

INTRODUCTION TO

**OLI Studio** 

V11.5

think simulation

getting the chemistry right

# Introduction to OLI Studio

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Version: OLI Studio V11.5

## **Contact Information**

Visit the Contact OLI Systems page at <u>https://www.olisystems.com/techsupport</u> 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: <u>https://info.olisystems.com/portal-instructions</u> Product Downloads: <u>http://downloads.olisystems.com/</u> OLI Systems YouTube Channel: <u>https://www.youtube.com/OLISystems</u> OLI Systems Wiki page: <u>http://wiki.olisystems.com/wiki/Main\_Page</u>

### Disclaimer

This manual was produced using the OLI Studio 11.5.1 build 5 (11.5.1.5). 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 Studio Software users. OLI Studio is a software suite containing several modules including Stream Analyzer, think simulation | getting the chemistry right and Corrosion Analyzer. A client's license determines which modules are enabled within the OLI Studio Software.

This introductory manual consists of one chapter showcasing the OLI Studio User Interface, and four main chapters showcasing the three main modules of OLI Studio: Stream Analyzer, Corrosion Analyzer, EVS Analyzer, and think simulation | getting the chemistry right.

If you have not yet installed the software, please install it following the instructions given in the Installation and Security page on our Wiki page at: <u>http://wiki.olisystems.com/wiki/Installation\_and\_security</u>.

# **OLI Studio Components**

## **Stream Analyzer**

Stream Analyzer is standalone software, and it is the main interface of the OLI Studio. 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: Mixed Solvent Electrolyte (MSE) model (Default) Aqueous (AQ) 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 Studio. A separate license enables this module. Corrosion Analyzer is a 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 a powerful statistical techniques that is used extensively to extrapolate damage (maximum pit depth) from small samples in the laboratory to larger area samples in the field.

# think simulation | getting the chemistry right

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

Brine, gas and oil analysis

Scaling scenarios

Compatibility testing of brines using the stream mixing function

Phase equilibrium calculation for 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 Studio Software User Interface

## **General View of the User Interface**

The OLI Studio 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 use, as well as how to navigate the OLI Studio User Interface, will be provided here.

Menu Bar	♦ OLI Studio (Version 11.5.1 Beta) - [Document]       -         ■ File Edit Streams Calculations Chemistry Tools View Window Help       -         ■ IF Edit Streams Calculations Chemistry Tools View Window Help       -         ■ IF Edit Streams Calculations Chemistry Tools View Window Help       -         ■ IF Edit Streams Calculations Chemistry Tools View Window Help       -         ■ IF Edit Streams       Ist Value 1: It	×
Actions Pane	Actions Actions Add Stream Add Mixer Add EVS Add Stream Add Mixer Add EVS Analysis Calculation Add Sirine Add Oil Add Gas Add Analysis Analysis Saturator Piot Template Manager • • • •	Description / Definition Pane
Plot Template Manager	Save	
Calculation Status Output	x     4       a     a       b     a       For Help, press F1     a	NUM

The screenshot shown above is what you will see when you first start OLI Studio. 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 Studio. documents in the window.

**Help:** Here you can have access to 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) it comes back to gray.



They are laid out in the following order:

Quick access to File:	D 🗃 🖬
Quick access to Edit:	አ 🖻 💼
Quick access to <b>Help:</b>	<b>? №</b> ?
Quick access to Chemistry:	L1 Va So L2 Re ± MSE ± MSE ± AQ
Quick access to <b>Tools:</b>	🏘 🎬 🛃 💱 🔊 😭 🎸

#### 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 and sometimes a critical fluid. It is 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:

MSE: Mixed Solvent Electrolyte databank (Default)

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

AQ: Aqueous databank

#### Icons in the Tools section

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

<u>Component search</u> :	<b>#</b> \$	This tool helps you to look for a component using Formula, CAS number, chemical name or using the periodic table.
<u>Names manager:</u>	NACL	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.
<u>Units manager:</u>	G≜ ∳F	This tool allows you to select or change to preferred units for all calculations.
<u>Customize toolbars:</u>		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:	<b>1</b>	This tool allows you to adjust or change default software settings.
Calculation options:	∧ 5⁄2	This tools allows you to include or exclude different types of properties into the calculations.

#### **Navigator Pane**

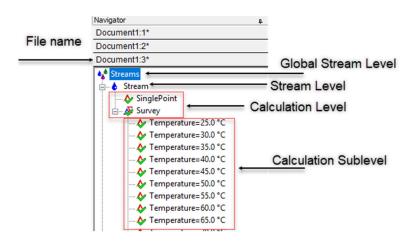
The Navigator Pane (or tree level) contains the list of streams and calculations that are active within a file. This view contains the icons and names of each action in a hierarchical tree. The Description/Definition pane changes depending on the level that is highlighted. A plus sign next to an object 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 for the working file.

**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 <u>Chapter II</u> of this manual.

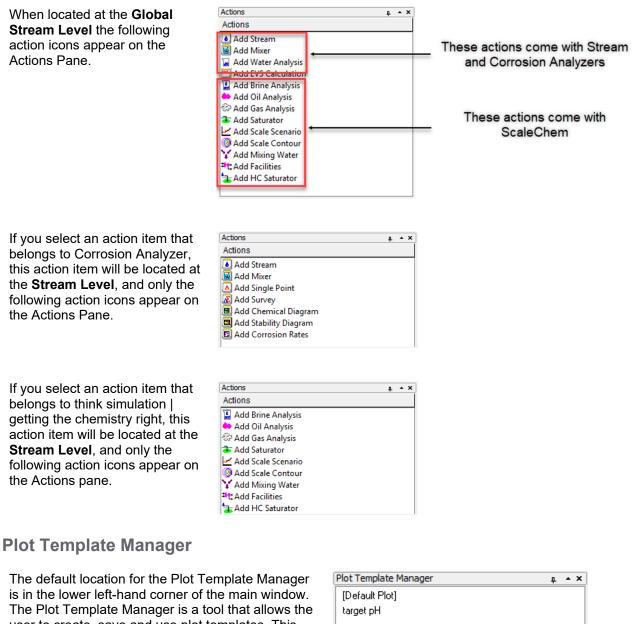
**Calculation Sublevel:** Some calculations, such as Survey calculations, have their own calculation sublevels. They can be expanded or maximized using the small icon (B or  $\doteq$ ) next to the calculation type.



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.

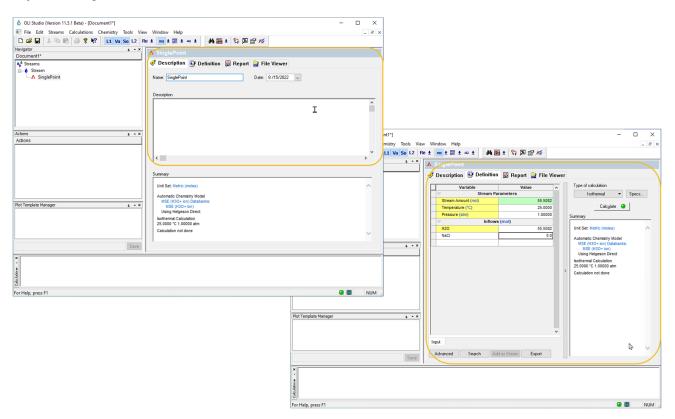


user to create, save and use plot templates. This tool allows a fast plotting and analysis of the user's results.



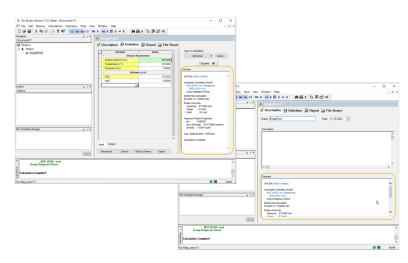
## **Description / Definition Pane**

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 Studio. 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 detailed 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 applications 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 can produce valid results in the following ranges:

Temperature	-50∘C to 300°C
Pressure	0 – 1500 bar
Ionic Strength	0 – 30 molal

The AQ-framework selects the PUBLIC<sup>1</sup> 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:

Aqueous (H<sup>+</sup> ion) – Public Database and selected by default Geochemical (AQ) Ceramics (AQ) Corrosion (AQ) Low Temperature (AQ) Alloys (AQ) Ion Exchange (AQ) Surface Complexation Double Layer Model (AQ) **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*<sup>th</sup> 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  $\gamma_i$  is the activity coefficient. This activity coefficient  $\gamma_i$ , 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 can produce results for the following ranges:

Temperature	-50°C – to 90% T <sub>crit</sub>
Pressure	0 – 1500 bar
Ionic Strength	no limit

The MSE framework contains the following databanks:

 $\begin{array}{l} \text{MSE} (\text{H}_3\text{O}^+ \, \text{ion}) - \text{Selected by default} \\ \text{Corrosion} \, (\text{MSE}) \\ \text{Geochemical} \, (\text{MSE}) \\ \text{Urea} \, (\text{MSE}) \\ \text{Surface Complexation Double Layer Model} \, (\text{MSE}) \end{array}$ 

<sup>&</sup>lt;sup>1</sup> 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 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 reproduce the critical behavior of nonelectrolyte systems more easily.

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:

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

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

 $\begin{array}{l} \text{MSE} (\text{H}_3\text{O}^+ \text{ ion}) - \text{Selected by default} \\ \text{MSE-SRK} (\text{H}_3\text{O}^+ \text{ ion}) - \text{Selected by default} \\ \text{Corrosion} (\text{MSE}) \\ \text{Geochemical} (\text{MSE}) \\ \text{Urea} (\text{MSE}) \\ \text{Surface Complexation Double Layer Model} (\text{MSE}) \end{array}$ 

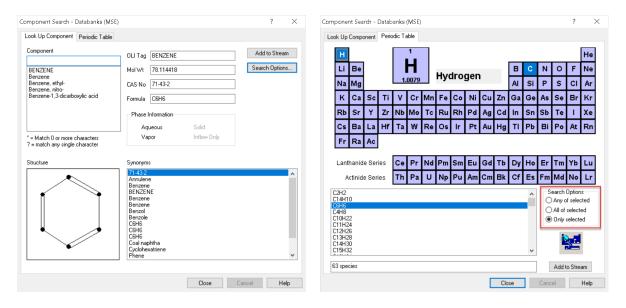
# **Component Search**

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.

Names Manag	ger		?	$\times$
Name Style	Search Criteria	Names Dictionary		
Displa     Displa     O     Displa     O     O	se Names Dictio			
	cted style will be u tables and lists. Cancel	used for displaying c		elp

## **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.

🗅 😅 🖬   🕹 🖻 💼   🍜 🤋 📢	L1 Va So L2 Re ± 🔤 ± 🗱 ± 🗛 ± 👫 🎬 ± 🛟 🔊 🖆 ۸
Navigator 4	• X [ .
Document1*	Default Units for Document ? X
<ul> <li>♦ Streams</li> <li>♦ Stream</li> <li>▲ SinglePoint</li> </ul>	Default Units
	Object Type All All Default Units Contour EVSStandard Metric Gas Moles V
Actions Actions Actions Add Stream Add EVS Calculation Add EVS Cal	HCSaturator Mixer Oil Customize Saturator Scenario Stream
Add Mixer     Add Brine Analysis       Add Water Analysis     Add Oil Analysis	Note: Changes made to default units only apply to new objects. Existing objects will not be modified.
Plot Template Manager #	OK Cancel Apply Help

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.

🗋 D 🚅 🖬   🏅 🖻 💼   🍜 💡 😵	L1 Va So L2 Re 🛓	MSE 🛨 MSE 🛨 🗛 🛨		💱 🔊 😭	肾
Navigator	🖡 🔺 💧 Stream				
Document1*	• Stream				
🐓 Streams	C Description	n 💕 Definition	🐼 Report		1.1
📩 💩 Stream	Units Manager - Stream	n	Ĩ	? ×	
▲ SinglePoint	Units Manager	-			_
					55
	Metric	∼ Batch ∽	Moles 🚿	· •	25 1.(
					55
	Customize				
Actions	<b>д</b> •				
Actions					
🖲 Add Stream 🛛 🔊 Add Survey	ок	Cancel	Apply	Help	
🖪 Add Mixer 📃 Add Chemi		Carlee	Ahhh	neip	
🔺 Add Single Point 🛛 🔲 Add Stabilit	y Diagram				

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

Metric 🗸 🗸	Batch 🗸	Moles 🗸 🗸
Metric	Batch	Moles
SI	Flowing	Mass Frac.
English		Conc.
Scale Metric		Mole Frac.
Scale		Molar Conc.
Scale English		Mass

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.

Variable	De -2	11-14-		Composition Parameters Corrosion	11-24-
	Basis	Units	^		Units
Stream Amount	Moles	mol		Temperature	°C
nflows	Moles	mol		Pressure	atm
•	t variables				
Aqueous Composition	Moles	mol	_	Time	hr
Vapor Composition	Moles	mol	_		
Solid Composition	Moles	mol	_	Alkalinity	mg HCO3/L
2nd Liquid Composition	Moles	mol	_	Density	g/ml
Total Composition	Moles	mol		Electrical Conductivity, molar	m2/ohm-mol
	s options		-	Specific Electrical Conductivity	µmho/cm
Moles		mol		Energy	cal
Mass		g N	<u>~</u>	Energy, Molar	cal/mol
		g		Entropy	cal/K
Concentration		kg Ib		Entropy, Molar	cal/mol K
Molar Concentration		mg		Fugacity	atm
Mass Fraction		(g/100)		Heat Capacity	cal/g K
Mole Fraction		metric ton	~	Ionic Strength (x-based)	mol/mol
	ок	ancel Heli	D	ОК	Cancel H

Variable	Units
Angular Velocity	cycle/min
Corrosion Rate	mm/yr
Corrosion Current Density	A/sq-m
Length/Diameter	cm
Potential	V (SHE)
Shear Stress	Pa
Volumetric Pipe Flow	m3/s
Velocity	m/s

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 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.

Customize		×	Customize X
Toolbars       Commands         Toolbars:       Standard         Full Screen       Chemistry Model Options         Chemistry Model Options       Tools	Show Tooltips     Cool Look     Large Buttons	New Reset	Toolbars       Commands         Categories:       Standard         Streams & Cales       ScaleChem         Chemistry       FP         Tools       FP         Select a category, then click a button to see its description. Drag the button to any toolbar         Description         Add an Isothermal calculation to the current stream.
	ОК	Cancel	OK Cancel

# **Calculation Options**

You can access the **Calculation Options** from the Menu Bar: **Tools > Options...** or via the quick access from

the Tool Bar <sup>M</sup>. This will open a new window. Under the **Calculation Options** tab you can enable or disable the following options:

#### General

Allows you to disable or enable the status dialog (a popup window that appears after pressing the calculate button)

bullonj

Diagnostics

Enable trace. This is a file containing the detailed solver output. It is generally used to diagnose why a calculation may have failed.

**Optional Properties** 

Diffusivities, electrical conductivity, heat capacity, activities, fugacities, and K-values, Gibbs free energy, entropy, thermal conductivity, surface tension, interfacial tension, Total Dissolved Solids, Scaling Induction Time, and pre-scaling tendencies.

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	Verbose	
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Electrical Conductivity		
Heat Capacity		
Activities, Fugacities, and	K-Values	
Gibbs Free Energy		
Entropy		
Thermal Conductivity		
Surface Tension		
Interfacial Tension		
Total Dissolved Solids (TD	S)- Rigorous method	
Scaling Induction Time(s)	Advanced	
Pre-scaling Tendencies		
Method Estimated	Rigorous	
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# **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.

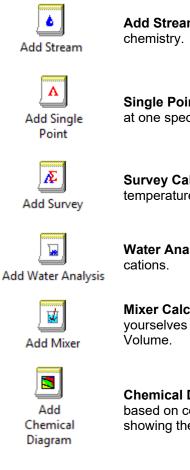
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Tip: If by accident we lose a tool bar, we can go to View > Toolbars >... and select the toolbar that is missing.

# Chapter II – OLI Studio: 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 Studio: 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 these calculation types.

# **Section 1. Single Point Calculations**

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

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*Isothermal:* The software computes solution properties based on a known chemical composition at a constant temperature and pressure.

*Isenthalpic:* A constant enthalpychange (loss/gain) is specified, and temperature or pressure is adjusted to meet the heat requirements.

**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).

*Dew Point:* The temperature or pressure is adjusted to reach a condition where a small amount of aqueous liquid (dew) begins to appear.

*Vapor Amount:* The temperature or pressure is adjusted to produce a user-specified amount (in moles) of vapor in the system.

**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.

*Isochoric:* The temperature or pressure is adjusted to produce the user-specified total volume (constant volume calculation).

**Set pH:** The software adjusts the flowrate of an acid or base titrant to maintain an aqueous solution at a user-specified pH.

*Precipitation Point:* The software adjusts the flowrate of a species until a small amount of solid precipitates. This can also be interpreted as the solid's solubility point.

*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.

**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.

*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.

*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.

#### 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<sub>3</sub> solution at 25 °C and 1 atm.

#### Starting the Simulation

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



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.

For this example, we are going to use the **MSE-Databank** (The default databank)

Type FeCI3 in the white cell below H2O inflows grid, and press <Tab> or <Enter>

Enter the value **1.0 mol** in the next cell.

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	Temperature (°C)	25.0000	Solids Only	
	Pressure (atm)	1.00000		
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	H20	55.5082	Unit Set: Metric (moles)	~
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*Note*: By default, the software populates the stream parameters table with 25°C, 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.

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 clicking** on the object and selecting rename.

Change the generic name Stream to pH of 1 m FeCl3

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

#### Go back to the **Definition** Tab

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#### Now, we are ready to perform a calculation

Go to the **Add Calculation** button Select **Single Point** 

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

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	H20	55.5082	Stability Diagram
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All the required variables have been entered, and the Calculate button has turned green. Click on the

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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

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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 us analyze the results of the simulation.

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	Temperature (°C)	25.0000	
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	H20	55,5082	Unit Set: Metric (moles)
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			Phase Amounts
			Aqueous 58.5583 mol
			Vapor 0.0 mol Solid 0.0110050 mol
			Aqueous Phase Properties pH 1.48627
			Ionic Strength 0.0556967 mol/mol
			Density 1.12834 g/ml
			Calc. elapsed time: 1.751 sec
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#### Analyzing 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 1.49

Let's analyze the simulation results in more detail

#### Click on the Report Tab

Scroll down and find Species Output (True Species). You will find a list of all the different species present in the aqueous phase.

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	Fe2(OH)2+4	1.75659e-5	1.75659e-5			
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Why is the **pH** so low?

The aqueous iron species complexes the hydroxide ions. The water dissociation reaction shifts in the direction that replenishes the hydroxide ions<sup>2</sup>.

This equilibrium is always present:

<sup>&</sup>lt;sup>2</sup> Le Châtelier's principle. P.W.Atkins. Physical Chemistry. W.H. Freeman and Company, San Francisco (1982) p 269.

$$H_2 O = H^+ + O H^{-3}$$

#### **Speciation Reactions**

First iron (III) chloride dissociates:

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

Then the Fe<sup>3+</sup> interacts with water; hydrolysis reaction:

$$Fe^{3+}$$
 + H<sub>2</sub>O  $\rightarrow$   $FeOH^{2+}$  +  $2H^+$ 

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 were shown as an illustration. The following is a list of all the species that are formed in the aqueous phase:

Fe <sup>+3</sup>	FeCl <sub>2</sub> <sup>+1</sup>	Fe(OH) <sub>3</sub> <sup>0</sup>	$H_2O^0$
FeCl <sup>+2</sup>	Fe(OH)2 <sup>+1</sup>	OH-1	HCI <sup>0</sup>
FeOH <sup>+2</sup>	H <sup>+1</sup>	FeCl4 <sup>-1</sup>	Fe <sub>2</sub> (OH) <sub>2</sub> +4
Cl <sup>-1</sup>	FeCl₃ <sup>0</sup>	Fe(OH)4 <sup>-1</sup>	

#### pH Calculation

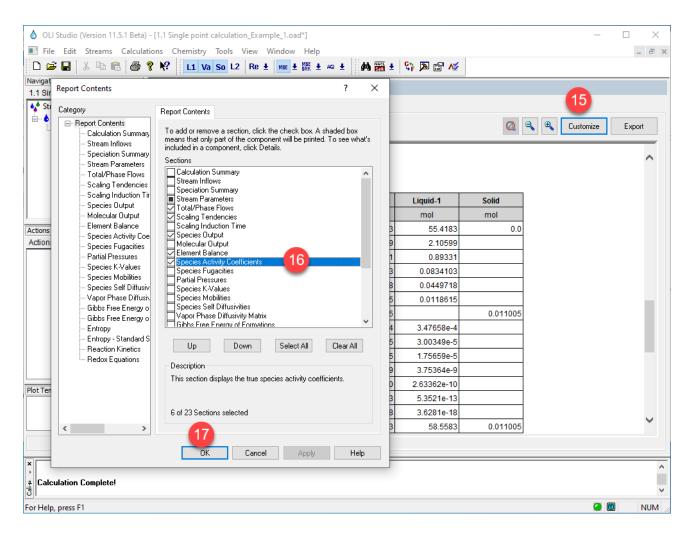
The pH is calculated using the following formula:

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

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.

<sup>&</sup>lt;sup>3</sup> This hydrolysis reaction is the generic form found in most aquatic textbooks. OLI uses this reaction in the AQ framework. In the MSE framework, a more advanced reaction is used: 2H2O=H3O+ + OH-

## Click on the Customize Button Select Species Activity Coefficients Click OK



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

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Actions	Fe2(OH)2+4	2.69634e-4	2.55176e-4			
	FeCl2+1 FeCl+2	7.70907	7.2957			
	Fe+3	0.132933	0.125805			
	FeO2-1	0.706024	0.668167			
	FeOH+2	0.162852	0.15412			
	FeO+1	0.706024	0.668167			
	H20	0.962773	0.911148			
	H3O+1	0.697601	0.660195			
	HCI - Lig1	0.825477	0.781214			
	HFeO2 - Liq1	0.962773	0.911148			
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Thus, the pH is:

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

$$pH = -\log[(0.049012)(0.660195)]$$

$$pH = -\log[0.032357]$$

$$pH = 1.49$$

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 us 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

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to Isothermal - acetic acid

Select the MSE thermodynamic Framework (selected by default)

Click on the Units Manager Icon, and the Units Manger window opens

<ul> <li>♦ OLI Studio (Version 11.5.1 Beta) - [1.1b</li> <li>■ File Edit Streams Calculations</li> <li>□ □ □ □ □ ↓ □ ↓ □ □ □ □ □ □ □ ↓</li> </ul>		4 ⊾ ₩ ∰ ± \$; > ≌ @ /#	- 0	× - = ×
Navigator	Isothermal - acetic acid			
1.1b Single point calculation_Exam				
	ダ Description 🔮 Definition 📓 Report			
⊨ b pH of 1 m FeCl3	Variable	Value	Add Calculation 👻	
SinglePoint	Stream Para			
sothermal - acetic acid	Stream Amount (mol)	55.5082	Special Conditions	
	Temperature (°C)	25.0000	Solids Only	
	Pressure (atm)	1.00000	Summary	
	□	mol)	Summary	
	H20	55.5082	Unit Set: Metric (moles)	$\sim$
			Automatic Chemistry Model	
Actions # * *			MSE (H3O+ ion) Databanks:	
Actions			MSE (H3O+ ion) Using Helgeson Direct	
🖲 Add Stream				
Add Mixer				
Add Single Point		;	•	
Add Survey				
Add Stability Diagram				
🖪 Add Corrosion Rates				
Plot Template Manager + ×				
		~		
	Input			
				$\sim$
Save	Advanced Search Add as Stream	Export	_ I	
×				
Call +				
<u> </u>				
For Help, press F1			🥥 🗉	NUM /

### Click on the Customize Button

Units Manager - Isothermal - acetic acid	?	×
Units Manager		
Metric ~ Batch ~ Moles	~	·
Customize 5		
OK Cancel Apply	Н	elp

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.

omposition	Parameters	Corrosion			
	Varia	ble	Basis	Units	
		Inflow var	iables		
Stream Ar	nount		Moles	mel	
Inflows			Mass Fraction 📃 🐱	6	
		Output var			
Aqueous	Composition		Moles	mol	
Vapor Cor	mposition		Concentration Molar Concentration	mol	
Solid Com	position		Mass Fraction	mol	
2nd Liquid	I Composition		Mole Fraction	mol	
Total Com	position		Moles	mol	
		Basis op	tions		
Moles				mol	
Mass				g	
Volume				L	
Concentra				mg/L	
Molar Con				mol/L	
Mass Frac				mass %	
Mole Fred	tion		1	mole %	

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

Mass Fraction	mass % 🔍
Mole Fraction	g/g
	mass %
	ppm (mass)

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

Go to the Add Calculation button and select Single Point. Select the default calculation type – Isothermal Change the name to *pH* using the <F2> key or by right-mouse click on the object and selecting rename Change the temperature to 75°C and pressure to 1 atm

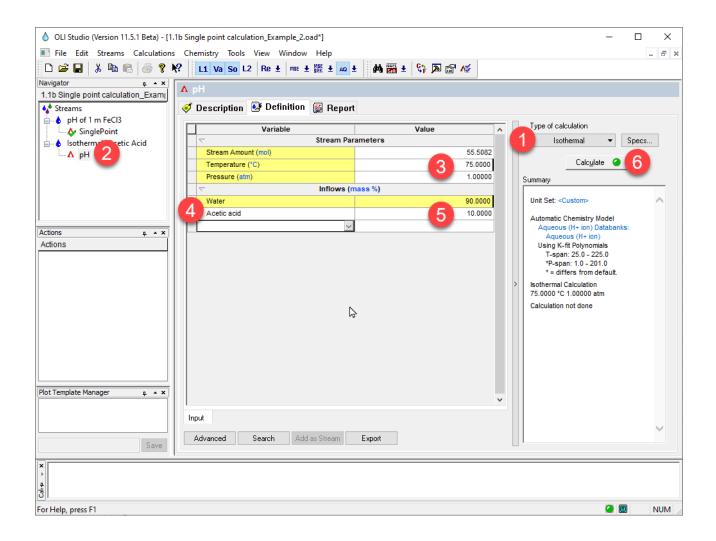
Type Acetic Acid in the white cell below H2O inflows grid, and press <Tab> or <Enter>

*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

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.

Click on the Calculate button



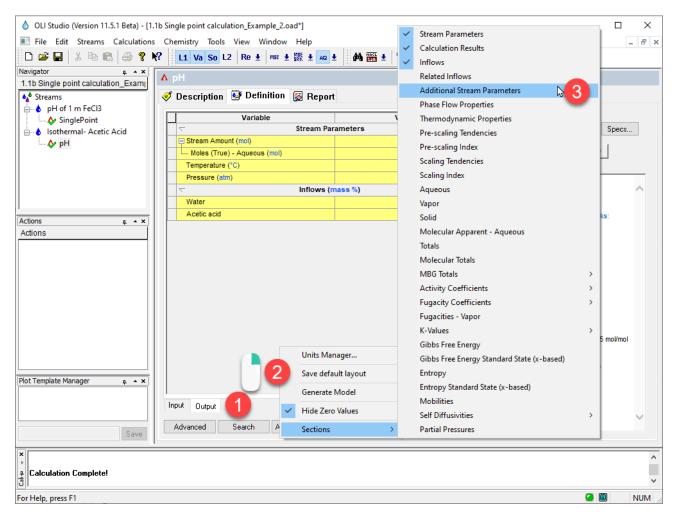
## Analyzing the Results

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

Click on the Output mini-tab at the bottom of the grid

Right-click on the gray area and select Sections

### 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.

< Description 🔮 Definition 📓 Repor	t		
Variable	Value	^	Type of calculation
	rameters		Isothermal 👻 Specs
딕 Stream Amount (mol)	55.5082		
Moles (True) - Liquid-1 (mol)	55.5082		Calc <u>u</u> late 🥝
Temperature (°C)	75.0000		Summary
Pressure (atm)	1.00000		
	mass %)		Unit Set: <custom></custom>
Water	89.9997		Automatic Chemistry Model
Acetic acid	9.99997		MSE (H3O+ ion) Databanks:
Additional Strea	m Parameters		MSE (H3O+ ion) Using Helgeson Direct
Density - Liquid-1 (g/ml)	0.983266	٦	Isothermal Calculation
Density - Total (g/ml)	0.983266		75.0000 °C 1.00000 atm
Dielectric Constant - Liquid-1	56.7447		Phase Amounts
Ionic Strength (m-based) - Liquid-1 (mol/kg)	5.61843e-3		Aqueous 1075.27 g
Ionic Strength (x-based) - Liquid-1 (mol/mol)	9.79429e-5		Aqueous Phase Properties
рН	2.29495		pH 2.29495
Standard Liquid Volume - Liquid-1 (L)	1.07368		Ionic Strength 9.79429e-5 mol/mol
Total Dissolved Solids (mg/L)	98415.9	J	Density 0.983266 g/ml
		1	Calc. elapsed time: 0.766 sec
			Calculation complete
			Calculation complete
		$\checkmark$	
Input Output			
output			
Advanced Search Add as Stream	Export		

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*.

# **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 software 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.  $1 \times 10^{-10}$  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					
Calculatio	n Settings	Stream Composition and Conditions			
Calculation Type	Single Point Calculation	Stream Amount	1 L		
Calculation Sub-type	Bubble Point	Temperature	25 °C		
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)

Add a new Stream

Click on the new Stream and press <F2> to change the name to Acetone Bubble Point

Select the MSE thermodynamic Framework

Click on the Names Manager Icon, and select the Display Name option, and click OK

Names Mana	ger		?	×
Name Style	Search Criteria	Names Dictionary		
Compone	nt Name Style —			
Displa	ay name			
	lse Names Dictio	nary		

Click on the hyperlink mol next to Stream Amount

Variable	Value	
$\nabla$	tream Parameters	
Stream Amount (mol)		55.5082
Temperature (°C)		25.0000
Pressure (atm)		1.00000
$\nabla$	Inflows (mol)	
Water		55.5082

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**.

omposition	Parameters	Corrosion				
	Varia	ble		Basis	Units	
		Inflo	w varia	bles		
Stream A	mount		,	Volume	L	
Inflows				Molar Concentratio 👡	mol/L	
		Outp	ut vari I			
Aqueous	Composition			loles	mol	
Vapor Co	mposition			Concentration	mol	
Solid Con	nposition			Aolar Concentration Aass Fraction	mol	
2nd Liqui	d Composition			Alle Fraction	mol	
Total Con	nposition			violes	mol	
		Bas	is optio	ons		
Moles					mol	
Mass					g	
Volume					L	
Concentr	ation				mg/L	
Molar Cor	ncentration				mol/L	
Mass Fra					mass %	
Mole Fred	stion				mole %	

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.

Go to the Add Calculation button and select Single Point calculation

# Change the SinglePoint name to Bubble Point Temperature using the <F2> key

Select Bubble point as Type of Calculation.

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** 

	Variable		Value					
	∽ \$	Stream Parameters						
	Stream Amount (L)			1.00000				
0	Temperature (°C)			25.0000				
•	Pressure (atm)			1.00000				
	Calculation Parameters							
	Calculate		Temperature	-				
	~	Inflows	Temperature					
H	Water		Pressure					
E	Acetone			1.00000				

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**".

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

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*.

## Analyzing the Results

Review the Summary Box. The temperature at the bubble point is computed to be **87.48°C** at 1 atm. Also notice that the **Vapor** amount is 5.27e-9 moles out of the total **Aqueous** amount of 52.79 moles. This is by design; the software sets the amount of vapor at 1/10<sup>th</sup> the moles of the stream amount.

Unit Set: <custom></custom>	
Automatic Chemistry Model MSE (H3O+ ion) Databanks: MSE (H3O+ ion) Using Helgeson Direct Bubble Point Calculation	
1.00000 atm 87.4831 ℃	
Phase Amounts Aqueous 52.7856 mol Vapor 5.27856e-9 mol Solid 0.0 mol	
Aqueous Phase Properties pH 6.23325 Ionic Strength 1.05633e-8 m Density 0.954351 g/ml	no l/mo
Calc. elapsed time: 0.762 sec	
Calculation complete	

Calculating the Bubble Point Pressure (Isothermal)

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

Select the Stream named Acetone Bubble point

Go to the Add Calculation button and select Single Point calculation

Change the SinglePoint name to Bubble Point Pressure using the <F2> key

Select **Bubble point** as Type of Calculation.

Change the Calculate-Temperature row to Calculate-Pressure

Calculate	Pressure 🔻		
Water			
Acetone	1.00000		

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

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

### Analyzing the Results

Review the Summary Box. The bubble point pressure is computed to be **0.0700550** at 25 °C. Also notice that the **Vapor** amount is 5.27e-9 moles out of the total **Aqueous** amount of 52.78 moles.

# **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 Studio: 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					
Calculatio	on Settings	Stream Composition and Conditions			
Calculation Type	Single Point Calculation	Stream Amount	Default – 55.5082 moles		
Calculation Sub-type	Dew Point	Temperature	120 °C		
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 <sub>4</sub>	95 mole %		
		H <sub>2</sub> S	3 mole %		

Calculating the Dew Point Temperature (Isobaric)

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to *Sour Natural Gas Dew Point* Select the **MSE** thermodynamic Framework

Click on the Names Manager Icon, and select the Formula option, and click OK

Names Mana	lames Manager ? X				
Name Style					
Compone					
O Display name					
V U	Use Names Dictionary				
Formula	ula				

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

Units Manager - Laden Gas Dew Point	?	×
Units Manager		
Metric V Batch V Moles Moles Mole Frac.	~	·
Molar Conc. Mass Conc. Mass Frac.		
OK Cancel Apply		Help

Enter the composition of the gas given in the table above

Go to the Add Calculation button and select Single Point calculation

### Change the *SinglePoint* name to *Dew Point Temperature* using the <F2> key

Select **Dew point** as Type of Calculation

Keep the Calculate-Temperature option

	Variable	Value			
	Stream Amount (mol)	55.5082			
0	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			

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

Create a **new** *SinglePoint* and name it *Dew Point Pressure*. Repeat the steps above, and select the Calculate-**Pressure** option

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*.

#### Analyzing the Results

Review the Summary Box. The calculated dew point temperature is 94.9154 °C . The calculated dew point pressure is 472.561

Dew Point	Dew Point
Temperature	Pressure
Unit Set: Metric (mole fraction)	Unit Set: Metric (mole fraction)
Automatic Chemistry Model	Automatic Chemistry Model
MSE (H3O+ ion) Databanks:	MSE (H3O+ ion) Databanks:
MSE (H3O+ ion)	MSE (H3O+ ion)
Using Helgeson Direct	Using Helgeson Direct
Dew Point Calculation	Dew Point Calculation
100.000 atm	120.000 °C
91.9154 °C	472.561 atm
Phase Amounts	Phase Amounts
Aqueous 5.55082e-5 mol	Aqueous 1.00000e-6 mol
Vapor 55.5082 mol	Vapor 55.5082 mol
Solid 0.0 mol	Solid 0.0 mol
Aqueous Phase Properties	Aqueous Phase Properties
pH 3.77521	pH 3.58375
Ionic Strength 3.15475e-6 mol/mol	Ionic Strength 5.08513e-6 mol/mol
Density 0.950536 g/ml	Density 0.953852 g/ml
Calc. elapsed time: 0.437 sec	Calc. elapsed time: 0.043 sec
Calculation complete	Calculation complete

**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).** 

o to: Species Output (True Species)		Q	🔍 🖲 Custo
Species Output (True Species)			
ow Filter Applied: Only Non Zero Values			
column Filter Applied: Only Non Zero Values			
	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

Note: This image is for the "Dew Point Pressure" calculation

The aqueous phase, also known as Liquid-1 in the MSE framework, is shown in the center column. The dissolved CH<sub>4</sub>, H<sub>2</sub>S, and CO<sub>2</sub> are 0.347, 0.305, and 0.043 mole % respectively.

# 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 °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.

Autoclave Calculation					
Calcula	ation Settings	Stream Composition and Conditions			
Calculation Type	Single Point Calculation	Stream Amount	Default – 55.5082		
Calculation Sub-type	Isochoric	Ambient Temperature	25 ℃		
Stream Name	Isochoric	H2O	Calculated		
Name Style	Display Formula	N2	77 moles		
Unit Set	Metric, Moles	02	21 moles		
Framework	MSE	CO2	1 mol		
Calculate	Pressure	Ar	0.04 moles		
Vessel Volume	10 L				

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to Isochoric

Select the MSE (default) thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the gas composition in the table above

Go to the Add Calculation button and select Single Point calculation

Change the SinglePoint name to 10L Vessel using the <F2> key

Select Isochoric as Type of Calculation

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			
	$\overline{\sim}$	Stream Parameters				
		Stream Amount (mol)	154.548			
•		Temperature (°C)	25.0000			
0		Pressure (atm)	1.00000			
	$\overline{\nabla}$	Calculation Pa	arameters			
		Total Volume (L)	10.0000			
		Calculate	Pressure 💌			
	$\overline{\sim}$	Inflows	(mol)			
		H2O	55.5082			
		N2	77.0000			
		02	21.0000			
		C02	1.00000			
		Ar	0.0400000			

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

# Analyzing the Results

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

Variable	Value	<b>^</b>	Type of calculation
Stream Parame	eters		Isochoric 💌 Specs
E Stream Amount (mol)	154.548		
- Moles (True) - Liquid-1 (mol)	55.6610		Calc <u>u</u> late 🥝
Moles (True) - Vapor (mol)	98.8871		Summary
Temperature (°C)	25.0000		
Calculation Resul	is (aim)		Unit Set: Metric (moles)
Pressure	304.866		Automatic Chemistry Model
🔨 iniiows (inc	, ij		MSE (H3O+ ion) Databanks:
H2O	55.5082		MSE (H3O+ ion)
N2	77.0000		Using Helgeson Direct
02	21.0000		Isochoric Calculation 25.0000 °C
C02	1.00000		304.866 atm
Ar	0.0400000	>	Phase Amounts
· · · · · ·			Aqueous 55.6610 mol
			Vapor 98.8871 mol Solid 0.0 mol
			Aqueous Phase Properties
			pH 3.94821
			lonic Strength 2.11978e-6 mol/mol Density 1.00310 g/ml
			Density 1.00510 g/m
			Calc. elapsed time: 0.746 sec
			Calculation complete
		¥	Calculation complete
nput Output			
Advanced Search Add as Stream I	Export		

About **304.9 atm** of pressure are needed to compress the 154.55 moles of gas and liquid into a 10-L volume vessel at 25 °C.

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

Total and Phase Flows (Amounts)

column Filter Applied: C	Only Non Zero Values		
	Total	Liquid-1	Vapor
	mol	mol	mol
Mole (True)	154.548	55.6610	98.8871
Mole (App)	154.548	55.6611	98.8871
	g	g	g
Mass	3874.62	1005.05	2869.56
	L	L	L
Volume	10.0001	1.00194	8.99811

The system is 10 L as defined (within the  $1/10^6$  tolerance). The water phase makes up slightly more 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.

# **Vapor Amount and Vapor Fraction**

The **vapor amount** and **vapor fraction** calculations are identical in nature to the <u>Bubble Point</u> calculation, except that instead of the software defining the vapor amount as  $1 \times 10^{-10}$  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				
Calculation Type	Single Point Calculation	Stream Amount	Default - 1 kg	
Calculation Sub-type	Vapor Fraction	Temperature	25 ℃	
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 <sub>4</sub>	1 mass %	

## Calculating the Vapor Fraction Temperature (Isobaric)

## Add a new Stream

Click on the new Stream and press <F2> to change the name to Brine Evaporation – Vapor Fraction

Select the **MSE** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

**Click** on the **Units Manager** lcon, and select Metric, Batch, Mass Frac. This will change all inflows to mass %.

Units Manager - Brine Evapo	ration - Vap	oor Fraction	?	×
Units Manager				
Metric ~	Batch	Mass Frac.	~	F
Customize		Moles Mole Frac. Molar Conc. Mass Conc. Mass Frac.		
OK	Cancel	Apply		Help

Enter the gas composition given in the table above.

Go to the Add Calculation button and select Single Point calculation

Change the *SinglePoint* name to *Vapor Fraction Temperature* using the <F2> key

Select Vapor Fraction as Type of Calculation

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.

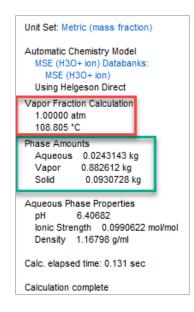
Keep the Calculate-Temperature option

	Variable	Value	^		
Г	Stream Parameters				
	Stream Amount (kg)	1.00000			
0	Temperature (°C)	25.0000			
•	Pressure (atm)	1.00000			
	Calculation P	arameters			
	Vapor Fraction (Vapor/Inflow [mol]) (mole %)	95.0000			
	Calculate	Temperature 💌			
	√ Inflows (n	nass%)			
	H2O	90.0000			
	NaCl	9.00000			
	CaSO4	1.00000			

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

#### Analyzing 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**.



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

mp to: Total and P	hase Flows (Amounts)	~		
Total and Phas column Filter Applied: (	e Flows (Amounts Only Non Zero Values	<u>s)</u>		
	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.

# 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 ℃	
Stream Name	Neutralizing Acid	Pressure	1 atm	
Name Style	Display Formula	H2O	Calculated	
Unit Set	Metric, Moles	СНЗСООН	1 mol	
Framework	MSE			

#### Setting the pH

Add a new Stream

Click on the new Stream and press <F2> to change the name to *Neutralizing Acid* 

Select the AQ thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles (default units). Click OK.

Units Manager - SinglePoint	?	$\times$
Metric V Batch V Moles	~	·
Customize		
OK Cancel Apply		Help

Enter 1 mol of CH3COOH as an inflow

Go to the Add Calculation button and select Single Point calculation

Select Set pH as Type of Calculation

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 **HCI** and **NaOH** (common) and so no additional specifications are required except to set the pH.

	Variable	Value			
<	C Stream Parameters				
	Stream Amount (mol)	56.5082			
	Temperature (°C)	25.0000			
	Pressure (atm)	1.00000			
1	Calculatio	n Parameters			
•	Target pH	0.0			
	Use Single Titrant	No			
	pH Acid Titrant	HCL			
1	pH Base Titrant	NAOH			
<	Inflo	ws (mol)			
	H20	55.5082			
	СНЗСООН	1.00000			

**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.

Calculation Options			?	×
Category Titrants Calculation Options	Select an acid and base	to adjust to meet the specified pl	H.	_
	Acid CH3COOH H2O HCL	Base CH3COOH H2O NAOH		

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.

# Enter 7 as the Target pH value Use the default titrants: HCL and NAOH

V	ariable	Value					
$\overline{\nabla}$							
Stream Amour	it (mol)		56.5082				
Temperature (	°C)		25.0000				
Pressure (atm	)		1.00000				
$\overline{\nabla}$	Calculation P	arameters					
Target pH			7.00000				
Use Single Titr	ant	No					
pH Acid Titran	t i	HCL					
pH Base Titran	t	NAOH					
$\overline{\nabla}$	Inflows	(mol)					
H20			55.5082				
СНЗСООН			1.00000				

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

## Analyzing the Results

Review the **Summary Box** or Click on the **Output-Minitab** to see the Results. About **0.996 moles** of NaOH is needed to neutralize 1 mole of acetic acid to 7 pH.

< Description 🥸 Definition 📓 Re	port				
Variable	Value	~		Type of calculation	
C Stream Pa	rameters			Set pH 🔹 Specs	1
E Stream Amount (mol)	57.5044				
Moles (True) - Liquid-1 (mol)	58.3648			Calc <u>u</u> late 🥝	
Temperature (°C)	25.0000			Summary	
Pressure (atm)	1.00000				_
Calculation R				Unit Set: Metric (moles)	^
pH titrant added: NaOH	0.996144 (mol)			Automatic Chemistry Model MSE (H3O+ ion) Databanks:	
H20	55.5082			MSE (H3O+ ion)	
СНЗСООН	1.00000			Using Helgeson Direct	
NaOH	0.996144			Set pH Calculation 25.0000 °C	
Input Output		>	>	1.0000 atm Target pH 7.00000 Acid Tirrant: HCI Total: 0.0 mol Base Tirrant: NaOH Total: 0.996144 mol Added: 0.996144 mol Added: 0.996144 mol Phase Amounts Aqueous 58.3648 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 7.0000 Ionic Strength 0.0147421 mol/mol Density 1.03528 g/ml	
Advanced Search Add as Strea	n Export			Calc. elapsed time: 1.301 sec	~

# **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<sub>3</sub>)

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<sub>3</sub>) 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 Conditions			•	
Calculation Type	Single Point Calculation	Stream Amount	Default - 1 kg	
Calculation Sub-type	Precipitation Point	Temperature 25 °C		
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	MSE	MgCl2 9325 ppm (mass)		
		CO2 431 ppm (mass)		
		CaCO3	0 ppm(mass)	

Calculating the Precipitation of Calcite (CaCO<sub>3</sub>)

Add a new Stream

Click on the new Stream and press <F2> to change the name to Solubility of CaCO3 – Precipitation Point

Select the **AQ** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

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.

Units Manager - Solubility of CaCO3 - Precipitation ? X
Units Manager
Metric V Batch V Mass Frac. V Moles Mass Frac. Molar Conc. Mole Frac. Conc. Mass
OK Cancel Apply Help

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

mposition	Parameters	Corrosion		
	Varia	ble	Basis	Units
		Inf	ow variables	
Stream Ar	nount		Mass	kg
Inflows			Mass Fraction	mass %
		Ou	put variables	
Aqueous	Composition		Mass Fraction	mass %
Vapor Co	mposition		Mass Fraction	mass %
Solid Com	position		Mass Fraction	mass %
	I Composition		Mass Fraction	mass %
Total Com	position		Mass Fraction	mass %
		В	isis options	
Moles				mol
Mass				kg
Volume				L
Concentra				mg/L
	centration			mol/L
Mass Fra				mass %
Mole Fred	tion			0/0
				mass % (ppm (mass)

Enter the stream composition given in the table <u>above</u>.

Go to the Add Calculation button and select Single Point calculation

Select Precipitation Point as Type of Calculation

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.

Variable	Value		~	Type of calculation
√ Stream Par	ameters	ters		Precipitation Point 🔻 Specs
Stream Amount (kg)	1.	00000		
Temperature (°C)	2	.0000		Calc <u>u</u> late 🥥
Pressure (atm)	1.	00000		Summary
	arameters			
Precipitant:	<select></select>			Unit Set: <custom></custom>
Adjusted Inflow:	<select></select>			Automatic Chemistry Model
√ Inflows (ppr	n (mass))	_		MSE (H3O+ ion) Databanks:
H2O	9.79	374e5		MSE (H3O+ ion)
CaCl2	1(	870.0		Using Helgeson Direct
MgCl2	93	25.00		Precipitation Point Calculation 25.0000 °C
C02	43	1.000		1.00000 atm
CaCO3		0.0		> Precipitate: Not specified.
				Adj. Inflow: Not specified.
				Calculation not done
				Please select a target solid. Please select a variable to adjust.
			×	
put				

## Select the CaCO3 (Calcite) as the Precipitant

### Select CaCO3 as the Adjusted Inflow

	Calculation Parameters									
•	Precipitant:	CaCO3 (Calcite)								
	Adjusted Inflow:	CaCO3 🗾								
	√ Inflows (pp)									
	H2O	CaCl2 MgCl2								
	CaCl2	C02								
	MgCl2	CaCO3								
	C02	431.000								
	CaCO3	0.0								

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

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



OLI Studio (Version 11.	5.1 Beta) - [1.7 Precipitation P	oint calculation_Example_8.oad*]			– 🗆 X
File Edit Streams	Calculations Chemistry	Tools View Window Help			- <i>E</i> ×
🗄 🗅 🚅 🔚 🕹 🖻 💼	🛯 🎒 📍 📢 🛛 L1 Va	So L2 Re ± MSE ± MSE ± AQ ±	🗄 🏘 🎆 🛃 💱 🔊 😭 🎸		
Navigator	τ • × [		· · · · ·		
1.7 Precipitation Point cal	Calculation Options		?	×	
- 🎸 Dew Point Tem					
Dew Point Pres		Precipitation Point			Type of calculation
10 L Vessel	Component Calculation Options	Hide Related Inflows	New Inflow	a	Precipitation Point 🔻 Specs
🖶 👌 Brine Evaporation -		Precipitant	Adjusted Variable		
🎸 Vapor Fraction		MgCl2.2CaCl2.6H20	H20	1	Calculate 🥥
Neutralizing Acid		MgCl2.12H2O	CaCl2		Summary
Solubility of CaCO		MgCl2.2H2O MgCl2.4H2O	MgCl2 CO2		Unit Set: <custom></custom>
🕹 Calcite Precipit		MgCl2.6H20 (Bischofite)	CaCO3		Automatic Chemistry Model
Actions		MgCl2.8H20			MSE (H3O+ ion) Databanks:
Actions		MgCl2.HCl.7H2O Mg(OH)2 (Brucite) - Sol			MSE (H3O+ ion) Using Helgeson Direct
		MgO (Periclase) - Sol			Precipitation Point Calculation
		CaCO3 (Aragonite) - Sol CaCO3 (Calcite) - Sol			25.0000 °C 1.00000 atm
					> Precipitate: CaCO3 (Calcite)
		Select the precipitant to precipitate a	and the adjusted variable to adjust until		Adj. Inflow: CaCO3 Total 313.080 ppm (mass)
		the solid forms.			Phase Amounts
				- 1	Aqueous 1.00032 kg Solid 1.00087e-13 kg
					Aqueous Phase Properties pH 6.06957
					Ionic Strength 0.0108617 mol/mol Density 1.01473 g/ml
Plot Template Manager					
Flot relipiate Manager					Calc. elapsed time: 1.577 sec
					Calculation complete
					· · · · · · · · · · · · · · · · · · ·
×					
>		ОК	Cancel Apply H	lelp	^
+ Calculation Complete!					~
For Help, press F1					

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

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*.

## Analyzing the Results

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

The software calculated that the solubility of CaCO<sub>3</sub> as Calcite in the solution under study is around  $\sim$ **313.1** ppm (mass). The pH of this solution is  $\sim$ 6.07.

Variable	Value	<b>^</b>		Type of calculation
Stream Par	ameters			Precipitation Point 👻 Specs
Stream Amount (kg)	1.00032			
— Mass - Liquid-1 (kg)	1.00032			Calc <u>u</u> late 🥝
Mass - Solid (kg)	1.00087e-13			Summary
Temperature (°C)	25.0000			
Pressure (atm)	1.00000			Unit Set: <custom></custom>
Calculation Result Adjusted Inflow: CaCO3	313.080			Automatic Chemistry Model MSE (H3O+ ion) Databanks:
C Intiows (ppn				MSE (H3O+ ion) Using Helgeson Direct
H2O	9.79064e5			Precipitation Point Calculation
CaCl2	10866.6			25.0000 °C
MgCl2	9322.05			1.00000 atm
C02	430.864		>	Precipitate: CaCO3 (Calcite)
CaCO3	313.080			Adj. Inflow: CaCO3 Total 313.080 ppm (mass)
				Phase Amounts Aqueous 1.00032 kg Solid 1.00087e-13 kg Aqueous Phase Properties pH 6.06957 Ionic Strength 0.0108617 mol/mol
out		*		Density 1.01473 g/ml Calc. elapsed time: 1.577 sec Calculation complete

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

<ul> <li>♦ OLI Studio (Version 11.5.1 B</li> <li>■ File Edit Streams Calc</li> <li>□ □ □ □ □ □ ↓ □ □ ↓ □ □ □ ↓</li> <li>Navigator</li> </ul>	ulations Chemistry Tools		8	□ × - ₽ ×
1.7 Precipitation Point Calcul	Report Contents Category Calculation Summary, Stream Inflows Speciation Summary, Stream Inflows Scaling Tendencies Scaling Induction Tir Species Culput Molecular Output Element Balance Species Fugacities Species Subbilities Species Solf Diffusiv Vapor Phase Diffusiv Species Solf Diffusiv Gibbs Free Energy o Entropy Entropy Entropy Entropy Serve Equations Species Reguations Species Reguations Species Reguations Species Reguations Species Reguent Species Regue	?     ×       Report Contents	Customize	Export
Plot Template Manager	< >>	This section displays the stream inflows. 6 of 23 Sections selected		~
Calculation Complete!		OK Cancel Apply Help		^ ~ 1) NUM

Notice that the concentrations have changed slightly. This is to accommodate the additional 313.1 ppm CaCO<sub>3</sub> 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	9.79064e5
CaCl2	10870.0	10866.6
MgCl2	9325.00	9322.05
CO2	431.000	430.864
CaCO3	0.0	313.080

# Example 9: Determining the Solubility of Aragonite (CaCO<sub>3</sub>)

**Calcite** is the thermodynamically stable phase of calcium carbonate. **Aragonite**, calcite's orthorhombic polymorph, is about 1.5 times more soluble than calcite<sup>4</sup>. 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.

## Starting the Simulation

Calculating the Precipitation of Aragonite (CaCO<sub>3</sub>)

Under the Stream Solubility of CaCO3 – Precipitation Point, Add a Single Point calculation

Select Precipitation Point as Type of Calculation

Change the SinglePoint name to Aragonite Precipitation using the <F2> key

Select the CaCO3 (Calcite) as the Precipitant

Select CaCO3 as the Adjusted Inflow

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

<sup>&</sup>lt;sup>4</sup> <u>https://www.sciencedirect.com/topics/earth-and-planetary-sciences/calcite</u>

### Click on Chemistry > Model Options

OLI Studio - [Single point calculations.oad*]								
File Edit Streams Calculations Chemistry Tools View Window Help								
	Pre-built Models >							
🛛 🖻 🖬 🕹 🛍 📾 🖗 🖇	Templates > se 🛓 MSE 🛓 🗛 🛨							
Navigator	Model Options							
Single point calculations.oad*	ecipitation							

#### Select the Phases tab

**Click** on the "+" next to the Ca(+2) box to display all the calcium containing solids Scroll down to find CaCO3 (Calcite) and **uncheck** this solid

Click OK continue.

Aragonite Precipitation Cher	nistry Model Options	?	×
Databanks Redox Phases	T/P Span  nclude Solid Phases  All Solids  C(+4)  Ca(+2)  Ca(+2)  Ca(OH)2 (Portlandite)  CaCO3 (Aragonite)  CaCO3 (Aragonite)  CaCO3 (Calcite)  CaCO2 (Hydrophilite)  CaCO2 (Hydrophilite)  CaCO2.2H2O (Sinjarite)  CaCO2.2H2O (Sinjarite)  CaCO2.2H2O (Calcite)  CaCO2.2H2O (Calcite)  CaCO2.2H2O (Calcite)  CaCO2.2H2O (Calcite)  CaCO2.2H2O (Calcite)  CaCO2.2H2O (Calcite)  CaCO2.2H2O (Calcite)	^	
	Calculate Scaling Tendencies for excluded so	> Y olids Hel	þ

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.

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

# Analyzing the Results

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

The software calculated that the solubility of CaCO<sub>3</sub> as Aragonite in the solution under study is around  $\sim$ 353.8 ppm (mass). The pH of this solution is  $\sim$ 6.15. You can see that the solubility of Aragonite is higher than the solubility of Calcite (313.1 ppm (mass)).

Description 🥸 Definition <u> </u>	Report		<b>— — — —</b>
Variable Value		^	Type of calculation
Stream Par	ameters		Precipitation Point 🔻 Specs
E Stream Amount (kg)	1.00036		
— Mass - Liquid-1 (kg)	1.00036		Calc <u>u</u> late 🥥
L Mass - Solid (kg)	1.00087e-13		Summary
Temperature (°C)	25.0000		
Pressure (atm)	1.00000		Unit Set: <custom></custom>
Calculation Result	s (ppm (mass))		Automatic Chemistry Model
Adjusted Inflow: CaCO3	353.836		MSE (H3O+ ion) Databanks:
T Inflows (ppr	n (mass))		MSE (H3O+ ion)
H2O	9.79024e5		Excluding 1 solid phase Using Helgeson Direct
CaCl2	10866.1		Precipitation Point Calculation
MgCl2	9321.67		25.0000 °C
C02	430.846		> 1.00000 atm
CaCO3	353.836		Precipitate: CaCO3 (Aragonite) Adj. Inflow: CaCO3
II			Total 353.836 ppm (mass)
			Phase Amounts
			Aqueous 1.00036 kg
			Solid 1.00087e-13 kg
			Aqueous Phase Properties
			pH 6.14902
			lonic Strength 0.0108837 mol/mol Density 1.01478 g/ml
			Density 1.01476 g/m
		~	Calc. elapsed time: 1.670 sec
put Output			Calculation complete
Advanced Search Add as Stre	eam Export		

# Example 10: Determining the Solubility of Dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>)

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 occur in geological time frames.

The species Dolomite is not present in the standard MSE database. However, it does exist in one of the specialty databases. This database is called *Geochemical (MSE)*.

### Starting the Simulation

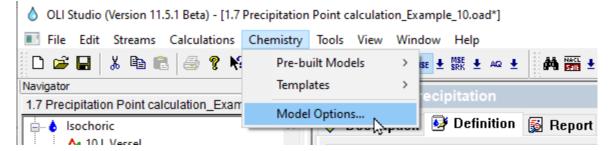
Calculating the Precipitation of Dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>)

Under the Stream Solubility of CaCO3 – Precipitation Point, Add a Single Point calculation

Change the SinglePoint name to Dolomite Precipitation using the <F2> key

Select Precipitation Point as Type of Calculation

### Click on Chemistry > Model Options



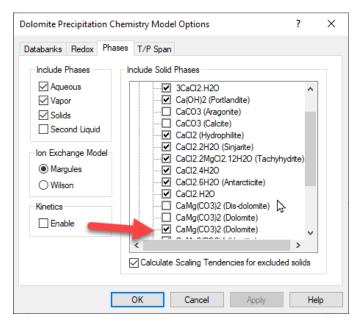
In the Databanks Tab, select the **Geochemical (MSE)** #1Databank. You can double click or use the right arrow #2 to add the databank. Then Click **OK**.

Dolomite Pr	ecipitati	on Chem	istry Model	Options		?	×
Databanks	Redox	Phases	T/P Span		n;*		
- Databank Availal	The M	SE (H3O+		k Selected MSE (H3O+ic	~	1	
BATE CASE Corros Densi Geoc Hone	ST RCL sion (MSI ty Databi hemical (	E) ase		MSE (H3U+ K	n)	↑ ↓	
< Databa	ank sear		from top to b rows to chan	ottom. ge the search ord	> er.		
			OK	Cancel	Apply	He	lp

You may have additional or fewer databases depending on previous installations and imported databases. Some are from OLI and some may be private (user) databases.

### Select the Phases tab

**Click** on the "+" next to the Ca(+2) box to display all the calcium containing solids Scroll down to find CaCO3 (Calcite) and CaCO3 (Aragonite) and **uncheck** these solids. The MSE model also has ordered and disordered dolomite. These also should be unchecked. See the figure below. Make sure to keep the second dolomite species checked. 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.

## Select the CaMg(CO3)2 (Dolomite) as the Precipitant

#### Select CaCO3 as the Adjusted Inflow

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

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

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*.

# Analyzing 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  $\sim$ 257.7 ppm (mass). The pH of this solution is  $\sim$ 5.95.

So far, we know that the solubilities of Calcite, Aragonite, and Dolomite in a MgCl<sub>2</sub>, CaCl<sub>2</sub> and CO<sub>2</sub> containing solution were 413.15, 552.87 and, 246.84 ppm (mass) respectively.

🛷 Description 👹 Definition 📓 Report							
Variable	Value	~	Type of calculation				
C Stream Par	rameters		Precipitation Point 👻 Specs				
E Stream Amount (kg)	1.00026						
— Mass - Liquid-1 (kg)	1.00026		Calc <u>u</u> late	<b>@</b>			
Mass - Solid (kg)	1.84402e-13		Summary N				
Temperature (°C)	25.0000						
Pressure (atm)	1.00000		Unit Set: <custom></custom>	^			
Calculation Result	ts (ppm (mass))		Automatic Chemistry Model				
Adjusted Inflow: CaCO3	257.706		MSE (H3O+ ion) Datab	oanks:			
☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐	✓ Inflows (ppm (mass))			Geochemical (MSE) MSE (H3O+ ion)			
H2O	9.79118e5		Excluding 4 solid phas	es			
CaCl2	10867.2		Using Helgeson Direct	t			
MgCl2	9322.57		Precipitation Point Calcul	ation			
C02	430.888		25.0000 °C 1.00000 atm Precipitate: CaMg(CO3)2 (Dolomite)				
CaCO3	257.706						
		Adj. Inflow: CaCO3 Total 257.706 ppm		n (mass)			
				Aqueous 1.00026 kg Solid 1.84402e-13 kg			
		*	Aqueous Phase Properti pH 5.95165 Ionic Strength 0.010 Density 1.01466 g/m	8318 mol/mol			
Input Output		Calc. elapsed time: 1.886	i sec				
Advanced Search Add as Stream Export							

# **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<sub>2</sub>S 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						
Calc	ulation Settings	Stream Composition and Conditions				
Calculation Type	Single Point Calculation	Stream Amount	Default – 55.5082			
Calculation Sub-type	Composition Point	Temperature	25 ⁰C			
Stream Name	Composition Point	Pressure	1 atm			
Name Style	Display Formula	H2O	55.5082 (default)			
Unit Set	Metric, Moles	H2S	0 moles			
Framework	MSE	Target H2S-Aq value	0.001 moles			

# Calculating the Vapor Fraction Temperature (Isobaric)

# Add a new Stream

Click on the new Stream and press <F2> to change the name to Composition Point

Select the MSE thermodynamic Framework (this is the default)

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition of the gas given in the table above

Go to the Add Calculation button and select Single Point calculation

Select Composition Point as Type of Calculation

Change the SinglePoint name to H2S dissolved in water using the <F2> key

Set the Target Species to H2S-Liq1 (i.e. the molecular H<sub>2</sub>S dissolved in the Aqueous phase)

Set the Target H2S value to 0.001 moles

Set the Adjusted Inflow to H2S

	Variable	Value
Г	Stream Part	rameters
	Stream Amount (mol)	55.5082
	Temperature (°C)	25.0000
	Pressure (atm)	1.00000
	Calculation P	Parameters
Π	Target Species:	H2S - Liq1
Π	Target H2S Value: (mol)	1.00000e-3
Π	Adjusted Inflow:	H2S 🗸
P	Inflows	(mol)
	H2O	55.5082
Г	H2S	0.0

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

## Analyzing the Results

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

Variable       Value         Stream Parameters       Composition Point Specs         Stream Amount (mol)       55.5093         Temperature (*C)       25.0000         Pressure (atm)       1.00000         Adjusted Inflow: H2S       1.01049e-3         H2O       55.5082         H2S       1.01049e-3         MSE (H3O+ ion)       Using Helgeson Direct         Composition Point       Summary         Unit Set: Metric (moles)       Automatic Chemistry Model         MSE (H3O+ ion)       Using Helgeson Direct         Composition Point       Source         H2S       1.01049e-3         H2S       1.01049e-3         MSE (H3O+ ion)       Using Helgeson Direct         Composition Point       Source         Jondo atm       Target H2S         Fixed at 1.0000e-3 mol       Aqueous 55.5093 mol         Vapor 0.0 mol       Solid 0.0 mol         Solid 0.0 mol       Solid 0.0 mol         Solid 0.0 mol       Solid 0.0 mol         Solid 0.997065 g/ml       Calculation complete	< Description 🔮 Definition 📓	Report		
Stream Amount (mol)       55.503         Moles (True) - Liquid-1 (mol)       55.503         Temperature (°C)       25.0000         Pressure (atm)       1.00000         Adjusted Inflow: H2S       1.01049e-3         H2O       55.5082         H2S       1.01049e-3         Wight H2S       1.01049e-3         Wight H2S       1.01049e-3         Wight H2S       1.01049e-3         Wight H2S       1.01049e-3         H2S       1.01049e-3         Wight H2S       1.01049e-3         H2S       1.01049e-3 <td< th=""><th>Variable</th><th>Value</th><th>~</th><th>Type of calculation</th></td<>	Variable	Value	~	Type of calculation
Imput       Unit       St.5093         Temperature (°C)       25.0000         Pressure (atm)       1.00000         Adjusted Inflow: H2S       1.01049e-3         M2O       55.5082         H2S       1.01049e-3         Using Helgeson Direct       Composition Point Calculation 25.0000 °C         1.00000 atm       Target H2S         Freed at 1.0000e-3 mol       Adjueus 55.5093 mol         Vapor 0.0 mol       Solidi 0.0 mol         Phase Amounts       Aqueous 55.5093 mol         Aqueous 55.5093 mol       Vapor 0.0 mol         Phase Amounts       Aqueous 55.5093 mol         Aqueous 55.5093 mol       Vapor 0.0 mol         Calculation complete       Calculation complete	Stream Pa	rameters		Composition Point 👻 Specs
Importature (*C)       25.0000         Temperature (*C)       25.0000         Pressure (atm)       1.0000e         Adjusted Inflow: H2S       1.01049e-3         H2O       55.5082         H2S       1.01049e-3         MSE (H3O+ ion) Databanks: MSE (H3O+ ion) Databanks: MSE (H3O+ ion) Databanks: MSE (H3O+ ion) Databanks: MSE (H3O+ ion) Using Helgeson Direct         Composition Point Calculation 25.0000 °C         H2S       1.01049e-3         Fixed at 1.0000e-3 mol Adji.Inflow: H2S         Total 1.01049e-3 mol Phase Amounts         Aqueous S5.5093 mol Vapor 0.0 mol Solid 0.0 mol         Aqueous Phase Properties pH 4.98095 Ionic Strength 1.88927e-7 mol/mol Density 0.997065 g/ml         Calc. elapsed time: 1.297 sec         Calculation complete	E Stream Amount (mol)	55.5093		
Pressure (atm)       1.00000         Calculation Results (mol)       1.01049e-3         M2       Inflows (mol)         H2S       1.01049e-3         H2S       1.01049e-3         Using Helgeson Direct       Composition Point Calculation 25.000 °C         1.00000 atm       Target H2S         Fixed at 1.0000e-3 mol       Adjuinflow: H2S         Total 1.01049e-3 mol       Phase Amounts         Aqueous 55.5093 mol       Vapor 0.0 mol         Solid 0.0 mol       Solid 0.0 mol         Solid 0.0 mol       Calculation complete	Moles (True) - Liquid-1 (mol)	55.5093		Calc <u>u</u> late 🥝
Calculation Results (mol)         Adjusted Inflow: H2S       1.01049e-3         H2O       55.5082         H2S       1.01049e-3         MSE (H3O+ ton)       Using Helgeson Direct         Composition Point Calculation       25.0000 °C         1.00000 atm       Target: H2S         Fixed at 1.0000e-3 mol       Adjuinflow: H2S         Vapor       0.0 mol         Solid       0.0 mol         Calc. elapsed time: 1.297 sec       Calculation complete	Temperature (°C)	25.0000		Summary
Adjusted Inflow: H2S       1.01049e-3         H2O       55.5082         H2S       1.01049e-3         MSE (H3O+ ion)       Using Helgeson Direct         Composition Point Calculation       25.0000 °C         1.00000 atm       Target: H2S         Fixed at 1.0000e-3 mol       Adj. Inflow: H2S         Total 1.01049e-3       Total 1.01049e-3 mol         Phase Amounts       Aqueous S5.5093 mol         Vapor 0.0 mol       Solid 0.0 mol         Solid 0.0 mol       Solid 0.0 mol         Solid 0.0 mol       Solid 0.0 mol         Calculation complete       Calculation complete	Pressure (atm)	1.00000		
Intlows (mol)       Automatic Chemistry Model         H20       55.5082         H2S       1.01049e-3         Using Helgeson Direct       Composition Point Calculation 25.0000 °C         25.0000 °C       1.00000 atm         Target: H2S       Fixed at 1.0000e-3 mol         Adj. Inflow: H2S       Total 1.01049e-3 mol         Phase Amounts       Aqueous 55.5093 mol         Vapor 0.0 mol       Solid 0.0 mol         Aqueous Phase Properties       PH         PH       4.98095         Ionic Strength 1.88927e-7 mol/mol       Density 0.997065 g/ml         Calc. elapsed time: 1.297 sec       Calculation complete	Calculation R	esults (mol)		Unit Set: Metric (moles)
Intlows (mol)       MSE (H30+ ion) Databanks: MSE (H30+ ion)         H20       55.5082         H2S       1.01049e-3         Composition Point Calculation 25.0000 °C       2.0000 °C         1.00000 atm       Target: H2S         Fixed at 1.0000e-3 mol       Adj. Inflow: H2S         Total 1.01049e-3 mol       Adj. Inflow: H2S         Total 1.01049e-3 mol       Solid 0.0 mol         Aqueous 55.5093 mol       Vapor 0.0 mol         Solid 0.0 mol       Solid 0.0 mol         Calc. elapsed time: 1.297 sec       Calculation complete	Adjusted Inflow: H2S	1.01049e-3		Automatic Chemistry Model
H2S       1.01049e-3         H2S       1.01049e-3         Using Helgeson Direct       Composition Point Calculation 25.0000 °C 1.00000 atm Target: H2S Fixed at 1.00000e-3 mol Adj. Inflow: H2S Total 1.01049e-3 mol         Adj. Inflow: H2S Total 1.01049e-3 mol         Adj. Inflow: H2S Total 1.01049e-3 mol         Solid 0.0 mol         Vapor 0.0 mol         Solid 0.0 mol         Aqueous Phase Properties PH 4.98095         Input         Dutput	Inflows	(mol)		MSE (H3O+ ion) Databanks:
H2S       1.010498-3         Composition Point Calculation 25.0000 °C         1.00000 atm         Target: H2S         Fixed at 1.0000e-3 mol         Adj. Inflow: H2S         Total       1.01049e-3 mol         Phase Amounts         Aqueous       55.5093 mol         Vapor       0.0 mol         Solid       0.0 mol         Aqueous Phase Properties         pH       4.98095         lonic Strength       1.88927e-7 mol/mol         Density       0.997065 g/ml         Calc. elapsed time: 1.297 sec       Calculation complete	H2O	55.5082		
Input       Output         Input       Output	H2S	1.01049e-3		
Input       Dutput         Input       Dutput              Target: H2S       Fixed at 1.00000e-3 mol         Adj. Inflow: H2S       Total 1.01049e-3 mol         Phase Amounts       Aqueous 55.5093 mol         Vapor       0.0 mol         Solid       0.0 mol         Solid       0.0 mol         Calc. elapsed time: 1.297 sec       Calculation complete				
Fixed at 1.0000e-3 mol         Adj. Inflow: H2S         Total 1.01049e-3 mol         Phase Amounts         Aqueous 55.5093 mol         Vapor 0.0 mol         Solid 0.0 mol         Aqueous Phase Properties         PH 4.98095         Ionic Strength 1.88927e-7 mol/mol         Density 0.997065 g/ml         Calc. elapsed time: 1.297 sec         Calculation complete				
Adj. Inflow: H2S Total 1.01049e-3 mol Phase Amounts Aqueous 55.5093 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 4.98095 lonic Strength 1.88927e-7 mol/mol Density 0.997065 g/ml Calc. elapsed time: 1.297 sec Calculation complete				
Input       Dutput         Input       Dutput				
Aqueous 55.5093 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 4.98095 Ionic Strength 1.88927e-7 mol/mol Density 0.997065 g/ml Calc. elapsed time: 1.297 sec Calculation complete				Total 1.01049e-3 mol
Vapor       0.0 mol         Solid       0.0 mol         Solid       0.0 mol         Aqueous Phase Properties         pH       4.98095         Ionic Strength       1.88927e-7 mol/mol         Dutput       Output         Calc. elapsed time: 1.297 sec         Calculation complete				
Input Dutput Dutput Output Output				
Input Output				
Input Output				Aqueous Phase Properties
Input Dutput Dut				
Input Output Calc. elapsed time: 1.297 sec Calculation complete				
Calculation complete			¥	Density 0.997065 g/ml
Calculation complete	Input Output			Calc. elapsed time: 1.297 sec
Advanced Search Add as Stream Export	Advanced Search Add as Sh	ream Export		Calculation complete

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	Liquid-1
	mol	mol
H2O	55.5082	55.5082
H2S	1.0e-3	1.0e-3
H3O+1	1.04872e-5	1.04872e-5
HS-1	1.04862e-5	1.04862e-5
OH-1	9.71758e-10	9.71758e-10
S-2	1.01628e-14	1.01628e-14
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  $H_3O^+$  and  $HS^-$  are nearly identical. This is because the following reactions:

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$$

 $H_3O^+$  is slightly higher because a second reaction, the dissociation of water also contributes to the  $H_3O^+$  formation.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

# **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**

<u>Calculating results at ambient conditions</u> <u>Increasing the volume of the vessel and its implications</u> <u>Increasing the final temperature and its implications</u> <u>Increasing the final pressure and its implications</u>

# Using a Reactive Gas

<u>Calculating results at final conditions</u> <u>Using a Reactive Gas and a NaOH solution</u>

# Example 12: Using an Inert Gas

#### **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<sub>2</sub>. The ambient temperature is 25 °C. The N<sub>2</sub> is presumed to be the gas that remains in the autoclave headspace after sparging (O<sub>2</sub> removal) is completed.

The amount of N<sub>2</sub> added is the combination of N<sub>2</sub> vapor filling the headspace, and N<sub>2</sub> that dissolves in the water (N<sub>2</sub> aqueous). Since N<sub>2</sub> has a low water solubility, this second amount is negligible. H<sub>2</sub>O also evaporates, so the headspace will be a mixed gas, N<sub>2</sub> and H<sub>2</sub>O.

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							
Calc	ulation Settings	Stream Composition and Conditions					
Calculation Type	Calculation Type Single Point Calculation S		Default – 55.5082				
Calculation Sub-type	Autoclave	Ambient Temperature	25 ℃				
Stream Name	Autoclave	Final Temperature	25 ℃				
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				

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to Autoclave

Select the **MSE-SRK** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the N2 as an inflow

Go to the Add Calculation button and select Single Point calculation

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

**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 instructions that additional specs are needed. The specifications need to be defined in the **Calculation Parameters** grid section.

## Click on the **Specs** button.

Variable	Value	^	Type of calculation	
Stream Par	ameters		Autoclave 👻 Spec	s
Stream Amount (mol)		55.5082		
Ambient: Temperature (°C)		25.0000	Calc <u>u</u> late 🥥	
Ambient: Pressure (atm)			Summary	
Calculation P	arameters			-
Final Temperature (°C)		0.0	Unit Set: Metric (moles)	
Final Pressure (atm)			Automatia Chamiata Madal	
Vessel Volume (L)		0.0	Automatic Chemistry Model MSE-SRK (H3O+ ion) Databanks:	
Compute results at which condition	Ambient		MSE-SRK (H3O+ ion)	
inflows	(moi)		MSE (H3O+ ion)	
H2O		55.5082	Second Liquid phase Using Helgeson Direct	
N2		0.0	Autoclave Calculation	
~			> Specifications:	
			Ambient Temperature 25.0000 °C Final Temperature 0.0 °C Final Pressure Vessel Volume 0.0 L Calculation not done	
			Volume of vessel is invalid. Use the specs button to select up to gases to consider.	5
ıt	$\triangleright$	~		

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**.

Calculation Options		?	×
Calculation Options Category Autoclave Calculation Options	Autoclave          Target Gas(es) (5 Max)         H20 · Vap         N2 · Vap         Selected         1         Specification Type         Partial Pressure(s)         Mole Fraction(s) in Aqueous Phase	?	×
	OK Cancel Apply	Hel	p

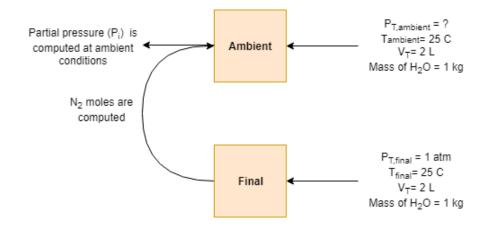
Set the Final Temperature to 25°C, the Final Pressure to 1 atm and the Vessel Volume to 2 L Set the Compute results at which Conditions to Ambient

Variable	Value					
Stream Amount (mol)	55.5082					
Ambient: Temperature (°C)	25.0000					
Ambient: Pressure (atm)						
	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 °C. The partial pressure of  $N_2$  will be calculated at a final temperature, 25 °C 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 shown in the image below.

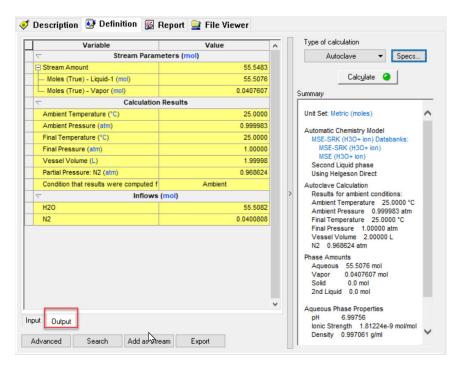


We are ready to perform the calculation. Click on the Calculate button or press the <F9> key

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*.

#### Analyzing 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 are the same, and by design, the autoclave calculation uses the identical inflows for ambient and final conditions.

The amount of N<sub>2</sub> added is 0.0400808 moles, which produces a ~0.9686 atm partial pressure. The computed N<sub>2</sub> 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 (N is 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	2.30275e-3
O(-2)	55 5082	33 3173	99 9977	2 30275e-3
N(0)	0.0801616	0.0481148	1.49271	98.5073

These results infer two effects:

As the final pressure ( $P_T$ ) increases, additional  $N_2$  will dissolve in the water, shifting the fraction of nitrogen to the liquid.

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.

#### 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**.

Right click on the Autoclave - Inert Gas single point calculation and select copy

Selecting the stream named Autoclave, right click on it and select paste

Rename the copied stream Autoclave – Inert Gas Vessel Vol 5L

Autoclave	Arrange > Cut	in <b>€ Auto</b> elswa in <b>¢</b> A	Arrange > Cut Copy	Autoclave Autoclave - Inert Gas Autoclave - Inert Gas Vessel Vol 5L
Actions	Copy 1	Actions	Paste 2	
Actions	Delete Rename	Actions Add Strea Add Mixe Add Singl	Delete Rename Add As Stream	
	Add As Stream Clear Results	Add Singi Add Surve	Clear Results Clear Status	
Plot Template Manager	Clear Status Calculation Options	Plot Template I	Calculation Options	

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

	Variable	Value	^		Type of calculation
Γ	√ Stream Pa	rameters			Autoclave 💌 Specs
	Stream Amount (mol)	55.5082			
	Ambient: Temperature (°C)	25.0000			Calc <u>u</u> late 🥥
	Ambient: Pressure (atm)				Summary
	Calculation F	Parameters	1		
	Final Temperature (°C)	25.0000	1		Unit Set: Metric (moles)
	Final Pressure (atm)	1.00000			Automatic Chemistry Model
	Vessel Volume (L)	5.00000			MSE-SRK (H3O+ ion) Databanks:
	Partial Pressure: N2 (atm)				MSE-SRK (H3O+ ion)
	Compute results at which condition	Ambient 💌			MSE (H3O+ ion) Second Liquid phase
	√ Inflows	(mol)	1		Using Helgeson Direct
	H2O	55.5082		>	Autoclave Calculation
	N2	0.0			Specifications:
					Ambient Temperature 25.0000 °C Final Temperature 25.0000 °C
					Final Pressure 1.00000 atm
					Vessel Volume 5.00000 L
					N2
					Calculation not done

At this point the system is defined as 1 kg  $H_2O$  (55.5082 moles) at an ambient temperature of 25 °C. The partial pressure of  $N_2$  will be calculated at a final temperature, 25 °C 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.

## Analyzing the Results

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

ኛ Description  🔯 Definition 🙀	Report 🚊 File Viewer	•			
Variable	Value		^		Type of calculation
C Stream Param	neters (mol)				Autoclave 💌 Specs
Stream Amount	5	5.6671			
- Moles (True) - Liquid-1 (mol)	5	5.5037			Calculate 🥝
Moles (True) - Vapor (mol)	0.1	63414		s	Summary
Calculation	Results			Шr	
Ambient Temperature (°C)	2	5.0000			Unit Set: Metric (moles)
Ambient Pressure (atm)	1	.00000			Automatic Chemistry Model
Final Temperature (°C)	2	5.0000			MSE-SRK (H3O+ ion) Databanks:
Final Pressure (atm)	1	.00000			MSE-SRK (H3O+ ion)
Vessel Volume (L)	5	.00004			MSE (H3O+ ion) Second Liquid phase
Partial Pressure: N2 (atm)	0.9	68642			Using Helgeson Direct
Condition that results were computed f	Ambient				Autoclave Calculation
	(mol)			>	Results for ambient conditions:
H20	5	5.5082			Ambient Temperature 25.0000 °C Ambient Pressure 1.00000 atm
N2	0.1	58888			Final Temperature 25.0000 °C
		_			Final Pressure 1.00000 atm Vessel Volume 5.00000 L N2 0.968642 atm
		\$			Phase Amounts Aqueous 55.5037 mol Vapor 0.163414 mol Solid 0.0 mol 2nd Liquid 0.0 mol
Input Output Advanced Search Add as Str	eam Export		~		Aqueous Phase Properties pH 6.99756 lonic Strength 1.81224e-9 mol/mol Density 0.997061 g/ml

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.

## 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<sub>2</sub>. The ambient temperature is 25  $^{\circ}$ C, and the final conditions will be 1 atm and 100  $^{\circ}$ C.

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** °C.

Copy the Autoclave – Inert Gas Vessel Vol 5L single point calculation and paste under the Autoclave Stream.

Name the new calculation object Autoclave – Inert Gas Tf=100C

Change the Final Temperature to 100°C and Calculate <F9>

Variable	Value	
	rameters	
Stream Amount (mol)	55.5082	
Ambient: Temperature (°C)	25.0000	
Ambient: Pressure (atm)		
	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	
H2O	55.5082	
N2	0.0	

At this point the system is defined as 1 kg H<sub>2</sub>O (55.5082 moles) at an ambient temperature of 25 °C. The partial pressure of N<sub>2</sub> will be calculated at a final temperature, 100 °C 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.

## Analyzing the Results

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

<b>Í</b>	Description 遂 Definition 📓	Report 🚊 File Viewer					
Г	Variable	Value		^		Type of calculation	
	Stream Param	neters (mol)			Autoclave - Spec		
	🖵 Stream Amount	55.50	37				
	- Moles (True) - Liquid-1 (mol)	55.50	31			Calc <u>u</u> late 🥥	
	Moles (True) - Vapor (mol)	5.54881e	-3			Summary	
	Calculation	n Results					
	Ambient Temperature (°C)	25.00	0			Unit Set: Metric (moles)	
	Ambient Pressure (atm)	0.03394	4			Automatic Chemistry Model	
	Final Temperature (°C)	100.0	0			MSE-SRK (H3O+ ion) Databanks:	
	Final Pressure (atm)	1.000	0			MSE-SRK (H3O+ ion)	
	Vessel Volume (L)	5.000	)1			MSE (H3O+ ion) Second Liquid phase	
	Partial Pressure: N2 (atm)	2.67276e	-3			Using Helgeson Direct	
	Condition that results were computed f	Ambient				Autoclave Calculation	
	√ Inflows	(mol)			>	Results for ambient conditions:	
	H2O	55.50	2			Ambient Temperature 25.0000 °C Ambient Pressure 0.0339414 atm	
	N2	4.38602e	-4			Final Temperature 100.000 °C	
		19 19				Final Pressure 1.00000 atm Vessel Volume 5.00000 L	
						N2 2.67276e-3 atm	
						Phase Amounts Aqueous 55.5031 mol Vapor 5.54881e-3 mol Solid 0.0 mol 2nd Liquid 0.0 mol	
Aqueous Phase Properties PH 6.99772 Input Output Advanced Search Add as Stream Export							

The amount of N<sub>2</sub> added is very small (~0.0004 moles). This is to be expected, because the vapor pressure of pure water at 100 °C is 1 atm. Therefore, a negligible amount of N<sub>2</sub> is needed to raise the pressure. Notice also that the calculated ambient pressure is 0.0339 atm. The vapor pressure of pure water at 25° 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 °C 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**.

OLI Studio - [Single point ca	alculations.oad*]			_	
File Edit Streams Calo	culations Chemistry Tools View Window Help	_			_ # ×
Report Contents	? ×	1 🚟 🛨 💱 🔊	😭 🎸		
Category	Report Contents	atm			
Peport Contents     Calculation Summary     Stream Inflows     Speciation Summary     Stream Parameters     Total/Phase Flows     Scaling Tendencies     Species Output     Molecular Output     Element Balance     Species Activity Coe     Species Activity Coe	To add or remove a section, click the check box. A shaded box means that only part of the component will be printed. To see what's included in a component, click Details. Sections Calculation Summary Stream Inflows Speciation Summary Stream Parameters Total/Phase Flows Scaling Tendencies Species Output	Report 🚘 Fil	e Viewer	Q Q Customize	Export
- Partial Pressures	Molecular Output	61.7478	mol	]	
- Species K-Values	Element Balance	25.0000	°C		
	Species Activity Coencients	38.0704	atm		
- Vapor Phase Diffusi	Partial Pressures			J	
Gibbs Free Energy o Gibbs Free Energy o	Species K-values     Species Mobilities				
Entropy	Species Self Diffusivities	6.99144			
Entropy - Standard S	Massar Dhaos Diffusiuitu Matriu	1.83405e-9	mol/mol		
Reaction Kinetics     Redox Equations	Up Down Select All Clear All	1.01846e-7	mol/kg		
	Description	78.4141			
	This section displays the vapor phase partial pressures.	0.543529	atm		
		0.0576240	µmho/cm		$\sim$
		1.00360	L		
	7 of 22 Sections selected				
× × >					
۲ ۲-span: ۱	OK Cancel Apply Help				6
Calculation Complete!	from default.				V
For Help, press F1				🤘 🛄	NUM /

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		

#### 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<sub>2</sub>. The ambient temperature is 25  $^{\circ}$ C, and the final conditions will be 100 atm and 100  $^{\circ}$ C.

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.** 

Copy the Autoclave – Inert Gas Tf=100C single point calculation and paste under the Autoclave Stream.

Name it Autoclave – Inert Gas Pf=100 atm

Change the Final Pressure to 100 atm and Calculate <F9>

	Variable	Value		
	Stream Amount (mol)	55.5082		
	Ambient: Temperature (°C)	25.0000		
	Ambient: Pressure (atm)			
$\overline{\nabla}$	Calculation P	arameters		
	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		
		(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 °C. The partial pressure of  $N_2$  will be calculated at a final temperature of 100 °C 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.

#### Analyzing the Results

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

Description 🤮 Definition 📓	Report 🚊 File Viev	wer	
Variable	Value		Type of calculation
Stream Param	neters (mol)		Autoclave 👻 Specs
C Stream Amount		67.9053	- 1
- Moles (True) - Liquid-1 (mol)		55.5441	Calc <u>u</u> late 🥥
Moles (True) - Vapor (mol)		12.3611	Summary
Calculation	Results		
Ambient Temperature (°C)		25.0000	Unit Set: Metric (moles)
Ambient Pressure (atm)		75.7159	Automatic Chemistry Model
Final Temperature (°C)		100.000	MSE-SRK (H3O+ ion) Databanks:
Final Pressure (atm)		100.000	MSE-SRK (H3O+ ion)
Vessel Volume (L)		5.00000	MSE (H3O+ ion) Second Liquid phase
Partial Pressure: N2 (atm)		75.6782	100.00000000000014 son Direct
Condition that results were computed f	Ambient		Autoclave Calculation
	(mol)		> Results for ambient conditions:
H2O		55.5082	Ambient Temperature 25.0000 °C Ambient Pressure 75.7159 atm
N2		12.3970	Final Temperature 100.000 °C
			Final Pressure 100.000 atm
			Vessel Volume 5.00000 L N2 75.6782 atm
			Phase Amounts
			Aqueous 55.5441 mol
			Vapor 12.3611 mol
			Solid 0.0 mol
			2nd Liquid 0.0 mol
			<ul> <li>Aqueous Phase Properties</li> </ul>
nput Output			pH 6.98515
- approx	lonic Strength 1.85714e-9 mol/mol		
Advanced Search Add as Stre	eam Export		Density 1.00012 g/ml

The computed ambient pressure  $P_{T,A}$  is 75.672 atm. Of this total, 75.68 atm is  $N_2$  ( $P_{N2}$ =75.68 atm) and 0.0377 atm is  $H_2O$  ( $P_{H2O}$ =0.0377 atm). Thus, to create a 100 atm final pressure, the autoclave would need to be charged with  $N_2$  at a regulator pressure of 75.68 atm.

According to the calculation, the amount of  $N_2$  in the autoclave is 12.397 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 °C.

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 select both the **Species Fugacities** and the **Partial Pressures** tables, and then click **OK**.

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

#### 100 °C and 1 atm

#### **Species Fugacities**

Row Filter Applied: Only Non Zero Values

Species	atm	
H20	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	0.0330213			
	N2	76.0121			

# Partial Pressures

Row Filter Applied: Only Non Zero Values			
Species	atm		
H2O	0.0376589		
N2	75.6782		

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 decreases until at short range, intermolecular forces begin to impact the molecular properties. The impact of these forces 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,

 $\varphi$  is the fugacity coefficient

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

# **Example 13: Using Reactive Gases**

#### **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<sub>2</sub>. The ambient temperature is 25 °C.

You will then modify the case further by adding NaOH so that additional CO<sub>2</sub> 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					
Calc	ulation Settings	Stream Composition and Conditions			
Calculation Type	Single Point Calculation	Stream Amount	Default – 55.5082		
Calculation Sub-type	Autoclave	Ambient Temperature	25 ℃		
Stream Name	Autoclave – Reactive Gas	Final Temperature	25 ℃		
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		

## Add a new Stream

Click on the new Stream and press <F2> to change the name to Autoclave Reactive Gas

Select the **MSE-SRK** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the CO2 and NaOH as inflows

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

Change the SinglePoint name to Autoclave - CO2 using the <F2> key

Select Autoclave as Type of Calculation

Click on the **Specs** button. This will open the **Calculation Options** window to set up the target gas.

Select CO2 and make sure to select the specification type Partial Pressure (default). Click OK.

۵	OLI Studio - [Single point cal	culations.oad*]					×
	File Edit Streams Calcu	lations Chemistry Tools View Window Help				-	ē x
	DLI	Cancel					
D	🗃 🖬 🕺 🗛 📾	🎖 💦 🛛 L1 Va So L2 Re ± MSE ± SKK ± AK		💱 🔊 😭 🎸 🗅			
Navi		A Autoclave – CO2	1				
	calculations oad*		? ×				
÷÷				File Viewer			
÷.	Category : Autoclave	Autoclave		Value ^		Type of calculation	a
÷.	Calculation Options	Target Gas(es) (5 Max)		55.5082		Autoclave 🔻 Specs	<u> </u>
÷		CO2 - Vap		25.0000		Calc <u>u</u> late 🥝	_
		H2U · Vap				Summary	
				0.0		Unit Set: Metric (moles)	_
				0.0			
				0.0		Automatic Chemistry Model MSE-SRK (H3O+ ion) Databanks:	
<						MSE-SRK (H3O+ ion) MSE (H3O+ ion)	
Acti		Selected 1		Ambient		Second Liquid phase Using Helgeson Direct	
Act		Selected 1		55.5082	>	Autoclave Calculation	
		Specification Type		0.0		Specifications: Ambient Temperature 25.0000 °C	
		Partial Pressure(s)		0.0		Final Temperature 0.0 °C Final Pressure	
		Mole Fraction(s) in Aqueous Phase				Vessel Volume 0.0 L	
						CO2 Calculation not done	
Plot						Volume of vessel is invalid.	
						You must specify the Final Pressure or Gas 1	
				~			
				port			Ť.
×Г		OK Cancel Apply	Help				^
	alculation Complete!						
							~
For H	lelp, press F1					1 🗐 🕑	JUM 🛛

Set the Final Temperature to 25°C, the Final Pressure to 1 atm and the Vessel Volume to 2 L Set the Compute results at which Condition to Final.

Variable	Value
	rameters
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
	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 💌
	Final
H2O	Ambient
CO2	0.0
NaOH	0.0

At this point the system is defined as 1 kg H<sub>2</sub>O (55.508 moles) at an ambient temperature of 25 °C. The partial pressure of CO<sub>2</sub> will be calculated at a final temperature, 25 °C and pressure, 1 atm in a 2 L vessel.

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

## Analyzing the Results

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

Variable	Value		^	Type of calculation	
Stream Param	eters (mol)			Autoclave 👻 Specs	
Stream Amount		55.5808			
- Moles (True) - Liquid-1 (mol)		55.5397		Calc <u>u</u> late 🥥	
- Moles (True) - Vapor (mol)		0.0409464		Summary	
Calculation	Results				_
Final Temperature (°C)		25.0000		Unit Set: Metric (moles)	1
Final Pressure (atm)		1.00000		Automatic Chemistry Model	
Vessel Volume (L)		2.00001		MSE-SRK (H3O+ ion) Databanks:	
Partial Pressure: CO2 (atm)		0.968445		MSE-SRK (H3O+ ion)	
Condition that results were computed f	Final			MSE (H3O+ ion) Second Liquid phase	
Inflows	(mol)			Using Helgeson Direct	
H2O		55.5082		Autoclave Calculation	
C02		0.0725227		Results for final conditions: Ambient Temperature 25.0000 °C Final Temperature 25.0000 °C Final Pressure 1.00000 atm Vessel Volume 2.00000 L CO2 0.968445 atm	
	Å			Phase Amounts Aqueous 55.5397 mol Vapor 0.0409464 mol Solid 0.0 mol 2nd Liquid 0.0 mol	
ut Output			*	Aqueous Phase Properties pH 3.91452 lonic Strength 2.21620e-6 mol/mol Density 0.997452 g/ml	

A total amount of 0.0725 moles of CO<sub>2</sub> added was computed by the software to set the autoclave total pressure to 1 atm. For comparison, the same scenario in Example 12-<u>1 Analyzing the Results</u> required 0.04 moles of N<sub>2</sub>. The difference is the amount of CO<sub>2</sub> that dissolved in the water. CO<sub>2</sub> is more soluble than N<sub>2</sub> in water.

To analyze the CO<sub>2</sub> 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	2.32772e-3
O(-2)	55.6533	33.3768	99.8552	0.144827
C(+4)	0.0725227	0.0434939	45.3215	54.6785

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

## Using Reactive Gas and NaOH solution

In this example, you will further modify the chemistry by adding NaOH so that additional CO<sub>2</sub> 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.** 

Copy the Autoclave – CO2 single point calculation and paste under the Autoclave Stream.

Name it Autoclave – CO2 – NaOH

#### Change the composition of NaOH to 0.1 moles and Calculate <F9>

Variable	Value					
C Stream Parameters						
Stream Amount (mol)	55.6082					
Ambient: Temperature (°C)	25.0000					
Ambient: Pressure (atm)						
Calculation F	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	√ Inflows (mol)					
H2O	55.5082					
C02	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 °C. The partial pressure of CO<sub>2</sub> will be calculated at a final temperature, 25 °C and final pressure, 1 atm in a 2 L vessel.

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

#### Analyzing 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<sub>2</sub> inflow is calculated to be 0.1716 moles. This is exactly 0.1 moles more than the calculation with only CO<sub>2</sub> (Example 13<u>-1</u>). The difference 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	1.28481e-3
Na+1	0.1	0.1	
HCO3-1	0.0998917	0.0998917	
CO2	0.0716555	0.0320887	0.0395668
CO3-2	5.42505e-5	5.42505e-5	
H3O+1	2.3994e-7	2.3994e-7	
ОН-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	0.0408516

You can see that ~0.1 moles of bicarbonate  $(HCO_3^-)$  is formed. This reaction is increasing the CO<sub>2</sub> gas requirement to reach a total final pressure of 1 atm.

# 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<sub>2</sub> 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						
Cal	culation Settings	Stream Composition and Conditions				
Calculation Type	Single Point Calculation	Stream Amount	Default – 1kg			
Calculation Sub-type	Custom	Temperature	30 °C			
Stream Name	Custom Calculation	Pressure	4 atm			
Name Style	Display Formula	H2O	Calculated			
Unit Set	Metric, Mass fraction – ppm (mass)	02	0 mol			
Framework	MSE					

#### Setting the pH

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to Custom Calculation

Select the MSE thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Mass Frac. This will change all inflows to mass %.

Click on the Customize button. This opens the Edit Units window.

Under Basis Options change mass fraction from mass % to ppm (mass)

Enter **O2** as an inflow and **0** moles

Change the T to 30 °C and P to 4 atm

Go to the Add Calculation button and select Single Point calculation

Change the SinglePoint name to Oxygen Solubility using the <F2> key

Select **Custom** as Type of Calculation

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.

alculation Options		?	>
Category	Custom		
Variables Calculation Options	Variables to Fix Filter All Enthalpy - Total H20 H20 - Sol H20 - Vap H30+1 Moles (True) - Liquid-1 02 - Liq1 02 - Vap 1	por	
	Variables to Free   Hide Related Inflows     H20     02	New Inflow	
	Pressure Temperature		
	Select an equal number of variables to be fixed and freed. Free be adjusted to meet the specified value of the fixed variables.	ed variables wil	i
	OK Cancel Apply	Hel	þ

In the Variables to Fix section, select Moles (True) Vapor, by double clicking or using the >> button. In the Variables to Free section, select O2 as the inflow. Then click OK. This will add a **Calculation Parameters** section, where 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 the Target: Moles (True) - Vapor is fix value. The Adjusted Inflow value font is green indicating that the software will adjust this value.

Variable	Value	Type of calculation
	neters	Custom 👻 Specs
Stream Amount (kg)	1.00000	
Temperature (°C)	30.0000	Calc <u>u</u> late 🥝
Pressure (atm)	4.00000	Summary
Calculation Para	ameters	
Target: Moles (True) - Vapor (mol)	0.0	Unit Set: <custom></custom>
Adjusted: O2 (ppm (mass))	0.0	Automatic Chemistry Model
	mass))	MSE (H3O+ ion) Databanks:
H2O	1.00000e6	MSE (H3O+ ion) Using Helgeson Direct
Adjusted: 02		Custom Calculation
		Fixed variable:
		Moles (True) - Vapor, target:
		0.0 mol
		Free variable: 02
		Calculation not done
		Moles (True) - Vapor must be
		greater than 0.0.
		×
nput		
		· · · · · · · · · · · · · · · · · · ·

Fix the Moles (True) Vapor to  $1e^{-7}$ 

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

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*.

# Analyzing the Results

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

Variable	Value	^	Type of calculation
Stream Param	eters		Custom 👻 Specs
Stream Amount (kg)	1.00	015	
— Mass - Liquid-1 (kg)	1.00	015	Calc <u>u</u> late 🥥
— Mass - Vapor (kg)	3.18493	e-9	Summary
Temperature (°C)	30.0	000	
Pressure (atm)	4.00	000	Unit Set: <custom></custom>
Calculation Re	sults		Automatic Chemistry Model
Target: Moles (True) - Vapor (mol)	1.00000	e-7	MSE (H3O+ ion) Databanks:
Inflows (ppm (n			MSE (H3O+ ion) Using Helgeson Direct
H2O	9.9985	le5	Custom Calculation
Adjusted: 02	146.	938	Fixed variable:
			146.938 ppm (mass)       Phase Amounts       Aqueous 1.00015 kg       Vapor 3.18493e-9 kg       Solid 0.0 kg       Aqueous Phase Properties       pH 6.91733       ionic Strength 2.18165e-9 mol/mol       Density 0.995710 g/ml       Calc. elapsed time: 1.053 sec       Calculation complete
t Output		*	

At 30°C and 4 atm the solubility of O<sub>2</sub> 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**.

Oxygen Solubility		<ul> <li>Stream Parameters</li> </ul>				
🖉 Description 🛛 💇 De	finition 📓 Rep	<ul> <li>Calculation Results</li> </ul>				
		<ul> <li>Inflows</li> </ul>		Type of calculation		
Var	iable	Related Inflows				
	Strea	Additional Stream Parameters		Custom    Specs		
Stream Amount (kg)     Mass - Liquid-1 (kg)		Phase Flow Properties		Calculate 🥝		
Mass - Vapor (kg)		Thermodynamic Properties				
Temperature (°C)		Pre-scaling Tendencies		immary		
Pressure (atm)		Pre-scaling Index		Unit Set: <custom></custom>		
$\nabla$	Calcu	Scaling Tendencies		Automatic Chemistry Model		
<ul> <li>Target: Moles (True) -</li> </ul>	Vapor (mol)	Scaling Index		MSE (H3O+ ion) Databanks:		
		Liquid-1		MSE (H3O+ ion) Using Helgeson Direct		
H2O		Vapor		Custom Calculation		
Adjusted: 02		Solid		Fixed variable:		
		Molecular Apparent	>	Moles (True) - Vapor, target: 1.00000e-7 mol		
		Totals		Free variable: O2. total:		
		Molecular Totals		146.938 ppm (mass)		
		MBG Totals	>	Phase Amounts		
		Activity Coefficients	Ś	Aqueous 1.00015 kg Vapor 3.18493e-9 kg		
		Fugacity Coefficients - Vapor		Solid 0.0 kg		
				Aqueous Phase Properties		
		Fugacities - Vapor				
	•	K-Values	>	(x-based) 9 mol/mol		
Units Ma	nager	Gibbs Free Energy		(m-based)		
		Gibbs Free Energy Standard State (x-based)		Calc. elapsed time: 0.046 sec		
Save defa	ult layout	Entropy		Calculation complete		
Generate	Model	Entropy Standard State (x-based) Mobilities				
Input Ou 🗸 Hide Zero	o Values	Self Diffusivities	>			
		Partial Pressures		×		

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

✓ K-Values - (m-bas	ed)
KH2O: 2H2O=H3OION+OHION	1.46564e-14
KH2OPPT: H2OPPT=H2O	1.32964
KH2OVAP: H2OVAP=H2O	23.8182
KO2VAP: 02VAP=02AQ	1.15985e-3

# **Reaction Kinetics**

Most of the chemistry and calculations that we have presented so far assume 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:

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

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 temperature dependence 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)  $E_a = \text{Activation energy} \left(\frac{joule}{gmole}\right)$   $R = \text{Universal gas constant} \left(8.314 \frac{joule}{gmole K}\right)$ T = Temperature (K)

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

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

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

#### 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:

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

where: *a*, *b*, ... *c*, *d* are stoichiometric coefficients

A, B, ... are reactant species

C, D, ... are product species

The rate law is of the form:

$$Rate = (k_f a_A^{r_1} a_B^{r_2} \dots - k_r a_C^{p_1} a_D^{p_2})$$

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)
$a_A, a_B, .$	=	Activities of reactant species $\left(\frac{mol}{m^3}\right)$
$r_1, r_2 \dots$	=	Reaction order of individual reactant species
		(normally from experimental data. Default is stoichiometric coefficients: a, b,)
$a_c, a_D, \ldots$	=	Activities of product species $\left(\frac{mol}{m^3}\right)$
$p_1, p_2,$	=	Reaction order of individual product species
		(normally from experimental data. Default is stoichiometric coefficients: c, d,)

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>i</i>
$EP_i$	Reaction order of product species <i>i</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, 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 200°C 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					
Calculatio	on Settings	Stream Composition and Conditions			
Calculation Type	Single Point Calculation	Stream Amount	Calculated		
Calculation Sub-type	Isothermal	Temperature	200 °C		
Stream Name	Standard Rxn Kinetics	Pressure100 atmWater55.5082CO22 moles	100 atm		
Single Point Name	Rxn Ammonia/CO2		55.5082		
Name Style	Display OLI Name (TAG)		2 moles		
Unit Set	Metric, Moles	NH3	2 moles		
Framework	AQ	UREA	0 moles		
Kinetics	Enabled				
Kinetics Holdup Time	ics Holdup Time 100 hours				
Number of Kinetic Steps	10				

#### Add a new Stream

**Click** on the new Stream and press **<F2>** to change the name to *Standard Rxn Kinetics* Select the **AQ** thermodynamic Framework Click on the Names Manager Icon, and select the OLI Name (TAG) option, and click OK.

Name Style	Search Criteria	Names Dictionary	
Compone	nt Name Style —		
	ay name		
V U	lse Names Dictior	hary	
◯ Form	ıla		
	lame (TAG)		
Show	mineral name aft	er solids	

Click on the Units Manager Icon, and select Metric, Batch, Moles.

Enter the stream composition, temperature and pressure given in the table above.

Go to the Add Calculation button and select Single Point calculation

Select Isothermal (default) as Type of Calculation.

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*.

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.

OLI Studio - [Single point calculations.oad*]			– 🗆 X
File Edit Streams Calculations Chemistry	Tools View Window Help		_ 8 ×
🗄 🗅 🚅 🖬 🕺 🖻 💼 🎒 🌮 😽 🛛 Pre-bu	ilt Models 🔰 se 🛓 MSE 🛓 🗛 🛓	M 🎬 🛃 💱 🔊 😭 🛷	
Navigator Templa		1	
Document1	CO2		
Single point calculations.oad*	Options 🗗 Definition 👩 R	eport 🚊 File Viewer	
🍓 Streams			Type of calculation
i.1.a pH of 1 m FeCl3	Variable	Value	
🖶 👌 1.1.b Isothermal - acetic acid	Stream Pa		Isothermal   Specs
🖶 👌 1.10. Custom Calculation	Stream Amount (mol)	59.5082	Calculate 🥥
🖶 👌 1.11.1. Arrhenius Rxn Kinetics	Temperature (°C)	200.000	
\Lambda Rxn Ammonia/CO2	Pressure (atm)	100.000	Summary
🖶 👌 1.2. Acetone Bubble Point	□ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □		
🖅 👌 1.3. Sour Natural Gas Dew Point	H20	55.5082	Unit Set: Metric (moles)
1.4. Isochoric calculation	C02	2.00000	Automatic Chemistry Model
1.5. Brine Evaporation - Vapor Fraction	NH3	2.00000	Aqueous (H+ ion) Databanks:
1.6. Neutralizing Acid	UREA	0.0	Aqueous (H+ ion) Using K-fit Polynomials
< >	<b>_</b>		T-span: 25.0 - 225.0
Actions g • ×	Aque	ous	*P-span: 1.0 - 201.0
Actions			* = differs from default.
Actions			> Isothermal Calculation 200.000 °C 100.000 atm
			Calculation not done
			Calculation not done
		¥	
	Input		
Plot Template Manager # * *			V
	Advanced Search Add as Strea	am Export	
Save			
×			
Calculation Complete!			
<u>+</u>			×

Rxn Ammonia/CO2 Chemi	stry Model Options	?	×
Databanks Redox Phas	es T/P Span		
Include Phases Aqueous Vapor Solids Second Liquid	Include Solid Phases 		
Ion Exchange Model Margules Wilson Kinetics Enable			
	Calculate Scaling Tendencies for exclude	d solids	
	OK Cancel Apply	He	elp

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.

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

Γ	Variable	Value	^		l ype of calculation
5	Stream Par	rameters			Isothermal 👻 Specs
	Stream Amount (mol)	59.5082			
	Temperature (°C)	200.000			Calc <u>u</u> late 🥝
	Pressure (atm)	100.000			Summary
5	Calculation P	arameters	1		
T	Kinetics Holdup Time (hr)	100.000			Unit Set: Metric (moles)
T	Number of Kinetics Steps	10	1		Automatic Chemistov Model
5	Stream Parameters     Isothermal     Specs       Stream Amount (mol)     59.5082     Calculation       Temperature (°C)     200.000     Calculate       Pressure (atm)     100.000     Summary       Calculation Parameters     Unit Set: Metric (moles)				
		55.5082			
Γ	C02	2.00000			
	NH3	2.00000			
T	UREA	0.0			* = differs from default.
				>	Isothermal Calculation

Kinetics Holdup time is equivalent to Residence Time. The Number of Kinetic Steps is equivalent to  $\Delta t$ . Thus Kinetics Holdup time =  $\Sigma \Delta t$ .

**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.

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

Select Kinetics under the Category window

Click the Add button to add a new reaction. This will open the Select a Reaction Window.

Calculation Options		?	×
Category	Rate Limited Reactions		
Calculation Options	Reactions:	Delete	-
	Rate Specification:		
	OK Cancel Apply	He	lp

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.

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

Select a Reaction:	×
<create new="" reaction=""></create>	<b>^</b>
CO2AQ+H2O=HION+HCO3ION	
CO2VAP=CO2AQ	
HCO3ION=HION+CO3ION	
NH2CO2ION+H2O=NH3AQ+HCO3ION	
NH3AQ+H2O=NH4ION+OHION	
NH3VAP=NH3AQ	
NH44H2CO33PPT=4NH4ION+2HCO3ION+CO3ION	
NH4HCO3PPT=NH4ION+HCO3ION	
UREAPPT=UREAAQ	
	÷
ОК	Cancel
	Carreet

This enables the option to enter a new reaction.

**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.

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

alculation Options		?	×
Category ; Calculation Options	Rate Limited Reactions		
Kinetics	Add Edit I	Delete	
	2NH3AQ+CO2AQ=UREAAQ+H2O		
	Rate Specification: STD		
	Rate Constants: Constant Value	Add	]
		Delete	]
	OK Cancel Apply	Help	)

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		$1.2 \times 10^{-10}$
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] <sup>2</sup>
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.

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

Calculation Options		? ×
Category	Rate Limited Reactions	
Calculation Options	Add Edit	Delete
	2NH3AQ+CO2AQ=UREAAQ+H2O	
	Rate Specification: STD V	
	Constant Value	Add
	KF	KF
	BR	KR
	ER1	AF
	ER2	AR
	EP1	BF
		BR
		ER1
		ER2
		EP1
		EP2
	OK Cancel Apply	Help

Type the constant values, and then click OK.

Calculation Options		? ×
Category	Rate Limited Reactions	
Calculation Options	Add         Edit           Reactions:         2NH3AQ+CO2AQ=UREAAQ+H2O	Delete
	Rate Specification: STD V	
	Rate Constants:	
	Constant Value KF 2000	Add
	AR 1.2e-10	Delete
	BR 3480.78	
	ER1 2	
	ER2 1	
	EP1 1	
	EP2 0	
	OK Cancel Appl	y Help

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

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*.

## Analyzing the Results

Click on the **Output-Minitab** to see the Results.

Right click on the gray area and select Sections> Molecular Apparent - Aqueous

Tools View Window Help         So L2       Re ±       MSE ±       MSE ±       MAR         A Rxn Ammonia/CO2         Image: Description       Image: Definition       Image: Definition         Image: Definition       Image: Definition       Image: Definition         Image	<ul> <li>Calculation Results</li> <li>Inflows</li> <li>Related Inflows</li> <li>Additional Stream Parameters</li> <li>Kinetics Reactions</li> <li>Phase Flow Properties</li> <li>Thermodynamic Properties</li> <li>Pre-scaling Tendencies</li> <li>Pre-scaling Index</li> <li>Scaling Tendencies</li> <li>Scaling Index</li> <li>Aqueous</li> <li>Vapor</li> <li>Solid</li> <li>Molecular Apparent - Aqueous</li> <li>Molecular Totals</li> <li>MBG Totals</li> </ul>		
Moles (True) - Aqueous (mol)     Moles (True) - Vapor (mol)     Temperature (°C)     Pressure (atm)     Calcu     Kinetics Holdup Time (hr)     Number of Kinetics Steps     C In	Scaling Index Aqueous Vapor Solid Molecular Apparent - Aqueous Totals Molecular Totals	Metric (moles) ic Chemistry Model bus (H+ ion) Databanks: ueous (H+ ion) K-fit Polynomials pan: 25.0 - 225.0 span: 1.0 - 201.0	^
CO2 NH3 Units Manager Save default layout Generate Model V Hide Zero Values	MBG Totals Activity Coefficients Fugacity Coefficients Fugacities - Vapor K-Values Gibbs Free Energy Gibbs Free Energy Standard State (x-based) Entropy Entropy Entropy Standard State (x-based) Mobilities Self Diffusivities Partial Pressures	<ul> <li>differs from default.</li> <li>al Calculation         *C 100.000 atm         mounts         bus 58.0473 mol         r 1.02509 mol         0.0 mol         s Phase Properties         6.66199         Strength 7.48750e-3 mol/mol         ty 0.888732 g/ml         ipsed time: 1.130 sec</li> <li>on complete</li> </ul>	

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.

## 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.

$$NH_{3(aq)} + H_2 0 \rightleftharpoons NH_4^+ + OH^-$$

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 ℃	
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			

Add a new Stream

Click on the new Stream and press <F2> to change the name to Non-Standard Rxn Kinetics

Select the **AQ** thermodynamic Framework

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

Click on the Units Manager Icon, and select Metric, Batch, Moles.

Enter the stream composition, temperature and pressure given in the table above.

Go to the Add Calculation button and select Single Point calculation

Change the *SinglePoint* name to *Ammonia Hydrolysis* using the <F2> key

Select Isothermal (default) as Type of Calculation.

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

1.11.2. Non-Standard Kinetics Chemistry Model Options ?	$\times$
Databanks Redox Phases T/P Span	
Include Phases Aqueous Vapor Solids Second Liquid Ion Exchange Model Margules Wilson Kinetics Enable Calculate Scaling Tendencies for excluded solids	
OK Cancel Apply He	lp

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

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

Select Kinetics under the Category window

**Click** the **Add** button to add a new reaction. This will open the **Select a Reaction** Window. **Select** the first reaction: NH3AQ+H2O=NH4ION+OHION, and then click **OK**.

Select a Reaction:		Х
<create new="" reaction=""> NH3AQ+H2O=NH4ION+OHION</create>		
NH3VAP=NH3AQ		
	OK Cance	el 🛛

Select the SPEC as the Rate Specification.

Calculation Options		?	×
Category	Rate Limited Reactions		
Calculation Options Kinetics	Add Edit Reactions: NH3AQ+H2O=NH4ION+OHION	Delete	
	Rate Specification: SPEC V		
	OL/ASAP DEFINES:		
	Variable Expression	Add	
		Delete	
	,		
	OK Cancel Apply	Help	)

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

$$Rate_{f} = k_{f} \cdot \gamma_{NH_{3,aq}} [NH_{3,aq}] \cdot \gamma_{H_{2}O} [H_{2}O] \qquad where \ k_{f} = 3$$
$$Rate_{r} = k_{r} \cdot \gamma_{NH_{4}^{+}} [NH_{4}^{+}] \cdot \gamma_{OH^{-}} [OH^{-}] \qquad where \ k_{r} = \frac{k_{f}}{K_{eq}}$$

Thus, the total rate is given by:

$$Rate = Rate_f - Rate_r$$

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

This 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<sup>5</sup>.

<sup>&</sup>lt;sup>5</sup> Commonly referred to as ASAP variables.

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  $\gamma$  are also taken as the natural log. So,  $\gamma_{OH^-}$  is written as Log<sub>e</sub>  $\gamma_{OH^-}$  = 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<sup>6</sup>:

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

Note: For a reaction rate to be considered in the program, your set of variables should include a RATEn statement where the "n" is the reaction rate equation number.

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

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

OL/ASAP DEFI	NES:	
Variable	Expression	Add
FXRATE	13AQ+ANH3AQ+LH2O+AH2O	Delete

<sup>&</sup>lt;sup>6</sup> 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 <u>Add</u> 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.

tegory		ited Reacti	ons	
— Calculation Optio — Kinetics	Rea NH3		Add Edit	Delete
	OL/	e Specificat ASAP DEFII Variable		Add
		XRATE	LNH3AQ+ANH3AQ+LH2O+AH	
		XRATE	LNH4ION+ANH4ION+LOHION+	Delete
		F1	3	
		R1	KF1/KEQ	
		ATE1	(KF1*EXP(FXRATE)-KR1*EXP(	

The completed equations

## 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 <u>Aqueous</u> section (not molecular aqueous):

ľ	Variable	Value			Type of calculation
	Stream Parameters				Isothermal 👻 Specs
	Stream Amount (mol)	55.6082			
	<ul> <li>Moles (True) - Aqueous (mol)</li> </ul>	55.6082			Calc <u>u</u> late 🥥
	Temperature (°C)	25.0000			Summary
	Pressure (atm)	1.00000			
	Calculation Results				Unit Set: Metric (moles)
	Kinetics Holdup Time (hr)	100.000			Automatic Chemistry Model
	Number of Kinetics Steps	10			AQ (H+ ion) Databanks:
	Inflows (mol)				Public
	H2O	55.5082			Isothermal Calculation 25.0000 °C 1.00000 atm
[	NH3	0.100000			
	Aqueous (mol)				Phase Amounts Aqueous 55.6082 mol
	H2O	55.5077	Ξ		Vapor 0.0 mol
	NH3	0.0994574			Solid 0.0 mol
	OHION	5.42587e-4			Aqueous Phase Properties
	NH4ION	5.42587e-4			pH 10.7171
	HION	1.97028e-11			lonic Strength 9.75731e-6 mol/mol Density 0.996159 g/ml
					Calc. elapsed time: 0.387 sec
					Calculation complete
			Ŧ		
2	ut Output			- 1	
1		2			

You can see that some ammonium ions have 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 the 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)	Ì
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

 $1.3 \times 10^{-3}$  moles of NH<sub>4</sub><sup>+</sup> have been created. By limiting the forward reactions, we allow the back reaction to take place and that only formed  $5.4 \times 10^{-4}$  moles of NH<sub>4</sub><sup>+</sup>.

# **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:

<u>Single Survey:</u> These calculations allow the user to designate one independent variable. The predefined single surveys include surveys by Temperature, Pressure, Composition, pH, Vapor Fraction and Vapor Amount. <u>Dual Survey:</u> These calculations allow the user to designate two independent variables. <u>Survey by changing the single point calculation type:</u> 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 another calculation type like **Precipitation Point**.

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.

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♦ Streams	< Description 🔮 Definition 🛍 Plot 📓	Report 🖨 File Viewer	
🛓 Stream			Survey by
Survey	Variable	Value ^	
	Stream Amount (mol)	55.5082	Temperature    Specs
	Temperature (°C)	55.5062	Temperature
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	□	(mol)	Composition
	H2O	55.5082	рН
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			No secondary survey selected
			Unit Set: Metric (moles)
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			Aqueous (H+ ion)
			Using K-fit Polynomials T-span: 25.0 - 225.0
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For Help, press F1			

## **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<sub>2</sub>O). The existing treatment strategy is to precipitate the nickel ions as Nickel Hydroxide (Ni(OH)<sub>2</sub>). 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:

Scenario 1: Wastewater without Additives Scenario 2: Wastewater with Cyanide Content 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. We will also be using the **AQ** thermodynamic model instead of the default MSE model.

#### Scenario 1: Wastewater without Additives

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

## Select the AQ-Databank (The default databank)

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

Click on the **Description** tab. This will display the description information

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

Add the following text to the Description box: "Nickel wastewater for the OLI Aqueous Modeling Course"

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

	OLI Studio - [Document1*]     File Edit Streams Calculations Chemistry Tools View Window Help     OLI E	-	□ × - ₽×
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	Nickel Waste Name: Nickel Waste Date: 4 / 8 /2019		
	Description		
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Į.	Add Single Point 🔲 Add Stability Diagra		
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Fo	or Help, press F1	0	NUM

Click on the **Definition** tab to start defining the wastewater stream

Click in the white box in the grid below the Inflows line. Add the formula Ni(OH)2

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)<sub>2</sub> 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

For the output results, we want output units in **ppm**. To change the output units, click on the <u>Units Manager</u> icon <sup>\$</sup>. This will open a new window.

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

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

File Edit Streams Calculations Chemistry	Tools View Window Help		_ <i>8</i> ×
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Nickel Waste	Variable Valu	Add Calculation 👻	
	Variable Valu		
	Stream Amount (mol)	55,5102 Special Conditions	
	Temperature (°C)	25.0000	
	Pressure (atm)	1.00000	
	☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐	Summary	
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34/6			

## Make sure you are on the Composition tab

## Change the Mass Fraction Units to ppm (mass)

## Click OK

Composition	Parameters	Corrosion			
	Varia	ble	Basis	Units	^
		In	ow variables		
Stream A	mount		Mass	kg	
Inflows			Mass Fraction	mass %	
		01	put variables		
Aqueous	Composition		Mass Fraction	mass %	
Vapor Co	omposition		Mass Fraction	mass %	
Solid Con	nposition		Mass Fraction	mass %	
2nd Liqui	d Composition		Mass Fraction	mass %	
Total Con	nposition		Mass Fraction	mass %	
		E	isis options		
Moles				mol	_
Mass				kg	
Volume				L	
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	ncentration			mol/L	
Mass Fra				mass %	┙ ,
Mole Fred	otion			g/g	
				mass % ppm (mass)	1

Our primary interest in this application is finding the optimum pH for nickel removal. To create a plot of Ni<sup>+2</sup> 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.

## Click on the Add Calculation button

## Select Survey

nickel waste.oad*	🜢 Nickel Waste 🍠 Description 🔯 Definition 🔯	Desert		
Streams	Variable		2	Add Calculation -
	Variable			
	Stream Amount (kg)	1.00019	S	Single Point
	Temperature (°C)	25.0000		Survey
	Pressure (atm)	1.00000		Chemical Diagram
	🔽 Inflows (pp	m (mass) <b>)</b>	Summary	Stability Diagram
	H20	9.99815e5	Unit Set	Corrosion Rates
	Ni(OH)2	185.335		Chemistry Model
Actions Add Stream Add Stream Add Chemical Diagra Add Mixer Add Stability Diagrar Add Single Point Add Survey Add Survey			>	fers from default.
Not Template Manager 🛛 🔒 🍝 🗙	Input Advanced Search Add as Str	~		

You can now add descriptive information about this calculation.

Enter a new **Survey name**: **Base Survey**. You can also double click on 'Survey' to change the name

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.

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

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

👌 OLI Studio (Version 11.5.1 Beta) - [2.1 - pH Survey -			- 🗆 ×
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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.

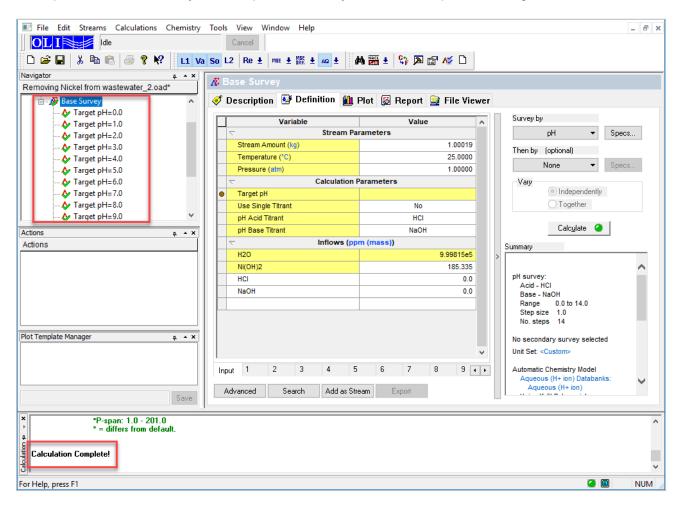
#### Select File

Select **Save As** from the menu. Give the name *Removing nickel from* wastewater

Click on the Calculate button

	Studio - [Removing Nickel from wastewater_2.oad	4]				- 🗆 X
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Re	Save Save As	Ctel+S	rvey tion 🥸 Definition 🛍 F	Plot 🔯 Report 🔜 File Vie	wer	
	Import Print Print Preview	> Ctrl+P	Variable Stream Par n Amount (kg) rature (°C)	Value ameters 1.00019 25.0000	^	Survey by           pH         Specs           Then by (optional)
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Acti	Removing Nickel from wastewater_2.oad     Removing Nickel from wastewater.oad     Removing Nickel from wastewater_1.oad		ngle Titrant id Titrant se Titrant Inflows (pp)	No HCL NAOH		Calculate
Ad	4 azeotrope_HCL-water_9.6.1.oad Exit		2	9.99815e5 185.335	>	pH survey: Acid - HCLIN
Plot Temp	late Manager g. A X					Base - NAOHIN Range 0.0 to 14.0 Step size 1.0 No. steps 14
		Input			~	No secondary survey selected Unit Set: <custom> Automatic Chemistry Model Aqueous (H+ ion) Databanks:</custom>
	Save	Advanced	Search Add as Stre	am Export		Aqueous (H+ ion)

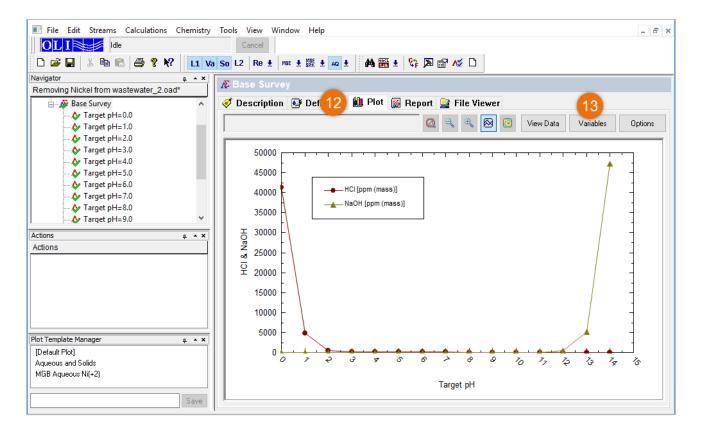
The program will run for a short time. When the orbit disappears, check the summary box to see if the calculation is complete. In the tree-view, you can expand the survey to see if all the points converged.



We can now obtain some graphical results.

#### Click on the Plot tab

Click on the Variables button

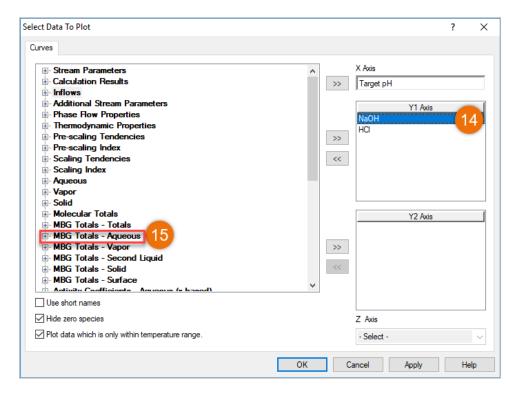


This will open a new window. The NaOH and HCI variables in the Y-Axis box should be displayed.

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

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.

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

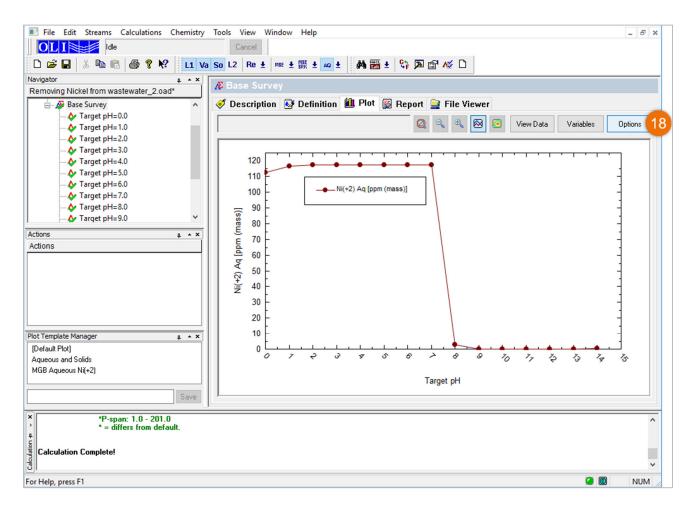
Click on the OK button.

Select Data To Plot					?	×
Curves						
• Inflows	^		X Axis			
Additional Stream Parameters     Phase Flow Properties			Target pH			
Thermodynamic Properties						
				Y1 Axis		
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• Vapor						
. Solid						
Molecular Totals						
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Cl(-1) Aq						
H(+1) Aq		>>				
		<<				
		~~				
	$\sim$					
Use short names						
Hide zero species			Z Axis			
Plot data which is only within temperature range.			- Select -			$\sim$
17	OK	Ca	ancel	Apply	He	elp

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.

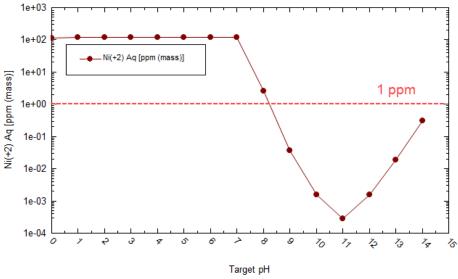
Above the plot window locate and select the **Options** button. This opens a new window.



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

Customize Plot		?	$\times$
Customize Plot Category — General — Legend — X Axis — Y Axis — Curves	Scale       Format       Title         Auto       Ø       Ø         Ø       Minimum       0.0         Ø       Maximum       2.1e-3         Ø       Major Unit       Ø         Ø       Minor Unit       Ø         Ø       Logarithmic scale       Ø	?	×
	21 OK Cancel Apply	Hel	þ

The modified plot is then displayed. The limit of 1 ppm for Ni<sup>+2</sup> is approximately 2 x 10<sup>-5</sup> moles. Above pH=9, we are several orders of magnitude below this limit. Additionally, you can see that a minimum amount of Ni<sup>2+</sup> 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.

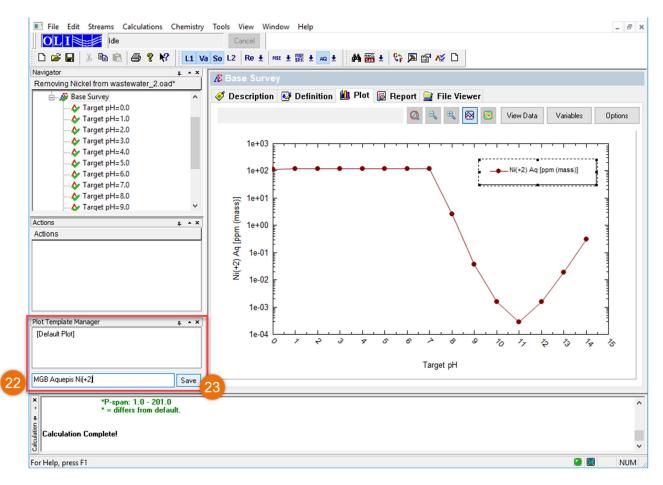


Note: The red line was put as a reference. it was not plot with the software.

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

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





Now there will be two plots on that list now. The first is the default plot, and the 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?

Click once more on the Variables button

**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

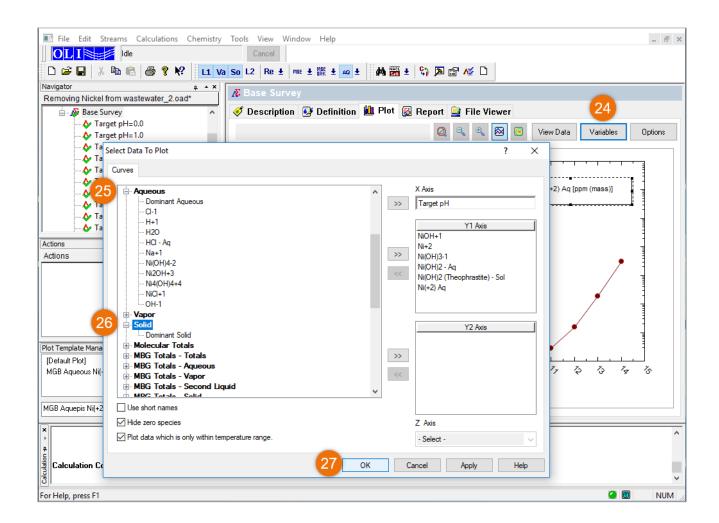
Ni+2

Ni(OH)3-1

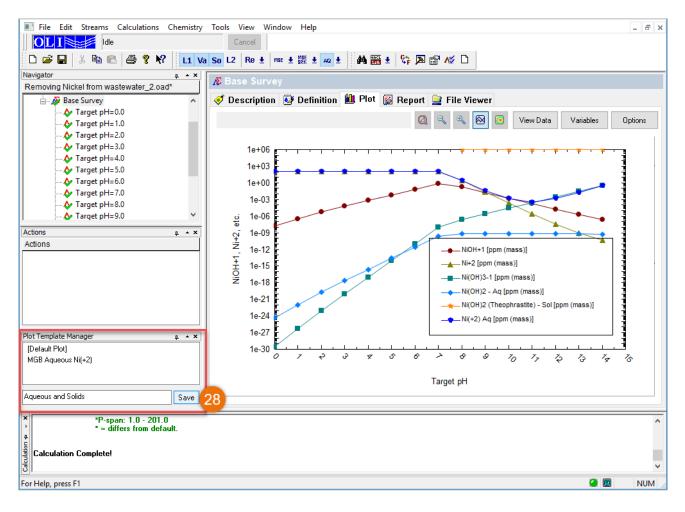
Add the following Solids species to the plot:

#### Ni(OH)2

#### 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.



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 cyanides, which brings us to the real waste treatment problem.

For this scenario, you will repeat many of the same steps as in <u>Scenario 1</u>. 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

Click on the Nickel Waste stream in the tree view in the left-hand window

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

	D 😅 🖬   X 🖻 🖻 🎒 😵 😽	L1 \	Va So L2 Re 🛓 MSE 🛓 MSE 🛓 AQ	👫 🎬 🛃 💱 🔊 😭	NS-		
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	nickel waste.oad*						
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	Nickel Waste	Г	Variable	Value		Add Calculation 👻	
	Base Sulvey		√ Stream	Parameters			
			Stream Amount (kg)		1.00019	Special Conditions	
			Temperature (°C)		25.0000	Solids Only	
			Pressure (atm)		1.00000	0	
			√ Inflows (	opm (mass))		Summary	_
			H2O		9.99815e5	Unit Set: <custom></custom>	~
			Ni(OH)2		185.335		
						Automatic Chemistry Model Aqueous (H+ ion) Databanks:	
						Aqueous (H+ ion)	
						Using K-fit Polynomials T-span: 25.0 - 225.0	
						*P-span: 1.0 - 201.0	
	Actions					* = differs from default.	
	Actions				>		
	Add Stream						
	Add Mixer Add Stability Add Single Point Add Corrosic						
2	Add Single Point B Add Corrosic						
	Add Survey						
	< >						
	Plot Template Manager # * *						
					~		
		<u> </u>					
		Ir	Input				U
			Advanced Search Add as Stre	ern Export			Ť
	Save						
	x	·					
	>						
	\$ 3						
	For Help, press F1					<b>2</b>	NUM
							11

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

Name: Waste Survey with CN

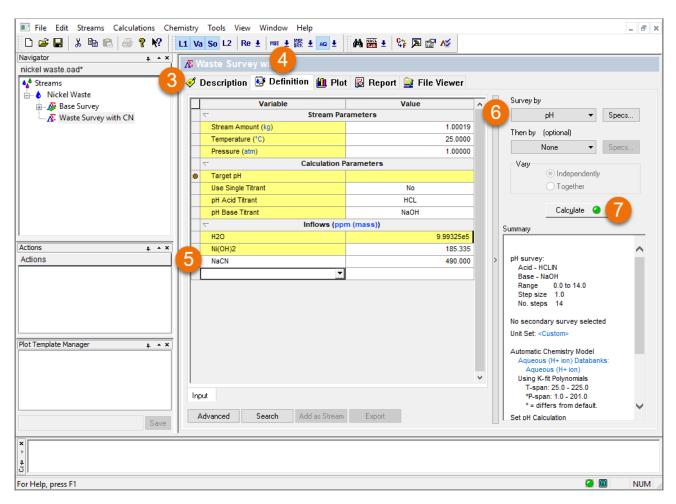
Description: pH survey with both Nickel and CN

Click on the Definition Tab

Add NaCN to the grid with a value of 490 ppm

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

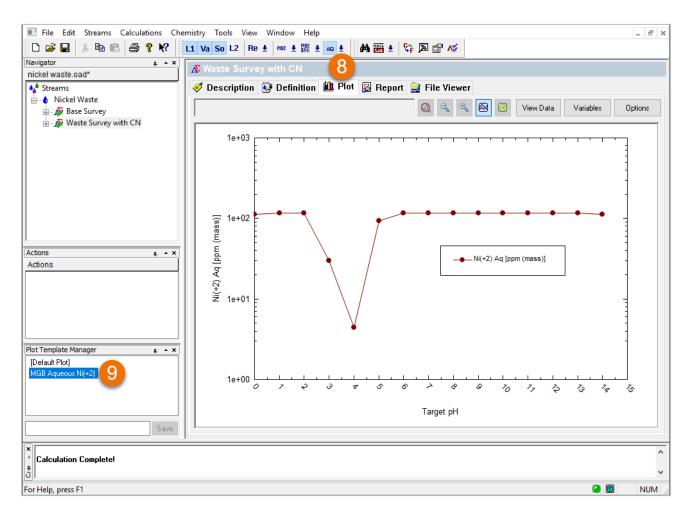
Click on the Calculate button.



Let's review the results.

## Click on the Plot tab

Go to the Plot Template Manager tool, and click 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.

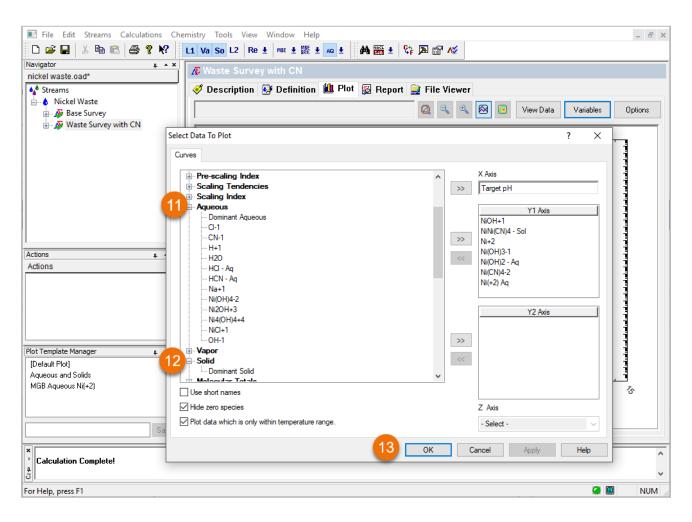
Let's analyze why this is happening. We can now modify the plot to display more variables. Select the **Aqueous** and **Solids** plot saved in the **Plot Template Manager**.

Click on Variables

Add the following new Aqueous species: Ni(CN)4-2

Add the following new Solid species: NiNi(CN)4-Solid

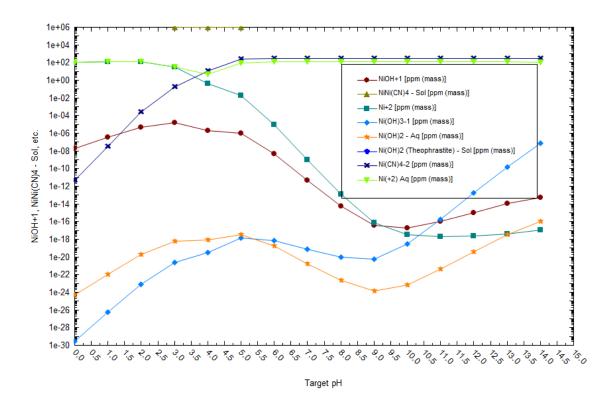
**Click OK** 



Let's analyze the results.

The culprit is the Ni(CN) $_{4}$ <sup>-2</sup> complex of nickel and cyanide. Basically, the plot of the total Ni in solution and the Ni(CN) $_{4}$ <sup>-2</sup> 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)<sub>4</sub> 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 many metal sulfide salts are highly insoluble.

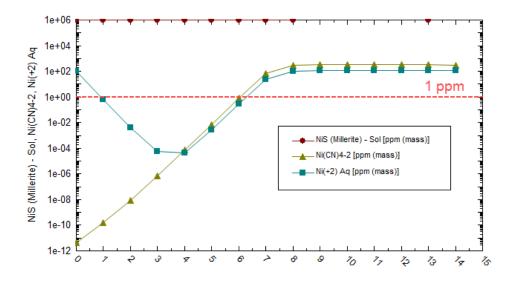
Create a new single point calculation and a survey as you did in the previous two scenarios.

#### 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:

## Aqueous Species: Ni(CN)4-2 Aqueous Species: Ni+2



The results reflect a "power struggle" between the Ni(CN)<sup>-2</sup> which is holding the nickel in solution and the NiS solid which clearly has a greater tendency to form than the NiNi(CN)<sub>4</sub> 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 Studio: 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)<sup>-2</sup> and not the cation (Ni+2) as the conventional wisdom might dictate.

## **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 Partitioning

The purpose of this first example is to present the basic Temperature survey. You will study how a four-phase mixture partitions with 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	
Calculatio	n Settings	Stream Compos	ition and Conditions
Calculation Type	Survey	Stream Amount	Calculated
Stream Name	Temperature Survey	Temperature Range	25-100 °C (Default)
Survey Name	4-Phase Partioning	Step Size	Increment by 5 °C (Default)
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

## Add a new Stream

Click on the new Stream and press <F2> to change the name to *Temperature Survey* Select the MSE-SRK thermodynamic Framework Click on the Names Manager Icon and select the Formula option Click on the Units Manager Icon, and select Metric, Batch, Moles Enter the composition of the stream given in the table above Go to the Add Calculation button and select Survey calculation Change the Survey name to 4-Phase Partitioning using the <F2> key Select Temperature as Type of Survey - Default Click on the Specs button. This will open the Survey Options Window

Variable		Value	<u>^</u>	Survey by	,
~	Stream Parameter	s		Te	mperature
Stream Amount (mol)		80.000		Then by	(optional)
Temperature (°C)				· ·	
Pressure (atm)		1.00000			None
,	Inflows (mol)			Vary	
H2O		50.0000			Independe
CH4		10.0000			<ul> <li>Together</li> </ul>
C10H22		10.0000			
NaCl		10.0000			Calc <u>u</u> late

The Temperature Range is entered in the **End Points** section. The default values for the Temperature Range are 25°C (Start) to 100°C (End). Leave the default values.

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**.

Survey Options	? ×
Category Var. 1 - Temperature Calculation Type Calculation Options	Survey Range Temperature Range Unit: *C Selected Range 25.0 to 100.0 in 15 steps of 5.0 New Delete
	<ul> <li>Linear</li> <li>Log</li> <li>Point List</li> <li>End Points</li> <li>End 100.000</li> <li>These are the default values</li> <li>Step Size</li> <li>Increment 5.0000</li> <li>Select one, the other is calculated</li> </ul>
	OK Cancel Apply Help

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

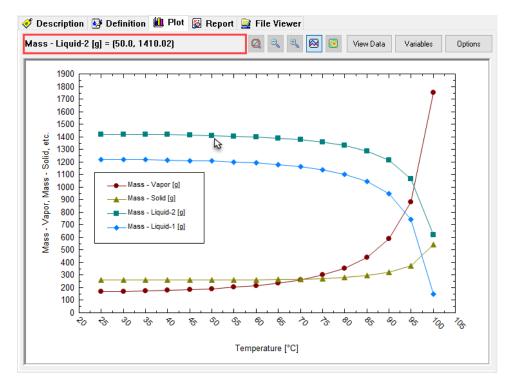
It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

## Analyzing 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 80°C, 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.

## **Pressure Survey**

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

### Example 19: Dissolution of CO<sub>2</sub> 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<sub>2</sub> in water (which is a direct reflection 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 ℃				
Unit Set	Metric, Moles	H2O	55.5082 moles				
Framework	MSE-SRK	CO2	10 moles				

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to *Pressure Survey* 

Select the **MSE-SRK** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition of the stream given in the table above

Go to the Add Calculation button and select Survey calculation

Change the Survey name to CO2 dissolved in water using the <F2> key

Select **Pressure** as Type of Survey

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

Γ	Variable	Value	^	-	Survey by		
~	Stream Parameters				Pressure 👻 Specs		
	Stream Amount (mol)	65.5082			Then by (op	otional)	
	Temperature (°C)	25.0000					
	Pressure (atm)				Nor	ne 🔻	Specs
<	√ Inflows (mol)				Vary		
	H2O	55.5082			<ul> <li>Independently</li> <li>Together</li> </ul>		
	C02	10.0000					

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**.

We are ready to perform the calculation. Click on the Calculate button or press the <F9> key It is time to save your file (File >Save as...) or using the save icon in the tool bar. You can save under the

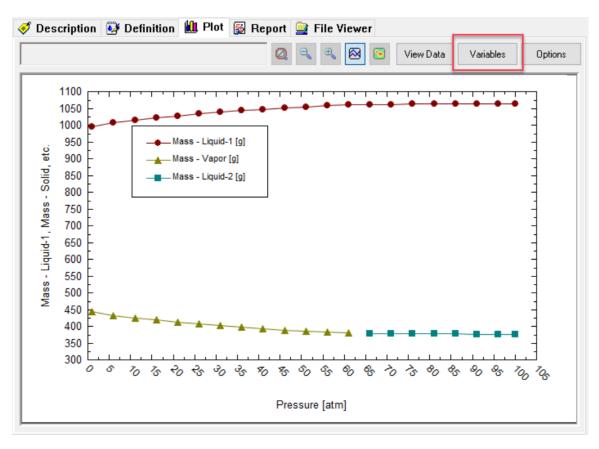
same file that we created before named as *Survey Calculations*.

## Analyzing the Results

Click on the **Plot** tab (<sup>LD</sup> 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<sub>2</sub> 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).

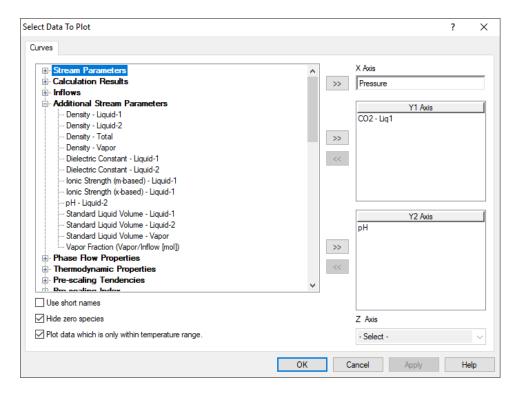


Click on the **Variables** button. This will open the **Select Data to Plot** window.

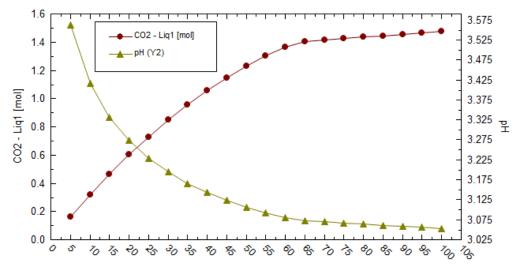
**Double click** or use the << button to remove the **Phase Amount** variables.

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

Look for Additional Stream Parameters section and click on the H 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 shows the selected variables: The dissolved CO<sub>2</sub> in the water (Liquid-1 Phase) in the Y1 Axis, and the pH in the Y2 Axis. Both variables are presented as a function of pressure.



Pressure [atm]

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:

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

$$CO_{2,aq} + 2H_2O \leftrightarrows H_3O^+ + HCO_3^-$$

$$HCO_3^- + H_2O \leftrightarrows H_3O^+ + CO_3^{2-}$$

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.

## **Composition Survey**

In the Survey by **Composition**, the 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<sub>3</sub>) as a function of CO<sub>2</sub>

Calcite is a scale that forms very easily in the production of oil and gas. It is known that adding  $CO_2$  to water dissolves Calcite. Likewise, removing CO2 from water precipitates calcite. 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	n Settings	Stream Composition and Conditions				
Calculation Type	Survey	Stream Amount	Calculated			
Stream Name	Composition Survey	Temperature	25 °C			
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			

#### Add a new Stream

**Click** on the new Stream and press **<F2>** to change the name to *Composition Survey* 

Select the MSE thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition of the stream given in the table above

Go to the Add Calculation button and select Survey calculation

Change the Survey name to Calcite Dissolution using the <F2> key

Select Composition as Type of Survey.

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.

To specify the component, click on the Specs button. This will open the Survey Options Window.

## Under the Component tab, select CO2

Survey Options		?	×
Category	Component Survey Range Component Inflows Hide Related Inflows CaCO3 CO2 H20 Select a component inflow which will be varied over t	New Inflow	
	OK Cancel A;	pply Help	

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**.

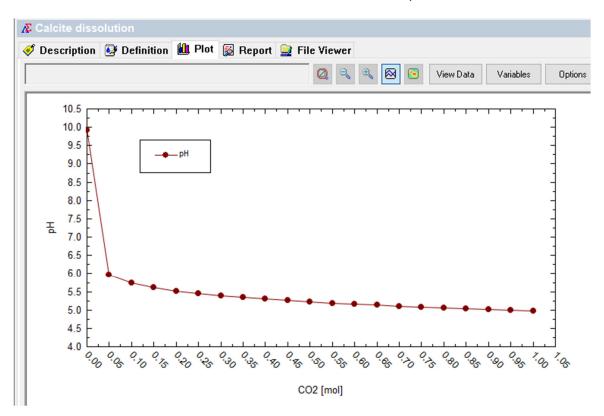
Survey Options		?	×
Category	Component Survey Range		
Var. 1 - Composition Calculation Type Calculation Options	Composition Range Unit: mol Selected Range 0.0 to 1.0 in 20 steps of 0.05	New	
	Linear O Log O Point List  End Points  Start 0.0  End 1.00000	Delete	
	Step Size Increment 0.0500000  Select one, th Number Steps 20	ne other is	
	OK Cancel Apply	Help	)

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

#### Analyzing the Results

Click on the **Plot** tab ( Plot ). The default plot is the pH as a function of total CO<sub>2</sub> in moles. As the concentration of CO2 increases, the pH decreases (as it was explained in the example <u>above</u>).

We are interested in understanding the dissolution of Calcite as a function of CO<sub>2</sub>. To see these results, we need to study how the moles of solid calcite change as the concentration of CO<sub>2</sub> increases.

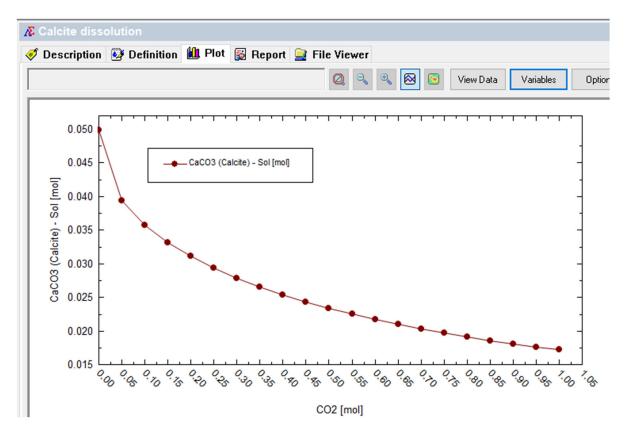


Click on the Variables button. This will open the Select Data to Plot window.

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

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 shows the selected variable: CaCO3 (Calcite) – Sol as a function of CO<sub>2</sub>.



As expected, the amount of CaCO<sub>3</sub> (Calcite) decreases with increasing CO<sub>2</sub>. In an oil production setting, when there is a significant pressure drop, CO<sub>2</sub> will be lost. This will decrease the solubility of CaCO<sub>3</sub> and will increase the likelihood of scale formation.

## 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 0.001 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					
Calculat	ion Settings	Stream Composition and Conditions			
Calculation Type	Survey	Stream Amount	Calculated		
Stream Name	ne pH Survey Temperature		25 °C		
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		

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to pH Survey

Select the AQ thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition of the stream given in the table above

Go to the Add Calculation button and select Survey calculation

Select **pH** as Type of Survey

Change the Survey name to Carbonic Acid System using the <F2> key

The calculation can be run without modification. The default titrants are **HCI** 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.

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

✓ Hide Related Inflows	New Inflow
Page	
	Base CO2 H2O NAOH

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

pH Titrants Survey F	lange
Target pH Range	Unit
Selected Range	
4.0 to 12.0 in 80 ste	ps of 0.1 New
	Delete
Linear	🔿 Log 💦 Point List
End Points	
Start	4.00000
End	12.0000
Step Size	
Increment	0.100000 💿 🔪 Select one, the other is
Number Steps	80 🔿 🗲 calculated

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

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*.

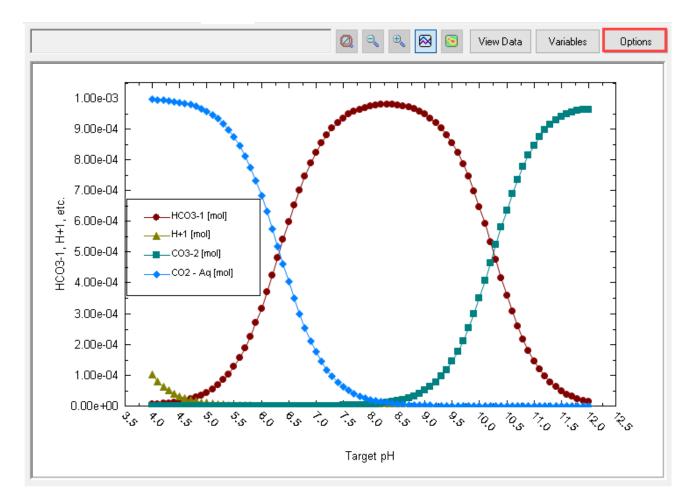
## Analyzing the Results

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.

Click on the Variables button

Remove the **NaOH** and **HCI** from the Y1 axis (double click or use the << button)

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.

Click on the Options button. This will bring the Customize Plot window

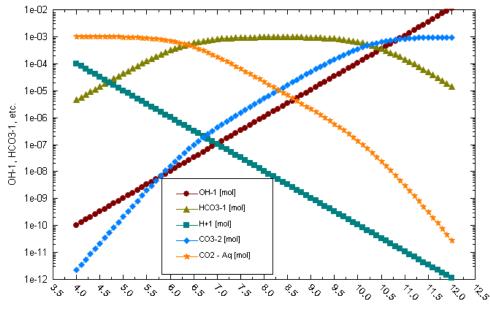
Select Y Axis in the Category window

Check the Logarithmic scale box, and then click OK.

Customize Plot		?	×
Customize Plot Category General 	Scale       Format       Title         Auto       0.0         Minimum       1.05e-3         Major Unit	?	×
	OK Cancel Apply	Help	>

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

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 HCI and H+.

## 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

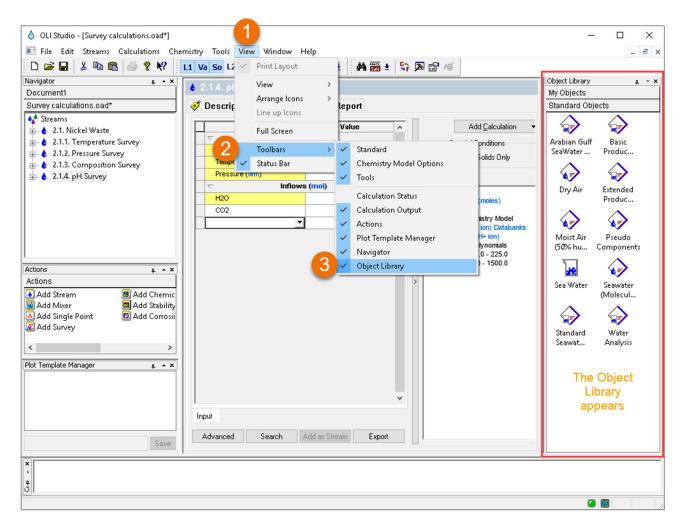
Seawater contains a variety of salts, and when seawater evaporates, these solids are left behind. The most abundant salt in seawater is sodium chloride (NaCl) which is commonly referred to by its mineral name halite.

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.

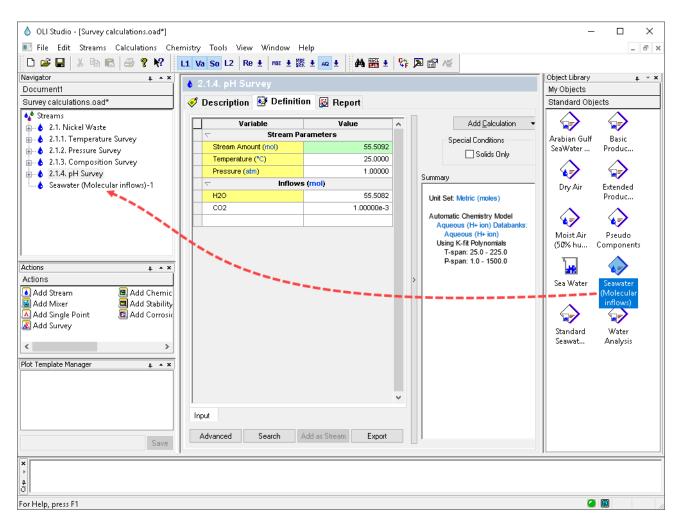
In this example we will also introduce the Object Library tool.

#### Starting the Simulation

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



냮냰냴냷냸냺냽넁넄넇너넊넍넎넗 Drag the **Seawater (Molecular inflows)** stream to the navigation panel (in the white space below the other streams and calculation objects) (Note: This object is in the AQ thermodynamic framework)



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

냮냰냴냷냸냺냽넁넄넇너넊넍넎넗 Vapor Fraction Survey 냮냰냴냷냸냺냽넁넄넇너넊넍넎넗 냮냰냴냷냸냺냽넁넄넇너넊넍넎넗 key 냮**냰냴냷냸냺냽넁넄넇너넊넍넎넗 냮냰냴냷냸냺냽넁넄넇너넊넍넎넗 낶냰냴냷냸냺냽넁넄넇너넊넍넎넗** Window

Click on the new Stream and press <F2> to change the name to

Go to the Add Calculation button and select Survey calculation

Change the Survey name to Seawater Evaporation using the <F2>

Select Vapor Fraction as Type of Survey

Click on the Specs button. This will open the Survey Options

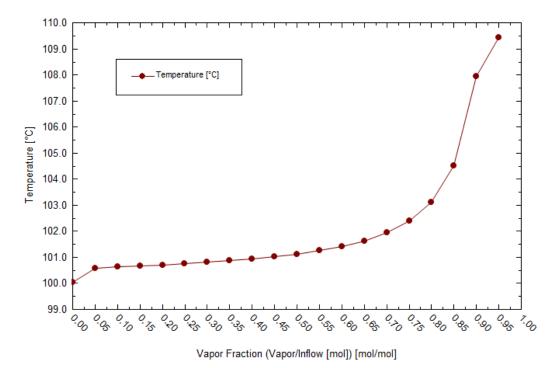
냮냰냴냷냸냺냽넁넄넇너넊넍넎넗 The default Vapor Fraction range is from 0-1 with an increment of 0.1. Change the **Vapor Fraction Range** to **Survey End** to 0.95. Set the **Step Size** to **0.05** increments. Then click **OK**.

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

냮냰냴냷냸냺냽넁넄넇너넊넍넎넗 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*.

## Analyzing the Results

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



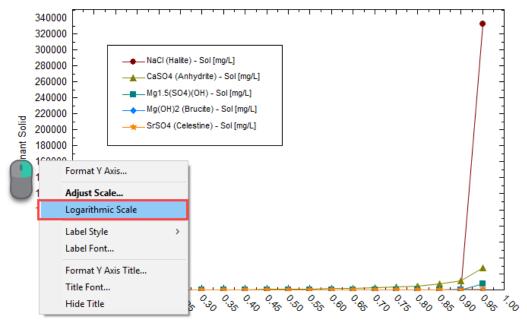
We are also interested to know which solid phases precipitate as the water evaporates.

#### Click on the Variables button

Remove **Temperature** from the Y1 axis (double click or use the << button)

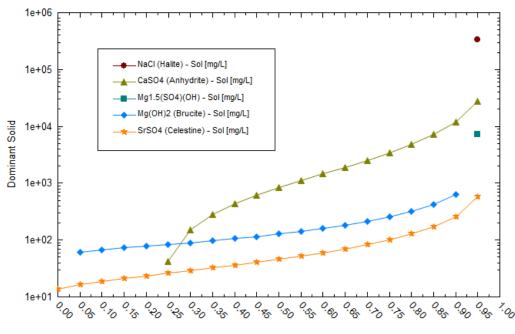
Look for **Solid** section and click on the 🗄 box to show all the available species. **Select** the option **Dominant Solids** and put it in the Y1 Axis using the >> button or by double clicking. When you are done, click **OK**.

The default plot is not very easy to read because halite dominates the solids and because the units are in mg/l and the liquid volume decreases from left-to-right on the plot. To see the plot more clearly, **right click** on any number in the Y axis, and select the **Logarithmic Scale** option.



Vapor Fraction (Vapor/Inflow [mol]) [mol/mol]

#### Plot in semilogarithmic scale



Vapor Fraction (Vapor/Inflow [mol]) [mol/mol]

As the water evaporates CaSO<sub>4</sub>,  $Mg(OH)_2$  and SrSO<sub>4</sub> salts precipitate at all temperatures. NaCl and a Mg/SO4/OH double salt starts to precipitate at 95% vapor fraction.

## **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 the red box in the image below. There are three options available in the optional survey, Temperature, Pressure and Composition.

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

1	Description 🤒 Definition 🛍 Plot	t 📓 Report 🚊 File Viewer			
Г	Variable	Value	~		Survey by
					Temperature 👻 Specs
	Stream Amount (mol) 55.5082		2 Then by (optional)		Then by (optional)
	Temperature (°C)				Pressure   Specs
	Pressure (atm)				
	⊂ Inflows				Vary 🔘 Is dee on deaths
	H2O	55.5082			Independently
					O Together
					Calculate 🥥
					Summary
				>	Temperature survey:
					Range 25.0 to 100.0 °C
					Step size 5.0 °C No. steps 15
					Pressure survey Range 1.0 to 10.0 atm
					Step size 1.0 atm
					No. steps 9
					Primary and secondary survey
					variables
					move independently Total points: 160
L			۷		Unit Set: Metric (moles)
h	put				
		<b>F</b> .			Automatic Chemistry Model
	Advanced Search Add as Stream	Export			Aqueous (TH IOI) Databalitis.

## **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<sub>2</sub> 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					
Calcu	lation 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 °C		
Unit Set	Metric, Moles	Step Size	Increment by 5 °C		
Framework	MSE-SRK	Vary	Independently		
		H2O	55.5082 moles		
		CO2	10 moles		

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to T/P Survey

Select the **MSE-SRK** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition of the stream given in the table above

Go to the Add Calculation button and select Survey calculation

Change the *Survey* name to *CO2 dissolution T/P* using the <F2> key

Select Temperature and then by Pressure

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

Change the **Temperature Range** to 5-100 °C. Set the **Step Size** to **5** °C increments.

Click on Var. 2 – Pressure, in the Category Window to define the Pressure Range.

Change the **Pressure Range** to 5-100 atm. Set the **Step Size** to **5 atm** increments. Then click **OK**.

Survey Options		?	×
Category Var. 1 - Temperature Var. 2 - Pressure - Calculation Type - Calculation Options	Survey Range Pressure Range Unit: atm Selected Range 5.0 to 100.0 in 19 steps of 5.0	New	
	● Linear ○ Log ○ Point List       End Points       Start       5.00000       End       100.000       Step Size       Increment       5.00000       Number Steps       13		_
	OK Cancel Apply	Help	

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

ø	🕈 Description  🕺 Definition 🛍 Plot	📓 Report 🚊 File Viewer		
Г	Variable	Value		Survey by
	C Stream Parameters			Temperature 👻 Specs
	Stream Amount (mol)	65.5082		Then by (optional)
	Temperature (°C)			
	Pressure (atm)			Pressure   Specs
	√ Inflows (n	nol)		Vary
	H2O	55.5082		Independently
	C02	10.0000		<ul> <li>Together</li> </ul>
	Input		*	Calculate Calcul
	Advanced Search Add as Stream	Export		Automatic Chemistry Model VIII MSE-SRK (H3O+ ion) Databanks:

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*.

## Analyzing 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<sub>2</sub> 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).

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

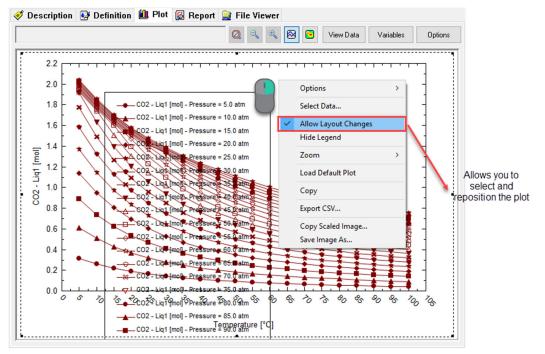
**Double click** or use the << button to remove the **Phase Amount** variables.

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

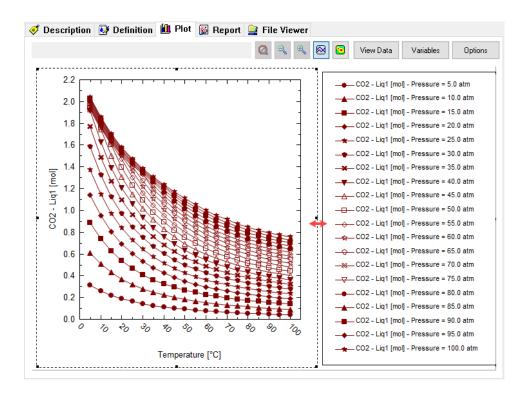
Select Data To Plot			?	×
Curves				
Stream Parameters     Calculation Results     Inflows     Additional Stream Parameters     Phase Flow Properties     Thermodynamic Properties     Pre-scaling Index     Scaling Index     Scaling Index     Liquid-1	X Axis Temperature CO2 - Liq1	Y1 Axis		
	>>	Y2 Axis		
Use short names	~			
Hide zero species	Z Axis			
Plot data which is only within temperature range.	Pressure			~
	OK Cancel	Apply	He	lp

The default plot now is showing the dissolved CO<sub>2</sub> in the water (Liquid-1 Phase) in the Y1 Axis as function of pressure. Unfortunately, the legend is covering the plot.

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.



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

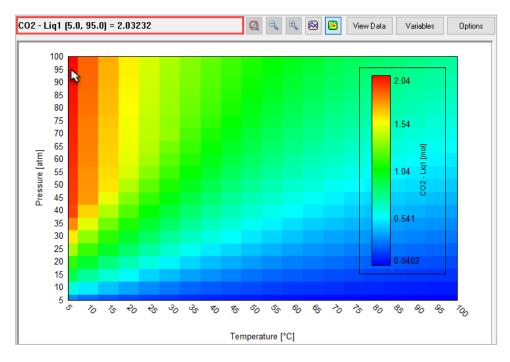


As the temperature increases (at a fixed pressure) the solubility of  $CO_2$  decreases. This is to be expected since at higher temperatures it is easy to overcome the vapor pressure and  $CO_2$  is released as gas. As the pressure increases (at a fixed temperature) the solubility of  $CO_2$  in solution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

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<sub>2</sub> 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 CO<sub>2</sub> dissolved in the Liquid-1 phase at each T and P value will be shown in the left corner box.

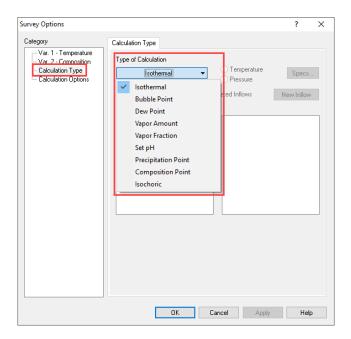


Note: The legend scale can also be optimized by either right-mouse-clicking on the Legend and selecting Options>Plot Options>Contour or clicking on the Options button in the upper right and selecting Contour. Both open to the Contour options window, where the color and range can be modified.

In the contour plot, you can see the effect of both Temperature (x-axis) and Pressure (y-axis) on the solubility of CO<sub>2</sub> 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 °C
Calculation Type	Precipitation Point	Step Size	Increment by 5 °C
Name Style	Display Formula	H2O	55.5082 moles
Unit Set	Metric, Moles	NaCl	0 moles
Framework	MSE		

Add a new Stream

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

Category		
Calculation Options	Calculation Type         Type of Calculation         Precipitation Point         ✓ Use Single Titrant         ✓ Hide Related Inflows         Solid Precipitate         HCL. 1H20         HCL 2H20         HCL 2H20         HCL 3420         NaCl (Halite) - Sol         NaOL 2H20 (hydrohalite)         NaOH - Sol         NaOH. 2H20         NaOH. 3.5H20         NaOH. 4H20	New Inflow

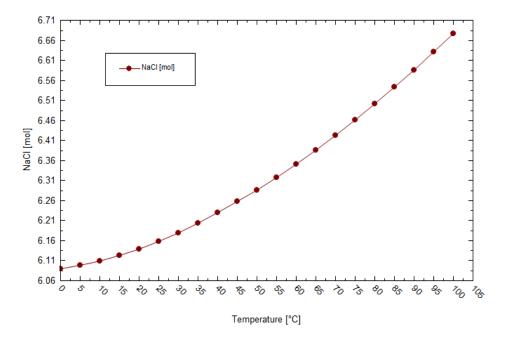
The **Calculation Parameters** section is now shown in the Definition Tab, highlighting the Precipitant (NaCl (Halite)) and the Adjusted Inflow (NaCl).

		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

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

## Analyzing 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<sub>2</sub>O at 25°C to 6.68 moles/1kg H<sub>2</sub>O at 100°C.

## 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 <u>Example 24</u> will be used.

#### Starting the Simulation

Under the **Solubility vs T** stream add a new Survey (see Stream information in Example 24) Change the **Survey** name to **Halite Solubility vs T and P** using the **<F2>** key Select Survey by **Temperature** and then by **Pressure** (This is a dual survey) Click on the **Temperature Specs** button. This will open the **Survey Options Window** Change the **Temperature Range** to 0-100 °C. Set the **Step Size** to **5** °C increments.

Click on **Var. 2 – Pressure**, in the Category Window to define the Pressure Range.

Change the Scale to Log, change the **Pressure Range** from 1 to 1000 atm, and set the Number of Steps to **3** (i.e. it will plot the following pressures: 1, 10, 100 and 1000 atm). Then click **OK**.

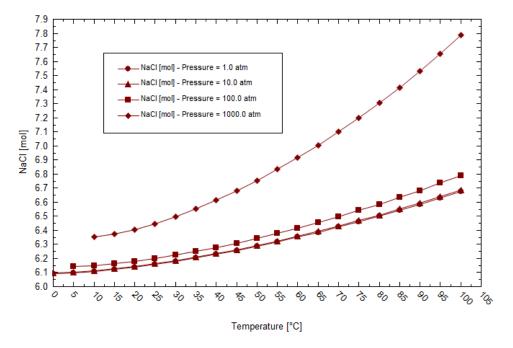
Survey Options		?	×
Category Var. 1 · Temperature Var. 2 · Pressure Calculation Type Calculation Options	Survey Range Pressure Range Unit: atm Selected Range 1.0 to 1000.0 in 3 steps of 333.0	New	
	O Linear       ● Log       ● Point List         End Points	the other is	
	OK Cancel Apply	Help	1

Click on Calculation Type, in the Category Window to define the Type of Calculation

Under Type of Calculation Change the Default Isothermal to **Precipitation Point** (use the drop-down arrow) Select **NaCl (Halite)-Sol** as the **Solid Precipitate** and **NaCl** as the **Adjusted Inflow**. Then click **OK**. We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key. 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*.

## Analyzing 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.

#### Return to the **Definition Tab**

Click on the Temperature Specs button.

Change the Temperature Range to 0-150 °C. Set the Step Size to 2 °C increments.

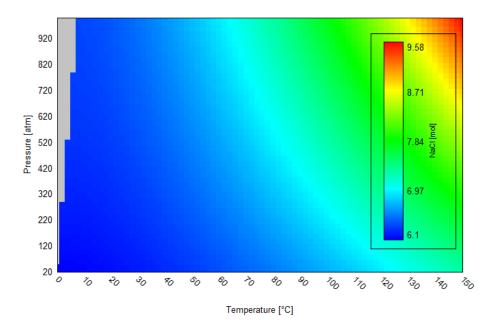
Click on Var. 2 – Pressure, in the Category Window to define the Pressure Range.

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.

Click the **Calculate** button. This calculation will take a few minutes to compute.

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

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to Composition survey - Azeotrope

Select the MSE thermodynamic Framework

Click on the Names Manager Icon and select the Display Name option

**Click** on the **Units Manager** Icon, and select Metric, Batch, Mass Frac.

Enter the composition of the stream given in the table above

Go to the Add Calculation button and select Survey calculation

Select Composition as the type of survey

Change the Survey name to Ethanol-Water Azeotrope using the <F2> key

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

## Under the Component tab, select Ethanol

Click on the **Survey Range tab.** Change the **Composition Range** to 0-100 mass%. Set the **Step Size** to **2** mass% increments.

Component Survey Range	Component Survey Range
Component Inflows	Composition Range Unit: mass %
Hide Related Inflows New Inflow	Selected Range
Ethanol	0.0 to 100.0 in 50 steps of 2.0 New
	Delete
	● Linear ○ Log ○ Point List
	End Points
	Start 0.0
	End 100.000
	Step Size
	Increment 2.00000      Select one, the other is
Select a component inflow which will be varied over the specified range.	Number Steps 50 Calculated

Click on Calculation Type, in the Category Window to define the Type of Calculation

Under Type of Calculation Change the Default Isothermal to **Bubble Point** (use the drop-down arrow). Then click **OK**.

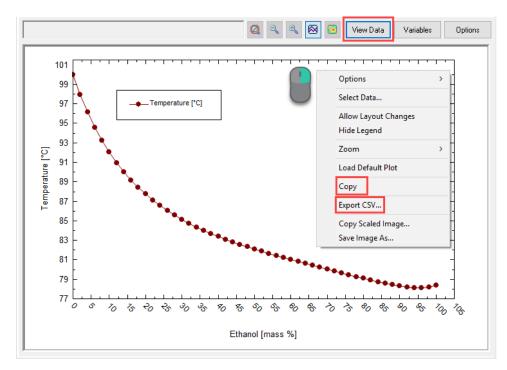
Survey Options		?	×
Category	Calculation Type		
Var. 1 - Composition 	Type of Calculation Bubble Point	Specs	
	Use Single Titrant Hide Related Inflows	New Inflow	
	OK Cancel A	Apply He	elp

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

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*.

#### Analyzing the Results

Click on the **Plot** tab (<sup>10</sup> 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 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

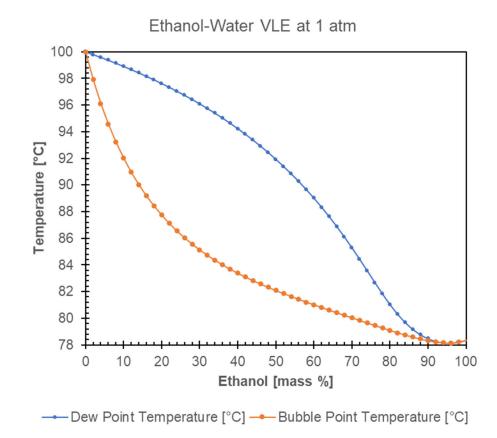
In this case let's use **Option 1**. Right click and **Copy** the data, then open your preferred plotting tool and **Paste** the data.

## Calculating the Dew Point

#### Return to the **Definition tab**

Click on the **Composition Specs** button. This will open the **Survey Options Window** Click on **Calculation Type**, in the Category Window to define the Type of Calculation Change the calculation type to **Dew Point** (use the drop-down arrow). Then click **OK**. **Recalculate**, and click on the **Plot tab** 

Right click and **Copy** the data, then open your preferred plotting tool and **Paste** the data **Plot** the two temperature curves vs mass% of ethanol and format as needed

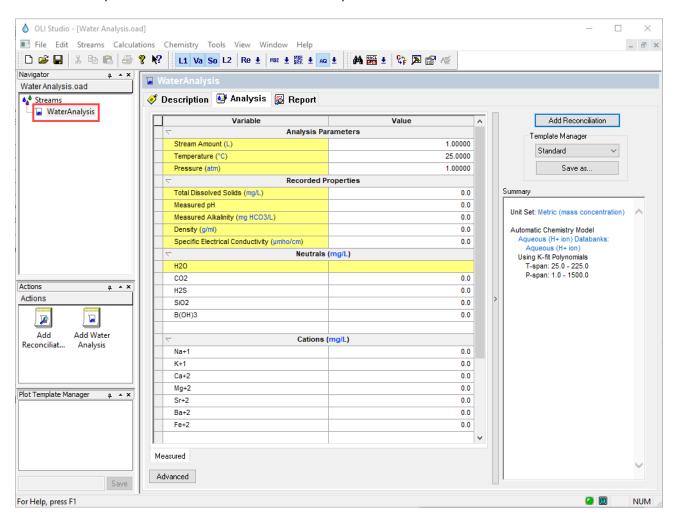


The azeotrope occurs at about 95% ethanol where the two curves intersect, at 78.15 °C.

# Section 3. Water Analysis (Ionic Inputs)

OLI Studio: 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.



## **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<sub>sp</sub>

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 ( $K_{sp}$ ).

$$ST = \frac{IAP}{K_{sp}}$$
 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

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

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

#### 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 25°C 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:

 $[Ca^{+2}] = 0.0093 m \qquad \gamma_{Ca^{+2}} = 0.4663$  $[SO_4^{-2}] = 0.0093 m \qquad \gamma_{SO_4^{-2}} = 0.4663$  $a_{H_2O} = 0.9997$ 

#### Calculating the IAP

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

$$IAP = a_{Ca^{+2}} \cdot a_{SO_4^{-2}} \cdot (a_{H_2O})^2$$
$$IAP = (m_{Ca^{+2}} \gamma_{Ca^{+2}}) \cdot (m_{SO_4^{-2}} \gamma_{SO_4^{-2}}) \cdot (a_{H_2O})^2$$
$$IAP = (0.0093 \times 0.4663) \cdot (0.0093 \times 0.4663) \cdot (0.9997)^2$$

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

$$SI = \log_{10} \frac{IAP}{K_{sp}} = \log_{10} ST$$
$$SI = \log_{10} (0.587)$$
$$SI \approx -0.231$$

# **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, Total Ions, 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.

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, Measured Total Inorganic Carbon (TIC), 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	
Measured TIC (mol C/L)	0.0	
Density (g/ml)	0.0	
Specific Electrical Conductivity (µmho/cm)	0.0	

The concentration of Neutrals, Total lons, 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 a **neutral**, simple 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 (n)	ng/L)
H2O	
C02	0.0
H2S	0.0
SiO2	0.0
B(OH)3	0.0
	ng/L)
P as PO4-3	0.0
Si as SiO2	0.0
B as B(OH)3	0.0
	g/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 (m)	g/L)
CI-1	0.0
S04-2	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.

$\nabla$	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
Cu	<b>v</b>
Display Name	OLI Name
OLI CSION	CSION
<sup>s</sup> ™Cu(+)	CUIION
\$ <sup>¶</sup> Cu(++)	CUION
<sup>\$™</sup> Cu(+1)	CUIION
SYN Cu(+2)	CUION

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>**.

	$\nabla$	Neutrals (mg/L)
	H2O	
	CO2	0.0
	H2S	0.0
	SiO2	0.0
	B(OH)3	0.0
8	OLI	0.0

# Water Analyses - Reported Elements as Total lons

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. Some of these ions are already entered into the **Total lons** section, and the software will do the conversion automatically.

Converting element	concentration to	species for Brine	e or Water Analysis
	••••••		

ICP data	Aqueous Species	Formula to enter	Formula weight multiplier
B, boron	Boric Acid	НЗВОЗ	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)
		HS-1 or SO4-2	S (mg/l) $\times$ 1.03 for HS-1 (mg/l)
S, Sulfur	Sulfate or Sulfide	(Cannot tell from total S only)	or
			S (mg/l) $\times$ 3.0 for SO4-2 (mg/l)

# 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 °C. 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 (Def	ault)	Total Dissolved S	Solids	Not recorded	
Temperature		25 ⁰C		Measured pH		6.7	
Pressure		1 atm		Measured Alkalir	nity	Not reco	orded
Name Style		Display	Formula	Density		Not reco	orded
Unit Set		Metric, E	Batch,	Specific Electrica	l	Not reco	orded
		Concen	tration	Conductivity			
Framework		MSE					
Calculation Type		Water A	nalysis				
Analysis Name		Basic W	ater Analysis				
			Comp	osition			
Neutrals	s (mg/L)		Cations	s (mg/L)	Anions (mg/L)		s (mg/L)
CO2	150		Na+1	1060	CI-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

### Add a Water Analysis

Click on the new Water Analysis and press <F2> to change the name to Basic Water Analysis

Select the MSE thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

**Click** on the **Units Manager** Icon, and select Metric, Batch, Concentration (it may be defined by default) Under the **Analysis** Tab, enter the Analysis Parameters, Recorded properties, and composition of the water given in the table above.

Go to the **Add Reconciliation** button of the top right corner or select **Add Reconciliation** from the Actions Panel.

gator + ×			
gator + * X Vater Analysis - Example_28.0ad	🖬 Basic Water Analysis		
	< Description 🧕 Analysis 📓 Repor	t	
Basic Water Analysis			
🔊 🔊 Reconcile	Variable	Value	Add Reconciliation
	Analysis Pa	arameters 1.00000	Template Manager
	Stream Amount (L) Temperature (°C)	25.0000	Standard V
	Pressure (atm)	1.0000	
	Recorded I		5047C 03
	Total Dissolved Solids (mg/L)	0.0	) Summary
	Measured pH	6.70000	0
	Measured Alkalinity (mg HCO3/L)	0.0	Unit Set: Metric (mass concentration)
	Measured TIC (mol C/L)	0.0	
	Density (g/ml)	0.0	MSE (H3O+ ion)
	Specific Electrical Conductivity (µmho/cm)	0.0	Using Helgeson Direct
	Neutrals	(mg/L)	
	H2O		
	CO2 H2S	150.000	
	Si02	0.0	
	B(OH)3	0.0	
	NH3	5.0000	
		s (mg/L)	
ns ▲ ×	P as PO4-3	0.0	
ons	Si as SiO2	0.0	
	B as B(OH)3	0.0	
Add Add Water conciliat Analysis	Cations		_
Analysis	Na+1 K+1	1060.00	
	Ca+2	773.000	
	Mg+2	177.000	
	Sr+2	0.180000	
	Ba+2	0.460000	
	Fe+2	62.1000	
Template Manager p • ×	Mn+2	2.80000	
Template Manager 📮 🔺 🗙	Al+3	0.740000	
	Anions		
	CI-1	3896.00	
	S04-2	54.0000	
	HC03-1 HS-1	0.0	
	HS-1 C2H302-1	0.0	
		. 0.0	
	Measured		

**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, four different types of reconciliation are enabled in the upper right corner of the window: (1) No Reconcile, (2) Reconcile pH, (3) Reconcile pH/Alkalinity, and Reconcile pH/Alkalining/TIC. 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.

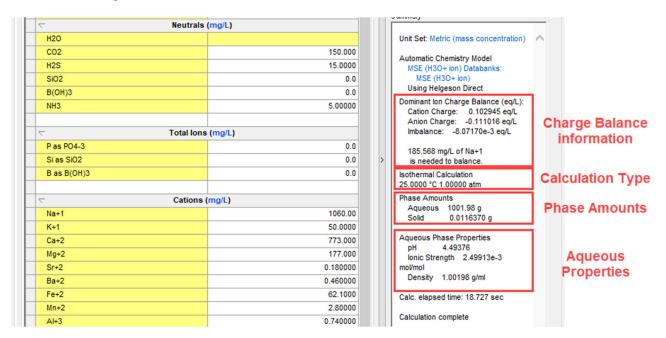
#### Select the **No Reconcile** option

OLI Studio (Version 11.5.1 Beta) - [3. Water Analysis - Exar	nple_28.oad*]		– 🗆 X
File Edit Streams Calculations Chemistry Tools	View Window Help		_ 8 ×
🗅 😅 🖬 👗 🛍 💼 🎒 🤻 🌾 📘 Va So L	2 Re 🛓 MSE 🛓 SRK 🛓 AQ 🛓 🚧 MACL 🛨	💱 🔊 🖆 🌾	
Navigator a A X			
3. Water Analysis - Example_28.oad*	Reconcile		
1 T	< Description 🔮 Reconciliation 🛃	Molecular Basis  📓 Report	
Basic Water Analysis	Variable	Value	Reconcilitation
Reconcile		Parameters	Specs
	Stream Amount (L)	1.00000	Reconcile
	Temperature (°C)	25.0000	No Reconcile
	Pressure (atm)	1.00000	O Reconcile pH
	Recorded	Properties	Reconcile pH/Alkalinity
	Total Dissolved Solids (mg/L)	0.0	Reconcile pH/Alkalinity/TIC
	Measured pH	6.70000	Calculate Alkalinity
	Measured Alkalinity (mg HCO3/L)	0.0	
	Measured TIC (mol C/L)	0.0	Calculate 🥝
	Density (g/ml)	0.0	
	Specific Electrical Conductivity (µmho/cm)	0.0	Summary
		s (mg/L)	
	H20		Unit Set: Metric (mass concentration)
	C02	150.000	Automatic Chemistry Model
	H2S	15.0000	MSE (H3O+ ion) Databanks:
	SiO2	0.0	MSE (H3O+ ion) Using Helgeson Direct
	B(OH)3	0.0	Dominant Ion Charge Balance (eq/L):
	NH3	5.00000	Cation Charge: 0.102945 eq/L
	Total lo	ns (mg/L)	Anion Charge: -0.111016 eq/L Imbalance: -8.07170e-3 eq/L
Actions + *	P as PO4-3	0.0	
Actions	Si as SiO2	0.0	185.568 mg/L of Na+1 is needed to balance.
	B as B(OH)3	0.0	Isothermal Calculation
			25.0000 °C 1.00000 atm
	Cation	s (mg/L)	Calculation not done
	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	
Plot Template Manager + ×	Mn+2	2.80000	
	Al+3	0.740000	
		s (mg/L)	
	CI-1	3896.00	
	S04-2	54.0000	
	HC03-1	0.0	
	HS-1	0.0	
	C2H3O2-1	0.0	
	Measured		
	Advanced Search Add as Stream	Export	× 1
Save	Hide do Official		
For Help, press F1			Image:

Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key 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  $-8.072 \times 10^{-3}$  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 °C 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
T Analysis Paran	neters
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	s (mg/L)
AICI3	3.61208
AI(OH)3	0.0262829
BaCl2	0.631654
BaSO4	0.0738067
CaCl2	2092.78
CaO	24.1565
C02	150.000
FeCl2	124.399
FeS	11.4757
H2O	9.95556e5
H2S	10.5511
KCI	95.3381
MgCl2	693.368
MnCl2	6.41382
NaCl	3166.36
NH3	4.99999
S03	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 Studio, by using the **Add as Stream** button, or it can be exported to a separate software like OLI Flowsheet: ESP , 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.

Save Selected Result S	treams	?	$\times$
Export Name: Molecular Include the followin			
Aqueous	Vapor		
Optional Phases that are no separately.	t included may be e	exported	
Aqueous			
Second Liquid			
	ОК	Car	ncel

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.

Leave the defaults and click **OK**. The program automatically adds a new stream in the navigation panel.

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E File Edit Streams Calculations C	mistry Tools View Window Help	_ 8 ×
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Navigator 4 • ×		
Document1	Molecular Export of Reconcile	
Water Analysis Calculations.oad	ダ Description 🔯 Definition 📓 Report	
▲ Streams	beschpton & connact (2 report	
Basic Water Analysis	Variable Value	Add <u>C</u> alculation 👻
Reconcile	C Stream Parameters	Special Conditions
Molecular Export of Reconcile	Stream Amount (L) 1.00000	Solids Only
	Temperature (°C) 25.0000	
	Pressure (atm) 1.00000	Summary
	C Inflows (mg/L)	
	H2O	Unit Set: Metric (mass concentration)
	CO2 150.000	Automatic Chemistry Model
	H2S 10.5511	MSE (H3O+ ion) Databanks:
	NH3 4.99999	MSE (H3O+ ion) Using Helgeson Direct
	AICI3 3.61208 BaCl2 0.631654	Using heigeson bliect
	CaCl2 2092.78	
I	CaO 24,1565	
Actions	FeCi2 124.399	
Actions	KCI 95.3381	
🙆 Add Stream 🔲 Add Stabi	MgCl2 693.368	
Add Mixer 🛛 🖾 Add Corre	MnCl2 6.41382	
Add Single Point	NaCl 3166.36	
Add Survey Add Chemical Diagram	S03 44.9809	
Add Chemical Diagram	SrCI2 0.325663	
< >	BaSO4 0.0738067	
Plot Template Manager a A X	FeS 11.4757	
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	v	
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		V
Course -	Advanced Search Add as Stream Export	1
Save		
For Help, press F1		Image:

#### 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.

🛷 Desa	ription 🥺 Reconciliation 🧕 🛛	lolecular Basis 🔯 Report 🚘 File Viewer	
Jump to:	Reconciliation Summary ~ Reconciliation Summary	📿 🔍 🔍 Customize Export	
Spe Charg	Stream Inflows Charge Balance Stream Parameters Total and Phase Flows (Amounts) Scaling Tendencies Species Dutput (True Species) Element 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 25°C 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	4.49376
Density, g/ml		1.00198
Water, mg/L		9.95555e5

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	9.95555e5
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	
CI-1	3896.00	
SO4-2	54.0000	
CO2	150.000	150.000
H2S	15.0000	15.0000
NH3	5.00000	4.99999
Mn+2	2.80000	
Al+3	0.740000	

The Charge Balance table contains the concentrations entered and the final balanced values. In this case only the sodium (Na+1) concentration was changed.

<u>Charge Balance</u> Cation Charge: Anion Charge: Imbalance: Adjusted Species:	-0.111	2945 eq/L 1016 eq/L 0e-3 eq/L Na+1		
Charged Species		Input	Balanced	Difference
		mg/L	mg/L	%
Na+1		1060.00	1245.57	17.5
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	
AI+3		0.740000	0.740000	
CI-1		3896.00	3896.00	
SO4-2		54.0000	54.0000	

0.0

0.0

0.0

0.0

0.0

0.0

17.51

HCO3-1

C2H3O2-1

HS-1

# **Exploring Reconciliation Options**

When reconciling a Water Analysis, there are three options for reconciliation:

**No Reconcile:** The software will run an electroneutrality reconciliation only, and then compute the water properties such as pH, density, etc., based on the <u>entered concentration of neutral, cations, and anions species</u>. In the <u>No Reconcile</u> 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. (<u>See electroneutrality options</u>).

**Reconcile pH:** The software will run both an <u>electroneutrality</u> and <u>pH reconciliation</u>. 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 **HCI** or **NaOH**, or you may select your preferred acids and bases to adjust the pH.

**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 HCI 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**<sub>2</sub> as the **alkalinity titrant**, H<sub>2</sub>**SO**<sub>4</sub> as the **alkalinity pH** titrant and **4.5** as the **alkalinity end point pH**.

**Reconcile pH/Alkalinity/TIC:** 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**<sub>2</sub> 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<sub>2</sub> 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 °C.

#### 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.

		V	Vater Analysis – I	<b>Reconcile Option</b>	S			
Analys	sis Parar	neters/Se	ettings	R	ecorded	Propertie	es	
Stream Amount		1 L (Def	ault)	Total Dissolved S	Solids	36500 n	ng/L	
Temperature		25 °C		Measured pH		7.8		
Pressure		1 atm		Measured Alkalir	nity	160 mg	HCO3/L	
Name Style		Display	Formula	Density		1.013		
Unit Set		Metric, I	Batch,	Specific Electrica	al	Not reco	orded	
		Concen	tration	Conductivity				
Framework		MSE						
Calculation Type		Water A	nalysis					
Stream Name		Water A	nalysis –					
		Reconc	ile Options					
			Comp	osition				
Neutrals	s (mg/L)		Cations	s (mg/L)		Anions	(mg/L)	
SiO2	16		Na+1	10000	CI-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	C2H3O	2-1	50	

### Calculating the pH

Setting the Water Analysis

#### Add a Water Analysis

**Click** on the new Water Analysis and press **<F2>** to change the name to *Water Analysis – Reconcile Options* Select the **MSE** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

**Click** on the **Units Manager** Icon, and select Metric, Batch, Concentration (it may be defined by default) Under the **Analysis** Tab, enter the Analysis Parameters, Recorded properties, and Composition of the water given in the table above. Go to the **Add Reconciliation** button of the top right corner or select **Add Reconciliation** from the Actions Panel, and name it **No Reconcile**.

Select the No Reconcile option (selected by default)

Variable	Value	Reconciliation
Analysis Par	ameters	Specs
Stream Amount (L)	1.0000	Reconcile
Temperature (°C)	25.000	) 💿 No Reconcile
Pressure (atm)	1.0000	) O Reconcile pH
Recorded Pr	operties	O Reconcile pH/Alkalinity
Total Dissolved Solids (mg/L)	0.0	Reconcile pH/Alkalinity/TIC
Measured pH	7.8000	
Measured Alkalinity (mg HCO3/L)	160.000	Calculate Alkalinity
Measured TIC (mol C/L)	0.0	
Density (g/ml)	1.0130	Calculate 🥥
Specific Electrical Conductivity (µmh	0.0	Summary
Neutrals (	mg/L)	
H2O		Unit Set: Metric (mass concentration)
C02	0.0	
H2S	0.0	Automatic Chemistry Model MSE (H3O+ ion) Databanks:
SiO2	16.000	MSE (H3O+ ion)
B(OH)3	0.0	Using Helgeson Direct
		Dominant Ion Charge Balance (eq/L):
Total lons	(mg/L)	Cation Charge: 0.563486 eq/L     Anion Charge: -0.596011 eg/L
P as PO4-3	0.0	
Si as SiO2	0.0	747.753 mg/L of Na+1
B as B(OH)3	0.0	is needed to balance
		Isothermal Calculation
Cations (r	ng/L)	25.0000 °C 1.00000 atm
Na+1	10000.0	Calculation not done
K+1	0.0	Π III
Ca+2	500.000	ī lietu ir statu ir s
Mg+2	1200.00	ī li li
Sr+2	200.000	
Ba+2	5.0000	
Fe+2	5.0000	
Anions (n	ng/L)	
CI-1	19000.0	
S04-2	2700.00	
HCO3-1	142.00	
HS-1	0.0	
C2H3O2-1	50.000	
HCOO-1	20.000	
As04-3	12.000	
sured		

**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.

#### Types of Balance for Electroneutrality

Click on the **Specs** button. This will open a new window.

econciliat	tion Data	1									?		Х
Balance	Calculat	ion Op	tions	Cor	nverge	ence							
Type of	balance	ĺ	Domin	ant lo	on)	•					New Ir	nflow	
Cation	s	~	Dor	nina	nt lor	n			1				
Na+1			Pro	rate									1
Ca+2			Pro	rate (	Catio	ns							
Mg+2 Sr+2			Pro	rate /	Anior	ıs							
Ba+2			Na/	CI									
Fe+2			Mal	ke-uj	p lon				-1				
			Use	r Cho	oice								
						Nee	ded t	o ba	lance:				
									L of Na				
	on the C evenly ba			nion	s	is r	neede	ed to	balanc	e.			
Cation c	harge:	0.56	63486	eq/L	-								
Anion cł	harge:	-0.59	96011	eq/L	-								
Imbalan	ce:	-0.032	25252	eq/L	-								

There are 7 different Types of Balance:

**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).

**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.

Prorate Cations: All cations are adjusted up or down equally

Prorate Anions: All anions are adjusted up or down equally

**Na+/CI-**: Sodium is added when there is an excess of negative charge. Chloride is added when there is an excess of positive charge.

**Make-up Ion**: This option allows for a single ion species to be adjusted. User selects an ion to increase or decrease.

**User Choice**: The software determines if an anion or cation is needed to balance the solution and the user choses the specific ion.

Keep the default option, **Dominant Ion**, as the balance type then press **OK** Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key 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.

Description 🤒 Reconciliation 🧕 Mo	olecular Basis			
mp to: Reconciliation Summary ~		0	🔍 Customize	Export
Reconciliation Summary Specification Charge Balance Method Dominant Ion	-			^
pH Reconciliation Type No reconciliation				
ph Reconciliation Type No reconciliation	Measured	Calculated		
Temperature, °C	Measured 25.0000	Calculated		
		Calculated		
Temperature, °C	25.0000	Calculated 7.48301		
Temperature, °C Pressure, atm	25.0000 1.00000			

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

Under the *Water Analysis – Reconcile Options* Stream go to the **Add Reconciliation** button **Click** on the new Reconcile-1 icon and press **<F2>** to change the name to *Reconcile pH* The default units, names and framework have been previously defined Select the **Reconcile pH** option

ا 🌶	Description 🧕 Reconciliation	🛛 🥸 Molecular Basis 🚦	🕺 R	ера	rt
Π	Variable	Value	^		Reconcililation
	Analysis Par	rameters			Specs
	Stream Amount (L)	1.00000			Reconcile
	Temperature (°C)	25.0000			🔿 No Reconcile
	Pressure (atm)	1.00000			Reconcile pH
	Recorded Pr	roperties			Reconcile pH/Alkalinity
	Total Dissolved Solids (mg/L)	0.0			Reconcile pH/Alkalinity/TIC
•	Measured pH	7.80000			Calculate Alkalinity
	Measured Alkalinity (mg HCO3/L)	160.000			
	Measured TIC (mol C/L)	0.0			Calculate 🥝
	Density (g/ml)	1.01300			
	Specific Electrical Conductivity (µmh	0.0			Summary
	Calculation Pa	arameters			
	Use Single pH Titrant	No			Unit Set: Metric (mass concentration) 🔥
	pH Acid Titrant	HCL			Automatic Chemistry Model
	pH Base Titrant	NAOH			MSE (H3O+ ion) Databanks:
	√ Neutrals	(mg/L)			MSE (H3O+ ion)
	H2O				Using Helgeson Direct
	CO2	0.0			Dominant Ion Charge Balance (eq/L): Cation Charge: 0.563486 eq/L
	H2S	0.0			Anion Charge: -0.596011 eq/L
	SiO2	16.0000			Imbalance: -0.0325252 eq/L
	B(OH)3	0.0			747.753 mg/L of Na+1
				>	is needed to balance.
		(mg/L)			Set pH Calculation
	P as PO4-3	0.0			Measured pH: 7.80000
	Si as SiO2	0.0			pH Titrants: Acid: HCI
	B as B(OH)3	0.0			Base: NaOH
					Calculation not done

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.

Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key 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.

np to: Reconciliation Summary 🗸 🗸		<b>Q Q</b>	🔍 Customize	Export
Reconciliation Summary				,
Specification				
Charge Balance Method Dominant Ion				
pH Reconciliation Type Reconcile pH				
	Measured	Calculated		
Temperature, °C	25.0000			
Pressure, atm	1.00000			
pH	7.80000	7.80000		
pH Titrant Acid: HCI, mg/L *	0.0			
pH Titrant Base: NaOH, mg/L *	0.0	44.6585		
	1.01300	1.02249		
Density, g/ml				

The measured and calculated pH are the same. The software added 44.6585 mg/L of NaOH to match the experimentally measured pH.

### **Calculating Alkalinity**

Now we will instruct the software to calculate Alkalinity.

Go back to the **Reconciliation Tab** and check the **Calculate Alkalinity** box.

Variable	Value		^	Reconcililation	
Analysis Pa	rameters			Specs	
Stream Amount (L)		1.00000		Reconcile	
Temperature (°C)		25.0000		O No Reconcile	
Pressure (atm)		1.00000		Reconcile pH	
Recorded P	roperties			Reconcile pH/Alkalinity	
Total Dissolved Solids (mg/L)		0.0		Reconcile pH/Alkalinity/TIC	
Measured pH		7.80000		Colordova Allesteine	
Measured Alkalinity (mg HCO3/L)		160.000		Calculate Alkalinity	
Measured TIC (mol C/L)		0.0		Coloulata 🙃 🛛	
Density (g/ml)		1.01300		Calc <u>u</u> late 🥥	
Specific Electrical Conductivity (µmho/c		0.0		Summary	
Calculation P	arameters				_
Alkalinity pH Titrant	H2SO4			Unit Set: Metric (mass concentration	)
Alkalinity End Point pH		4.50000	τ.	Automatic Chemistry Model	
Use Single pH Titrant	No			MSE (H3O+ ion) Databanks:	
pH Acid Titrant	HCL			MSE (H3O+ ion)	
pH Base Titrant	NAOH			Using Helgeson Direct	
Neutrale	(mg/L)			Dominant Ion Charge Balance (eq/L) Cation Charge: 0.563486 eq/L	
H2O				Anion Charge: -0.596011 eq/L	
C02		0.0		Imbalance: -0.0325252 eq/L	
H2S		0.0		747.753 mg/L of Na+1	
SiO2		16.0000		is needed to balance.	
B(OH)3		0.0		Set pH Calculation	
				Measured pH: 7.80000	
Total lons	; (mg/L)			pH Titrants: Acid: HCI	
P as PO4-3		0.0	~	Base: NaOH	
				Calculation not done	
sured					

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.

Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key.

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.

Reconciliation Summary Specification Charge Balance Method Dominant Ion pH Reconciliation Type Reconcile pH Alkalinity pH Titrant: H2SO4

	Measured	Calculated
Temperature, °C	25.0000	
Pressure, atm	1.00000	
pH	7.80000	7.80000
pH Titrant Acid: HCI, mg/L *	0.0	
pH Titrant Base: NaOH, mg/L *	0.0	44.6585
Alkalinity, mg HCO3/L	160.000	249.667
Density, g/ml	1.01300	1.02249
Water, mg/L		9.88319e5

\* Calculated value indicates added or removed amount.

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

Under the Water Analysis - Reconcile Options Stream go to the Add Reconciliation button

Click on the new Reconcile-1 icon and press <F2> to change the name to Reconcile pH/Alkalinity

The default units, names and framework have been previously defined

Select the Reconcile pH/Alkalinity option

1	Description 🧕 Reconciliat	on 🔯 Molecular Basis 🚦	鰯 Report 🚊 File Viewer
	Variable	Value	Reconciliation
	Analys	s Parameters	Specs
	Stream Amount (L)	1.0	.00000 Reconcile
	Temperature (°C)	25.	5.0000 O No Reconcile
	Pressure (atm)	1.0	.00000 O Reconcile pH
		ed Properties	Reconcile pH/Alkalinity
	Total Dissolved Solids (mg/L)		0.0 O Reconcile pH/Alkalinity/TIC
ō	Measured pH	7.8	.80000
۰	Measured Alkalinity (mg HCO3/L)	160	60.000 Calculate Alkalinity
	Measured TIC (mol C/L)		0.0
	Density (g/ml)	1.0	.01300 Calculate Q
	Specific Electrical Conductivity (µn	ho/c	0.0 Summary
		on Parameters	
	Alkalinity Titrant	C02	Unit Set: Metric (mass concentration)
	Alkalinity pH Titrant	H2SO4	Automatic Chemistry Model
	Alkalinity End Point pH	4.5	.50000 MSE (H3O+ ion) Databanks:
	Use Single pH Titrant	No	MSE (H3O+ ion)
	pH Acid Titrant	HCL	Using Helgeson Direct
	pH Base Titrant	NAOH	Dominant Ion Charge Balance (eq/L):
	✓ Neut	rals (mg/L)	Reconcile pH Alkalinity Calculation Alkalinity: 160.000 mg HCO3/L
	H2O		Titration End Pt: 4.50000
	CO2		0.0 Alkalinity Titrant: CO2 Alkalinity pH Titrant: H2SO4
	H2S		0.0 pH Reconciliation:
	SiO2	16.	6.0000 Measured pH: 7.80000
	B(OH)3		0.0 pH Titrants: Acid: HCI
			Base: NaOH
		lons (mg/L)	Calculation not done
м	easured		
			✓
	Advanced Search Add a	s Stream Export	
		N	

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.

Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key 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.

np to: Reconciliation Summary ~			2 9 0	Customize	Export
Reconciliation Summary					
Specification					
Charge Balance Method Dominant Ion					
pH Reconciliation Type Reconcile pH and A	lkalinity				
Alkalinity pH Titrant: H2SO4					
	Measured	Calculated	]		
Temperature, °C	Measured 25.0000	Calculated	]		
		Calculated			
Pressure, atm	25.0000	Calculated 7.80000	-		
Pressure, atm pH	25.0000 1.00000		•		
Pressure, atm pH pH Titrant Acid: HCI, mg/L *	25.0000 1.00000 7.80000	7.80000	•		
Pressure, atm pH pH Titrant Acid: HCI, mg/L * pH Titrant Base: NaOH, mg/L *	25.0000 1.00000 7.80000 0.0	7.80000			
Pressure, atm pH pH Titrant Acid: HCI, mg/L * pH Titrant Base: NaOH, mg/L *	25.0000 1.00000 7.80000 0.0	7.80000 14.9320	-		
Pressure, atm pH pH Titrant Acid: HCI, mg/L * pH Titrant Base: NaOH, mg/L * Alkalinity Titrant: CO2, mg/L *	25.0000 1.00000 7.80000 0.0 0.0	7.80000 14.9320 -35.0147	-		

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 Studio: Stream Analyzer, Pre-scaling tendencies are turned OFF by default. We need to enable this option.

#### Setting the Water Analysis

Go back to the Reconciliation tab of the Reconcile pH/Alkalinity water analysis

Click on the **Calculation Options** icon *Leven*. This will open the Calculation Options window. Check the **Pre-scaling Tendencies** box and select the **Rigorous method**. Then click **OK**.

Calculation Options - Reconcile pH/Alkalinity	?	×
Calculation Options Convergence		
General Diagnostics Show status dialog Verbose		
Optional Properties		
Diffusivities and Mobilities		
Diffusivities Matrix		
Viscosity		
Electrical Conductivity		
Heat Capacity		
Activities, Fugacities, and K-Values		
Gibbs Free Energy		
Entropy		
Thermal Conductivity		
Surface Tension		
Interfacial Tension		
Total Dissolved Solids (TDS)- Rigorous method		
Scaling Induction Time(s) Advanced		
Pre-scaling Tendencies Method Estimated  Rigorous		
OK Cancel Apply	Help	D

Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key

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

### Analyzing the Results

np to: Scaling Tendencies 🗸 🗸		Q	€ €	Customize	Export
Scaling Tendencies	-				
Row Filter Applied: Values > 1.0e-4					
Solids	Post-Scale	Pre-Scale	1		
SrSO4 (Celestine (celestite))	1.00000	4.54260	1		
CaCO3 (Calcite)	1.00000	10.8568	1		
FeCO3 (Siderite)	1.00000	43.4174	1		
BaSO4 (Barite)	1.00000	134.339	1		
H2O	0.774208	0.774173	1		
CaCO3 (Aragonite)	0.736014	7.99073	1		
SrCO3 (Strontianite)	0.330589	14.9453	1		
CaSO4.2H2O (Gypsum)	0.211114	0.230285	1		
CaSO4 (Anhydrite)	0.166722	0.181878	1		
SiO2 (lechatelierite)	0.143303	0.122612	1		
CaSO4.0.5H2O (Bassanite)	0.0500906	0.0546430	1		
Mg3Si2O5(OH)4 (Poor-crystalline Antigorite)	0.0200948	11431.9	1		
Na2SO4.10H2O (Mirabilite)	3.05314e-3	3.24993e-3	1		
NaCI.2H2O (hydrohalite)	2.98497e-3	2.97781e-3	1		
NaCl (Halite)	2.93868e-3	2.93190e-3	1		
CaHAsO4.1H2O	2.86125e-3	2.95330e-3	1		
MgCO3	1.78918e-3	0.0187455	1		
Fe(OH)2 (Amakinite)	6.69700e-4	0.255146	1		
MgSO4.7H2O (Epsomite)	5.97715e-4	6.29050e-4	1		
NaHCO3 (Nahcolite)	4.64170e-4	5.10099e-4	1		
Na2SO4 (Thenardite)	4.46418e-4	4.75411e-4	]		
MgSO4.12H2O	4.20631e-4	4.42580e-4	]		
Mg(OH)2 (Brucite)	2.76487e-4	0.0254191	]		
MgSO4.6H2O (Hexahydrite)	2.62743e-4	2.76530e-4	]		
Na2SO4.CaSO4 (Glauberite)	1.70179e-4	1.97708e-4	]		
MgSO4.5H2O (Pentahydrite)	9.50880e-5	1.00082e-4	]		
BaCO3 (Witherite)	3.29741e-5	0.0440846	]		
Mg3Si2O5(OH)4 (Antigorite amorphous)	5.44916e-10	3.10002e-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 enter 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:

The first is to start with a PVT curve and create pseudocomponents using one of the three thermodynamic methods coded into the software.

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 11. .

A brief introduction of how to enter PVT curves and/or pseudocomponents will be shown in the examples below.

# **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

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to *Crude Oil* Select the **MSE-SRK** thermodynamic Framework Click on the **Names Manager** Icon and select the **Formula** option Click on the **Units Manager** Icon, and select Metric, Batch, Moles **Enter** the conditions of the Stream T= 25 °C and 1 atm

Crude Oil Stream							
Calculat	tion Settings	Conditions					
Stream Name	Crude Oil	Stream Amount	Default				
Name Style	Display Formula	Temperature	25 ℃				
Unit Set	Metric, Moles	Pressure	1 atm				
Framework	MSE-SRK						

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.

Variable	Valu	le	<b>^</b>	Add <u>C</u> alculation 🛛 🔻
Strea	m Parameters			Special Conditions
Stream Amount (mol)		55.5082		·
Temperature (°C)		25.0000		Solids Only
Pressure (atm)		1.00000		C
	flows (mol)			Summary
H2O		55.5082		Unit Set: Metric (moles)
ASSAY	-			
Shift +	Enter			Automatic Chemistry Model MSE-SRK (H3O+ ion) Databanks: MSE-SRK (H3O+ ion) MSE (H3O+ ion) Second Liquid phase Using Helgeson Direct

Note: After typing the name of your Assay, immediately press Shift + Enter command keys together.

Use the information provided in the table below to complete the grid.

	Assay Information					
Calculation	Settings	Distillation Data				
Assay amount	1000 moles	Volume %	Temperature, °C			
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:

Variable		Value		^	Add <u>C</u> alculation 🔫
	Stream Para	ameters			Special Conditions
Stream Amount (mol)			1055.51		
Temperature (°C)			25.0000		Solids Only
Pressure (atm)			1.00000		C
~	Inflows (	(mol)			Summary
H2O			55.5082		Unit Set: Metric (moles)
ASSAY			1000.00		
<ul> <li>Assay Data Type</li> </ul>		ASTM D86			Automatic Chemistry Model MSE-SRK (H3O+ ion) Databanks:
- Average Bulk Density Ty	pe	API Gravity			MSE-SRK (H3O+ ion) Databanks: MSE-SRK (H3O+ ion)
– API Gravity			40.0000		MSE (H3O+ ion)
- Distillation Curve Cuts			10		Second Liquid phase Using Helgeson Direct
- Distillation Data		Edit			
- Thermo Method		API-8	-		Species ASSAY is not valid.

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.

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.

Assay ASSAY	<b>⊳</b>	?	$\times$
Distillation Data			
Volume %	Temperature °C		
1.000	30.00		
5.000	30.00		
10.00	50.00		
20.00	60.00		
40.00	80.00		
60.00	120.0		
80.00	150.0		
90.00	180.0		
95.00	200.0		
95.00	200.0		
99.00	220.0		
100.0	240.0		
OK	Cancel Apply	He	elp

The Distillation Curve Cuts will eventually become individual pseudocomponents, each with its own critical parameters and thermodynamic reference data.

At this point we are ready to perform a calculation. Add a Single Point calculation, and then select an **Isothermal** calculation.

Change the SinglePoint name to Assay using the <F2> key

Click on the Calculate button or press the <F9> key to run the simulation 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.

#### 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.

Variable	Value		~		Type of calculation
	rameters				Isothermal 👻 Specs
		1055.51			
- Moles (True) - Liquid-1 (mol)		55.0810			Calculate 🥝
Moles (True) - Liquid-2 (mol)		1000.43			Summary
Temperature (°C)		25.0000			
Pressure (atm)		1.00000			Unit Set: Metric (moles)
	s (mol)				Automatic Chemistry Model
H2O		55.5082			MSE-SRK (H3O+ ion) Databanks:
ASSAY_243K		87.6615			MSE-SRK (H3O+ ion) MSE (H3O+ ion)
- Thermo Method	API-8				Second Liquid phase
<ul> <li>Normal Boiling Point (°C)</li> </ul>		-30.2796			Using Helgeson Direct
<ul> <li>Specific Gravity</li> </ul>		0.717259			Isothermal Calculation
L Molecular Weight		47.1866		>	25.0000 °C 1.00000 atm
ASSAY_278K		82.2275			Phase Amounts Aqueous 55.0810 mol
ASSAY_307K		200.849			Vapor 0.0 mol
ASSAY_337K		173.140			Solid 0.0 mol
ASSAY_370K		109.658			2nd Liquid 1000.43 mol
ASSAY_403K		131.728			Aqueous Phase Properties
ASSAY_431K		110.846			pH 6.99753
ASSAY_464K		57.0493			lonic Strength 1.81246e-9 mol/mol Density 0.997043 g/ml
ASSAY_496K		35.2169			
ASSAY_524K		11.6247			Calc. elapsed time: 1.137 sec
			۷		Calculation complete
nput Output					
Carpa					

# 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.

np to: Species Output (True Species) ~		0	) 🔍 🔍 Cu	stomize Expor
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	

# **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

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to Crude Oil - Pseudocomponents

Select the MSE-SRK thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the conditions of the Stream T= 15 °C and 1 atm

Change H2O from the default value to 20 moles

Crude Oil Stream				
Calcul	ation Settings	Conditions		
Stream Name	Crude Oil - Pseudocomponents	Stream Amount	Calculated	
Name Style	Display Formula	Temperature	15 ℃	
Unit Set	Metric, Moles	Pressure	1 atm	
Framework	MSE-SRK	H2O	20 moles	

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 a pseudocomponent rather than look for a species or pure component from the database.

Variable		Value	<u>^</u>	Add <u>C</u> alculation 👻
$\overline{\nabla}$	Stream Para	ameters		Special Conditions
Stream Amount (mol)		20.0000		
Temperature (°C)		15.0000		Solids Only
Pressure (atm)		1.00000		
$\overline{}$	Inflows	(mol)		Summary
H2O		20.0000		Unit Set: Metric (moles)
PC1	-			
•			1	Automatic Chemistry Model
				MSE-SRK (H3O+ ion) Databanks:

Note: After typing the name of your pseudocomponent, immediately press Ctrl + Enter command keys together.

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 (°C)	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:

1	Variable	Value	Add <u>C</u> a	lculation 🛛 💌
<	Stream	Parameters	Special Condi	iono
	Stream Amount (mol)	1000.0		
	Temperature (°C)	15.000	Solid	s Uniy
	Pressure (atm)	1.0000	C	
<	- Inflov	vs (mol)	Summary	
	H2O	20.000	Unit Set: Metric (mole	es)
PĢ	] PC1	100.00		
	<ul> <li>Thermo Method</li> </ul>	APL8	Automatic Chemistry MSE-SRK (H3O+ i	
	<ul> <li>Normal Boiling Point (°C)</li> </ul>	33.000	MSE-SRK (H30	
	<ul> <li>Specific Gravity</li> </ul>	0.72000	MSE (H3O+ ion	
	- Molecular Weight		Second Liquid pha Using Helgeson D	
l	Calculated Properties		Using heigeson D	
PĢ	] PC2	200.00		
	— Thermo Method	API-8		
	<ul> <li>Normal Boiling Point (°C)</li> </ul>	60.000		
	<ul> <li>Specific Gravity</li> </ul>	0.76000		
	<ul> <li>Molecular Weight</li> </ul>			
t	Calculated Properties			
P Ģ	] PC3	250.00		
	<ul> <li>Thermo Method</li> </ul>	API-8		
	<ul> <li>Normal Boiling Point (°C)</li> </ul>	100.00		
	<ul> <li>Specific Gravity</li> </ul>	0.80000		
	- Molecular Weight			
t	Calculated Properties			
P G	] PC4	250.00		
	<ul> <li>Thermo Method</li> </ul>	API-8		
	<ul> <li>Normal Boiling Point (°C)</li> </ul>	140.00		
	- Specific Gravity	0.85000		
	- Molecular Weight			
l	Calculated Properties			
	PC5	180.00		
	- Thermo Method	API-8		
	<ul> <li>Normal Boiling Point (°C)</li> </ul>	190.00		
	- Specific Gravity	0.9000		
	- Molecular Weight			
	+ Calculated Properties			
	• • • • • • • • • • • • • • • • • • • •			
			¥	

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.

Variable	Value
C Stream P	arameters
Stream Amount (mol)	1000.00
Temperature (°C)	15.0000
Pressure (atm)	1.00000
	rs (mol)
H2O	20.0000
P 📮 PC1	100.000
- Thermo Method	API-8
- Normal Boiling Point (°C)	33.0000
- Specific Gravity	0.720000
- Molecular Weight	
Calculated Properties	
- Calc:Molecular Weight	70.3287
- Calc:Specific Gravity	0.720000
<ul> <li>Calc:Boiling Point (°C)</li> </ul>	33.0000
<ul> <li>Calc:Critical Temperature (°C)</li> </ul>	213.813
- Calc:Critical Pressure (atm)	42.1427
- Calc:Critical Volume (L/mol)	0.271026
- Calc:Acentric Factor	0.197144
- Calc:HREF Vapor	-1.28412e5
- Calc:GREF Vapor	-9686.26
- Calc:SREF Vapor	343.881
- Calc:CPREF Vapor	103.303
- Calc:VREF	24.4483
- Calc:HREF Aqueous	-1.39845e5
- Calc:GREF Aqueous	9148.86
- Calc:SREF Aqueous	242.360
- Calc:CPREF Aqueous	244.429
Calc:Rackett	0.277609
P 📮 PC2	200.000
- Thermo Method	API-8
- Normal Boiling Point (°C)	60.0000
- Specific Gravity	0.760000
- Molecular Weight	
Calculated Properties	
P 🖓 PC3	250.000
- Thermo Method	API-8
	100.000
Input	

The values in the green boxes can be edited to match data from other programs.

At this point we are ready to perform a calculation. **Add** a **Single Point** calculation, and then select an **Isothermal** calculation.

Change the SinglePoint name to Pseudocomponents using the <F2> key

Click on the Calculate button or press the <F9> key to run the simulation

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

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.

np to: Species Output (True Species) 🛛 🗸 🗸	·	2	🕽 🔍 🔍 Cu	ustomize Expo
Species Output (True Species) Row Filter Applied: Only Non Zero Values solumn 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.

<ul> <li>♦ OLI Studio - [Mixers.oad]</li> <li>■ File Edit Streams Calculations Ch</li> <li>□ □ □ □ □ ↓ □ □ ↓ □ □ □ 0 ? ?</li> <li>Navigator + + ×</li> </ul>		× _ s ×
Mixers.oad	Mixer  Description Definition Plot Report File Vi  Available Streams Stream - [AQ] Stream - [AQ]	iewer Mixing Method Single Point Mix Specs Single Point Mix Volume Ratio Multiplier Summay
Actions 4 • × Actions	Variable         Value           Multiplier         Stream Parameters           Total Inflow         Temperature (*C)           Pressure (atm)         Feasure (atm)	25.0000 1.00000
Plot Template Manager	Input Advanced Search Add as Stream Export	• •
₽ Ŭ For Help, press F1		[] NUM     []

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.

# **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	nL

#### 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 $2 \times 0$
1	Stream $2 \times 1$
1	Stream $2 \times n$

# 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)<sub>2</sub> 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)<sub>2</sub> 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						
1 <sup>st</sup>	Stream	2 <sup>nc</sup>	<sup>d</sup> Stream			
Stream Name	Ca(OH)2	Stream Name	HCI			
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 °C	Temperature	25 °C			
Pressure	1 atm	Pressure	1 atm			
H2O	Calculated	H2O	Calculated			
Ca(OH)2	10 mass%	HCI	10 mass%			

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.

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.

A				
OLI Studio - [Mixer calculations.oad*]			_	
File Edit Streams Calculations Chemistre	y Tools View Window Help			_ 8 ×
🗋 D 😅 🖬 🗼 ங 💼 🦪 🤗 🕺 🗖 🖬	Va So L2 Re 🛓 MSE ± MSE ± AGE ±	🚧 🎆 🛓 💱 🔎 😭 💅		
Navigator 🛛 🗛 🔺		<u></u>		
Water Analysis Calculations.oad	A Basic Mixing			
Hydrocarbons and Pseudocomponents.oad	🦪 Description 🔮 Definition 📶	Plot 👼 Report		
Mixer calculations.oad*			Mixing Method	
🍓 Streams	Available Streams	Selected		Specs
👌 Ca(OH)2	Ca(OH)2 · [MSE] HCI · [MSE]			opecs
HCI			Type of calculation	
Basic Mixing			Isothermal 👻	
	Window that displa		Coludar 0	
	streams availa	ble for mixing	Calc <u>u</u> late 🥥	
			Summary	
	Variable	Value 🔺		
	Multiplier		Need at least 1 input stream.	
		Parameters		
	Total Inflow			
Actions I A X	Temperature (°C)	25.000		
Actions	Pressure (atm)	1.00000	>	
	Window that allows			
	the mixing c	onditions		
Plot Template Manager # * *				
		¥		
	lum d			
	Input			
	Advanced Search Add as Stre	eam Export		Ť
Save				
× Calculation Complete!				
For Help, press F1				

**Select** the Ca(OH)2 stream from the available streams and use the >> button to put it under the **Selected** window

Select the HCl stream from the available streams and use the >> button to put it under the Selected window

1	Description 🤒	Definiti	on 🛍 P	lot 👼 Report			
	Available Streams Selected Ca(OH)2 HCI						Mixing Method Single Point Mix  Specs Type of calculation Isothermal Calculate Summary
Г	Variable	Value	Ca(OH)2	HCI	~		
	Multiplier		1.00000	1.00000			Unit Set: Metric (moles)
			Stream P	arameters			Automatic Chemistry Model
	Total Inflow		1000.00 g	1000.00 g			MSE (H3O+ ion) Databanks: MSE (H3O+ ion)
	Temperature (°C)	25.0000	25.0000	25.0000			Using Helgeson Direct
	Pressure (atm)	1.00000	1.00000	1.00000			Isothermal Calculation
						>	25.0000 °C 1.00000 atm Single Point Mix Calculation not done

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.

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.

1	Description 🔮	Definition 📶	Plot 髮 Repor	t			
A	vailable Streams	×					Mixing Method Single Point Mix  Specs Type of calculation Adiabatic Calculate Summary
F	Variable Multiplier	Value	Ca(OH)2 1.00000	HCI 1.00000	^		Unit Set: Metric (moles)
F		Stream	Parameters				Automatic Chemistry Model
F	Total Inflow		1000.00 g	1000.00 g			MSE (H3O+ ion) Databanks:
0	Temperature (°C)	25.0000	25.0000	25.0000			MSE (H3O+ ion) Using Helgeson Direct
•	Pressure (atm)	1.00000	1.00000	1.00000			Isenthalpic Calculation
_	sut				¥	,	0.0 cal 1.00000 atm Single Point Mix Calculation not done
	Advanced Sea	irch Add as Str	eam Export				

Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

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 °C to approximately ~48.65 °C at a constant pressure of 1 atm. This indicates that the enthalpy (or heat) of mixing is exothermic.

## **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<sub>2</sub>

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. Note that we have switched thermodynamic frameworks to the **AQ** framework. Please make sure that this framework is selected for both streams in this example.

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						
1 <sup>st</sup>	Stream	2 <sup>nd</sup> 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 °C	Temperature	30 °C			
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

Add a Single Point - Isothermal calculation for each stream

Change the name to pH 0.1 m HF and pH 0.1 m CaCl2 respectively using the <F2> key

Calculate the isothermal calculation for each stream

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

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. 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.

< Description 🧕 Definit	ion 🛍 Plot 📓 Report
Available Streams Ca(0H)2 - (MSE) HCI - (MSE) 0.1 HF - (AQ) 0.1 CaCI2 - (AQ) Basic Mixing - (MSE) pH 0.1 HF - (AQ) pH 0.1 CaCI2 - (AQ)	Selected

Select the 0.1 HF – [AQ] stream. Use the >> button to move it to the Selected window Select the 0.1 CaCl2 stream. Use the >> button to move it to the Selected window Select Single Point Mix as the Mixing Method and Isothermal as the Type of Calculation Leave the default values for the multipliers (1.0) and change the temperature at which the mixture takes place to 30 °C.

< Description 🔮	Definitio	on 🛍 Plot 📓 I	Report			
Available Streams		Se	elected			Mixing Method
pH 0.1 HF - [AQ]			.1 HF			Single Point Mix 👻 Specs
pH 0.1 CaCl2 - [AQ]		>> 0	.1 CaCl2			Type of calculation
						Isothermal  Calculate
						Summary
Variable	Value	0.1 HF	0.1 CaCl2	^		Unit Set: Metric (moles)
Multiplier		1.00000	1.00000			Unit Set. Metric (moles)
		Stream Parameter	s			Automatic Chemistry Model
Total Inflow		55.6082 mo	55.6082 mol			Aqueous (H+ ion) Databanks: Aqueous (H+ ion)
Temperature (°C)	30.0000	30.0000	30.0000			Using K-fit Polynomials
Pressure (atm)	1.00000	1.00000	1.00000			T-span: 25.0 - 225.0
					>	P-span: 1.0 - 1500.0 Isothermal Calculation 30.0000 *C 1.00000 atm Single Point Mix
						Calculation not done

Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key 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*. **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<sub>2</sub> 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<sub>2</sub>.

#### Titrating HF with CaCl<sub>2</sub>

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...)

**Click** on the **Specs** button. This will open a new window indicating you to select the Stream to vary In the **Select Stream** tab **Select** the 0.1m CaCl2 stream

Volume Survey Options			?	×
Category Variable - Volume Calculation Options	Select Stream Select inlet str	Survey Range eam to vary		
	0.1 CaCl2 0.1 HF			

**Select** the **Survey Range** tab. Change the Volume Range from 0 L to 1 L. Change the **Number of Steps** to 50. Then click **OK**.

Volume Survey Options		?	×
Category	Select Stream Survey Range		
Category Variable - Volume Calculation Options	Select Stream       Survey Range         Volume Range       Unit:         Selected Range       0.0 to 1.0 in 1 steps of 1.0 <ul> <li>Incear</li> <li>Log</li> <li>Point List</li> </ul> End Points       Start         Increment       1.00000         Step Size       Select one, the calculated         Number Steps       50	New Delete	
	OK Cancel Apply	Help	

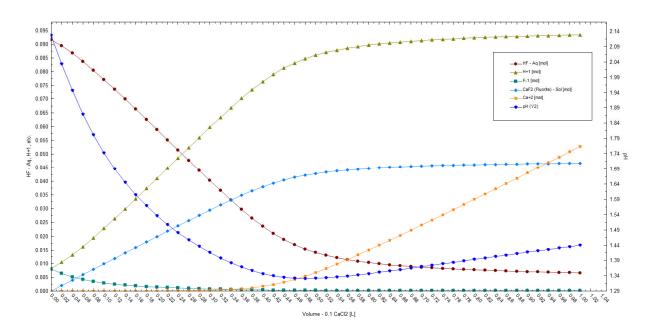
Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key It is time to **save** your file (**File >Save as...) or** using the **save** icon in the tool bar. You can save under the same file that we created before named as *Mixer Calculations*.

Titration Results and Plotting

**Click** on the **Plot** tab. **Note:** You will see an empty plot, since we need to define the variables that we want to report.

**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).

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<sub>2</sub> 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<sub>2</sub> 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:

$$Ca^{+2} + 2F^- \rightarrow CaF_{2(s)}$$

As we add more CaCl<sub>2</sub> in solution, more CaF<sub>2</sub> 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:

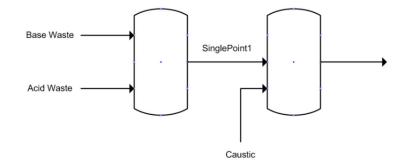
$$HF \to H^+ + F^-$$

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<sub>2</sub>, the solid reaches a steady value, indicating that the solid has reached its saturation (maximum formation) value.

## **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)

Parameter	Value	Units
Stream Name	Base Waste	
Temperature	25.0	°C
Pressure	1.0	Atmospheres
Stream Amount	55.5082 (Default)	Mole
H <sub>2</sub> O	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 <sub>2</sub> O	55.5082	Mole
HCI	0.1	Mole
H2SO4	1.0	Mole
Stream Name	Caustic	
Temperature	25.0	°C
Pressure	1.0	Atmospheres
H <sub>2</sub> O	55.5082	Mole
NaOH	1.0	Mole

Cascading	Mixer	Stream	Data
-----------	-------	--------	------

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.

OLI Studio - [Chapter 8 Tour.oad*]			
File Edit Streams Calculations Chemi	star Taols View Window Halp		
	IVa So 2 <sup>nd</sup> Re ± 11 ± 12 ± 44 m ± €	} 🛛 🔂 📈	
Navigator # * *	A Circula Dation 0		
Chapter 8 Tour.oad*	▲ SinglePoint-2		
- Stream	🦪 Description 🥸 Definition 📓 Report 🚊	File Viewer	
🗄 - 👰 Survey 📃			Type of calculation
🖃 👌 Stream-1	Variable	Value	
😥 🛷 Survey-1	Stream Parameters		Isothermal   Specs
- Stream-2	Stream Amount (mol)	56.5082	Bubble/Dew Point
😥 🔊 🖓 Survey-2	Temperature (*C)	25.0000	<ul> <li>Temperature</li> </ul>
👌 Citric Acid	Pressure (atm)	1.00000	Pressure
NaOH	C Inflows (mol)		
• - A Mixer	H2O	55.5082	Calculate 🥝
😑 🍐 Base Waste	NaOH	1.00000	
SinglePoint			Summary
index = 1 → Acid Waste Index = 1 → Acid Waste Index = 1 → Acid Waste			Unit Set: Metric (moles)
□ A Caustic			Unit Set. Metric (moles)
SinglePoint-2			Automatic Chemistry Model
The singler on t-2			AQ (H+ ion) Databanks: Public
Actions a * X		E	Isothermal Calculation
Actions			25.0000 °C 1.00000 atm
Actions			Phase Amounts
			Aqueous 57.5082 mol
			Vapor 0.0 mol
			Solid 0.0 mol
			Aqueous Phase Properties
			pH 13.8891
			lonic Strength 0.0173888 mol/mol Density 1.03546 g/ml
Plot Template Manager			
Plot remplate Manager # * *			Calc. elapsed time: 0.250 sec
			Calculation complete
		-	
	/ Input Output		
	Input Output		
	Advanced Search Add as Stream E:	from	
Save			,
For Help, press F1			Image:

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.

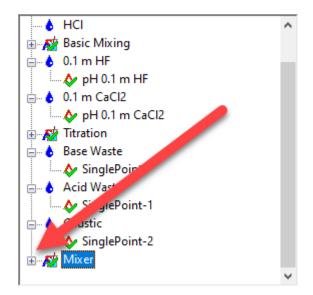


We can now add the "Base Waste" and "Acid Waste" stream as we have done in previous examples. The only difference here is that we are selecting an **Adiabatic** calculation instead of the default isothermal calculation.

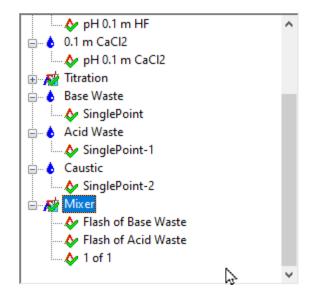
Description 🔮	Definition <u> </u> Plot	😡 Report 📄 File Viewer	
Available Streams		Selected	Mixing Method
Stream Stream-1 Stream-2 Citric Acid NaOH Caustic Mixer - [AQ] SinglePoint - [AQ] SinglePoint - [AQ]	× ×	Base Waste Acid Waste	Single Point Mix  Specs Type of calculation Adiabatic Bubble/Dew Point Type of calculation Bubble/Dew Point Type Pressure Type 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.

ian of the cacl2 and the cacl2 below by pH 0.1 m Cacl2	^	Description	🥺 Definit	ion 📶 Plot	👼 Report	📄 File Vie	wer
Titration	A	vailable Streams			Selected		
Base Waste	Ba	austic - [AQ] asic Mixing - [MSE		>>			
<ul> <li>Acid Waste</li> <li>SinglePoint-1</li> </ul>	pł	H 0.1 m HF - [AQ] H 0.1 m CaCl2 - [A itration - [AQ]		<<			
Caustic	Si	inglePoint - [ÁQ] inglePoint-1 - [ÁQ]					
→ SinglePoint-2		inglePoint-2 - [AQ] ixer - [AQ]	- v				
🗸 🎸 Flash of Base Waste		Variable			/alue		~
V Flash of Acid Waste		Multiplier					
↓ 1 of 1				Stream Param	eters		
Mixer-1	v    -	Total Inflow					

When we add a subsequent mixer, we will see all 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 OLI Flowsheet: ESP.) We want to connect the output from our first mixer (Mixer) to the inlet of the **Caustic** stream. Click the object

#### Mixer -(AQ).

Then add the Caustic stream. Select the type of calculation as Isothermal.

Description	🥸 Defini	tion 🚻 Pl	ot 👼 Report 🚂 File Vi	wer	
Available Streams			Selected		Mixing Method
0.1 m HF 0.1 m CaCl2 Base Waste Acid Waste pH 0.1 m HF - [AQ] pH 0.1 m CaCl2 - [A( Titration - [AQ] SinglePoint - [AQ] SinglePoint-1 - [AQ]	1	>> ~	Mixer Caustic		Single Point Mix   Specs  Type of calculation  Isothermal  Calc <u>u</u> late
Singler officer - [AQ]	*			9	Summary
Variable	Value	Mixer	Caustic	<u> </u>	
	Value	Mixer 1.00000	Caustic 1.00000	— I r	Unit Set: Metric (moles)
Variable	Value		1.00000	— I r	
Variable	Value	1.00000	1.00000	— I r	Unit Set: Metric (moles) Automatic Chemistry Model Aqueous (H+ ion) Databanks:
Variable Multiplier		1.00000 Stream Par 113.236 mol	1.00000 ameters	— I r	Unit Set: Metric (moles)

We are now ready to calculate the second mixer. Press the calculate button.

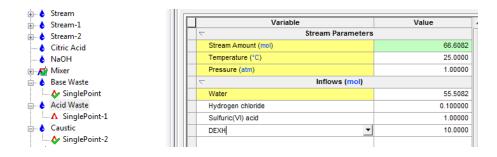
The resultant pH should be approximately 1.0. We want to increase this value. Change the <u>Multiplier</u> value for Caustic Stream from 1.0 to 2.4

Variable	Value	Mixer-1	Caustic	
Multiplier		1.00000	2.4000	
Stream Parameters 7				
Total Inflow		113.236 mol	56.5082 mol	
Temperature (°C)	25.0000	25.0000	25.0000	
Pressure (atm)	1.00000	1.00000	1.00000	

Click the calculate button again. The new pH should be approximately 12.1.

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<sup>7</sup> to the grid with a value of 10.0 moles.

<sup>&</sup>lt;sup>7</sup> 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-1 in our example) and then reduce the *Caustic Multiplier back to* **1.0** 

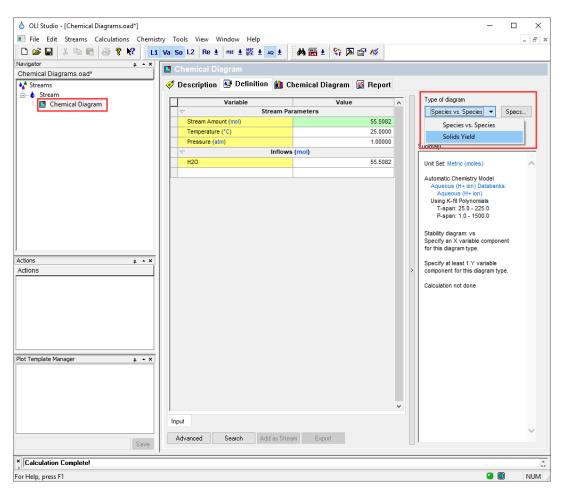
To recalculate all the objects at once, press the control+F9 keys and all objects will be calculated. Now if you look at the summary of Mixer2 you will see that the pH has changed to approximately 10.

Stream-1       >>       Caustic       Type of calculation         Stream-2       Isothermal       Isothermal       Isothermal         NaQH       Base Waste       Calculate       Isothermal       Isothermal         SinglePoint - [AQ]       -       Calculation       Isothermal       Isothermal         Variable       Value       Mixer-1       Caustic       Calculation       Isothermal       Isothermal         Multiplier       1.00000       1.00000       1.00000       Automatic Chemistry Model       AQ (H+ ion) Databanks: Public       Public       Isothermal Calculation       25.0000 ct.000000 atm       Single Point Mix       Calculation Mix         Pressure (at       1.00000       1.00000       1.00000       Single Point Mix       Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal       Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol       Solid 0.0 mol         Solid       0.0 mol       Solid       0.0 mol Solid       Solid 0.0158132 mol/mol Density 1.05177 g/ml         Calc. elapsed time: 0.582 sec       -       -	Des	scription	P Definition	🛍 Plot 员	Report		
Stream-1       >>       Caustic       Type of calculation         Stream-2       Isothermal       Isothermal       Isothermal         NaQH       Base Waste       Calculate       Isothermal       Isothermal         SinglePoint - [AQ]       -       Calculate       Isothermal       Isothermal         Variable       Value       Mixer-1       Caustic       Calculation       Isothermal       Isothermal         Multiplier       1.00000       1.00000       Automatic Chemistry Model       AQ (H+ ion) Databanks: Public       Public       Isothermal Calculation       25.0000 ct.00000 dtm       Single Point Mix         Calculation Results: Temperature (at       1.00000       1.00000       1.00000       Single Point Mix         Calculation Results: Temperature 25.0000 vC Heat Duty -11867.3 cal       Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol       Aqueous Phase Properties pH 10.0788 bonic Strength 0.0158132 mol/mol Density 1.05177 g/ml	Availat	ble Streams		Selected	1	Π	Mixing Method
Stream-2       Image: Chick Acid         Chick Acid       Stream Parameters         Multiplier       1.00000         Stream Parameters       Image: Chick Acid         Total Inflow       123,236 mol         Temperature       25.0000         Pressure (at       1.00000         Pressure (at       1.00000         Temperature       25.0000         Stope Point (at       1.00000         Proble       Isothermal         Isothermal       Calculation         Calculation       Calculation         Multiplier       1.00000         Total Inflow       123,236 mol         Stope Pressure (at       1.00000         Noncold       1.00000         Proble       Isothermal Calculation         Single Point Mix       Calculation         Calculation Results:       Temperature         Temperature       25.0000 °C         Heat Duty -11867.3 cal       Phase Amounts         Aqueous Phase Properties       PH         PH       10.0788         Solid       0.0 mol         Solid       0.0 mol         Calculation Strength       0.0158132 mol/mol         Density       0.058132 mol/mol<			<b>_</b>				Single Point Mix 🔹 Specs
Chric Acid       Image: Control of the second				Caustic			Type of calculation
Value       Mixer-1       Caustic         Mutiplier       1.00000       1.00000         Stream Parameters       Automatic Chemistry Model         AQ (H+ ion) Databanks:       Public         Isole value       1.00000       1.00000         Pressure (at       1.00000       1.00000         Pressure (at       1.00000       1.00000         Pressure (at       1.00000       1.00000         Pressure (at       1.00000       1.00000         Aqueous       179.430 mol         Vapor       0.0 mol         Solid       0.0 fis8132 mol/mol         Density       1.05177 g/ml         Calc. elapsed time: 0.582 sec		cid	= <	<			
Mixer - [AQ]       •         Variable       Value         Multiplier       1.00000         Stream Parameters         Total Inflow       123.236 mol         Temperature       25.0000         Pressure (at       1.00000         1.00000       1.00000         Multiplier       1.00000         Temperature       25.0000         Pressure (at       1.00000         Multiplier       1.00000         Multiplier       1.00000         Variable       Value         Multiplier       1.00000         Temperature       25.0000         Summary       Value         Multiplier       1.00000         Multiplier       1.00000 <t< td=""><td>Base W</td><td></td><td></td><td></td><td></td><td></td><td>- Tood to man</td></t<>	Base W						- Tood to man
SinglePoint - [AQ]       •         Variable       Value       Mixer-1       Caustic         Multiplier       1.00000       1.00000       Automatic Chemistry Model         AC (H+ ion) Databanks:       Public       Bothermal Calculation         Total Inflow       123.236 mol       56.5082 mol       25.0000         Pressure (at       1.00000       1.00000       1.00000         Pressure (at       1.00000       1.00000       Single Point Mix         Calculation Results:       Temperature 25.0000 °C       Heat Duty -11867.3 cal         Phase Amounts       Aqueous 179.430 mol       Vapor 0.0 mol         Solid       0.0 mol       Solid       0.0 mol         Solid       0.0 mol       Solid       0.0 mol         Solid       0.0 tis8132 mol/mol       Density 1.05177 g/ml         Calc. elapsed time: 0.582 sec       •							Calculate 🥥
Multiplier       1.0000       1.0000         Stream Parameters       Automatic Chemistry Model         Total Inflow       123.236 mol       56.5082 mol         Temperature       25.0000       25.0000         Pressure (at       1.00000       1.00000         Single Point Mix       Calculation Results: Temperature 25.000 °C         Phase Amounts       Aqueous 179.430 mol         Vapor 0.0 mol       Solid         Solid       0.0 mol         Solid       0.0 mol         Solid       0.0 mol			-				Summary
Multiplier       1.00000       1.00000         Stream Parameters         Total Inflow       123.236 mol       56.5082 mol         Temperature       25.0000       25.0000       25.0000         Pressure (at       1.00000       1.00000       1.00000         Single Point Mix       Calculation Results: Temperature 25.0000 °C 1.00000 atm       Single Point Mix         Calculation Results:       Temperature 25.0000 °C 1.00000 atm       Single Point Mix         Calculation Results:       Temperature 25.0000 °C 1.00000 atm       Single Point Mix         Calculation Results:       Temperature 25.0000 °C       Heat Duty -11867.3 cal         Phase Amounts       Aqueous 179.430 mol       Vapor 0.0 mol         Solid       0.0 mol       Solid       0.0 mol         Solid       0.0 tis1132 mol/mol       Density 1.05177 g/ml       Calc. elapsed time: 0.582 sec		Variable	Value	Mixer-1	Caustic		
Total Inflow       123.236 mol       56.5082 mol         Temperature       25.0000       25.0000         Pressure (at       1.00000       1.00000         1.00000       1.00000       1.00000         Single Point Mix       Calculation Results: Temperature 25.0000 °C         Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol         Aqueous Phase Properties PH 10.0788 Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml         Calc. elapsed time: 0.582 sec	N	Aultiplier		1.00000	1.00000		Unit Set: Metric (moles)
Temperature       25.0000       25.0000       25.0000         Pressure (at       1.00000       1.00000       1.00000         Single Point Mix       Calculation Results: Temperature 25.0000 °C       Calculation Results: Temperature 25.0000 °C         Heat Duty - 11867.3 cal       Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol       Phase Properties pH 10.0158132 mol/mol Density 1.05177 g/ml         Calc. elapsed time: 0.582 sec			Stream	Parameters			
Temperature         25.0000         25.0000         25.0000           Pressure (at         1.00000         1.00000         1.00000         1.00000           Single Point Mix         Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal         Single Point Mix           Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol         Aqueous Phase Properties pH 10.0788 Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml         Calc. elapsed time: 0.582 sec	Т	Fotal Inflow		123.236 mol	56.5082 mol		
<ul> <li>Single Point Mix</li> <li>Single Point Mix</li> <li>Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal</li> <li>Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol</li> <li>Solid 0.0 mol</li> <li>Solid 0.0 mol</li> <li>Solid 0.0 mol</li> <li>Solid 0.0 mol</li> <li>Density 1.05187132 mol/mol Density 1.05177 g/ml</li> <li>Calc. elapsed time: 0.582 sec</li> </ul>							
Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 10.0788 Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml Calc. elapsed time: 0.582 sec	P	Pressure (at	1.00000	1 00000			
Temperature 25.0000 °C Heat Duty -11867.3 cal Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 10.0788 Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml Calc. elapsed time: 0.582 sec					1.00000		
Temperature 25.0000 °C Heat Duty -11867.3 cal Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 10.0788 Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml Calc. elapsed time: 0.582 sec					1.00000	>	25.0000 °C 1.00000 atm
Phase Amounts Aqueous 179,430 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 10.0788 Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml Calc. elapsed time: 0.582 sec					1.00000	>	25.0000 °C 1.00000 atm Single Point Mix
Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 10.0788 Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml Calc. elapsed time: 0.582 sec					1.00000	>	25.0000 °C 1.00000 atm Single Point Mix Calculation Results: Temperature 25.0000 °C
Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 10.0788 Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml Calc. elapsed time: 0.582 sec					1.0000	>	25.0000 °C 1.00000 atm Single Point Mix Calculation Results: Temperature 25.0000 °C Heat Unity11867 3.cal
Solid 0.0 mol Aqueous Phase Properties pH 10.0788 Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml Calc. elapsed time: 0.582 sec					1.0000	>	25.0000 °C 1.00000 atm Single Point Mix Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal
Aqueous Phase Properties pH 10.0788 lonic Strength 0.0158132 mol/mol Density 1.05177 g/ml Calc. elapsed time: 0.582 sec					1.0000	>	25.0000 °C 1.00000 atm Single Point Mix Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal Phase Amounts Aqueous 179.430 mol
PH 10.0788 Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml Calc. elapsed time: 0.582 sec					1.0000	>	25.0000 °C 1.00000 atm Single Point Mix Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol
Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml Calc. elapsed time: 0.582 sec					1.0000	>	25.0000 °C 1.00000 atm Single Point Mix Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol
Density 1.05177 g/ml     Calc. elapsed time: 0.582 sec					1.0000	>	25.0000 °C 1.00000 atm Single Point Mix Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties
Calc. elapsed time: 0.582 sec					1.0000	>	25.0000 °C 1.00000 atm Single Point Mix Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 10.0788
					1.0000	>	25.0000 °C 1.00000 atm Single Point Mix Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 10.0788 Ionic Strength 0.0158132 mol/mol
nput Calculation complete					1.0000	>	25.0000 °C 1.00000 atm Single Point Mix Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 10.0788 Ionic Strength 0.0158132 mol/mol
					1.0000	>	25.0000 °C 1.00000 atm Single Point Mix Calculation Results: Temperature 25.0000 °C Heat Duty -11867.3 cal Phase Amounts Aqueous 179.430 mol Vapor 0.0 mol Solid 0.0 mol Aqueous Phase Properties pH 10.0788 Ionic Strength 0.0158132 mol/mol Density 1.05177 g/ml

# 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<sup>78</sup>.

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.



<sup>&</sup>lt;sup>8</sup> 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.

# **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<sub>3</sub>O<sub>2</sub>)<sub>3</sub> – K<sub>3</sub>PO<sub>4</sub> 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. <u>https://doi.org/10.1179/143307510X12599329343123</u>.

#### 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 <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> – K <sub>3</sub> PO <sub>4</sub> Chemical Diagram				
Calculat	tion Settings	Stream Composition and Conditions		
Stream Name	Chemical Diagrams	Stream Amount	Calculated	
Name Style	Display Formula	Temperature	25 °C	
Unit Set	Metric, Batch, Moles	Pressure	1 atm	
Framework	AQ	H2O	55.5082 moles	
Type of Calculation	Chemical Diagram	La[C2H3O2]3 <sup>Note</sup>	0.1 moles	
		K3PO4	0.1 moles	
		HNO3	0.0 moles	
		NaOH	0.0 moles	

Note: Notice the use of square brackets instead of the traditional parenthesis

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to Chemical Diagrams

Select the AQ thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

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.

Go to the **Add Calculation** button and select **Chemical Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane

Select Species vs Species as Type of Diagram - Default

Change the Chemical Diagram name to Lanthanum/Phosphate using the <F2> key

OLI Studio (Version 11.5.1 Beta) - [6.1 Chemical Dia	agrams - Example_37.oad*]		– 🗆 X
File Edit Streams Calculations Chemistry			_ <i>B</i> ×
		🕯 📷 🛨 💱 🗩 😭 📈	
Navigator 6.1 Chemical Diagrams - Example_37.oad*	Lanthanum/Phosphate		
• Streams	I Description 🤮 Definition 🛍 (	hemical Diagram 📓 Benort	📦 File Viewer
🚊 👌 Chemical Diagrams			
Lanthanum/Phosphate	Variable	Value	Type of diagram
	Stream Amount (mol)	55.7082	Species vs. Species 🔻 Specs
	Temperature (°C)	25.0000	Calculate 🥝
	Pressure (atm)	1.00000	
		mol)	Summary
	H2O	55.5082	Unit Set: Metric (moles)
	La[C2H3O2]3	0.100000	Automatia Obernistes Martal
	K3P04	0.100000	Automatic Chemistry Model Aqueous (H+ ion) Databa ks:
	HNO3	0.0	Aqueous (H+ ion) Using K-fit Polynomials
	NaOH	0.0	T-span: 25.0 - 225.0
			P-span: 1.0 - 1500.0
Actions			Stability diagram: vs
Actions			Only one redox system
			<ul> <li>can be selected for display in Species vs Species diagrams.</li> </ul>
			Specify an X variable component for this diagram type.
			Specify at least 1 Y variable component for this diagram type.
			Calculation not done
Plot Template Manager # * *			
		¥	
	Input		
Save	Advanced Search Add as Stre	am Export	
For Help, press F1	I		

Notice that the calculation is not ready

Click on the Specs button. This will open the Chemical Diagram Options window

In the **Display Choices** tab, select the **No Aqueous lines** button and check the box for **Lanthanum** as the subsystems to display

Chemical Diagram Options		?	×
Category Display Axes	Display Choices         Aqueous and Solid Lines         Superimpose lines         No Aqueous lines         Only Aqueous lines         Display Subsystem         Potassium         Sodium         Nitrogen         Phosphorus		
	OK Cancel Apply	Help	1

Click on the Axes category. The dialog changes to display the X Axis tab.

In the **Variable** section select the **pH** option. Leave the default **pH Range**: 0-14. This also enables the **Titrants** button.

Chemical Diagram Options		?	×
Category — Display — Axes	X Axis Y Axis Variable Species Amount PH Range Start 0 End 14 Log scale	Species Inflow ☐ Hide Related Inflows H2O HNO3 K3PO4 La[C2H3O2]3 NaOH	
	OK	Cancel Apply He	elp

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.

Select Titrants		?	×		
Titrants					
Hide Related Inflows		New Inf	low		
Acid	Base		_		
H2O HNO3 K3PO4 La[C2H3O2]3	H2O HNO3 K3PO4 La[C2H3O2]3				
NaOH	NaOH				
Select the acid and the base which will be used to vary the pH.					
OK Ca	ncel Apply	Н	elp		

Select the **Y** Axis tab. Select the **Species Amount** button as the variable to change Select La[C2H3O2]3 and K3PO4 species

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.

#### Click OK

Chemical Diagram Option	5	? ×
Category	X Axis Y Axis	
Display Axes	Variable Species Amount Temperature Inflow Range Start 1e-014 mol End 1 mol Uog scale	Species (maximum of 4) Inflow(s) Hide Related Inflows H20 HINO3 Solution (SPO4 La[C2H3O2]3 NAON
	0	K Cancel Apply Help

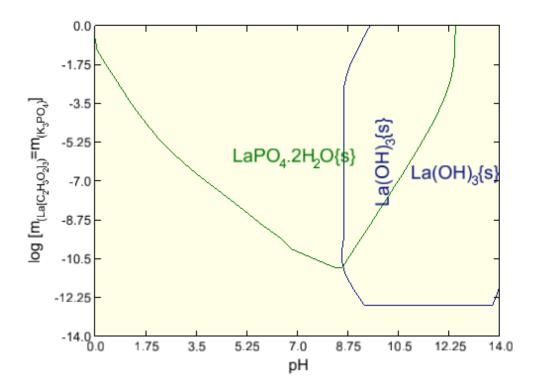
We are ready to perform the calculation. Click on the Calculate button or press the <F9> key

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*.

#### Analyzing 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<sup>-</sup> 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

**Copy** the *Lanthanum/Phosphate* chemical diagram calculated in the Example 37: La(C2H3O2)<sub>3</sub> – K3PO4 Chemical Diagram, and **paste** it under the *Chemical Diagrams* stream.

Change the name to Lanthanum 50% increase using the <F2> key

Change the Lanthanum Acetate amount to 0.15 moles

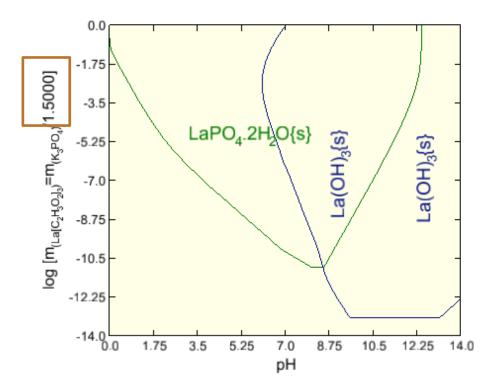
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🗋 🗅 🚔 🖬 👗 🖷 🛍 🦪 🖇 😢	L1 Va So L2 Re ± MSE ± MSE ± AQ ±	🚧 🎬 🛓 💱 🔊 😭 🎸		
Navigator # * X	Lanthanum 50% increase			
Chemical Diagrams.oad*				
🍫 Streams 🧳	<sup>f</sup> Description 🔮 Definition <u> ا</u> Chemi	cal Diagram 👔 Report		
Lanthanum/Phosphate	Variable	Value		Type of diagram
Lanthanum 50% increase	Stream Para	ameters		Species vs. Species 🔻 Specs
	Stream Amount (mol)	55.7582		
	Temperature (°C)	25.0000		Calculate 🥥
	Pressure (atm)	1.00000	9	Summary
	Calculation Pa			
	Use Single Titrant pH Acid Titrant	No HNO3		Unit Set: Metric (moles)
	pH Base Titrant	NaOH		Automatic Chemistry Model
				Aqueous (H+ ion) Databanks: Aqueous (H+ ion)
	H20	55.5082		Using K-fit Polynomials
	La[C2H3O2]3	0.150000		T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0
Actions	K3PO4	0.100000		
Actions	HNO3	0.0	>	Stability diagram: La[C2H3O2]3 vs pH
	NaOH	0.0		User-selected titrants Acid: HNO3
				Base: NaOH
				Range on La[C2H3O2]3:
				1.00000e-14 to 1.00000 mol
				Range on pH: 0.0 to 14.0000
				Subsystems
Plot Template Manager # *				Lanthanum Calculation complete
				Calculation complete
		~		
	nput Output			
	Advanced Search Add as Stream	Export		×
Save				
X Calculation Completed				
Calculation Complete!				~
For Help, press F1				

We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar.

#### Analyzing the Results

Click on the **Chemical Diagram** tab ( **Memical Diagram**). 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 thirds example we will use the original amount of the lanthanum acetate species and see the effect of this increase in temperature and pressure on the chemical diagram.

#### Starting the Simulation

**Copy** the *Lanthanum/Phosphate* chemical diagram calculated in the Example 37: La(C2H3O2)<sub>3</sub> – K3PO4 Chemical Diagram, and **paste** it under the *Chemical Diagrams* stream.

Change the name to Lanthanum HTHP using the <F2> key

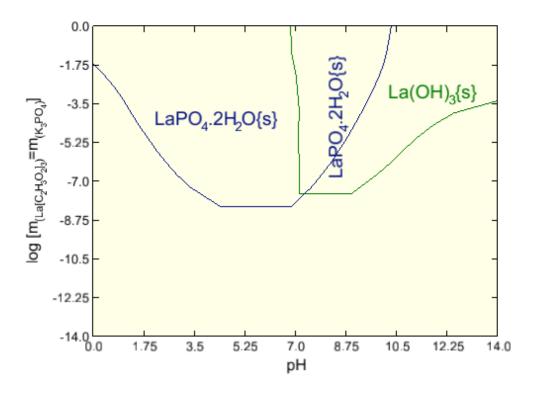
**Change** the temperature to 200 °C and the pressure to 25 atmospheres

💧 OLI Studio - [Chemical Diagrams.oad*]			– 🗆 ×
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Chemical Diagrams.oad*	_anthanum HTHP		
♦ Streams	Description 🛃 Definition 📶 Chemi	ical Diagram 📓 Report	
🚊 👌 Chemical Diagrams			1 <b>-</b> - <i>i</i> :
	Variable	Value 🔨	Type of diagram
🖳 💭 Lanthanum 50% increase	C Stream Par		Species vs. Species 💌 Specs
Lanthanum HTHP	Stream Amount (mol)	55.7082	
	Temperature (°C)	200.000	Calc <u>u</u> late 🥥
	Pressure (atm)	25.0000	Summary
	Calculation P		
	Use Single Titrant	No	Unit Set: Metric (moles)
	pH Acid Titrant	HNO3	Automatic Chemistry Model
	pH Base Titrant	NaOH	Aqueous (H+ ion) Databanks:
			Aqueous (H+ ion) Using K-fit Polynomials
	H2O	55.5082	T-span: 25.0 - 225.0
	La[C2H3O2]3	0.100000	P-span: 1.0 - 1500.0
Actions a A X	K3PO4	0.100000	
Actions	HNO3	0.0	Stability diagram: La[C2H3O2]3 vs pH Auto-selected titrants
	NaOH	0.0	Acid: HNO3
			Base: NaOH
			Range on La[C2H3O2]3:
			1.00000e-14 to 1.00000 mol
			Range on pH: 0.0 to 14.0000
			Subsystems
Plot Template Manager 📮 🔺 🗙			Lanthanum
			Calculation not done
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× OIDTOT IIIISIICU.			^
Calculation Complete!			Ŷ
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We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar.

#### Analyzing 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 200°C 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 Studio: Corrosion Analyzer

Corrosion Analyzer is a module within the OLI Studio. 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 (Potential vs pH and Potential vs species 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.



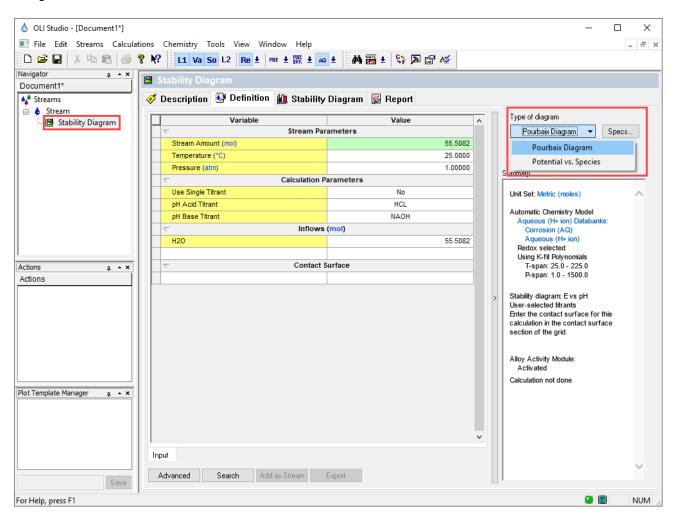
Add Corrosion Rates

**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

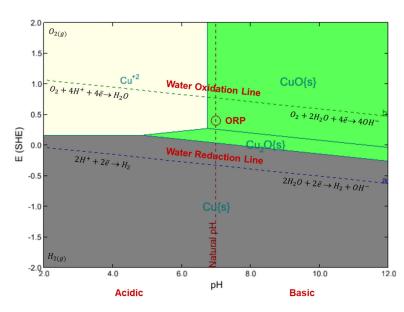
In this section you are going to learn how to set up a Stability Diagram and how to interpret the results when using this tool.



## 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 °C 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<sub>2</sub>O 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.

## 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: 
$$H^+ + 2\bar{e} \otimes H_2$$

Basic: 
$$2H_2O + 2\bar{e} \otimes H_2 + OH^-$$

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.

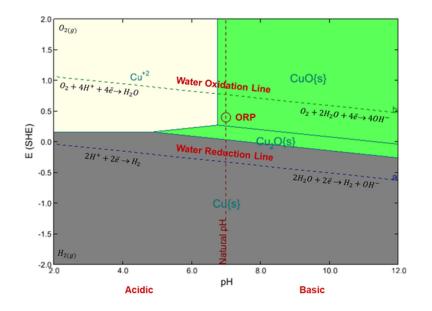
In oxygen-containing solutions,  $O_2$  can be reduced to  $H_2O$  (as shown by line **b**). Depending of the pH that reactions that can occur are the following:

Acidic: 
$$O_2 + 4H^+ + 4\bar{e} \otimes H_2 O$$

Basic: 
$$O_2 + 2H_2O + 4\bar{e} \otimes 4OH^-$$

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 25°C and 1 atm

# **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 Studio icon on the desktop, which will take you to the OLI Studio 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 Condition						
Stream Name	Fe-H2O System	Stream Amount	Calculated			
Name Style	Display Formula	Temperature	25 ⁰C			
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					

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to Fe-H2O System

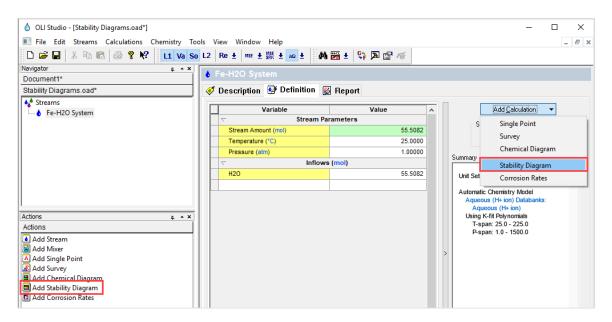
Select the **AQ** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition, temperature and pressure of the stream given in the table above

Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane.



#### Select Pourbaix Diagram as Type of Survey - Default

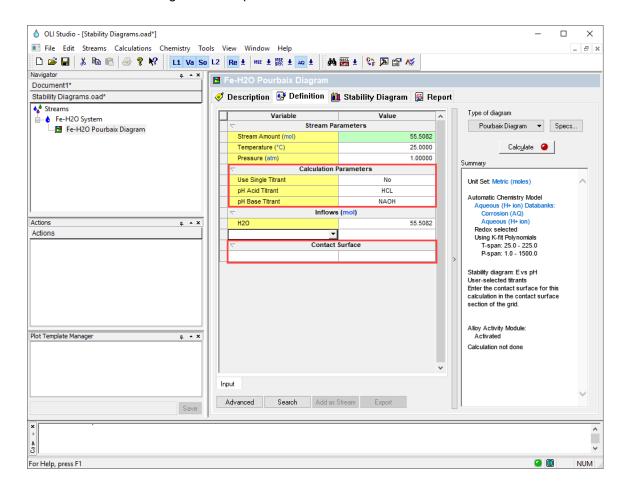
Click on the new Stability Diagram and press <F2> to change the name to Fe-H2O Pourbaix Diagram

**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 HCI 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.



Leave the default titrants for this calculation: HCl and NaOH

## Under the Contact Surface grid type Fe

Note:	You also	have the o	option to	use the	drop-down	arrow to	search fo	or the	metal or	alloy o	of interest.
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Navigator # * *	Fe-H2O Pourbaix Diagram		
Document1*			
Stability Diagrams.oad*	< Description 🤮 Definition 🛍	l Stability Diagram 🛛 📓 Rep	ort
🍫 Streams	Variable	Value	Type of diagram
Fe-H2O System	Stream Par		Pourbaix Diagram 🔻 Specs
📕 Fe-H2O Pourbaix Diagram	Stream Amount (mol)	55.5082	
	Temperature (°C)	25.0000	Calcylate 🥝
	Pressure (atm)	1.00000	
	Calculation P	arameters	Summary
	Use Single Titrant	No	Unit Set: Metric (moles)
	pH Acid Titrant	HCL	
	pH Base Titrant	NAOH	Automatic Chemistry Model Aqueous (H+ ion) Databanks:
1	□	(mol)	Corrosion (AQ)
Actions a * ×	H2O	55.5082	Aqueous (H+ ion) Redox selected
Actions			Using K-fit Polynomials
	Contact 5	Surface	T-span: 25.0 - 225.0
	Fe 🔽		P-span: 1.0 - 1500.0
	Display Name	OLI Name ^	Stability diagram: Evs pH
	OLI F2	F2	User-selected titrants
	▲ F2	F2	Enter the contact surface for this calculation in the contact surface
	本 Fe	FEEL	section of the grid.
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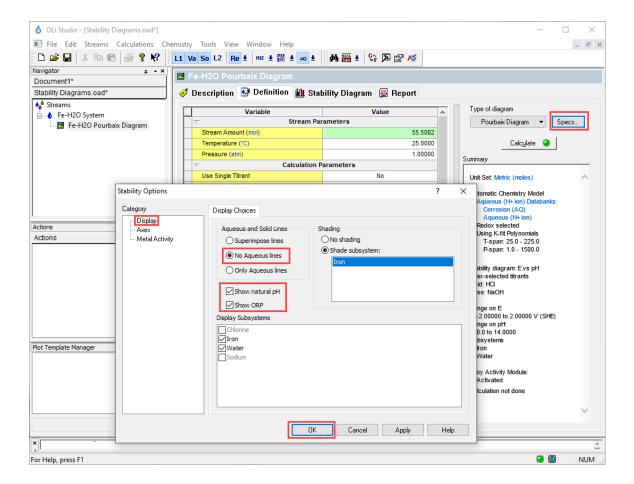
At this point all the basic inputs to create a Pourbaix Diagram have been defined. Notice that in the summary box the following default plotting settings have been defined: Potential range: -2 to 2 V vs SHE and pH range: 0-14. You can modify these default values before running the calculation.

Stability Diagrams.oad*       Image: Constraint of the stability of	Value ers 55.5082 25.0000 1.00000 eters No HCI NaOH 55.5082 0.0. 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0	0     Calculate       0     Summary       Unit Set: Metric (moles)     Automatic Chemistry Model       Aqueous (H-ion)     Aqueous (H-ion)       2     Aqueous (H+ion)       0     Redox selected       0     Using K-fit Polynomiais       0     T-span: 25.0 - 225.0       P-span: 1.0 - 1500.0       >     Stability diagram: E vs pH
▲ Fe-H2O System       ✓       Stream Paramet         ✓       Stream Amount (mol)       ✓         ✓       Temperature (°C)       ●         ✓       Calculation Paramet       ●         ØH Acid Titrant       ●       ●         ØH Base Titrant       ●       ●         H2O       ●       ●         H2O       ●       ●         H2O       ●       ●         ✓       Contact Surface ●       ●	ers 55.5082 25.0000 1.00000 ters No HCI NaOH 55.5082 0.0 0.0	2       Pourbaix Diagram       Specs         0       Calculate       Summary         Unit Set: Metric (moles)       Automatic Chemistry Model         Aqueous (H+ ion) Databanks:       Corrosion (AQ)         0       Redox selected         0       Using K-fit Polynomials         0       T-span: 25.0 - 225.0         P-span: 1.0 - 1500.0       Stability diagram: E vs pH
Actions       4 ~ X         Actions       4 ~ X	55.5082 25.0000 1.00000 eters No HCI NaOH 55.5082 0.0. 0.0 0.0	2       Calculate         0       Summary         Unit Set: Metric (moles)       Automatic Chemistry Model         Aqueous (H+ ion) Databanks:       Corrosion (AQ)         2       Aqueous (H+ ion)         0       Redox selected         Using K-fit Polynomials       T-span: 25.0 - 225.0         0       P-span: 1.0 - 1500.0         5       Stability diagram: E vs pH
Actions     4 ★ ★       Actions     4 ★ ★	25.000 1.0000 HCI NaOH 55.5082 0.0 0.0	0     Calculate       0     Summary       Unit Set: Metric (moles)     Automatic Chemistry Model       Aqueous (H-ion)     Aqueous (H-ion)       2     Aqueous (H+ion)       0     Redox selected       0     Using K-fit Polynomiais       0     T-span: 25.0 - 225.0       P-span: 1.0 - 1500.0       >     Stability diagram: E vs pH
Actions <ul> <li>★ *X</li> <li>Actions</li> <li>★ *X</li> </ul>	1.00000 ters No HCI NaOH 55.5082 0.0 0.0 0.0	0         Summay           Unit Set: Metric (moles)         ////////////////////////////////////
Actions 4 * X Actions Contact Surface (	eters No HCI NaOH 55.5082 0.0 0.0 0.0	Summary Unit Set: Metric (moles) Automatic Chemistry Model Aqueous (H+ ion) Databanks: Corrosion (AQ) Aqueous (H+ ion) Redox selected Using K-fit Polynomials T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0 Stability diagram: E vs pH
Actions + ★X Actions + ★X	No HCI NaOH 55.5082 0.0 0.0 0.0 0.0	Unit Set: Metric (moles)         Automatic Chemistry Model         Aqueous (H+ ion) Databanks:         Corrosion (AQ)         Aqueous (H+ ion)         Redox selected         Using K-fit Polynomials         T-span: 25.0         P-span: 1.0 - 1500.0         Stability diagram: E vs pH
Actions + *X	HCI NaOH 55.5082 0.0 0.0 0.0 0.0	Automatic Chemistry Model Aqueous (1+ ion) Databanks: Corrosion (AQ) Aqueous (1+ ion) Redox selected Using K-fit Polynomials Using K-fit Polynomials - r-span: 25.0 - 225.0 P-span: 1.0 - 1500.0
Actions	NaOH 55.5082 0.0 0.0	Aqueous (H+ ion) Databanks:           Corrosion (AQ)           2         Aqueous (H+ ion)           0         Redox selected           0         Using K-fit Polynomials           1         -span: 25.0 - 225.0           0         P-span: 1.0 - 1500.0
Actions	55.5082 0.0 0.0	Aqueous (H+ ion) Databanks:           Corrosion (AQ)           2         Aqueous (H+ ion)           0         Redox selected           0         Using K-fit Polynomials           1         -span: 25.0 - 225.0           0         P-span: 1.0 - 1500.0
ctions ↓ • × ctions ↓ • ×	0.0 0.0 0.0	2         Aqueous (H+ion)           0         Redox selected           0         Using K-fit Polynomials           0         T-span: 25.0 - 225.0           0         P-span: 1.0 - 1500.0           >         Stability diagram: E vs pH
ctions	0.0 0.0 0.0	Redox selected           Using K-fit Polynomials           T-span: 25 0 - 225.0           P-span: 1.0 - 1500.0           Stability diagram: E vs pH
ctions L · × kctions Contact Surface (	0.0	Using x-int Polynomials           0         T-span: 25.0 - 225.0           0         P-span: 1.0 - 1500.0           >         Stability diagram: E vs pH
ctions p · · × Actions Contact Surface (	0.0	0 P-span: 1.0 - 1500.0
Actions  Actions Contact Surface (		Stability diagram: E vs pH
Actions Contact Surface	nol)	
		User-selected titrants Acid: HCI
		Base: NaOH
		Range on E:
		-2.00000 to 2.00000 V (SHE)
		Range on pH:
		0.0 to 12.0000 Subsystems
		Iron
lot Template Manager # * *		Water
		Alloy Activity Module:
		Activated
		<ul> <li>Calculation not done</li> </ul>
Input		
Advanced Search Add as Stream E	port	

Click on the **Specs** button. This will open the **Stability Diagram Options** Window Under the **Display** Category you will see the **Display Choices** tab. Under this tab make sure to select the following options: No Aqueous lines Show natural pH Show ORP Under **Display Subsystems** check the **Iron** and **Water** boxes

Under Shading select the option Shade Subsystem and select Iron.

Click OK to close the window



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.

Stability Options		?	$\times$
Category Display Axes Metal Activity	Plot Variables XAxis PH Range Start End 12 Titrants PH Titrants	Y Axis Potential Range Start -2 V (SHE) End 2 V (SHE)	
	ОК	Cancel Apply H	Help

**Change** the X Axis or pH range to 2-12

Leave the default values for the Y Axis of Potential Range (-2 to 2 V SHE)

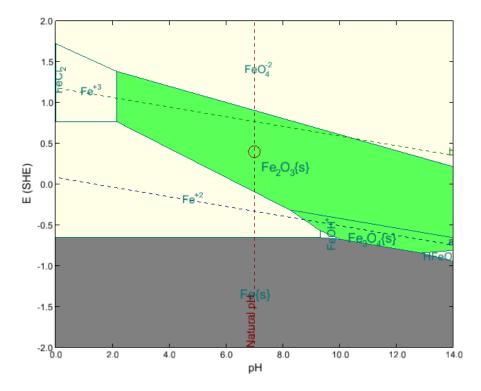
Click **OK** to close the window

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

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 °C 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<sup>+2</sup>. 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  $Fe_3O_4$ , 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 °C and 1 atm. The point at which the natural pH and the ORP intersects (7 pH, 0.4 V SHE) indicates that Fe<sub>2</sub>O<sub>3</sub> (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.,  $Fe^{2+}$ .

# **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<sup>+6</sup> 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 ℃			
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			

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 **Add Stability Diagram** icon in the Actions Pane. Select the **AQ** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

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

Select Pourbaix Diagram as Type of Survey - Default

**Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O Selective Oxidation* Under the **Contact Surface** grid type **Fe** 

## Changing the Default Titrant

In the **Calculation Parameters** grid, **click** on HCI (which is default titrant). A drop-down arrow appears, **click** on it and **select** H2SO4. NaOH has been selected by default.

Calculation Parameters			
Use Single Titrant	No		
pH Acid Titrant	HCL 💌		
pH Base Titrant	H2O		
⊂ Inflows	1H2SO4 Fe		
H2O	HCL		
H2SO4	NAOH		

Note: You can also change the default titrant using the Specs button

## Click on the Specs button

Select the Axes option under the Category window Click on pH Titrants. This will open a new window

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Navigator	Fe-H2O Selective Oxidation	
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Stability Diagrams.oad		
Fe-H2O System	Variable Value   Type of diagr	
🛛 👺 Fe-H2O Pourbaix Diagram	C Stream Parameters Pourbaix	Diagram 🔻 Specs
Fe-H2O Selective Oxidation	Stream Amount (mol) 55.5082 Stability Options ?	X e 🥥
	stability options	
	Category Plot Variables	
	Display Axes Axes	· · · ·
	Metal Activity pH Range Potential Range	odel
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	End 14 End 2 V(SHE)	
		als
	Titrants	5.0
Actions	BH Titrants	0.0
Actions		рН
		V (SHE)
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	OK Cancel Apply He	lp .
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	Advanced Search Add as Stream Export	$\sim$
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For Help, press F1	,	NUM //

Select H2SO4 as the Acid titrant, and NaOH as the Base titrant. Then click OK to exit both windows.

Select Titrants		?	$\times$
Titrants			
Hide Related Inflows		New Inf	low
Acid	Base		
Fe H2O	Fe H2O		
H2SO4 NaOH	H2SO4 NaOH		_
Select the acid and the base which w		1.	
OK Cano	cel Apply	Н	elp

The screen should look like the image below after all the inputs and definitions have been entered:

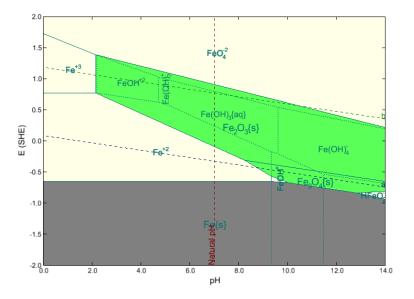
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Document1	Fe-H2O Selective Oxidation		
Stability Diagrams.oad*	🛷 Description 🤒 Definition 🛍 Stabili	ty Diagram 📓 Benort 💷 File V	liewer
• Streams		, oragioni (22 report 22 rio	
🗒 🔥 Fe-H2O System	Variable	Value	Type of diagram
🕞 💀 Fe-H2O Pourbaix Diagram	Stream Param		Pourbaix Diagram 🔻 Specs
Fe-H2O Selective Oxidation	Stream Amount (mol)	55.5082	
	Temperature (°C) Pressure (atm)	25.0000	Calculate 🥥
	Calculation Para		Summary
	Use Single Titrant	No	Unit Set: Metric (moles)
	pH Acid Titrant	H2SO4 -	official decimients (moles)
	pH Base Titrant	NAOH	Automatic Chemistry Model
		ol)	Aqueous (H+ ion) Databanks: Corrosion (AQ)
	H2O	55.5082	Aqueous (H+ ion) Redox selected
	H2SO4	0.0	Using K-fit Polynomials
	Fe	0.0	T-span: 25.0 - 225.0
Actions a A X			P-span: 1.0 - 1500.0
Actions	Contact Surface	(mol)	Stability diagram: E vs pH
	Fe		Auto-selected titrants Acid: H2SO4
			Base:
			Range on E: -2.00000 to 2.00000 V (SHE)
			Range on pH:
			0.0 to 14.0000 Subsystems
			Iron
Plot Template Manager a. * ×			Water
			Alloy Activity Module:
			Activated
		¥	Calculation not done
	Input		
	Adversed County Add Co	5 mod	$\sim$
Save	Advanced Search Add as Stream	Export	1
For Help, press F1	, 		

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

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

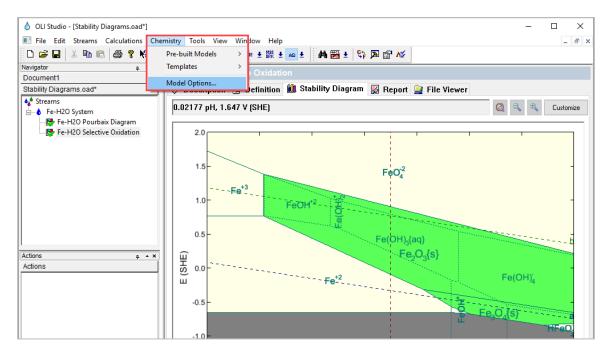
Click on the **Chemical Diagram** tab ( Stability Diagram ). This tab displays the Pourbaix Diagram for the Fe-H2O system at 25 °C and 1 atm.



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

In the Menu bar go to **Chemistry > Model Options.** This will open a new window



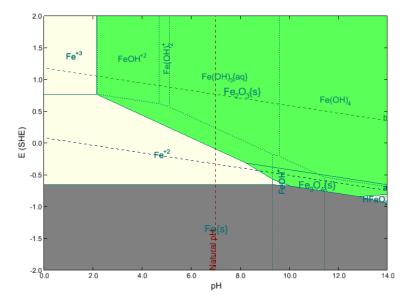
Select the **Redox** tab, expand the Iron Subsystems by clicking on the '+' icon, and **uncheck** the **Fe(+6)** oxidation state. Note that if you have an inflow component with this oxidation state it will remain in the calculation. Click the **OK** button to save your changes and close the window.

Fe-H2O Selective Oxidation Chemistry Model Options	?	×
Databanks Redox Phases T/P Span		
Include Redox Chemistry		
Include Subsystems	_	
□····································		
OK Cancel Apply	Hel	p

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 ( **U** Stability Diagram ). In the figure below, you can see that the region dominated by the FeO<sub>4</sub><sup>2-</sup> ion is not present.



# Modeling the Effects of Hydrogen Sulfide on Corrosion

## Example 42: The Effect of Hydrogen Sulfide on the Corrosion of Iron

The H<sub>2</sub>S (S<sup>-2</sup>) forms a relatively insoluble precipitate with Fe<sup>+2</sup>. 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 ⁰C
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

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 **Add Stability Diagram** icon in the Actions Pane. Select the **AQ** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition, temperature and pressure of the stream given in the table above. Add 1e-4 moles of H2S as an inflow.

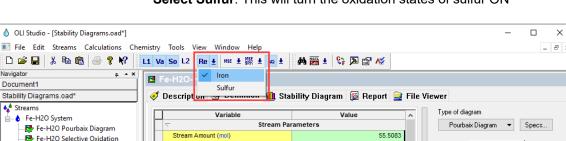
Select **Pourbaix Diagram** as Type of Survey – Default

**Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-H2O-H2S System* Under the **Contact Surface** grid type **Fe** 

The screen should look like the image below after all the inputs and definitions have been entered:

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Navigator # * *	E Fe-H2O-H2S System			
Document1				
Stability Diagrams.oad*	🛛 🎻 Description 🧕 Definition 🛍 Stal	bility Diagram 📓 Report 🚊 File '	Viewer	
🍓 Streams	Variable	Value	Type of diagram	
🚊 👌 Fe-H2O System	Stream Par			
🔤 🐺 Fe-H2O Pourbaix Diagram			Pourbaix Diagram 🔻 Specs	
	Stream Amount (mol)	55.5083		
Fe-H2O-H2S System	Temperature (°C)	25.0000	Calculate 🥥	
	Pressure (atm)	1.00000	Summary	
	Calculation P	arameters	Summary	
	Use Single Titrant	No	Unit Set: Metric (moles)	
	pH Acid Titrant	HCL		
	pH Base Titrant	NAOH	Automatic Chemistry Model	
		(mol)	Aqueous (H+ ion) Databanks: Corrosion (AQ)	
	H20	55,5082	Aqueous (H+ ion)	
	H2S	1.00000e-4	Redox selected	
	Fe	0.0	Using K-fit Polynomials	
	re	0.0	T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0	
Actions <u>a</u> • ×			1-3pan. 1.0 - 1000.0	
Actions	Contact Sur	face (mol)	Stability diagram: E vs pH	
100010	Fe		Auto-selected titrants	
			Acid:	

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.



Calculation Parameters

Inflows (mol)

Temperature (°C)

Use Single Titrant

pH Acid Titrant

pH Base Titrant

H20

H2S

Fe

Pressure (atm)

Go to the Redox button (Re), and click on the drop-down arrow Select Sulfur. This will turn the oxidation states of sulfur ON

No

HCL

NAOH

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

25.0000

1.00000

55.5082

0.0

1.00000e-4

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

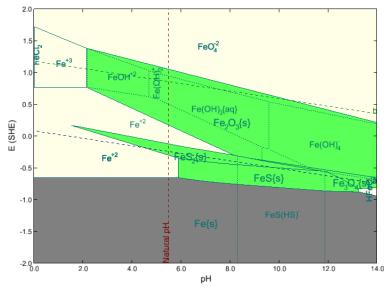
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🍂 Streams

Fe-H2O-H2S System

Click on the Chemical Diagram tab ( M Stability Diagram ). This tab displays the Pourbaix Diagram for the Fe-H2O-H2S system at 25 °C and 1 atm.



Inspection of the diagram reveals a profound effect of H<sub>2</sub>S on the corrosion of iron. New stability fields of FeS and FeS<sub>2</sub> are observed. Elemental iron is found to be in equilibrium with FeS over for pH values ranging from ca. 6.0 to 12.5.

Calc<u>u</u>late 🥝

Unit Set: Metric (moles)

Automatic Chemistry Model

Corrosion (AQ) Aqueous (H+ ion)

Using K-fit Polynomials

T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0

Redox selected

Aqueous (H+ ion) Databanks

Since the Fe/FeS equilibrium line lies below the H<sup>+</sup> reduction line (a), a process consisting of the reduction of H<sup>+</sup> to H<sup>0</sup> 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.

# **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 °C	
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			

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 **Add Stability Diagram** icon in the Actions Pane. Select the **AQ** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

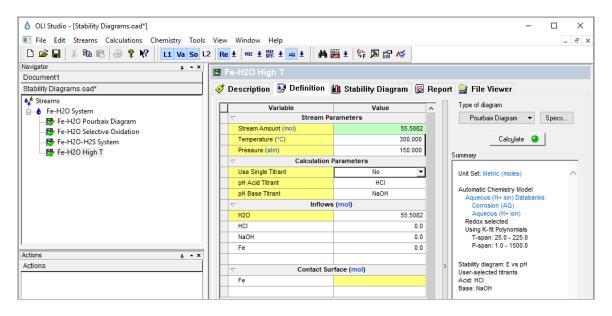
Enter the composition, temperature and pressure of the stream given in the table above

Select **Pourbaix Diagram** as Type of Survey – Default

Click on the new Stability Diagram and press <F2> to change the name to Fe-H2O High T

Under the Contact Surface grid type Fe

The screen should look like the image below after all the inputs and definitions have been entered:

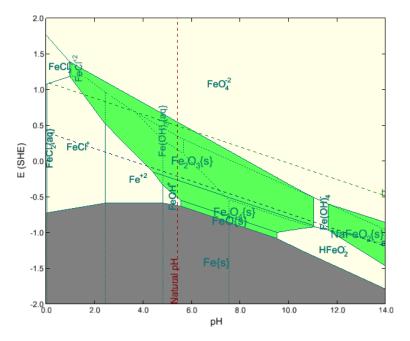


We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

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 °C 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 °C
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	HCI	0 moles (Acid Titrant)
		DEA <sup>9</sup>	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

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 **Add Stability Diagram** icon in the Actions Pane Select the **AQ** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition, temperature and pressure of the stream given in the table above

Select **Pourbaix Diagram** as Type of Survey – Default

Click on the new Stability Diagram and press <F2> to change the name to Fe-H2O-Alkanoamines

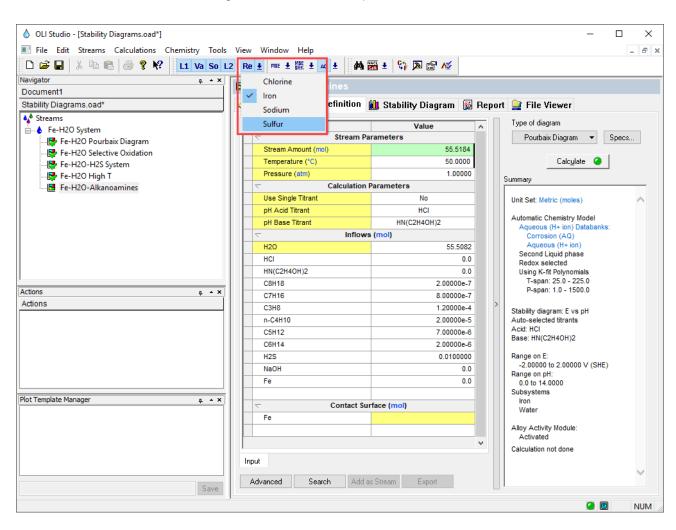
Under the Contact Surface grid type Fe

Change the Base Titrant to DEA

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.

<sup>&</sup>lt;sup>9</sup> 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



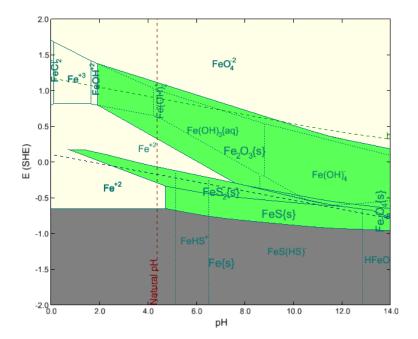
The screen should look like the image below after all the inputs and definitions have been entered:

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

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 °C and 1 atm.



# 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				
Calculat	Calculation Settings Stream Composition and Conditions			
Stream Name	Cu-H2O System	Stream Amount	Calculated	
Name Style	Display Formula	Temperature	25 ⁰C	
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	

## Add a new Stream

Click on the new Stream and press <F2> to change the name to Cu-H2O System

Select the **AQ** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition, temperature and pressure of the stream given in the table above

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 Select **Pourbaix Diagram** as Type of Survey – Default

**Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Cu-H2O-NH3* Under the **Contact Surface** grid type **Cu** 

The screen should look like the image below after all the inputs and definitions have been entered:

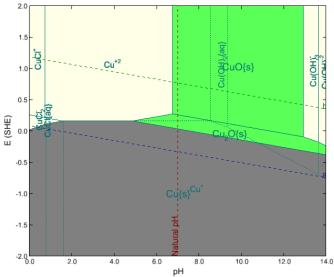
? Re	🛓 MSE 🛨 MSE 🛨 🗛 🛨 🎼 🚧 🖥	🎬 🛨 💱 🔊 😭 🎸	
	Cu-H2O-NH3 Complexation		Re
	Variable	Value	^
	Stream Part	rameters	
	Stream Amount (mol)	55.5082	
	Temperature (°C)	25.0000	
	Pressure (atm)	1.00000	
	Calculation F	Parameters	
	Use Single Titrant No		
	pH Acid Titrant	HCL	
	pH Base Titrant	NAOH	
		(mol)	
	H2O	55.5082	
	NH3	0.0	
	Cu	0.0	]
		face (mol)	
	Cu		

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

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 ( Mustability Diagram ). This tab displays the Pourbaix Diagram for the Cu-



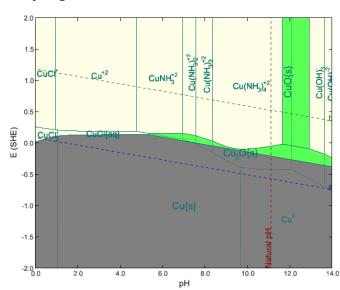
H20 system at 25 °C and 1 atm.

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

Go to the **Definition** tab, and change the amount of NH3 from 0 to 0.1 moles **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 °C and 1 atm in a 0.1 m of NH3 solution.

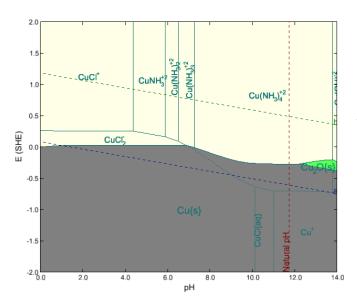
Notice that a large area of corrosive liquid has appeared in the stability field for the copper oxides. This means that it is thermodynamically possible for the ammonia to break down the passivation layer of copper oxide in the presence of oxygen. Notice that in the absence of oxygen (the  $\boldsymbol{a}$  line only), copper is still stable.

Now repeat the exercise with 1.5 moles of NH3

Go to the **Definition** tab, and change the amount of NH3 from 0 to 1.5 moles **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 °C 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 °C
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

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to Au-H2O System Select the AQ thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition, temperature and pressure of the stream given in the table above

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 Select **Pourbaix Diagram** as Type of Survey – Default

**Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Au-H2O* Under the **Contact Surface** grid type **Au** 

The screen should look like the image below after all the inputs and definitions have been entered:

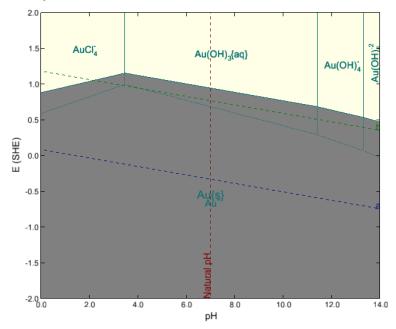
_		🗄 🛨 🚾 🛨 🛛 🊧 Irbaix Diagram	🎬 ± 💱 🔊 🖆 🔏	
1	Description	🥸 Definition	🛍 Stability Diagram 🚦	R
	V	ariable	Value	^
	$\nabla$	Stream F	arameters	
	Stream Amo	unt (mol)	55.508	2
	Temperature	e (°C)	25.000	0
	Pressure (at	im)	1.0000	0
	$\overline{\nabla}$	Calculation	Parameters	
	Use Single T	ïtrant	No	
	pH Acid Titra	ant	HCL	
	pH Base Titr	ant	NaOH	
	$\overline{\nabla}$	Inflow	/s (mol)	
	H2O		55.508	2
	NaCN		0.	0
	Au		0.	0
		-	·	
	$\nabla$	Contact S	urface (mol)	
	Au			

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

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 ( **U** Stability Diagram ). This tab displays the Pourbaix Diagram for the Au-H2O system at 25 °C 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.

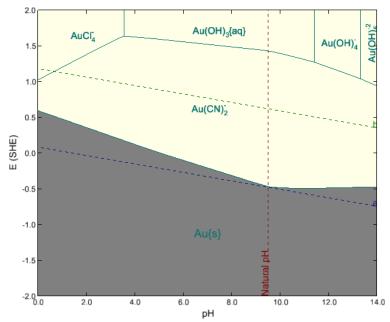
One of the most commonly used leaching processes for **gold extraction** is the **cyanidation** process. This process is a hydrometallurgical technique for extracting gold from low-grade ores by converting the gold to a water-soluble coordination complex. Basically, this approach adds cyanide salts to water. We are going to simulate this using the software.

## Effect of Cyanide on the Stability of Gold

Go to the **Definition** tab, and change the amount of NaCN from 0 to 1e-4 moles **Click** on the **Calculate** button or press the **<F9>** key

## Analyzing the Results

Click on the **Chemical Diagram** tab ( Use Stability Diagram ). This tab displays the Pourbaix Diagram for the Au-H2O-NaCN system at 25 °C 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.

# 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				
Calculat	tion Settings	Stream Composition and Conditions		
Stream Name	Inhibitors	Stream Amount	Calculated	
Name Style	Display Formula	Temperature	25 ⁰C	
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			

## Add a new Stream

Click on the new Stream and press <F2> to change the name to *Inhibitors* 

Select the AQ thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition, temperature and pressure of the stream given in the table above

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

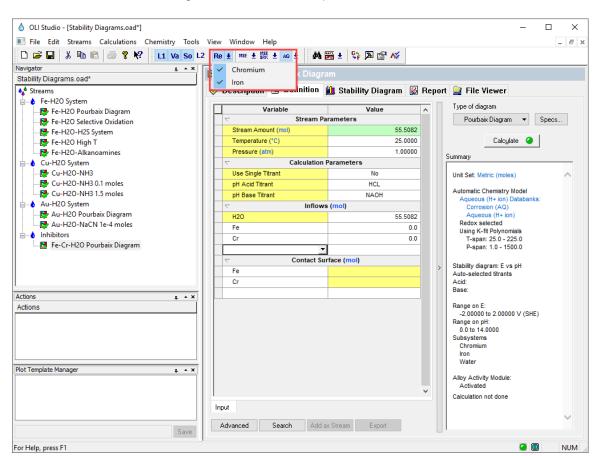
Select Pourbaix Diagram as Type of Survey – Default

Click on the new Stability Diagram and press <F2> to change the name to Fe-Cr-H2O Pourbaix Diagram

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:

**Click** the **Specs** button and under the Display Choices tab check the following options: No aqueous lines

## Show ORP

Stability Options		?	×
Category Display Axes Metal Activity	Display Choices Aqueous and Solid Lines Superimpose lines O Superimpose lines O No Aqueous lines O Only Aqueous lines Show natural pH Show ORP Display Subsystems Ochromium Chromium Fron M Water Potassium Sodium		
	OK Cancel Apply	Help	1

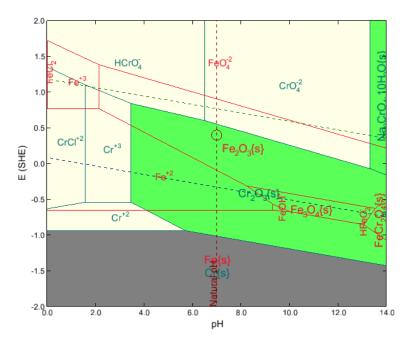
Click OK to close the Stability Options window

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

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 °C and 1 atm.



As you can see in this diagram, the shaded chrome passivating solid (Cr(OH)<sub>3ppt</sub>) 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<sup>2+</sup>, 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 ⁰C	
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			

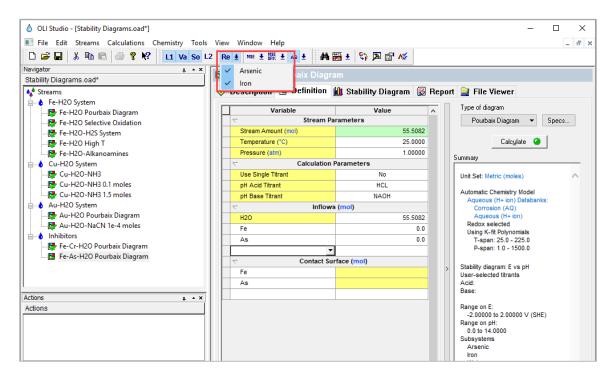
Under the *Inhibitors* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane Select **Pourbaix Diagram** as Type of Survey – Default

**Click** on the new *Stability Diagram* and press **<F2>** to change the name to *Fe-As-H2O Pourbaix Diagram* 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:



**Click** the **Specs** button and under the Display Choices tab check the following options: No aqueous lines Show ORP

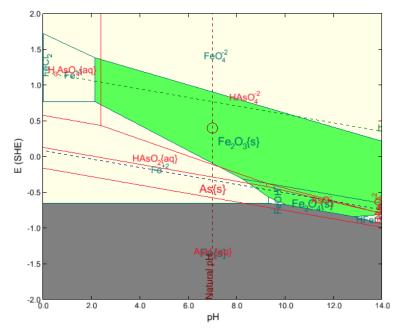
Stability Options		?	×
Category Cat	Display Choices Aqueous and Solid Lines Superimpose lines Only Aqueous lines Shade subsystem: Arsenic Iron Display Subsystems Same Arsenic Iron Water	2	
	OK Cancel Apply	Help	I

Click OK to close the Stability Options window

We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key 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 ( **U** Stability Diagram ). This tab displays the Pourbaix Diagram for the Fe-As-H2O system at 25 °C 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.

# 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 °C 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				
Calculat	tion Settings	Stream Composition and Conditions		
Stream Name	Cathodic Protection	Stream Amount	Calculated	
Name Style	Display Formula	Temperature	30 °C	
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			

## Add a new Stream

Click on the new Stream and press <F2> to change the name to Cathodic Protection

Select the AQ thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

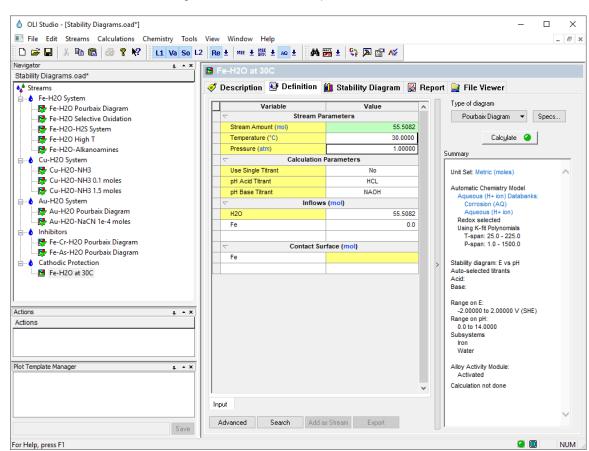
Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition, temperature and pressure of the stream given in the table above

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 Select **Pourbaix Diagram** as Type of Survey – Default

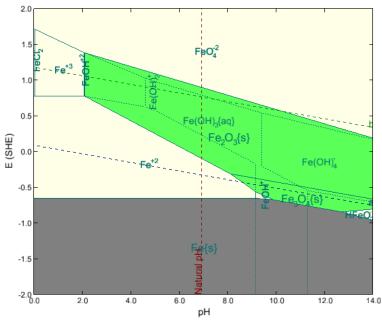
Click on the new *Stability Diagram* and press <F2> to change the name to *Fe-H2O at 30C and 1 atm* Under the **Contact Surface** grid type **Fe** 



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 °C and 1 atm.



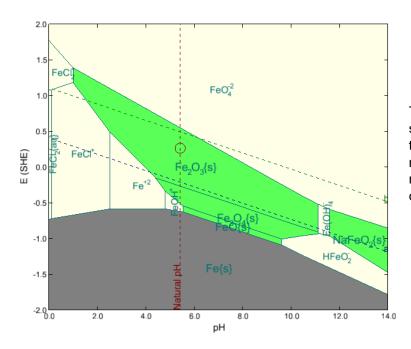
In the whole pH range, cathodic protection will require shifting the potential to moderately negative values.

## Iron at 300 °C and 100 atm

# Go to the **Definition** tab, and change the Temperature and Pressure to 300°C and 100 atm **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 °C and 100 atm.

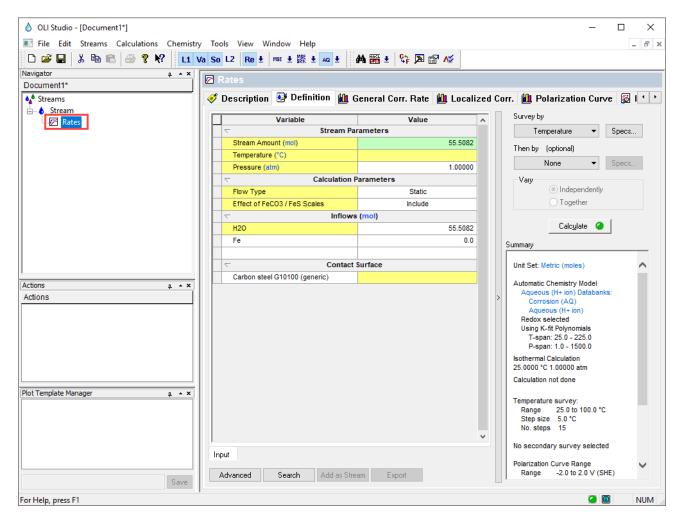


The immunity range in acidic and neutral solutions is weakly affected by temperature. However, the immunity range in alkaline solutions is shifted to much lower potentials which makes cathodic protection much more difficult.

# 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.



# 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. Note: As of version 11.5 and earlier, only the AQ thermodynamic framework supports the corrosion rate calculation.

## Example 50: Corrosion rate of an oxygenated 0.1 m NaCl solution

## Starting the Simulation

To start the software, double-click the OLI Studio icon on the desktop, which will take you to the OLI Studio 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				
Calcu	lation Settings	Stream Composition and Conditions		
Stream Name	CR of carbon steel	Stream Amount	Calculated	
Name Style	Display Formula	Temperature	25 ℃	
Unit Set	Metric, Batch, Moles	Pressure	1 atm	
Framework	AQ	H2O	55.5082 moles	
Calculation Type	Corrosion Rates	02	2.5e-4 moles	
Contact Surface	Carbon Steel G10100 (generic)	NaCl	0.1 moles	

## Add a new Stream

Click on the new Stream and press <F2> to change the name to CR of carbon steel

Select the AQ thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Moles

Enter the composition, temperature and pressure of the stream given in the table above

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.

👌 OLI Studio - [Corrosion Rates.oad*]			– 🗆 X				
I File Edit Streams Calculations Chemistry T	🗉 File Edit Streams Calculations Chemistry Tools View Window Help						
🗅 🚔 🖬 🐍 🗁 💡 📌 🛛 L1 Va So L2 Re ± MSE ± 驟 ± 🚾 ± 🚧 🎬 ± 💱 為 😭 ۸%							
Navigator + * X							
Corrosion Rates.oad*							
🏘 Streams	🦪 🖉 Description 🛃 Definition	General Corr. Rate 📶 Localize	ed Corr. 🛍 Polarization Curve 💷				
🚊 👌 CR of carbon steel			Survey by				
Single CR	Variable	Value					
	Stream Par	Temperature   Specs					
	Stream Amount (mol)	55.5085	Then by (optional)				
	Temperature (°C)						
	Pressure (atm)	1.00000	None   Specs				
	Calculation P	Vary					
	Flow Type	Static	<ul> <li>Independently</li> </ul>				
	Effect of FeCO3 / FeS Scales	Include	<ul> <li>Together</li> </ul>				
		(mol)					
	H2O	55.5082	Calc <u>u</u> late 🥝				
	02	2.50011e-4	Summary				
	NaCl	0.100000	Summary				
	-		Unit Set: <custom></custom>				
J	Contact S						
Actions # * ×	Carbon steel G10100 (generic)		Automatic Chemistry Model Aqueous (H+ ion) Databanks:				
Actions	··· /		Aqueous (ITT IOII) Databaliks.				

**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.

Contact Surface			
OLI Name	^		
Carbon steel G1010			
Carbon steel 1018			
Stainless steel 304			
Stainless steel 316			
Alloy 254SMO			
Dunley stainless 2205	~		
	OLI Name Carbon steel G1010 Carbon steel 1018 Stainless steel 304 Stainless steel 316 Alloy 254SMO		

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.

Calculation Parameters			
Flow Type	Static 🔽		
Effect of FeCO3 / FeS Scales	Static		
	Pipe Flow Rotating Disk		
H2O	Rotating Cylinder		
02	Complete Agitation		
NaCl	Defined Shear Stress Approximate Multiphase Flow		
Fe	0.0		

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.

#### Leave the default alloy Carbon steel G10100 (generic) as the contact surface

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.

2	기 Single CR					
1	Description 🔮 Definition 🚻	General Corr. Rate 🛍 Lo	calize	d C	orr. 🛍 Polarization Curve 🚺	
	Variable	Value	^	9	Survey by	
		ameters			Single Point Rate 🔻 Specs	
	Stream Amount (mol)	55.5085			Single Point Rate	
	Temperature (°C)	25.0000		4	Temperature	
	Pressure (atm)	1.00000			Pressure	
	Calculation P	arameters				
	Flow Type	Static			Composition	
	Effect of FeCO3 / FeS Scales	Include			рН	
		(mol)			Pipe Flow	
	H2O	55.5082			Rotating Disk	
	02	2.50011e-4		Sι	Rotating Cylinder	
	NaCl	0.100000		Ē.		
					Thermal Aging Temp.	
	Contact S	Surface			Thermal Aging Time	
	Carbon steel G10100 (generic)				Shear Stress	
			>		Liquid Flow in Pipe	
				11.1		

**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 like the pH survey available in OLI Studio: Stream Analyzer. The specification requires a titrant acid and base to change the pH.

*Temperature Survey* – The default range is from 25-100 °C. 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<sub>2</sub>.6H<sub>2</sub>O). 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.

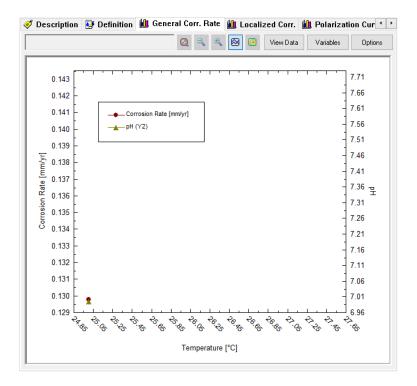
Flow Velocity Survey – In systems that are flowing, the flowrate of the stream can be varied.

Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

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

Click on the **General Corr. Rate** tab ( M General Corr. Rate ). This tab displays a plot showing the results of corrosion rate and pH.



Click on the View Data button to see the results in tabulated form.

	Temperature	Corrosion Rate	pН
	°C	mm/yr	
1	25.0000	0.129801	6.99516

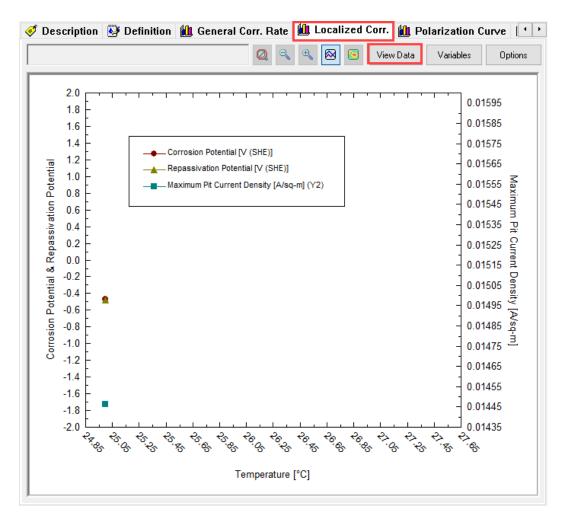
The predicted corrosion rate of carbon steel at 25 °C and 1 atm is ~0.13 mm/year when exposed to an oxygenated 0.1 m NaCl solution. It is important to highlight that this predicted corrosion rate is the corrosion rate once the system has reached a steady state.

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)

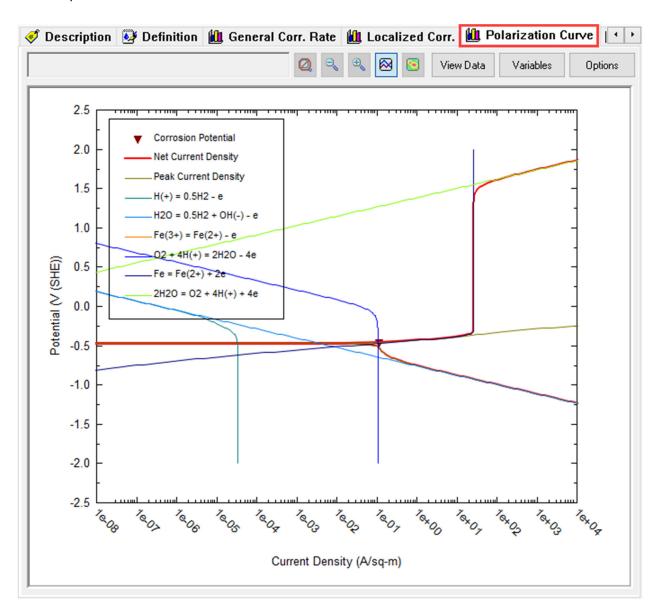


Click on the View Data button to see the results in tabulated form.

	Temperature	<b>Corrosion Potential</b>	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 °C 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.

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.

# Exploring corrosion rate calculation options

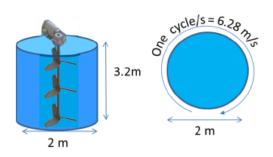
## Example 51: Corrosion in a Water-Filled Carbon Steel Tank

In the following example you are going to study the corrosion rate of a carbon steel tank with a volume of 10 m<sup>3</sup> 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:

Sometimes the water in the tank remains static (mixer off), closed to the atmosphere Some other times the tank is fully mixed (complete agitation) The tank when operating has a variable speed mixer with a rotation speed between 0 and 12,000 rpm 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 °C		
Name Style	Display Name	Pressure	1 atm		
Unit Set	Metric, Batch, Concentration	Water	Calculated		
Framework	AQ				
Contact surface	Carbon Steel G10100 (generic)				

Add a new Stream

**Click** on the new Stream and press **<F2>** to change the name to *CR vs flow* Select the **AQ** thermodynamic Framework

Click on the Names Manager Icon, and select the *Display Name* option, and click OK Click on the Units Manager Icon, and select the *Metric, Batch, Conc.* option, and click OK

Units Manager -	CR vs flow				?	×
Units Manager						
Metric	~	Batch	~	Conc.	~	·

In the Definition tab, notice that the units of the Stream Amount changed from moles (mol) to liters (L).

Enter the composition, temperature and pressure of the stream given in the table above Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane.

Change the Rates name to Static Flow, 25C using the <F2> key.

Leave the default Flow Type as Static

Leave the default alloy Carbon steel G10100 (generic) as the contact surface

**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.

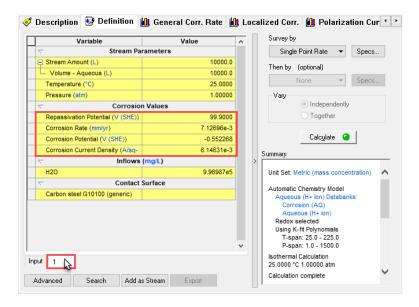
♦ OLI Studio - [Corrosion Rates.oad]								
File Edit Streams Calculations Chemistry Tools	View Window Help			_ & ×				
🗅 🖙 🖬 🐇 ங 💼 🥔 😵 🎌 🛛 L1 Va So L2 🛛 Re 🛨 🗰 🛨 🎆 🛨 🚾 🛨 👫 🎆 🛨 💱 🔎 🕼								
Navigator a 🔺 🗙	Z Static Flow, 25C							
Corrosion Rates.oad								
🏘 Streams	< Description 🦉 Definition	🛍 General Corr. Rate 🛍	J Loc	alized Corr. 🛍 Polarization Cur 🚹				
🗄 🔥 CR of carbon steel				Survey by				
CR vs flow	Variable	Value	^	Single Point Rate   Specs				
Static Flow, 25C	Stream Amount (L)	10000.0		Single Foint hate + Specs				
	Temperature (°C)	25.0000		Then by (optional)				
	Pressure (atm)	1.00000		None 👻 Specs				
	Calculation Parameters			Vary				
	Flow Type	Static		<ul> <li>Independently</li> </ul>				
	Effect of FeCO3 / FeS Scales	Include		<ul> <li>Together</li> </ul>				
	□ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □							
<u> </u>	H20			Calc <u>u</u> late 🥝				
Actions a * X	Fe	0.0		Summary				
Actions			>					
	Contact	Surface		Unit Set: Metric (mass concentration)				
	Carbon steel G10100 (generic)			Automatic Chemistry Model				
			Aqueous (H+ ion) Databanks:					
				Corrosion (AQ) Aqueous (H+ ion)				
				Redox selected				
Plot Template Manager 🛛 🖡 🔺 🗙		Using K-fit Polynomials T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0						
Input				Isothermal Calculation				
		25.0000 °C 1.00000 atm						
Advanced Search Add as Stream Export				Calculation not done				
Save	Haraitota Statelii Ada	export		,				

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

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

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 Change the **Rates** name to **Turbulent Flow**, **25C** using the **<F2>** key. Change the default Flow Type to **Complete Agitation** Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface Go to the **Survey by** option and select **Single Point Rate**.

8.1 Corrosion Rates - Example_b1.oad*	🦪 Description 🛃 Definition 🛍	General Corr. Rate 📶 Localize	d Corr. 🛍 Polarization Curve 👼 🕩
🗄 📿 Single CR	Variable	Value 🔺	Currey by
CR vs flow	🤝 🗠 Stream Par	rameters	Single Point Rate 🔻 Specs
🗄 🐼 Static Flow, 25C	Stream Amount (L)	1.00000	These has the family of
Turbulance Flow, 25C	<ul> <li>Density correlation</li> </ul>	Parent stream condition	Then by (optional)
	- Stream: Temperature (°C)	25.0000	None 👻 Specs
	Stream: Pressure (atm)	1.00000	Vary
	Temperature (°C)	25.0000	<ul> <li>Independently</li> </ul>
	Pressure (atm)	1.00000	<ul> <li>Together</li> </ul>
	Calculation P	arameters	
	Calculation Type	Isothermal	Calc <u>u</u> late 🥝
	Flow Type	Complete Agitation	Summary
Actions <u> </u>	Effect of FeCO3 / FeS Scales	Include	Summary
Actions		(mg/L)	> Unit Set: Metric (mass concentration)
	H2O		
	Fe	0.0	Automatic Chemistry Model Aqueous (H+ ion) Databanks:
			Corrosion (AQ)
	Contact S	Surface	Aqueous (H+ ion)

#### 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.

Variable	Value		~	Survey by
Stream Param	eters			Single Point Rate 🔻 Specs
Stream Amount (L)	100	0.00		Then by (optional)
Volume - Aqueous (L)	100	0.00		
Temperature (°C)	25.0	000		None   Specs
Pressure (atm)	1.00	000		Vary
Corrosion Va	lues			<ul> <li>Independently</li> </ul>
Repassivation Potential (V (SHE))	99.9	000		<ul> <li>Together</li> </ul>
Corrosion Rate (mm/yr)	0.0196	420		
Corrosion Potential (V (SHE))	-0.535	169		Calc <u>u</u> late 🥝
Corrosion Current Density (A/sq-	0.0169	394		Summary
Inflows (mg	/L)			>
H2O	9.9698	7e5		Unit Set: Metric (mass concentration)
Contact Surf	ace			Automatic Chemistry Model
Carbon steel G10100 (generic)				Aqueous (H+ ion) Databanks:
				Corrosion (AQ)
				Aqueous (H+ ion) Redox selected
				Using K-fit Polynomials
			- 1	T-span: 25.0 - 225.0
			~	P-span: 1.0 - 1500.0
at 1				Isothermal Calculation 25.0000 °C 1.00000 atm
				Calculation complete

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

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 Change the **Rates** name to **Varying Flow, 25C** using the **<F2>** key Go to the *Survey by* button and select **Rotating Disk** Under the **Calculation Parameters** grid. change the **Disk Diameter** to **200 cm** 

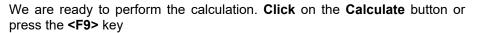
**Note:** At this point the vertical dimensions of the tank are unimportant. We will assume that the tank can be modeled like a rotating cylinder. The propeller rotates at 1200 rpm, although it is not expected that the wall velocity will approach this value, and so a lower value will be used (we still want it to be high enough to see the effects of shear).

The next step is to set the speed of the mixer. Go to the **Specs** button next to the **Rotating Disk** option Change the Disk Rotation Speed Range from 0 to 300 cycles/min with an increment of 10 cycles/min. Then click **OK**.

Category	Survey Range
Var. 1 - Disk Rotation Speed Polarization Curve Calculation Type Calculation Options	Disk Rotation Speed Range Unit: cycle/min Selected Range [00 to 300 tim 30 steps of 10.0
	Delete
	● Linear 🛛 Log 🔷 Point List
	End Points
	Start 0.0
	End 300.000
	Step Size
	Increment 10.0000      Select one, the other is
	Number Steps 30 O Scalculated

Leave the default alloy Carbon steel G10100 (generic) as the contact surface

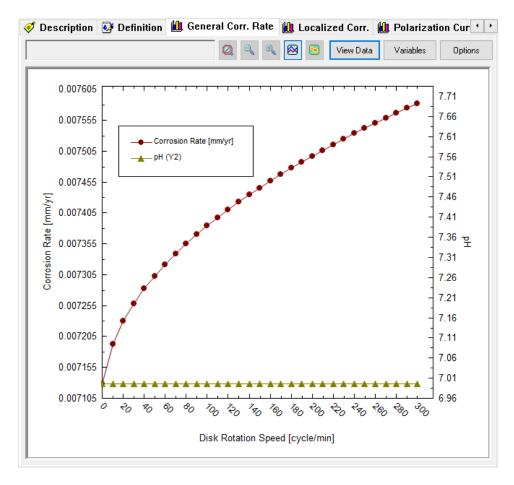
👌 OLI Studio (Version 11.5.1 Beta) - [8.1 Corrosion Ra	ates - Example_51.oad*]		– 🗆 X
File Edit Streams Calculations Chemistry	Tools View Window Help		_ & ×
🗅 😅 🖬   % 🖻 💼   🍜 💡 🕺 💶 🗤	So L2 Re ± MSE ± MSE ± AQ ±	🖫 🛨 💱 🔎 😭 🌾	
Navigator + *	Varying Flow, 25C		
8.1 Corrosion Rates - Example_51.oad*			
🏘 Streams	<li>Description 🤒 Definition 🛍 Generation</li>	eral Corr. Rate  🛍 Localized C	orr. 🛍 Polarization Curve 📓 🚺
🚔 👌 CR of carbon steel			Survey by
🗄 📿 Single CR	Variable	Value ^	
CR vs flow	E Stream Amount (L)	1.00000	Rotating Disk 👻 Specs
🗄 🐼 Static Flow, 25C		Parent stream condition	Then by (optional)
Turbulance Flow, 25C	Density correlation     Stream: Temperature (°C)	25.0000	None 👻 Specs
Varying Flow, 25C	Stream: remperature ( C)	1.00000	
	Temperature (°C)	25.0000	Vary     Independently
	Pressure (atm)	1.00000	
	Calculation Param		- r ogether
	Calculation Type	Isothermal	Calculate 🥝
	Flow Type	Rotating Disk	
	Disk Diameter (cm)	200.000	Summary
	Disk Rotation Speed (cycle/min)	200.000	Unit Set: Metric (mass concentration)
	Effect of FeC03 / FeS Scales	Include	onit Set. Metric (mass concentration)
			Automatic Chemistry Model
	H20	-/	Aqueous (H+ ion) Databanks: Corrosion (AQ)
Actions	Fe	0.0	Aqueous (H+ ion)
Actions			Redox selected
	Contact Surfac	> >	Using K-fit Polynomials T-span: 25.0 - 225.0
	Carbon steel G10100 (generic)		P-span: 1.0 - 1500.0
			Isothermal Calculation
			25.0000 °C 1.00000 atm
			Calculation not done
			Rotating Disk survey:
			Range 0.0 to 300.0 cycle/min
			Step size 10.0 cycle/min
			No. steps 30
Plot Template Manager 🔒 🔺 🖌			No secondary survey selected



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 ( Mu 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.

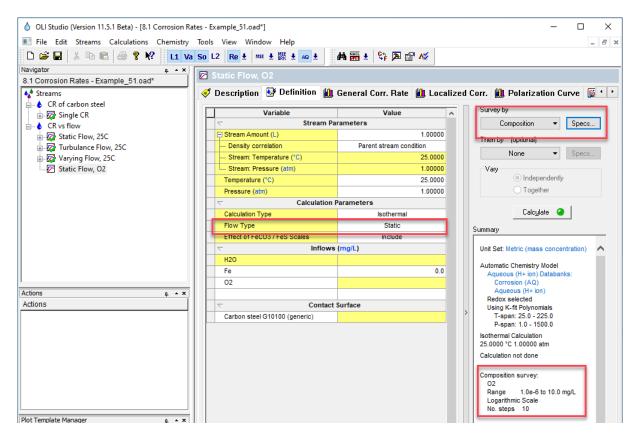
Under the stream '*CR vs Flow*' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane Change the **Rates** name to **Static Flow, O2** using the **<F2>** key **Add** Oxygen (O2) to the inflow grid Leave the default Flow Type as **Static Composition Go** to the *Survey by* button and select **Composition** 

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.

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**.

Composition Rates Calculation	on	? ×	Composition Rates Calculation	I.	?	×
Category Var. 1 - Composition Polarization Curve Catculation Type Catculation Options	Component Survey Range Component Inflows Hide Related Inflows Fe 02 Select a component inflow which will be varied over	New Inflow	Category Var. 1 - Composition Polarization Curve Catculation Type Catculation Options	Component Survey Range Component Survey Range Selected Range 106-6 to 10.0 in 10 steps of 1.0 C Linear  C Linear	Unit: mg/L Delet Point List Select one, the other is Select one, the other is	
	OK Cancel	Apply Help		OK C	Cancel Apply H	lelp

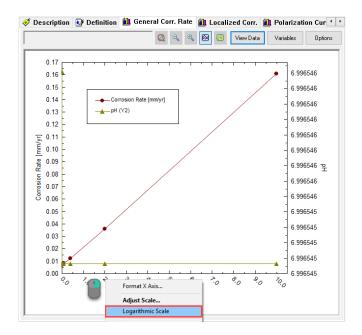
Leave the default alloy Carbon steel G10100 (generic) as the contact surface



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

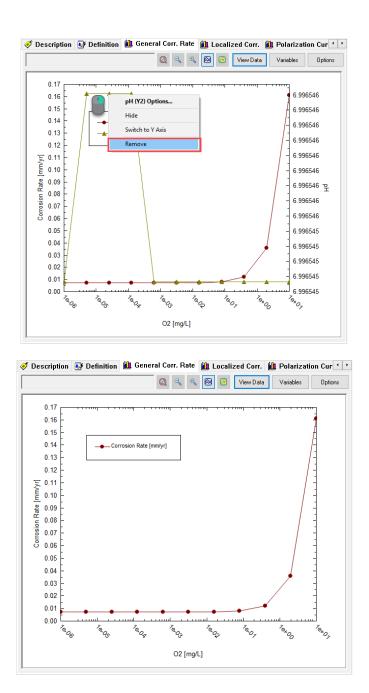
#### Analyzing the Results

Click on the **General Corr. Rate** tab ( Mu General Corr. Rate ). This tab displays a plot showing the results of corrosion rate and pH.



Right-mouse click on the X-axis and change it to Logarithmic Scale

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  $\mu$ g/l. Aerated water contains approximately 8 mg/l O<sub>2</sub>. 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<sub>2</sub> and CO<sub>2</sub>) at ambient conditions

The atmosphere contains ~400 ppmV CO<sub>2</sub>. At this concentration 0.6 mg/l CO<sub>2</sub> is dissolved in water as molecular CO<sub>2</sub>, this CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> impact, you will recalculate the corrosion rate using two CO<sub>2</sub> concentrations: 0 and 0.6 ppm.

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 Change the **Rates** name to **Static Flow, O2 and CO2** using the **<F2>** key **Add** Oxygen (O2) and carbon dioxide (CO2) to the inflow grid Leave the default Flow Type as **Static** 

Go to the *Survey by* button and select Survey by **Composition** and then by **Composition** (as shown below)

Survey by			
Compos	ition	•	Specs
Then by (opti	ional)		
Compos	ition	•	Specs
Vary	Indepen	dently	
	Togethe		•

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.

Under the **Category** section, make sure to select **Var. 1** -**Composition**. Go to the **Component** tab, and select O2

Composition Rates Calculatio	n	?	×
Calegory Var. 1 - Composition - Var. 2 - Composition - Polarization Curve - Calculation Type - Calculation Options	Component Survey Range Component Inflows CD2 Fe D2 Select a component inflow which will be varied over the	New Inflow	
	OK Cancel Appl	y Help	,

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**.

Composition Rates Calculatio	n	?	×
Category Var. 1 - Composition Var. 2 - Composition Polarization Curve – Calculation Type – Calculation Diptions	Component Survey Range Composition Range Unit: mg/L Selected Range 10.0e-6 to 10.0 in 10 steps of 1.0	New Delete	
	O Linear ● Log O Point List End Points Start 1.00000e-6 End 10.0000 Step Size Increment 1.0000 ○ Select one, Number Steps 10 ◎ Select one,	the other is	
	OK Cancel Apply	Help	

Under the Category section, select Var. 2 -Composition. Go to the Component tab, and select CO2

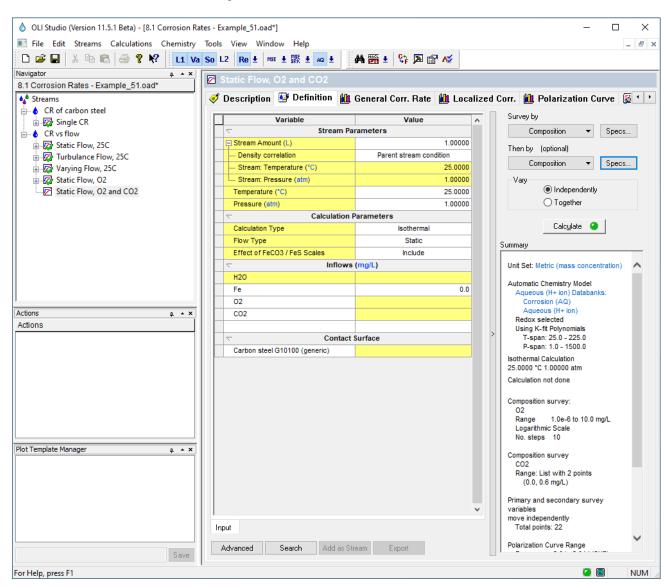
Category     Component Survey Range       Var. 1 - Composition     Component Inflows       Polarization Curve     Component Inflows       Calculation Options     Hide Related Inflows       Cicl     Fe       02     02
Select a component inflow which will be varied over the specified range.

Then select the **Survey Range** tab. Select the Point List option. Create two points with values of 0 and 0.6 mg/L. Then click **OK**.

Category	Component Survey Range		
War. 1 - Composition     War. 2 - Composition     Polarization Curve     Calculation Type     Calculation Dptions	Composition Range Unit: mg/L Selected Range Point List: 0.0 to 0.0	New Delete	
	◯ Linear ◯ Log		
	Value           1         0.0           2         0.0	Add Point Remove Pts	

Leave the default alloy Carbon steel G10100 (generic) as the contact surface

Your screen should look like the image below.



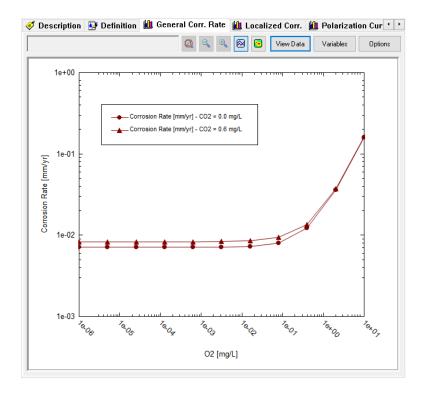
We are ready to perform the calculation. Click on the Calculate button or press the <F9> key

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 ( M General Corr. Rate ). This tab displays a plot showing the results of corrosion rate and pH.

Right-mouse click on the X-axis and change it to Logarithmic Scale Right-mouse click on the Y-axis and change it to Logarithmic Scale Right-mouse click on the pH curve and select Remove Series



The effects of CO<sub>2</sub> are small, particularly in relation to the oxygen effects. The Corrosion rates at low O<sub>2</sub> content are about 0.0071 mm/yr with no CO<sub>2</sub> and 0.0083 mm/yr with 0.6 mg/l CO<sub>2</sub>; a small difference between two small rates. At 10 mg/l O<sub>2</sub> the corrosion rate is 0.16 mm/y and it is the same with and without CO<sub>2</sub>. Thus, CO<sub>2</sub> has no effect on corrosion at high O<sub>2</sub> concentrations meaning that the surface is corroded by oxygen and small concentrations of CO<sub>2</sub> does not change this rate.

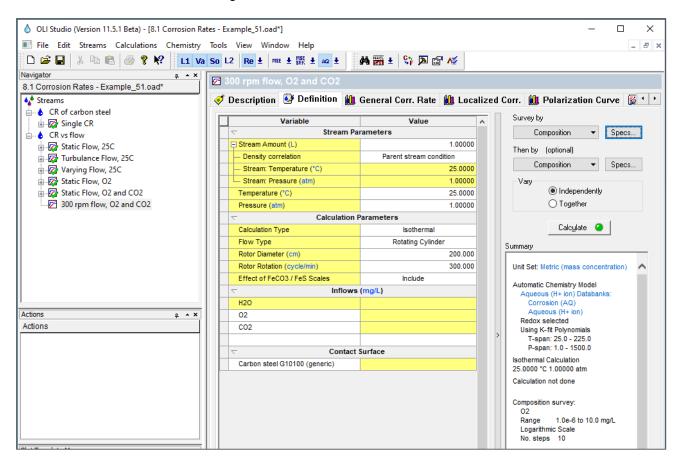
Sixth operation condition: 300 cycles/min flow, tank open to the atmosphere (aerated with  $O_2$  and  $CO_2$ ) at ambient conditions

Lastly, you will look at the effects of shear rates on the tank in contact with CO2 and O2.

**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*'

🍫 Streams			🍫 Streams	
🚊 💧 CR of carbon steel			🚊 👌 CR of carb	bon steel
👜 🐼 Single CR			🗈 🐼 Single	
🗄 👌 CR vs flow			📩 🔥 CR vs flow	
🗄 🐼 Static Flow, 250	0		🌐 🌠 St	Arrange >
🗉 🐼 Turbulent Flow			🕕 🐼 Ti	Cut
👜 🐼 Varying Flow, 2	25C		🖮 🌠 Vi	
🛓 🐼 Static Flow, O2			🎰 🐼 St 🔜	Сору
🕀 🐼 Static Flow, 🕰	and CO2		🗄 😡 St	Paste
	Arrange	>		Delete
	Cut			Rename
	Сору			
	Paste			Add As Stream
				Clear Results
	Delete			Clear Status

Change the *Static Flow, O2 and CO2-1* name to *300 rpm flow, O2 and CO2* using the <F2> key Add Oxygen (O2) and carbon dioxide (CO2) to the inflow grid Change the Flow Type from *Static* to *Rotating Cylinder* Set the Rotor Diameter to 200 cm Set the Rotor Rotation to 300 cycles/min Leave the default alloy Carbon steel G10100 (generic) as the contact surface



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

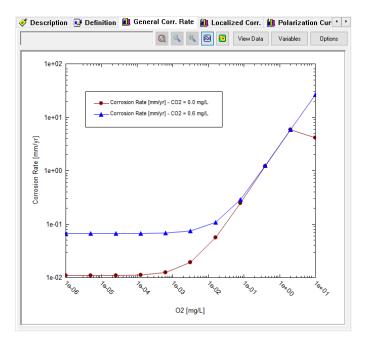
#### Analyzing the Results

Click on the General Corr. Rate tab ( Mu General Corr. Rate ). This tab displays a plot showing the results of corrosion rate and pH.

Right-mouse click on the X-axis and change it to Logarithmic Scale Right-mouse click on the Y-axis and change it to Logarithmic Scale Right-mouse click on the pH curve and select Remove Series Double click on the CO2=0.6 mg/L. This will open a new window. Change the color to blue.

urve Properties			?	×
Curves				
Corrosion Rate [mm/yr] - C Corrosion Rate [mm/yr] - C				
Auto Legend Text			 	
Corrosion Rate [mm/yr	] - CO2 = 0.6 mg/L			
Auto Line Style	Auto Line Weight	Auto Color		<b>_</b>
Auto Symbol	Auto Scaling Factor	Hidden		
Filled Triangle V	4			

The plot should look like the image below.



The 0.6 mg/L CO<sub>2</sub> curve shifted to higher values at low O<sub>2</sub> concentrations compared to no CO<sub>2</sub> presence. Now, when comparing the corrosion rate for the 0.6 mg/L CO<sub>2</sub> 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<sub>2</sub> concentrations (right side of the plot) is also pronounced. Corrosion is still dominated by O<sub>2</sub> attack, but the rate is now over 10 mm/year, about 100x greater than the static conditions.

## 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 ⁰C	
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	

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to Gas Condensate

Select the **AQ** thermodynamic Framework

Click on the Names Manager Icon and select the Formula option

Click on the Units Manager Icon, and select Metric, Batch, Mole Fraction

Enter the composition, temperature and pressure of the stream given in the table above

Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane.

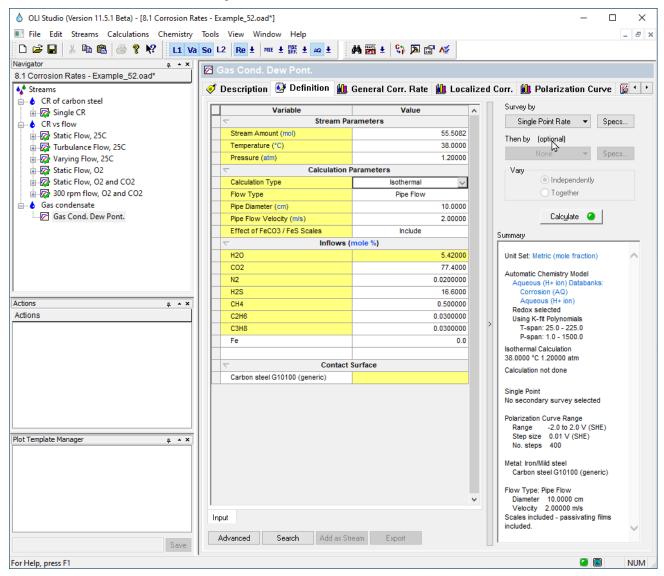
Go to the Survey by option and select Single Point Rate. Change the name to Gas Cond. Dew Point.

Change the Flow Type from Static to Pipe Flow.

Specify the Pipe Diameter = 10 cm and the Pipe Flow Velocity = 2 m/s.

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.

Click on the Specs button. This will open a new window

#### Under the Category section, select Calculation Type

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**. Notice that the input grid has been updated:

Calculation Parameters					
Calculation Type	Dew Point 🗸				
Calculate	Temperature				
Flow Type	Pipe Flow				
Pipe Diameter (cm)	10.0000				
Pipe Flow Velocity (m/s)	2.00000				
Effect of FeCO3 / FeS Scales	Include				
Inflows (m	aolo VI				

You could have also used the drop-down arrow next to the "Calculation Type" box to directly pick a dew point (or any other required) calculation type.

Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key 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 ( M General Corr. Rate ).

Click on the View Data button to see the results in tabulated form.

	Temperature	Corrosion Rate	pН
	°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.

Click on the **Polarization Curve** tab ( Polarization Curve). Before interpreting this plot, we will format it for easy viewing.

Click on the **Options** button. This will open a new window.

l	🗓 Po	larization C	urve	👼 Re	port	1	۲
3	<b>5</b>	View Data	Var	iables	Op	otions	

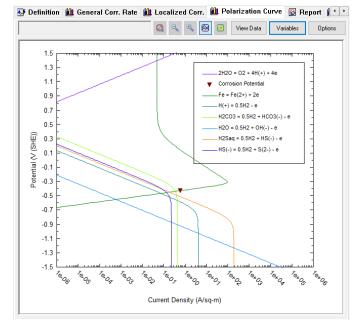
Under the **Category** section select **X** axis. Change the **Minimum** to 1e-6 and **Maximum** to 1e6. Now, select **Y** axis. Change the **Minimum** to -1.5 and **Maximum** to 1.5. Then **click OK**. Click on the **Variables** button. This will open a new window.



Select Data To Plot ?  $\times$ Survey Points & Reactions Half-Reactions O2 + 4H(+) + 4e on Potential Fe(3+) = Fe(2+) - e 2CO3 = 0.5H2 + HCO3(-) - e 20 = 0.5H2 + OH(-) - e 12Saq = 0.5H2 + HS(-) - e = 0.5H2 + S(2-) - e Net Current Density O2 + 4H(+) = 2H2O - 4e Peak Current Density Clear all reactions Select all reactions OK Cancel Apply Help

Remove the following variables by unchecking them. See image below. Then  $\ensuremath{\text{Click OK}}$  .

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<sup>2</sup>.

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

**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.

Change the name to **DEA** using the **<F2>** key.

Add DEA in the inflows grid. (It should have changed to the formula name: HN(C2H4OH)2 Go to the Type of Calculation option and select Set pH Change the Target pH to 7.5 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.

Document1	• × 💧 🗋			
Corrosion Rates.oad*		Description 🧕 Definition	👼 Report 🚊 File Viewer	
🔥 Streams		Variable	Value	Type of calculation
CR of carbon steel			arameters	Set pH
CR vs flow		Stream Amount (mol)	1.00000e5	opode
Gas Condensate		Temperature (°C)	38.0000	Calculate 🥝
A DEA		Pressure (atm)	1.20000	Summary
		Calculation	Parameters	Summary
	•	Target pH	7.50000	Unit Set: Metric (mole fraction)
		Use Single Titrant	No	Automatic Chemistry Model
		pH Acid Titrant	HCL	Aqueous (H+ ion) Databanks:
		pH Base Titrant	HN(C2H4OH)2	Aqueous (H+ ion)
		√ Inflows	(mole %)	Using K-fit Polynomials T-span: 25.0 - 225.0
		H2O	5.42000	P-span: 1.0 - 1500.0
		CO2	77.4000	Set pH Calculation
		N2	0.0200000	38.0000 °C 1.20000 atm
· · ·	* ×	H2S	16.6000	Target pH 7.50000
ctions		CH4	0.500000	Acid Titrant:
		C2H6	0.0300000	Base Titrant: HN(C2H4OH)2
		C3H8	0.0300000	Calculation not done
		HN(C2H4OH)2	0.0	
ot Template Manager a	• X			
			¥	
	Inp	ut		
				$\sim$
	ave A	Advanced Search Add	as Stream Export	

Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

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

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.

## Click on the Report Tab and go to the Total and Phase Flows and Species Output tables

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
С3Н8	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

Total and Phase Flows (Amounts) olumn 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

Recalculating the corrosion rate with DEA

We first need to capture the condensate from the DEA pH calculation. We want only the liquid portion to perform our corrosion rate calculation. This would represent the first drop of condensate from the gas stream.

OLI Studio (Version 11.5.1 Beta) - [8.1 Corrosion R	ates - Example_52.oad*]		- 0	×
File Edit Streams Calculations Chemistry	Tools View Window Help			- 8 ×
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8.1 Corrosion Rates - Example_52.oad*	A DEA			
🎄 Streams	< Description 🔮 Definition 📓	Report 🚊 File Viewer		
En of carbon steel	Variable	Value A	Type of calculation	
En Single CK	Stream Par		Set pH 👻 Specs.	
Static Flow, 25C	Stream Amount (mol)	1.0000e5		_
Turbulance Flow, 25C	Temperature (°C)	38.0000	Calc <u>u</u> late 🥝	
Varying Flow, 25C	Pressure (atm)	1.20000	Summary	
🖶 🌠 Static Flow, O2	Calculation P		Summary	
😥 🐼 Static Flow, O2 and CO2	Target pH	7.50000	Unit Set: Metric (mole fraction)	^
300 rpm flow, O2 and CO2	Use Single Titrant	No		
🖃 🔥 Gas condensate	pH Acid Titrant	HCI	Automatic Chemistry Model Aqueous (H+ ion) Databanks:	
Gas Cond. Dew Pont.	pH Base Titrant	HN(C2H4OH)2	Aqueous (H+ ion) Databaliks.	
DEA	□ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □		Using K-fit Polynomials	
	H2O	5.42000	T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0	
J	C02	77,4000	Set pH Calculation	
Actions	N2	0.0200000	38.0000 °C	
Actions	H2S	16.6000	1.20000 atm	
	CH4	0.50000	Target pH 7.50000 Acid Titrant: HCI	
	C2H6	0.0300000	Total: 0.0 mole %	
	C3H8	0.0300000	Base Titrant: HN(C2H4OH)2	
	HN(C2H4OH)2	0.0	Total: 5.97097e-4 mole % Added: 5.97097e-4 mole %	
	HCI	0.0	Phase Amounts	
		0.0	Aqueous 31.6197 mol	
			Vapor 99968.5 mol	
Plot Template Manager 🛛 🖡 🔺 🗙			Solid 0.0 mol	
			Aqueous Phase Properties	
			pH 7.50001	
			lonic Strength 0.0160371 mol/mol Density 1.02648 g/ml	
		k v		
	Input Output	43	Calc. elapsed time: 0.111 sec	
			Calculation complete	$\sim$
Save	Advanced Search Add as Str	eam Export		
Save				
× P-span: 1.0 - 1500.0				
•				
문 문 Calculating Rates for 1 of 1				
Calculating Rates for 1 of 1 Calculation Complete!				
				$\checkmark$
For Help, press F1			<b>a</b> E	NUM

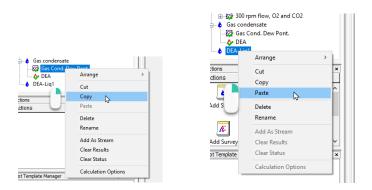
#### Click the Add as Stream button

Save Selected Result	Streams	?	$\times$
Export Name: DEA-Liq1 Include the followin	ng phases in the st	ream(s)	
Aqueous	Vapor		
Second Liquid	Solids		
Optional Phases that are no separately.	ot included may be	exported	
Aqueous			
Second Liquid			
Solid			
	ОК	Car	ncel

Uncheck the following boxes: **Second Liquid, Vapor,** and **Solids.** This removes these phases from the saved stream. Click the **OK** button

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.

 Copy 'Gas Cond. Dew Point' corrosion calculation from the <u>Gas condensate</u> stream, and paste it under the stream '<u>DEA-Liq1</u>'



Change the name to *Gas Cond. Dew Point DEA* using the <F2> key

The added DEA is already in the inflows gird.

Leave the default alloy **Carbon steel G10100 (generic)** as the contact surface Change the calculation type to **Isothermal** 

OLI Studio (Version 11.5.1 Beta) - [8.1 Corrosion Ra	ites - Example_52.oad*]		- 0	×
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Navigator + ×				
8.1 Corrosion Rates - Example_52.oad*	🖻 Gas Cond. Dew PontDEA			
CR of carbon steel	🛷 Description 🤒 Definition 🛍 G	Separal Corr. Date 🏙 Localized	Corr MI Polarization Curve	<b>5</b> • •
Single CR	V Description 🔄 Somition 🛄 C			<u>2</u>
	Variable	Value A	Survey by	
Burger Static Flow, 25C	Stream Para	ameters	Single Point Rate 🔻 Spec	s
Turbulance Flow, 25C	Stream Amount (mol)	32.0613	Then by (optional)	
🗄 📈 Varying Flow, 25C	Temperature (°C)	38.0000		
🗄 📈 Static Flow, O2	Pressure (atm)	1.20000	None 👻 Spec	\$
🗄 🐼 Static Flow, O2 and CO2	Calculation Pa	remotore	Vary	
	Calculation Type	Isothermal 🗸	<ul> <li>Independently</li> </ul>	
🖨 🖕 Gas condensate	Flow Type	PIPE FIOW	<ul> <li>Together</li> </ul>	
	Pipe Diameter (cm)	10.0000		
DEA	Pipe Flow Velocity (m/s)	2.00000	Calculate 🥥	
E DEA-Liq1	Effect of FeCO3 / FeS Scales	Include	Summary	
🗄 - 🌠 Gas Cond. Dew PontDEA 🗸 🗸	🖂 🗠 Inflows (n	nole %)		
1 dellara	H2O	96.5139	Unit Set: Metric (mole fraction)	^
Actions # * X	C02	1.41875	Automatic Chemistry Model	
Actions	N2	2.53014e-7 >	Aqueous (H+ ion) Databanks:	
	H2S	0.206530	Corrosion (AQ)	
	CH4	1.35263e-5	Aqueous (H+ ion) Redox selected	
	C2H6	8.96017e-7	Using K-fit Polynomials	
	C3H8	6.96702e-7	T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0	
	HN(C2H4OH)2	1.86081		
	Fe	0.0	Isothermal Calculation 38.0000 °C 1.20000 atm	
			Calculation complete	
Plot Template Manager # * ×	Contact S	urface		
	Carbon steel G10100 (generic)		Single Point	
			No secondary survey selected	
		~	Polarization Curve Range	
	Input 1		Range -2.0 to 2.0 V (SHE)	
	mpac		Step size 0.01 V (SHE) No. steps 400	U
	Advanced Search Add as Stre	am Export		Ť
Save				
× P-span: 1.0 - 1500.0	-			
P-span: 1.0 - 1500.0				^
Calculation Dates for 1 of 1				
Calculating Rates for 1 of 1 Calculation Complete!				
Calc				*
For Help, press F1			<b>2</b> 🗐	NUM //

Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

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 ( M General Corr. Rate ).

Click on the View Data button to see the results in tabulated form.

	Temperature	Corrosion Rate	pН
	°C	mm/yr	
1	38.0000	0.480601	7.50001

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 like 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

Copy 'Gas Cond. Dew Point' corrosion calculation, and paste it under the stream 'Gas Condensate'

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.

#### Change the contact surface to Super13%Cr stainless steel

OLI Studio (Version 11.5.1 Beta) - [8.1 Corrosion Ra	tes - Example 52 gad*1		- 0	×
File Edit Streams Calculations Chemistry				- 8 ×
🗅 😅 🖬 👗 🛍 🛍 🎒 💡 💦 💶 Va	So L2 Re ± MSE ± MSE ± AQ ±	🚧 🎬 🛃 💱 🔊 😭 🌾		
Navigator 🛛 🖡 🔺 🗙	Gas Cond. 13%Cr			
8.1 Corrosion Rates - Example_52.oad*				
😥 🐼 Single CR 📃 🔨	< Description 🤮 Definition 🚻	General Corr. Rate 🛍 Localized	Corr. 🛍 Polarization Curve	۰ ا 👰
CR vs flow	Variable	Value	Survey by	
Italian Construction Construction Construction     Italian Construction Construction Construction Construction     Italian Construction Construction Construction Construction	Stream Pa		Single Point Rate 🔻 Spec	
Varying Flow, 25C	Stream Amount (mol)	1.0000e5		
Static Flow, O2	Temperature (°C)	38.0000	Then by (optional)	_
Burger Static Flow, O2 and CO2	Pressure (atm)	1.20000	None 🔻 Spec	S
300 rpm flow, O2 and CO2	Calculation F	arameters	Vary	
🖃 👌 Gas condensate	Calculation Type	Dew Point	<ul> <li>Independently</li> </ul>	
	Calculate	Temperature	<ul> <li>Together</li> </ul>	
DEA	Flow Type	Pipe Flow		
Gas Cond. 13%Cr 🗸	Pipe Diameter (cm)	10.0000	Calc <u>u</u> late 🥝	
Actions	Pipe Flow Velocity (m/s)	2.00000	Summary	
Actions	T Inflows (	mole %)		_
	H2O	5.42000	Unit Set: Metric (mole fraction)	^
	C02	77.4000	Automatic Chemistry Model	
	N2	0.0200000	Aqueous (H+ ion) Databanks:	
	H2S	16.6000	Corrosion (AQ)	
	CH4	0.500000	Aqueous (H+ ion) Redox selected	
	C2H6	0.0300000	Using K-fit Polynomials	
	C3H8	0.0300000	T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0	
	Fe	0.0	Dew Point Calculation	
			1.2000 atm	
	Contact	Surface	Calculation not done	
Plot Template Manager # * ×	Super13Cr stainless steel 🗸			
			Single Point	
			No secondary survey selected	
		~	Polarization Curve Range	
	Input		Range -2.0 to 2.0 V (SHE) Step size 0.01 V (SHE)	
	in post		No. steps 400	$\sim$
Save	Advanced Search Add as Str	eam Export	1	
Save				
× P-span: 1.0 - 1500.0				^
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Calculating Rates for 1 of 1			Ţ	
Calculating Rates for 1 of 1 Calculation Complete!				
3				¥
For Help, press F1			🥥 🔳	NUM /

Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key

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 **Report** tab to see the results. (You may need to use the ◀► buttons to move the tabs and find the Report tab).

Go to the Calculated Rates table

	~		0 9	Customize Export
СЗН8	0.0300000 0.0	300000		,
			-	
Calculated Rates				
			1	
Corrosion Rate	1.20223e-3	mm/yr		
Corrosion Rate Corrosion Potential	1.20223e-3 -0.263434	mm/yr V (SHE)		
		-		

The corrosion rate of Super 13%Cr is several orders of magnitude lower when compared to the corrosion rate for Carbon Steel, i.e. at 0.0012 mm/year for 13%Cr vs 0.7 mm/year for Carbon Steel. This is consistent with the use of Super 13% Cr to protect against  $CO_2$  corrosion.

Click on the **Polarization Curve** tab ( <sup>M Polarization Curve</sup>).

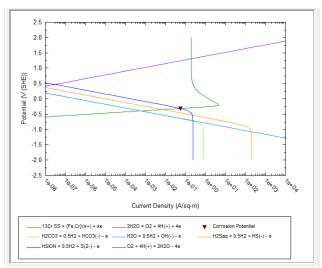
Click on the Variables button. This will open a new window.

🛍 Polarization Curve			📓 Report 🚺 🕐		
3 🖻	View Data	Var	iables	Op	otions

Remove the following variables by unchecking them. See image below. Then Click OK.

elect Data To Plot	?	$\times$
Survey Points & Reactions		
Half-Reactions		
13Cr SS = {Fe,Cr}(x+) + xe		
2H2O = O2 + 4H(+) + 4e Corrosion Potential		
Fe(3+) = Fe(2+) - e		
H(+) = 0.5H2 - e		
H2CO3 = 0.5H2 + HCO3(-) - e		
H2O = 0.5H2 + OH(-) - e		
H2Saq = 0.5H2 + HS(-) - e		
HSION = 0.5H2 + S(2-) - e		
Net Current Density		
02 + 4H(+) = 2H2O - 4e		
Peak Current Density		
Clear all reactions Select all reactions		
OK Cancel Ac	ply	Help

The polarization curve (after some layout modifications) should look like the image below.

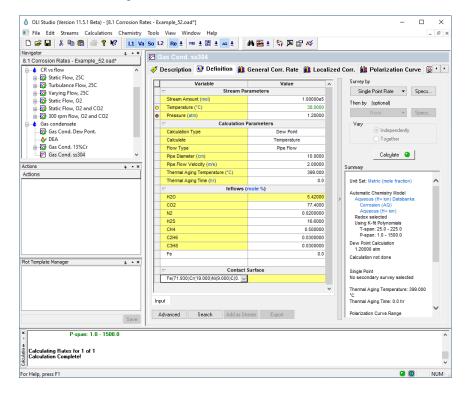


The layout of the plot was changed for easy reading. To change layout, you can right click on any part of the plot and select the option *Alloy Layout Changes* to modify the appearance of your plot.

The corrosion potential of Super 13%Cr is -0.25 V vs SHE and the corresponding corrosion current  $i_{corr}$ =0.001A/m<sup>2</sup>. The  $i_{corr}$  for Carbon Steel was 0.61 A/m<sup>2</sup>, this means that 13%Cr is 10x more resistant to corrosion under the same conditions.

Stainless Steel 304

**Copy** 'Gas Cond. Dew Point' corrosion calculation, and **paste** it under the stream 'Gas Condensate' Change the name to **Gas Cond. SS304** using the **<F2>** key **Change** the **contact surface** to Stainless Steel 304



Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key 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 **Report** tab to see the results. (You may need to use the ◀► buttons to move the tabs and find the Report tab).

Go to the Calculated Rates table

#### Calculated Rates

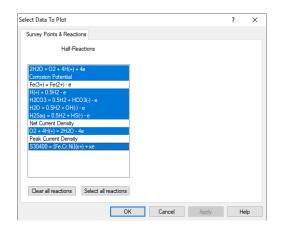
Corrosion Rate	2.40183e-3	mm/yr
Corrosion Potential	-0.293505	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	2.21614e-3	A/sq-m

The corrosion rate of 304 SS is now 0.0024 mm/year. This is a negligible value.

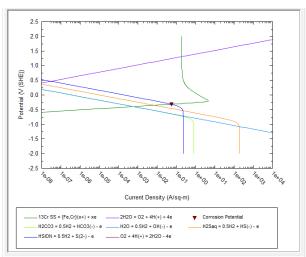
Click on the **Polarization Curve** tab ( Mental Polarization Curve).

Click on the Variables button. This will open a new window.

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<sup>2</sup>. 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

## **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 calculation 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.  $x_{Cr}^* = 0.11 \text{ or } 0.12$ ). This parameter can be calculated as the area of the depletion profile below the threshold concentration  $x_{Cr}^*$ , divided by bulk Cr concentration,  $x_{Cr}^0$ :

$$\delta(x_{Cr}^*) = \frac{1}{x_{Cr}^0} \int_0^{z^*} (x_{Cr}^* - x_{Cr}(z)) dz$$

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.

# 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:

Chromium and molybdenum depletion profiles in the vicinity of grain boundaries, which result from heat treatment of austenitic alloys.

Depletion parameters for sensitized austenitic alloys, which provide an indicator of whether the alloy is susceptible to intergranular corrosion.

Effect of thermal aging on the repassivation potential of austenitic alloys, which provides a threshold condition for localized corrosion (pitting or crevice corrosion).

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 °C	
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			

#### Add a new Stream

Click on the new Stream and press <F2> to change the name to Thermal Aging

Select the AQ thermodynamic Framework (selected by default)

Click on the Units Manager Icon and select Metric, Batch, Moles

Click on the Names Manager Icon and select Display Name

Enter the stream composition and conditions specified in the table above

#### 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.

#### Select the Survey by Thermal Aging Time

Change the name from *Rates* to *Alloy 600* using the <F2> key or by **right-mouse click** on the object and select rename

Select Alloy 600 from the Contact Surface grid

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.

👌 OLI Studio - [Corrosion Rates.oad*]			– 🗆 ×
■ File Edit Streams Calculations Cł	hemistry Tools View Window Help		_ 8 ×
🗈 😅 🖬 🐇 🖻 💼 🎒 😵	L1 Va So L2 Re ± MSE ± MSE ± AQ ±	🚧 🎬 🛃 💱 🔊 😭 🎸	
Navigator # * *	Alloy 600		
Corrosion Rates.oad*			
🍫 Streams	< Ø Description 🔮 Definition 🛍 Gene	eral Corr. Rate  🛍 Localized Corr.	🛍 Polarization Curve 📓 Report 🚹
🖶 🗄 CR of carbon steel	Variable	Malua	Survey by
E CR vs flow	Stream Par	Value ^	Thermal Aging Time 🔻 Specs
🖶 🔥 Gas Condensate	Stream Amount (mol)	55.5482	
Localized Corrosion     Thermal Aging	Temperature (°C)	60.0000	Then by (optional)
Alloy 600	Pressure (atm)	1.00000	None 👻 Specs
Andy out	Calculation P		Vary
	Flow Type	Static	<ul> <li>Independently</li> </ul>
	Thermal Aging Temperature (°C)	700.000	Together
	Thermal Aging Time (hr)		
	□ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □	(mol)	Calculate 🥝
	Water	55.5082	
	Sodium chloride	0.0400000	Summary
Actions	Nickel	0.0	Unit Set: Metric (moles)
Actions			>
	Contact S	urface	Automatic Chemistry Model Aqueous (H+ ion) Databanks:
	Alloy 600		Corrosion (AQ)
			Aqueous (H+ ion)
			Redox selected Using K-fit Polynomials
			T-span: 25.0 - 225.0
			P-span: 1.0 - 1500.0
Plot Template Manager 📮 🔺 🗙			Isothermal Calculation 60.0000 °C 1.00000 atm
			Calculation not done
			Calculation not done
		¥	Thermal Aging Time survey:
	-		Range 0.0 to 10.0 hr
	Input		Step size 2.0 hr No. steps 5
	Advanced Search Add as Stream	Export	
Save			
For Help, press F1			Image:

Now we need to specify the Thermal Aging Time range. **Click** on the **Specs** button. This will open a new window.

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).

Rates Calculation		?	$\times$
Category - Var. 1 - Thermal Aging Time - Polarization Curve - Thermal Aging - Calculation Type - Calculation Options	Survey Range Thermal Aging Time Range Unit: hr Selected Range U0 to 220 in 5 steps of 4.4	New	
	Clog Point List      Control Content      Content		_
< >>	OK Cancel Apply	Help	

Under the Category section, select the Thermal Aging option.

Rates Calculation	?	>
Category Var. 1 - Thermal Aging T Polarization Curve - Thermal Aging - Calculation Type - Calculation Options	Erp Directly from Correlation:         Image: No         Yes           Alley Composition wt%:         Fe         6.534         Cr         16.408         Ni         75.032           Mo+W         0         c         0.026         N         0           Carbide Stoichiometry:         Fe         0         Cr         7         Ni         0           Carbide Stoichiometry:         Fe         0         Cr         7         Ni         0           Carbide Thermochemistry:         A         405190         B         -25.765         Cr         Diffusion Coefficient:         D         4.40190         Q         2.43000         0           Carbide Thermochemistry:         A         405190         B         -25.765         Cr         Diffusion Coefficient:         D         Q         Q         2.43000         Q         Q         Cr         Site:         12.3         Revert to Default         Revert to Default         Revert to Default         Site:         12.3         Revert to Default         Site:         Site:         12.3         Site:         12.3         Site:         Site:         12.3         Site:         Site:         12.3         Site:         Site:         Site:         Site:         12.3	
< >>	OK Cancel Apply H	elp

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

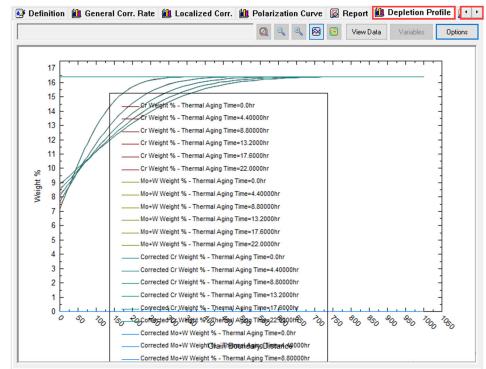
Also, you can indicate whether the repassivation potential ( $E_{rp}$ ) should be calculated directly from the correlation developed by Anderko et al. (2008), which expresses  $E_{rp}$  as a function of alloy composition or not. If it is not calculated directly, then the repassivation potential is calculated first using the alloy-specific parameters for the alloy of interest and only the decrement of  $E_{rp}$  (i.e.,  $E_{rp}$ , thermally aged –  $E_{rp, bulk alloy}$ ) 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.

For now, we will accept the default settings. Click OK.

Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key 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

Click on the **Depletion Profile** tab (<sup>▲ Depletion Profile</sup>). 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  $\mu$ m). 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

Click on the **Options** button. This will open a new window.

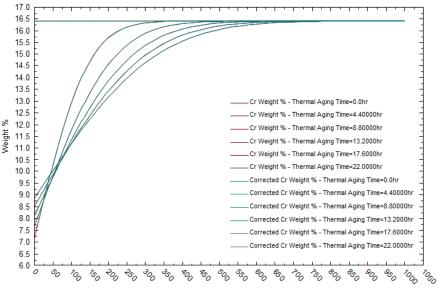
Since alloy 600 does not contain Mo or W, eliminate the Mo+W curves. To do this, go to the **Category** section and select the **Curves** option

Highlight the Mo+W weight % curves by pressing the Shift key and the down key (**Shift +**  $\downarrow$ ). After highlighting these curves, check the **Hidden** button.

Customize Plot		?	×
Customize Plot Category General Legend -XAxis -YAxis Curves	Curves  Cr Weight % - Thermal Aging Time=17.6000hr Cr Weight % - Thermal Aging Time=22.000hr Mo+W Weight % - Thermal Aging Time=24.0000hr Mo+W Weight % - Thermal Aging Time=26.0000hr Mo+W Weight % - Thermal Aging Time=13.2000hr Mo+W Weight % - Thermal Aging Time=17.6000hr Mo+W Weight % - Thermal Aging Time=20.000hr Mo+W Weight %	?	
	OK Cancel Apply	He	elp

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.



Grain Boundary Distance

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

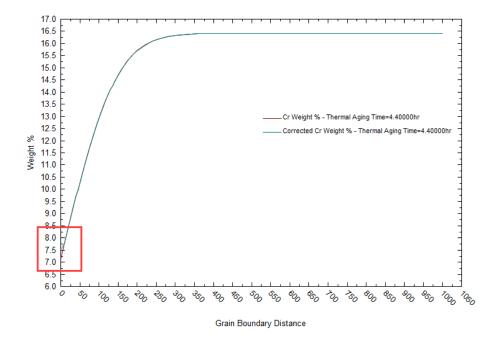
Now, let's focus on the differences between the uncorrected and corrected depletion profiles. To have a clear picture of the difference between them, we will analyze the depletion profiles results obtained at 4.4 hours of thermal aging.

Click on the **Options** button, and select the **Curves** category 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  $\mu$ m). 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.

Copy the Alloy 600 corrosion calculation, and then **paste** it under the **Thermal Aging Stream Rename** the new calculation as **Alloy 600 – Cr depletion** 

Go back to the **Definition** tab and click the **Specs** button

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

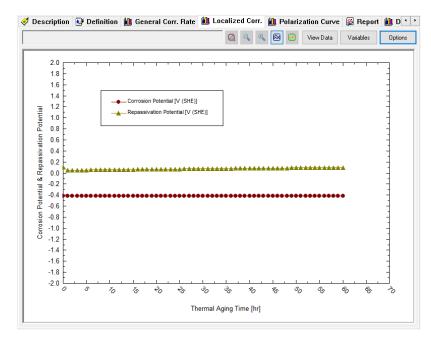
OLI Studio - [Corrosion Rates.oad*	1		- 🗆 X
- · ·	, is Chemistry Tools View Window Help		_ <i>E</i> ×
🗓 🖆 🔚 🐇 🖻 💼 🥌 💡		+ i dda 🚟 + 😳 Da 🕾 📈	- D' X
Navigator n + X			
Corrosion Rates.oad*	Alloy 600-Cr depletion		
🍫 Streams	< Description 🛂 Definition 📶 General	Corr. Rate 🛍 Localized Corr. 🛍 Pola	arization Curve 📓 Report 🛍 D 💶 🕨
🗄 🗄 CR of carbon steel			Survey by
E CR vs flow	Variable	Value	Thermal Aging Time - Specs
🖶 💧 Gas Condensate	Stream Amount (mol)	55.5482	Theimal Aging Time
Localized Corrosion	Temperature (°C)	60.0000	Then by (optional)
Alloy 600	Pressure (atm)	1.00000	None 👻 Specs
Alloy 600-Cr depletion	Calculation Pa		Vary
	Flow Type	Static	<ul> <li>Independently</li> </ul>
	Thermal Aging Temperature (°C)	700.000	<ul> <li>Together</li> </ul>
	Thermal Aging Time (hr)		
	⊂ Inflows (	mol)	Calc <u>u</u> late 🥝
	Water	55.5082	Summary
	Sodium chloride	0.0400000	Summary
< >			Unit Set: Metric (moles)
	Contact Su	ırface	Automatic Chemistry Model
Actions	Alloy 600		Aqueous (H+ ion) Databanks:
Actions		/	Corrosion (AQ)
			Aqueous (H+ ion) Redox selected
			Using K-fit Polynomials
			T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0
			Isothermal Calculation
			60.0000 °C 1.00000 atm
			Calculation not done
Plot Template Manager 📮 🔺 🗙			
			Thermal Aging Time survey:
			Range 0.0 to 60.0 hr Step size 1.0 hr
			No. steps 60
		¥	
	Input		No secondary survey selected
	t quart		Thermal Aging Temperature: 700.000 🗸
Save	Advanced Search Add as Stream E	Export	°C
For Help, press F1			

Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key

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

Click on the Localized Corr. tab ( Localized Corr.). By default, this tab will show a plot of the corrosion potential and repassivation potential.



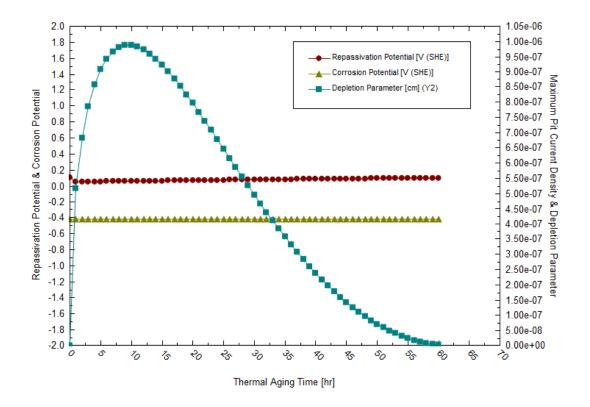
Let's add a new parameter to the plot: The Depletion Parameter.

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**.

Select Data To Plot	? ×
Curves	
	A X Axis
Stream Parameters     Calculation Results	>> Thermal Aging Time
Corrosion Values Consoin Current Density Consoin Rate	Y1 Axis Repassivation Potential Corrosion Potential
Depletion Parameter     Section Parameter     Additional Stream Parameters	~
Phase Flow Properties     Thermodynamic Properties     Pre-scaling Tendencies	
Pre-scaling Index     Scaling Tendencies     Scaling Index	Y2 Axis Maximum Pit Current Density
Aqueous     Vapor     Solid	
Molecular Totals     MBG Totals - Totals     MBG Totals - Areasure	<< v
Use short names	
Hide zero species	Z Axis
Plot data which is only within temperature range.	- Select - 🗸 🗸
	OK Cancel Apply Help

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 °C	
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			

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** 

Change the name from *Rates* to *Alloy 825* using the <F2> key or by right-mouse click on the object and select rename

Select the Survey by Thermal Aging Temperature option

Change the stream composition and conditions to the specified values in the table above

Select Alloy 825 from the Contact Surface grid

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

Navigator # * *	Alloy 825	
Corrosion Rates.oad*		
🏘 Streams	< ダ Description 🧕 Definition 🛍 General Corr. Rate 🛔	🗓 Localized Corr. 🛍 Polarization Curve 📓 Report 🛍 D 💶
🖶 👌 CR of carbon steel		Value Survey by
🗄 🔥 CR vs flow	Variable	Value A
🕀 👌 Gas Condensate	Stream Parameters	Thermal Aging Temp. 👻 Specs
🗄 👌 Localized Corrosion	Stream Amount (mol)	55.5111 Then by (optional)
🛓 🗄 Thermal Aging	Temperature (°C)	95.0000
🗄 📈 Alloy 600	Pressure (atm)	1.00000 None V Specs
Alloy 600-Cr depletion	Calculation Parameters	Vary
Alloy 825	Flow Type	Static   Independently
	Thermal Aging Temperature (°C)	
	Thermal Aging Time (hr)	15.0000
< >		Calculate 🥝
	Water	55.5082 Summary
Actions	Sodium chloride	2.84600e-3
Actions	Nickel	0.0 Unit Set: Metric (moles)
		Automatia Chamistra Madal
	Contact Surface	Automatic Chemistry Model Aqueous (H+ ion) Databanks:
	Alloy 825	Corrosion (AQ)
		Aqueous (H+ ion)

Now we need to specify the Thermal Aging Temperature range. **Click** on the **Specs** button. This will open a new window.

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**.

Rates Calculation	?	$\times$
Category	Survey Range	
Var. 1 • Thermal Aging Tempe Polarization Curve Thermal Aging Calculation Type Calculation Options	Thermal Aging Temperature Range Unit: "C Selected Range 550.0 to 500.0 in 7 steps of 50.0 New Delete	
	Linear O Log O Point List End Points Start 550.000	
	End 900.000 Step Size	
	Number Steps 7	
< >		
	OK Cancel Apply He	elp

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

Click on the **Depletion Profile** tab (<sup>Depletion Profile</sup>). If you don't see it in your screen, use the **I** 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.

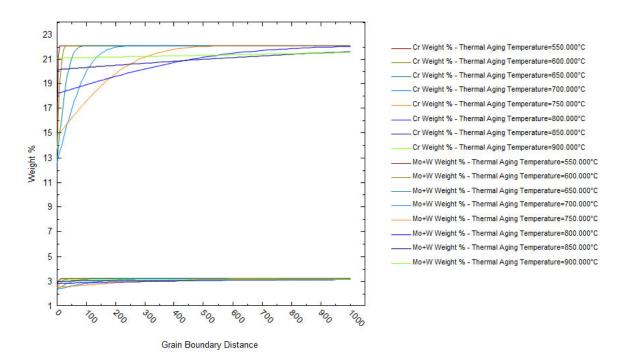
🛍 General Corr. Rate 👔	🛍 Localized Corr. 🛍 Polarization Curve 📓 Report 🛍 Depletion Profile 📄 File Viewer 🛀
	👰 🔍 🎕 🐼 😨 View Data Variables Options
23 21 19 17 15 15 15 15 15 15 15 15 15 15 15 15 15	Ct-Weight % - Thermal Aging Temperature-550 000°C         Cr Weight % - Thermal Aging Temperature-650 000°C         Cr Weight % - Thermal Aging Temperature-750 000°C         Cr Weight % - Thermal Aging Temperature-750 000°C         Cr Weight % - Thermal Aging Temperature-750 000°C         Cr Weight % - Thermal Aging Temperature-850 000°C         Mo-W Weight % - Thermal Aging Temperature-950 000°C         Mo-W Weight % - Thermal Aging Temperature-850 000°C
	Corrected Cr Weight % - Thermal Aging Temperature=750.000°C

For clarity, let's customize the plot by removing the corrected depletion profiles and leaving only the uncorrected (or directly calculated) ones.

Click on the **Options** button, and select the **Curves** category, highlight the Corrected curves and check the hidden box. Then click **OK**.

Customize Plot		?	×
Category General Legend X Axis Uurves	Curves Corrected Mo+W Weight % · Thermal Aging Temperature=550.000°C Corrected Mo+W Weight % · Thermal Aging Temperature=650.000°C Corrected Mo+W Weight % · Thermal Aging Temperature=650.000°C Corrected Mo+W Weight % · Thermal Aging Temperature=700.000°C Corrected Mo+W Weight % · Thermal Aging Temperature=800.000°C Corrected Mo+W Weight % · Thermal Aging Temperature=900.000°C		^
	Auto Line Style     Auto Line Weight     Auto Color     1 pt     Auto Symbol     Auto Scaling Factor     None     4		]•
	OK Cancel Apply	Н	elp

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.

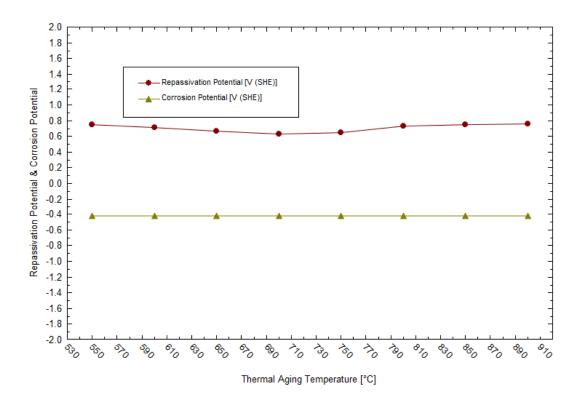
As shown in the plot above, the depletion profile is very narrow at the lowest temperature, i.e., 550 °C. On the other hand, it becomes flat at high temperatures, and it has a high minimum. The high minimum value is particularly important because it indicates that the local depletion of Cr and Mo is 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

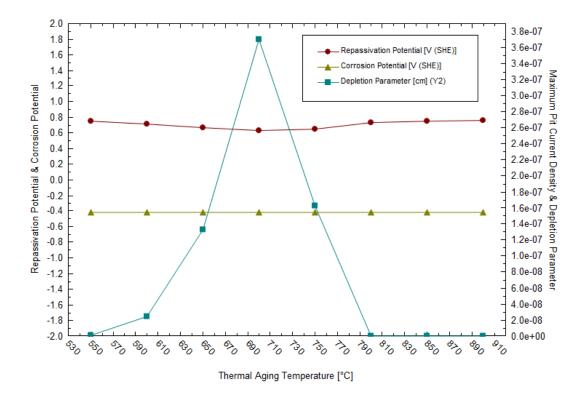
Click on the **Localized Corr.** tab ( M Localized Corr.). By default, this tab will show a plot of the corrosion potential and repassivation potential.



Let's add a new parameter to the plot: The Depletion Parameter.

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.

# 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 -  $\chi$ ,  $\sigma$ , M<sub>23</sub>C<sub>6</sub>-type carbide, and secondary austenite ( $\gamma_2$ ). 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	4 Stream Amount Calculated		
Calculation Type	Corrosion Rates	Temperature	60 °C	
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	02	0.02 moles	
		N2	0.08 moles	

Note: The oxygen and nitrogen have been added to simulate the presence of air

## Add a new Stream

Click on the new Stream and press <F2> to change the name to *Thermal Aging – Alloy 2324* Select the AQ thermodynamic Framework (selected by default) Click on the **Units Manager** Icon and select Metric, Batch, Moles Click on the **Names Manager** Icon and select *Display Name* Enter the stream composition and conditions specified in the table above Go to the Add Calculation button and select Corrosion Rates Select the Survey by Composition 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.

## 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.

OLI Studio - [Corrosion Rates.oad*	1		- 🗆 X		
-					
11	ns Chemistry Tools View Window Help		_ & ×		
🗋 🗅 🚅 🖬 👗 🐚 🛍 🎒 🍞	K? L1 Va So L2 Re ± MSE ± MSE ± AQ ±	: 🗚 🎬 🛨 💱 🔊 😭 🎸			
Navigator 👖 🔺 🗙	Alley 2204 hafens aning				
Corrosion Rates.oad*	Alloy 2324 -before aging				
🏘 Streams	< < Description 🥸 Definition 🛍 General	Corr. Rate 🛍 Localized Corr. 🛍	Polarization Curve 📓 Report 🛍 💶		
🗄 🗠 🍐 CR of carbon steel			Survey by		
🛓 🗄 CR vs flow	Variable	Value			
🖶 👌 Gas Condensate	Stream Para		Composition    Specs		
🛓 💧 Localized Corrosion	Stream Amount (mol)	55.6082	Then by (optional)		
🗄 🖕 🍐 Thermal Aging	Temperature (°C)	60.0000	None   Specs		
Thermal Aging -Alloy 2324	Pressure (atm)	1.00000			
Alloy 2324 -before aging	Calculation Pa		Vary Independently		
	Flow Type	Static	O Together		
	Thermal Aging Temperature (°C)	399.000			
	Thermal Aging Time (hr)	0.0	Calculate 🥝		
	Inflows (	55.5082			
	Water		Summary		
	Sodium chloride	0.0			
	Oxygen	0.0200000	Unit Set: Metric (moles)		
Actions a + ×	Nitrogen	0.080000	Automatic Chemistry Model		
Actions	Iron	0.0	Aqueous (H+ ion) Databanks:		
	Contact Si		Corrosion (AQ) Aqueous (H+ ion)		
	Stainless steel 316	inace	Redox selected		
	Stalliess steel 310		Using K-fit Polynomials T-span: 25.0 - 225.0		
			P-span: 1.0 - 1500.0		
			Isothermal Calculation		
			60.0000 °C 1.00000 atm		
			Calculation not done		
Plot Template Manager a. • ×					
			Composition survey: No Inflow selected		
			No secondary survey selected		
	1	*	Thermal Aging Temperature: 399.000		
	Input		°C .		
	Advanced Search Add as Stream	Francis	Thermal Aging Time: 0.0 hr		
Save Save					
For Help, press F1	1				
For help, press Fi			w w NUM		

We will be running a composition survey to see how the concentration of NaCl affects the propensity for localized corrosion.

We need to specify the NaCl concentration range. Click on the Specs button. This will open a new window.

Under the Component tab select Sodium Chloride

Composition Rates Calculation	on		?	×
Category	Component	Survey Range		
Var. 1 - Composition — Polarization Curve — Thermal Aging — Calculation Type — Calculation Options	Compone Hide Iron Nitroger Oxygen Sodium Water	nt Inflows Related Inflows	New Inflow	
		OK Cancel	Apply Help	

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.

atogon .	
Category Var. 1 - Composition – Polarization Curve – Thermal Aging – Calculation Type – Calculation Options	Component Survey Range Composition Range Unit mol Selected Range 1.0e-4 to 6.0 in 20 steps of 0.239995 New Delete
	C Linear ● Log O Point List End Points Start 1.00000e-4 End 6.00000 Step Size Increment 0.233335 Number Steps 20 ⊙ Select one, the other is Calculated

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.

First, click on the **Yes** button next to "Erp directly from correlation:"

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
С	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:

omposition Rates Calculati		?	
Category	Thermal Aging		
Var. 1 - Composition - Polarization Curve - Thermal Aging - Calculation Type - Calculation Options	Erp Directly from Correlation:         O No         Yes           Alloy Composition wt%:         Fe         67.245         Cr         25.4         Ni         5.75           Mo+W         1.5         C         0.025         N         0.08		
	Carbide Stoichiometry:		
	Fe 0 Cr 19.74 Ni 0		
	Mo+W 3.26 C 6 N 0		
	Carbide Thermochemistry: A 41221 B -966		
	Cr Diffusion Coefficient: D0 0.00016818 Q -2890	100	]
	Mo, W Diffusion Coefficient: D0 7.93e-005 Q -2740	100	1
	Cr Sensitization Threshold wt% 12 Grain Size: Revert to Defau	100 .lt	
	OK Cancel Apply	Heli	

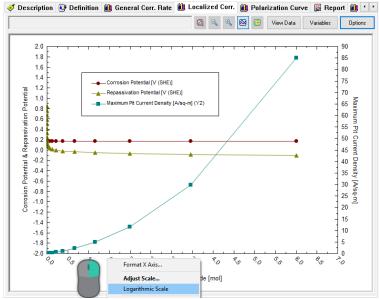
Click **OK** to accept the changes

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

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

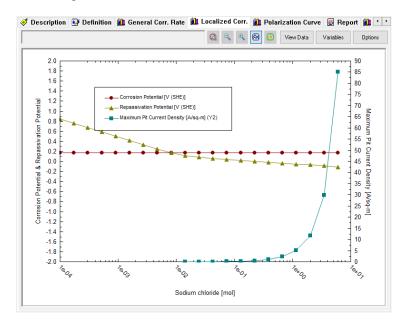
Click on the **Localized Corr.** tab ( Localized Corr. ). By default, this tab will show a plot of the corrosion and repassivation potentials as a function of NaCl concentration. In the Y2 axis the Maximum Pit Current Density is also plotted.



To visualize the results better, change the horizontal axis to a logarithmic scale.

#### 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  $\sim$ 0.3 molal. Above this concentration, the repassivation potential drops below the corrosion potential and, therefore, localized corrosion can be stabilized at these conditions.

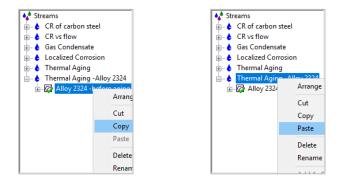
## Example 56: Prediction of Localized Corrosion for Alloy 2324 After Thermal Aging

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 chromiumdepleted secondary austenite phase is responsible for a much-increased tendency for localized corrosion. We will use this experimental data to approximate the localized corrosion tendency of alloy 2324.

## Starting the Simulation

Copy the Alloy 2324-before aging calculation and paste it under the Thermal Aging – Alloy 2324 stream



**Rename** the calculation as *Alloy 2324 – after aging* by using the **<F2>** key or by **right-mouse click** on the object and select rename

Click on the **Specs** button. This will open a new window.

Under the **Category** section, select the **Thermal Aging** option. The screen will be populated with default parameters for type 316 stainless steel.

Click on the **Yes** button next to "*Erp directly from correlation:*" – because we will be running calculations for a completely new phase

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
С	0.017
Ν	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.

Var. 1 - Composition Var. 1 - Composition - Polarization Curve - Thermal Aging - Calculation Type - Calculation Options	Themal Aging           Erp Directly from Correlation:         No              • Yes            Alloy Composition wt%:         Fe              80.774         Cr              12.512         Ni              5.314           Mo+W         1.339         C              0.017         N              0.164           Catbide Stoichiometty:         Fe         0              Cr              19.74         Ni              0               Auxiliary (Cr)               0.164           Catbide Stoichiometty:         Fe         0              Cr              19.74         Ni              0               Auxiliary (Cr)               No              0.164           Catbide Thermochemistry:         A              41221              B              966           Cr Diffusion Coefficient:         D0              0.00016818              2293000           Mo, w/ Diffusion Coefficient:         D0              7.38-005              Q              274000           Cr Sensitization Threshold wt%:              12              Grain Size: 100           Revert to Default

Click **OK** to accept the changes

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

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

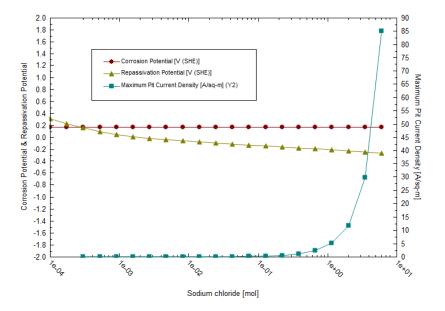
## Analyzing the results

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.

## 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 Studio: EVS Analyzer

## Section 10. EVS Overview

## **Overview and Theoretical Foundation**

Engineering systems may have many 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<sub>f</sub>, 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:

$$P_f = 1 - \exp\left\{-\frac{\exp\left[-d - \left(u + \alpha \ln\frac{S}{s}\right)\right]}{\alpha}\right\}$$
(1)

where location parameter, u, and scale parameter,  $\alpha$ , 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  $\alpha(t)$ , 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  $\alpha$  in terms of time of the hyperbolic form:

$$u = \frac{a_1 t}{1 + a_2 t} \text{ and } \alpha = a_3 t \tag{2}$$

where a<sub>1</sub>, a<sub>2</sub>, and a<sub>3</sub> 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 answer 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:

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.

We can expect that when the depth of the pit increases some critical value, the nucleation of cracks can occur. A purely statistical method cannot predict such a transition. This method also cannot predict any catastrophic event.

This method cannot be used for design of new constriction, because it relies upon calibration upon a preexisting system.

## **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:

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

Probability of failure for a given penetration depth and the area of the system as a function of observation time

Probability of failure for a given observation time and the area of the system as a function of penetration depth

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<sup>2</sup> immersed in Kingston tape water at 25 °C. The experimental data is summarized in the table below.

Maximum pit depth (in  $\mu$ m) developed on Alcan 2S-O coupons with immersed in Kingston tape water for different observation times. Area of all coupons is s $\approx$ 129 cm<sup>2</sup>

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

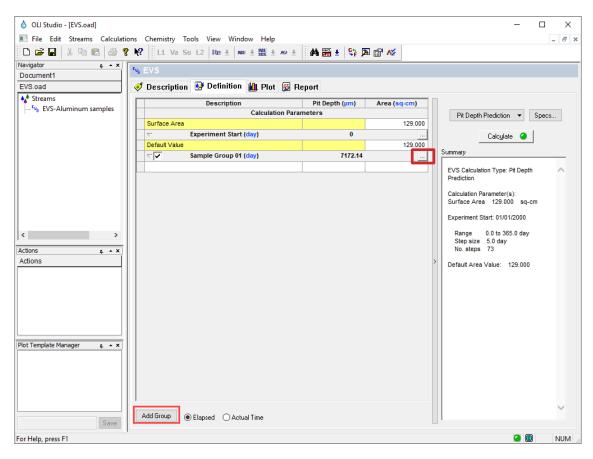
Starting the Simulation

Add a new EVS calculation. Select the Add EVS Calculation icon in the Actions Pane

Actions	
🖲 Add Stream	
📕 Add Mixer	
🗔 Add Water Analysis	
🛅 Add EVS Calculation	
🕌 Add Brine Analysis	

**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*.

All samples have a constant area s =  $129 \text{ cm}^2$ . Under the **Calculation Parameters** grid, enter  $129 \text{ cm}^2$  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.

By default, **Sample group 01** is created. Click on the <u>init</u> button to edit this field. This will open a new window.

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.

EVS Sample Group Info Editor	3	' ×
Title:		
One Week		
Elapsed: (day)		
7		
Included for Calculation		
ОК	Cancel	

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.

Click on the Add Group button (located at the bottom of the window). This will open a new window.

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.

Enter the **Pit Depth** data (second column) obtained for 1 month.

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)
	Cone 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
on for this group	10	692.000	129.000
by un-checking			
nformation is not	Three Months (day)	89.9999	
for the calculation	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 8		
	9	740.000	129.000
	10	760.000	129.000
	- 10	/60.000	129.000
	One Year (day)	365.0	
		640.000	129.000
	2	680.000	129.000
	3	700.000	129.000
	4	760.000	129.000
		100.000	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.

Click on the Specs button. This will open a new window.

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** 

EVS Calculation Options	? ×
Survey Range	
Pit Depth Prediction Range Unit: day	
Selected Range	
0.0 to 365.0 in 50 steps of 7.3	New
	Delete
End Points	
Start 0.0	
End 365.000	
Step Size	
Increment 7.30000 O 🔪 Select one,	the other is
Number Steps 50 💿 🗲 calculated	
OK Cancel Apply	Help

Before running the calculation, we are going to study two different cases:

The first case will include the experimental data for 1 week and 1 month - short term experiments

The second case will include all the experimental data - long term experiments

Predicting the Worst Pit Depth for 1 year of service life using short term experiments (Experimental Data for 1 week and 1 month)

Description	Pit Depth (µm)	Area (sq-cm)
Calculation	Parameters	
Surface Area		129.000
C Experiment Start (day)	0	
Default Value		129.000
Cone 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
C One Month (day)	30.0	
1	460.000	129.000
2	500.000	129.000
3	510.000	129.00
4	580.000	129.00
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	129.00
2	578.000	129.00
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	129.00
9	760.000	129.000
10	798.000	129.000
Six Months (day)	180.0	
1	620.000	129.00

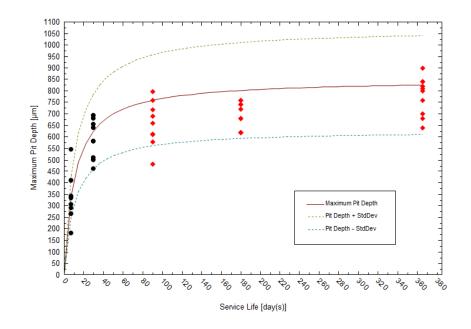
## Check the boxes for 1 week and 1 month only to include them into the calculations

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

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

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.



Click on the Report tab, and to the Calculation Results table.

The predicted depth of the deepest pit at 365 days is  $610.43\mu m \le 825.373\mu m \le 1040.31\mu m$  (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)

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.

Go back to the **Definition** tab

**Include** (check) the experimental data for 3 months, 6 months and 1 year

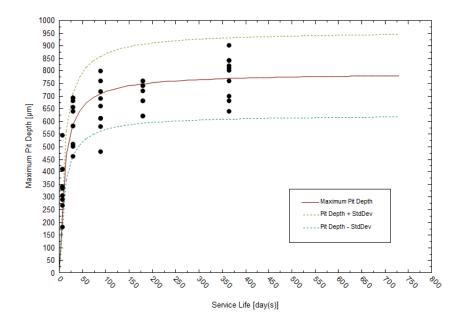
Click on the Specs button. This will open a new window

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** 

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

#### Analyzing the results

## Click on the Plot tab ( Plot ).



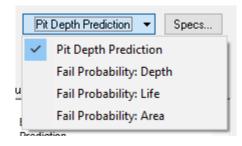
Click on the **Report** tab, and to the **Calculation Results** table.

The predicted depth of the deepest pit at 730 days (1 year) is 617.57  $\mu$ m  $\leq$  780.873  $\mu$ m  $\leq$  944.18  $\mu$ m.

## **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<sup>2</sup> have to have in order to ensure acceptable performance (probability of failure  $P_f < 5\%$  at design service life, t<sub>s</sub> =5 years?

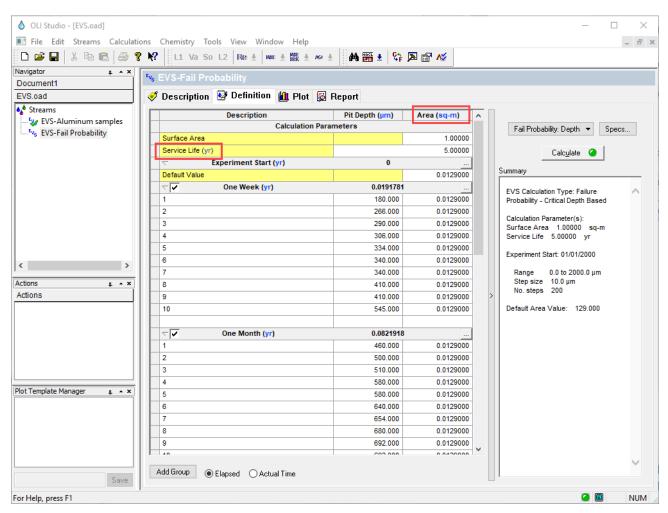
Starting the Simulation

Use the data enter in the example above. Change the Calculation Type to Fail Probability: Depth

Under the **Calculation Parameters** grid, enter 1 m<sup>2</sup> for the **Surface Area** and 5 years for the **Service Life.** Change units by clicking on the **blue** hyperlinks.

Make sure all data sets are selected (checked)

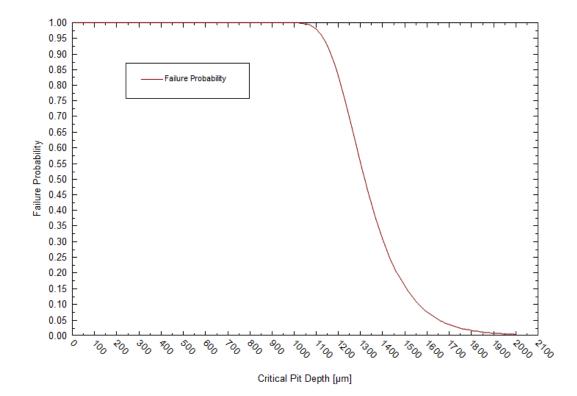
Your screen should look like the image below.



We are now ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar.

## Analyzing the results

Click on the **Plot** tab ( Plot ). You will see a plot of predicted probability of failure



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  $\mu$ m.

## 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  $\mu$ m with area S=10 m<sup>2</sup> in order to ensure acceptable performance i.e. probability of failure, Pf< 5 %?

Starting the Simulation

## Change the Calculation Type to Fail Probability: Life

Under the **Calculation Parameters** grid, enter 10 m<sup>2</sup> for the **Surface Area** and 1850  $\mu$ m 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.

Click on the **Specs** button. This will open a new window.

Change the **Service Life** range as follows: Start=0 years, End=3 years and Increments=0.2 years. Then click **OK**.

EVS Calculation Options	?	×
Survey Range		
Failure Probability - Service Life Based Unit:		
Selected Range 0.0 to 3.0 in 15 steps of 0.2		
	New	
	Delete	
● Linear ○ Log ○ Point List		
End Points		
Start 0.0		
End 3.00000		
Step Size		
Increment 0.200000 💿 🔪 Select one, the	e other is	
Number Steps 15		
OK Cancel Apply	He	lp

Your screen should look like the image below.

#### 🛷 Description 🔮 Definition 🛍 Plot 📓 Report

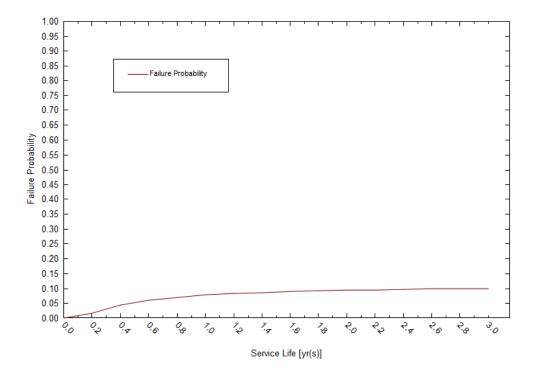
Description	Pit Depth (µm)	Area ( <mark>sq-m</mark> )
Calculatio	n Parameters	
Surface Area		10.0000
Critical Pit Depth	1850.00	
Experiment Start (yr)	0	
Default Value		0.0129000
Cone Week (yr)	0.0191781	
1	180.000	0.0129000
2	266.000	0.0129000
3	290.000	0.0129000
4	306.000	0.012900
5	334.000	0.012900
6	340.000	0.0129000
7	340.000	0.012900
8	410.000	0.0129000
9	410.000	0.0129000
10	545.000	0.012900
Cone Month (yr)	0.0821918	
1	460.000	0.012900
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	0.012900
9	692.000	0.0129000
40	000.000	0.040000

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

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

#### Analyzing the results

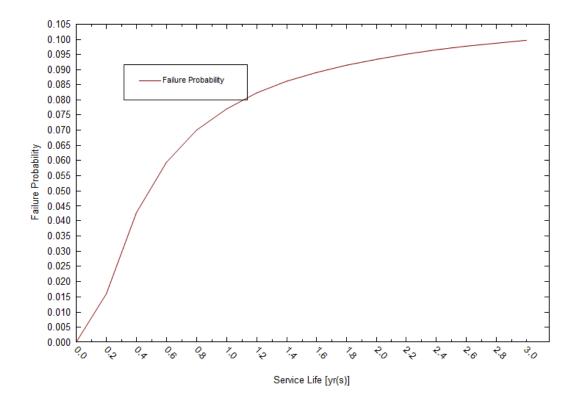
Click on the **Plot** tab ( Plot ). You will see a plot of predicted probability of failure. We need to modify the plot to see the results in more detail.



**Double click** on the **Y axis**. This will open a new window. **Check** the boxes Minimum and Maximum. Then click **OK**.

Y Axis - Properties			?	×
Scale				
Auto				
Minimum	0.0			
Maximum	1.0			
Major Unit				
Minor Unit				
Logarithmic scale				
ОК С	ancel	Apply	He	elp

The plot should look like the image below



The maximum probability of failure seems to be at around 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  $\mu$ m and service life t=5 years in order to ensure acceptable performance i.e. probability of failure, P<sub>f</sub> < 5 %?

#### Starting the Simulation

#### Change the Calculation Type to Fail Probability: Area

Under the **Calculation Parameters** grid, enter 2000  $\mu$ m 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.

Click on the **Specs** button. This will open a new window.

Change the **Surface Area** range as follows: Start=0 sq-m, End=100 sq-m and Number of steps=50. Then click **OK**.

EVS Calculation Options	?	×
Survey Range		
Failure Probability - Surface Area Based Unit: Sqm		
Selected Range 0.0 to 100.0 in 50 steps of 2.0	New	_
	New Delete	;
● Linear ◯ Log ◯ Point List		
End Points		-
Start 0.0		
End 100.000		
Step Size		-
Increment 2.00000 O 🔪 Select one, t	he other is	
Number Steps 50 💿 🕤 calculated		
OK Cancel Apply	He	lp

Your screen should look like the image below.

Description	Pit Depth (µm)	Area ( <mark>sq-m</mark> )
Calculation F	Parameters	
Critical Pit Depth	2000.00	
Service Life (yr)		5.0000
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	0.012900
2	500.000	0.0129000
3	510.000	0.012900
4	580.000	0.012900
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
40	000.000	0.040000

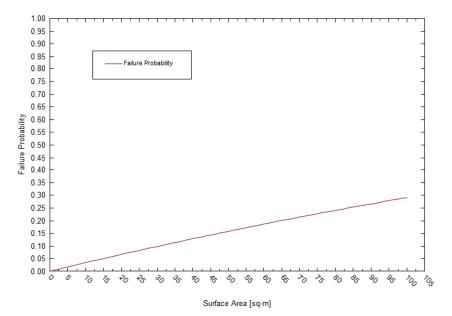
#### 🛷 Description 🔯 Definition 🛍 Plot 📓 Report

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

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

## Analyzing the results

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%.

Click on the **Report** tab, and to the **Calculation Results** table.

We can conclude that acceptable performance is reached at <14 m<sup>2</sup>.

#### 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].

	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	

Pit depths (mm) for pipeline between Samara and Moscow

#### Calculation the Depth of the Deepest Pit

Starting the Simulation

Add a new **EVS** calculation. Select the Add **EVS** Calculation icon in the Actions Pane

Actions	
💧 Add Stream	
🗷 Add Mixer	
🙀 Add Water Analysis	
😬 Add EVS Calculation	
불 Add Brine Analysis	

**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*.

Under the Calculation Parameters grid, enter 1 cm<sup>2</sup> 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.

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:

OLI Studio - [EVS.oad*]	charity Task Man Water Hite	- 🗆 X
🗅 😅 🖬   👗 🛍 📾 🎒	ons Chemistry Tools View Window Help ▶ 1 1 Va So L2 Ree ± Maar ± 10000 ± 1000 ± 1000 ± 1000 ± 1000 ± 1000 ± 1000 ± 100000 ± 10000 ± 100000000	_ & ×
Document1 EVS.oad*	<ul> <li>EVS-Pipeline samples</li> <li>Description Definition 1 Plot Report</li> </ul>	
<ul> <li>Streams</li> <li>EVS-Aluminum samples</li> <li>EVS-Fail Probability</li> <li>EVS-Pipeline samples</li> </ul>	Description         Pit Depth (µm)         Area (sq-cm)           Calculation Parameters         1.00000	Pit Depth Prediction
····· •§ Evo-ripeline samples		Calculate 🥥
		EVS Calculation Type: Pit Depth Arediction

There are experimental data sets for 8 different periods of time. This means that we need to enter 8 different sample groups.

By default, **Sample group 01** is created. Click on the <u>use</u> button to edit this field. This will open a new window.

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'

EVS Sample Group Info Editor	?	×
Title:		
Sample Group 01		
Elapsed: (hr) 1440.0		
Included for Calculation		
OK Cancel		

Enter the **Pit Depth** data (second column) obtained for 1440 hours.

	-			
	Description		Pit Depth (mm)	Area (sq-cm)
	Calculat	ion Para	meters	
Surface Area				1.00000
Expension	eriment Start (hr)		0	
Default Value				1.00000
Sam	ple Group 01 (hr)		1440.0	
1			0.100000	1.00000
3			0.300000	1.00000
4			0.400000	1.00000
5			0.900000	1.00000
6			0.300000	1.00000

Now we need to add 7 more groups.

Click on the Add Group button (located at the bottom of the window. This will open a new window.

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.

Enter the Pit Depth data (second column) obtained for 5040 hours.

Click on the Add Group button, and repeat the same procedure for 5760, 8959, 12624, 17688, 28032 and 28272 hours.

(S-Pipeline-Pit Depth Predictic escription Description Sample Group 01 (hr)          Sample Group 02 (hr)         Sample Group 03 (hr)	ot <u> </u> Report	Area (sq-cm)	^	Pit Depth Prediction
Sample Group 01 (hr) Sample Group 02 (hr)	1440.0 0.100000 0.300000 0.400000 0.900000 0.300000 5040.0 0.490000	1.00000 1.00000 1.00000 1.00000 1.00000	^	Calcylate 🥥
Sample Group 02 (hr)	0.100000 0.300000 0.400000 0.900000 0.300000 5040.0 0.490000	1.00000 1.00000 1.00000 1.00000		Calcylate 🥥
	0.300000 0.400000 0.900000 0.300000 5040.0 0.490000	1.00000 1.00000 1.00000 1.00000		
	0.400000 0.900000 0.300000 5040.0 0.490000	1.00000 1.00000 1.00000		
	0.900000 0.300000 5040.0 0.490000	1.00000 1.00000		
	0.300000 5040.0 0.490000	1.00000		Summary
	<b>5040.0</b> 0.490000			
	0.490000			EVS Calculation Type: Pit Depth
	0.490000			Prediction
Sample Group 03 (hr)		1.00000		Calculation Parameter(s):
Sample Group 03 (hr)		1.00000		Surface Area 1.00000 sq-cm
Sample Group 03 (hr)				Experiment Start: 01/01/2000
	5760.0			Pance 0.0 to 97600.0 br
	1.57000	1.00000		Range 0.0 to 87600.0 hr Step size 1752.0 hr
	1.20000	1.00000		No. steps 50
				Default Area Value: 1.00000
Sample Group 04 (hr)	8959.0			
	1.40000	1.00000		
	1.95000	1.00000		
	1.80000	1.00000		
	1.60000	1.00000		
	2.10000	1.00000		
	1.40000	1.00000	>	
Sample Group 05 (hr)	12624.0			
	1.70000	1.00000		
	2.10000	1.00000		
	1.65000	1.00000		
	2.21000	1.00000		
	1.40000	1.00000		
Sample Group 06 (hr)	17688.0			
	1.90000	1.00000		
	2.08000	1.00000		
	1.88000	1.00000		
	2.40000	1.00000		
	1.55000	1.00000		
Sample Group 07 (hr)	28032.0			
	2.40000	1.00000		
	1.71000	1.00000		
	28272.0			

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.

Click on the Specs button. This will open a new window.

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** 

EVS Calculation Options	?	×
Survey Range		
Pit Depth Prediction Range Unit: hr		
Selected Range 0.0 to 30000.0 in 15 steps of 2000.0	New Delete	
Linear O Log O Point List End Points		
Start 0.0 End 30000.0		
Step Size Increment 2000.00 Number Steps 15 Select one, the calculated	other is	-
OK Cancel Apply	He	lp

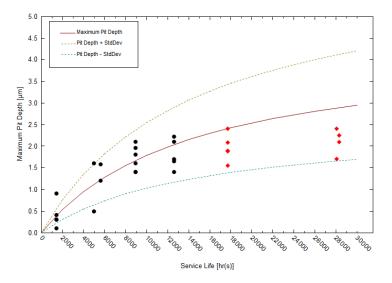
Before running the calculation, we are going to study two different cases: The first case will include the experimental data from groups 01 to 05 The second case will include all the experimental data from groups 01 to 08

Calculation including Groups 01 to 05

#### Check the boxes for Group 01 to 05

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



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.

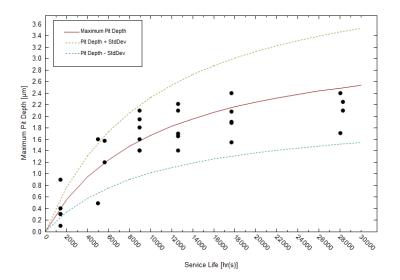
Calculation including Groups 01 to 08

#### Check the boxes for Group 01 to 08

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

#### Click on the Plot tab ( M 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.

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  $\mu$ m ≤2.54  $\mu$ m ≤3.53  $\mu$ m.

#### 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 ( $2 \times 2 \times 1/2$  in) in a 10% ferric chloride solution at 50 °C.

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

#### Pit Depth Data for an area of s= 25.8 cm<sup>2</sup>, depth in $\mu$ m

#### Calculation the Depth of the Deepest Pit

Starting the Simulation

Add a new EVS calculation. Select the Add EVS Calculation icon in the Actions Pane

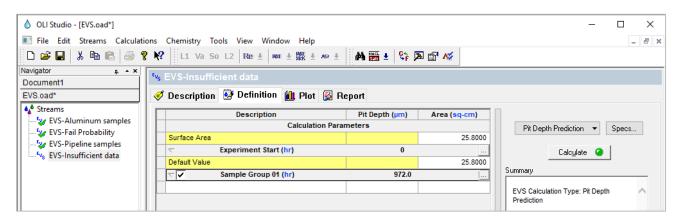
Actions	
🖲 Add Stream	
📕 Add Mixer	
🗔 Add Water Analysis	
😁 Add EVS Calculation	
🕌 Add Brine Analysis	

**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*.

Under the Calculation Parameters grid, enter 25.8 cm<sup>2</sup> for the Surface Area and Default Value cells.

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.

By default, **Sample group 01** is created. Click on the <u>...</u> button to edit this field. This will open a new window. **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'** 

EVS Sample Group Info Editor	?	$\times$
Title:		
Sample Group 01		
Elapsed: (hr)		
40.5		
Included for Calculation		
OK Cancel		

Enter the Pit Depth data (second column) obtained for 40.5 hours.

Now we need to add 8 more groups.

Click on the **Add Group** button (located at the bottom of the window. This will open a new window. **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**.

Enter the Pit Depth data (second column) obtained for 144.17 hours.

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.

lavigator a • × Document1	% EVS-Ins					
EVS.oad	🦪 Descrip	tion 🤮 Definition 👔 Plot	Benort			
Streams	V Desemp					
- WEVS-Aluminum samples		Description	Pit Depth (µm) A	trea (sq-cm)		
- W EVS-Fail Probability	Surface A		Parameters	25.8000	Fit Depth Prediction 👻 Spec	28
		Experiment Start (hr)	0	25.0000		
EVS-Insufficient data	Default Va		·	25.8000	Calculate 🥝	
		Sample Group 01 (hr)	40.5	20.0000	Summary	
	1	cample croup or (m)	775.000	25.8000		
					EVS Calculation Type: Pt Depth Prediction	
	~~	Sample Group 02 (hr)	144.17			
	1		1326.00	25.8000	Calculation Parameter(s): Surface Area 25.8000 sq-cm	
	2		1176.00	25.8000		
					Experiment Start: 01/01/2000	
	~	Sample Group 03 (hr)	215.33		Range 0.0 to 8760.0 hr	
	1		912.000	25.8000	Step size 120.0 hr	
	2		1173.00	25.8000	No. steps 73	
					Default Area Value: 25.8000	
	~ ~	Sample Group 04 (hr)	292.5			
	1		912.000	25.8000		
	2		1173.00	25.8000		
	~~	Sample Group 05 (hr)	331.0			
	1	sample Group os (m)	1361.00	25.8000		
tions a • × tions	2		1534.00	25.8000		
aions	-		1004.00	20.0000	>	
	~~	Sample Group 06 (hr)	378.5			
11	1		1613.00	25.8000		
	2		1641.00	25.8000		
	~ ~	Sample Group 07 (hr)	453.25			
	1		2101.00	25.8000		
	2		2024.00	25.8000		
		Sample Group 08 (hr)	477.0			
t Template Manager a + ×	1 2		1722.00	25.8000		
	3		1/98.00	25.8000		
			1430.00	25.0000		
	~~	Sample Group 09 (hr)	528.0			
	1		0.0	25.8000		
	1		0.0	25.8000		

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.

Click on the Specs button. This will open a new window.

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** 

EVS Calculation Options	? ×
Survey Range	
Pit Depth Prediction Range Unit: hr	
Selected Range	
0.0 to 580.0 in 50 steps of 11.6	New
	Delete
● Linear ◯ Log ◯ Point List	
End Points	
Start 0.0	
End 580.000	
Step Size	
Increment 11.6000 O 🔪 Select one, t	he other is
Number Steps 50 💿 🕤 calculated	
OK Cancel Apply	Help

Before running the calculation, we are going to study two different cases:

The first case will include the experimental data from groups 01 to 03 The second case will include all the experimental data from groups 01 to 09

Calculation including Groups 01 to 03

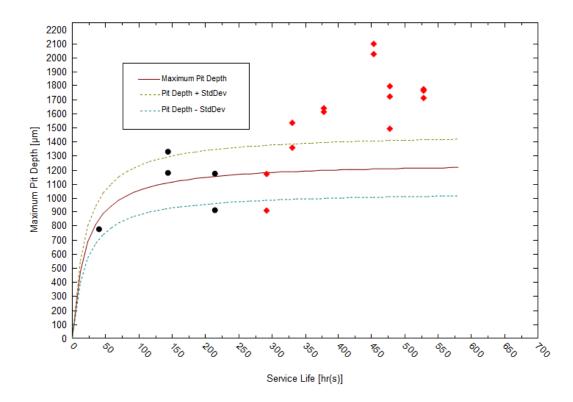
Check the boxes for Group 01 to 03

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

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

#### Click on the Plot tab ( M 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.

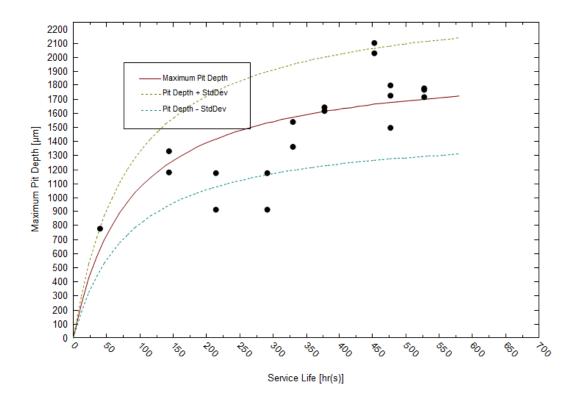
#### Calculation including Groups 01 to 09

#### Check the boxes for Group 01 to 09

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

#### Click on the Plot tab ( M 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.

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  $\mu$ m ≤ 1724.09  $\mu$ m ≤1724.09  $\mu$ m.

## Chapter V – OLI Studio: ScaleChem

think simulation | getting the chemistry right is a module within the OLI Studio. A separate license enables this module.

## Why Use OLI Studio: ScaleChem?

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. think simulation | getting the chemistry right 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. think simulation | getting the chemistry right 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.

think simulation | getting the chemistry right 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 calculation objects that can be used in think simulation | getting the chemistry right. 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 think simulation | getting the chemistry right software: Brine Analysis, Oil Analysis and Gas Analysis.



think simulation | getting the chemistry right 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, pseudocomponents or all three.



Add Gas Analysis 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<sub>4</sub>) 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 think simulation | getting the chemistry right: Saturator, Facilities, Scale Scenario, Scale Contour, and Mixing Water. A brief definition of each type of calculation is given below.



Add Saturator **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 Add Scale Scenario object calculates the scaling of minerals from a fluid as temperature and pressure changes, e.g. at different production locations..



Add Scale Contour 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.

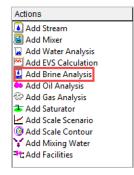
In this chapter we will model a hypothetical field and learn how to use and set up each one of the objects presented above.

# Section 11. Entering a Brine Analysis in think simulation | getting the chemistry right

### **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.

	Stream	ns	Calcul	ations	Che	mis	try	Тос	ls	View	W	indo
	4	\dd	Stream				Va	So	L2	Re	±	IASE
	A	٨dd	New A	nalysis			;					
-	S	cale	Chem			>		Ad	d O	il		
l .						_		Ad	d G	as		
	nalysis oncile			Na	ame:	Stre		Ad	d Bi	rine		



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.

	Variable	Value	Balanced	Entry Options
Na+1 K+1		itions (mg/L)		Units
	Na+1	0.0	0.0	mg/L
	K+1	0.0	0.0	Display
	Ca+2	0.0	0.0	Formula
	Mg+2	0.0	0.0	
	Sr+2	0.0	0.0	Show Non-zero Only
	Ba+2	0.0	0.0	Show Balanced Column
	Fe+2	0.0	0.0	Template Manager
				remplate Manager
		nions (mg/L)		Standard $\checkmark$
	CI-1	0.0	0.0	Save as
	S04-2	0.0	0.0	Suve usin
	HCO3-1	0.0	0.0	
	HS-1	0.0	0.0	Balance Options
	C2H3O2-1	0.0	0.0	Туре
				Dominant Ion
		utrals (mg/L)		
	CO2	0.0	0.0	
	H2S	0.0	0.0	
	SiO2	0.0	0.0	
	B(OH)3	0.0	0.0	

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 a **neutral**, simply type the species either using the formula name or its chemical 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.

	Variable	Value	Balanced	Entry Options
K+1       0.0       0.0         Ca+2       0.0       0.0         Mg+2       0.0       0.0         Sr+2       0.0       0.0         Ba+2       0.0       0.0         Fe+2       0.0       0.0         Display       ✓       Show Non-zero OL         Display Name       OLI Name       ✓         ✓ Cs+1       CSION       Standard         OLI CSION       CSION       Save as         SWN Cu(++)       CUION       Balance Options         SWN Cu(+1)       CUIION       Type	Cations (	mg/L)		Units
K+1       0.0       0.0         Ca+2       0.0       0.0         Mg+2       0.0       0.0         Sr+2       0.0       0.0         Ba+2       0.0       0.0         Fe+2       0.0       0.0         Display       Show Non-zero O         Cu       Image: Constraint of the state of	Na+1	0.0	0.0	ma/L
Ca+2     0.0     0.0       Mg+2     0.0     0.0       Sr+2     0.0     0.0       Ba+2     0.0     0.0       Fe+2     0.0     0.0       Display Name     OLI Name     ^       Cs+1     CSION     Standard       OLT CSION     CSION     Save as       SW Cu(+)     CUION     SWCu(+1)	K+1	0.0	0.0	
Mg+2         0.0         0.0           Sr+2         0.0         0.0           Ba+2         0.0         0.0           Fe+2         0.0         0.0           Display Name         OLI Name         Template Manager           Pisplay Name         OLI Name         Standard           A: Cs+1         CSION         Save as           0LT CSION         CUION         Save as           SW Cu(+)         CUION         Balance Options           SWCu(+1)         CUION         Type	Ca+2	0.0	0.0	
Ba+2         0.0         0.0           Fe+2         0.0         0.0           Cu         ✓         Template Manager           Display Name         OLI Name         Standard           *: Cs+1         CSION         Standard           out CSION         CSION         Save as           sm Cu(+)         CUION         Balance Options           sm Cu(+1)         CUION         Type	Mg+2	0.0	0.0	Formula
Fe+2         0.0         0.0           Cu         ✓         Template Manager           Display Name         OLI Name         Standard           .< Cs+1	Sr+2	0.0	0.0	Show Non-zero Only
Cu     ✓     Template Manager       Display Name     OLI Name     Standard                 Cs+1         CSION                 OIT CSION         CSION                 SWCu(+)         CUION                 SWCu(++)               SWCu(+1)             CUIION	Ba+2	0.0	0.0	Show Balanced Column
Cu     OLI Name     Standard       Display Name     OLI Name     Standard       ^t Cs+1     CSION     Save as       0LT CSION     CSION     Save as       Strik Cu(+)     CUION     Balance Options       Strik Cu(+1)     CUION     Type	Fe+2	0.0	0.0	Template Manager
Image: Construction         CSION         Save as           0LT CSION         CSION         Save as           SW Cu(+)         CUION         Balance Options           SW Cu(+1)         CUION         Type	Cu 🗸			relipiate Manager
OLICSION     CSION       SYNCu(+)     CUIION       SYNCu(++)     CUION       SYNCu(+1)     CUIION	Display Name	OLI N	lame	▲ Standard
OLI CSION         CSION           SYN Cu(+)         CUIION           SYN Cu(++)         CUION           SYN Cu(+1)         CUION	▲ Cs+1	CSIO	N	Save as
S™Cu(++)     CUION     Balance Options       S™Cu(+1)     CUIION     Type	LICSION	CSIO	N	
sm(cu(++) CUION Type	<sup>ም</sup> Cu(+)	CUIIC	N	
	"NCu(++)	CUION		Balance Options
SYN Cu(+2) CUION Dominant Ion	<sup>w</sup> Cu(+1)	CUIIC	N	Туре
	₩Cu(+2)	CUIO	N	V Dominant Ion
CO2 0.0 0.0	C02	0.0	0.0	
H2S 0.0 0.0	H2S	0.0	0.0	
SiO2 0.0 0.0	SiO2	0.0	0.0	
B(OH)3 0.0 0.0	B(OH)3	0.0	0.0	

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>**.

Neu	Dominiant Ion		
CO2	0.0	0.0	
H2S	0.0	0.0	
SiO2	0.0	0.0	
B(OH)3	0.0	0.0	
oli	0.0	0.0	

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.

 De:	scriptio	n 🔮 Design	题 Пера	ort					
Reconcile Data Entry		ulate Brine Properti ) Concentration Dai ) Gas-Phase CO2 C ) Measured pH and ) Measured pH Only ) Measured pH, Alkk ] Calculate Alkalinity	ta Only ontent (mole Alkalinity / alinity, TIC	%)	Specs	Calculate 🥥 to form			
ec		Properties	1	N	leasured	Calculated			
<u>۳</u>	Temp	erature (°C)			25.0000				
$\mathbf{i}$	Press	sure (atm)		1.00000					
	pН				0.0				
Alkalinity (mg HCO3/L)				0.0					
	Dens	ity (g/ml)			0.0				
	Elec	Cond, specific (µm	ho/cm)		0.0				
	Total	Dissolved Solids (r	ng/L)	0.0					
			Compo	sition A	djustments				
	Char	ge Balance Unknov	vn.						

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	
рН	0.0	
Alkalinity (mg HCO3/L)	0.0	
ensity (g/ml)	0.0	
lec Cond, specific (µmho/cm)	0.0	
Total Dissolved Solids (mg/L)	0.0	
Comp	osition 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<sup>10</sup>, 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.

If you don't have a measured property value, for example, the Specific Electrical Conductivity, just leave it blank.

<sup>&</sup>lt;sup>10</sup> 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.

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. think simulation | getting the chemistry right 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:

Concentration Data Only Gas-phase CO2 content (mole%) Measured pH and Alkalinity Measured pH Only Measured pH, Alkalinity, TIC

Additionally, there is the option to calculate the alkalinity value by checking the **Calculate Alkalinity** box.

Calculate Brine Properties Using:			
Concentration Data Only	Specs	Calc <u>u</u> late	0
Gas-Phase CO2 Content (mole%)	· · ·		
O Measured pH and Alkalinity	Allow solids to form		
O Measured pH Only			
Measured pH, Alkalinity, TIC			
Calculate Alkalinity			

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.

### **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.

	Aqueous Species	Formula to enter	Formula weight multiplier
B, boron	Boric Acid	НЗВОЗ	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)
		HS-1 or SO4-2	S (mg/l) $\times$ 1.03 for HS-1 (mg/l)
S, Sulfur	Sulfate or Sulfide	(cannot tell from total S only)	or
			S (mg/l) $\times$ 3.0 for SO4-2 (mg/l)

#### Converting element concentration to species for Brine Analysis

## **Reconciliation Options in the Brine Analysis - Definitions**

When reconciling a Brine Analysis, there are five options for reconciliation:

**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. (<u>See electroneutrality options</u>).

**Gas-phase CO2 content (mole%):** Frequently it is simpler and more stable to measure the gas-phase CO<sub>2</sub> 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. think simulation | getting the chemistry right performs a CO<sub>2</sub> 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<sub>2</sub> is adjusted to match a saturated gas composition.

**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 HCI or NaOH, or you may select your preferred acids and bases to adjust the pH.

**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 to a different alkalinity titrant if you prefer.

**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**: 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.

## 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. We will calculate the **pH** and **scaling tendency** of a brine sample based upon its measured composition at 1 atm and 25 °C.

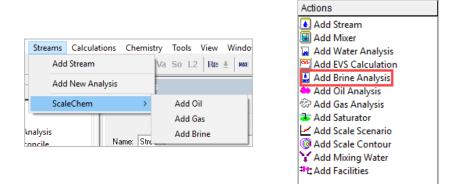
#### Starting the Simulation

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											
Cation	s (mg/L)	Anions (n	ng/L)	Neutra	als (mg/L)	Measured Properties						
Na+1	20400	CI-1	37000	CO2	150	рН	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**

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



Click on the new Brine and press <F2> to change the name to *Brine Analysis* Select the AQ thermodynamic Framework (remember that MSE is the default so please switch it) Click on the Names Manager Icon and select the Formula option (default) Click on the Units Manager Icon, and select Metric, Concentration (default) Under the Design Tab, enter the Cation, Anion, and Neutrals composition given in the table above. Your screen should look like the image below:

Variable	Value	Balanced	Entry Options	Summary
Catio	ns (mg/L)		Units	Unit Set: Metric (mass concentration
Na+1	20400.0	20400.0	mg/L v	
K+1	400.000	400.000	Display	Automatic Chemistry Model Aqueous (H+ ion) Databanks:
Ca+2	3800.00	3800.00		Aqueous (H+ ion)
Mg+2	830.000	830.000	Formula 🗸	No Solid phase(s)
Sr+2	15.0000	15.0000	Show Non-zero Only	Using K-fit Polynomials T-span: 25.0 - 225.0
Ba+2	0.700000	0.700000	Show Balanced Column	P-span: 1.0 - 1500.0
Fe+2	10.0000	10.0000		Stream Parameters:
			Template Manager	Temperature (°C) 25.0000
Anior	ns (mg/L)		Standard 🗸	Pressure (atm) 1.00000
CI-1	37000.0	38938.1		Stream amount (L) 1.00000
S04-2	2200.00	2200.00	Save as >	Dominant Ion Charge Balance
HCO3-1	0.0	0.0		(eq/L):
HS-1	0.0	0.0	Balance Options	Cation Charge 1.15621
C2H3O2-1	715.000	715.000	Туре	Anion Charge -1.10155
			Dominant Ion V	Imbalance 0.0546661
Neutra	als (mg/L)			lon(s) needed to balance (mg/
CO2	150.000	150.000		CI-1 1938.077
H2S	15.0000	15.0000		Concentration Data Only.
SiO2	0.0	0.0		
B(OH)3	0.0	0.0		

**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 concentration ion is used to adjust the electroneutrality. In our example,1938.077 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.

Select **Dominant Ion** as balance option

Click on the **Reconcile** (vertical blue tab)

Notice that the five different types of reconciliations are available in in the upper left corner of the window (see image below). Also, you can see the **Calculate Alkalinity box** ( $\[equal Calculate Alkalinity]\]) option, which allows you to compute the alkalinity, based on the concentration entered.$ 

**Select** the **Concentration Data Only** option. This option means that the software will compute the water properties based on the current concentration of neutral, cation, and anion species. The calculation will not use the measured pH, or the measured alkalinity entered (if any).

Enter the measured properties: pH = 7.1 and Alkalinity = 715 as mg HCO3/L

Reconcile Data Entry	Calculate Brine Properties Using: Concentration Data Only Gas-Phase CO2 Content (mole%) Measured pH and Alkalinity Measured pH Only Measured pH, Alkalinity, TIC Calculate Alkalinity	Specs	Calcylate 🥥		Unit Set: Metric (mass concentration) Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion) No Solid phase(s) Using K-fit Polynomials T-span: 25.0 - 225.0
Se [	Properties	Measured	Calculated	1	P-span: 1.0 - 1500.0 Stream Parameters:
<u>۳</u>	Temperature (°C)	25.0000			Temperature (°C) 25.0000
$ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	Pressure (atm)	1.00000			Pressure (atm) 1.00000
	pH	7.10000			Stream amount (L) 1.00000
	Alkalinity (mg HCO3/L)	715.000		>	
	Density (g/ml)	0.0			Dominant Ion Charge Balance (eg/L):
	Elec Cond, specific (µmho/cm)	0.0			Cation Charge 1.15621
	Total Dissolved Solids (mg/L)	0.0			Anion Charge -1.10155
	Comp		Imbalance 0.0546661		
	Add Charge Balance (mg/L CI-1)				lon(s) needed to balance (mg/L):
					CI-1 1938.077 Concentration Data Only.

Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key

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=5.31 and Alkalinity=263.0 mg HCO3-1/L vs the measured values of pH=7.1 and Alkalinity=715 mg HCO3-1/L.

< Des	cription 🤒 Design 📓 Report 🕻	🤰 File Viewer			
Reconcile Data Entry	Calculate Brine Properties Using: Concentration Data Only Gas-Phase CO2 Content (mole%) Measured pH and Alkalinity Measured pH Only Measured pH, Alkalinity, TIC Calculate Alkalinity	Specs	Calculate 🥥		Summary Unit Set: Metric (mass concentration) Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion) No Solid phase(s) Using K-fit Polynomials T-span: 25.0 - 225.0
e l	Properties	Measured	Calculated		P-span: 1.0 - 1500.0
~	Temperature (°C)	25.0000			Stream Parameters:
	Pressure (atm)	1.00000			Temperature (°C) 25.0000 Pressure (atm) 1.00000
	pН	7.10000	5.31413		Stream amount (L) 1.00000
	Alkalinity (mg HCO3/L)	715.000	263.001		
	Density (g/ml)	0.0	1.04487		Dominant Ion Charge Balance (eq/L):
	Elec Cond, specific (µmho/cm)	0.0	91637.7		Cation Charge 1.15621
	Total Dissolved Solids (mg/L)	0.0	67370.0	>	Anion Charge -1.10155
	Compo	sition Adjustments		T	Imbalance 0.0546661
	Add Charge Balance (mg/L CI-1)		1938.08		lon(s) needed to balance (mg/L):
					CI-1 1938.077
					Concentration Data Only.
					Phase Amounts:
					Aqueous (g) 1044.87
					Aqueous Phase Properties:
					pH 5.31413
					Ionic Strength (mol/mol) 0.0226409
					Density (g/ml) 1.04487
					Calc. elapsed time: 9.227 sec.
					Calculation complete
L					The brine is supersaturated with 2

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 °C, 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 5.31. The density of this solution is 1.04487 g/ml. Remember, for this example the software used only the concentration of neutrals, cations, and anions in solution to do a reconciliation.

Click on the **Report** tab and scroll down to the **Pre and Post Scaling Tendencies** table.

Scale Mineral	Pre-scaling	Pre-index	Post-scaling	Post-index
BaSO4 (Barite)	9.41306	0.973731	9.41306	0.973731
CaCO3 (Calcite)	0.0252328	-1.59803	0.0252328	-1.59803
CaSO4.2H2O (Gypsum)	0.936931	-0.0282926	0.936931	-0.0282926
CaSO4 (Anhydrite)	0.738602	-0.131590	0.738602	-0.131590
FeCO3 (Siderite)	2.71223e-3	-2.56667	2.71223e-3	-2.56667
FeS (Pyrrhotite)	16.3375	1.21319	16.3375	1.21319
KCI (Sylvite)	6.72353e-4	-3.17240	6.72353e-4	-3.17240
FeS (Mackinawite)	0.278931	-0.554504	0.278931	-0.554504
NaCl (Halite)	0.0122286	-1.91262	0.0122286	-1.91262
SrCO3 (Strontianite)	2.96599e-4	-3.52783	2.96599e-4	-3.52783
SrSO4 (Celestine)	0.200644	-0.697574	0.200644	-0.697574

Pre and Post Scaling Tendencies

From this table, you can see that Barite and Pyrrhotite solids have been predicted to be supersaturated.

For more detailed information about scaling tendencies, you can go to Scaling section on page 179.

#### 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	CI(-1)	38938.1	C02	107.419
Na(+1)	20400.0	HCO3- (*)	59.0364	H2S	15.0000
Ba(+2)	0.700000	SO4-2	2200.00		
Ca(+2)	3800.00	Acetate-	545.141		
Fe(+2)	10.0000				
Mg(+2)	830.000				
Sr(+2)	15.0000				

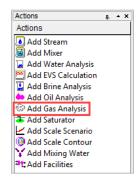
This table shows the composition of the brine after the reconciliation (calculation) has taken place.

# Section 12. Entering a Gas Analysis in think simulation | getting the chemistry right

### **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.

	Streams	Calculat	tions	Chemis	try	Tools	View	Wi	ndo
	Ad	d Stream			Va	So L2	Re	±	IASE
-	Add New Ana		alysis		;				
ľ	Sca	leChem		>		Add O	il		1
[						Add G	as		
	nalysis oncile		Na	me: Stre		Add B	rine		



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.

Component         Value         Normalized           H20         0.0         0.0         0.0           N2         0.0         0.0         0.0           CO2         0.0         0.0         0.0           H25         0.0         0.0         0.0           C2H6         0.0         0.0         0.0           C3H8         0.0         0.0         0.0           FCH10         0.0         0.0         0.0           FCH12         0.0         0.0         0.0           C5H12         0.0         0.0         0.0           C6H14         0.0         0.0         0.0           Capt Manager	2	Compone	nt	Value	Normalized	Entry Options
N2       0.0       0.0         CO2       0.0       0.0         H2S       0.0       0.0         C2H6       0.0       0.0         C3H8       0.0       0.0         iC4H10       0.0       0.0         iC4H10       0.0       0.0         ic5H12       0.0       0.0         C6H14       0.0       0.0         C6H14       0.0       0.0         Group Manager       Group Manager	0		5	Subtotal: 0.0/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)	Units
CO2       0.0       0.0         H2S       0.0       0.0         C2H6       0.0       0.0         C3H8       0.0       0.0         C3H8       0.0       0.0         I+C4H10       0.0       0.0         I+C5H12       0.0       0.0         C5H12       0.0       0.0         C6H14       0.0       0.0         Group Manager       Group Manager		H2O		0.0	0.0	mole %
H2S       0.0       0.0         ✓ CH4       0.0       100.000         C2H6       0.0       0.0         C3H8       0.0       0.0         □ i+C4H10       0.0       0.0         □ n-C4H10       0.0       0.0         □ C5H12       0.0       0.0         □ C5H12       0.0       0.0         □ C6H14       0.0       0.0         □ C6H14       0.0       0.0         □ C6H14       0.0       0.0         □ C6H14       0.0       0.0		N2			0.0	Display
H2S       0.0       0.0         ✓ CH4       0.0       100.000         C2H6       0.0       0.0         C3H8       0.0       0.0         I+C4H10       0.0       0.0         I+C4H10       0.0       0.0         I+C5H12       0.0       0.0         C5H12       0.0       0.0         C6H14       0.0       0.0         ✓       ✓       Makeup         Group Manager       Group Manager		C02		0.0	0.0	Formula
C3H8       0.0       0.0         i-C4H10       0.0       0.0         n-C4H10       0.0       0.0         i-C5H12       0.0       0.0         C5H12       0.0       0.0         C6H14       0.0       0.0         C6H14       0.0       0.0         C6H14       0.0       0.0         C7       C7       0.0         C6H14       0.0       0.0         C7       C7       C7		H2S		0.0	0.0	
C3H8       0.0       0.0         i-C4H10       0.0       0.0         n-C4H10       0.0       0.0         i-C5H12       0.0       0.0         C5H12       0.0       0.0         C6H14       0.0       0.0         C6H14       0.0       0.0         C6H14       0.0       0.0         C7       C7       0.0         C6H14       0.0       0.0         C7       C7       C7		CH4		0.0	100.000	
i-C4H10         0.0         0.0           n-C4H10         0.0         0.0           i-C5H12         0.0         0.0           C5H14         0.0         0.0           C6H14         0.0         0.0           Group Manager         Group Manager	ž	C2H6		0.0	0.0	Show Normalized Column
n-C4H10         0.0         0.0           i-C5H12         0.0         0.0           C5H12         0.0         0.0           C6H14         0.0         0.0		СЗН8		0.0	0.0	Template Manager
i         i						-
C5H12         0.0         0.0           C6H14         0.0         0.0           Makeup         Group Manager						Standard \
C6H14 0.0 0.0 0.0 Normalize Options Makeup Group Manager				0.0	0.0	Save as
Normalize Options       Makeup       Group Manager						
Group Manager		C6H14		0.0	0.0	u h e u
Group Manager			~			
Use Groups Add						
						Use Groups Add

We will start in the **Inflows** (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 chemical 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.

	Component	Value	Normalized	Entry Options
		Subtotal: 0.0/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)	Units
	H20	0.0	0.0	mole %
	CH4 CH4	0.0	100.000	Display
	N2	0.0	0.0	Formula
	C02	0.0	0.0	
	H2S	0.0	0.0	Show Non-zero Only
	C2H6	0.0	0.0	Show Normalized Colum
	СЗН8	0.0	0.0	Template Manager
4	i-C4H10	0.0	0.0	
	n-C4H10	0.0	0.0	Standard
	i-C5H12	0.0	0.0	Save as
	C5H12	0.0	0.0	
	C6H14	0.0	0.0	
	i-C8H18	V 0.0	0.0	Normalize Options
	Display Name	OLI N	ame	Makeup Y
	▲ i-C4H10	ISOBU	ITANE	Group Manager
	▲i-C5H12	IPENT	AN	Use Groups Add
	∧i-C8H18	MEPN	ITAN224	
	▲12	IOD2E	L	
	SIN IBA	IBUTY	LAMN	
	0LI IRENIZENE	IRENI7	FNF	× .

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>**.

	Component	Value	Normalized	Entry Options
Г		Subtotal: 0.0/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)	Units
F	H2O	0.0	0.0	mole %
	CH4	0.0	100.000	Display
	N2	0.0	0.0	Formula
	C02	0.0	0.0	
	H2S	0.0	0.0	Show Non-zero Only
	C2H6	0.0	0.0	Show Normalized Colu
	СЗН8	0.0	0.0	Template Manager
	i-C4H10	0.0	0.0	remplate Hanager
	n-C4H10	0.0	0.0	Standard
	i-C5H12	0.0	0.0	Save as
	C5H12	0.0	0.0	buve usini
	C6H14	0.0	0.0	
	i-C8H18	0.0	0.0	Normalize Options
	OLI	0.0	0.0	Makeup

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 °F (15.56°C) and 14.7 psia (1.002 atm).

) Des	s cr	iption	🚱 Design 🚱 Definition 📓 Report		
Inflows	F	H20	Component	Normalized Subtotal: 100.000/100.000 (mole %) 0.0	Calculate Condition
Reconcile		CH4		100.000	Conditione Value
					Show Non-zero Only

## A Basic Gas Analysis

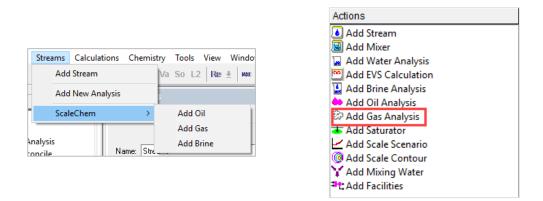
A brief introduction to the gas analysis tool will be shown in the example below. As we go through the example, the basic definitions, functionalities, and reporting for the *Gas Analysis object* will be shown.

#### Example 61: Basic Gas Analysis

The Gas Analysis object provides a quick way to enter a pure-component hydrocarbon gas.

#### Setting the Gas Analysis

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



**Click** on the new Gas Analysis and press **<F2>** to change the name to *Gas Analysis* 

Select the **AQ** thermodynamic Framework (Remember that MSE is the default so you need to change it)

Click on the Names Manager Icon and select the Formula option (default)

Click on the Units Manager Icon, and select Metric, Mole Frac. (default)

Under the Inflows Tab, enter the gas composition given in the table below

Gas	Analysis Compositi	on
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:

	Component	Value	Normalized	Entry Options
		Subtotal: 100.000/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)	Units
H E H	120	1.80000	1.80000	mole %
	12	3.00000	3.00000	Display
	002	1.50000	1.50000	Formula
	12S	0.500000	0.500000	
V (	CH4	65.5000	65.5000	Show Non-zero Only
	22H6	14.0000	14.0000	Show Normalized Colu
	C3H8	8.00000	8.00000	Template Manager
i i i	-C4H10	1.00000	1.00000	-
	n-C4H10	3.00000	3.00000	Standard
- F	-C5H12	0.500000	0.500000	Save as
	C5H12	0.700000	0.700000	
	C6H14	0.500000	0.500000	
				Normalize Options
				Makeup
				Group Manager
				Use Groups Ad

Note: There are several options to the right of the data entered.

**Entry options:** Here you can select the preferred units, and display name. You also have the option to show the non-zero values only – sometimes the composition of species is zero – and also show the normalized (yellow) column – this option is useful when the values don't add up to 100 mole%.

**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.

**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.

Click on **Reconcile** (vertical blue tab). The reconciliation calculation will be calculated at 15.556 C and 1.00231 atm (standard conditions).

🦪 Description 🔮 Design	Definition	🔯 Report
------------------------	------------	----------

0	Component	Normalized	Reconciled Gas	Calc <u>u</u> late 🤇	
		Subtotal: 100.000/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)	Condition	
	H20	1.80000	1.75645	Condition	
-	N2	3.00000	3.00133	Conditions	Value
Þ	C02	1.50000	1.50066	Temperature (°C)	15.5556
collelle	H2S	0.500000	0.500221	Pressure (atm)	1.00231
	CH4	65.5000	65.5290		
	C2H6	14.0000	14.0062	1	
	СЗН8	8.00000	8.00355		
	i-C4H10	1.00000	1.00044	Show Non-zero Only	
	n-C4H10	3.00000	3.00133	Snow Non-zero Only	
	i-C5H12	0.500000	0.500222		
	C5H12	0.700000	0.700310		
	C6H14	0.500000	0.500222		

Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key

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.

Г	Component	Normalized	Reconciled Gas	Calcylate 🥝		Summary
		Subtotal: 100.000/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)			Unit Set: Metric (mole fraction)
IF	H2O	1.80000	1.75645	Condition		
Ŀ	N2	3.00000	3.00133	Conditions Value		Automatic Chemistry Model Aqueous (H+ ion) Databanks;
ŀ	C02	1.50000	1.50066	Temperature (°C) 15.5556		Aqueous (H+ ion)
ŀ	H2S	0.500000	0.500221	Pressure (atm) 1.00231		Second Liquid phase
ŀ	CH4	65.5000	65.5290			Using K-fit Polynomials T-span: 25.0 - 225.0
ŀ	C2H6	14,0000	14.0062	J		P-span: 1.0 - 1500.0
ŀ	C3H8	8.0000	8.00355			Stream Parameters:
ŀ	i-C4H10	1.00000	1,00044			Temperature (°C) 15.5556
ŀ	n-C4H10	3.00000	3.00133	Show Non-zero Only		Pressure (atm) 1.00231
ŀ	i-C5H12	0.50000	0.500222			Makeup Normalization: CH4.
ŀ	C5H12	0.70000	0.700310			Equilibrium Calculation.
ŀ		0.50000	0.500222		1	Phase Amounts:
ŀ	C6H14	0.500000	0.500222			Aqueous (mol) 0.0443282
ŀ						Vapor (mol) 99.9557
						Solid (mol) 0.0
						2nd Liquid (mol) 0.0
						Aqueous Phase Properties:
						pH 4.75177
						Ionic Strength (mol/mol) 3.20592e-7
						Density (g/ml) 0.999257
						Calc. elapsed time: 0.940 sec. Calculation complete

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 15.556°C 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.

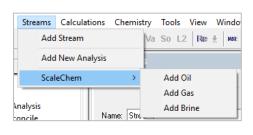
The **Aqueous Phase Properties** information shows the computed pH, ionic strength, and density of the solution.

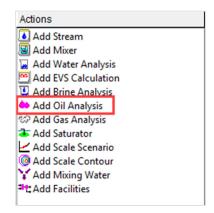
Click on the **Report** tab. Here you will see a more complete representation of the results at equilibrium.

# Section 13. Entering an Oil Analysis in think simulation | getting the chemistry right

## **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 three different tabs for this analysis. The Description, Design, 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 chemical 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.

	Component	Value	Normalized	<ul> <li>Entry Options</li> </ul>
n-C4H10		0.0	0.0	Units
i-C5H12		0.0	0.0	mole %
C5H12		0.0	0.0	Display
C6H14		0.0	0.0	
C7H16		0.0	0.0	
i-C8H18		0.0	0.0	Show Non-zero On
n-C8H18		0.0	0.0	Show Normalized C
C9H20		0.0	0.0	Template Manager
C10H22		0.0	0.0	· · · ·
C11H24		0.0	0.0	Standard
C12H26		0.0	0.0	Save as
C13H28		0.0	0.0	
C14H30		0.0	0.0	
C15H32		0.0	0.0	
C16H34		0.0	0.0	Prorate
C17H36		0.0	0.0	
C18H38		0.0	0.0	
C19H40		0.0	0.0	
C20H42		0.0		
C21H44		0.0	0.0	
C22H46		0.0		
C23H48		0.0	0.0	
C24H50		0.0	0.0	
C25H52		0.0	0.0	
C30H62		0.0	0.0	
C35H72		0.0	0.0	

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.

ſ						
ombined	Component	Molecular Weight	Nomal Boiling Point (°C)	Specific Gravity	Thermo Method	Value (mole %)
Ö	<enter a="" name=""></enter>					
Pseudocomponents						

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.

	Componer <enter a="" name=""></enter>	nt mole 9	<u> </u>			Distillation D	ata Grid		
					Volume%			Temperature (°C)	
	ntry Options								
T	уре /	ASTM D86	$\sim$						
2 Th	hermo Method 🛛	API-8	$\sim$						
De	ensity 0.00	Specific Gravity	$\sim$						
	o, of Cuts		0						
	Display As	ssay Cuts							
	Entry C ay Properties	options	I						
	Name	Mole %	Mol V	Vt. NBP (	°C) Sp (	Gr Cr Temp	°C) Cr Pres (atm)	Cr Vol (L/mol)	Acentric Fact

**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.

Entry Options	
Туре	ASTM D86 V
Thermo Method	ASTM D86 ASTM D1160
Density 34.00	ASTM D2887 TBP CURVE

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.

Thermo I	Method	API-8 V
Density	34.00	API-8 API-5
No. of C	uts	Cavett 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 three, average bulk density options: Specific Gravity, API gravity and Watson K.

Density	34.00	Specific Gravity 🔍 🗸
No. of C	uts	Specific Gravity API Gravity Watson K

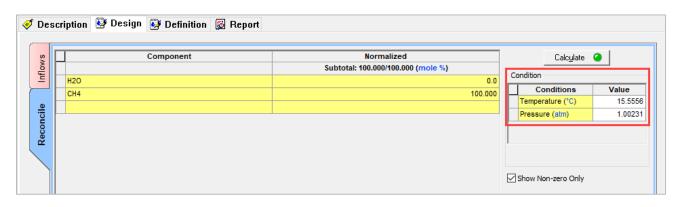
**Specific Gravity** (SG) is the ratio of the material density to water. think simulation | getting the chemistry right requires specific gravity to be between 0.228 and 1.6. **API Gravity** is defined as API Gravity = (141.5/SG) – 131.5

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 393-396.

**Distillation Data Grid:** In this section the distillation data is entered.

The **Reconcile** tab is where the equilibrium calculations are performed and 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 °F (15.556°C) and 14.7 psia (1.002 atm).



## **Basic Definitions for the Oil Analysis Tool**

#### **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.

#### 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:

$$T_c = 24.2787 \times T_b^{0.58848} \times SG^{0.3596}$$
$$\ln P_c = \frac{3.12281\rho + 9}{T_b^{2.3125}SG^{2.3201}} \text{ if } T_b < 1000 \text{ °F}$$

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

$$\Delta = \frac{8.75 + 1.978(\log T_b) \times T_b}{1.8} \text{ if } T_c < 536.67 \text{ R}$$

If 536.67<Tc<593 R, the above result for  $\Delta$  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:

$$T_{c} = 768.0712 + 1.7133693 \times T_{b} - 0.0010834 \times T_{b}^{2} - 0.008921258 \times T_{b} \times API + (3.8890584\rho - 7) + T_{b}^{3} \times 5.309492\rho - 6 \times T_{b}^{2} \times API + 3.27116\rho - 8 \times (T_{b} \times API)^{2}$$

$$\begin{split} log P_c &= 2.829046 + 0.0009412 \times T_b - 3.047475\rho - 5 \times T_b^2 - 2.087611\rho - 5 \times API \times T_b + 1.5184103\rho - 9 \times T_b^3 \\ &+ 1.1047809\rho - 8 \times API \times T_b^2 - 4.82716\rho - 8 \times API^2 \times T_b + 1.3949619\rho - 10 \times (API \times T_b)^2 \\ V_c &= \frac{Z_c \times T_c \times 10.73}{P_c} \end{split}$$

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

$$\Delta = \frac{8.75 + 1.978(\log T_b) \times T_b}{1.8} \text{ if } T_c < 536.67 \text{ R}$$

If 536.67<Tc<593 R, the above result for  $\Delta$  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

$$\Delta = \frac{8.75 + 1.978(\log T_b) \times T_b}{1.8} \text{ if } T_c < 536.67 \text{ R}$$

If 536.67<Tc<593 R, the above result for  $\Delta$  is multiplied by f:

$$f = \left(T_c - \frac{536.67}{T_c - T_b}\right)^{0.38}$$

$$\Delta = \left(\frac{(0.98907 \times SG)(\Delta - 592.4439)}{MW}\right)^{0.5}$$

#### Average Bulk Density

#### Specific Gravity

Unitless, relative to pure water (H<sub>2</sub>O) 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.

# Putting together a complete calculation in think simulation | getting the chemistry right

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 task we will show the main interface of a Brine Analysis, followed by an example of a brine (water analysis) and calculate its scaling tendency. Steps for the simulation will be given with bullet points.

Add Brine Analysis from Actions Panel.

<b>.</b>
Add Brine
Analysis

Click on the description Tab. If the *Description* tab is not currently displayed, click on the tab.

🖪 Brine		
< Description	🛃 Design	👼 Report
Name: Brine		

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	
Cation	s mg/L	Anions mg	g/L	Measured Properties	
Na+1	36000	CI-	57000	Temperature	25 C
K+1	300	SO4-2	250	Pressure	1 atm
Ca2+	600	H3CO3-1	600	рН	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

~	Variable	Value	Balanced	Entry Options
12	Cation	s (mg/L)		Units
Data Entry	Na+1	36000.0	36116.0	ma/L ~
Dat	K+1	300.000	300.000	Display
	Ca+2	600.000	600.000	
	Mg+2	150.000	150.000	Formula ~
-ie	Sr+2	80.0000	80.0000	Show Non-zero Only
Reconcile	Ba+2	5.00000	5.00000	Show Balanced Column
Å	Fe+2	0.0	0.0	
				Template Manager
	Anion	s (mg/L)	Standard V	
	CI-1	57000.0	57000.0	
	S04-2	250.000	250.000	Save as
3	HC03-1	600.000	600.000	
	HS-1	0.0	0.0	Balance Options
	C2H3O2-1	0.0	0.0	Type
				Dominant Ion V
	Neutra	ls (mg/L)		
	CO2	0.0	0.0	
	H2S	0.0	0.0	
	SiO2	0.0	0.0	
	B(OH)3	0.0	0.0	

#### Select Formula

0.0	Display
0.0	
0.0	OLI Tag 🗸 🗸
0.0	Display Name Formula
0.0	OLI Tag

You can display an easier-to-read table by showing only the species that have actual concentrations.

Select the Show non-zero only box

	Variable	Value	Balanced	Entry Options
i i	Cation		Units	
Data Entry	Na+1	36000.0	36116.0	mg/L 🗸
Dat	K+1	300.000	300.000	Display
	Ca+2	600.000	600.000	
	Mg+2	150.000	150.000	Formula 🗸
Reconcile	Sr+2	80.0000	80.0000	Show Non-zero Only
cou	Ba+2	5.00000	5.00000	Show Balanced Column
Å				
	Anion	Template Manager		
	CI-1	57000.0	57000.0	Standard 🗸
	S04-2	250.000	250.000	0
	HCO3-1	600.000	600.000	Save as
	Neutra	ls (mg/L)		Balance Options
				Туре
				Dominant Ion 🗸 🗸

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**.

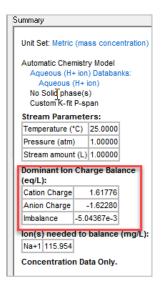
	Variable	Value	Balanced
Data Entry	Cation	s (mg/L)	
a	Na+1	36000.0	36116.0
Dat	K+1 43	300.000	300.000
	Ca+2	600.000	600.000
	Mg+2	150.000	150.000
Reconcile	Sr+2	80.0000	80.0000
Co	Ba+2	5.00000	5.00000
Å.			
	Anions	s (mg/L)	
	CI-1	57000.0	57000.0
	S04-2	250.000	250.000
	HCO3-1	600.000	600.000
	Neutra	ls (mg/L)	

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.

Balance Options	
Туре	
Dominant Ion	-
Dominant Ion	-
Prorate Cation	
Prorate Anion	
Makeup Ion	

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.* 

Select *Concentration Data Only* Option Check the *Calculate Alkalinity* box Enter the measured pH (7.67), density (1.064 g/mL) and TDS (96280 mg/L) 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.

Reconcile Data Entry	Calculate Brine Properties Using: Concentration Data Only Gas-Phase CO2 Content (mole %) Measured pH and Alkalinity Measured pH Only Calculate Alkalinity	Specs	Calcylate 🥥
LO C	Properties	Measured	Calculated
Re	Temperature (°C)	25.0000	
	Pressure (atm)	1.00000	
	pH	7.67000	
	Alkalinity (mg HCO3/L)	600.000	
	Density (g/ml)	1.06400	
	Elec Cond, specific (µmho/cm)	0.0	
	Total Dissolved Solids (mg/L)	96280.0	
	Cor	nposition Adjustments	
	Add Charge Balance (mg/L Na+1)		

Select the Calculate button or press the <F9> key

Reconcile Data Entry		Calculate Brine Properties Using:		Specs Allow solids to form		Calculate 🥥
8		Properties		Measured		Calculated
Re		Temperature (°C)		25.0000		
		Pressure (atm)		1.00000		
		pH		7.67000		7.42904
		Alkalinity (mg HCO3/L)		600.000		564.260
		Density (g/ml)		1.06400		1.06134
		Elec Cond, specific (µmho/cm)		0.0		1.26085e5
		Total Dissolved Solids (mg/L)		96280.0		95090.6
			osition Adjustments	_		
		Co	mp	osmon Adjustments		

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.

Aqueous Phase Prop	erties:
<sub>д</sub> рн	7.42904
lonic Strength (mol/mol)	0.0288607
Density (g/ml)	1.06134
Calc. elapsed time: 7. Calculation complete The brine is supersatura solids: BaSO4 (Barite), CaCO3 SrCO3 (Strontianite) Alkalinity: 564.260mg HC	ted with 3 (Calcite),

More details of the Brine composition can be found in the **<u>Report</u>** Tab.

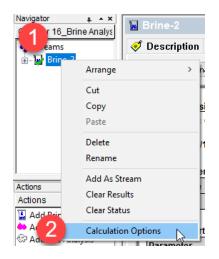
In the Report tab, scroll down to the Pre and Post Scaling Tendencies, where you will find the results of Scaling Tendencies with Solids off.

np to: Brine Analysis Dat	a	$\sim$		<b>Q Q</b>	🔍 Customize E	Expor
Pre and Post Scaling T	endencies	Λ			_	
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		
KCI (Sylvite)	7.36476e-4	-3.13284	7.36476e-4	-3.13284		
NaCI (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	CI(-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					

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:

Right click on the brine analysis icon Select *Calculation Options* 



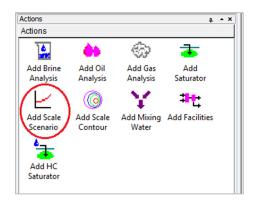
## Enable Pre-scaling Tendencies

Calculation Options - Brine-2	?	$\times$
ScaleChem Calculation Options ScaleChem Convergence		
General Diagnostics Show status dialog Enable trace Verbose		
Optional Properties		
Diffusivities and Mobilities		
Diffusivities Matrix		
Viscosity		
Electrical Conductivity		
Heat Capacity		
Activities, Fugacities, and K-Values		
Gibbs Free Ellyrgy		
Entropy		
Thermal Conductivity		
Surface Tension		
✓ Interfacial Tension		
Pre-scaling Tendencies		
OK Cancel Apply	Help	1

# 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.

Design 📶 Plot 📓 I	Report 🚊 File V	liewer
be Na	me	Flow
elected Inlet Name		
Component	Value (	mol/hr)
	be Na	elected Inlet Name

## 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 think simulation | getting the chemistry right 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.

File Edit Streams Calculation	ns Chemistry Tools View Window H	elp	_ 5	×
		± 🙀 ± 🛛 🚧 🚟 ± 💱 🔉 😭	N	
Chapter 16_Brine Analysis*	Brine Scale Scenario			
	Description 🤮 Design 🛍 Plot 📓	Report 🔜 File Viewer		
Brine-2				
Brine Scale Scenario	Type N	ame Flow	Calculate 🥝	
	S Type N <select></select>		Calculate Alkalinity	
			Summary	
	onditions		Unit Set: Scale Metric	
	ပိ		Automatic Chemistry Model Aqueous (H+ ion) Databanks:	
			Aqueous (H+ ion)	
	Detail Info of Selected Inlet Name		Custom K-fit P-span At least one inlet should be selected.	
	Component	Value (mol/hr)	At least one inlet should be selected. Selected Solids:	
Actions		values (month)	No Solid Selected.	
Actions			Calculation not done	

- 4. Select the Inlets tab
- 5. Select the right corner of the first cell in the Type column then select Brine (bbl/day). You may need to change units by clicking the blue hyperlink.

ets	Туре	Name	Flow
Inlets	<select></select>		
$\land$	Whole Fluid		
suo			
Conditions			
ပိ			
$\land$			
Solid	Detail Info of Selected Inlet I	Name	
S	Compone	nt Va	lue (mol/hr)

6. Select Brine from the drop-down menu in the Name column.

🛷 Des	cri	iption 🔮 Design	🛍 Plot 📓 Report 🚊 F	ile Viewer
<u> </u>	_			
ts		Туре	Name	Flow
nlets		Brine	-	
		<select></select>	Brine [AQ]	
			h	2

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)

<b>«</b>	De	scr	iption	🥸 Desig	n 🛍 Plot	<u> </u> Report	🤰 File Viewer	
	Inlets	P	<enter i<="" th=""><th>Locatio Location Name</th><th></th><th>Temperature (</th><th>Pressure (bar)</th><th>Drop Solid</th></enter>	Locatio Location Name		Temperature (	Pressure (bar)	Drop Solid
	Conditions			G				
	Solid		Auto Ste Steps:	p 5 Go		coom Đ Q Q		

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.

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

#### Scale Scenario Locations

The diagram within the Conditions screen and the list of locations in the Summary window 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 specified conditions.

I	Location	Temperature (°C)	Pressure (bar)	Drop Solids		Cale	lculate 🥝	1
	Reservoir	125.000	275.000					
IJ	Bottom hole	125.000	280.000			Calcu	ulate Alkalinit	y
	Downhole	115.000	190.000			Summary		
	Midwell	105.000	130.000					
	Wellhead	100.000	100.000			Unit Set: <custon< td=""><td>n&gt;</td><td></td></custon<>	n>	
	Choke	90.0000	80.0000			Automatic Chemis	stry Model	
	Separator	60.0000	30.0000			Aqueous (H+ i	ion) Databan	ks:
	<enter location="" name=""></enter>					Aqueous (H		
γI						Excluding 74 s Using K-fit Poly		
L	Auto Step Sort Zoom					T-span: 25.0		
L	Steps: 5 Go T P 🔍 🔍 🙋					P-span: 1.0	- 1500.0	
						Inlets:		
11				^		Brine (bbl/day) E	3rine 1400.0	0
					, s	Locations Terr	nperature F	Pressu
	Reservoir Bottom	Downhole				Locations	(°C)	(ba
	T:125.0 P:275.0 T:125.0	T:115.0 P:190.0	T:105 P:130			Reservoir	125.000	275.0
	P:280.0	P:150.0	F:130	.0		Bottom	125.000	280.0
			┛ └──┮			hole		
						Downhole	115.000	190.0
						Midwell	105.000	130.0
	<b>\</b>					Wellhead Choke	100.000	100.0
			7			Separator	90.0000 60.0000	30.00
	Wellhead Choke	Separator						30.00
	T:100.0 T:90.0 P:100.0 P:80.0	T:60.0 P:30.0				Selected Solids		
	1.100.0	1.00.0				No Solid Selected	i.	
						Calculation not do	ane	
1								

The graphical view clearly shows the five locations and their Temperature and Pressure conditions.

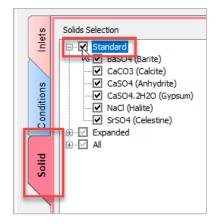
The Drop Solids checkbox column is designed to help the users decide if they want to carry forward solids from certain locations or not.

## Solid Tab

- 10. Select the **Solid** Tab
- 11. Make sure that the solid button in the menu bar is selected.



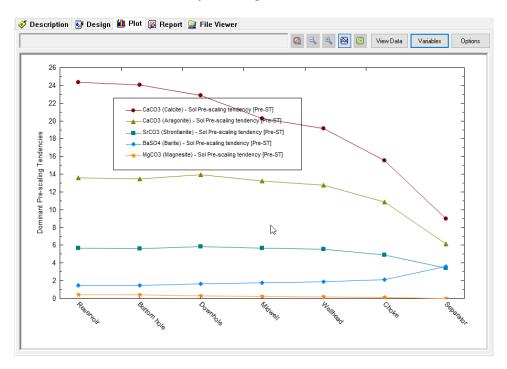
12. Select the Standard checkbox



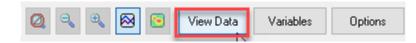
13. Press the Calculate button of select the <F9> key

#### 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

Double click on the Add Gas Analysis object in the Actions Panel

Actions					
Actions					
•	w.	12	evs		
Add Stream	Add Mixer	Add Water Analysis	Add EVS Calculation	Add Brine Analysis	
45	$\odot$	3	4	0	
Add Oil Analysis	Add Gas Analysis	Add Saturator	Add Scale Scenario	Add Scale Contour	
× 1	파는	+			
Add Mixing Water	Add Facilities	Add HC Saturator			

This adds a Gas object to the Navigator panel.

Select the **Description** tab, then rename the object Gas Analysis.

Navigator # * *	🗇 Gas Analysis
Chapter 16_Brine Analysis*	
♦♠ Streams	< < Description 🧕 Design 🛃 Defin
Brine Scale Scenario     Gas Analysis     S	Name:  Gas Analysis

Enter the following composition and values in the Inflows grid:

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

Gas Analysis

The Inflows grid will look like one below..

\$ L	Component	Value	Normalized	Entry Options
Inflows		Subtotal: 100.0	Subtotal: 100.000/	Units
1 2	H20	1.80000	1.80000	mole %
	N2	3.00000	3.00000	Display
	C02	1.50000	1.50000	Formula
Reconcile	H2S	0.500000	0.500000	
5	CH4 CH4	65.5000	65.5000	Show Non-zero Only
æ    –	C2H6	14.0000	14.0000	
	СЗН8	8.00000	8.00000	Template Manager
	i-C4H10	1.00000	1.00000	
	n-C4H10	3.00000	3.00000	Standard
	i-C5H12	0.500000	0.500000	Save as
	C5H12	0.700000	0.700000	
	C6H14	0.500000	0.500000	
		-		Normalize Options
				Makeup

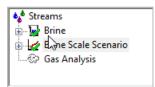
This is the extent of the gas entry step. There are modifications that can be part of the gas analysis entry step (in the Reconcile Tab), but in this case, they are not considered. Now that the gas is entered, the scale scenario considered in Task-2 will be recomputed.

2		Component		Reconciled Ga		Calc <u>u</u> late	<b>@</b>				
			Subtotal: 10	Subtotal: 100.0	-0	ondition			Unit Set: Metric (	mole fracti	on)
=	H20	)	1.80000	1.75645	-				Automatic Chemi	strv Model	
	N2		3.00000	3.00133	Sa	aturate With	None 🔻		Aqueous (H+		anks:
2	CO	2	1.50000	1.50066		Conditions	Value		Aqueous (H Second Liquid		
	H29	3	0.500000	0.500221		Temperature (°C)	15.5556		Custom K-fit P		
5	CH4	ļ.	65.5000	65.5290	E	Pressure (atm)	1.00231		Stream Parame		
1	C2H	16	14.0000	14.0062	E				Temperature (°C		1
	C3H	18	8.00000	8.00355					Pressure (atm)	1.00231	
	i-C4	H10	1.00000	1.00044					Makeup Normaliz	ation: CH4	1
	n-C	4H10	3.00000	3.00133	$\mathbb{N}$	Show Non-zero Only			Equilibrium Ca		
	i-C5	iH12	0.500000	0.500222					Phase Amount		
	C5H	112	0.700000	0.700310					Aqueous (mol)		8
	C6H	114	0.500000	0.500222				, s	Vapor (mol)	99.955	-
						L.		Í	Solid (mol)	0.000	-
						-0			2nd Liquid (mol)		-
									Lind Liquid (mol)		
									Aqueous Phas	e Proper	ties:
									pH		4.75178
									Ionic Strength (r	nol/mol) 3.3	20591e-7
									Density (g/ml)		0.999257

# 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.

Select the Brine Scale Scenario icon in the navigator panel



Select the **Design** Tab (horizontal tab) if not automatically sent there Select the *Inlets* tab (vertical) if not automatically sent there In the *Type* Column Add *Gas* 

s l	Туре	Name	Flow
Inlets	Brine (bbl/day)	Brine	1400.00
= [	Gas (std E3m3/day)	•	
	Brine		
	Whole Fluid		
tions	Gas	N	

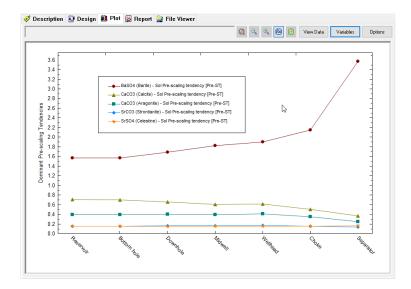
In the Name column select Gas Analysis

ŝ	Туре	Name	Flow
Inlet	Brine (bbl/day)	Brine	1400.00
_	Gas (std E3m3/day)	<b>•</b>	
	<select></select>	Gas Analysis	

Enter a flowrate of 250 std E3m3/day in the flow cell

		Туре	Name	Flow
Inlets	Brine (bl	ol/day)	Brine	1400.00
=	Gas (std	E3m3/day)	Gas Analysis	250.000
	<select></select>	· · · · · · · · · · · · · · · · · · ·		

Calculate (Press <F9>) Select <u>Plot</u> Tab



### Select Variables button

Remove all the variables from the Y1 Axis and the Y2 axis by double-clicking on the variables (this removes them 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.

Expand the Pre-scaling Tendencies button by clicking the + sign Double-click on the CaCO3 (Calcite) variable to move it to the Y1 Axis Expand the Additional Stream Parameters and add pH to the Y2 axis Click <u>**OK**</u>

urves	
Thermodynamic Properties	X Axis
Pre-scaling Tendencies     Dominant Pre-scaling Tendencies     BaSO4 (Bartie) - S01 Pre-scaling tendency     GaC03 (Calctel - S01 Pre-scaling tendency     GaC03 (Calctel - S01 Pre-scaling tendency     GaC04 2/120 (Gypsum) Pre-scaling tendency     NaCl (Halte) - S01 Pre-scaling tendency     SrS04 (Calestre) - S01 Pre-scaling tendency     Scaling Tendencies     Scaling Index	>> Locations Y1 Avis
Aqueous     Vapor     Second Liquid     Solid     Molecular Totals	V >>
Solids	<<
Standard V	
Use short names	
✓ Hide zero species	Z Axis
Plot data which is only within temperature range.	- Select -

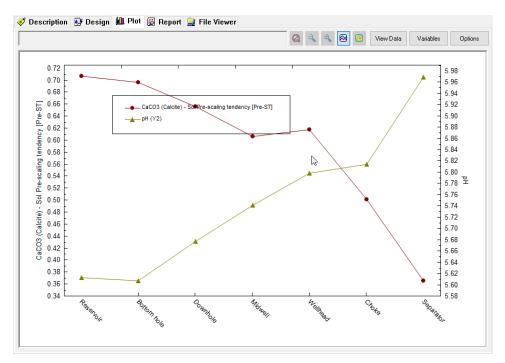
If you are in the *View Data* view, then the table should be similar to the one below.

	Locations	CaCO3 (Calcite) Pre-scali ng tendenc y Scaling Tendenc y Pre-ST	рН
1	Reservoir		5.61211
2	Bottom hole		
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	0.365394	5.96805

Calcite is sub-saturated (S<1) at all locations.

Select the View plot button

The decreasing calcite saturation trend and the increasing pH is easier to see from the plot view.



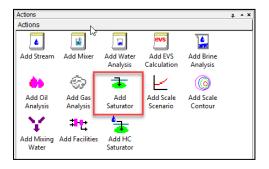
# Task 5 – Creating a Saturator Object

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 NaCI. This assumes 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

Navigator + * Chapter 16_Scale Scenario with S	🚁 Reservoir	
Streams	< Description 🥸 Design 📓 Report	📄 F
<ul> <li>→ → Brine</li> <li>→ → → Reconciled-Brine-1</li> <li>→ → Brine Scale Scenario</li> <li>→ → Gas Analysis</li> <li>→ → Reservoir</li> </ul>	Name: Reservoir	D

#### 3) Select the **Design** Tab

🦪 De	scri	ption 🧕 Design 📓	Report 🚊	File Viewer			
_							
Inlets		Туре	Nar	ne	Flow	Calc <u>u</u> late 🥝	
=		<select></select>				Calculate Alkalinity	
						Summary	_
Solid						Unit Set: Scale Metric	$\sim$
						Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion) Custom K-fit P-span	
	F		ditions		Value	At least one inlet should be selected	
		Temperature (°C)				for Reservoir.	
		Pressure (bar)				Selected Solids:	
	De	tail Info of Selected Inlet Na				Calculation not done	
$\square$	┢	Compone	nt	Va	lue (mol/hr)		

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 (see the image below for the flows)
- 5) Enter the Gas calculated in Task 3 (see the image below for the flows)
- 6) Enter the Reservoir conditions: 125 C and 275 bar in the conditions section.

П	Туре	Name	Flow	Calculate 🥝	
	Brine (m3/day)	Brine	200.00	00 Calculate Alkalinity	
	Gas (std E3m3/day)	Gas Analysis	250.00	00	
ם ו	<select></select>			Summary	
				Unit Set: Scale Metric	
				Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion)	
ľ-		ditions	Value	Second Liquid phase Excluding 83 solid phases	
H	Temperature (°C)	Iditions	value 125.00		
	Pressure (bar)		275.00	··· · · · · · · · · · · · · · · · · ·	
				Brine (m3/day) Brine 200.00	
Det	ail Info of Selected Inlet Name	2		Gas (std Gas E3m3/day) Analysis 250.00	)
	Compone	ent	Value (mole %)	comordayy y mayore	
П	Compone			Warning: no solid selected for	

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).

Mineral to saturate	Inflow to vary
BaSO4 (Barite)	BaSO4
aCO3 (Calcite)	CaCO3
Select Solid>	

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

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
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
BaSO4	Barite	2.64658e-5	9.27644e-6	1.00000	1.82516e-6	1.00000	0.0
SrSO4	Celestine	0.0	0.0	0.148191	-0.829178	0.148191	-0.829178
SrCO3	Strontianite			0.209852	-0.678087	0.209852	-0.678087
CaCO3	Calcite	1.13495e-5	3.97806e-6	1.00000	-4.82687e-8	1.00000	0.0
KCI	Sylvite			2.14382e-4	-3.66881	2.14382e-4	-3.66881
CaSO4.2H2O	Gypsum	0.0	0.0	0.0179366	-1.74626	0.0179365	-1.74626
CaSO4	Anhydrite	0.0	0.0	0.0934633	-1.02936	0.0934633	-1.02936

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 Excess Solute 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.

Select *Brine Scale Scenario* in the Navigator Pane and rename it **Reservoir Scale Scenario** Select the **Design** tab In the *Inlets* tab in the **Type** column delete the Brine and Gas from the Type column (click the small gray box to the left of the name which will highlight the entire row, then press the delete key) Add *Whole Fluid* In the **Name** column select *Reservoir* In the **Flow** column select *< Automatic* >

🦻 Desi	cription 🛛 🕺 Desigr	🛍 Plot 📓 Report	📄 File Viewer
s [	Туре	Name	Flow
Inlets	Whole Fluid (m3/day)	Reservoir	<automatic> 💌</automatic>
=	<select></select>		

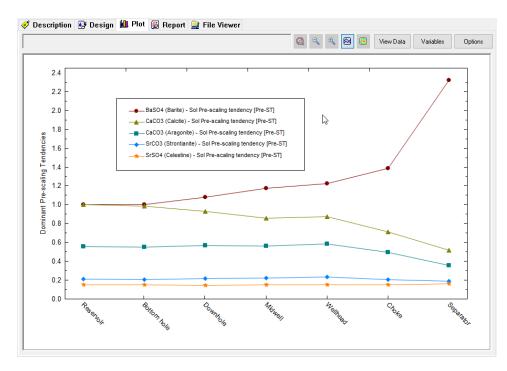
**Note:** The Whole Fluid type refers to all the phases within the fluid. The Automatic option takes the final flow rate phase of the separator and automatically enters this as the flow rate in the Scale Scenario calculation.

Go to the Solid tab and make sure that the Standard box is checked

2	Solids Selection
Inlets	□▼ Standard
	BaSO4 (Barite)
	CaCO3 (Calcite)
<u>ه</u>	CaSO4 (Anhydrite)
Conditions	CaSO4.2H2O (Gypsum)
ভ	NaCl (Halite)
Ö	SrSO4 (Celestine)
	Expanded
	i
P	
Solid	

Calculate (Press <F9>)

Select <u>Plot</u> tab and select *View Plot* (note: you may have to delete the existing entry and then reselect the dominant pre-scaling tendencies from the variables list)



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.

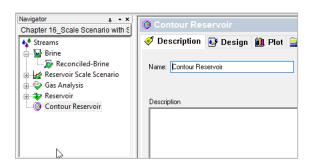
The basis of this calculation is that water in the pores of a rock matrix is at equilibrium with the mineral surface. Some questions to consider are whether it is reasonable to assume that a reservoir gas, oil, water, and rock are in equilibrium. Furthermore, we should also consider over what vertical 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.

## Add Scale Contour Rename the Object **Contour Reservoir**



Select the <u>Design</u> Tab Select the *Inlets* (vertical) tab Select the bottom right corner of the 1st cell in the Inlet grid and choose *Whole Fluid* Select *Reservoir* in the 2nd column Keep the *<Automatic>* flow rate option in the 3rd column

🕈 Description 😼 Design 🛍 Plot 🚊 File Viewer				
	Turne	Nama	Flower	
lets	Type Whole Fluid (m3/day)	Name	Flow	

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.

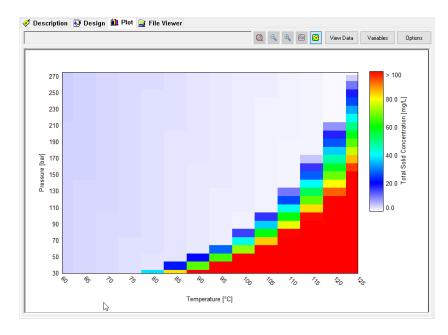
Change the Start to 60 Change the End to 125 Select the Increment radio button Enter 5 as the increment Uncheck the Log box (if it is checked) In the Pressure Range box, change the Start to 30 Change the End to 275 Select the Increment radio button (uncheck the Log box first) Change the Increment to 10

🔞 Cor	tour Reservoir			
🦪 De	scription 🔯 Desigi	n 📶 Plot	📄 File Viewer	
Inlets	Temperature Ra	nge	۹C	~
Conditions	Start	60.0 125.0	Increment     Number Steps	<b>5.0</b> 13
Co	Pressure Range			
Solid	Start	30.0	lncrement	× 10.0
	End	275.0	O Number Steps	25

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	ł.

Select the **Solid** Tab Check the Standard box Calculate. The calculation should take less than 5 min to complete When calculation is done, go to the <u>Plot</u> 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).

# 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 anticipation of next steps when using the interface.

# Task 1 – Add a Brine

Add a *Brine Analysis* from the Action Panel Rename the Brine in the **Description** Tab, and name it WTXWTR

Navigator Document1*	д <b>- х</b>	WTXWTR
🍫 Streams		< Description 🛃 Design 🚦
WTXWTR		Name: WTXWTR
		West Texas Water Supply

Go to the **Design** Tab and enter the following composition in the **Data Entry** (vertical) tab:

Name: Type of water: Comment:	WTXWTR Aquifer Water West Texas Water Supply			
Species Na <sup>+</sup> Ca <sup>+2</sup> Mg <sup>+2</sup> Fe <sup>+2</sup> Cl <sup>-1</sup> SO4 <sup>-2</sup> HCO3 <sup>-</sup>	Concel 3074 910 249 0.77 4474 2960 439	ntration mg/L mg/L mg/L mg/L mg/L mg/L		
HS <sup>-1</sup>	146.2	mg/L		

Check the Show non-zero Only box (under Entry Options)

Go to the *Reconcile* (vertical) tab

Select the measured pH and alkalinity Option

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 (°F)	
	Pressure (ps	

Temperature	77 F
Pressure	14.7 psia
рН	7.98
Alkalinity end Point pH	439 mg/L as HCO3-
Titration pH	4.5
Density	(will be estimated)

-		t 🚉 File Viewer		Summary
e Data Entry	Calculate Brine Properties Using: Concentration Data Only Gas-Phase CO2 Content (mole% Measured pH and Alkalinity Measured pH Only Calculate Alkalinity	5) Specs	Calculate 🥥	Unit Set: <custom> Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion) No Solid phase(s) Custom K-fit P-span</custom>
Reconcile	Properties	Measured	Calculated	Stream Parameters:
š	Temperature (°F)	77.0000	Guidalatou	Temperature (°F) 77.0000
	Pressure (psia)	14,7000		Pressure (psia) 14.7000
	pH	7.98000		Stream amount (L) 1.00000
	Alkalinity (mg HCO3/L)	439.000		Dominant Ion Charge Balance
	Alkalinity End Point pH	4.50000		(eq/L): Cation Charge 0.199639
	Density (g/ml)	0.0		Anion Charge -0.199436
	Elec Cond, specific (umho/cm)	0.0		Imbalance 2.02957e-4
	Total Dissolved Solids (mg/L)	0.0	2	
		ition Adjustments		Ion(s) needed to balance (mg/L):
	Added titrant (mg/L)			Measured pH and Alkalinity.
	Add Charge Balance (mg/L CI-1)			measureu pri anu Aikaillilly.

Click the Calculate Button

# Task 2 – Add a Second Brine

Add a Brine Analysis, name it SSC-Brine Enter the composition given below in the **Data Entry** (vertical) Tab

~ [	Variable	Value	Balance	Entry Options
	Catior	ns (mg/L)		Units
e l	Na+1	20400.0	20400.0	mg/L
Data Entry	K+1	402.000	402.000	
	Ca+2	3800.00	3800.00	Formula
	Mg+2	829.000	829.000	Formula
	Sr+2	15.2000	15.2000	Show Non-zero Only
Reconcile	Ba+2	0.70000	0.70000	Show Balanced Column
<u>د اا</u> م	Fe+2	9.50000	9.50000	Template Manager
				remplate Manager
	Anior	is (mg/L)		Standard 🗸 🗸
	CI-1	37000.0	38934.7	Save as
	SO4-2	2200.00	2200.00	
	HCO3-1	0.0	0.0	
	B(OH)4-1	4.00000	4.00000	
	HS-1	0.0	0.0	iype
	C2H3O2-1	715.000	715.000	Dominant Ion
		-		
		als (mg/L)		
	CO2	0.0	0.0	
	H2S	0.0	0.0	

## Go to **Reconcile** tab

Select *pH* and Alkalinity calculation type, and enter the information provided in the figure below.

Reconcile Data Entry		Calculate Brine Properties Using: Concentration Data Only Gas-Phase CO2 Content (mo Measured pH and Alkalinity Measured pH Only Calculate Alkalinity	le%)	Specs	Calculate 🥥
C I		Properties	P	Measured	Calculated
Re		Temperature (°C)		25.0000	
		Pressure (atm)			
		рН		7.10000	
	Г	Alkalinity (mg HCO3/L)		715.000	
	Г	Alkalinity End Point pH		4.50000	
		Density (g/ml)		0.0	
		Elec Cond, specific (µmho/cm)		0.0	
		Total Dissolved Solids (mg/L)		0.0	
		Comp	osition A	djustments	
		Added titrant (mg/L)			
		Add Charge Balance (mg/L CI-1)			

Click the Calculate button

# Task 3 – Add a Gas

From the Actions Panel click on *Add Gas Analysis* Input the name in the **Description** tab. Name it *LightHC* 

Navigator	<b>μ ▲ Χ</b>	Con Line Har	
Document1*		S LightHC	
崎 Streams		🦪 Description	🔮 Design
WTXWTR      Gradient Stress Stre		Name: LightHC	
$\searrow$		Description	

Go to the **Design** Tab and enter the following composition in the **Inflows** (vertical) tab Enter the following composition:

Component	Composition
Carbon dioxide (CO2)	10 mole %
Water (H2O)	15 mole %

🛷 De	s	crij	ption	🥸 Design	🥸 Defi	nition 📓	Report 📄 File Viewer
_							
NS			Con	nponent	Value	Normalize	
Inflows					Subtotal:	Subtotal: 1	IO Units
E			H2	0	15.0000	15.000	0 mole % ~
		ſ	N2		0.0	0.	0 Display
	١.	ſ	CC	)2	10.0000	10.000	0 Formula V
Reconcile			H2	S	0.0	0.	0
20			🗸 СН	4	0.0	75.000	
Re			C2	H6	0.0	0.	O Show Normalized Column
			C3	H8	0.0	0.	0 Template Manager
	I		i-C	4H10	0.0	0.	
			n-(	C4H10	0.0	0.	0 Standard V
			i-C	5H12	0.0	0.	0 Save as
			C5	H12	0.0	0.	0
		ſ	C6	H14	0.0	0.	
							Normalize Options
							Makeup $\checkmark$
							Course Manager
							Group Manager
				2			Use Groups Add
				- 0			
	L						

think simulation | getting the chemistry right 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.

<u>ه</u> [	Component	Normali	Reconcile	Calc <u>u</u> late	0
Inflows		Subtota	Subtotal:		
트	H2O	15.0000	1.75794	Condition	
	CO2	10.0000	11.5567	Saturate With	lone 🔻
e	CH4	75.0000	86.6854	Conditions	Value
Reconcile				Temperature (°C)	15.5556
S				Pressure (atm)	1.00231

Go to the *Reconcile* (vertical) Tab

Leave the default conditions for Temperature and Pressure Calculate

# Task 4 – Add an Oil

From the Actions Panel click *Add Oil Analysis*. Enter the name in the **Description** Tab. Name it *OIL-1* 

Navigator	μ <b>. ×</b> ×			
Document1*		🌢 OIL-1		
🍁 Streams		🦪 Description	🥺 Design	😼 Report
		Name: OIL-1		
3		Description		

Go to the **Design** tab This tab is divided into: Combined Tab: Here pure components (organic and inorganic) are entered. Pseudocomponent Tab Assay Tab: Here distillation curves are entered. Reconcile Tab

For this example, we will enter pure component and pseudocomponent data.

Go to the *Combined* tab 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.

Component	Value	Normalized	Entry Options	Summary	
Inflows	Subtota	Subtotal: 100.0	Units	Unit Set: Metric (mole	fraction)
H2O	0.0	0.0	mole %		
CH4	20.5300	58.2990	Display	Automatic Chemistry AQ (H+ ion) Databa	
C6H14	8.59500	24.4072	Formula	Public	
CO2	6.09000	17.2938	Show Non-zero Only	Second Liquid pha Custom K-fit P-spa	
		6	Show Normalized Column	Stream Parameter	
				Temperature (°C) 15	.0000
			Template Manager	Pressure (atm) 1.0	0000
			Standard 💌	Prorate Normalization	
			Save as	Inflows:	100.000
				Pseudocomponents:	0.0
			Normalize Options	Assay:	0.0
			Prorate	Equilibrium Calcula	tion.

## Go to the Pseudocomponent tab

Combined	Component	Molecular Weight	Nomal Boiling Point (°C)	Specific Gravity	Thermo Method	Value (mole %)
<u>ا</u> ق	<enter a="" na<="" th=""><th></th><th></th><th></th><th></th><th></th></enter>					
Reconcile Assay Pseudocom	3					

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:

Combined	Component	Molecular Weight	Nomal Boiling Point (°F)	Specific Gravity	Thermo Method	Value (mole %)
3 II	PC1	98.4300	100.210		API-8	27.5700
	PC2	170.340	216.320		API-8	29.3500
Pseudocom	PC3	282.550	343.780		API-8	7.1900
ö	PC4	506.000	645.000		API-8	0.680000
P	<enter a="" na<="" td=""><td></td><td></td><td></td><td></td><td></td></enter>					

Go to the *Reconcile* (vertical) tab

Here you will see how well the pseudocomponent will predict the phase behavior of the hydrocarbon sample.

In the Condition option (below calculate button) enter T=204 F and P=1 atm. Click on the *Add boiling point curve* (red square shown)

	Component	Normalized	Calculate 🥥
	Inflows	Subtotal: 35.2132/	Unit Set: <custom></custom>
	H20	0.0	Condition
	CH4	20.5290	Saturate With None  Automatic Chemistry Model Aqueous (H+ ion) Databanks:
'     ł	C6H14	8.59457	Conditions Value
	C02	6.08970	Second Liquid phase
			Temperature (°F)         204.000         Custom K-fit P-span           Pressure (psia)         14.6960         Stream Parameters:
	Pseudocompo	Subtotal: 64.7868/	Temperature (°F) 204.000
	PC1	27.5686	Pressure (psia) 14.6960
	PC2	29.3485	
	PC3	7.18964	Show Non-zero Only
	PC4	0.679966	Boling Point Corve
			Add boiling point curve Pseudocomponents: 64.7868
finner			Assay: 0.0
			Equilibrium Calculation.
		23	
Keconcile			
žΙ			

A new calculation appears in the navigation panel below OIL1 Object.

🐓 Streams	
🗄 🕎 WTXWTR	
LightHC	
🖶 📥 OIL-1	
🖉 Boiling	
-	
22	

This is a survey by Pressure. Click on the specs button and specify the conditions below. Change pressure units if necessary.

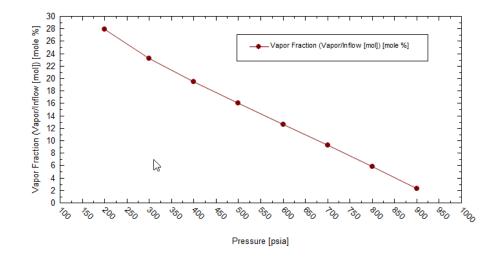
Survey by	
Pressure	Specs
Then by (optional)	13
None •	Specs

Enter a pressure range:

Start	200 psia
End	2000 psia
Decrement	100 psia

Click the Calculate button.

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.

Go back to OIL-1 in the Action panel



Click on the Design tab

In the Conditions option use T= 77 F and 14.7 psia.

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.

From the Actions Panel, click on the Add Mixing Water logo.



After double clicking the logo, you will the object in the Navigation Panel.

Navigator	<b>д ▲ Х</b>	Y ME	lingWater	. 4
Document1		T IVILX	ingvvater	
Chapter 18-Calculations overview*		🚽 🍼 De	scription	🥺 Design
🍓 Streams				
🗄 🙀 WTXWTR		Name:	MixingWate	er-1
🗄 🌍 LightHC				
🗄 🧄 🕹 OIL-1		Descri	ption	
🗄 🚽 Scenario				
🗄 🖓 SSC-Brine				

Click on the **Design** tab to enter more information.

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.

🎺 Des	cription 🥸 Design 🛍 Plot 📓	Report 📄 File Vi
( v)		
Inlets	First Brint (bbl/day)	WTXWTR
	Second Brine (DDVday)	SSC_Brine
	Gas (std E3m3/day)	Light-HC
suo	Oil (bbl/day)	OIL-1
Iditions	<select></select>	

This should pop the following window up. Click on Inlets tab and change the units.

Inlets tab looks like below. Changing units on Brine:

Edit Units - Mixing Water-1	? X
	Batch System Flowing System
Composition Parameters Corrosion Inlets	
Variable	Units
Brine Quantity	bbl/day 🔍
Oil Quantity	bbl/day
Gas Quantity	std Mft3/day
Whole Fluid Quantity	m3/day

The final Mixer with inflows entered should look like the image below:

	Туре	Name	Flow			Cal	c <u>u</u> late 🥝
	First Brine (bbl/day)	WTXWTR		1000.00			ulate Alkalinity
	Second Brine (bbl/day)	SSC-Brine					and the Airkanin Ircy
	Gas (std Mft3/day)	LightHC		230.000		Summary	
	Oil (bbl/day)	OIL-1		7.00000		Unit Set: <custon< td=""><td>112</td></custon<>	112
	<select></select>						
		ditions	Value	400.000		Aqueous (H Second Liquid Excluding 116 Custom K-fit P	phase solid phases
	Temperature (°F) Pressure (psia)			200.000		Inlets:	-span
	Pressure (psia)			200.000	>	Brine (bbl/day)	WTXWTR
De	tail Info of Selected Inlet Nam	e				Brine (bbl/day)	SSC- 1000. Brine
-	Compone	nt	Value (mg/L)			Gas (std Mft3/day)	LightHC 230.0
						Oil (bbl/day)	OIL-1 7.000
						Oil (bbl/day) Brine Ratio:	OIL-1 7.000
						Brine Ratio: WTXWTR SSC- 1.00000	Brine 0.0
						Brine Ratio: WTXWTR SSC- 1.00000 0.800000 0.20	Brine

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.

Leave the default values

Inlets	Select Type Er	nter Values	
Ē	Ratio	WTXWTR	SSC_Brine
		1.00000	0.0
	Total flow: 1000.00 bbl/day	0.800000	0.20000
5	Steps: 5 Auto Step	0.600000	0.400000
	Auto Step	0.400000	0.600000
		0.200000	0.80000
		0.0	1.0000

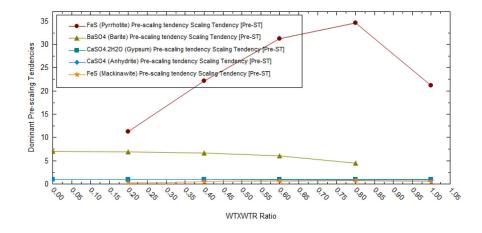
#### Go to the Solid tab

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).

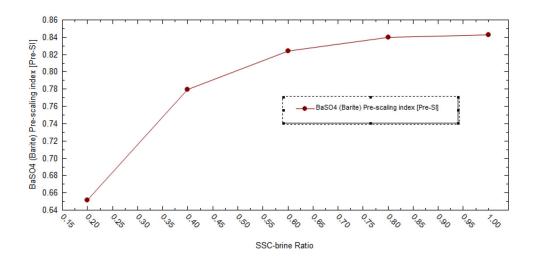
	ng Water-1 scription 🐼 Design 🚻 Plot
Conditions Inlets	Solids Selection  Solids Selection  Standard  Garcel BaSO4 (Barite)  CaCO3 (Calcite)  Garcel CaSO4 (Anhydrite)  Garcel CaSO4 (Anhydrite)  Garcel CaSO4.2H2O (Gypsum)  FecCO3 (Siderite)  FesS  FesS  FesS  FesS  FesS (Pyrrhotite)
Solid	NaCl (Halite) ⊡ SrSO4 (Celestine) Expanded All

Click on the Calculate button.

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

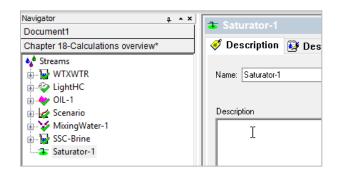
Water and gas samples at the surface are not necessarily representative of conditions in the reservoir. The processing of the samples may involve significant changes in the chemistry.

The Saturate option (often referred to as "Saturate at reservoir conditions") allows the user to "Back-calculate" the conditions downhole.

Select Add Saturator from the Actions Panel.



Rename the object in the descriptions tab. Name it Saturator-1



Go to <u>Design</u> tab And go to *Inlets* (vertical) tab

We will select objects that we have already defined.

Enter a Brine flow of 1000 bbl/day (SSC-brine) Enter a Gas flow of 230 std Mft3/day (LightHC) Enter T=77 F and P=14.7 psia

Set these units as custom units for all new objects in Units manager.

Units Manager - Saturator-1		?	×
Units Manager			
<custom> ~</custom>	~	$\sim$	•
Customize			
OK Cancel	Apply		Help

The window should look like the image below.

Flow
1000.00
230.000
Value
77.0000
14.7000
mole %)
(

Go to **Solid** (vertical) tab Check the Standard box

We need to select solids inflow to vary for Saturator1. Under the table Select Mineral to saturate, choose the solid to vary from the dropdown list.

Select BaSO4 (solid) and hit enter. Automatically the inflow to vary BaSO4 will appear.

< De	scription 🕺 Design 🙀 Report	📄 File Viewer
Solid	Solid Selection (check solids allowed	e) ite) y(Gypsum) rite)
	Mineral to saturate	Inflow to vary
	BaSO4 (Barite)	BaSO4
	<select solid=""></select>	

To study the Saturator-1 (Brine and Gas mix) at various locations we need to add a Scaling Scenario object.

OLI StudioTest - [Chapter 18-Calculations overview*]		- 0	ı ×
File Edit Streams Calculations Chemistry Tools	View Window Help		- 8 ×
	Cancel		
🗅 🗃 🖬 🕺 🛍 🖻 🎯 🤋 🎌 🛛 Aq Va So :	* Re ± 物 ± 物 ± 🙀 ± 🗱 🍁 🎬 ± 💱 🎜 🖆 🌾		
Navigator a + *	∠ Scenario-1		
Document1			
Chapter 18-Calculations overview*	< Description 🔮 Design 🏨 Plot 📓 Report 🚍 File Viewer		
▲ Streams			
in → 🔂 WTXWTR	V Type Name Flow	Calculate 🥝	
🗑 🍣 LightHC	Select> Type Name Flow		
👜 🔶 OIL-1		Calculate Alkalinity	
👜 🚂 Scenario		Summary	
MixingWater-1			
SSC-Brine		Unit Set: Scale Metric	^
Scenario-1	Conditions	Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion)	
Actions a * *	T	Custom K-fit P-span	
Actions	Detail Info of Selected Inlet Name	At least one inlet should be selected	d.
📱 🤲 🗇 🚠 🕯	Component Value (mol/hr)	Selected Solids:	
🔛 🔶 🗇 🚠 🔓		No Solid Selected.	
Add Brine Add Oil Add Gas Add		Calculation not done	
Analysis Analysis Analysis Saturator			
🕑 🎯 🍸 🏨			
Add Scale Add Scale Add Mixing Add Facilities			
Scenario Contour Water			
Plot Template Manager + * *			$\sim$
Save	1		
	j.		
*			
ore			
ceg			
cáculáron O.e. +			
For Help, press F1		🥥 🗉	NUM

Name the new Scale Scenario as Saturator-1 Scale Scenario under the Description tab.

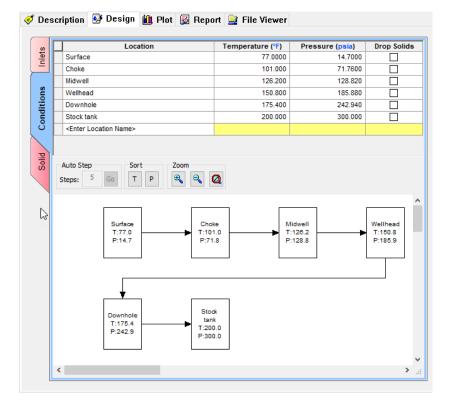
Navigator # * X	La Commenten A Coole Coome
Document1	🛃 Saturator-1 Scale Scena
Chapter 18-Calculations overview*	< Description 🔯 Design
Streams UTXWTR Gradient Constraints Const	Name: Saturator-1 Scale Scenario

Go to the **Design** Tab Under the **Inlets** (vertical) tab, select *Brine* under the *Type column* Make sure to select Saturator-1, as is shown in the picture below:

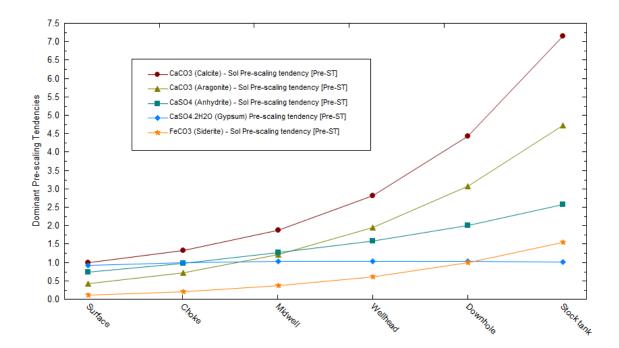
🦪 Des	scr	iption 🥺 Design <u>세</u> Plo	t 📓 Report 🚊 File Viewer	
ţs		Туре	Name	Flow
Inlets	Г	Brine	•	
_		<select></select>	WTXWTR [AQ]	
			Seturates 4 (AQ)	
<u>0</u>			Saturator-1 [AQ]	

Flow will be automatically controlled. Locations can be input under the **Conditions** tab.

Go to *Conditions* (vertical) tab, and enter the information provided in the figure below:



Go to **Solid** tab and check the Standard box Click the Calculate Button Go to **Plot** tab



After the calculation is complete, the plot for scale scenario shows that other solids are appearing.

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
KCI	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.

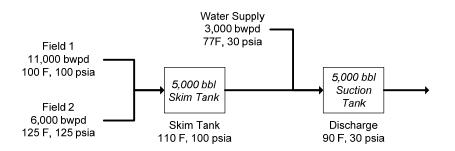
Post-Scale: The saturation ratio AFTER solids precipitate (if solids are selected).

S, ST - Saturation, Scale Tendency: The ratio of the concentration (activity) to its solubility (S=1).

SI - Scale Index: Log(S).

## **Introducing the Facilities Object**

This section presents a new calculation object: *Facilities*. The Facilities is a simplified process simulator; it mixes and separates. think simulation | getting the chemistry right 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			
CI-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			
рН	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:

Open a new Window for Simulation

Create the above brines: Field 1, Field 2 and Water Supply

Use the Add Brine Analysis object as you have done before to create them.

The Data Entry Windows should look like this:

				1	_					_ (				
Ш	Variable	Value	Balanced A		≥	Vari		_	anced	^	Entry	Variable	Value	Balance
		s (mg/L)			Entry	K+1		.0	0.0		Ē.	K+1	0.0	0
	Na+1	38209.0	38370.4		Data	Ca+2	4480.		480.00		Data	Ca+2	910.000	910.00
	K+1	0.0	0.0		Da	Mg+2	1191.	_	191.00		E L	Mg+2	249.000	249.00
	Ca+2	6600.00	6600.00	2		Sr+2		.0	0.0	2		Sr+2	0.0	0
	Mg+2	1531.00	1531.00			Ba+2	-0 (	.0	0.0			Ba+2	0.0	0
	Sr+2	0.0	0.0		econcile	Fe+2	6.600	00 6.	60000		econcile	Fe+2	0.770000	0.7700
	Ba+2	0.0	0.0		CO						5	67		
	Fe+2	120.000	120.000		۳,		Anions (mg/L)				e l	Ar	nions (mg/L)	
						CI-1	51134		1257.9	L L		CI-1	4474.00	4637.
	Anion	s (mg/L)				S04-2	1840.		840.00			S04-2	2960.00	2960.
	CI-1	73150.0	73150.0			HCO3-1	677.0		\$77.000			HC03-1	439.000	439.0
	S04-2	2453.00	2453.00			HS-1	146.2	_	46.200			HS-1	0.0	(
	HCO3-1	421.000	421.000			C2H3O2-1	(	.0	0.0			C2H3O2-1	0.0	(
	HS-1	244.000	244.000											
	C2H3O2-1	0.0	0.0				Neutrals (mg/L)					Ner	utrals (mg/L)	
1						C02		.0	0.0			C02	0.0	(
1	Neutra	ls (ma/L)				H2S		.0	0.0			H2S	0.0	(
1	C02	0.0	0.0			SiO2		.0	0.0			Si02	0.0	
	H2S	0.0	0.0			B(OH)3	(	.0	0.0			B(OH)3	0.0	
-	Si02	0.0	0.0							~				

Reconcile these three brines for measured pH and alkalinity.

Make sure that the *Allow solids to form* box is uncheck at the bottom of the reconciliation options for all the brines.

🖌 Field	cription 🔯 Design 📓 Report 🚊	File Viewer	
Data Entry	Calculate Brine Properties Using: Calculate Alkalinity Calculate Alkalinity	Specs	Calcylate 🥝
Reconcile	Properties	Measured	Calculated
Re	Temperature (°F)	100.000	
	Pressure (psia)	100.000	
	pH	6.97000	6.97000
	Alkalinity (mg HCO3/L)	421.000	420.990
	Alkalinity End Point pH	4.50000	
	Density (g/ml)	0.0	1.07666
	Elec Cond, specific (µmho/cm)	0.0	1.84894e5
	Total Dissolved Solids (mg/L)	0.0	1.22617e5
	Comp	osition Adjustments	
	Added titrant (mg/L) HCI		227.307
			-238.440
	Add carbonate (mg/L CO2)		-230.440

Select Add Facilities from the Action Panel.



Go to the **Description** Tab and rename the object as Facilities-1

🧷 Descrij	otion 💫	Design	🛍 Plot	🚳 Report	📮 File V	iewer
Name: Faci	lities-1			Date:	6 /21/2016	•
Description						

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.

Go to the **Design** tab 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.

Double click on the node name (where it says: Node 1) and type "Skim Tank".

#t;	Faci	ilities-1			
<b></b>	Des	scription 🧕 Design	🛍 Plot 🔯 Repor	t 🚊 File Viewer	
1					
	Inflow Specs			Â	Calculate 🥥
	w S	Skim	+	E	Calculate Alkalinity
	Inflo	Tank			Summary
					Unit Set: Scale Metric
	Solid				Automatic Chemistry Model AQ (H+ ion) Databanks:
l	S				Public
					Custom K-fit P-span Some node(s) do not have inlet.
				-	Node(s):
		<		•	Skim Tank: No inlet
		Node Input Current Node: Skim Tank	Drop Solids	Zoom	
				۹ ۹ 🙆	Selected Solids:
		Add Delete			No Solid Selected.
		h	ditions	Value	Calculation not done
		Temperature (°C)		15.0	
		Pressure (bar)		1.01325	
		Туре	Name	Flow	
		<select></select>			

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

Make sure to select drop solids checkbox at the Skim Tank node.

When complete, your screen should look like this.

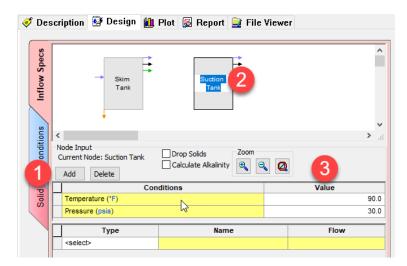
Conditions Inflow Specs	Skim Tank Node Input Current Node: Skim Tank	Drop Solids LuXalculate Alkalinity	▲ ↓ ↓
Ō		nditions	Value
	Temperature (°F)		110.0
Solid	Pressure (psia)		100.0
S	Туре	Name	Flow
	Brine (bbl/day)	Field 1	11000.0
	Brine (bbl/day)	Field 2	6000.00
	<select></select>		

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.

Click on the Add button to add a second Node Change the name of the node to Suction Tank Change the conditions of this node to 90 F and 30 psia.

When complete your screen should look like the image below:

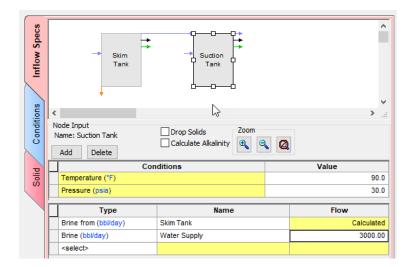


When a brine is calculated in a facilities calculation, we have the option of allowing any produced solids to be considered (that is they traveled along with the brine) or to *eliminate* them as they precipitate out. We will eliminate the solids in this case. The orange downward arrow from Skim Tank indicate dropped solids.

We are also adding the Water Supply to this tank.

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).

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.

Click on the Calculate button, or press <Ctrl+F9>

Go to the **<u>Report</u>** tab, and check for the Pre-scaling Tendencies and Scaling Tendencies 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 – Scaling Inhibition**

# Introduction

OLI has developed a rigorous Nucleation and Inhibition tool for mineral scaling formation. The two tools help users predict the onset of precipitation in a process environment and also how to delay it. Both tools are built on OLI's fundamental thermodynamic framework and extends these predictions into kinetics using the Classical Nucleation Theory [ref]. This theory use the energetics of the solution and the solid to predict the time needed for a supersaturated solution to start precipitating. This is the transition time between when a metastable solution finally starts to precipitate. The background and details of nucleation is offered by Wikipedia: <a href="https://en.wikipedia.org/wiki/Classical\_nucleation\_theory">https://en.wikipedia.org/wiki/Classical\_nucleation\_theory</a>

# What is a mineral scale?

Mineral scaling occurs when there are changes in process conditions, such as pressure and temperature changes, dissolved gases, or when mixing incompatible waters. When scales accumulate in fixed diameter volumes, like membrane pores, production tubing, or process piping, flow is restricted. Action is then needed to remove the scale and restore flow.

A scale deposit may occur as single mineral phases, but more commonly, it is a combination of different elements. Common scales include CaCO<sub>3</sub> (calcite) and BaSO<sub>4</sub> (barite) in oil and gas production, CaCO<sub>3</sub>, struvite, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Mg-Silicates, and silica in water treatment, Jarosite, CaSO<sub>4</sub>, and CaCO<sub>3</sub> (calcite) in mineral processing, and additional scale types in other chemical processes.

Scale deposition involves two distinct steps. The first is the nucleation step, this is the time between when a supersaturated water goes from no solids to forming the stable, microscopic crystals. The second is the crystal growth step. In this step, the microscopic crystals grow until the concentration in the water reduces to the point where the solution is no longer supersaturated.

The duration of this nucleation step is known as the "induction time". It is the time that passes from the creation of supersaturated solution to the detection of first solids. This time is critical, because the longer this time can be delayed the greater chance that the solids do not form in an area that affects operations.

# Scale formation - how OLI predicts this induction time?

OLI has developed a state-of-the-art tool that predicts this induction time. This enables users to assess the risk of mineral scale forming more accurately in their process. This is a major advancement compared to existing technology, in which the scaling tendency value plus empirical rules of thumb are used to assess scale risk in a process.

Figure 2 is a plot showing the output of the new model. The x-axis is the inverse square of the Scale Index. The scale index is a base-10, logarithm of the scale tendency.

$$SI^{-2} = \left(log10(ST)\right)^{\frac{1}{2}}$$

A lower SI<sup>-2</sup> value (left side of the plot) means a higher supersaturation.

The Y-axis is the time it takes before stable crystals begin to form (in seconds). As the liquid supersaturation increases (increasing the driving force for precipitation), the time it takes for the solids to form shrinks.

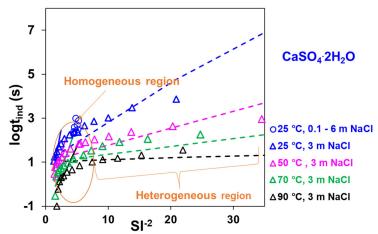


Figure 0-1 - Calculated and experimental gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O) induction times in the CaSO<sub>4</sub>-NaCl solution at 25, 50, 70, and 90 °C. Symbols are experimental data, whereas lines represent MSE+CNT model calculations

There are two distinct slopes to the plot, the far-left slope is the Homogeneous nucleation region, while the right slope is the heterogeneous region. The homogeneous nucleation region represents a liquid that is highly supersaturated, and where little time elapses before solids start precipitating. The heterogeneous region is where the liquid is only slightly saturated, and solids only start to form if there is dust or other types of particles in the water that makes it easier for the solids to form. Both time regions are important to modeling induction time properly, and the OLI database contains the required parameters for these calculations.

## V11.5 Nucleation Induction Time model

OLI Studio V11.5 is the first delivery of this new technology. We have created a database that will predict the induction time for four of the most common scales, calcite (CaCO<sub>3</sub>), barite (BaSO<sub>4</sub>), gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O), and Celestine (SrSO<sub>4</sub>). In future releases, the predictions will be extended to other solids.

## Scale Inhibition - how OLI is used to predict treatment?

Scale inhibitors are a type of chemical that interacts with the nascent crystallites and prevents them from becoming stable. They effectively delay the formation of a stable crystal by poisoning its surface. Scale inhibitors are an essential part of engineering, because when added to the process water, they delay the formation of these crystals, allowing a process to remain free of solids. Scale inhibitors are used in many applications, including cooling tower water, as a pre-treatment to RO membranes, and oil and gas production wells.

Because scale inhibitors represent the key solution to unwanted mineral scaling, OLI created a database that predicts this time delay. Thus, an OLI Studio user can now predict a more accurate scale risk analysis for their process and simultaneously develop a chemical treatment plan. Six of the most common scale inhibitors are

included in the V11.5 software; NTMP/ATMP, DTPMP, HEDP, EDTPMP, PPCSA, and PMA (see footnote for chemical names)<sup>11</sup>.

# Using the Nucleation Model in OLI Studio

The nucleation model is a post-process to all OLI calculations. Therefore, the only impact on any calculation is that a new table will be available in the Report tab, or a new set of categories will be available in the Plots tab. When scale inhibitors are added, then its speciation is included in the calculation. Usually the inhibitor concentrations are low (in the parts per million) so there will be minimal performance difference. There will be the same changes to the report and plot, since the inhibitor speciation will be added to the output, and its effects on nucleation will also be shown.

# Performing induction time calculations in V11.5

The V11.5 release contains nucleation induction times ( $t_{ind}$ ) for four mineral phases; CaCO<sub>3</sub> (calcite), BaSO<sub>4</sub> (barite), SrSO<sub>4</sub> (celestine), and CaSO<sub>4</sub>.2H<sub>2</sub>O (Gypsum). The release also contains inhibition  $t_{ind}$  for six scale inhibitors, HEDP, NTMP/ATMP, DTPMP, EDTMP, PMA, and PBTC. The nucleation model is developed in the MSE framework (database) and its prediction range extends across the range of this framework.

OLI Tag Name	Chemical Formula	IUPAC Names
DTPMP	C9H28N3O15P5	Diethylenetriamine penta(methylene phosphonic acid)
HEDP	C2H8O7P2	1-hydroxyethane 1,1-diphosphonic acid
NTMP/ATMP	C3H12NO9P3	Nitrilotris(methylenephosphoric acid)
PMLA	C40H40O40	Poly maleic acid
PBTC	C7H11O9P	2-phosphono-butane-1,2,4-tricarboxylic acid
EDTMP	C6H20N2O12P4	Ethylenediamine tetra(methylene phosphonic acid)

<sup>&</sup>lt;sup>11</sup> 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), amino tris (methylenephosphonic acid) (NTMP), diethylenetriamine penta (methylene phosphonic acid) DTPMP, ethylenediamine tetra (methylene phosphonic acid) (EDTPMP), and polymaleic acid (PMA)

## Setting up the automatic calculation

Induction time calculations are activated within the **Calculation Options** popup window (Figure 0-2). When checked, the model sub-routine is included as a post process to the calculation being run. The induction time calculation is available for the Single Point and Survey calculation of a Stream, in a Mixer calculation, and in the five ScaleChem calculations (Saturator, Scale Scenario, Facilities, Contour, Mixing Waters).

Start the software. There should be no streams or calculations in the Navigator panel

Select Tools>Options>Calculation Options

Check the **Scaling Induction Time(s)** box at the bottom of the popup window. Then press OK to close the window.

Calculation Options - SinglePo	pint		?	$\times$
Calculation Options Converge	ence			
General Show status dialog		agnostics Enable trace Verbose		
Optional Properties				
Diffusivities and Mobilit	ies			
Diffusivities Matrix	t			
Viscosity				
Electrical Conductivity				
Heat Capacity				
Activities, Fugacities, a	and K-Valu	Jes		
Gibbs Free Energy				
Entropy				
Thermal Conductivity				
Surface Tension				
Interfacial Tension				
Total Dissolved Solids (	TDS)- Rig	orous method		
Scaling Induction Time	(s)	Advanced		
Pre-scaling Tendencies				

Figure 0-2 - Calculation Options window showing the Scaling Induction Time(s) check box

## Example #1 – Induction times for CaCO<sub>3</sub>, BaSO<sub>4</sub>, and SrSO<sub>4</sub> in a Stream

The following stream contains low concentrations of CaCO<sub>3</sub>, BaSO<sub>4</sub>, and SrSO<sub>4</sub> in a NaCl brine at 25°C. We will use a few single point, isothermal calculations to show how the model works.

#### Step #1 – Create a basic induction time calculation

Add a stream and label it Basic Calculation (MSE model)

Add the four inflows and mole amounts:  $CaCO_3 - 0.001$ ;  $BaSO_4 - 0.00005$ ;  $SrSO_4 - 0.008$ ; and NaCl - 0.1.

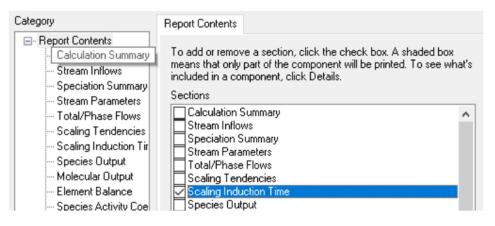
Basic Calculation						
ダ Description 🔯 Definition 📓 Rep						
Variable	Value					
Stream Par	ameters					
Stream Amount (mol)	55.6173					
Temperature (°C)	25.0000					
Pressure (atm)	1.00000					
	(mol)					
H2O	55.5082					
CaCO3	1.00000e-3					
BaSO4	5.00000e-5					
SrSO4	8.00000e-3					
NaCl	0.100000					

Figure 0-3 - New Stream containing low concentrations of CaCO3, BaSO4, and SrSO4 in a 0.1 NaCl electrolyte solution.

Add a single point calculation and label it No Inhibitor

When the calculation is complete, click on the **Report** tab. Then click on the **Customize** button in the upper right of the screen.

Deselect all boxes and then check the Scaling Induction Time box only





Review the column data in the Scale Induction Time(s) table

#### Scaling Induction Time(s)

	Induction Time	Scaling	Scaling
Solids	min	Tendency	Index
CaSO4.2H2O (Gypsum)	n/a	0.0256792	-1.59042
CaCO3 (Calcite)	8.66935	12.8217	1.10795
SrSO4 (Celestine (celestite))	7.02197	20.9219	1.32060
BaSO4 (Barite)	0.397590	275.421	2.44000

The three solid phases are supersaturated as shown in the Scaling Tendency column, and their induction times vary from 0.4 to 8.7 minutes. This means that barite will form in about 25 seconds while the other solids will take several minutes longer before they start to precipitate.

#### Step #2 – Adding scale inhibitors

Add a new single point calculation and label it With Inhibitor

You may have noticed already that there are + boxes to the left of CaCO<sub>3</sub>, BaSO<sub>4</sub> and SrSO<sub>4</sub>. These boxes expose a sub grid containing the available scale inhibitors for that specific mineral

Click on the + sign adjacent to BaSO<sub>4</sub> to expose the sub grid.

Click on the <select to add> box and select the NTMP – C3H12NO9P3 inhibitor. It will now appear at the bottom of the grid

	📮 BaSO4	5.00000e-5
	Available Inhibitors	<select add="" to=""></select>
	SrSO4	8.00000e-3
	NaCl	0.100000
I	C3H12NO9P3	2.00000e-4

Give it an amount of 2e-4 moles (this is about 60 mg/l) and calculate

Click on the Report tab and once again, turn on only the Induction Time table using the Customize window

#### Scaling Induction Time(s)

	Induction Time	Scaling	Scaling	
Solids	min	Tendency	Index	
CaSO4.2H2O (Gypsum)	n/a	0.0256380	-1.59112	
CaCO3 (Calcite)	n/a	0.159813	-0.796387	
BaSO4 (Barite)	1692.73	279.068	2.44571	
SrSO4 (Celestine (celestite))	7.28424	20.7554	1.31713	

The induction time for BaSO<sub>4</sub> increased to 1692 minutes, a time that would likely prevent the solid from precipitating in the process. The calcite induction time now shows n/a, which means that the compute time exceeds the maximum limit of 10,000 hours. Only the SrSO<sub>4</sub> induction time remained the same.

Return to the Definition tab and select the + adjacent to SrSO<sub>4</sub>. Select the HEDP – C2H8O7P2 inhibitor and give it a value of 2e-4 (~41 mg/l).

	P BaSO4	5.00000e-5
	Available Inhibitors	<select add="" to=""></select>
	SrSO4	8.00000e-3
	NaCl	0.100000
I	C3H12NO9P3	2.00000e-4
I	C2H8O7P2	2.00000e-4

#### Re-calculate and view the Report table

Scaling Induction Time(s)

	Induction Time	Scaling	Scaling
Solids	min	Tendency	Index
CaSO4.2H2O (Gypsum)	n/a	0.0266380	-1.57450
CaCO3 (Calcite)	n/a	5.11185e-3	-2.29142
BaSO4 (Barite)	n/a	278.957	2.44554
SrSO4 (Celestine (celestite))	140.909	20.7065	1.31611

The SrSO<sub>4</sub> induction time has increased to 141 minutes and both barite and calcite no longer have values (n/a). The HEDP inhibited both SrSO<sub>4</sub> and BaSO<sub>4</sub>. At these concentrations, the water would now be considered inhibited (and possibly overdosed!).

#### Step #3 – Using a concentration survey to compute the best inhibitor concentration

In the previous steps you created a supersaturated solution and then reduced its propensity to precipitate by adding a scale inhibitor. The inhibitor concentrations used were not optimized. You will use the survey calculation to vary the inhibitor concentration and find a reasonable value.

Add a Survey calculation and label it Inhibitor survey

Expand the BaSO4 box and select NTMP - C3H12NO9P3 again

Change the Survey by from Temperature to Composition

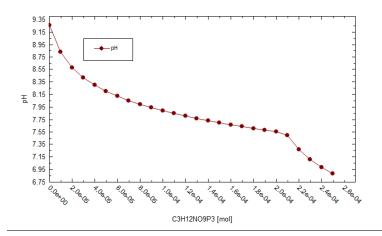
Open the **Specs** window, select NTMP as the component

Set the concentration range to star start at 0, end at 2.5e-4, and have 25 steps

	<ul> <li>Linear</li> </ul>	🔿 Log	<ul> <li>Point List</li> </ul>
Component Survey Range	End Points		
Component Inflows	Start	0.0	
BaSO4	Step Size		
C3H12N09P3	51ep 512e		
CaCO3	Increment	1.00000e-5	○
H20	Number Steps	25	a a law data al
NaCl SrSO4	Number Steps	23	
SrSO4			

#### Calculate and select the Plot tab

The scale inhibitor has a significant impact on the pH because NTMP is a hexavalent acid. This will affect scale tendencies for carbonate solids if added in this way. Right now, we are looking at BaSO<sub>4</sub>, and so we will ignore the impact on calcite



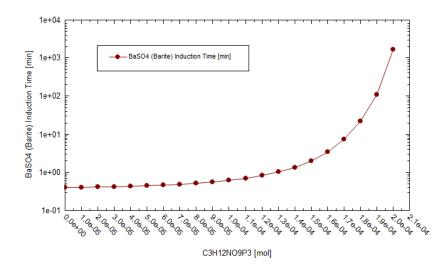
Click the Variables button to open the Curves window

Remove the pH from the Y1 axis and add the BaSO4 induction time from the Scaling Induction Times category



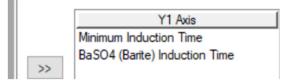
Set the y-axis to log scale

The plot now shows the barite induction times as the inhibitor is added. The induction times increase from 1 minute to 1692 minutes when the concentration increases from 1.3e-4 to 2.0e-4 moles (52 to 80 mg/L). Somewhere in this rage would be the optimal inhibitor concentration.

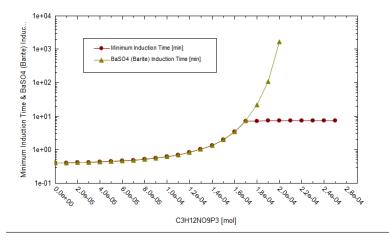


You will notice that the plot does not extend to the final concentration of 2.5e-4 NTMP. It is because at this point the induction time exceeded the 10,000 hr maximum value.

Add the Minimum Induction Time variable (located under the Scaling Induction Times category) to the plot



This new plot offers a different perspective to the user's interpretation. You can now see that the two curves diverge at 1.8e-4 moles. Because this inhibitor concentration barite is the solid phase that is the fastest to precipitate. As more inhibitor is added, barites induction time increases and eventually becomes greater than the next solid that forms, which in this case is SrSO<sub>4</sub>. So, the software is computing that below 1.8e-4 moles inhibitor, barite will be the first solid to form. Above this concentration SrSO<sub>4</sub> is the first solid to form. This would also mean that a second scale inhibitor should be added to keep SrSO<sub>4</sub> from nucleating.



#### Step #4 - Using a temperature survey to test induction times

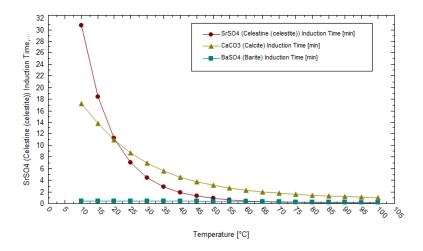
Induction times depend on both the scaling tendency of the solid (driving force for precipitation) and the temperature (reaction rates). Therefore, changes to either will result in different induction times for the solid.

Add a new Survey calculation and label it t\_ind vs T

Set the temperature range from 10 to 100 °C by 5 °C increments, click OK and then and calculate

Select the Plot tab and plot the induction times for the three solids, CaCO<sub>3</sub>, BaSO<sub>4</sub>, and SrSO<sub>4</sub>

The plot shows how temperature affects induction times. At 10 °C, CaCO<sub>3</sub> and SrCO<sub>3</sub> induction times are at 18 and 31 minutes, respectively. At 100 °C, the induction times for the 3 of them are less than 1 minute.



## Example #2 – Using induction times in a Mixer calculation

A common cause of scaling is when two incompatible streams are mixed together. For example, one stream containing a high calcium concentration and the other containing high concentrations of carbonate. The software will compute the induction times during the time of mixing using the Mixer block. This next example shows this.

- 1) Add a stream and label it *Cations*
- 2) Add CaCl<sub>2</sub> and NaCl to the grid. Set the values to 0.005 and 0.1 moles, respectively

√ Inflows (mol)			
H2O	55.5082		
CaCl2	5.00000e-3		
NaCl	0.100000		

- 3) Add a second stream and label it Anions
- 4) Add Na<sub>2</sub>CO<sub>3</sub> and NaCl to the grid. Set the values at 0.005 and 0.1 moles, respectively

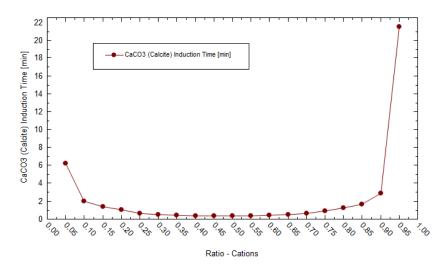
√ Inflows	(mol)
H2O	55.5082
Na2CO3	5.00000e-3
NaCl	0.100000

- 5) Add a Mixer calculation and label it Incompatibility
- 6) Move the Cations and Anions streams to the Selected Section
- 7) Set the Mixing Method to Ratio
- 8) Open the Specs window and select Cations as the Ratio stream.
- 9) Under the **Survey Range** tab set the steps to 20

Av.	ailable Streams			Selected				Mixing Method	
lo Vit	ic Calculation - [MSE] Inhibitor - [MSE] h Inhibitor - [MSE] glePoint - [MSE]	]		Cations Anions				Ratio   Type of calculation Isothermal Calculate	Spec
_								Summary	
1	Variable	Value	Cations	Anions		^		Unit Set: Metric (moles)	
-	Multiplier							Automatic Chamistor Madel	
	Multiplier		<varied></varied>	am Parameters	00000			Automatic Chemistry Model	
	Multiplier Total Inflow			am Parameters	32 mol	1		Automatic Chemistry Model MSE (H3O+ ion) Databanks:	
		25.0000	Stre	am Parameters 55.61			>	MSE (H3O+ ion) Databanks: MSE (H3O+ ion)	
	Total Inflow	25.0000 1.00000	Stre 0.0 mol	am Parameters 55.61 2	32 mol		>	MSE (H3O+ ion) Databanks:	

- 10) Calculate and go to the Plot tab
- 11) Plot the CaCO<sub>3</sub> induction times

The plot shows that induction times are lowest (fastest to form) at a 50:50 mixture and highest at the far ends of the plot. In fact, at the 0 and 100% points, no induction times are shown because there is no calcium in the 0% calculation and no carbonate in the 100% calculation.



Scale inhibitors can also work in the mixer calculation but to do this, the user must create a separate stream and add it to the mixer like it would occur in a process.

12) Create a new stream and label it 0.1 molal NTMP

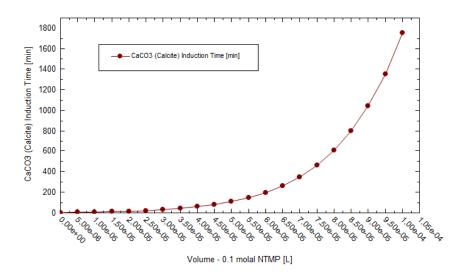
Again, we are disregarding practical units in this example so that we can focus on the procedure of studying induction times.

- 13) Add NTMP to the grid and give it a value of 0.1 mole
- 14) Return to the Incompatibility mixer and add the 0.1 molal NTMP stream to the Selected window
- 15) Change the mixing type from Ratio to Volume
- 16) Open the Specs window and select the 0.1 molal NTMP as the adjustable stream
- 17) Set the start and end to 0 L and 1e-4 L, respectively. Set the steps to 20.

۵	vailable Streams				Selected		Mixing Method	
B. N	asic Calculation - [MSE o Inhibitor - [MSE] fith Inhibitor - [MSE] nglePoint - [MSE]	[]		>>	Cations Anions 0.1 molal NTMP		Type of calculation Isothermal Calculate	pecs.
					Summary			
	Variable	Value	Cations 1.00000	Anions 1.00000	0.1 molal NTMP	^	Unit Set: Metric (moles)	
	Multiplier				iters			
				n Paramete			Automatic Chemistry Model MSE (H3O+ ion) Databanks:	
	Total Inflow		55.6132 mol		0.0 mol		MSE (H3O+ ion)	
	Temperature (°C)	25.0000	25.0000	25.0000	25.0000	>	Vsing Helgeson Direct	
Pressure (atm) 1.00000 1.00000 1.00000		1.00000	1.00000		Isothermal Calculation 25.0000 °C 1.00000 atm			
							Volume survey: Range 0.0 to 1.0e-4 L Step size 5.0e-6 L No. steps 20	

- 18) **Run** the calculation and click on the **Plot** tab when done
- 19) Add the CaCO3 induction time to the plot and click OK

As NTMP is added to the mixture, the calcite induction time increases from less than one minute to over 1600 minutes. Somewhere in this addition would be the optimal treatment value, and that would depend on how long the solid needs to remain in solution. For example, 200 minutes is over three hours, a time that would probably be enough for a fluid to exit any process unit, like an RO or mixing tank. This would correlate with a 6e-5 L or 0.060 mL dosage per the two liters of mixed material.



An alternative way to plot this would be to use the MBG-Liquid 1 variables. Instead of plotting the volume of the NTMP added, you can plot the concentration of NTMP in solution. This concentration would be the minimum inhibitor concentration desired, or perhaps the residual concentration that you want to keep in solution.

- 20) Open the Variables button and expand the MBG Totals Liquid 1 category
- 21) Move NTMP(-6) to the X-axis

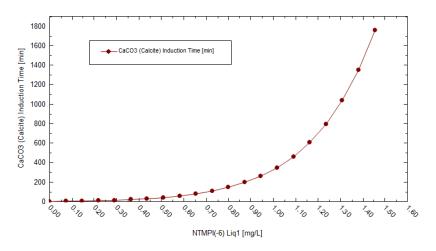
^		X Axis
	>>	NTMPI(-6) Liq1

- 22) Close the Variables window and open the Units Manager (
- 23) Click on the **Customize** button and change the Aqueous Composition from moles to Concentration

Edit Units - Ir	ncompatibilty	(			?	×
			<ul> <li>Bate</li> </ul>	ch System	O Flowing S	ystem
Composition	Parameters	Corrosion				
	Varia	ble	Basi	s	Units	^
		Infl	ow variables			
Stream An	nount		Moles		mol	
Inflows	Inflows				mol	
		Out	put variables			
Aqueous	Composition		Concentration	n 🗸	mg/L	

24) Close the units manager and review the plot

According to the calculation, a residual NTMP concentration of about 0.6 mg/l will keep CaCO<sub>3</sub> from precipitating for 60 minutes. A concentration of 1 mg/L will inhibit precipitation for about 6 hours (348 minutes).



## More Induction time options

The induction time calculation is a post-process calculation, meaning that it calculates the scale tendencies and t<sub>ind</sub> after the system converges to equilibrium. This means that the software will keep the target solids in solution

so that it can calculate its supersaturation. Competing solids that remove precipitating ions from the water can impact the induction times. For example, BaSO<sub>4</sub> is supersaturated, but CaSO<sub>4</sub> also precipitates, and in doing so, removes sulfate from solution. This sulfate removal affects the final BaSO<sub>4</sub> induction time. The software must be able to accommodate conditions where such mass actions impact the calculation. It does this in the **Calculation Options** window.

Click on any of the calculations you created using this chapter

Select the Specs button and then the Calculation Options tab (or category)

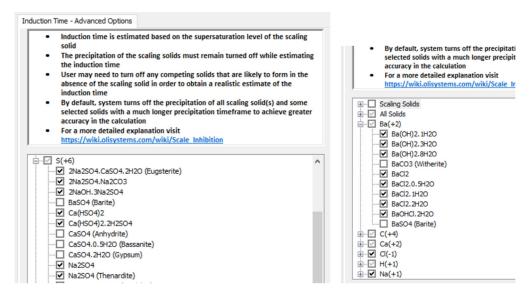
Click on the Advanced button adjacent to the Scaling Induction Times(s) check box

Total Dissolved Solids (TDS)- Rigorous method					
Scaling Induction Time(s) Advanced					
Pre-scaling Tendencies					

Expand the S(+6) category in the window

The text in the upper section of the window explains how the induction times work. It explains that the induction times are based on the supersaturation level of the specific solid and that for this solid to be supersaturated, it must not precipitate during the induction time calculation. In addition to the target solid, any competing solids that might change the concentration in the supersaturation equation (Ba and SO<sub>4</sub> if the calculation is for BaSO<sub>4</sub>) also needs to be turned off. Otherwise, the supersaturation of the target solid will be lowered and a less accurate induction time value will be computed.

So, in this case, potential competing solids for BaSO<sub>4</sub> include three CaSO<sub>4</sub> phases and BaCO<sub>3</sub>. These are turned off by default. There are many other Ba- and SO4-containing solids that can form, and if you see them forming in your induction time calculation, you can go to this window and turn them all off.



You may also decide that these competing solid <u>should</u> affect the induction time of your target solid. In that case, you turn those solids on. When that happens, reduced concentration of the target solid's ions will be used to compute the induction time.

# Chapter VII – Naming Conventions in OLI Studio and Definitions

OLI naming conventions are important to understand as they become critical in performing advanced features in OLI Studio. The following chapter explains OLI naming conventions, when they're important, and provides key definitions for understanding these conventions.

# Naming the Phases of Species

Let's say for example you want to type the following reaction in the OLI reaction kinetics tool:

#### $2NH_{3(AQ)}\text{+}CO_{2(AQ)}\text{=}CH4N2O_{(AQ)}\text{+}H2O$

**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

# **Ionic Strength**

## 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<sub>2</sub>O. Therefore, the ionic strength is 1.0 molal.

$$I = \frac{1}{2} \left( (z_{Na^+})^2 (m_{Na^+}) + (z_{Cl^-})^2 (m_{Cl^-}) \right)$$

$$I = \frac{1}{2} \left( (1)^2 (1) + (-1)^2 (1) \right) = 1$$

Now, consider a 1.0 molal solution of CaCl<sub>2</sub>. This solution has 1.0 mole of  $Ca^{+2}$  ions and 2.0 moles of  $Cl^{-}$  ions in 1 kg of H<sub>2</sub>O. Therefore, the ionic strength is 3.0 molar, or it can be said that a 1.0 molal solution of CaCl<sub>2</sub> behaves similar to a 3.0 molar solution of NaCl.

$$I = \frac{1}{2} \left( (z_{Ca^+})^2 (m_{Ca^+}) + (z_{Cl^-})^2 (m_{Cl^-}) \right)$$
$$I = \frac{1}{2} \left( (2)^2 (1) + (-1)^2 (2) \right) = 3$$

#### 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.

## 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.

Variable	Value	<u>^</u>	Type of calculation	
Stream P	arameters	Isothermal 👻 S		
Stream Amount (mol)	58.5082			
Temperature (°C)	25.0000		Calculate 🥝	
Pressure (atm)	1.00000		Summary	
- Inflow	s (mol)			
H2O	55.5082		Unit Set: Metric (moles)	
NaCl	1.00000		Automatic Chemistry Model	
CaCl2	1.00000		Aqueous (H+ ion) Databanks:	
CaCO3	1.00000		Aqueous (H+ ion)	
MBG Totals	- Totals (mol)		Using K-fit Polynomials T-span: 25.0 - 225.0	
H(+1)	111.016		P-span: 1.0 - 1500.0	
Na(+1)	1.00000		Isothermal Calculation	
Ca(+2)	2.00000		25.0000 °C 1.00000 atm	
0(-2)	58.5082		Phase Amounts Aqueous 60.5083 mol Vapor 0.0 mol	
CI(-1)	3.00000			
C(+4)	1.00000	/	Solid 0.999980 mol	
MBG Totals - A	Aqueous (mol)		A sussess Disease Disease time	
H(+1)	111.016		Aqueous Phase Properties pH 8.02574	
0(-2)	55.5083		Ionic Strength 0.0661064 mol/mol	
CI(-1)	3.00000		Density 1.11694 g/ml	
Ca(+2)	1.00002		Calc. elapsed time: 1.291 sec	
Na(+1)	1.00000			
C(+4)	1.97427e-5		Calculation complete	
MBG Totals	- Solid (mol)			
0(-2)	2.99994			
C(+4)	0.999980			
Ca(+2)	0.999980			
		×		
t Output				

# Volume vs. Volume at Standard Conditions vs. Standard Liquid Volume

## Volume

This is the volume of the system at a specified temperature, pressure, and composition.

## **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: 15°C and Pressure: 1.0023 atm

Liquid-1: Temperature: 25°C and Pressure: 1 atm

Liquid-2: Temperature: 15°C and Pressure: 1 atm

## **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<sub>2</sub>O: 55.5082 mole, NaCI: 1 mole, 25°C, 1 atm (using OLI Studio 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 <sup>3</sup> )
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
CI-1	1
Na+1	1
H3O+1	1.33E-07
OH-1	1.33E-07
NaOH	5.30E-14
HCI	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 <sup>3</sup> )	0.00103827
	Volume (L)	1.03827

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