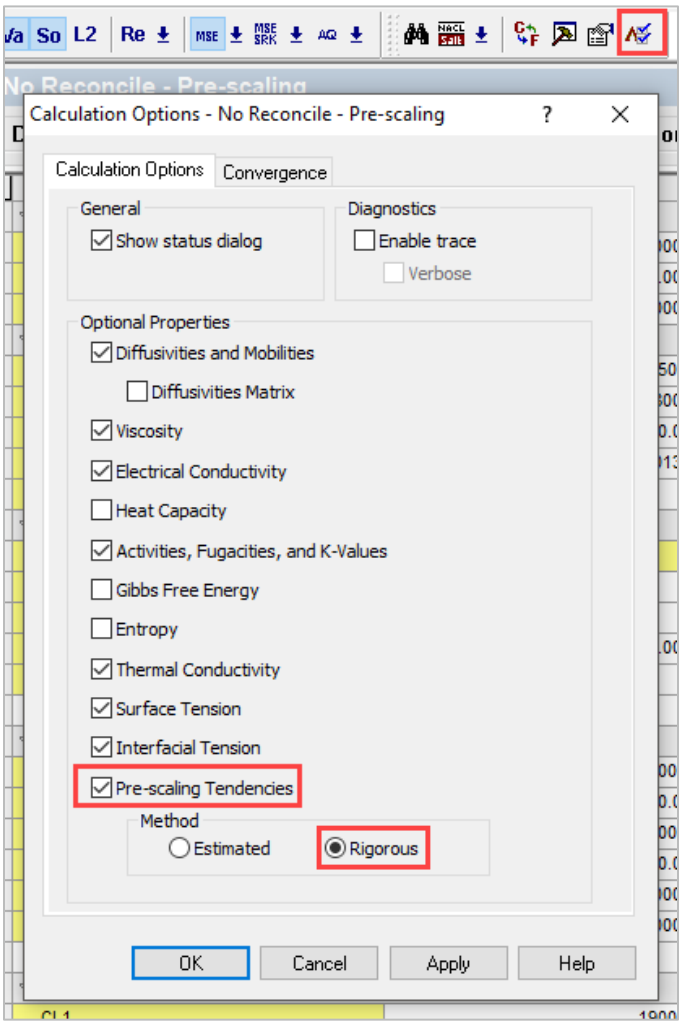
The measured and calculated pH and alkalinity values are the same. The software added 14.9320 mg/L of HCl to match the experimentally measured pH and removed 35.0147 mg/L of CO2 to match the experimentally measured alkalinity value.

Calculating Pre-scaling Tendencies

Now we will instruct the software to calculate Pre-scaling tendencies. In OLI Analyzer: Stream Analyzer, Pre-scaling tendencies are turned OFF by default. We need to enable this option.

Setting the Water Analysis

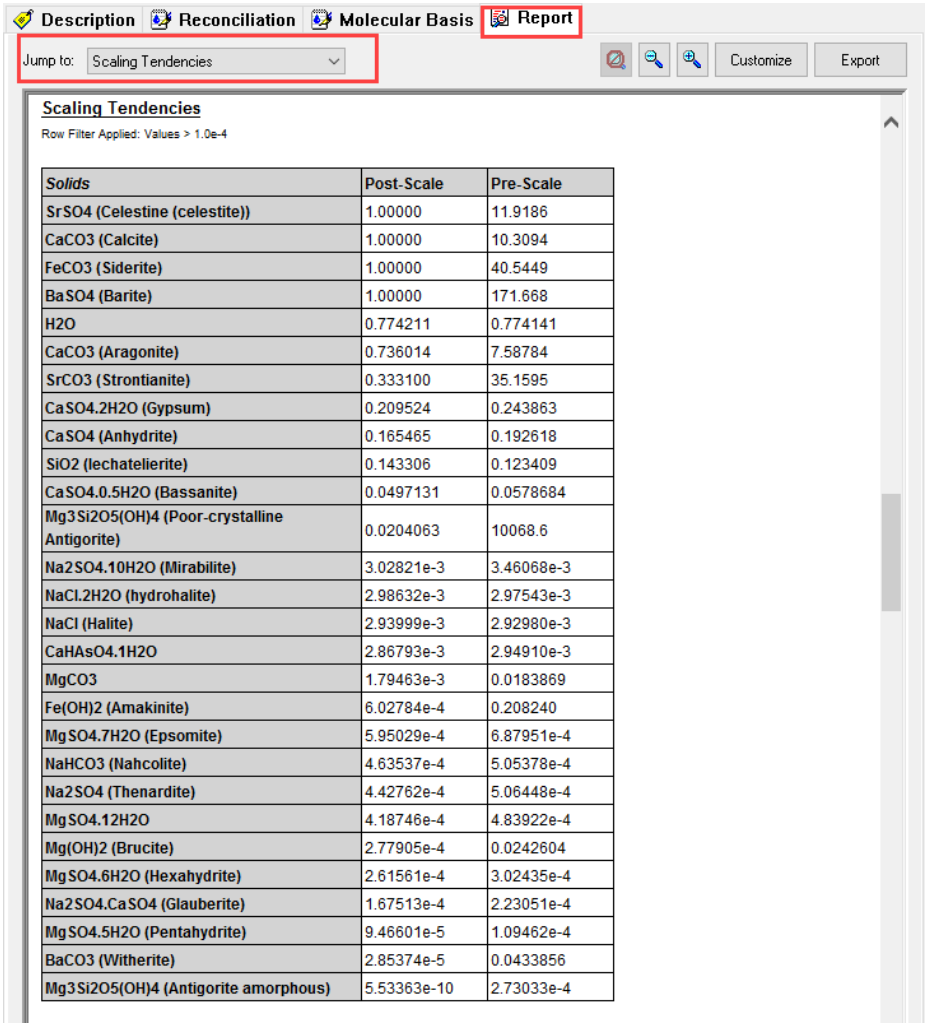
1. Go back to the **Reconciliation** tab of the *Reconcile pH/Alkalinity* water analysis
2. Click on the **Calculation Options** icon . This will open the Calculation Options window.
3. Check the **Pre-scaling Tendencies** box and select the **Rigorous method**. Then click **OK**.



4. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
5. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Analyzing the Results

1. Go to the **Report** Tab and search for the **Scaling Tendencies** Table.



Scaling Tendencies

Row Filter Applied: Values > 1.0e-4

Solids	Post-Scale	Pre-Scale
SrSO4 (Celestine (celestite))	1.00000	11.9186
CaCO3 (Calcite)	1.00000	10.3094
FeCO3 (Siderite)	1.00000	40.5449
BaSO4 (Barite)	1.00000	171.668
H2O	0.774211	0.774141
CaCO3 (Aragonite)	0.736014	7.58784
SrCO3 (Strontianite)	0.333100	35.1595
CaSO4.2H2O (Gypsum)	0.209524	0.243863
CaSO4 (Anhydrite)	0.165465	0.192618
SiO2 (lechatelierite)	0.143306	0.123409
CaSO4.0.5H2O (Bassanite)	0.0497131	0.0578684
Mg3Si2O5(OH)4 (Poor-crystalline Antigorite)	0.0204063	10068.6
Na2SO4.10H2O (Mirabilite)	3.02821e-3	3.46068e-3
NaCl.2H2O (hydrohalite)	2.98632e-3	2.97543e-3
NaCl (Halite)	2.93999e-3	2.92980e-3
CaHAsO4.1H2O	2.86793e-3	2.94910e-3
MgCO3	1.79463e-3	0.0183869
Fe(OH)2 (Amakinite)	6.02784e-4	0.208240
MgSO4.7H2O (Epsomite)	5.95029e-4	6.87951e-4
NaHCO3 (Nahcolite)	4.63537e-4	5.05378e-4
Na2SO4 (Thenardite)	4.42762e-4	5.06448e-4
MgSO4.12H2O	4.18746e-4	4.83922e-4
Mg(OH)2 (Brucite)	2.77905e-4	0.0242604
MgSO4.6H2O (Hexahydrite)	2.61561e-4	3.02435e-4
Na2SO4.CaSO4 (Glauberite)	1.67513e-4	2.23051e-4
MgSO4.5H2O (Pentahydrite)	9.46601e-5	1.09462e-4
BaCO3 (Witherite)	2.85374e-5	0.0433856
Mg3Si2O5(OH)4 (Antigorite amorphous)	5.53363e-10	2.73033e-4

This table reports both the Post-Scale and Pre-scale Tendencies. See the section 3.1 Basic Terminology to see a more detailed explanation.

The Scaling Tendencies (reported in the software as **Post-Scale**), are essentially saturation ratios. When the scaling tendency for a given mineral is equal to 1.0 (saturation conditions) it indicates that the mineral is in equilibrium with water, a solid phase has formed. A scaling tendency below 1.0 indicates sub-saturation and that the solid phase will not form. A solid is at risk of forming when the scale tendency value is greater than 1.0 (supersaturation conditions).

The Pre-Scaling Tendencies (reported in the software as **Pre-Scale**), is defined as the scaling tendency before any solids are formed (this can be seen as all the species suspended in solution).

Note: The Post-Scale and the Pre-Scale tendencies are equivalent if the solid phase is turned OFF.

Section 4. Hydrocarbons and Pseudocomponents

So far, we have learned how to enter molecular and ionic inflows in Stream Analyzer. Stream Analyzer also allows you to enter assays or pseudocomponents in order to crude oils as streams.

Crude oils are complex groups of organic molecules containing hundreds, perhaps thousands of pure components in a single oil. Modeling crude oils using pure components is impractical, because analyzing for each pure component is cost prohibitive and the number of species would make calculations overwhelming. A convenient solution to this problem and to modeling the properties of a crude oil is to create pseudo components.

Crude Oil properties may be defined through a distillation curve, where each boiling point range is a progression of molecular weights, densities, solubilities, viscosities and other properties associated with that section. It is reasonable for low boiling point molecules to be low molecular weight, low density, low viscosity, and more soluble in water. We can dice boiling point curves using well accepted methods standard to create pseudocomponents that in combination reflect the property of the whole oil.

There are two ways to create a crude oil stream on Stream Analyzer:

1. The first is to start with a PVT curve and create pseudocomponents using one of the three thermodynamic methods coded into the software.

2. The second is to enter the pseudocomponent data directly and using the same thermodynamic methods to predict the component properties.

The three thermodynamic methods are: API, Lee Kesler, and Cavett. More details about this method can be found in Section 10. .

A brief introduction of how to enter PVT curves and/or pseudocomponents will be shown in the examples below.

4.1. Entering a PVT Analysis

Example 32: Creating an Assay

In this example, we are going to learn how to enter a simple PVT analysis in order to create a *Crude Oil* Stream.

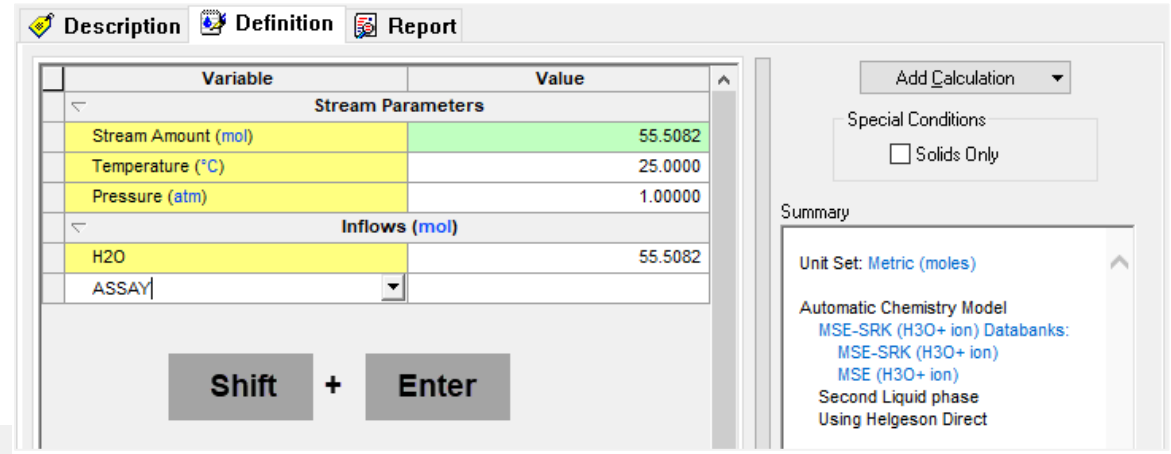
Starting the Simulation

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Crude Oil*
3. Select the **MSE-SRK** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. **Enter** the conditions of the Stream T= 25 ºC and 1 atm

Crude Oil Stream			
Calculation Settings		**Conditions**	
Stream Name	Crude Oil	Stream Amount	Default
Name Style	Display Formula	Temperature	25 ºC
Unit Set	Metric, Moles	Pressure	1 atm
Framework	MSE-SRK		

7. In the inflows grid, in the white cell below H2O, type ASSAY and then press **<Shift + Enter>.** You can assign other name to your Assay; however, you are limited to 5 characters for the name of the Assay.

   Note: The <Shift + Enter> action instructs the software to create an Assay rather than look for a species or pure component from the database.

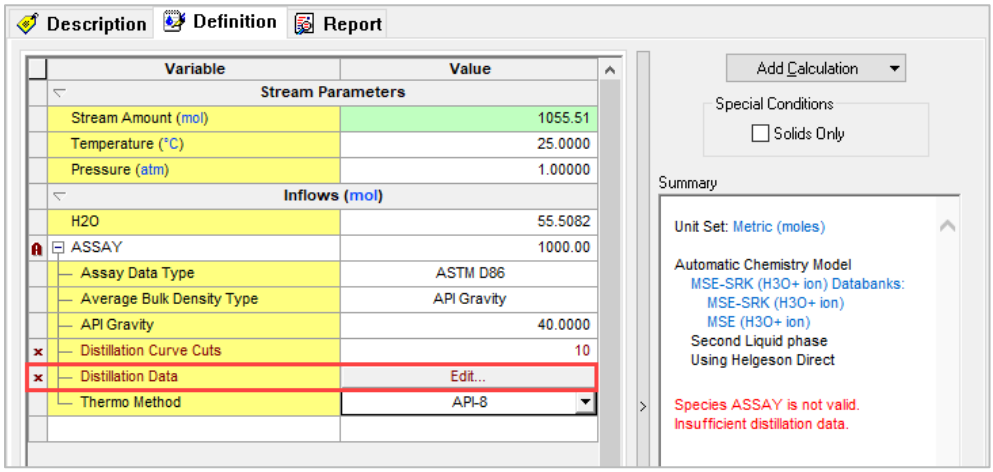


Note: After typing the name of your Assay, immediately press Shift + Enter command keys together.

8. Use the information provided in the table below to complete the grid.

Assay Information			
Calculation Settings		**Distillation Data**	
Assay amount	1000 moles	**Percent Distilled**	**Temperature, ºC**
Assay Data Type	ASTM D86	1	20
Average Bulk Density Type	API Gravity	5	30
API Gravity	40	10	50
Distillation Curve Cuts	10	20	60
Distillation Data	See next two columns	40	80
Thermo Method	API-8	60	120
		80	150
		90	180
		95	200
		99	220
		100	240

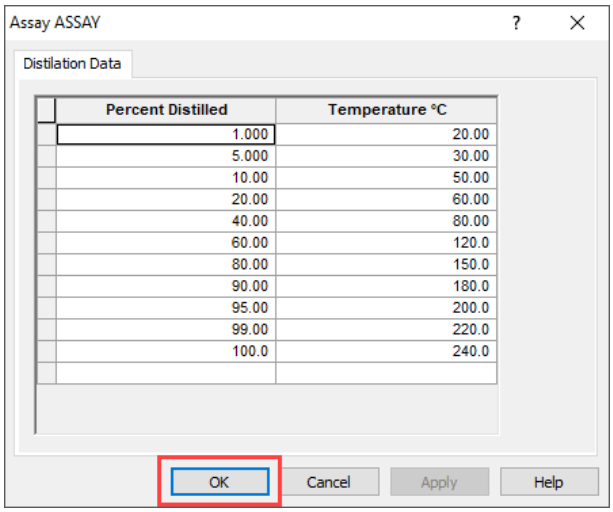
Your screen should look like the image below:



Note: You can change the Assay Data Type, the Average Bulk Density Type and the Thermo Method options by clicking on the white cells. This will enable a drop-down arrow that will show you the different options.

9. Click on the **Edit** button next to the Distillation Data. This will open a new window. Complete the Distillation Data using the information given in the table above. Then click **OK**.

   Note: Ctrl+C and then Ctrl+V can be used to copy and paste the data in the Distillation Data table.



The Distillation Curve Cuts will eventually become individual pseudocomponents, each with its own critical parameters and thermodynamic reference data.

10. At this point we are ready to perform a calculation. **Add** a **Single Point** calculation, and then select an **Isothermal** calculation.
11. Change the ***SinglePoint*** name to ***Assay*** using the **<F2>** key
12. **Click** on the **Calculate** button or press the **<F9>** key to run the simulation
13. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Save the calculations of this section under the name *Hydrocarbons and Pseudocomponents.*

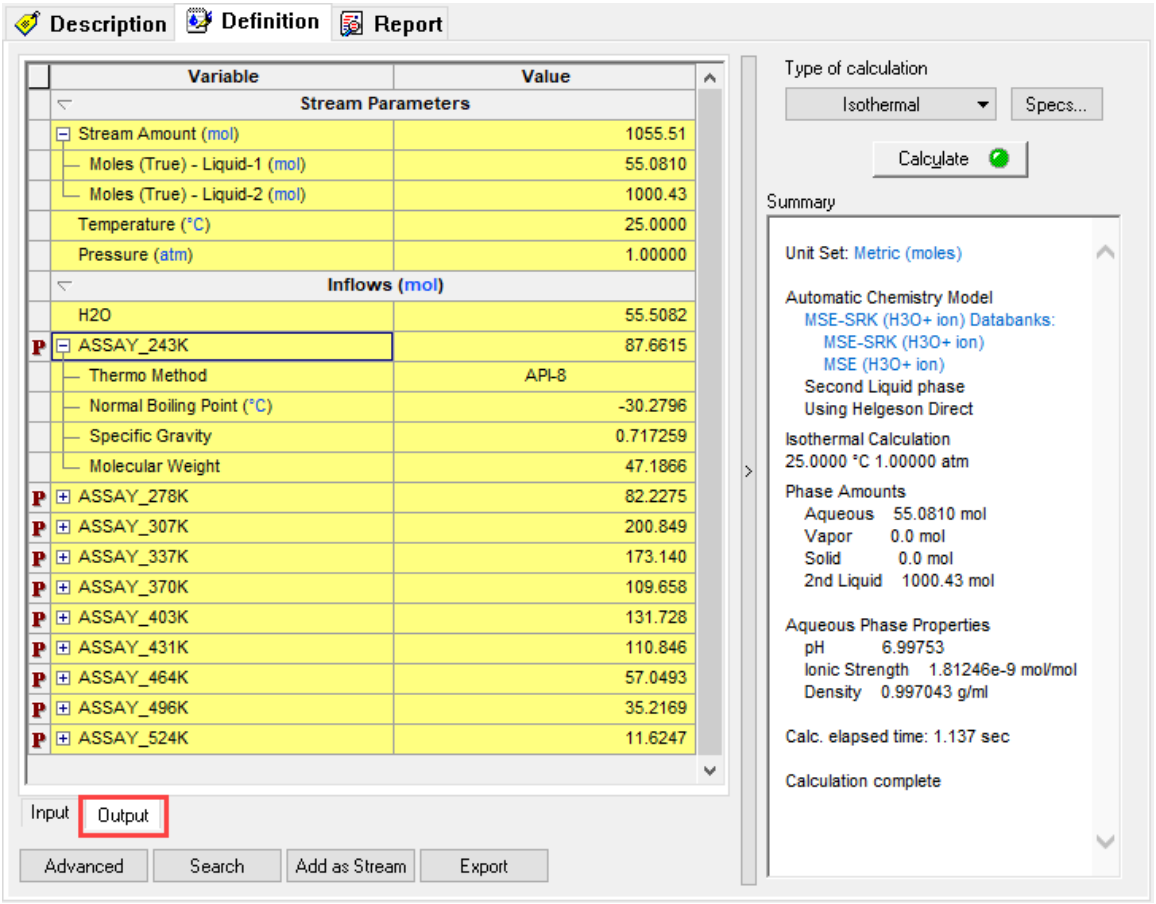
Analyzing the Results

We will review the results first in the Output Tab and the in the Report Tab.

1. Click on the **Output Tab**

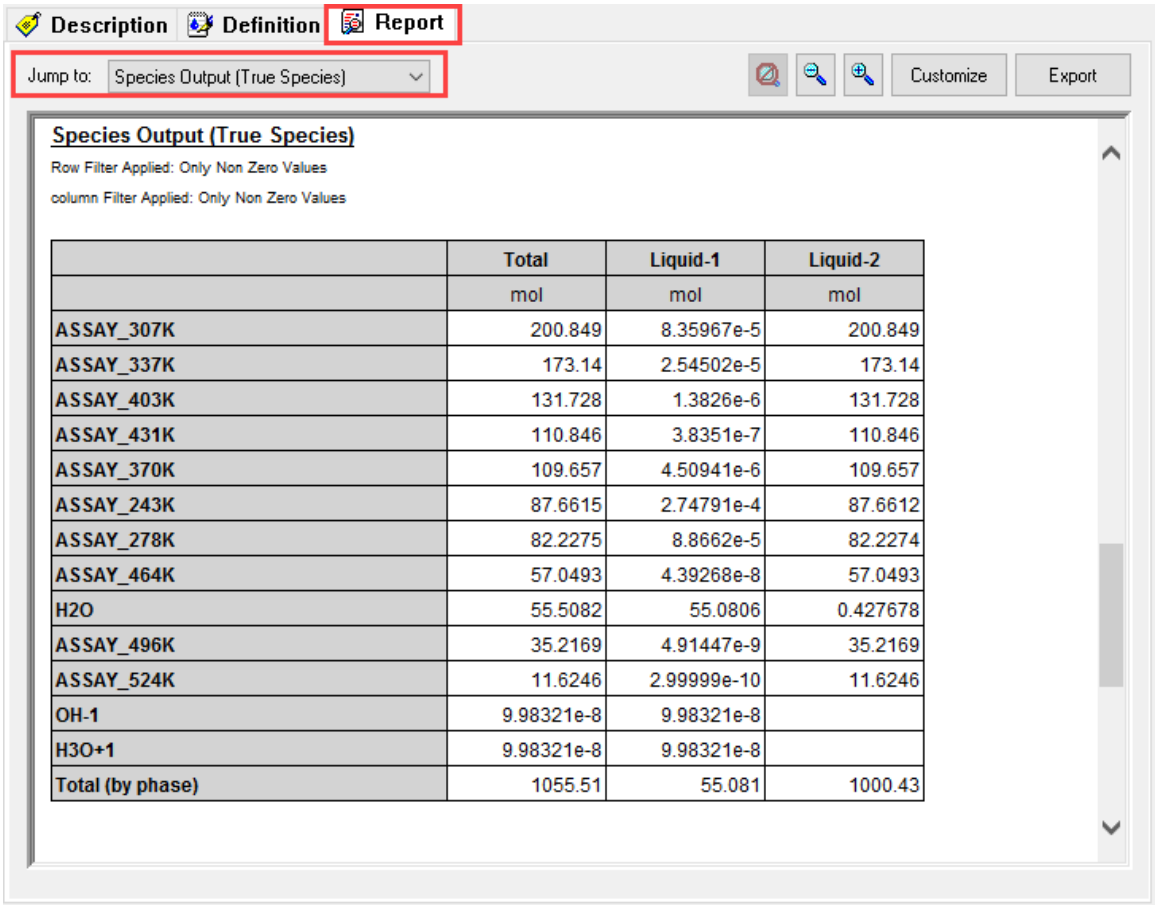
   The Output Tab shows a grid with 10 different pseudocomponents, identified with the letter P, corresponding to each distillation cut of the crude. Notice that the name of each cut is the combination of the oil name (ASSAY for this example) plus its boiling point in K.

   The '+' sign adjacent to each Assay expands a sub-table that contains the critical properties of each cut. These properties are: Normal boiling point, density and molecular weight.



2. Click on the **Report Tab and** scroll down to the **Species Output** table.

This table shows how the pseudocomponents are distributed between the Liquid-1 and Liquid-2 phases. Notice how the Liquid-1 (or aqueous) solubility decreases with each increasing boiling point.



Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Liquid-2
	mol	mol	mol
ASSAY_307K	200.849	8.35967e-5	200.849
ASSAY_337K	173.14	2.54502e-5	173.14
ASSAY_403K	131.728	1.3826e-6	131.728
ASSAY_431K	110.846	3.8351e-7	110.846
ASSAY_370K	109.657	4.50941e-6	109.657
ASSAY_243K	87.6615	2.74791e-4	87.6612
ASSAY_278K	82.2275	8.8662e-5	82.2274
ASSAY_464K	57.0493	4.39268e-8	57.0493
H2O	55.5082	55.0806	0.427678
ASSAY_496K	35.2169	4.91447e-9	35.2169
ASSAY_524K	11.6246	2.99999e-10	11.6246
OH-1	9.98321e-8	9.98321e-8	
H3O+1	9.98321e-8	9.98321e-8	
Total (by phase)	1055.51	55.081	1000.43

4.2. Entering Pseudocomponents to a Stream

There are times when the user does not have (or does not want to use) distillation data. Rather the user had the individual properties for a single pseudocomponent. OLI allows the user to enter the individual pseudocomponents. In the following example we will illustrate how.

Example 33: Creating Pseudocomponents

In this example, we will enter two properties - boiling point and density. The software will use one of four thermodynamic models – API-8, API-5, Cavett or Kessler-Lee – to calculate critical properties of pseudocomponents.

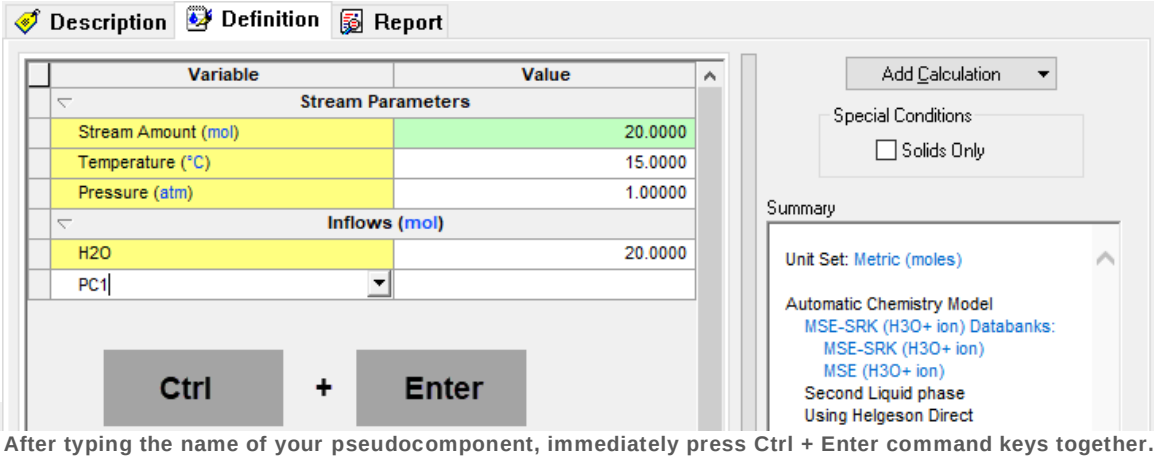
Starting the Simulation

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Crude Oil - Pseudocomponents*
3. Select the **MSE-SRK** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. **Enter** the conditions of the Stream T= 15 ºC and 1 atm
7. **Change** H2O from the default value to 20 moles

Crude Oil Stream			
Calculation Settings		**Conditions**	
Stream Name	Crude Oil - Pseudocomponents	Stream Amount	Calculated
Name Style	Display Formula	Temperature	15 ºC
Unit Set	Metric, Moles	Pressure	1 atm
Framework	MSE-SRK	H2O	20 moles

8. In the inflows grid, in the white cell below H2O, type PC1 and then press **<Crtl + Enter>**

Note: The <Crtl + Enter> action instructs the software to create an pseudocomponent rather than look for a species or pure component from the database.

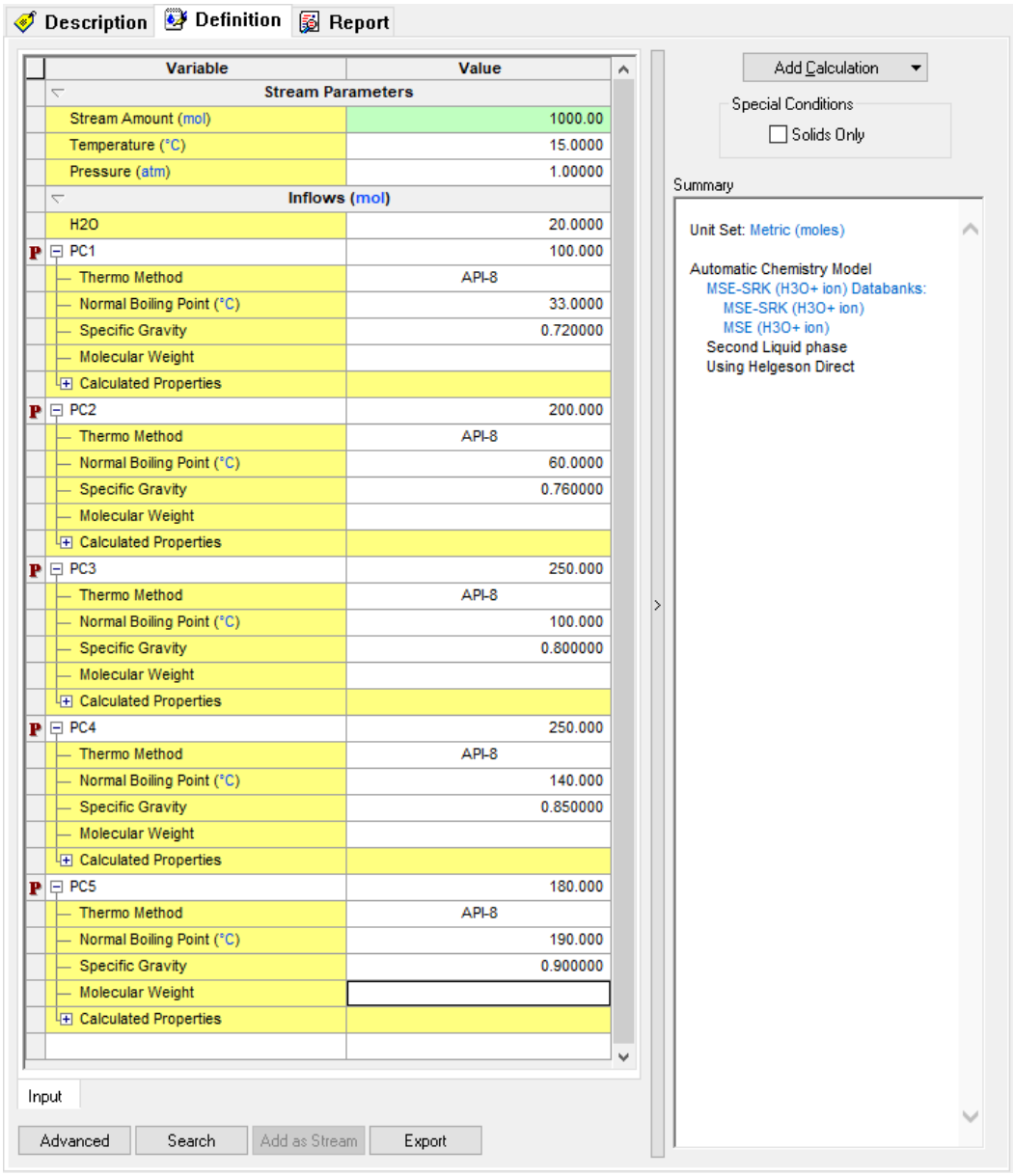


Note: After typing the name of your pseudocomponent, immediately press Ctrl + Enter command keys together.

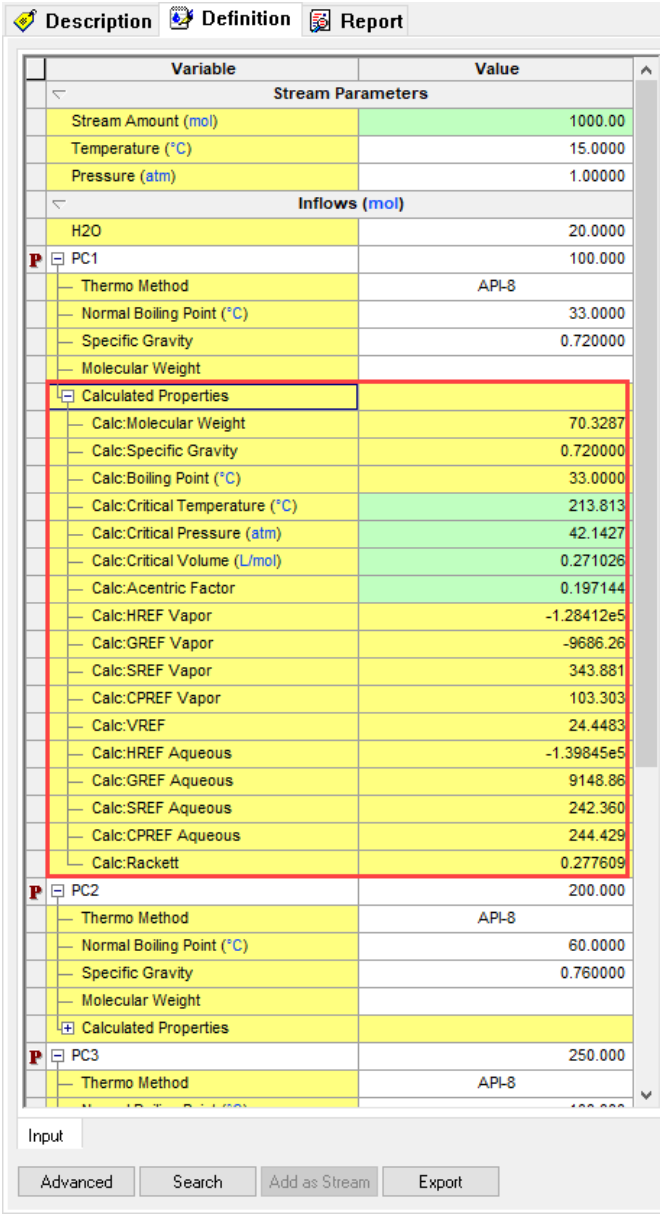
9. Repeat step 8 four more time with the following names: PC2, PC3, PC4 and PC5. Use the information provided in the table below to complete the grid. The molecular weight will be calculated by the software. In general, only two of the three parameters need be entered.

Pseudocomponents Information					
Pseudocomponent name	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**
Inflow (moles)	100	200	250	250	180
Thermo Method	API-8	API-8	API-8	API-8	API-8
Boiling Point (ºC)	33	60	100	140	190
Specific Gravity	0.72	0.76	0.8	0.85	0.9

Your screen should look like the image below:



Notice that at the bottom of each pseudocomponent there is a "+" and a field called calculated properties. Stream Analyzer immediately predicts all the calculated properties for each pseudocomponent. Click the "+" sign next to PC1 to expand and see these properties.



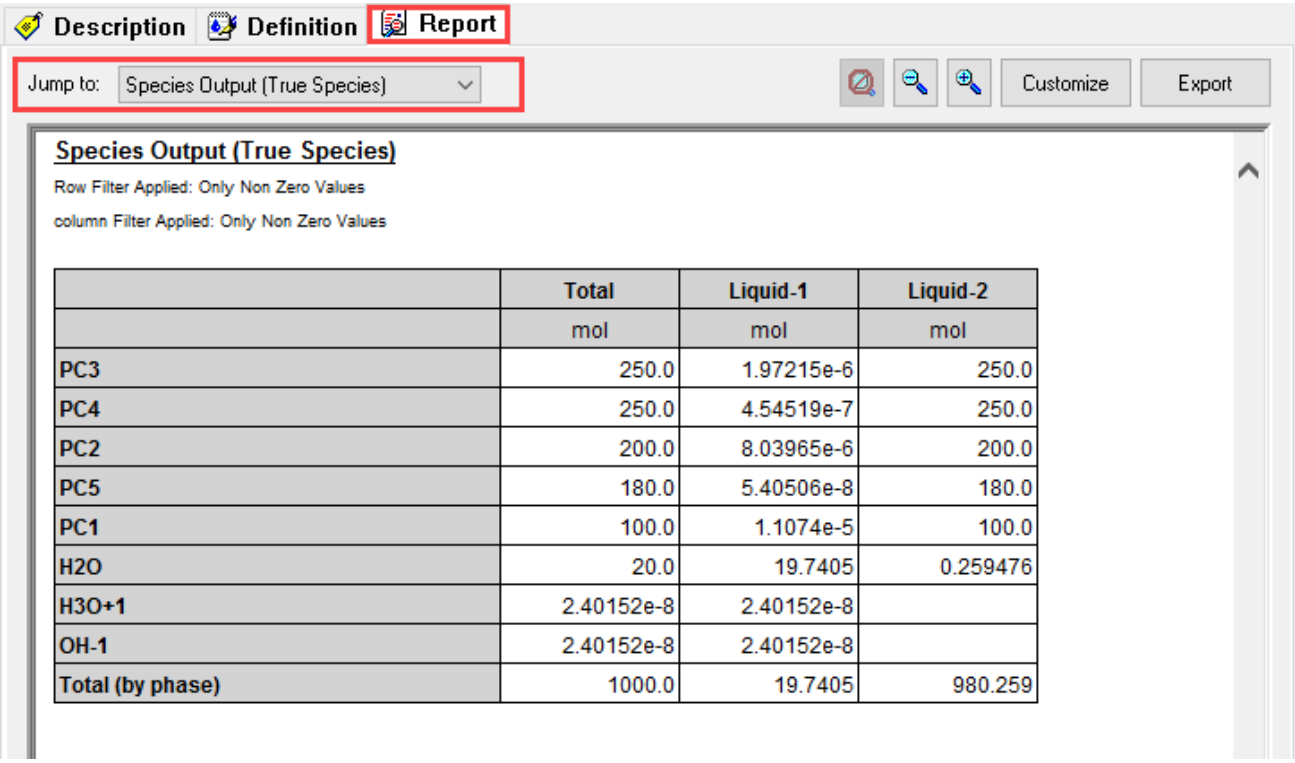
The values in the green boxes can be changed to match data from other programs.

10. At this point we are ready to perform a calculation. **Add** a **Single Point** calculation, and then select an **Isothermal** calculation.
11. Change the ***SinglePoint*** name to ***Pseudocomponents*** using the **<F2>** key
12. **Click** on the **Calculate** button or press the **<F9>** key to run the simulation
13. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Save the calculations of this section under the name *Hydrocarbons and Pseudocomponents.*

Analyzing the Results

1. Click on the **Report Tab and** scroll down to the **Species Output** table.

This table shows how the pseudocomponents are distributed between the Liquid-1 and Liquid-2 phases.



Species Output (True Species)

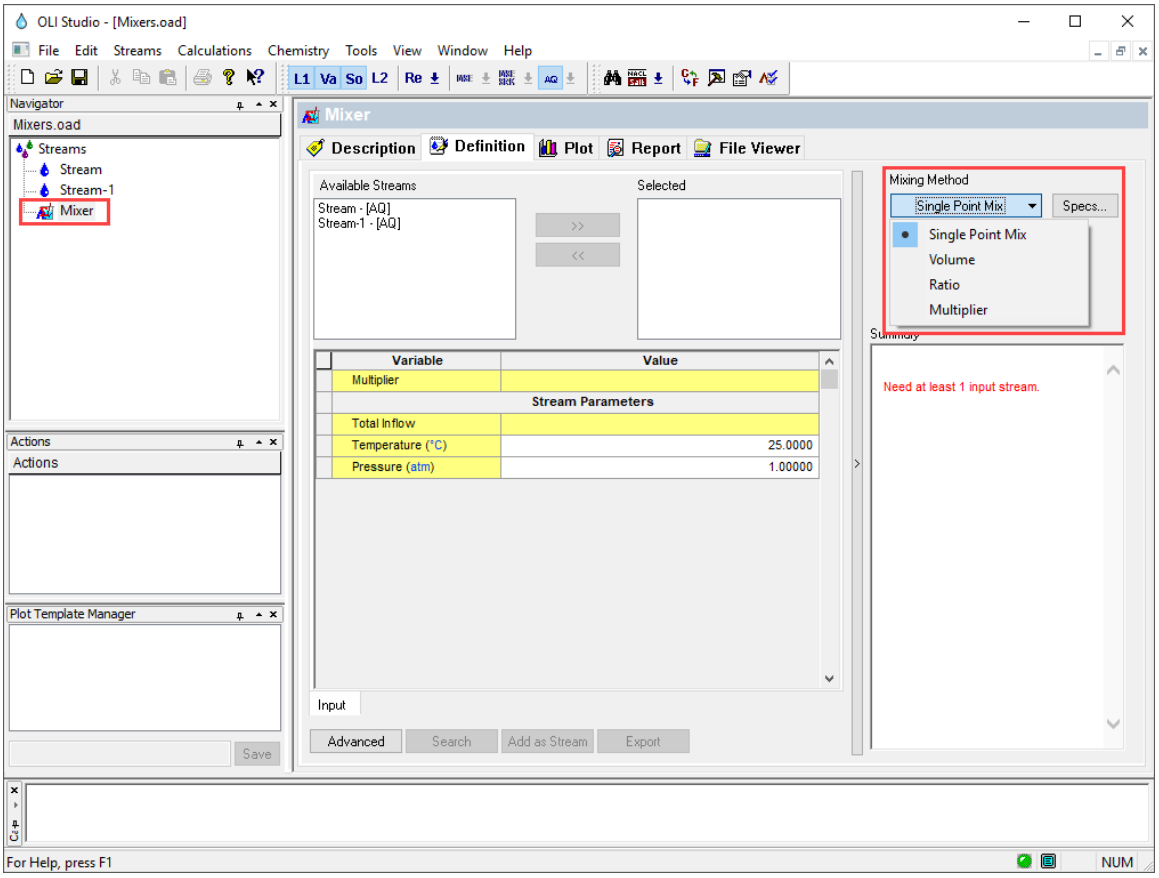
Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Liquid-2
	mol	mol	mol
PC3	250.0	1.97215e-6	250.0
PC4	250.0	4.54519e-7	250.0
PC2	200.0	8.03965e-6	200.0
PC5	180.0	5.40506e-8	180.0
PC1	100.0	1.1074e-5	100.0
H2O	20.0	19.7405	0.259476
H3O+1	2.40152e-8	2.40152e-8	
OH-1	2.40152e-8	2.40152e-8	
Total (by phase)	1000.0	19.7405	980.259

Section 5. Mixers

Mixers are a useful tool to mix one or more streams. This tool allows you to mix Molecular Streams or Reconciled Streams.



In this section, you will learn how to set up a **Mixer** and differentiate the different mixing options to get the most out of your simulation results.

5.1. Mixing Options (Definitions)

The Mixer Object has four different mixing options: Single point mix, Volume, Ratio, and Multiplier. A quick summary of what each mixing options allows you to do is summarized here.

Single Point Mix

This option allows you to multiply up or down a stream inflow. When selecting the streams to mix, this option will enable the multiplier option for both streams. You can leave the default values that are set by default to 1.0 or change the multiplier values to any other number.

Volume

In this option, one stream stays at a constant volume, while the other stream's volume changes within a range specified by the user, as is illustrated in the table below:

Stream 1	Stream 2
1 L	1 L
1 L	2 L
…	…
1 L	n L

Ratio

In the ratio mixing type, both streams change at the same time. For example, stream will be 100% and Stream will be 0%, then Stream 1 will be 90% and Stream 2 will be 10%, and so on, until it reaches Stream 1 0% and Stream 2 100%.

Stream 1	Stream 2
100 %	0 %
90 %	10%
…	…
0 %	100 %

Multiplier

In this mixing option, one stream stays constant, while the other stream changes using a multiplier. The range of the multiplier values is given by the user.

Stream 1	Stream 2
1	Stream 2 × 0
1	Stream 2 × 1
…	…
1	Stream 2 × n

5.2. A Basic Mixer Calculation

A brief introduction to the Mixer tool will be shown in the example below. As we go through the example, basic definitions, functionalities and reporting for the *Mixer tool* will be introduced.

Example 34: Calculating the Heat of Mixing

You will mix 1 L of a 10 wt% $Ca(OH)_2$ solution with 1 L of a 10% HCl solution, and then you will ask the software to calculate the **heat of mixing** and **the final temperature** of the mixture.

Starting the Simulation

In this example we need to create two different streams: a 10 wt% $Ca(OH)_2$ solution and a 10% HCl solution.

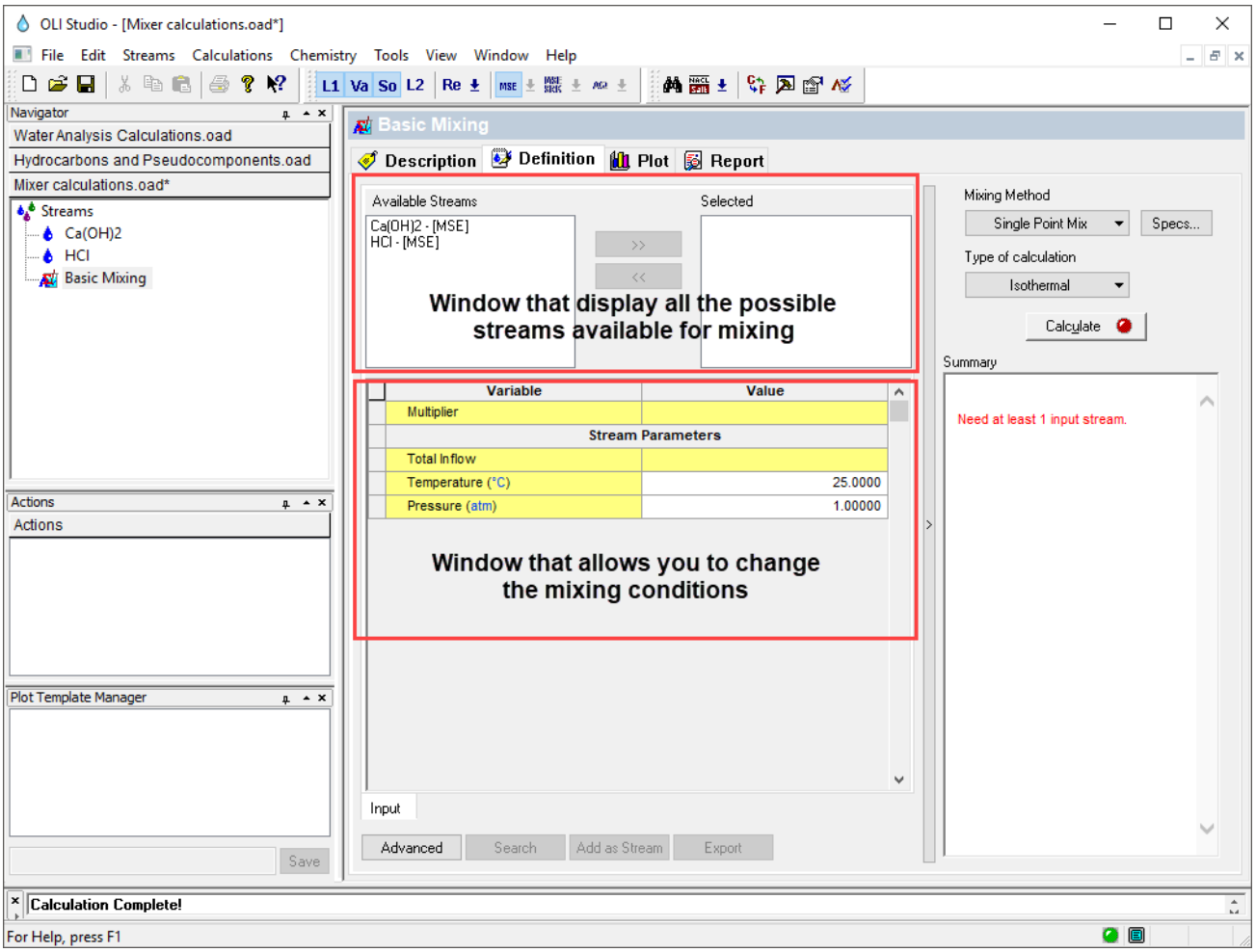
Use the inputs and parameters from the table below to create each stream. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Basic Mixing Calculation			
1st Stream		**2nd Stream**	
Stream Name	Ca(OH)2	Stream Name	HCl
Name Style	Display Formula	Name Style	Display Formula
Unit Set	Metric, Batch, Mass Frac.	Unit Set	Metric, Batch, Mass Frac.
Framework	MSE	Framework	MSE
Stream Amount	1 kg	Stream Amount	1 kg
Temperature	25 ºC	Temperature	25 ºC
Pressure	1 atm	Pressure	1 atm
H2O	Calculated	H2O	Calculated
Ca(OH)2	10 mass%	HCl	10 mass%

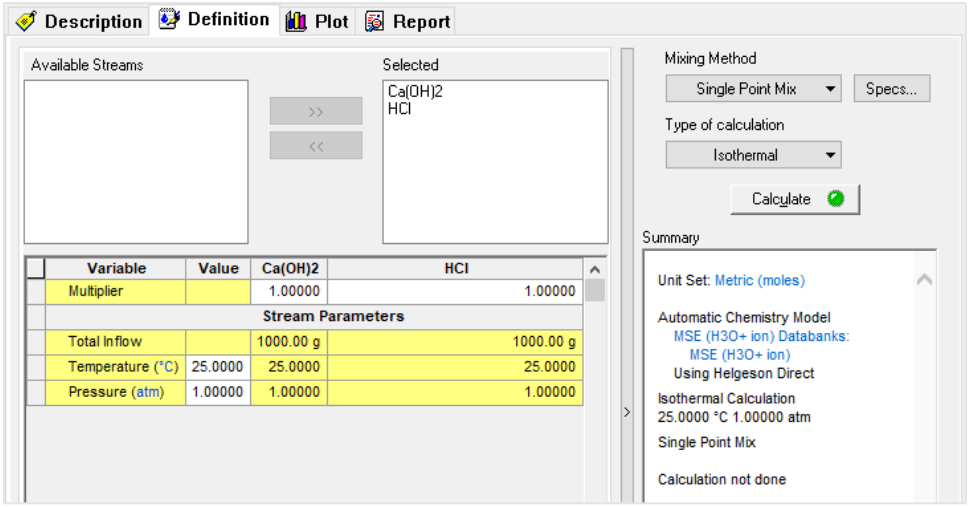
1. After creating the streams, **Add a Mixer.** The Mixer object can be accessed from the Menu Bar by selecting Calculations > **Add Mixer** or by selecting the **Add Mixer** in the Actions Pane.
2. Press **<F2>** to rename the mixer to *Basic Mixing*

Notice that the display layout for the Mixer tool is slightly different. There are two different windows (see image below).

- The first window displays all possible streams available for the mix calculation. There is no limit to the number of streams to be mixed.
- The second window allows you to change the mixing conditions, e.g. temperature, and pressure of the mixing.



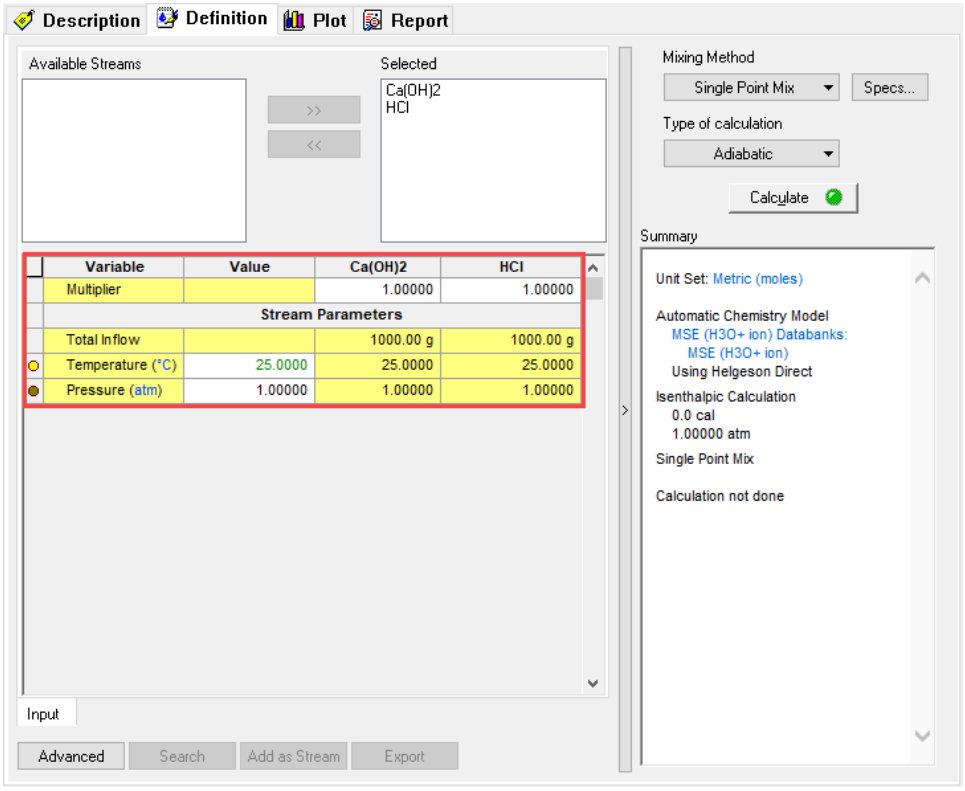
3. **Select** the Ca(OH)2 stream from the available streams and use the **>>** button to put it under the **Selected** window
4. **Select** the HCl stream from the available streams and use the **>>** button to put it under the **Selected** window



Also notice that the default calculation is the **Single Point Mix** Method at **Isothermal** conditions. In this example, we want to calculate the heat of mixing and the final temperature of the mixture. Thus, an adiabatic calculation is required to see this effect.

5. Click on the **Type of Calculation** button and select the **Adiabatic** calculation option

   Note: Once the streams for the mixing have been selected, notice that the multipliers of both streams: Ca(OH)2 and HCl can be edited. This specific calculation will be carried out at a constant pressure of 1 atm, and the final temperature of the mixture will be calculated.



6. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

7. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it and name it as *Mixer Calculations*.

Analyzing the Results

Review the Summary Box. After mixing these two streams, the temperature increased from 25 ºC to approximately 48.65 ºC at a constant pressure of 1 atm. This indicates that that the enthalpy (or heat) of mixing is exothermic, and the software calculated this value to be approximately -7.25×10^6 calories.

5.3. A Titration Experiment

In this example, you will explore the volume mixing option to recreate a titration experiment. As we go through the example, different functionalities, reporting and plotting for the *Mixer tool* will be introduced.

Example 35: HF Titration with $CaCl_2$

In this example, first, we will create two new streams, a 0.1 m HF solution and a 0.1 m $CaCl_2$ solution. What is the pH of these individual streams?

Second, we will mix these two streams in equal amounts. What is the final pH of the mixture?

And finally, the 0.1 m HF solution will be titrated with a 0.1 m CaCl2 solution. What will the titration curve look like?

Starting the Simulation

For this example, we need to create two different streams: a 0.1 m HF solution and a 0.1 m CaCl2 solution.

Use the inputs and parameters from the table below to create each stream. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Titration Calculation			
1st Stream		**2nd Stream**	
Stream Name	0.1 m HF	Stream Name	0.1 m CaCl2
Name Style	Display Formula	Name Style	Display Formula
Unit Set	Metric, Batch, Moles	Unit Set	Metric, Batch, Moles
Framework	AQ	Framework	AQ
Stream Amount	Calculated	Stream Amount	Calculated
Temperature	30 ºC	Temperature	30 ºC
Pressure	1 atm	Pressure	1 atm
H2O	55.5082 moles	H2O	55.5082 moles
HF	0.1 moles	CaCl2	0.1 moles

Calculating the pH of the individual streams

1. Add a **Single Point** – **Isothermal** calculation for each stream
2. **Change** the name to ***pH 0.1 m HF*** *and* ***pH 0.1 m CaCl2*** respectively using the **<F2>** key
3. **Calculate** the isothermal calculation for each stream
4. **Check** the pH values of the individual streams in the **Summary Box**

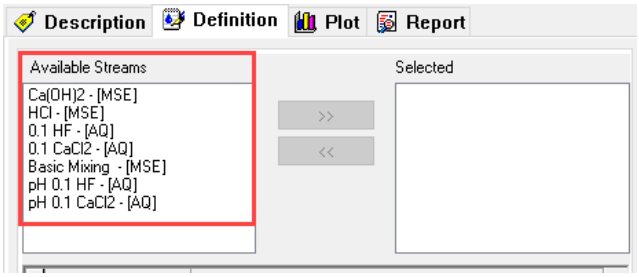
Results – pH of the individual streams

pH 0.1 m HF	**pH 0.1 m CaCl2**
2.13	6.82

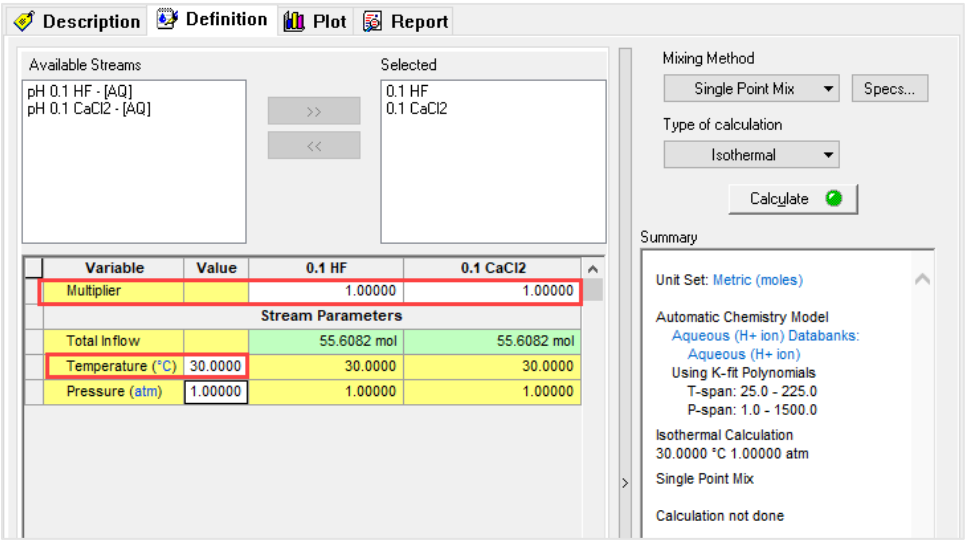
Calculating the pH of the Mixture

5. After creating the streams, **Add a Mixer.** The Mixer object can be accessed from the Menu Bar by selecting Calculations > **Add Mixer** or by selecting the **Add Mixer** in the Actions Pane.
6. Press **<F2>** to rename the mixer to *Titration*

Note: Notice that the Available Streams window is showing all the available streams for the mixing calculation. Also notice that this window is showing both: *Streams* and *Single Point calculations*. Additionally, in front of the name of the available streams, the thermodynamic framework appears within brackets, e.g. AQ, MSE or MSE-SRK. This is important because in order to carry out mixing calculations, the selected streams need to use the same thermodynamic framework.



7. **Select** the 0.1 HF – [AQ] stream. Use the **>>** button to move it to the **Selected** window
8. **Select** the 0.1 CaCl2 stream. Use the **>>** button to move it to the **Selected** window
9. Select **Single Point Mix** as the Mixing Method and **Isothermal** as the Type of Calculation
10. **Leave** the default values for the multipliers (1.0) and **change** the temperature at which the mixture takes place to 30 ºC.



11. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
12. At this point is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Mixer Calculations*.
13. **Check** the pH values of the individual streams in the **Summary Box**

Results – pH of the individual streams

The resultant pH is 1.44. How can this be? An acid stream (the HF stream had a pH of approximately 2.13) and a nominally basic stream (the $CaCl_2$ stream had a pH of 6.82) are mixed and the pH is outside the value of either stream.

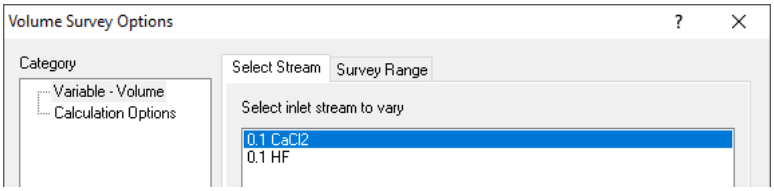
We will continue using Stream Analyzer to further examine the chemistry in more detail. We will titrate the HF stream with $CaCl_2$.

Titrating HF with $CaCl_2$

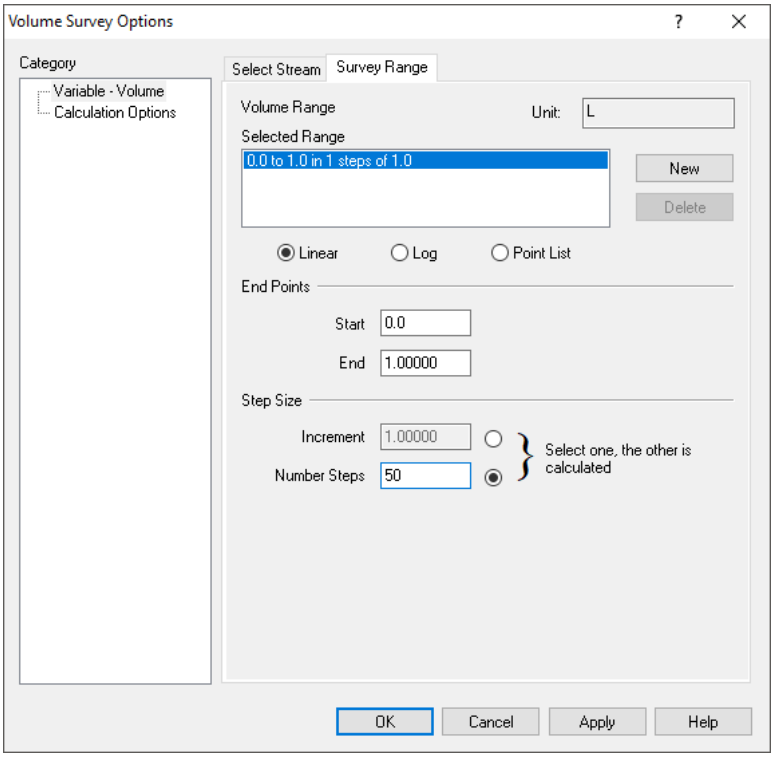
14. **Change** the **Single Point Mix** as the Mixing Method to the **Volume** option.

    Note: You will receive a warning message: Need 1 stream selected as the variable stream (Specs...)

15. **Click** on the **Specs** button. This will open a new window indicating you to select the Stream to vary
16. In the **Select Stream** tab **Select** the 0.1m CaCl2 stream



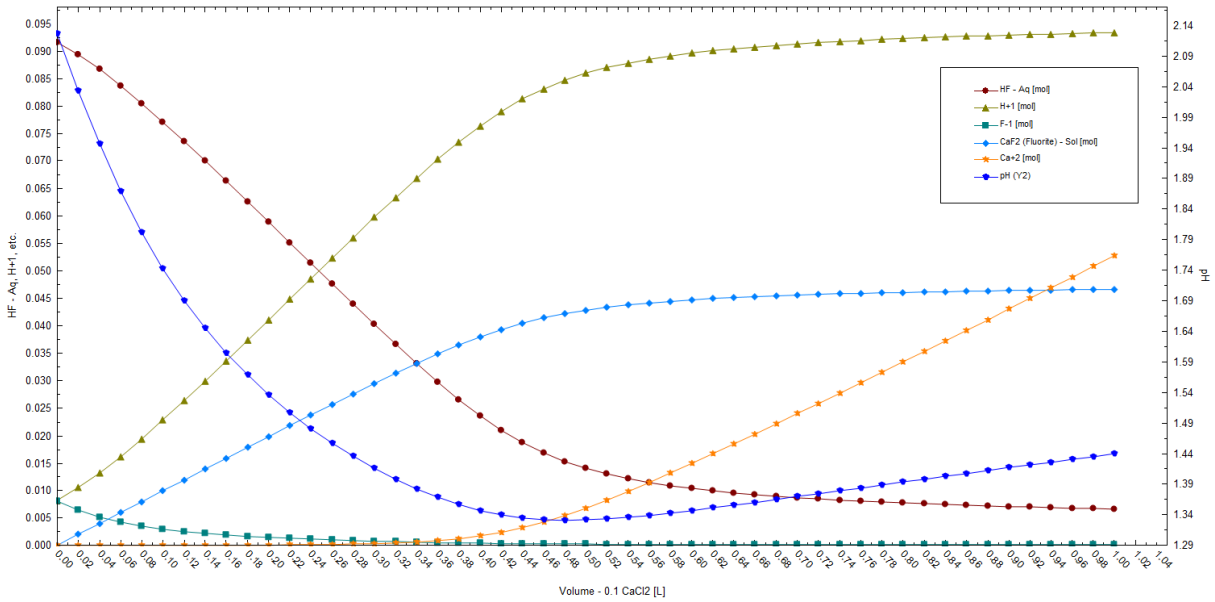
17. **Select** the **Survey Range** tab. Change the Volume Range from 0 L to 1 L.
18. Change the **Number of Steps** to 50. Then click **OK**.



19. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
20. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Mixer Calculations*.

Titration Results and Plotting

1. **Click** on the **Plot** tab. **Note:** You will see an empty plot, since we need to define the variables that we want to report.
2. **Click** on the **Variables** button and expand the **Aqueous** section. **Select** and put the following species in the **Y1 axis** using the **>>** button: HF-Aq, H+1, F-1, Ca+2. Expand the **Solid** section and **select** CaF2(s).
3. Next, expand the **Additional Parameters** Section and Select **pH**. Put it in the **Y2 Axis** using the **>>** button. Then click **OK**.



As you can see, adding $CaCl_2$ to this solution lowers the pH to values as low as 1.33. The pH does begin to slowly increase after 0.48 L of $CaCl_2$ have been added.

Why the unusual pH behavior? You can see that a small amount of Ca^{+2} in solution, causes the formation of the solid CaF_2. This effectively removes F^- from solution according to the following equation:

$$Ca^{+2} + 2\,F^- \rightarrow CaF_{2(s)}$$

As we add more $CaCl_2$ in solution, more CaF_2 is formed. As a result, the molecular HF decreases, because it dissociates in order to maintain the equilibrium, by producing more F^- ions. This shifts the following equilibrium to the right:

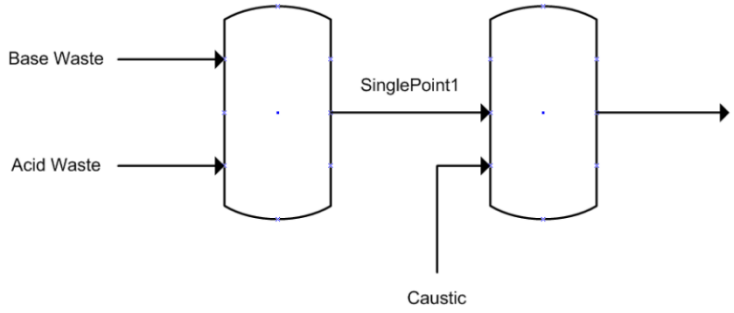
$$HF \leftrightarrow H^+ + F^-$$

This causes an increase of H^+ in solution, and as a result a decrease in the pH. At some point, at around 0.48 L of 0.1 m $CaCl_2$, the solid reaches a steady value, indicating that the solid has reached its saturation value.

5.4. Cascading Mixers

Example 36: Cascading Mixers

In this example, we will mix two streams, one basic and one acidic, and mix them together under adiabatic conditions. The output of this mixer will then be used as the input to a second mixer where a new caustic stream is added. The schematic in the figure below illustrates the layout.

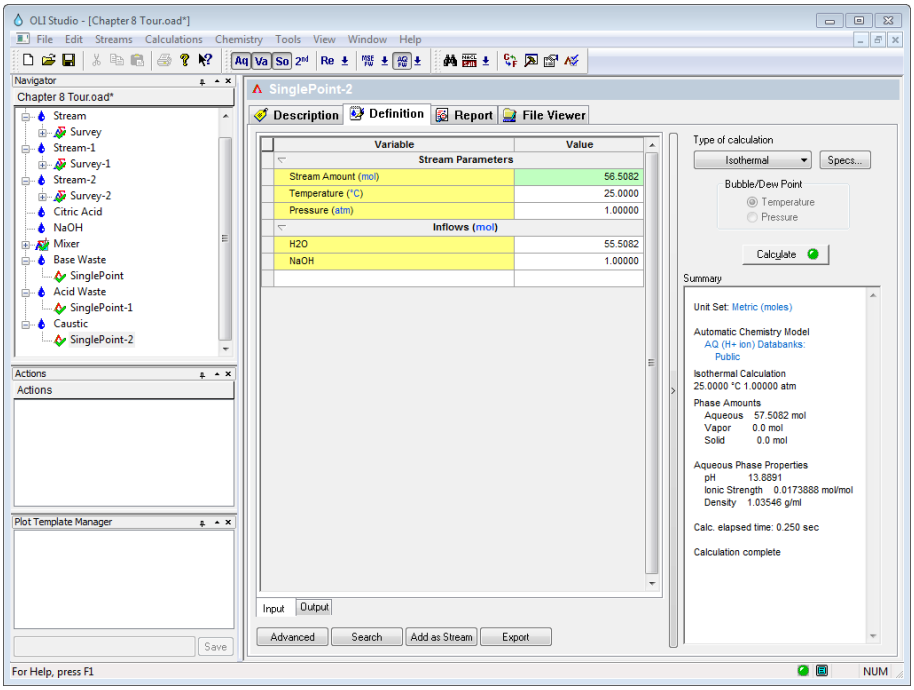


For this example, we need to create three streams. You have already done this in other examples, so we will only give you the input data (for all streams, we will use the AQ – default – thermodynamic framework)

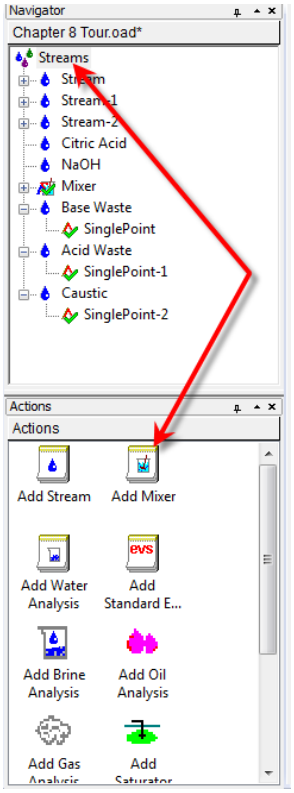
Cascading Mixer Stream Data

Parameter	Value	Units
Stream Name	Base Waste	
Temperature	25.0	°C
Pressure	1.0	Atmospheres
Stream Amount	55.5082 (Default)	Mole
H_2O	55.5082	Mole
CO2	0.1	Mole
NH3	0.01	Mole
SO2	0.01	Mole
Stream Name	Acid Waste	
Temperature	25.0	°C
Pressure	1.0	Atmospheres
H_2O	55.5082	Mole
HCl	0.1	Mole
H2SO4	1.0	Mole
Stream Name	Acid Waste	
Temperature	25.0	°C
Pressure	1.0	Atmospheres
H_2O	55.5082	Mole
NaOH	1.0	Mole

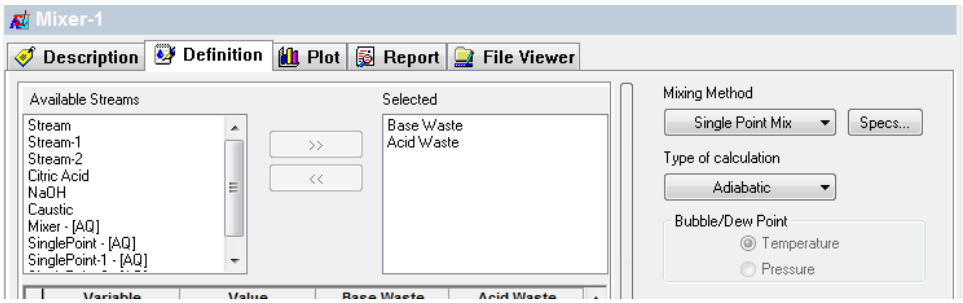
To test that our streams are representing their respective names, perform a single point isothermal flash on each stream. When you are done you should have a window that looks like the image below.



Now we are ready to begin. Click on the “Streams” at the top of the tree-view in the left-hand window and then select Add Mixer from the actions panel.

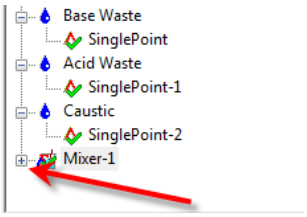


We can now add the “Base Waste” and “Acid Waste” stream as we have done in previous examples. The only difference here is that we are selecting an **Adiabatic** calculation instead of the default isothermal calculation.

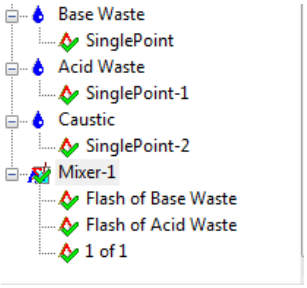


Let's calculate this mixer. Click the Calculate button. If everything is set up correctly the resultant mixed pH should be approximately 0.3.

In the stream tree-view panel, locate your mixer and click the "+" sign.

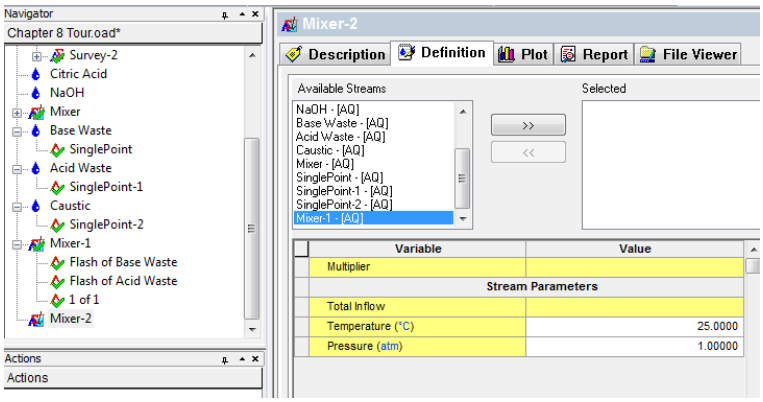


Click the "+" sign to expand the tree.



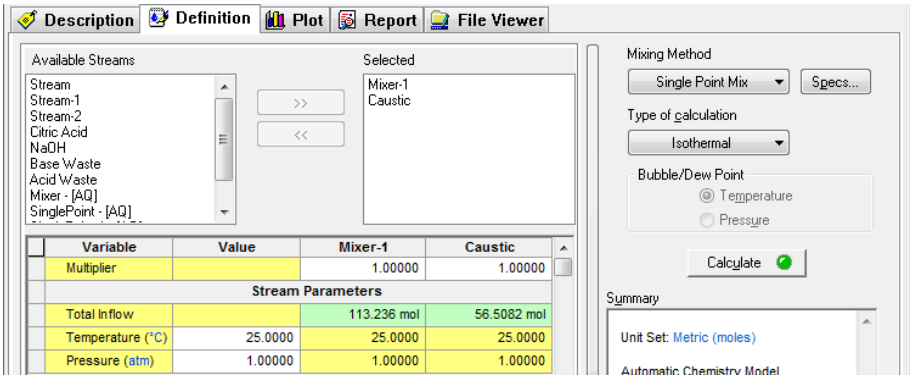
You can see that the program has performed an equilibrium calculation on each of our input streams as well as calculated the mixer. The results of the mixer are stored in the object "1 of 1".

We will now add a second mixer from the actions panel.



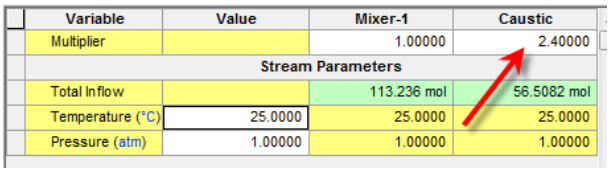
When we add a subsequent mixer, we will see all of our previous objects still displayed. It is possible to reuse a stream that we already used (this is not possible in OLI's other simulators such as ESP FS.) We want to connect the output from our first mixer (Mixer1) to the inlet of the **Caustic** stream. Click the object **Mixer-1-(AQ)**.

Then add the Caustic Reagent. Select the type of calculation as Isothermal.



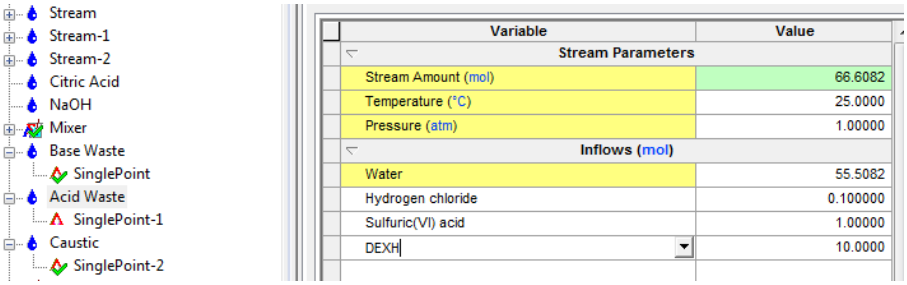
We are now ready to calculate the second mixer. Press the calculate button.

The resultant pH should be approximately 1.0. We want to increase this value. Change the **Multiplier** value for Caustic Stream from 1.0 to 2.4



Click the calculate button again. The new pH should be approximately 12.4.

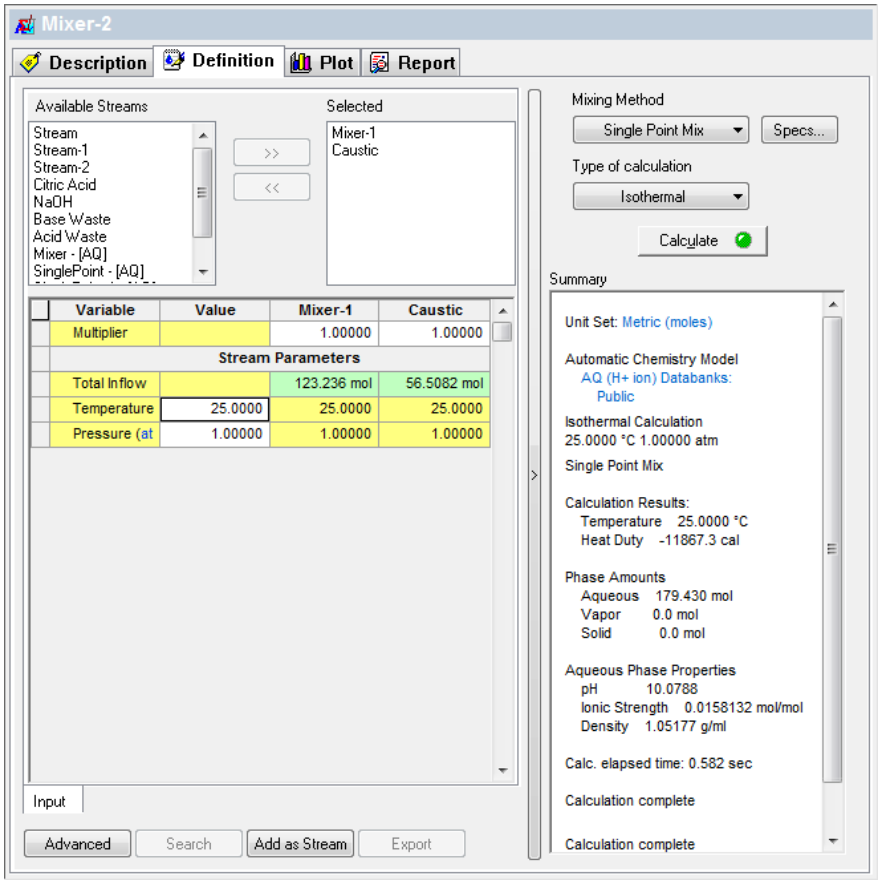
The real value of the cascading mixer is the quick ability to re-calculate the objects if we want to change something. Let's add some diethanolamine to the series of calculations. Click the **Acid Waste** stream (not the single point calculation below it) and add the component DEXH[6] to the grid with a value of 10.0 moles.



[6] This is the OLI Tag name for diethanolamine, which is easier to type if you know the name.

Return to the last mixer you created (Mixer-2 in our example) and then reduce the ***Caustic Multiplier back to 1.0***

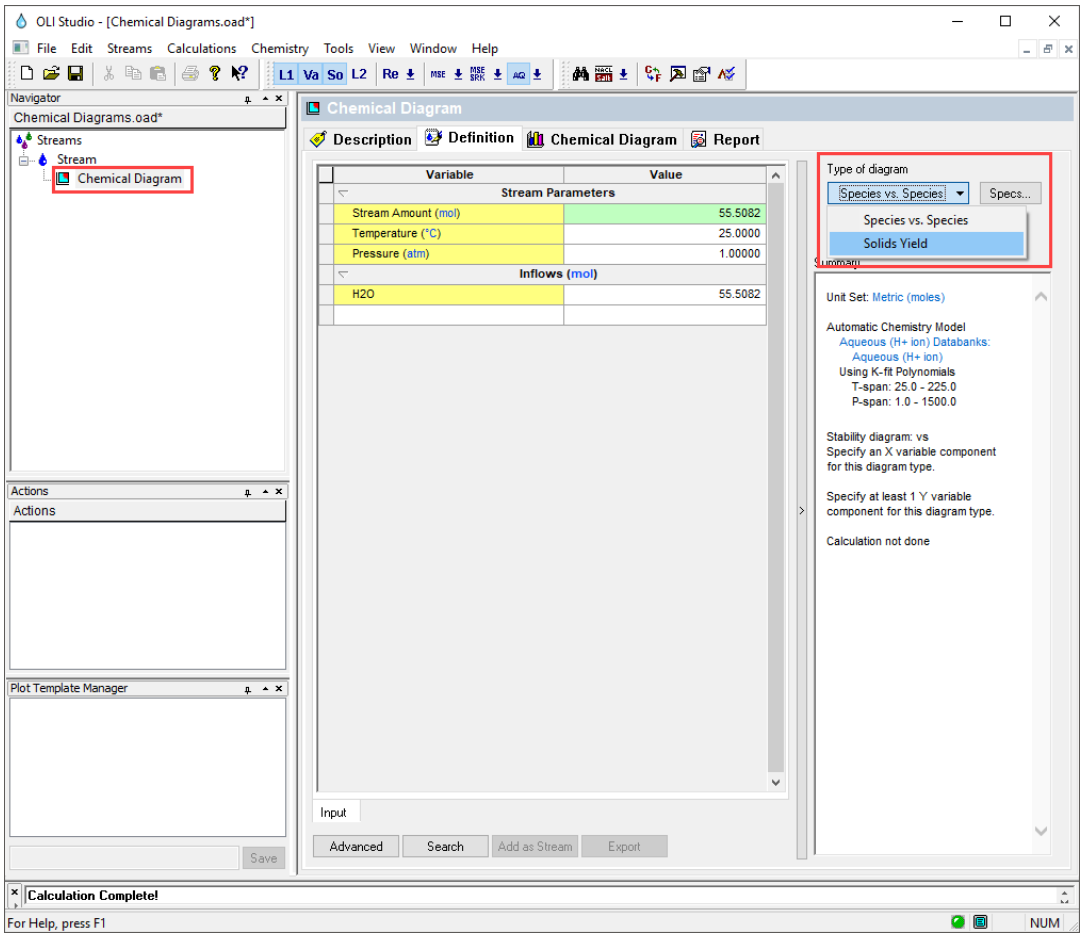
To recalculate all the objects at once, press the control+F9 keys and all objects will be calculated. Now if you look at the summary of Mixer2 you will see that the pH has changed to approximately 10.



Section 6. Chemical Stability Diagrams

"Predicting the stability of chemical compounds as a function of solution chemistry is crucial towards understanding the electrochemical characteristics of materials in real-world applications. There are several commonly considered factors that affect the stability of a chemical compound, such as metal ion concentration, mixtures of ion concentrations, pH, buffering agents, complexation agents, and temperature. Chemical stability diagrams graphically describe the relative stabilities of chemical compounds, ions, and complexes of a single element as a function of bulk solution chemistry (pH and metal ion concentration) and also describe how solution chemistry changes upon the thermodynamically driven dissolution of a species into solution as the system progresses towards equilibrium"[7].

Stream Analyzer has the capability of building chemical stability diagrams by using the *Chemical Diagram tool* that allows to study the precipitation of species as function of ion concentration and other parameters such as pH. In this section we will explore with different examples how to set up cases to use the Chemical Diagram tool.



[7] Santucci, R.J., McMahon, M.E. and Scully, J.R., 2018. Utilization of chemical stability diagrams for improved understanding of electrochemical systems: evolution of solution chemistry towards equilibrium. npj Materials Degradation, 2(1), p.1.

6.1. Building a Chemical Diagram

In this section, first we will go through the steps of building a basic chemical diagram, and then we will explore how the concentration of species and other variables such as temperature and pressure have a significant influence on the stability of chemical species.

Example 37: $La(C2H_3O_2)_3$ – K_3PO_4 Chemical Diagram

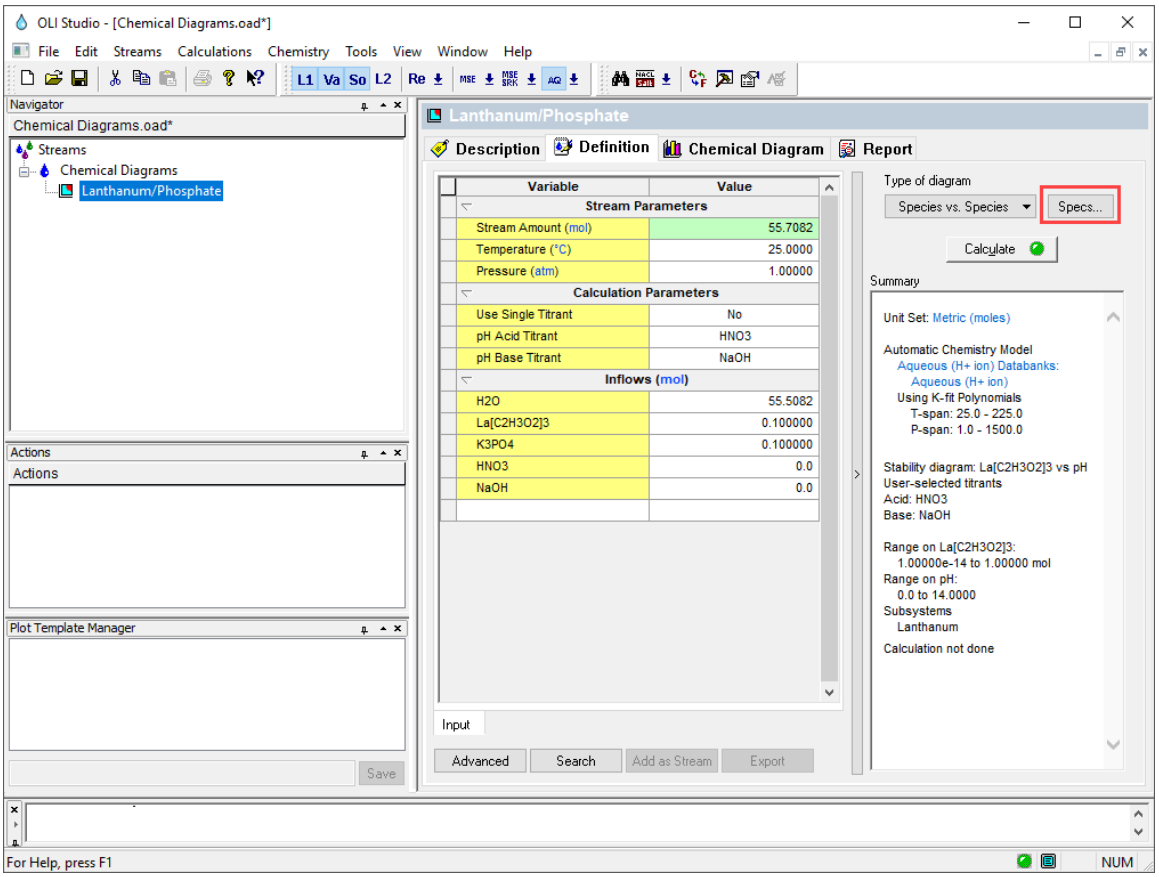
For this example, we are going to reproduce the work found in the following paper: *Andelman, T., Tan, M. C., & Riman, R. (2010). Thermochemical engineering of hydrothermal crystallization processes. Materials Research Innovations, 14(1), 9-15. https://doi.org/10.1179/143307510X12599329343123.*

Starting the Simulation

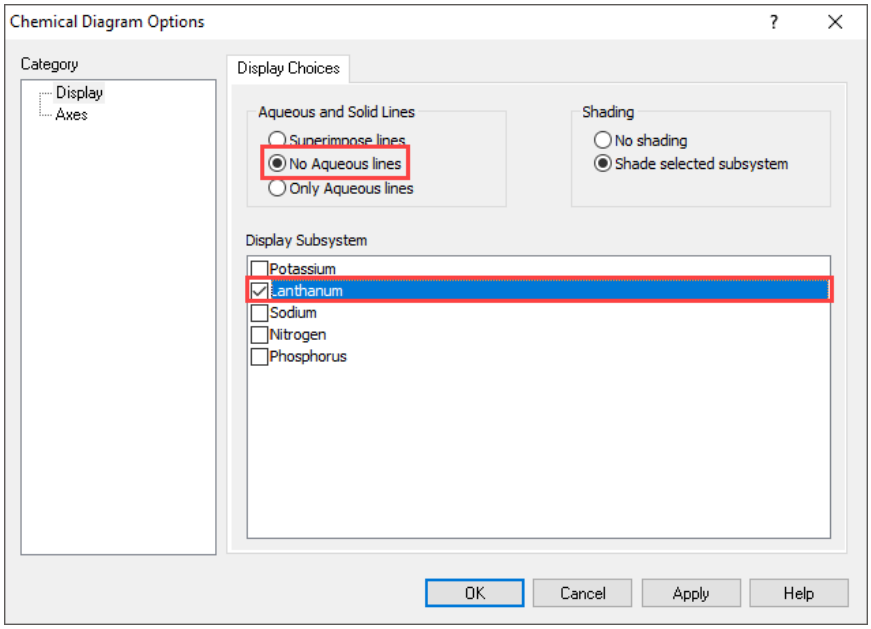
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

$La(C2H_3O_2)_3$ – K_3PO_4 Chemical Diagram			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Chemical Diagrams	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 ºC
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	H2O	55.5082 moles
Type of Calculation	Chemical Diagram	La[C2H3O2]3	0.1 moles
		K3PO4	0.1 moles
		HNO3	0.0 moles
		NaOH	0.0 moles

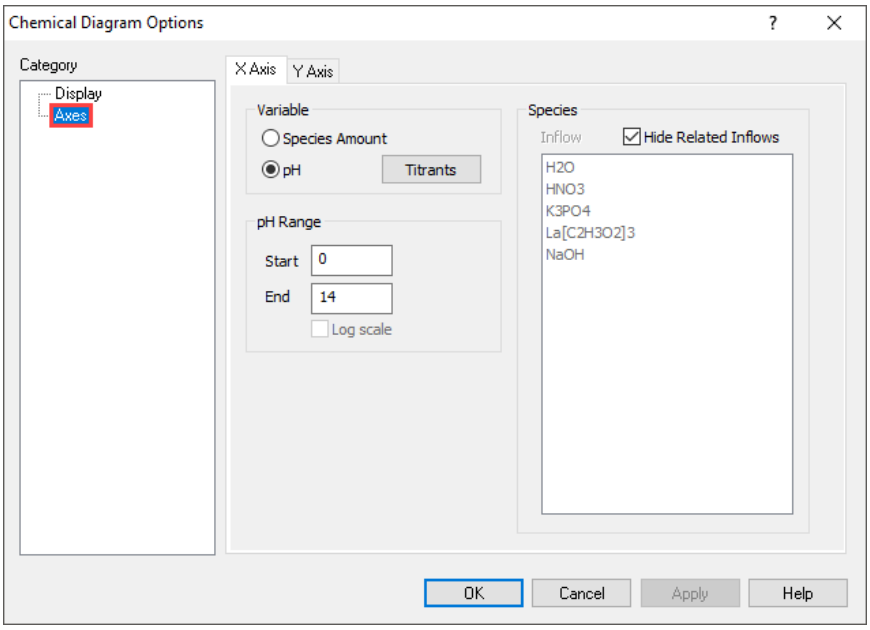
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Chemical Diagrams*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition of the stream given in the table above. Notice that the concentrations of La(C2H3O2)3 and K3PO4 are held at a 1:1 molal ratio.
7. Go to the **Add Calculation** button and select **Chemical Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane
8. Select **Species vs Species** as Type of Diagram – Default
9. Change the ***Chemical Diagram*** name to ***Lanthanum/Phosphate*** using the **<F2>** key



10. Click on the **Specs** button. This will open the **Chemical Diagram Options** window
11. In the **Display Choices** tab, select the **No Aqueous lines** button and check the box for **Lanthanum** as the subsystems to display

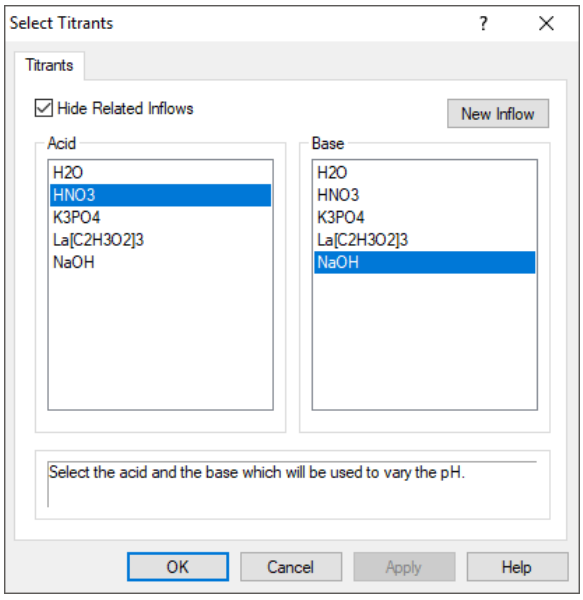


12. Click on the **Axes** category. The dialog changes to display the **X Axis** tab.
13. In the **Variable** section select the **pH** option. Leave the default **pH Range**: 0-14. This also enables the **Titrants** button.



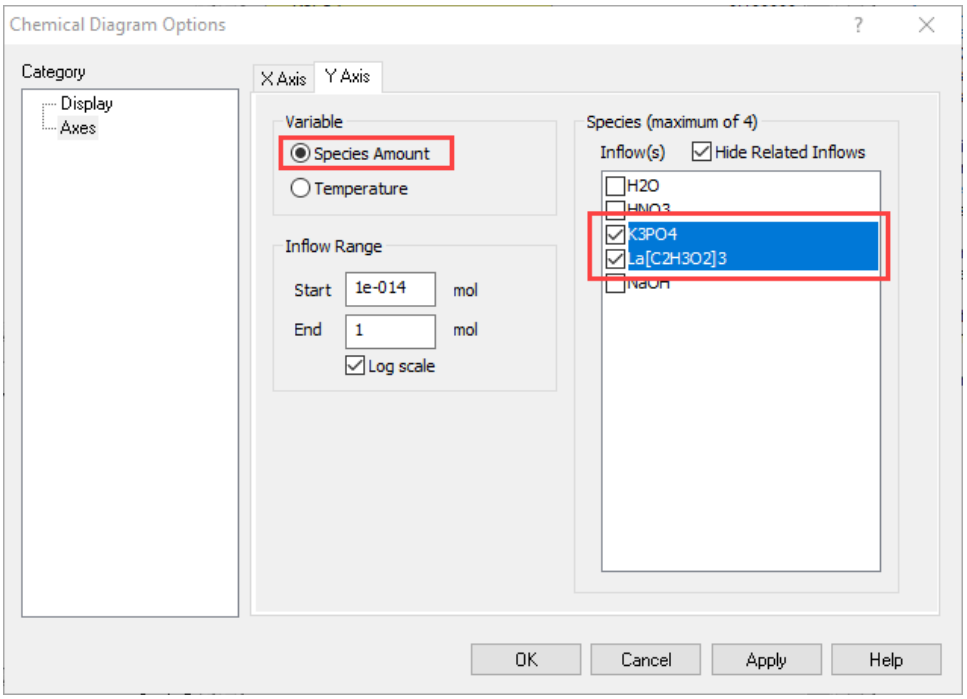
14. Click on the **Titrants** button. Select **HNO3** as the **acid titrant** and **NaOH** as the **base titrant**. Then click **OK**.

    Note: These titrants were added in the stream definition, and that's why they appear as possible titrants.



15. Select the **Y Axis** tab. Select the **Species Amount** button as the variable to change
16. Select La[C2H3O2]3 and K3PO4 species
17. For the Inflow Range keep the default range: from 1E-14 to 1.0 moles on a log scale.

    Note: This means we will have initially 1.0E-14 moles of $La(C_2H_3O_2)_3$ and 1.0E-14 moles of K_3PO_4 increasing equally until we have 1.0 moles of each.
18. Click **OK**

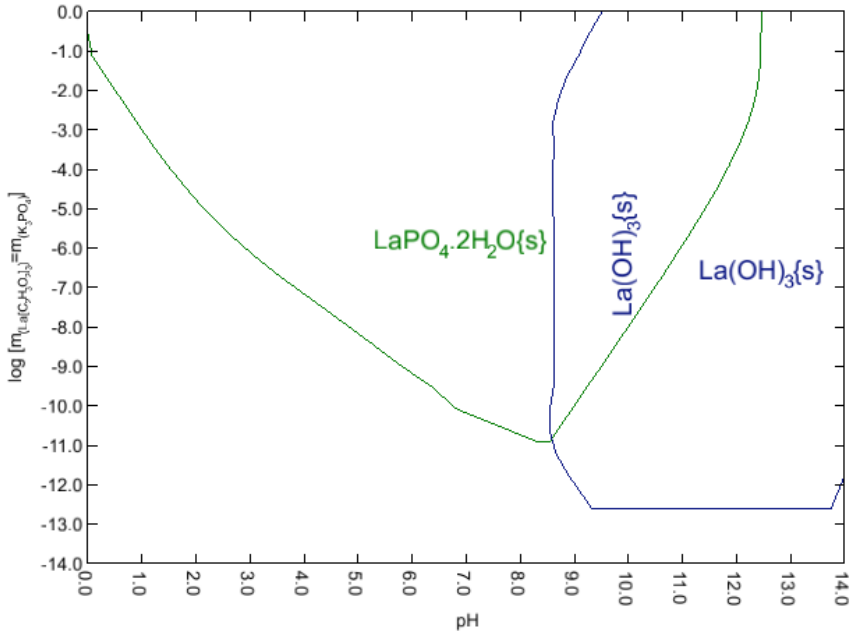


19. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
20. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it and name it *Chemical Diagrams.*

Anaylyzing the Results

Click on the **Chemical Diagram** tab (Chemical Diagram). This tab displays the Species vs pH diagram for the Lanthanum species.

The X axis of the diagram is pH, varied by adding HCl or NaOH, and the Y axis variable is the concentrations of La(C2H3O2)3 and K3PO4, held at a 1:1 molar ratio. From this figure, we can see that at room temperature there is a large pH range over which lanthanum phosphate will be the thermodynamically stable product. As pH increases, and more OH^- ions are present, La(OH)3 begins to form. The pH range in which La(OH)3 forms is the right bounded region in the diagram. The area below the lines is where only aqueous species exist.

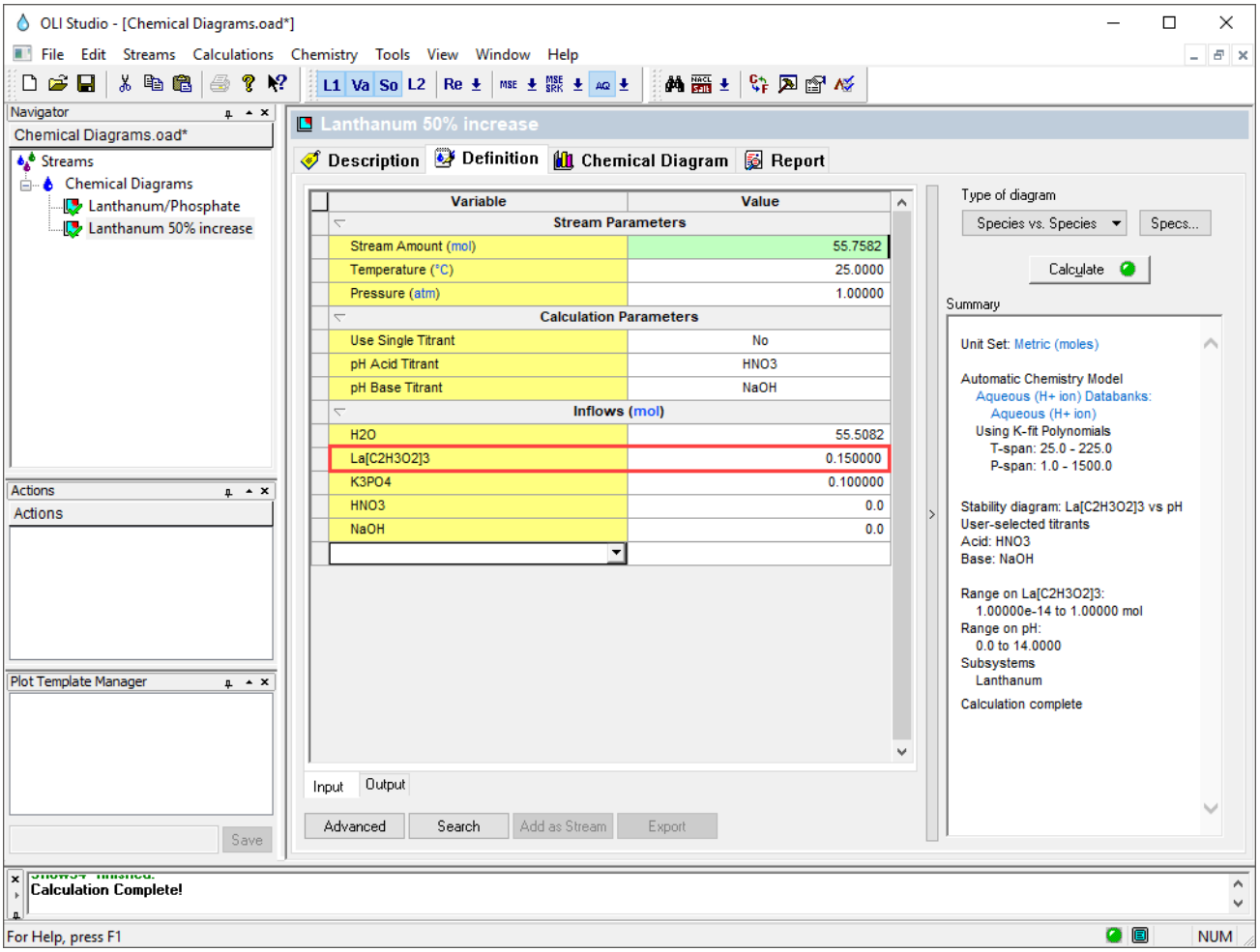


Example 38: Adding 50% Lanthanum Acetate

In this second example we will add 50% more to the lanthanum acetate species and see the effect of this increase in concentration on the chemical diagram.

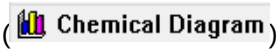
Starting the Simulation

1. **Copy** the *Lanthanum/Phosphate* chemical diagram calculated in the Example 37: $La(C2H3O2)_3$ – K3PO4 Chemical Diagram, and **paste** it under the *Chemical Diagrams* stream.
2. **Change** the name to ***Lanthanum 50% increase*** using the **<F2>** key
3. **Change** the Lanthanum Acetate amount to 0.15 moles



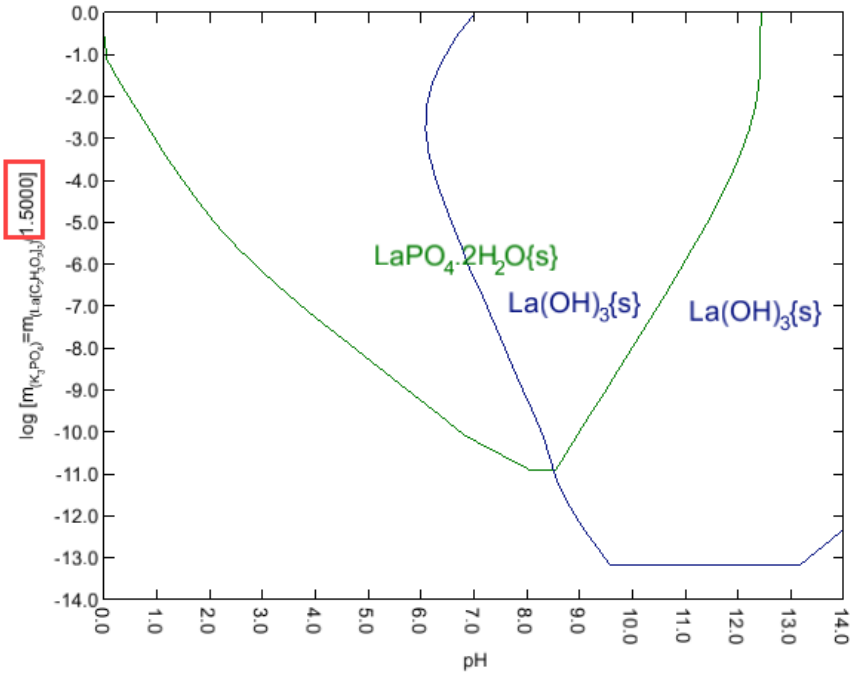
4. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
5. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Anaylyzing the Results

Click on the **Chemical Diagram** tab (

). It is important to note that the Y axis label has changed to reflect the increased amount of the lanthanum acetate.

From this figure, we can see that by increasing amount of Lanthanum acetate it favors the stability of La(OH)3 over a wider range of pH.

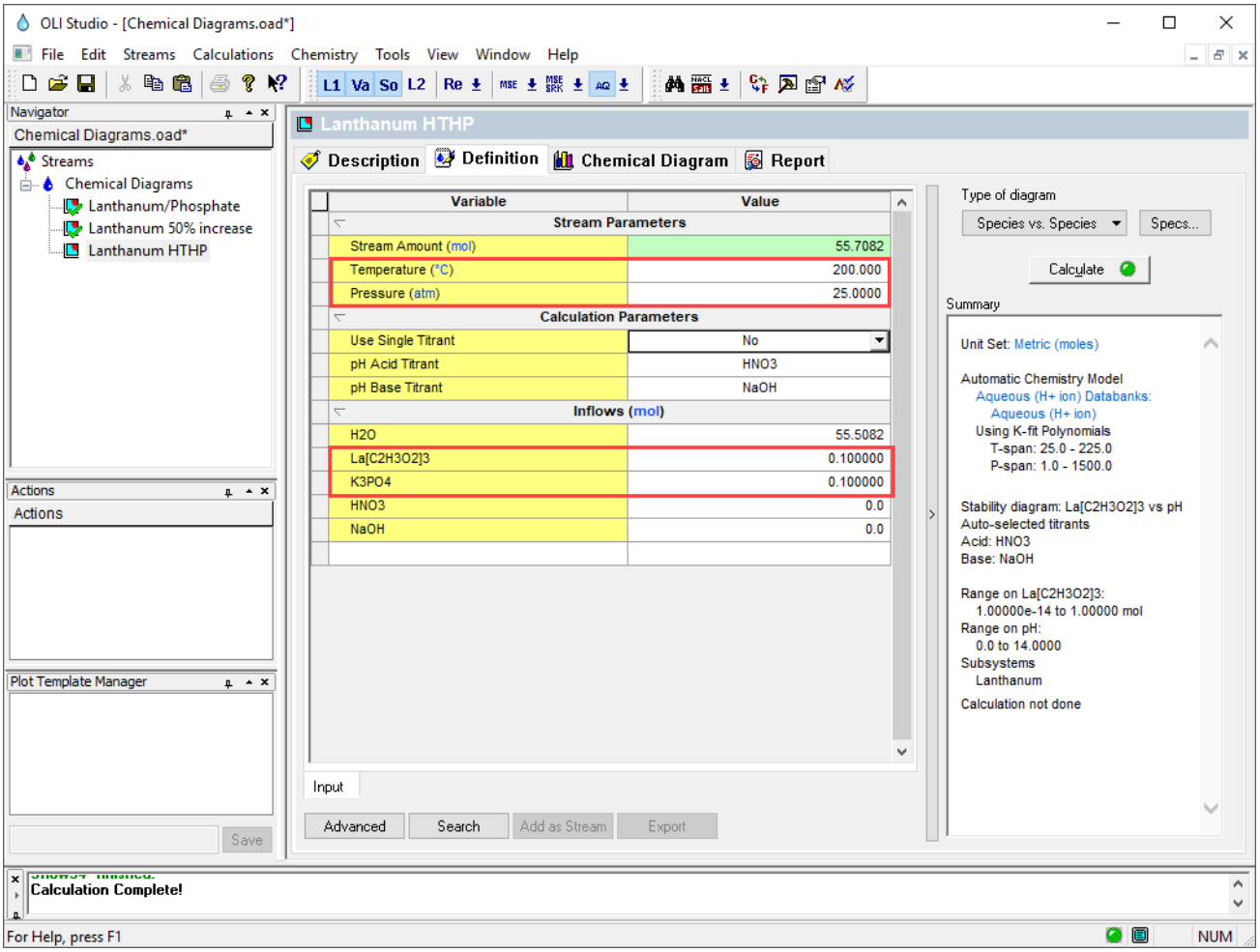


Example 39: Changing temperature and pressure

In this second example we will add 50% more to the lanthanum acetate species and see the effect of this increase in concentration on the chemical diagram.

Starting the Simulation

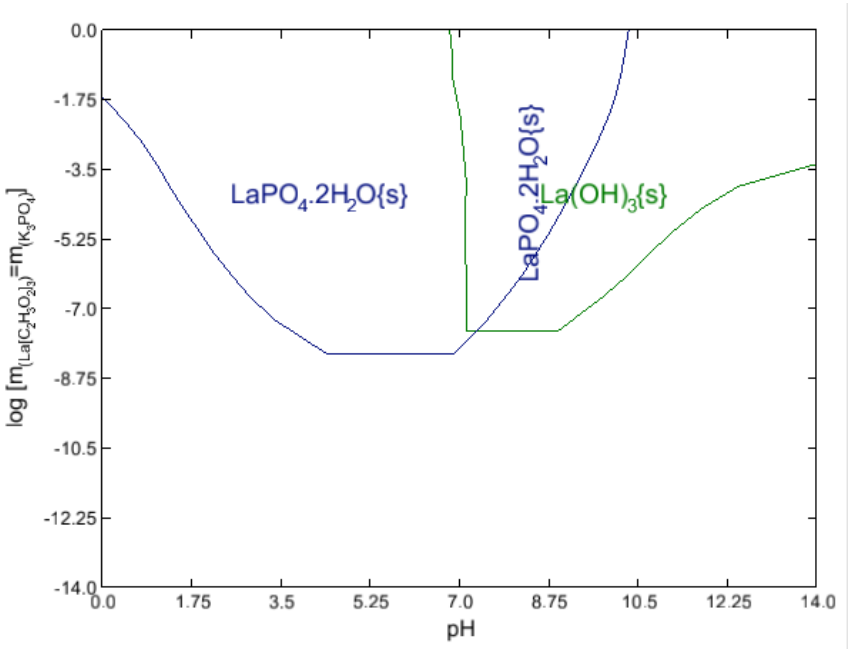
1. **Copy** the *Lanthanum/Phosphate* chemical diagram calculated in the Example 37: $La(C2H3O2)_3$ – K3PO4 Chemical Diagram, and **paste** it under the *Chemical Diagrams* stream.
2. **Change** the name to ***Lanthanum HTHP*** using the **<F2>** key
3. **Change** the temperature to 200 ºC and the pressure to 25 atmospheres



6. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
7. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Anaylyzing the Results

Click on the **Chemical Diagram** tab (Chemical Diagram). This figure shows the stability diagram for La(C2H3O2)3 and K3PO4 over a range of pH values at 200ºC and 25 atm. Under these conditions, there is a decrease in the pH range over which LaPO4 is the stable product. This is because as temperature increases, the insoluble rare earth hydroxides [RE(OH)3] become more stable. The aqueous area of the single-phase increases at elevated temperatures due to the increased solubility of the different species. Again, at high pH values, only La(OH)3 will form.

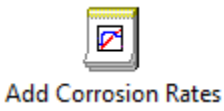


Chapter III – OLI Analyzer: Corrosion Analyzer

Corrosion Analyzer is a module within the OLI Analyzer. A separate license enables this module. Corrosion Analyzer is first-principles corrosion prediction tool. As in Stream Analyzer, 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.

There are two different types of calculations that can be carried out in Corrosion Analyzer: Corrosion Rates and Stability Diagrams. A brief definition of each type of calculation is given below.

Stability Diagram is used to predict the stability of metals, metal ions, oxides, etc. as a function of T, P and solution composition. With this tool you can draw conclusions about the ranges of immunity to corrosion, possible passivation and dissolution of metals in the presence of species that promote or inhibit corrosion.

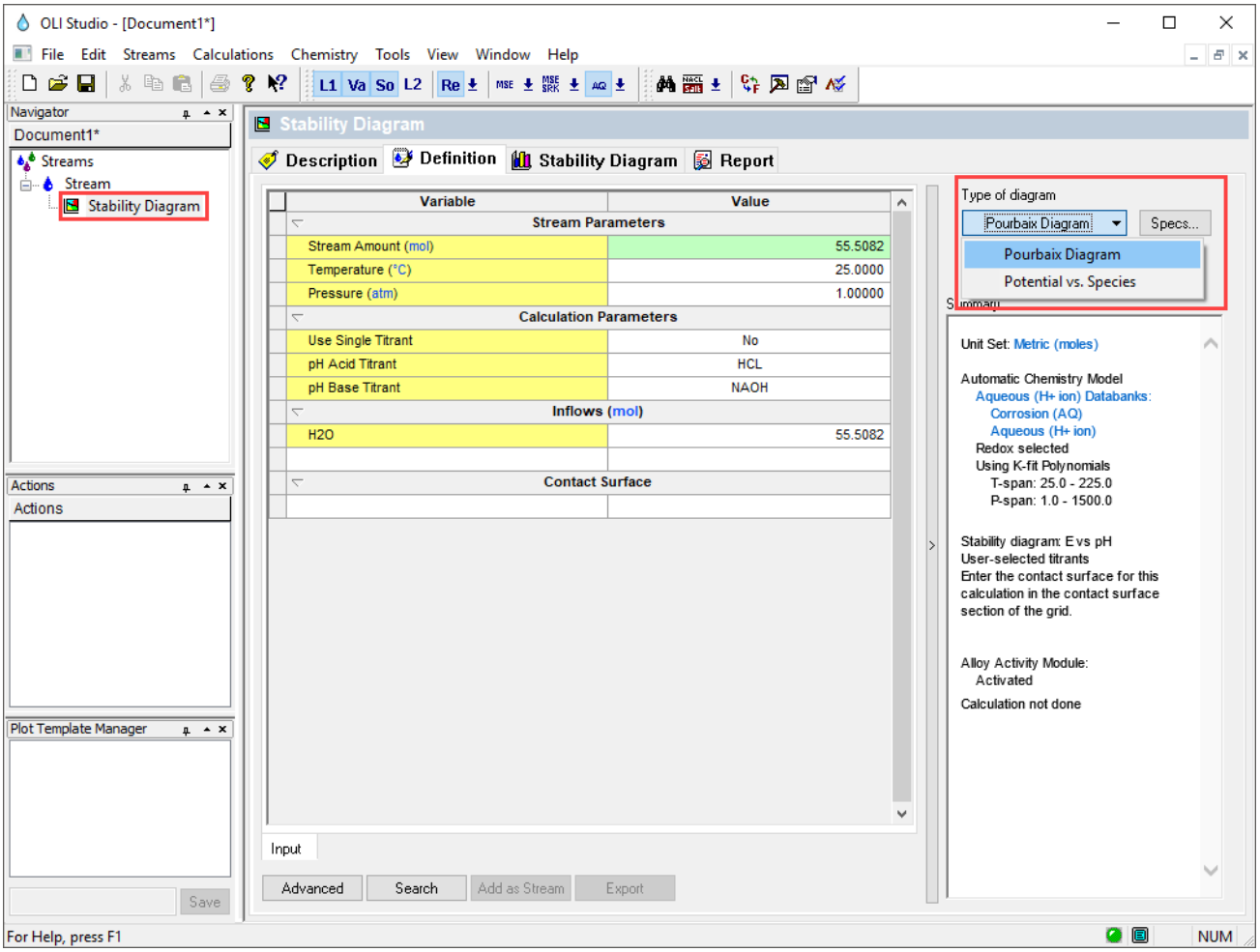


Corrosion Rates is used to predict the general corrosion rate, the propensity for localized corrosion (pitting or crevice corrosion) to occur, polarization curves, and heat treatment effects of metallic materials at one specific equilibrium state. The effects of temperature, pressure, pH, concentration of species, and velocity on corrosion are also included.

In this chapter several examples will be provided to cover these calculation types.

Section 7. Stability Diagrams

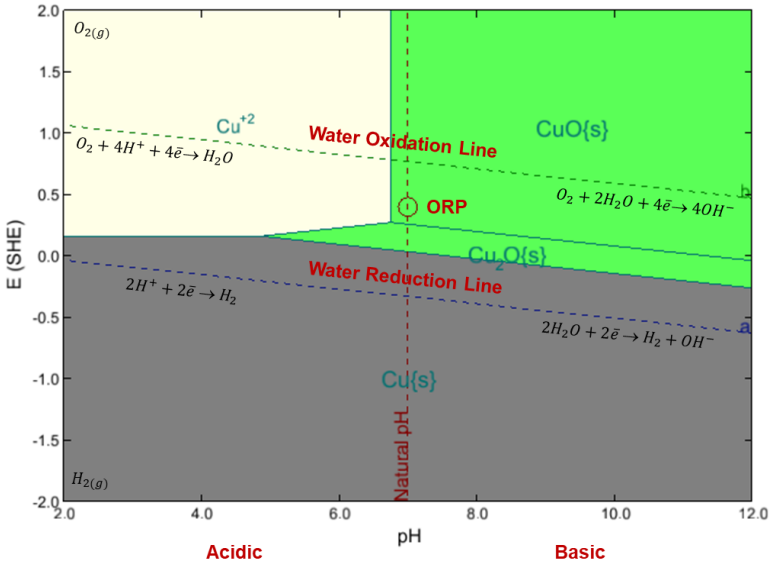
In this section you are going to learn how to set up a Stability Diagram and how to interpret the results when using this tool.



7.1. How to Interpret a Stability Diagram

A Stability Diagram also known as Pourbaix Diagram or simply Potential vs pH diagram, maps out the possible stable species in an aqueous environment at different pH and potential combinations. This diagram, however, does not provide information of reaction rates or kinetic effects.

A schematic representation of the Pourbaix diagram for copper in water at 25 ºC and 1 atm is shown in the image below.



The gray color represents the immune to corrosion region. It is the stability field of the elemental metal. Cu is the base metal in the above plot.

The green color represents the range of possible passivation. It is the 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. In the above plot, the green area contains CuO and Cu_2O as the solid phases produced by oxidation of Cu.

The light-yellow color represents the corrosion region. It is the stability field(s) of dissolved (ionic or neutral) metal species in which neither the metal nor passivating solids are stable. In the plot above, Cu^{2+} is the ionic species that is the most stable.

The diagonal dashed lines, represented by the letters a and b are the water reduction and water oxidation lines, respectively.

Below the water reduction line (a): Water decomposes to form H_2 gas. Above the water oxidation line (b): Water decomposes to form O_2 gas. The region within these lines (a and b) is called the stability region of water.

The lines that divide different species in the Pourbaix diagram show the equilibrium conditions. These lines represent the equilibrium for chemical and electrochemical reactions.

Finally, as a reference, the values of the Natural pH and the Oxidation Reduction Potential (ORP) are superimposed on the diagram. The natural pH line of the water sample is the water's computed pH before it is adjusted using with acid or base to create the diagram. The ORP is represented by the red circle and indicates the initial electrochemical potential of the water phase. This is the value before the potential is adjusted using a potentiostat, for example.

7.2. How to determine if 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*** in the plot below). Depending of the pH that reactions that can occur are the following:

$$Acidic: \ H^+ + 2\bar{e} \ ® \ H_2$$

$$Basic: \ 2H_2O + 2\bar{e} \ ® \ H_2 + OH^-$$

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.

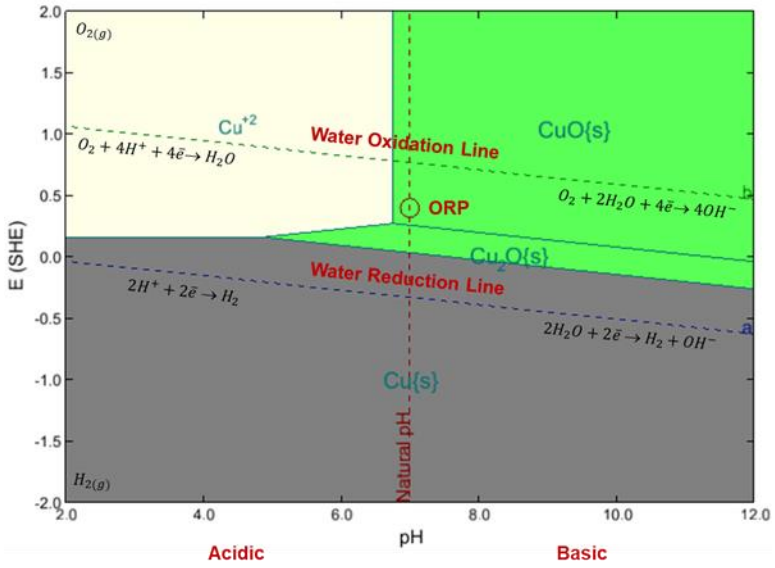
In oxygen-containing solutions, O_2 can be reduced to H_2O (as shown by line ***b***). Depending of the pH that reactions that can occur are the following:

$$Acidic: \ O_2 + 4H^+ + 4\bar{e} ® \ H_2O$$

$$Basic: \ O_2 + 2H_2O + 4\bar{e} ® \ 4OH^-$$

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.



Stability diagram for Copper in Water at 25ºC and 1 atm

7.3. Building a Pourbaix Diagram

Example 40: Pourbaix Diagram of Fe-H2O System

After completing this example, you will learn how to set up a Pourbaix Diagram using the **Stability Diagram** tool.

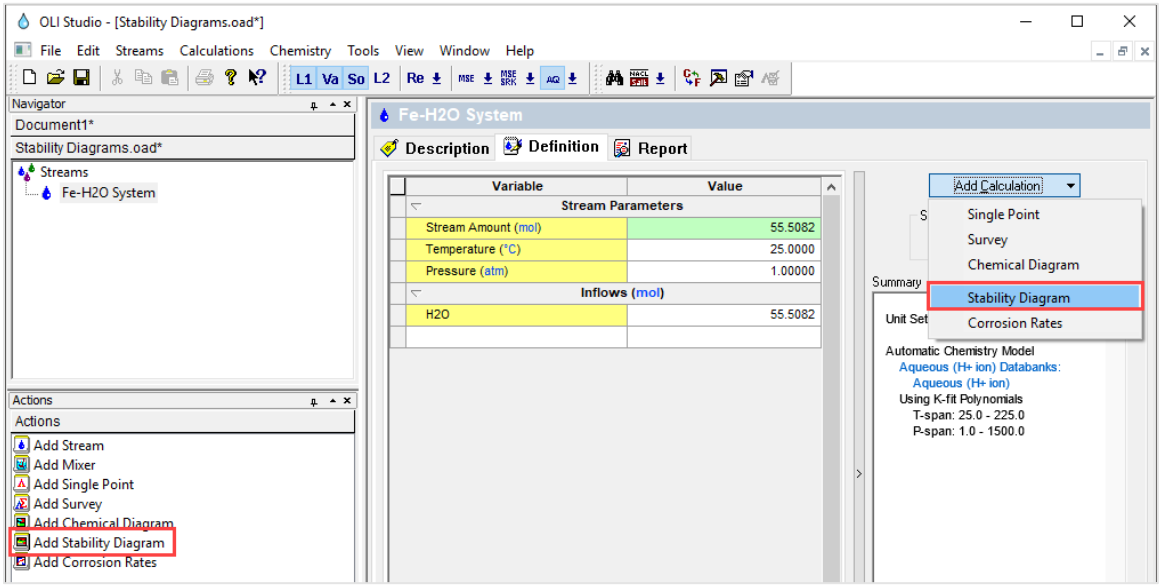
Starting the Simulation

To start the software, double-click the OLI Analyzer icon on the desktop, which will take you to the OLI Analyzer interface where you can start creating your calculations.

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Stability Diagram Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Fe-H2O System	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 ºC
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	2-12
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe		

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Fe-H2O System*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition, temperature and pressure of the stream given in the table above
7. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane.



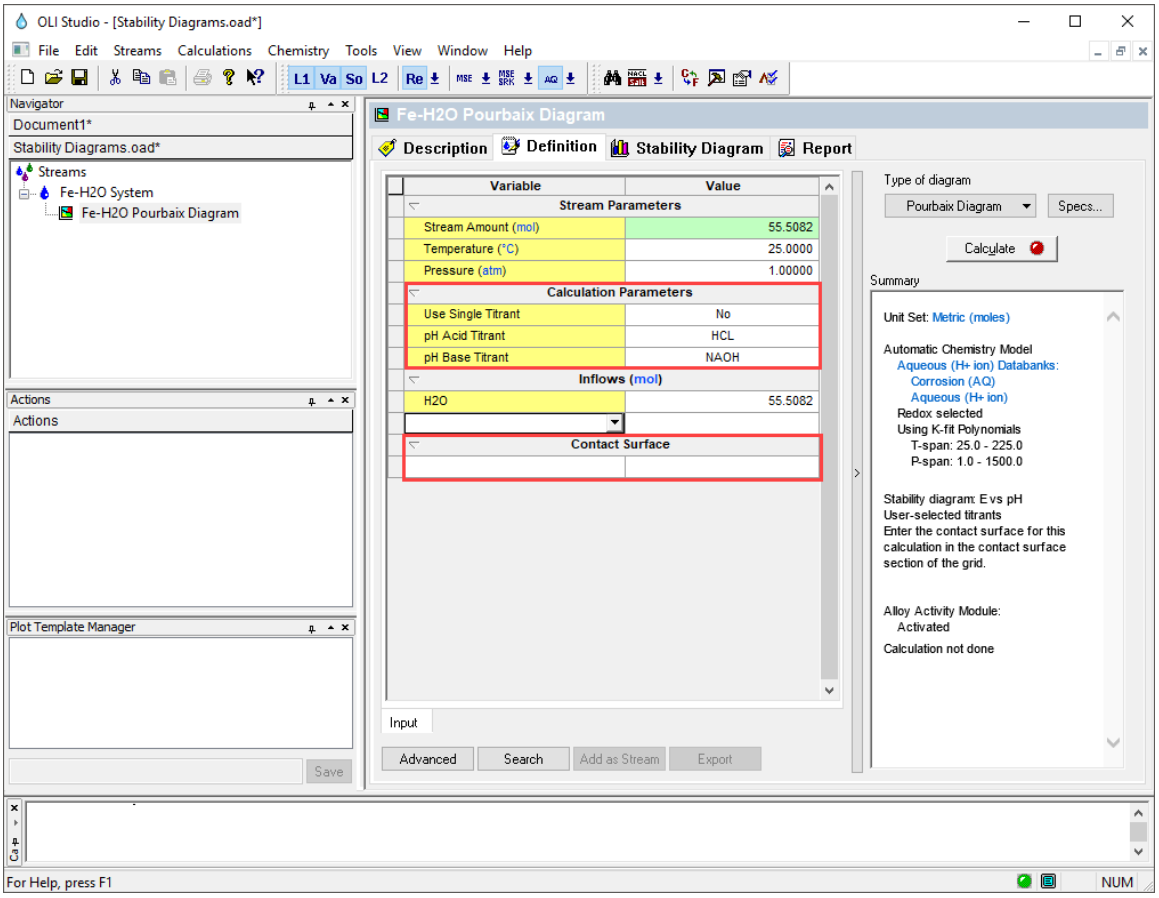
8. Select **Pourbaix Diagram** as Type of Survey – Default
9. **Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O Pourbaix Diagram*

Note: Notice that two new sections appear in the **Definition** tab: **Calculation Parameters** and **Contact Surface** grids. Additionally, the Redox button is turned ON.

In the **Calculation Parameters** grid is where the pH titrants need to be defined. These default pH titrants selected by default are HCl and NaOH. You have the option to change the default titrants to your preferred titrants.

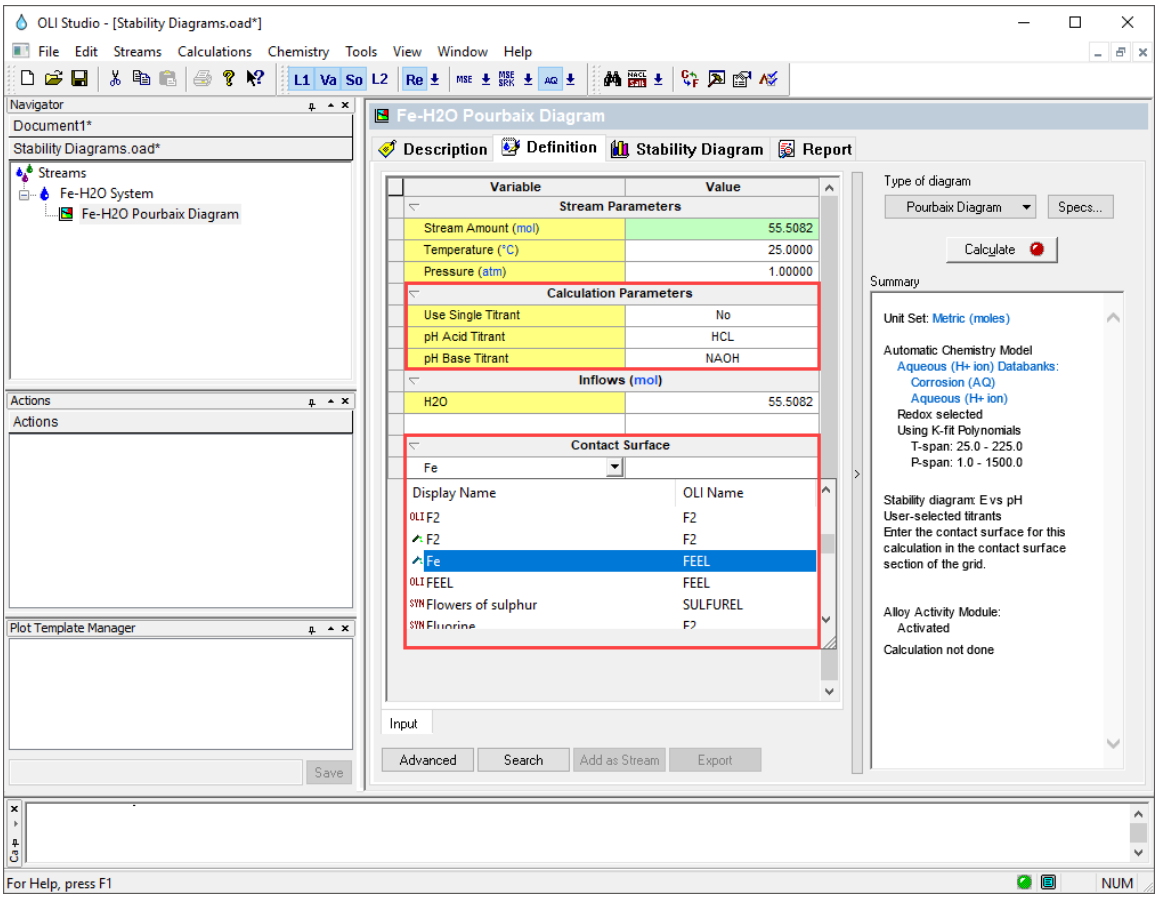
In the **Contact Surface** grid is where the metal or alloy of interest needs to be defined. E.g. Fe, Cu, carbon steel, etc.

The **Redox** button (Re) is turned ON for this calculation since reduction and oxidation reactions are need it to create the Pourbaix Diagram. This option will enable the different oxidation states of the selected metal.

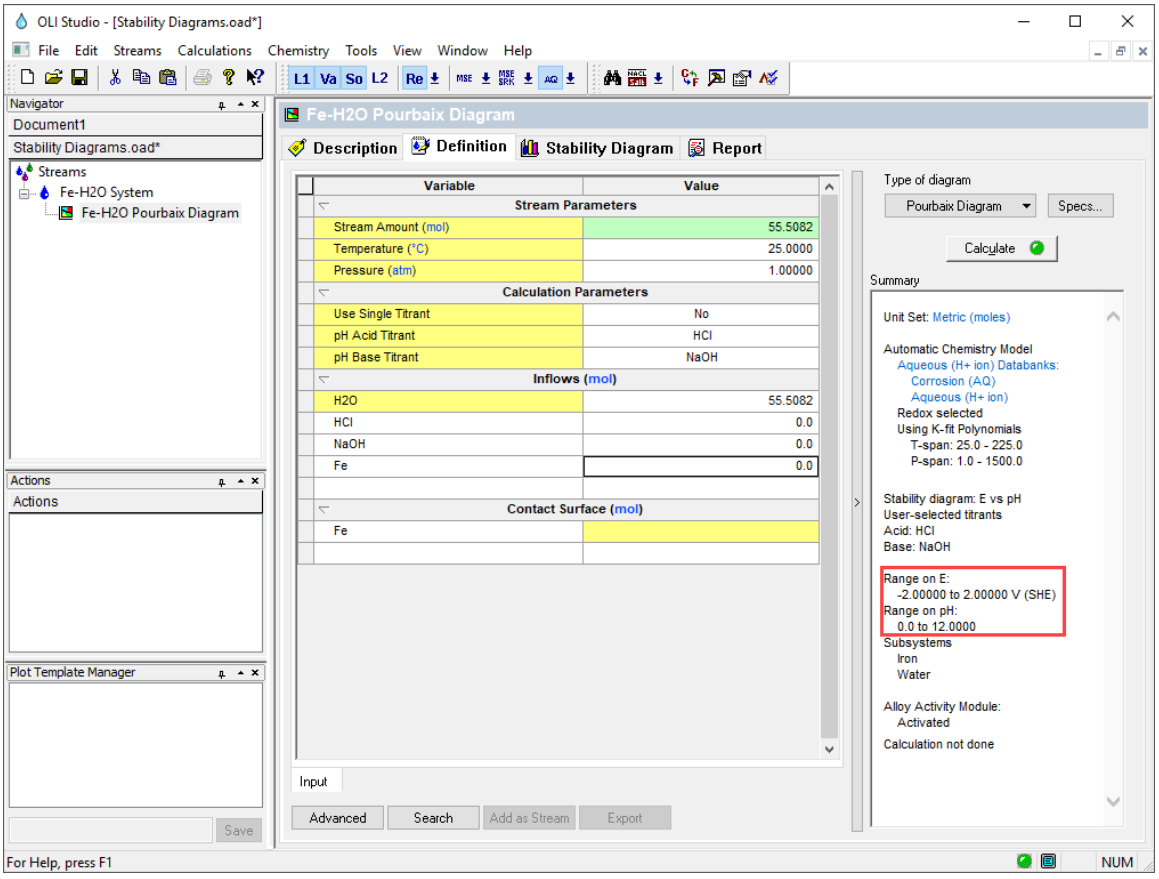


10. Leave the default titrants for this calculation: HCl and NaOH
11. Under the **Contact Surface** grid type **Fe**

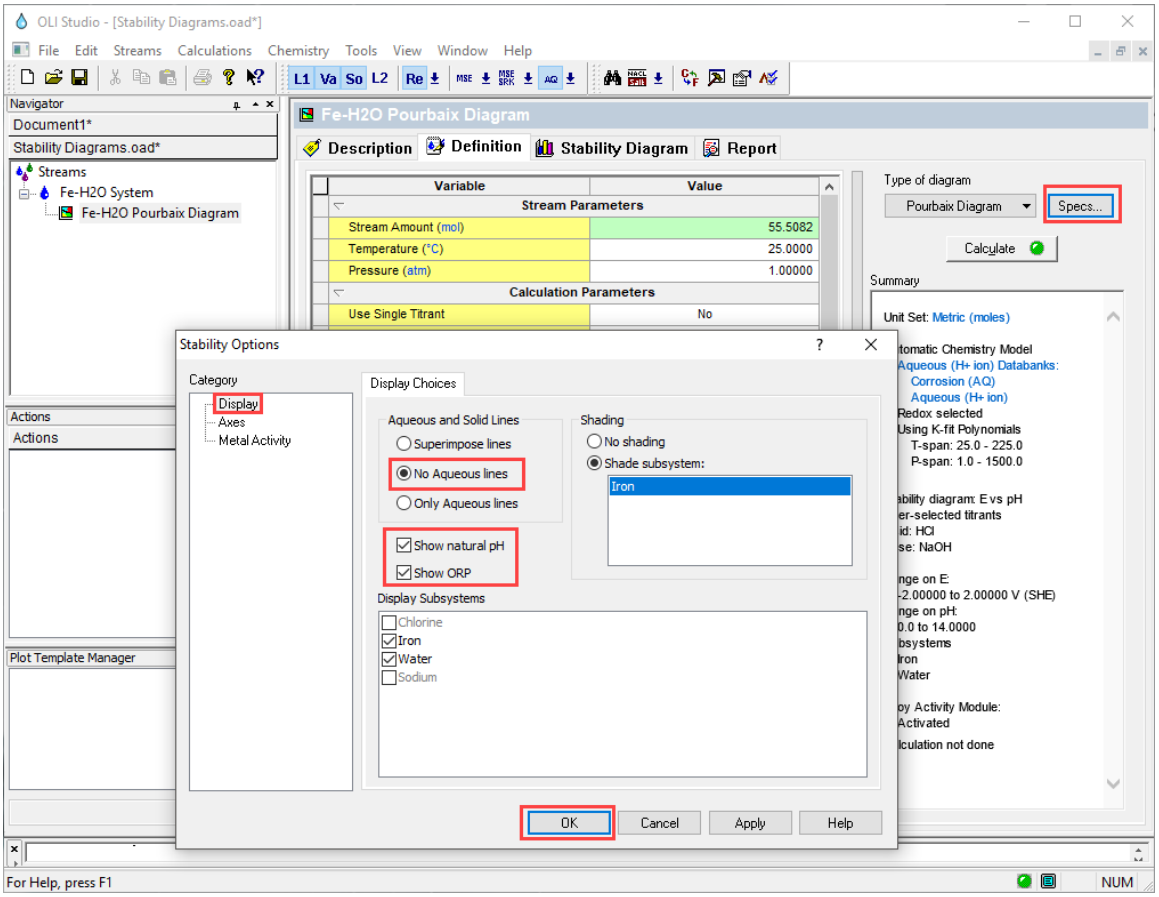
Note: You also have the option to use the drop-down arrow to search for the metal or alloy of interest.



At this point all the basic inputs to create a Pourbaix Diagram have been defined. Notice that in the summary box the following default plotting settings have been defined: Potential range: -2 to 2 V vs SHE and pH range: 0-14. You can modify these default values before running the calculation.

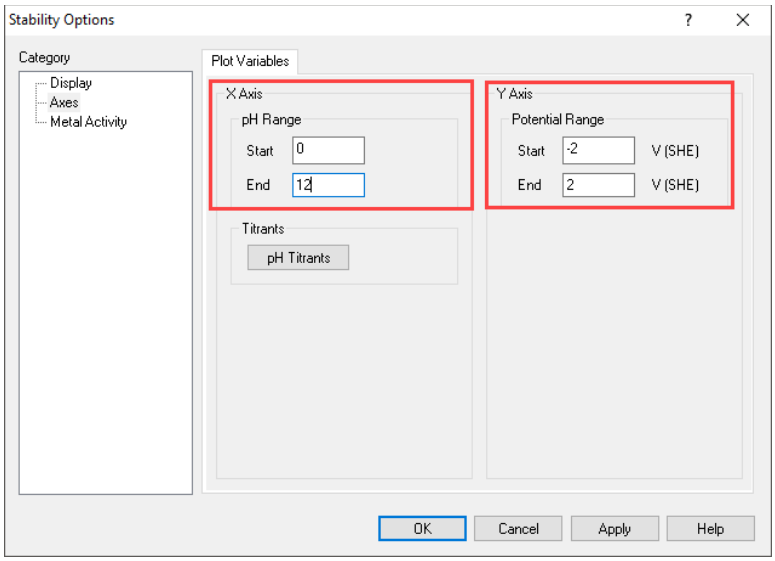


15. Click on the **Specs** button. This will open the **Stability Diagram Options** Window
16. Under the **Display** Category you will see the **Display Choices** tab. Under this tab make sure to select the following options:
    i. No Aqueous lines
    ii. Show natural pH
    iii. Show ORP
17. Under **Display Subsystems** check the **Iron** and **Water** boxes
18. Under **Shading** select the option **Shade Subsystem** and select **Iron.**
19. Click **OK** to close the window



20. **Click** on the **Axes** Category. This will show you the Plot Variables tab.

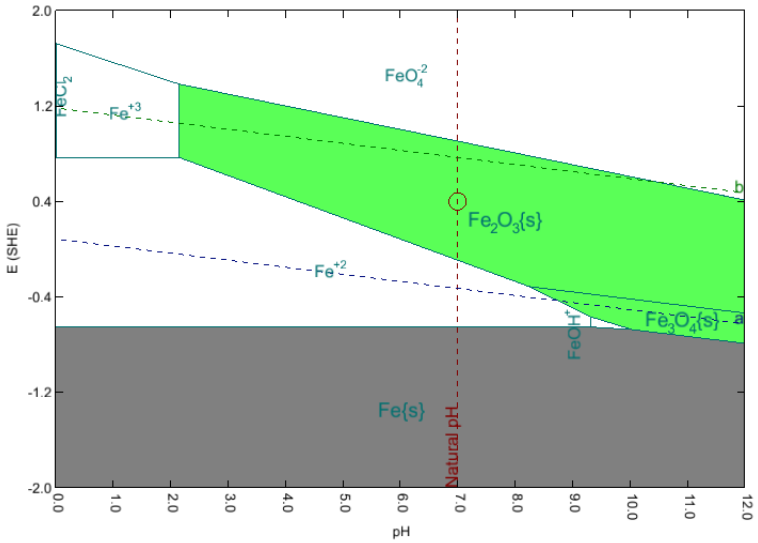
    Note: In the **Axes** Category you can modify the axes of the Pourbaix Diagram and change the default titrants.



21. **Change** the X Axis or pH range to 2-12
22. **Leave** the default values for the Y Axis of Potential Range (-2 to 2 V SHE)
23. Click **OK** to close the window
24. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
25. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it and name it as *Stability Diagrams.*

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-H2O system at 25 ºC and 1 atm.



The obtained diagram is useful for assessing the corrosion behavior of iron in pure water.

Elemental iron (gray section) is stable from -2 to -0.6 V SHE. At a potential greater than -0.6 V SHE, Fe oxidizes to Fe^{+2}. If the pH is above 10, the boundary is at a lower potential for example, -0.7 V SHE at 12 pH.

The software computes that Fe_3O_4 (magnetite) is stable between a pH range of ~8.3 and 12. This is also known as the *Passive Film* that protects the iron surface from active corrosion. At higher potentials, the software computes Fe_2O_3 (hematite). Hematite is the dehydrated form of $Fe(OH)_3$ and FeOOH, two forms of rust. These phases provide less corrosion protection the iron surface than the magnetite. These two phases are represented in the plot by the green color.

The white sections of the plot represent the dominant iron-containing species dissolved in solution. The species with the largest range is Fe^{+2}. The software computes stability for this species from -0.6 V to 0.77 V SHE, at low pH, and it is no longer stable at pH 10. Active corrosion of the iron surface is predicted if the pH is between 0 and 10. The actual corrosion rate cannot be predicted from this plot, nor can the pH of the water film (diffusion layer) in contact with the iron surface. Therefore, the pH range of 0 to 10 is a guideline and not a direct prediction.

The natural pH and the oxidation reduction potential (ORP) of water, which is represented by the red circle, are showing that when placing Fe in pure water at 25 ºC and 1 atm. The point at which the natural pH and the ORP intersects (7 pH, 0.4 V SHE) indicates that Fe_2O_3 (hematite) is the most stable species that forms.

Additionally, notice that the oxidation of iron can be coupled with the reduction of water because water reduction line (line a) lies 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 e.g. Fe^{2+}.

7.4. Selective Oxidation and Reduction Chemistry

Occasionally you may want to remove a specific oxidation state for an element when building a Stability Diagram. There are a variety of reasons to perform such an activity, one being that a specific oxidation state may be kinetically unavailable for the reaction. Another case is that perhaps you need to compare and contrast two systems. We will explore how to do this in the following example.

Example 41: Turning off the Fe^{+6} oxidation state in the Stability Diagram

In this example you will create a Stability diagram for iron in water at ambient conditions (see previous example for details on how to create this stream), learn how to change the default titrants and turn off/on different specific oxidation states of the metal of interest.

Starting the Simulation

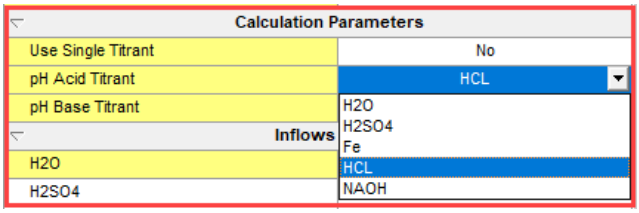
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Stability Diagram Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Fe-H2O System	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 ºC
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe	H2SO4	0 moles
		NaOH	0 moles

1. Under the *Fe-H2O System* add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane.
2. Select the **AQ** thermodynamic Framework
3. **Click** on the **Names Manager** Icon and select the **Formula** option
4. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
5. Enter the composition, temperature and pressure of the stream given in the table above. **Add** H2SO4 and NaOH as inflows. **Note**: H2SO4 and NaOH will be used as titrants to adjust pH
6. Select **Pourbaix Diagram** as Type of Survey – Default
7. **Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O Selective Oxidation*
8. Under the **Contact Surface** grid type **Fe**

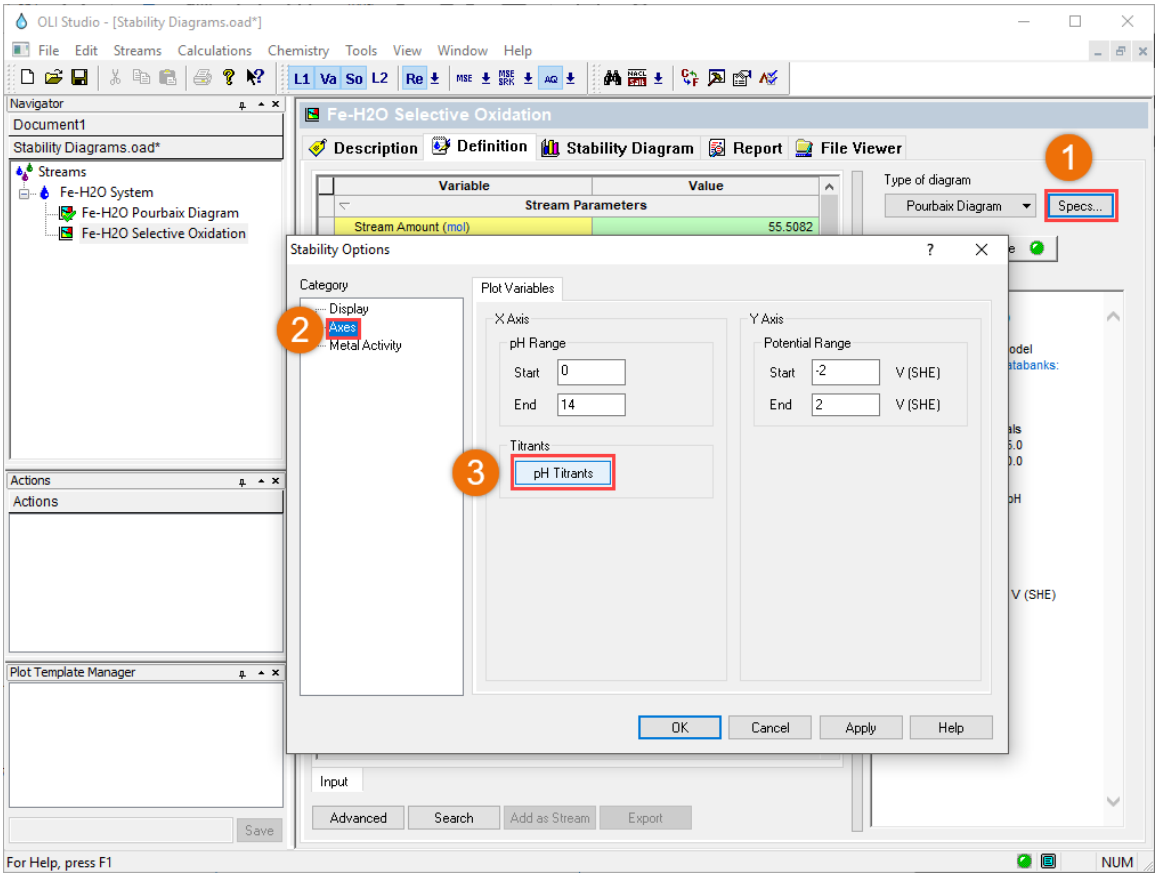
Changing the Default Titrant

9. In the **Calculation Parameters** grid, **click** on HCl (which is default titrant). A drop-down arrow appears, **click** on it and **select** H2SO4. NaOH has been selected by default.

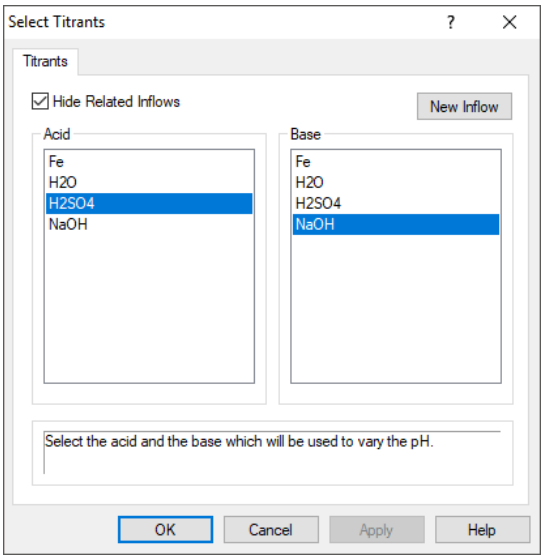


Note: You can also change the default titrant using the **Specs** button

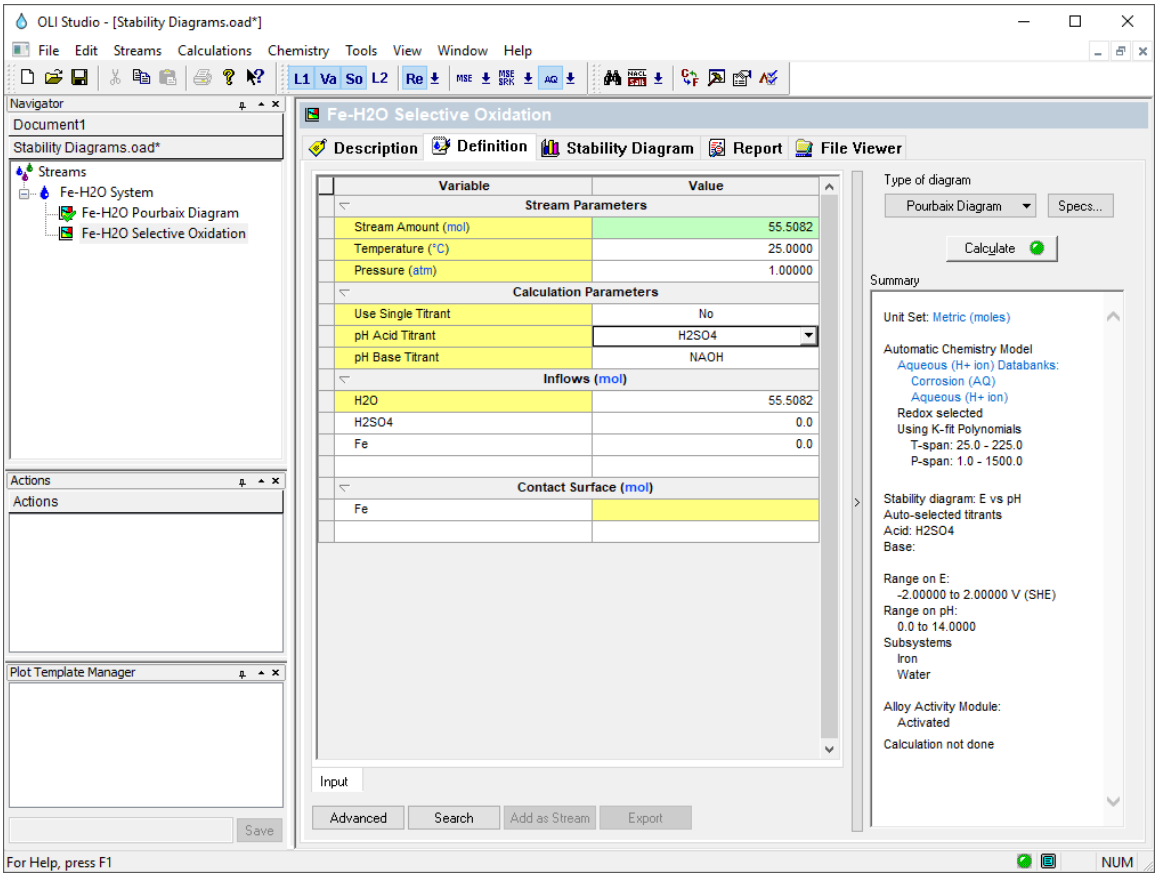
1. **Click** on the **Specs** button
2. **Select** the **Axes** option under the **Category** window
3. **Click** on **pH Titrants.** This will open a new window



4. **Select H2SO4** as the **Acid** titrant, and **NaOH** as the **Base** titrant. Then **click OK** to exit both windows.



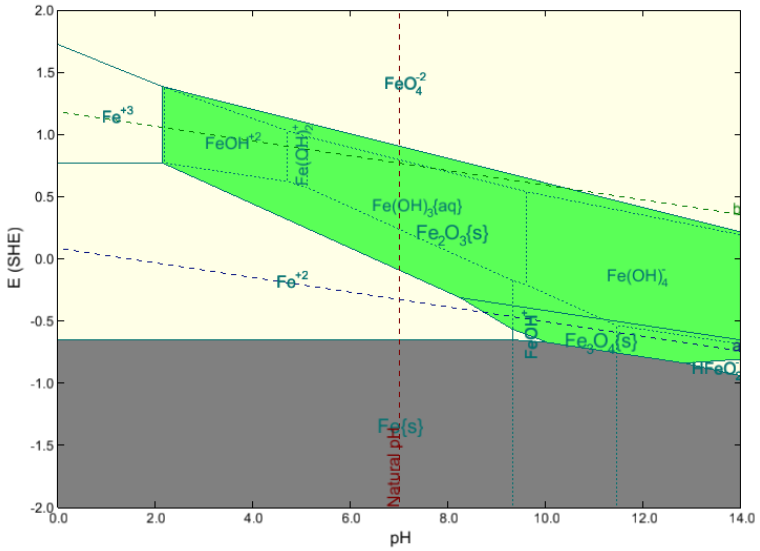
The screen should look like the image below after all the inputs and definitions have been entered:



10. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
11. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams.*

Analyzing the Results

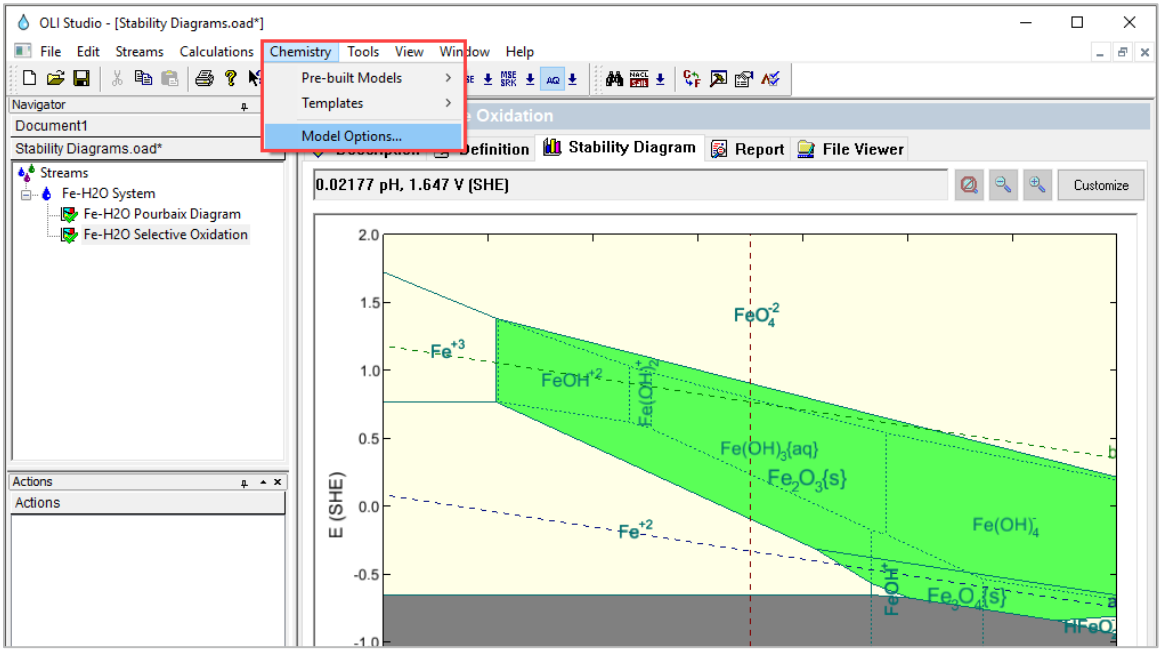
Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-H2O system at 25 ºC and 1 atm.



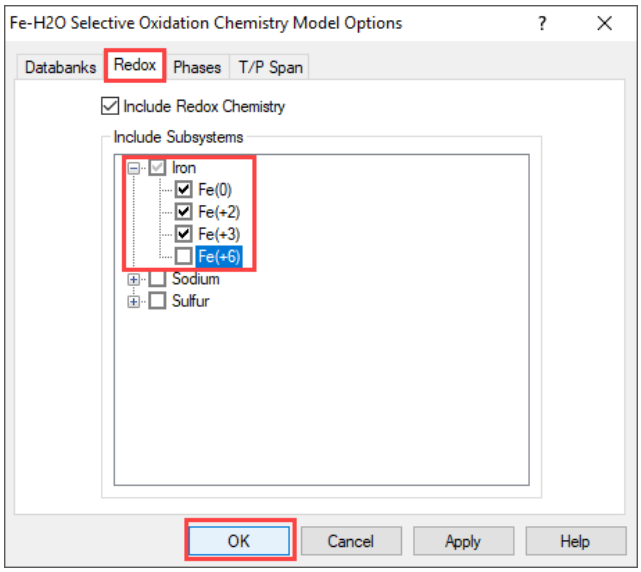
Marcell Pourbaix did not consider the FeO_4^{2-} ion in his work. This is iron in the +6 oxidation state for which there was little thermodynamic data available in the1960s. To reproduce his work, we need to remove the redox subsystem that pertains to Fe(+6).

Selective Redox, removing an undesired oxidation state

1. In the Menu bar go to **Chemistry > Model Options.** This will open a new window



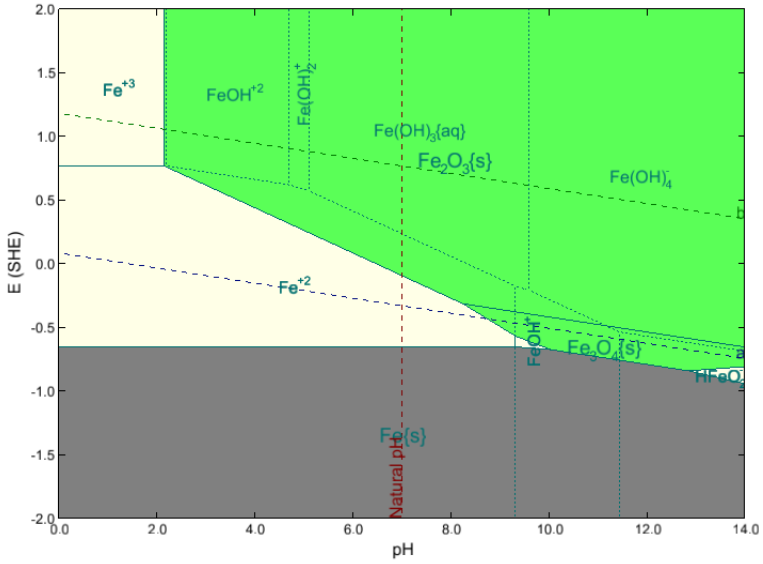
2. Select the **Redox** tab, expand the Iron Subsystems by clicking on the **'+'** icon, and **uncheck** the **Fe(+6)** oxidation state. Note that if you have an inflow component with this oxidation state it will remain in the calculation. Click the **OK** button to save your changes and close the window.



12. We are ready to recalculate to consider the changes. Press the **<F9>** key or go to the **Definition** tab and click on the **Calculate** button.

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). In the figure below, you can see that the region dominated by the FeO_4^{2-} ion is not present.



7.5. Modeling the Effects of Hydrogen Sulfide on Corrosion

Example 42: The Effect of Hydrogen Sulfide on the Corrosion of Iron

The H_2S (S^{-2}) forms a relatively insoluble precipitate with Fe^{+2}. This precipitate has the potential to cover the metal surface and enhance the pH region where iron is protected from the water. We will model this using the Stability Diagram tool.

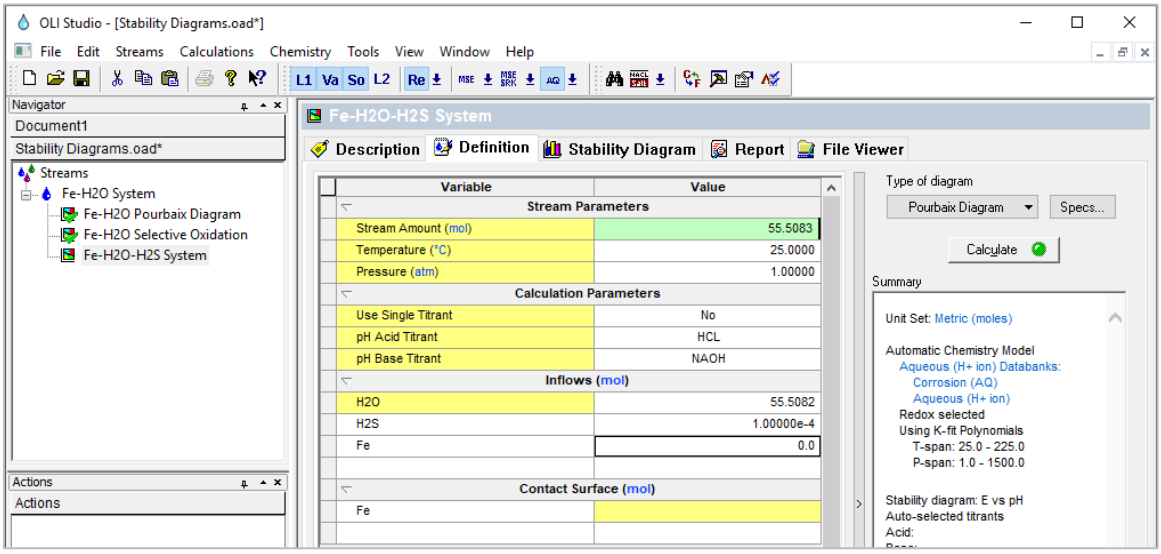
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Stability Diagram Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Fe-H2O System	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 ºC
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe	H2S	1e-4 moles

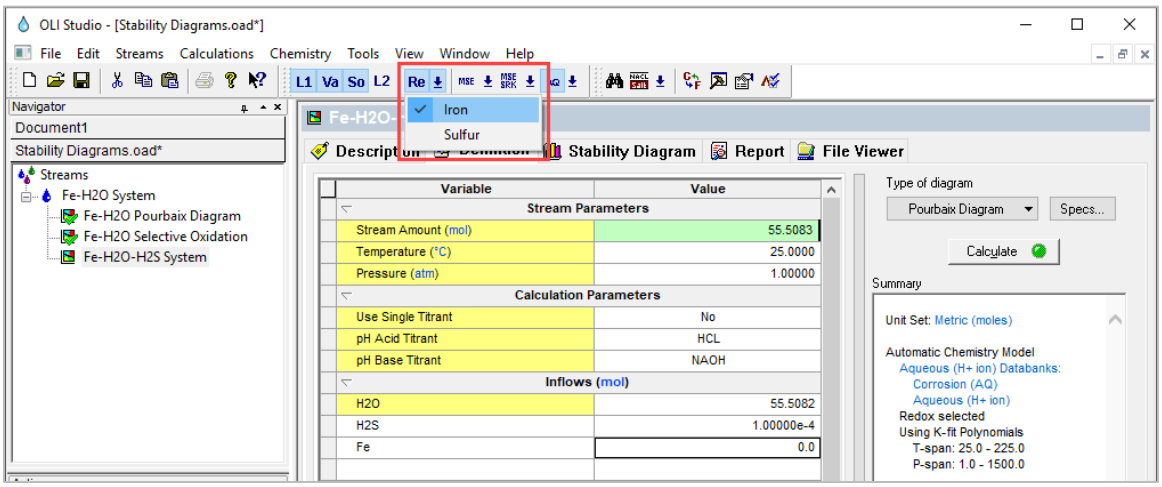
1. Under the *Fe-H2O System* add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane.
2. Select the **AQ** thermodynamic Framework
3. **Click** on the **Names Manager** Icon and select the **Formula** option
4. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
5. Enter the composition, temperature and pressure of the stream given in the table above. **Add 1e-4 moles of H2S** as an inflow.
6. Select **Pourbaix Diagram** as Type of Survey – Default
7. **Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O-H2S System*
8. Under the **Contact Surface** grid type **Fe**

The screen should look like the image below after all the inputs and definitions have been entered:



Note: By default, only the transition metals are turned ON. The different oxidation states of elements that are not transition metals are not turned on automatically. You need to turn them ON manually.

9. **Go** to the **Redox** button (**Re**), and **click** on the drop-down arrow
10. **Select Sulfur**. This will turn the oxidation states of sulfur ON

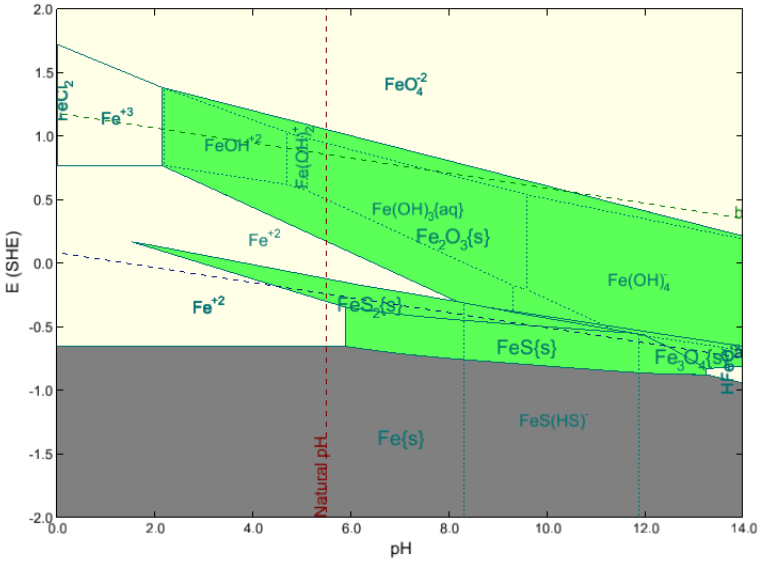


11. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
12. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams.*

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-H2O-H2S system at 25 ºC and 1 atm.

Inspection of the diagram reveals a profound effect of H_2S on the corrosion of iron. New stability fields of FeS and FeS_2 are observed. 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 to occur 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 is frequently present.

7.6. Modeling Corrosion at High Temperature

Example 43: High Temperature Iron in Water

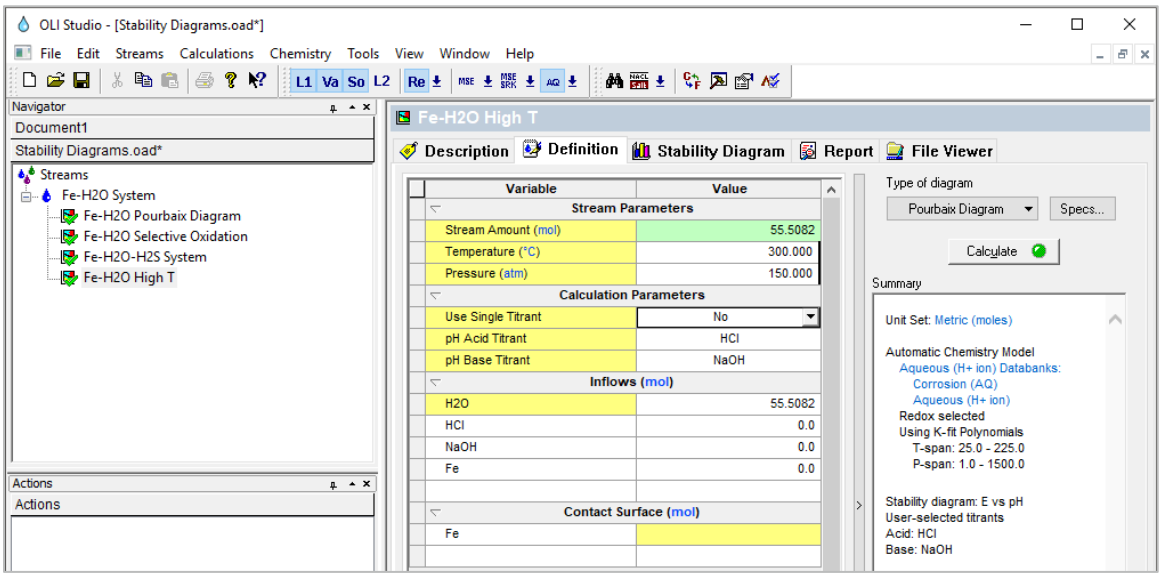
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Stability Diagram Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Fe-H2O System	Stream Amount	Calculated
Name Style	Display Formula	Temperature	300 ºC
Unit Set	Metric, Batch, Moles	Pressure	150 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe		

1. Under the *Fe-H2O System* add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane.
2. Select the **AQ** thermodynamic Framework
3. **Click** on the **Names Manager** Icon and select the **Formula** option
4. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
5. Enter the composition, temperature and pressure of the stream given in the table above
6. Select **Pourbaix Diagram** as Type of Survey – Default
7. **Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O High T*
8. Under the **Contact Surface** grid type **Fe**

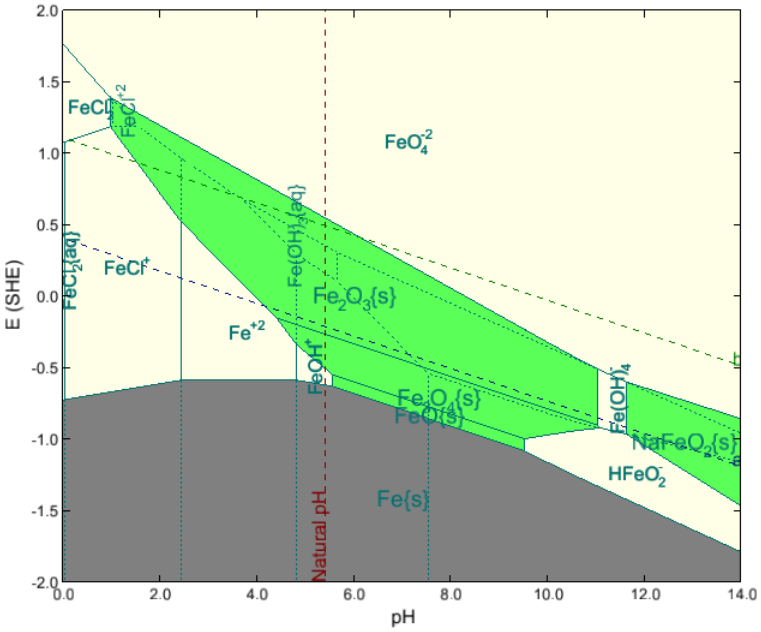
The screen should look like the image below after all the inputs and definitions have been entered:



9. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
10. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams.*

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-H2O system at 300 ºC and 150 atm.



We can see from the diagram above that passivation is only possible at moderate pH's.

Example 44: Neutralization of Refinery Streams with Alkanolamines

In this example you will create a stability diagram for alkaline neutralization in an oil refinery.

Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

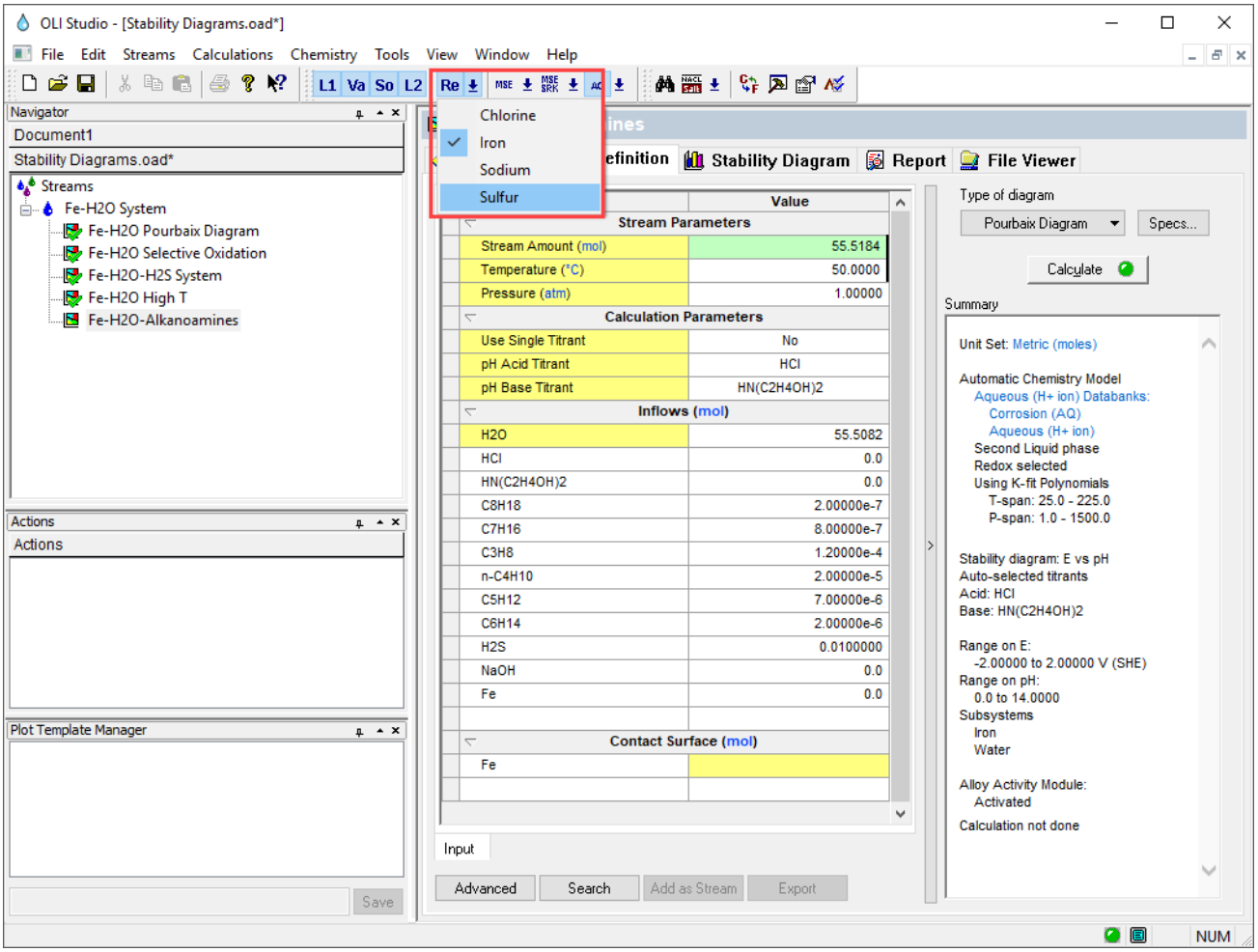
Stability Diagram Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Fe-H2O System	Stream Amount	Calculated
Name Style	Display Formula	Temperature	50 ºC
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe	HCl	0 moles (Acid Titrant)
		DEA[8]	0 moles (Base Titrant)
		C8H18	2E-07 moles
		C7H16	8E-07 moles
		C3H8	1.2E-04 moles
		C4H10	2E-05 moles
		C5H12	7E-6 moles
		C6H14	2E-6 moles
		H2S	0.01 moles

1. Under the *Fe-H2O System* add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane
2. Select the **AQ** thermodynamic Framework
3. **Click** on the **Names Manager** Icon and select the **Formula** option
4. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
5. Enter the composition, temperature and pressure of the stream given in the table above
6. Select **Pourbaix Diagram** as Type of Survey – Default
7. **Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O-Alkanoamines*
8. Under the **Contact Surface** grid type **Fe**
9. **Change** the **Base Titrant** to **DEA**
10. **Turn Redox ON** for Sulfur. **Click** on the drop-down arrow next to the **Re** button and select **Sulfur**

    Note: You can also enable Redox reactions via the menu bar: ***Chemistry*** > ***Model Options*** > ***Redox*** tab. Make sure that Sulfur is checked.

[8] The "ESP" name for this species is DEXH, which can be used as an input to make your life easier. The formula name is: HN(C2H4OH)2

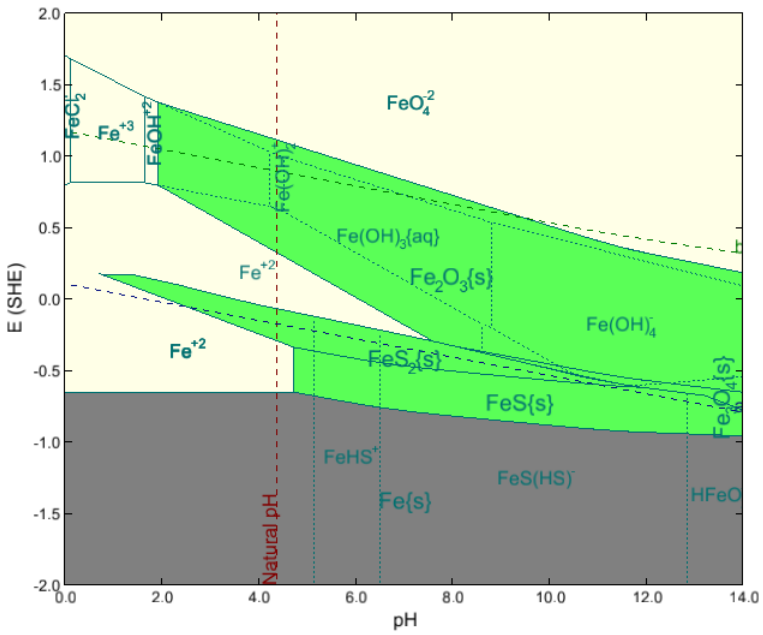
The screen should look like the image below after all the inputs and definitions have been entered:



11. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
12. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams.*

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-H2O system at 50 ºC and 1 atm.



7.7. Modeling the Effects of Complexation on Corrosion

In this section we will simulate the reaction of Copper with Ammonia and Gold metal with Cyanide. This section attempts to answer the question of how strong complexing agents affect the passivation of these metals.

Example 45: Copper and Ammonia

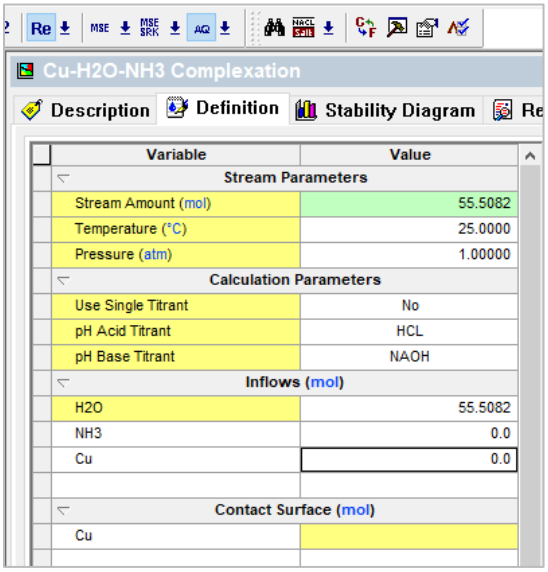
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Stability Diagram Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Cu-H2O System	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 ºC
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Cu	NH3	0 moles

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Cu-H2O System*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition, temperature and pressure of the stream given in the table above
7. Under the *Cu-H2O System* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane
8. Select **Pourbaix Diagram** as Type of Survey – Default
9. **Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Cu-H2O-NH3*
10. Under the **Contact Surface** grid type **Cu**

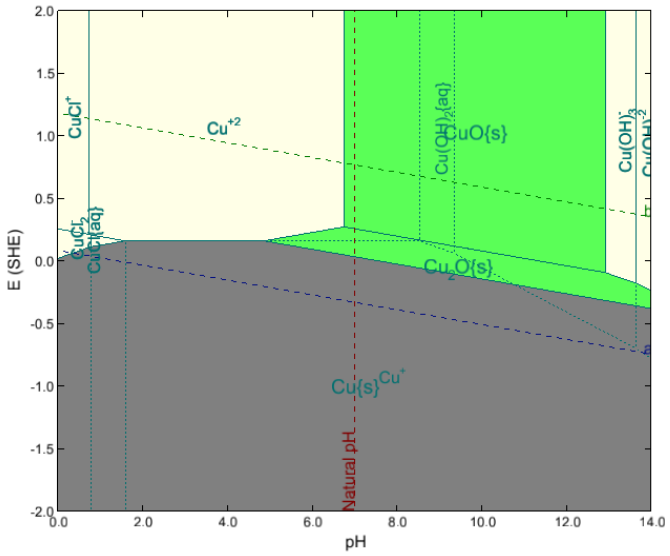
The screen should look like the image below after all the inputs and definitions have been entered:



13. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
14. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams.*

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Cu-H2O system at 25 ºC and 1 atm.



In the absence of oxygen (looking at only the ***a*** line), we can see that the copper equilibrium line lays above the hydrogen ***a*** line. This means there is insufficient oxidizing power in the water to corrode copper metal in pure water.

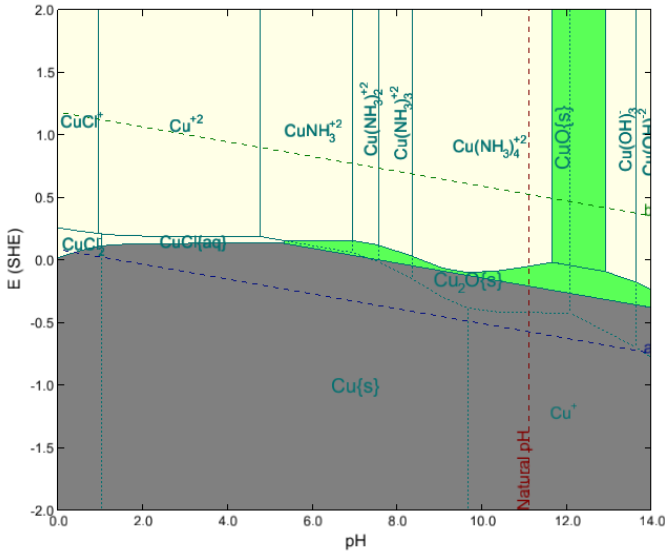
What happens if Ammonia (NH_3) is added to the solution? The next step is to understand the effect of NH_3 on the stability of copper.

Effect of NH3 on the Stability of Copper

1. Go to the **Definition** tab, and change the amount of NH3 from 0 to 0.1 moles
2. **Click** on the **Calculate** button or press the **<F9>** key

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Cu-H2O-NH3 system at 25 ºC and 1 atm in a 0.1 m of NH3 solution.



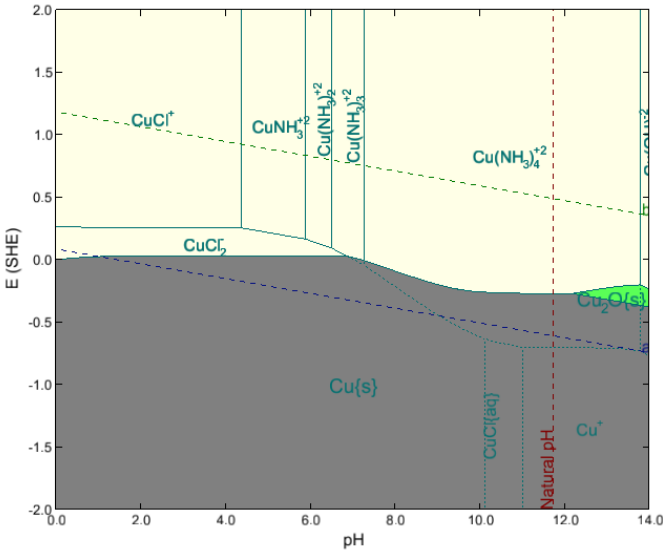
Notice that a large area of corrosive liquid has appeared in the stability field for the copper oxides. This means that it is thermodynamically possible for the ammonia to break down the passivation layer of copper oxide in the presence of oxygen. Notice that in the absence of oxygen (the ***a*** line only), copper is still stable.

Now repeat the exercise with ***1.5 moles of NH3***

1. Go to the **Definition** tab, and change the amount of NH3 from 0 to 1.5 moles
2. **Click** on the **Calculate** button or press the **<F9>** key

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Cu-H2O-NH3 system at 25 ºC and 1 atm in a 1.5 m of NH3 solution.



At this concentration of ammonia, most, if not all the passivating copper oxide has been reacted away. Only at very high pH values are there any stable oxides.

Example 46: Gold in the presence of Cyanides

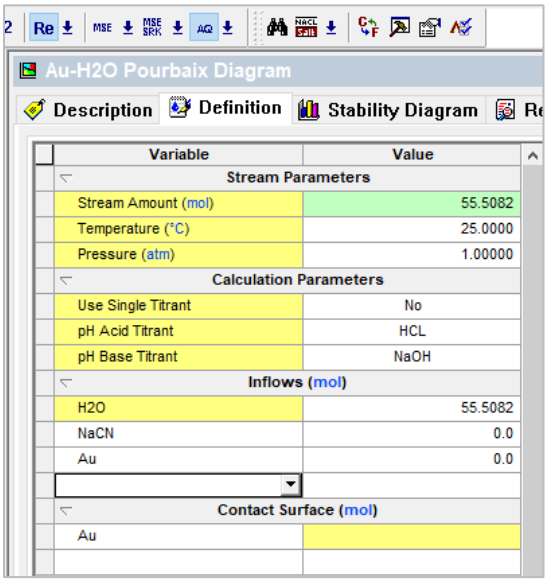
Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Stability Diagram Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Au-H2O System	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 ºC
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Au	NaCN	0 moles

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Au-H2O System*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition, temperature and pressure of the stream given in the table above
7. Under the *Au-H2O System* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane
8. Select **Pourbaix Diagram** as Type of Survey – Default
9. **Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Au-H2O*
10. Under the **Contact Surface** grid type **Au**

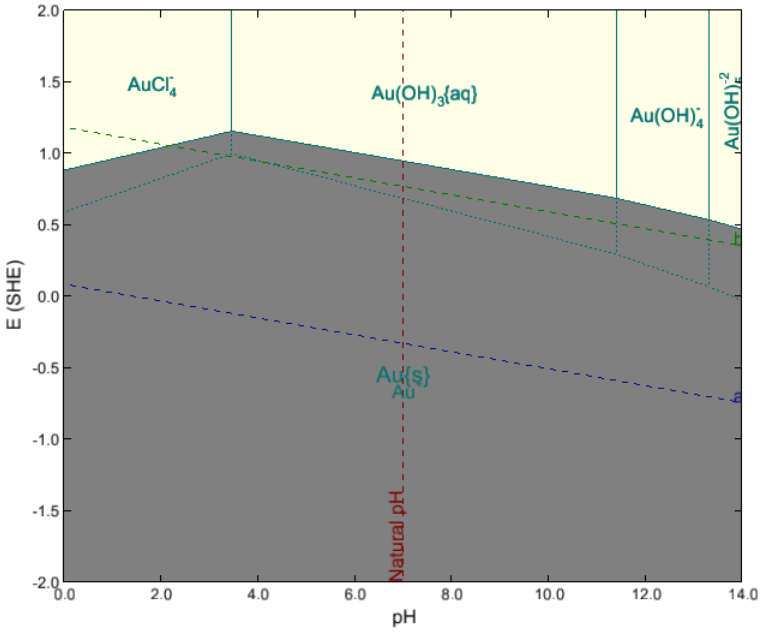
The screen should look like the image below after all the inputs and definitions have been entered:



11. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
12. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams.*

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Au-H2O system at 25 ºC and 1 atm.



You can see that without oxygen, gold metal is immune to corrosion. The hydrogen line ***a*** is below the gold equilibrium line. In the presence of oxygen, gold is still immune to corrosion except at very low pH.

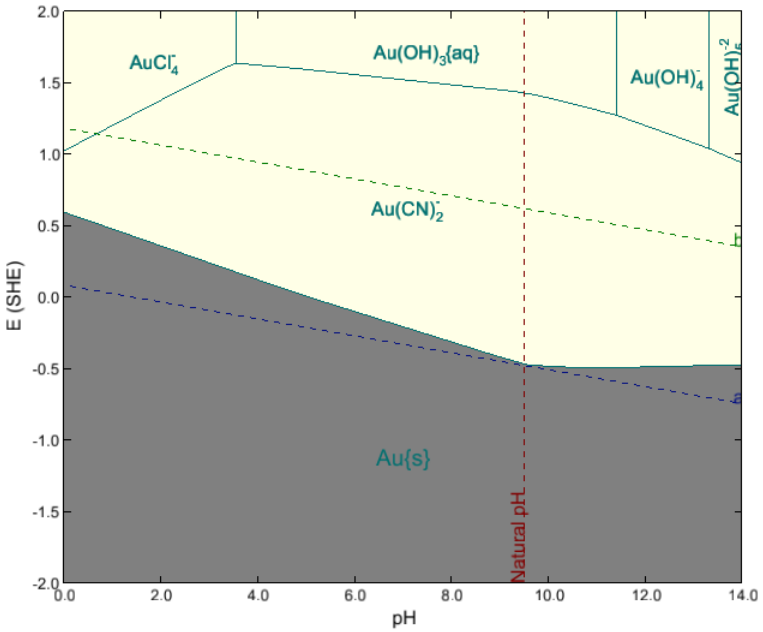
One of the most commonly used leaching processes for **gold extraction** is the **cyanidation** process. This process is a hydrometallurgical technique for extracting gold from low-grade ores by converting the gold to a water-soluble coordination complex. Basically, this approach adds cyanide salts to water. We are going to simulate this using the software.

Effect of Cyanide on the Stability of Gold

1. Go to the **Definition** tab, and change the amount of NaCN from 0 to 1e-4 moles
2. **Click** on the **Calculate** button or press the **<F9>** key

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Au-H2O-NaCN system at 25 ºC and 1 atm.



In the presence of oxygen, gold completely corrodes with cyanide. This is primarily due to the formation of the gold complex: $Au(CN)_2^-$. This complex is stable over all regions where water is also stable. This means that now gold can be processed in water in a variety of conditions.

7.8. Modeling the Effect of Oxidizing Inhibitors on Corrosion

In this chapter we will look at the effect of modeling corrosion inhibitors. We will do this by superimposing two stability diagrams over one another. If one solid field overlaps the corrosion range of the other system, then passivation is likely.

Example 47: Iron in the presence of chromates

Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

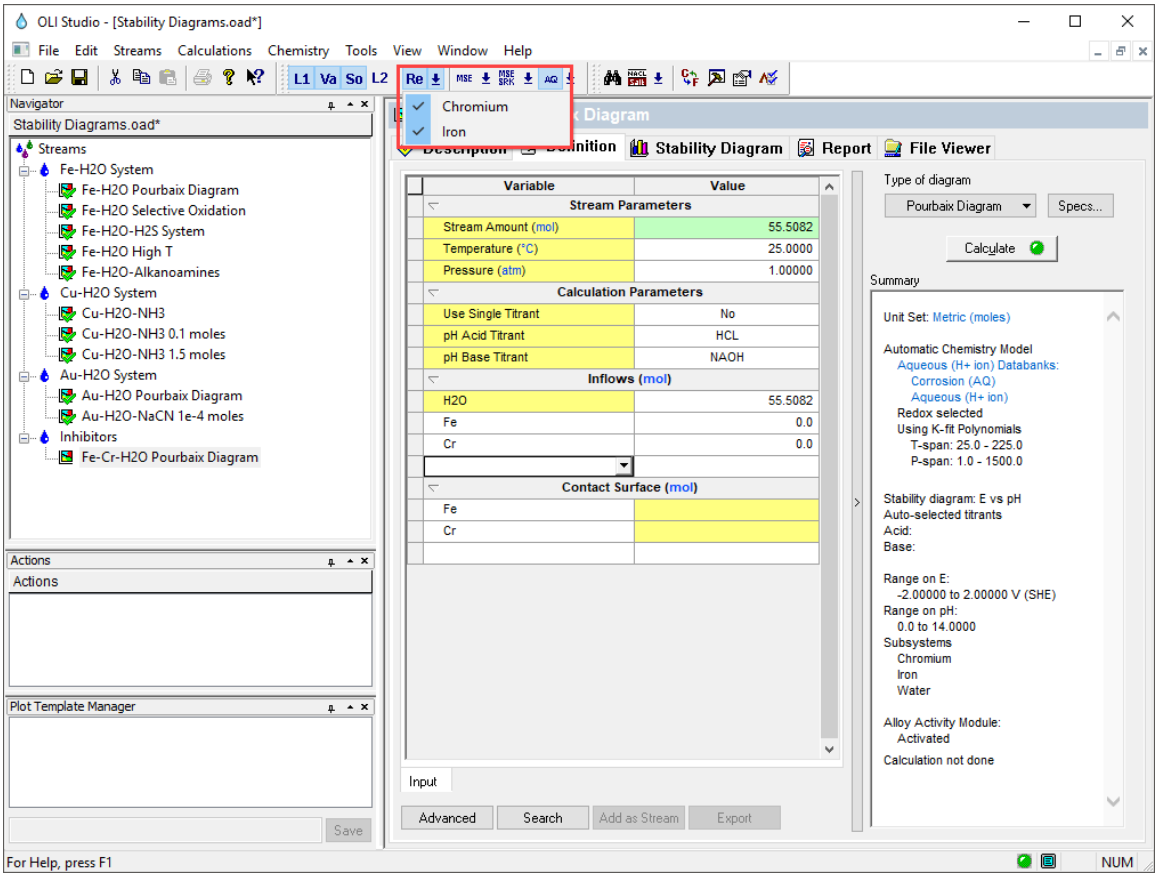
Stability Diagram Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Inhibitors	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 ºC
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe		
Contact Surface	Cr		

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Inhibitors*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition, temperature and pressure of the stream given in the table above
7. Under the *Inhibitors* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane
8. Select **Pourbaix Diagram** as Type of Survey – Default
9. **Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-Cr-H2O Pourbaix Diagram*
10. Under the **Contact Surface** grid type **Fe** and then **Cr**

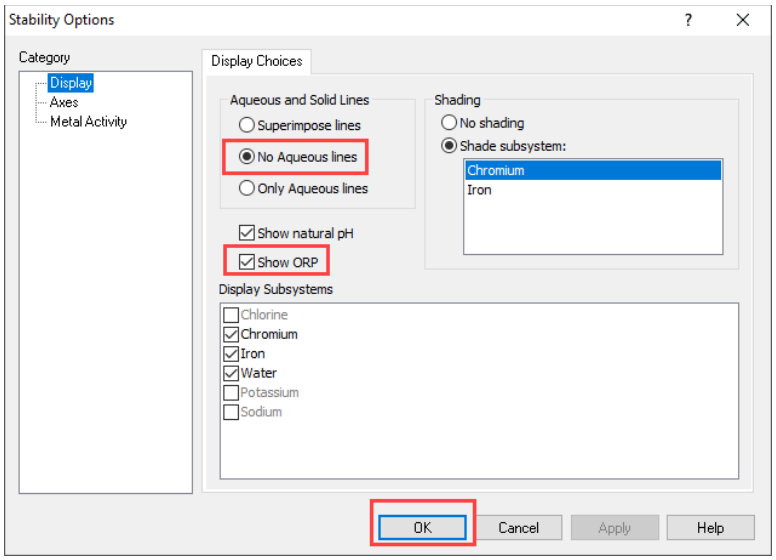
Note: Make sure that both **Fe** and **Cr** are enabled for Redox reactions. Use the arrow next to the **Re** button to expand the list.

You can also enable Redox reactions via the menu bar: ***Chemistry*** > ***Model Options*** > ***Redox*** tab. Make sure that Fe and Cr boxes are checked.

The screen should look like the image below after all the inputs and definitions have been entered:



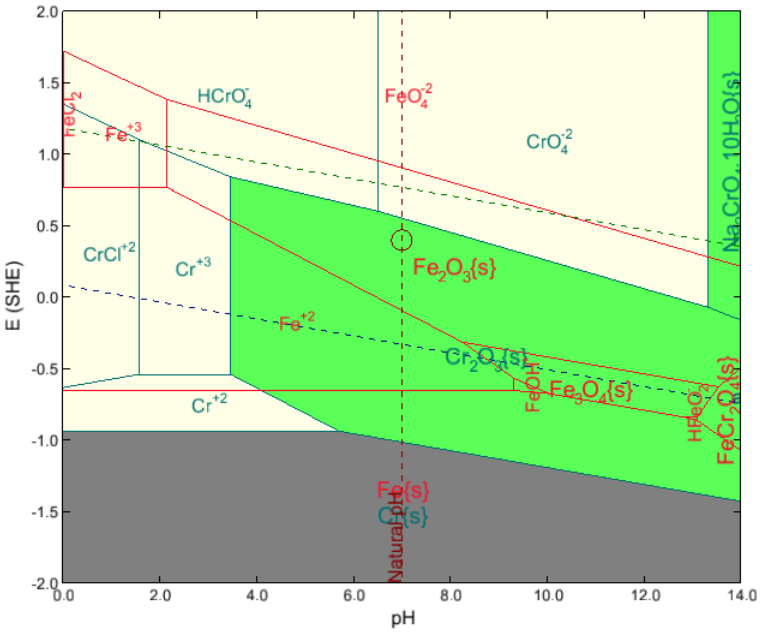
11. **Click** the **Specs** button and under the Display Choices tab check the following options:
    a) No aqueous lines
    b) Show ORP



12. Click **OK** to close the Stability Options window
13. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
14. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams.*

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-Cr-H2O system at 25 ºC and 1 atm.



As you can see in this diagram, the shaded chrome passivating solid ($Cr(OH)_{3ppt}$) overlays the corrosive region of the iron system. This means that there is potential for passivating the metal in that region.

The $Cr(OH)_3$ field overlaps with the corrosion range of Fe in most of the pH range. This causes inhibition because of the coupling of: Oxidation of Fe to Fe^{2+}, reduction of chromates to $Cr(OH)_3$, and the deposition of a protective layer of $Cr(OH)_3$.

Example 48: Iron in the presence of arsenates

Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

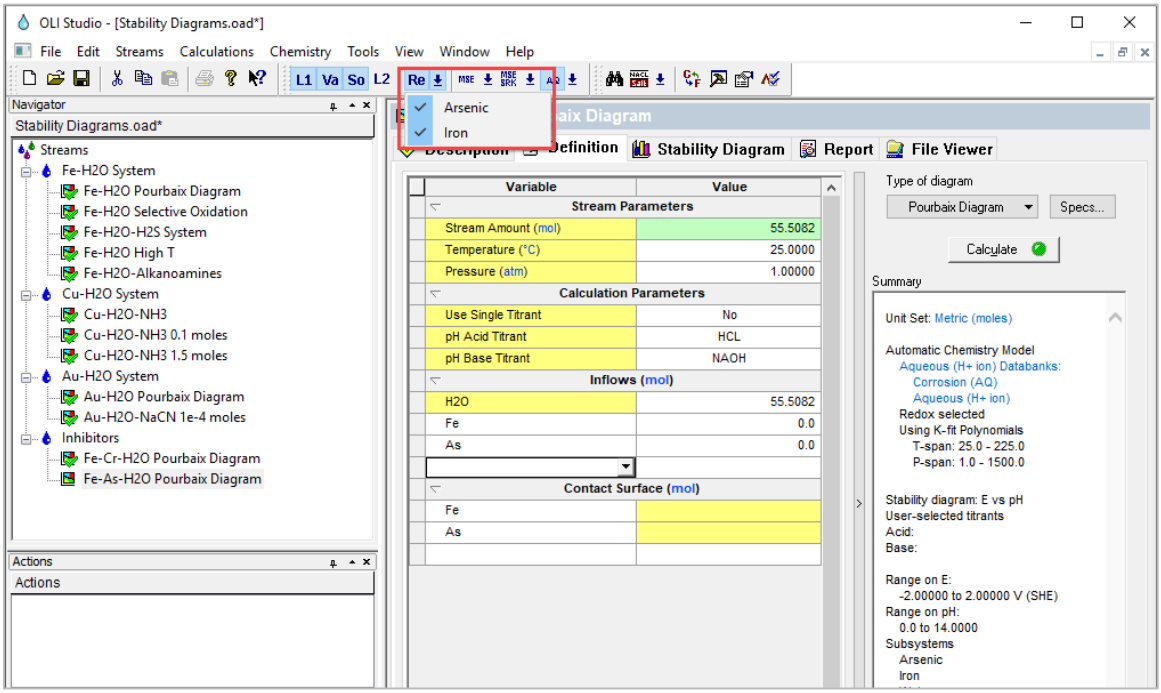
Stability Diagram Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Inhibitors	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 ºC
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe		
Contact Surface	As		

1. Under the *Inhibitors* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane
2. Select **Pourbaix Diagram** as Type of Survey – Default
3. **Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-As-H2O Pourbaix Diagram*
4. Under the **Contact Surface** grid type **Fe** and then **As**

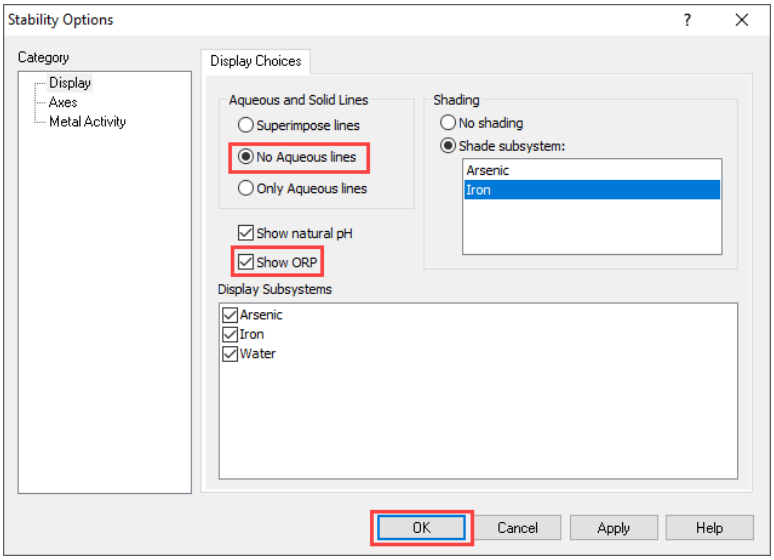
   Note: Make sure that both **Fe** and **As** are enabled for Redox reactions. Use the arrow next to the **Re** button to expand the list.

   You can also enable Redox reactions via the menu bar: ***Chemistry*** > ***Model Options*** > ***Redox*** tab. Make sure that Fe and As boxes are checked.

The screen should look like the image below after all the inputs and definitions have been entered:



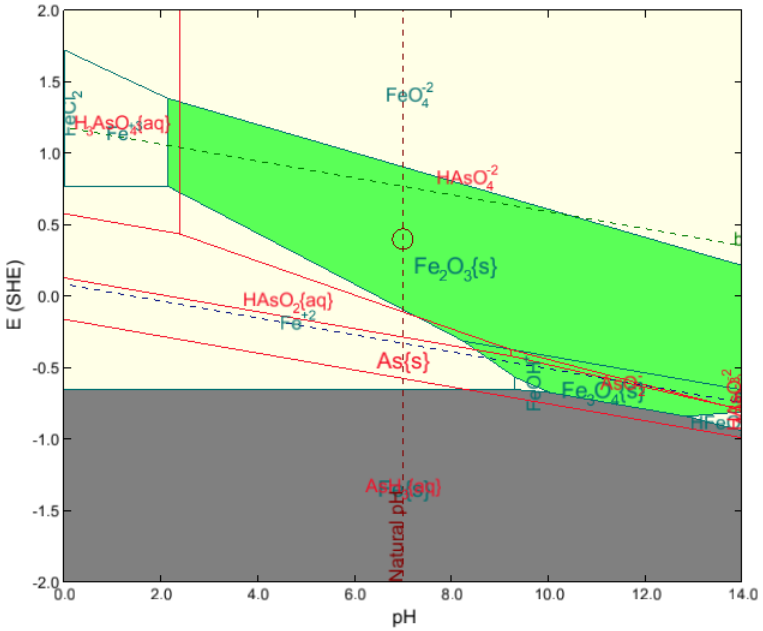
5. **Click** the **Specs** button and under the Display Choices tab check the following options:
   c) No aqueous lines
   d) Show ORP



6. Click **OK** to close the Stability Options window
7. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
8. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams.*

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-As-H2O system at 25 ºC and 1 atm.



The elemental arsenic field overlaps with the corrosion range of Fe in most of the pH range provided that the conditions are reducing (absence of oxygen). This promotes inhibition because of the coupling of: Oxidation of Fe to Fe^{+2} and the reduction of arsenates to elemental As. This promotes the deposition of a protective layer of As. This can only work in reducing environments; otherwise the protective layer of As will oxidize and dissolve.

7.9. Implications of Stability Diagrams on Cathodic Protection

Cathodic protection works by shifting the potential of the metal into its immunity range. Stability diagrams can help you to answer the following questions:

- What is the potential range that ensures that the metal stays in the immunity range?
- What is the effect of environmental variables on the immunity domain?

We will explore the Fe-H2O system at different temperatures and pressures to answer these questions.

Example 49: Effect of Temperature and Pressure on the Pourbaix Diagram of Fe-H2O System

Starting the Simulation

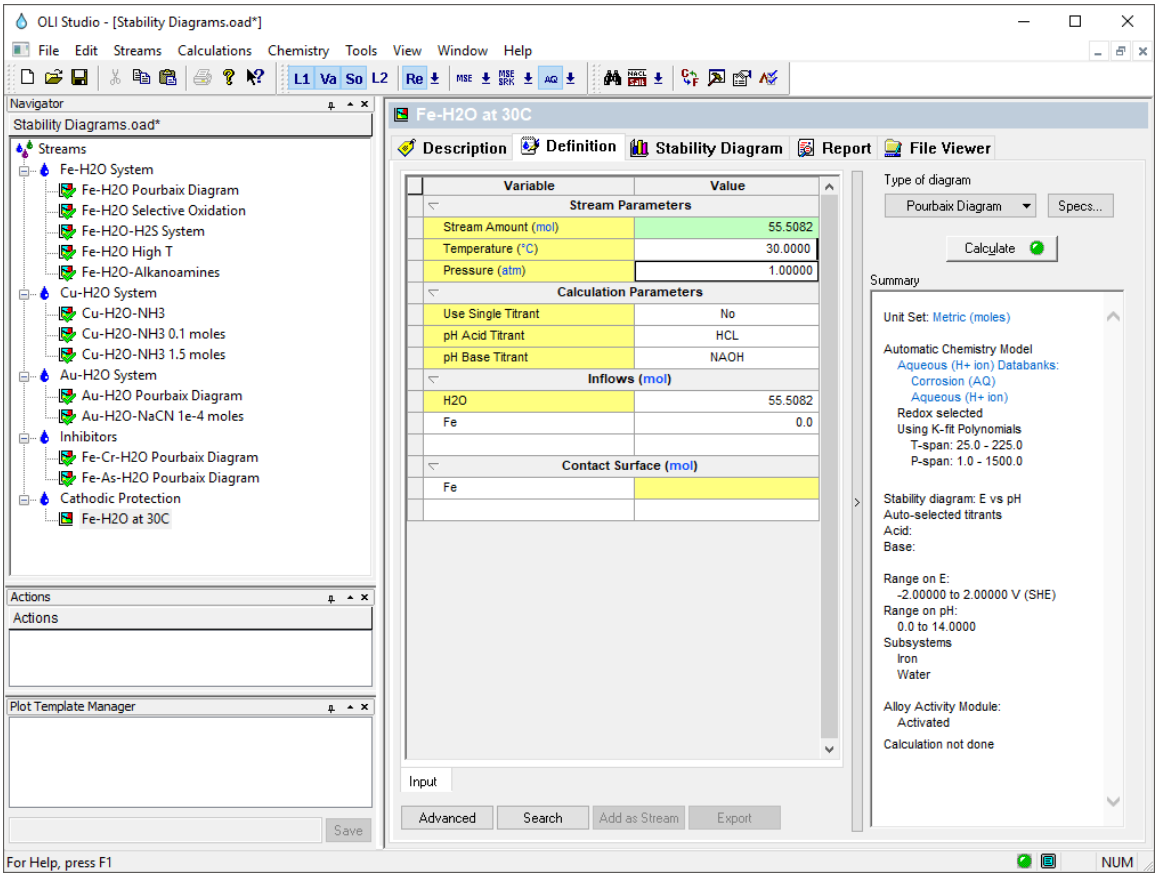
Iron at 30 ºC and 1 atm

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Stability Diagram Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Cathodic Protection	Stream Amount	Calculated
Name Style	Display Formula	Temperature	30 ºC
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe		

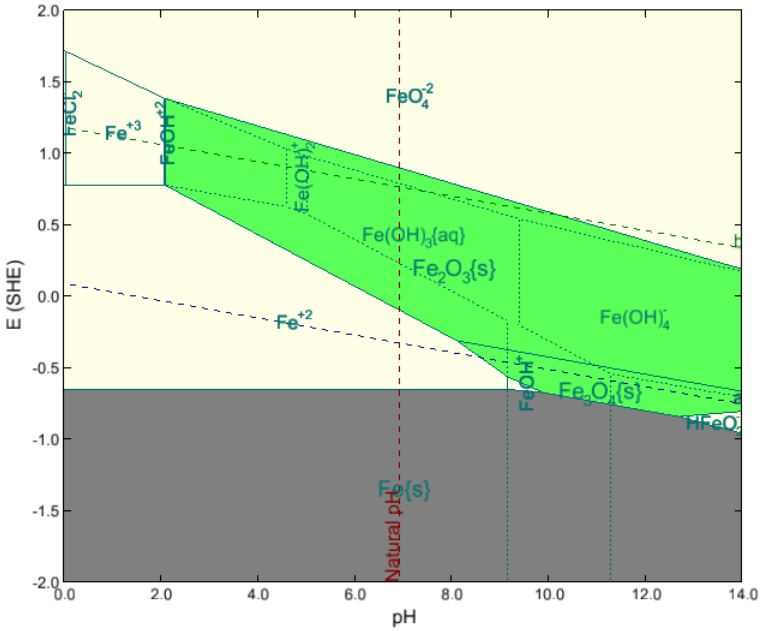
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Cathodic Protection*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition, temperature and pressure of the stream given in the table above
7. Under the *Cathodic Protection* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane
8. Select **Pourbaix Diagram** as Type of Survey – Default
9. **Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O at 30C and 1 atm*
10. Under the **Contact Surface** grid type **Fe**

The screen should look like the image below after all the inputs and definitions have been entered:



Analyzing the Results

Click on the **Chemical Diagram** tab (**Stability Diagram**). This tab displays the Pourbaix Diagram for the Fe-H2O system at 30 ºC and 1 atm.



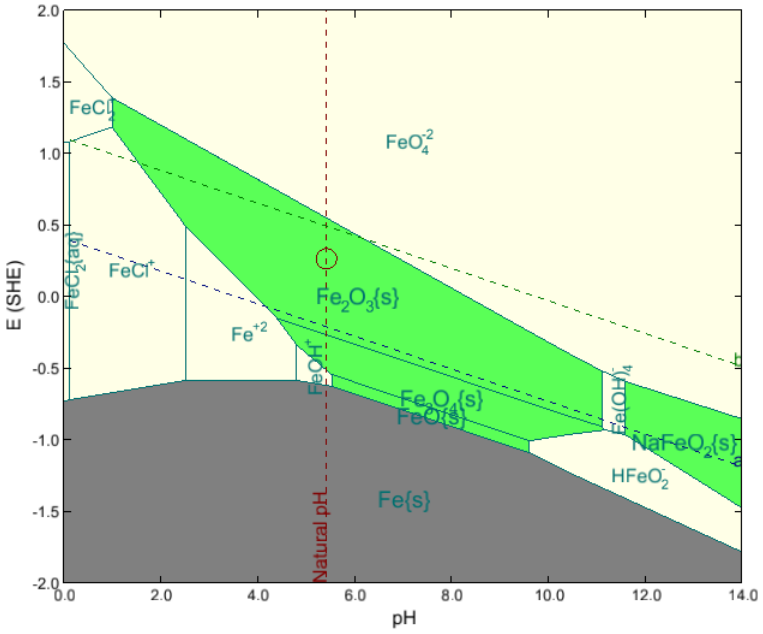
In the whole pH range, cathodic protection will require shifting the potential to moderately negative values.

Iron at 300 ºC and 100 atm

1. Go to the **Definition** tab, and change the Temperature and Pressure to 300ºC and 100 atm
2. **Click** on the **Calculate** button or press the **<F9>** key

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Cu-H2O-NH3 system at 300 ºC and 100 atm.

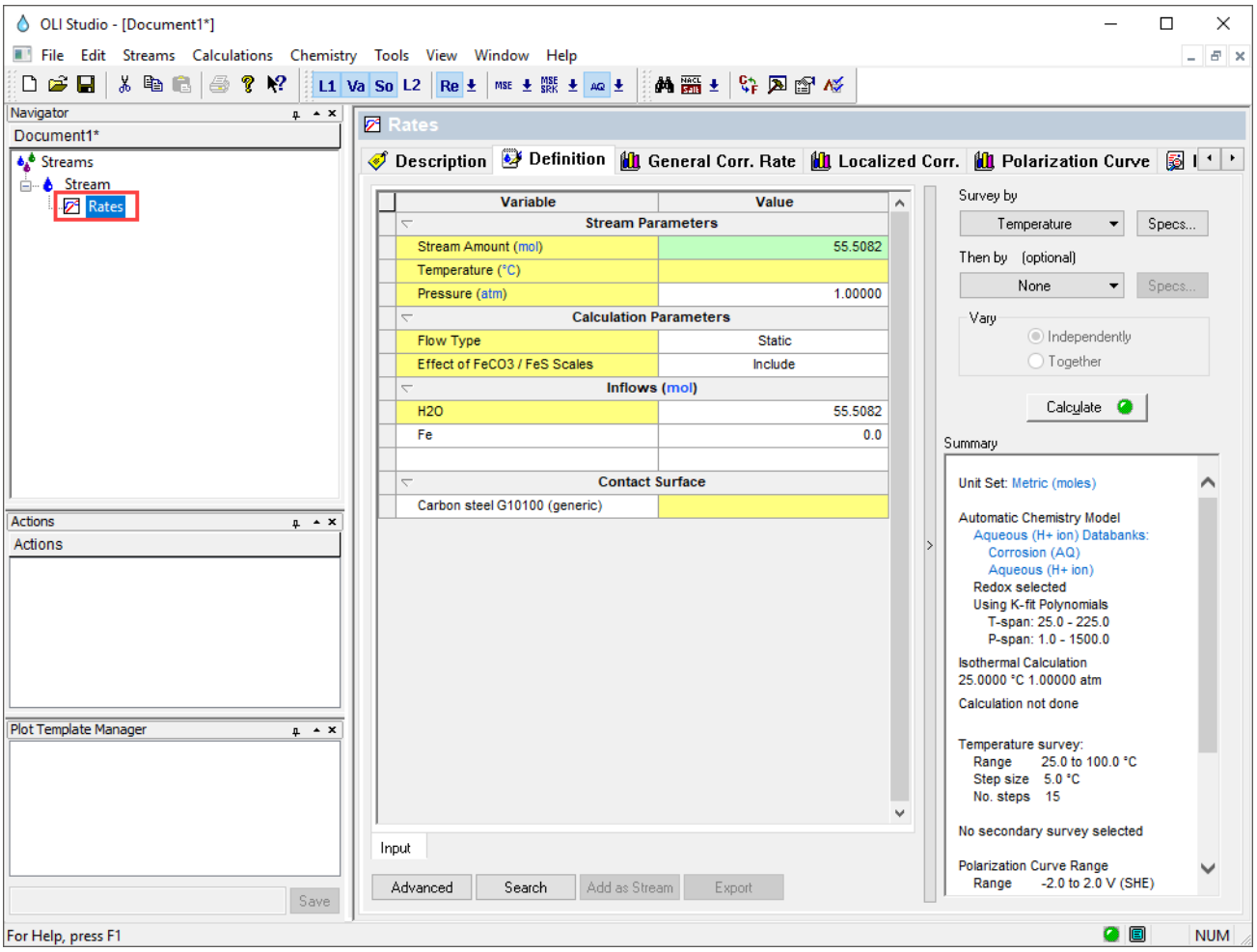


The immunity range in acidic and neutral solutions is weakly affected by temperature. However, the immunity range in alkaline solutions is shifted to much lower potentials which makes cathodic protection much more difficult.

Section 8. Introduction to Rates of Corrosion

In this section you are going to learn how to set up a Corrosion Rate calculation, how to study the effect of different variables on the corrosion rates of different alloys, such as temperature, pH, flow velocity, etc., and how to interpret the results when using this tool.

We will also explore how to interpret the results for the propensity to localized corrosion, polarization curves and heat treatment effects.



8.1. A Basic General Corrosion Rate Calculation

A brief introduction to the corrosion rate tool will be shown in the example below. As we go through the example, the basic definitions, functionalities and reporting for the *Corrosion rate* tool will be introduced.

Example 50: Corrosion rate of an oxygenated 0.1 m NaCl solution

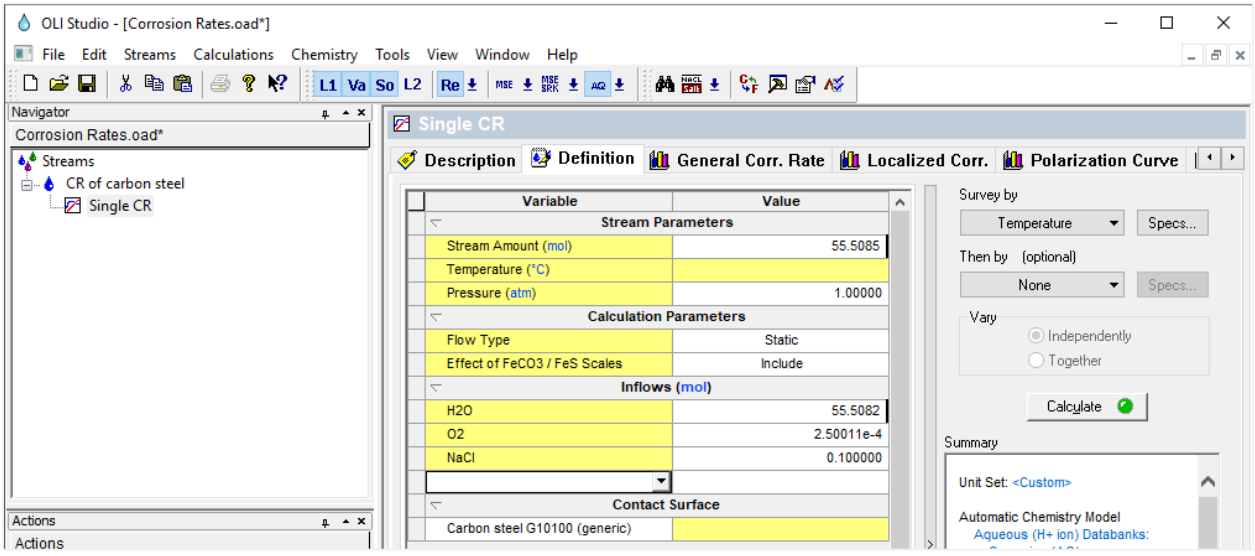
Starting the Simulation

To start the software, double-click the OLI Analyzer icon on the desktop, which will take you to the OLI Analyzer interface where you can start creating your calculations.

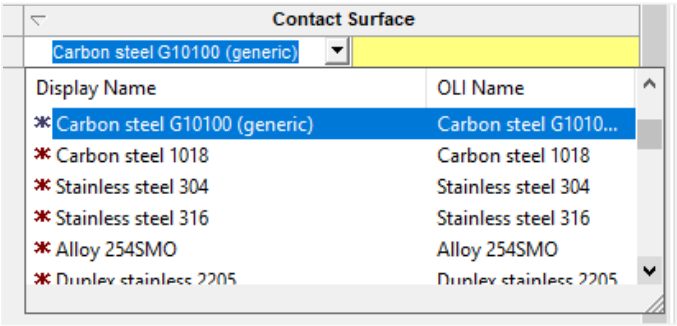
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Corrosion Rate Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	CR of carbon steel	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 ºC
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	H2O	55.5082 moles
Calculation Type	Corrosion Rates	O2	2.5e-4 moles
Contact Surface	Carbon Steel G10100 (generic)	NaCl	0.1 moles

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *CR of carbon steel*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Moles
6. Enter the composition, temperature and pressure of the stream given in the table above
7. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane. Your screen should look like the image below.

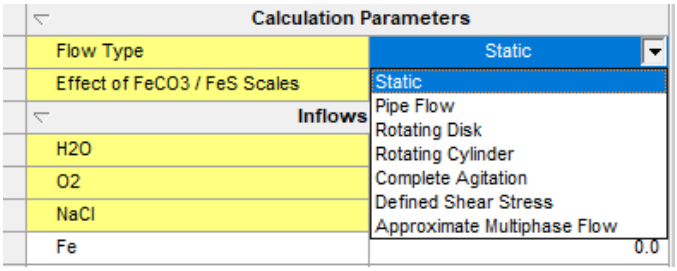


Note: By default, the software has selected **Carbon steel G10100 (generic)** as the default contact surface to perform the corrosion rates on. You can click on the white space of the **Carbon steel G10100 (generic)** name, and it will show a drop-down arrow. You can then click on the dropdown arrow, and you will be able to see and select any alloy present in the **Alloy** database.



Additionally, the **Calculation Parameters** grid shows two options: (1) Flow Type and (2) Effect of FeCO3 /FeS scales on corrosion rates.

By default, the software selects **Static** as **Flow Type**. There are 7 options for Flow Type, and a brief description of the first five options will be given below.



Static
The solution is not flowing in this calculation.

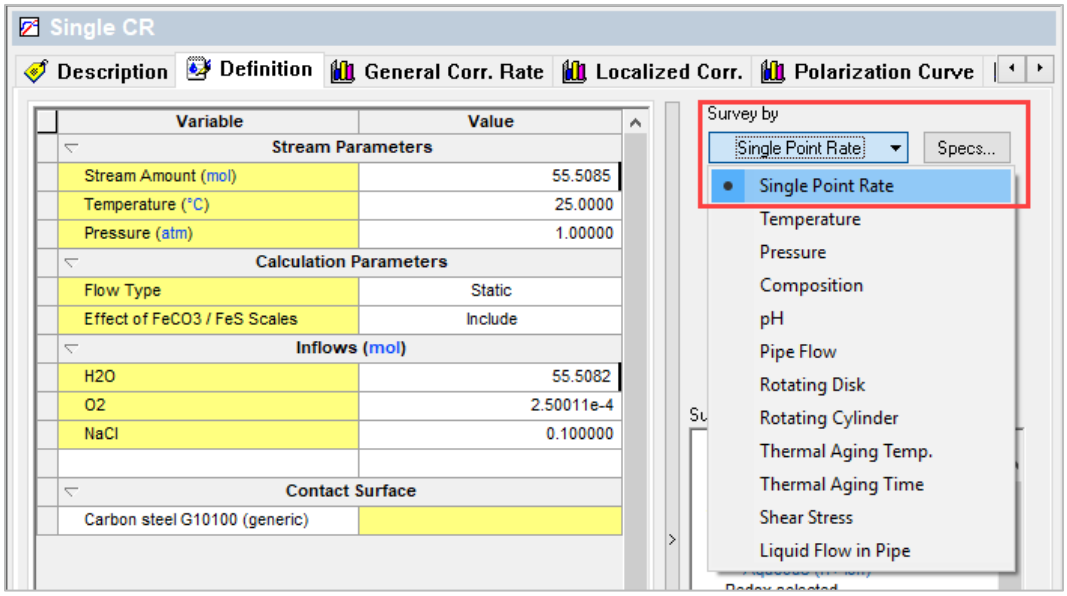
Pipe Flow
The fluid is flowing through a pipe. The pipe diameter and flow velocity must be defined. The default pipe diameter is 0.1 meters and the default flow velocity is 2 m/s.

Rotating disk
This reproduces a type of experiment that is used quite frequently in the laboratory. A disk is rotated to bring fluid to the surface of the electrode in a predictable manner. The diameter of the disk is specified as well as the revolutions per minute (RPM). The default diameter is 0.01 meters and the default RPM is 5000 RPM.

Rotating Cylinder
This reproduces a type of experiment that is used quite frequently in the laboratory. A cylindrical rotor is rotated to bring fluid to the surface of the electrode in a predictable manner. The diameter of the rotor is specified as well as the revolutions per minute (RPM). The default diameter is 0.01 meters and the default RPM is 5000 RPM.

Complete Agitation
In this calculation, the liquid phase is completely agitated, and no mass transfer limitations apply.

8. Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface
9. **Go** to the **Survey by** option and select **Single Point Rate**. This option will allow you to calculate the corrosion rate at the temperature and pressure specified.



Note: You can also study the effect of other variables such as temperature, pressure, (chemical species) composition, pH, pipe flow, etc. on the corrosion rate. The effect of these variables can be set up as a survey calculation. In the upcoming corrosion rate examples, survey calculations to study corrosion rates will be shown in more detail.

A brief description of the most common survey types for studying corrosion rates are given below.

pH Survey – This calculation is similar to the pH survey available in OLI Analyzer: Stream Analyzer. The specification requires a titrant acid and base to change the pH.

Temperature Survey – The default range is from 25-100 ºC. Any range may be used by changing the Range option. The user should consider that some points in the survey may not converge due to phase changes (e.g., boiling off of aqueous liquids).

Composition Survey – The composition of a chemical compound, for example NaCl, can be varied to study its effects on corrosion rates. The range of the chemical compound defaults from 0 to 1 mole with an increment of 0.1 moles. This range can be changed via the Range option.

Care should be taken when adding salts that can form hydrates (e.g., $CaCl_2.6H_2O$). When these hydrated salts begin to precipitate from solution, large amounts of water may be complexed with the crystal. The solution may dehydrate, and non-convergence may be the result.

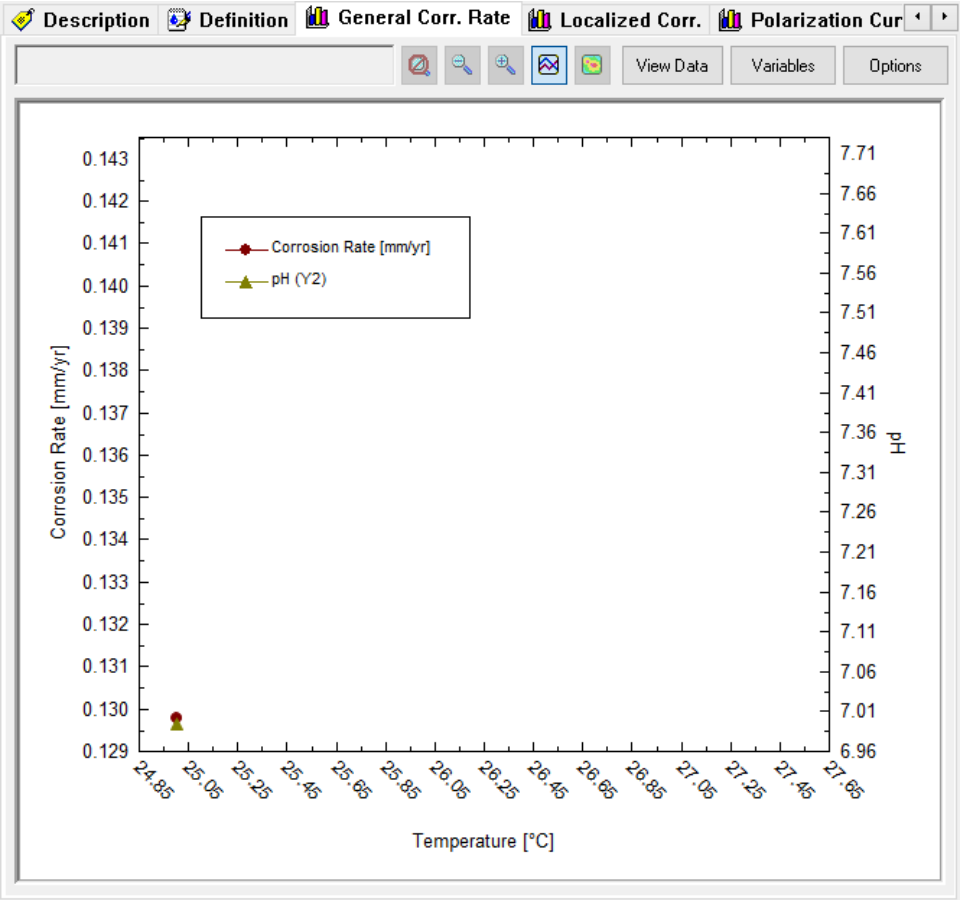
Pressure Survey – The pressure of the system can also be varied. The default range can be changed via the Range option. Care should be taken when working at very low pressures since the solution may inadvertently boil off the liquid and non-convergence may result.

Flow Velocity Survey – In systems that are flowing, the flowrate of the stream can be varied.

10. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
11. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Create a new file and name it: *Corrosion Rates.*

Analyzing the Results

1. Click on the **General Corr. Rate** tab (General Corr. Rate). This tab displays a plot showing the results of corrosion rate and pH.

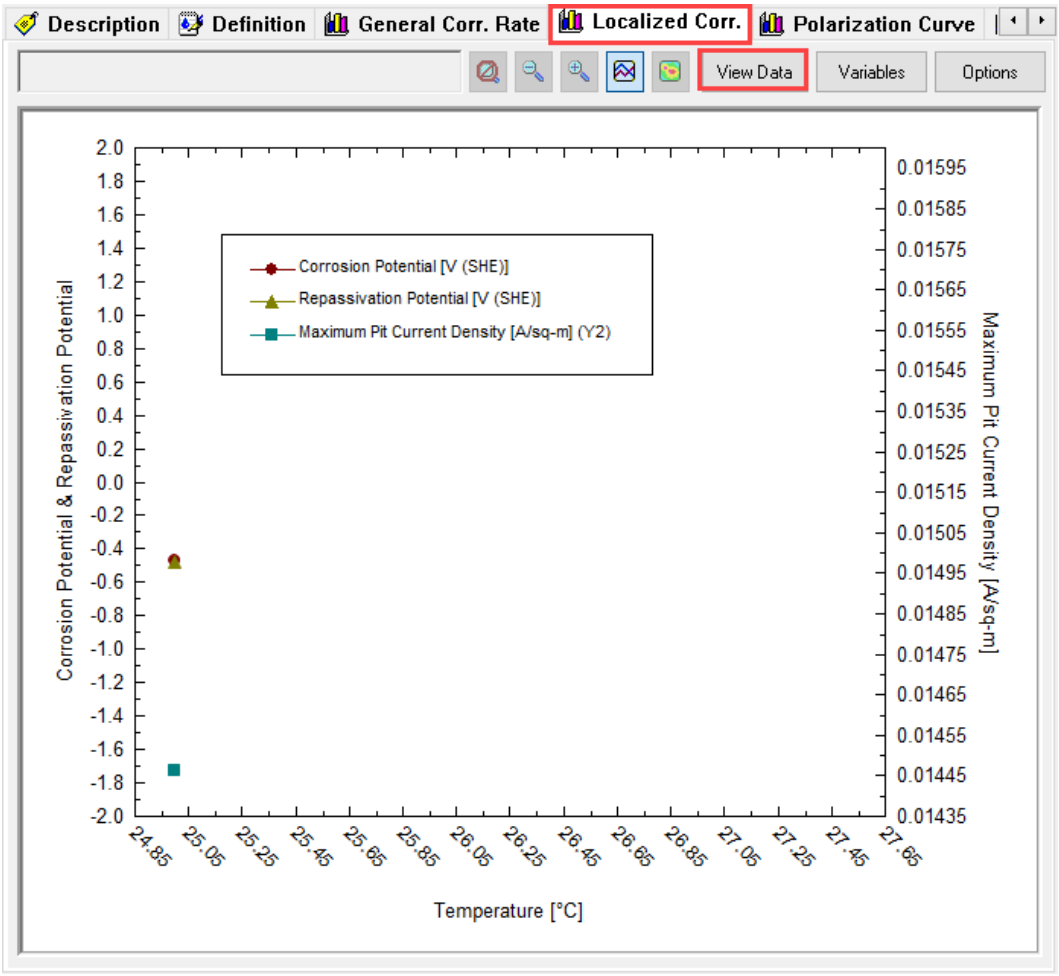


2. **Click** on the **View Data** button to see the results in tabulated form.

	Temperature	Corrosion Rate	pH
	°C	mm/yr	
1	25.0000	0.129801	6.99516

The predicted corrosion rate of carbon steel at 25 ºC and 1 atm is ~0.13 mm/year when exposed to an oxygenated 0.1 m NaCl solution. It is important to highlight that this predicted corrosion rate is the corrosion rate once the system has reached a steady state.

3. Click on the **Localized Corr. Rate** tab (Localized Corr.). This tab displays a plot showing the results of three different calculated data:
   - Corrosion Potential (red dot)
   - Repassivation Potential (yellow triangle)
   - Maximum Pit Current Density (blue square)

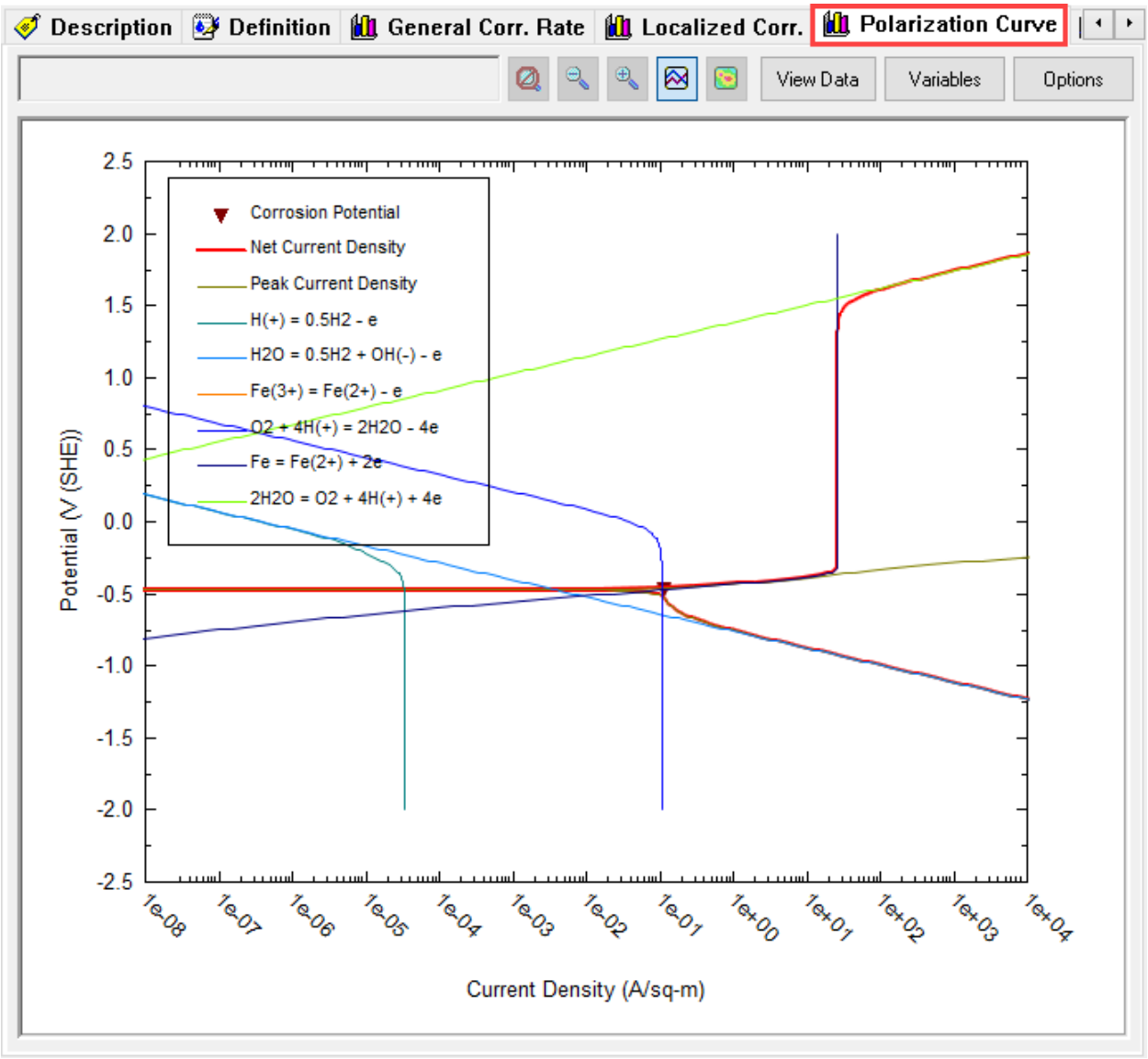


4. **Click** on the **View Data** button to see the results in tabulated form.

	Temperature	Corrosion Potential	Repassivation Potential	Maximum Pit Current Density
	°C	V (SHE)	V (SHE)	A/sq-m
1	25.0000	-0.472418	-0.481902	0.0144636

Notice that in this case, the corrosion potential has a higher value than the repassivation potential. This indicates that carbon steel at 25 ºC and 1 atm when exposed to an oxygenated 0.1 m NaCl solution will likely suffer localized corrosion (pitting or crevice corrosion). The maximum pit current density gives the worst-case pitting rate for these conditions.

5. Now, click on the **Polarization Curve** tab (Polarization Curve). This tab displays a plot showing the calculated polarization curve of carbon steel.



The net polarization curve is given by the red curve. This red curve is obtained by adding up all the currents of the half reactions at a given potential. The corrosion potential is calculated by applying the mixed potential theory, and it is represented by this red triangle. Once the corrosion potential is obtained, the corrosion current density also is computed and subsequently the corrosion rate.

8.2. Exploring corrosion rate calculation options

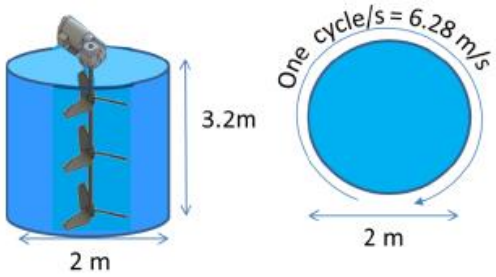
Example 51: Corrosion in a Water-Filled Carbon Steel Tank

In the following example you are going to study the corrosion rate of a carbon steel tank with a volume of 10 m^3 tank (3.2 cm high and 200 cm in diameter) that is filled to the top with water. The tank's wall thickness is 1.27 cm.

These are the operation conditions:

1. Sometimes the water in the tank remains static (mixer off), closed to the atmosphere
2. Some other times the tank is fully mixed (complete agitation)
3. The tank when operating has a variable speed mixer with a rotation speed between 0 and 12,000 rpm
4. At other times, the tank is open to the atmosphere. The effects of O_2, CO_2 and flow will be studied.

We will evaluate each instance to compute the corrosion risk.



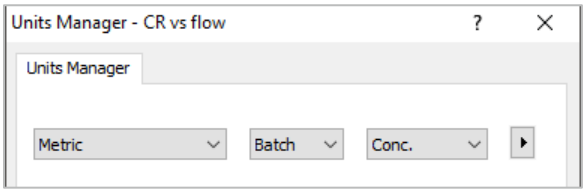
Starting the Simulation

First operation condition: Static flow, tank closed to the atmosphere at ambient conditions

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Corrosion rate calculation of tank as a function of flow			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	CR vs flow	Stream Amount	10000 L
Calculation Type	Corrosion Rates	Temperature	25 ºC
Name Style	Display Name	Pressure	1 atm
Unit Set	Metric, Batch, Concentration	Water	Calculated
Framework	AQ		
Contact surface	Carbon Steel G10100 (generic)		

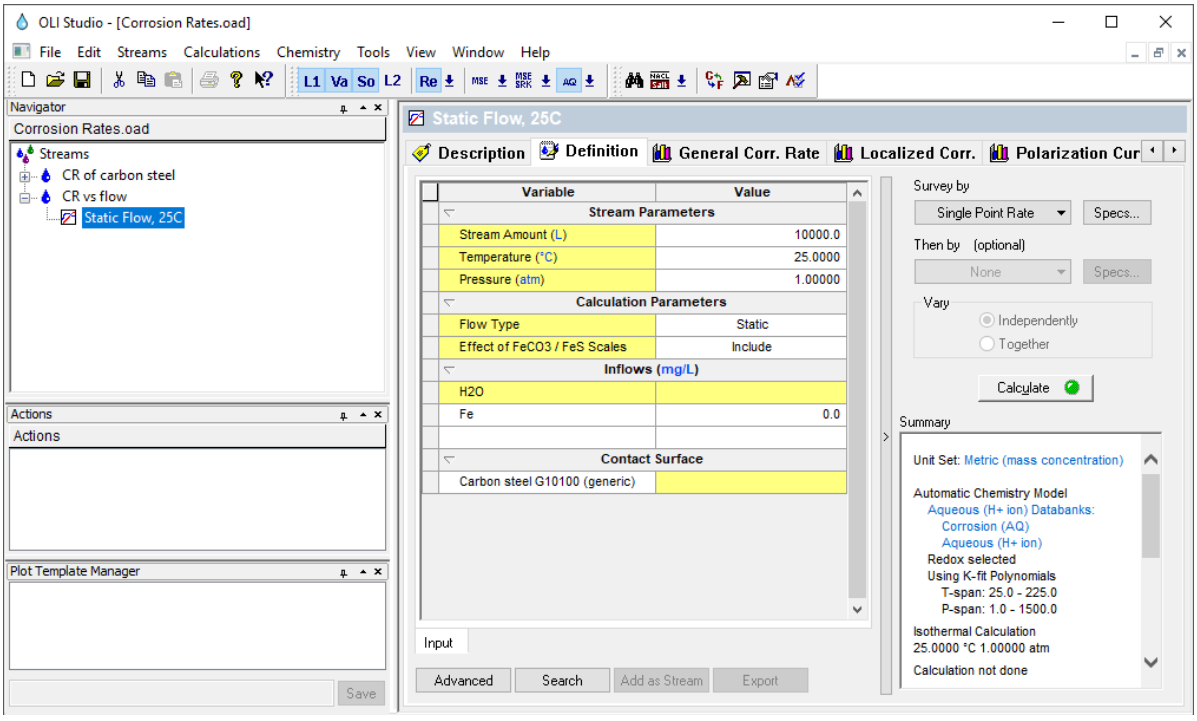
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *CR vs flow*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon, and select the ***Display Name*** option, and click **OK**
5. **Click** on the **Units Manager** Icon, and select the ***Metric, Batch, Conc.*** option, and click **OK**



In the Definition tab, notice that the units of the Stream Amount changed from moles (mol) to liters (L).

6. Enter the composition, temperature and pressure of the stream given in the table above
7. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane.
8. Change the ***Rates*** name to ***Static Flow, 25C*** using the **<F2>** key.
9. Leave the default Flow Type as **Static**
10. Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface
11. **Go** to the **Survey by** option and select **Single Point Rate**. This option will allow you to calculate the corrosion rate at the temperature and pressure specified.

Your screen should look like the image below.

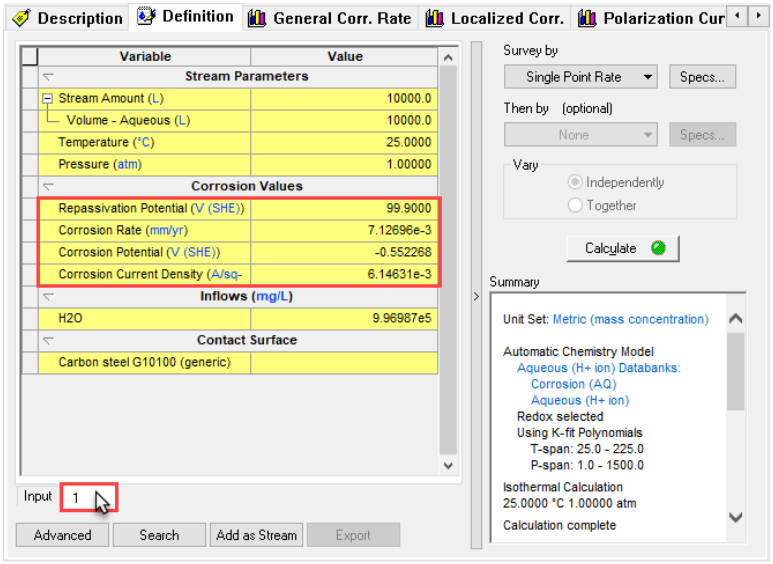


12. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key.

13. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

Analyzing the Results

Click on the output tab labeled **1** (next to the input tab), and check the results located in the **Corrosion Values** tab.

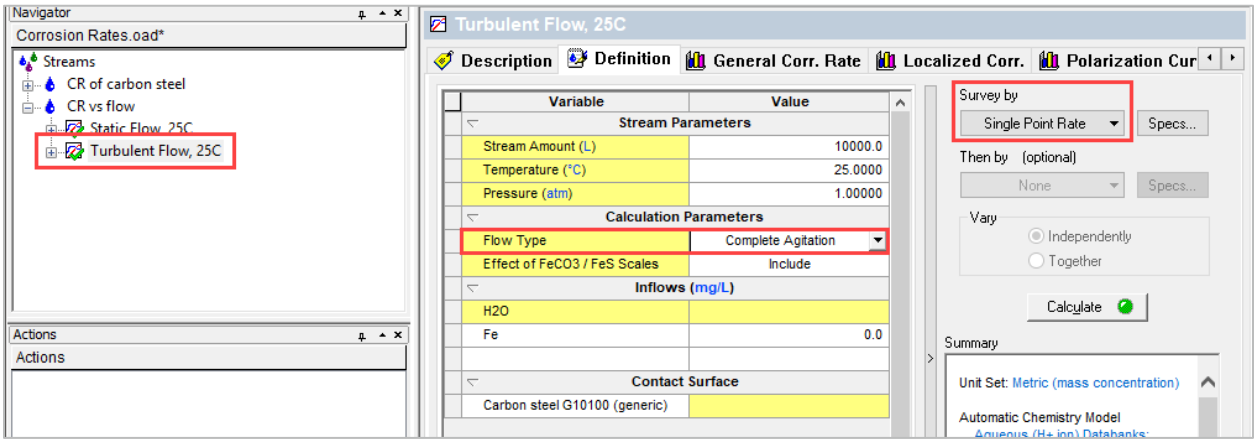


The corrosion rate is 7.13e-3 mm/yr. This is a negligible rate, since the thickness of the tank is ~12.7 mm, then corroding half the wall thickness would take about 900 years.

Second operation condition: Turbulent flow, tank closed to the atmosphere at ambient conditions

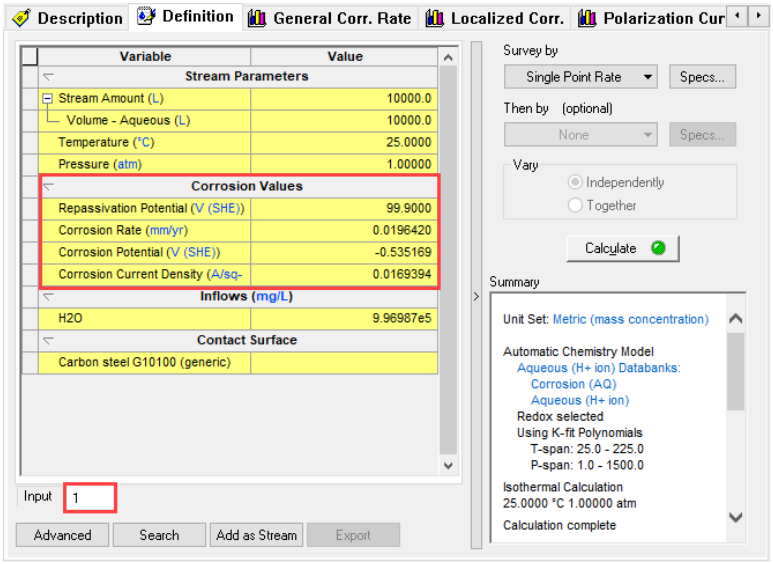
1. Under the stream '*CR vs Flow*' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane
2. Change the ***Rates*** name to ***Turbulent Flow, 25C*** using the **<F2>** key.
3. Change the default Flow Type to **Complete Agitation**
4. Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface
5. Go to the **Survey by** option and select **Single Point Rate**.

Your screen should look like the image below.



Analyzing the Results

Click on the output tab labeled **1** (next to the input tab), and check the results located in the **Corrosion Values** tab.



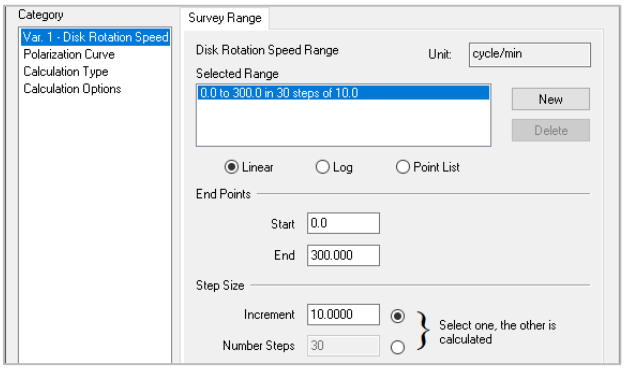
The corrosion rate increased 0.0196 mm/year, still a relatively low value.

Third operation condition: Varying flow, tank closed to the atmosphere at ambient conditions

1. Under the stream '*CR vs Flow*' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane
2. Change the ***Rates*** name to ***Varying Flow, 25C*** using the **<F2>** key
3. Go to the *Survey by* button and select **Rotating Disk**
4. Under the **Calculation Parameters** grid. change the **Disk Diameter** to **200 cm**

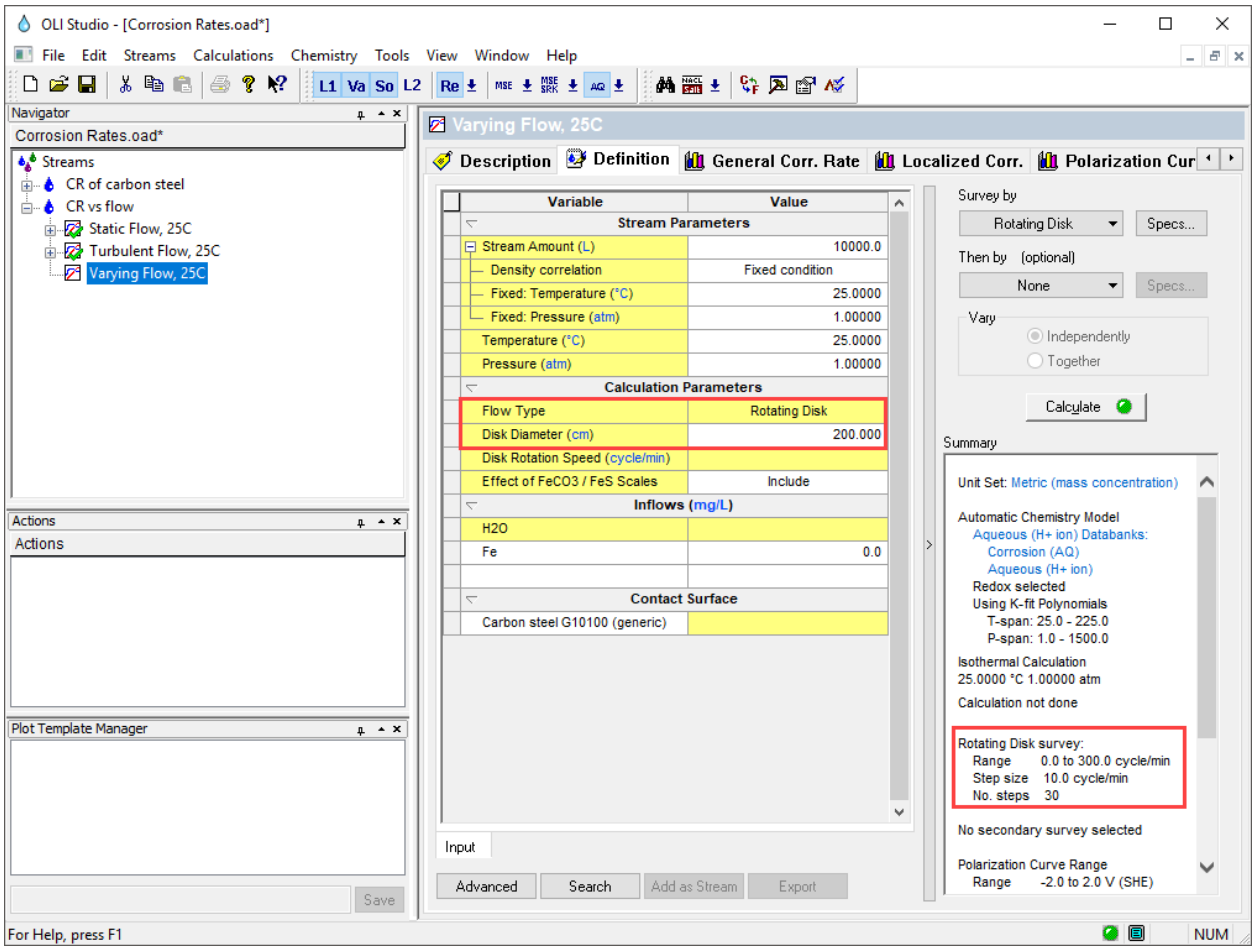
Note: At this point the vertical dimensions of the tank are unimportant. We will assume that the tank can be modeled like a rotating cylinder. The propeller rotates at 1200 rpm, although it is not expected that the wall velocity will approach this value, and so a lower value will be used (we still want it to be high enough to see the effects of shear).

5. The next step is to set the speed of the mixer. Go to the **Specs** button next to the **Rotating Disk** option
6. Change the Disk Rotation Speed Range from 0 to 300 cycles/min with an increment of 10 cycles/min. Then click **OK**.



7. Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.

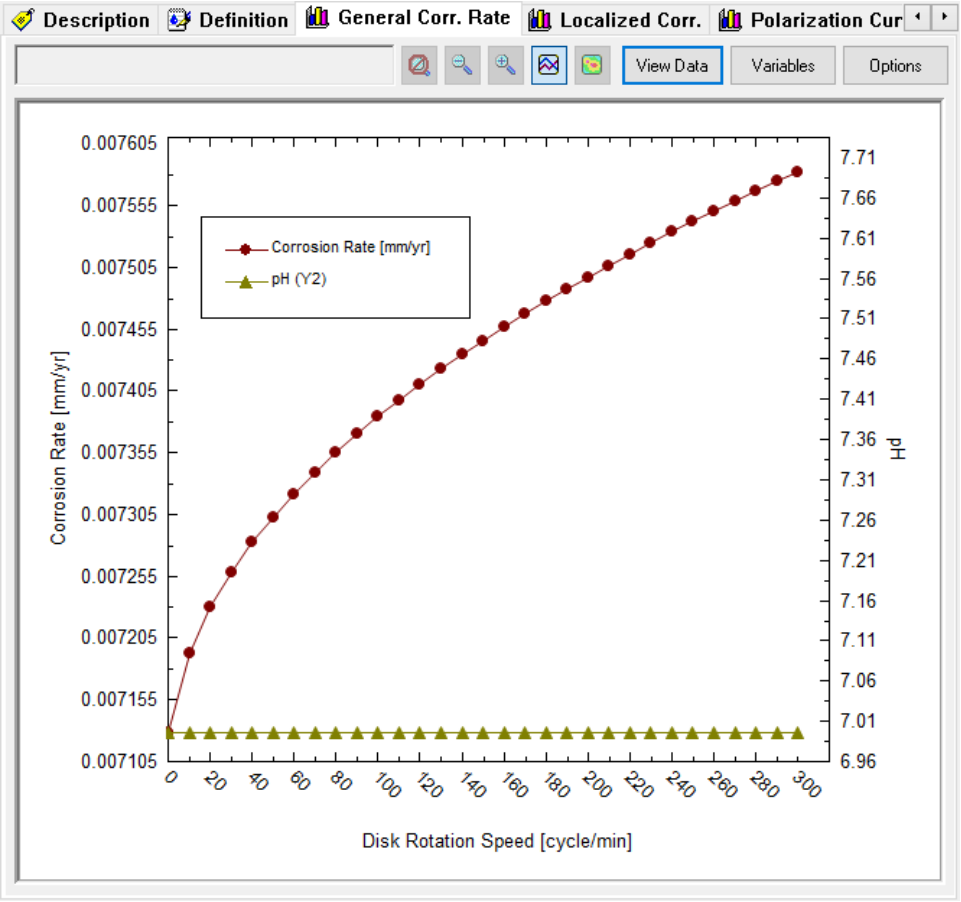


8. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

9. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

Analyzing the Results

Click on the **General Corr. Rate** tab (General Corr. Rate). This tab displays a plot showing the results of corrosion rate and pH.



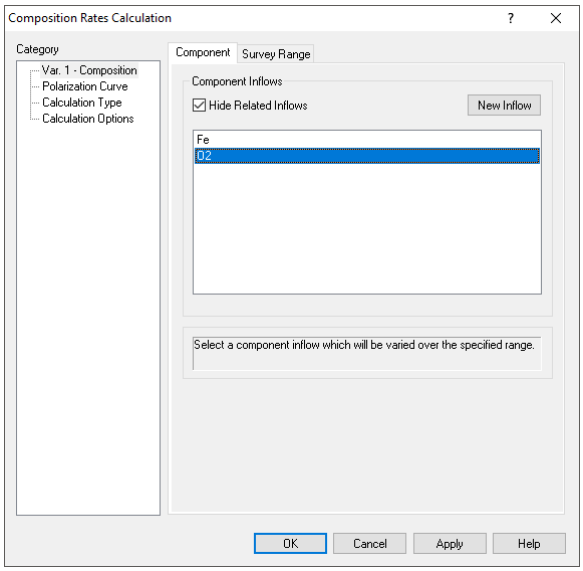
The corrosion rate is computed to increase as the bulk liquid velocity increases from 0 to 300 rpm near the wall surface. The reason is straightforward; the higher velocity reduces the static water film thickness on the metal surface. This *diffusion layer* film limits the mass transfer of corrosion products and bulk chemicals to and from the surface. As the liquid velocity (and therefore shear force) increases, the film thickness decreases, and the concentration gradient increase. This increases the flux of materials to and from the surface, which increase corrosion rates.

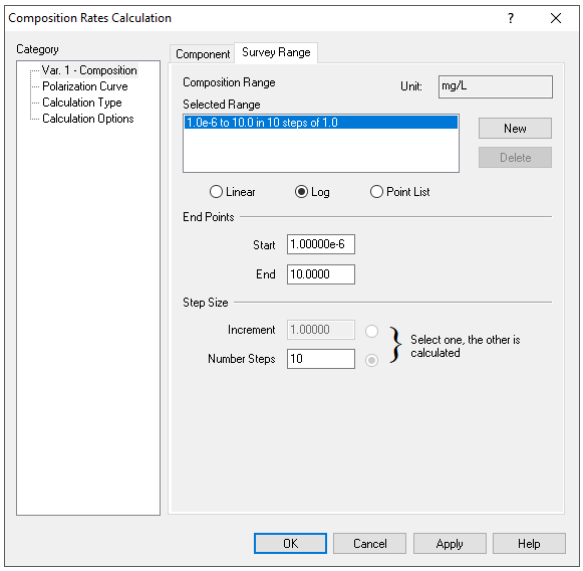
Fourth operation condition: Static flow, tank open to the atmosphere (aerated with O_2 only) at ambient conditions

Open steel tanks are in contact with oxygen in the air. To simulate this, follow the steps below.

1. Under the stream '*CR vs Flow*' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane
2. Change the ***Rates*** name to ***Static Flow, O2*** using the **<F2>** key
3. **Add** Oxygen (O2) to the inflow grid
4. Leave the default Flow Type as **Static**

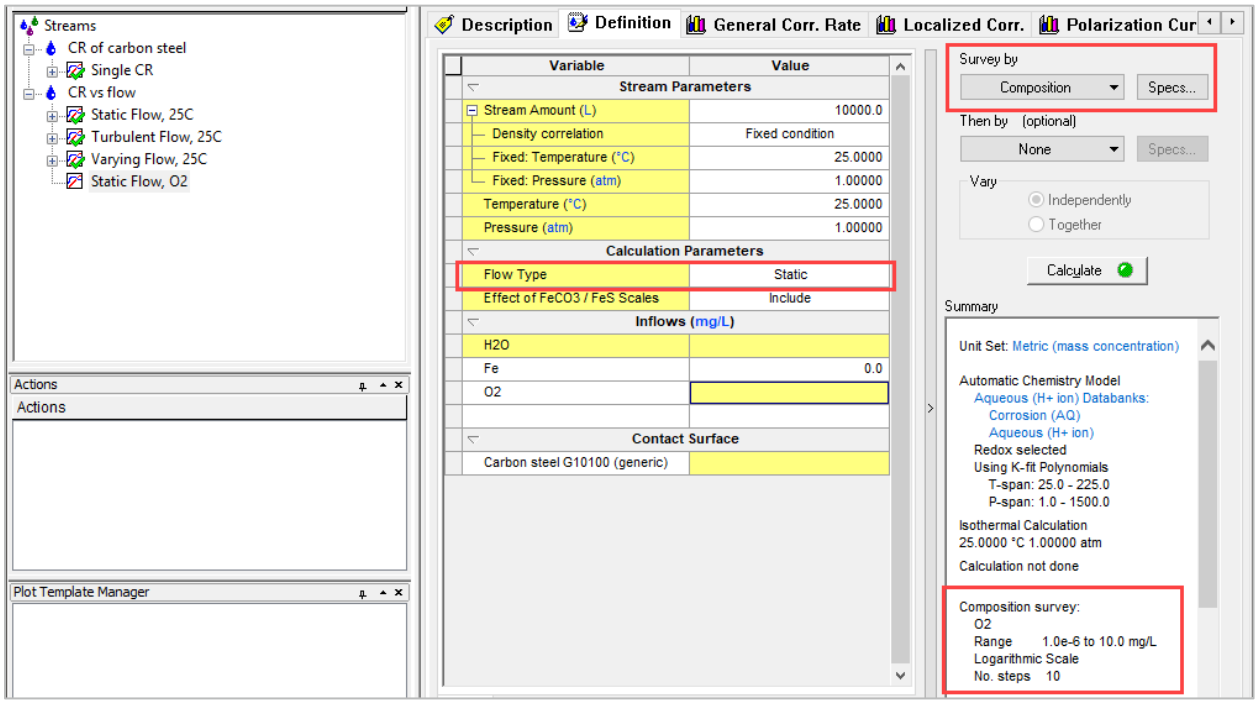
5. Go to the *Survey by* button and select **Composition**
6. Change the **Disk Diameter** to **200 cm**
7. The next step is the concentration range of oxygen. Go to the **Specs** button next to the **Composition** option. This will open a new window.
8. Under **component** select (click on) O2. Then select the **Survey Range** tab and enter the Survey Range as follows: Log Scale, Start=1e-6, End=10, Steps=10. Then click **OK**.





9. Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.

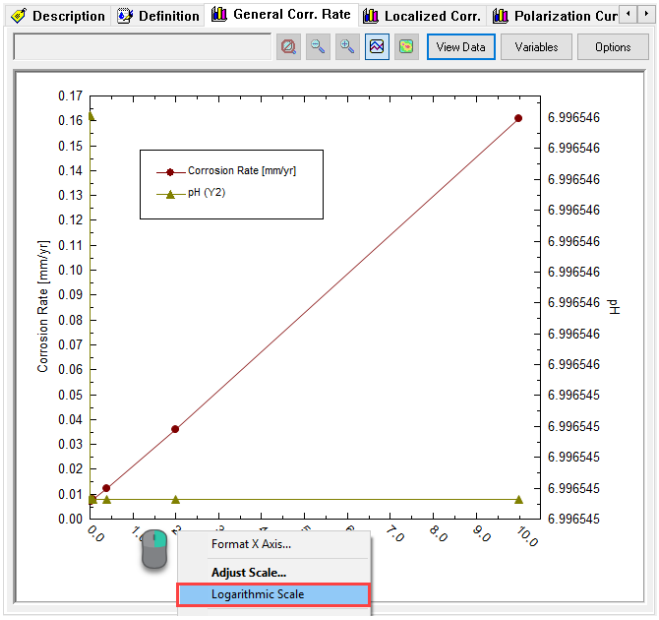


10. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
11. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

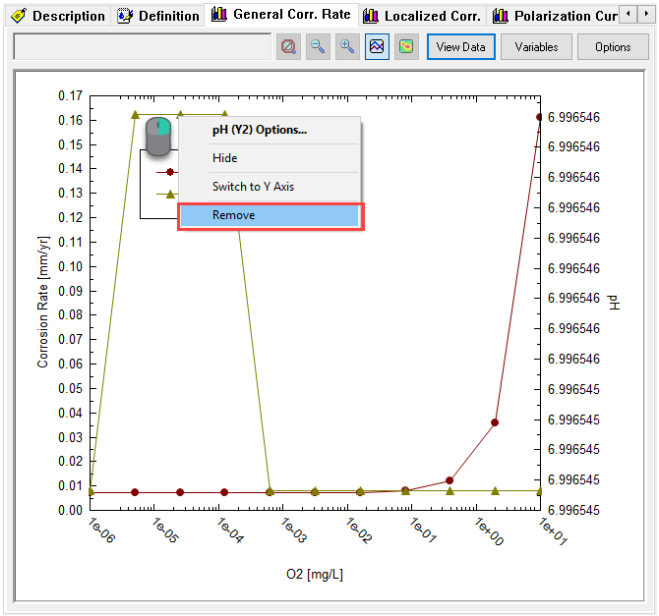
Analyzing the Results

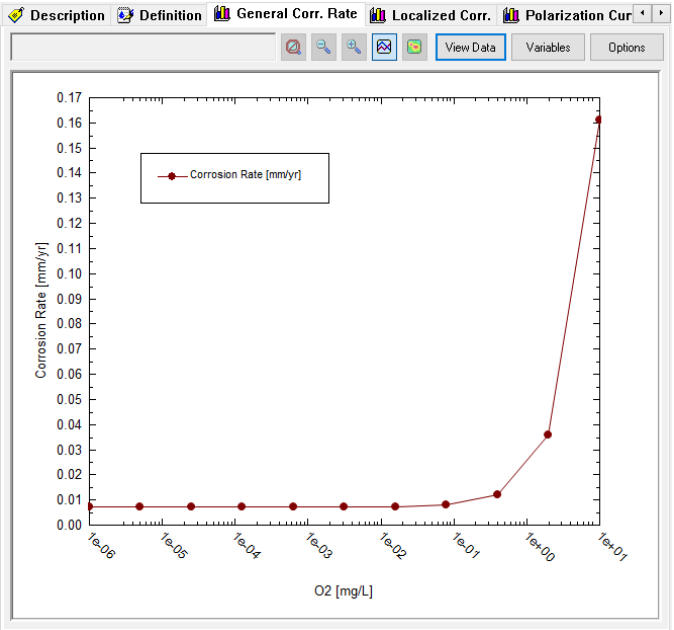
Click on the **General Corr. Rate** tab (General Corr. Rate). This tab displays a plot showing the results of corrosion rate and pH.

1. **Right-mouse click** on the **X-axis** and change it to **Logarithmic Scale**



2. **Right-mouse click** on the **pH** curve and select **Remove**





The resulting plot shows the impact of oxygen on the corrosion rate. Corrosion increases by a factor of 20 once the concentration increases beyond 100 µg/l. Aerated water contains approximately 8 mg/l O_2. Corrosion on the tank wall is 0.16 mm/yr. At this rate, 50% of the 12.3 mm wall will be dissolved in 40 years.

Fifth operation condition: Static flow, tank open to the atmosphere (aerated with O_2 and CO_2) at ambient conditions

The atmosphere contains ~400 ppmV CO_2. At this concentration 0.6 mg/l CO_2 is dissolved in water as molecular CO_2, this CO_2 hydrolyzes water to form the following reactants:

$$CO_2 + H_2O = H^+ + HCO_3^-$$

The resulting pH is about 5.6 at ambient conditions.

The impact of CO_2 on corrosion is two-fold, as two separate reactions occur at the metal surface:

$$H^+ + e^- \leftrightarrow \frac{1}{2}H_2$$

$$HCO_3^- + e^- = \frac{1}{2}H_2 + CO_3^{-2}$$

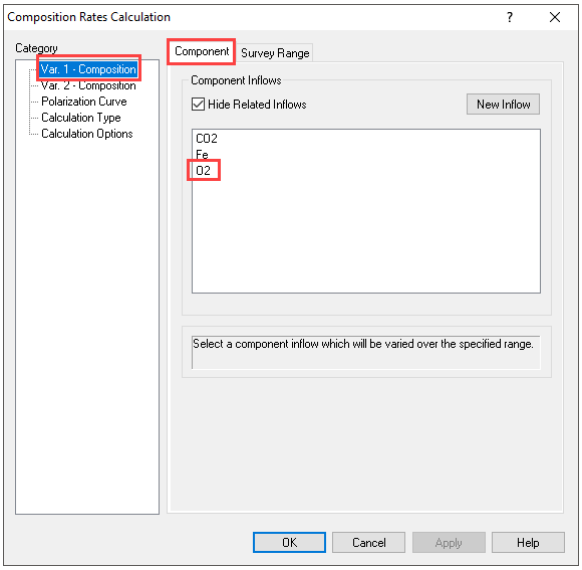
To test the CO_2 impact, you will recalculate the corrosion rate using two CO_2 concentrations: 0 and 0.6 ppm.

I. Under the stream '*CR vs Flow*' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane
II. Change the ***Rates*** name to ***Static Flow, O2 and CO2*** using the **<F2>** key
III. **Add** Oxygen (O2) and carbon dioxide (CO2) to the inflow grid
IV. Leave the default Flow Type as **Static**

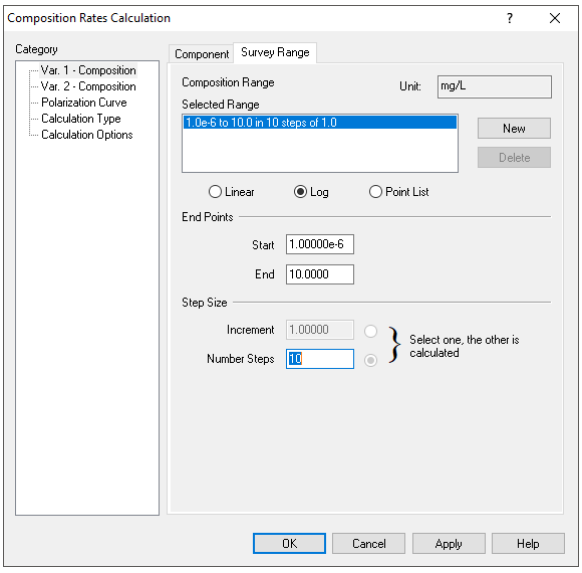
V. Go to the *Survey by* button and select Survey by **Composition** and then by **Composition** (as shown below)

VI. The next step is the concentration range of oxygen and carbon dioxide. Go to the **Specs** button next to the **Composition** option. This will open a new window.

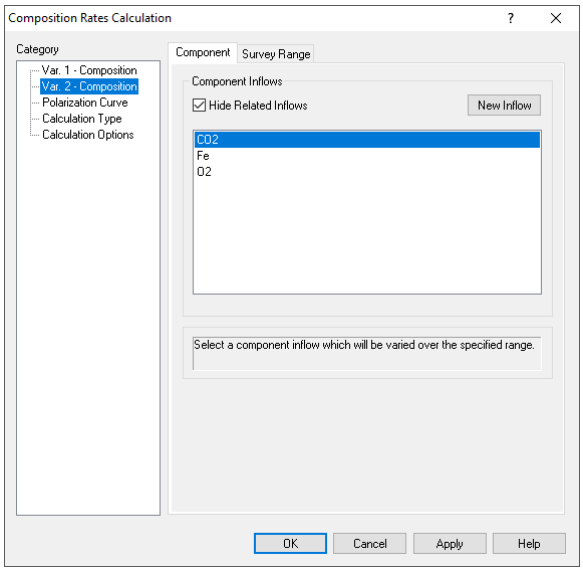
VII. Under the **Category** section, make sure to select **Var. 1 -Composition**. Go to the **Component** tab, and select O2



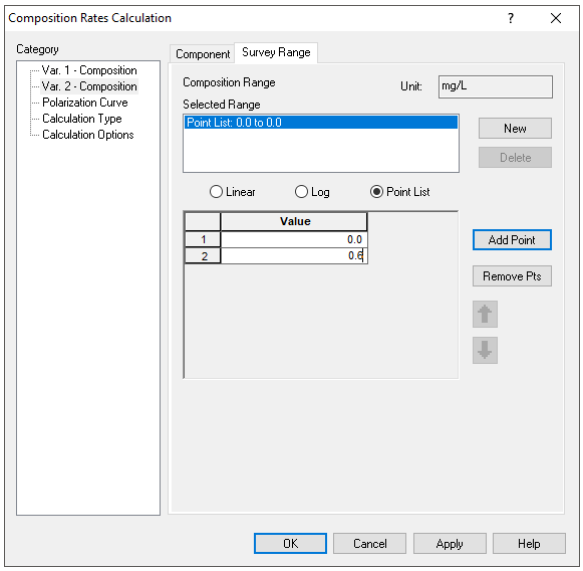
VIII. Then select the **Survey Range** tab and enter the Survey Range as follows: Log Scale, Start=1e-6, End=10, Steps=10. Then click **OK**.



IX. Under the **Category** section, select **Var. 2 -Composition**. Go to the **Component** tab, and select CO2

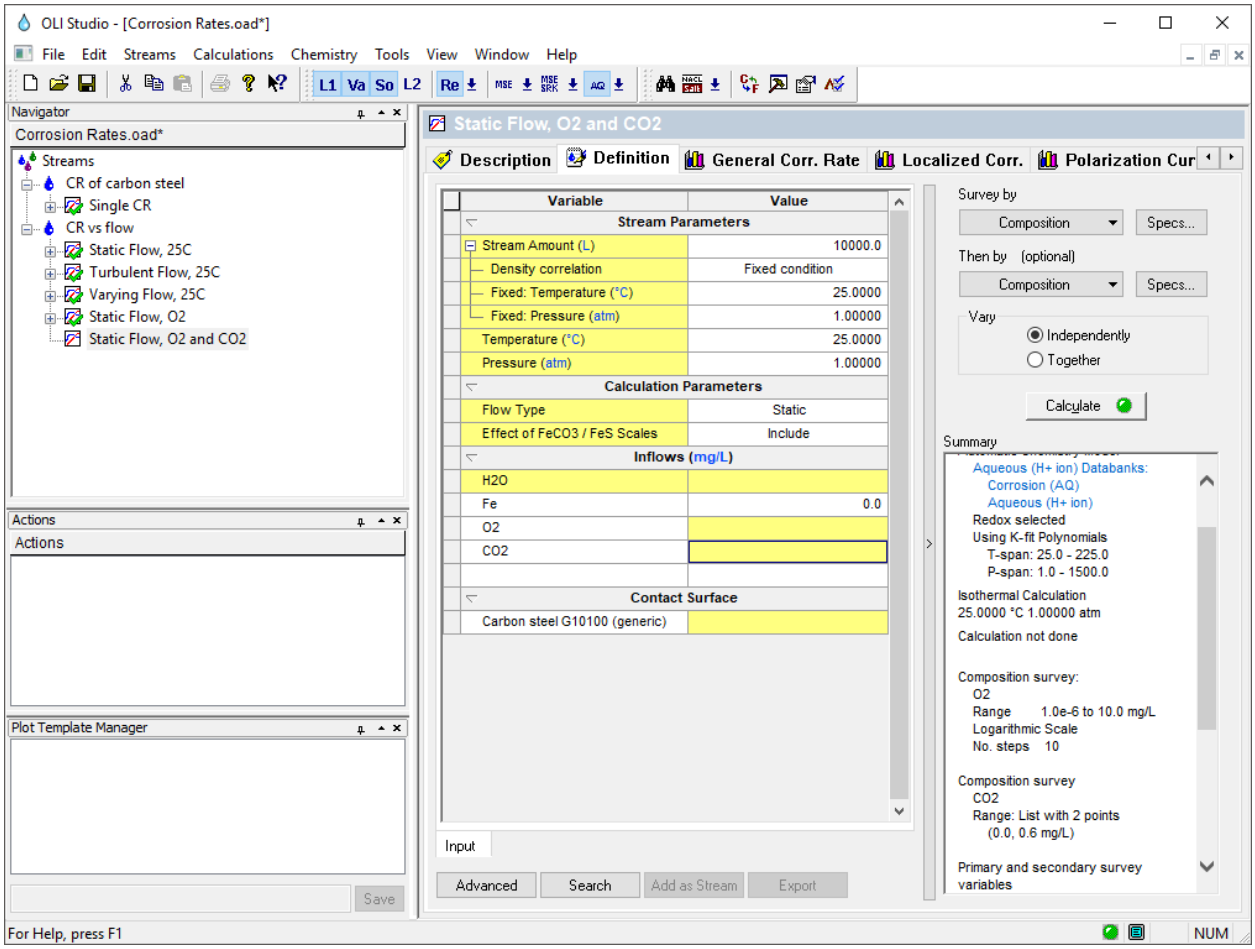


X. Then select the **Survey Range** tab. Select the Point List option. Create two point with values of 0 and 0.6 mg/L. Then click **OK**.



XI. Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.

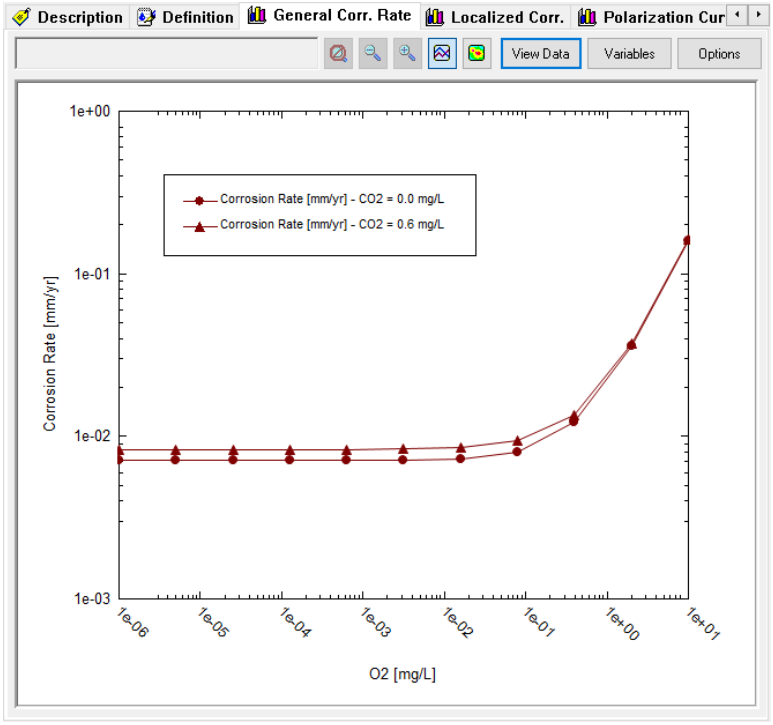


12. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

13. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

Click on the **General Corr. Rate** tab (General Corr. Rate). This tab displays a plot showing the results of corrosion rate and pH.

1. **Right-mouse click** on the **X-axis** and change it to **Logarithmic Scale**
2. **Right-mouse click** on the **Y-axis** and change it to **Logarithmic Scale**
3. **Right-mouse click** on the **pH** curve and select **Remove Series**

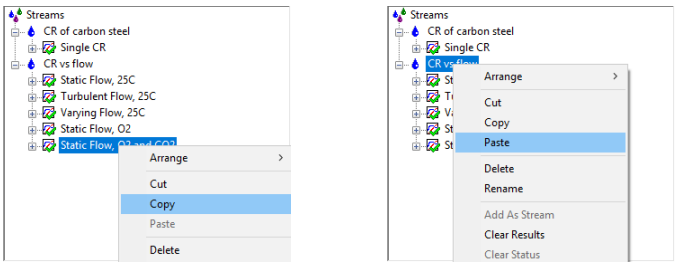


The effects of CO_2 are small, particularly in relation to the oxygen effects. The Corrosion rates at low O_2 content are about 0.0071 mm/yr with no CO_2 and 0.0083 mm/yr with 0.6 mg/l CO_2; a small difference between two small rates. At 10 mg/l O_2 the corrosion rate is 0.16 mm/y and it is the same with and without CO_2. Thus, CO_2 has no effect on corrosion at high O_2 concentrations meaning that the surface is corroded by oxygen and small concentrations of CO_2 does not change this rate.

Sixth operation condition: 300 cycles/min flow, tank open to the atmosphere (aerated with O_2 and CO_2) at ambient conditions

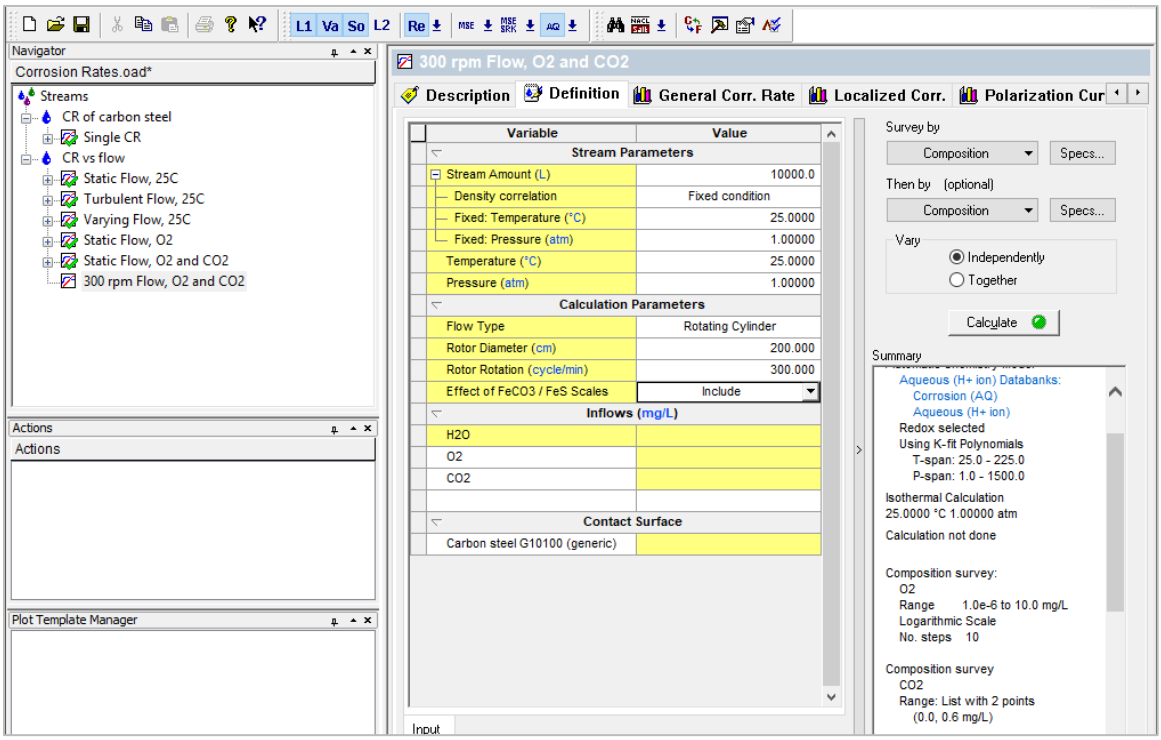
Lastly, you will look at the effects of shear rates on the tank in contact with CO_2 and O_2.

1. **Copy** (right-mouse click or Ctrl+C) *'Static Flow, O2 and CO2'* corrosion calculation, and **paste** (right-mouse click or Ctrl+V)under the stream '*CR vs Flow*'



2. Change the ***Static Flow, O2 and CO2-1*** name to ***300 rpm flow, O2 and CO2*** using the **<F2>** key
3. **Add** Oxygen (O2) and carbon dioxide (CO2) to the inflow grid
4. Change the Flow Type from **Static** to **Rotating Cylinder**
5. **Set** the **Rotor** D**iameter** to 200 cm
6. **Set** the **Rotor Rotation** to 300 cycles/min
7. Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.

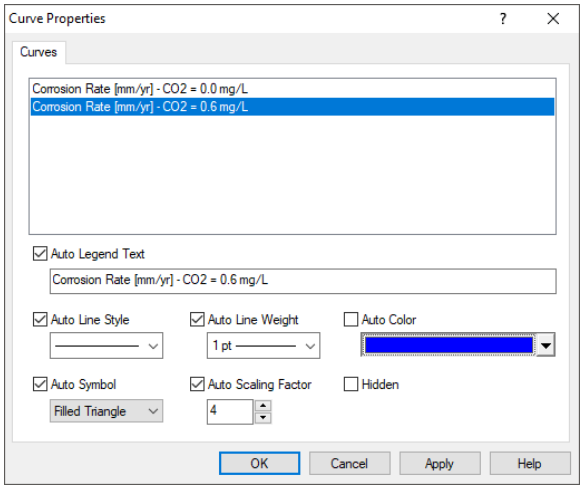


8. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
9. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

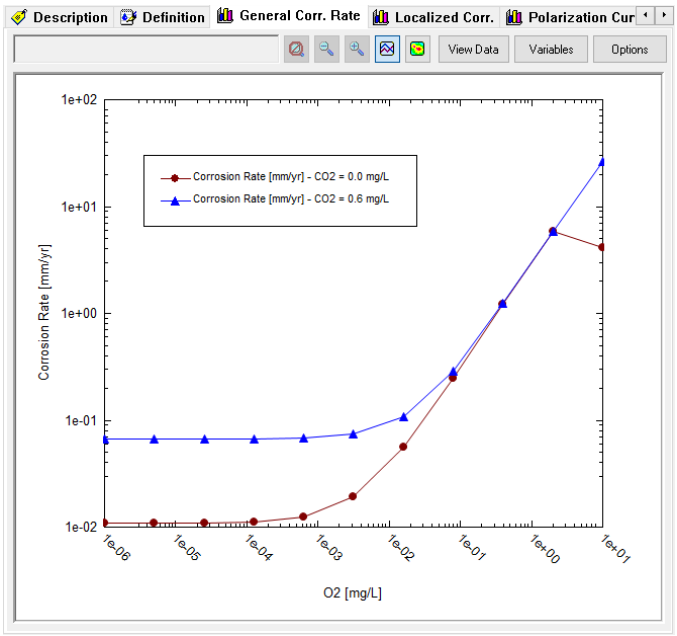
Analyzing the Results

Click on the **General Corr. Rate** tab (General Corr. Rate). This tab displays a plot showing the results of corrosion rate and pH.

1. **Right-mouse click** on the **X-axis** and change it to **Logarithmic Scale**
2. **Right-mouse click** on the **Y-axis** and change it to **Logarithmic Scale**
3. **Right-mouse click** on the **pH** curve and select **Remove Series**
4. **Double click** on the CO2=0.6 mg/L. This will open a new window. Change the color to blue.



The plot should look like the image below.



The 0.6 mg/L CO_2 curve shifted to higher values at low O_2 concentrations compared to no CO_2 presence. Now, when comparing the corrosion rate for the 0.6 mg/L CO_2 concentration at 300 rpm vs static conditions, the rates are 0.067 mm/year and 0.008 mm/year respectively. The effect of shear at high O_2 concentrations (right side of the plot) is also pronounced. Corrosion is still dominated by O_2 attack, but the rate is now over 10 mm/year, about 100x greater than the static conditions.

8.3. Gas condensate corrosion

Example 52: Condensed overhead gas and mitigation strategies

An alkanolamine gas sweetening plant has corrosion problems in the condensed overhead gas.

Diethanolamine is used to neutralize an acid gas containing carbon dioxide (CO_2) and hydrogen sulfide (H_2S). The diethanolamine is regenerated and the acid gases are driven off in a stripper. The off gas from this stripper is saturated with water vapor. As these gases cool, they will condense. This condensate can be very corrosive. The plant's service life can be shortened considerably due to these condensed acid gases.

In this example, you will calculate the gas dew point temperature, remove the condensed aqueous phase and perform a Corrosion Rate calculation with the condensed water. Lastly, you will consider mitigation strategies for the pipes.

You are introducing *fluid velocity* and *liquid condensation* into the calculation. The software uses a diffusion layer model to compute mass transfer to and from corroding surfaces. Higher rates produce thinner layers, resulting in faster mass transfer rates, and thus higher corrosion rates. The liquid condensation point is straightforward; it calculates the temperature (or pressure) where the first liquid drop forms.

Starting the Simulation

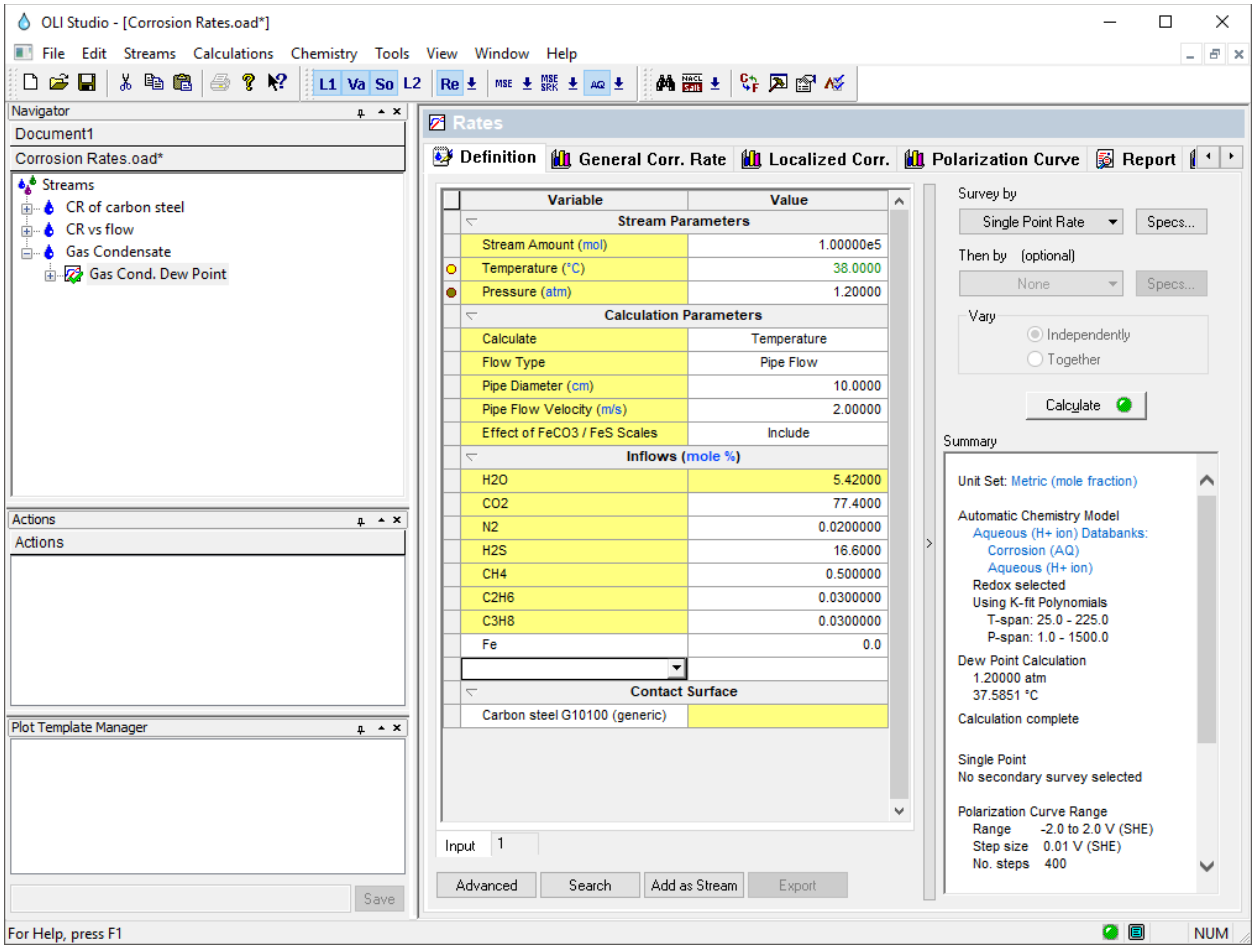
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Corrosion Rate Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Gas condensate	Stream Amount	1e5 moles
Name Style	Display Formula	Temperature	38 ºC
Unit Set	Metric, Batch, Mole Fraction	Pressure	1.2 atm
Framework	AQ	H2O	Calculated (mole%)
Calculation Type	Corrosion Rates	CO2	77.4
Survey	Single Point Rate	N2	0.02
Flow Type	Pipe Flow	H2S	16.6
Pipe Diameter	10 cm	CH4	0.5
Pipe Flow Velocity	2 m/s	C2H6	0.03
Contact Surface	Carbon Steel G10100 (generic)	C3H8	0.03

1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Gas Condensate*
3. Select the **AQ** thermodynamic Framework
4. **Click** on the **Names Manager** Icon and select the **Formula** option
5. **Click** on the **Units Manager** Icon, and select Metric, Batch, Mole Fraction
6. Enter the composition, temperature and pressure of the stream given in the table above
7. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane.
8. **Go** to the **Survey by** option and select **Single Point Rate.** Change the name to **Gas Cond. Dew Point.**

9. **Change** the Flow Type from Static to **Pipe Flow.**
10. **Specify** the **Pipe Diameter** = 10 cm and the **Pipe Flow Velocity** = 2 m/s.
11. Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.



Now that the gas condensate stream is created, the next task is to isolate the condensed water at the dew point temperature.

12. **Click** on the **Specs** button. This will open a new window
13. Under the **Category** section, select **Calculation Type**
14. Change the Type of Calculation from Isothermal to **Dew Point.** Make sure that radio button for temperature is selected since we are going to calculate the Dew Point temperature for this example. Then click **OK**.
15. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
16. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

Analyzing the Results

1. Click on the **General Corr. Rate** tab (General Corr. Rate).

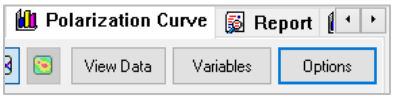
2. **Click** on the **View Data** button to see the results in tabulated form.

	Temperature	Corrosion Rate	pH
	°C	mm/yr	
1	37.5851	0.704502	3.92719

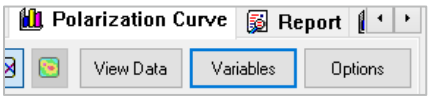
   Notice that the calculated dew temperature is 37.6°C, corrosion rate is 0.7 mm/year, and the dew point pH is 3.9. To further interpret the results of this calculation, we are going to study the polarization curve.

3. Click on the **Polarization Curve** tab (Polarization Curve). Before interpreting this plot, we will format it for easy viewing.

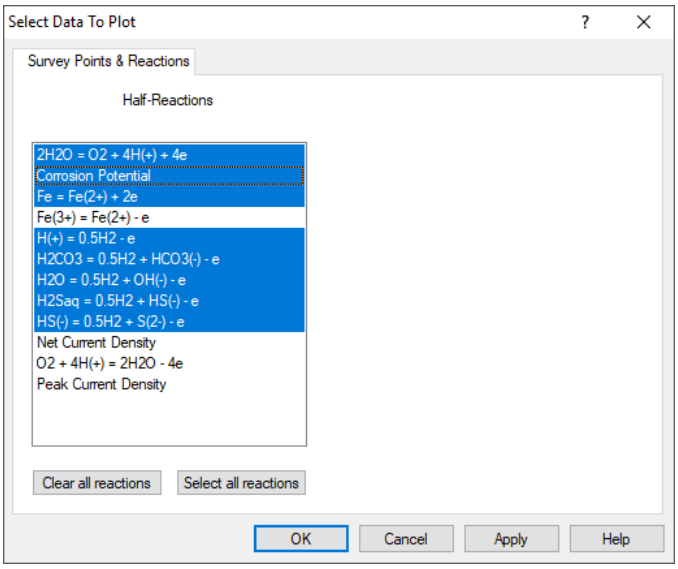
4. Click on the **Options** button. This will open a new window.



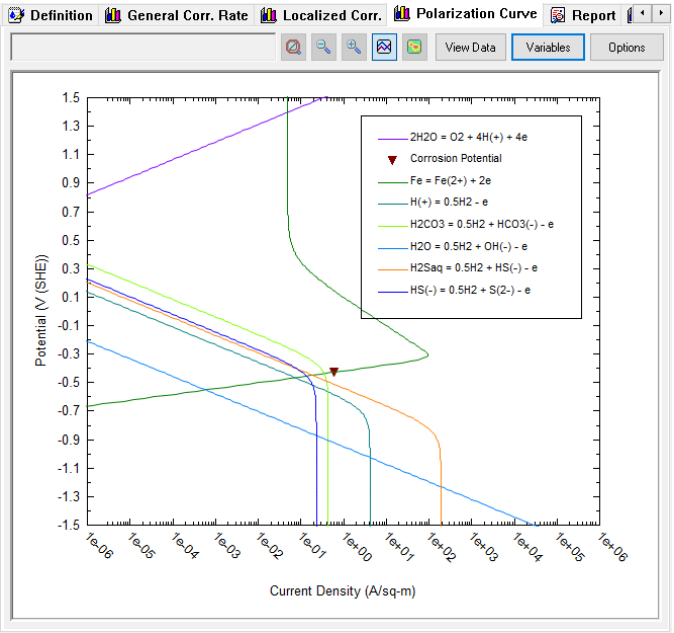
5. Under the **Category** section select **X axis.** Change the **Minimum** to 1e-6 and **Maximum** to 1e6.
6. Now, select **Y axis.** Change the **Minimum** to -1.5 and **Maximum** to 1.5. Then **click OK.**
7. Click on the **Variables** button. This will open a new window.



8. Remove the following variables by unchecking them. See image below. Then **Click OK.**



9. Your polarization curve should look like the image below.



You can click and drag the legend of the polarization curve to your desired position.

This is a measured potential vs. current density plot. The anodic portion (green curve) is the carbon steel. There are cathodic reactions. The sum of the cathodic currents adds up to the anode curve at a single point: The corrosion potential (represented by the inverted red triangle ▼) with a value of -0.43 V vs SHE. At the corrosion potential, the anodic and cathodic currents are equal, and this value is also known as the i_{corr}. For this example, i_{corr}=0.61 A/m^2.

Notice that the cathodic reaction that contributes the most to corrosion is H_2CO_3 (light green line). The next contributors are H_2S (orange line) and HS^{-1}(blue line) equally. After that is H^+ (turquoise line). Water reduction (light blue line), contributes the least to corrosion.

Mitigation Strategies

There are several mitigating solutions to this corrosion problem.

One is adding insulation to prevent temperature drops. The dew point is very close to the overhead gas temperature so this may not be a suitable option. Adding heat to keep the temperature above the dew point is usually considered along with insulation.

Changing the chemistry to change the partial oxidation and reduction processes is also an option.

Changing alloys could mitigate the corrosion problems as well.

We will explore the change of chemistry and change of alloys for this example.

Adjusting the solution chemistry

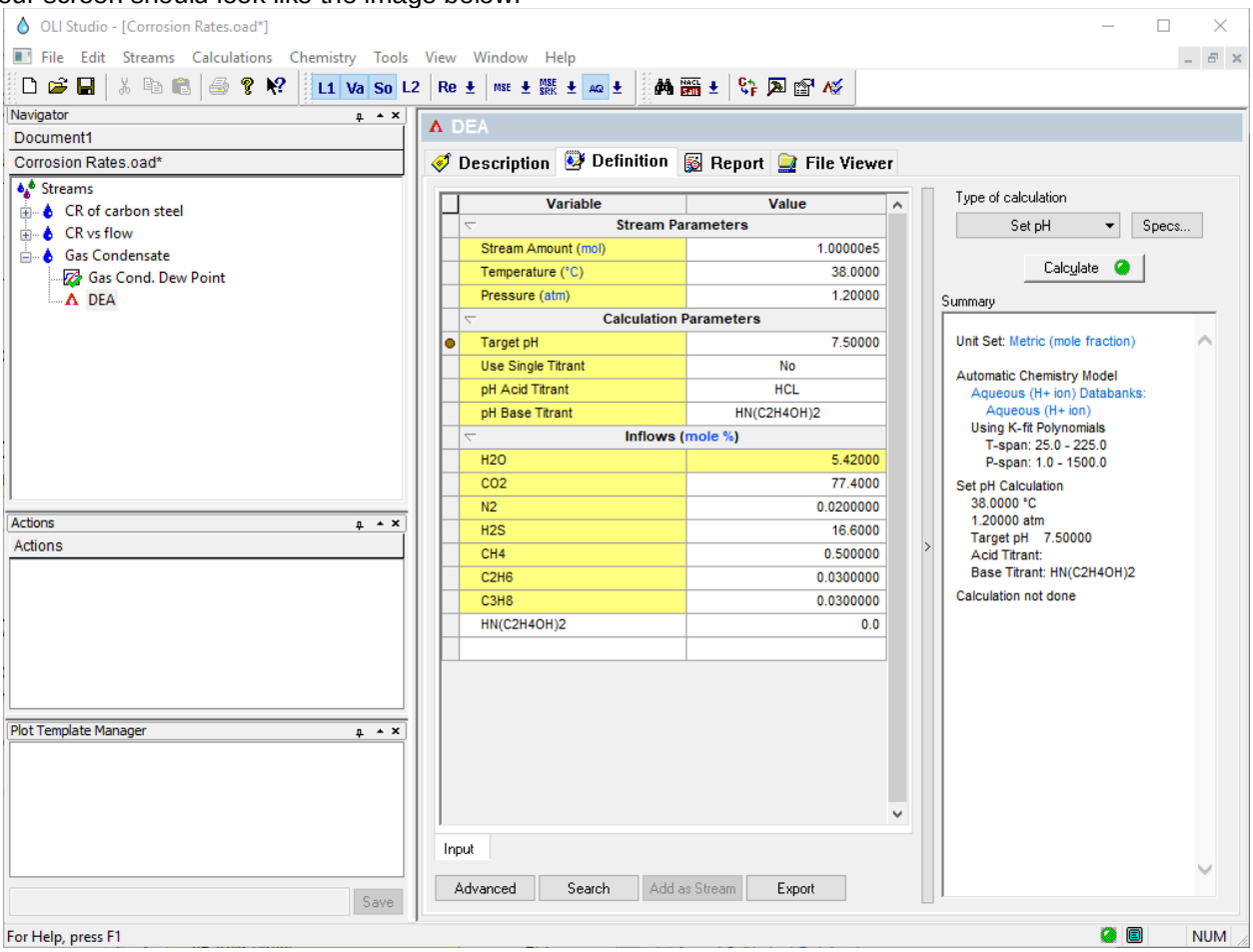
The condensate pH is approximately 3.9. We can try to add a base to increase the pH. In this section, we will add Diethanolamine to raise the pH to 7.5.

Single Point– Set pH Calculation

1. **Click** on the '*Gas Condensate'* stream and **go** to the **Add Calculation** button and select **Single Point** calculation or by selecting the **Add Single Point** icon in the Actions Pane.
2. Change the name to ***DEA*** using the **<F2>** key.
3. **Add DEA** in the inflows grid. (It should have changed to the formula name: HN(C2H4OH)2
4. **Go** to the **Type of Calculation** option and select **Set pH**
5. **Change** the **Target pH** to 7.5
6. Click on the drop-down arrow for the pH Base Titrant and select DEA (or HN(C2H4OH)2)

We have set up the calculation to adjust the amount of DEA to match the target value of pH=7.5.

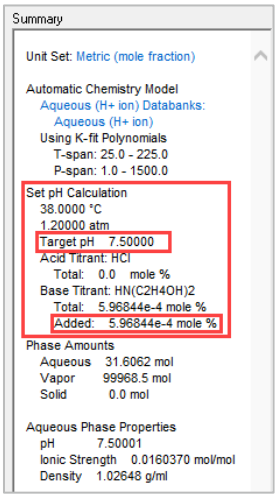
Your screen should look like the image below.



7. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

8. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

1. Check the summary box to analyze the results.



The pH is set to 7.5 and the inflow of DEA to the total gas is approximately 5.97e-4 mole%.

The DEA concentration in the condensing water and the amount remaining in the vapor phase can both be viewed in the Report tab.

2. **Click** on the **Report Tab** and go to the **Total and Phase Flows** and **Species Output** tables

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mol	mol	mol
Mole (True)	1.00000e5	31.6062	99968.5
Mole (App)	1.00001e5	32.0477	99968.5
	g	g	g
Mass	4.08064e6	642.188	4.08000e6
	L	L	L
Volume	2.11456e6	0.625619	2.11456e6

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

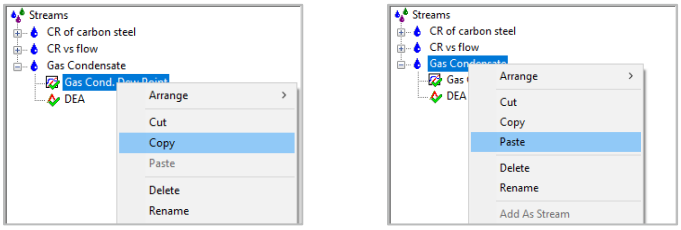
column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mole %	mole %	mole %
CO2	77.3994	0.0416672	77.4239
H2S	16.5999	0.0271211	16.6052
H2O	5.41962	96.6827	5.39076
CH4	0.499999	1.37153e-5	0.500157
C2H6	0.03	9.08534e-7	0.0300094
C3H8	0.03	7.06434e-7	0.0300094
N2	0.02	2.56549e-7	0.0200063
NH2(C2H4OH)2(+1)	5.02996e-4	1.59145	
HCO3-1	3.689e-4	1.16718	
C5H10NO4-1	6.87352e-5	0.217474	
HS-1	5.7612e-5	0.182281	
HN(C2H4OH)2	2.51153e-5	0.0778779	5.01249e-7
CO3-2	3.86988e-6	0.0122441	
S-2	3.93925e-9	1.24636e-5	
OH-1	6.55471e-10	2.07387e-6	
H+1	2.47871e-11	7.8425e-8	
Total (by phase)	100.0	100.0	100.0

Recalculating the corrosion rate with DEA

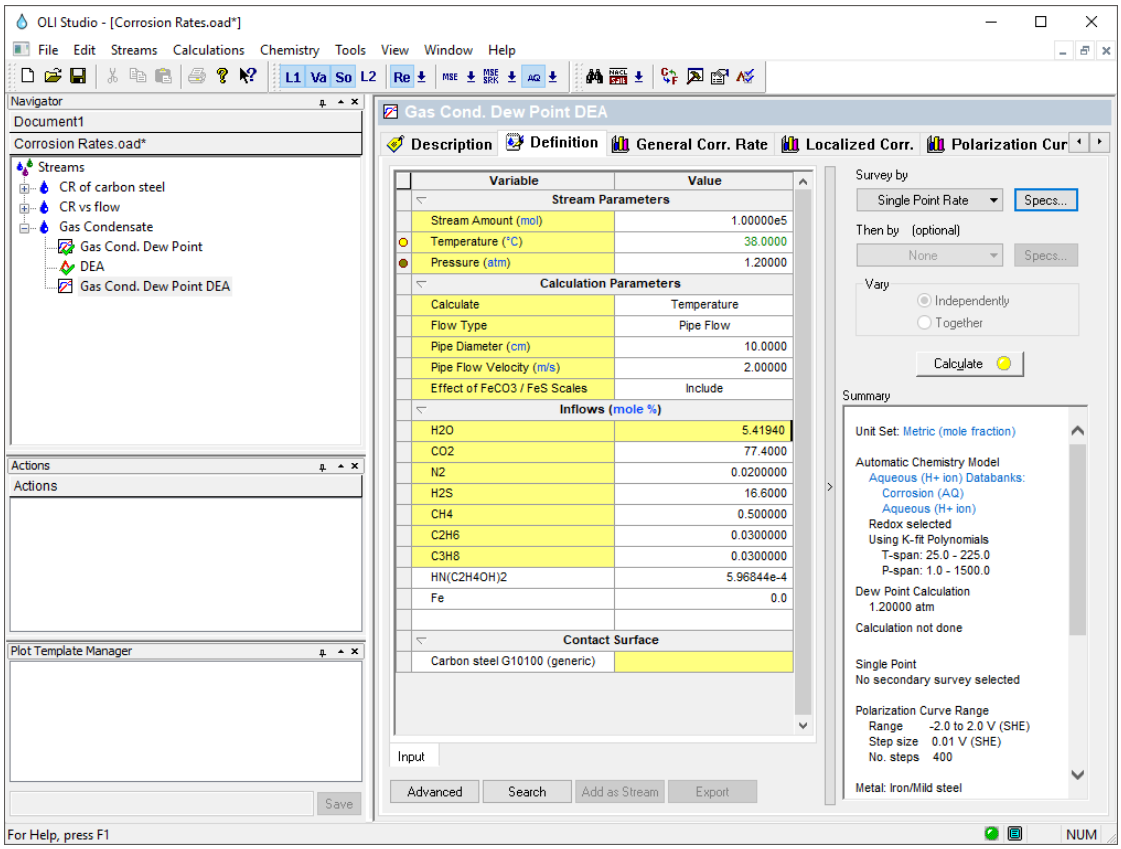
We now can recalculate the corrosion rate with DEA in the stream. This represents some DEA entrained in the vapor phase as the gas leaves the regenerator.

1. **Copy** *'Gas Cond. Dew Point'* corrosion calculation, and **paste** it under the stream '*Gas Condensate*'



2. Change the name to ***Gas Cond. Dew Point DEA*** using the **<F2>** key
3. **Add DEA** to the inflows gird and give it the value computed in the set pH calculation. (DEA =5.96844e-4 mole%)
4. Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface

Your screen should look like the image below.



9. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

10. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

Analyzing the Results

1. Click on the **General Corr. Rate** tab (General Corr. Rate).

2. **Click** on the **View Data** button to see the results in tabulated form.

	Temperature	Corrosion Rate	pH
	°C	mm/yr	
1	33.5105	1.10650	7.59719

Notice that the corrosion rate has decreased from 0.7 mm/year to 0.48 mm year. The pH is 7.6, and it remained similar to the target value of 7.5. Based on these results neutralizing the pH had a partial effect on corrosion reduction.

Changing the Alloy

Since treating the acid gas with a base is probably not a good idea for metal hydroxides, perhaps we can change the alloy. We will add a new corrosion rates calculation and test different alloys.

13%Cr Stainless Steel

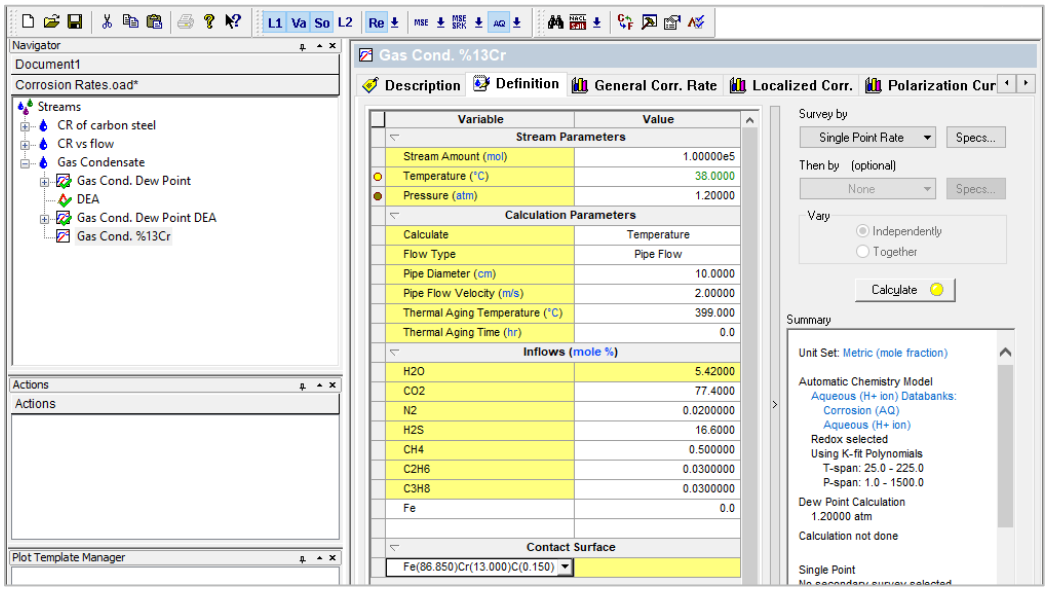
1. **Copy** *'Gas Cond. Dew Point DEA'* corrosion calculation, and **paste** it under the stream '*Gas Condensate*'

2. Change the name to ***Gas Cond. 13%Cr*** using the **<F2>** key.

   Notice that in the inflows, copying and pasting does not bring the DEA and its composition to this corrosion calculation. The reason why is because the DEA was added at the corrosion rate calculation level, and not at the stream level.

3. **Change** the **contact surface** to 13%Cr stainless steel

Your screen should look like the image below.



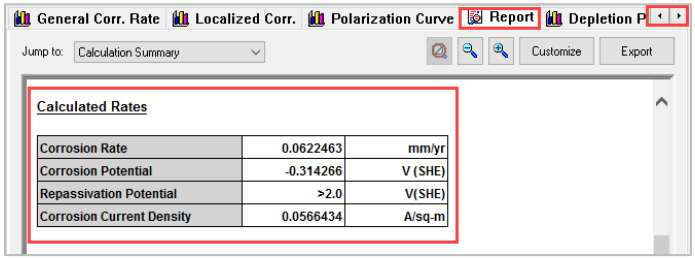
4. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

5. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

Analyzing the Results

i. Click on the **Report** tab to see the results. (You may need to use the ◄► buttons to move the tabs and find the Report tab).

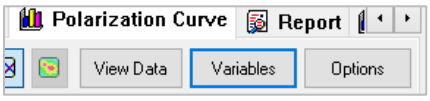
ii. Go to the **Calculated Rates** table



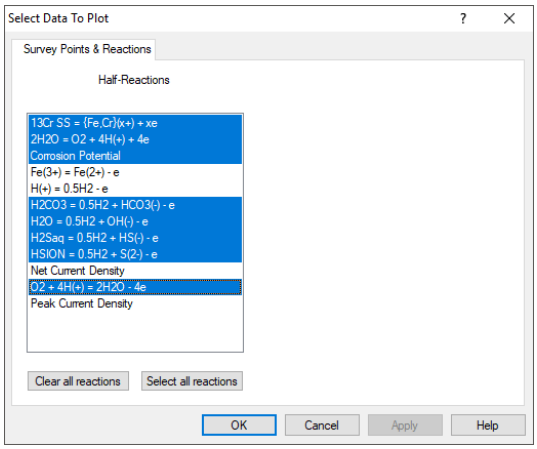
The corrosion rate of 13%Cr is one order of magnitude lower when compared to the corrosion rate for Carbon Steel, i.e. at 0.06 mm/year for 13%Cr vs 0.7 mm/year for Carbon Steel. This is consistent with the use of 13% Cr to protect against CO_2 corrosion.

iii. Click on the **Polarization Curve** tab (Polarization Curve).

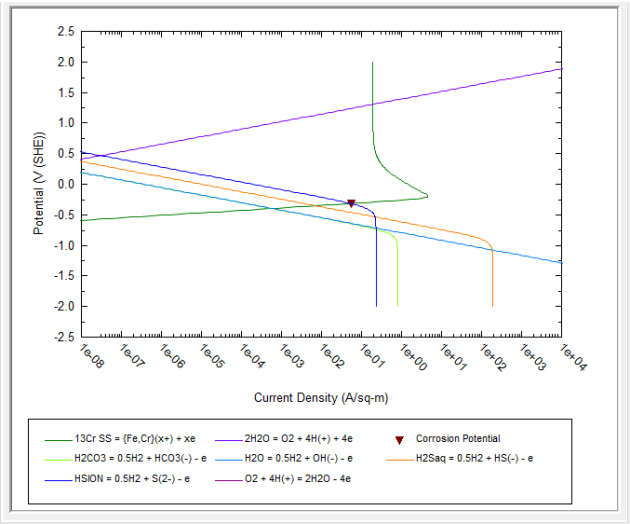
iv. Click on the **Variables** button. This will open a new window.



v. Remove the following variables by unchecking them. See image below. Then **Click OK.**



vi. The polarization curve (after some layout modifications) should look like the image below.



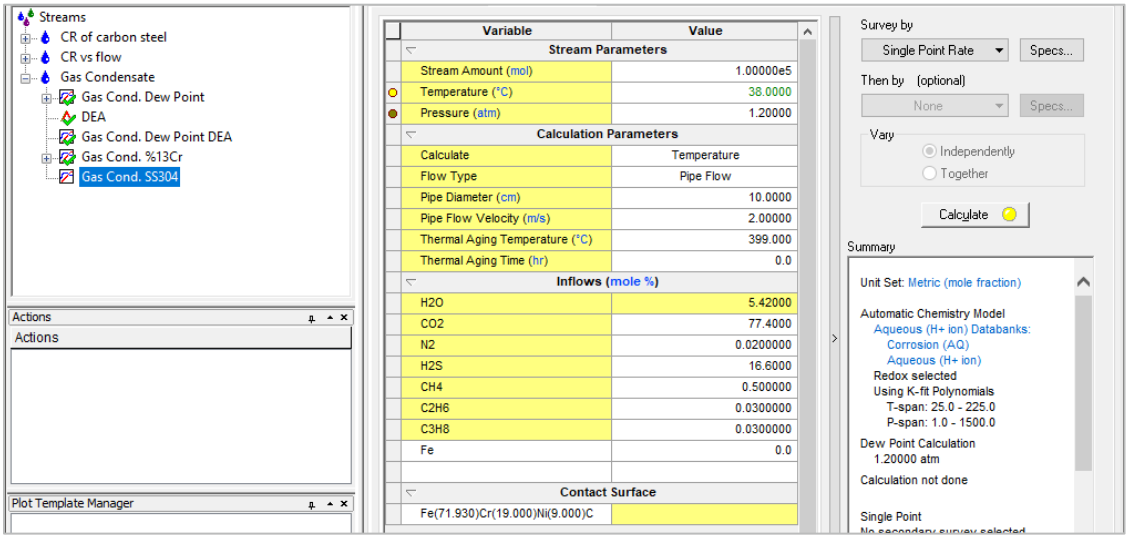
The layout of the plot was changed for easy reading. To change layout, you can right click on any part of the plot and select the option *Alloy Layout Changes* to modify the appearance of your plot.

The corrosion potential of 13%Cr is -0.31 V vs SHE and the corresponding corrosion current i_{corr}=0.06 A/m^2. The i_{corr} for Carbon Steel was 0.61 A/m^2, this means that 13%Cr is 10x more resistant to corrosion under the same conditions.

Stainless Steel 304

1. **Copy** *'Gas Cond. Dew Point DEA'* corrosion calculation, and **paste** it under the stream '*Gas Condensate*'
2. Change the name to ***Gas Cond. SS304*** using the **<F2>** key
3. **Change** the **contact surface** to Stainless Steel 304

Your screen should look like the image below.



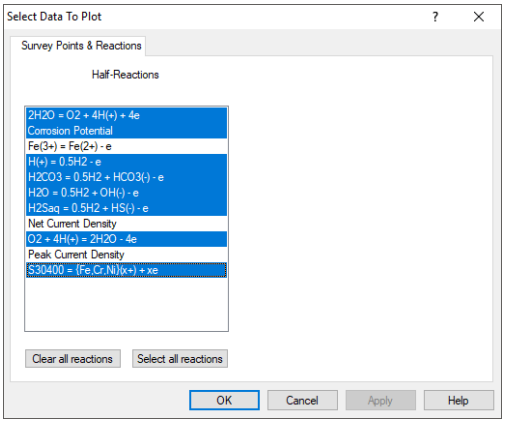
4. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
5. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

1. Click on the **Report** tab to see the results. (You may need to use the ◄► buttons to move the tabs and find the Report tab).
2. Go to the **Calculated Rates** table

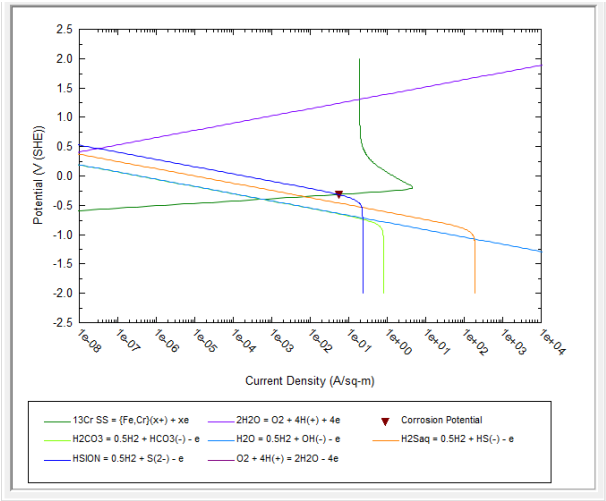
Corrosion Rate	3.57108e-3	mm/yr
Corrosion Potential	-0.172583	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	3.29499e-3	A/sq-m

The corrosion rate of 304 SS is now 0.0036 mm/year. This is a negligible value.

3. Click on the **Polarization Curve** tab (Polarization Curve).
4. Click on the **Variables** button. This will open a new window.
5. Remove the following variables by unchecking them. See image below. Then **Click OK.**



The polarization curve (after some layout modifications) should look like the image below.



The layout of the plot was changed for easy reading. To change layout, you can right click on any part of the plot and select the option Alloy Layout Changes to modify the appearance of your plot.

The corrosion potential of SS304 is -0.17 V vs SHE and the corresponding corrosion current i_{corr}=3.3e-3 A/m^2. With this low corrosion current density, sour gas regeneration can be remedied using a higher-grade alloy such as SS304.

Section 9. Thermal Aging and Variations in Alloy Composition

9.1. Overview and Basic Terminology

Localized corrosion of engineering alloys is a complex function of metallurgical factors and environmental conditions. Among metallurgical factors, effects of thermal instabilities are of interest for assessing the performance and expected service life of industrial components fabricated from nominally corrosion-resistant stainless steels and nickel-base alloys.

Fabrication processes such as heat treatment and welding are known to introduce microstructural changes that may affect both the mechanical and corrosion performance of an alloy. In particular, thermal instability of stainless steels and nickel-base alloys may lead to the formation of complex metal carbides of the type M_3C_2, M_7C_3, M_6C, or $M_{23}C_6$ in which the metallic component M represents Cr, Mo, W, and Fe. The carbide is chromium- or molybdenum-rich depending on the carbide type, which in turn depends on the alloy composition and temperature. Also, various chromium-rich intermetallic phases can form in many alloys. Precipitation of such phases may occur at temperatures ranging from 500 to 900 °C depending on alloy composition. Formation of grain boundary carbides often results in the depletion of chromium and, possibly, molybdenum in the vicinity of the grain boundary because of the slow diffusion of substitutional elements such as chromium relative to the interstitial carbon.

Similarly, the corrosion resistance of welded components may be affected by the segregation of alloying elements and precipitation of intermetallic phases, carbides or nitrides in the solidified weld and unmixed zones as well as the precipitation of carbides and other phases in the heat-affected zone adjacent to the weld.

Sensitization of Fe-Ni-Cr-Mo alloys and its effects on intergranular attack and intergranular stress corrosion cracking is the most directly observed effect of Cr depletion. It may result in intergranular attack and intergranular stress corrosion cracking. Localized corrosion can be also affected by Cr and Mo depletion.

Corrosion Analyzer contains the following technology that can help address these issues:

- A grain boundary microchemistry model for predicting the chromium and molybdenum depletion in the vicinity of grain boundaries as a result of carbide formation;
- An electrochemical model for calculating the repassivation potential of Fe-Ni-Cr-Mo-W alloys as a function of alloy composition and environmental conditions including temperature and concentrations of aqueous solution species;
- A procedure for calculating the observable repassivation potential that corresponds to macroscopic localized corrosion by applying the electrochemical model to the depletion profiles and performing suitable integration.

More details about this technology are described by Anderko et al. (2008), Tormoen et al. (2009), Anderko et al. (2009), and Sridhar et al. (2009).

Alloy Chemistry

Simulations can be performed, in general, for alloys that belong to the Fe-Ni-Cr-Mo-W-N-C family (i.e., for stainless steels and nickel-base alloys).

Depletion profiles in the vicinity of grain boundaries and depletion parameters can be obtained for austenitic alloys (including stainless steels and Ni-base alloys). Also, the effect of Cr and Mo depletion on localized

corrosion can be calculated. This effect can be examined using the repassivation potential, which provides a threshold potential for the stabilization of localized corrosion (Anderko et al., 2009).

For other alloys from the Fe-Ni-Cr-Mo-W-N-C family, the repassivation potential can be calculated if the alloy composition is known. This also includes experimental alloys and separate phases that may be formed as a result of various forms of heat treatment (Sridhar et al., 2009).

Calculation types

Thermal aging is an additional phenomenon that can be simulated within the framework of corrosion kinetics. All calculations types and, in particular, survey types, that are supported for corrosion kinetics are also supported in conjunction with the study of thermal aging.

If it is desired to make calculations on a thermally aged sample, the thermal aging temperature and time need to be specified in the **Calc Parameters** section in the **Definition** tab. The default values are 399 °C for the thermal aging temperature and 0.0 hours for the thermal aging time. If either of these default values is used, no thermal aging effects will be predicted. Thus, by default, Corrosion Analyzer performs calculations on samples that have not been thermally aged.

Thermal Aging Temperature Survey

This calculation makes it possible to vary the thermal aging temperature within a certain range. A fixed value of thermal aging time is assumed as specified by the user. Typically, the temperatures for which thermal aging effects can be observed range from ~500 °C to ~900 °C, with the effects being most pronounced in the middle of this range.

Thermal Aging Time Survey

This calculation can be used to examine the effect of aging time at a fixed thermal aging temperature.

Output Specific to Thermal Aging

The following output can be generated:

- Chromium and molybdenum depletion profiles, i.e., the variation of Cr and Mo concentration within the grain as a function of grain boundary.

- The depletion parameter, which provides compact information on the extent to which the depletion process reduces the grain boundary concentration below a certain critical value of, which can be defined by well-known criteria for maintaining passivity (e.g. $x_{Cr}^{*} = 0.11\ or\ 0.12$). This parameter can be calculated as the area of the depletion profile below the threshold concentration x_{Cr}^{*}, divided by bulk Cr concentration, x_{Cr}^{0}:

  $$\delta(x_{Cr}^{*}) = \frac{1}{x_{Cr}^{0}} \int_{0}^{z^{*}} \left(x_{Cr}^{*} - x_{Cr}(z)\right) dz$$

  where z^{*} is the distance from the grain boundary that corresponds to the threshold concentration x_{Cr}^{*}.

- The repassivation potential, which is a key parameter for determining whether localized corrosion can occur, may be affected by thermal aging in a rather complex way.

9.2. Thermal Aging and Variations in Alloy Composition

We will show examples of simulating the effects of thermal aging on Fe-Ni-Cr-Mo-W-C-N alloys (i.e., stainless steels and nickel-base alloys). Specifically, we will show how to predict:

1. Chromium and molybdenum depletion profiles in the vicinity of grain boundaries, which result from heat treatment of austenitic alloys;
2. Depletion parameters for sensitized austenitic alloys, which provide an indicator of whether the alloy is susceptible to intergranular corrosion.
3. Effect of thermal aging on the repassivation potential of austenitic alloys, which provides a threshold condition for localized corrosion (pitting or crevice corrosion).
4. The repassivation potential of alloys with compositional variations that may or may not result from thermal aging. This facility can also be used for bulk alloys that are not in the database or to hypothetical or experimental alloys as long as they belong to the Fe-Ni-Cr-Mo-W-C-N family. An example will be given for a duplex alloy, either annealed or thermally treated.

Example 53: Thermal aging of alloy 600

We will be studying the behavior of thermally aged alloy 600 in a dilute aqueous solution of sodium chloride, and will simulate how the time of thermal aging affects alloy 600 at a fixed thermal aging temperature of 700°C.

Starting the Simulation

Thermal Aging Calculation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Thermal Aging Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Thermal Aging	Stream Amount	Calculated
Calculation Type	Corrosion Rates	Temperature	60 ºC
Survey by	Thermal Aging Time	Pressure	1 atm
Name Style	Display Name	H2O	Default – 55.5082 moles
Unit Set	Metric, Batch, Moles	NaCl	0.04 moles
Framework	AQ		

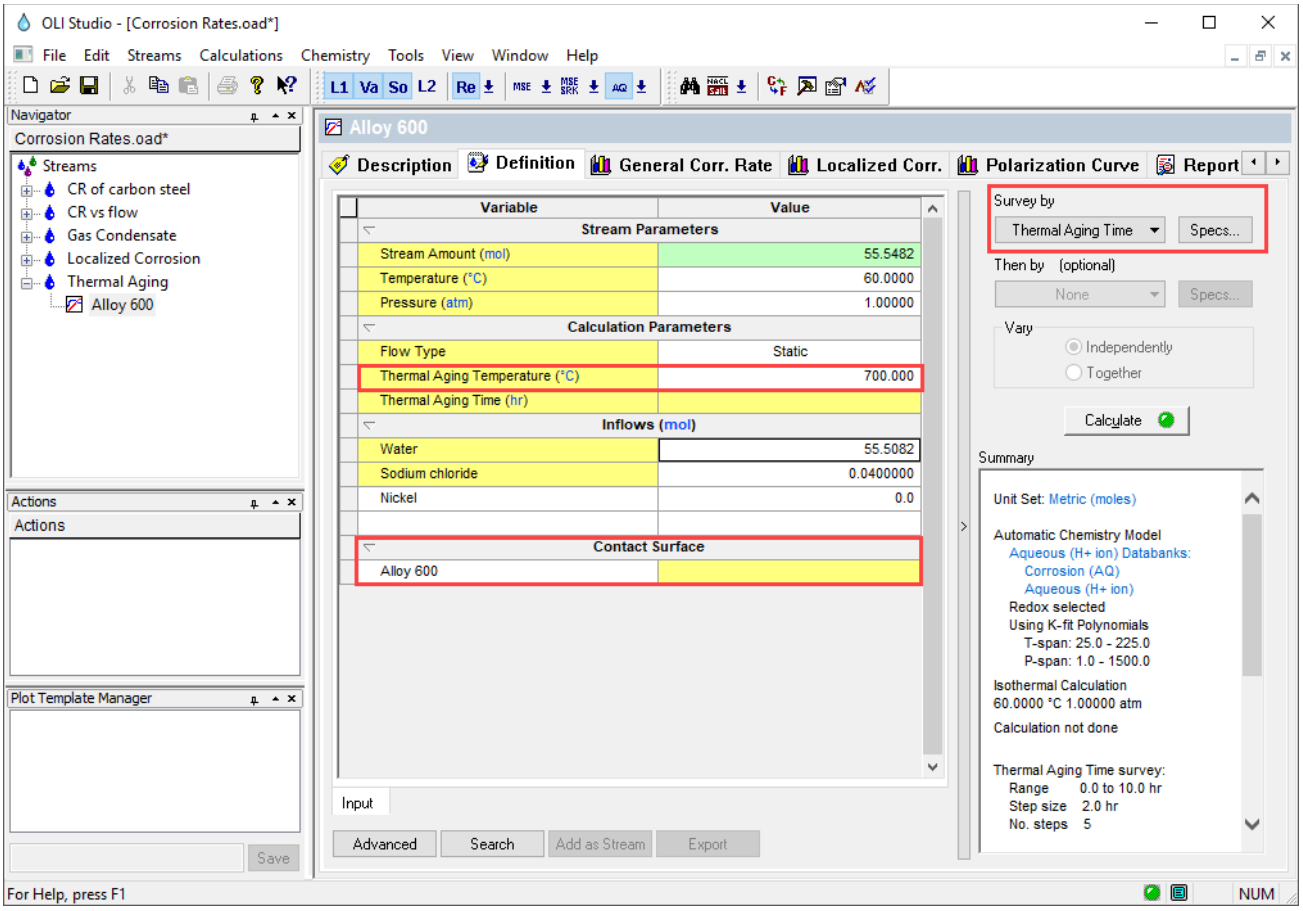
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Thermal Aging*
3. Select the AQ thermodynamic Framework (selected by default)
4. **Click** on the **Units Manager** Icon and select Metric, Batch, Moles
5. **Click** on the **Names Manager** Icon and select *Display Name*

6. **Enter** the stream composition and conditions specified in the table above
7. **Go** to the **Add Calculation** button and select **Corrosion Rates**

   Note: Even though the thermal aging simulation facilities do not predict corrosion rates per se, they belong to the category of corrosion kinetics and, therefore, they are included in the Corrosion Rates section of the Corrosion Analyzer.
8. **Select** the Survey by **Thermal Aging Time**
9. **Change** the name from ***Rates*** to ***Alloy 600*** using the **<F2>** key or by **right-mouse click** on the object and select rename
10. Select ***Alloy 600*** from the **Contact Surface** grid
11. In the **Calculation Parameters** grid, change the default value for the **Thermal Aging Temperature** to 700°C.

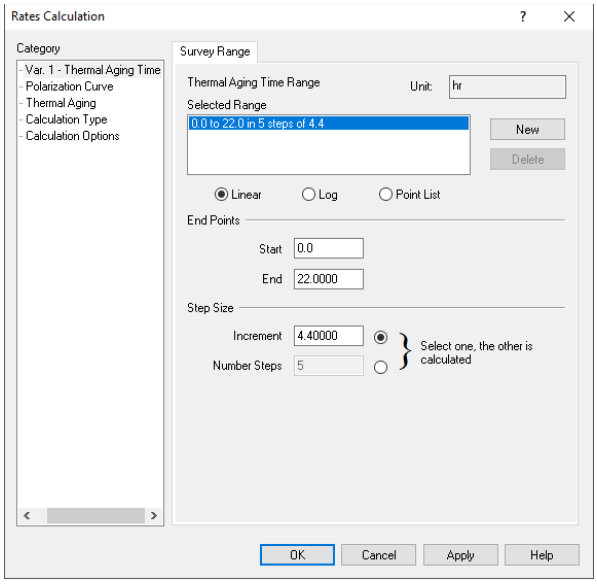
    Note that the default value for the **Thermal Aging Temperature** is 399 °C, which is a low value so that, in the default case, no effects of thermal aging are being calculated.

Your screen should look like the image below.

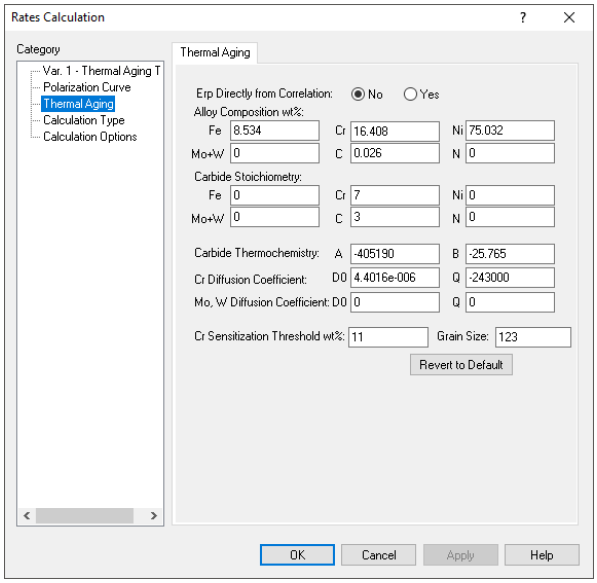


12. Now we need to specify the Thermal Aging Time range. **Click** on the **Specs** button. This will open a new window.

13. Under the **Survey Range** tab, change the range for Thermal Aging Time from 0 to 22 hours with an increment of 4.4 hours (of 5 steps).



14. Under the **Category** section, select the **Thermal Aging** option.



In this **Thermal Aging** Category, you can change all parameters that are necessary for calculating chromium and (if applicable) molybdenum depletion profiles. You can change:

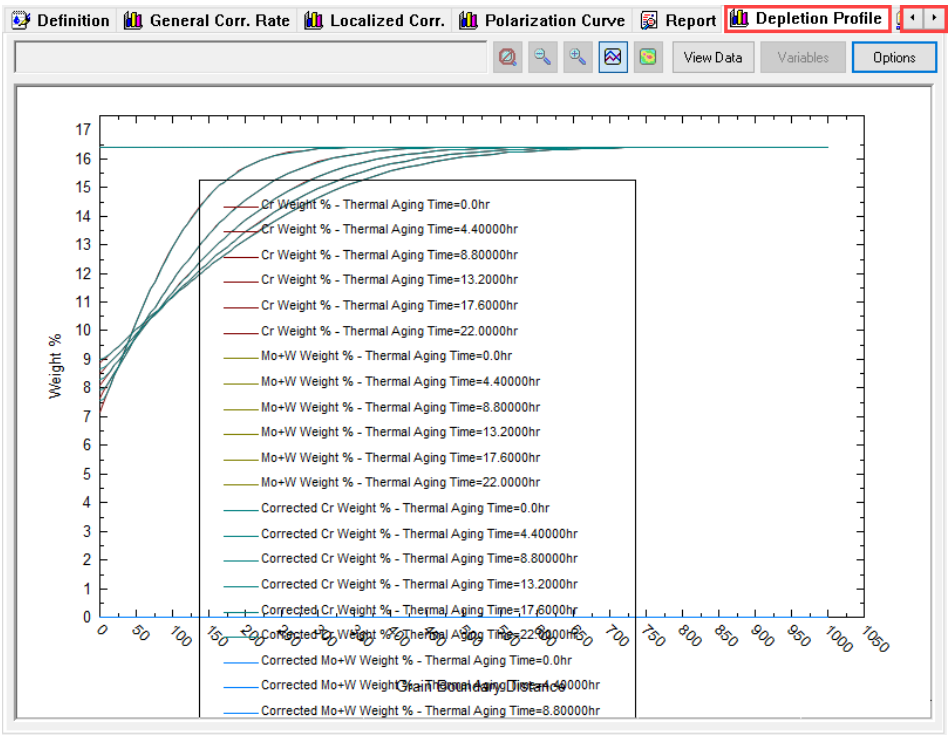
- The alloy composition (for example, to analyze the effect of a different carbon content);
- The stoichiometry of the carbide phase that may form at the grain boundary; the typical carbide stoichiometry is M_7C_3 or $M_{23}C_6$ (where M = Cr, Mo) but can be adjusted
- The parameters that define the equilibrium constant for the formation of the carbide
- The diffusion coefficient of Cr and, if applicable, Mo
- The threshold concentration of Cr for sensitization. This threshold concentration is used for calculating the depletion parameter.
- The average grain size, which affects the process of healing of chromium depletion as a function of time

Also, you can indicate whether the repassivation potential (E_{rp}) should be calculated directly from the correlation developed by Anderko et al. (2008), which expresses E_{rp} as a function of alloy composition or not. If it is not calculated directly, then the repassivation potential is calculated first using the alloy-specific parameters for the alloy of interest and only the decrement of E_{rp} (i.e., $E_{rp,\ \text{thermally aged}} - E_{rp,\ \text{bulk alloy}}$) is obtained from the correlation. This decrement is then added to the alloy-specific E_{rp} value. This option is set by default to "No" because this maximizes the accuracy of calculations for alloys that are already in the database.

15. For now, we will accept the default settings. Click **OK**.
16. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
17. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous section named *Corrosion Rates.*

Analyzing the Results

1. Click on the **Depletion Profile** tab (Depletion Profile). If you don't see it in your screen, use the ◄► buttons to move the tabs.



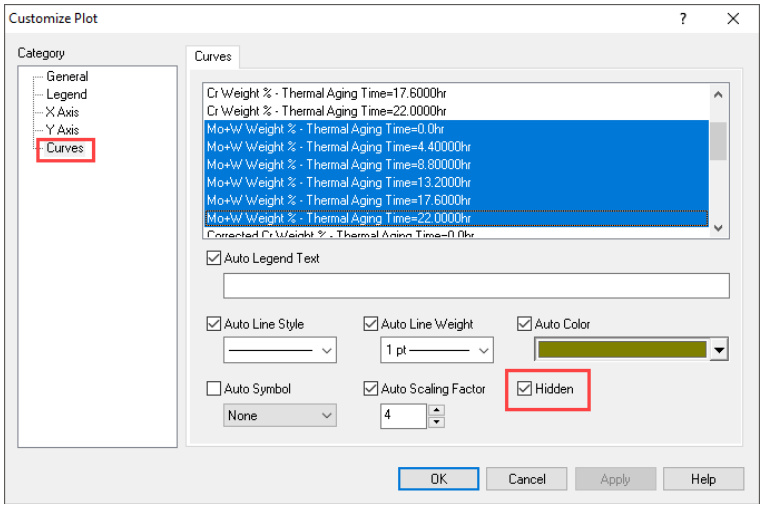
Note: Since alloy 600 does not contain any molybdenum, the molybdenum curves will always be equal to zero.

This plot will show the concentrations of chromium and molybdenum within a grain as a function of the distance from the grain boundary (in μm). You will see that, for each condition, there are four lines:

- **Cr weight %:** concentration of Cr in weight %
- **Mo+W weight %:** sum of the concentrations of molybdenum and tungsten in weight %
- **Corrected Cr weight %:** concentration of Cr corrected for beam scattering and related effects so that it can be directly compared with experimental results. The procedure for calculating the correction is described by Anderko et al. (2009).
- **Corrected Mo+W weight %:** sum of the concentrations of Mo and W corrected in the same way as those for Cr.

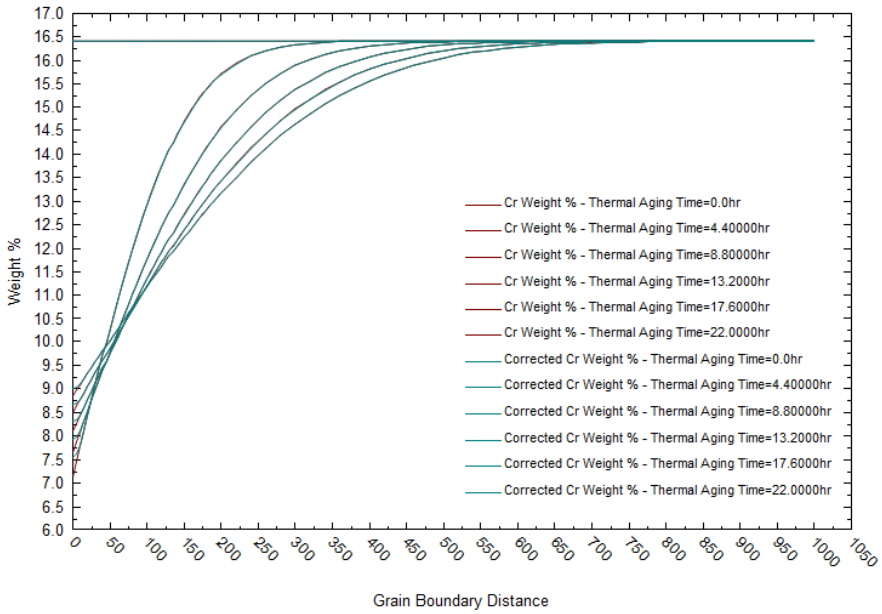
Let's customize the plot

2. Click on the **Options** button. This will open a new window.
3. Since alloy 600 does not contain Mo or W, eliminate the Mo+W curves. To do this, go to the **Category** section and select the **Curves** option
4. Highlight the Mo+W weight % curves by pressing the Shift key and the down key (**Shift +** ↓). After highlighting these curves, check the **Hidden** button.



5. After hiding the Mo+W weight % curves, do the same for the Corrected Mo+W weight % curves. Then click **OK**.

The plot should look like the image below.



The legend of this plot was modified for clarity. The border style of the legend was modified by double clicking on the legend, and selecting *None* as the Border Style

Differences between Uncorrected and Corrected Depletion Profiles

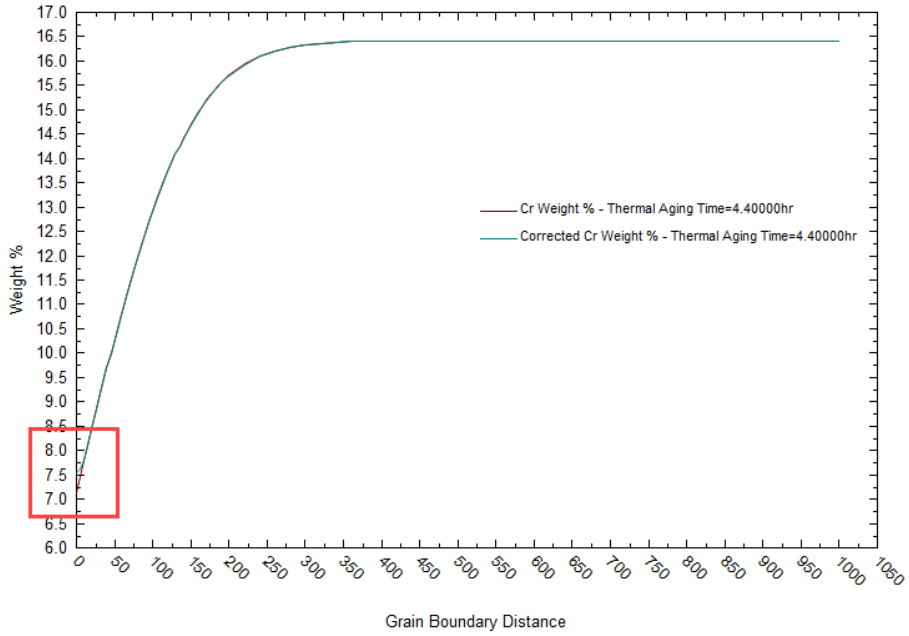
Now, let's focus on the differences between the uncorrected and corrected depletion profiles. To have a clear picture of the difference between them, we will analyze the depletion profiles results obtained at 4.4 hours of thermal aging.

6. Click on the **Options** button, and select the **Curves** category
7. Highlight all curves except the ones labeled as:

Cr Weight % - Thermal Aging Time = 4.40000 hr, and
Corrected Cr Weight % - Thermal Aging Time = 4.40000 hr

Check the **Hidden** box, then click **OK**.

Your plot should look that the image below.



In the obtained plot, you can see the difference between the two curves for small distances from the grain boundary (roughly below 30 μm). The corrected concentration is much more rounded in the vicinity of the minimum because instrumental measurement effects. At larger distances from the grain boundary, there is no difference between the two curves.

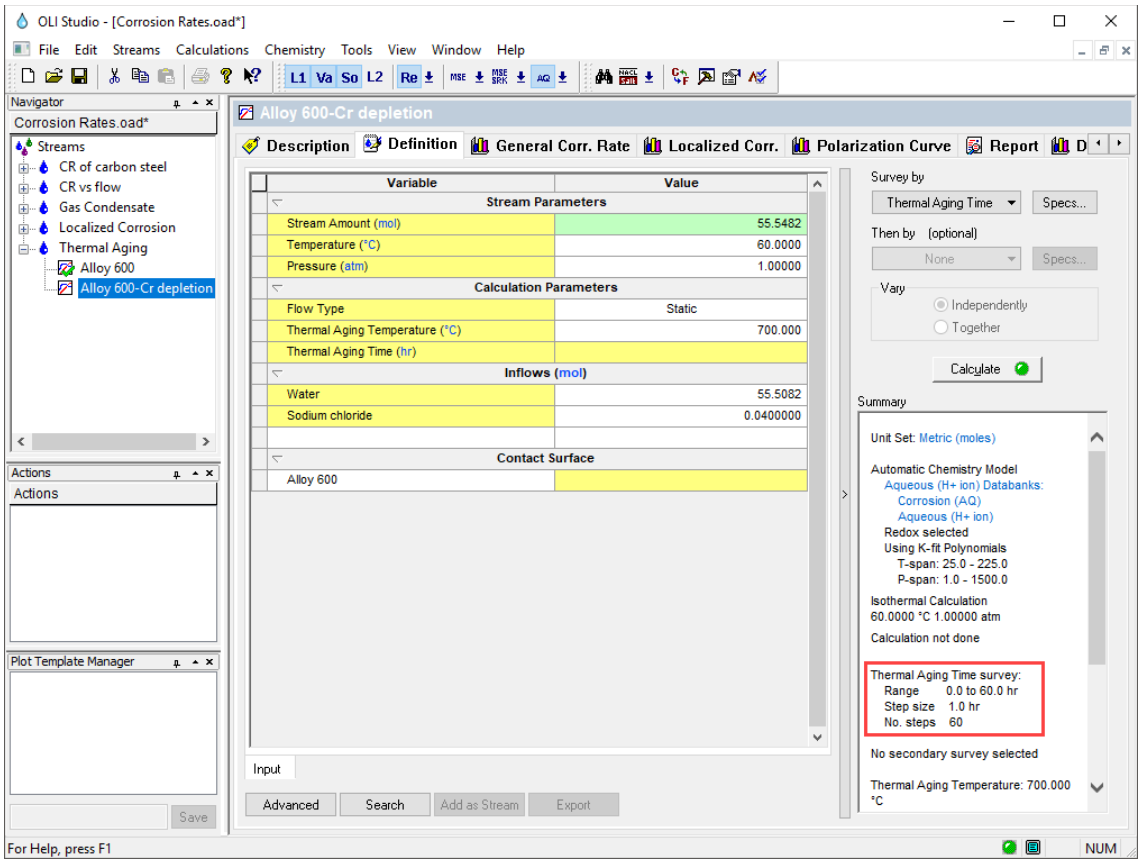
Effect of Cr depletion on corrosion

After analyzing the depletion profiles, let's focus on the effects of Cr depletion on corrosion. We will do it by analyzing two parameters – the depletion parameter and the repassivation potential.

To have more meaningful results, let's expand the range of thermal aging time and reduce the interval for calculations.

1. **Copy** the Alloy 600 corrosion calculation, and then **paste** it under the **Thermal Aging Stream**
2. **Rename** the new calculation as **Alloy 600 – Cr depletion**
3. Go back to the **Definition** tab and click the **Specs** button
4. In the **Var.1 Thermal Aging Time** category, change the Survey Range as follows: **Start**=0 hours, **End**= 60 hours with an **Increment**= 1 hour. Then click **OK.**

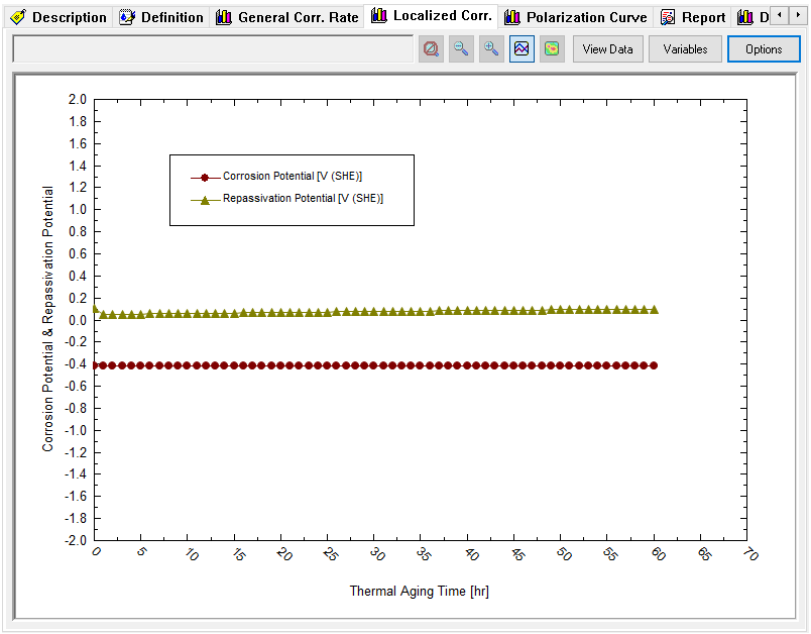
Your screen should look like the image below



5. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

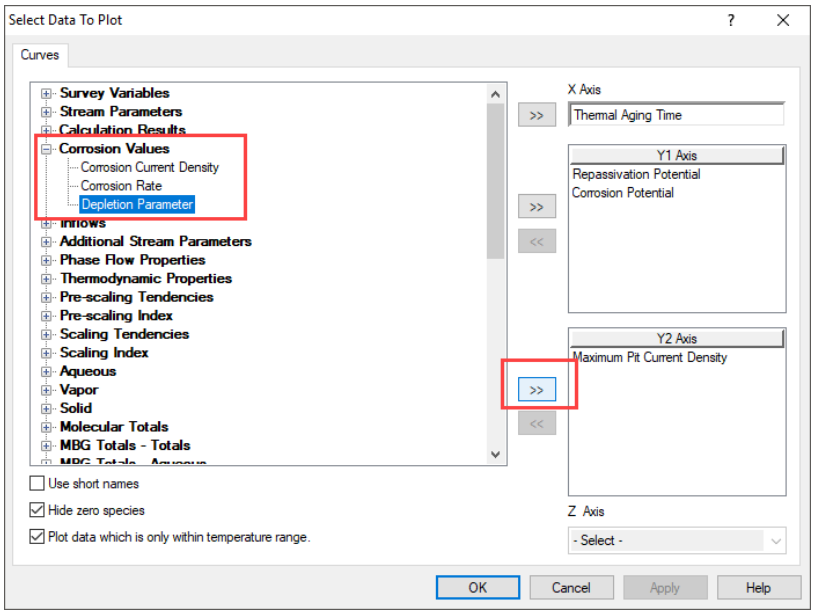
6. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous section named *Corrosion Rates.*

1. Click on the **Localized Corr.** tab (Localized Corr.). By default, this tab will show a plot of the corrosion potential and repassivation potential.

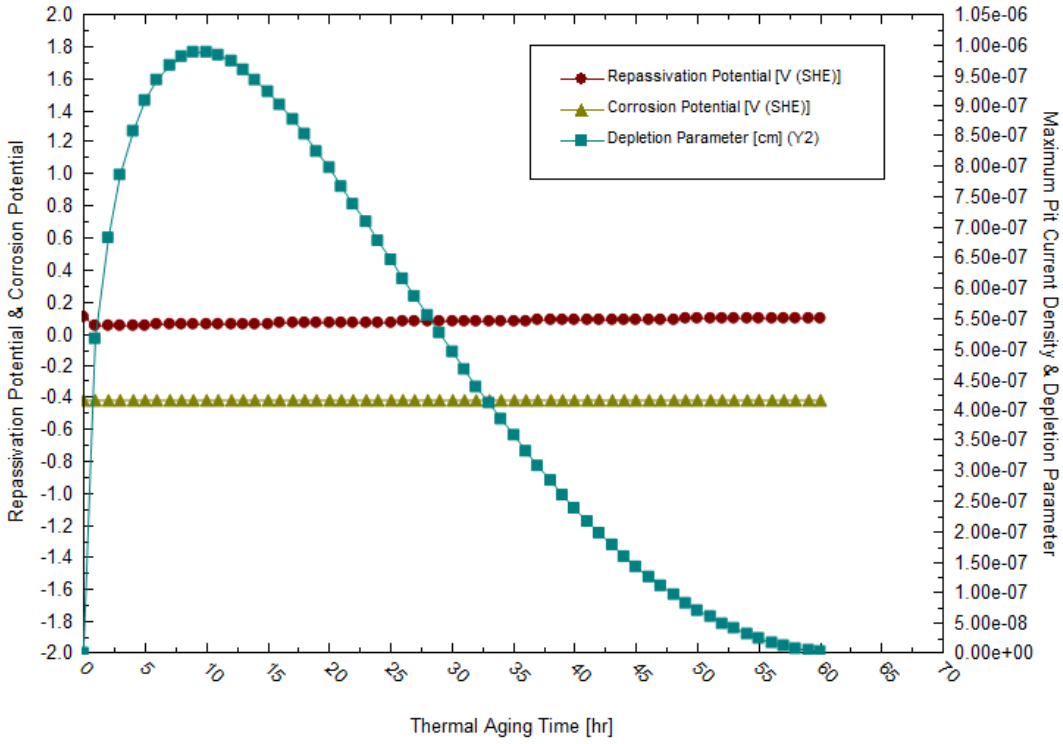


Let's add a new parameter to the plot: The ***Depletion Parameter***.

2. Click on the **Variables** button. This will open a new window.
3. Look for the **Corrosion Values** section, click on the '+' icon, and select the **Depletion Parameter** option. Click on the **>>** button that belongs the **Y2 Axis**. This action will place the new variable under the Y2 Axis. Then click **OK**.



The plot should look like the image below.



It is clear that the depletion parameter reaches a maximum for aging time of about 10 hours. Since the depletion parameter is a measure of the susceptibility of an alloy to intergranular corrosion, we can expect that the alloy will be most susceptible to intergranular corrosion at intermediate aging times. When the depletion parameter is zero, intergranular corrosion or intergranular stress corrosion cracking are unlikely. The decrease of the depletion parameter as a function of time is a manifestation of the phenomenon of healing of Cr depletion.

The repassivation potential shows a minimum as a function of aging time (see the option **View Data**). This indicates that the tendency of the alloy to undergo localized corrosion is enhanced as a result of thermal aging. However, the effect of thermal aging on the repassivation potential of alloy 600 is small (cf. Tormoen et al., 2009, Anderko et al., 2009). The repassivation potential shows a minimum at low aging times (ca. 1-2 hours). Therefore, the susceptibility to localized corrosion is enhanced the most for these aging times. It is noteworthy that the maximum in the depletion parameter does not coincide with the minimum in the repassivation potential. This is due to the fact that intergranular corrosion (which is related to the depletion parameter) and localized corrosion (which is controlled by the repassivation potential) are subject to different mechanisms. A general discussion of these differences is given by Tormoen et al. (2008).

In general, the alloy will be susceptible to localized corrosion if the corrosion potential exceeds the repassivation potential. In the above example, the corrosion potential is low because we have no oxidizing agents in the system. Therefore, the alloy will not undergo localized corrosion at the conditions of this example. However, a rise in the corrosion potential due to the presence of oxidizing agents may cause localized corrosion.

Example 54: Thermal aging of alloy 825

Alloy 825 is appreciably different from alloy 600 because it contains molybdenum and, also, substantially more chromium in addition to other alloying elements.

In this example, we will simulate how the temperature of thermal aging affects alloy 825 at a fixed thermal aging time of 15 hours.

Starting the Simulation

Thermal Aging Calculation

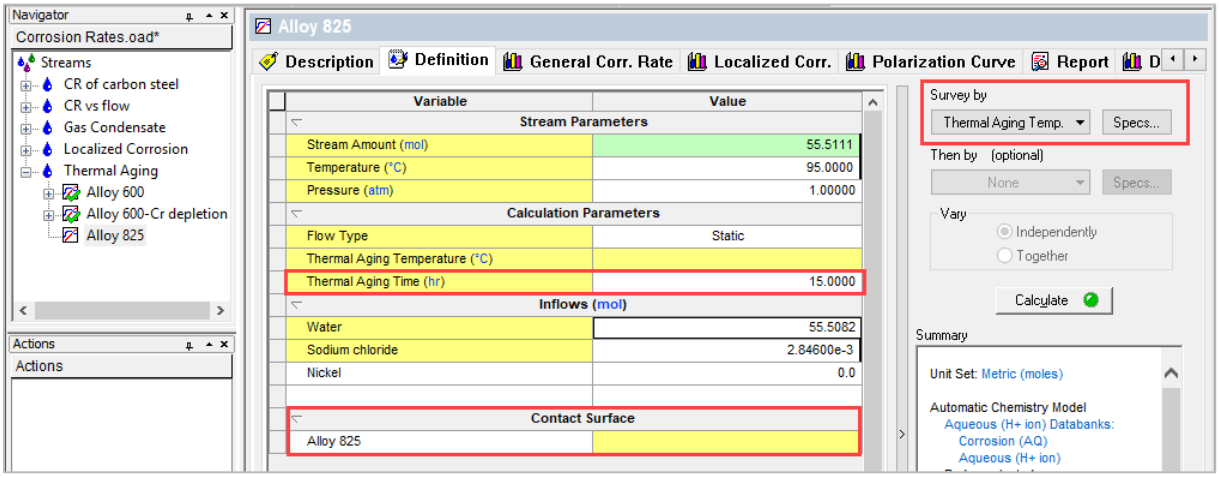
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Thermal Aging Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Thermal Aging	Stream Amount	Calculated
Calculation Type	Corrosion Rates	Temperature	95 ºC
Survey by	Thermal Aging Temperature	Pressure	1 atm
Name Style	Display Name	H2O	Default – 55.5082 moles
Unit Set	Metric, Batch, Moles	NaCl	2.846e-3 moles
Framework	AQ		

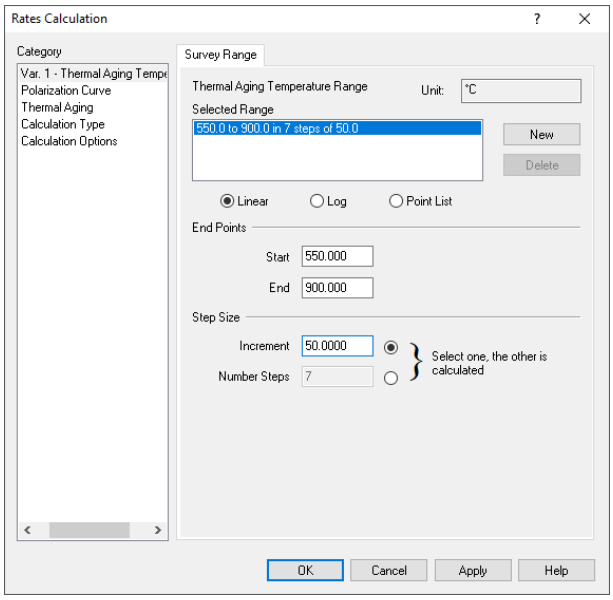
1. Under the Thermal Aging stream add a new calculation rate. Go to the **Add Calculation** button and select **Corrosion Rates** or select the **Add Corrosion Rates** icon in the **Actions panel**
2. **Change** the name from ***Rates*** to ***Alloy 825*** using the **<F2>** key or by **right-mouse click** on the object and select rename
3. **Select** the Survey by **Thermal Aging Temperature** option
4. **Change** the stream composition and conditions to the specified values in the table above
5. Select ***Alloy 825*** from the **Contact Surface** grid
6. In the **Calculation Parameters** grid, change the default value for the **Thermal Aging Time** to 15 hours

   Note that the default value for the **Thermal Aging Temperature** is 0 hours, which means that no thermal aging is considered by default.

Your screen should look like the image below



18. Now we need to specify the Thermal Aging Temperature range. **Click** on the **Specs** button. This will open a new window.
19. Under the **Survey Range** tab, change the range for **Thermal Aging Temperature** from 550 to 900 °C with increments of 50 °C. We will keep the other parameters at their default values. Click **OK.**

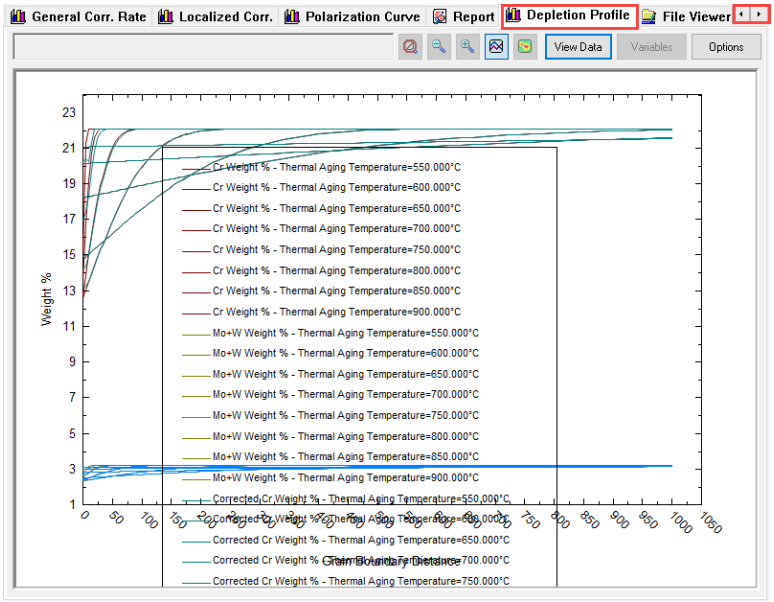


20. We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
21. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous section named *Corrosion Rates.*

Analyzing the results

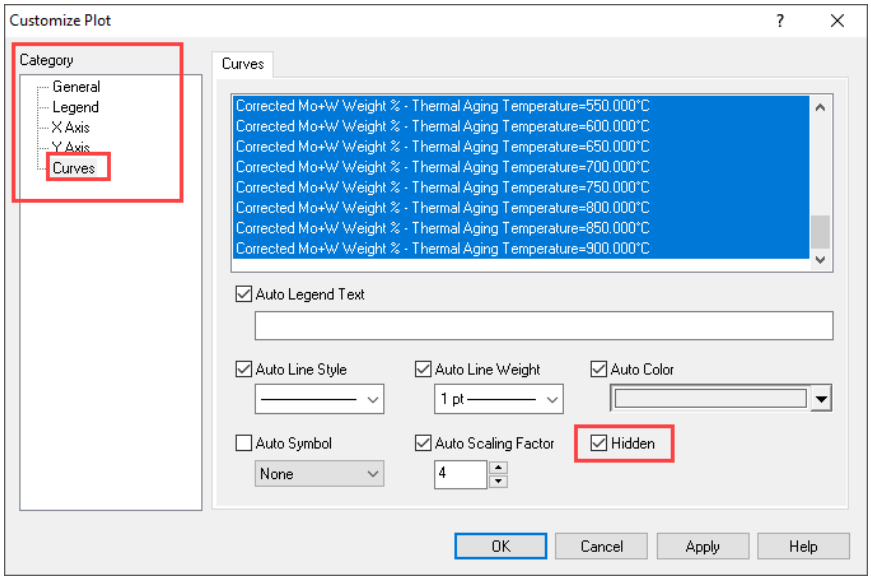
1. Click on the **Depletion Profile** tab (Depletion Profile). If you don't see it in your screen, use the ◄► buttons to move the tabs.

Since alloy 825 contains Mo in addition to Cr, you will see the depletion profiles for both Cr and Mo.

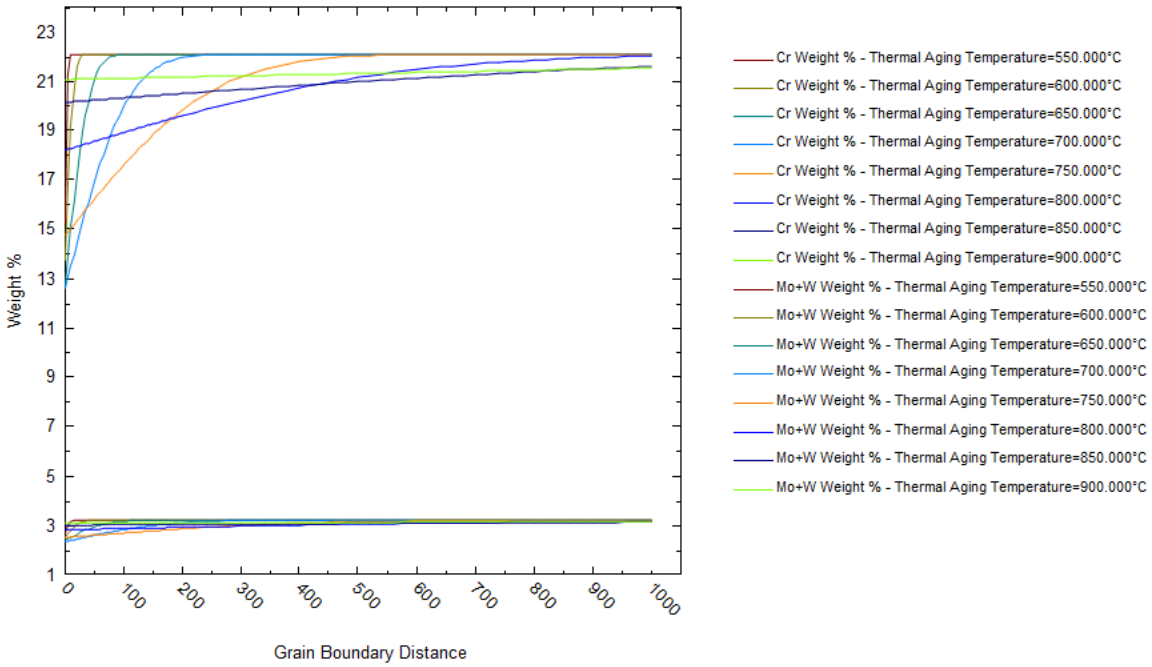


For clarity, let's customize the plot by removing the corrected depletion profiles and leaving only the uncorrected (or directly calculated) ones.

2. Click on the **Options** button, and select the **Curves** category, highlight the Corrected curves and check the hidden box. Then click **OK**.



Your plot should look like the image below



The plot was modified by right clicking on it and selecting the option *Allow Layout Changes*. This option allows to move and rearrange the plot and legend. Additionally, the color of the lines was changed for each temperature in order to distinguish the temperature effect.

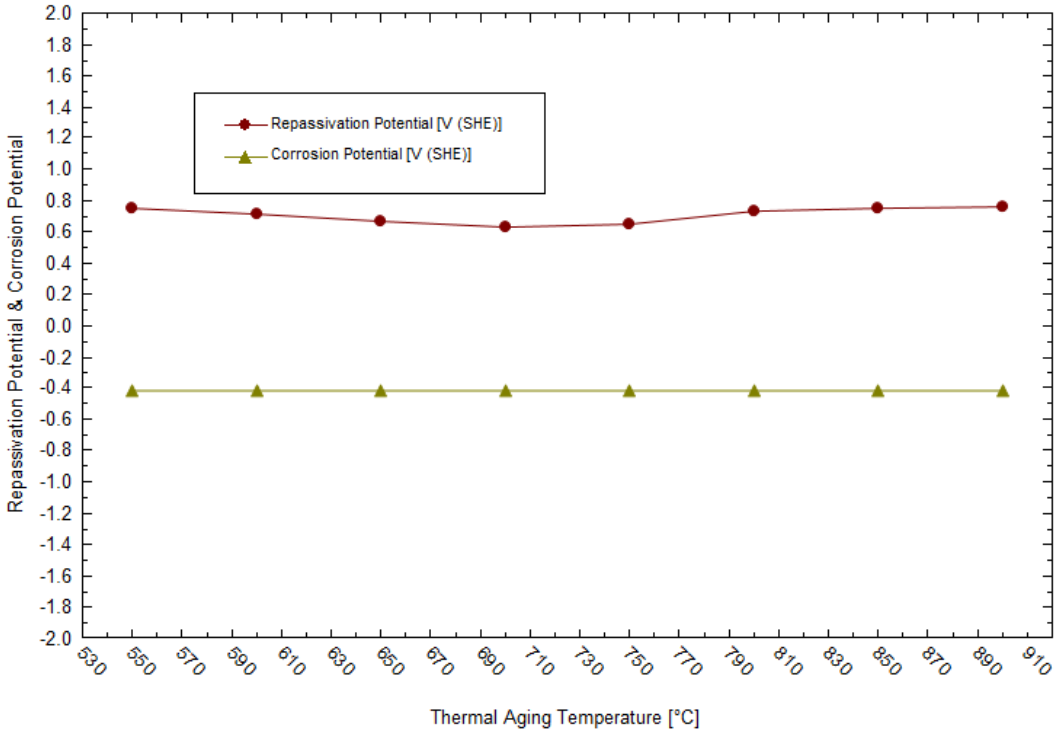
As shown in the plot above, the depletion profile is very narrow at the lowest temperature, i.e., 550 °C. On the other hand, it becomes flat at high temperatures and it has a high minimum. The high minimum value is particularly important because it indicates that the local depletion of Cr and Mo is much less severe at high temperatures (due to much faster diffusion of substitutional elements and subsequent healing).

It should be noted that the Mo profile qualitatively parallels the Cr profile but has somewhat different slopes because of differences in diffusion coefficients of Cr and Mo.

Effect of Cr and Mo depletion on corrosion

To look at the effect of Cr and Mo depletion on corrosion

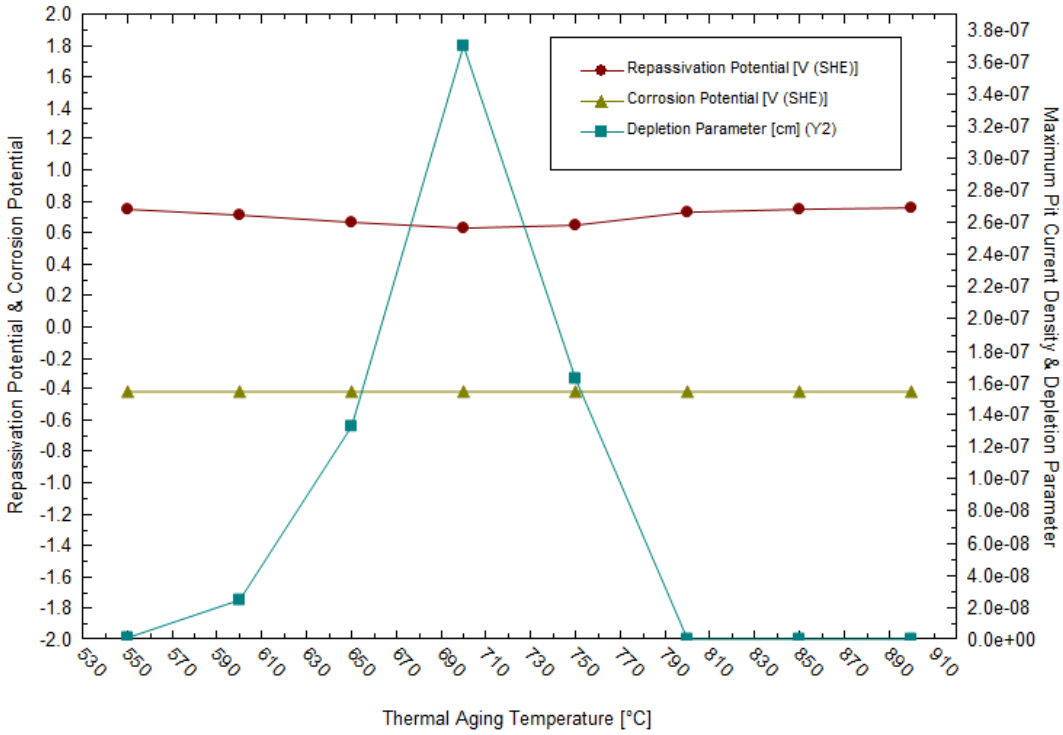
3. Click on the **Localized Corr.** tab (Localized Corr.). By default, this tab will show a plot of the corrosion potential and repassivation potential.



Let's add a new parameter to the plot: The ***Depletion Parameter***.

4. Click on the **Variables** button. This will open a new window.

Look for the **Corrosion Values** section, click on the '+' icon, and select the **Depletion Parameter** option. Click on the **>>** button that belongs the **Y2 Axis**. This action will place the new variable under the Y2 Axis. Then click **OK.**



It is evident that both the depletion parameter and repassivation potential show their extreme values at intermediate temperatures of thermal aging. In the case of the depletion parameter, it is a maximum and, in the case of the repassivation potential, it is a minimum. This is in agreement with experimental data (Anderko et al., 2009). Non-zero values of the depletion parameter indicate the possibility of intergranular corrosion. A depression in the repassivation potential indicates an increased tendency for localized corrosion.

9.3. Thermal Aging and Localized Corrosion of Annealed and Thermally Aged Duplex Alloy 2324

In the previous examples, we used the Corrosion Analyzer's capabilities to predict the Cr and Mo depletion profiles for austenitic stainless steels and nickel-base alloys. However, we are not limited to such calculations.

We can also use the Corrosion Analyzer to predict the localized corrosion behavior of other alloys and other phases, including those that are not stored in the database. This facility is based on a generalized correlation for predicting the repassivation potential of Fe-Ni-Cr-Mo-W-N alloys as a function of alloy composition (Anderko et al., 2008). This correlation can be applied to both bulk alloys that are not in the database and to phases that may result from thermal aging.

In this section, we will go through two simulations:

- First, we will predict the tendency for localized corrosion for the duplex alloy 2324 in an aerated chloride solution. Alloy 2324 (a.k.a. AISI 329) is not in the database, so the repassivation potential will be calculated from the generalized correlation (Anderko et al., 2008). The corrosion potential will be calculated for a similar alloy because the corrosion potential does not differ much for many Fe-Cr-Ni-Mo alloys in the passive state in neutral solutions.

- Second, we will predict the localized corrosion tendency for alloy 2324 after thermal aging. Thermal aging of duplex steels in the temperature range of 900°C to 600°C leads to the formation of various phases - χ, σ, $M_{23}C_6$-type carbide, and secondary austenite (γ_2). The secondary austenite phase is primarily responsible for the increased tendency of the alloy for localized corrosion. This is due to a very significant depletion of chromium in the secondary austenite over relatively wide spatial areas (Sridhar et al., 2009). Since the composition of the secondary austenite cannot be predicted at present, we will use experimental microstructural data (Sridhar et al., 2009) in conjunction with the generalized correlation for the repassivation potential.

Example 55: Prediction of Localized Corrosion for Alloy 2324 Before Thermal Aging in an Aerated NaCl Solution

Starting the Simulation

Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Thermal Aging Calculation			
Calculation Settings		**Stream Composition and Conditions**	
Stream Name	Thermal Aging – Alloy 2324	Stream Amount	Calculated
Calculation Type	Corrosion Rates	Temperature	60 ºC
Survey by	Composition	Pressure	1 atm
Name Style	Display Name	H2O	Default – 55.5082 moles
Unit Set	Metric, Batch, Moles	NaCl	0 moles
Framework	AQ	O2	0.02 moles
		N2	0.08 moles

Note: The oxygen and nitrogen have been added to simulate the presence of air

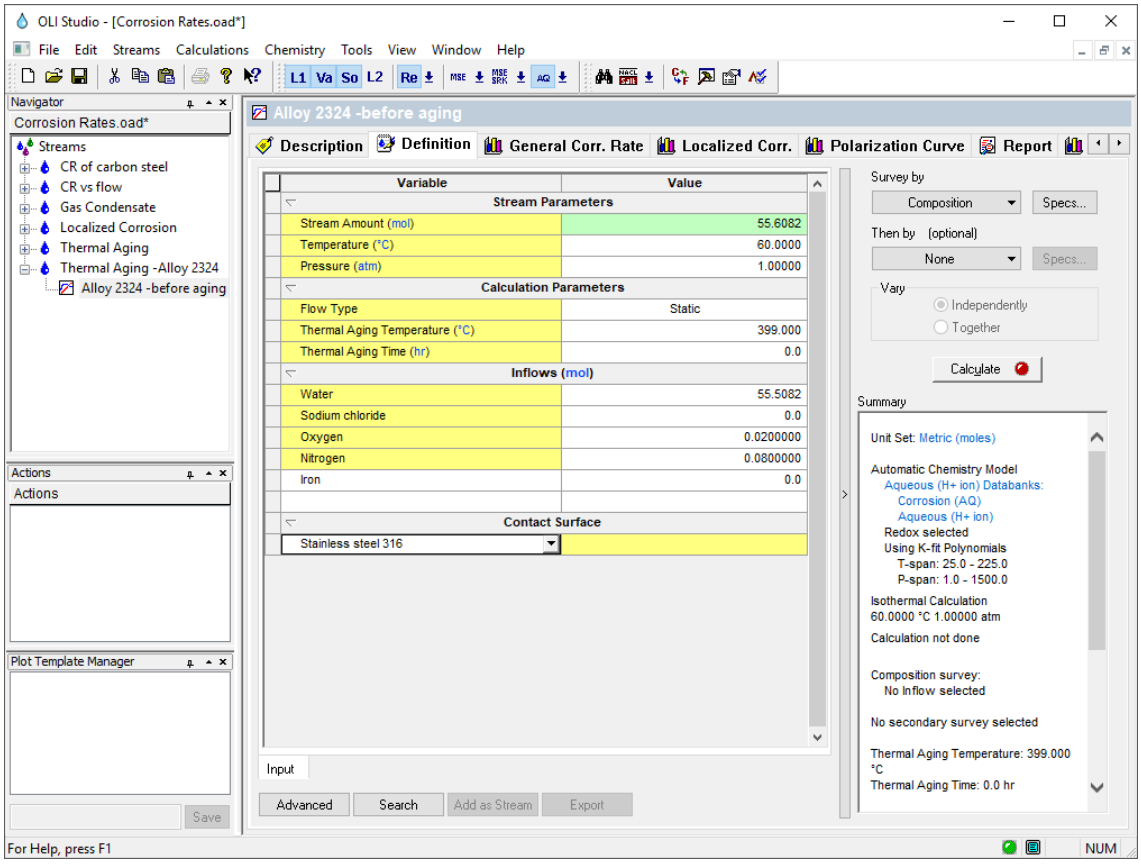
1. Add a new **Stream**
2. **Click** on the new Stream and press **<F2>** to change the name to *Thermal Aging – Alloy 2324*
3. Select the AQ thermodynamic Framework (selected by default)
4. **Click** on the **Units Manager** Icon and select Metric, Batch, Moles
5. **Click** on the **Names Manager** Icon and select *Display Name*
6. **Enter** the stream composition and conditions specified in the table above
7. **Go** to the **Add Calculation** button and select **Corrosion Rates**
8. **Select** the Survey by **Composition**
9. **Change** the name from ***Rates*** to ***Alloy 2324 – before aging*** using the **<F2>** key or by **right-mouse click** on the object and select rename

Since alloy 2324 is not available in the database, we will select stainless steel 316 as the contact surface. This will ensure that the predicted corrosion potential is very similar to that for alloy 2324.

10. Select ***Stainless Steel 316*** from the **Contact Surface** grid

Unlike in the previous examples, do not make any changes in the **Calc Parameters** section. We will not make Cr depletion calculations; rather, we will be specifying the **compositions of the phases**.

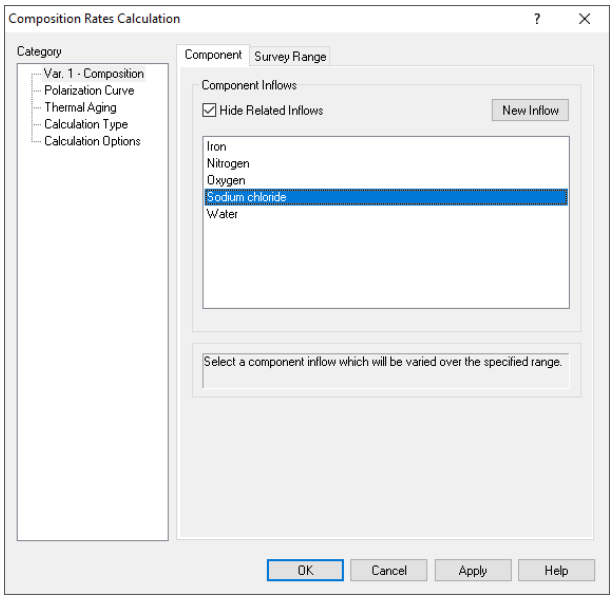
Your screen should look like the image below.



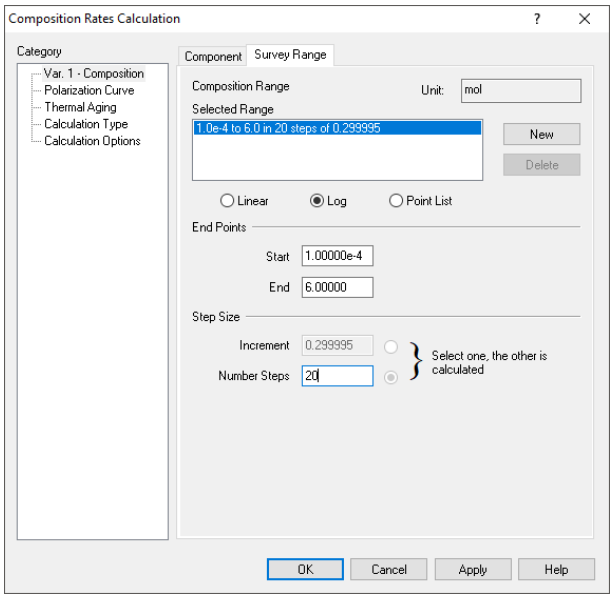
We will be running a composition survey to see how the concentration of NaCl affects the propensity for localized corrosion.

11. We need to specify the NaCl concentration range. **Click** on the **Specs** button. This will open a new window.

12. Under the **Component** tab select **Sodium Chloride**



13. Click on the **Survey Range** tab and change the concentration range as follows: Start=0.001 moles, End=6 moles, and number of steps=20. Then, click on the Log radio button.



14. Under the **Category** section, select the **Thermal Aging** option. The screen will be populated with default parameters for type 316 stainless steel.

In the following steps we are going to enter the alloy 2324 composition and use the repassivation potential (E_{rp}) correlation (embedded in the software) to calculate the E_{rp} of the alloy. This is necessary because no

parameters for alloy 2324 are stored in the databank and we have to rely exclusively on the correlation to predict the repassivation potential.

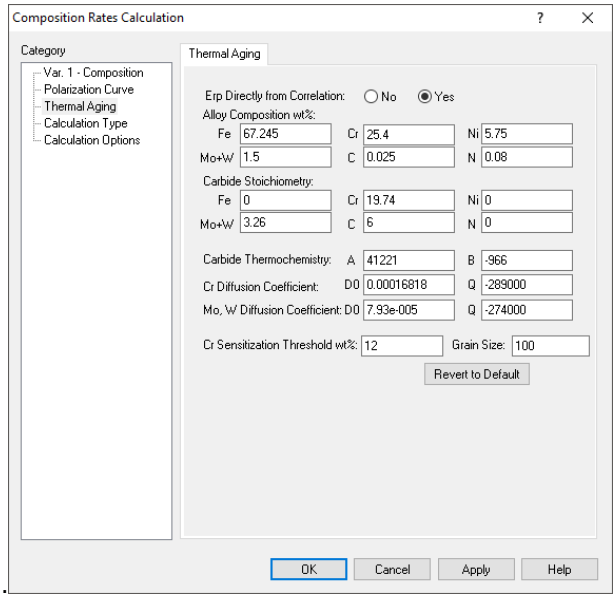
15. First, click on the **Yes** button next to "*Erp directly from correlation:"*
16. Then, enter the composition of alloy 2324 by replacing the default values for alloy 316.

    Enter the following composition of alloy 2324:

Element	Composition (wt%)
Fe	67.245*
Cr	25.4
Ni	5.75
Mo+W	1.5
C	0.025
N	0.08

*which is the balance that includes many minor elements

The remaining parameters in the Thermal Aging screen can remain the same because we will not be using them in this example (i.e., we will not be calculating any depletion profiles). After entering the values, the screen should look as follows:



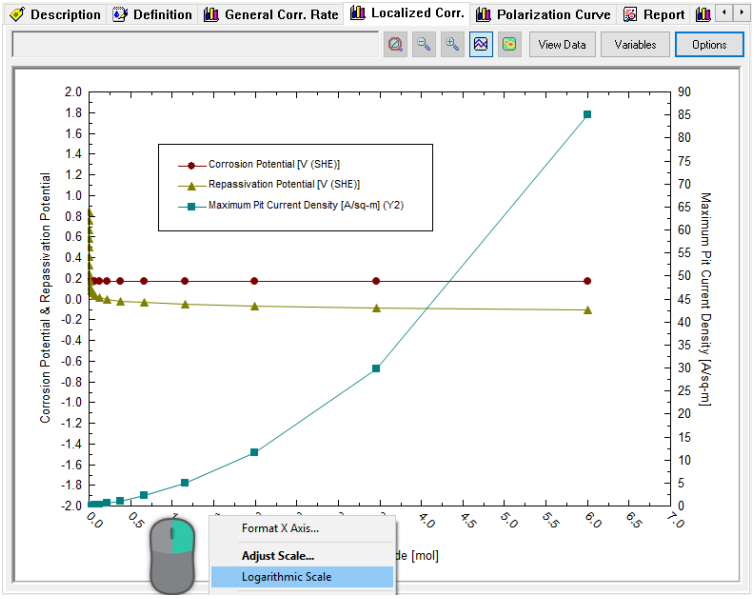
17. Click **OK** to accept the changes

18. We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

19. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under the same file created in the previous section named *Corrosion Rates.*

Analyzing the results

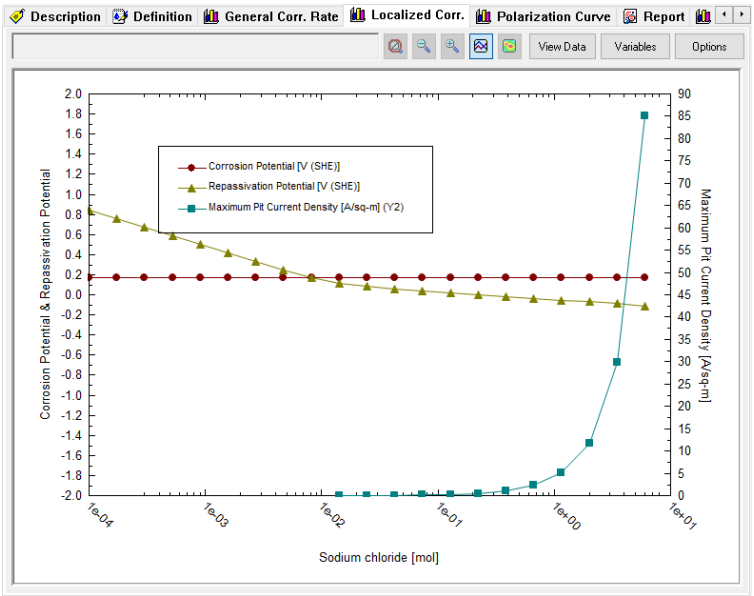
1. Click on the **Localized Corr.** tab (Localized Corr.). By default, this tab will show a plot of the corrosion and repassivation potentials as a function of NaCl concentration. In the Y2 axis the Maximum Pit Current Density is also plotted.



To visualize the results better, change the horizontal axis to a logarithmic scale.

2. **Right-mouse click** on the X Axis and select **Logarithmic Scale**

The plot should look like the image below.



These results indicate that alloy 2324 is susceptible to localized corrosion in aerated solutions when the chloride concentration exceeds ~0.3 molal. Above this concentration, the repassivation potential drops below the corrosion potential and, therefore, localized corrosion can be stabilized at these conditions.

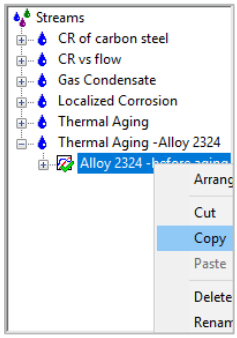
Example 56: Prediction of Localized Corrosion for Alloy 2324 After Thermal Aging

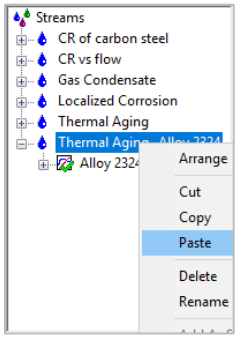
Now, we will perform the same prediction of localized corrosion calculations for thermally aged alloy 2324. We will run the same concentration survey as in the previous case so that we can compare the results for bulk alloy 2324 with those for a heat-treated sample.

Sridhar et al. (2009) found that after aging alloy 2205 at 700 °C for 24 hours, the formation of a chromium-depleted secondary austenite phase is responsible for a much-increase tendency for localized corrosion. We will use this experimental data to approximate the localized corrosion tendency of alloy 2324.

Starting the Simulation

1. **Copy** the *Alloy 2324-before aging* calculation and **paste** it under the *Thermal Aging – Alloy 2324* stream





2. **Rename** the calculation as *Alloy 2324 – after aging* by using the **<F2>** key or by **right-mouse click** on the object and select rename

3. Click on the **Specs** button. This will open a new window.

4. Under the **Category** section, select the **Thermal Aging** option. The screen will be populated with default parameters for type 316 stainless steel.

5. Click on the **Yes** button next to "*Erp directly from correlation:"* – because we will be running calculations for a completely new phase

6. Then, enter the composition of the secondary austenite phase by replacing the default values for alloy 316.

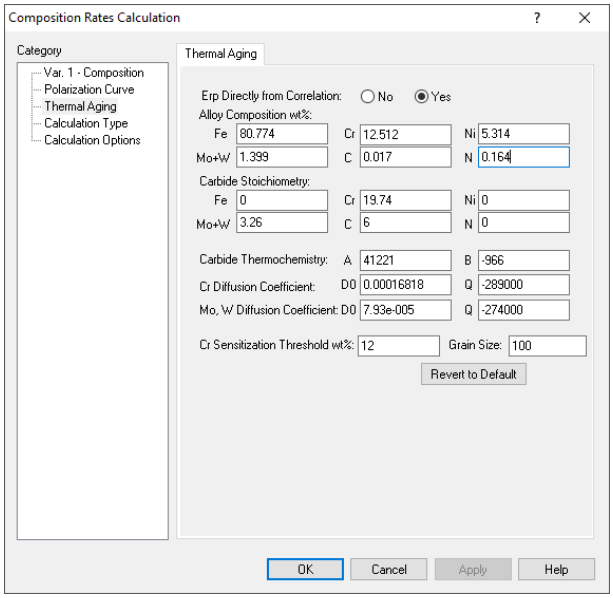
   Note: we are using experimental data obtained for alloy 2205 for illustration purposes). For more details how these compositions were determined, see the paper of Sridhar et al. (2009).

   Enter the following composition:

Element	Composition (wt%)
Fe	80.774*
Cr	12.512
Ni	5.134
Mo+W	1.399
C	0.017
N	0.164

*which is the balance that includes many minor elements

The remaining parameters in the Thermal Aging screen can remain the same because we will not be using them in this example (i.e., we will not be calculating any depletion profiles). After entering the values, the screen should look like the image below.



7. Click **OK** to accept the changes
8. We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
9. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. You can save it under

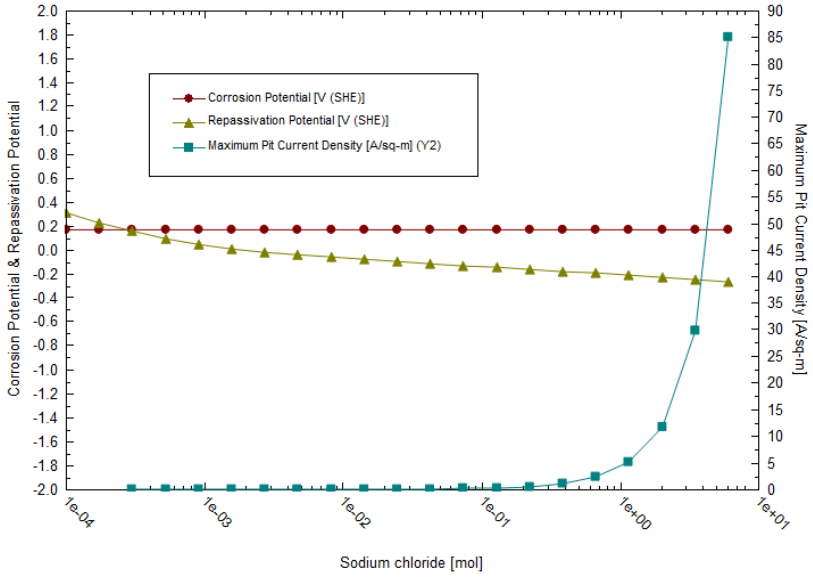
Analyzing the results

1. Click on the **Localized Corr.** tab (Localized Corr.). By default, this tab will show a plot of the corrosion and repassivation potentials as a function of NaCl concentration. In the Y2 axis the Maximum Pit Current Density is also plotted.

To visualize the results better, change the horizontal axis to a logarithmic scale.

2. **Right-mouse click** on the X Axis and select **Logarithmic Scale**

The plot should look like the image below.



The obtained plot shows that the repassivation potential is much lower than that for bulk alloy 2324. Because of the strong depression of the repassivation potential, the corrosion potential exceeds the repassivation potential at chloride concentrations of ~0.0007 m. Thus, localized corrosion is predicted to be possible at concentrations above 0.0007 m. This indicates a very strong increase in the propensity for localized corrosion compared with bulk alloy 2324, for which the predicted threshold is ~0.3 m.

In general, you can use this facility to predict the repassivation potential for any alloys, including unknown and experimental ones, as long as they belong to the Fe-Ni-Cr-Mo-W-N-C family.

Chapter IV – OLI Analyzer: EVS Analyzer

10.1. Overview and Theoretical Foundation

Engineering systems may have a large number of pits and corroded areas of varying degree of severity. The first perforation, whose time and location will be a matter of probability, may cause the failure of the construction. Accordingly, the probability of such failure must be known as accurately as possible.

Extreme value statistics (EVS) is one of the most powerful statistical techniques that have been used extensively to extrapolate damage (maximum pit depth) from small samples in the laboratory to larger area samples in the field (see, for example, Eldridge G. 1957, Shibata T. et al. 1988, Kowaka et al. 1994). Thus, it was shown (Shibata T. et al. 1988) that probability of failure of a construction, P_f, i.e. the probability that at least one pit reaches the critical dimension, d, (for example wall thickness) in the system with area S is described by the equation:

$$P_f = 1 - \exp\left\{-\frac{exp\left[-d-\left(u+\alpha\, ln\frac{S}{s}\right)\right]}{\alpha}\right\} \quad (1)$$

where location parameter, *u*, and scale parameter, α, are measured by using small samples with constant area, s. Equation (1) is to extrapolate corrosion damage from a small reference area, such as a coupon to a larger operation area, S. This is the classical use of Extreme Value Statistics.

Experimental studies demonstrate that both the shape and location parameters are time dependent. However, those dependencies must be established empirically and since no theory contained within classical EVS is available for the functional forms of u(t) and α(t), it is necessary to know answer (prediction) in advance for predicting the damage at long times. This has proven to be a severe constrains of the applicability of classical EVS.

This problem can be overcome by applying damage function analysis (DFA) method that considers propagation of corrosion damage by drawing an analogy between the growth of a pit and the movement of a particle (Engelhardt and Macdonald, 2004). In many cases DFA yields an analytical expression for u and α in terms of time of the hyperbolic form:

$$u = \frac{a_1 t}{1+a_2 t} \; and \; \alpha = a_3 t \quad (2)$$

where a_1, a_2, and a_3 are readily determined by calibration from short term data in order to predict damage over the longer time. Namely, equations (2) are used now by OLI software for predicting damage in corroding systems. It must be noted that a different (power) form of such dependencies has been used by Laycock et al. 1990.

Input and Output Specific to EVS

For applying this technique the user has to provide a set of experimental data (x_i, t_i, s_i), i = 1,2,…,N, where x_i is the depth of the deepest pit over area s_i, of a metal exposed to corrosion attack. The separate area, s_i, could be distinct coupons from a designed experiment or random samples at various times from different locations in the system. Experiments must be performed for at least two different times.

The output of the code yields the probability of failure as a function of time for a large system with area S. The code also allows the user to answers on several engineering questions, for example, what service life, t, will have the pipe with the width, d, and length L in order to ensure acceptable performance (probability of failure, P_f).

Advantages and Disadvantages of EVS

The advantage of this approach is self-evident. The prediction of corrosion damage for long times will be done by using experimental data for short times without requiring the explicit determination of any information about the kinetic parameters of the system. However, such approach has evident disadvantages, as follows:

1. The results of the analysis cannot be transferred for predicting corrosion damage to other systems (for example pipelines) due to the different technological and environmental conditions that generally exist. The results cannot be used for predicting damage in the same system if technological and environmental conditions change.

2. We can expect that when the depth of the pit increases some critical value, the nucleation of cracks can occur. It is clear that a purely statistical method cannot predict such a transition. This method also cannot predict any catastrophic event.

3. This method cannot be used for design of new constriction, because it relies upon calibration upon a pre-existing system.

10.2. Extreme Value Statistics for Predicting Pitting Damage

We will show examples of applications of Extreme Value Statistics for predicting pitting damage. Specifically, we will show how to predict:

1. The depth of the deepest pit in the engineering structure or laboratory systems as a function of time and the surface area of the system

2. Probability of failure for a given penetration depth and the area of the system as a function of observation time

3. Probability of failure for a given observation time and the area of the system as a function of penetration depth

4. Probability of failure for a given penetration depth and observation time as a function of the area of the system

Foundations of Extreme Value Statistics can be found in the following references: (Aziz, 1956, Kowaka et al. 1994, Laycock et al. 1990, Engelhardt and Macdonald, 2004).

Example 57: Corrosion of Aluminum Alloy in Tap Water

In this example, we will consider the classical data for pitting corrosion (Aziz, 1956). In this paper, we can find particularly the experimental data for the maximum pit depths developed on Alcan 2S-O coupons with area s≈129 cm^2 immersed in Kingston tape water at 25 ^{0}C . The experimental data is summarized in the table below.

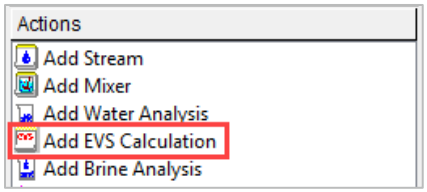
Maximum pit depth (in μm) developed on Alcan 2S-O coupons with immersed in Kingston tape water for different observation times. Area of all coupons is s≈129 cm^2

Coupon #	One Week	One Month	Three Months	Six Month	One Year
	7 days	30 days	90 days	180 days	365 days
1	180	460	480	620	640
2	266	500	578	620	680
3	290	510	610	620	700
4	306	580	610	680	760
5	334	580	610	680	800
6	340	640	660	720	810
7	340	654	690	740	820
8	410	680	718	740	840
9	410	692	760	760	840
10	545	692	798	760	900

Calculating the Depth of the Deepest Pit

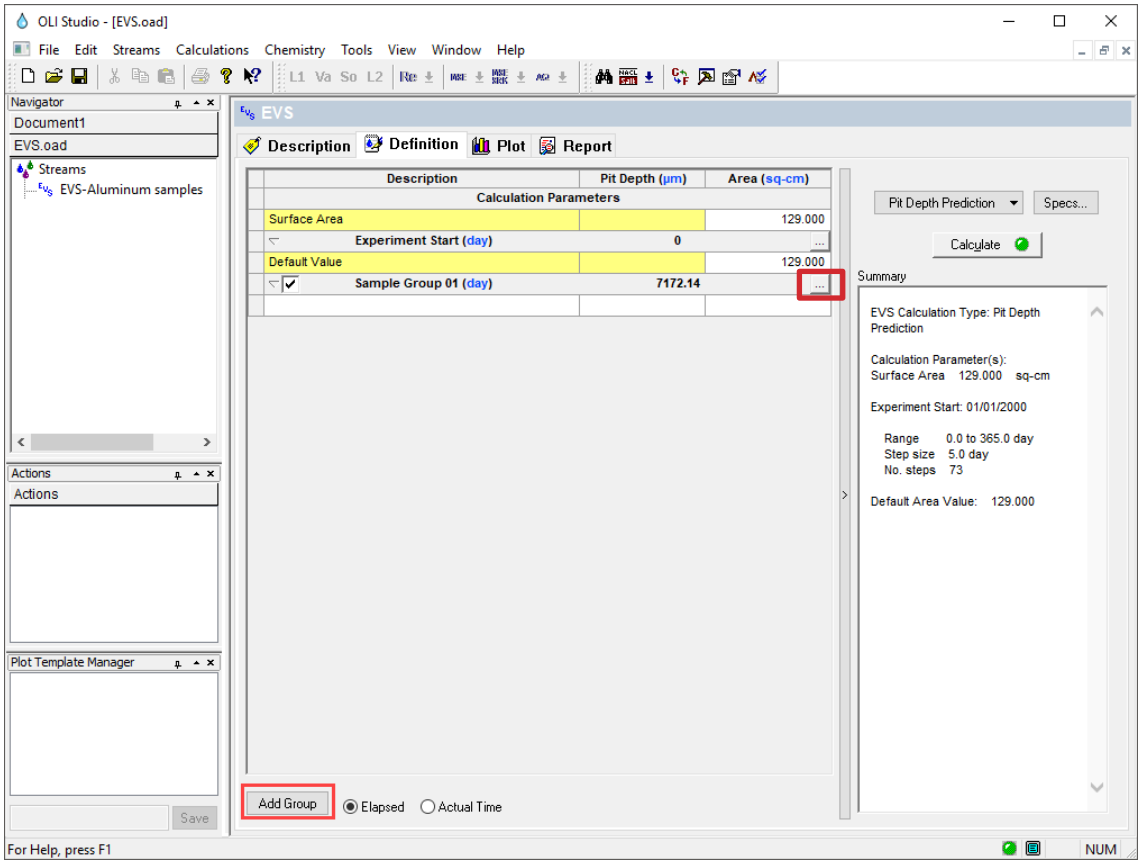
Starting the Simulation

1. Add a new **EVS** calculation. Select the A**dd EVS Calculation** icon in the Actions Pane



2. **Click** on the new EVS calculation and press **<F2>** to change the name to *EVS-Aluminum samples.* Notice that the default calculation is the *Pit Depth Prediction.*

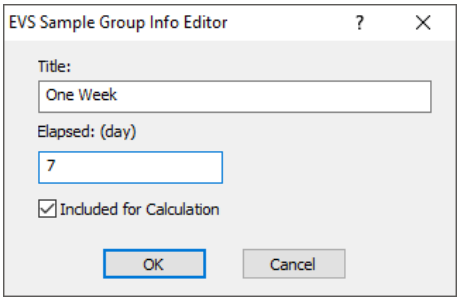
3. All samples have a constant area s = 129 cm^2. Under the **Calculation Parameters** grid, enter 129 cm^2 for the **Surface Area** and **Default Value** cells.



There are experimental data sets for 5 different periods of time. This means that we need to enter 5 different sample groups.

4. By default, **Sample group 01** is created. Click on the … button to edit this field. This will open a new window.

5. **Change** the title to **One Week**, enter the number **7** for the number of **elapsed days**, and **check** the box **'Include for Calculation'.** Then click **OK.**



6. Enter the **Pit Depth** data (second column) obtained for 1 week

Description	Pit Depth (µm)	Area (sq-cm)
Calculation Parameters		
Surface Area		129.000
Experiment Start (day)	0	
Default Value		129.000
One Week (day)	7.0	
1	180.000	129.000
2	266.000	129.000
3	290.000	129.000
4	306.000	129.000
5	334.000	129.000
6	340.000	129.000
7	340.000	129.000
8	410.000	129.000
9	410.000	129.000
10	545.000	129.000

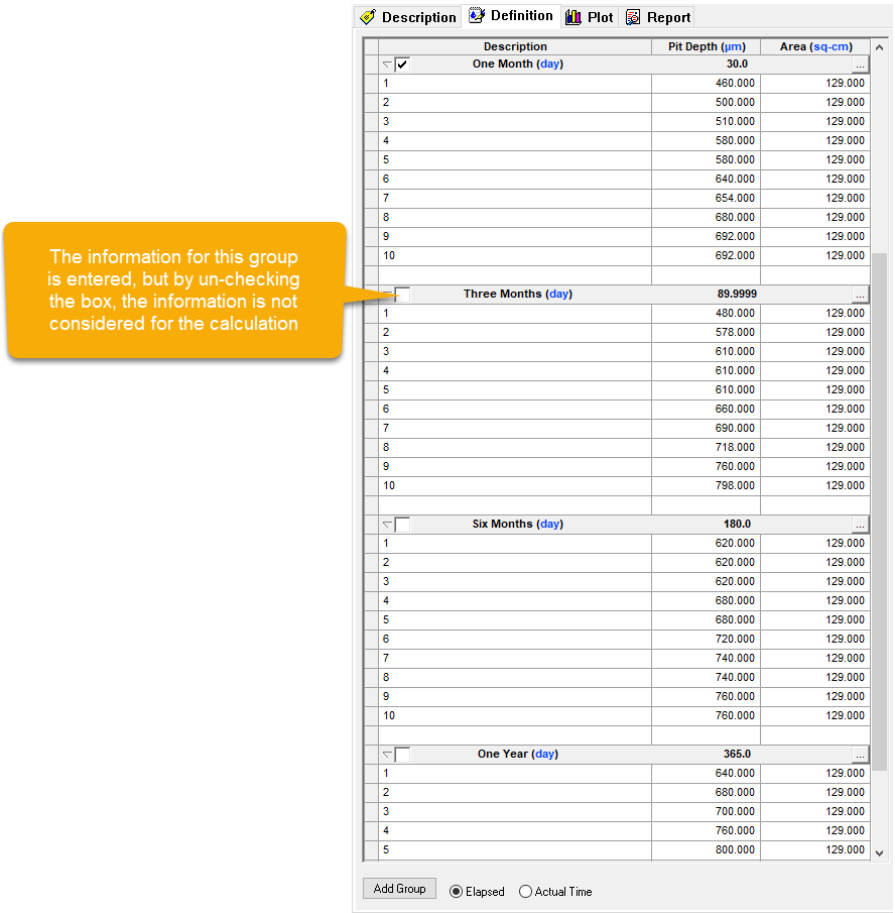
Now we need to add 4 more groups.

7. Click on the **Add Group** button (located at the bottom of the window). This will open a new window.

8. **Change** the title to **One Month**, enter the number 30 for the number of **elapsed days**, and **check** the box **'Include for Calculation'.** Then click **OK.**

9. Enter the **Pit Depth** data (second column) obtained for 1 month.

10. Click on the **Add Group** button, and repeat the same procedure for one month, three months, six months and one year.



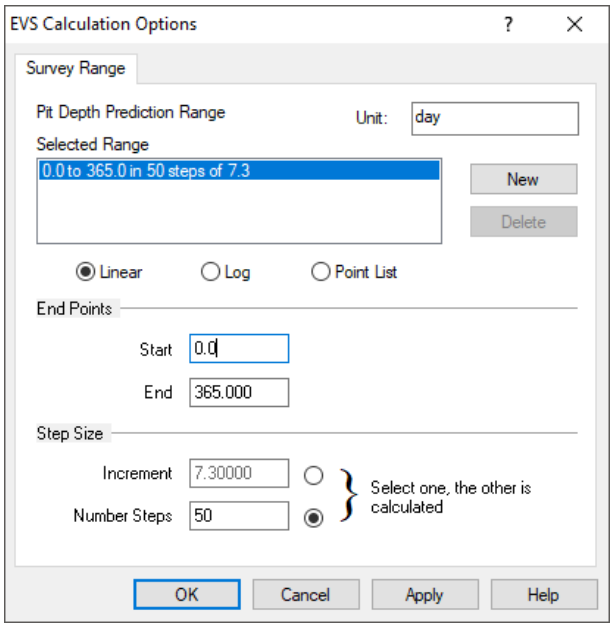
Description	Pit Depth (μm)	Area (sq-cm)
One Month (day)	30.0	
1	460.000	129.000
2	500.000	129.000
3	510.000	129.000
4	580.000	129.000
5	580.000	129.000
6	640.000	129.000
7	654.000	129.000
8	680.000	129.000
9	692.000	129.000
10	692.000	129.000
Three Months (day)	89.9999	
1	480.000	129.000
2	578.000	129.000
3	610.000	129.000
4	610.000	129.000
5	610.000	129.000
6	660.000	129.000
7	690.000	129.000
8	718.000	129.000
9	760.000	129.000
10	798.000	129.000
Six Months (day)	180.0	
1	620.000	129.000
2	620.000	129.000
3	620.000	129.000
4	680.000	129.000
5	680.000	129.000
6	720.000	129.000
7	740.000	129.000
8	740.000	129.000
9	760.000	129.000
10	760.000	129.000
One Year (day)	365.0	
1	640.000	129.000
2	680.000	129.000
3	700.000	129.000
4	760.000	129.000
5	800.000	129.000

Note the following:

- Here, for the description of different experiments we simply used the number of the corresponding row in Table 1. However, this description can be done in an arbitrary form.
- For each group, the order of samples relative depth can be arbitrary (not necessary in ascending order as in Table 1)
- If coupons have different areas each area must be specified in the column **Area**
- Radio button **Elapsed** means the time after corrosion attack is used in calculations and namely this time is used usually in scientific publication. However, it is possible to use also **Actual Time** of the experiments.

At this point, the experimental data has been entered. Now we need define the period of time for which we want to do the prediction of failure due to pitting.

11. **Click** on the **Specs** button. This will open a new window.
12. Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 days, End=365 days, and number of steps=50. Then click **OK**

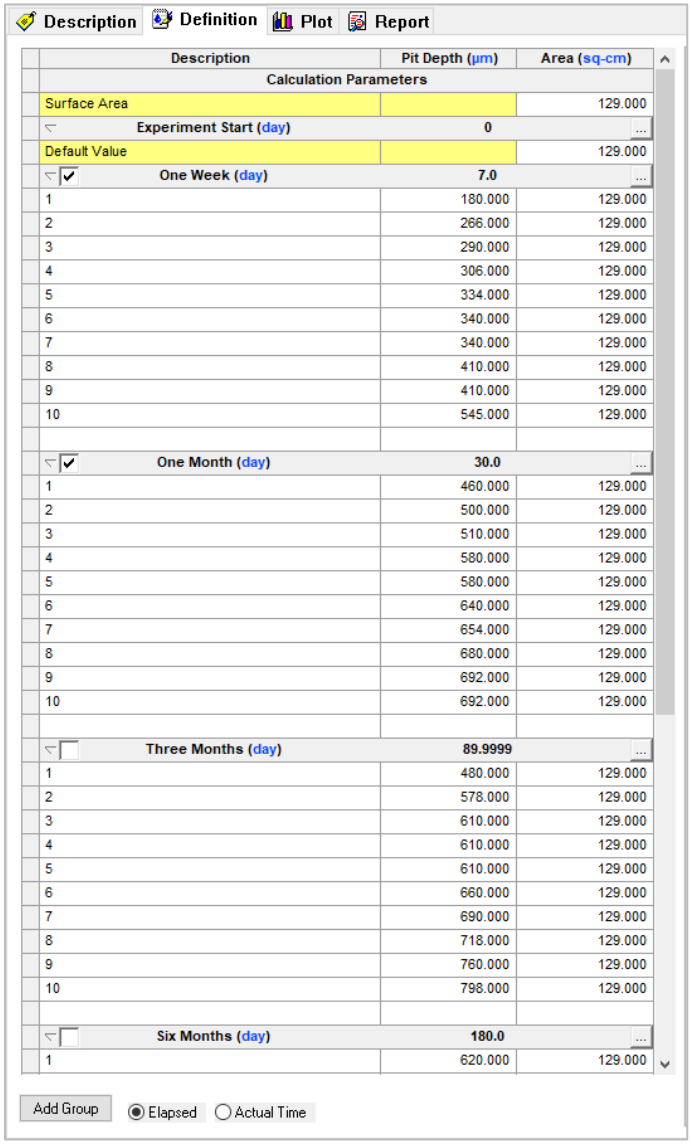


Before running the calculation, we are going to study two different cases:

I. The first case will include the experimental data for 1 week and 1 month – short term experiments

II. The second case will include all the experimental data – long term experiments

13. **Check** the boxes for 1 week and 1 month only to include them into the calculations



Description	Pit Depth (μm)	Area (sq-cm)
Calculation Parameters		
Surface Area		129.000
Experiment Start (day)	0	
Default Value		129.000
One Week (day)	7.0	
1	180.000	129.000
2	266.000	129.000
3	290.000	129.000
4	306.000	129.000
5	334.000	129.000
6	340.000	129.000
7	340.000	129.000
8	410.000	129.000
9	410.000	129.000
10	545.000	129.000
One Month (day)	30.0	
1	460.000	129.000
2	500.000	129.000
3	510.000	129.000
4	580.000	129.000
5	580.000	129.000
6	640.000	129.000
7	654.000	129.000
8	680.000	129.000
9	692.000	129.000
10	692.000	129.000
Three Months (day)	89.9999	
1	480.000	129.000
2	578.000	129.000
3	610.000	129.000
4	610.000	129.000
5	610.000	129.000
6	660.000	129.000
7	690.000	129.000
8	718.000	129.000
9	760.000	129.000
10	798.000	129.000
Six Months (day)	180.0	
1	620.000	129.000

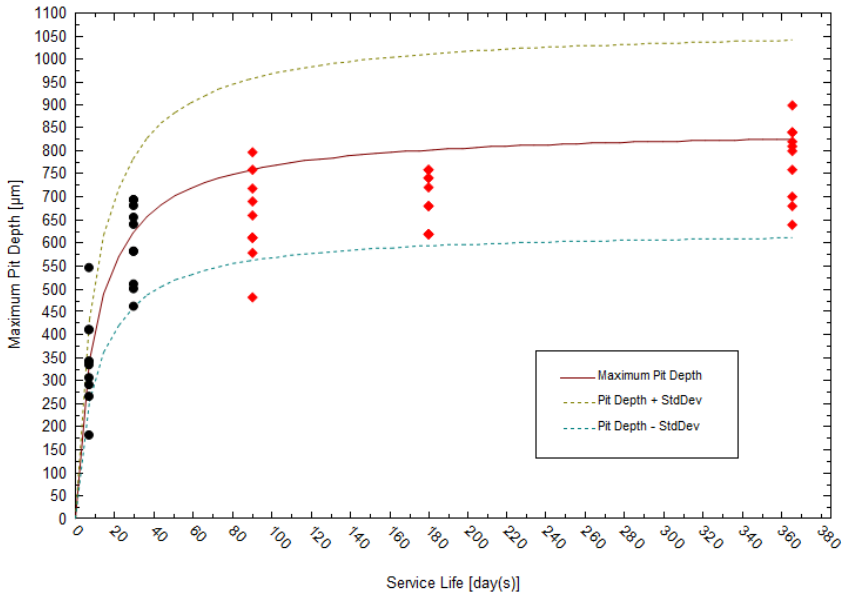
14. We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

15. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Save this new file as *EVS calculations.*

Analyzing the results

16. Click on the **Plot** tab (Plot). You will see a plot of the predicted mean value of the depth of the deepest pit, x_m and the plots of values $x_m - \sigma$ and $x_m + \sigma$, where σ is the standard deviation of x_m.

    It is important to note that only data for short term experiments (for 1 week and 1 month) are shown as black circles in the plot. The additional data are shown as red diamonds, only for demonstrating the accuracy of prediction.



17. Click on the **Report** tab, and to the **Calculation Results** table.

    The predicted depth of the deepest pit at 365 days is 610.43µm ≤ 825.373µm ≤ 1040.31µm (based on the short-term experimental data).

Predicting the Worst Pit Depth for 2 years of service life using long term experiments (all data sets)

18. The accuracy of prediction increases when additional group of experiments are included into consideration. For this case we are going to add the experimental data for 3 months, 6 months and 1 year.

19. Go back to the **Definition** tab

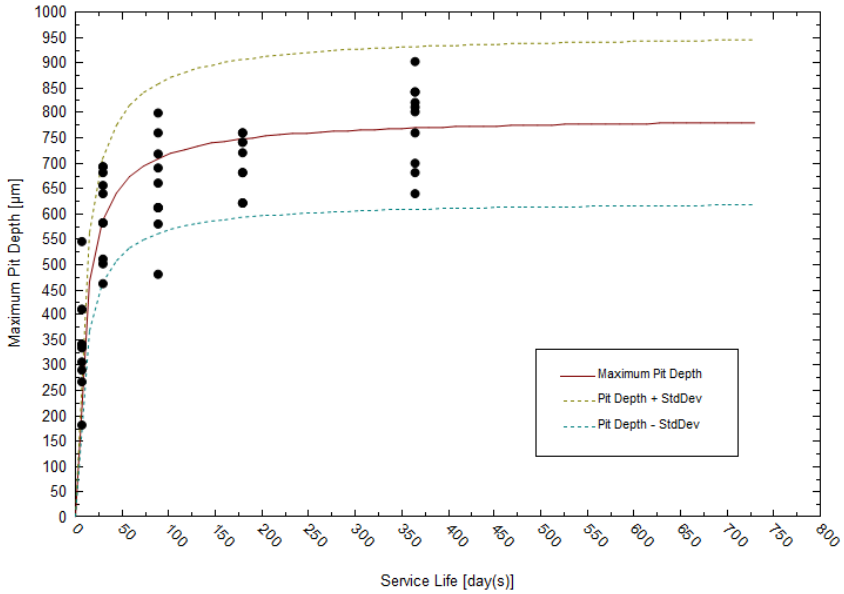
20. **Include** (check) the experimental data for 3 months, 6 months and 1 year

21. **Click** on the **Specs** button. This will open a new window

22. Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 days, End=730 days, and number of steps=50. Then click **OK**

23. Then **Click** on the **Calculate** button or press the **<F9>** key

24. Click on the **Plot** tab (Plot).



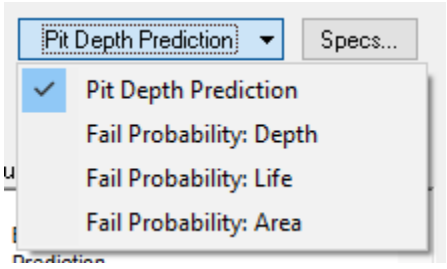
25. Click on the **Report** tab, and to the **Calculation Results** table.

The predicted depth of the deepest pit at 730 days (1 year) is 617.57 µm ≤ 780.873 µm ≤ 944.18 µm.

Calculating Fail Probabilities

When doing engineering design, information regarding the probability of failure is of importance to consider. The next set of calculations will involve calculating the Probability of Failure for a given:

- Penetration depth
- Observation time (life)
- Area of the system



Fail Probability: Depth

Let's start with the calculation of Probability of Failure for a given penetration depth and the area of the system as a function of observation time.

We are going to answer the following question:

- Which thickness, d, does an aluminum pipe with the area of S= 1 m^2 have to have in order to ensure acceptable performance (probability of failure P_f< 5% at design service life, t_s =5 years?

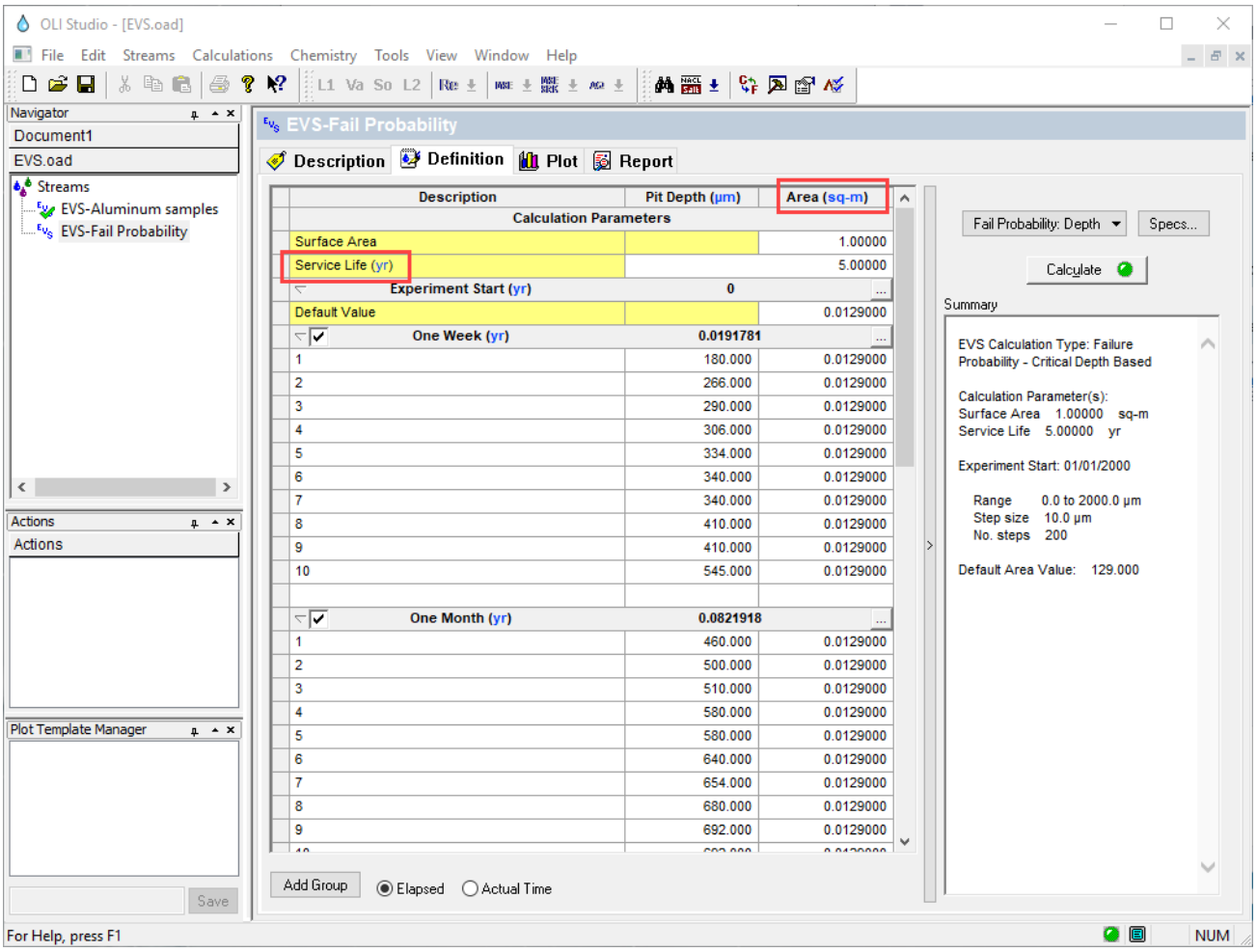
Starting the Simulation

1. Use the data enter in the example above. **Change** the Calculation Type to **Fail Probability: Depth**

2. Under the **Calculation Parameters** grid, enter 1 m^2 for the **Surface Area** and 5 years for the **Service Life.** Change units by clicking on the **blue** hyperlinks.

3. Make sure all data sets are selected (checked)

Your screen should look like the image below.

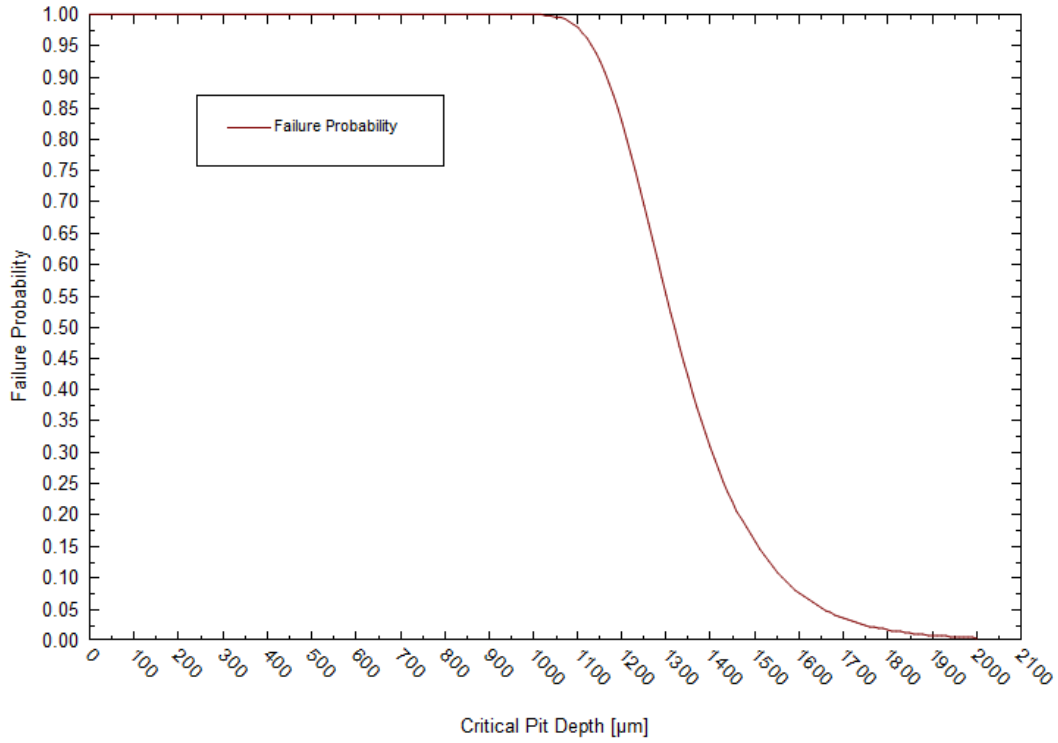


4. We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

5. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Analyzing the results

6. Click on the **Plot** tab (Plot). You will see a plot of predicted probability of failure



7. Click on the **Report** tab, and to the **Calculation Results** table.

We can conclude that the acceptable pipe wall width is reached at d > 1950 µm.

Fail Probability: Life

Let's continue with the calculation of Probability of failure for a given service time (life) and the area of the system as a function of penetration depth.

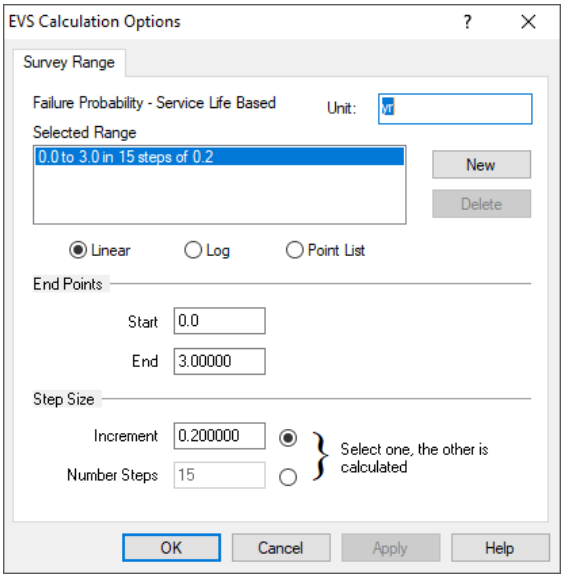
We are going to answer the following question:

- What service life, t, will have the aluminum pipe with the width, d=1850 µm with area S=10 m^2 in order to ensure acceptable performance i.e. probability of failure, P_f< 5 %?

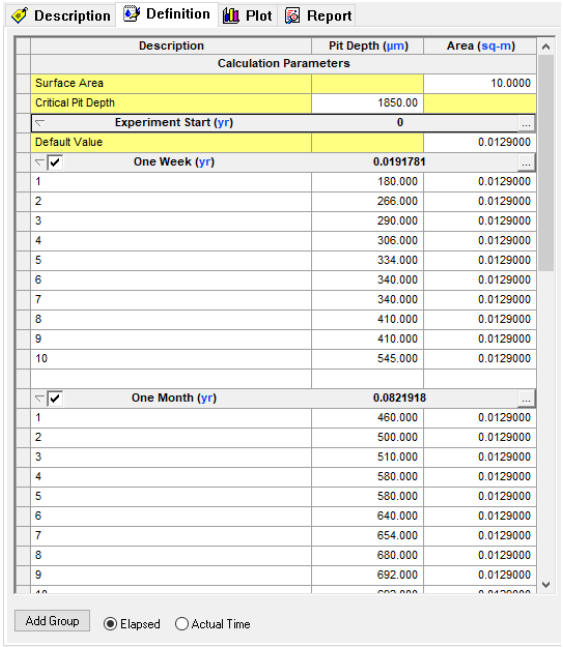
1. **Change** the Calculation Type to **Fail Probability: Life**
2. Under the **Calculation Parameters** grid, enter 10 m^2 for the **Surface Area** and 1850 μm for the **Critical Pit Depth.** Change units by clicking on the **blue** hyperlinks (If needed).

For this calculation we need to specify the period of time at which we want to bound the calculation.

3. Click on the **Specs** button. This will open a new window.
4. Change the **Service Life** range as follows: Start=0 years, End=3 years and Increments=0.2 years. Then click **OK**.



Your screen should look like the image below.



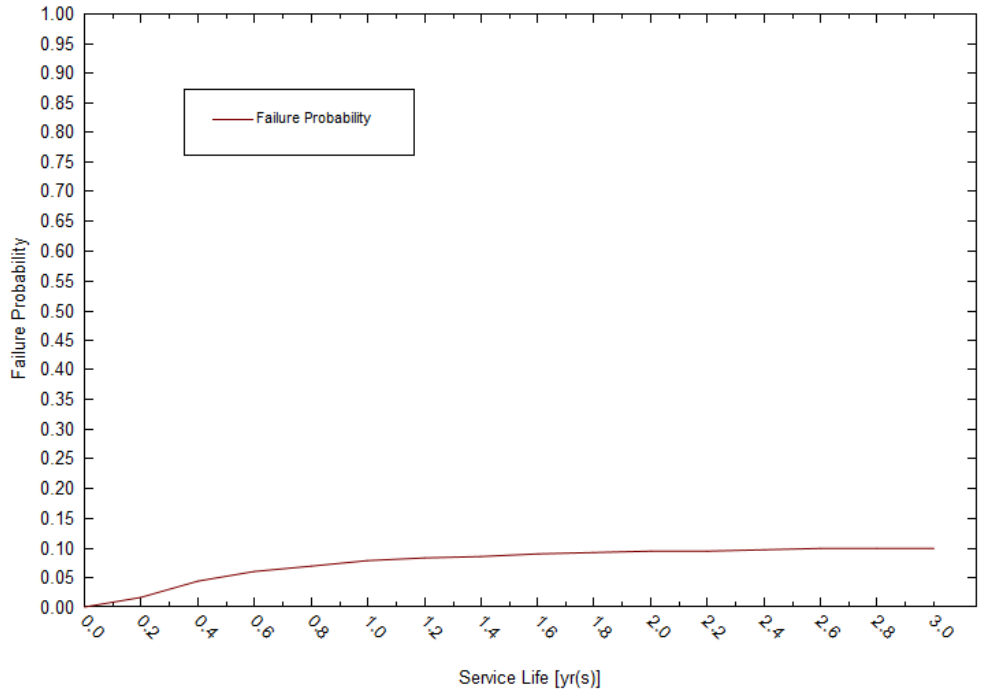
Description	Pit Depth (μm)	Area (sq-m)
Calculation Parameters		
Surface Area		10.0000
Critical Pit Depth	1850.00	
Experiment Start (yr)	0	
Default Value		0.0129000
One Week (yr)	0.0191781	
1	180.000	0.0129000
2	266.000	0.0129000
3	290.000	0.0129000
4	306.000	0.0129000
5	334.000	0.0129000
6	340.000	0.0129000
7	340.000	0.0129000
8	410.000	0.0129000
9	410.000	0.0129000
10	545.000	0.0129000
One Month (yr)	0.0821918	
1	460.000	0.0129000
2	500.000	0.0129000
3	510.000	0.0129000
4	580.000	0.0129000
5	580.000	0.0129000
6	640.000	0.0129000
7	654.000	0.0129000
8	680.000	0.0129000
9	692.000	0.0129000

5. We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

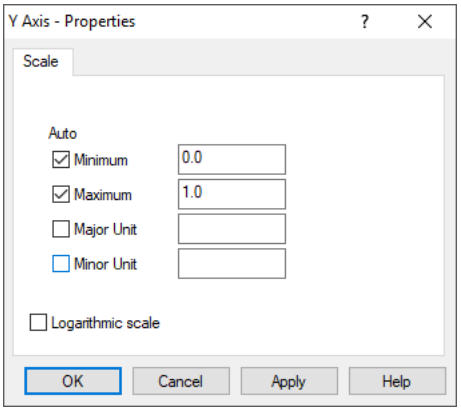
6. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Analyzing the results

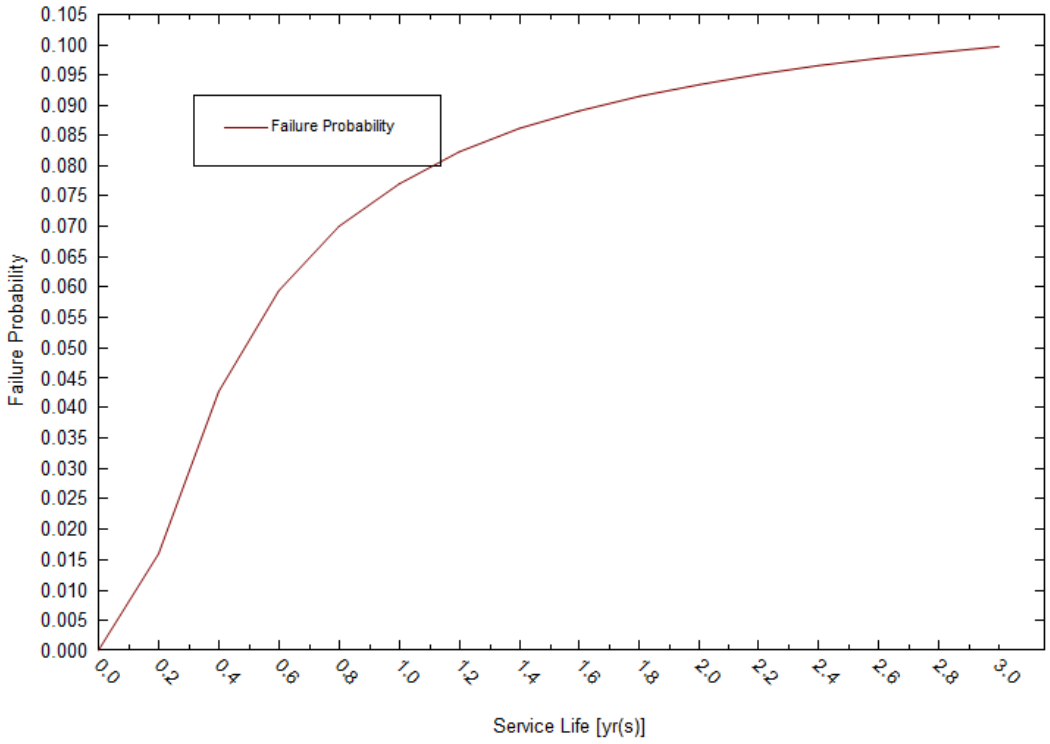
7. Click on the **Plot** tab (Plot). You will see a plot of predicted probability of failure. We need to modify the plot to see the results in more detail.



8. **Double click** on the **Y axis**. This will open a new window.
9. **Check** the boxes Minimum and Maximum. Then click **OK**.



The plot should look like the image below



The maximum probability of failure seems to be at around 10%.

10. Click on the **Report** tab, and to the **Calculation Results** table.

We can conclude that the lifetime of this pipe before failing is <0.6 years.

Fail Probability: Area

Finally, let's do the the calculation of Probability of failure for a given penetration depth and service time as a function of the area of the system.

We are going to answer the following question:

- What area, S, can have the aluminum pipe with the width, d=2000 μm and service life t=5 years in order to ensure acceptable performance i.e. probability of failure, $P_f < 5$ %?

Starting the Simulation

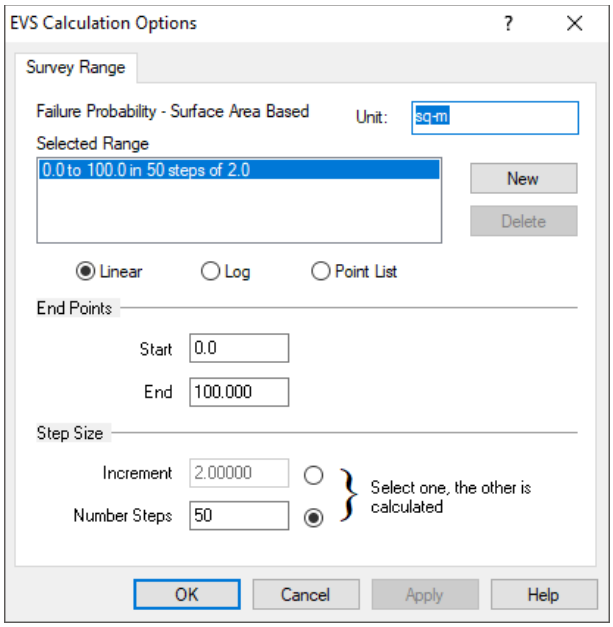
1. **Change** the Calculation Type to **Fail Probability: Area**

2. Under the **Calculation Parameters** grid, enter 2000 μm for **Critical Pit Depth** and 5 years for the **Service Life.** Change units by clicking on the **blue** hyperlinks (If needed).

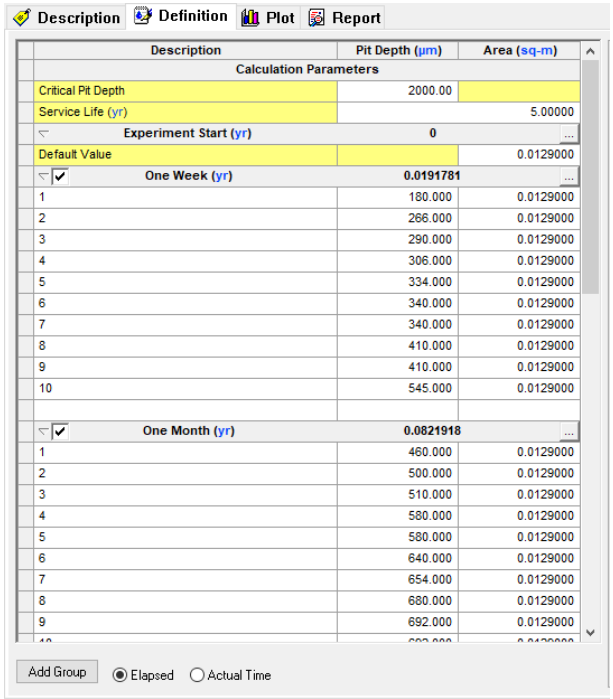
For this calculation we need to specify the surface area range that we want to survey.

3. Click on the **Specs** button. This will open a new window.

4. Change the **Surface Area** range as follows: Start=0 sq-m, End=100 sq-m and Number of steps=50. Then click **OK**.



Your screen should look like the image below.



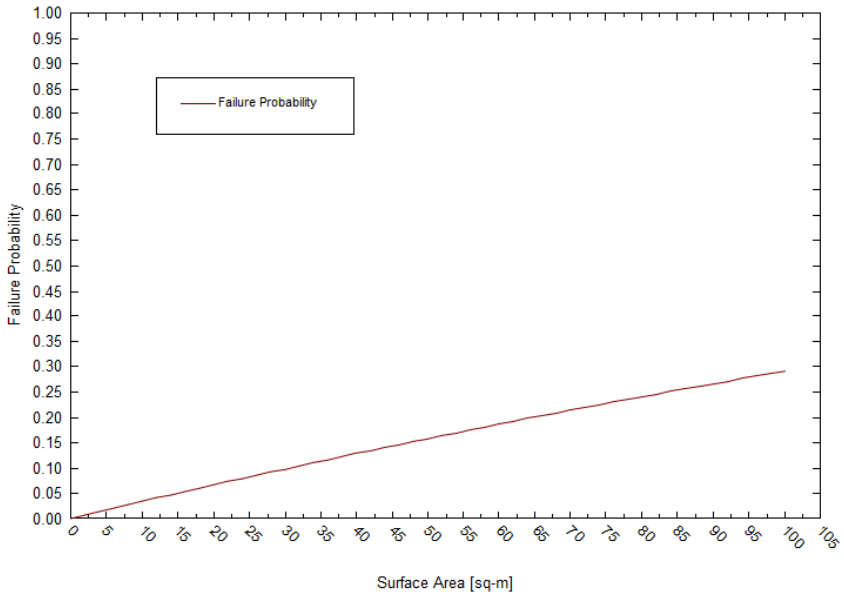
Description	Pit Depth (µm)	Area (sq-m)
Calculation Parameters		
Critical Pit Depth	2000.00	
Service Life (yr)		5.00000
Experiment Start (yr)	0	
Default Value		0.0129000
One Week (yr)	0.0191781	
1	180.000	0.0129000
2	266.000	0.0129000
3	290.000	0.0129000
4	306.000	0.0129000
5	334.000	0.0129000
6	340.000	0.0129000
7	340.000	0.0129000
8	410.000	0.0129000
9	410.000	0.0129000
10	545.000	0.0129000
One Month (yr)	0.0821918	
1	460.000	0.0129000
2	500.000	0.0129000
3	510.000	0.0129000
4	580.000	0.0129000
5	580.000	0.0129000
6	640.000	0.0129000
7	654.000	0.0129000
8	680.000	0.0129000
9	692.000	0.0129000

5. We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

6. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar.

Analyzing the results

7. Click on the **Plot** tab (Plot). You will see a plot of predicted probability of failure. We need to modify the plot to see the results in more detail.



The maximum probability of failure seems to be at around 30%.

8. Click on the **Report** tab, and to the **Calculation Results** table.

We can conclude that acceptable performance is reached at <14 m^2.

Example 58: Failure Analysis due to Corrosion in Pipelines

In this example, we will show how in some cases reliable prediction of corrosion damage can be done by using a very limited number of experimental points.

In the table below, you can see the results of direct measurements of the depth of the deepest pits in the pipeline between Samara and Moscow [Zikerman, 1972].

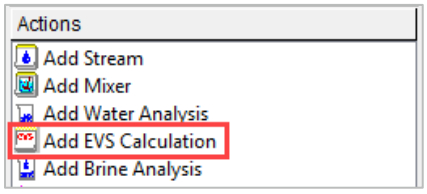
Pit depths (mm) for pipeline between Samara and Moscow

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
Sample	**1440 h**	**5040 h**	**5760 h**	**8959 h**	**12624 h**	**17688 h**	**28032 h**	**28272 h**
1	0.1			1.4	1.7	1.9		2.1
2		0.49		1.95	2.1	2.08		2.25
3	0.3	1.6		1.8				
4	0.4			1.6	1.65	1.88		
5	0.9		1.57	2.1	2.21	2.4	2.4	
6	0.3		1.2	1.4	1.4	1.55	1.71	

Calculation the Depth of the Deepest Pit

Starting the Simulation

1. Add a new **EVS** calculation. Select the A**dd EVS Calculation** icon in the Actions Pane



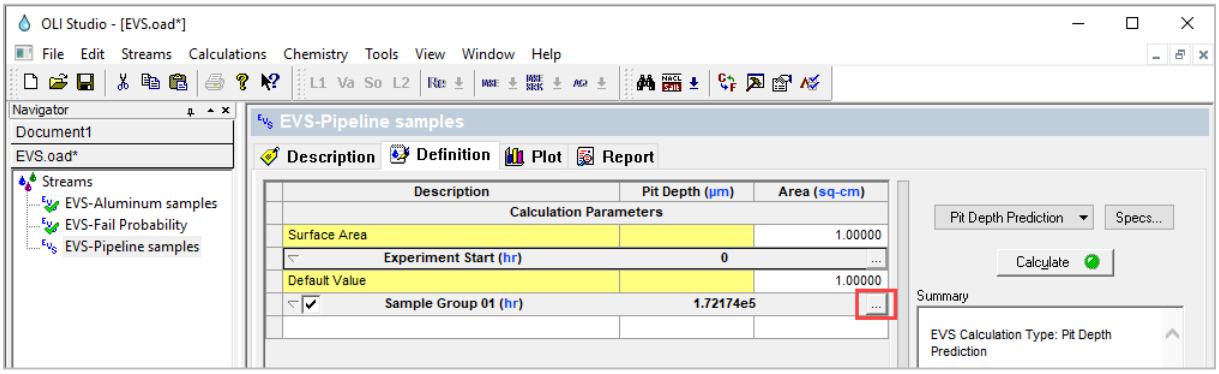
2. **Click** on the new EVS calculation and press **<F2>** to change the name to *EVS-Pipeline samples.* Notice that the default calculation is the *Pit Depth Prediction.*

3. Under the **Calculation Parameters** grid, enter 1 cm^2 for the **Surface Area** and **Default Value** cells.

   Note: Because the area of the pipelines metal was not changed with time the information about this area is not needed for extrapolation of corrosion damage in time.

4. Since the data is in hours, click on the blue hyperlink **day** and change it to hours (**hr**) (for both: The **Experiment Start** and the **Sample Group**.

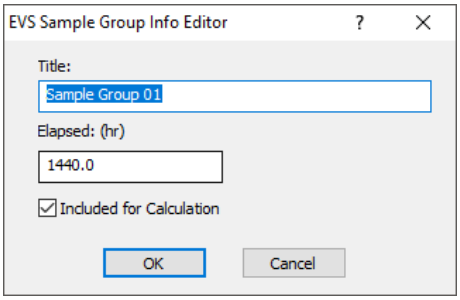
Your screen should look like the image below:



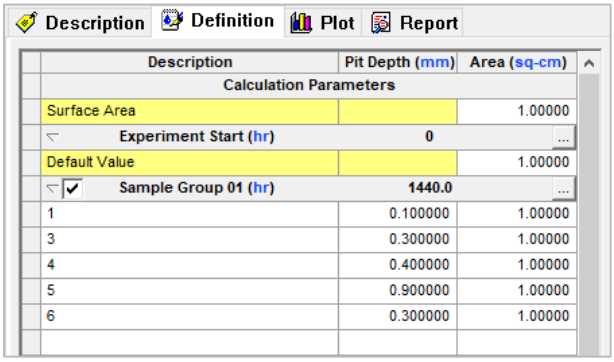
There are experimental data sets for 8 different periods of time. This means that we need to enter 8 different sample groups.

5. By default, **Sample group 01** is created. Click on the … button to edit this field. This will open a new window.

6. **Leave** the default name as **Sample Group 01**, enter the number **1440** for the number of **elapsed hours**, and **check** the box **'Include for Calculation'**



7. Enter the **Pit Depth** data (second column) obtained for 1440 hours.

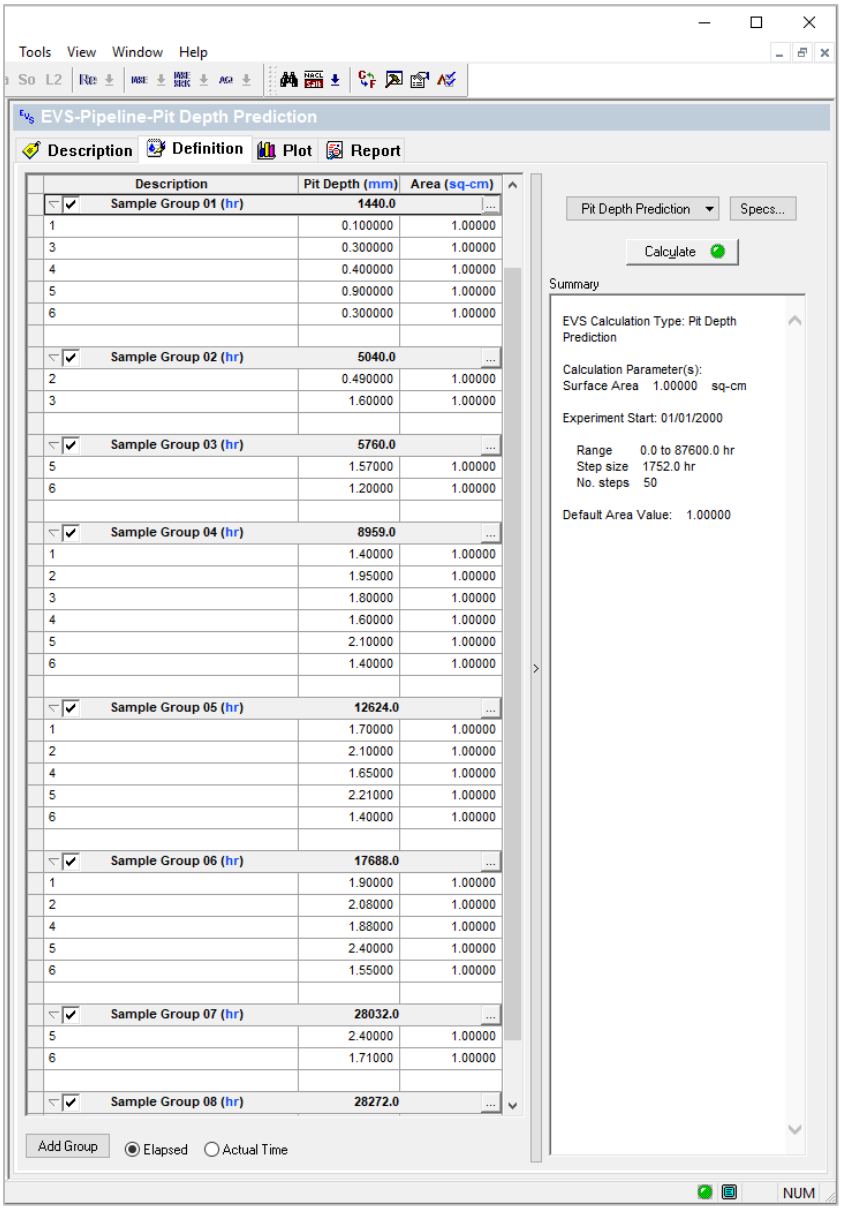


Now we need to add 7 more groups.

8. Click on the **Add Group** button (located at the bottom of the window. This will open a new window.

9. **Leave** the default name as **Sample Group 02,** enter the number 5040 for the number of **elapsed hours**, and **check** the box **'Include for Calculation'**. Then click **OK.**
10. Enter the **Pit Depth** data (second column) obtained for 5040 hours.
11. Click on the **Add Group** button, and repeat the same procedure for 5760, 8959, 12624, 17688, 28032 and 28272 hours.

Once you have entered all the experimental data, your screen should look like the image below.

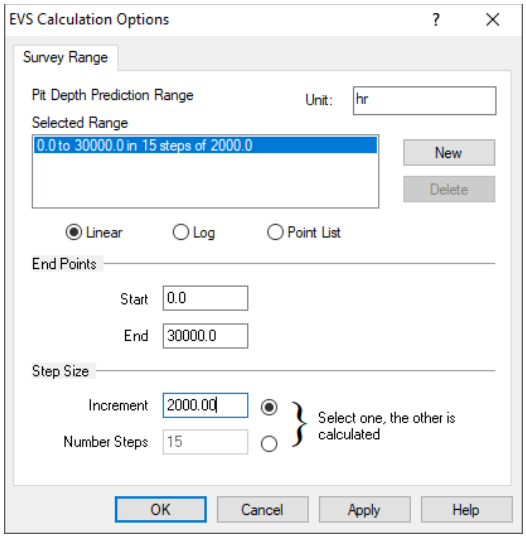


Make sure that all the groups are selected (checked) to be considered for the calculation.

At this point, the experimental data has been entered. Now we need define the period of time for which we want to do the prediction of failure due to pitting.

12. **Click** on the **Specs** button. This will open a new window.

13. Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 hours, End=30000 hours, and Increment=2000 hours. Then click **OK**



Before running the calculation, we are going to study two different cases:

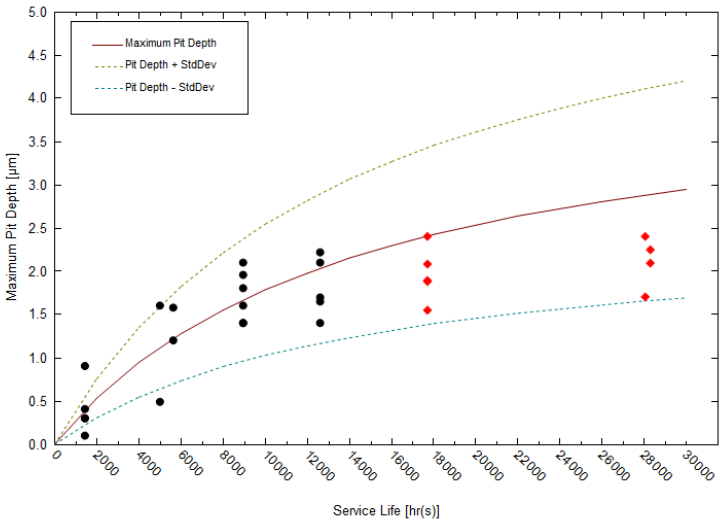
I. The first case will include the experimental data from groups 01 to 05
II. The second case will include all the experimental data from groups 01 to 08

Calculation including Groups 01 to 05

14. **Check** the boxes for Group 01 to 05
15. We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
16. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Save it under the same file that we previously created as *EVS calculations.*

Analyzing the results

17. Click on the **Plot** tab (Plot). You will see a plot of the predicted mean value of the depth of the deepest pit, x_m and the plots of values $x_m - \sigma$ and $x_m + \sigma$, where σ is the standard deviation of x_m.



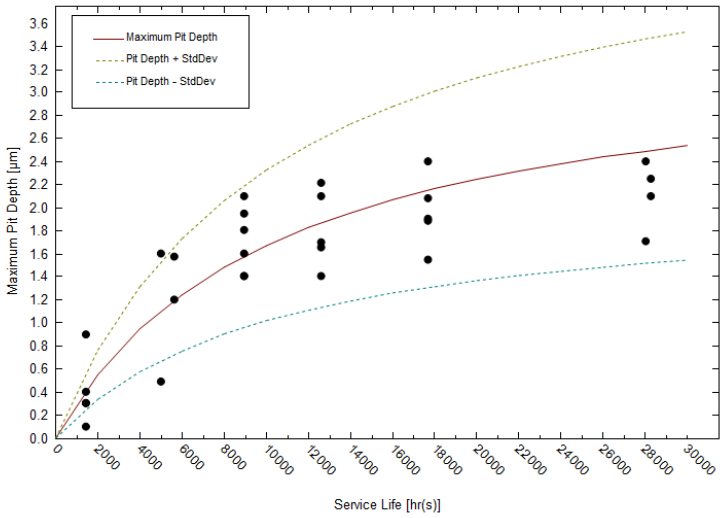
As previously noted, only the points in black mean that were used for predicting propagation of corrosion damage. The red diamonds mean that were not taken into account for the calculation and are shown only for demonstrating the accuracy of prediction.

Calculation including Groups 01 to 08

18. **Check** the boxes for Group 01 to 08
19. We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
20. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Save it under the same file that we previously created as *EVS calculations.*

Analyzing the results

21. Click on the **Plot** tab (Plot).



The plot above show how the predicted results improved with increasing number of subsequent inspections.

Note: The predictions can be substantially improved if they were obtained on the same part of the pipe where conditions are approximately the same.

22. Click on the **Report** tab, and to the **Calculation Results** table.

You can see here that at 30,000 hours the maximum pit depth predicted is 1.55 µm ≤2.54 µm ≤3.53 µm.

Example 59: Predicting the Pit Depth with Insufficient Data

In some cases, the data that provided by the user may be insufficient for reliable prediction of corrosion damage. The table below, shows experimental data (obtained from Laycock et al. 1990) for depths of the deepest pits that were measured on 316L coupons (2 x 2 x 1/2 in) in a 10% ferric chloride solution at 50 ^{0}C.

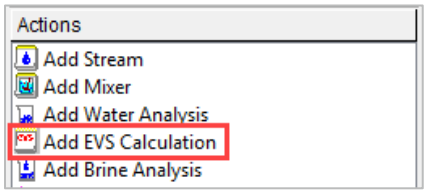
Pit Depth Data for an area of s= 25.8 cm^2, depth in µm

Sample	Grp 1	Grp 2	Grp3	Grp 4	Grp 5	Grp 6	Grp 7	Grp 8	Grp 9
	40.5 h	144.17 h	215.33 h	292.5 h	331.0 h	378.5 h	453.25 h	477.0 h	528.0 h
1	775	1326	1036	912	1361	1613	2101	1722	1714
2		1176	1199	1173	1534	1641	2024	1798	1767
3								1496	1775

Calculation the Depth of the Deepest Pit

Starting the Simulation

1. Add a new **EVS** calculation. Select the A**dd EVS Calculation** icon in the Actions Pane

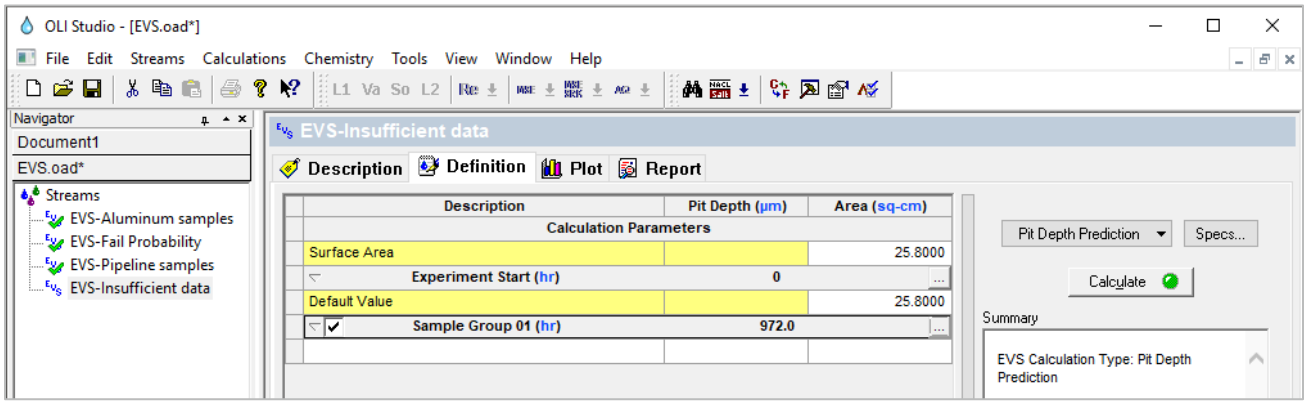


2. **Click** on the new EVS calculation and press **<F2>** to change the name to *EVS-Insufficient Data.* Notice that the default calculation is the *Pit Depth Prediction.*

3. Under the **Calculation Parameters** grid, enter 25.8 cm^2 for the **Surface Area** and **Default Value** cells.

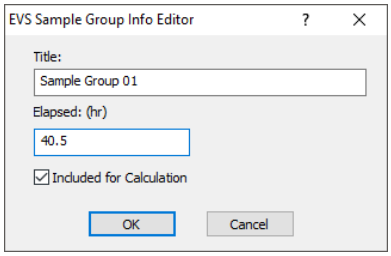
4. Since the data is in hours, click on the blue hyperlink **day** and change it to hours (**hr**) (for both: The **Experiment Start** and the **Sample Group**.

Your screen should look like the image below:



There are experimental data sets for 9 different periods of time. This means that we need to enter 9 different sample groups.

5. By default, **Sample group 01** is created. Click on the [...] button to edit this field. This will open a new window.
6. **Leave** the default name as **Sample Group 01**, enter the number **40.5** for the number of **elapsed hours**, and **check** the box **'Include for Calculation'**

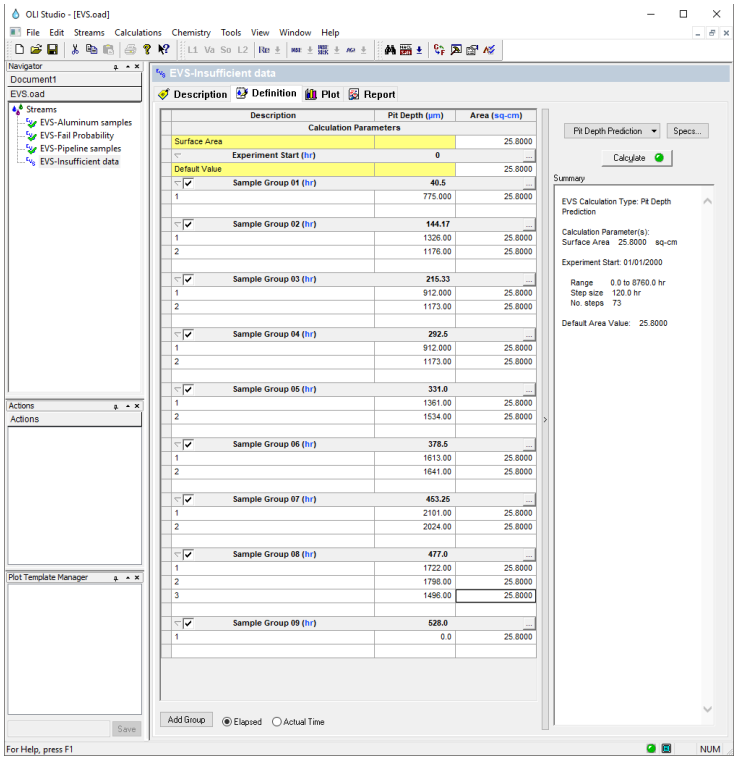


7. Enter the **Pit Depth** data (second column) obtained for 40.5 hours.

Now we need to add 8 more groups.

8. Click on the **Add Group** button (located at the bottom of the window. This will open a new window.
9. **Leave** the default name as **Sample Group 02,** enter the number 144.17 for the number of **elapsed hours**, and **check** the box **'Include for Calculation'**. Then click **OK.**
10. Enter the **Pit Depth** data (second column) obtained for 144.17 hours.
11. Click on the **Add Group** button, and repeat the same procedure for the rest of the experimental data (groups)

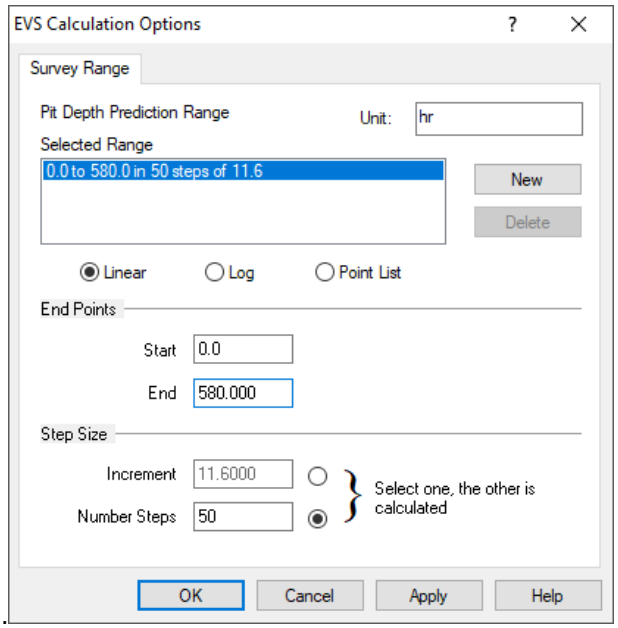
Once you have entered all the experimental data, your screen should look like the image below.



At this point, the experimental data has been entered. Now we need define the period of time for which we want to do the prediction of failure due to pitting.

12. **Click** on the **Specs** button. This will open a new window.

13. Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 hours, End=580 hours, and number of steps=50 hours. Then click **OK**



Before running the calculation, we are going to study two different cases:

I. The first case will include the experimental data from groups 01 to 03
II. The second case will include all the experimental data from groups 01 to 09

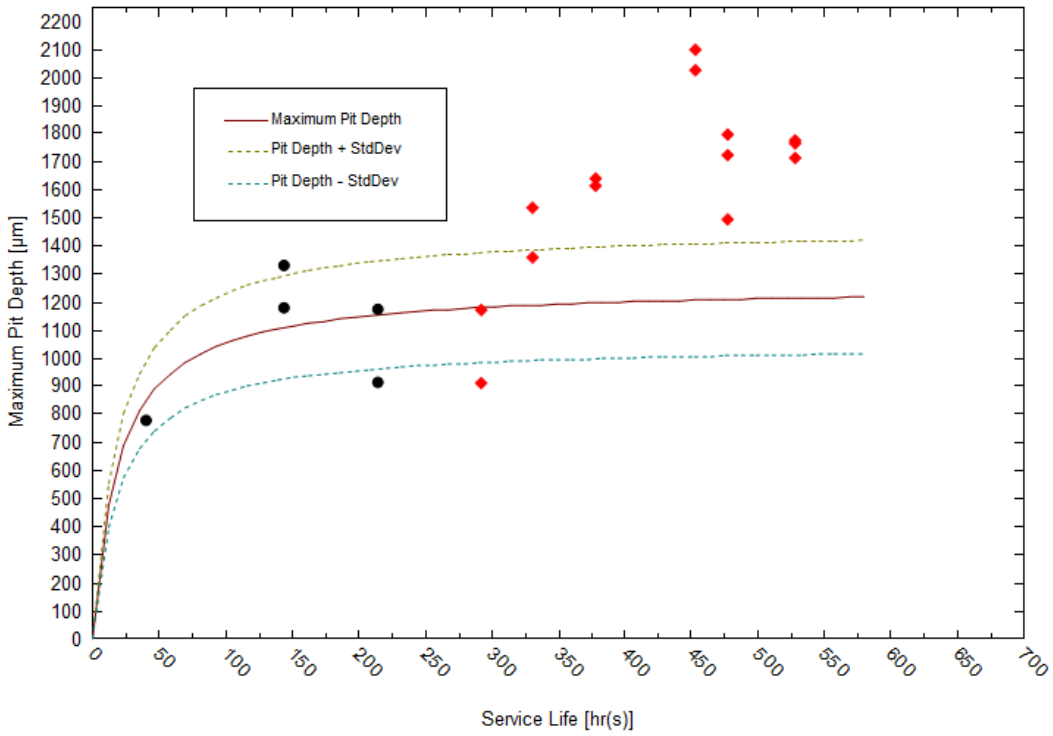
Calculation including Groups 01 to 03

14. **Check** the boxes for Group 01 to 03

15. We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

16. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Save it under the same file that we previously created as *EVS calculations.*

17. Click on the **Plot** tab (Plot).

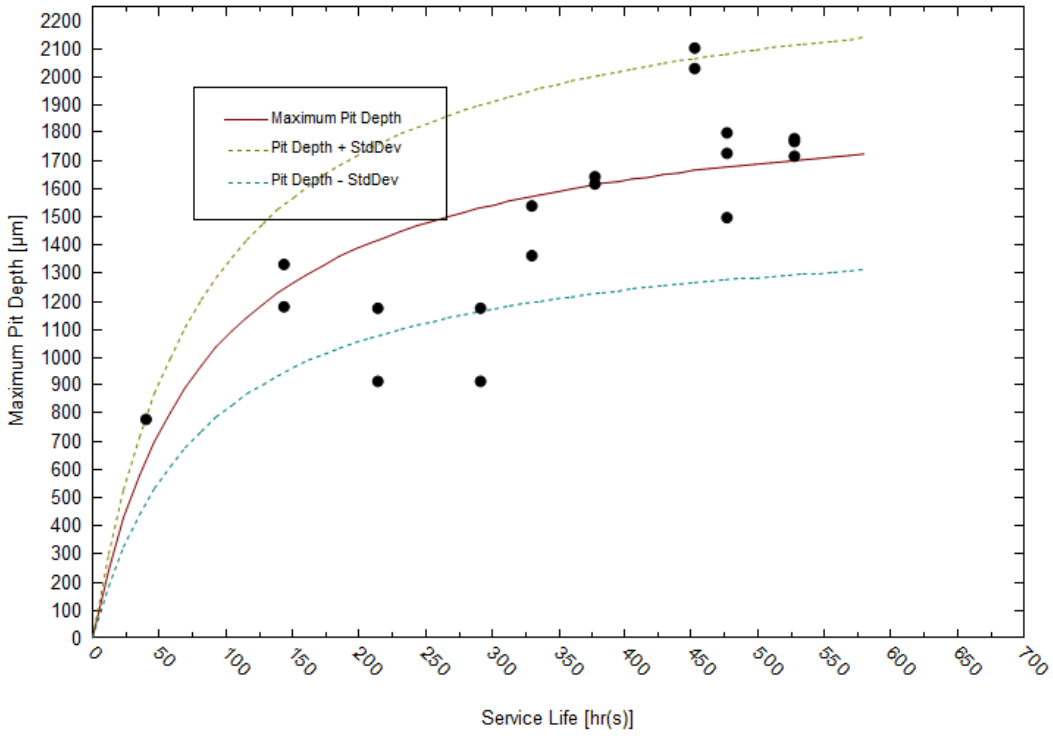


We see that in this case the prediction cannot be considered satisfactory. The reason is that for the first, second, and third observation times the observed mean value of deepest pit decreases. Obviously, such behavior of maximum pit depth has no physical foundation. Generally speaking, such situation is the result of an insufficient numbers of experiments (used coupons) for given observation times. Accordingly, we can expect that after increasing the number of used coupons the situation can improve.

Calculation including Groups 01 to 09

18. **Check** the boxes for Group 01 to 09
19. We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
20. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Save it under the same file that we previously created as *EVS calculations.*

21. Click on the **Plot** tab (Plot).



The plot above show how the predicted results improved with increasing number of subsequent inspections.

The plot above also shows that the results of approximation of the full set of available experimental data from Laycock et al. 1990) can be reasonably approximated by using EVS approach.

Additionally, these results show that insufficient number of coupons (measurements at given observation times) can be compensated by increasing numbers of observation at different times.

22. Click on the **Report** tab, and to the **Calculation Results** table.

You can see here that at 580 hours the maximum pit depth predicted is 1309.93 μm ≤ 1724.09 μm ≤1724.09 μm.

Chapter V – OLI Analyzer: ScaleChem Analyzer

ScaleChem Analyzer is a module within the OLI Analyzer. A separate license enables this module.

Why Use OLI Analyzer: ScaleChem Analyzer?

Scale problems arise when fluid, initially in equilibrium with its environment, is disturbed and becomes unstable. The unstable fluid results in H_2O, CO_2, and H_2S partitioning across the water, oil, and gas phases, corrosion of metal surfaces, and precipitation/dissolution of solids. ScaleChem Analyzer recognizes all three effects, which are all important to the oil and gas production professional.

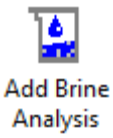
Precipitates form when mineral-forming elements increase the concentration of produced waters beyond supersaturation, or the saturation point. The primary causes of supersaturation are pressure, temperature, phase partitioning, and fluid mixing. ScaleChem Analyzer quantifies the effects on mineral scale potential while calculating the physical and chemical properties of fluid and gas phases. Industry professionals can use the software's calculations to help determine the best methods to deal with scaling situations.

ScaleChem Analyzer can be used to calculate scaling at one or more user specified temperatures and pressures. Other calculation options include the ability to mix waters at user specified ratios to find compatible waters, and the ability to saturate a water with respect to one or more solids to simulate reservoir conditions.

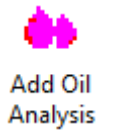
There are different types of inputs and calculations objects that can be used in ScaleChem Analyzer. A brief definition of each type of calculation is given below.

Input Objects

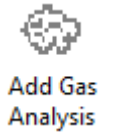
There are three different types of input objects, also referred to as analysis types, in the ScaleChem Analyzer software: Brine Analysis, Oil Analysis and Gas Analysis.



ScaleChem Analyzer refers to all waters and aqueous samples as brines. This option is added by double clicking on the **Add Brine Analysis.** A brine can be a surface water, an injection water, a formation water, a production water or any other type of aqueous fluid you can create. Brine compositions are entered in terms of ionic concentrations. In addition, the brine pH, total inorganic carbon and alkalinity can also be specified.



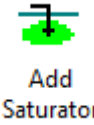
Add Oil Analysis allows you to enter an oil (non-aqueous phase). The oil sample may consist of pure component hydrocarbons (e.g., alkanes), distillation data, pseudocomponent or all three.



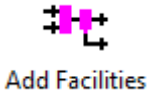
Add Gas Analysis allows you to enter any hydrocarbon mixture which may or may not contain water, carbon dioxide or hydrogen sulfide. The default hydrocarbon is methane (CH_4) but the hydrocarbon list may be expanded to include higher carbon numbers.

Calculation Objects

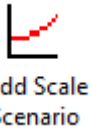
There are five different types of calculations that can be carried out in ScaleChem Analyzer: Saturator, Facilities, Scale Scenario, Scale Contour, and Mixing Water. A brief definition of each type of calculation is given below.



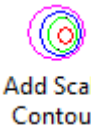
Add Saturator object combines fluids at the specified temperature and pressure and saturates the combined phases with the selected minerals.



Add Facilities mixes and separates fluids. It is used to simulate production operations.



Add Scale Scenario object calculates the scaling of minerals from a fluid as temperature and pressure changes, e.g. at different production locations during production.



Add Scale Contour object calculates the scaling of minerals from a fluid over a matrix of temperature and pressure. It creates a 2D contour plot visual.

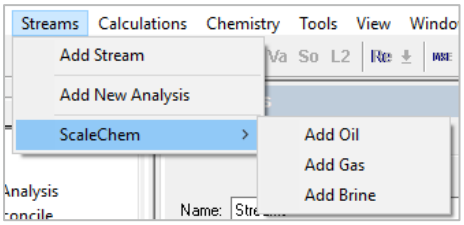
Add Mixing Water object mixes two potentially incompatible brines together to identify at what ratios the scale will form.

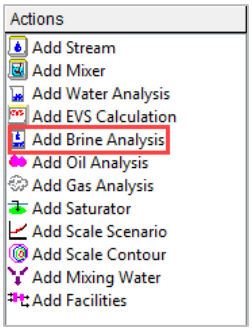
In these chapter we will model a hypothetical field and learn how to use and set up each one of the objects presented above.

Section 10. Entering a Brine Analysis in ScaleChem Analyzer

11.1. Entering Data for a Brine Analysis

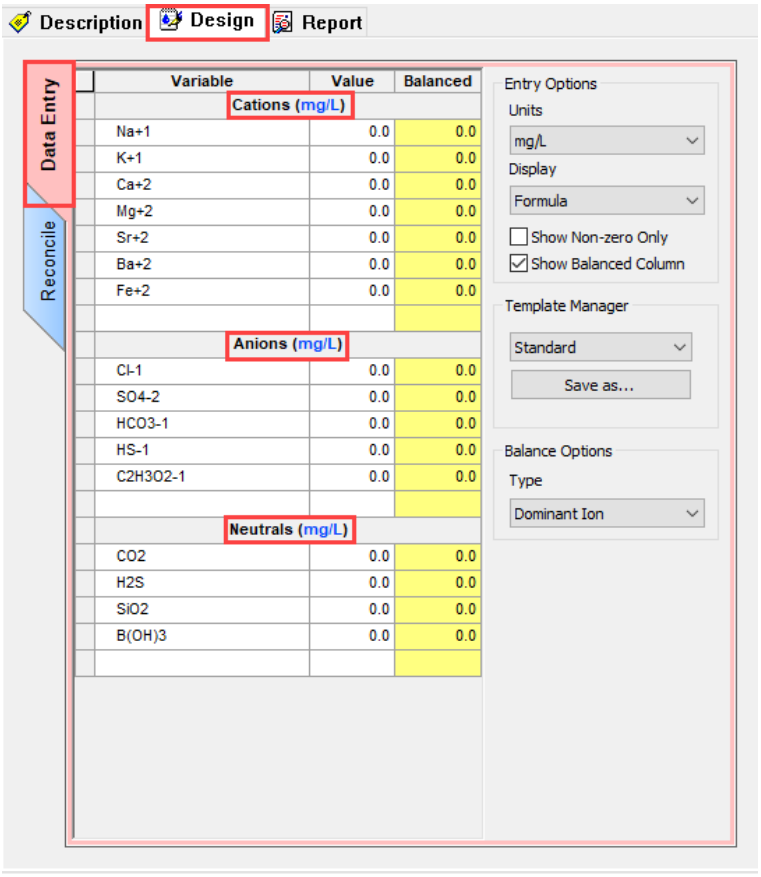
To add a **Brine Analysis,** go to the toolbar menu and click on **Streams** > **ScaleChem > Add Brine,** or by selecting the **Add Brine Analysis** icon in the Actions Pane.





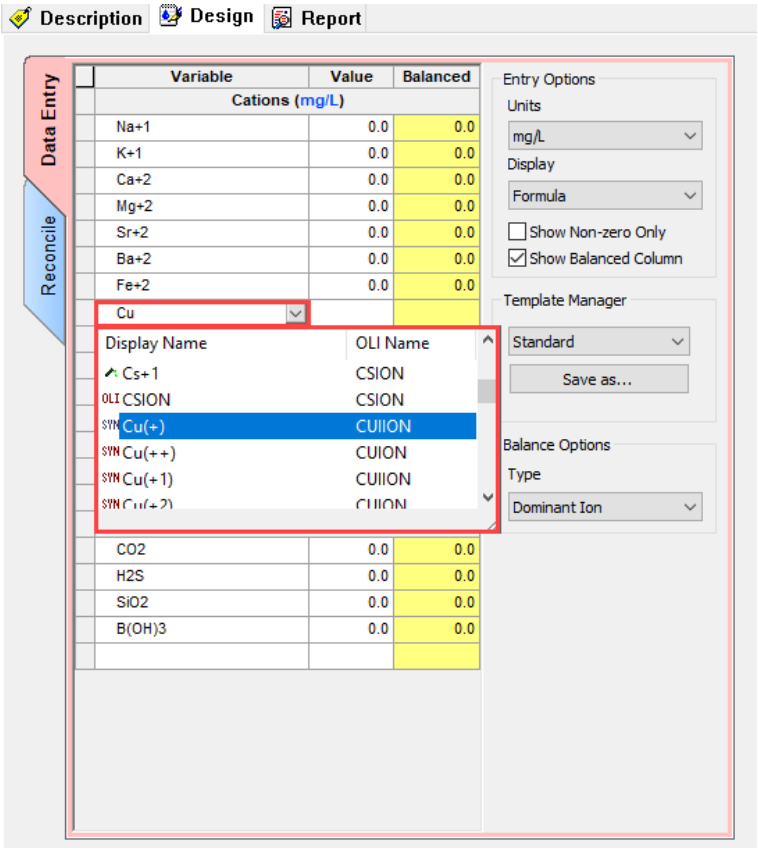
You will see three different tabs for this analysis. The **Description, Design** and **Report** tab.

The Brine Analysis open in the **Design,** which has 2 different sub-tabs: **Data Entry** and **Reconcile**, where we need to enter the laboratory analysis information.

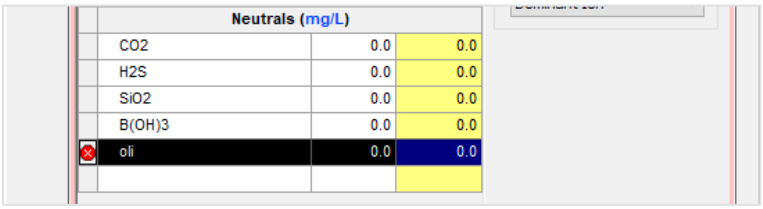


We will start in the **Data Entry** (red) sub-tab. Here you enter the concentration of Cations, Anions, and Neutrals. This sub-tab comes already prepopulated with some of the most common cations, anions, and neutrals species found in laboratory water/brine analyses (by default the units are in **mg/L**). If your species is not present in the prepopulated grid, simply click on the white grid and type the ion or neutral of interest. If it is a **cation**, type the element followed by a plus (+) sign and the corresponding oxidation state, e.g. Cu+2. If it is an **anion**, type the element followed by a minus (-) sign and the corresponding oxidation state, e.g. Br-1. If it is a **neutral**, simple type the species either using the formula name or its name, as has been shown in the previous sections.

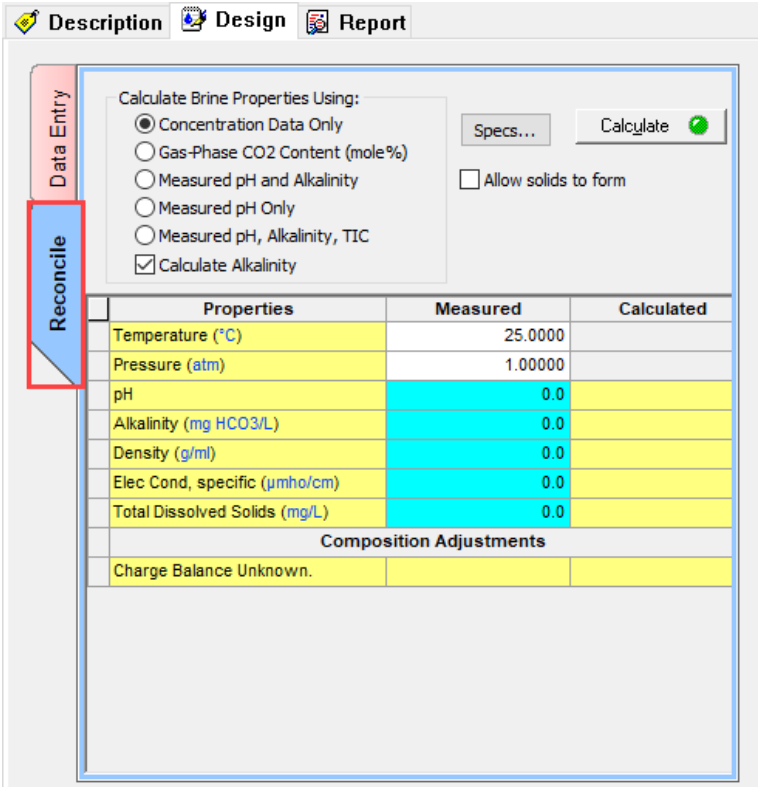
The Brine Analysis grid also contains search aids to find a specific cation, anion or neutral species. The first search aid is the drop list located in each the cation, anion, and neutral grid sections. The list is alphabetic and is activated using the drop-down arrow within the cell, after the first few letters of the ion is typed.



If a name is misspelled or if the text is unrecognized, then a red 'X' appears to the left of the name. This name needs to be corrected or the row deleted before proceeding. To delete the row, simply select the wrong entry (which will turn black) and hit the key **<Delete>**.



The **Reconcile** sub-tab is used to define the measured properties of the brine. In this **Reconcile** sub-tab, we will tell the software how to reconcile the brine.



The first step, however, is to enter the brine measured properties and conditions. To do this we need to start in the **Properties | Measured | Calculated** table.

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
pH	0.0	
Alkalinity (mg HCO3/L)	0.0	
Density (g/ml)	0.0	
Elec Cond, specific (µmho/cm)	0.0	
Total Dissolved Solids (mg/L)	0.0	
Composition Adjustments		
Charge Balance Unknown.		

By default, the values of temperature, and pressure are 25°C and 1 atm. The **aqua-blue** cells indicate the values that you need to enter if they were measured at the temperature and pressure specified, these are: Measured pH, Measured Alkalinity[9], Density, Specific Electrical Conductivity and Total Dissolved Solids (TDS).

You can always change the units of these properties by clicking on the units highlighted in **blue**. This action will open the Units Manager Window.

[9] This is generally a reliable value, unless solids have precipitated in the sample. Alkalinity is often but not always the same value as the bicarbonate ion (HCO_3^-). ScaleChem Analyzer can reconcile on a measured alkalinity by adjusting the solution composition.

If you don't have a measured property value, let's say for example, the Specific Electrical Conductivity, just leave it blank.

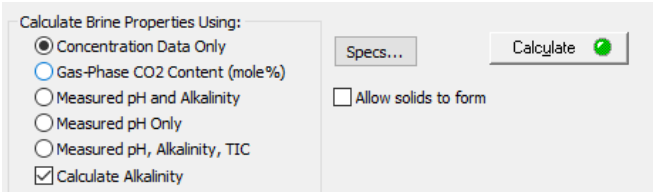
The yellow cells, under the **Calculated** column, will contain calculated values by the software and will be shown once the simulation is run.

When reviewing laboratory analysis of brine samples, it is quite common for the positive ions (cations) and the negatively charged ions (anions) in solution to not balance. This may be due to the precision limits of the various experimental procedures used to measure the ions - i.e. some ions may not have been analyzed. These solutions must have a neutral charge. ScaleChem Analyzer will adjust/modify inflows in order to balance the charges and make the solution neutral. This adjusting procedure is referred to as **Reconciliation**.

There are 5 different types of **Reconciliation Options**:

a) Concentration Data Only
b) Gas-phase CO2 content (mole%)
c) Measured pH and Alkalinity
d) Measured pH Only
e) Measured pH, Alkalinity, TIC

Additionally, there is the option to calculate the alkalinity value by checking the **Calculate Alkalinity** box.



When the Reconciliation Option is selected, the software will calculate the properties of the brine

A more detailed description of each reconciliation option is given in Section 11.3. Reconciliation Options in the Brine Analysis below.

11.2. Brine Analyses - Reporting Elements

Brine analysis data obtained from ICP measurements will contain concentrations for B, P, S, and Si. These elements do not exist in the water, rather they exist as dissolved ions. If they are part of your analysis, then you should convert them to the following before entering them into the Brine Analyses object.

Converting element concentration to species for Brine Analysis

ICP data	Aqueous Species	Formula to enter	Formula weight multiplier
B, boron	Boric Acid	H3BO3	B (mg/l) × 5.72 = H3BO3 (mg/l)
Si, Silicon	Silica	SiO2	Si (mg/l) × 2.14 = SiO2 (mg/l)
P, Phosphorus	Dihydrogen Phosphate	H2PO4-1	P (mg/l) × 3.13 = H2PO4 (mg/l)
S, Sulfur	Sulfate or Sulfide	HS-1 or SO4-2 (cannot tell from total S only)	S (mg/l) × 1.03 for HS-1 (mg/l) or S (mg/l) × 3.0 for SO4-2 (mg/l)

11.3. Reconciliation Options in the Brine Analysis - Definitions

When reconciling a Brine Analysis, there are five options for reconciliation:

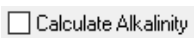
1. **Concentration Data Only:** The software will run an electroneutrality reconciliation only, and then compute the water properties such as pH, density, etc., based on the entered concentration of neutral, cations, and anions species. In the **Concentration Data Only** option you may allow the program to pick the species to adjust for electroneutrality or you may manually choose the species to perform the adjustment. (See electroneutrality options).

2. **Gas-phase CO2 content (mole%):** Frequently it is simpler and more stable to measure the gas-phase CO_2 that is separated from the brine at the sampling point. When matched with another measured variable, usually alkalinity, the concentration of the carbonate species and the pH can be calculated. ScaleChem Analyzer performs a CO_2 gas fraction calculation by taking the P_{CO2} and the calculated alkalinity (based on the water analysis data) to reconcile the system for pH and carbonate properties. The CO_2 is adjusted to match a saturated gas composition.

3. **Measured pH Only:** Many brines analyses report a measured pH. This pH may or may not match the pH calculated by the software. The cause may be an incomplete and/or inaccurate brine description. The software will run both an electroneutrality and pH reconciliation. This type of reconciliation will match your recorded pH. Additionally, the software will compute the water properties such as, density, electrical conductivity, etc. The pH of the solution is automatically adjusted by the software by adding either HCl or NaOH, or you may select your preferred acids and bases to adjust the pH.

4. **Measured pH and Alkalinity:** The purpose of the Measured pH and Alkalinity reconciliations is to match the computed pH and alkalinity values with those you measured. The software will run an electroneutrality, pH and alkalinity reconciliation. Additionally, the software will compute the water properties such as density, electrical conductivity, etc. The pH of the solution is automatically adjusted by the software by adding either HCl or NaOH or you may select your preferred acids and bases to adjust the pH. The Alkalinity is automatically calculated by the software, using CO_2 as the alkalinity titrant, H_2SO_4 as the alkalinity pH titrant and 4.5 as the alkalinity end point pH. You can also change a different alkalinity titrant if you prefer.

5. **Measured pH, Alkalinity, TIC:** The purpose of this reconciliation is to match the measured pH, total alkalinity and the total inorganic carbon (TIC). The Total Inorganic Carbon (TIC) is adjusted using CO_2 as the alkalinity titrant, H_2SO_4 as the alkalinity pH titrant and 4.5 as the alkalinity end point pH. The software adjusts the acetate concentration (organic acids) to match the total Alkalinity value by adding or removing acetic acid. You cannot however change the CO_2 or acetic acid for the alkalinity adjustment. These are fixed by the software. The target pH is obtained simultaneously by HCl or NaOH. You may select your preferred acids and bases to adjust the pH instead of the default HCl and NaOH.

Additionally, there is the option to **Calculate Alkalinity**: 

. It is important to note, that this is only an alkalinity calculation based on the concentration entered, it is not an alkalinity reconciliation.

11.4. A Basic Brine Analysis

A brief introduction to the brine analysis tool will be shown in the example below. As we go through the example, the basic definitions, functionalities and reporting for the *Brine Analysis object* will be shown.

Example 60: Basic Brine Analysis

In this example, we will input dissolved species concentrations and other measured properties into a **Brine Analysis** object to model a hypothetical water sample. Will calculate the **pH** and **scaling tendency** of a brine sample based upon its measured composition at 1 atm and 25 ºC.

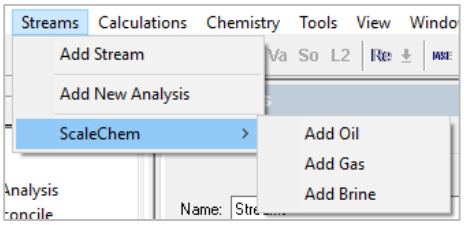
Starting the Simulation

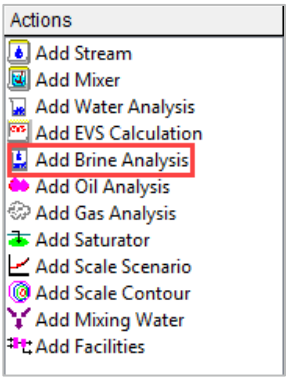
Use the inputs and parameters from the table below to create the brine analysis. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Brine Analysis Composition							
Cations (mg/L)		**Anions (mg/L)**		**Neutrals (mg/L)**		**Measured Properties**	
Na+1	20400	Cl-1	37000	CO2	150	pH	7.1
K+1	400	SO4-2	2200	H2S	15	Alkalinity as HCO3-, mg/L	715
Ca+2	3800	HCO3-1	0				
Mg+2	830	HS-1	0				
Sr+2	15	C2H3O2-1	715				
Ba+2	0.7						
Fe+2	10						

Setting the Water Analysis

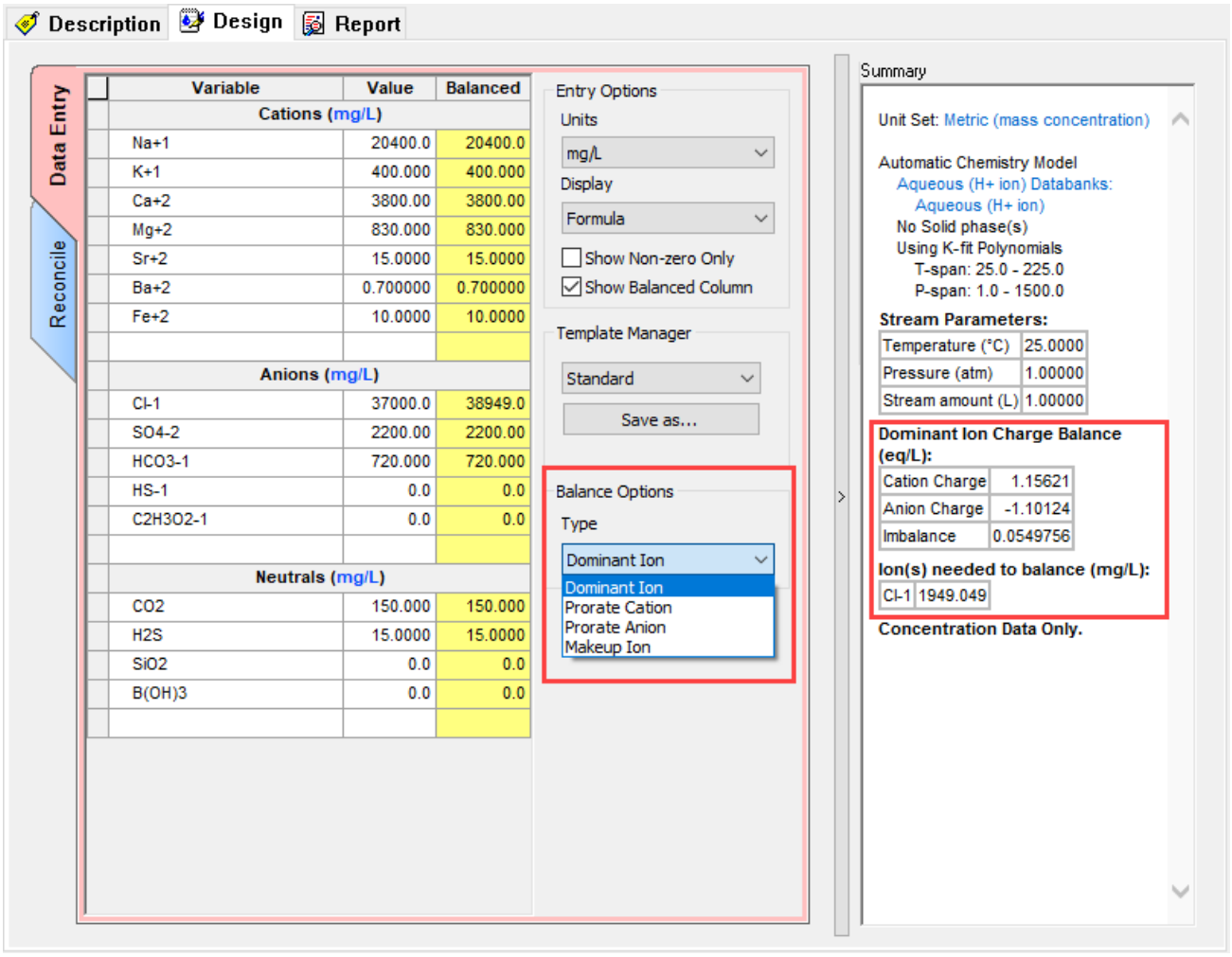
1. Add a **Brine Analysis.** Go to the toolbar menu and click on **Streams** > **ScaleChem > Add Brine,** or by selecting the **Add Brine Analysis** icon in the Actions Pane





2. **Click** on the new Brine and press **<F2>** to change the name to *Brine Analysis*
3. Select the **AQ** thermodynamic Framework (default)
4. **Click** on the **Names Manager** Icon and select the **Formula** option (default)
5. **Click** on the **Units Manager** Icon, and select Metric, Concentration (default)
6. Under the **Design** Tab, enter the **Cation, Anion,** and **Neutrals** composition given in the table above.

Your screen should look like the image below:



Note: It is highly unusual for the data to be electrically neutral. Therefore, the software reconciles the sample for **electroneutrality**. After entering each species concentrations, you will notice that the software shows a yellow column named **Balanced**. The software balances charges according to the selected option and displays this in the yellow column.

There are 4 different Balance Options:

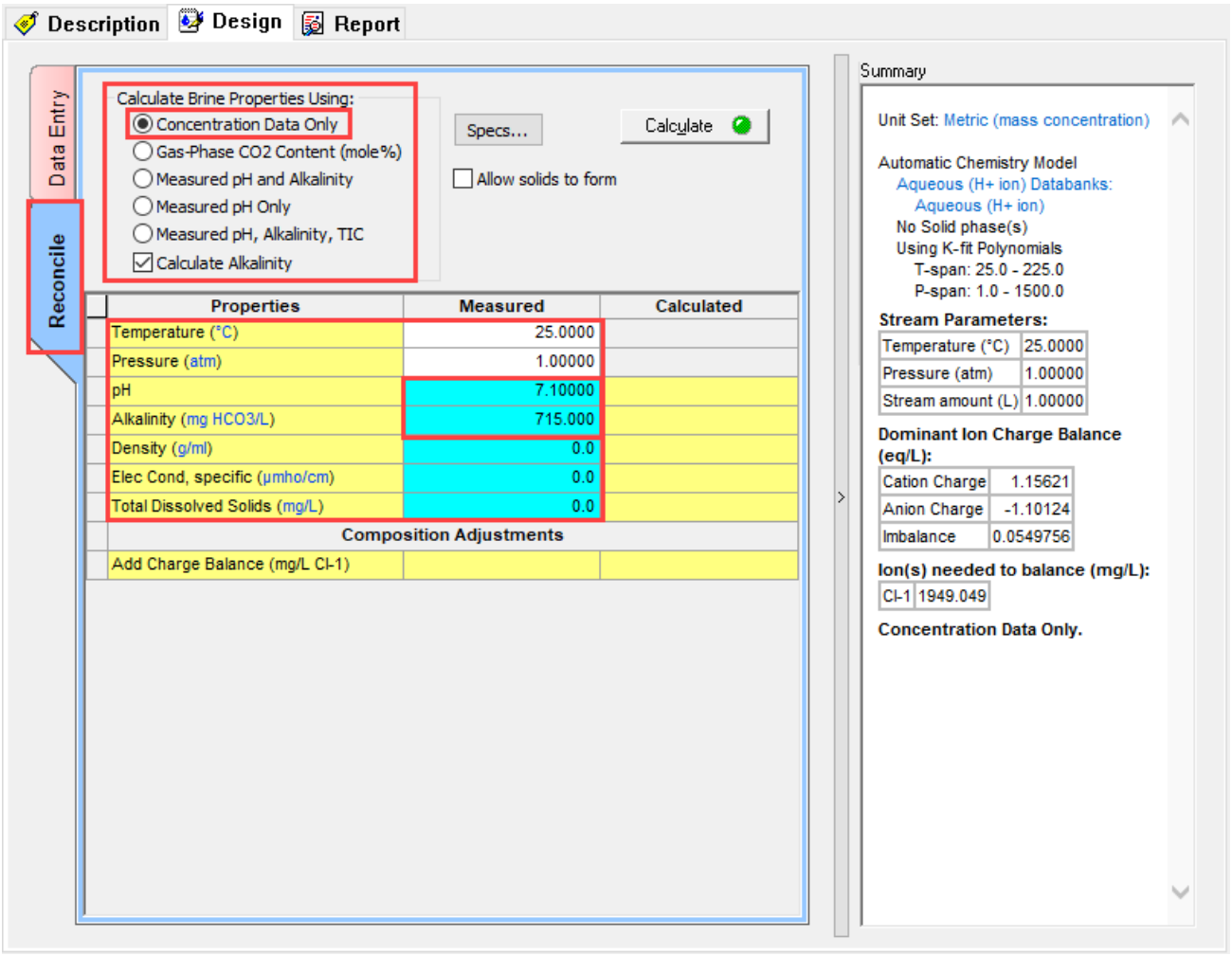
1) **Dominant Ion**: This is the default method. The largest counter ion is used to adjust the electroneutrality. In our example,1949.049 mg/L of Cl-1 are added since there is an excess of positive charge (see the above image).
2) **Prorate Cations**: All cations are adjusted up or down equally
3) **Prorate Anions**: All anions are adjusted up or down equally
4) **Make-up Ion**: This option allows for a single ion species to be adjusted. User selects an ion to increase or decrease.
5) Under the **Design** Tab, enter the **Cation, Anion,** and **Neutrals** composition given in the table above.

7. Select **Dominant Ion** as balance option
8. Click on the **Reconcile** (vertical blue tab)

Notice that there that five different types of reconciliation are available in in the upper left corner of the window (see image below). Also, you can see the **Calculate Alkalinity box** (Calculate Alkalinity) option, which allows you to compute the alkalinity, based on the concentration entered.

9. **Select** the **Concentration Data Only** option. This option means that the software will compute the water properties based on the current concentration of neutral, cations, and anions species. The calculation will not use the measured pH, or the measured alkalinity entered (if any).

10. Enter the **measured properties**: pH = 7.1 and Alkalinity = 715 as mg HCO3/L

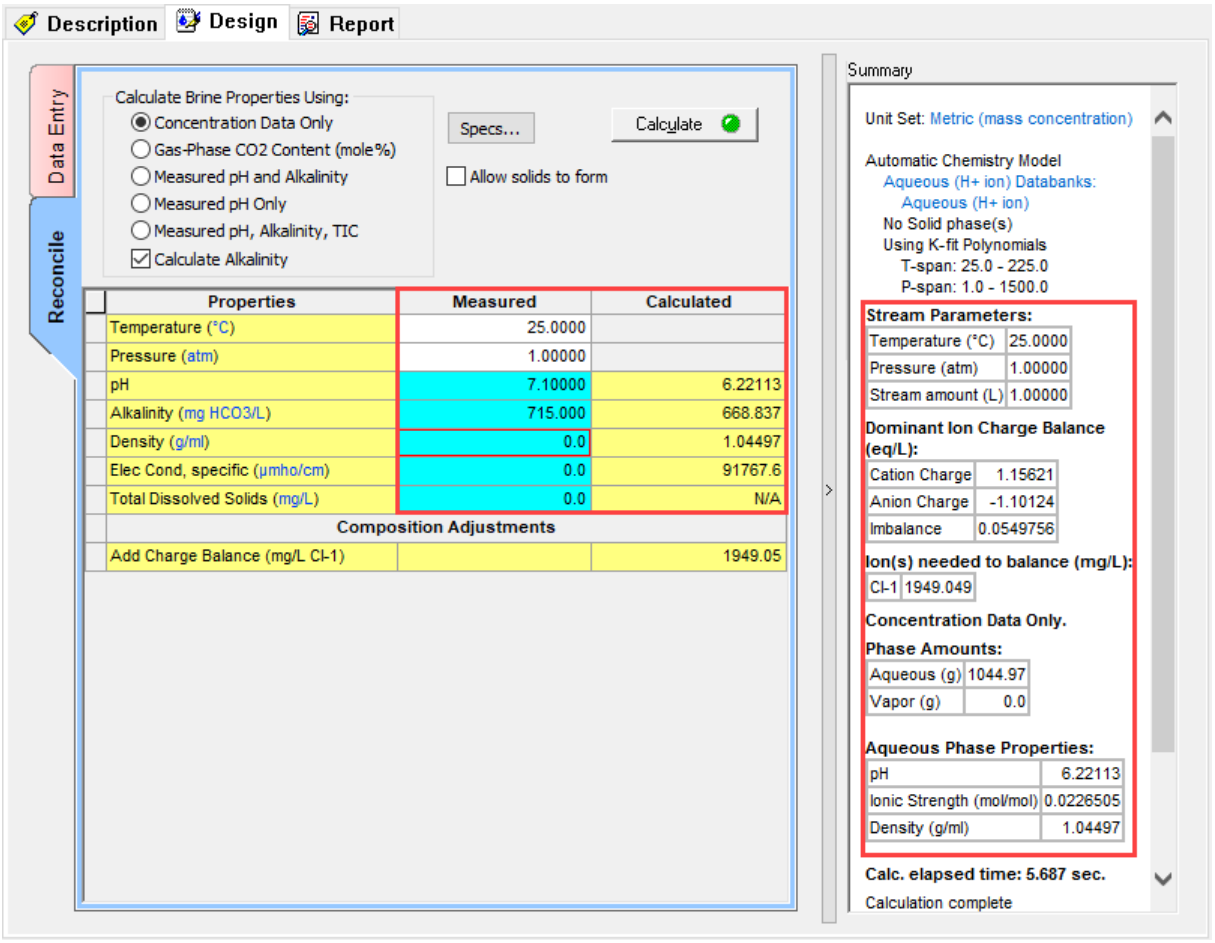


11. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

12. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Create a new file and name it: *ScaleChem Analysis Calculations.*

Analyzing the Results

Once the calculation is done, the **Calculated** column displays the results obtained based on the concentrations entered in the **Data Entry** tab. Notice that the calculated results are pH=6.22 and Alkalinity=669 mg HCO3-1/L vs the measured values of pH=7.1 and Alkalinity=715 mg HCO3-1/L.



To the right you can see the results summarized in the **Summary Box**.

The top section contains the **Stream Parameters** information. In this example, the software performed the calculation at 25 ºC, 1 atm, and a total Stream amount of 1 L.

The **Dominant Ion Charge Balance** section shows the type of balance that was used to reach electroneutrality, which cation/anion was deficient, and how much of it was added.

The **Phase amounts** section shows the distribution of species in the different phases. This analysis contains two phases: aqueous and vapor.

The **Aqueous Phase Properties** information shows the computed pH, ionic strength, and density of the solution. It is important to note here that the measured pH is 7.1 and the computed pH is 6.22. The density of this solution is 1.04497 g/ml. Remember, for this example the software used only the concentration of neutrals, cations and anions in solution to do a reconciliation.

1. Click on the **Report** tab, and scroll down to the **Pre and Post Scaling Tendencies** table.

Pre and Post Scaling Tendencies

Scale Mineral	Pre-scaling	Pre-index	Post-scaling	Post-index
BaSO4 (Barite)	9.44533	0.975217	9.44533	0.975217
CaCO3 (Calcite)	2.44082	0.387535	2.44082	0.387535
CaSO4.2H2O (Gypsum)	0.938902	-0.0273798	0.938902	-0.0273798
CaSO4 (Anhydrite)	0.740543	-0.130450	0.740543	-0.130450
FeCO3 (Siderite)	0.178450	-0.748484	0.178450	-0.748484
FeS (Pyrrhotite)	500.789	2.69966	500.789	2.69966
KCl (Sylvite)	6.72458e-4	-3.17233	6.72458e-4	-3.17233
FeS (Mackinawite)	8.54999	0.931965	8.54999	0.931965
NaCl (Halite)	0.0122161	-1.91307	0.0122161	-1.91307
SrCO3 (Strontianite)	0.0290888	-1.53627	0.0290888	-1.53627
SrSO4 (Celestine)	0.203964	-0.690447	0.203964	-0.690447

From this table, you can see that Barite, Calcite, Pyrrhotite and Mackinawite solids have been predicted to be supersaturated.

For more detailed information about scaling tendencies you can go to Scaling section in page 175.

2. Scroll down to the **Brine Composition** table

Brine Composition

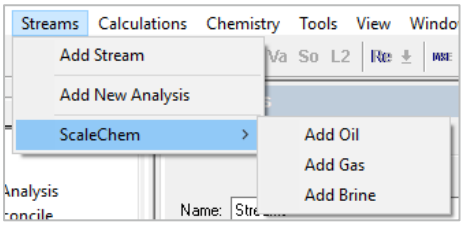
Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)
K(+1)	400.000	Cl(-1)	38949.0	CO2	158.990
Na(+1)	20400.0	HCO3- (*)	707.535	H2S	14.9948
Ba(+2)	0.700000	SO4-2	2203.08		
Ca(+2)	3800.00				
Fe(+2)	10.0000				
Mg(+2)	830.000				
Sr(+2)	15.0000				

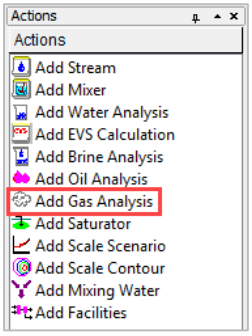
This table shows the composition of the brine after the reconciliation (calculation) has taken place.

Section 11. Entering a Gas Analysis in ScaleChem Analyzer

12.1. Entering Data for a Gas Analysis

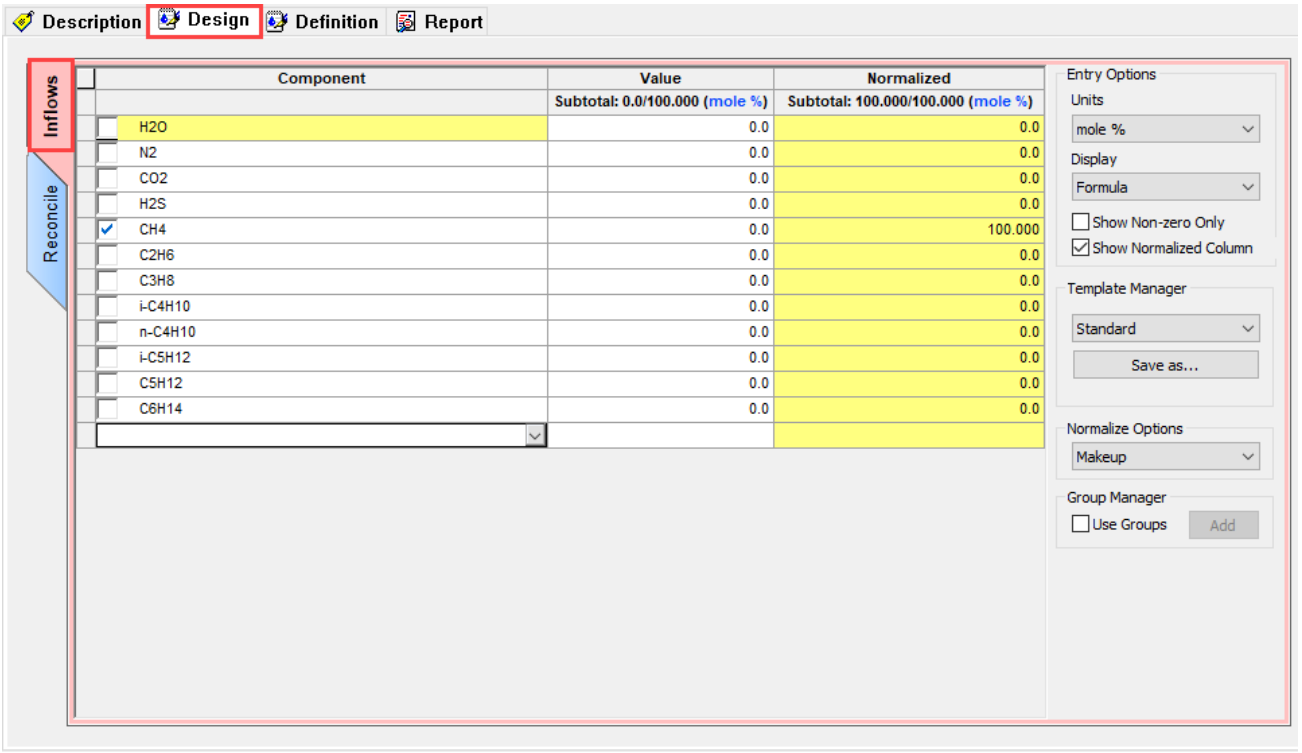
To add a **Gas Analysis,** go to the toolbar menu and click on **Streams** > **ScaleChem > Add Gas,** or by selecting the **Add Gas Analysis** icon in the Actions Pane.





You will see four different tabs for this analysis. The **Description, Design, Definition** and **Report** tab.

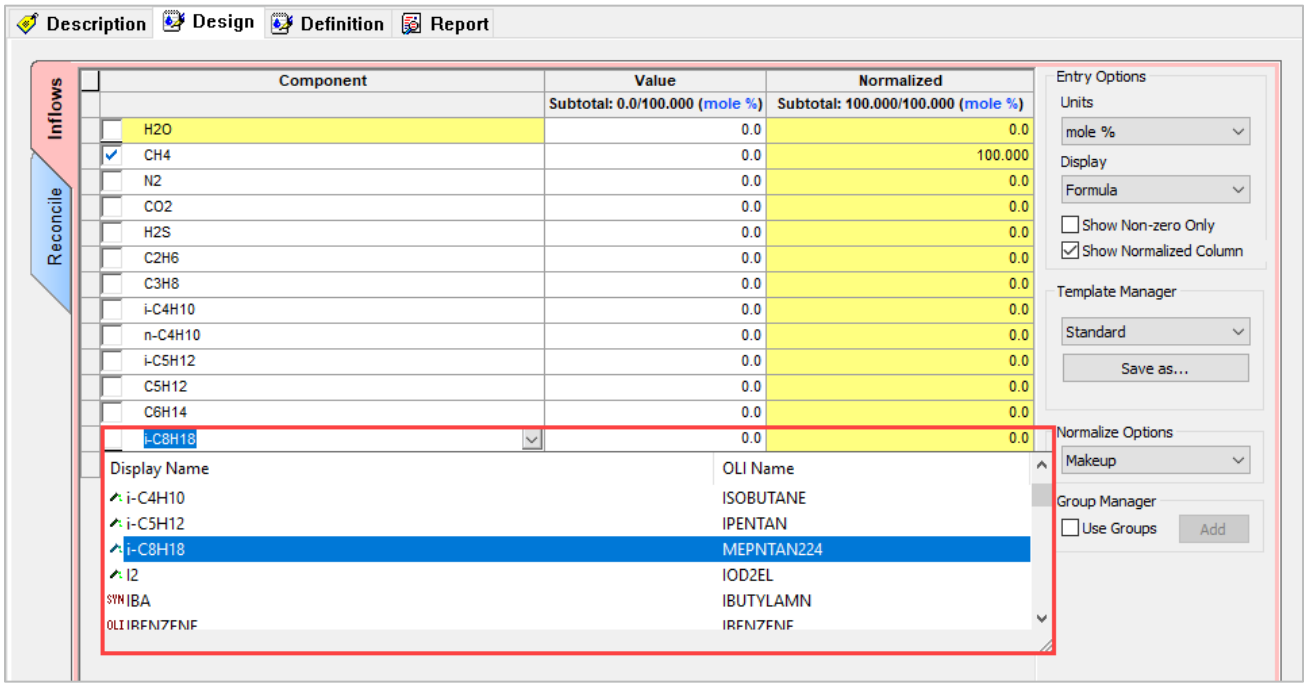
The gas analysis opens in the **Design** tab, which has 2 different sub-tabs: **Inflows** and **Reconcile**, where we need to enter the laboratory gas analysis information.



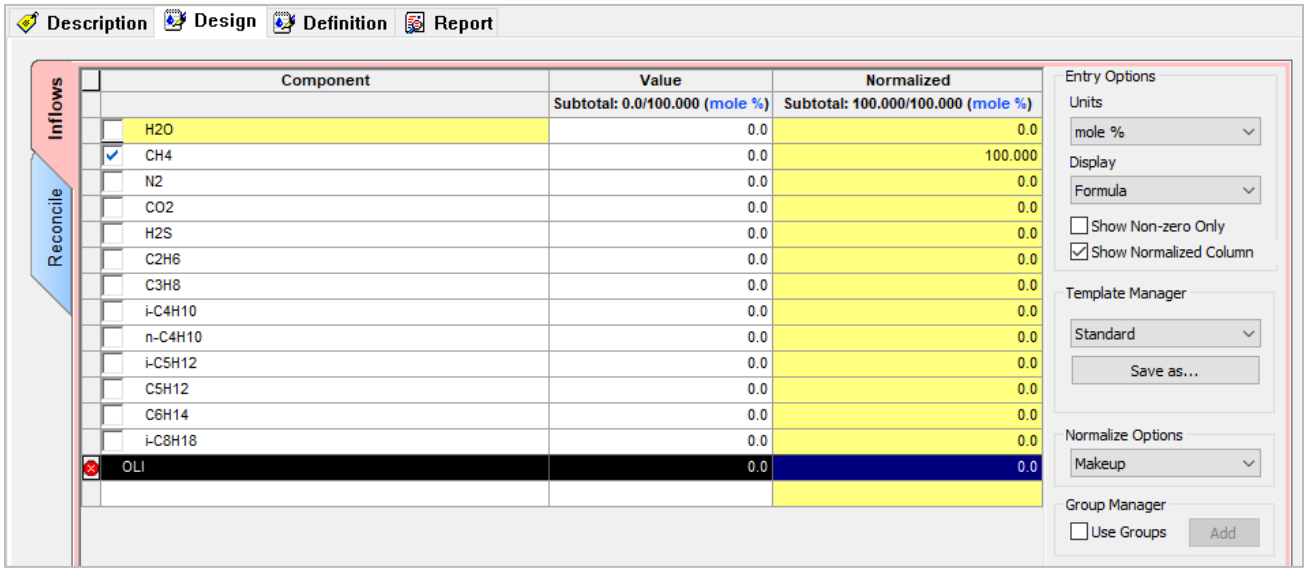
We will start in the **Data Entry** (red) sub-tab. Here you enter the concentration of a pure-component hydrocarbon gas, in **mole %** units. The standard list of component extents to C6 alkanes.

If there is a component that is not present in the prepopulated grid, simply click on the white grid and type the species of interest, using the formula name or its name, as has been shown in the previous sections. Let's say for example, you want to add Isooctane. Type isooctane or i-C8H18 in the white cell to add it to the list.

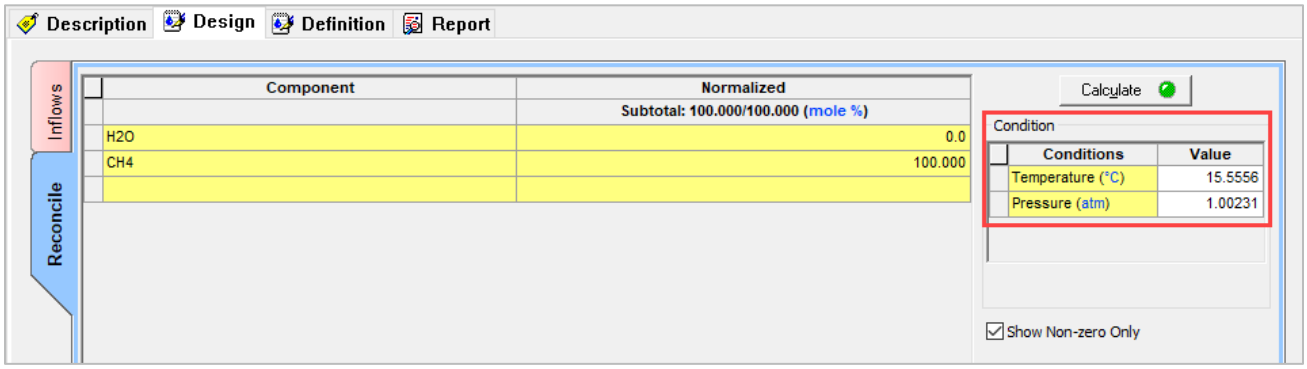
There is also the option of using the drop-down arrow, that allows you to search for the specific components you want to add.



If a name is misspelled or if the text is unrecognized, then a red 'X' appears to the left of the name. This name needs to be corrected or the row deleted before proceeding. To delete the row, simply select the wrong entry (which will turn black) and hit the key **<Delete>**.



The **Reconcile** sub-tab is used to calculate the properties of the gas at the temperature and pressure conditions specified. By default, the values of temperature, and pressure are 60 ºF (15.56ºC) and 14.7 psia (1 atm).



12.2. A Basic Gas Analysis

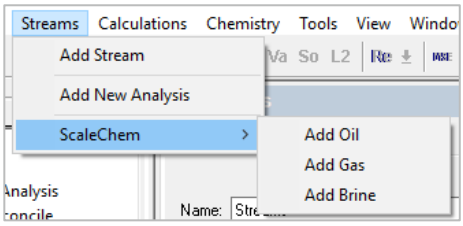
A brief introduction to the gas analysis tool will be shown in the example below. As we go through the example, the basic definitions, functionalities and reporting for the *Gas Analysis object* will be shown.

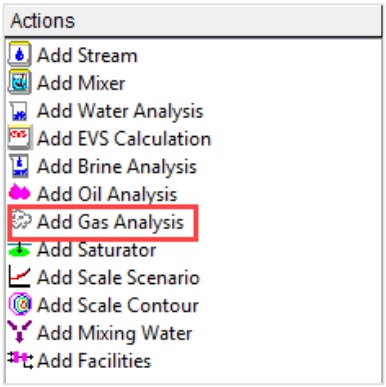
Example 61: Basic Gas Analysis

The Gas Analysis object provides a quick way to enter a pure-component hydrocarbon gas.

Setting the Gas Analysis

1. **Add a Gas Analysis.** Go to the toolbar menu and click on **Streams** > **ScaleChem > Add Gas,** or by selecting the **Add Brine Analysis** icon in the Actions Pane

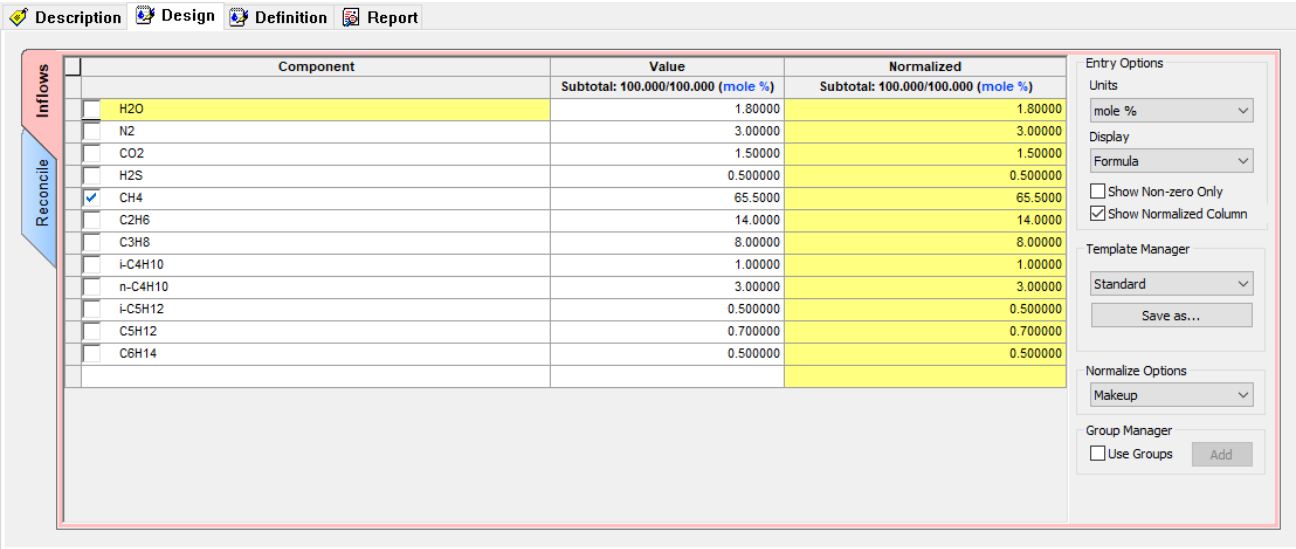




2. **Click** on the new Gas and press **<F2>** to change the name to *Gas Analysis*
3. Select the **AQ** thermodynamic Framework (default)
4. **Click** on the **Names Manager** Icon and select the **Formula** option (default)
5. **Click** on the **Units Manager** Icon, and select Metric, Concentration (default)
6. Under the **Inflows** Tab, enter the gas composition given in the table below

Gas Analysis Composition		
Formula	**Component Name**	**Mole %**
H2O	Water	1.80
N2	Nitrogen	3.00
CO2	Carbon Dioxide	1.50
H2S	Hydrogen Sulfide	0.50
CH4	Methane	65.5
C2H6	Ethane	14.0
C3H8	Propane	8.00
i-C4H10	Isobutane	1.00
n-C4H10	n-Butane	3.00
i-C5H12	Isopentane	0.50
C5H12	n-Pentane	0.70
C6H14	n-Hexane	0.50

Your screen should look like the image below:



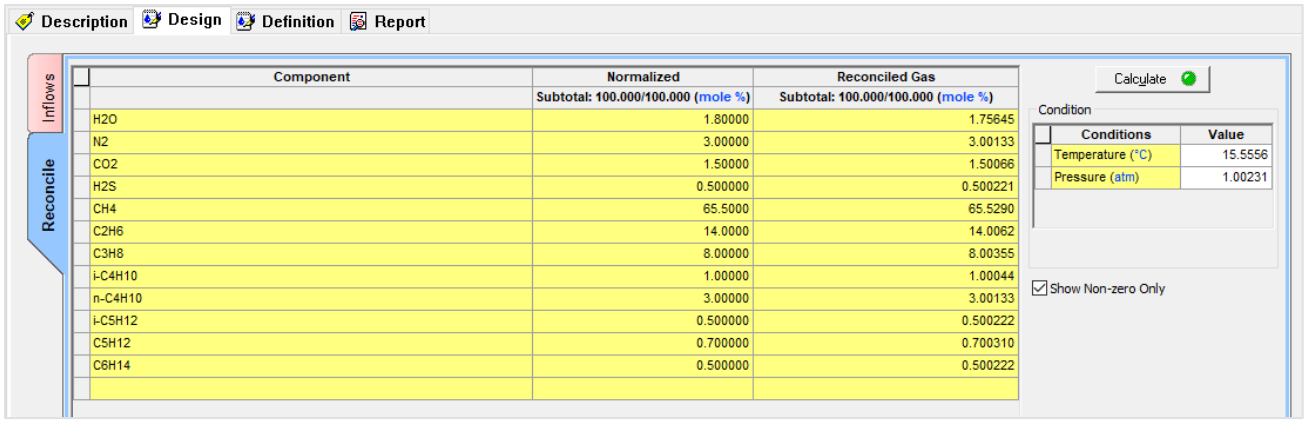
Note: There are several options to the right of the data entered.

1) **Entry options:** Here you can select the prefer units, and display name. You also have the options to show the non-zero values only – sometimes the composition of species is zero – and show normalized (yellow) column – this option is useful when the values don't add up to 100 mole%.

2) **Template manager:** Here you can select the standard (default) template or the extended template – which includes hydrocarbons with longer chains. You can also create and save your own template for future use.

3) **Normalize options:** When your analysis does not add up 100 mole% you can select between two options: Make-up and Prorate. For the Make-up option, the default gas used is CH4.

7. Click on the **Reconcile** (vertical blue tab). The reconciliation calculation will be calculated at 15.556 C and 1.00231 atm (standard conditions).

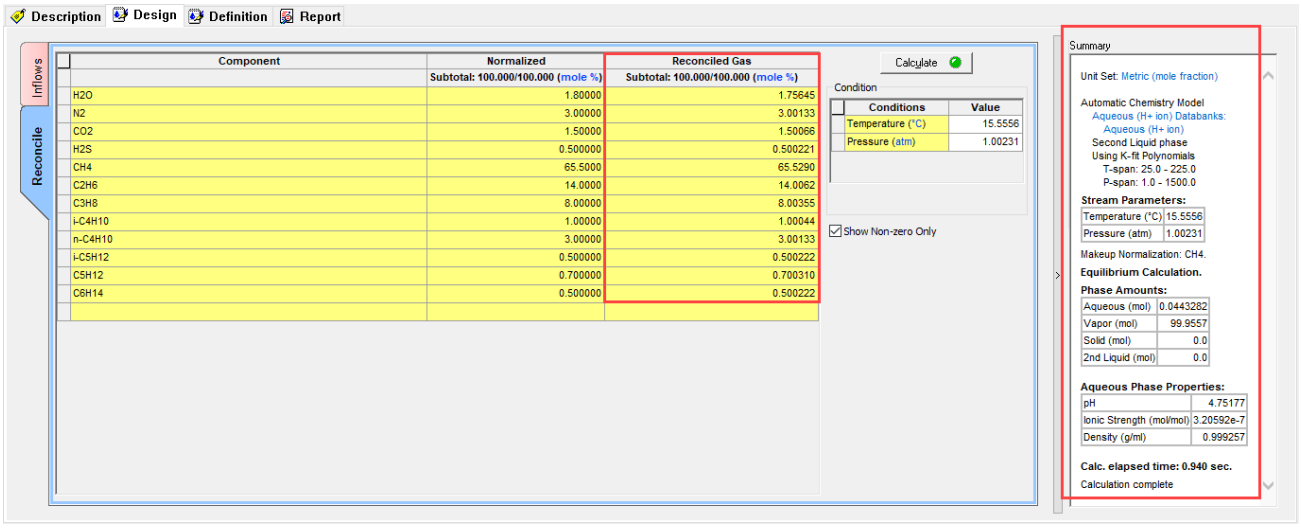


8. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

9. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Create a new file and name it: *ScaleChem Analysis Calculations.*

Analyzing the Results

Once the calculation is done, the **Reconciled Gas** column displays the results at equilibrium conditions.



To the right you can see the results summarized in the **Summary Box**.

The top section contains the **Stream Parameters** information. In this example, the software performed an equilibrium calculation at 15.556ºC and 1.00231 atm.

The **Phase amounts** section shows the distribution of species in the different phases. This analysis contains two phases: aqueous and vapor.

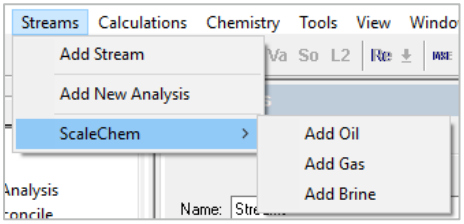
The **Aqueous Phase Properties** information shows the computed pH, ionic strength, and density of the solution.

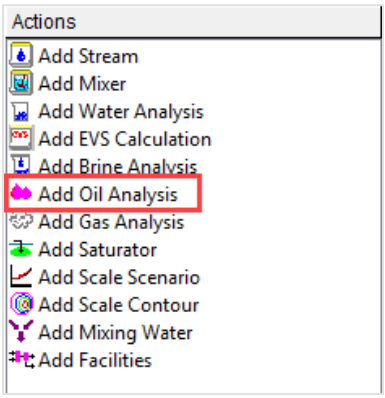
3. Click on the **Report** tab. Here you will see a more complete representation of the results at equilibrium.

Section 12. Entering an Oil Analysis in ScaleChem Analyzer

13.1. Entering Data for an Oil Analysis

To add an **Oil Analysis,** go to the toolbar menu and click on **Streams** > **ScaleChem > Add Oil,** or by selecting the **Add Oil Analysis** icon in the Actions Pane.



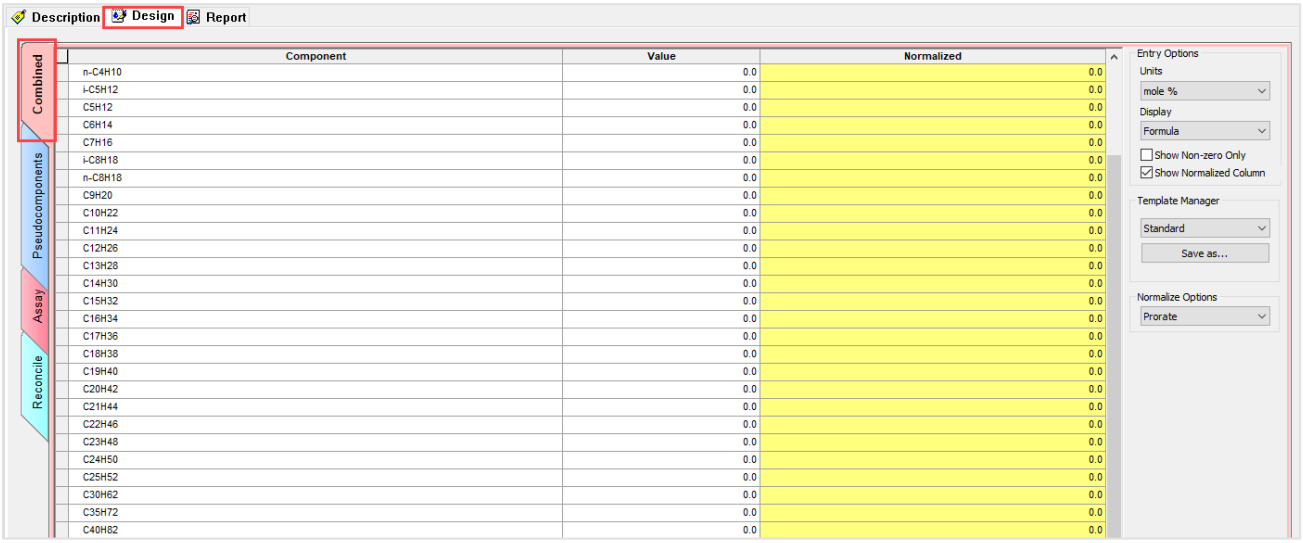


You will see four different tabs for this analysis. The **Description, Design, Definition** and **Report** tab.

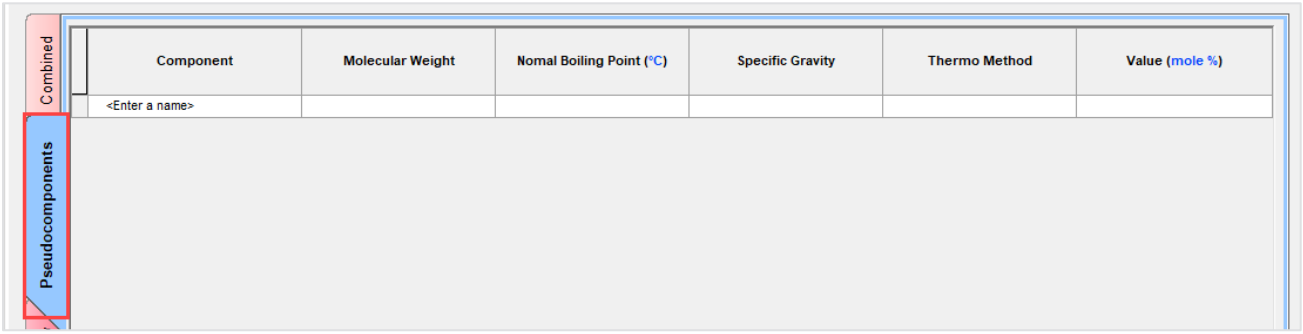
The oil analysis opens in the **Design** tab, which has 4 different sub-tabs: **Combined, Pseudocomponents, Assay** and **Reconcile.**

In the **Combined** (red) sub-tab, pure components (organic and inorganic) are entered. If there is a component that is not present in the prepopulated grid, simply click on the white grid and type the species of interest, using the formula name or its name, as has been shown in the previous sections. Let's say for example, you want to add Isooctane. Type isooctane or i-C8H18 in the white cell to add it to the list.

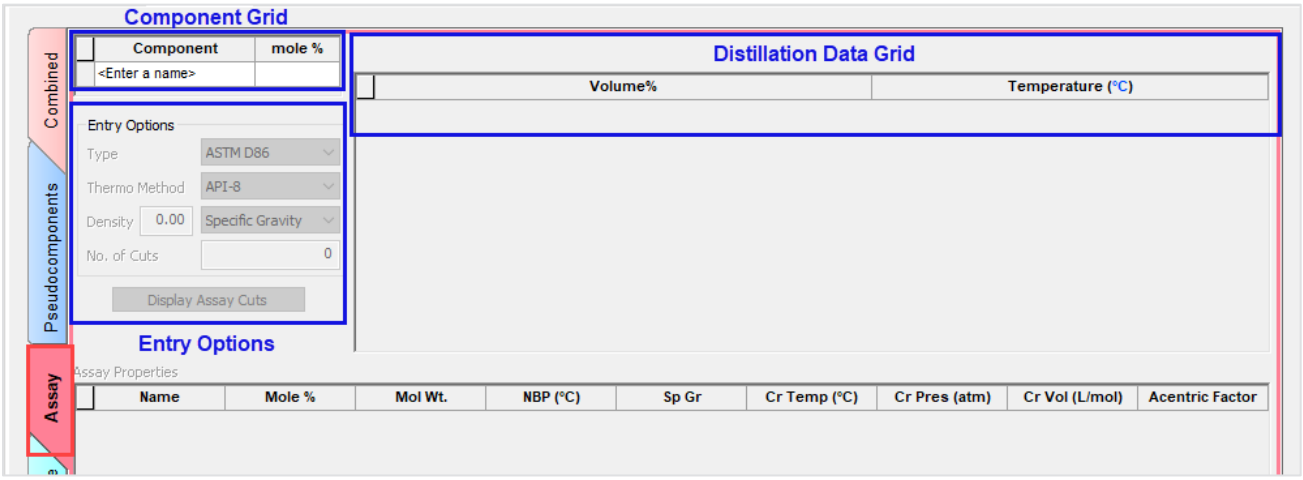
Also, you can use the **show non-zero only** option to hide all the zero values – since they are not needed.



In the **Pseudocomponents** (blue) sub-tab, you can enter pseudocomponents. Here you need to provide the molecular weight, NBP, SG, Thermodynamic Method and the mole% information.



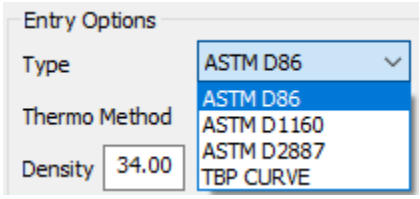
In the **Assay** (red) sub-tab, distillation curves can be entered. The Assay screen contains three data entry grids: Component, Entry Options and Distillation Data.



Component Grid: In the component grid you can name your assay. No more than 5 letters are allowed for the name. The mole% instructs the software that the mole% entered represents the total hydrocarbon mass.

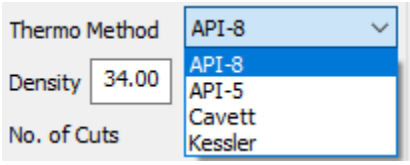
Entry Options Grid: In this grid there are four pieces of information that the user needs to fill out: The Assay Type, the Thermo Method, Density and No. of Cuts.

There are four Assay types. These are experimental methods used to create distillation curves.



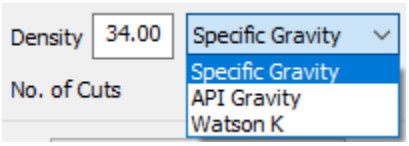
- **ASTM D86** runs at atmospheric pressures and is used for all oil types
- **ASTM D1160** runs at vacuum pressure and is used for heavy oils
- **ASTM D2887** runs on a gas chromatograph and is used for light oils
- **TBP** is the true boiling point curve

There are also four methods for calculating thermodynamic properties, referred to as **Thermo Method** in the software, and these are: API-8, API-5, Cavett and Lee-Kessler.



- The **API-8** and **API-5** are methods that use specific gravity to determine critical parameters.
- **Cavett** is a method to determine critical parameters using the API gravity
- **Lee-Kessler** is a method to determine critical parameters by using the Watson K

There are thee average bulk density options: Specific Gravity, API gravity and Watson K.



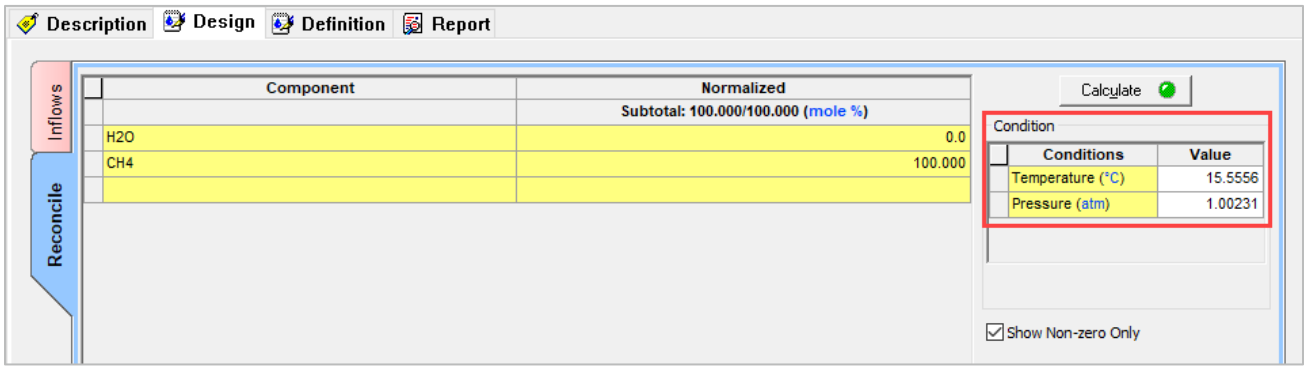
- **Specific Gravity** (SG) is the ratio of the material density to water. ScaleChem Analyzer requires specific gravity to be between 0.228 and 1.6.
- **API Gravity** is defined as API Gravity = (141.5/SG) – 131.5
- **Watson K** is a method that relates density to boiling point

A more detailed description of the different assay types, thermodynamic methods and density calculation methods is found in the Basic Definitions for the Oil Analysis Tool section on pages 375-378.

Distillation Data Grid: In this section the distillation data is entered.

And in the **Reconcile** tab, is where the equilibrium calculations are performed.

The **Reconcile** sub-tab is used to calculate the properties of the gas at the temperature and pressure conditions specified. By default, the values of temperature, and pressure are 60 ºF (15.56ºC) and 14.7 psia (1 atm).



13.2. Basic Definitions for the Oil Analysis Tool

13.2.1. Hydrocarbon Petroleum Fractions

Frequently a hydrocarbon analysis is the only data available for entry into the software. This analysis is usually a distillation curve where the volume distilled as a function of temperature of a petroleum fraction has been analyzed. This information must be turned into a vapor, organic and aqueous component for use in the simulator.

ASTM D86

Used for light and medium petroleum products and is carried out at atmospheric pressure. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline.

ASTM D1160

Used for heavier petroleum products and is often carried out under vacuum. Sometimes as low as 1 mm Hg. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline.

ASTM D2887

Uses gas chromatography to produce the distillation curve and is applicable to a wide range of petroleum products. The results are always reported on a volume percent basis. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline

True Boiling Point (TBP)

These curves, in practice, are difficult to obtain. The other methods are usually used instead.

13.2.2. Thermodynamic Methods (pseudo-components and petroleum fractions)

The methods used within OLI to calculate the critical temperature and pressure are the API, Cavett and Lee-Kesler methods.

API Method

Uses the specific gravity to estimate the critical parameters. The specific gravity, if not entered, can be estimated from the API gravity or the Watson K. The boiling points are taken from the assay data. API version 5 (API-5) and API version 8 (API-8) are currently supported.

The API method is selected by the user. Tc, Pc, and Vc are calculated as follows:

$$T_c = 24.2787 \times T_b^{0.58848} \times SG^{0.3596}$$

$$\ln P_c = \frac{3.12281\rho + 9}{T_b^{2.3125} SG^{2.3201}} \; if \; T_b < 1000\,°\mathrm{F}$$

Otherwise

$$\ln P_c = 8.3634 - \frac{0.566}{SG} - \left(0.24244 + \frac{2.2898}{SG}\right) + \left(\frac{0.11857}{SG^2}\right) \times 0.001 \times T_b$$
$$+ \left(1.4685 + \frac{3.648}{SG} + \frac{0.47127}{SG^2}\right) \times \left|\rho - 7 \times T_b^2 - \left(0.42019 + \frac{1.6977}{SG^2}\right)\right| \rho - 10 \times T_b^3$$

$$V_c = \frac{Z_c \times T_c \times 10.73}{P_c}$$

Where,

Tc = Critical temperature in Rankine
Pc = Critical pressure in psia
Zc = Critical compressibility factor

$$Z_c = \frac{1}{3.43 + 6.7\rho - 9 \times \Delta^2}$$

And

$$\Delta = \frac{8.75 + 1.978(\log T_b) \times T_b}{1.8} \; if \; T_c < 536.67 \; R$$

If 536.67<Tc<593 R, the above result for Δ is multiplied by f:

$$f = \left(T_c - \frac{536.67}{T_c - T_b}\right)^{0.38}$$

If Tc>593 R,

$$\Delta = \left(\frac{(0.98907 \times SG)(\Delta - 592.4439)}{MW}\right)^{0.5}$$

Cavett

This method uses the API gravity method to determine the critical properties. The API gravity, if not entered can be estimated from the actual specific gravity or the Watson K. The boiling points for the pseudo-components are taken from the assay.

If the Cavett method is chosen by the user, Tc, Pc and Vc are calculated as follows:

$$T_c = 768.0712 + 1.7133693 \times T_b - 0.0010834 \times T_b^2 - 0.008921258 \times T_b \times API + (3.8890584\rho - 7)$$
$$+ T_b^3 \times 5.309492\rho - 6 \times T_b^2 \times API + 3.27116\rho - 8 \times (T_b \times API)^2$$

$$logP_c = 2.829046 + 0.0009412 \times T_b - 3.047475\rho - 5 \times T_b^2 - 2.087611\rho - 5 \times API \times T_b + 1.5184103\rho - 9 \times T_b^3$$
$$+ 1.1047809\rho - 8 \times API \times T_b^2 - 4.82716\rho - 8 \times API^2 \times T_b + 1.3949619\rho - 10 \times (API \times T_b)^2$$

$$V_c = \frac{Z_c \times T_c \times 10.73}{P_c}$$

Where,
Tc = Critical temperature in Rankine
Pc = Critical pressure in psia
Zc = Critical compressibility factor

$$Z_c = \frac{1}{3.43 + 6.7\rho - 9 \times \Delta^2}$$

And

$$\Delta = \frac{8.75 + 1.978(\log T_b) \times T_b}{1.8} \; if \; T_c < 536.67 \; R$$

If 536.67<Tc<593 R, the above result for Δ is multiplied by f:

$$f = \left(T_c - \frac{536.67}{T_c - T_b}\right)^{0.38}$$

If Tc>593 R,

$$\Delta = \left(\frac{(0.98907 \times SG)(\Delta - 592.4439)}{MW}\right)^{0.5}$$

Lee-Kesler

This method uses the Watson K and the specific gravity (which can be estimated via the Watson K) to determine the critical parameters.

If the Lee-Kesler method is selected by the user, Tc, Pc, and Vc are calculated as follows:

$$T_c = 341.7 + \frac{811}{SG} + (0.4244 + 0.1174\,SG) \times T_b + (0.4669 - 3.2623\,SG) + \frac{100{,}000}{T_b}$$

$$\ln P_c = 8.3634 - \frac{0.566}{SG} - \left(0.24244 + \frac{2.2898}{SG} + \frac{0.11857}{SG^2}\right) \times 0.001 \times T_b + \left(1.4685 + \frac{3.648}{SG} + \frac{0.47127}{SG^2}\right) \times \left|\rho - 7 \times T_b^2 - \left(0.42019 + \frac{1.6977}{SG^2}\right)\right| \rho - 10 \times T_b^3$$

$$V_c = \frac{Z_c \times T_c \times 10.73}{P_c}$$

Where,
Tc = Critical temperature in Rankine
Pc = Critical pressure in psia
Zc = Critical compressibility factor

$$Z_c = \frac{1}{3.43 + 6.7\rho - 9 \times \Delta^2}$$

And

$$\Delta = \frac{8.75 + 1.978(\log T_b) \times T_b}{1.8} \; if \; T_c < 536.67 \; R$$

If 536.67<Tc<593 R, the above result for Δ is multiplied by f:

$$f = \left(T_c - \frac{536.67}{T_c - T_b}\right)^{0.38}$$

If Tc>593 R,

$$\Delta = \left(\frac{(0.98907 \times SG)(\Delta - 592.4439)}{MW}\right)^{0.5}$$

13.2.3. Average Bulk Density

Specific Gravity

Unitless, relative to pure water (H_2O) at 15 °C which has a density of 1.0 g/mL

API Gravity

Degrees API (°API). This is calculated via the following equation:

$$API(60F) = \left(\frac{141.5}{s.g.(60F)}\right) - 131.5$$

where, SG is the specific gravity at 60 °F.

Watson K

The Watson K has no units but is calculated via:

$$K = \left(\frac{NBP^{1/3}}{SG}\right)$$

where NBP is the normal Boiling point.

13.3. A Basic Gas Analysis

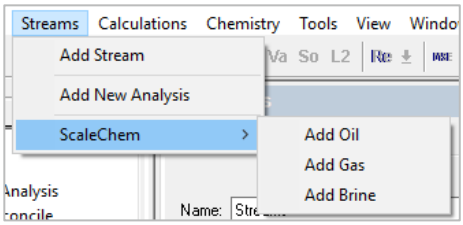
A brief introduction to the gas analysis tool will be shown in the example below. As we go through the example, the basic definitions, functionalities and reporting for the *Gas Analysis object* will be shown.

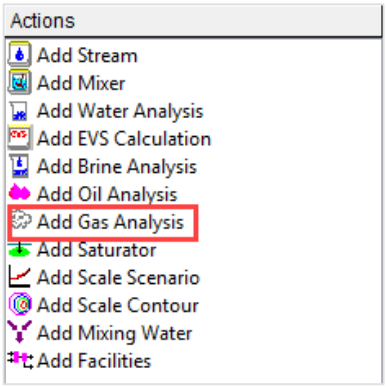
Example 62: Basic Gas Analysis

The Gas Analysis object provides a quick way to enter a pure-component hydrocarbon gas.

Setting the Gas Analysis

10. **Add a Gas Analysis.** Go to the toolbar menu and click on **Streams** > **ScaleChem > Add Gas,** or by selecting the **Add Brine Analysis** icon in the Actions Pane

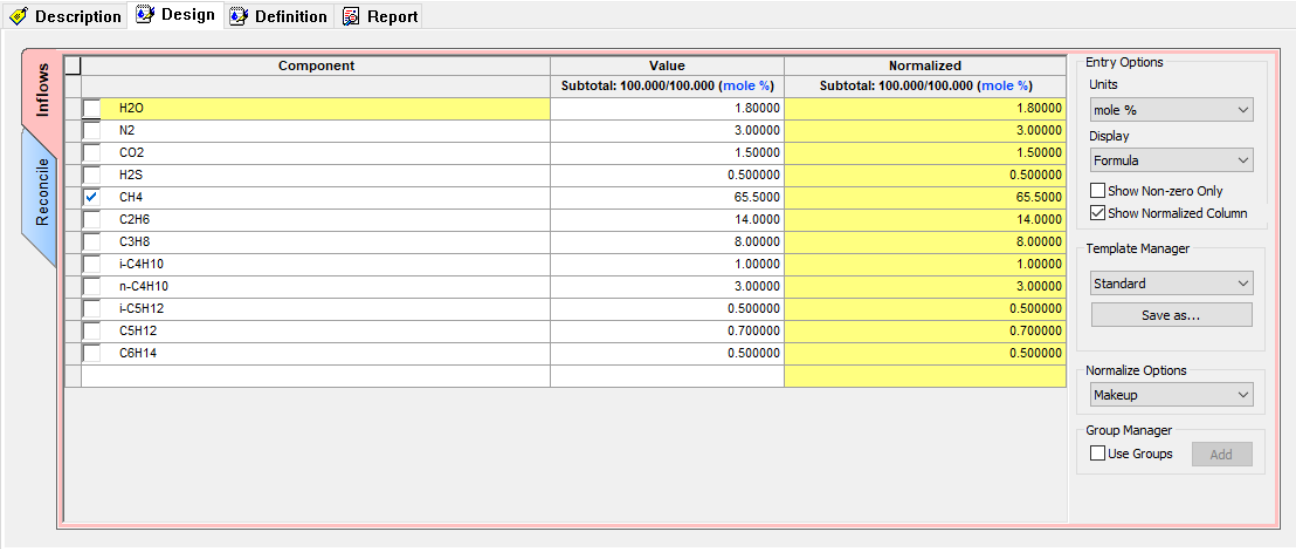




11. **Click** on the new Gas and press **<F2>** to change the name to *Gas Analysis*
12. Select the **AQ** thermodynamic Framework (default)
13. **Click** on the **Names Manager** Icon and select the **Formula** option (default)
14. **Click** on the **Units Manager** Icon, and select Metric, Concentration (default)
15. Under the **Inflows** Tab, enter the gas composition given in the table below

Gas Analysis Composition		
Formula	**Component Name**	**Mole %**
H2O	Water	1.80
N2	Nitrogen	3.00
CO2	Carbon Dioxide	1.50
H2S	Hydrogen Sulfide	0.50
CH4	Methane	65.5
C2H6	Ethane	14.0
C3H8	Propane	8.00
i-C4H10	Isobutane	1.00
n-C4H10	n-Butane	3.00
i-C5H12	Isopentane	0.50
C5H12	n-Pentane	0.70
C6H14	n-Hexane	0.50

Your screen should look like the image below:



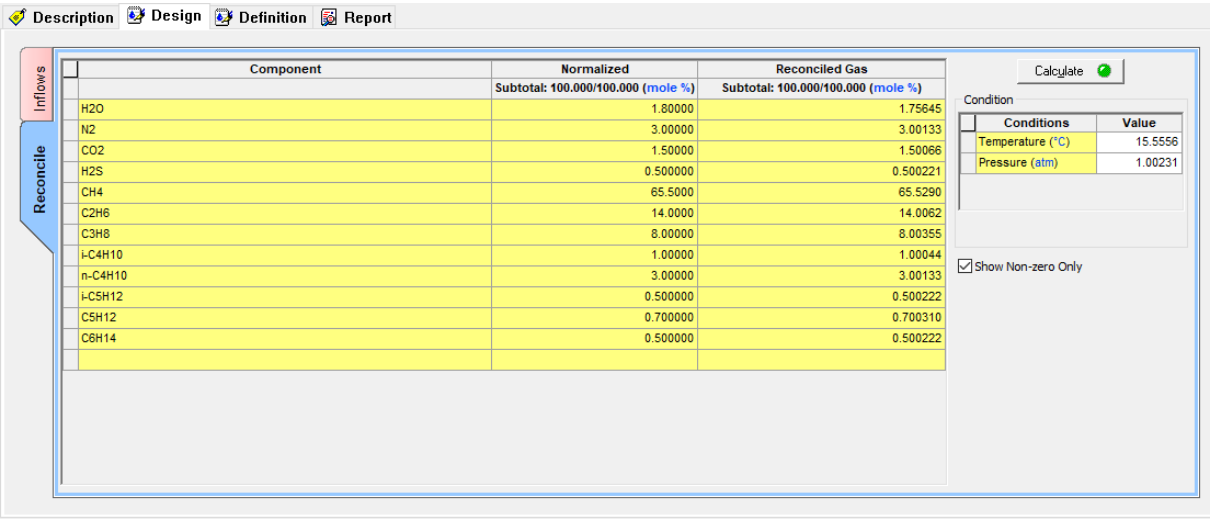
Note: There are several options to the right of the data entered.

4) **Entry options:** Here you can select the prefer units, and display name. You also have the options to show the non-zero values only – sometimes the composition of species is zero – and show normalized (yellow) column – this option is useful when the values don't add up to 100 mole%.

5) **Template manager:** Here you can select the standard (default) template or the extended template – which includes hydrocarbons with longer chains. You can also create and save your own template for future use.

6) **Normalize options:** When your analysis does not add up 100 mole% you can select between two options: Make-up and Prorate. For the Make-up option, the default gas used is CH4.

16. Click on the **Reconcile** (vertical blue tab). The reconciliation calculation will be calculated at 15.556 C and 1.00231 atm (standard conditions).

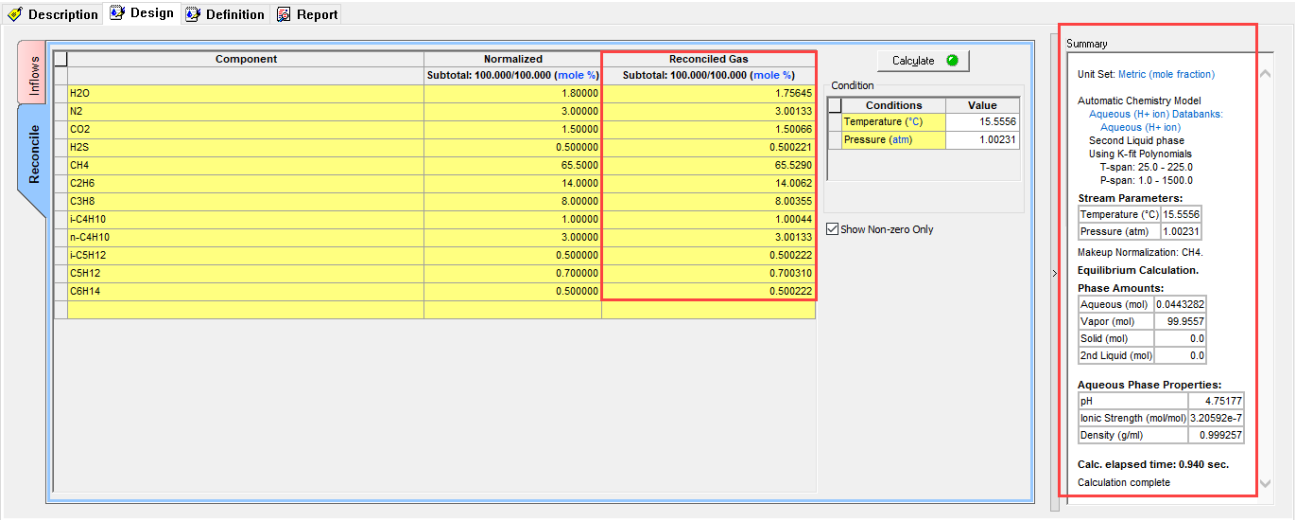


17. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

18. It is time to **save** your file (**File >Save as…) or** using the **save** icon in the tool bar. Create a new file and name it: *ScaleChem Analysis Calculations.*

Analyzing the Results

Once the calculation is done, the **Reconciled Gas** column displays the results at equilibrium conditions.



To the right you can see the results summarized in the **Summary Box**.

The top section contains the **Stream Parameters** information. In this example, the software performed the

The **Phase amounts** section shows the distribution of species in the different phases. This analysis contains two phases: aqueous and vapor.

The **Aqueous Phase Properties** information shows the computed pH, ionic strength, and density of the solution.

4. Click on the **Report** tab.

Here you will see a more complete representation of the results at equilibrium.

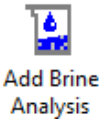
13.4. Putting together a complete calculation in ScaleChem Analyzer

Now that we have defined some terms, we are now ready to begin entering the information required to run a calculation. In this calculation we will be entering the concentrations of a single brine.

Task 1 – Create a Brine Analysis

In this tour we will show the main interface of a Brine Analysis, followed by an example of a brine (water analysis) and calculate its scale tendency. Let's begin. Steps for the simulation will be given with bullet points.

1. Add Brine Analysis from Actions Panel.



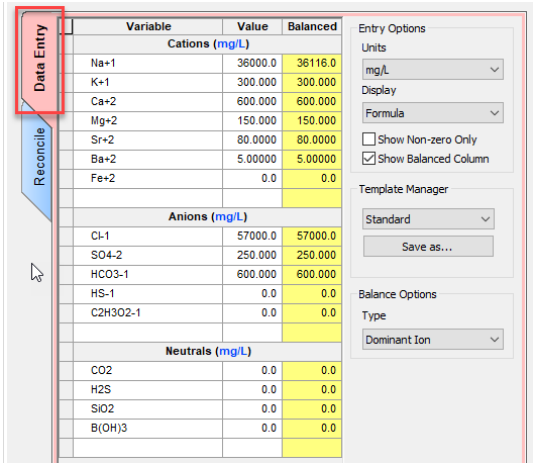
2. Click on the description Tab. If the ***Description*** tab is not currently displayed, click on the tab.

The chemistry of the brine needs to be entered. This information includes concentrations, alkalinity, pH and density. The table below describes the hypothetical water that we will create:

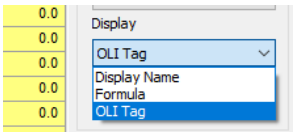
Brine Analysis

Cations mg/L		Anions mg/L		Measured Properties	
Na+1	36000	Cl-	57000	Temperature	25 C
K+1	300	SO4-2	250	Pressure	1 atm
Ca2+	600	H3CO3-1	600	pH	7.67
Mg2+	150			Alkalinity	600
Sr+2	80			Density (mg/L)	1.064
Ba+2	5			Total Dissolved Solids (mg/L)	96280

The screen should look like the image below

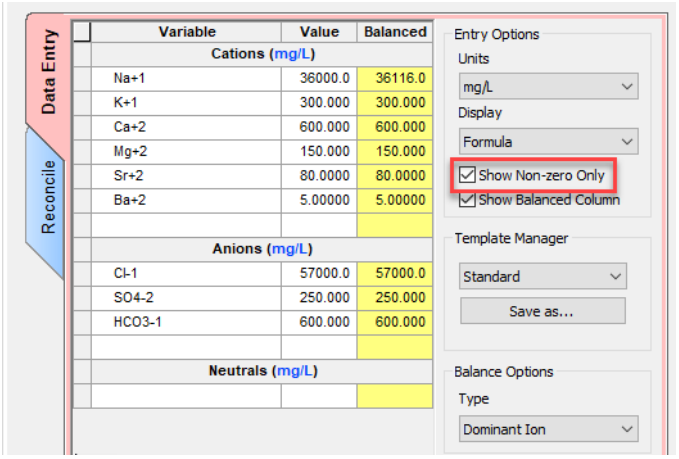


3. Select **Formula**



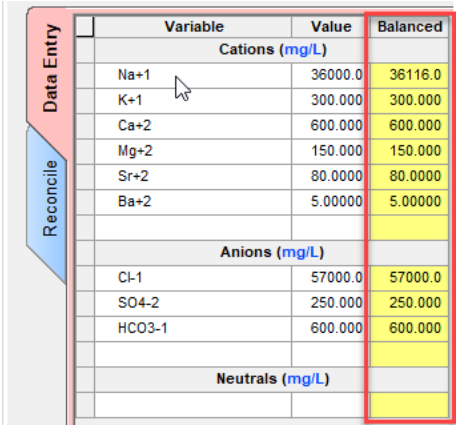
You can display an easier-to-read table by showing only the species that have actual concentrations.

4. Select the Show **non-zero only** box

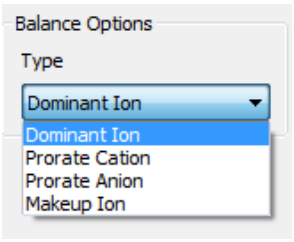


Another thing to consider is which **Balance Option** to select.

It is highly unusual for the data to be electrically neutral. Therefore, samples are reconciled for Electroneutrality. After entering each species concentrations, you will notice that Balanced values show up in the column next to values. The Column header says **Balanced.**

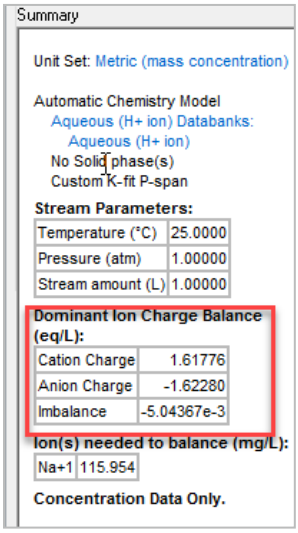


When adding or removing ions to balance charge, the solute mass is altered. We must decide as to whether we keep the mass of the solution constant (thereby adjusting the amount of water) or keeping the amount of water constant and adjusting the solution mass.



5. Select **Dominant Ion** balance option type.

You can review the Dominant Ion Charge and Ions needed to balance in the tables presented in the Summary Box.

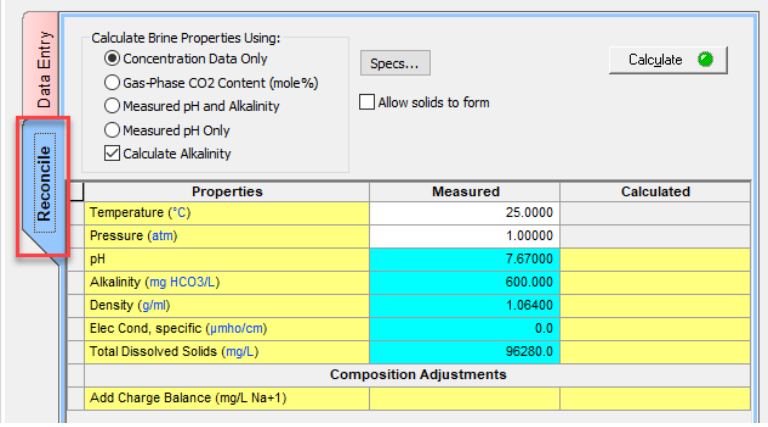


The summary box shows additional detail about the brine's chemistry and balance option. The stream parameters table shows default values. The Dominant Ion Charge Balance shows the total cations or anions, and the total imbalance.

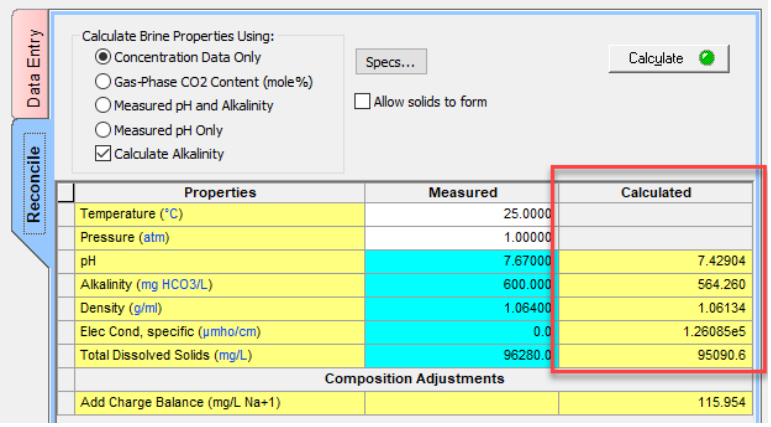
Now is time to enter the measured property data in the ***Reconcile Tab.***

6. Select ***Concentration Data Only*** Option
7. Check the ***Calculate Alkalinity*** box
8. Enter the measured pH (7.67), density (1.064 g/mL) and TDS (96280 mg/L)
9. Leave the ***Allow solids to form*** unchecked.

We will leave the **Allow solids to form** unchecked because generally the industry uses acid to preserve water samples, which prevent solids to form. Acidified samples contain the unprecipitated ion concentration, which is what we entered into the brine. In this step, we will eliminate solids because allowing solids to form would change the brine's composition significantly.

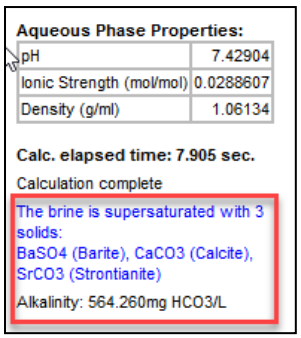


10. Select the **Calculate** button or press the **<F9>** key



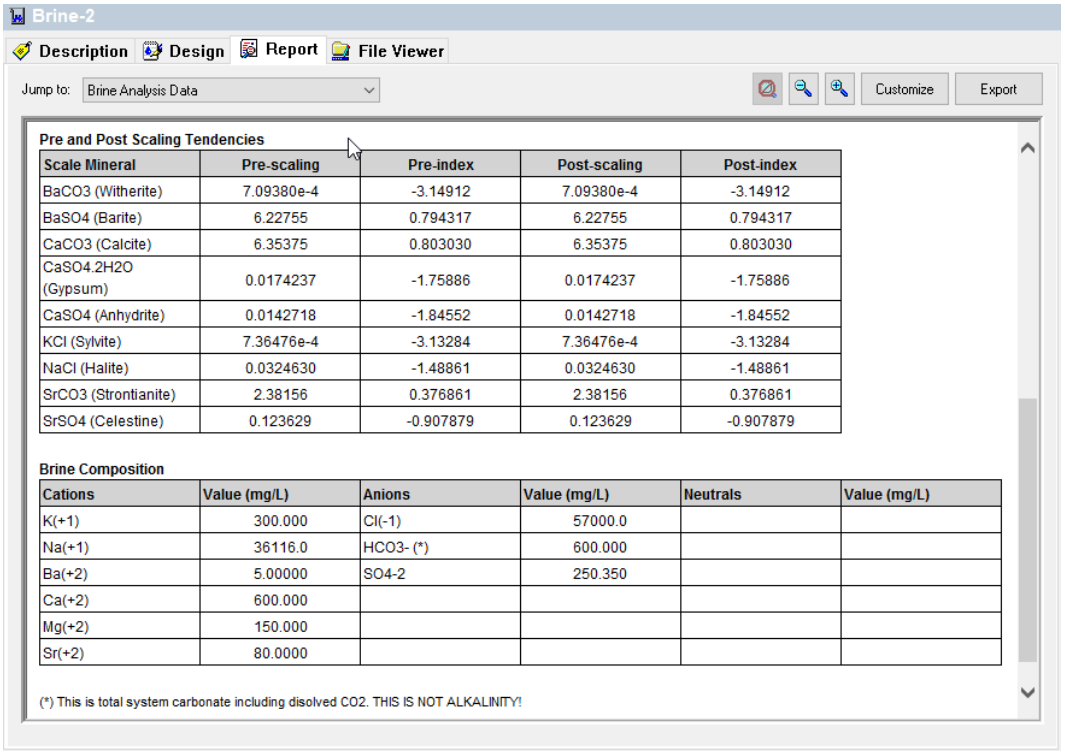
Once the calculation is done, the calculated column displays results based on the concentration that were entered in the Data Entry Tab. The calculated results of note are pH=7.43 and 564.26 mg/L as HCO3 in total alkalinity.

Experimental inaccuracies in sample measurement may, on occasion, result in a calculation that indicates that solid is supersaturated. This can normally be ignored providing that the super saturation is not excessive.



More details of the Brine composition can be found in the **Report** Tab.

In the Report tab, scroll down to the Pre and Post Scaling Tendencies, where you will find the results of Scaling Tendencies with Solids off.



Pre and Post Scaling Tendencies

Scale Mineral	Pre-scaling	Pre-index	Post-scaling	Post-index
BaCO3 (Witherite)	7.09380e-4	-3.14912	7.09380e-4	-3.14912
BaSO4 (Barite)	6.22755	0.794317	6.22755	0.794317
CaCO3 (Calcite)	6.35375	0.803030	6.35375	0.803030
CaSO4.2H2O (Gypsum)	0.0174237	-1.75886	0.0174237	-1.75886
CaSO4 (Anhydrite)	0.0142718	-1.84552	0.0142718	-1.84552
KCl (Sylvite)	7.36476e-4	-3.13284	7.36476e-4	-3.13284
NaCl (Halite)	0.0324630	-1.48861	0.0324630	-1.48861
SrCO3 (Strontianite)	2.38156	0.376861	2.38156	0.376861
SrSO4 (Celestine)	0.123629	-0.907879	0.123629	-0.907879

Brine Composition

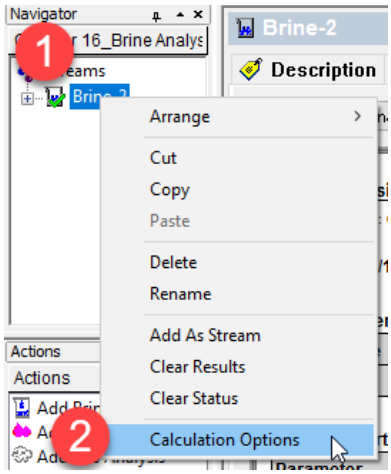
Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)
K(+1)	300.000	Cl(-1)	57000.0		
Na(+1)	36116.0	HCO3- (*)	600.000		
Ba(+2)	5.00000	SO4-2	250.350		
Ca(+2)	600.000				
Mg(+2)	150.000				
Sr(+2)	80.0000				

(*) This is total system carbonate including disolved CO2. THIS IS NOT ALKALINITY!

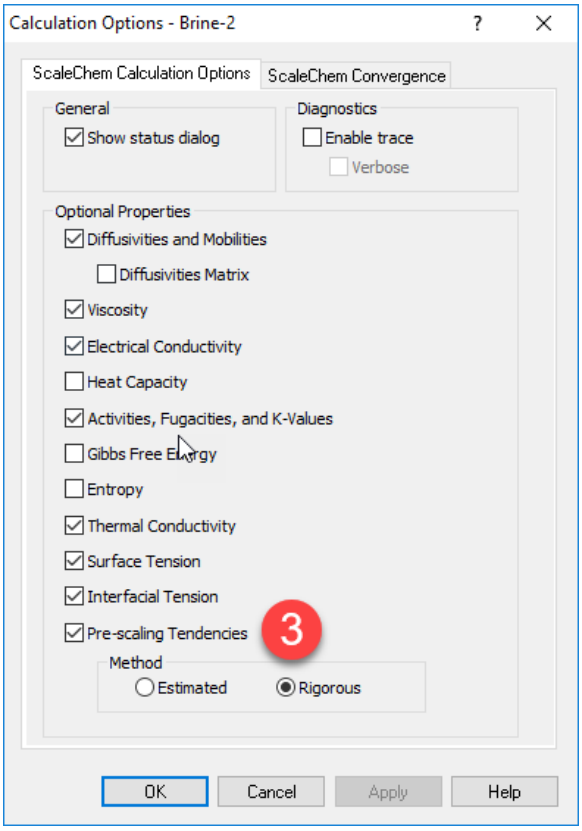
If we would have allowed solids to form, these concentrations would not be as close to the initial values.

Note: If scaling tendencies did not show up in the Report Tab, follow these steps:

11. Right click on the brine analysis icon
12. Select ***Calculation Options***



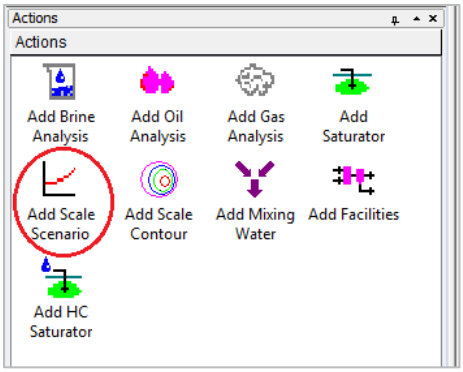
13. Enable ***Pre-scaling Tendencies***



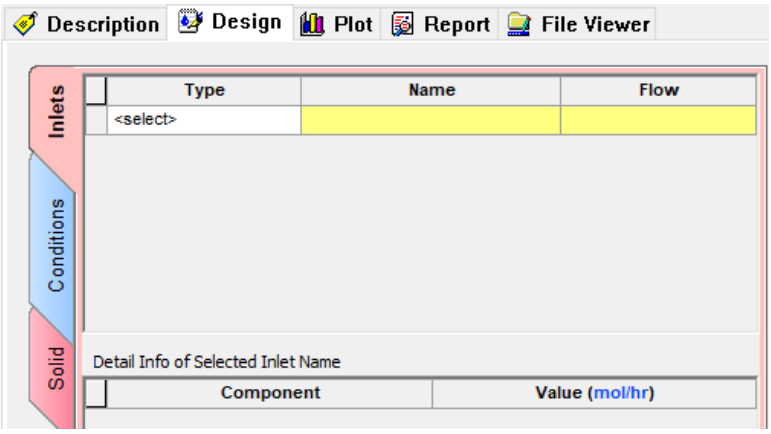
Task 2 – Create a Scaling Scenario

The next task is to calculate the brine scaling tendencies. Once the Brine Analysis data is entered and the sample reconciled, we can begin the ***Scaling Scenario*** calculation.

1. Select ***Add Scale Scenario*** from Actions panel.



Once we add a ***Scale Scenario*** object, the software opens to a new ***Design*** screen containing three vertical tabs: ***Inlets, Conditions***, and ***Solid***. We will work in each of these sections to set up the scaling calculation.



Inlet Tab

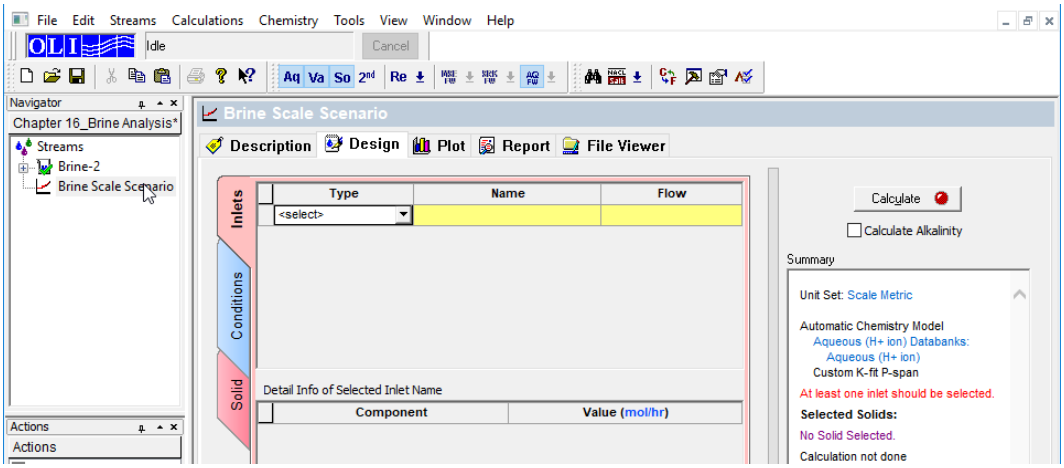
Type You can select the brine, gas or hydrocarbon of interest

Name Click in the Name field. As you position the cursor in the field, a Down Arrow will appear. You can then select from a list of brines, gases or oils already entered into this ScaleChem Analyzer document.

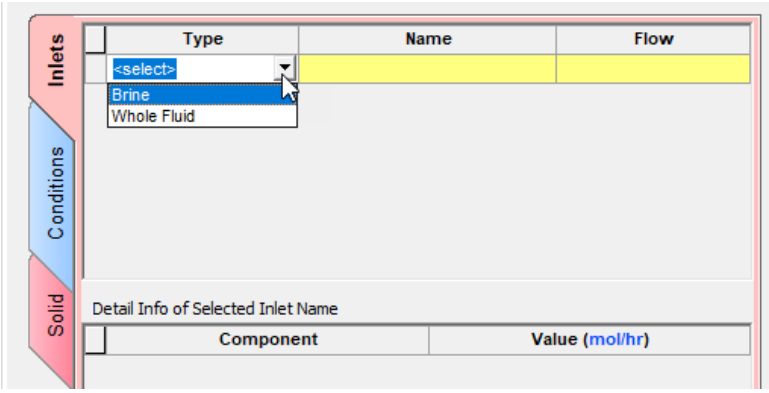
Flow Enter the flow rate for the gas, hydrocarbon or brine.

2. Click on the **Description** tab and rename the Scale Scenario as " Brine Scale Scenario".
3. Then click the **Design** tab.

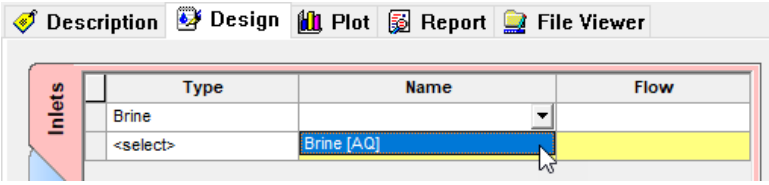
Your screen should now look like image below.



4. Select the ***Inlets*** tab
5. Select the right corner of the first cell in the Type column then select Brine (bbl/day)



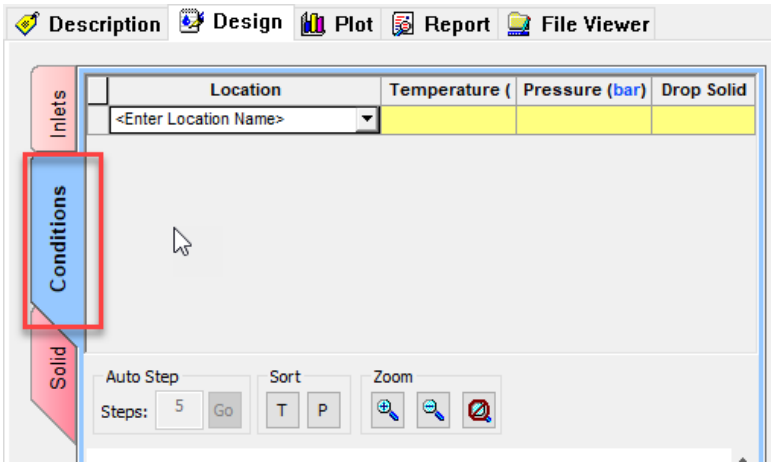
6. Select Brine from the drop-down menu in the Name column.



7. Enter 1400 (bbl/day) in the Flow Column. Please change units if necessary.

Conditions Tab

8. Select the ***Conditions*** Tab (vertical blue tab on the left-hand side of the Design screen)



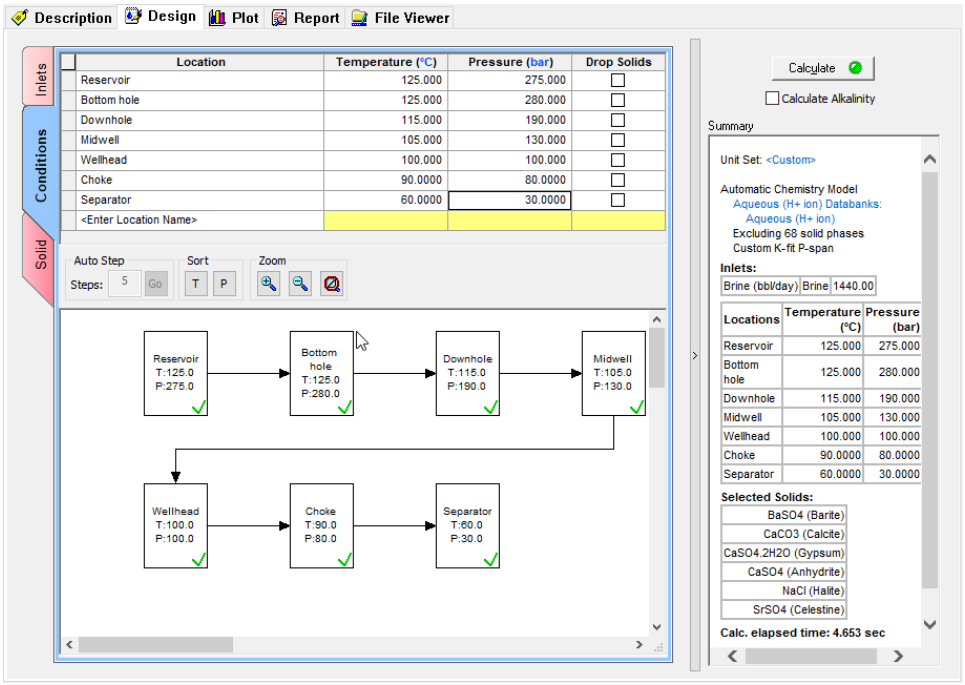
The ***Conditions*** section is where we enter points along the production scheme. The first column is Location. We can use the dropdown menu in each row to select a location or type in our own location name.

9. Type in the following conditions or use the dropdown menu within the Location cells.

Scale Scenario Locations

Location	Temperature (C)	Pressue (bar)
Reservoir	125	275
Bottomhole	125	280
Downhole	115	190
Midwell	105	130
Wellhead	100	100
Choke	90	80
Separator	60	30

The diagram within the Conditions screen and the list of locations in the **Summary** box both show the locations in the order that we entered. This screen has options for zooming, auto steps, sorting by temperature or pressure, and dropping solids at particular conditions.



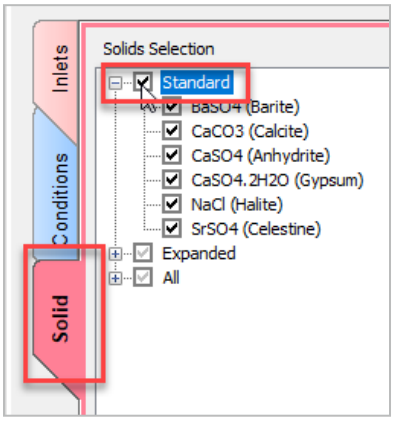
The graphical view clearly shows the five locations and their Temperature and pressure conditions.

The Drop Solids checkbox column at the very end of the grid is designed to help the users decide if they want to carry forward solids from certain locations or not.

Solid Tab

10. Select the ***Solid*** Tab
11. Make sure that the solid button in the menu bar is selected.

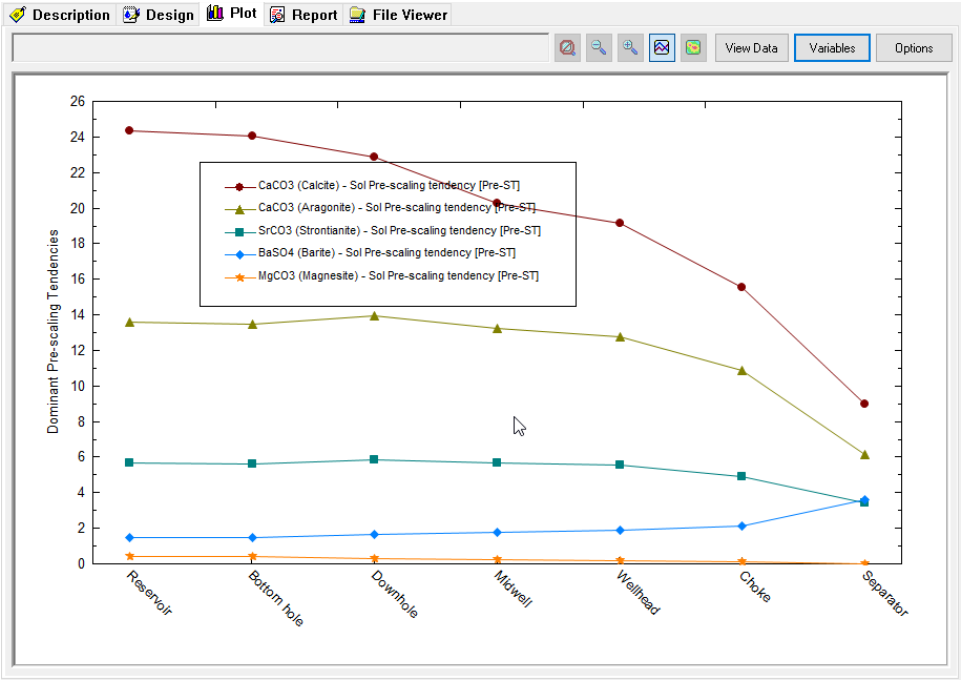
12. Select the Standard checkbox



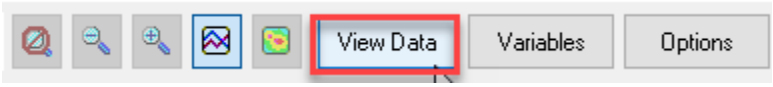
13. Press the **Calculate** button of select the <F9> key

14. Select the **Plot Tab**

You can customize which curves are visible by selecting the *Variables* button.



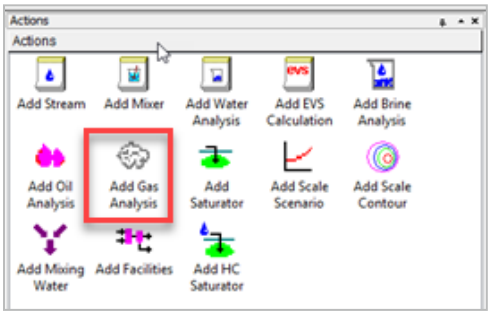
15. Select the View Data button



The *View Data* button shows the pre-scaling tendency at each location. We can copy the results of this table to a program like Excel by selecting the top left cell then selecting <Ctrl>+<C> on the keyboard.

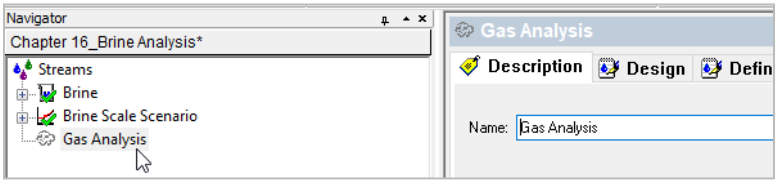
Task 3 – Create a Gas Analysis

1. Double click on the ***Add Gas Analysis*** object in the Actions Panel



This adds a Gas object to the Navigator panel.

2. Select the **Description** tab, then rename the object Gas Analysis.

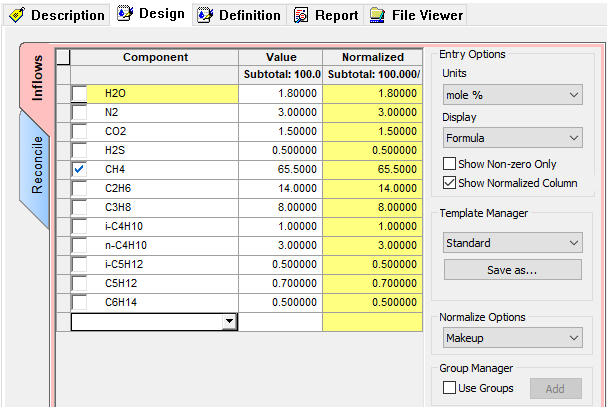


Enter the following composition and values in the Inflows grid:

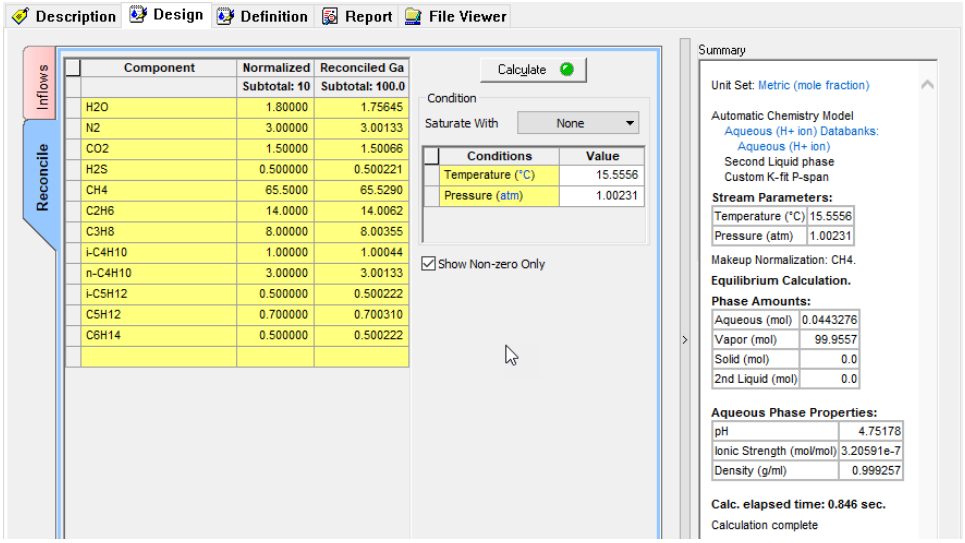
Gas Analysis

Formula	Component Name	mole %	Formula	Component Name	mole %
H2O	Water	1.80	C3H8	Propane	8.00
N2	Nitrogen	3.00	i-C4H10	Isobutane	1.00
CO2	Carbon dioxide	1.50	n-C4H10	n-Butane	3.00
H2S	Hydrogen sulfide	0.50	i-C5H12	Isopentane	0.50
CH4	Methane	65.5	n-C5H12	n-Pentane	0.70
C2H6	Ethane	14.0	n-C6H14	n-Hexane	0.50

The *Inflows* grid will look like one of the two below, depending on the Names view you select.



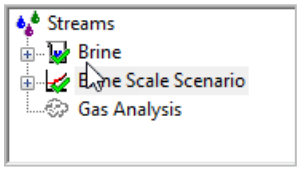
This is the extent of the gas entry step. There are modifications that can be part of the gas analysis entry step (in the Reconcile Tab), but in this case, they are not considered. Now that the gas is entered, the scale scenario considered in Task-2 will be recomputed.



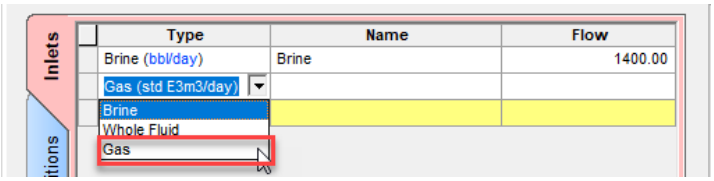
Task 4 – Recalculate Scale Scenario with Gas

The gas analysis will be added to the Scale Scenario so that it is considered during the scale evaluation.

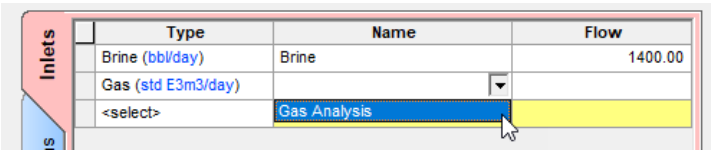
1. Select the Brine Scale Scenario icon in the navigator panel



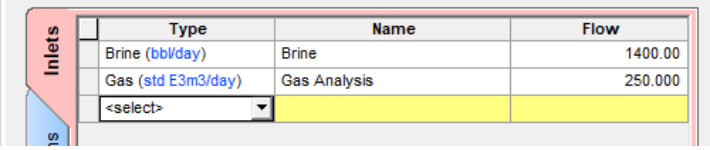
2. Select the **Design** Tab (horizontal tab) if not automatically sent there
3. Select the ***Inlets*** tab (vertical) if not automatically sent there
4. In the ***Type*** Column Add ***Gas***



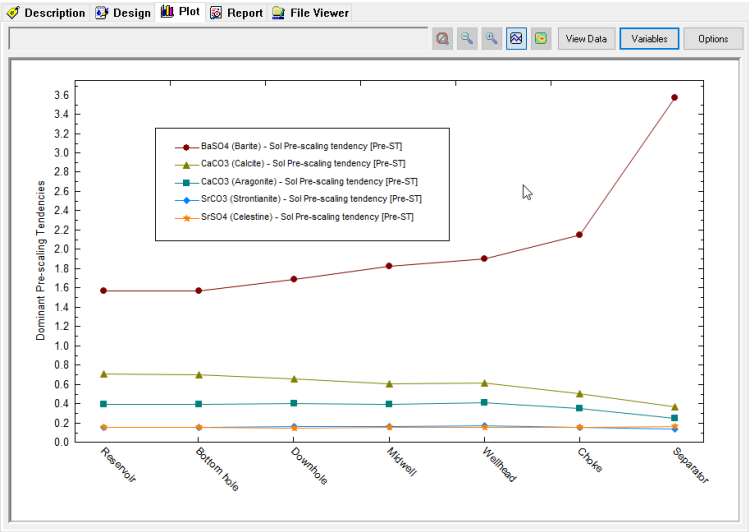
5. In the ***Name*** column select ***Gas Analysis***



6. Enter a flowrate of 250 std E3m3/day in the flow cell



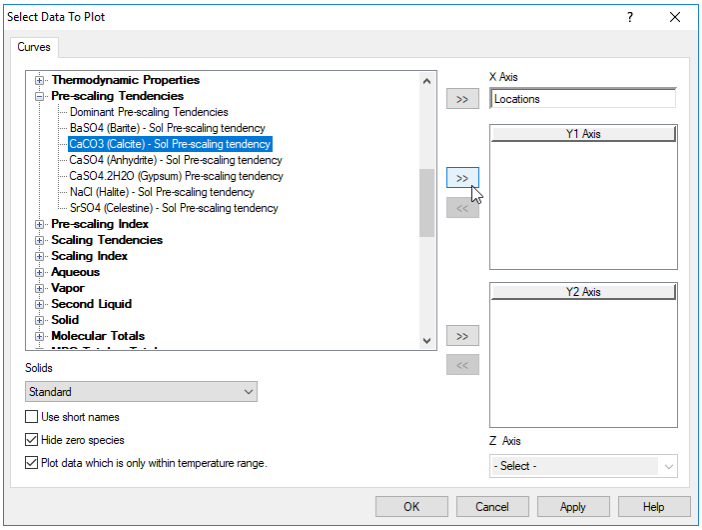
7. Calculate (Press <F9>)
8. Select **Plot** Tab



9. Select Variables button
10. Remove all the variables from the Y1 Axis and the Y2 axis by double-clicking on the variables (this removes then from the list). Alternatively, highlight each variable and click on the double-arrow.

You will replace the existing variables with the calcite pre-scaling tendency.

11. Expand the Pre-scaling Tendencies button by clicking the + sign
12. Double-click on the CaCO3 (Calcite) variable to move it to the Y1 Axis
13. Expand the Additional Stream Parameters and add pH to the Y2 axis
14. Click ***OK***



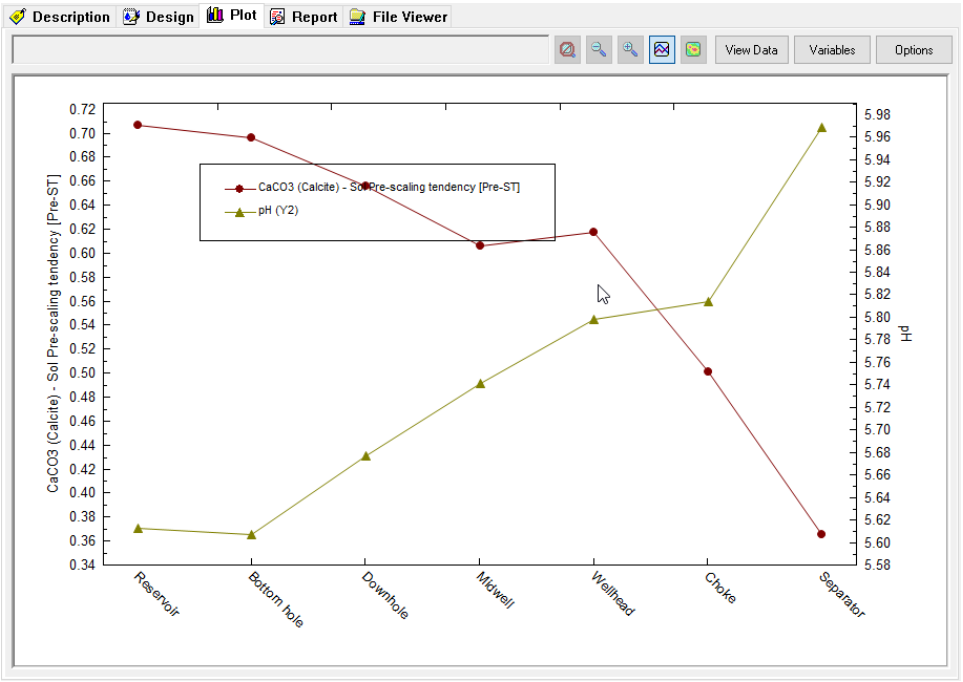
If you are in the *View Data* view, then the table should be similar to the one below.

	Locations	CaCO3 (Calcite) - Sol Pre-scaling tendency	pH
		Pre-ST	
1	Reservoir	0.705312	5.61211
2	Bottom hole	0.694891	5.60661
3	Downhole	0.655192	5.67654
4	Midwell	0.604697	5.74096
5	Wellhead	0.616784	5.79768
6	Choke	0.500689	5.81369
7	Separator	1.24448	6.14419

Calcite is sub-saturated (S<1) at all locations, except the separator.

15. Select the *View plot* button

The decreasing calcite saturation trend and the increasing pH is easier to see from the plot view.

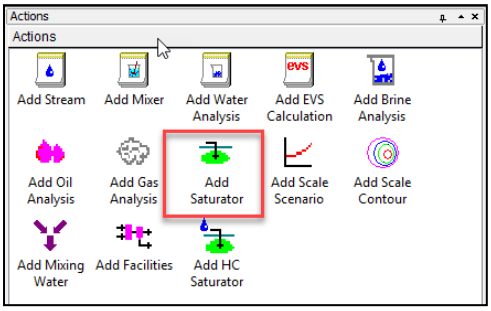


Task 5 – Creating a Saturator Object

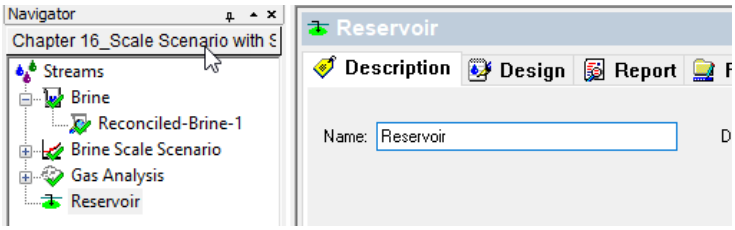
You will use the *Saturator* object to set the reservoir minerals at equilibrium with the produced fluid. It is reasonable, in some cases, to saturate the produced fluid with common evaporite and secondary minerals like CaCO3, CaSO4.H2O, FeCO3, and NaCl. This is based on the assumption that as the reservoir fluid flows through the rock pores, there is sufficient time to interact with the surface minerals. This is based on a second assumption that the vertical column of liquid and gas are in complete equilibrium and that the saturating minerals are distributed throughout the reservoir matrix, such that complete water-mineral contact is possible.

In this case we are going to simulate a particular oil & gas well: ABC. This well produces from calcite-cemented sandstone. Barite is also present in minor quantities in the rock matrix. You will, therefore, create a reservoir called ABC Reservoir and saturate the Brine (previously calculated) with calcite and barite. You will then recalculate the Brine Scale Scenario.

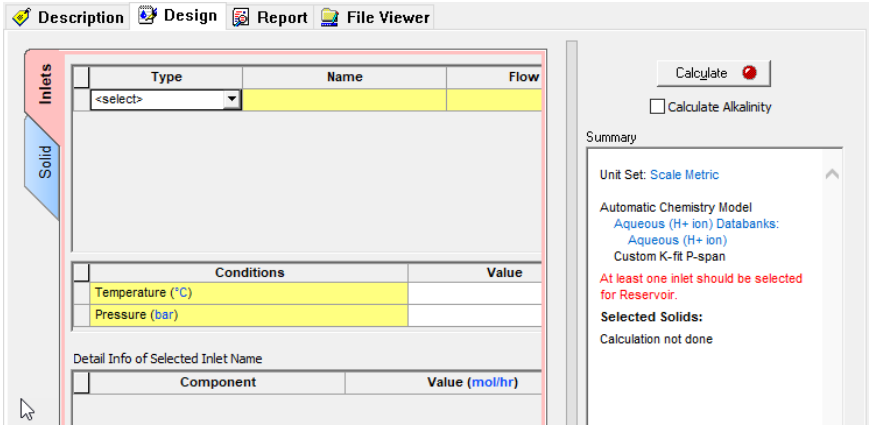
1. Add a Saturator Object



2. Select the **Description** Tab to rename the Object **Reservoir**



3. Select the **Design** Tab



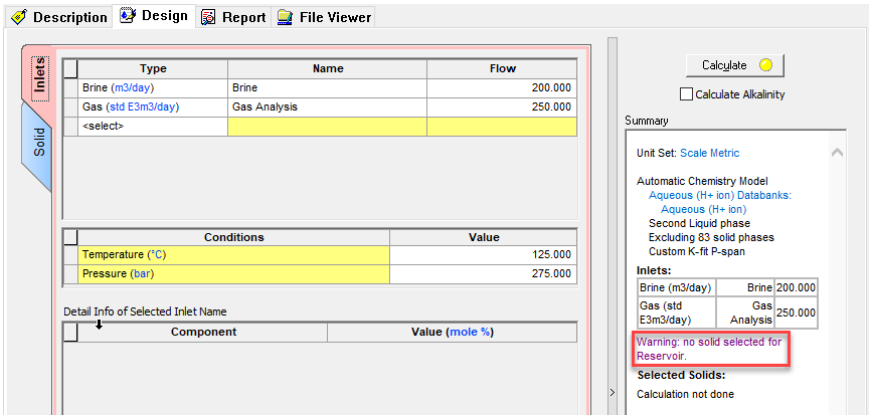
The Saturator has two vertical tabs: Inlets and Solid.

In the **Inlets** Tab the Fluids are entered in the top grid and the Conditions are entered in the bottom grid.

Solids are selected and saturated in the **Solid** Tab.

4. Enter the Brine calculated in Task 1
5. Enter the Gas calculated in Task 3

6. Enter the Reservoir conditions: 125 C and 275 bar in the conditions section.



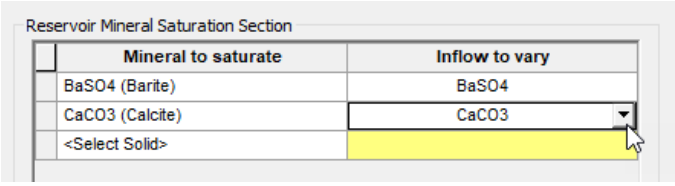
The Saturator's calculate button is yellow. This is because solids have not been selected yet. A warning also appears in the summary box. A yellow button is allowable, and a calculation may continue; it is merely a warning that the case is incomplete.

7. Select the ***Solid*** Tab (vertical tab)
8. Select the Standard checkbox

This last step instructs the software to allow the selected solids to precipitate – to include solid-liquid equilibrium equation in the calculation. It **does not** instruct the software to saturate these solids. Rather, if the phase is supersaturated, then it will precipitate. It is in the lower section that saturated solids are chosen.

This section contains two columns. The first (Solid) is the mineral to be saturated, and the second (inflow) is the cation and anion to be adjusted. If, for example, Barite is subsaturated in the existing fluid, then Ba+2 and SO4-2 are added. The amount of each added is stoichiometrically equivalent; one Ba+2 with one SO4-2, which maintains charge balance. If, for example, (again) Calcite is supersaturated, then equal mole amounts of Ca+2 and CO3-2 will be removed from the fluid. This inflow will be positive if the solid is subsaturated in the existing fluid, or it will be negative if the solid is supersaturated.

9. Use the Solid drop-down menus to select BaSO4 (Barite) and CaCO3 (Calcite) as solids to saturate
10. Use the Inflow drop-down menu to select BaSO4 and CaCO3 as solids to saturate (it should have been selected automatically).



At this point, the Calculate button is green indicating that the specifications are complete.

11. Calculate (or press the <F9> key)
12. Click the **Report** tab

The Saturator Report tab contains several tables: Saturation Details, Inlet Summary, Stream/Phase Properties, Pre and Post Scaling Tendencies, Brine Composition, Gas Composition, and if selected an inlet summary.

- Scroll down to the Pre and Post Scaling Tendencies Table

Pre and Post Scaling Tendencies

Formula	Mineral	Excess Solute	Excess Solute	Pre-Scale	Pre-Scale	Post-Scale	Post-Scale
		mg/L	lb/1000bbl	S, ST	SI, Index	S, ST	SI, Index
CaSO4.2H2O	Gypsum	0.0	0.0	0.0179366	-1.74626	0.0179365	-1.74626
SrSO4	Celestine	0.0	0.0	0.148191	-0.829178	0.148191	-0.829178
SrCO3	Strontianite			0.209852	-0.678087	0.209852	-0.678087
BaSO4	Barite	2.64658e-5	9.27644e-6	1.00000	1.82534e-6	1.00000	0.0
CaSO4	Anhydrite	0.0	0.0	0.0934633	-1.02936	0.0934633	-1.02936
CaCO3	Calcite	1.13495e-5	3.97806e-6	1.00000	-4.81593e-8	1.00000	0.0
Mg(OH)2	Brucite			4.98480e-4	-3.30235	4.98479e-4	-3.30235
NaCl	Halite	0.0	0.0	0.0245553	-1.60985	0.0245553	-1.60985
KCl	Sylvite			2.14382e-4	-3.66881	2.14382e-4	-3.66881

Excess solute or Max Scale: The solids amount forming at equilibrium.
Pre-Scale: The saturation ratio before solids precipitate.
Post-Scale: The saturation ratio AFTER solids precipitate (if solids are selected).
S, ST – Saturation, Scale Tendency: The ratio of the concentration (activity) to its solubility (S=1).
SI – Scale Index: Log(S).

The Max scale column shows that trace amounts of BaSO4 and CaCO3 are present in the water. These exceedingly small values (in the parts-per-trillion range) are the specifications or targets for the calculation. The software sets these target solid concentrations and then adjusts up or down, the BaSO4 and CaCO3 inflows until it reaches these targets. These part-per-trillion values may look arbitrary, but in fact the values are equivalent to 1e-10 moles of solid/kg water.

Notice also, that the pre-scale tendency for BaSO4 and CaCO3 are set to 1.0, by saturation definition. That is, these are not calculated, they are defined. The remaining scale tendencies are computed.

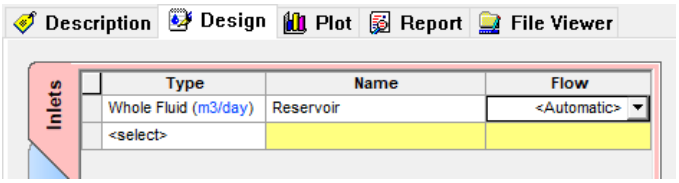
Task 6 – Recalculate the Scale Scenario with the Saturated Reservoir

Considerable time is spent creating what is hoped to be a more representative brine. The Brine is reconciled for charge balance, and where needed, alkalinity and pH; the gas is saturated with water as needed (though not done in this case), and lastly the fluids are set to equilibrium with important reservoir minerals. It is only after these steps are complete, and that there is confidence that the assumptions and calculations are representative of the process, that a final scaling calculation is run.

The **Reservoir** calculation contains the representative fluid. It is, therefore, the output of this calculation that will be used in all subsequent calculations. To access this output, a new Type of fluid, Whole Fluid is defined. The Whole Fluid type represents 100% of the contents of a previous calculation, regardless of phase.

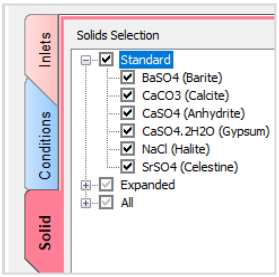
You will use the Whole Fluid from the Reservoir to rerun the scaling calculations.

1. Select *Brine Scale Scenario* in the Navigator Pane and rename it **Reservoir Scale Scenario**
2. Select the **Design** tab
3. In the ***Inlets*** tab in the **Type** column delete the Brine and Gas from the Type column
4. Add ***Whole Fluid***
5. In the **Name** column select ***Reservoir***
6. In the **Flow** column select <***Automatic***>

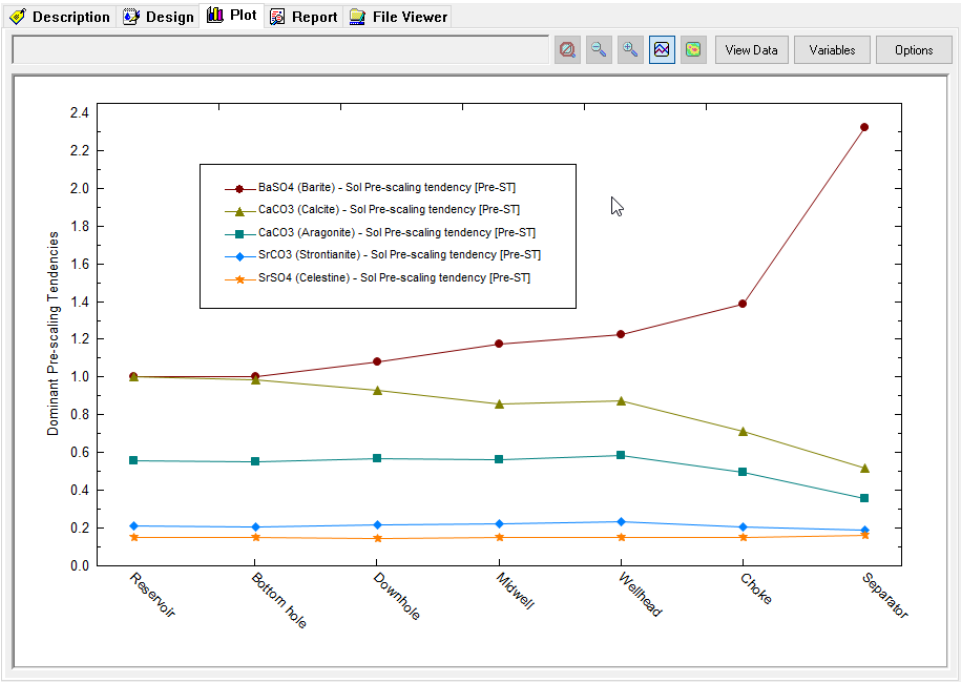


Note: The Whole Fluid type refers to all the phases within the fluid. The Automatic option takes the final flow rate phase of the separator and automatically enters this as the flow rate in the Scale Scenario calculation.

7. Go to the ***Solid*** tab and make sure that the Standard box is checked



8. Calculate (Press <F9>)
9. Select **Plot** tab and select *View Plot*



The Saturator is a tool for normalizing the thermodynamics of a reservoir system. The purpose of this calculation is to apply the constraint of solid-liquid equilibrium on a system to create a specific compositional starting point.

The basis of this calculation is that water in the pores of a rock matrix is at equilibrium with the mineral surface. Some questions to consider are whether it is reasonable to assume that a reservoir gas, oil, water, and rock

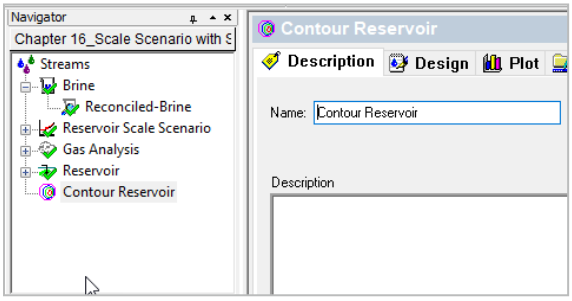
are in equilibrium. Furthermore, we should also consider over what vertical and radial distance we can make this claim.

Regardless of the inconsistencies, the industry widely accepts this approach. It is up to the analyst to decide if the Saturator produces a more representative fluid than the original data.

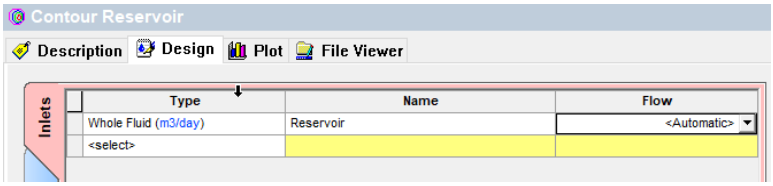
Task 7 – Add a Contour Diagram

An alternative to the *Scale Scenario* calculation is the *Contour Diagram*. The conditions defined in the Scale Scenario are specific to production locations, and generally no more than ten are entered. By comparison, the conditions defined in the Contour Diagram are a range of temperatures and pressures. The object then computes a matrix of temperature and pressure conditions and creates a presentation-quality contour diagram.

1. Add Scale Contour
2. Rename the Object **Contour Reservoir**



3. Select the **Design** Tab
4. Select the ***Inlets*** (vertical) tab
5. Select the bottom right corner of the 1st cell in the Inlet grid and choose ***Whole Fluid***
6. Select ***Reservoir*** in the 2nd column
7. Keep the ***<Automatic>*** flow rate option in the 3rd column

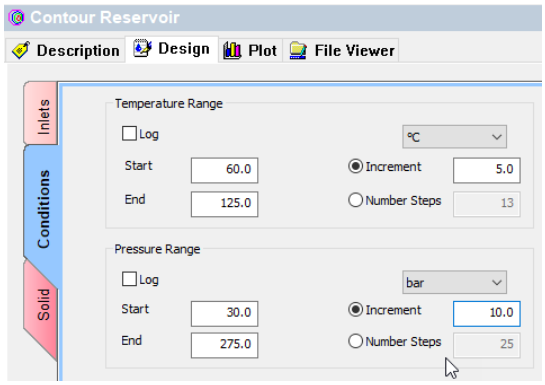


8. Click Conditions (vertical) tab

The minimum and maximum conditions are at the Separator 60C, 30 bar and Reservoir 125C, 275 bar. These are the start and end range of the study. To create a reasonable number of calculations (~300) and to keep the matrix somewhat symmetric, we will use increments of 2 C and 10 bar.

9. Change the Start to 60
10. Change the End to 125
11. Select the Increment radio button
12. Enter 5 as the increment
13. Uncheck the Log box (if it is checked)

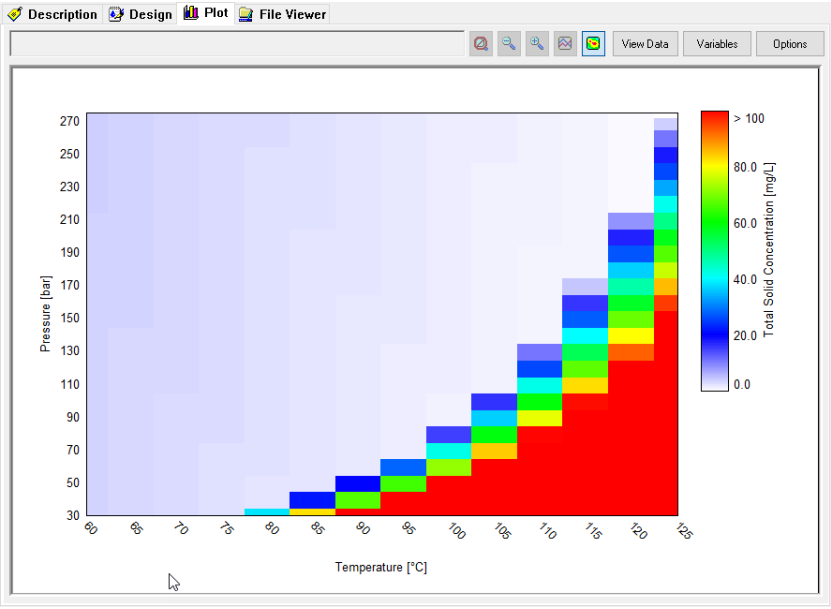
14. In the Pressure Range box, change the Start to 30
15. Change the End to 275
16. Select the Increment radio button (uncheck the Log box first)
17. Change the Increment to 10



This produces a matrix of 13 temperature and 15 pressure steps. This produces a 14x16 matrix, or 224 calculations.

	Temperature	Pressure
Units	°C	bar
Start	60.0	1.01325
Stop	125.0	10.1325
Step Size	5.0	0.60795
No. Steps	13.0	15.0
Calculations	224	

10. Select the ***Solid*** Tab
11. Check the Standard box
12. Calculate. The calculation should take less than 10 min to be complete
13. When calculation is done, go to the **Plot** tab



The default plot is the total solids forming. The color scale represents a different numerical range. The red cells indicate heavier solid precipitation, and the faint purple-white in the center and left of the screen indicate that little to no scale forms. The upper right corner is the Reservoir conditions (125C and 275 bar). The lower left represents Separator conditions (60C and 30 bar). At both points, minimal solids are computed to form. The fluid traveling through the piping traverses this plot as temperature and pressure decreases. Layering production conditions (e.g., early to late life) over this plot provides an indication as to whether production will be at risk now or in the future. For example, if the pressure decline is significant (e.g., 60 bar), then the fluid will be unstable at the higher temperatures (bottom of well).

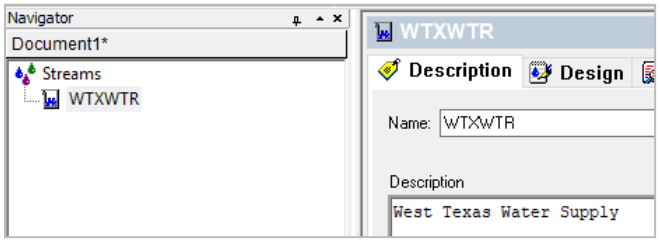
13.5. Overview of Brine, Gas and Oils and Introducing Mixer, and Saturator Objects

Other calculation options include the ability to mix waters at user specified ratios to find compatible waters, and the ability to saturate a water with respect to one or more solids to simulate reservoir conditions.

This chapter will cover the same calculation objects using fewer instructions and will introduce *Mixing, Saturator* and *Facility* Calculations. Its purpose is to reinforce what was learned in the previous chapter and to promote the anticipating of next steps when using the interface.

Task 1 – Add a Brine

1. Add a *Brine Analysis* from the Action Panel
2. Rename the Brine in the **Description** Tab, and name it WTXWTR

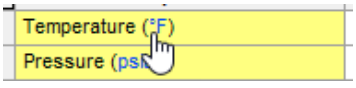


3. Go to the **Design** Tab and enter the following composition in the ***Data Entry*** (vertical) tab:

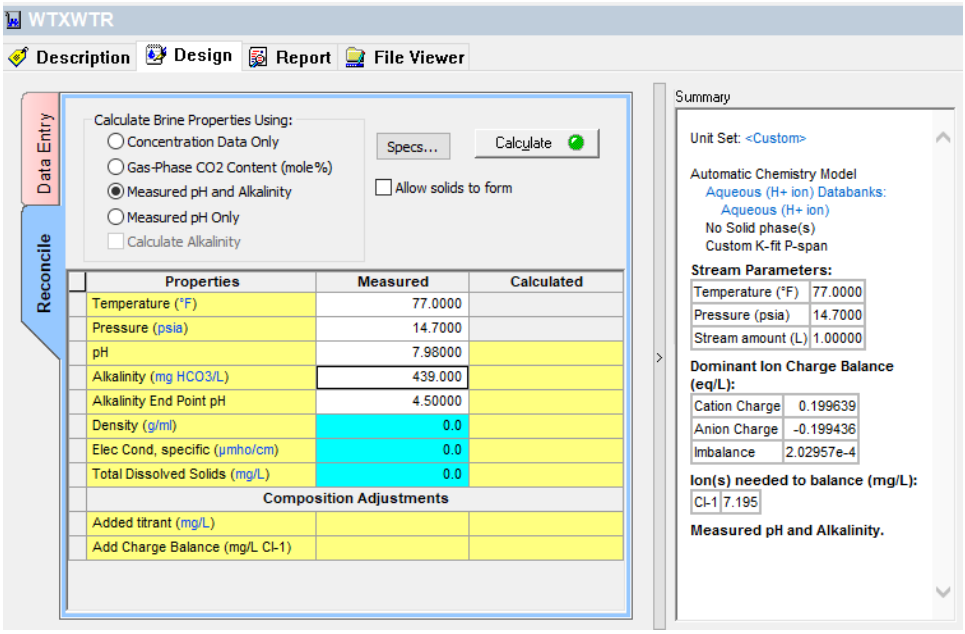
Name:	WTXWTR
Type of water:	Aquifer Water
Comment:	West Texas Water Supply

Species	Concentration	
Na^{+}	3074	mg/L
Ca^{+2}	910	mg/L
Mg^{+2}	249	mg/L
Fe^{+2}	0.77	mg/L
Cl^{-1}	4474	mg/L
SO_4^{-2}	2960	mg/L
HCO_3^{-}	439	mg/L
HS^{-1}	146.2	mg/L

4. Check the *Show non-zero Only* box (under Entry Options)
5. Go to the ***Reconcile*** (vertical) tab
6. Select the measured pH and alkalinity Option
7. Enter the following conditions (change units if necessary)
   - To change units just click on the hyperlink next to the variable that you want to change.



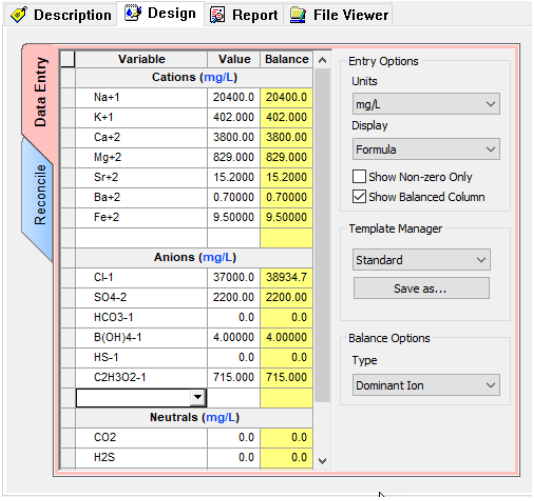
Temperature	77 F
Pressure	14.7 psia
pH	7.98
Alkalinity end Point pH	439 mg/L as HCO3-
Titration pH	4.5
Density	(will be estimated)



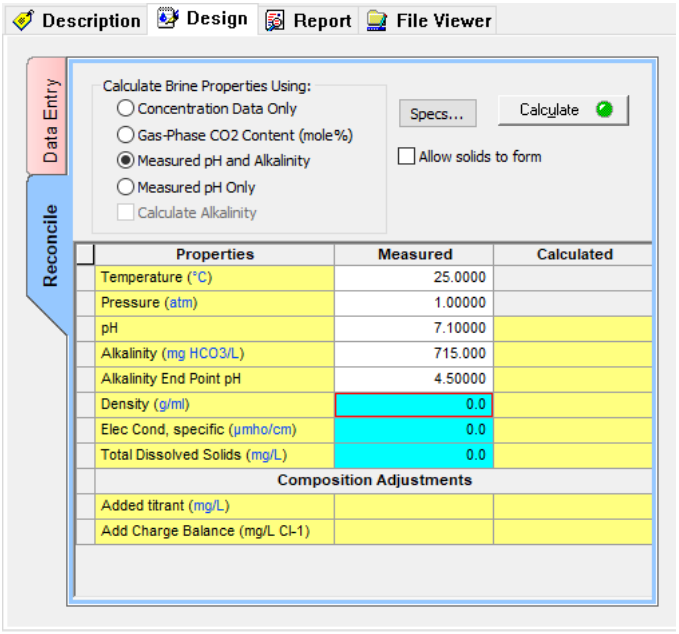
8. Click the **Calculate** Button

Task 2 – Add a Second Brine

1. Add a Brine Analysis
2. Enter the composition given below in the ***Data Entry*** (vertical) Tab



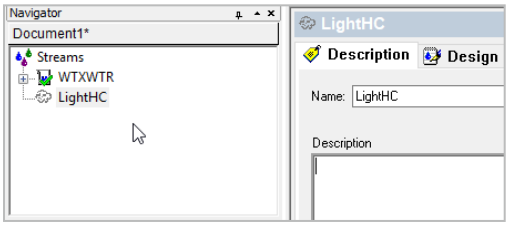
3. Go to ***Reconcile*** tab
4. Select *pH and Alkalinity* calculation type, and enter the information provided in the figure below.



5. Click the Calculate button

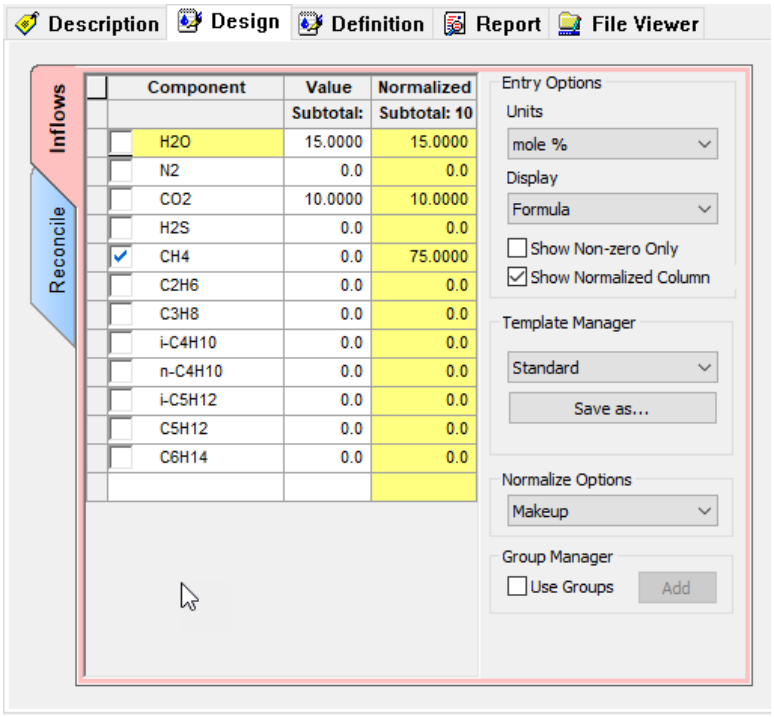
Task 3 – Add a Gas

1. From the Actions Panel click on *Add Gas Analysis*
2. Input the name in the **Description** tab. Name it *LightHC*



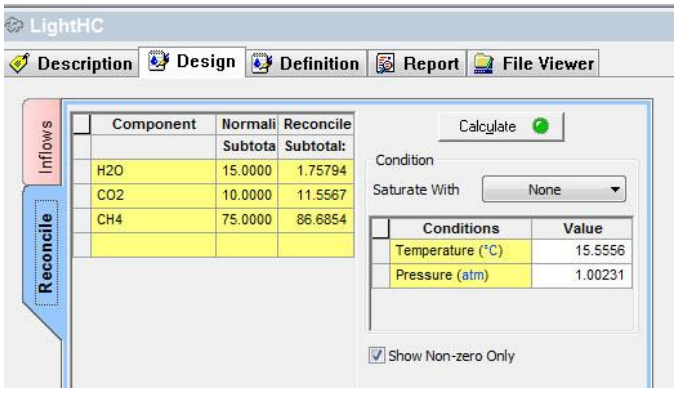
3. Go to the **Design** Tab and enter the following composition in the ***Inflows*** (vertical) tab
4. Enter the following composition:

Component	Composition
Carbon dioxide (CO2)	10 mole %
Water (H2O)	15 mole %



ScaleChem Analyzer will assume that all of the hydrocarbon gas is methane (CH4). So, in this case the software normalizes the gas adding 75 mole% of CH4.

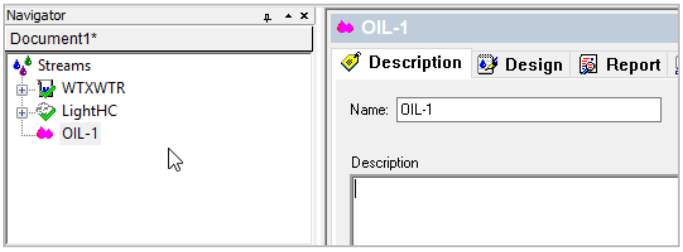
5. Go to the ***Reconcile*** (vertical) Tab



6. Leave the default conditions for Temperature and Pressure
7. Calculate

Task 4 – Add an Oil

1. From the Actions Panel click *Add Oil Analysis*.
2. Enter the name in the **Description** Tab. Name it *OIL-1*



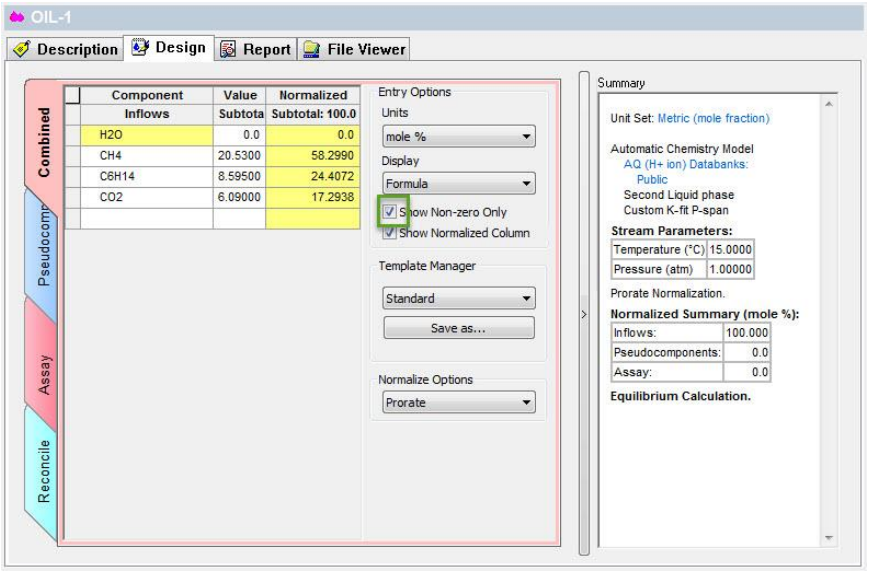
3. Go to the **Design** tab
    a. This tab is divided into:
        i. Combined Tab: Here pure components (organic and inorganic) are entered.
        ii. Pseudocomponent Tab
        iii. Assay Tab: Here distillation curves are entered.
        iv. Reconcile Tab

For this example, we will enter pure component and pseudocomponent data.

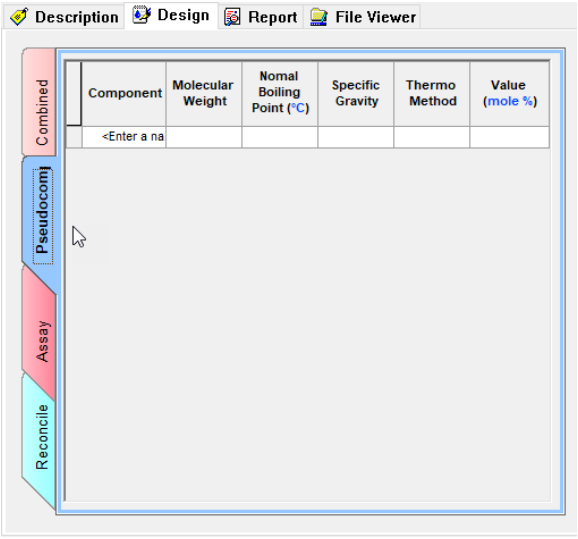
4. Go to the ***Combined*** tab
5. Enter the following composition:

Methane (CH4)	20.53mole %
Hexane (C6H14)	8.595mole %
CO2	6.09mole %

Note: You will have to scroll down to find the CO2 entry.



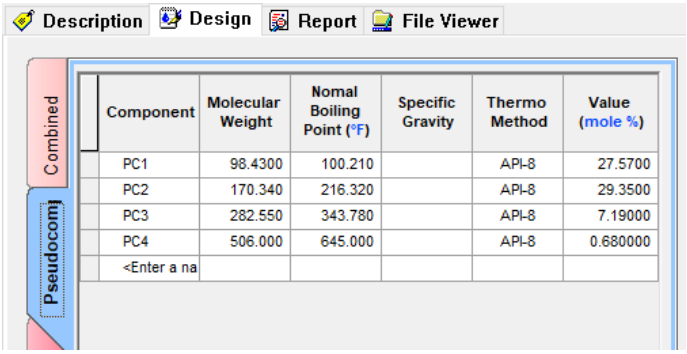
6. Go to the ***Pseudocomponent*** tab



7. Add the following pseudocomponents:

Name	MW (g/mol)	nBP (F)	Thermo Method	Value mole %
PC1	98.43	100.21	API	27.57
PC2	170.34	216.32	API	29.35
PC3	282.55	343.78	API	7.19
PC4	506.0	645.00	API	0.68

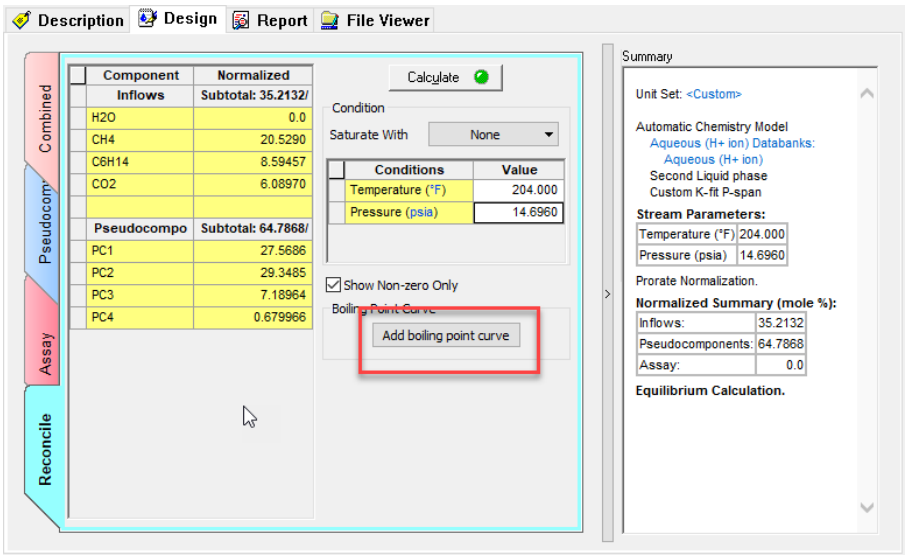
The completed input looks like this:



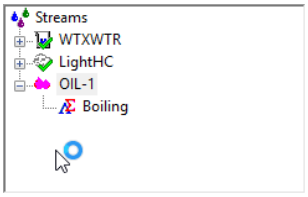
8. Go to the ***Reconcile*** (vertical) tab

   Here you will see how well the pseudocomponent will predict the phase behavior of the hydrocarbon sample.

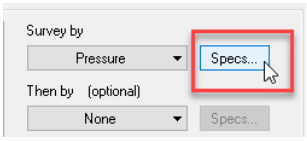
9. In the Condition option (below calculate button) enter T=204 F and P=1 atm.
10. Click on the *Add boiling point curve* (red square shown)



11. A new calculation appears in the navigation panel below OIL1 Object.



12. This is a survey by Pressure. Click on the specs button and specify the conditions below. Change pressure units if necessary.

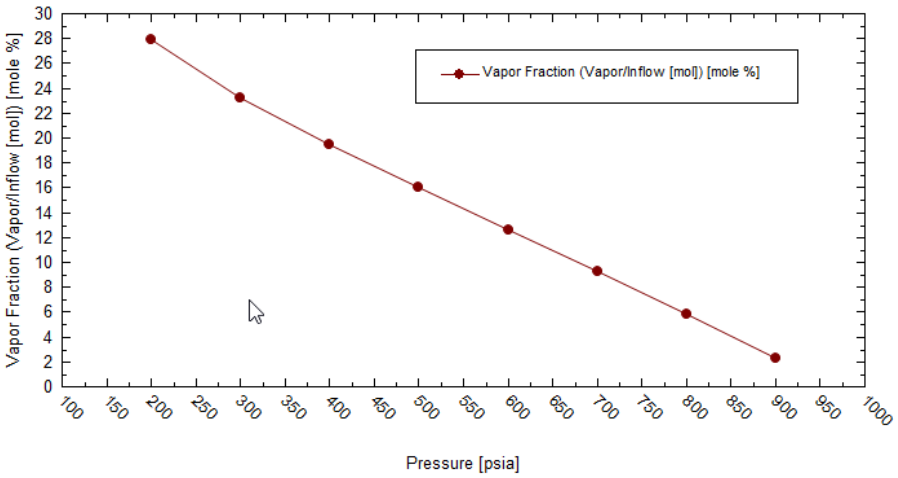


13. Enter a pressure range:

Start	200 psia
End	2000 psia
Decrement	100 psia

14. Click the **Calculate** button.

15. Click on the plot tab, you will see the following graph: You could adjust the parameters by clicking on curves.

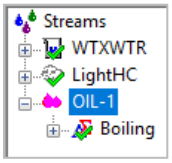


If the curve does not meet expectations, you will have to adjust the mole percentages or the pseudocomponent properties. This is a manual iterative approach. You can see the actual data by clicking the View data button.

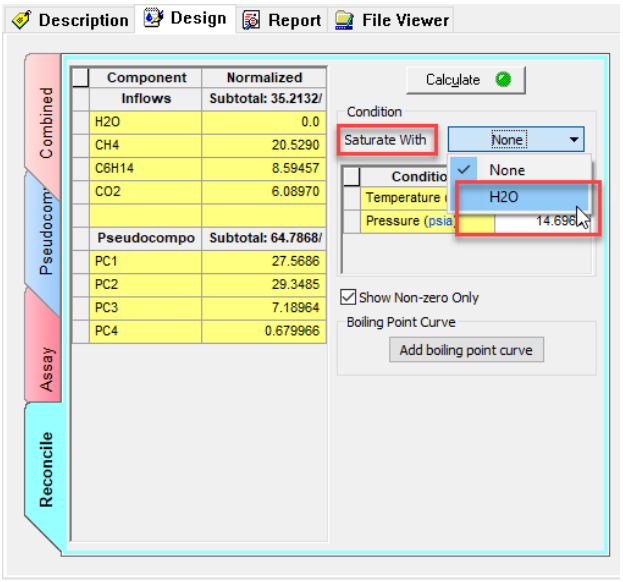
	Pressure	Vapor Fraction (Vapor/Inflow [mol])
	psia	mole %
1	200.000	27.8711
2	300.000	23.1977
3	400.000	19.4660
4	500.000	16.0216
5	600.000	12.6532
6	700.000	9.26672
7	800.000	5.80919
8	900.000	2.24433
9	1000.00	
10	1100.00	
11	1200.00	
12	1300.00	
13	1400.00	
14	1500.00	
15	1600.00	
16	1700.00	
17	1800.00	
18	1900.00	
19	2000.00	

Frequently the hydrocarbon is saturated with water. We will simulate this part.

16. Go back to OIL-1 in the Action panel



17. Click on the **Design** tab
18. Click on the *Saturate with* drop down. Select H2O



19. In the Conditions option use T= 77 F and 14.7 psia.
    Note: The software requires an initial "Guess" for the concentration of the water.

20. Click on the **Calculate** button.

When done, the software will create a *Reconciled OIL-1* in the Navigator pane.

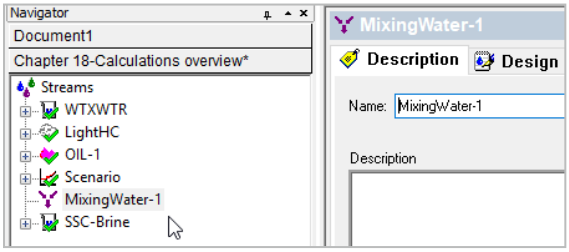
The Brine, Gas and Oil that we already calculated will be used for the upcoming Mixer, Saturator and Facilities Calculations.

Task 5 – Adding a Mixer Calculation

The Mixer calculation determines if two waters (brines) can be mixed. Frequently the mixing of two waters will cause precipitates to form which were not present in original brines. This can lead to the plugging of a formation when an injection water is mixed with the natural fluids in the formation.

1. From the Actions Panel, click on the Add Mixing Water logo.

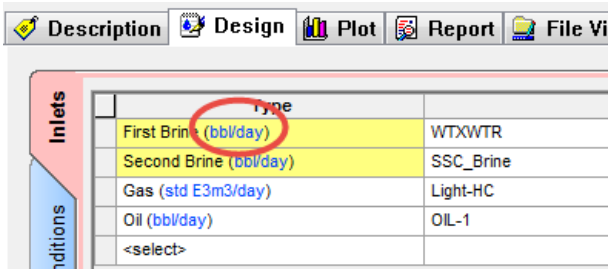
2. After double clicking the logo, you will the object in the Navigation Panel.



3. Click on the **Design** tab to enter more information.

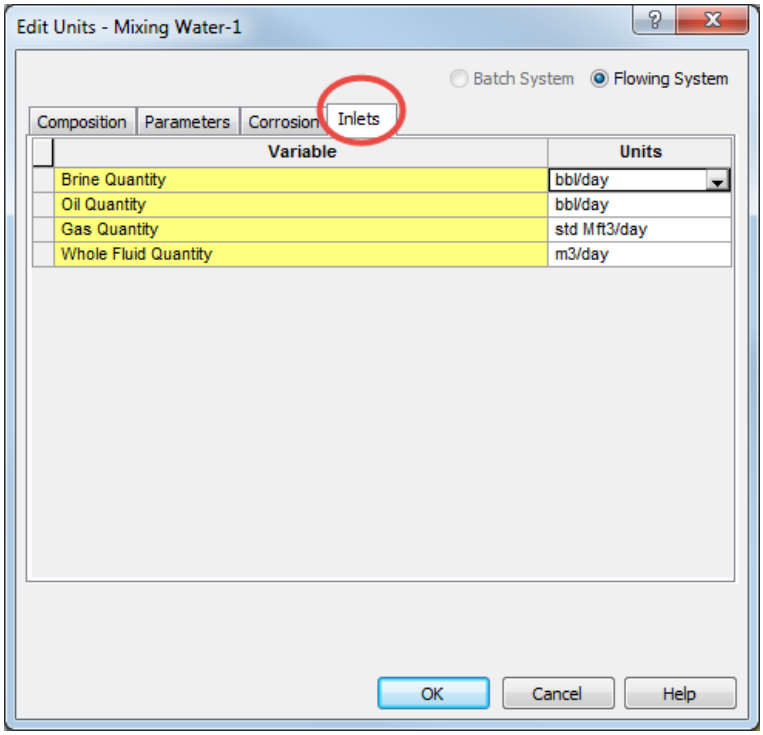
4. Select your Brines, Gas and Oil s as shown in the figure below. Enter the indicated brine flow rate of 1000 bbl/day, gas flow of 230 stdMft3/day and oil flow of 7 bbl/day.

   Note: To change units on brine, oil and gas, click on the hyperlinked (**blue**) units inside of the bracket next to Inlets First Brine, Second Brine etc. This is under the column heading Type.

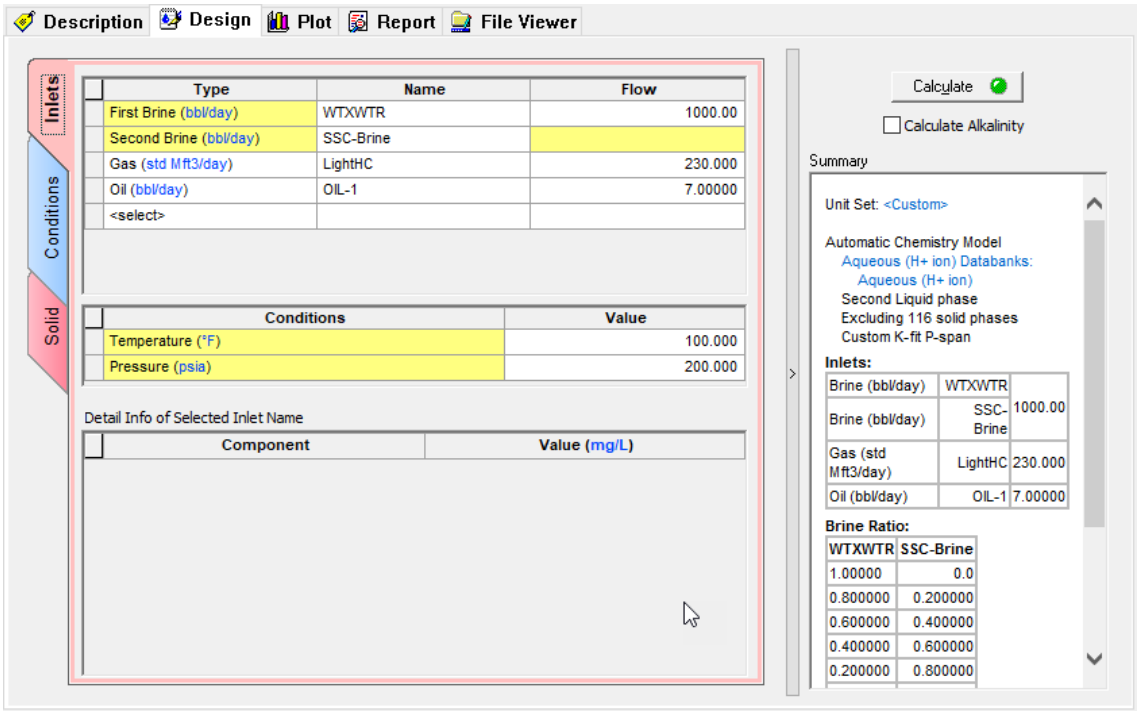


This should pop the following window up. Click on Inlets tab and change the units.

Inlets tab looks like below. Changing units on Brine:

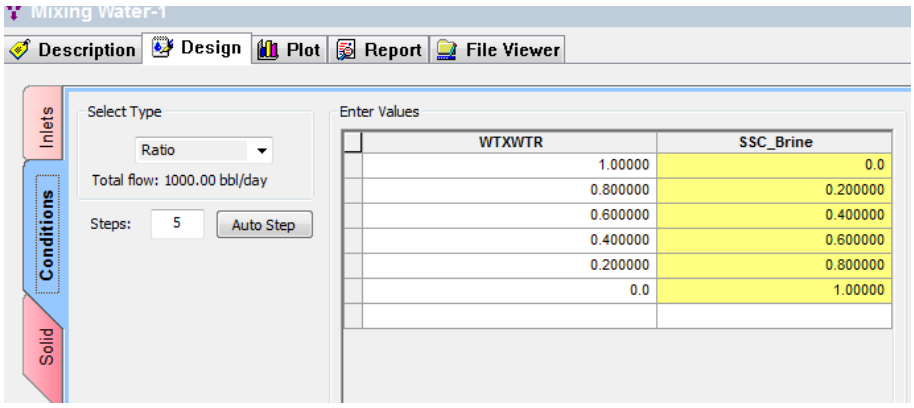


The final Mixer with inflows entered should look like the image below:



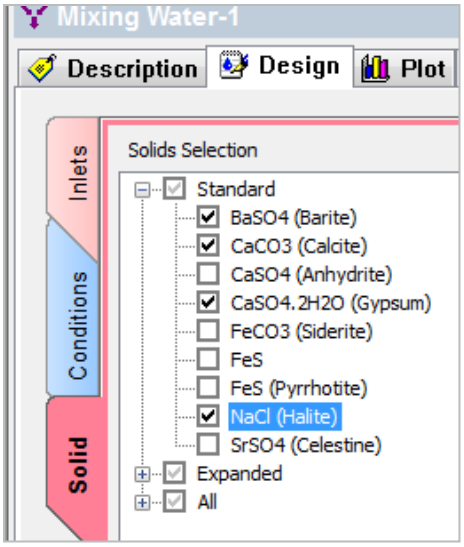
5. Go to the ***Conditions*** tab.
   In this example, we are mixing the brines at 100 F and 200 psia. The first brine specified (WTXWTR) is the one we compare to when evaluating the ratios. In this case we start out with all brine WTXWTR and none of the SSC_Brine and end up with none of brine WTXWTR and all of the SSC_Brine.

6. Leave the default values



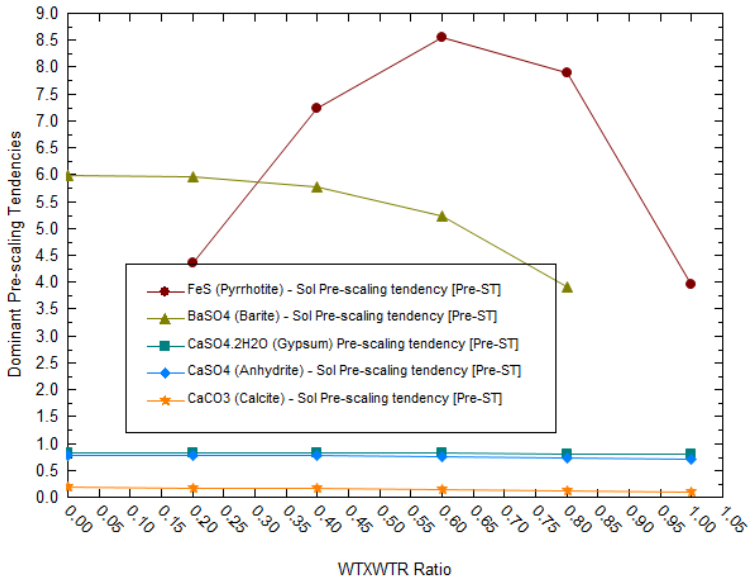
7. Go to the ***Solid*** tab

For this calculation we are only selecting a few of the possible solids. Mark a check box next to desired solids (BaSO4, CaCO3, CaSO4.2H2O, NaCl).

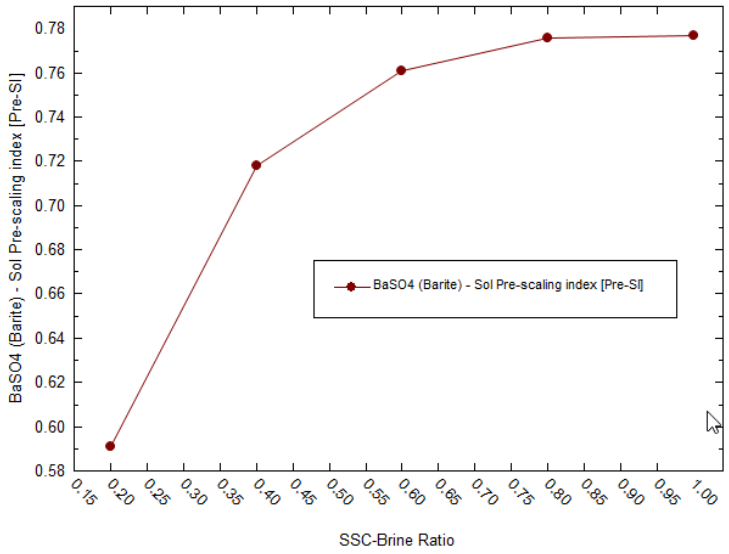


8. Click on the Calculate button.

9. Click on the **Plot** tab.



To study the effects better go to the variables button and eliminate other solids precipitated by the << arrow. Keep only one solid (in this case BaSO4). The ratio is relative to the first brine specified. This means at a ratio of 0.0 (all the first brine and none of the second) we have no BaSO4 scaling. As we add the second brine, the amount of BaSO4 increases. These waters are perhaps incompatible.



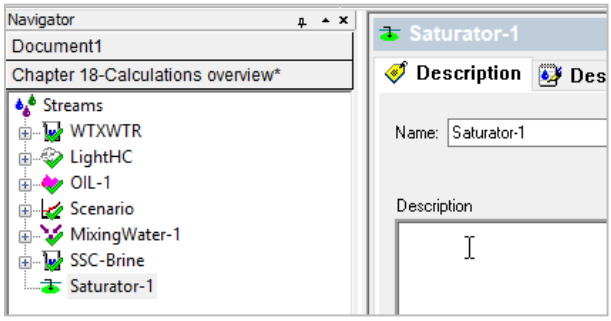
Task 5 – Adding a Saturator Calculation

Water and gas samples at the surface are not necessarily representative of conditions in the reservoir. The processing of the samples may involve significant changes in the chemistry.

The Saturate option (often referred to as "Saturate at reservoir conditions") allows the user to "Back-calculate" the conditions downhole.

1. Select ***Add Saturator*** from the Actions Panel.

2. Rename the object in the descriptions tab. Name it Saturator-1

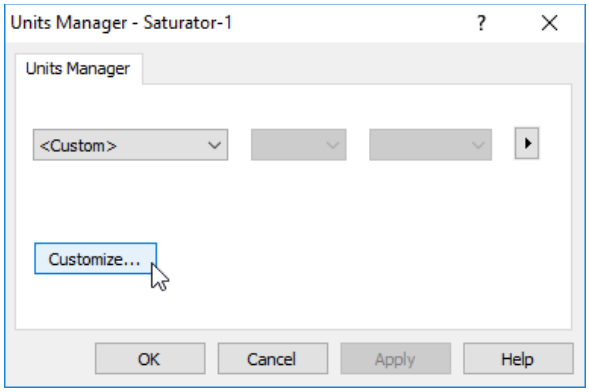


3. Go to **Design** tab
4. And go to ***Inlets*** (vertical) tab

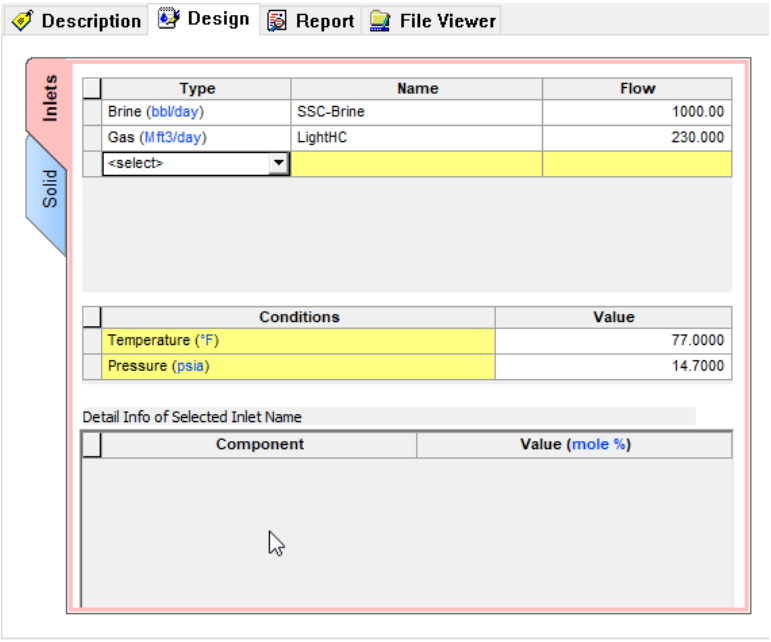
We will select objects that we have already defined.

5. Enter a Brine flow of 1000 bbl/day

6. Enter a Gas flow of 230 std Mft3/day
7. Enter T=77 F and P=14.7 psia
8. Set these units as custom units for all new objects in Units manager.



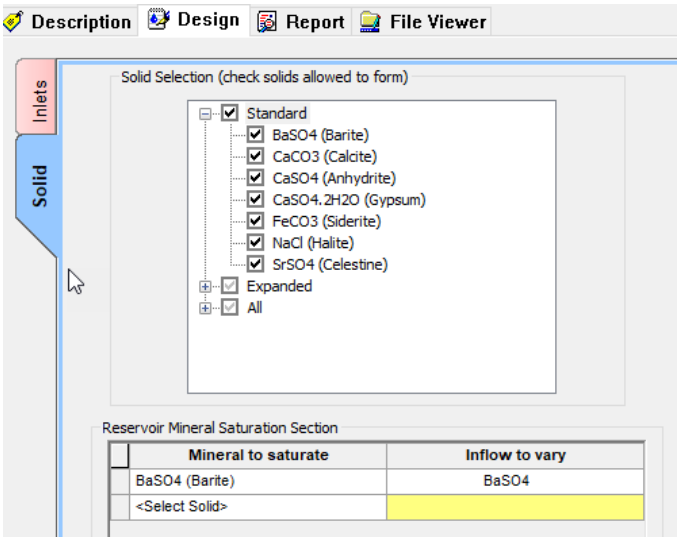
The window should look like the image below.



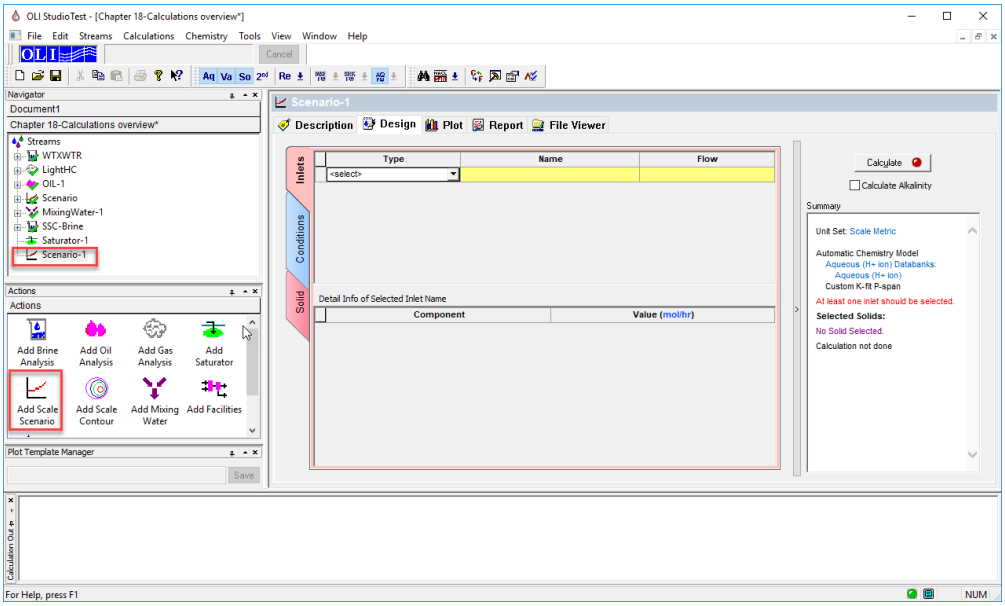
9. Go to ***Solid*** (vertical) tab
10. Check the Standard box

We need to select solids inflow to vary for Saturator1. Under the table *Select Inflows to Vary*, choose the solid to vary from the dropdown list.

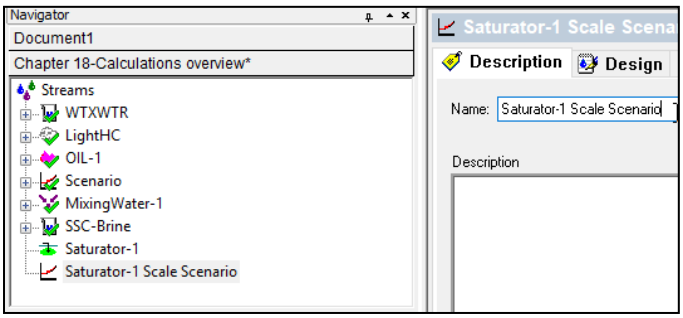
11. Select BaSO4 (solid) and hit enter. Automatically the inflow to vary BaSO4 will appear.



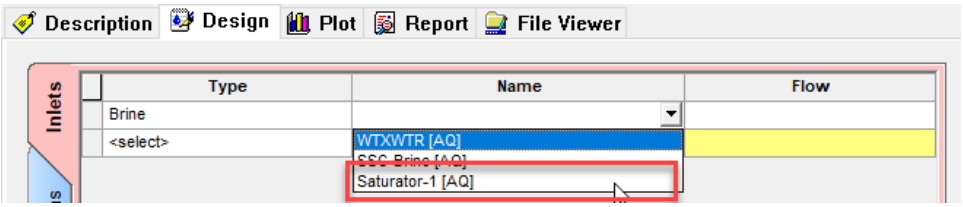
To study the Saturator-1 (Brine and Gas mix) at various locations we need to add a Scaling Scenario object.



12. Name the new Scale Scenario as *Saturator-1 Scale Scenario* under the **Description** tab.

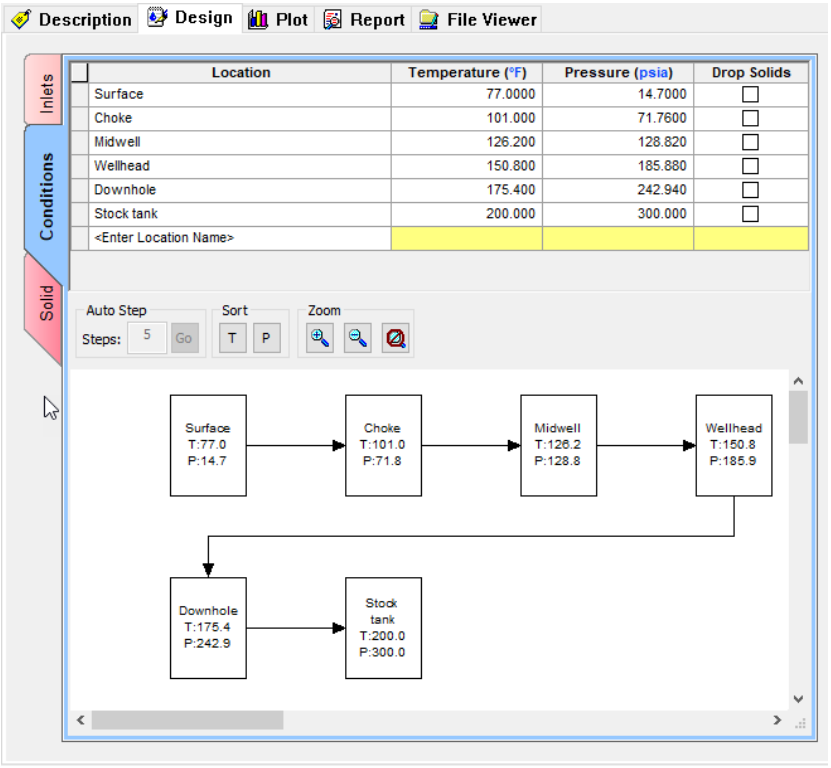


13. Go to the **Design** Tab
14. Under the **Inlets** (vertical) tab, select *Brine* under the *Type column*
15. Make sure to select Saturator-1, as is shown in the picture below:

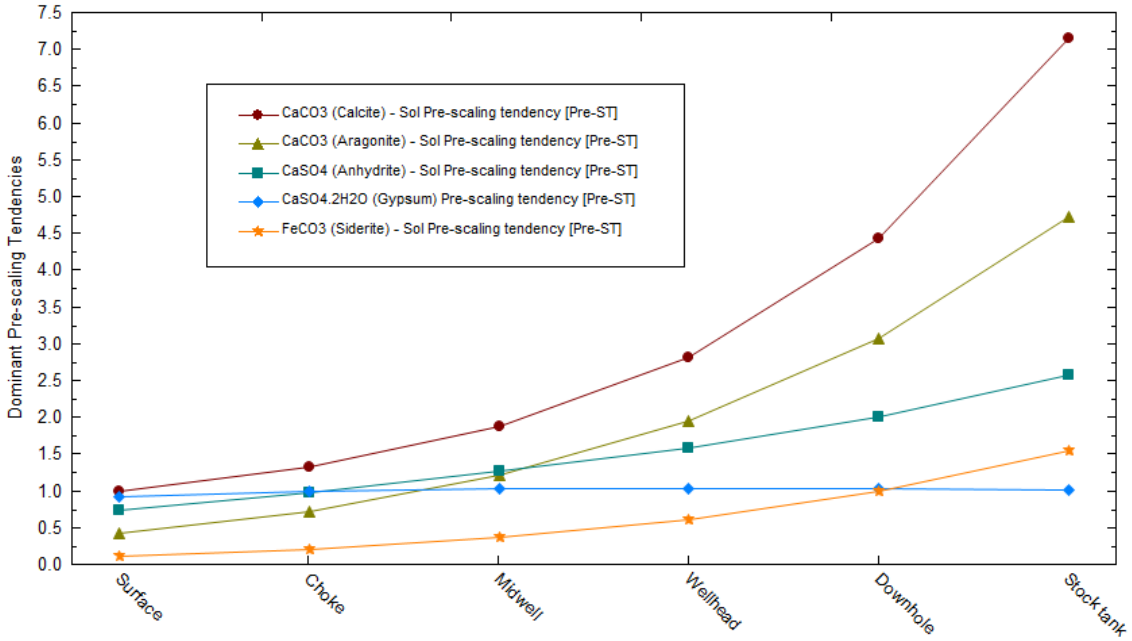


Flow will be automatically controlled. Locations can be input under the ***Conditions*** tab.

16. Go to ***Conditions*** (vertical) tab, and enter the information provided in the figure below:



17. Go to ***Solid*** tab and check the Standard box
18. Click the Calculate Button
19. Go to **Plot** tab



After the calculation is complete, the plot for scale scenario shows that other solids are appearing.

20. Go to the **Report** tab, and look for Pre and Post Scaling Tendencies

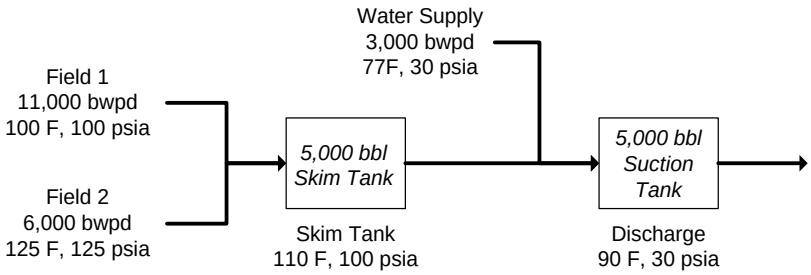
Pre and Post Scaling Tendencies

Formula	Mineral	Excess Solute	Excess Solute	Pre-Scale	Pre-Scale	Post-Scale	Post-Scale
		mg/L	lb/1000bbl	S, ST	SI, Index	S, ST	SI, Index
CaSO4.2H2O	Gypsum	0.0	0.0	0.928262	-0.0323294	0.928262	-0.0323294
FeCO3	Siderite	0.0	0.0	0.114350	-0.941763	0.114350	-0.941763
SrSO4	Celestine	0.0	0.0	0.203747	-0.690908	0.203747	-0.690908
SrCO3	Strontianite			0.0120481	-1.91908	0.0120481	-1.91908
BaSO4	Barite	0.0	0.0	1.00000	-2.23307e-11	1.00000	0.0
CaSO4	Anhydrite	0.0	0.0	0.731753	-0.135635	0.731753	-0.135635
CaCO3	Calcite	0.0	0.0	1.00000	-1.46285e-11	1.00000	0.0
NaCl	Halite	0.0	0.0	0.0121174	-1.91659	0.0121174	-1.91659
KCl	Sylvite			6.71059e-4	-3.17324	6.71059e-4	-3.17324

Excess solute or Max Scale: The solids amount forming at equilibrium.
Pre-Scale: The saturation ratio before solids precipitate.
Post-Scale: The saturation ratio AFTER solids precipitate (if solids are selected).
S, ST – Saturation, Scale Tendency: The ratio of the concentration (activity) to its solubility (S=1).
SI – Scale Index: Log(S).

13.6. Introducing the Facilities Object

This section presents a new calculation object: *Facilities*. The Facilities is a simplified process simulator; it mixes and separates. ScaleChem Analyzer has the ability to link together several individual calculations to create a flow sheet facility. An example of a facility calculation is shown in the figure below.



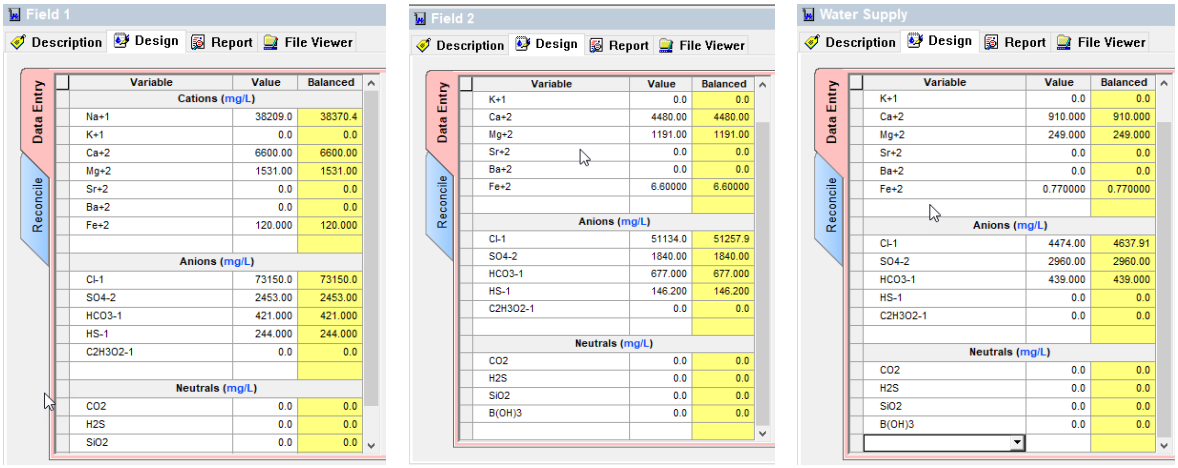
It is a simple process in which two field brines mix in a skim tank. The discharge from this tank then mixes with a water supply in a discharge tank. Below are the compositions and conditions of the inlet fluids.

Name	Field 1 mg/L	Field 2 mg/L	Water Supply mg/L
Na+	38209	27078	3074
Ca+2	6600	4480	910
Mg+2	1531	1191	249
Fe+2	120	6.6	0.77
Cl-1	73150	51134	4474
SO4-2	2453	1840	2960
HCO3-	421	677	439
HS-1	244	146.2	0
Conditions			
Temperature	100 F	125 F	77 F
Pressure	100 psia	125 psia	30 psia
pH	6.97	7.53	7.98
Alkalinity (As HCO3 mg/L)	421	677	439
Alkalinity End Point pH	4.5	4.5	4.5

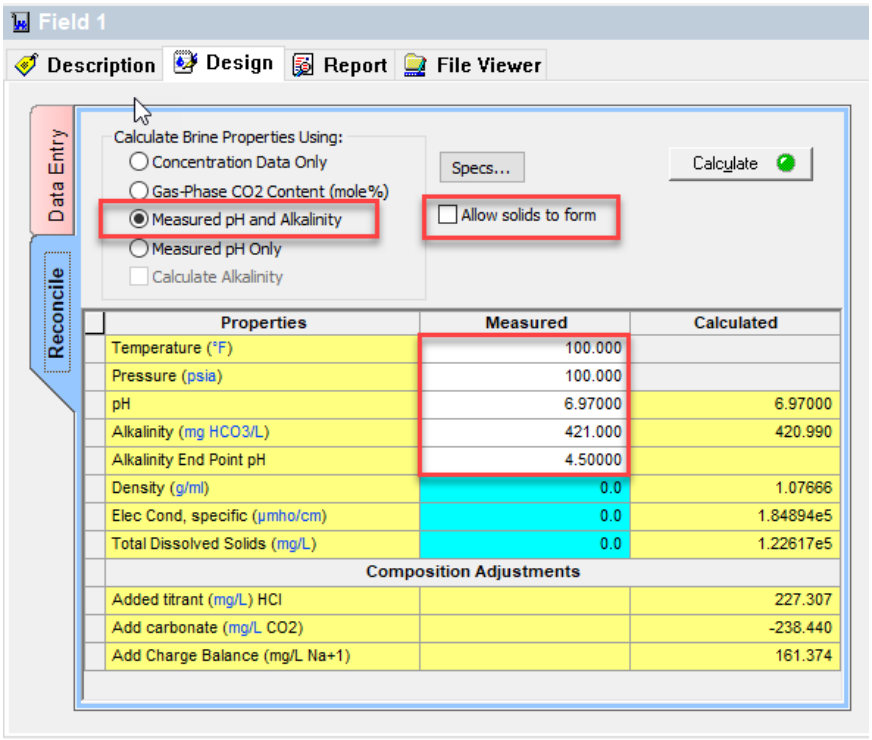
Follow the steps below:

1. Open a new Window for Simulation
2. Create the above brines: Field 1, Field 2 and Water Supply
3. Use the *Add Brine Analysis* object as you have done before to create them.

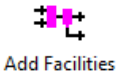
The ***Data Entry*** Windows should look like this:



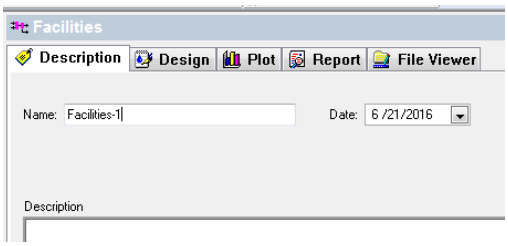
4. *Reconcile* these three brines for *measured pH and alkalinity.*
5. Make sure that the *Allow solids to form* box is uncheck at the bottom of the reconciliation options for all the brines.



6. Select ***Add Facilities*** from the Action Panel.



7. Go to the **Description** Tab and rename the object as Facilities-1

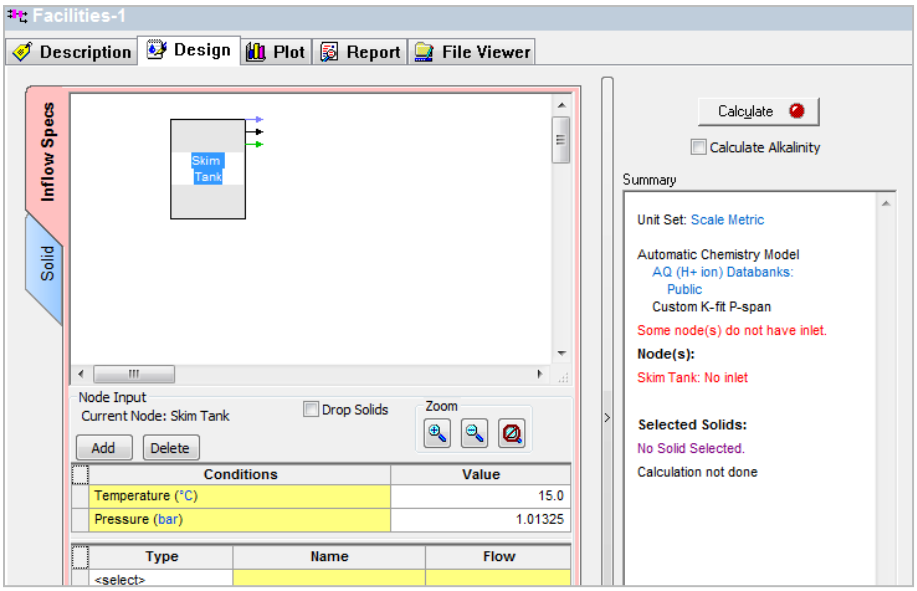


The facilities calculation is based upon transferring information between calculations through nodes. These nodes can be thought of as pseudo brines and gases. These pseudo brines are not stored as individual brine rather they are used internally in the calculation. The concentration and flow rates for these nodes can be viewed in the output.

8. Go to the **Design** tab
9. Go to the **Inflow Specs** (vertical tab)

Within ***Inflow Specs***, we can add Nodes via Node input options. There will be one default node added.

10. Double click on the node name (where it says: Node 1) and type "Skim Tank".

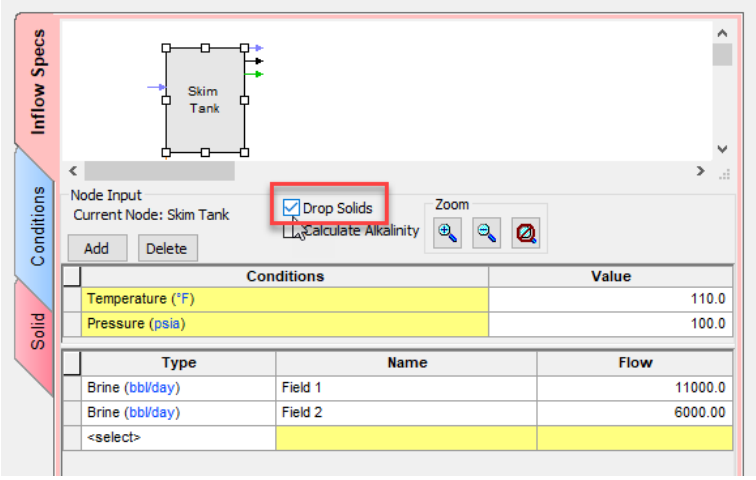


11. Enter the name, description, conditions, and streams for the Skim Tank shown in the table below:

	Flow	Temperature, F	Pressure, psia
Field 1	11000 bbl/day	100	100
Field 2	6000 bbl/day	125	125
Water Supply	3000 bbl/day	77	30
Skim Tank	5000 bbl/day	110	100
Suction Tank	5000 bbl/day	90	30

12. Make sure to select drop solids checkbox at the Skim Tank node.

When complete, your screen should look like this.

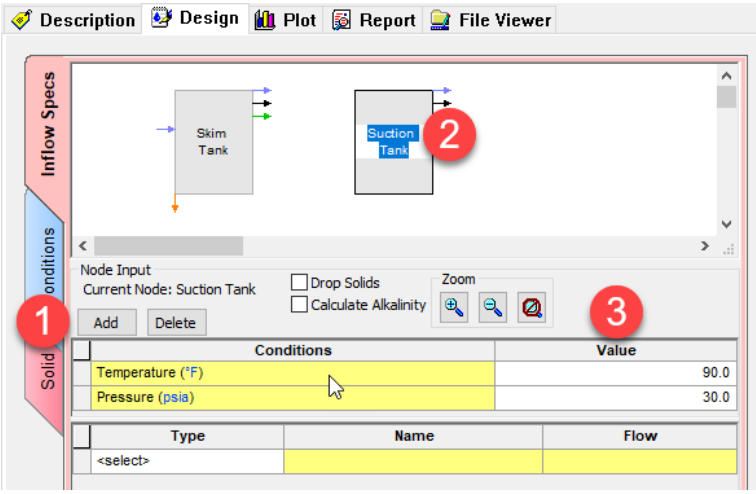


The output of this calculation will go to the next node.

Next, enter the information for the second node, Suction Tank. We will select the output brine of the Skim tank, which is a ***brine from node.*** The temperature and pressure as well as the flow of the brine are calculated.

13. Click on the Add button to add a second Node
14. Change the name of the node to Suction Tank
15. Change the conditions of this node to 90 F and 30 psia.

When complete your screen should look like the image below:

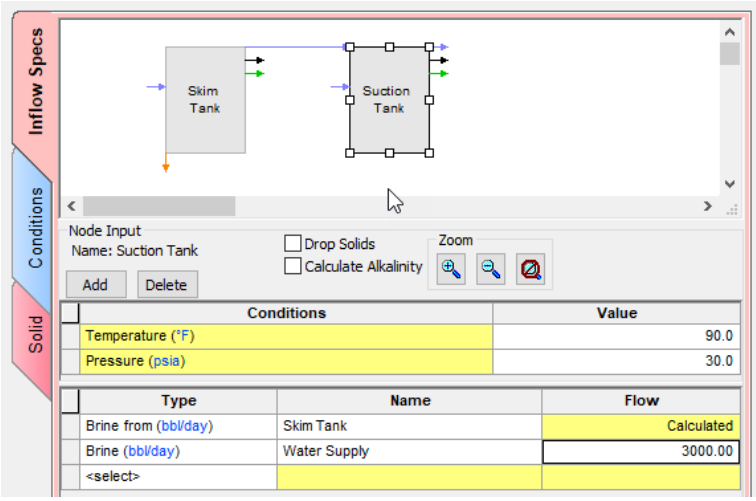


When a brine is calculated in a facilities calculation, we have the option of allowing any produced solids to be considered (that is they traveled along with the brine) or to ***eliminate*** them as they precipitate out. We will eliminate the solids in this case. The orange downward arrow from Skim Tank indicate dropped solids.

We are also adding the **Water Supply** to this tank.

16. In the Type column and first row select *Brine from*. In the Name column select *Skim Tank.* The *Flow* is calculated (since it comes from the Skim Tank).
17. In the Type column and second row select *Brine*. In the Name column select *Water Supply.* Enter 3000 bbl/day in the Flow column.

When complete the screen should look like the image below.



18. Click on the Calculate button, or press <Ctrl+F9>
19. Go to the **Report** tab, and check for the Pre-scaling Tendencies and Scaling Tendencies
20. See the Results

Pre-Scaling Tendencies

Column Filter Applied: Values > 1.0e-4

Temperature Filter Applied: Active TRange Only.

Nodes	CaCO3 (Aragonite)	CaCO3 (Calcite)	CaSO4.2H2O (Gypsum)	CaSO4 (Anhydrite)	FeCO3 (Siderite)	Fe(OH)2 (Amakinite)
Temp Range °C	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
Skim Tank	5.20710	8.91186	1.24207	1.39847	0.165109	3.48775e-4
Suction Tank	4.83533	9.86145	1.18226	1.09089	0.147451	1.58132e-4

Nodes	FeS (Pyrrhotite)	FeS (Mackinawite)	MgCO3.3H2O (Nesquehonite)	MgCO3 (Magnesite)	Mg(OH)2 (Brucite)	MgSO4.7H2O (Epsomite)
Temp Range °C	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
Skim Tank	41958.3	906.834	4.47209e-3	9.15709e-3	1.05810e-3	1.11430e-3
Suction Tank	41552.1	781.107	3.37396e-3	4.74809e-3	3.15204e-4	1.21290e-3

Based on these results, it is clear to see that the software predicts the formation of several solids in this process. Solids with a Pre-Scaling Tendency > 1 are predicted to form.

Chapter VI – Naming Conventions in OLI Analyzer and Definitions

1. Naming the Phases of Species

- Let's say for example you want to type the following reaction in the OLI reaction kinetics tool:

$$2NH_{3(AQ)}+CO_{2(AQ)}=CH4N2O_{(AQ)}+H2O$$

Note: You must use the ***OLI Tag Name*** for this step, and additionally specify the phase of the reactants and products. Water is a special case; it is written only as H2O.

As a general rule:

- For an aqueous phase: AQ
- For a vapor/gas phase: VAP
- For a solid phase: PPT
- For a hydrated solid: SOLIDNAME.nH2O, where n is the hydration number
- For an ion: ION

You can find the OLI TAG Name of your specific species using the **Component Search Tool.**

In OLI terminology the above reaction will look like:

2NH3AQ+CO2AQ=UREAAQ+H2O

2. Ionic Strength

2.1. Ionic Strength (molal based or m-based)

The ionic strength is a quantity representing the strength of the electric field in a solution, and it is equal to the sum of the molalities of each type of ion present multiplied by the square of their charges, as represented by the following equation:

$$I = \frac{1}{2}\sum_{i=1}^{n}(z_i^2 m_i)$$

Where n is the number of charged species

For example, a 1.0 molar solution of NaCl has 1.0 moles of Na^+ions and 1.0 moles of Cl^- ions in 1 kg of H_2O. Therefore, the ionic strength is 1.0 molal.

$$I = \frac{1}{2}((z_{Na^+})^2(m_{Na^+}) + (z_{Cl^-})^2(m_{Cl^-})$$

$$I = \frac{1}{2}((1)^2(1) + (-1)^2(1) = 1$$

Now, consider a 1.0 molal solution of $CaCl_2$. This solution has 1.0 moles of Ca^{+2} ions and 2.0 moles of Cl^{-} ions in 1 kg of H_2O. Therefore, the ionic strength is 3.0 molar, or it can be said that a 1.0 molal solution of $CaCl_2$ behaves similar to a 3.0 molar solution of NaCl.

$$I = \frac{1}{2}((z_{Ca^+})^2(m_{Ca^+}) + (z_{Cl^-})^2(m_{Cl^-})$$

$$I = \frac{1}{2}((2)^2(1) + (-1)^2(2) = 3$$

2.2. Ionic Strength (mole fraction based or x-based)

In this case the ionic strength is calculated using the mole fraction rather than the molality:

$$I = \frac{1}{2}\sum_{i=1}^{n}(z_i^2 x_i)$$

Where n is the number of charged species.

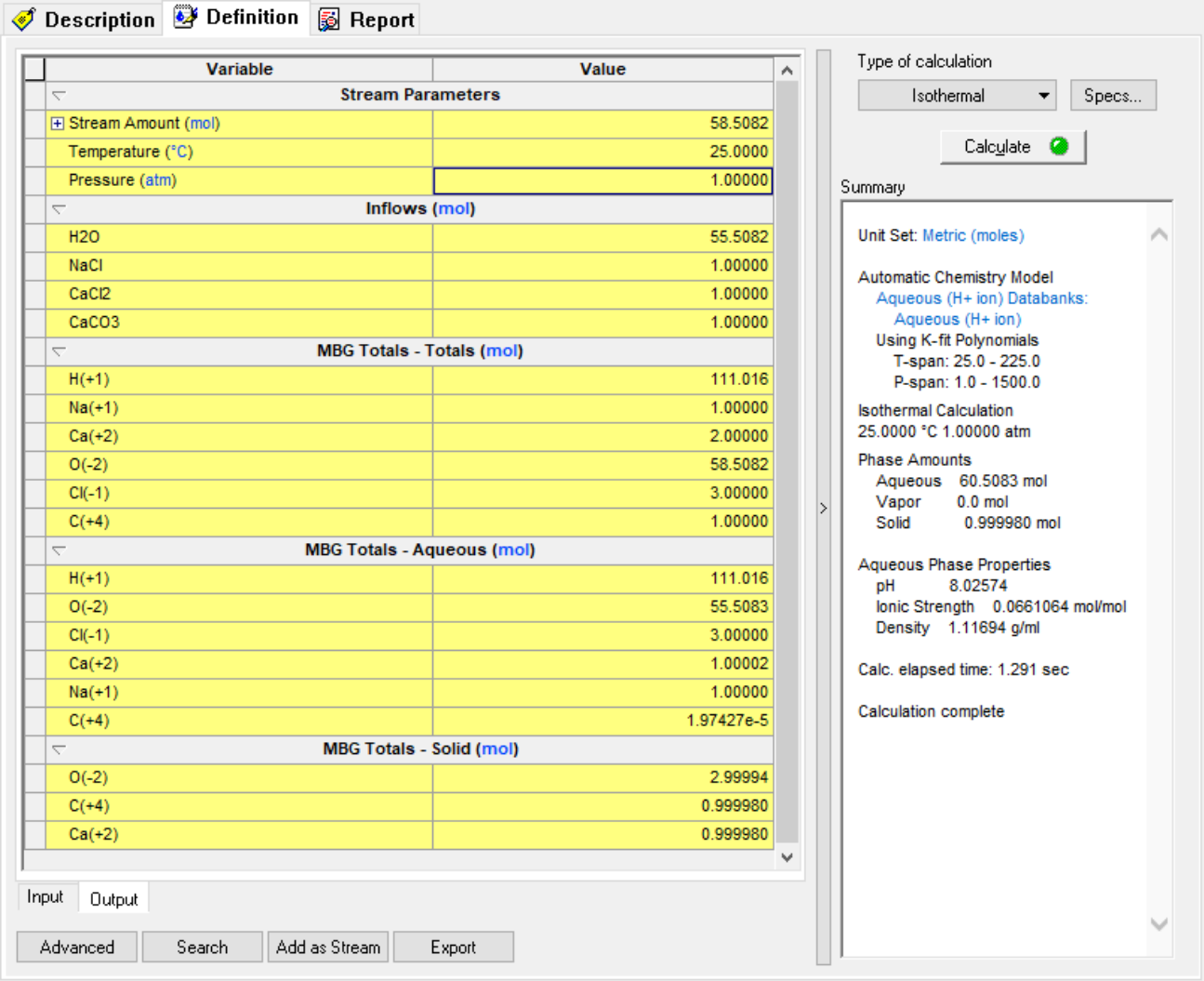
3. Material Balance Group (MBG)

MGB is an abbreviation for Material Balance Groups. The **MGB** variable is a sum of all the species with the same oxidation state. OLI gives this information as Total or for the specific phase requested (Aqueous, Vapor, Solid, and Organic) or as absorbed to the surface.

For example, if we have the following system:

- 55.5082 moles of H2O
- 1 mol of NaCl
- 1 mol of CaCl2
- 1 mol of CaCO3

The distribution of the elements with their respective oxidation states are given as MBG for the total system, and for the phases that are predicted to form, as shown in the image below.



4. Volume vs. Volume at Standard Conditions vs. Standard Liquid Volume

4.1. Volume

This is the volume of the system at a specified temperature, pressure and composition.

4.2. Volume at Standard Conditions

It is also known as the Standard Volume. This is the calculated volume of each phase (using the composition of each phase) at standard conditions. The standard conditions for each phase: vapor, liquid-1, and liquid-2 are predefined in the software, and can be changed.

The standards conditions are:

Vapor: Temperature: 15ºC and Pressure: 1.0023 atm

Liquid-1: Temperature: 25ºC and Pressure: 1 atm

Liquid-2: Temperature: 15ºC and Pressure: 1 atm

4.3. Standard Liquid Volume

This is a transport unit. Standard liquid volume is the calculated standard liquid volume based on true species. You can see it as the contribution of volume of each true species to the total liquid volume.

An example

Standard liquid volume calculation of Liquid-1 phase (MSE), H_2O: 55.5082 mole, NaCl: 1 mole, 25ºC, 1 atm (using OLI Analyzer 9.5.4).

Standard liquid volume of material balance group (MBG) (accessible through Databank > literature >Material codes > VOLU).

MBG name	Standard liquid volume of MBG, VOLU (m^3)
H(+1)	1.41E-05
Na(+1)	1.82E-05
O(-2)	-1.02E-05
Cl(-1)	1.72E-05

True species composition after speciation:

True species (Name)	Composition (COMP), mole
H2O	55.5082
Cl-1	1
Na+1	1
H3O+1	1.33E-07
OH-1	1.33E-07
NaOH	5.30E-14
HCl	2.07E-15

Standard liquid volume of the phase calculation, considering MBG group contribution in each true species:

MBG Name	Contribution	Contribution Value
H(+1)	1.41E-05×(55.5082×2 + 1.33E-07×3 + 1.33E-07×1 + 5.30E-14×1 + 2.07E-15×1)	1.57E-03
Na(+1)	1.82E-05× (1×1 + 5.30E-14×1)	1.82E-05
O(-2)	-1.02E-05× (55.5082×1 + 1.33E-07×1 + 1.33E-07×1 + 5.30E-14×1)	-5.65E-04
Cl(-1)	1.72E-05× (1×1 + 2.07E-15×1)	1.72E-05
	Volume (m^3)	0.00103827
	Volume (L)	1.03827

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