

INTRODUCTION TO

OLI Studio

V10

think simulation

getting the chemistry right

Introduction to OLI Studio

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Version: OLI Studio v10

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if you need to contact Support, an online request form is located at the OLI Systems Tech Support page at https://www.olisystems.com/contact-tech-support. Other useful links and resources are:

- OLI Systems Support Email: <u>oli.support@olisystems.com</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 / OLI Analyzer 10.0 build 1 (10.0.1). As time progresses, new data and refinements to existing data sets can result in values that you obtain being slightly different than what is presented in this manual. This is a natural progress and cannot be avoided. When large systematic changes to the software occur, this manual will be updated.

Table of Contents

ABOUT THIS MANUAL	6
OLI STUDIO COMPONENTS	6
ScaleChem	6
Corrosion Analyzer	7
CHAPTER I – THE OLI STUDIO SOFTWARE USER INTERFACE	8
General View of the User Interface	
Menu Bar	8
Tool Bar	
Navigator Pane	
Actions Pane	
Plot Template Manager	
Description / Definition Pane	
Summary Pane	
Calculation Status Output	14
Thermodynamic Frameworks and their Databases	15
Aqueous (AQ) Thermodynamic Framework	
Mixed Solvent Electrolyte (MSE) Thermodynamic Framework	16
Mixed Solvent Electrolyte with Soave-Redlich-Kwong Equation of State (MSE-SRK) Thermodynamic Framework	16
Component Search	18
Names Manager	19
Units Manager	20
Customize Toolbars	22
Calculation Options	23
Object Library	24
CHAPTER II – OLI STUDIO : STREAM ANALYZER	25
Section 1. Single Point Calculations	26
1.1. Isothermal	
1.2. Bubble Point	
1.3. Dew Point	-
1.4. Isochoric (constant volume)	
1.5. Vapor Amount and Vapor Fraction	

1.6.	Set pH	57
1.7.	Precipitation Point	60
1.8.	Composition Point	
1.9.	Autoclave	
1.10.	. Custom	
1.11.	Reaction Kinetics	
Sectio	n 2. Survey Calculations	114
2.1.	Single Surveys	115
2.2.	Dual Surveys	157
Sectio	n 3. Water Analysis (Ionic Inputs)	173
3.1.	Basic Terminology	174
3.2.	Entering Data for Water Analysis	177
3.3.	Water Analyses - Reported Elements	178
3.4.	A Basic Water Analysis	179
3.5.	Exploring Reconciliation Options	
Sectio	n 4. Hydrocarbons and Pseudocomponents	200
4.1.	Entering a PVT Analysis	200
4.2.	Entering Pseudocomponents to a Stream	205
Sectio	n 5. Mixers	209
5.1.	Mixing Options (Definitions)	210
5.2.	A Basic Mixer Calculation	211
5.3.	A Titration Experiment	214
5.4.	Cascading Mixers	218
Sectio	n 6. Chemical Stability Diagrams	223
6.1.	Building a Chemical Diagram	
CHAF	PTER III – OLI STUDIO: CORROSION ANALYZER	233
Sectio	n 7. Stability Diagrams	234
7.1.		
7.2.	How to determine if corrosion in the absence of oxygen is possible?	
7.3.	Building a Pourbaix Diagram	
7.4.	Selective Oxidation and Reduction Chemistry	
7.5.	Modeling the Effects of Hydrogen Sulfide on Corrosion	
7.6.	Modeling Corrosion at High Temperature	
7.7.	Modeling the Effects of Complexation on Corrosion	
7.8.	Modeling the Effect of Oxidizing Inhibitors on Corrosion	
7.9.	Implications of Stability Diagrams on Cathodic Protection	
Sectio	n 8. Introduction to Rates of Corrosion	
8.1.	A Basic General Corrosion Rate Calculation	
8.2.	Exploring corrosion rate calculation options	
8.3.	Gas condensate corrosion	
Sectio	n 9. Thermal Aging and Variations in Alloy Composition	
9.1.	Overview and Basic Terminology	

9.2.	Thermal Aging and Variations in Alloy Composition	304
9.3.	Thermal Aging and Localized Corrosion of Annealed and Thermally Aged Duplex Alloy 232	4 318
Section	10. Extreme Value Statistics (EVS)	326
10.1.	Overview and Theoretical Foundation	
10.2.	Extreme Value Statistics for Predicting Pitting Damage	328
CHAP	FER IV –OLI STUDIO. : SCALECHEM	353
	Jse OLI Studio. : ScaleChem?	
	Objects	
•	ation Objects	
Section	11. Entering a Brine Analysis in OLI Studio: ScaleChem	355
11.1.	Entering Data for a Brine Analysis	355
11.2.	Brine Analyses - Reporting Elements	358
11.3.	Reconciliation Options in the Brine Analysis - Definitions	359
11.4.	A Basic Brine Analysis	360
Section	12. Entering a Gas Analysis in OLI Studio: ScaleChem	
12.1.	Entering Data for a Gas Analysis	365
12.2.	A Basic Gas Analysis	367
Section	13. Entering an Oil Analysis in OLI Studio: ScaleChem	370
13.1.	Entering Data for an Oil Analysis	
13.2.	Basic Definitions for the Oil Analysis Tool	
13.3.	A Basic Gas Analysis	378
13.4.	Putting together a complete calculation in ScaleChem	
13.5.	Overview of Brine, Gas and Oils and Introducing Mixer, and Saturator Objects	
13.6.	Introducing the Facilities Object	420
INDEX		425

About This Manual

This manual will provide an introductory guide for new OLI Studio Software users. The OLI Studio is a software suite containing several modules including, Stream Analyzer, ScaleChem 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 three main chapters showcasing the three main modules of OLI Studio: Stream Analyzer, ScaleChem and Corrosion Analyzer.

If you have not yet installed the software, please install it following the instructions given in Installation and Security page in our Wikipage at: <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:
 - Aqueous (AQ) model
 - Mixed Solvent Electrolyte (MSE) model
 - Mixed Solvent Electrolyte and Soave-Redlich-Kwong (MSE-SRK) model
- Thermophysical properties: Stream Analyzer has thermophysical models to predict surface tension, interfacial tension, viscosity, electrical conductivity, thermal conductivity, diffusivity, and osmotic pressure.
- Molecular and ionic inflows: Stream Analyzer accepts molecular inflows, typical of a process stream, and ion inflows, typical of a sample water analysis.

ScaleChem

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

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



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. 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.

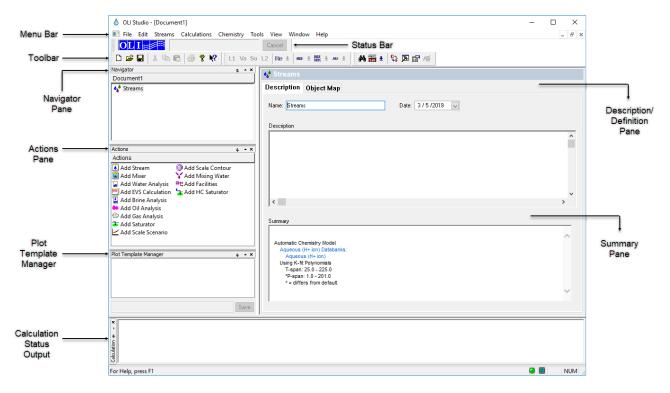
Effects of temperatures, pressure, pH, concentration, and velocity on corrosion are also included. Capabilities and features of Corrosion Analyzer are:

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

Chapter I – The OLI Studio Software User Interface

General View of the User Interface

In the OLI Studio Software, 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 be using within the software, as well as how to navigate the OLI Studio User Interface, will be provided here.



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 the Technical Support or any content that you may need related to OLI Software.

Tool Bar

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



They are laid out in the following order:

Quick access to File:	🗅 📂 🔚
Quick access to Edit:	X 🗈 🛍
Quick access to Help:	? № ?
Quick access to Chemistry:	L1 Va So L2 Re ± MSE ± MSE ± AQ ±
Quick access to Tools :	🛤 🎬 🛃 💱 🔊 😭 🌾

Icons in the Chemistry section

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

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

L1: Liquid 1 or water-rich phase

Va: Vapor phase

So: Solid phase

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

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

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

AQ: Aqueous databank

MSE: Mixed Solvent Electrolyte databank

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

Icons in the Tools section

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

<u>Component search</u> :	# \$	This tool helps you to look for a component using Formula, CAS number, or via 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.
Customize toolbars:		This tool allows you to remove or add preferred tools to the Tool Bar. For example, you can add or remove Chemistry from the Tool Bar.
<u>General options:</u>		This tool allows you to adjust or change default software settings.
Calculation options:	N	This tools allows you to include or exclude different types of properties into the calculations.

Navigator Pane

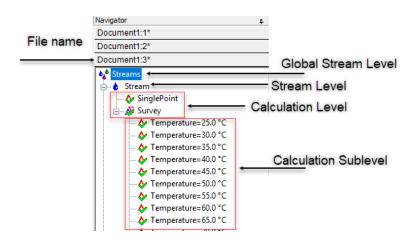
The Navigator Pane (or tree level) contains the list of streams and calculations that are active within a file. This view contains the icons and names of each action in a hierarchical tree. The Description/Definition pane changes depending on the level that is highlighted. A plus sign next to an object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

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

Stream Level: Chemistry options such as phase selection, REDOX reactions, and the thermodynamic databanks can be selected as this level.

Calculation Level: Calculation types such as Single point calculations, Survey calculations, etc., are subordinate to streams, and appear in this level. A more detailed explanation of calculation types can be found in <u>Chapter II</u> of this manual.

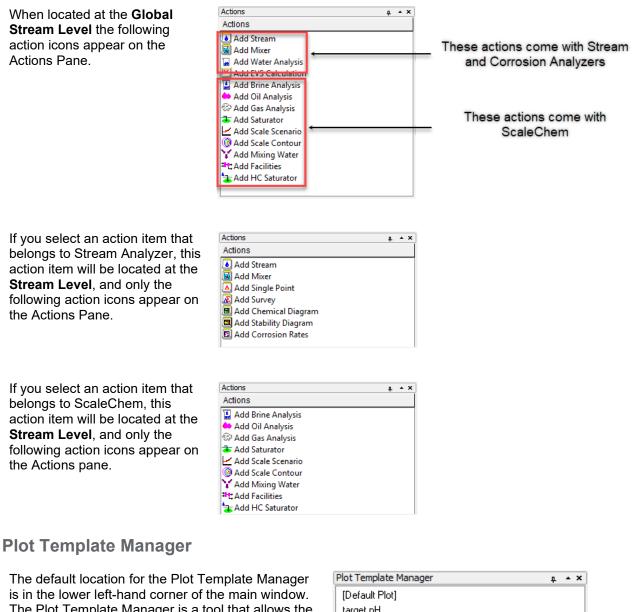
Calculation Sublevel: Some calculations, such as Survey calculations, have their own calculation sublevels. They can be expanded or maximized using the small icon (\oplus or $\dot{\oplus}$) next to the calculation type.



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.

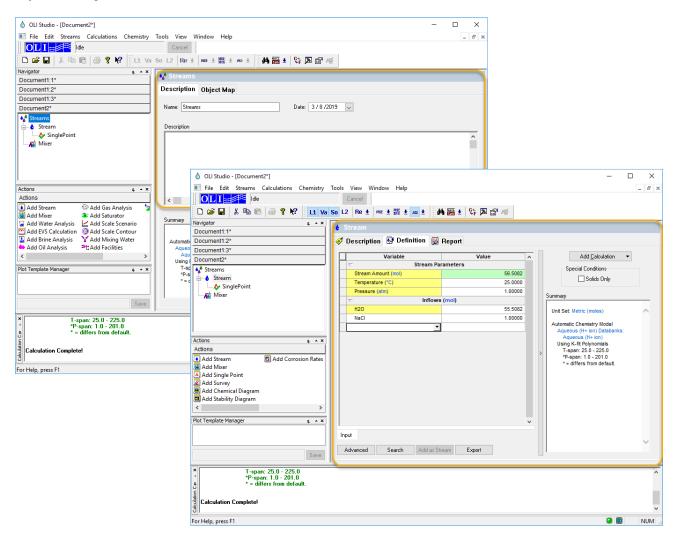


is in the lower left-hand corner of the main window. The Plot Template Manager is a tool that allows the user to create, save and use plot templates. This tool allows a fast plotting and analysis of the users results.

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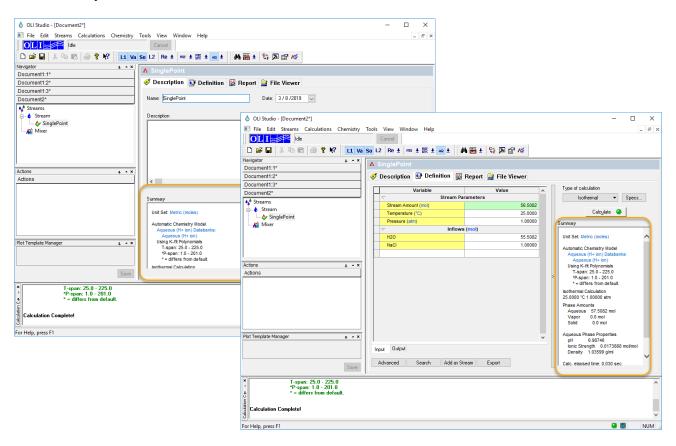
Description / Definition Pane

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 detail description of each framework is given below:

Aqueous (AQ) Thermodynamic Framework

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

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

The AQ framework utilizes the Bromley-Zemaitis activity model:

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

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

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

The AQ-framework selects the PUBLIC¹ database by default. Frequently there is more to the chemistry than what is covered in the PUBLIC database. The following is a partial list of additional databases available in the AQ framework:

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

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

Mixed Solvent Electrolyte (MSE) Thermodynamic Framework

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

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

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

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

Temperature	-50°C – to 90% T _{crit}
Pressure	0 – 1500 bar
Ionic Strength	no limit

The MSE framework contains the following databanks:

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

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

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

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

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

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

- 1. MSE $(H_3O^+ \text{ ion})$ Selected by default
- 2. MSE-SRK (H₃O⁺ ion) Selected by default
- 3. Corrosion (MSE)
- 4. Geochemical (MSE)
- 5. Urea (MSE)
- 6. Surface Complexation Double Layer Model (MSE)

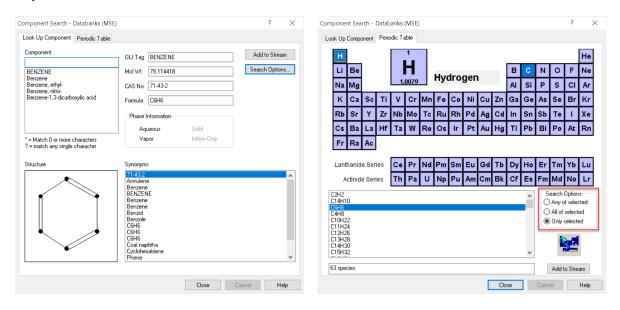
Component Search

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

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

The **Component Search** option opens 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
- 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 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	se Names Diction			
	cted style will be u tables and lists. Cancel	used for displaying of Apply		elp

Units Manager

calculation objects.

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

🗅 🚅 🖬 🕹 🖻 💼 💼 🎒 🦞 👯 [1	4) (c. 1.2) [The 1] was 1 [W] 1 was 1 [] [] 44 [He] 1 [] [] [] [] [] [] [] [] []
	1 Va So L2 Re ± MME ± \$\$\$\$ ± MA ± \$\$\$\$\$\$ ₩ ± \$\$\$\$\$ \$\$\$ MME ± \$\$\$\$\$ \$\$\$ \$\$\$\$ \$\$\$\$ \$
	• X .
Document1*	Default Units for Document ? X
🔥 Streams 🖃 🖕 Stream	Default Units
└····▲ SinglePoint	
	Object Type All 🗸
	All Brine Contour EVSStandard Metric Gas HCSaturator MixingWater
Actions 4	Oil
Actions	Customize Saturator Scenario
🚺 Add Stream 🧧 Add EVS Calculatic	Stream
📕 Add Mixer 🛛 🔛 Add Brine Analysi:	WaterAnalysis
🚡 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.

🗅 🚅 🖬 👗 🛍 🛍 🎒 😵 🕌	L1 Va So L2 Re ± MSE ± 🗱 ± 🗛 ± 👫 ± 💱 🗚 😭 4
· · · · · · · · · · · · · · · · · · ·	↓ ▲ × • Stream
Document1*	
💑 Streams	Content Description Definition Report
🚊 🕹 Stream	Units Manager - Stream ? X
▲ SinglePoint	Units Manager
	5
	Metric V Batch V Moles V 🕨 🙎
	5
]	Customize
Actions	h •
Actions	
🛃 Add Stream 🛛 🔊 🔊 Add Survey	
📓 Add Mixer 🛛 🔳 Add Chemical	Diag OK Cancel Apply Help
🖪 Add Single Point 🛛 🖪 Add Stability D	

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.

nposition Parameters Corrosion				Composition Parameters Corrosion	
Variable	Basis	Units	^	Variable	Units
Stream Amount	Moles	mol		Temperature	°C
Inflows	Moles	mol		Pressure	atm
Outj	put 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
Basis options			Specific Electrical Conductivity	µmho/cm	
Moles		mol		Energy	cal
Mass		g 📐	<u>~</u>	Energy, Molar	cal/mol
Volume		g	4	Entropy	cal/K
Concentration		kg		Entropy, Molar	cal/mol K
Molar Concentration		dl		Fugacity	atm
Mass Fraction		rng (a/100)		Heat Capacity	cal/g K
Mole Fraction		metric ton	-	Ionic Strength (x-based)	mol/mol
			_	Ionic Strength (in based)	molika

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.

56.5082				
25.0000				
1.00000				
√ Inflows (mol) √				
55.5082				
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.

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	OK	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 ^M. This will open a new window. Under the **Calculation Options** tab you can enable or disable the following options:

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

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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.

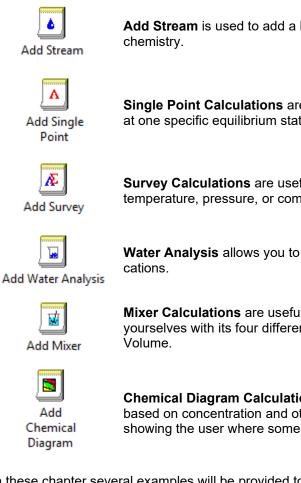
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× Calculation Complete!			
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Tip: If by accident we lose a tool bar, we can go to View > Toolbars >... and select the toolbar that is missing.

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

Section 1. Single Point Calculations

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

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Isothermal	The software computes solution properties based on a known composition, at a constant temperature and pressure.
lsenthalpic	A constant heat loss/gain is applied to the calculation and a temperature or pressure can be adjusted to meet this new heat content.
Bubble Point	The temperature or pressure is adjusted to reach a condition where a small amount of vapor begins to appear.

Dew Point	The temperature or pressure is adjusted to reach a condition where a small amount of aqueous liquid appears.
Vapor Amount	The temperature or pressure is adjusted to produce a (user) specified amount of vapor.
Vapor Fraction	The temperature or pressure is adjusted to produce a (user) specified amount of vapor as a fraction of the total quantity.
Isochoric	The temperature or pressure is adjusted to produce the (user) specified total volume.
Set pH	The software adjusts the flowrate of a species to calculate the (user) specified pH of the aqueous solution.
Precipitation Point	The software adjusts the flowrate of a species until a small amount of solid precipitates.
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 reconciliates the alkalinity of a solution by adjusting a titrant, by default the software uses CO ₂ .
Autoclave	It is an isochoric (constant volume) calculation in which mass, pressure and temperature are allowed to vary. This simulates a closed pressure vessel. ²
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 the Custom single point calculation, we can select from a wider variety of variables.

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.

² You may have to enable this calculation from Tools | Options | Enable Features Under Development

1.1. Isothermal

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

Example 1: Speciation and its importance for pH calculations

After completing this example, you will learn how to set up an **Isothermal calculation** and will also get a better understanding of the importance of full speciation on the calculation of pH. Let's calculate the pH of a 1 m FeCl₃ solutions 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.



- 1. Let's create a new stream. Click on the **Add Stream** located in the **Action Pane**. When a stream is created only H2O is present in the grid. Its cell is yellow because it cannot be removed, it is a permanent inflow.
- 2. For this example, we are going to use the **AQ-Databank** (The default databank)
- 3. Type FeCI3 in the white cell below H2O inflows grid, and press <Tab> or <Enter>
- 4. Enter the value **1.0 mol** in the next cell.

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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.

- 5. Click the **Description** tab to change the name of the Stream. You can also change the name using the **<F2>** key or by **right-mouse click** on the object and selecting rename.
- 6. Change the generic name Stream to pH of 1 m FeCl3
- 7. Add the following Description: Isothermal calculation calculating the pH of FeCl3 1 molal solution
- 8. Go back to the **Definition** Tab

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Now, we are ready to perform a calculation

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

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

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11. All the required variables have been entered, and the Calculate button has turned green. Click on the

Calculate 🥥 button. You can also press the **<F9>** key to run the calculation.

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

Red – Insufficient specifications for a calculation

Yellow - Incomplete specifications but calculation can continue

Green – Completed specifications, the calculation is ready

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

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

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Anaylyzing the Results

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

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

Let's analyze the simulation results in more detail

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

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		Total	Aqueous		
		mol	mol		
	H2O	55.503	55.503		
	CF1	2,97833	2.97833		
	Fe+3	0.983345	0.983345		
	FeCI2+1	9.83218e-3	9.83218e-3		
Actions	H+1	5.2894e-3	5.2894e-3		
Actions	FeOH+2	5.27572e-3	5.27572e-3		
	FeCH-2	1.30791e-3	1.30791e-3		
	FeCl3 (Molysite)	2.25081e-4	2.25081e-4		
	FeCl4-1	6.4732e-6	6.4732e-6		
	Fe(OH)2+1	6.35892e-6	6.35892e-6		
	Fe2(OH)2+4	4.78545e-7	4.78545e-7		
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Why is the **pH** so low?

The aqueous iron species complexes the hydroxide ions. The water dissociation shifts in the direction to replenish the hydroxide ions³.

This equilibrium is always present:

$$H_2 O = H^+ + O H^-$$

³ Le Châtelier's principle. P.W.Atkins. Physical Chemistry. W.H. Freeman and Company, San Francisco (1982) p 269.

Speciation Reactions

First iron (III) chloride dissociates:

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

Then the Fe³⁺ interacts with water; hydrolysis reaction:

$$Fe^{3+}$$
 + H₂O \rightarrow $FeOH^{2+}$ + 2H⁺

Then another water molecule enters into the reaction:

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

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

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

Fe⁺ ³	FeCl ₂ +1	Fe(OH)₃⁰	H_2O^0
FeCl ⁺²	Fe(OH)2 ⁺¹	OH-1	HCl⁰
FeOH ⁺²	H ⁺¹	FeCl4 ⁻¹	Fe ₂ (OH) ₂ +4
Cl ⁻¹	FeCl ₃ 0	Fe(OH)4 ⁻¹	

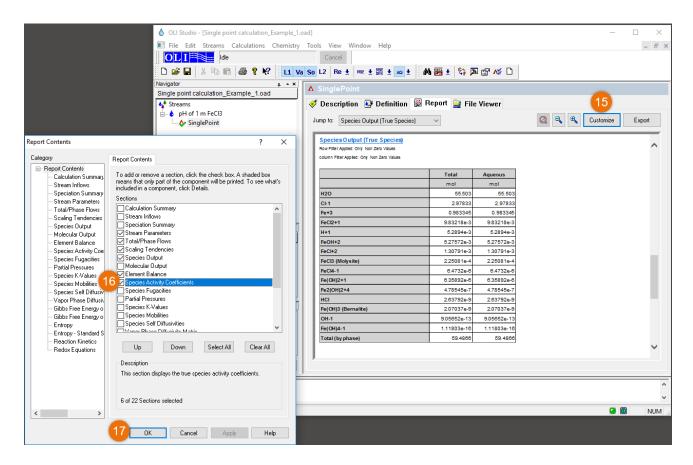
pH Calculation

The pH is calculating using the following formula:

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

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

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



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

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	Fe(OH)2+1	0.701115	0.654164		
	Fe(OH)3 - Aq	2.56304	2.3914		
	Fe(OH)4-1	1.87391	1.74842		
	FeOH+2	0.269701	0.25164		
Disk Tamalaka Managan	H2O	1.01807	0.949897		
Plot Template Manager 📮 🔺	HCI-Aq	2.56304	2.3914		
	H+1	1.2348	1.15211		
	OH-1	1.87255	1.74715		
					~
Save					
Jave					
×					^
Calculation Complete!					
<u></u>					•
For Help, press F1					Image:

Thus, the pH is:

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

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

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

$$pH = 2.2151$$

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

Example 2: Calculating the pH of an acetic acid solution

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

Starting the Simulation

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

Image: Constraint of the second se	Cancel 3 4 So L2 Re ± Mst ± St ± A mathematical A m	
sothermal	Image: Stream Parameters Add Calculation Stream Amount (mol) 55.5082 Temperature (°C) 25.0000 Pressure (atm) 1.00000 H2O 55.5082 Unit Set: Metric (moles) Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion) Databanks: Add Calculation (H+ ion) Databanks: Aqueous (H+ ion) Databanks: Add Calculation (H+ ion) *= differs from default.	
Isothermal - acetic acid	Stream Amount (mol) 55.5082	
		Summary
Actions Actions Actions Add Stream Add Stability Diagra Add Single Point Add Corrosion Rate Add Single Point Add Survey Add Chemical Diagram Plot Template Manager A A X		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
Save	Input Advanced Search Add as Stream Export	·

5. Click on the Customize Button

Units Manager - Isothermal - acetic acid	?	×
Units Manager		
Metric \checkmark Batch \checkmark Moles	~	۲
Customize		
OK Cancel Apply		Help

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

	othermal - ac			Batch Syste	? m) Flowing Sy	/st
mposition	Parameters	Corrosion				
	Varia	ble		Basis	Units	
		In	flow vari	ables		
Stream Ar	nount			Moles		
Inflows				Moles 🔍	5	
		Οι	utput vari			
Aqueous	Composition			Moles	mol	
Vapor Cor	mposition			Concentration	mol	
Solid Com	position			Molar Concentration Mass Fraction	mol	
2nd Liquid	I Composition			Mole Fraction	mol	
Total Com	position			Moles	mol	
		E	Basis opt	ions		
Moles					mol	
Mass					g	
Volume					L	
Concentra	ation				mg/L	
Molar Con	centration				mol/L	
Mass Frac					mass %	-
Mole Fred	tion				mole %	
			6	OK Can	cel Heli	

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.

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

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

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

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

6. Click on the **Calculate** button

OLI Studio - [Single point calculations.oad*]			- 🗆 ×
E File Edit Streams Calculations Chemistry	Tools View Window Help		_ 8 ×
	Cancel		
	a So L2 Re ± Mse ± skk ± AQ ± 6	M 🎬 🛃 💱 🔉 😭 📈 🗋	
Navigator			
Single point calculations.oad*	▲ pH		
🍓 Streams	< Description 🥸 Definition 📓	Report 🚊 File Viewer	
📄 🗄 İsothermal	Variable	Value	Type of calculation
lsothermal	Stream Pa		Isothermal - Specs
bisothermal - acetic acid	Stream Amount (mol)	55.5082	isotroma opecs
2		75.0000	Calculate 🥝
-	Pressure (atm)	1.00000	Summary
	☐	mass %)	
	Water	90.000	Unit Set: <custom></custom>
	4 Acetic acid	5 10.0000	Automatic Chemistry Model
			Aqueous (H+ ion) Databanks: Aqueous (H+ ion)
]			Using K-fit Polynomials
Actions # * X			T-span: 25.0 - 225.0 *P-span: 1.0 - 201.0
Actions			* = differs from default.
			> Isothermal Calculation
			75.0000 °C 1.00000 atm
			Calculation not done
Plot Template Manager 🛛 📮 🔺 🗙			
	Input		
			↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓
Save	Advanced Search Add as Str	eam Export	
	J		
			^
Calculation Complete!			~
For Help, press F1			
rorricip, press ri			

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

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

♦ OLI Studio - [Single point calculations.oad*] ■ File Edit Streams Calculations Chemistry ● ● ● ● ● ● ● ● ● ● ● ● ● ● ● ● ● ● ●	Cancel		Stream Parameters Calculation Results Inflows Related Inflows Additional Stream Parameters Phase Flow Properties Thermodynamic Properties Pre-scaling Tendencies	×
Single point calculations.oad*	▲ pH		Pre-scaling Index	
Actions	✓ Description Image: Provide the second	F	Scaling Tendencies Scaling Index Aqueous Vapor Solid Molecular Apparent - Aqueous Totals Molecular Totals MBG Totals Activity Coefficients Fugacity Coefficients Fugacities - Vapor K-Values Scaling Tendencies Scaling Tendecies Scaling Tendencies Scaling Tendecies Scalin	ipecs
	Units Manager		Gibbs Free Energy Gibbs Free Energy Standard State (x-based)	
	Save default layout		Entropy	
	Generate Model		Entropy Standard State (x-based)	
Plot Template Manager	Hide Zero Values		Mobilities Self Diffusivities	
	Sections >		Partial Pressures	iol/mol
Save	Output Advanced Search Add as Stream Expo	rt	Calc. elapsed time: 0.029 sec Calculation complete	
Calculation Complete!			 Image: Control of the second se	NUM

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

Variable	Value	Type of calculation
Stream Para	ameters	Isothermal 👻 Specs
Stream Amount (mol)	55.5082	
 Moles (True) - Aqueous (mol) 	55.5133	Calc <u>u</u> late 🥥
Temperature (°C)	75.0000	Summary
Pressure (atm)	1.00000	
Inflows (m)	ass %)	Unit Set: <custom></custom>
Water	90.0000	Automatic Chemistry Model
Acetic acid	10.0000	Aqueous (H+ ion) Databanks:
Additional Stream	n Parameters	Aqueous (H+ ion)
Density - Aqueous (g/ml)	0.773294	Using K-fit Polynomials T-span: 25.0 - 225.0
Density - Total (g/ml)	0.773294	*P-span: 1.0 - 201.0
lonic Strength (m-based) - Aqueous (m	5.17899e-3	* = differs from default.
lonic Strength (x-based) - Aqueous (m	9.02834e-5	Isothermal Calculation 75.0000 °C 1.00000 atm
рН	2.32267	Phase Amounts
Standard Liquid Volume - Aqueous (L)	1.07368	Aqueous 1075.27 g
		Vapor 0.0 g
		Solid 0.0 g
		Aqueous Phase Properties
		pH 2.32267
		lonic Strength 9.02834e-5 mol/mol Density 0.773294 g/ml
		×
		Calc. elapsed time: 0.029 sec
ut Output		Calculation complete

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

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

1.2. Bubble Point

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

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

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

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

Starting the Simulation

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

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

Calculating the Bubble Point Temperature (Isobaric)

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

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

5. Click on the hyperlink mol next to Stream Amount

Variable		Value
∇	Stream Pa	rameters
Stream Amount (mol)		55.5082
Temperature (°C)	< -	25.0000
Pressure (atm)		1.00000
∇	Inflows	(mol)
Water		55.5082

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

mposition	Parameters	Corrosion			
	Varia	ble	Basis	Units	
		Inflow	variables		
Stream A	mount		Volume	L	
Inflows			Molar Concentratio	🧹 mol/L	
		Outpu	t vari Mass		
Aqueous	Composition		Moles	mol	
Vapor Co	mposition		Concentration Molar Concentration	mol	
Solid Com	nposition		Molar Concentration	mol	
2nd Liqui	d Composition		Mole Fraction	mol	
Total Com	nposition		Moles	mol	
		Basi	s options		
Moles				mol	
Mass				g	
Volume				L	
Concentra				mg/L	
	ncentration			mol/L	
Mass Fra				mass %	
Mole Fred	stion			mole %	

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

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

Variable Value Stream Parameters Stream Amount (L) 1.00000 25.0000 Temperature (°C) Ó Pressure (atm) 1.00000 Calculation Parameters Calculate Temperature Ŧ Inflows Temperature Pressure Water 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**".
- 12. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key.
- 13. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save under the same file that we created before named as *Single Point Calculations*.

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

Unit Set: <custom></custom>	
Automatic Chemistry Model MSE (H3O+ ion) Databanks MSE (H3O+ ion) Using Helgeson Direct	8:
Bubble Point Calculation 1.00000 atm 87.1143 °C	
Phase Amounts Aqueous 50.7382 mol Vapor 5.07382e-9 mol Solid 0.0 mol	1
Aqueous Phase Properties pH 6.23654 lonic Strength 1.04844e- Density 0.954131 g/ml	8 mol/mol
Calc. elapsed time: 0.725 sec	:
Calculation complete	

Calculating the Bubble Point Pressure (Isothermal)

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

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

	Calculation Parameters Calculate Pressure					
	√ Inflows (mol/L)					
	Water					
	Acetone	1.00000				

- 6. Click on the Calculate button or press the <F9> key.
- 7. It is time to save your file (File >Save as...) or using the save icon in the tool bar.

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

Unit Set: <custom></custom>	
Automatic Chemistry Model MSE (H3O+ ion) Databanks: MSE (H3O+ ion) Using Helgeson Direct	
Bubble Point Calculation 25.0000 °C 0.0700550 atm	
Phase Amounts Aqueous 52.7833 mol Vapor 5.27833e-9 mol Solid 0.0 mol	
Aqueous Phase Properties pH 6.99771 lonic Strength 1.81463e-9 r Density 0.990973 g/ml	nol/mol
Calc. elapsed time: 0.047 sec	
Calculation complete	

1.3. Dew Point

The **Dew Point** is defined as the temperature at which a condensable component of a gas, for example water vapor in the air, starts to condensate into 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	type Dew Point Temperature		120 °C		
Stream Name	Sour Natural Gas Dew Point	Pressure	100 atm		
Name Style	Style Display Formula H2O		Calculated		
Unit Set	Metric, Mole Fraction	CO2	1 mole %		
Framework	MSE	CH ₄	95 mole %		
		H ₂ S	3 mole %		

Calculating the Dew Point Temperature (Isobaric)

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



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

Units Manager - Laden Gas Dew Point	?	\times
Units Manager		
Metric V Batch V Moles Moles Mole Frac Molar Con Mass Conc. Mass Frac	ic.	Þ
OK Cancel Apply	H	ielp

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

	Variable	Value			
		rameters			
	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			

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

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

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 1.00000e-6 mol
Aqueous 5.55082e-5 mol	Vapor 55.5082 mol
Vapor 55.5082 mol	Solid 0.0 mol
Solid 0.0 mol	Solid 0.0 mor
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 a/ml	Density 0.953852 g/ml
contraction of the second seco	
Calc. elapsed time: 0.437 sec	Calc. elapsed time: 0.043 sec
Calculation complete	Calculation complete
Calc. elapsed time: 0.437 sec	Calc. elapsed time: 0.043 sec

Note: The software sets the amount of liquid to 1/10⁶ of the stream amount for the dew point calculation.

You can study the composition of the acid gases such as CO₂ and H₂S 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)**.

ump to: Species Dutput (True Species) 🗸 🔍 Customize					
Species Output (True Species)					
Row Filter Applied: Only Non Zero Values					
olumn 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		

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

1.4. Isochoric (constant volume)

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

$$PV = nRT$$

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

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

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

In this example, you will add 1 kg water to a 10 L vessel and then fill the void (head space) with Air. The temperature is 25 °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				
Calc	ulation Settings	Stream Composition and Conditions		
Calculation Type	Single Point Calculation	Stream Amount Default – 55.5		
Calculation Sub-type	Isochoric	Ambient Temperature	25 °C	
Stream Name	Isochoric	H2O	Calculated	
Name Style	Display Formula	N2 77 moles		
Unit Set	Metric, Moles	02	21 moles	
Framework	AQ	CO2	1 mol	
Calculate	Pressure	Ar	0.04 moles	
Vessel Volume	10 L			

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

	Variable	Value
	√ Stream Par	ameters
	Stream Amount (mol)	154.548
•	Temperature (°C)	25.0000
0	Pressure (atm)	1.00000
	Calculation Pa	arameters
	Total Volume (L)	10.0000
	Calculate	Pressure 🔻
	√ Inflows	(mol)
	H2O	55.5082
	N2	77.0000
	02	21.0000
	CO2	1.00000
	Ar	0.0400000

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

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

	Variable	Value	^	Type of calculation
	√ Stream Par	ameters		Isochoric 💌 Specs
	Stream Amount (mol)	154.548		
	 Moles (True) - Aqueous (mol) 	55.6901		Calc <u>u</u> late 🥝
	Moles (True) - Vapor (mol)	98.8582		Summary
•	Temperature (°C)	25.0000		
	Calculation Re	sults (atm)		Unit Set: Metric (moles)
0	Pressure	305.676		Automatic Chemistry Model
	√ Inflows	(mol)		Aqueous (H+ ion) Databanks:
	H2O	55.5082		Aqueous (H+ ion)
	N2	77.0000		Using K-fit Polynomials T-span: 25.0 - 225.0
	02	21.0000		*P-span: 1.0 - 201.0
	C02	1.00000		* = differs from default.
	Ar	0.0400000		Isochoric Calculation
				25.0000 °C 305.676 atm
				Phase Amounts
				Aqueous 55.6901 mol Vapor 98.8582 mol
			~	Solid 0.0 mol
Int	out Output			Aqueous Phase Properties
	Carpa			pH 3.82308
4	Advanced Search Add as Stream	Export		Ionic Strength 2.73634e-6 mol/mol

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

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

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

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

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

1.5. Vapor Amount and Vapor Fraction

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

Example 6: Evaporating a Brine

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

Starting the Simulation

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

Vapor Fraction / Vapor Amount Point Calculation					
Calculation Settings Stream Composition and Condition					
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 ₄	1 mass %		

Calculating the Vapor Fraction Temperature (Isobaric)

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

Units Manager - Brine Evaporation - Vapor Fraction	?	×
Units Manager		
Metric V Batch V Moles Mole Frac. Molar Conc.	~	Þ
Customize Mass Conc. Mass Frac.		
OK Cancel Apply		Help

- 18. Enter the gas composition given in the table <u>above</u>.
- 19. Go to the Add Calculation button and select Single Point calculation
- 20. Select Vapor Fraction as Type of Calculation
- 21. Change the SinglePoint name to Vapor Fraction Temperature using the <F2> key
- 22. Enter 95 as the Vapor Fraction amount.
- Note: The software will convert the 1 kg to mole units and will put 95% of this in the vapor phase.
- 23. Keep the Calculate-Temperature option

	Variable	Value	Ţ		
	√ Stream Par	ameters	1		
	Stream Amount (kg)	1.00000	1		
0	Temperature (°C)	25.0000	1		
•	Pressure (atm)	1.00000	1		
	Calculation Parameters				
	Vapor Fraction (Vapor/Inflow [mol]) (mole %)	95.0000	1		
	Calculate	Temperature 💌	1		
	√ Inflows (n	nass %)	1		
	H2O	90.0000	1		
	NaCl	9.00000	1		
	CaSO4	1.00000	1		
			1		

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

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

Unit Set: Met	tric (mass frac	ction)
MSE (H3C MSE (H	hemistry Mode D+ ion) Databa I3O+ ion) geson Direct	
Vapor Fract 1.00000 a 108.805 °		
	0.0243143 k 0.882612 kg	-
pH lonic Strei	ase Properties 6.40682 ngth 0.09906 1.16798 g/ml	
Calc. elapse	ed time: 0.131 s	sec

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

np to: Total and Ph	ase Flows (Amounts)	~		
Total and Phase column Filter Applied: O	Provide Flows (Amounts) Non Zero Values			
	Total	Liquid-1	Vapor	Solid
	mol	mol	mol	mol
Mole (True)	51.6887	1.20091	48.9923	1.49547
Mole (App)	51.5708	1.08307	48.9923	1.49547
	kg	kg	kg	kg
Mass	0.999999	0.0243143	0.882612	0.0930728
	L	L	L	cm3
Volume	1518.82	0.0208174	1518.76	41.7748

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

1.6. Set pH

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

Example 7: Neutralizing Acetic Acid

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

Starting the Simulation

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

Set pH Calculation					
Calculatio	on 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	СН3СООН	1 mol		
Framework	AQ				

Setting the pH

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

its Manager - Sing Jnits Manager				1	×
Metric	~	Batch 🗸 🗸	Moles	~	►
Customiza					
Customize					

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

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

	Variable	Value			
	Stream Pa	rameters			
	Stream Amount (mol)	56.5082			
	Temperature (°C)	25.0000			
	Pressure (atm)	1.00000			
	Calculation F	Parameters			
•	Target pH	0.0			
	Use Single Titrant	No			
	pH Acid Titrant	HCL			
	pH Base Titrant	NAOH			
Inflows (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			?	\times
Category Titrants Calculation Options	Select an acid and base	to adjust to meet the specified ;	oH. New Inflow	
	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.

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

	Variable	Value
	√ Stream Pa	arameters
	Stream Amount (mol)	56.5082
	Temperature (°C)	25.0000
	Pressure (atm)	1.00000
	Calculation	Parameters
•	Target pH	7.00000
	Use Single Titrant	No
	pH Acid Titrant	HCL
	pH Base Titrant	NAOH
	√ Inflow	s (mol)
	H2O	55.5082
	СНЗСООН	1.00000

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

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

Stream Parameters Set pH Specs Stream Amount (mol) 57.5053 Calculate Moles (True) - Aqueous (mol) 58.3044 Calculate Temperature (*C) 25.0000 Calculation Results (mol) pH titrant added: NaOH 0.997023 Moles (True) - Material (mol) Mutomatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion) Using K-ft Polynomials T-span: 25.0 - 225.0 *-span: 1.0 - 201.0 * = differs from default. Set pH Calculation 25.0000 °C 1.00000 atm NaOH 0.997023 wt Output	Variable	Value	-	\	l ype of calculation
Moles (True) - Aqueous (mol) 58.3044 Temperature (*C) 25.0000 Pressure (atm) 1.00000 Calculation Results (mol) 0.997023 PH titrant added: NaOH 0.997023 H2O 55.5082 CH3COOH 1.00000 NaOH 0.997023 V "-span: 25.0 - 225.0 'P-span: 1.0 - 201.0 * '* = differs from default. Set pH Calculation Set pH Calculation 25.0000 °C 1.00000 atm Target pH 7.00000 Acid Titrant: HCl Totai: 0.0 mol Base Titrant: NaOH Totai: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol Vapor 0.0 mol Vapor 0.0 mol	Stream Pa	arameters			Set pH 💌 Specs
Temperature (*C) 25.0000 Pressure (atm) 1.00000 Calculation Results (mol) 0.997023 PH titrant added: NaOH 0.997023 Inflows (mol) 4utomatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion) Using K-fit Polynomials T-span: 25.0 - 225.0 V *= differs from default. Set pH Calculation 25.0000 °C 1.00000 atm Target pH 7.00000 Acid Titrant: HCI Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol	Stream Amount (mol)	57	7.5053		
Pressure (atm) 1.00000 Pressure (atm) 0.0000 pH titrant added: NaOH 0.997023 H2O 55.5082 CH3COOH 1.00000 NaOH 0.997023 V * = differs from default. Set pH Calculation 25.000 °C 1.00000 atm Target pH 7.00000 Acid Titrant: HCl Total: 0.0 mol Base Titrant: NaOH O.997023 mol Aqueous \$8.3044 mol Vapor 0.0 mol	Moles (True) - Aqueous (mol)	58	8.3044		Calc <u>u</u> late 🥝
Pressure (atm) 1.0000 Calculation Results (mol) 0.997023 PH titrant added: NaOH 0.997023 H2O 55.5082 CH3COOH 1.00000 NaOH 0.997023 * = differs from default. Set pH Calculation 25.000 °C 1.00000 atm Target pH 7.00000 atm Target pH 7.00000 atm Target pH 7.00000 atm Added: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol	Temperature (°C)	25	5.0000		Summary
pH titrant added: NaOH 0.997023 Inflows (mol) Automatic Chemistry Model H2O 55.5082 CH3COOH 1.00000 NaOH 0.997023 * = differs from default. Set pH Calculation 25.000 °C 1.00000 atm Target pH 7.0000 Acid Titrant: HCl Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol	Pressure (atm)	1.	00000		
Inflows (mol) Automatic Chemistry Model H2O 55.5082 CH3COOH 1.00000 NaOH 0.997023 * = differs from default. Set pH Calculation 25.0000 °C 1.00000 atm Target pH 7.00000 Acid Titrant: HCl Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol	Calculation I	Results (mol)			Unit Set: Metric (moles)
Inflows (mol) Aqueous (H+ ion) Databanks: H2O 55.5082 CH3COOH 1.00000 NaOH 0.997023 * = differs from default. Set pH Calculation 25.000 °C 1.00000 atm Target pH 7.00000 atm Target pH 7.00000 Acid Titrant: HCl Total: 0.997023 Total: 0.997023 Phase Amounts Aqueous 58.3044 mol Vapor 0.0 mol	pH titrant added: NaOH	0.9	97023		Automatic Chemistry Model
CH3COOH 1.00000 NaOH 0.997023 * = differs from default. Set pH Calculation 25.0000 °C 1.00000 atm Target pH 7.00000 Acid Titrant: HCl Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol Yapor 0.0 mol	- Inflow	s (mol)			-
CH3COOH 1.00000 NaOH 0.997023 > *= differs from default. Set pH Calculation 25.0000 °C 1.00000 atm Target pH 7.00000 Acid Titrant: NaOH Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol	H2O	55	5.5082		
NaOH 0.997023 *P-span: 1.0 - 201.0 * = differs from default. Set pH Calculation 25.0000 °C 1.00000 atm Target pH 7.00000 Acid Titrant: HCI Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol Vapor 0.0 mol Vapor 0.0 mol Vapor 0.0 mol	СНЗСООН	1.	00000		
 * = differs from default. Set pH Calculation 25.0000 °C 1.00000 atm Target pH 7.00000 Acid Titrant: HCI Total: 0.0 mol Base Titrant: NaOH Total: 0.0997023 mol Added: 0.997023 mol Phase Amounts Aqueous 58.3044 mol Vapor 0.0 mol 	NaOH	0.9	97023		
25.0000 °C 1.00000 atm Target pH 7.0000 Acid Titrant: HCl Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol				>	
 1.00000 atm Target pH 7.00000 Acid Titrant: HCl Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol Phase Amounts Aqueous 58.3044 mol Vapor 0.0 mol 					Set pH Calculation
Target pH 7.00000 Acid Titrant: HCI Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Phase Amounts Aqueous 58.3044 mol Vapor 0.0 mol					
Acid Titrant: HCI Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Added: 0.997023 mol Phase Amounts Aqueous 58.3044 mol Vapor 0.0 mol					1.00000 atm
Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 Total: 0.997023 mol Added: 0.997023 Phase Amounts Aqueous 58.3044 mol Vapor 0.0 mol					
Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Phase Amounts Aqueous 58.3044 mol Vapor 0.0 mol					
Total: 0.997023 mol Added: 0.997023 mol Phase Amounts Aqueous 58.3044 mol Vapor 0.0 mol			- 1	Ш	Acid Titrant: HCI
Added: 0.997023 mol Phase Amounts Aqueous 58.3044 mol Vapor 0.0 mol			- 1		Acid Titrant: HCI Total: 0.0 mol
Phase Amounts Aqueous 58.3044 mol Vapor 0.0 mol				l	Acid Titrant: HCI Total: 0.0 mol Base Titrant: NaOH
Aqueous 58.3044 mol Vapor 0.0 mol				l	Acid Titrant: HCI Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol
Vapor 0.0 mol					Acid Titrant: HCI Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol
					Acid Titrant: HCI Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Phase Amounts
				,	Acid Titrant: HCI Total: 0.0 mol Base Titrant: NaOH Total: 0.997023 mol Added: 0.997023 mol Phase Amounts Aqueous 58.3044 mol

1.7. Precipitation Point

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

Example 8: Determining the Solubility of Calcite (CaCO₃)

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 (CaCO₃) 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^{-1} as well as dissolved CO_2 .

Starting the Simulation

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

Precipitation Point Calculation					
Calculation Settings Stream Composition and Conditions					
Calculation Type	Single Point Calculation	Stream Amount	Default - 1 kg		
Calculation Sub-type	Precipitation Point	Temperature	25 °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	AQ	MgCl2	9325 ppm (mass)		
		CO2	431 ppm (mass)		
		CaCO3	0 ppm(mass)		

Calculating the Precipitation of Calcite (CaCO₃)

- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to Solubility of CaCO3 Precipitation Point
- 3. Select the **AQ** thermodynamic Framework
- 4. Click on the Names Manager lcon 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 - Precipit	ation ?	×
Units Manager		
Qustomize	Mass Frac. V Moles Mass Frac. Molar Conc. Mole Frac. Conc. Mass	
OK Cancel	Apply	Help

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

nposition	Parameters	Corrosion		
	Varial	ble	Basis	Units
		Inflov	v variables	
Stream Ar	nount		Mass	kg
Inflows			Mass Fraction	mass %
		Outpu	ıt variables	
Aqueous	Composition		Mass Fraction	mass %
Vapor Co			Mass Fraction	mass %
Solid Com	•		Mass Fraction	mass %
2nd Liquid	I Composition		Mass Fraction	mass %
Total Com	position		Mass Fraction	mass %
		Basi	s options	
Moles				mol
Mass				kg
Volume				L
Concentra				mg/L
	centration			mol/L
Mass Frac				mass %
Mole Fred	tion			n/o mass %
				ppm (mass)

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

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

Variable	Value	^		Type of calculation
	Parameters			Precipitation Point 👻 Specs
Stream Amount (kg)	1.000	0		
Temperature (°C)	25.00	0		Calc <u>u</u> late 🥥
Pressure (atm)	1.000	0		Summary
	n Parameters			
Precipitant:	<select></select>			Unit Set: <custom></custom>
Adjusted Inflow:	<select></select>			Automatic Chemistry Model
√ Inflows	ppm (mass))			Aqueous (H+ ion) Databanks:
H2O	9.79374	:5		Aqueous (H+ ion)
CaCl2	10870	.0		Using K-fit Polynomials T-span: 25.0 - 225.0
MgCl2	9325.	0		*P-span: 1.0 - 201.0
C02	431.0	0	>	* = differs from default.
CaCO3	(.0		Precipitation Point Calculation
				25.0000 °C 1.00000 atm
		_		Precipitate: Not specified.
				Adj. Inflow: Not specified.
				Calculation not done
				Please select a target solid.
				Please select a variable to adjust.
		×		
put				

11. Select the CaCO3 (Calcite) as the Precipitant

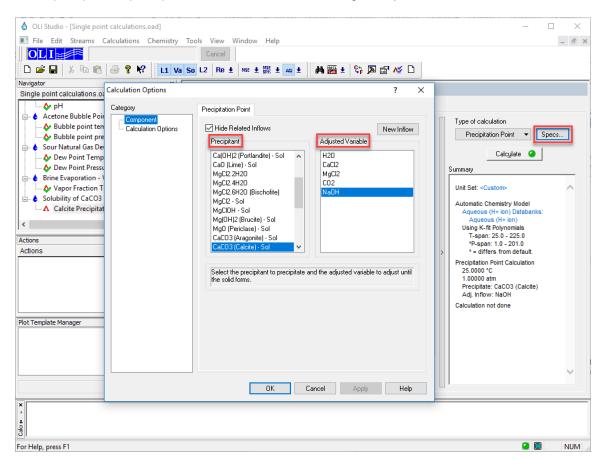
12. Select NaOH as the Adjusted Inflow

	Calculation Parameters						
•	Precipitant:	CaCO3 (Calcite)					
	Adjusted Inflow:	CaCO3 🗸					
		/s (ppi H2O					
	H2O	CaCl2 MgCl2					
	CaCl2	CO2					
	MgCl2	CaCO3					
	CO2	431.000					
	CaCO3	0.0					

The **Precipitant** refers to the independent variable – in this calculation, the solid phase selected will precipitate at amount of $1.0x10^{-10}$ times the stream amount.

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





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

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

The software calculated that the solubility of CaCO₃ as Calcite in the solution under study is around \sim 431.15 ppm (mass). The pH of this solution is \sim 5.97.

Variable	Value	~		Type of calculation
Stream Pa	rameters			Precipitation Point 👻 Specs
E Stream Amount (kg)	1.00041			
- Mass - Aqueous (kg)	1.00041			Calc <u>u</u> late 🥥
Mass - Solid (kg)	5.46166e-8			Summary
Temperature (°C)	25.0000			
Pressure (atm)	1.00000			Unit Set: <custom></custom>
Calculation Result	ts (ppm (mass))			Automatic Chemistry Model
Adjusted Inflow: CaCO3	413.146			Aqueous (H+ ion) Databanks:
	m (mass))			Aqueous (H+ ion)
H2O	9.78970e5			Using K-fit Polynomials T-span: 25.0 - 225.0
CaCl2	10865.5			*P-span: 1.0 - 201.0
MgCl2	9321.15		>	* = differs from default.
C02	430.822			Precipitation Point Calculation 25.0000 °C
CaCO3	413.146			1.00000 atm
				Precipitate: CaCO3 (Calcite) Adj. Inflow: CaCO3 Total 413.146 ppm (mass)
				Phase Amounts Aqueous 1.00041 kg Vapor 0.0 kg Solid 5.46166e-8 kg
Input Output		~		Aqueous Phase Properties pH 5.96733 lonic Strength 0.0107625 mol/mol Density 101414 n/ml
Advanced Search Add as Stre	eam Export			Density 1.01414 g/ml

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

٥ (Ll Studio - [Single point ca	alculations.oad*]			_	
🔳 Fi	ile Edit Streams Calo	ulations Chemistry Tools View Window Help				_ & ×
		Cancel	_			
Repo	ort Contents	? ×		a 🔊 🖓 🔊		
N Cat	tegory	Report Contents				
	 Report Contents Calculation Summary Stream Inflows Speciation Summary Stream Parameters Total/Phase Flows Scaling Tendencies Species Output Molecular Output Element Balance Species Activity Coe Species Kurky 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 Speciation Summary Stream Inflows Speciation Summary Stream Parameters Total/Phase Flows Scaling Tendencies Species Output Melecular Output Element Balance Species Erugacities Partial Pressures Species Erugacities Partial Pressures Species Sci Diffusivities Species Sel Diffusivities Species Sel Diffusivities Species Sel Diffusivities Up Down Select All Clear All Description This section displays the stream inflows. 6 of 22 Sections selected	eport Fil 1.00026 25.0000 1.00000 6.08996 0.0106874 0.599793 13.7558 34706.8 0.0161381 0.958261 1.07583 0.988618	kg °C atm mol/mol mol/kg atm m2/ohm-mol cP	Customize	Export
<	>		0.986447	L		\sim
		OK Cancel Apply Help		, - ,		

Notice that the concentrations have changed slightly. This is to accommodate the additional 413.15 ppm CaCO₃ needed to meet the calculation specifications.

Stream Inflows

Row Filter Applied: Only Non Zero Values

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

Example 9: Determining the Solubility of Aragonite (CaCO₃)

Calcite is the thermodynamically stable phase of calcium carbonate. **Aragonite**, calcite's orthorhombic polymorph, is about 1.5 times more soluble than calcite⁴. At surface conditions, aragonite spontaneously turns into calcite over geologic time, but at higher pressures aragonite, the denser of the two, is the preferred structure.

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

Starting the Simulation

Calculating the Precipitation of Aragonite (CaCO₃)

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

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

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

6. 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	recipitation		
Single point calculations.oad*		ecipitation		

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

Aragonite Precipitation Chemistry Model Options	? ×
Databanks Redox Phases T/P Span Include Phases Include Solid Phases ✓ Aqueous Include Solid S ✓ Vapor C(+4) ✓ Solids Ca(+2)	
Second Liquid)
Calculate Scaling Tendencies for e	xcluded solids
OK Cancel Appl	y Help

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

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

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

The software calculated that the solubility of CaCO₃ as Aragonite in the solution under study is around ~552.87 ppm (mass). The pH of this solution is ~6.21. You can see that the solubility of Aragonite is higher than the solubility of Calcite (~431.15 ppm (mass)).

Variable	Value	~		Type of calculation	
🗢 Stream Par	rameters			Precipitation Point 👻 Specs	
F Stream Amount (kg)	1.00055			- 1	
- Mass - Aqueous (kg)	1.00055			Calc <u>u</u> late 🥝	
Mass - Solid (kg)	5.46166e-8			Summary	
Temperature (°C)	25.0000				
Pressure (atm)	1.00000			Unit Set: <custom></custom>	^
Calculation Result	ts (ppm (mass))			Automatic Chemistry Model	
Adjusted Inflow: CaCO3	552.873			Aqueous (H+ ion) Databanks:	
Inflows (ppr	m (mass))			Aqueous (H+ ion)	
H20	9.78833e5			Excluding 1 solid phase	
CaCl2	10864.0			Using K-fit Polynomials T-span: 25.0 - 225.0	
MgCl2	9319.85		>	*P-span: 1.0 - 201.0	
C02	430.762			* = differs from default.	
CaCO3	552.873			Precipitation Point Calculation	
Solid (ppm	(mass))			25.0000 °C 1.00000 atm	
CaCO3 (Aragonite)	1.00000e6			Precipitate: CaCO3 (Aragonite) Adj. Inflow: CaCO3 Total 552.873 ppm (mass)	
		*		Phase Amounts Aqueous 1.00055 kg Vapor 0.0 kg Solid 5.46166e-8 kg	
Input Output Advanced Search Add as Stre	eam Export			Aqueous Phase Properties pH 6.21344 Ionic Strength 0.0107870 mol/mol	~

Example 10: Determining the Solubility of Dolomite (CaMg(CO₃)₂)

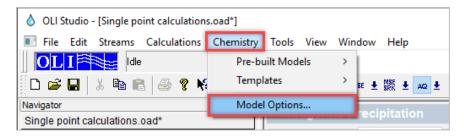
The third carbonate mineral to mention is **Dolomite**, which is something like calcite with a very high concentration of magnesium in it. Under some conditions there can be much more magnesium added in, and when the amount of magnesium becomes roughly the same as the calcium, the resulting mineral is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

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

Starting the Simulation

Calculating the Precipitation of Dolomite (CaMg(CO₃)₂)

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



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

	Dolomite Precipitation Chemistry Model Options	?	Х
	Databanks Redox Phases T/P Span		
	Databanks		
	Thermodynamic Framework		
	Aqueous (H+ ion)		
	Available Selected		
You may have more or less databanks depending on previous	Corrosion (AQ) Ceramics (AQ) Low Temperature (AQ) Alloys (AQ) Ion Exchange (AQ) Surface Complexation D	1	
installations and	JMM Databank		
imported databanks	< >> < >>		
	Import Databank Databank search order is from top to Use the Up and Down arrows to chan search order.		
	OK Cancel Apply	Help	>

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

Dolomite Precipitation Chemistry Model Options ? X					
Databanks Redox Phase	es T/P Span				
Include Phases	Include Solid Phases				
Aqueous Vapor Solids Second Liquid Ion Exchange Model Margules	Ca(+2) Ca(OH)2 (Portlandite) CaCO3 (Aragonite) CaCO3 (Calcite) CaCO3 (Calcite) CaCO3 (Calcite) CaCO3 (Calcite) CaCO2 (Hydrophilite) CaCI2.2H2O (Sinjarite) CaCI2.2H2O	^			
Wilson Kinetics	CaCl2.6H2O (Antarcticite) CaCl2.CaO.2H2O CaCl2.H2O CaCl2.H2O CaMg(CO3)2 (Dis-dolomite) CaMg(CO3)2 (Dolomite) CaMg(CO3)2 (Or-dolomite) CaMg(CO3)4 (Huntite)	v			
Calculate Scaling Tendencies for excluded solids					

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

10. Select the CaMg(CO3)2 (Dolomite) as the Precipitant

11. Select CaCO3 as the Adjusted Inflow

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

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

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 246.84 ppm (mass). The pH of this solution is \sim 5.63.

So far, we know that the solubilities of Calcite, Aragonite, and Dolomite in a MgCl₂, CaCl₂ and CO₂ containing solution were 413.15, 552.87 and, 246.84 ppm (mass) respectively.

1	🛷 Description 🔯 Definition 📓 Report 🚘 File Viewer					
Г	Variable	Value	~	Type of calculation		
	Stream Par	rameters		Precipitation Point 🔻 Specs		
	📮 Stream Amount (kg)	1.00025		- 1		
	 Mass - Aqueous (kg) 	1.00025		Calc <u>u</u> late 🥥		
	Mass - Solid (kg)	1.00626e-7		Summary		
	Temperature (°C)	25.0000				
	Pressure (atm)	1.00000		Unit Set: <custom></custom>		
	Calculation Result	s (ppm (mass))		Automatic Chemistry Model		
	Adjusted Inflow: CaCO3	246.838		Aqueous (H+ ion) Databanks:		
	Inflows (ppr	m (mass))		Geochemical (AQ) Aqueous (H+ ion)		
	H20	9.79133e5		Excluding 2 solid phases		
	CaCl2	10867.3		Using K-fit Polynomials		
	MgCl2	9322.70		> T-span: 25.0 - 225.0 *P-span: 1.0 - 201.0		
	C02	430.894		* = differs from default.		
	CaCO3	246.838		Precipitation Point Calculation		
	∇ Solid (ppm (mass)) 25.0000 °C					
	CaMg(CO3)2 (Dolomite)	1.00000e6		1.00000 atm Precipitate: CaMg(CO3)2 (Dolomite)		
				Adj. Inflow: CaCO3		
				Total 246.838 ppm (mass)		
				Phase Amounts		
				Aqueous 1.00025 kg Vapor 0.0 kg		
			*	Solid 1.00626e-7 kg		
lr	Input Output					
	Advanced Search Add as Stream Export					

1.8. Composition Point

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

Example 11: Targeting dissolved H₂S in water below 0.001 m

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

Starting the Simulation

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

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

Calculating the Vapor Fraction Temperature (Isobaric)

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

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

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

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

🛷 Description 😼 Definition 📓 Report 🚘 File Viewer					
Г	Variable	Value	~	Type of calculation	
	Stream Part	rameters		Composition Point 👻 Specs	
	E Stream Amount (mol)	55.5093		- 1	
	L Moles (True) - Aqueous (mol)	55.5093		Calc <u>u</u> late 🥥	
	Temperature (°C)	25.0000		Summary	
	Pressure (atm)	1.00000			
	Calculation Re	esults (mol)		Unit Set: Metric (moles)	
	Adjusted Inflow: H2S	1.01019e-3		Automatic Chemistry Model	
	Inflows	(mol)		Aqueous (H+ ion) Databanks:	
	H2O	55.5082		Aqueous (H+ ion) Using K-fit Polynomials	
	H2S	1.01019e-3		T-span: 25.0 - 225.0	
				*P-span: 1.0 - 201.0	
				> * = differs from default.	
				Composition Point Calculation 25.0000 °C	
				1.0000 atm	
				Target: H2S	
				Fixed at 1.00000e-3 mol Adj. Inflow: H2S	
				Total 1.01019e-3 mol	
				Phase Amounts	
				Aqueous 55.5093 mol	
				Vapor 0.0 mol Solid 0.0 mol	
			~		
In	put Output			Aqueous Phase Properties	
				pH 4.99328 Ionic Strength 1.83642e-7 mol/mol	
	Advanced Search Add as Stre	eam Export			

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

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

Species Output (True Species)

Row Filter Applied: Only Non Zero Values column Filter Applied: Only Non Zero Values

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

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

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

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

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

1.9. Autoclave

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

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

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

For the autoclave calculation 2 examples will be shown:

Using an Inert Gas

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

Using a Reactive Gas

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

Example 12: Using an Inert Gas

1. Calculating Results at Ambient Conditions

In this example, you will add 1 kg water to a 2 L autoclave and then fill the void (head space) with N₂. The ambient temperature is 25 °C. The N₂ is presumed to be the gas that remains in the autoclave headspace after sparging (O₂ removal) is completed.

The amount of N₂ added is the combination of N₂ vapor filling the headspace, and N₂ that dissolves in the water (N₂ aqueous). Since N₂ has a low water solubility, this second amount is negligible. H₂O also evaporates, so the headspace will be a mixed gas, N₂ and H₂O.

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	Single Point Calculation	Stream Amount	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			

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

8. Select Autoclave as Type of Calculation

9. Change the *SinglePoint* name to Autoclave – Inert Gas using the <F2> key

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

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

1	Description 🧕 Definition 📓 F	Report 🚊 File Viewer			
Г	Variable	Value	~		Type of calculation
		rameters			Autoclave 👻 Specs
	Stream Amount (mol)	55.5082			
	Ambient: Temperature (°C)	25.0000			Calc <u>u</u> late 🥝
	Ambient: Pressure (atm)				Summary
	Calculation P	arameters	L		
	Final Temperature (°C)	0.0	L		Unit Set: Metric (moles)
	Final Pressure (atm)		L		Automatic Chemistry Model
	Vessel Volume (L)	0.0	L		Aqueous (H+ ion) Databanks:
	Compute results at which condition	Ambient			Aqueous (H+ ion) Using K-fit Polynomials
					T-span: 25.0 - 225.0
	H2O	55.5082			*P-span: 1.0 - 201.0 * = differs from default.
	N2	0.0		>	Autoclave Calculation
	<u> </u>				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 5 gases to consider.
_	Advanced Search Add as Stre	am Export			~

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

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	Help	2

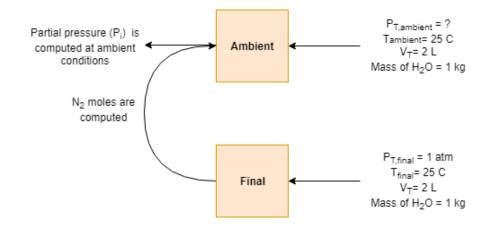
12. Set the Final Temperature to 25°C, the Final Pressure to 1 atm and the Vessel Volume to 2 L13. Set the compute results at Ambient Conditions

Variable	Value
	rameters
Stream Amount (mol)	55.5082
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: 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 showed in the image below.



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

Anaylyzing the Results

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

		Variable		Value	;	~		Type of calculation	
	~	Sti	ream Param	eters (mol)				Autoclave 👻 Specs	
[🚽 Stream Ar	mount			55.5483			- 1	
	- Moles (T	rue) - Liquid-1 (n	nol)		55.5076			Calc <u>u</u> late 🥝	
	- Moles (T	rue) - Vapor (mo	l)		0.0407594			Summary	
	∇		Calculation	Results					
	Ambient T	emperature (°C)			25.0000			Unit Set: Metric (moles)	
	Ambient P	ressure (atm)			1.00000			Automatic Chemistry Model	
	Final Temp	perature (°C)			25.0000]		MSE-SRK (H3O+ ion) Databanks:	
	Final Pres	sure (atm)			1.00000			MSE-SRK (H3O+ ion) MSE (H3O+ ion)	
	Vessel Vo	olume (L)			2.00001			Second Liquid phase	
	Partial Pre	ssure: N2 (atm)			0.968642			Using Helgeson Direct	
	Condition	that results were	computed f	Ambier	nt		>	Autoclave Calculation	
	∇		Inflows	(mol)				Results for ambient conditions: Ambient Temperature 25,0000 °C	
	H2O				55.5082			Ambient Pressure 1.00000 atm	
	N2				0.0400796			Final Temperature 25.0000 °C	
								Final Pressure 1.00000 atm Vessel Volume 2.00000 L	
								N2 0.968642 atm	
								Phase Amounts	
								Aqueous 55.5076 mol Vapor 0.0407594 mol	
						~	11	Solid 0.0 mol	
-								2nd Liquid 0.0 mol	
Inpu	ut Output	1						Aqueous Phase Properties	
A	dvanced	Search	Add as Stre	am Export				pH 6.99756	

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

The amount of N₂ added is 0.0400796 moles, which produces a ~0.9686 atm partial pressure. The computed N₂ inflow compares to the Ideal Gas value of 0.040874 moles, a ~2% deviation.

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

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

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

Element Distribution

These results infer two effects:

- 1. As the final pressure (P_T) increases, additional N₂ will dissolve in the water, shifting the fraction of nitrogen to the liquid.
- 2. As the total autoclave volume (V_T) increases relative to the input liquid (which stays constant), additional water will evaporate, shifting the water to the vapor. This case will be shown next.

2. Increasing the Vessel Volume to 5 L

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

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

Autoclave	Arrange >	ien i Autoe lav i ≬ A	Arrange >	Autoclave - Inert Gas
	Cut		Сору	
Actions	Сору	Actions	Paste 2	
Actions	Paste	Actions	Delete	
	Delete	🛓 Add Strea	Rename	
	Rename	Add Mixe Add Singl	Add As Stream	
	Add As Stream	🔊 Add Surve	Clear Results	
	Clear Results	<	Clear Status	
Plot Template Manager	Clear Status	Plot Template I	Calculation Options	
	Calculation Options			

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

Π	Variable	Value	~		Type of calculation
	√ 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	arameters			
	Final Temperature (°C)	25.0000			Unit Set: Metric (moles)
	Final Pressure (atm)	1.00000			Automatic Chemistry Model
	Vessel Volume (L)	5.00000			MSE-SRK (H30+ ion) Databanks:
	Partial Pressure: N2 (atm)		1		MSE-SRK (H3O+ ion)
	Compute results at which condition	Ambient 💌			MSE (H3O+ ion) Second Liquid phase
	√ Inflows	(mol)			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
					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.

Anaylyzing the Results

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

< Description 🔮 Definition 📓	Report 🚊 File Viewer		
Variable	Value		Type of calculation
Stream Parar	neters (mol)		Autoclave 💌 Specs
E Stream Amount	55.6671		
— Moles (True) - Liquid-1 (mol)	55.5037		Calc <u>u</u> late 🥝
Moles (True) - Vapor (mol)	0.163399		Summary
Calculatio	n Results		
Ambient Temperature (°C)	25.0000		Unit Set: Metric (moles)
Ambient Pressure (atm)	1.00000		Automatic Chemistry Model
Final Temperature (°C)	25.0000		MSE-SRK (H3O+ ion) Databanks:
Final Pressure (atm)	1.00000		MSE-SRK (H30+ ion)
Vessel Volume (L)	4.99998		MSE (H3O+ ion) Second Liquid phase
Partial Pressure: N2 (atm)	0.968642		Using Helgeson Direct
Condition that results were computed to	Ambient		> Autoclave Calculation
	(mol)		Results for ambient conditions: Ambient Temperature 25,0000 °C
H2O	55.5082		Ambient Pressure 1.00000 atm
N2	0.158874		Final Temperature 25.0000 °C
-		1	Final Pressure 1.00000 atm Vessel Volume 5.00000 L
			N2 0.968642 atm
			Phase Amounts
			Aqueous 55.5037 mol
		-	Vapor 0.163399 mol Solid 0.0 mol
I		*	2nd Liquid 0.0 mol
Input Output			
			Aqueous Phase Properties
Advanced Search Add as Str	eam Export		

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

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

3. Increasing the Final Temperature

In this example, you will add 1 kg water to a 5 L autoclave and then fill the void (head space) with N₂. 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.

- 1. **Copy** the *Autoclave Inert Gas Vessel Vol 5L* single point calculation and **paste** under the **Autoclave** Stream.
- 2. Name it Autoclave Inert Gas Tf=100C
- 3. Change the Final Temperature to 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
√ Inflows	(mol)
H2O	55.5082
N2	0.0

At this point the system is defined as 1 kg H₂O (55.5082 moles) at an ambient temperature of 25 °C. The partial pressure of N₂ 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.

Anaylyzing the Results

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

< Description 🤒 Definition 📓 F	Report 🚊 File Viewer		
Variable	Value		Type of calculation
Stream Param	eters (mol)		Autoclave 💌 Specs
E Stream Amount	55.5087		
- Moles (True) - Liquid-1 (mol)	55.5031		Calculate 🥥
Moles (True) - Vapor (mol)	5.54762e-3		Summary
Calculation	Results		
Ambient Temperature (°C)	25.0000		Unit Set: Metric (moles)
Ambient Pressure (atm)	0.0339414		Automatic Chemistry Model
Final Temperature (°C)	100.000		MSE-SRK (H3O+ ion) Databanks:
Final Pressure (atm)	1.00000		MSE-SRK (H3O+ ion) MSE (H3O+ ion)
Vessel Volume (L)	5.00009		Second Liquid phase
Partial Pressure: N2 (atm)	2.67276e-3		Using Helgeson Direct
Condition that results were computed f	Ambient		> Autoclave Calculation
			Results for ambient conditions: Ambient Temperature 25.0000 °C
H2O	55.5082		Ambient Pressure 0.0339414 atm
N2	4.38508e-4		Final Temperature 100.000 °C
			Final Pressure 1.00000 atm Vessel Volume 5.00000 L N2 2.67276e-3 atm
Input Output		¥	Phase Amounts Aqueous 55.5031 mol Vapor 5.54762e-3 mol Solid 0.0 mol 2nd Liquid 0.0 mol
Advanced Search Add as Stre	am Export		Aqueous Phase Properties pH 6.99772

The amount of N₂ 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 N₂ 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 c	alculations.oad*]			_	
File Edit Streams Calo	culations Chemistry Tools View Window Help	_			_ & ×
Report Contents	? ×	I 🚟 🛨 💱 🔊	😭 🎸		
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	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 Stream Parameters Total/Phase Flows Scaling Tendencies	Report 🚘 Fil	e Viewer	Q Q Customize	Export
- Species Activity Coe - Species Fugacities - Partial Pressures - Species K-Values		61.7478	mol		
- Species Mobilities	Species Activity Coefficients	25.0000	°C		
	Species Fugacities Species Avalues Species Notalities	38.0704	atm		
Entropy Entropy - Standard S	Species Self Diffusivities	6.99144			
- Reaction Kinetics		1.83405e-9 1.01846e-7	mol/mol mol/kg		
F Redox Equations	Up Down Select All Clear All	78,4141	monkg		
	Description	0.543529	atm		
	This section displays the vapor phase partial pressures.	0.0576240	µmho/cm		<u> </u>
		1.00360	L		· ·
	7 of 22 Sections selected				
	OK Cancel Apply Help 1.U - 2U1.U from default.				~
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		

4. Increasing the Final Pressure

In this example, you will add 1 kg water to a 5 L autoclave and then fill the void (head space) with N₂. 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.**

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

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

At this point the system is defined as 1 kg H_2O (55.5082 moles) at an initial temperature of 25 °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.

Anaylyzing the Results

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

< Description 🤒 Definition 📓 Re	port 🚊 File Viewer	
Variable Value		Type of calculation
Stream Param	eters (mol)	Autoclave 🔻 Specs
E Stream Amount	67.8251	- 1
- Moles (True) - Liquid-1 (mol)	55.5441	Calc <u>u</u> late 🥝
Moles (True) - Vapor (mol)	12.2810	Summary
Calculation	Results	
Ambient Temperature (°C)	25.0000	Unit Set: Metric (moles)
Ambient Pressure (atm)	75.6205	Automatic Chemistry Model
Final Temperature (°C)	100.000	
Final Pressure (atm)	100.000	
Vessel Volume (L)	5.00000	MSE (H3O+ ion) Second Liquid phase
Partial Pressure: N2 (atm)	75.5829	Using Helgeson Direct
Condition that results were computed for	Ambient	> Autoclave Calculation
☐	(mol)	Results for ambient conditions:
H2O	55.5082	Ambient Temperature 25.0000 °C Ambient Pressure 75.6205 atm
N2	12.3169	Final Temperature 100.000 °C
		Final Pressure 100.000 atm Vessel Volume 5.00000 L N2 75.5829 atm
		 Phase Amounts Aqueous 55.5441 mol Vapor 12.2810 mol Solid 0.0 mol 2nd Liquid 0.0 mol
Advanced Search Add as Stream	Export	Aqueous Phase Properties pH 6.98517 Ionic Strenoth 1.85708e-9 mol/mol

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

According to the calculation, the amount of N_2 in the autoclave is 12.3169 moles. This amount of N_2 plus the 55.5082 moles of H_2O produces a final pressure of 100 atm in a 5 L autoclave at 100 °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 enable both the **Species Fugacities** and the **Partial Pressures** options, and then click **OK**.

For comparison purposes, the **Species Fugacities** and the **Partial Pressures** for 100 °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
H2O	0.0312529
N2	2.67376e-3

Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.0312686
N2	2.67276e-3

100 °C and 100 atm

Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.033019
N2	75.9152

Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.0376507
N2	75.5829

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

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

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

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

Where, φ is the fugacity coefficient

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

Example 13: Using and Reactive Gas

1. Calculating Results at Final Conditions

In this example, you will add 1 kg water to a 2 L autoclave and then fill the void (head space) with CO₂. The ambient temperature is 25 °C.

You will then modify the case further by adding NaOH so that additional CO₂ dissolves in water to form bicarbonate.

Starting the Simulation

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

Autoclave Calculation			
Calculation Settings		Stream Composition and Conditions	
Calculation Type	Single Point Calculation	Stream Amount	Default – 55.5082
Calculation Sub-type	Autoclave	Ambient Temperature	25 ℃
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	Final Conditions	CO2	0 moles
		NaOH	0 moles

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

OLI Studio - [Single point calculations.oad*]	
File Edit Streams Calculations Chemistry Tools View Window Help	_ 8 ×
OLI I Ide Cancel	
🗅 🖆 🖬 👗 🚳 😵 🛠 🛛 L1 Va So L2 Re ± 🔤 ± 🙀 ± 🦛 ±	
Navigator + * X Single point calculations and* Autoclave - CO2	
Calculation Ontions 2 X	
Category Autoclave Target Gas(es) (5 Max)	
Autoclave Target Gas(es) (5 Max)	ecs
H2U - Vap 25.0000 Laiculate	
0.0 Unit Set: Metric (moles)	\sim
0.0 Automatic Chemistry Model MSE-SRK (H3O+ ion) Databank	s:
Ambient MSE-SRK (H30+ ion) MSE (H30+ ion)	
Acti Selected 1 Selected 1	
Act 55.5082 > Autoclave Calculation	
Ambient Temperature 25.000	0°C
Mole Fraction(s) in Aqueous Phase	
Vessel Volume 0.0 L CO2	
Plot	
Plot Volume of vessel is invalid. You must specify the Final Press	ire
v or Gas 1	
bort	\sim
OK Cancel Apply Help	^
A Calculation Complete!	
3 For Help, press F1	V NUM

12. Set the Final Temperature to 25°C, the Final Pressure to 1 atm and the Vessel Volume to 2 L

13. Set the **compute results** at **Final** Conditions. Click on the cell to enable the drop-down arrow.

Variable	Value
Stream Pa	rameters
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation	Parameters
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	2.00000
Partial Pressure: CO2 (atm)	
Compute results at which condition	Ambient 🗾
	Final
H2O	Ambient
C02	0.0
NaOH	0.0

At this point the system is defined as 1 kg H₂O (55.508 moles) at an ambient temperature of 25 °C. The partial pressure of CO₂ will be calculated at a final temperature, 25 °C and pressure, 1 atm in a 2 L vessel.

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

Anaylyzing the Results

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

Variable	Value	~		Type of calculation	
C Stream Parameters (mol)				Autoclave 👻 Specs	
Stream Amount	55.5808				
- Moles (True) - Liquid-1 (mol)	55.5397			Calc <u>u</u> late 🥝	
Moles (True) - Vapor (mol)	0.0409453			Summary	
Calculation	Results				
Final Temperature (°C)	25.0000			Unit Set: Metric (moles)	^
Final Pressure (atm)	1.00000			Automatic Chemistry Model	
Vessel Volume (L)	2.00003			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	0.0725216			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	

A total amount of 0.0725 moles of CO₂ 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 Anaylyzing the Results</u> required 0.04 moles of N₂. The difference is the amount of CO₂ that dissolved in the water. CO₂ is more soluble than N₂ in water.

To analyze the CO₂ distribution in more detail, go to the **Report** Tab, and Scroll down until you find the **Element Distribution** table.

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

Element Distribution

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

2. Using a Reactive Gas and a NaOH solution

In this example, you will further modify the chemistry by adding NaOH so that additional CO₂ dissolves in water to form bicarbonate. This will increase the gas requirement.

Starting the Simulation

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

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

Variable	Value
Stream Pa	rameters
Stream Amount (mol)	55.6082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation	Parameters
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	2.00000
Partial Pressure: CO2 (atm)	
Compute results at which condition	Final
Inflows	(mol)
H2O	55.5082
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_2 will be calculated at a final temperature, 25 °C and final pressure, 1 atm in a 2 L vessel.

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

Anaylyzing the Results

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

√ Inflows (mol)			
H2O	55.5082		
CO2	0.171600		
NaOH	0.100000		

The CO₂ inflow is calculated to be 0.1716 moles. This is exactly 0.1 moles more than the calculation with only CO₂ (Example 13-1) and results from the acid-base reaction with the 0.1 moles of NaOH.

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

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor
	mol	mol	mol
H2O	55.5083	55.507	1.28477e-3
Na+1	0.1	0.1	
HCO3-1	0.0998917	0.0998917	
CO2	0.0716542	0.0320887	0.0395654
CO3-2	5.42505e-5	5.42505e-5	
H3O+1	2.3994e-7	2.3994e-7	
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	0.0408502

You can see that ~0.1 moles of bicarbonate (HCO_3^-) have been formed. This reaction is increasing the CO₂ gas requirement to reach a total final pressure of 1 atm.

1.10. Custom

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

Example 14: Solubility of Oxygen in Water

With a custom calculation, we are going to calculate the solubility of O₂ 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					
Calc	ulation Settings	Stream Composition and Conditions			
Calculation Type	Single Point Calculation	Stream Amount	Default – 1kg		
Calculation Sub-type	ation Sub-type Custom		30 ℃		
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

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

Note: In the Calculation Options window, you have the option to select the **Variables to Fix** and the **Variables to Free**. In this example, the Variable to Fix is the number of Moles (True) of Vapor which will be given a small value of 1×10^{-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.

Calculation Options		?	×
Category	Custom		
Variables Calculation Options	Variables to Fix Filter All V Enthalpy - Total H20 H20 - Sol H20 - Vap H30 +1 Moles (True) - Liquid-1 02 - Liq1 02 - Vap 1 1		
	Variables to Free Hide Related Inflows H20 Pressure Temperature (<) 1	w Inflow	
	Select an equal number of variables to be fixed and freed. Freed va be adjusted to meet the specified value of the fixed variables.	riables will Help	

14. In the Variables to Fix section, select Moles (True) Vapor, by double clicking or using the >> button.

15. In the Variables to Free section, select O2 as the inflow. Then click OK.

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

ኛ Description 🧕 Definition 📓 Report	🚘 File Viewer		
Variable	Value	Type of calculation	
Stream Pa	rameters	Custom 👻 Specs	1
Stream Amount (kg)	1.00000		
Temperature (°C)	30.0000	Calc <u>u</u> late 🥥	
Pressure (atm)	4.00000	Summary	
Calculation F	Parameters		_
 Target: Moles (True) - Vapor (mol) 	0.0	0 Unit Set: <custom></custom>	\sim
Adjusted: O2 (ppm (mass))	0.0	Automatic Chemistry Model	
□ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □		MSE (H3O+ ion) Databanks:	
H2O	1.00000e6	6 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.	
I		✓	
Input			
Advanced Search Add as Stream	Export		\sim
Auvanceu Sedichi Auu as Stieam	Export		

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

Anaylyzing the Results

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

Variable	Value	~	Type of calculation
Stream Paramete	ers		Custom - Specs.
Stream Amount (kg)	1.000	15	
— Mass - Liquid-1 (kg)	1.000	15	Calculate 🥝
— Mass - Vapor (kg)	3.184936	-9	Summary
Temperature (°C)	30.00	00	
Pressure (atm)	4.000	00	Unit Set: <custom></custom>
Calculation Resu	Its		Automatic Chemistry Model
Target: Moles (True) - Vapor (mol)	1.00000e	-7	MSE (H3O+ ion) Databanks:
Inflows (ppm (ma	ss))		MSE (H3O+ ion)
H2O	9.99854	85	Using Helgeson Direct
Adjusted: 02	146.9	38	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
tt Output		~	

At 30°C and 4 atm the solubility of O₂ 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 So		~	Stream Parameters		1
	n 🥸 Definition	🖾 Dee 🗸	Calculation Results		
Description	i 🛃 Dennadni (👳 нер 🗸	Inflows		
	Variable		Related Inflows		Type of calculation
$\overline{\nabla}$		Strea	Additional Stream Parameters		Custom - Specs
E Stream Am			Phase Flow Properties		
	quid-1 (kg)		Thermodynamic Properties		Calculate 🥥
Mass - Va			Pre-scaling Tendencies		immary
Pressure (Pre-scaling Index		Unit Set: <custom></custom>
	uuny	Calcu	Scaling Tendencies		
Target: Mol	les (True) - Vapor (mol)		-		Automatic Chemistry Model MSE (H3O+ ion) Databanks:
~		Inflow	Scaling Index		MSE (H3O+ ion)
H2O			Liquid-1		Using Helgeson Direct Custom Calculation
Adjusted: 0	02		Vapor		Fixed variable:
			Solid		Moles (True) - Vapor, target: 1.00000e-7 mol
			Molecular Apparent	>	Free variable:
			Totals		O2, total: 146.938 ppm (mass)
			Molecular Totals		Phase Amounts
			MBG Totals	>	Aqueous 1.00015 kg
			Activity Coefficients	>	Vapor 3.18493e-9 kg Solid 0.0 kg
			Fugacity Coefficients - Vapor		
			Fugacities - Vapor		Aqueous Phase Properties
			K-Values	>	(x-based) -9 mol/mol
			Gibbs Free Energy		(m-based)
	Units Manager		Gibbs Free Energy Standard State (x-based)		Calc. elapsed time: 0.046 sec
	Save default layout		Entropy		Calculation complete
\bigcirc	Generate Model		Entropy Standard State (x-based) Mobilities		
Input 🛛 🗸	Hide Zero Values		Self Diffusivities	>	
	Sections	>	Partial Pressures		

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

K-Values - (m-based)				
KH2O: 2H2O=H3OION+OHION	1.46564e-14			
KH2OPPT: H2OPPT=H2O	1.32964			
KH2OVAP: H2OVAP=H2O	23.8182			
K02VAP: 02VAP=02AQ	1.15985e-3			

1.11. Reaction Kinetics

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

For the stoichiometric reaction below:

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

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 dependence with temperature can be studied using the Arrhenius Equation, as shown below.

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

where: k = Reaction rate constant (*units depend on reaction order*)

A = Arrhenius frequency factor (has same units as k) $E_a = \text{Activation energy} \left(\frac{joule}{gmole}\right)$ $R = \text{Universal gas constant} \left(8.314 \frac{joule}{gmole K}\right)$ T = Temperature (K)

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

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

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

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

1.11.1. Standard Rate Law

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

For the reaction below:

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

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:

$$Rate = \left(k_{f}a_{A}^{r1}a_{B}^{r2}...-k_{r}a_{C}^{p1}a_{D}^{p2}\right)$$

where:

Rate	=	Reaction rate $\frac{mol}{h}$
k_f	=	Forward reaction rate constant (units depend on reaction order)
k_r	=	Reverse reaction rate constant (units depend on reaction order)
$a_A, a_B, .$		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 ,	=	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, Arrhenius factors, and activation energies (divided by the universal gas constant). For the species reaction order coefficients, the reaction stoichiometric values are assumed. To complete the standard rate expression definition, the reaction temperature and initial reactant molality are included in the process stream composition definition.

Example 15: Reaction of Ammonia and Carbon Dioxide

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

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

This reaction will take place in a plug flow reactor at 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				
Calculation 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	Pressure	100 atm	
Single Point Name	Rxn Ammonia/CO2	Water	55.5082	
Name Style	Display OLI Name (TAG)	CO2	2 moles	
Unit Set	Metric, Moles	NH3	2 moles	
Framework	AQ	UREA	0 moles	
Kinetics	Enabled			
Kinetics Holdup Time	100 hours			
Number of Kinetic Steps	10			

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

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



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

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

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

OLI Studio - [Single point calculations.oad*]	1				- 0	x i
File Edit Streams Calculations Chen	mistry Tools V	iew Window Help				_ & ×
D 🚅 🖬 X 🖻 💼 🍜 🤋 K	Pre-built Models	> SE 🛨 MSE 🛨 AQ 🛨	M 🎆 🛃 💱 🔊 😭 🛷			
Navigator	Templates	>				
Document1		CO2				
Single point calculations.oad*	Model Options	Definition 📓 R	eport 🚊 File Viewer			
♦ Streams	T			_	Type of calculation	
🛓 👌 1.1.a pH of 1 m FeCl3		Variable	Value	^		_
🖶 👌 1.1.b Isothermal - acetic acid		Stream Pa			Isothermal 🔻 Sper	cs
🖶 👌 1.10. Custom Calculation		am Amount (mol)	59.5082		Calculate 🥝	
🖶 👌 1.11.1. Arrhenius Rxn Kinetics		perature (°C)	200.000		Calculate 😈	
\Lambda Rxn Ammonia/CO2		sure (atm)	100.000		Summary	
🛊 🖞 👌 1.2. Acetone Bubble Point		Inflows				
🖅 👌 1.3. Sour Natural Gas Dew Point	H20		55.5082		Unit Set: Metric (moles)	<u> </u>
1.4. Isochoric calculation	CO2		2.00000		Automatic Chemistry Model	
1.5. Brine Evaporation - Vapor Fraction	NH3		2.00000		Aqueous (H+ ion) Databanks:	
1.6. Neutralizing Acid			0.0	_	Aqueous (H+ ion) Using K-fit Polynomials	
< >		<u> </u>			T-span: 25.0 - 225.0	
Actions a A		Aque	ous		*P-span: 1.0 - 201.0	
Actions	<u>-</u>				* = differs from default.	
Actions				>	Isothermal Calculation 200.000 °C 100.000 atm	
					Calculation not done	
					Calculation not done	
					1	
					1	
					1	
					1	
					1	
					1	
					1	
				~	1	
	Input				1	
Plot Template Manager # * *					1	\sim
	Advance	ed Search Add as Stree	am Export		(I	
Save				_		
×						^
Calculation Complete!						
<u>+</u>						*
					2 E	NUM

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

Rxn Ammonia/CO2 Chem	istry Model Options	?	\times
Databanks Redox Pha	ses T/P Span		
Include Phases Aqueous Vapor Solids Second Liquid Ion Exchange Model Margules Wilson	Include Solid Phases All Solids C (+4) F − ✓ H(+1) F − ✓ N(-3) F − ✓ O(-2) F − ✓ UREA		
Kinetics	Calculate Scaling Tendencies for exc	luded solids	
[OK Cancel Apply	Hel	lp

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

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

	Variable	Value	^		Type of calculation
<	Stream Par	rameters			Isothermal 💌 Specs
	Stream Amount (mol)	59.5082			
	Temperature (°C)	200.000			Calc <u>u</u> late 🥝
	Pressure (atm)	100.000			Summary
4	Calculation P	arameters	1		
Γ	Kinetics Holdup Time (hr)	100.000			Unit Set: Metric (moles)
Г	Number of Kinetics Steps	10	1		Automatic Chemistry Model
7	Inflows	(mol)	1		Aqueous (H+ ion) Databanks:
	H2O	55.5082			Aqueous (H+ ion)
	C02	2.00000			Using K-fit Polynomials T-span: 25.0 - 225.0
	NH3	2.00000			*P-span: 1.0 - 201.0
	UREA	0.0			* = differs from default.
				>	Isothermal Calculation

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

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

Calculation Options		?	×
Category	Rate Limited Reactions		
Calculation Options	Reactions:	Delete	
	Rate Specification:		
	OK Cancel Ap	pply H	Help

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

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

S	Select a Reaction:	Х
	Create New Reaction> CO2AQ+H2O=HION+HCO3ION CO2VAP=CO2AQ HCO3ION=HION+CO3ION	^
	NH2CO2ION+H2O=NH3AQ+HCO3ION NH3AQ+H2O=NH4ION+OHION NH3VAP=NH3AQ NH4H2CO33PPT=4NH4ION+2HCO3ION+CO3ION NH4HCO3PPT=NH4ION+HCO3ION	
	UREAPPT=UREAAQ 1 ΙRFΔVΔP=I IRFΔΔΟ	~
	OK Cancel	

This enables the option to enter a new reaction.

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

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

As a general rule:

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

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

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

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

Now, let's start entering the rate constants.

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

$$R = k_f [NH_3]^2 [CO_2] - kr [NH_2 CONH_2]$$

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

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

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

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

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

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

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

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

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

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

Calculation Options			? ×	_
Category	Rate Limited Reacti	ons		
Calculation Options	Reactions: 2NH3AQ+CO2J	Add Edit	Delete	
	Rate Specificat Rate Constants		Add	
	KF	2000	Add	
	AR	1.2e-10	Delete	
	BR	3480.78		
	ER1	2		
	ER2	1		
	EP1	1		
	EP2	0]	
	OK	Cancel App	Help]

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

Anaylyzing the Results

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

Tools View Window Help So L2 Re ± mst ± ﷺ ± ma : Rxn Ammonia/CO2 Description Definition Variable Variable Variable Variable Variable Variable Variable Variable Costreat Holes (True) - Aqueous (mol) Moles (True) - Aqueous (mol) Temperature (*C) Pressure (atm) Costreat Kinetics Holdup Time (hr) Number of Kinetics Steps Cost NH3 Units Manager	 Calculation Results Inflows Related Inflows Additional Stream Parameters Kinetics Reactions Phase Flow Properties Thermodynamic Properties Pre-scaling Tendencies Scaling Tendencies Scaling Index Aqueous Vapor Solid Molecular Apparent - Aqueous Molecular Totals MBG Totals Activity Coefficients Fugacities - Vapor K-Values Gibbs Free Energy Gibbs Free Energy Standard State (x-based) 	> > >		
Units Manager Save default layout Generate Model Hide Zero Values	Fugacities - Vapor K-Values Gibbs Free Energy		Imounts pus 58.0473 mol r 1.02509 mol 0.0 mol s Phase Properties	

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	2.0	09657e-3		

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

1.11.2. Non-standard Rate Law

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

Example 16: Ammonia Hydrolysis

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

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

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					

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

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

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 VWison Kinetics Enable Calculate Scaling Tendencies for excluded solids	
OK Cancel Apply He	ŧlp

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

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

Select a Reaction:			\times
<create new="" reaction=""> NH3AQ+H2O=NH4ION+OHION NH3VAP=NH3AQ</create>			
	OK	Cancel	

16. Select the SPEC as the Rate Specification.

Calculation Options		?	×
Category	Rate Limited Reactions		
Calculation Options	Add Edit Reactions: NH3AQ +H2O =NH4ION +OHION Rate Specification: SPEC	Delete	
	OL/ASAP DEFINES:	Add Delete]
	OK Cancel Apply	Help	0

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

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

Thus, the total rate is given by:

$$Rate = Rate_f - Rate_r$$

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

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

We now need to turn these values into "OLI" terms⁵.

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

Similarly, activity coefficients γ are also taken as the natural log. So, γ_{OH^-} is written as Log_e γ_{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 window⁶:

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

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

0	L/ASAP DEFIN	NES:	
	Variable	Expression	Add
	FXRATE	13AQ+ANH3AQ+LH2O+AH2O	Delete

⁵ Commonly referred to as ASAP variables.

⁶ 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.

Iculation Options	
ategory	Rate Limited Reactions
Calculation Option Kinetics	s Add Edit Delete Reactions: NH3AQ+H2O=NH4ION+OHION
	Rate Specification: SPEC OL/ASAP DEFINES: Variable Expression
	FXRATE LNH3AQ+ANH3AQ+LH2O+AH
	RXRATE LNH4ION+ANH4ION+LOHION+ Delete
	KF1 3
	KR1 KF1/KEQ
	RATE1 (KF1*EXP(FXRATE)-KR1*EXP(
	OK Cancel Apply Help

The completed equations

The variable VOLLIQ is the volume of the liquid phase in Liters. OLI requires the rate to be in mol/m³ we need to divide by 1000.

Click the OK button.

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

Now Calculate

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

< Description 🔮 Definition 🔯 Report	👔 File Viewer			
Variable	Value		Π	Type of calculation
Stream Parameters				Isothermal 👻 Specs
E Stream Amount (mol)	55.6082			
Moles (True) - Aqueous (mol)	55.6082			Calc <u>u</u> late 🥝
Temperature (°C)	25.0000		lls	iummary
Pressure (atm)	1.00000		Шř	
Calculation Results				Unit Set: Metric (moles)
Kinetics Holdup Time (hr)	100.000			Automatic Chemistry Model
Number of Kinetics Steps	10			AQ (H+ ion) Databanks:
				Public
H2O	55.5082			Isothermal Calculation 25.0000 °C 1.00000 atm
NH3	0.100000			Phase Amounts
Aqueous (mol)				Aqueous 55.6082 mol
H2O	55.5077	Ξ		Vapor 0.0 mol
NH3	0.0994574			Solid 0.0 mol
OHION	5.42587e-4		11	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		
Input Output	N.			
Advanced Search Add as Stream E	xport			Ψ.

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

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

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

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

 1.3×10^{-3} moles of NH₄⁺ have been created. By limiting the forward reactions, we allow the back reaction to take place and that only formed 5.4×10^{-4} moles of NH₄⁺.

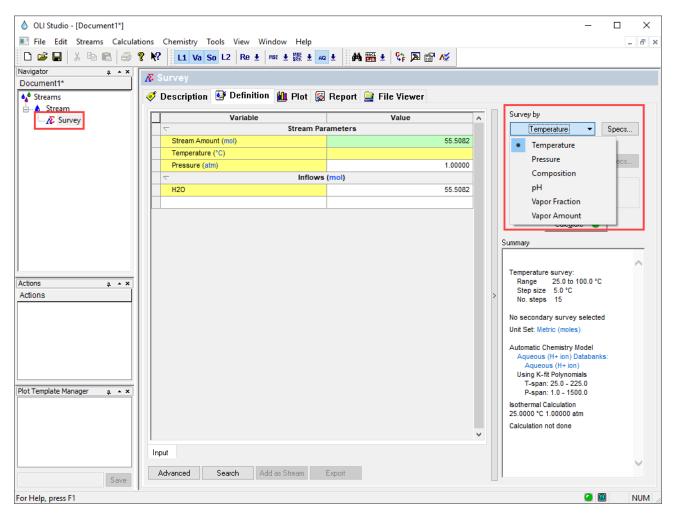
Section 2. Survey Calculations

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 survey by Temperature, Pressure, Composition, pH, Vapor Fraction and Vapor Amount.
- 2. <u>Dual Survey</u>: These calculations allow the user to designate two independent variables.
- 3. <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 the **Precipitation Point** calculation type.

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



2.1. Single Surveys

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

Example 17: Removal of Nickel from Wastewater

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

The wastewater in this case study contains nickel ions at a concentration of 0.002 m (or moles/ 1 kg H₂O). The existing treatment strategy is to precipitate the nickel ions as Nickel Hydroxide (Ni(OH)₂). The soluble nickel remaining after precipitation needs to be less than 1 ppm, which is the maximum contaminant level allowed.

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

This example will be divided into three different scenarios:

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

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

Scenario 1: Wastewater without Additives

We begin by starting the Stream Analyzer Program. This may be accomplished by *clicking* on the OLI Studio : Stream Analyzer 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.



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

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

	👌 OLI Studio - [Document1*]	-	>	×
	File Edit Streams Calculations Chemistry Tools View Window Help		- 8	×
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	Navigator + + × Document1*			
	Vocument 3 Ø Description 🐼 Definition 🖗 Report			
	Nickel Waste			
	Name: Nickel Waste			
	Description			
	Nickel waste water for the OLI Aqueous Modeling Course		 ^	
	Actions 👢 🔺 🗙		~	
2	Actions <		>	
5	Add Mixer B Add Chemical Diage Summary			
	Add Single Point Add Stability Diagra			
	Plot Template Manager + × 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			
	* = differs from default.		\sim	
	Save			
	Calculation +			
	Tor Help, press F1	a 🗉	NUN	M
	· · · · · · · · · · · · · · · · · · ·			

- 6. Click on the **Definition** tab to start defining the wastewater stream
- 7. Click in the white box in the grid below the Inflows line. Add the formula Ni(OH)2
- Click in the white box next to the species you just entered and enter the value 0.002. Press <Enter> to update the list

Note: Stream Analyzer will automatically change the name of the species to the selected display name. In this instance, the name you entered was Ni(OH)₂ but it may have changed to a different form. If it changed you can specify which display name to use in the Names Manager icon

- 9. For the output results, we want output units in **ppm**. To change the output units, click on the <u>Units Manager</u> icon ^C. This will open a new window.
- 10. Change moles to Mass Frac. Using the drop-down arrow
- 11. Click on the **Customize** button. The **Units Manager** window will appear.

File Edit Streams Calculations Chemistry		9	_ 8 ×
	Cancel		
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Removing Nickel from wastewater_2.oad*	Jescrip 6 Definition		
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1	Stream	Parameters	Special Conditions
	Stream Amount (mol)	55.5102	
	Temperature (°C)	25.0000	
	Pressure (atm)	1.00000	Summary
	H20	55.5082	Unit Set: Metric (moles)
	7 Ni(OH)2	8 2.00000e-3	
J			Automatic Chemistry Model Aqueous (H+ ion) Databanks:
Actions g • ×			Aqueous (H+ ion)
Actions	Units Manager - Nickel	Waste ? ×	Using K-fit Polynomials T-span: 25.0 - 225.0
🙆 Add Stream 🔲 Add Stability Diagra	Units Manager		*P-span: 1.0 - 201.0
Add Mixer Add Corrosion Rate Add Single Point		-	* = differs from default.
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Add Chemical Diagram	meuic		55.5102 mol
< >			
Plot Template Manager			
	Customize	1	
	Input		
	Advanced	Cancel Apply Help	¥
Save			

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

13. Click OK

omposition	Parameters	Corrosion			
	Varia	ble	Basis	Units	-
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Stream A	mount		Mass	kg	
Inflows			Mass Fraction	mass %	
		Outp	ut variables		
Aqueous	Composition		Mass Fraction	mass %	
Vapor Co	mposition		Mass Fraction	mass %	
Solid Com	nposition		Mass Fraction	mass %	
2nd Liquid	d Composition		Mass Fraction	mass %	
Total Com	nposition		Mass Fraction	mass %	
		Bas	is options		
Moles				mol	
Mass				kg	
Volume				L	
Concentra	ation			mg/L	
Molar Cor	ncentration			mol/L	
Mass Fra	ction			mass % 📃	4.,
Mole Fred	tion			g/g	
				mass % ppm (mass)	-

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

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

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

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

Streams	< Description 🤡 Definition 📓	Report	•
Nickel Waste	Variable	Value ^	
	Stream Pa		S Single Point
	Stream Amount (kg)	1.00019 25.0000	Survey
	Temperature (°C) Pressure (atm)	1.0000	Chemical Diagram
	Inflows (pr		Summary Stability Diagram
	H2O	9.99815e5	Unit Set Corrosion Rates
	Ni(OH)2	185.335	Automatic Chemistry Model
ctions Add Stream Add Stream Add Mixer Add Single Point Add Single Point Add Survey C C C C C C C C C C C C C C C C C C C		~	*P-span: 1.0 - 201.0 * = differs from default.

You can now add descriptive information about this calculation.

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

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

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

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

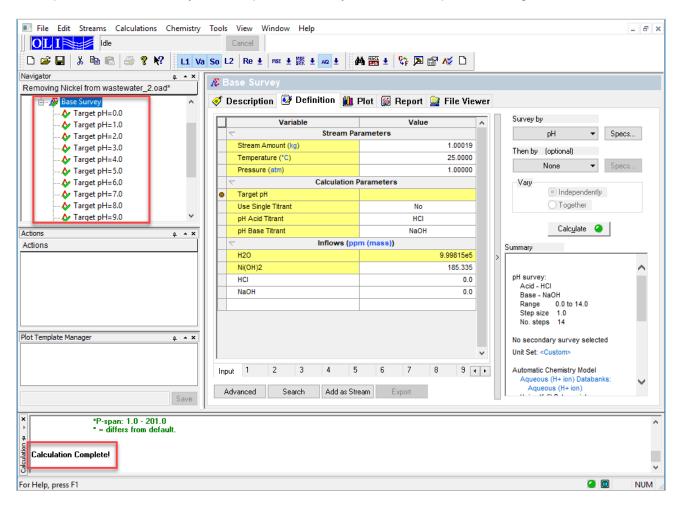
File Edit Streams Calculations Chemistry	Tools View Window Help		_ & ×
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nickel waste.oad*	Æ Base Sun 6		
♦₅♦ Streams	📝 Description 🥵 Definition 🚻	Plot 📓 Report 🚊 File Vie	wer
📄 💧 Nickel Waste	Variable	Value	Survey by
Base Survey	Stream Par		pH Specs
_	Stream Amount (kg)	1.00019	
	Temperature (°C)	25.0000	Temperature
	Pressure (atm)	1.00000	Pressure ecs
	Calculation P	arameters	Composition
	Target pH		• рн 8
	Use Single Titrant	No	Vapor Fraction
	pH Acid Titrant	HCI	Vapor Amount
	pH Base Titrant	NaOH	cale <u>a</u> rate 🖉
	C Inflows (ppr		Summary
Actions	H2O	9.99815e5	
Actions	Ni(OH)2	185.335	> pH survey:
	HCI	0.0	Acid - HCI
	NaOH	0.0	Base - NaOH
			Range 0.0 to 14.0 Step size 1.0
			No. steps 14
			No secondary survey selected
			Unit Set: <custom></custom>
Plot Template Manager 🛛 🖡 🔺 🗙			one out. Soustone
			Automatic Chemistry Model
			Aqueous (H+ ion) Databanks: Aqueous (H+ ion)
			Using K-fit Polynomials
	Input		T-span: 25.0 - 225.0 *P-span: 1.0 - 201.0
			*= differs from default.
Save	Advanced Search Add as Str	eam Export	
	J.		

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

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

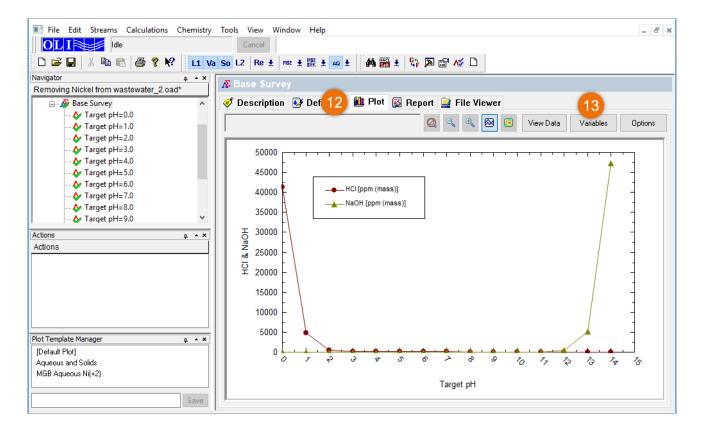
	DLI S	Studio - [Removing Nickel from wastewater_2.	oad]				– 🗆 ×
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		New	Ctrl+N				
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Nav Re		Close Save	C+rl+S	irvey			
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Ė		Import	>	Variable	Value	~	Survey by
		Print	Ctrl+P	Stream Par	ameters		pH 🔻 Specs
		Print Preview		n Amount (kg)	1.00019		Then by (optional)
		Print Setup		rature (°C)	25.0000		None Specs
		Properties		ure (atm) Calculation P			Varu
		Properties		pH			 Independently
		1 Removing Nickel from wastewater_2.oad		ingle Titrant	No		 Together
		2 Removing Nickel from wastewater.oad		id Titrant	HCL		
Acti		3 Removing Nickel from wastewater_1.oad		se Titrant	NAOH		Calculate 🥥 🚺
Act		4 azeotrope_HCL-water_9.6.1.oad		Inflows (ppr			Summary
		Exit			9.99815e5 185.335	>	>
	_		-	2	105.335		pH survey:
							Acid - HCLIN Base - NAOHIN
							Range 0.0 to 14.0
							Step size 1.0 No. steps 14
		ate Manager <u>" </u>					
Plot I	empi	late Manager 🛛 🖡 🔺 🗙				- 1	No secondary survey selected
						~	Unit Set: <custom></custom>
			Input				Automatic Chemistry Model
			Advanced	d Search Add as Stre	am Export		Aqueous (H+ ion) Databanks:
		Save	Advanced	Add as offe	un export		

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



We can now obtain some graphical results.

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



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

- 13. Select them and then Click on the left double-arrow (<<) button which will remove NaOH and HCI from the list. You can also select and double click to remove them.
- 14. Scroll down the left-hand window to find **MBG Totals Aqueous** and expand the list by clicking the 🗄 box.

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

Select Data To Plot		? X
Curves		
Stream Parameters Calculation Results Inflows Additional Stream Parameters Phase Flow Properties Thermodynamic Properties Pre-scaling Tendencies Pre-scaling Index Scaling Index	X Axis Target pH X Axis Target pH X Axis X Axis Target pH X Axis	wis 14
Aqueous Vapor Vapor Solid Molecular Totals MBG Totals - Totals MBG Totals - Aqueous MBG Totals - Aqueous MBG Totals - Solid MBG Totals - Solid MBG Totals - Solid MBG Totals - Surface Activity Conflicients - Aqueous (5 based)	>>> <<	Axis
Use short names		
Hide zero species	Z Axis	
Plot data which is only within temperature range.	- Select -	~
	OK Cancel Apply	Help

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

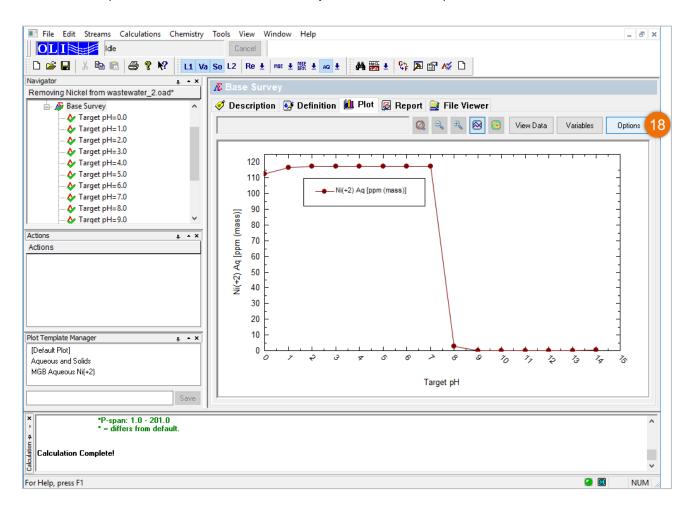
- 15. **Double-Click** the **Ni(+2)** item or select it and use the >> button.
- 16. Click on the OK button.

Select Data To Plot					?	Х
Curves						
Inflows Additional Stream Parameters Phase Flow Properties Thermodynamic Properties	^	>>	X Axis Target pH	1 Axis		
Pre-scaling Tendencies Pre-scaling Index Scaling Index Scaling Index Scaling Index Aqueous Vapor		>>				
Solid Molecular Totals MBG Totals - MBG Totals - MBG Totals - Aqueous			Y	2 Axis		
Dominant MBG Totals - Aqueous Cl(-1) Aq H(+1) Aq Na(+1) Aq Na(+1) Aq Ni(+2) Aq		>>				
Use short names	*					
Hide zero species			Z Axis			_
Plot data which is only within temperature range.			- Select -			~
17	OK	С	ancel App	oly	Hel	p

You will see the new plot.

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

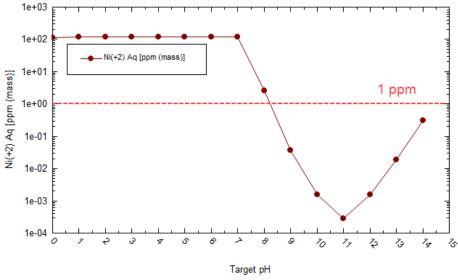
17. Above the plot window locate and select the **Options** button. This opens a new window.



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

Customize Plot		?	×
Category General Legend X Axis Y Axis Curves	Scale Format Title Auto Minimum 0.0		
Curves	Maximum 2.1e-3 Major Unit		
2	O 🗹 Logarithmic scale		
	21 OK Cancel Apply	He	lp

The modified plot is then displayed. The limit of 1 ppm for Ni⁺² is approximately 2 x 10⁻⁵ moles. Above pH=9, we are several orders of magnitude below this limit. Additionally, you can see that a minimum amount of Ni²⁺ in the aqueous phase seems to occur in the pH=11 range. This is the result of nickel solids forming and leaving the aqueous phase.

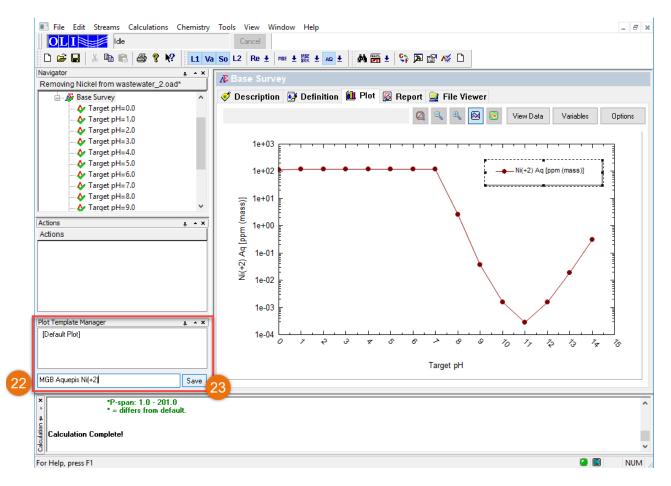


Note: The red line was put as a reference. it was not plot with the software.

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

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

22. Click Save



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

What else is important in this solution?

- 23. Click once more on the Variables button
- 24. Add the following Aqueous species to the plot. (you may need to scroll up or down to find all the species):

Ni(OH)2

NiOH+1

Ni+2

Ni(OH)3-1

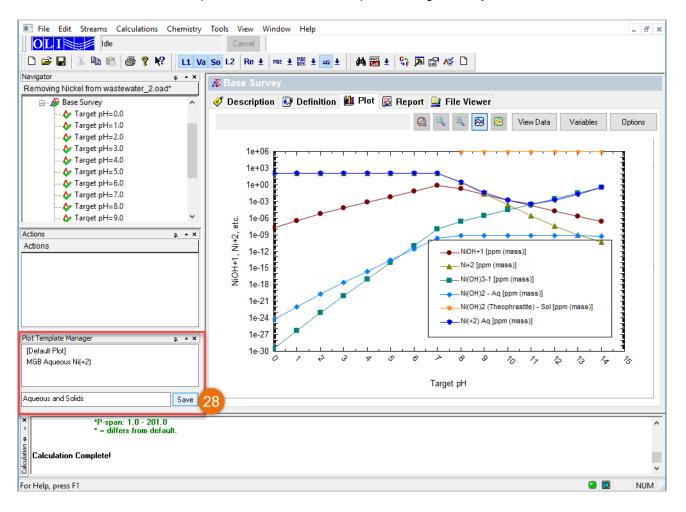
25. Add the following Solids species to the plot:

Ni(OH)2

26. Click on the OK button when done

File Edit Streams Calculations Chemistr	Cancel	∞ ± Ma 語 ± 9; ▶ 雷 ペ D	- & X
Navigator # * × Removing Nickel from wastewater_2.oad* Image: the state of	Base Survey	ion M Plot Report File Viewer	24 Variables Options
Plot Template Mana Default Plot] MGB Aqueopis Ni(+2 NiGB Aqueopis Ni(+2 Plot data which is only within t	<u>.</u>	X Axis X Axis Target pH Y1 Axis NOH+1 N+2 Ni(OH)3-1 Ni(OH)2 Aq Ni(OH)2 (Theophrastite) - Sol Ni(+2) Aq Y2 Axis Z Axis - Select -	1 [ppm (mass)]
For Help, press F1	27	OK Cancel Apply Help	@

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



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

Scenario 2: Wastewater with Cyanide Content

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

For this scenario, you will repeat many of the same steps as in <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

- 1. 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 🖨 🖬 ½ 🗈 💼 姜 😵 🛠 Navigator + ▲ ★ × nickel waste.oad*	L1 Va So L2 Re ± Mse ± Mse ± ac ±	🗚 🎬 ± 🔤 🔉 🖻 🖄	k - A - A
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Save	Input Advanced Search Add as Stream	Export	<u> </u>
+ 3 For Help, press F1			[] NUM []

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

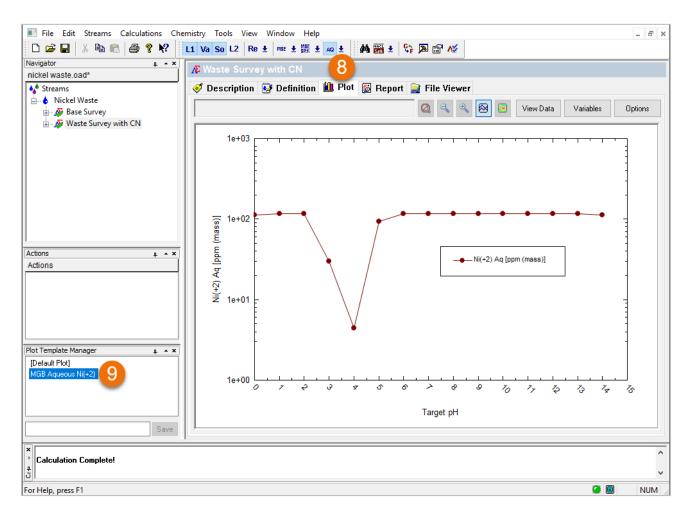
Name: *Waste Survey with CN* Description: *pH survey with both Nickel and CN*

- 4. Click on the Definition Tab
- 5. Add NaCN to the grid with a value of 490 ppm
- 6. **Click** on the **Survey By** button and select **pH**. Note that HCl and NaOH are the default titrants and are automatically added
- 7. Click on the Calculate button.

📧 File Edit Streams Calculations Cher	nistry Tools View Window Help L1 Va So L2 Re ± MSE ± MSE ± AQ ±	aa 🎬 + 😋 🖻 🕾 💉	_ 5 ×
Navigator + + × [
nickel waste.oad*	🔊 Waste Survey wi		
streams 3	🦪 Description 🔮 Definition 🛍 Plot	鰯 Report 🚊 File Viewer	
📄 👌 Nickel Waste	Variable	Value	Survey by
Base Survey	Stream Para		6 pH Specs
Waste Survey with CN	Stream Amount (kg)	1.00019	
	Temperature (°C)	25.0000	Then by (optional)
	Pressure (atm)	1.00000	None Specs
	Calculation Pa	rameters	Vary
	Target pH		 Independently
	Use Single Titrant	No	◯ Together
	pH Acid Titrant	HCL	
	pH Base Titrant	NaOH	Calc <u>u</u> late 🥝
		(mass))	Summary
J	H2O	9.99325e5	
Actions + • ×	Ni(OH)2	185.335	^
Actions	5 NaCN	490.000	> pH survey: Acid - HCLIN
	<u> </u>		Base - NaOH
			Range 0.0 to 14.0 Step size 1.0 No. steps 14 No secondary survey selected Unit Set <custom></custom>
Plot Template Manager + * x	Input		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 * = differs from default. ✓
Save	Advanced Search Add as Stream	Export	I Set oH Calculation
a Tor Help, press F1			[] NUM []

Let's review the results.

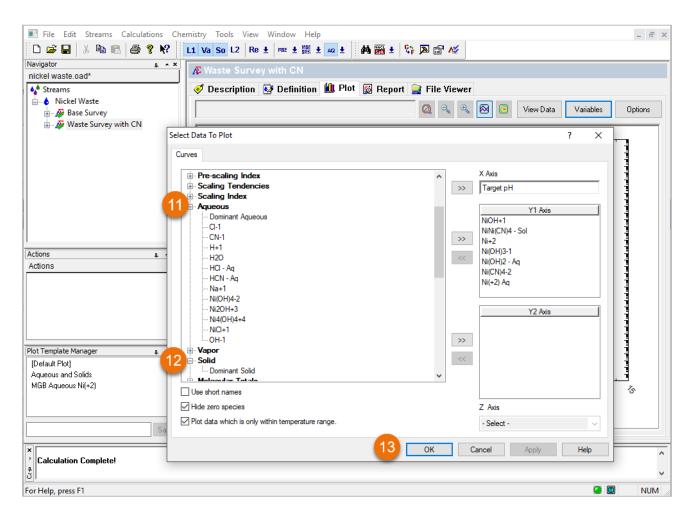
- 8. Click on the Plot tab
- 9. Go to the Plot Template Manager tool, and click on MGB Aqueous Ni(+2)



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**.

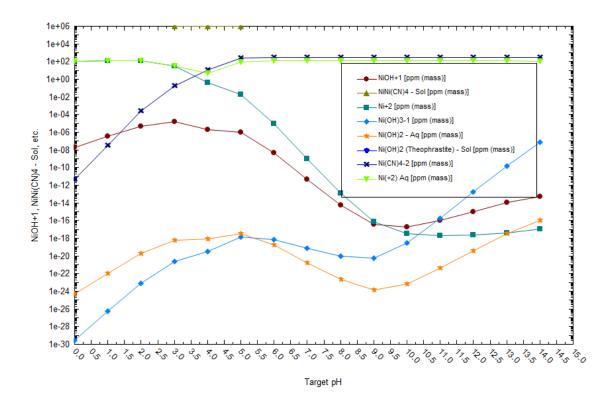
- 10. Click on Variables
- 11. Add the following new Aqueous species: Ni(CN)4-2
- 12. Add the following new Solid species: NiNi(CN)4-Solid
- 13. Click OK



Let's analyze the results.

The culprit is the Ni(CN) $_{4}$ ⁻² complex of nickel and cyanide. Basically, the plot of the total Ni in solution and the Ni(CN) $_{4}$ ⁻² complex overlap over the interval pH=5 to 12. This means that virtually all nickel in solution is in the form of this complex.

This complex thus holds the Ni in solution and does not allow the nickel hydroxide to even form. Instead, a much weaker precipitate, the NiNi(CN)₄ salt forms over a narrow range of pH with 4.0 being the optimum.



Scenario 3: Wastewater with Sulfide Salts

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

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

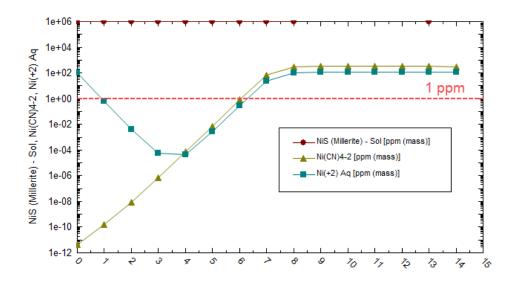
Add 490 ppm of NaCN

Add 340 ppm of H2S

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

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

3. Solid Species: NiS-Solid



The results reflect a "power struggle" between the Ni(CN)⁻² which is holding the nickel in solution and the NiS solid which clearly has a greater tendency to form than the NiNi(CN)₄ solid. As a result, our optimum pH is still around 4.0 and we are now around 10^{-5} ppm total nickel in solution which is a bit below 1 ppm.

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

Final Thoughts...

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

The actual removal achieved with sulfide may not be quite enough to satisfy the regulations. This is useful information to have. In addition, with the power of OLI 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)⁻² and not the cation (Ni+2) as the conventional wisdom might dictate.

2.1.1. Temperature Survey

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

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

The purpose of this first example is to present the basic Temperature survey. You will study how a four-phase mixture partitions as a function of temperature. The system composition will be basic, containing one primary phase component, H₂O (liquid), CH₄ (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					
Calculat	tion Settings	Stream Composition and Conditions			
Calculation Type	Survey	Stream Amount	Calculated		
Stream Name	Temperature Survey	Temperature Range	25-100 °C		
Survey Name	4-Phase Partioning	Step Size	Increment by 5 °C		
Name Style	Display Formula	Pressure	1 atm		
Unit Set	Metric, Moles	H2O	50 moles		
Framework	MSE-SRK	CH4	10 moles		
		C10H22	10 moles		
		NaCl	10 moles		

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

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

Variable	Value	Survey by
√ Stre	am Parameters	Temperature 👻 Spe
Stream Amount (mol)	80	80.0000 Then by (optional)
Temperature (°C)		
Pressure (atm)	1.0	1.00000 None - Spe
√	Inflows (mol)	Vary
H2O	50	50.0000 Independently
CH4	10	10.0000 O Together
C10H22	10	10.0000
NaCl	10	10.0000 Calc <u>u</u> late 🥝

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

Survey Options		?	×
Category Var. 1 - Temperature Calculation Type Calculation Options	Survey Range Temperature Range Selected Range 25.0 to 100.0 in 15 steps of 5.0	New	
	Linear O Log O Point List End Points End 100.000 End 100.000 These are the default values Step Size Increment 5.00000 Number Steps 15 Select one, the o calculated calculated select one, the o calculated select	9	
	OK Cancel Apply	Help	

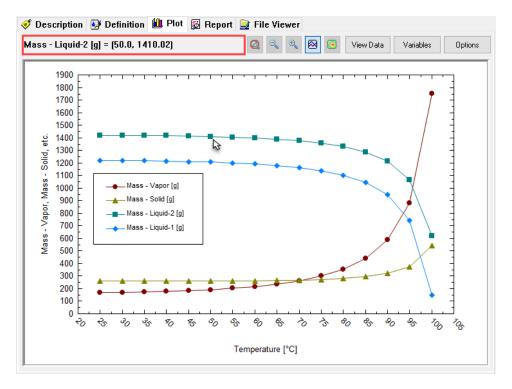
- 13. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 14. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

Anaylyzing the Results

Click on the Plot tab (Plot).

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

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

2.1.2. 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 CO₂ 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 CO₂ in water (which is a direct reflect of VLE) will be studied as a function of pressure.

Starting the Simulation

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

Pressure Survey Calculation					
Calculation Settings Stream Composition and Condition					
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		

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

Γ	Variable	Variable Value A Survey by				
1	Stream Parameters			Pressure 👻 Specs		
	Stream Amount (mol)	65.5082		Then by (optional)		
Γ	Temperature (°C)	25.0000				
T	Pressure (atm)			None Specs		
,	√ Inflows (mol)			Vary		
	H2O	55.5082		 Independently 		
t	C02	10.0000		🔿 Together		

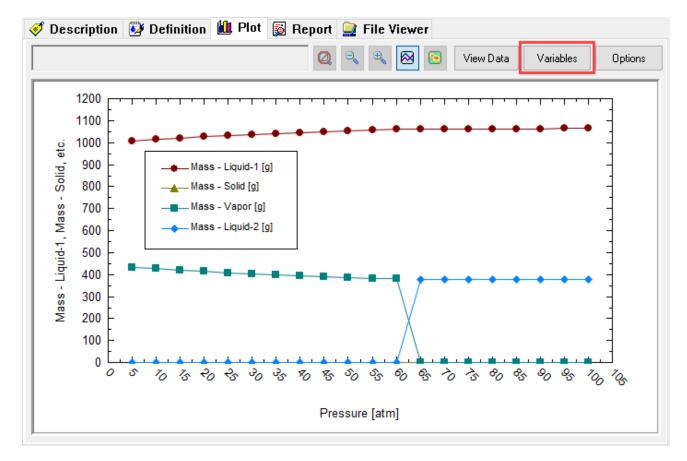
- 11. The default pressure range is from 1-10 atm with an increment of 1 atm. Change the **Pressure Range** to 5-100 atm. Set the **Step Size** to 5 atm increments. Then click **OK**.
- 12. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 13. It is time to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

Anaylyzing the Results

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

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

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

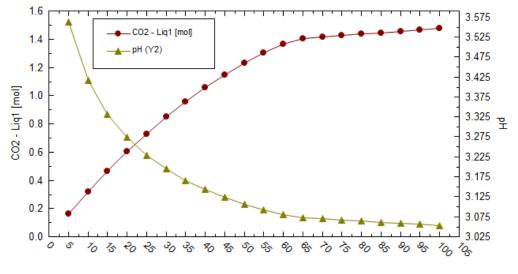


1. Click on the Variables button. This will open the Select Data to Plot window.

- 2. Double click or use the << button to remove the Phase Amount variables.
- 3. Look for Liquid-1 and click on the ⊞ box to show all the available variables. Select CO2-Liq1 and put it in the Y1 Axis using the >> button.
- 4. Look for Additional Stream Parameters section and click on the ⊞ box to show all the available variables. Select **pH** and put it in the Y2 Axis using the >> button. Then click **OK**.

ect Data To Plot	?					
urves						
Stream Parameters	A X Axis					
Calculation Results	>> Pressure					
Additional Stream Parameters	Y1 Axis					
Density - Liquid-1	CO2 - Lig1					
Density - Liquid-2	002 - 541					
Density - Total	>>					
Density - Vapor						
Dielectric Constant - Liquid-1	<<					
Dielectric Constant - Liquid-2						
Ionic Strength (m-based) - Liquid-1						
— Ionic Strength (x-based) - Liquid-1						
pH - Liquid-2						
Standard Liquid Volume - Liquid-1	Y2 Axis					
	pH					
Standard Liquid Volume - Vapor	pri					
	>>					
Phase Flow Properties						
Thermodynamic Properties	<<					
Pre-scaling Tendencies						
· Dra acolina Index	•					
Use short names						
Hide zero species	Z Axis					
Plot data which is only within temperature range.	- Select -					
	OK Cancel Apply	Help				

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



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:

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

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

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

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

2.1.3. Composition Survey

In the Survey by **Composition**, 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 (CaCO₃) as a function of CO₂

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

Starting the Simulation

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

Composition Survey Calculation									
Calculation	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						

- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to Composition Survey
- 3. Select the MSE thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 6. Enter the composition of the stream given in the table above
- 7. Go to the Add Calculation button and select Survey calculation
- 8. Select **Composition** as Type of Survey.
- Change the Survey name to Calcite Dissolution using the <F2> key
 Note: In the summary box a message in red appears: 'Component not selected for composition survey variable'. This means that we need to select the component that we want to vary. In this example CO2.
- 10. To specify the component, click on the Specs button. This will open the Survey Options Window.

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

Survey Options		?	×
Category	Component Survey Range Component Inflows Image: Component Inflows CaC03 Co2 H2D Image: Component Inflow which will be varied over the server of t	New Inflow specified range.	
	OK Cancel App	y Help	,

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

Category	Component Survey Range		
- Var. 1 - Composition - Calculation Type - Calculation Options		New	
	 Linear Log Point List End Points End 1.00000 Step Size Increment 0.0500000 Increment Select of calculation 	one, the other is red	
	OK Cancel As	oply Hel	n

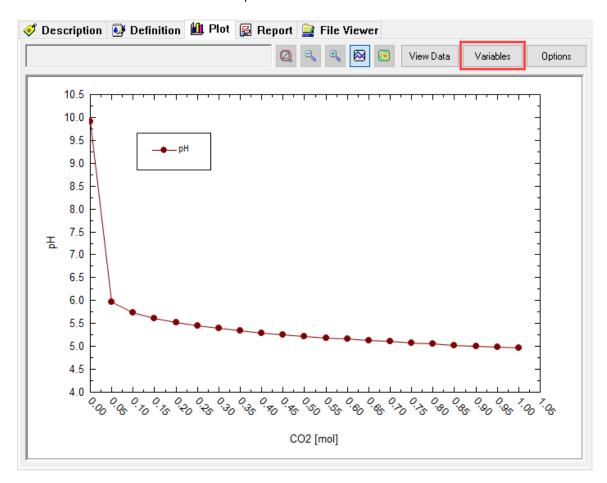
- 13. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 14. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

Anaylyzing the Results

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

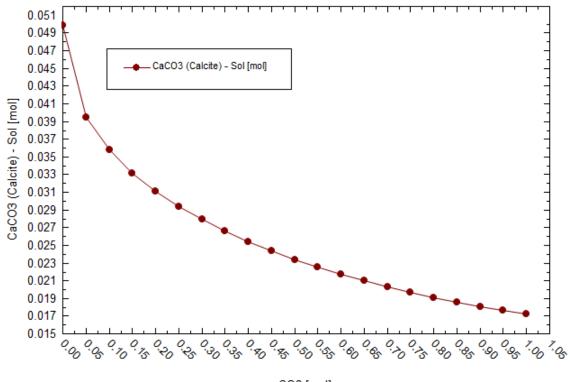
We are interested in understanding the dissolution of Calcite as a function of CO_2 . To see these results, we need to study how the moles of solid calcite change as the concentration of CO_2 increases.

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



- 2. Double click or use the << button to remove the pH variable
- 3. Look for **Solid** section and click on the ⊞ box to show all the available variables. **Select CaCO3 (Calcite)** - **Sol** and put it in the Y1 Axis using the >> button. Click **OK**.

The default plot now is showing the selected variable: CaCO3 (Calcite) - Sol as a function of CO2.



CO2 [mol]

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

2.1.4. pH Survey

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

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

In this survey calculation, a 1 molal CO₂ solution is titrated with HCl and NaOH. Instead of defining the amount of acid/base to add, the pH will be specified, and the software will compute the amounts of HCl and NaOH needed.

Starting the Simulation

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

pH Survey Calculation					
Calculation	n Settings	Stream Composition and Conditions			
Calculation Type	Survey	Stream Amount	Calculated		
Stream Name	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		

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

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

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

Use Single Titrant	Hide Dela	ted Inflows	New Inflow
Jose single ritrant		neu mnows	New Inflow
Acid		Base	
CO2		CO2	
H2O		H2O	
HCL		NAOH	

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

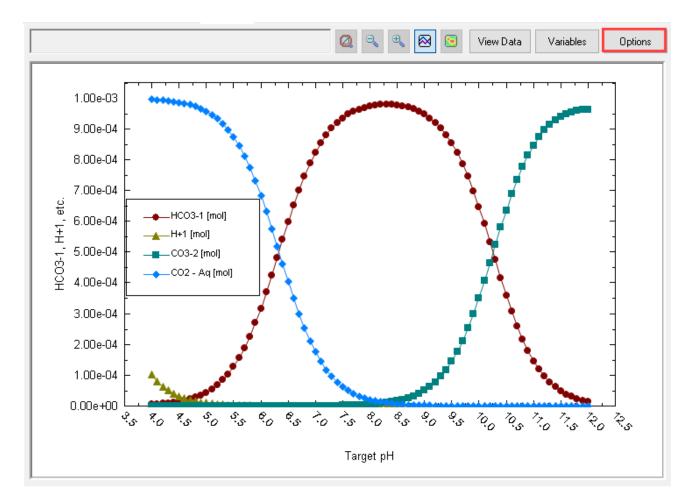
pH Titrants Survey F	ange	
Target pH Range	ι	Jnit:
Selected Range		
4.0 to 12.0 in 80 ste	os of 0.1	New
		Delete
Linear	◯ Log ◯ Poir	nt List
End Points		
Start	4.00000	
End	12.0000	
Step Size		
Increment	0.100000	Select one, the other is
Number Steps	80 🛛 🔿 🖌	calculated

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

Anaylyzing the Results

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

- 1. Click on the Variables button
- 2. Remove the **NaOH** and **HCI** from the Y1 axis (double click or use the << button)



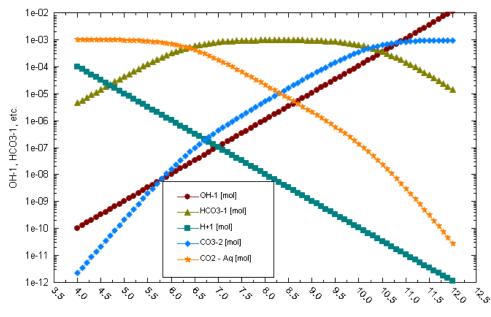
You can also present this plot on a semi-log scale.

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

Customize Plot		?	×
Category General Legend X Axis Y Axis Curves	Scale Format Title Auto Image: Comparison of the second seco		
	OK Cancel Apply	Hel	2

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+.

2.1.5. Vapor Fraction / Vapor Amount Survey

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

Example 22: Seawater Evaporation

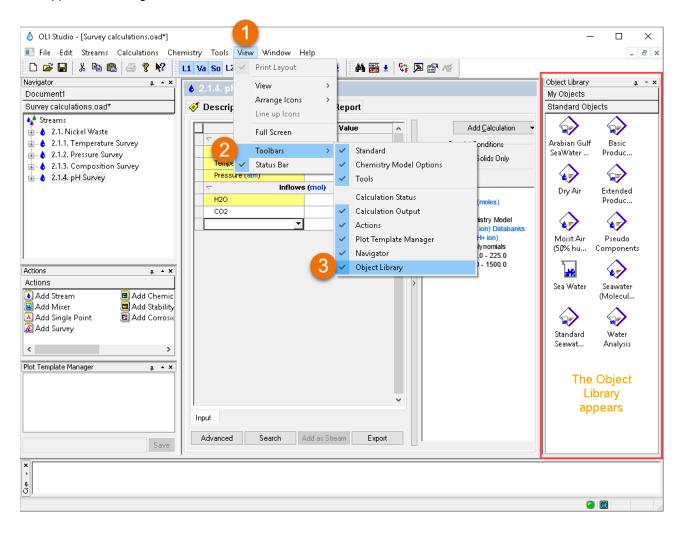
Seawater contains a variety of salts, and when seawater evaporates, these solids are left behind. The most abundant salt in seawater is sodium chloride (NaCl) which is also technically referred to as halite.

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

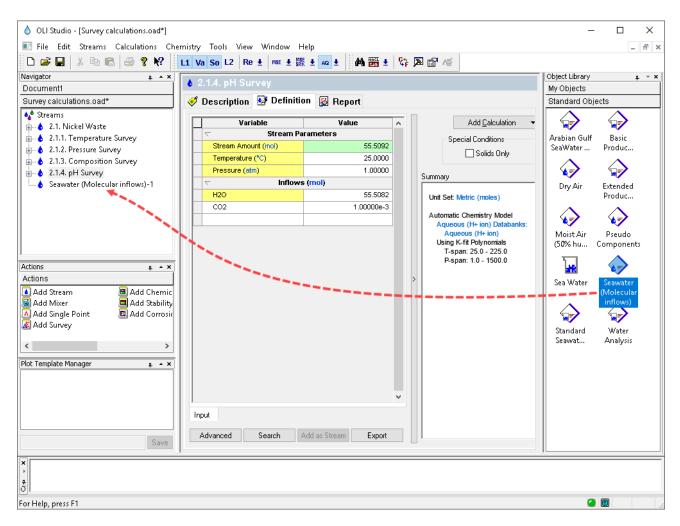
In this example we will also introduce the Object Library tool.

Starting the Simulation

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



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

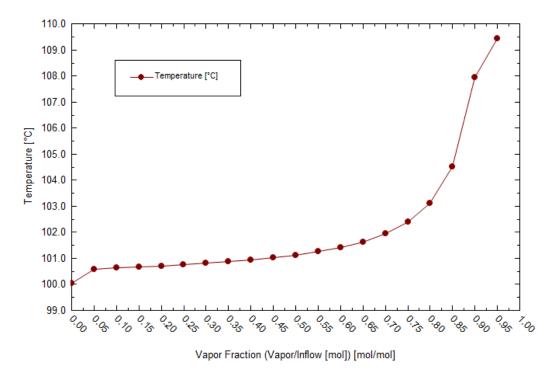


The inputs and parameters are automatically populated when selecting the Seawater (molecular inflows) form the Object Library.

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

Anaylyzing the Results

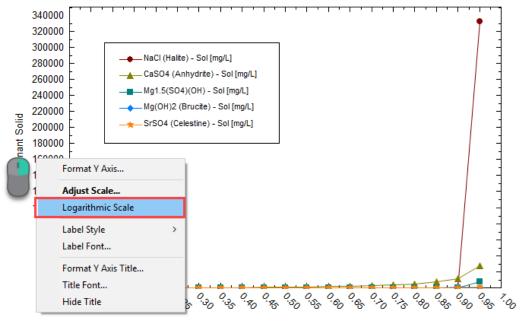
Click on the **Plot** tab (Plot). The default plot is the Vapor Fraction plot (as the dependent variable) vs Temperature. It shows that seawater boils initially at 100°C, and at near complete evaporation (95%) the temperature is 109.4°C.



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

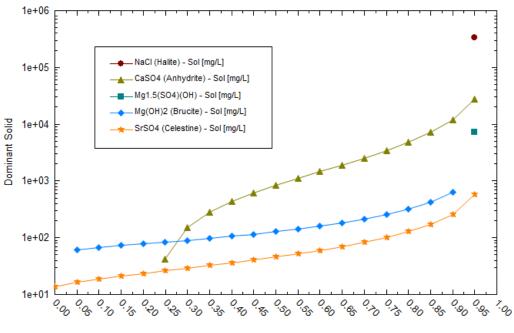
- 1. Click on the **Variables** button
- 2. Remove **Temperature** from the Y1 axis (double click or use the << button)
- 3. Look for **Solid** section and click on the ⊞ box to show all the available species. **Select** the option **Dominant Solids** and put it in the Y1 Axis using the >> button or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

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



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

Plot in semilogarithmic scale



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

As the water evaporates CaSO₄, Mg(OH)₂ and SrSO₄ salts precipitate at all temperatures. NaCl and a Mg/SO4 double salt start to precipitate at 95% vapor fraction.

2.2. Dual Surveys

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

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

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

1	🛷 Description 🔯 Definition 🛍 Plot 👼 Report 🚍 File Viewer						
	Variable	Value	~		Survey by		
	Stream Parameters				Temperature 👻 Specs		
	Stream Amount (mol)	55.5082			Then by (optional)		
	Temperature (°C)						
	Pressure (atm)				Pressure Specs		
					Vary		
	H2O	55.5082			Independently		
					◯ Together		
					Calculate 🥥		
				>	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		
In	put		¥		move independently Total points: 160 Unit Set: Metric (moles)		
	Advanced Search Add as Stream	Export			Automatic Chemistry Model		

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 CO₂ 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		

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

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

Survey Options		?	×
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 © Linear O Log O Point List	? New Delete	×
	End Points Start 5.00000 End 100.000 Step Size Increment 5.00000 Number Steps 19 Select one, the of calculated	ther is	
	OK Cancel Apply	Help	

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

	Value	~	Survey by
Stream Pa	arameters		Temperature 👻 Specs
Stream Amount (mol)	65	5.5082	Then by (optional)
Temperature (°C)			
Pressure (atm)			Pressure
√ Inflow:	s (mol)		Vary
H2O	55	5082	Independently
C02	10	0.0000	 Together
			Calculate 🥥
			Summary
			> Temperature survey:
			Range 5.0 to 100.0 °C
			Step size 5.0 °C
			Step size 5.0 °C
			Step size 5.0 °C No. steps 19 Pressure survey Range 5.0 to 100.0 atm
			Step size 5.0 °C No. steps 19 Pressure survey Range 5.0 to 100.0 atm Step size 5.0 atm
			Step size 5.0 °C No. steps 19 Pressure survey Range 5.0 to 100.0 atm Step size 5.0 atm No. steps 19
			Step size 5.0 °C No. steps 19 Pressure survey Range 5.0 to 100.0 atm Step size 5.0 atm No. steps 19 Primary and secondary survey
			Step Size 5.0 °C No. steps 19 Pressure survey Range 5.0 to 100.0 atm Step Size 5.0 atm No. steps 19 Primary and secondary survey Variables
		*	Step size 5.0 °C No. steps 19 Pressure survey Range 5.0 to 100.0 atm Step size 5.0 atm No. steps 19 Primary and secondary survey

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

Anaylyzing the Results

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

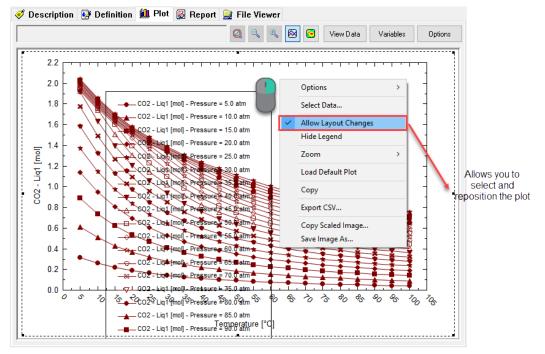
We are interested in the solubility of CO₂ in water, i.e. in the Liquid-1 phase. We can change the default plot to show the molecular CO2 dissolved in water (CO2-Liq1).

- 1. Click on the Variables button. This will open the Select Data to Plot window.
- 2. Double click or use the << button to remove the Phase Amount variables.
- 3. Look for Liquid-1 and click on the ⊞ box to show all the available variables. Select CO2-Liq1 and put it in the Y1 Axis using the >> button. Then click OK.

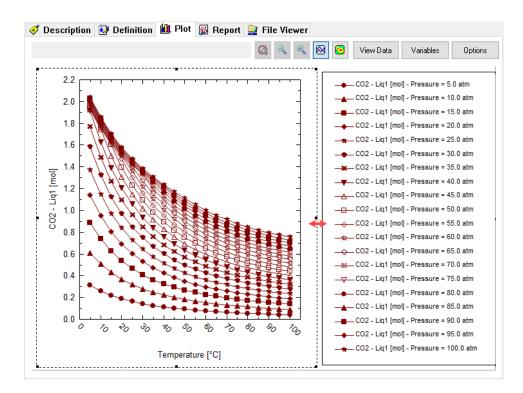
ct Data To Plot		?	
rves			
Stream Parameters	A X Axis		
Calculation Results	>> Temperature		
Additional Stream Parameters	Y1 Axis		
Phase Flow Properties	CO2 - Lig1	,	
Thermodynamic Properties			
Pre-scaling Tendencies	>>		
Pre-scaling Index			
Scaling Tendencies	<<		
Scaling Index			
E-Liquid-1			
Dominant Liquid-1 			
	Y2 Axis		
0H-1	>>		
	<<		
Malaaular Tatala	~		
Use short names			
Hide zero species	Z Axis		
Plot data which is only within temperature range.	Pressure		
	OK Cancel Apply		Help

The default plot now is showing the dissolved CO₂ in the water (Liquid-1 Phase) in the Y1 Axis as function of pressure. Unfortunately, the legend is covering the plot.

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



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

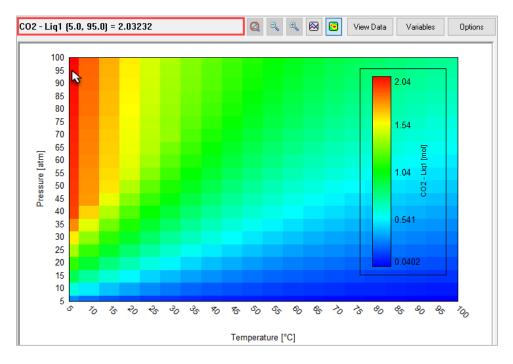


As the temperature increases (at a fixed pressure) the solubility of CO_2 . This is to be expected since at higher temperatures it is easy to overcome the vapor pressure and CO_2 is released as gas. As the pressure increases (at a fixed temperature) the solubility of CO_2 in solution increases.

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

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

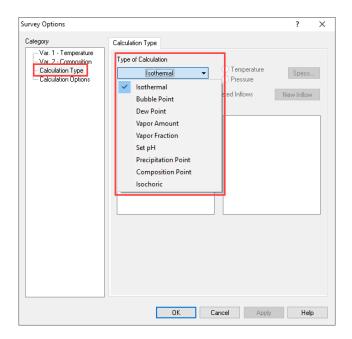


Note: The legend scale can also be optimized by either right-mouse-clicking on the Legend and selecting **Options>Plot Options>Contour** or clicking on the **Options** button in the upper right and selecting **Contour**. Both open to the Contour options window, where the color and range can be modified.

In the contour plot, you can see the effect of both Temperature (x-axis) and Pressure (y-axis) on the solubility of CO₂ 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

Sections 2.1 and 2.2 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					

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

Category Var. 1 - Temperature Calculation Type 	Calculation Type Type of Calculation Precipitation Poin Use Single Titrant Solid Precipitate H2D - Sol HCL.1H2D HCL.2H2D		Temperature Pressure Related Inflows Adjusted Inflow	Specs New Inflow	
- Calculation Type	Precipitation Poin Use Single Titrant Solid Precipitate H20 - Sol HCL.1H20	Hide F	 Pressure Related Inflows Adjusted Inflow 		
	Solid Precipitate H2D - Sol HCL.1H2D		Adjusted Inflow	New Inflow	
	H20 - Sol HCL.1H20	^			
	HCL 3H20 NaCl (Haitre) - Sol NaCL2H20 (tydrohaitre) NaOH - Sol NaOH.1H20 NaOH.2H20 NaOH.2H20 NaOH.35H20 NaOH.4H20	~	NaCl		
	ОК		ancel Apply	Help	

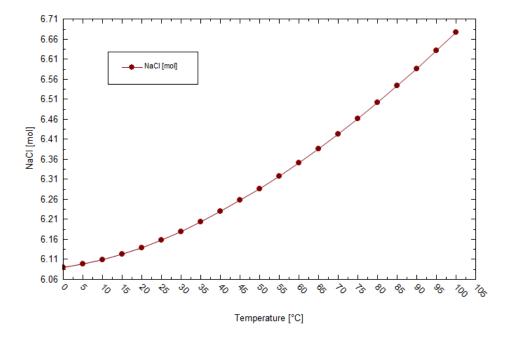
The **Calculation Parameters** section is now shown in the Definition Tab, highlighting the Precipitant (NaCl (Halite)) and the Adjusted Inflow (NaCl).

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

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

Anaylyzing the Results

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



Halite solubility increases slightly with temperature, from 6.16 moles/1kg H_2O at 25°C to 6.68 moles/1kg H_2O 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 $\frac{\text{Example 24}}{\text{Example 24}}$ will be used.

Starting the Simulation

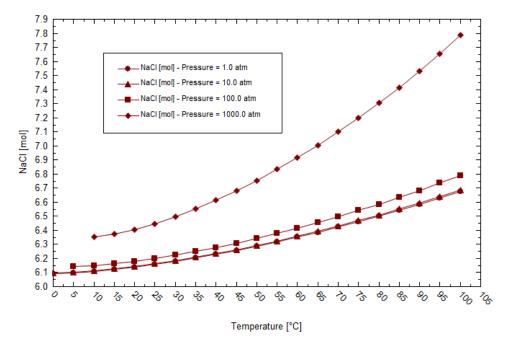
- 1. Under the **Solubility vs T** stream add a new Survey (see Stream information in Example 24)
- 2. Change the Survey name to Halite Solubility vs T and P using the <F2> key
- 3. Select Survey by **Temperature** and then by **Pressure** (This is a dual survey)
- 4. Click on the Temperature Specs button. This will open the Survey Options Window
- 5. Change the **Temperature Range** to 0-100 °C. Set the **Step Size** to **5** °C increments.
- 6. 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 Delete	
	O Linear ● Log O Point List End Points Start 1.00000 End 1000.00 Step Size Increment 333.000 Number Steps 3 ● } Select one, the calculated of the second se	ne other is	
	OK Cancel Apply	Help	

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

Anaylyzing the Results

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



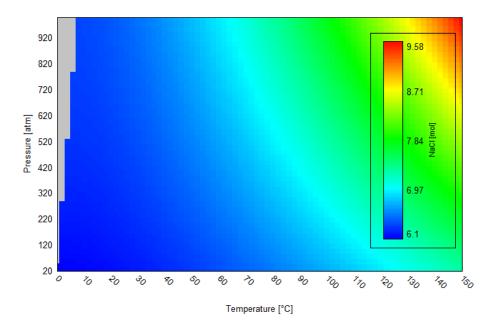
The effect of pressure is significant between 100 and 1000 atm relative to the effects between 1 and 100 atm.

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

- 1. Return to the Definition Tab
- 2. Click on the Temperature Specs button.
- 3. Change the **Temperature Range** to 0-150 °C. Set the **Step Size** to **2** °C increments.
- 4. 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.

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



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

Composition Survey with a Bubble and Dew Point Calculation

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

Example 26: Ethanol-Water Azeotrope

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

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

Starting the Simulation

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

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

Calculating the Bubble Point

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

- 11. Under the Component tab, select Ethanol
- 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 O calculated

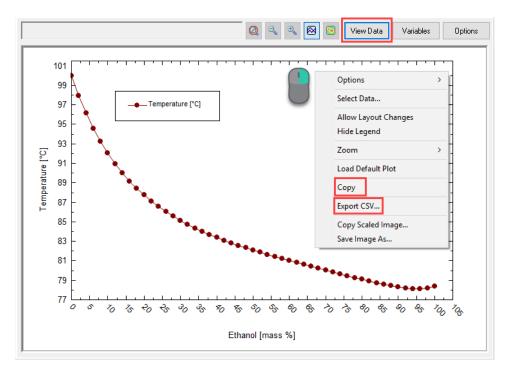
- 13. Click on **Calculation Type**, in the Category Window to define the Type of Calculation
- 14. Under Type of Calculation Change the Default Isothermal to **Bubble Point** (use the drop-down arrow). Then click **OK**.

Survey Options			?	×
Category	Calculation Type			
Var. 1 - Composition Calculation Type Calculation Options Solvent	Type of Calculation Bubble Point -	Temperature Pressure	Specs	
	🗹 Use Single Titrant 🗹 Hide	e Related Inflows	New Inflow	
	ОК	Cancel	Apply He	lp

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

Anaylyzing the Results

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



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

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

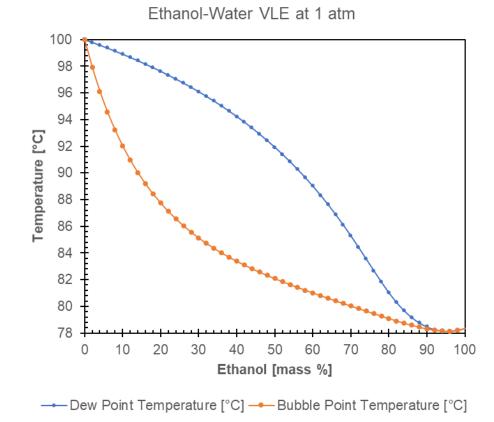
- Option 2: Right-click on the white region of the plot to open the drop-down menu and select Export CSV.
- Option 3: Click on the View Data button, select all data by clicking on the upper left corner of the table, and copy the data using Ctrl+C.

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

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

Calculating the Dew Point

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

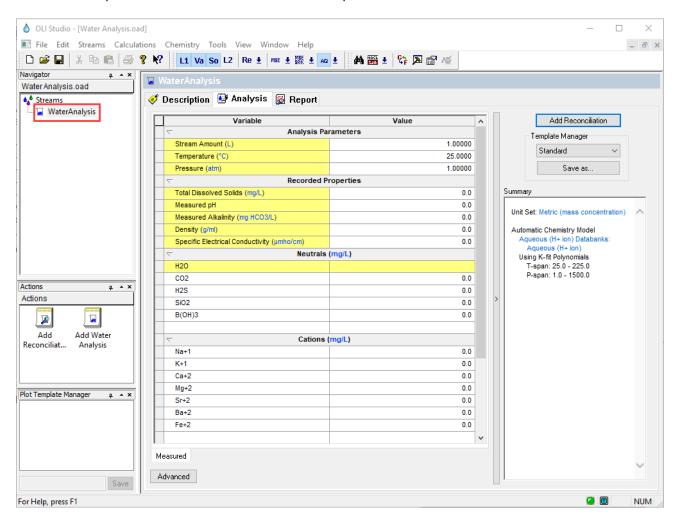


The azeotrope occurs at about 95% ethanol where the two curves intersect, at 78.15 °C.

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.



3.1. Basic Terminology

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

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

Scaling

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

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

Solubility Product Constant, K_{sp}

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

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

With equilibrium constant K_{sp} defined as:

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

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

$$a_i = m_i \gamma_i$$

Ion Activity Product, IAP

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

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

Scaling Tendency and Scale Index

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

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

Scaling tendencies are essentially saturation ratios. Thus, if

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

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

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

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

Thus, if

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

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

Pre-scaling Tendency and Scale Index

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

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

Difference between Post-scale and Pre-scale

Pre-Scale: The saturation ratio before solids precipitate.

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

Another way to interpret these two definitions is:

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

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

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:

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

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

Calculating the Scaling Tendency

$$ST = \frac{1.879 \times 10^{-5}}{3.2 \times 10^{-5}}$$
$$ST \approx 0.587$$

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

Calculating the Scaling Index

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

3.2. Entering Data for Water Analysis

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

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

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

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

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

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

Neutrals (mg/	L)
H2O	
C02	0.0
H2S	0.0
SiO2	0.0
B(OH)3	0.0
Cations (mg/	L)
Na+1	0.0
K+1	0.0
Ca+2	0.0
Mg+2	0.0
Sr+2	0.0
Ba+2	0.0
Fe+2	0.0
Anions (mg/l)	_)
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.

∇	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	
Display Name	OLI Name
OLI CSION	CSION
^{syn} Cu(+)	CUIION
\$\\Cu(++)	CUION
^{SYN} 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>**.

	Variable	Value
	Density (g/ml)	0.0
	Specific Electrical Conductivity (µmho/cm)	0.0
	Neutrals	(mg/L)
	H2O	
	C02	0.0
	H2S	0.0
	SiO2	0.0
	B(OH)3	0.0
8	OLI	0.0

3.3. Water Analyses - Reported Elements

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

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

3.4. A Basic Water Analysis

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

Example 28: Ground Water Analysis

Will calculate the **pH** and **density** of a Ground Water sample based upon its measured composition at 1 atm and 25 °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		1 L (Default)		Total Dissolved Solids		Not recorded		
Temperature		25 ℃		Measured pH		6.7		
Pressure		1 atm		Measured Alkalinity		Not recorded		
Name Style		Display Formula		Density		Not recorded		
Unit Set		Metric, Batch, Concentration		Specific Electrical Conductivity		Not recorded		
Framework		MSE			,			
Calculation Type		Water Analysis						
		Basic Water Analysis						
Composition								
Neutrals (mg/L)			Cations (mg/L)		Anions (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

- 1. Add a Water Analysis
- 2. Click on the new WaterAnalysis and press <F2> to change the name to Basic Water Analysis
- 3. Select the **MSE** thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Concentration (it may be defined by default)

- 6. Under the **Analysis** Tab, enter the Analysis Parameters, Recorded properties, and composition of the water given in the table above.
- 7. Go to the **Add Reconciliation** button of the top right corner or select **Add Reconciliation** from the Actions Panel.

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Navigator 👖 🔺 🖌		145					
Document1	📱 Basic Water Analysis						
Water Analysis.oad*	< Description 🛃 Analysis 🙀 Repo	rt					
♦♣ [♠] Streams	Construction Construction						
Basic Water Analysis	Variable	Value	 Add Reconciliation 				
	C Analysis Pa	rameters	Template Manager				
	Stream Amount (L)	1.00000	Standard V				
	Temperature (°C)	25.0000					
	Pressure (atm)	1.00000	Save as				
	Recorded F						
	Total Dissolved Solids (mg/L)	0.0	Summary				
	Measured pH	6.70000	Unit Set: Metric (mass concentration)				
	Measured Alkalinity (mg HCO3/L)	0.0	one see metric (nass concentration)				
	Density (g/ml)	0.0	Automatic Chemistry Model				
	Specific Electrical Conductivity (µmho/cm)	0.0	MSE (H3O+ ion) Databanks: MSE (H3O+ ion)				
		(mg/L)	Using Helgeson Direct				
	H2O						
	C02	150.000					
	H2S	15.0000					
	Si02	0.0					
	B(OH)3	0.0					
	NH3	5.00000					
Actions	Cations						
Actions	Na+1	1060.00					
Add Reconciliation	K+1	50.0000					
😡 Add Water Analysis	Ca+2	773.000					
	Mg+2	177.000					
	Sr+2	0.180000					
	Ba+2	0.460000					
	Fe+2	62.1000					
	Mn+2	2.80000					
	Al+3	0.740000					
Plot Template Manager # * *							
	CI-1	3896.00					
	S04-2	54.0000					
	HC03-1	0.0					
	HS-1	0.0					
	C2H3O2-1	0.0					
			v				
	Measured						
	measureu						
	Advanced						
Save							
For Help, press F1			Image:				

Note: You may notice that after selecting **Add Reconciliation** option, the navigator panel displays a sub-stream called **Reconcile**, and this **Reconcile** sub-stream opens a new tab named **Reconciliation**. The Reconcile sub-stream copies the original inputs entered in the *Water Analysis*. Any changes made in the sub-stream will not change the original Water Analysis.

Additionally, three different types of reconciliation are enabled in the upper right corner of the window: (1) No Reconcile, (2) Reconcile pH and (3) Reconcile pH/Alkalinity. These types of reconciliation will be described in more detail later in the next section.

The selected default calculation is **No Reconcile**. This option means that the software will compute the water properties based on the current concentration of neutral, cations, and anions species. The calculation will not use the measured pH, or the measured alkalinity entered (if any).

The Calculate Alkalinity box (Calculate Alkalinity) allows you to compute the alkalinity, also based on the concentration entered.

 OLI Studio - [Water Analysis.oad*] File Edit Streams Calculations C 	Chemistry Tools View Window Help		>
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Navigator n • ×	Reconcile		
Document1			
Water Analysis.oad*	🛷 Description 🧕 Reconciliation 🛃 Mol	ecular Basis 📓 Report 🚊 File	Viewer
🍓 Streams			Reconcililation
🖮 🖬 Basic Water Analysis	Variable	Value ^	Specs
🔤 🚂 Reconcile	Stream Amount (L)	1.00000	Reconcile
	Temperature (°C)	25,0000	No Reconcile
	Pressure (atm)	1.00000	O Reconcile pH
	Recorded Prope		O Reconcile pH/Alkalinity
	Total Dissolved Solids (mg/L)	0.0	
	Measured pH	6.70000	Calculate Alkalinity
	Measured Alkalinity (mg HCO3/L)	0.0	
	Density (g/ml)	0.0	Calculate 🥥
	Specific Electrical Conductivity (µmho/cm)	0.0	
	Section 2 Control Conductivity (printediny)		Summary
	H2O		Unit Set: Metric (mass concentration)
	C02	150.000	one out metric (mass concentration)
	H2S	15.0000	Automatic Chemistry Model
	SiO2	0.0	MSE (H3O+ ion) Databanks: MSE (H3O+ ion)
	B(OH)3	0.0	Using Helgeson Direct
	NH3	5.00000	Dominant Ion Charge Balance (eq/L):
			Isothermal Calculation
actions # * ×	Cations (mg	1)	25.0000 °C 1.00000 atm
Actions	Na+1	1060.00	Calculation not done
	K+1	50.0000	
	Ca+2	773.000	
	Mg+2	177.000	
	Sr+2	0.180000	
	Ba+2	0.460000	
	Fe+2	62,1000	
	Mn+2	2.80000	
	Al+3	0.740000	
lot Template Manager 📮 🔺 🗙	Anions (mg/	L)	
errempierer nameger 🕌 🔶	CI-1	3896.00	
	S04-2	54.0000	
	HC03-1	0.0	
	HS-1	0.0	
	C2H3O2-1	0.0	
		÷	
	Measured		
		-	×
Save	Advanced Search Add as Stream	Export	J I
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8. Select the No Reconcile option

- 9. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 10. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Create a new file and name it: *Water Analysis Calculations.*

Analyzing the Results

Viewing the Summary Box

Review the Summary Box. Let's analyze it in detail since it contains several pieces of important information, as shown in the image below.

Specific Electrical Conductivity (unno/cm)	0.0	Summary
$\overline{\nabla}$	Neutrals (mg/L)		
H2O			Unit Set: Metric (mass concentration)
CO2	150	00	Automatic Chemistry Model
H2S	15.0	00	MSE (H3O+ ion) Databanks:
SiO2		0.0	MSE (H3O+ ion)
B(OH)3		0.0	Using Helgeson Direct
NH3	5.00	00	Dominant Ion Charge Balance (eq/L): Cation Charge: 0.102945 eg/L
			Anion Charge: -0.111016 eq/L Charge Balance
$\overline{\nabla}$	Cations (mg/L)		Imbalance: -8.07170e-3 eq/L Information
Na+1	106	00	185.568 mg/L of Na+1
K+1	50.0	00	is needed to balance.
Ca+2	773	00 >	Isothermal Calculation Calculation Type
Mg+2	177	00	25.0000 °C 1.00000 atm
Sr+2	0.180	00	Phase Amounts
Ba+2	0.460	00	Aqueous 1001.98 g Vapor 0.0 g Phase Amounts
Fe+2	62.1	00	Solid 0.0115758 g
Mn+2	2.80	00	
Al+3	0.740	00	Aqueous Phase Properties pH 4.47595
		_	Ionic Strength 2.49905e-3 Aqueous Propertie
	Anions (mg/L)		mol/mol
CI-1	389	00	Density 1.00198 g/ml
S04-2	54.0	00	Calc. elapsed time: 30.438 sec
HCO3-1		0.0	
HS-1).0	Calculation complete
C2H3O2-1		0.0	

The top section contains the **charge balance information** showing the total equivalent charge (positive and negative), and the charge imbalance. This example has a negative imbalance of -8.072×10^{-3} eq/L, indicating that more cations are needed in solution in order to reach electroneutrality. The software calculates that 185.568 mg/L of Na+ are needed to balance the solution. The software adds this amount of Na+ to the solution. This information can be further confirmed in the **Report Tab** in the Charge Balance table.

The **calculation type information** shows the calculation type the software used. In this example, the software performed a default isothermal calculation at 25 °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	
$\overline{\nabla}$	Analysis Para	meters	
ę s	Stream Amount (L)	1.00000	
-	Volume - Liquid-1 (L)	1.00000	
L	Volume - Solid (cm3)	2.40298e-3	
т	emperature (°C)	25.0000	
P	Pressure (atm)	1.00000	
$\overline{\nabla}$	Molecular Tota	ls (mg/L)	1
A	AICI3	3.61208	1
A	AI(OH)3	0.0262829	1
E	BaCl2	0.631654	
E	BaSO4	0.0738067	
C	CaCl2	2092.78	ľ
C	CaO	24.1565	ľ
C	02	150.000	1
F	eCl2	124.399	ľ
F	eS	11.4757	1
Н	120	9.95556e5	ľ
Н	125	10.5511	ľ
ĸ	(CI	95.3381	ľ
h	/gCl2	693.368	ľ
N	InCl2	6.41382	Ì
Ν	laCl	3166.36	ľ
Ν	IH3	4.99999	ľ
S	603	44.9809	1
	GrCl2	0.325663	ŕ

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 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.

1. Click on the **Add as Stream** button. This will open a new window

Save Selected Result Streams $?$ \times						
Export Name: Molecular	Export of Reconcile					
Include the followin	g phases in the str	eam(s)				
Aqueous	Vapor					
Second Liquid	Solids					
Optional Phases that are no separately.	t included may be e	xported				
Aqueous						
Vapor						
Second Liquid						
Solid						
	ОК	Car	ncel			

Note: By default, the name of the stream is **Molecular Export of Reconcile**. You can change the name if you prefer. Additionally, you can include or exclude the phases that you want to export into your stream by checking or unchecking the corresponding boxes.

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

👌 OLI Studio - [Water Analysis Calculation	is.oad]		- 🗆 ×
I File Edit Streams Calculations C	hemistry Tools View Window Help		- 8
i 🗅 🚅 🖬 👗 🗈 🖻 🖉 🨵	L1 Va So L2 Re ± MSE ± MSE ± AQ ±	• 👬 🛤 • 🚱 🔊 🔊 🗸	
Navigator + *			
Document1	Molecular Export of Reconcile		
Water Analysis Calculations.oad	🦪 Description 🥸 Definition 📓 Reg	nort	
♦▲● Streams		Port	
Basic Water Analysis	Variable	Value A	Add Calculation 👻
Reconcile	Stream P	Parameters	Special Conditions
Molecular Export of Reconcile	Stream Amount (L)	1.00000	Solids Only
	Temperature (°C)	25.0000	
	Pressure (atm)	1.00000	Summary
	□ ⊂ Inflow	s (mg/L)	Summery
	H2O		Unit Set: Metric (mass concentration)
	C02	150.000	Automatic Observations Mandal
	H2S	10.5511	Automatic Chemistry Model MSE (H3O+ ion) Databanks:
	NH3	4.99999	MSE (H3O+ ion)
	AICI3	3.61208	Using Helgeson Direct
	BaCl2	0.631654	
	CaCl2	2092.78	
	CaO	24.1565	
Actions a * X	FeCI2	124.399	
Actions	KCI	95.3381	>
💩 Add Stream 🔲 Add Stabi	MgCl2	693.368	
Add Mixer 🛛 Add Corri A Add Single Point	MnCl2	6.41382	
Add Single Point	NaCl	3166.36	
Add Chemical Diagram	S03	44.9809	
	SrCl2	0.325663	
< >	BaSO4	0.0738067	
Plot Template Manager a • ×	FeS	11.4757	
Plot Template Manager # * *	AI(OH)3	0.0262829	
		~	
	Innut		
	Input		
	Advanced Search Add as Stream	Export	
Save			
For Help, press F1			

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.

🛷 Desc	ription 🥹 Reconciliation 🧕 M	olecular Basis 📓 Report 🚘 File Viewer
Jump to:	Reconciliation Summary ~ Reconciliation Summary	🝳 🔍 🔍 Customize Export
Spe Charg	Stream Inflows Charge Balance J Gream Parameters Total and Phase Flows (Amounts) Scaling Tendencies Species Output (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	
рН	6.70000	4.47595
Density, g/ml		1.00198

9.95554e5

The Stream Inflows table summarizes all the species that were entered in the water analysis grid.

Stream Inflows

Water, mg/L

Row Filter Applied: Only Non Zero Values

	Input	Output
Species	mg/L	mg/L
H2O	1.00000e6	9.95554e5
Na+1	1060.00	
K+1	50.0000	
Ca+2	773.000	
Mg+2	177.000	
Sr+2	0.180000	
Ba+2	0.460000	
Fe+2	62.1000	
Mn+2	2.80000	
AI+3	0.740000	
CO2	150.000	150.000
H2S	15.0000	15.0000
CI-1	3896.00	
SO4-2	54.0000	
NH3	5.00000	4.99999

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

<u>Charge Balance</u> Cation Charge: Anion Charge: Imbalance: Adjusted Species:	0.102945 eq/L -0.111016 eq/L -8.07170e-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		
HCO3-1		0.0	0.0		

0.0

0.0

0.0

0.0

17.51

HS-1

C2H3O2-1

3.5. 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 entered concentration of neutral, cations, and anions species. In the No Reconcile option you may allow the program to pick the species to adjust for electroneutrality or you may manually choose the species to perform the adjustment. (See electroneutrality options).
- 2. Reconcile pH: The software will run both an electroneutrality and pH reconciliation. This type of reconciliation will match your recorded pH. Additionally, the software will compute the water properties such as, density, electrical conductivity, etc. The pH of the solution is automatically adjusted by the software by adding either HCl or NaOH, or you may select your preferred acids and bases to adjust the pH.
- **3. Reconcile pH/Alkalinity:** The software will run an electroneutrality, pH and alkalinity reconciliation. This type of reconciliation will match your recorded pH and alkalinity values. Additionally, the software will compute the water properties such as density, electrical conductivity, etc. The pH of the solution is automatically adjusted by the software by adding either HCI or NaOH or you may select your preferred acids and bases to adjust the pH. The Alkalinity is automatically calculated by the software, using CO₂ as the alkalinity titrant, H₂SO₄ as the alkalinity pH titrant and 4.5 as the alkalinity end point pH. You can also change a different alkalinity titrant if you prefer.

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.

Water Analysis – Reconcile Options							
Analys	sis Parar	neters/Se	ettings	Recorded Properties			
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 Analysis					
Stream Name		Water Analysis –					
		Reconcile 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	C2H3O2	2-1	50

Calculating the pH

Setting the Water Analysis

- 1. Add a Water Analysis
- 2. Click on the new WaterAnalysis and press <F2> to change the name to Water Analysis Reconcile Options
- 3. Select the **MSE** thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Concentration (it may be defined by default)
- 6. Under the **Analysis** Tab, enter the Analysis Parameters, Recorded properties, and Composition of the water given in the table above.

- 7. Go to the **Add Reconciliation** button of the top right corner or select **Add Reconciliation** from the Actions Panel, and name it **No Reconcile**.
- 8. Select the No Reconcile option (selected by default)

1	Description	🥸 Reconciliation	2	Molecular Basis	😼 Report		Fil	e Viewer
		Variable		Value	•	~		Reconcililation
	~	Analysi	s Pai	rameters				Specs
	Stream Amou	unt (L)			1.00000			Reconcile
	Temperature	(°C)			25.0000			No Reconcile
	Pressure (at	m)			1.00000			O Reconcile pH
	$\overline{\nabla}$	Record	ed Pi	roperties				Reconcile pH/Alkalinity
	Total Dissolv	ed Solids (mg/L)			36500.0			Calculate Alkalinity
	Measured pH	ł			7.80000			
	Measured Al	kalinity (mg HCO3/L)			160.000			
	Density (g/m)			1.01300			Calc <u>u</u> late 🥝
	Specific Elec	trical Conductivity (µmho/c			0.0			Summary
	$\overline{\nabla}$	Neut	rals	(mg/L)				
	H2O							Unit Set: Metric (mass concentration)
	CO2				0.0	-		Automatic Chemistry Model
	H2S				0.0	-		MSE (H3O+ ion) Databanks:
	SiO2				16.0000	-		MSE (H3O+ ion) Using Helgeson Direct
	B(OH)3		_		0.0	-		Dominant Ion Charge Balance (eq/L):
	L							Isothermal Calculation
	∇	Catio	ons (mg/L)	40000.0			25.0000 °C 1.00000 atm
	Na+1				10000.0	-	>	Calculation not done
	Ca+2				500.000	-		
	Mg+2				1200.00	-		
	Sr+2 Ba+2				200.000	-		
⊢	Fe+2				5.00000	-		
	1642				5.0000	-		
⊢	$\overline{\nabla}$	Anic	ne (mg/L)				
	CI-1	Allis	/10 (19000.0			
	S04-2				2700.00	-		
	HCO3-1				142.000	-		
	As04-3		_		12.0000			
	HCOO-1				20.0000			
	C2H3O2-1				50.0000			
						~		
М	easured							
_								V
	Advanced	Search Add as Stre	eam	Export] I

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

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

Reconciliation Data	I	? ×					
Balance Calculat	on Options Convergence						
Type of balance	Dominant Ion 🔻	New Inflow					
Cations	 Dominant Ion 						
Na+1	Prorate						
Ca+2	Prorate Cations						
Mg+2 Sr+2	Prorate Anions						
Ba+2	Na/CI						
Fe+2	Make-up Ion	-1					
	User Choice						
Needed to balance: Charges on the Cations and Anions must be evenly balanced Cation charge: 0.563486 eq/L Anion charge: -0.596011 eq/L							
Imbalance:	-0.0325252 eq/L						
[OK Cancel	Apply Help					

There are 7 different Types of Balance:

- 1. Dominant Ion: This is the default method. The largest counter ion is used to adjust the electroneutrality. In our example,747.753 mg/L of Na+1 are added since there is an excess of negative charge (see the above image).
- 2. **Prorate**: This option keeps the relative amount of the counter ions (for this example, the cations) the same and are adjusted up or down equally until reaching electroneutrality.
- 3. Prorate Cations: All cations are adjusted up or down equally
- 4. Prorate Anions: All anions are adjusted up or down equally
- 5. Na+/CI-: Sodium is added when there is an excess of negative charge. Chloride is added when there is an excess of positive charge.
- 6. Make-up Ion: This option allows for a single ion species to be adjusted. User selects an ion to increase or decrease.
- 7. User Choice: The software determines if an anion or cation is needed to balance the solution and the user choses the specific ion.

- 10. Keep the default option, Dominant Ion, as the balance type then press OK
- 11. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 12. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save under the same file that we created before named *Water Analysis Calculations*.

Analyzing the Results

Once you run the simulation there are two options to analyze the results: The summary box and the Report

1. Go to the **Report** Tab and look at the **Reconciliation Summary** Table.

Description 🔯 Reconciliation 🛃 M	lolecular Basis	🔯 Report 📄	File Viewer		
mp to: Reconciliation Summary ~]		0 0	Customize	Export
Reconciliation Summary Specification					,
Charge Balance Method Dominant Ion					
Charge Balance MethodDominant IonpH Reconciliation TypeNo reconciliation					
-			I		
-	Measured	Calculated			
-	Measured 25.0000	Calculated			
pH Reconciliation Type No reconciliation		Calculated			
pH Reconciliation Type No reconciliation	25.0000	Calculated 7.48368			
pH Reconciliation Type No reconciliation 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

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

Variable	Value	^	Reconcililation
Analysis Paramet	ters		Specs
Stream Amount (L)	1.000	00	Reconcile
Temperature (°C)	erature (°C) 25.00		O No Reconcile
Pressure (atm)	1.000	00	Reconcile pH
Recorded Propert	ties		Reconcile pH/Alkalinity
Total Dissolved Solids (mg/L)	3650	0.0	Calculate Alkalinity
Measured pH	7.800	00	
Measured Alkalinity (mg HCO3/L)	160.0	00	
Density (g/ml)	1.013	00	Calc <u>u</u> late 🥝
Specific Electrical Conductivity (µmho/cm		0.0	Summary
Calculation Parame	eters		
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
C02		0.0	Dominant Ion Charge Balance (eq/L):
H2S		0.0	Set pH Calculation Measured pH: 7.80000
SiO2	16.00	00	pH Titrants:
B(OH)3		0.0	Acid: HCI
			> Base: NaOH
Cations (mg/L))		Calculation not done
Na+1	1000		
Ca+2	500.0	00	
Mg+2	1200		
Sr+2	200.0		
Ba+2	5.000		
Fe+2	5.000	00	
C Anions (mg/L)			
CI-1	1900	_	
S04-2	2700	_	
HC03-1	142.0	_	
As04-3	12.00	_	
HC00-1	20.00	_	
C2H3O2-1	50.00	00	
		\checkmark	
easured			
easuleu			

Note that by selecting the *Reconcile pH* option, now the measured pH is a fixed value (and brown dot appears in front of this cell). To match the measured pH, the software added a Calculation Parameters section which indicates the acid and basic pH titrants to adjust the pH. By default, HCl and NaOH are selected by the software. This is similar to the set pH single point calculation.

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

Analyzing the Results

1. Go to the **Report** Tab and look at the **Reconciliation Summary** Table.

mp to: Reconciliation Summary ~		(2 ⊖ ⊕	Customize	Export
Reconciliation Summary					,
Specification					
Charge Balance Method Dominant Ion					
pH Reconciliation Type Reconcile pH					
			1		
	Measured	Calculated			
		culculated			
Temperature, °C	25.0000	Culculated			
Temperature, ⁰C Pressure, atm	25.0000	culculated			
		7.80000			
Pressure, atm	1.00000				
Pressure, atm pH	1.00000 7.80000		I		
Pressure, atm pH pH Titrant Acid: HCI, mg/L *	1.00000 7.80000 0.0	7.80000			

The measured and calculated pH are the same. The software added 44.5892 mg/L of NaOH to match the experimentally measured pH.

Calculating Alkalinity

Now we will instruct the software to calculate Alkalinity.

	Variable	Value A	Reconciliation
	Analysis Para		Specs
	Stream Amount (L)	1.00000	Reconcile
	Temperature (°C)	25.0000	◯ No Reconcile
	Pressure (atm)	1.00000	Reconcile pH
	Recorded Pro	operties	Reconcile pH/Alkalinity
	Total Dissolved Solids (mg/L)	36500.0	
	Measured pH	7.80000	Calculate Alkalinity
	Measured Alkalinity (mg HCO3/L)	160.000	
	Density (g/ml)	1.01300	Calc <u>u</u> late 🥝
	Specific Electrical Conductivity (µmho/cm	0.0	
	Calculation Par	rameters	Summary
11 m 14 m 414 m m 4 m	Alkalinity pH Titrant	H2SO4	Unit Set: Metric (mass concentration)
linity titrants	Alkalinity End Point pH	4.50000	
	Use Single pH Titrant	No	Automatic Chemistry Model MSE (H3O+ ion) Databanks:
pH titrants	pH Acid Titrant	HCL	MSE (H3O+ ion)
	oH Base Titrant	NAQH	Using Helgeson Direct
	Neutrals (r	ng/L)	Dominant Ion Charge Balance (eq/L):
	H20		Cation Charge: 0.563486 eq/L Anion Charge: -0.596011 eq/L
	C02	0.0	Imbalance: -0.0325252 eq/L
	H2S	0.0	747.750 6 No. 4
	Si02	16.0000	> 747.753 mg/L of Na+1 is needed to balance.
	B(OH)3	0.0	Set pH Calculation
			Measured pH: 7.80000
	Cations (n	ng/L)	pH Titrants: Acid: HCI
	Na+1	10000.0	Base: NaOH
	Ca+2	500.000	Calculation not done
	Mg+2	1200.00	
	Sr+2	200.000	
	Ba+2	5.00000	
	Fe+2	5.00000	
	Anions (m		
	CI-1 S04-2	19000.0	
	HC03-1	142.000	
	As04-3	142.000	
	HC00-1	20.0000	
	C2H3O2-1		
	C2H3O2-1	50.0000	
	Measured		
r	Advanced Search Add as Stream	Export	

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

Notice that by selecting the Calculate Alkalinity box two more rows were added to the Calculation Parameters section: Alkalinity pH Titrant and Alkalinity End Point pH, besides the pH titrants rows. These two new rows indicate that the software will add H_2SO_4 (selected by default) until the pH reduces to 4.5. The software then converts the amount of additional H_2SO_4 into the alkalinity value.

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

Analyzing the Results

1. Go to the **Report** Tab and look at the **Reconciliation Summary** Table.

mp to: Reconciliation Summary ~		(2	€	Customize	Export
Reconciliation Summary						
Specification						
Charge Balance Method Dominant Ion						
pH Reconciliation Type Reconcile pH						
Alkalinity pH Titrant: H2SO4						
	Measured	Calculated				
	Medsureu	Calculated				
Temperature, °C	25.0000	Calculated				
Temperature, °C Pressure, atm		Calculated				
	25.0000	7.80000				
Pressure, atm	25.0000					
Pressure, atm pH	25.0000 1.00000 7.80000					
Pressure, atm pH pH Titrant Acid: HCI, mg/L *	25.0000 1.00000 7.80000 0.0	7.80000				
Pressure, atm pH pH Titrant Acid: HCl, mg/L * pH Titrant Base: NaOH, mg/L *	25.0000 1.00000 7.80000 0.0 0.0	7.80000 44.5892	I			

The calculated alkalinity value is different to the measured value. This is because the software is not doing an alkalinity reconciliation, rather the software is using only the concentration data to calculate alkalinity. You can see this as single point alkalinity calculation.

Note that in this example, the alkalinity being reported because we checked the **Calculate Alkalinity** box; if the box wasn't checked we would not see the calculated value in the Reconciliation Summary table.

Example 31: Water Analysis – Reconcile pH/Alkalinity Option

In this example we will reconcile the sample by **pH and alkalinity** and also calculate the **pre-scaling tendencies** of the same Produced Water sample used in the previous Example 29: Water Analysis – No Reconcile Option.

Starting the Simulation

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

	Variable	Value	Reconcililation
	Analysis Par		Specs
	Stream Amount (L)	1.00000	Reconcile
	Temperature (°C)	25.0000	🔿 No Reconcile
	Pressure (atm)	1.00000	O Reconcile pH
	Recorded Pr	operties	Reconcile pH/Alkalinity
	Total Dissolved Solids (mg/L)	36500.0	
	Measured pH	7.80000	Calculate Alkalinity
•	Measured Alkalinity (mg HCO3/L)	160.000	
	Density (g/ml)	1.01300	Calc <u>u</u> late 🥝
	Specific Electrical Conductivity (umho/cm	0.0	Summary
	Calculation Pa	arameters	Summary
	Alkalinity Titrant	C02	Unit Set: Metric (mass concentration)
alinity titrants	Alkalinity pH Titrant	H2SO4	
•	Alkalinity End Point pH	4.50000	Automatic Chemistry Model MSE (H3O+ ion) Databanks:
	Use Single pH Titrant	No	MSE (H30+ ion)
pH titrants	pH Acid Titrant	HCL	Using Helgeson Direct
·	pH Base Titrant	NAOH	Dominant Ion Charge Balance (eq/L):
	Neutrals ([mg/L]	Reconcile pH Alkalinity Calculation
	H2O		Alkalinity: 160.000 mg HCO3/L Titration End Pt: 4.50000
	CO2	0.0	Alkalinity Titrant: CO2
	H2S	0.0	Alkalinity pH Titrant: H2SO4
	SiO2	16.0000	pH Reconciliation: Measured pH: 7.80000
	B(OH)3	0.0	pH Titrants:
			Acid: HCI
	Cations (mg/L)	Base: NaOH
	Na+1	10000.0	Calculation not done
	Ca+2	500.000	
	Mg+2	1200.00	
	Sr+2	200.000	
	Ba+2	5.00000	
	Fe+2	5.00000	
	Anions (r	mg/L)	
	CI-1	19000.0	
	S04-2	2700.00	
	HCO3-1	142.000	
	As04-3	12.0000	
	HCOO-1	20.0000	
	C2H3O2-1	50.0000 V	
Mo	asured		

Note that by selecting the *Reconcile pH/Alkalinity* option, now both the measured pH and alkalinity values are fixed values (and brown dot appears in front of this cell).

To match the measured alkalinity value, the software added a **Calculation Parameters** section which indicates the alkalinity titrant and the pH titrant used to adjust the alkalinity. CO2 is used by default as the alkalinity titrant. This is similar to an *alkalinity* single point calculation.

To match the measured pH, the software also added a **Calculation Parameters** section which indicates the acid and basic pH titrants to adjust the pH. By default, HCl and NaOH are selected by the software. This is similar to the *set pH* single point calculation. Also notice that the alkalinity box is grayed out. This is because we have asked the software to match the measured alkalinity value. This means that calculated alkalinity value is no longer needed.

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

Analyzing the Results

1. Go to the **Report** Tab and look at the **Reconciliation Summary** Table.

Description 🧕 Reconciliation 🎒 Ma	lecular Basis	😼 Report		
mp to: Reconciliation Summary ~		¢	🔍 🔍 Customize	Export
Reconciliation Summary				/
Specification				
Charge Balance Method Dominant Ion				
pH Reconciliation Type Reconcile pH and A	Ikalinity			
Alkalinity pH Titrant: H2SO4	-			
			_	
	Measured	Calculated		
T ()0				
Temperature, °C	25.0000			
Pressure, atm	25.0000 1.00000			
		7.80000		
Pressure, atm	1.00000	7.80000 14.9320		
Pressure, atm pH	1.00000 7.80000			
Pressure, atm pH pH Titrant Acid: HCI, mg/L *	1.00000 7.80000 0.0			
Pressure, atm pH pH Titrant Acid: HCI, mg/L * pH Titrant Base: NaOH, mg/L *	1.00000 7.80000 0.0	14.9320		
Pressure, atm pH pH Titrant Acid: HCl, mg/L * pH Titrant Base: NaOH, mg/L * Alkalinity Titrant: CO2, mg/L *	1.00000 7.80000 0.0 0.0	-35.0147		

The measured and calculated pH and alkalinity values are the same. The software added 14.9320 mg/L of HCI 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

- 1. Go back to the Reconciliation tab of the Reconcile pH/Alkalinity water analysis
- 2. Click on the **Calculation Options** icon *M*. This will open the Calculation Options window.
- 3. Check the **Pre-scaling Tendencies** box and select the **Rigorous method**. Then click **OK**.

C	Calculation Options - No Reconcile - Pre-scaling ? X	
	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	
	Method O Estimated I Rigorous	
	O LEANING O NIGHT	

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

Analyzing the Results

1. Go to the Report Tab and search for the Scaling Tendencies Table.

00 00 00 211 014 100 524 465 306 7131 4063 21e-3	Pre-Scale 11.9186 10.3094 40.5449 171.668 0.774141 7.58784 35.1595 0.243863 0.192618 0.123409 0.0578684 10068.6 3.46068e-3				,
00 00 00 211 014 100 524 465 306 7131 4063 21e-3	11.9186 10.3094 40.5449 171.668 0.774141 7.58784 35.1595 0.243863 0.192618 0.123409 0.0578684 10068.6				
00 00 00 211 014 100 524 465 306 7131 4063 21e-3	11.9186 10.3094 40.5449 171.668 0.774141 7.58784 35.1595 0.243863 0.192618 0.123409 0.0578684 10068.6				
00 00 211 014 100 524 465 306 7131 4063 21e-3	10.3094 40.5449 171.668 0.774141 7.58784 35.1595 0.243863 0.192618 0.123409 0.0578684 10068.6				
00 00 211 0014 100 524 465 306 7131 4063 21e-3	40.5449 171.668 0.774141 7.58784 35.1595 0.243863 0.192618 0.123409 0.0578684 10068.6				
00 211 0014 524 465 306 7131 4063 21e-3	171.668 0.774141 7.58784 35.1595 0.243863 0.192618 0.123409 0.0578684 10068.6				
211 014 100 524 465 306 7131 4063 21e-3	0.774141 7.58784 35.1595 0.243863 0.192618 0.123409 0.0578684 10068.6				
014 100 524 465 306 7131 4063 21e-3	7.58784 35.1595 0.243863 0.192618 0.123409 0.0578684 10068.6				
100 524 465 306 7131 4063 21e-3	35.1595 0.243863 0.192618 0.123409 0.0578684 10068.6				
524 465 306 7131 4063 21e-3	0.243863 0.192618 0.123409 0.0578684 10068.6				
465 306 7131 4063 21e-3	0.192618 0.123409 0.0578684 10068.6	-			
306 7131 4063 21e-3	0.123409 0.0578684 10068.6	-			
7131 4063 21e-3	0.0578684 10068.6				
4063 21e-3	10068.6				- 1
21e-3		7			
	2 460690-2				
32e-3	3.400006-3	7			
	2.97543e-3				
99e-3	2.92980e-3				- 1
93e-3	2.94910e-3				
63e-3	0.0183869				
84e-4	0.208240				
29e-4	6.87951e-4				
37e-4	5.05378e-4	7			
62e-4	5.06448e-4	1			
46e-4	4.83922e-4	7			
05e-4	0.0242604	7			
61e-4	3.02435e-4				
13e-4	2.23051e-4				
01e-5	1.09462e-4				
74e-5	0.0433856	7			
	84e-4 29e-4 37e-4 62e-4 46e-4 05e-4 61e-4 13e-4 01e-5 74e-5 63e-10	29e-4 6.87951e-4 37e-4 5.05378e-4 62e-4 5.06448e-4 46e-4 4.83922e-4 05e-4 0.0242604 61e-4 3.02435e-4 13e-4 2.23051e-4 01e-5 1.09462e-4	29e-4 6.87951e-4 37e-4 5.05378e-4 62e-4 5.06448e-4 46e-4 4.83922e-4 05e-4 0.0242604 61e-4 3.02435e-4 13e-4 2.23051e-4 01e-5 1.09462e-4 74e-5 0.0433856	29e-4 6.87951e-4 37e-4 5.05378e-4 62e-4 5.06448e-4 46e-4 4.83922e-4 05e-4 0.0242604 61e-4 3.02435e-4 13e-4 2.23051e-4 01e-5 1.09462e-4 74e-5 0.0433856	29e-4 6.87951e-4 37e-4 5.05378e-4 62e-4 5.06448e-4 46e-4 4.83922e-4 05e-4 0.0242604 61e-4 3.02435e-4 13e-4 2.23051e-4 01e-5 1.09462e-4 74e-5 0.0433856

This table reports both the Post-Scale and Pre-scale Tendencies. See the section 3.1 Basic Terminology to see a more detailed explanation.

The Scaling Tendencies (reported in the software as **Post-Scale**), are essentially saturation ratios. When the scaling tendency for a given mineral is equal to 1.0 (saturation conditions) it indicates that the mineral is in equilibrium with water, a solid phase has formed. A scaling tendency below 1.0 indicates sub-saturation and that the solid phase will not form. A solid is at risk of forming when the scale tendency value is greater than 1.0 (supersaturation conditions).

The Pre-Scaling Tendencies (reported in the software as **Pre-Scale**), is defined as the scaling tendency before any solids are formed (this can be seen as all the species suspended in solution).

Note: The Post-Scale and the Pre-Scale tendencies are equivalent if the solid phase is turned OFF.

Section 4. Hydrocarbons and Pseudocomponents

So far, we have learned how to enter molecular and ionic inflows in Stream Analyzer. Stream Analyzer also allows you to enter assays or pseudocomponents in order to crude oils as streams.

Crude oils are complex groups of organic molecules containing hundreds, perhaps thousands of pure components in a single oil. Modeling crude oils using pure components is impractical, because analyzing for each pure component is cost prohibitive and the number of species would make calculations overwhelming. A convenient solution to this problem and to modeling the properties of a crude oil is to create pseudo components.

Crude Oil properties may be defined through a distillation curve, where each boiling point range is a progression of molecular weights, densities, solubilities, viscosities and other properties associated with that section. It is reasonable for low boiling point molecules to be low molecular weight, low density, low viscosity, and more soluble in water. We can dice boiling point curves using well accepted methods standard to create pseudocomponents that in combination reflect the property of the whole oil.

There are two ways to create a crude oil stream on Stream Analyzer:

- 1. The first is to start with a PVT curve and create pseudocomponents using one of the three thermodynamic methods coded into the software.
- 2. The second is to enter the pseudocomponent data directly and using the same thermodynamic methods to predict the component properties.

The three thermodynamic methods are: API, Lee Kesler, and Cavett. More details about this method can be found in Section 11. Basic Terminology.

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

4.1. Entering a PVT Analysis

Example 32: Creating an Assay

In this example, we are going to learn how to enter a simple PVT analysis in order to create a Crude Oil Stream.

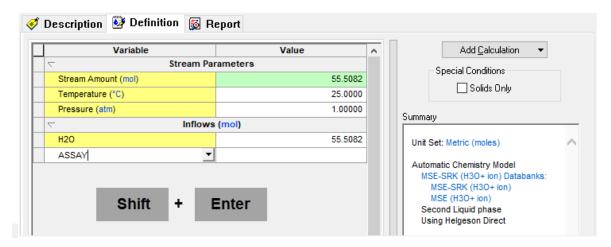
Starting the Simulation

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

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

7. In the inflows grid, in the white cell below H2O, type ASSAY and then press **<Shift + Enter>.** You can assign other name to your Assay; however, you are limited to 5 characters for the name of the Assay.

Note: The <Shift + Enter> action instructs the software to create an Assay rather than look for a species or pure component from the database.



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

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

	Assay Information				
Calculation	Calculation Settings		tion Data		
Assay amount	1000 moles	Percent Distilled	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 🔫
		ameters				Special Conditions
	Stream Amount (mol)		1055.51			
	Temperature (°C)		25.0000			Solids Only
	Pressure (atm)		1.00000			
	√ Inflows	(mol)				ummary
	H2O		55.5082			Unit Set: Metric (moles)
A I	📮 ASSAY		1000.00			
	— Assay Data Type	ASTM D86				Automatic Chemistry Model
	 Average Bulk Density Type 	API Gravity				MSE-SRK (H3O+ ion) Databanks: MSE-SRK (H3O+ ion)
	– API Gravity		40.0000			MSE (H3O+ ion)
x	Distillation Curve Cuts		10			Second Liquid phase Using Helgeson Direct
×	 Distillation Data 	Edit				Using heigeson birect
	— Thermo Method	API-8	-		>	Species ASSAY is not valid.
						Insufficient distillation data.

Note: You can change the Assay Data Type, the Average Bulk Density Type and the Thermo Method options by clicking on the white cells. This will enable a drop-down arrow that will show you the different options.

9. Click on the **Edit** button next to the Distillation Data. This will open a new window. Complete the Distillation Data using the information given in the table above. Then click **OK**.

Note: Ctrl+C and then Ctrl+V can be used to copy and paste the data in the Distillation Data table.

Percent Distilled	Temperature °C
1.00	
5.00	
10.0	
20.0	
40.0	
60.0	
80.0	
90.0	
95.0	
99.0	
100	.0 240.0

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

- 10. At this point we are ready to perform a calculation. **Add** a **Single Point** calculation, and then select an **Isothermal** calculation.
- 11. Change the *SinglePoint* name to *Assay* using the **<F2>** key
- 12. Click on the Calculate button or press the <F9> key to run the simulation
- 13. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Save the calculations of this section under the name *Hydrocarbons and Pseudocomponents.*

Analyzing the Results

We will review the results first in the Output Tab and the in the Report Tab.

1. Click on the **Output Tab**

The Output Tab shows a grid with 10 different pseudocomponents, identified with the letter P, corresponding to each distillation cut of the crude. Notice that the name of each cut is the combination of the oil name (ASSAY for this example) plus its boiling point in K.

The '+' sign adjacent to each Assay expands a sub-table that contains the critical properties of each cut. These properties are: Normal boiling point, density and molecular weight.

Variable	Value		^	Type of calculation		
	ameters			Isothermal 💌 Specs		
E Stream Amount (mol)		1055.51		- 1		
- Moles (True) - Liquid-1 (mol)		55.0810		Calc <u>u</u> late 🥝		
Moles (True) - Liquid-2 (mol)		1000.43		Summary		
Temperature (°C)		25.0000				
Pressure (atm)		1.00000		Unit Set: Metric (moles)		
√ Inflows ((mol)			Automatic Chemistry Model		
H2O		55.5082		MSE-SRK (H30+ ion) Databanks:		
P 📮 ASSAY_243K		87.6615		MSE-SRK (H3O+ ion)		
- Thermo Method	API-8			MSE (H3O+ ion) Second Liquid phase		
 Normal Boiling Point (°C) 		-30.2796		Using Helgeson Direct		
- Specific Gravity		0.717259		Isothermal Calculation		
Molecular Weight		47.1866	>	25.0000 °C 1.00000 atm		
P		82.2275		Phase Amounts		
P		200.849		Aqueous 55.0810 mol Vapor 0.0 mol		
P		173.140		Solid 0.0 mol		
P		109.658		2nd Liquid 1000.43 mol		
P ASSAY_403K		131.728		Aqueous Phase Properties		
P		110.846		pH 6.99753		
P		57.0493		lonic Strength 1.81246e-9 mol/mol Density 0.997043 g/ml		
P		35.2169		Density 0.997043 g/mi		
P		11.6247		Calc. elapsed time: 1.137 sec		
			×	Calculation complete		
nput Output						

2. Click on the **Report Tab and** scroll down to the **Species Output** table.

This table shows how the pseudocomponents are distributed between the Liquid-1 and Liquid-2 phases. Notice how the Liquid-1 (or aqueous) solubility decreases with each increasing boiling point.

np to: Species Output (True Species)	\sim	2	🎗 🔍 🔍 Cu	istomize Export
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	
ОН-1	9.98321e-8	9.98321e-8		
H3O+1	9.98321e-8	9.98321e-8		
Total (by phase)	1055.51	55.081	1000.43	

4.2. Entering Pseudocomponents to a Stream

There are times when the user does not have (or does not want to use) distillation data. Rather the user had the individual properties for a single pseudocomponent. OLI allows the user to enter the individual pseudocomponents. In the following example we will illustrate how.

Example 33: Creating Pseudocomponents

In this example, we will enter two properties - boiling point and density. The software will use one of four thermodynamic models – API-8, API-5, Cavett or Kessler-Lee – to calculate critical properties of pseudocomponents.

Starting the Simulation

- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to Crude Oil Pseudocomponents
- 3. Select the MSE-SRK thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 6. Enter the conditions of the Stream T= 15 °C and 1 atm
- 7. Change H2O from the default value to 20 moles

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

8. In the inflows grid, in the white cell below H2O, type PC1 and then press <Crtl + Enter>

Note: The <Crtl + Enter> action instructs the software to create an pseudocomponent rather than look for a species or pure component from the database.

Variable	Value	^	Add <u>C</u> alculation 🔹
	ameters		Special Conditions
Stream Amount (mol)	20.0000		
Temperature (°C)	15.0000	0 Solids Only	
Pressure (atm)	1.00000		
√ Inflows ((mol)		Summary
H2O	20.0000		Unit Set: Metric (moles)
PC1			
		1	Automatic Chemistry Model
			MSE-SRK (H3O+ ion) Databanks: MSE-SRK (H3O+ ion) MSE (H3O+ ion)

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	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:

Variable	Value		~	Add <u>C</u> alculation 🔫
Stream	n Parameters			Special Conditions
Stream Amount (mol)		1000.00		
Temperature (°C)		15.0000		Solids Only
Pressure (atm)		1.00000		Summary.
√ Infl	ows (mol)			Summary
H2O		20.0000		Unit Set: Metric (moles)
PPC1		100.000		
 Thermo Method 	API-8			Automatic Chemistry Model MSE-SRK (H3O+ ion) Databanks:
 Normal Boiling Point (°C) 		33.0000		MSE-SRK (H3O+ ion)
 Specific Gravity 		0.720000		MSE (H3O+ ion)
— Molecular Weight				Second Liquid phase Using Helgeson Direct
- PC2		200.000		
 Thermo Method 	API-8			
 Normal Boiling Point (°C) 		60.0000		
 Specific Gravity 		0.760000		
 Molecular Weight 				
Calculated Properties				
₽ PC3		250.000		
 Thermo Method 	API-8			
 Normal Boiling Point (°C) 		100.000		1
 Specific Gravity 		0.800000		
— Molecular Weight				
Calculated Properties				
⊐ PC4		250.000		
 Thermo Method 	API-8			
 Normal Boiling Point (°C) 		140.000		
 Specific Gravity 		0.850000		
— Molecular Weight				
Calculated Properties				
쿠 PC5		180.000		
 Thermo Method 	API-8			
 Normal Boiling Point (°C) 		190.000		
 Specific Gravity 		0.900000		
— Molecular Weight				
Calculated Properties				
			*	
ut				

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
	Stream Pa	arameters
	Stream Amount (mol)	1000.00
	Temperature (°C)	15.0000
	Pressure (atm)	1.00000
	√ Inflow	s (mol)
	H2O	20.0000
P	₽ PC1	100.000
	— Thermo Method	API-8
	 Normal Boiling Point (°C) 	33.0000
	 Specific Gravity 	0.720000
	 Molecular Weight 	
	Le Calculated Properties	
	 Calc:Molecular Weight 	70.3287
	 Calc:Specific Gravity 	0.720000
	 Calc:Boiling Point (°C) 	33.0000
	 Calc:Critical Temperature (°C) 	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
	L Calc:Rackett	0.277609
P	₽ PC2	200.000
	— Thermo Method	API-8
	 Normal Boiling Point (°C) 	60.0000
	 Specific Gravity 	0.760000
	— Molecular Weight	
	E Calculated Properties	
P	PC3	250.000
	— Thermo Method	API-8
		100.000

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

- 10. At this point we are ready to perform a calculation. **Add** a **Single Point** calculation, and then select an **Isothermal** calculation.
- 11. Change the *SinglePoint* name to *Pseudocomponents* using the <F2> key
- 12. Click on the Calculate button or press the <F9> key to run the simulation
- 13. It is time to save your file (File >Save as...) or using the save icon in the tool bar. Save the calculations of this section under the name Hydrocarbons and Pseudocomponents.

Analyzing the Results

1. Click on the **Report Tab and** scroll down to the **Species Output** table.

This table shows how the pseudocomponents are distributed between the Liquid-1 and Liquid-2 phases.

np to: Species Output (True Species)	~	2) 🔍 🔍 Ci	istomize Expo
Species Output (True Species)				
Row Filter Applied: Only Non Zero Values				
column Filter Applied: Only Non Zero Values				
	Total	Liquid-1	Liquid-2	
	mol	mol	mol	
PC3	250.0	1.97215e-6	250.0	
PC4	250.0	4.54519e-7	250.0	
PC2	200.0	8.03965e-6	200.0	
PC5	180.0	5.40506e-8	180.0	
PC1	100.0	1.1074e-5	100.0	
H2O	20.0	19.7405	0.259476	
H3O+1	2.40152e-8	2.40152e-8		
OH-1	2.40152e-8	2.40152e-8		
Total (by phase)	1000.0	19.7405	980.259	

Section 5. Mixers

Mixers are a useful tool to mix one or more streams. This tool allows you to mix Molecular Streams or Reconciled Streams.

♦ OLI Studio - [Mixers.oad] ■ File Edit Streams Calculations Ch □ □ □ □ □ ↓ & □ □ ↓ Navigator Mixers.oad ♦ Streams	L1 Va So L2 Re ± MMR ± Mixer		r	- c	×
- ∲ Stream-1 - ∲ Stream-1 - ∰ Mixer	Available Streams Stream - [AQ] Stream 1 - [AQ]	Selected		Mixing Method Single Point Mix Sp Single Point Mix Volume Ratio Multiplier Stummary	ecs
	Variable Multiplier Total Inflow	Value Stream Parameters		Need at least 1 input stream.	^
Actions	Temperature (°C) Pressure (atm) Input Advanced Search	25.00 1.000 Add as Stream Export	_		~
Save					
For Help, press F1				2	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.

5.1. Mixing Options (Definitions)

The Mixer Object has four different mixing options: Single point mix, Volume, Ratio, and Multiplier. A quick summary of what each mixing options allows you to do is summarized here.

Single Point Mix

This option allows you to multiply up or down a stream inflow. When selecting the streams to mix, this option will enable the multiplier option for both streams. You can leave the default values that are set by default to 1.0 or change the multiplier values to any other number.

Volume

In this option, one stream stays at a constant volume, while the other stream's volume changes within a range specified by the user, as is illustrated in the table below:

Stream 1	Stream 2
1 L	1 L
1 L	2 L
1 L	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 2×0
1	Stream 2×1
1	Stream $2 \times n$

5.2. A Basic Mixer Calculation

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

Example 34: Calculating the Heat of Mixing

You will mix 1 L of a 10 wt% Ca(OH)₂ solution with 1 L of a 10% HCl solution, and then you will ask the software to calculate the **heat of mixing** and **the final temperature** of the mixture.

Starting the Simulation

In this example we need to create two different streams: a 10 wt% Ca(OH)₂ solution and a 10% HCl solution.

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

Basic Mixing Calculation						
1 st	Stream	2 nd 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 ℃			
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.
- 2. Press **<F2>** to rename the mixer to *Basic Mixing*

Notice that the display layout for the Mixer tool is slightly different. There are two different windows (see image below).

- The first window displays all possible streams available for the mix calculation. There is no limit to the number of streams to be mixed.
- The second window allows you to change the mixing conditions, e.g. temperature, and pressure of the mixing.

OLI Studio - [Mixer calculations.oad*]			_	
File Edit Streams Calculations Chemist	ry Tools View Window Help			- 8 ×
🗈 🚅 🖬 X 🖻 💼 🚑 🤋 📢 🚺	Va So L2 Re ± MSE ± MSE ± AGA ±	🚧 🎬 🛃 💱 🔊 😭 😽		
Navigator + ×				
Water Analysis Calculations.oad	A Basic Mixing			
Hydrocarbons and Pseudocomponents.oad	🦪 Description 🔯 Definition 🛍	Plot 👼 Report		
Mixer calculations.oad*	Available Streams		Mixing Method	
🏘 Streams	Ca(OH)2 · [MSE]	Selected		Specs
👌 Ca(OH)2	Luci niori	>>		opeca
HCI		<<	Type of calculation	
Basic Mixing			Isothermal 👻	
	Window that displ		Calculate 🥝	
	streams availa	ible for mixing		
			Summary	
	Variable	Value ^		~
	Multiplier		Need at least 1 input stream.	
	Total Inflow	Parameters		
	Temperature (°C)	25.0000		
Actions	Pressure (atm)	1.0000		
Actions			>	
	Window that allow			
	the mixing of	conditions		
Plot Template Manager 📮 🔺 🗙				
		~		
	Input			
				\sim
Save	Advanced Search Add as St	ream Export		
	-			
Calculation Complete!				al. b.t
For Help, press F1			🥝 🗉	

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

🞺 Des	cription 🧕	Definiti	on 🛍 Pi	lot 髮 Report			
Availab	le Streams		>>> <<	Selected Ca(OH)2 HCI			Mixing Method Single Point Mix Specs Type of calculation Isothermal Calculate Summary
	Variable	Value	Ca(OH)2	HCI	^		
M	ultiplier		1.00000	1.00000			Unit Set: Metric (moles)
			Stream P	arameters			Automatic Chemistry Model
Т	otal Inflow		1000.00 g	1000.00 g			MSE (H3O+ ion) Databanks: MSE (H3O+ ion)
Т	emperature (°C)	25.0000	25.0000	25.0000			Using Helgeson Direct
P	ressure (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.

5. Click on the **Type of Calculation** button and select the **Adiabatic** calculation option

Note: Once the streams for the mixing have been selected, notice that the multipliers of both streams: Ca(OH)2 and HCl can be edited. This specific calculation will be carried out at a constant pressure of 1 atm, and the final temperature of the mixture will be calculated.

vailable Streams	×	Ca(OH)2 HCI	Selected Ca(DH)2 HCI			Mixing Method Single Point Mix Specs Type of calculation Adiabatic Calculate Summary		
Variable Multiplier Total Inflow Temperature (*C) Pressure (atm)	Value Stream 25.0000 1.00000	Ca(OH)2 1.00000 Parameters 1000.00 g 25.0000 1.00000	HCI 1.00000 1000.00 g 25.0000 1.00000	<	>	Unit Set: Metric (moles) Automatic Chemistry Model MSE (H3O+ ion) Databanks: MSE (H3O+ ion) Using Helgeson Direct Isenthalpic Calculation 0.0 cal 1.00000 atm Single Point Mix Calculation not done		

- 6. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
- 7. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it and name it as *Mixer Calculations*.

Analyzing the Results

Review the Summary Box. After mixing these two streams, the temperature increased from 25 °C to approximately 48.65 °C at a constant pressure of 1 atm. This indicates that the enthalpy (or heat) of mixing is exothermic, and the software calculated this value to be approximately -7.25×10⁶ calories.

5.3. A Titration Experiment

In this example, you will explore the volume mixing option to recreate a titration experiment. As we go through the example, different functionalities, reporting and plotting for the *Mixer tool* will be introduced.

Example 35: HF Titration with CaCl₂

In this example, first, we will create two new streams, a 0.1 m HF solution and a 0.1 m $CaCl_2$ solution. What is the pH of these individual streams?

Second, we will mix these two streams in equal amounts. What is the final pH of the mixture?

And finally, the 0.1 m HF solution will be titrated with a 0.1 m CaCl2 solution. What will the titration curve look like?

Starting the Simulation

For this example, we need to create two different streams: a 0.1 m HF solution and a 0.1 m CaCl2 solution.

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

Titration Calculation						
1 st	Stream	2 nd 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 ℃			
Pressure	1 atm	Pressure	1 atm			
H2O	55.5082 moles	H2O	55.5082 moles			
HF	0.1 moles	CaCl2	0.1 moles			

Calculating the pH of the individual streams

- 1. Add a Single Point Isothermal calculation for each stream
- 2. Change the name to pH 0.1 m HF and pH 0.1 m CaCl2 respectively using the <F2> key
- 3. Calculate the isothermal calculation for each stream
- 4. Check the pH values of the individual streams in the Summary Box

Results – pH of the individual streams

pH 0.1 m HF	pH 0.1 m CaCl2
2.13	6.82

Calculating the pH of the Mixture

- 5. After creating the streams, **Add a Mixer.** The Mixer object can be accessed from the Menu Bar by selecting Calculations > **Add Mixer** or by selecting the **Add Mixer** in the Actions Pane.
- 6. Press **<F2>** to rename the mixer to *Titration*

Note: Notice that the Available Streams window is showing all the available streams for the mixing calculation. Also notice that this window is showing both: *Streams* and *Single Point calculations*. Additionally, in front of the name of the available streams, the thermodynamic framework appears within brackets, e.g. AQ, MSE or MSE-SRK. This is important because in order to carry out mixing calculations, the selected streams need to use the same thermodynamic framework.

< Description 🧕 Definit	ion 🛍 Plot 📓 Report
Available Streams Ca(OH)2 - [MSE] HCI - [MSE] 0.1 HF - [AQ] 0.1 CaCl2 - [AQ] Basic Mixing - [MSE] pH 0.1 HF - [AQ] pH 0.1 CaCl2 - [AQ]	Selected

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

ø	Description 🧕	Definiti	on 🛍 Plot 📓 F	leport			
P	wailable Streams H 0.1 HF - [AQ] H 0.1 CaCl2 - [AQ]		0.	lected 1 HF 1 CaCl2			Mixing Method Single Point Mix Specs Type of calculation Isothermal Calculate Summary
Г	Variable	Value	0.1 HF	0.1 CaCl2	^		
Г	Multiplier		1.00000	1.00000			Unit Set: Metric (moles)
			Stream Parameters	3			Automatic Chemistry Model
	Total Inflow		55.6082 mol	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

- 11. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
- 12. At this point is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save under the same file that we created before named as *Mixer Calculations*.
- **13. Check** the pH values of the individual streams in the **Summary Box**

Results - pH of the individual streams

The resultant pH is 1.44. How can this be? An acid stream (the HF stream had a pH of approximately 2.13) and a nominally basic stream (the CaCl₂ 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 CaCl₂.

Titrating HF with CaCl₂

14. Change the Single Point Mix as the Mixing Method to the Volume option.

Note: You will receive a warning message: Need 1 stream selected as the variable stream (Specs...)

15. Click on the Specs button. This will open a new window indicating you to select the Stream to vary16. In the Select Stream tab Select the 0.1m CaCl2 stream

Volume Survey Options		?	\times
Category Variable - Volume Calculation Options	Select Stream Select inlet str 0.1 CaCl2 0.1 HF		

17. Select the Survey Range tab. Change the Volume Range from 0 L to 1 L.

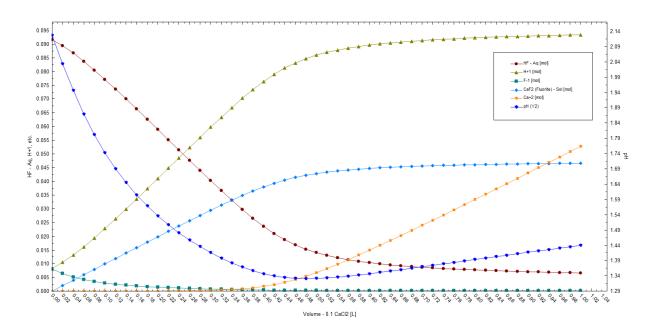
18. Change the Number of Steps to 50. Then click OK.

Volume Survey Options		?	Х
Category	Select Stream Survey Range		
Calculation Options	Volume Range Unit: L Selected Range 0.0 to 1.0 in 1 steps of 1.0	New Delete	
	Linear O Log O Point List		
	End Points Start 0.0 End 1.00000		
	Step Size Increment 1.00000 O Number Steps 50 O	other is	
	OK Cancel Apply	Help	

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

Titration Results and Plotting

- 1. Click on the Plot tab. Note: You will see an empty plot, since we need to define the variables that we want to report.
- 2. Click on the Variables button and expand the Aqueous section. Select and put the following species in the Y1 axis using the >> button: HF-Aq, H+1, F-1, Ca+2. Expand the Solid section and select CaF2(s).
- 3. Next, expand the **Additional Parameters** Section and Select **pH**. Put it in the **Y2 Axis** using the >> button. Then click **OK**.



As you can see, adding CaCl₂ 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 CaCl₂ 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 CaCl₂ in solution, more CaF₂ is formed. As a result, the molecular HF decreases, because it dissociates in order to maintain the equilibrium, by producing more F^- ions. This shifts the following equilibrium to the right:

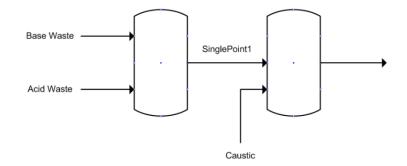
$$HF \leftrightarrow H^+ + F^-$$

This causes an increase of H^+ in solution, and as a result a decrease in the pH. At some point, at around 0.48 L of 0.1 m CaCl₂, the solid reaches a steady value, indicating that the solid has reached its saturation value.

5.4. Cascading Mixers

Example 36: Cascading Mixers

In this example, we will mix two streams, one basic and one acidic, and mix them together under adiabatic conditions. The output of this mixer will then be used as the input to a second mixer where a new caustic stream is added. The schematic in the figure below illustrates the layout.

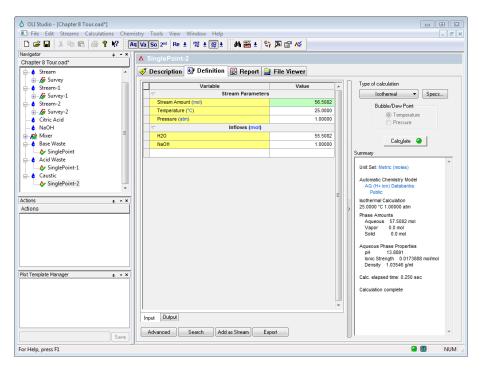


For this example, we need to create three streams. You have already done this in other examples, so we will only give you the input data (for all streams, we will use the AQ – default – thermodynamic framework)

Parameter	Value	Units
Stream Name	Base Waste	
Temperature	25.0	°C
Pressure	1.0	Atmospheres
Stream Amount	55.5082 (Default)	Mole
H ₂ 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 ₂ O	55.5082	Mole
HCI	0.1	Mole
H2SO4	1.0	Mole
Stream Name	Acid Waste	
Temperature	25.0	°C
Pressure	1.0	Atmospheres
H ₂ 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 Figure 0-6 below:



Now we are ready to begin. Click on the "Streams" at the top of the tree-view in the left-hand window and then select Add Mixer from the actions panel.



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

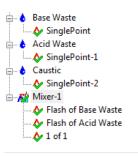
Mixer-1 🖉 Description	Definition 🛍 Pla	ot 😡 Report 📄 File Viewe	r
Available Streams		Selected	Mixing Method
Stream Stream-1 Stream-2 Citric Acid NaOH Caustic Mixer - [AQ] SinglePoint-1 - [AQ] SinglePoint-1 - [AQ]		Base Waste Acid Waste	Single Point Mix Specs Type of calculation Adiabatic Bubble/Dew Point Type of calculation Pressure Pressure

Let's calculate this mixer. Click the Calculate button. If everything is set up correctly the resultant mixed pH should be approximately 0.3.

In the stream tree-view panel, locate your mixer and click the "+" sign.

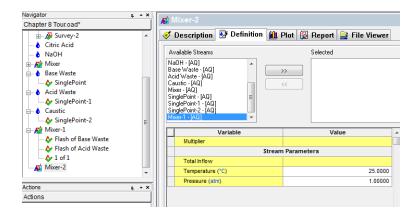


Click the "+" sign to expand the tree.



You can see that the program has performed an equilibrium calculation on each of our input streams as well as calculated the mixer. The results of the mixer are stored in the object "1 of 1".

We will now add a second mixer from the actions panel.



When we add a subsequent mixer, we will see all of our previous objects still displayed. It is possible to reuse a stream that we already used (this is not possible in OLI's other simulators such as OLI Flowsheet.) We want to connect the output from our first mixer (Mixer1) to the inlet of the <u>Caustic</u> stream. Click the object Mixer1-(AQ) as highlighted in Figure 0-11 above.

🛷 Description 🔮	Definition 🛍 P	lot <u> </u> Report	🚽 File Viewer		
Available Streams		Selected			Mixing Method
Stream	^	Mixer-1			Single Point Mix 🔻 Specs
Stream-1 Stream-2		> Caustic			Type of calculation
Citric Acid NaOH	= <	<			Isothermal 🔻
Base Waste					Bubble/Dew Point
Acid Waste Mixer - [AQ]					 Temperature
SinglePoint - [AQ]	-				O Press <u>u</u> re
Variable	Value	Mixer-1	Caustic 4	-	- 1
Multiplier		1.00000	1.00000		Calc <u>u</u> late 🥥
	Stream	Parameters			Summary
Total Inflow		113.236 mol	56.5082 mol		A
Temperature (°C)	25.0000	25.0000	25.0000		Unit Set: Metric (moles)
Pressure (atm)	1.00000	1.00000	1.00000		Automatic Chemistry Model

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

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

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

Variable	Value	Mixer-1	Caustic		
Multiplier		1.00000	2.40000		
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 12.4.

The real value of the cascading mixer is the quick ability to re-calculate the objects if we want to change something. Let's add some diethanolamine to the series of calculations. Click the **Acid Waste** stream (not the single point calculation below it) and add the component DEXH⁷ to the grid with a value of 10.0 moles.

🖮 👌 Stream		
🗄 🔥 Stream-1	Variable	Value
🖶 💧 Stream-2	Stream Parameters	
Citric Acid	Stream Amount (mol)	66.6082
NaOH	Temperature (°C)	25.0000
🖅 🙀 Mixer	Pressure (atm)	1.00000
🔄 🔥 Base Waste	Inflows (mol)	
↓ SinglePoint	Water	55.5082
🗐 👌 Acid Waste	Hydrogen chloride	0.100000
▲ SinglePoint-1	Sulfuric(VI) acid	1.00000
🗐 🕹 Caustic	DEXH	10.0000
SinglePoint-2		

⁷ This is the OLI Tag name for diethanolamine, which is easier to type if you know the name.

Return to the last mixer you created (Mixer-2 in our example) and then reduce the *Caustic Multiplier back to* **1.0**

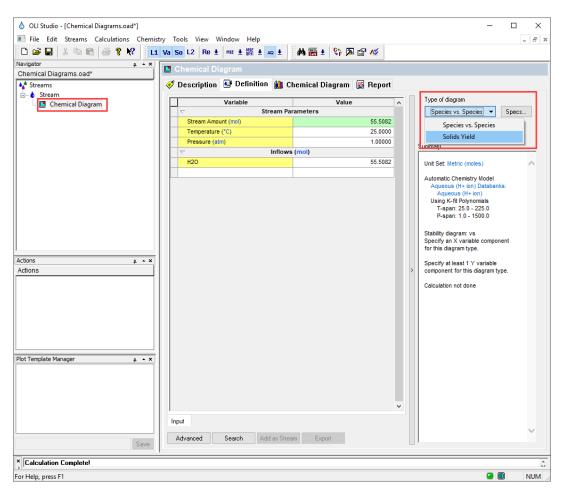
To recalculate all the objects at once, press the control+F9 keys and all objects will be calculated. Now if you look at the summary of Mixer2 you will see that the pH has changed to approximately 10.

🛃 N	/lixer-2						
🦪 I	Description	🥸 Definition	🛍 Plot 📓	Report			
Str Str Citr Na Ba: Aci	vailable Streams eam eam-1 eam-2 ric Acid 00H se Waste se Waste ser - [AQ] glePoint - [AQ]		Selected Mixer-1 Caustic	I			Mixing Method Single Point Mix Specs Type of calculation Isothermal Calculate Summary
	Variable	Value	Mixer-1	Caustic			
Н	Multiplier	Value	1.00000	1.00000			Unit Set: Metric (moles)
		Stream	Parameters				Automatic Chemistry Model
H	Total Inflow		123.236 mol	56.5082 mol			AQ (H+ ion) Databanks:
	Temperature	25.0000	25.0000	25.0000			Public
	Pressure (at	1.00000	1.00000	1.00000			Isothermal Calculation 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
					-		Calc. elapsed time: 0.582 sec
Inp	put				Ŧ		Calc. elapsed time: 0.582 sec Calculation complete

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"⁸.

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.



⁸ Santucci, R.J., McMahon, M.E. and Scully, J.R., 2018. Utilization of chemical stability diagrams for improved understanding of electrochemical systems: evolution of solution chemistry towards equilibrium. npj Materials Degradation, 2(1), p.1.

6.1. Building a Chemical Diagram

In this section, first we will go through the steps of building a basic chemical diagram, and then we will explore how the concentration of species and other variables such as temperature and pressure have a significant influence on the stability of chemical species.

Example 37: La(C2H₃O₂)₃ – K₃PO₄ 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 ₃ O ₂) ₃ – K ₃ PO ₄ Chemical Diagram				
Calculation Settings Stream Composition and Conditions				
Stream Name	Chemical Diagrams	Stream Amount	Calculated	
Name Style	Display Formula	Temperature	25 ℃	
Unit Set	Metric, Batch, Moles	Pressure	1 atm	
Framework	AQ	H2O	55.5082 moles	
Type of Calculation	Chemical Diagram	La[C2H3O2]3	0.1 moles	
		K3PO4	0.1 moles	
		HNO3	0.0 moles	
		NaOH	0.0 moles	

- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to Chemical Diagrams
- 3. Select the **AQ** thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 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
- 8. Select Species vs Species as Type of Diagram Default
- 9. Change the *Chemical Diagram* name to *Lanthanum/Phosphate* using the <F2> key

♦ OLI Studio - [Chemical Diagrams.oad*] ■ File Edit Streams Calculations Chemistry Tools Vie □ <td< th=""><th></th><th>🗄 ± 🛟 🔊 😭 🖉</th><th> ×</th></td<>		🗄 ± 🛟 🔊 😭 🖉	×
Navigator + * X		u ≖ ¢F two ⊞, n⊗	
Chemical Diagrams.oad*	Lanthanum/Phosphate		
♦ Streams	< Description 🧕 Definition	🚹 Chemical Diagram 📓	Report
🖕 👌 Chemical Diagrams			
Lanthanum/Phosphate	Variable	Value ^	Type of diagram
	Stream Pa		Species vs. Species 🔻 Specs
	Stream Amount (mol)	55.7082	Citata A
	Temperature (°C)	25.0000	Calculate 🥥
	Pressure (atm)		Summary
	Use Single Titrant	No	Unit Cate Matrix (malas)
	pH Acid Titrant	HNO3	Unit Set: Metric (moles)
	pH Base Titrant	NaOH	Automatic Chemistry Model
			Aqueous (H+ ion) Databanks: Aqueous (H+ ion)
	H2O	55.5082	Using K-fit Polynomials
	La[C2H3O2]3	0.100000	T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0
Actions a • ×	K3PO4	0.100000	-span. 1.0 - 100.0
Actions	HNO3	0.0	Stability diagram: La[C2H3O2]3 vs pH
Actions -	NaOH	0.0	User-selected titrants Acid: HNO3
			Base: NaOH
Plot Template Manager a * *		~	Range on La[C2H3O2]3: 1.00000e-14 to 1.00000 mol Range on pH: 0.0 to 14.0000 Subsystems Lanthanum Calculation not done
Save	Input Advanced Search Ad	d as Stream Export	~
x .			 Image: Control of the second se

- 10. Click on the Specs button. This will open the Chemical Diagram Options window
- 11. In the **Display Choices** tab, select the **No Aqueous lines** button and check the box for **Lanthanum** as the subsystems to display

Chemical Diagram Options		?	' ×	(
Category	Display Choices			
- Display Axes	Aqueous and Solid Lines Superimpose lines No Aqueous lines Only Aqueous lines Display Subsystem Potassium	Shading No shading Shade selected subsyste	m	
	Foldsstum Sodum Nitrogen Phosphorus			
	ОК	Cancel Apply	Help	

- 12. Click on the **Axes** category. The dialog changes to display the **X Axis** tab.
- 13. In the **Variable** section select the **pH** option. Leave the default **pH Range**: 0-14. This also enables the **Titrants** button.

Chemical Diagram Options		?	×
Chemical Diagram Options Category Display Axes	X Axis Y Axis Variable Species Amount PH Titrants PH Range Start 0 End 14 Log scale	? Species Inflow Mide Related Inflows H2O HNO3 K3PO4 La[C2H3O2]3 NaOH	
	ОК	Cancel Apply	Help

14. Click on the **Titrants** button. Select **HNO3** as the **acid titrant** and **NaOH** as the **base titrant**. Then click **OK**.

Note: These titrants were added in the stream definition, and that's why they appear as possible titrants.

Select Titrants	? ×
Titrants	
Hide Related Inflows	New Inflow
Acid	Base
H2O HNO3 K3PO4 La[C2H3O2]3 NaOH	H2O HNO3 K3PO4 La[C2H3O2]3 NaOH
Select the acid and the base which w	ill be used to vary the pH.
OK Can	cel Apply Help

- 15. Select the Y Axis tab. Select the Species Amount button as the variable to change
- 16. Select La[C2H3O2]3 and K3PO4 species
- 17. For the Inflow Range keep the default range: from 1E-14 to 1.0 moles on a log scale.
 Note: This means we will have initially 1.0E-14 moles of La(C₂H₃O₂)₃ and 1.0E-14 moles of K₃PO₄
 - increasing equally until we have 1.0 moles of each.
- 18. Click **OK**

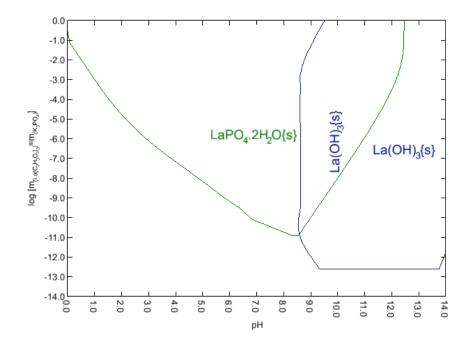
Chemical Diagram Options		?	×
Category Display Axes	X Axis Y Axis Variable Species Amount ○ Temperature Inflow Range Start 1e-014 mol End 1 mol ✓ Log scale Start 1e-014 mol	4) e Related Inflows	
	OK Cancel	Apply H	lelp

- 19. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 20. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it and name it *Chemical Diagrams*.

Anaylyzing the Results

Click on the **Chemical Diagram** tab (**Chemical Diagram**). This tab displays the Species vs pH diagram for the Lanthanum species.

The X axis of the diagram is pH, varied by adding HCl or NaOH, and the Y axis variable is the concentrations of La(C2H3O2)3 and K3PO4, held at a 1:1 molar ratio. From this figure, we can see that at room temperature there is a large pH range over which lanthanum phosphate will be the thermodynamically stable product. As pH increases, and more OH⁻ ions are present, La(OH)3 begins to form. The pH range in which La(OH)3 forms is the right bounded region in the diagram. The area below the lines is where only aqueous species exist.



Example 38: Adding 50% Lanthanum Acetate

In this second example we will add 50% more to the lanthanum acetate species and see the effect of this increase in concentration on the chemical diagram.

Starting the Simulation

- 1. **Copy** the *Lanthanum/Phosphate* chemical diagram calculated in the Example 37: La(C2H₃O₂)₃ K₃PO₄ Chemical Diagram, and **paste** it under the *Chemical Diagrams* stream.
- 2. Change the name to *Lanthanum 50% increase* using the **<F2>** key
- 3. Change the Lanthanum Acetate amount to 0.15 moles

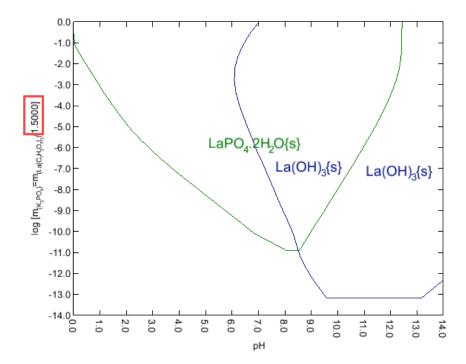
	1		– – ×
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	Chemistry Tools View Window Help		_ & ×
🗅 🚅 🖬 👗 🖻 🛍 🥌 💡 🌾	L1 Va So L2 Re ± MSE ± SSK ± AQ ±	🛃 🚟 🛨 💱 🔊 😭 🎸	
Navigator + • ×	Lanthanum 50% increase		
Chemical Diagrams.oad*			
• Streams	< Description 🛃 Definition 🛍 Chem	ical Diagram 📓 Report	
Chemical Diagrams Unthanum/Phosphate	Variable	Value	Type of diagram
Lanthanum/Phosphate	Stream Par		Species vs. Species 💌 Specs
	Stream Amount (mol)	55.7582	
	Temperature (°C)	25.0000	Calc <u>u</u> late 🥝
	Pressure (atm)	1.00000	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:
	H20	55,5082	Aqueous (H+ ion) Using K-fit Polynomials
	La[C2H3O2]3	0.150000	T-span: 25.0 - 225.0
1	K3P04	0.100000	P-span: 1.0 - 1500.0
Actions # * X	HNO3	0.0	Stability diagram: La[C2H3O2]3 vs pH
	NaOH	0.0	User-selected titrants Acid: HNO3
	▼		Base: NaOH
			Baaaa aa Lar(2011202)20
			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
	1	×	
	Input Output		
			\sim
Save	Advanced Search Add as Stream	Export	
Calculation Complete!			^
			¥
For Help, press F1			Image: State of the state of

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

Anaylyzing the Results

Click on the **Chemical Diagram** tab (**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 second example we will add 50% more to the lanthanum acetate species and see the effect of this increase in concentration on the chemical diagram.

Starting the Simulation

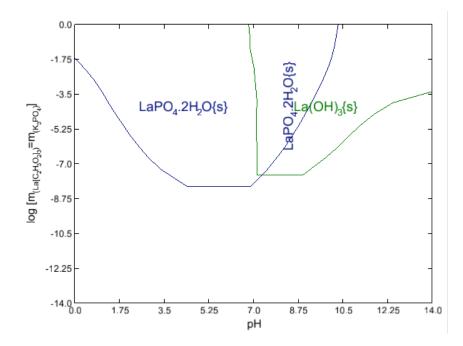
- 1. **Copy** the *Lanthanum/Phosphate* chemical diagram calculated in the Example 37: La(C2H₃O₂)₃ K₃PO₄ Chemical Diagram, and **paste** it under the *Chemical Diagrams* stream.
- 2. Change the name to Lanthanum HTHP using the <F2> key
- 3. Change the temperature to 200 °C and the pressure to 25 atmospheres

OLI Studio - [Chemical Diagrams.oad*]]				– 🗆 ×
File Edit Streams Calculations	Chem	istry Tools View Window Help			_ & ×
🗄 🗅 🚅 🖬 🛛 X 🖻 🛍 🦪 🤗 💔	L	1 Va So L2 Re ± MSE ± MSE ± AQ ±	🖌 🛗 🛨 💱 🔊 😭 🎸		
Navigator + ▲ ×	1.1.			_	
Chemical Diagrams.oad*		anthanum HTHP			
♦ Streams	ا 🃎	Description 📑 Definition 🛍 Chem	ical Diagram 📓 Report		
🗄 🗄 Chemical Diagrams				_	Type of diagram
🐶 Lanthanum/Phosphate	Ц	Variable	Value	^	
Lanthanum 50% increase		Stream Par			Species vs. Species 💌 Specs
Lanthanum HTHP		Stream Amount (mol) Temperature (°C)	55.7082		Calculate 🥥
		Pressure (atm)	25.0000		
		Calculation P		4	Summary
		Use Single Titrant	No v	1	Unit Cat. Matrix (malas)
		pH Acid Titrant	HNO3	4	Unit Set: Metric (moles)
		pH Base Titrant	NaOH		Automatic Chemistry Model
					Aqueous (H+ ion) Databanks: Aqueous (H+ ion)
		H2O	55.5082		Using K-fit Polynomials
		La[C2H3O2]3	0.100000		T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0
Actions		K3P04	0.100000		P-Span. 1.0 - 1500.0
Actions		HNO3	0.0		Stability diagram: La[C2H3O2]3 vs pH
		NaOH	0.0		Auto-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 not done
				¥	
	-				
	Inp	u			
	A	dvanced Search Add as Stream	Export		· · · · · · · · · · · · · · · · · · ·
Save					
× SHOTTST IIIIBIICU.					^
Calculation Complete!					Ç.
Ear Halp, proce E1					
For Help, press F1					NUM //

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

Anaylyzing the Results

Click on the **Chemical Diagram** tab (**Chemical Diagram**). This figure shows the stability diagram for La(C2H3O2)3 and K3PO4 over a range of pH values at 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. A brief definition of each type of calculation is given below.



Add Stability Diagram

Stability Diagram is used to predict the stability of metals, metal ions, oxides, etc. as a function of T, P and solution composition. With this tool you can draw conclusions about the ranges of immunity to corrosion, possible passivation and dissolution of metals in the presence of species that promote or inhibit corrosion.

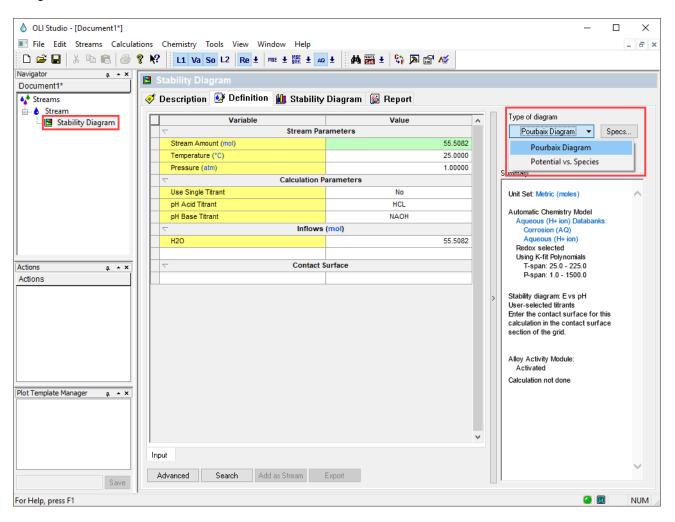


Corrosion Rates is used to predict the general corrosion rate, the propensity for localized corrosion (pitting or crevice corrosion) to occur, polarization curves, and heat treatment effects of metallic materials at one specific equilibrium state. The effects of temperature, pressure, pH, concentration of species, and velocity on corrosion are also included.

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

Section 7. Stability Diagrams

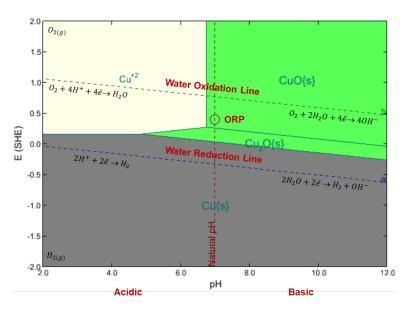
In this section you are going to learn how to set up a Stability Diagram and how to interpret the results when using this tool.



7.1. How to Interpret a Stability Diagram

A Stability Diagram also known as Pourbaix Diagram or simply Potential vs pH diagram, maps out the possible stable species in an aqueous environment at different pH and potential combinations. This diagram, however, does not provide information of reaction rates or kinetic effects.

A schematic representation of the Pourbaix diagram for copper in water at 25 °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 Cu₂O as the solid phases produced by oxidation of Cu.

The light-yellow color represents the corrosion region. It is the stability field(s) of dissolved (ionic or neutral) metal species in which neither the metal nor passivating solids are stable. In the plot above, Cu^{2+} is the ionic species that is the most stable.

The diagonal dashed lines, represented by the letters a and b are the water reduction and water oxidation lines, respectively.

Below the water reduction line (a): Water decomposes to form H_2 gas. Above the water oxidation line (b): Water decomposes to form O_2 gas. The region within these lines (a and b) is called the stability region of water.

The lines that divide different species in the Pourbaix diagram show the equilibrium conditions. These lines represent the equilibrium for chemical and electrochemical reactions.

Finally, as a reference, the values of the Natural pH and the Oxidation Reduction Potential (ORP) are superimposed on the diagram. The natural pH line of the water sample is the water's computed pH before it is adjusted using with acid or base to create the diagram. The ORP is represented by the red circle and indicates the initial electrochemical potential of the water phase. This is the value before the potential is adjusted using a potentiostat, for example.

7.2. How to determine if corrosion in the absence of oxygen is possible?

In the absence of oxygen, the most common reduction reaction is the reduction of the proton to elemental hydrogen (as shown by line **a** in the plot below). Depending of the pH that reactions that can occur are the following:

Acidic:
$$H^+ + 2\bar{e} \rightarrow H_2$$

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

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.

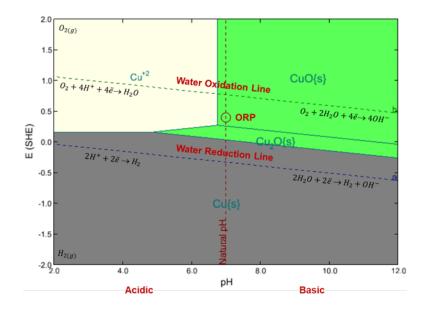
In oxygen-containing solutions, O_2 can be reduced to H_2O (as shown by line **b**). Depending of the pH that reactions that can occur are the following:

Acidic:
$$O_2 + 4H^+ + 4\bar{e} \rightarrow H_2O$$

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

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

7.3. Building a Pourbaix Diagram

Example 40: Pourbaix Diagram of Fe-H2O System

After completing this example, you will learn how to set up a Pourbaix Diagram using the **Stability Diagram** tool.

Starting the Simulation

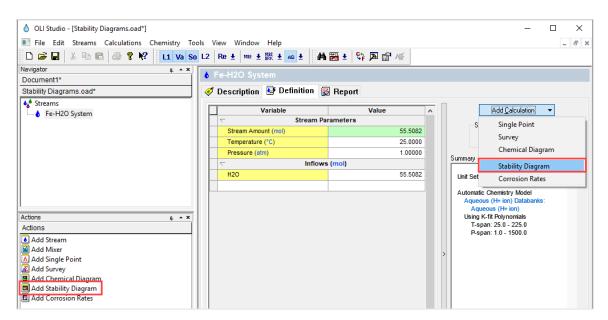
To start the software, double-click the OLI Studio icon on the desktop, which will take you to the OLI Studio interface where you can start creating your calculations.



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 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	2-12
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe		

- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to Fe-H2O System
- 3. Select the **AQ** thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 6. Enter the composition, temperature and pressure of the stream given in the table above
- 7. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane.



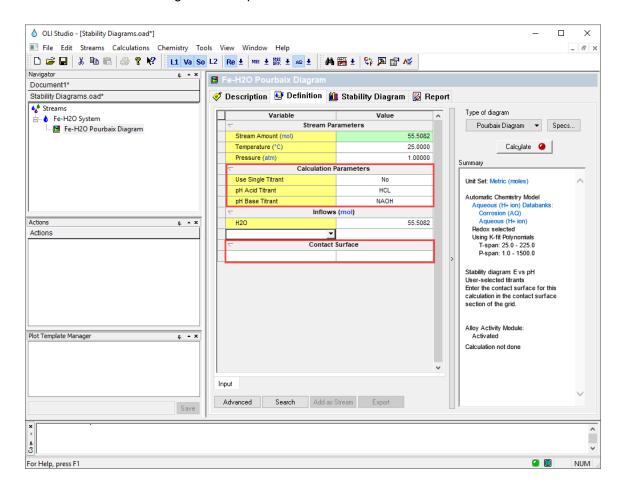
- 8. Select Pourbaix Diagram as Type of Survey Default
- 9. Click on the new Stability Diagram and press <F2> to change the name to Fe-H2O Pourbaix Diagram

Note: Notice that two new sections appear in the **Definition** tab: **Calculation Parameters** and **Contact Surface** grids. Additionally, the Redox button is turned ON.

In the **Calculation Parameters** grid is where the pH titrants need to be defined. These default pH titrants selected by default are 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.



- 10. Leave the default titrants for this calculation: HCl and NaOH
- 11. Under the Contact Surface grid type Fe

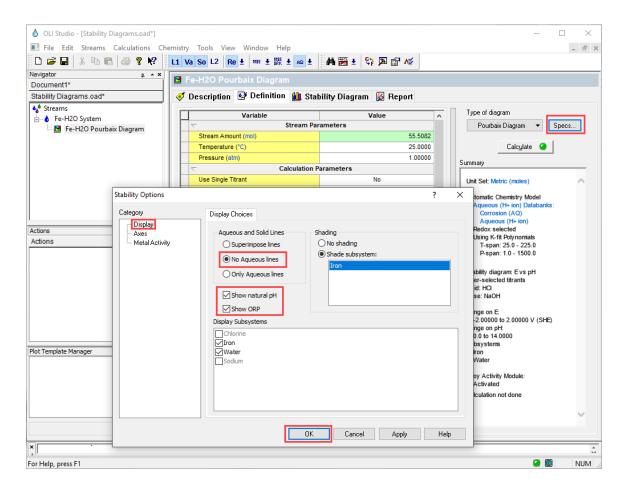
Note: You also have the option to use the drop-down arrow to search for the metal or alloy of interest.

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	Temperature (°C)	25.0000	Calculate 🥝	
	Pressure (atm)	1.00000		
	Calculation I		Summary	
	Use Single Titrant	No	Unit Set: Metric (moles)	~
	pH Acid Titrant	HCL		
	pH Base Titrant	NAOH	Automatic Chemistry Model Aqueous (H+ ion) Databanks:	
J	☐	s (mol)	Corrosion (AQ)	
Actions # * ×	H20	55.5082	Aqueous (H+ ion)	
Actions			Redox selected Using K-fit Polynomials	
	Contact	Surface	T-span: 25.0 - 225.0	
	Fe 💌		P-span: 1.0 - 1500.0	
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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*	🛷 Description 🧕 Definition 🛍 Stability	Di El D	
Streams		• •- •	Type of diagram
🛓 🔥 Fe-H2O System	Variable	Value	
Fe-H2O Pourbaix Diagram	Stream Parame		Pourbaix Diagram 🔻 Specs
	Stream Amount (mol)	55.5082	
	Temperature (°C)	25.0000	Calc <u>u</u> late 🥥
	Pressure (atm)	1.00000	Summary
	Calculation Para		
	Use Single Titrant	No	Unit Set: Metric (moles)
	pH Acid Titrant	HCI NaOH	Automatic Chemistry Model
	pH Base Titrant		Aqueous (H+ ion) Databanks:
	H20	55.5082	Corrosion (AQ) Aqueous (H+ ion)
	HCI	0.0	Redox selected
	NaOH	0.0	Using K-fit Polynomials
	Fe	0.0	T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0
tions + • ×	re	0.0	
ctions	Contact Surface	(mol)	Stability diagram: E vs pH
	Fe	. (mon)	User-selected titrants Acid: HCI
	16		Base: NaOH
			Range on E: -2.00000 to 2.00000 V (SHE)
			Range on pH:
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- 15. Click on the Specs button. This will open the Stability Diagram Options Window
- 16. Under the **Display** Category you will see the **Display Choices** tab. Under this tab make sure to select the following options:
 - i. No Aqueous lines
 - ii. Show natural pH
 - iii. Show ORP
- 17. Under **Display Subsystems** check the **Iron** and **Water** boxes
- 18. Under Shading select the option Shade Subsystem and select Iron.
- 19. Click OK to close the window



20. Click on the Axes Category. This will show you the Plot Variables tab.

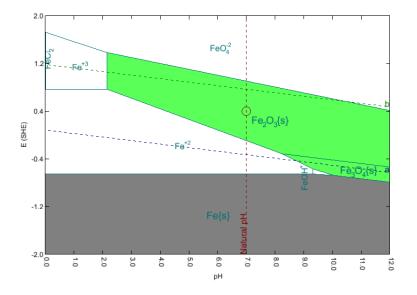
Note: In the **Axes** Category you can modify the axes of the Pourbaix Diagram and change the default titrants.

Stability Options		? ×
Category Display Axes Metal Activity	Plot Variables X Axis pH Range Start End 12 Titrants pH Titrants	YAxis Potential Range Start -2 V (SHE) End 2 V (SHE)
	OK	Cancel Apply Help

- 21. Change the X Axis or pH range to 2-12
- 22. Leave the default values for the Y Axis of Potential Range (-2 to 2 V SHE)
- 23. Click **OK** to close the window
- 24. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 25. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it and name it as *Stability Diagrams*.

Analyzing the Results

Click on the **Chemical Diagram** tab (Use 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⁺². If the pH is above 10, the boundary is at a lower potential for example, -0.7 V SHE at 12 pH.

The software computes that Fe₃O₄ (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 Fe₂O₃ (hematite). Hematite is the dehydrated form of Fe(OH)₃ and FeOOH, two forms of rust. These phases provide less corrosion protection the iron surface than the magnetite. These two phases are represented in the plot by the green color.

The white sections of the plot represent the dominant iron-containing species dissolved in solution. The species with the largest range is Fe^{+2} . The software computes stability for this species from -0.6 V to 0.77 V SHE, at low pH, and it is no longer stable at pH 10. Active corrosion of the iron surface is predicted if the pH is between 0 and 10. The actual corrosion rate cannot be predicted from this plot, nor can the pH of the water film (diffusion layer) in contact with the iron surface. Therefore, the pH range of 0 to 10 is a guideline and not a direct prediction.

The natural pH and the oxidation reduction potential (ORP) of water, which is represented by the red circle, are showing that when placing Fe in pure water at 25 °C and 1 atm. The point at which the natural pH and the ORP intersects (7 pH, 0.4 V SHE) indicates that Fe₂O₃ (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. Fe²⁺.

7.4. Selective Oxidation and Reduction Chemistry

Occasionally you may want to remove a specific oxidation state for an element when building a Stability Diagram. There are a variety of reasons to perform such an activity, one being that a specific oxidation state may be kinetically unavailable for the reaction. Another case is that perhaps you need to compare and contrast two systems. We will explore how to do this in the following example.

Example 41: Turning off the Fe⁺⁶ oxidation state in the Stability Diagram

In this example you will create a Stability diagram for iron in water at ambient conditions (see previous example for details on how to create this stream), learn how to change the default titrants and turn off/on different specific oxidation states of the metal of interest.

Starting the Simulation

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

Stability Diagram Calculation				
Calculation Settings		Stream Composition and Conditions		
Stream Name	Fe-H2O System	Stream Amount Calculated		
Name Style	Display Formula	Temperature	25 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	H2SO4	0 moles	
		NaOH	0 moles	

- 1. Under the *Fe-H2O System* add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane.
- 2. Select the **AQ** thermodynamic Framework
- 3. Click on the Names Manager Icon and select the Formula option
- 4. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 5. Enter the composition, temperature and pressure of the stream given in the table above. **Add** H2SO4 and NaOH as inflows. **Note**: H2SO4 and NaOH will be used as titrants to adjust pH
- 6. Select Pourbaix Diagram as Type of Survey Default
- 7. Click on the new Stability Diagram and press <F2> to change the name to Fe-H2O Selective Oxidation
- 8. Under the Contact Surface grid type Fe

Changing the Default Titrant

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

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

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

Select Titrants		?	×
Titrants			
Hide Related Inflows		New I	nflow
Acid	Base		
Fe H2O	Fe H2O		
H2SO4 NaOH	H2SO4 NaOH		
Select the acid and the base which will		H.	
OK Cance	el Apply		Help

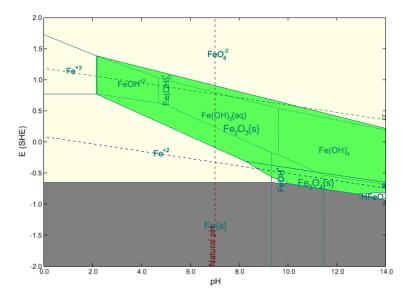
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Navigator + ×	Fe-H2O Selective Oxidation		
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♦ Streams			
E-H2O System	Variable	Value ^	Type of diagram
	Stream Par		Pourbaix Diagram 👻 Specs
Fe-H2O Selective Oxidation	Stream Amount (mol)	55.5082	
	Temperature (°C)	25.0000	Calculate 🥥
	Pressure (atm)	1.00000	Summary
	Calculation P	No No	
	Dise Single Hirant	H2S04	Unit Set: Metric (moles)
	pH Base Titrant	NAOH	Automatic Chemistry Model
			Aqueous (H+ ion) Databanks: Corrosion (AQ)
	H20	55,5082	Aqueous (H+ ion)
	H2SO4	0.0	Redox selected
	Fe	0.0	Using K-fit Polynomials T-span: 25.0 - 225.0
			P-span: 1.0 - 1500.0
Actions # * *	Contact Sur	face (mol)	
Actions	Fe		Stability diagram: E vs pH Auto-selected titrants Acid: H2SO4 Base:
Not Template Manager 1, • ×			Range on E: -2.00000 to 2.00000 V (SHE) Range on pH: 0.0 to 14.0000 Subsystems Iron Water
	Input	۲	Alloy Activity Module: Activated Calculation not done
Save	Advanced Search Add as Stream	Export	×

- 10. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 11. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams*.

Analyzing the Results

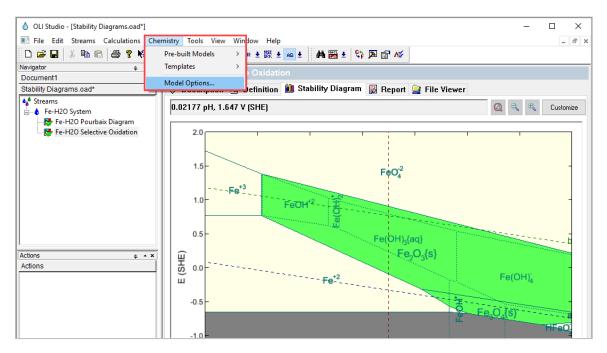
Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-H2O system at 25 °C and 1 atm.



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

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



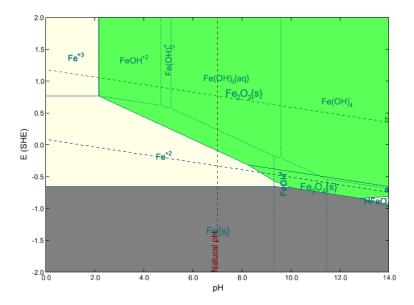
2. Select the **Redox** tab, expand the Iron Subsystems by clicking on the '+' icon, and **uncheck** the **Fe(+6)** oxidation state. Note that if you have an inflow component with this oxidation state it will remain in the calculation. Click the **OK** button to save your changes and close the window.

Fe-H2O Selective Oxidation Chemistry Model Options	?	Х
Databanks Redox Phases T/P Span		
Include Redox Chemistry		
Include Subsystems	_	
□····· ✓ Iron □···· ✓ Fe(0) □··· ✓ Fe(+2) □··· ✓ Fe(+3) □··· ③··· Sodium ③··· Sulfur		
OK Cancel Apply	Help	D

12. We are ready to recalculate to consider the changes. Press the **<F9>** key or go to the **Definition** tab and click on the **Calculate** button.

Analyzing the Results

Click on the **Chemical Diagram** tab (I Stability Diagram). In the figure below, you can see that the region dominated by the FeO₄²⁻ ion is not present.



7.5. Modeling the Effects of Hydrogen Sulfide on Corrosion

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

The H₂S (S⁻²) forms a relatively insoluble precipitate with Fe⁺². This precipitate has the potential to cover the metal surface and enhance the pH region where iron is protected from the water. We will model this using the Stability Diagram tool.

Starting the Simulation

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

Stability Diagram Calculation				
Calculation Settings		Stream Composition and Conditions		
Stream Name	Fe-H2O System	Stream Amount	Calculated	
Name Style	Display Formula	Temperature	25 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	

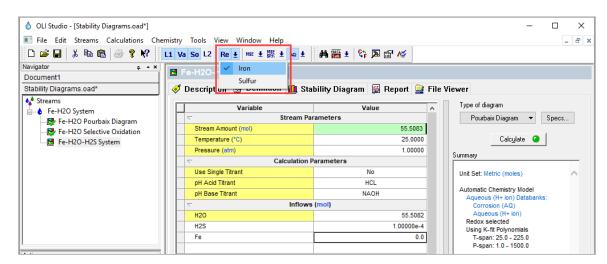
- 1. Under the *Fe-H2O System* add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane.
- 2. Select the **AQ** thermodynamic Framework
- 3. Click on the Names Manager Icon and select the Formula option
- 4. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 5. Enter the composition, temperature and pressure of the stream given in the table above. Add 1e-4 moles of H2S as an inflow.
- 6. Select **Pourbaix Diagram** as Type of Survey Default
- 7. Click on the new Stability Diagram and press <F2> to change the name to Fe-H2O-H2S System
- 8. Under the Contact Surface grid type Fe

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

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Fe-H2O Selective Oxidation	Temperature (°C)	25.0000	Calculate 🥥		
Fe-H2O-H2S System	Pressure (atm)	1.0000			
			Summary		
	Use Single Titrant	No	Unit Set: Metric (moles)		
	pH Acid Titrant	HCL	Automatic Chemistry Model		
	pH Base Titrant	NAOH	Aqueous (H+ ion) Databanks:		
	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	(mol)	Corrosion (AQ)		
	H2O	55.5082	Aqueous (H+ ion) Redox selected		
	H2S	1.00000e-4	Using K-fit Polynomials		
	Fe	0.0	T-span: 25.0 - 225.0		
1			P-span: 1.0 - 1500.0		
Actions # * ×	Contact Sur				
Actions	Fe		Stability diagram: E vs pH Auto-selected titrants		
			Auto-selected titrants Acid:		
1			Deser		

Note: By default, only the transition metals are turned ON. The different oxidation states of elements that are not transition metals are not turned on automatically. You need to turn them ON manually.

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

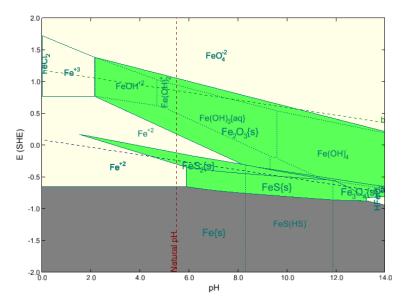


- 11. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 12. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams*.

Analyzing the Results

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

Inspection of the diagram reveals a profound effect of H₂S on the corrosion of iron. New stability fields of FeS



and FeS_2 are observed. Elemental iron is found to be in equilibrium with FeS over for pH values ranging from ca. 6.0 to 12.5.

Since the Fe/FeS equilibrium line lies below the H⁺ reduction line (**a**), a process consisting of the reduction of H⁺ to H⁰ 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 Fe₃O₄ (magnetite) in the absence of H₂S. This has important implications for corrosion in refinery installations, where H₂S is frequently present.

7.6. Modeling Corrosion at High Temperature

Example 43: High Temperature Iron in Water

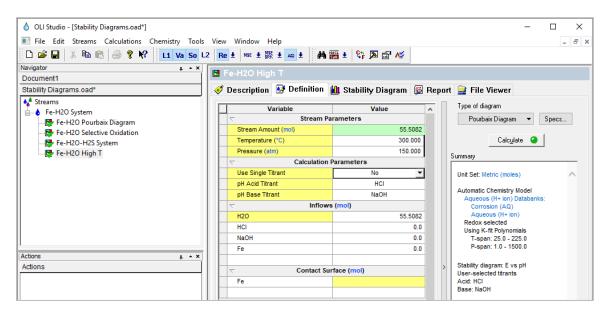
Starting the Simulation

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

Stability Diagram Calculation				
Calculation Settings		Stream Composition and Conditions		
Stream Name	Fe-H2O System	Stream Amount	Calculated	
Name Style	Display Formula	Temperature	300 °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			

- 1. Under the *Fe-H2O System* add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane.
- 2. Select the **AQ** thermodynamic Framework
- 3. Click on the Names Manager Icon and select the Formula option
- 4. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 5. Enter the composition, temperature and pressure of the stream given in the table above
- 6. Select Pourbaix Diagram as Type of Survey Default
- 7. Click on the new Stability Diagram and press <F2> to change the name to Fe-H2O High T
- 8. Under the Contact Surface grid type Fe

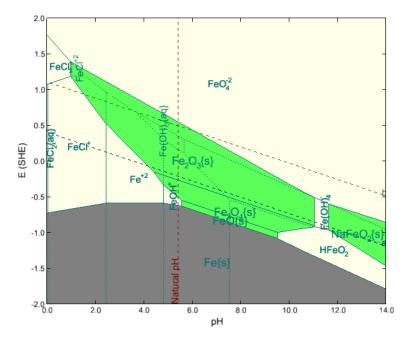
The screen should look like the image below after all the inputs and definitions have been entered:



- 9. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 10. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams*.

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-H2O system at 300 °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 ⁹	0 moles (Base Titrant)
		C8H18	2E-07 moles
		C7H16	8E-07 moles
		C3H8	1.2E-04 moles
		C4H10	2E-05 moles
		C5H12	7E-6 moles
		C6H14	2E-6 moles
		H2S	0.01 moles

- 1. Under the *Fe-H2O System* add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane
- 2. Select the **AQ** thermodynamic Framework
- 3. Click on the Names Manager Icon and select the Formula option
- 4. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 5. Enter the composition, temperature and pressure of the stream given in the table above
- 6. Select **Pourbaix Diagram** as Type of Survey Default
- 7. Click on the new Stability Diagram and press <F2> to change the name to Fe-H2O-Alkanoamines
- 8. Under the Contact Surface grid type Fe
- 9. Change the Base Titrant to DEA
- 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.

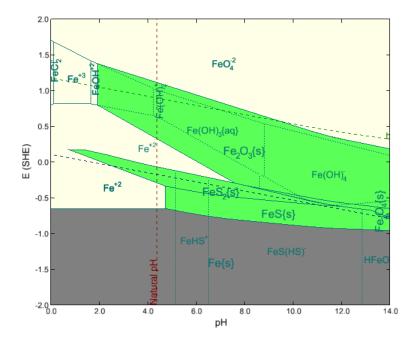
⁹ The "ESP" name for this species is DEXH, which can be used as an input to make your life easier. The formula name is: HN(C2H4OH)2

💽 File Edit Streams Calculations Chemistry T		🎬 ± 💱 🔉 😭 💉	_ 8
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Document1	ines		
Stability Diagrams.oad*		🛍 Stability Diagram 📓 Rep	ort 📑 File Viewer
s ^e Streams	Sodium	200	
E-H2O System	Sulfur	Value 🔨	Type of diagram
		Parameters	Pourbaix Diagram 🔻 Specs
	Stream Amount (mol)	55.5184	
	Temperature (°C)	50.0000	Calc <u>u</u> late 🥝
	Pressure (atm)	1.00000 n Parameters	Summary
Fe-H2O-Alkanoamines	Use Single Titrant	No	
	pH Acid Titrant	HCI	Unit Set: Metric (moles)
	pH Base Titrant	HN(C2H4OH)2	Automatic Chemistry Model
		vs (mol)	Aqueous (H+ ion) Databanks: Corrosion (AQ)
	H20	55.5082	Aqueous (H+ ion)
	нсі	0.0	Second Liquid phase Redox selected
	HN(C2H4OH)2	0.0	Using K-fit Polynomials
	C8H18	2.0000e-7	T-span: 25.0 - 225.0
ctions 🛛 🖡 🔺	× C7H16	8.00000e-7	P-span: 1.0 - 1500.0
Actions	C3H8	1.20000e-4	Stability diagram: E vs pH
	n-C4H10	2.00000e-5	Auto-selected titrants
	C5H12	7.00000e-6	Acid: HCI Base: HN(C2H4OH)2
	C6H14	2.00000e-6	
	H2S	0.0100000	Range on E: -2.00000 to 2.00000 V (SHE)
	NaOH	0.0	Range on pH:
	Fe	0.0	0.0 to 14.0000
lot Template Manager 🛛 🔒 🔺	×		Subsystems Iron
		urface (mol)	Water
	Fe		Alloy Activity Module:
			Activated
		¥	Calculation not done
	Input		
	Advanced Search Add	as Stream Export	↓ ✓

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

- 11. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 12. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams*.

Click on the **Chemical Diagram** tab (**U** Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-H2O system at 50 °C and 1 atm.



7.7. Modeling the Effects of Complexation on Corrosion

In this section we will simulate the reaction of Copper with Ammonia and Gold metal with Cyanide. This section attempts to answer the question of how strong complexing agents affect the passivation of these metals.

Example 45: Copper and Ammonia

Starting the Simulation

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

Stability Diagram Calculation				
Calculation Settings Stream Composition and Conditions				
Stream Name	Cu-H2O System	Stream Amount	Calculated	
Name Style	Display Formula	Temperature	25 °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	Cu	NH3	0 moles	

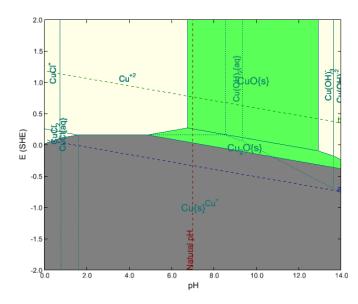
- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to Cu-H2O System
- 3. Select the **AQ** thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 6. Enter the composition, temperature and pressure of the stream given in the table above
- Under the Cu-H2O System Stream add a new Stability Diagram calculation. Go to the Add Calculation button and select Stability Diagram calculation or by selecting the Chemical Diagram icon in the Actions Pane
- 8. Select **Pourbaix Diagram** as Type of Survey Default
- 9. Click on the new Stability Diagram and press <F2> to change the name to Cu-H2O-NH3
- 10. Under the **Contact Surface** grid type **Cu**

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

2	Re	🛨 MSE 🛨 MSE 🛨 🗛 🛨 🦛	🎬 🛨 💱 🔊 😭 🎸			
E	Cu-H2O-NH3 Complexation					
	🛷 Description 🔮 Definition 🏙 Stability Diagram 📓 R					
		Variable	Value	^		
		Stream Page 1	arameters			
		Stream Amount (mol)	55.5082			
		Temperature (°C)	25.0000			
		Pressure (atm)	1.00000			
		Calculation	Parameters			
	Use Single Titrant		No			
		pH Acid Titrant	HCL			
		pH Base Titrant	NAOH			
			s (mol)			
		H2O	55.5082			
		NH3	0.0			
		Cu	0.0	1		
				1		
		Contact Su	rface (mol)			
		Cu				

- 13. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 14. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams*.

Click on the **Chemical Diagram** tab (**U** Stability Diagram). This tab displays the Pourbaix Diagram for the Cu-H2O 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.

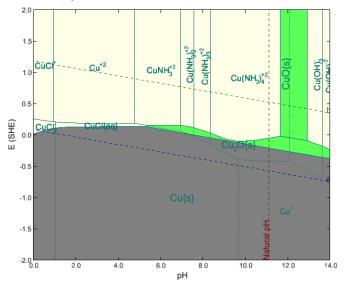
What happens if Ammonia (NH_3) is added to the solution? The next step is to understand the effect of NH_3 on the stability of copper.

Effect of NH3 on the Stability of Copper

- 1. Go to the **Definition** tab, and change the amount of NH3 from 0 to 0.1 moles
- 2. Click on the Calculate button or press the <F9> key

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Cu-H2O-NH3 system at 25 °C and 1 atm in a 0.1 m of NH3 solution.



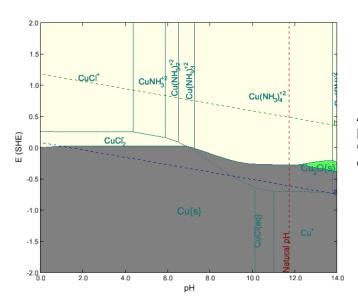
Notice that a large area of corrosive liquid has appeared in the stability field for the copper oxides. This means that it is thermodynamically possible for the ammonia to break down the passivation layer of copper oxide in the presence of oxygen. Notice that in the absence of oxygen (the *a* line only), copper is still stable.

Now repeat the exercise with 1.5 moles of NH3

- 1. Go to the **Definition** tab, and change the amount of NH3 from 0 to 1.5 moles
- 2. Click on the Calculate button or press the <F9> key

Analyzing the Results

Click on the **Chemical Diagram** tab (**Stability Diagram**). This tab displays the Pourbaix Diagram for the Cu-H2O-NH3 system at 25 °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 ℃	
Unit Set	Metric, Batch, Moles	Pressure	1 atm	
Framework	AQ	pH Range	0-14 (Default)	
Calculation Type	Stability Diagram	H2O	55.5082 moles	
Contact Surface	Au	NaCN	0 moles	

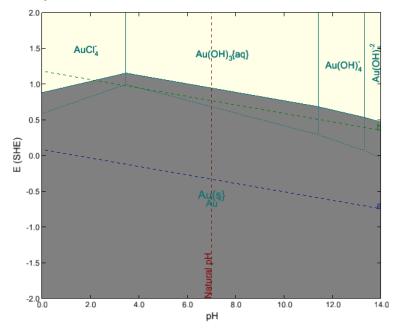
- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to Au-H2O System
- 3. Select the **AQ** thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 6. Enter the composition, temperature and pressure of the stream given in the table above
- Under the Au-H2O System Stream add a new Stability Diagram calculation. Go to the Add Calculation button and select Stability Diagram calculation or by selecting the Chemical Diagram icon in the Actions Pane
- 8. Select Pourbaix Diagram as Type of Survey Default
- 9. Click on the new Stability Diagram and press <F2> to change the name to Au-H2O
- 10. Under the Contact Surface grid type Au

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

Au-H2O Pourbaix Diagra		
Variable	Value	
	Parameters	
Stream Amount (mol)	55.5082	
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
	on Parameters	
Use Single Titrant No		
pH Acid Titrant	HCL	
pH Base Titrant	NaOH	
∇ Inflo	ows (mol)	
H2O	55.5082	
NaCN	0.0	
Au	0.0	
	-	
	Surface (mol)	
Au		

- 11. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 12. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams*.

Click on the **Chemical Diagram** tab (**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.

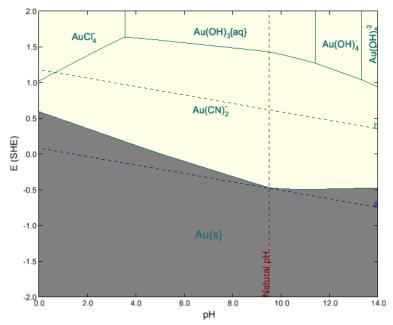
One of the most commonly used leaching processes for **gold extraction** is the **cyanidation** process. This process is a hydrometallurgical technique for extracting gold from low-grade ores by converting the gold to a water-soluble coordination complex. Basically, this approach adds cyanide salts to water. We are going to simulate this using the software.

Effect of Cyanide on the Stability of Gold

- 1. Go to the Definition tab, and change the amount of NaCN from 0 to 1e-4 moles
- 2. Click on the Calculate button or press the <F9> key

Analyzing the Results

Click on the **Chemical Diagram** tab (**U** 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.

7.8. Modeling the Effect of Oxidizing Inhibitors on Corrosion

In this chapter we will look at the effect of modeling corrosion inhibitors. We will do this by superimposing two stability diagrams over one another. If one solid field overlaps the corrosion range of the other system, then passivation is likely.

Example 47: Iron in the presence of chromates

Starting the Simulation

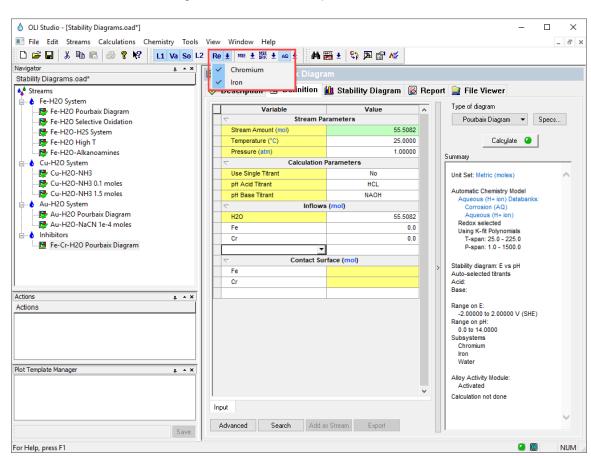
Use the inputs and parameters from the table below to create the stream's composition. Certain inputs, such as the name style, units, etc. will require further adjustments, and will be described as necessary.

Stability Diagram Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Inhibitors	Stream Amount	Calculated
Name Style	Display Formula	Temperature	25 °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		
Contact Surface	Cr		

- 1. Add a new Stream
- 2. Click on the new Stream and press **<F2>** to change the name to *Inhibitors*
- 3. Select the **AQ** thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 6. Enter the composition, temperature and pressure of the stream given in the table above
- 7. Under the *Inhibitors* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane
- 8. Select **Pourbaix Diagram** as Type of Survey Default
- 9. Click on the new Stability Diagram and press <F2> to change the name to Fe-Cr-H2O Pourbaix Diagram
- 10. Under the Contact Surface grid type Fe and then Cr

Note: Make sure that both **Fe** and **Cr** are enabled for Redox reactions. Use the arrow next to the **Re** button to expand the list.

You can also enable Redox reactions via the menu bar: *Chemistry* > *Model Options* > *Redox* tab. Make sure that Fe and Cr boxes are checked.



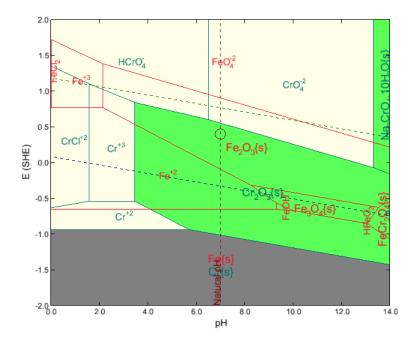
The screen should look like the image below after all the inputs and definitions have been entered:

- 11. Click the Specs button and under the Display Choices tab check the following options:
 - a) No aqueous lines
 - b) Show ORP

Stability Options		?	Х
Category	Display Choices Aqueous and Solid Lines Superimpose lines Only Aqueous lines Shading Shade subsystem: Chromium Iron Show natural pH Show ORP Display Subsystems Chromium Chromium Tron Water Potassium Sodium		
	OK Cancel Apply	Hel	p

- 12. Click **OK** to close the Stability Options window
- 13. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 14. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams*.

Click on the **Chemical Diagram** tab (**Use 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 $(Cr(OH)_{3ppt})$ overlays the corrosive region of the iron system. This means that there is potential for passivating the metal in that region.

The $Cr(OH)_3$ field overlaps with the corrosion range of Fe in most of the pH range. This causes inhibition because of the coupling of: Oxidation of Fe to Fe²⁺, 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 °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		
Contact Surface	As		

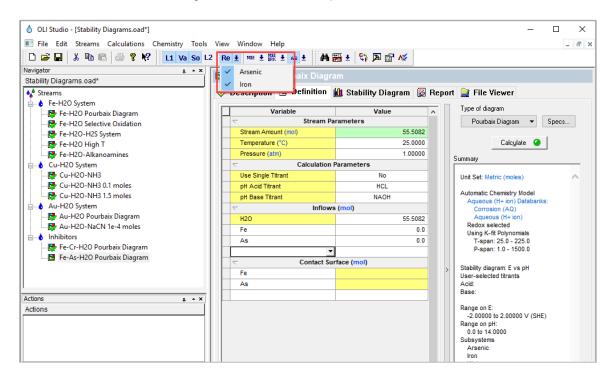
1. Under the *Inhibitors* Stream add a new Stability Diagram calculation. Go to the **Add Calculation** button and select **Stability Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane

- 2. Select Pourbaix Diagram as Type of Survey Default
- 3. Click on the new Stability Diagram and press <F2> to change the name to Fe-As-H2O Pourbaix Diagram
- 4. Under the Contact Surface grid type Fe and then As

Note: Make sure that both **Fe** and **As** are enabled for Redox reactions. Use the arrow next to the **Re** button to expand the list.

You can also enable Redox reactions via the menu bar: *Chemistry > Model Options > Redox* tab. Make sure that Fe and As boxes are checked.

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

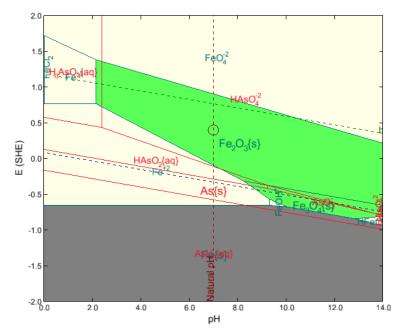


- 5. Click the Specs button and under the Display Choices tab check the following options:
 - c) No aqueous lines
 - d) Show ORP

Stability Options		?	Х
Category Display Axes Metal Activity	Display Choices Aqueous and Solid Lines Superimpose lines Only Aqueous lines Only Aqueous lines Show natural pH Show ORP Display Subsystems Arsenic Tron Water		
	OK Cancel Apply	Не	lp

- 6. Click **OK** to close the Stability Options window
- 7. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 8. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Stability Diagrams*.

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.

7.9. Implications of Stability Diagrams on Cathodic Protection

Cathodic protection works by shifting the potential of the metal into its immunity range. Stability diagrams can help you to answer the following questions:

- What is the potential range that ensures that the metal stays in the immunity range?
- What is the effect of environmental variables on the immunity domain?

We will explore the Fe-H2O system at different temperatures and pressures to answer these questions.

Example 49: Effect of Temperature and Pressure on the Pourbaix Diagram of Fe-H2O System

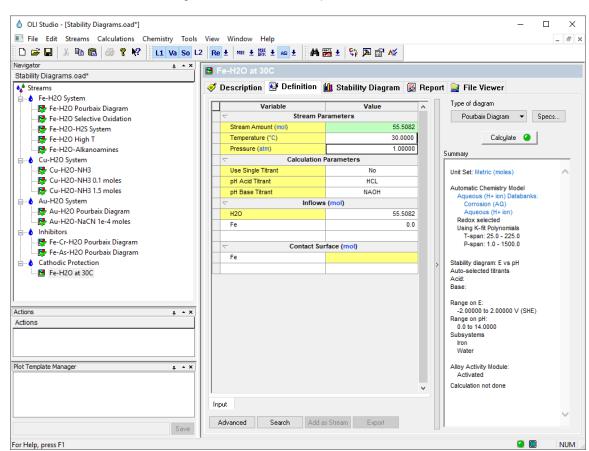
Starting the Simulation

Iron at 30 °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			
Calculation Settings Stream Composition and Conditions			
Stream Name	Cathodic Protection	Stream Amount	Calculated
Name Style	Display Formula	Temperature	30 ℃
Unit Set	Metric, Batch, Moles	Pressure	1 atm
Framework	AQ	pH Range	0-14 (Default)
Calculation Type	Stability Diagram	H2O	55.5082 moles
Contact Surface	Fe		

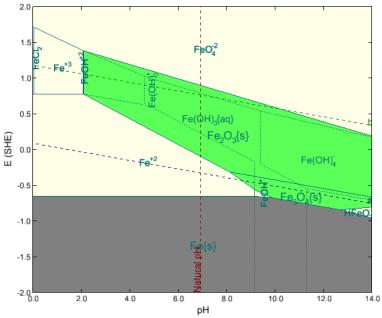
- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to Cathodic Protection
- 3. Select the **AQ** thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 6. Enter the composition, temperature and pressure of the stream given in the table above
- Under the Cathodic Protection Stream add a new Stability Diagram calculation. Go to the Add Calculation button and select Stability Diagram calculation or by selecting the Chemical Diagram icon in the Actions Pane
- 8. Select Pourbaix Diagram as Type of Survey Default
- 9. Click on the new Stability Diagram and press <F2> to change the name to Fe-H2O at 30C and 1 atm
- 10. Under the Contact Surface grid type Fe



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

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Fe-H2O system at 30 °C and 1 atm.



In the whole pH range, cathodic protection will require shifting the potential to moderately negative values.

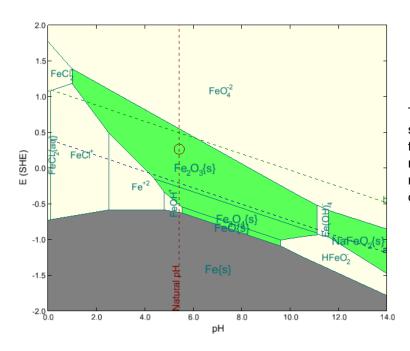
think simulation | getting the chemistry right

Iron at 300 °C and 100 atm

- 1. Go to the Definition tab, and change the Temperature and Pressure to 300°C and 100 atm
- 2. Click on the Calculate button or press the <F9> key

Analyzing the Results

Click on the **Chemical Diagram** tab (Stability Diagram). This tab displays the Pourbaix Diagram for the Cu-H2O-NH3 system at 300 °C and 100 atm.

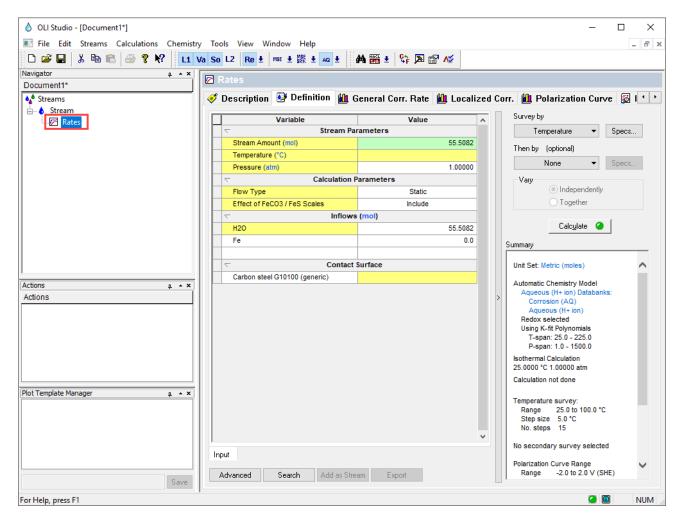


The immunity range in acidic and neutral solutions is weakly affected by temperature. However, the immunity range in alkaline solutions is shifted to much lower potentials which makes cathodic protection much more difficult.

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.



8.1. A Basic General Corrosion Rate Calculation

A brief introduction to the corrosion rate tool will be shown in the example below. As we go through the example, the basic definitions, functionalities and reporting for the *Corrosion rate* tool will be introduced.

Example 50: Corrosion rate of an oxygenated 0.1 m NaCl solution

Starting the Simulation

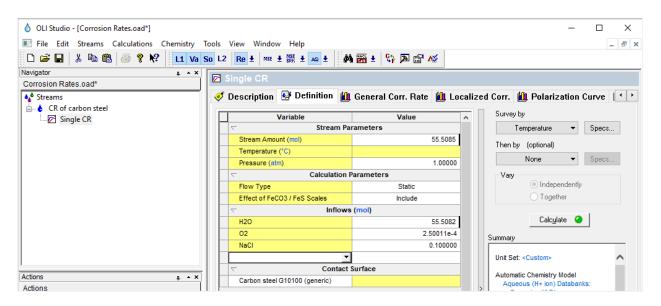
To start the software, double-click the OLI Studio icon on the desktop, which will take you to the OLI Studio interface where you can start creating your calculations.



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	Calculation 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	

- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to CR of carbon steel
- 3. Select the AQ thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Moles
- 6. Enter the composition, temperature and pressure of the stream given in the table above
- 7. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane. Your screen should look like the image below.



Note: By default, the software has selected **Carbon steel G10100 (generic)** as the default contact surface to perform the corrosion rates on. You can click on the white space of the **Carbon steel G10100 (generic)** name, and it will show a drop-down arrow. You can then click on the dropdown arrow, and you will be able to see and select any alloy present in the **Alloy** database.

Contact Sur	face
Carbon steel G10100 (generic)	
Display Name	OLI Name
🛪 Carbon steel G10100 (generic)	Carbon steel G1010
* Carbon steel 1018	Carbon steel 1018
★ Stainless steel 304	Stainless steel 304
★ Stainless steel 316	Stainless steel 316
* Alloy 254SMO	Alloy 254SMO
₩ Dunley stainless 2205	Dunley stainless 2205

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				
√ Inflows	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.

- 8. Leave the default alloy Carbon steel G10100 (generic) as the contact surface
- 9. Go to the Survey by option and select Single Point Rate. This option will allow you to calculate the corrosion rate at the temperature and pressure specified.

🗹 Single CR					
< Description 🔮 Definition 🛍	General Corr. Rate 🛍 Lo	ocalized Corr. 🛍 Polarization Curve 🖂 🕇			
Variable	Value	Survey by			
	Stream Parameters				
Stream Amount (mol)	55.5085	Single Point Rate			
Temperature (°C)	25.0000	Temperature			
Pressure (atm)	1.00000	Pressure			
Calculation F					
Flow Type	Static	Composition			
Effect of FeCO3 / FeS Scales	Include	pH			
☐ ☐ Inflows	(mol)	Pipe Flow			
H2O	55.5082	Rotating Disk			
02	2.50011e-4	Su Rotating Cylinder			
NaCl	0.100000	Thermal Aging Temp.			
		Thermal Aging Time			
Contact Contact	Contact Surface				
Carbon steel G10100 (generic)		Shear Stress			
		Liquid Flow in Pipe			
		Daday salastad			

Note: You can also study the effect of other variables such as temperature, pressure, (chemical species) composition, pH, pipe flow, etc. on the corrosion rate. The effect of these variables can be set up as a survey calculation. In the upcoming corrosion rate examples, survey calculations to study corrosion rates will be shown in more detail.

A brief description of the most common survey types for studying corrosion rates are given below.

pH Survey – This calculation is similar to the pH survey available in OLI 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.

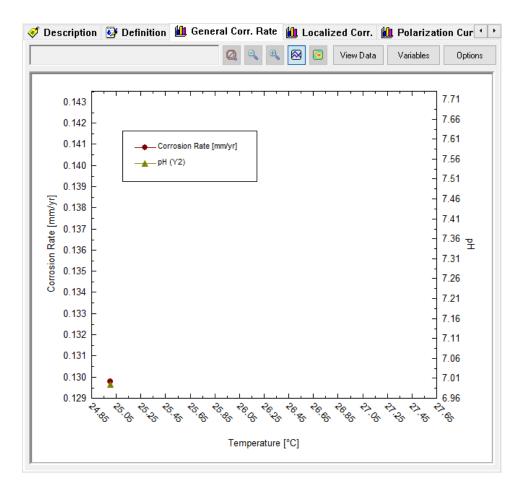
Care should be taken when adding salts that can form hydrates (e.g., CaCl₂.6H₂O). When these hydrated salts begin to precipitate from solution, large amounts of water may be complexed with the crystal. The solution may dehydrate, and non-convergence may be the result.

Pressure Survey – The pressure of the system can also be varied. The default range can be changed via the Range option. Care should be taken when working at very low pressures since the solution may inadvertently boil off the liquid and non-convergence may result.

Flow Velocity Survey – In systems that are flowing, the flowrate of the stream can be varied.

- 10. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 11. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Create a new file and name it: *Corrosion Rates.*

1. Click on the **General Corr. Rate** tab (M General Corr. Rate). This tab displays a plot showing the results of corrosion rate and pH.

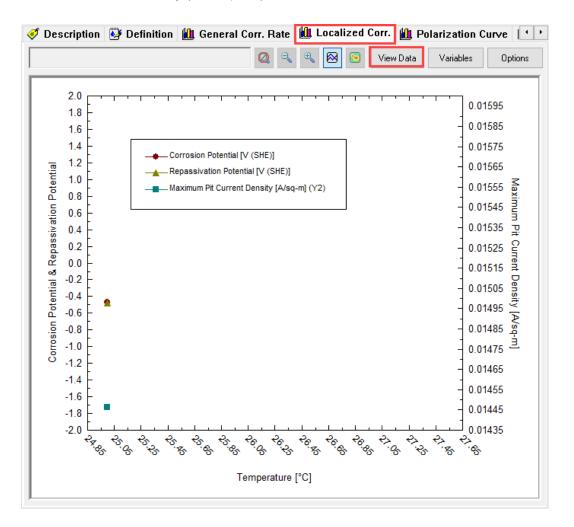


2. Click on the View Data button to see the results in tabulated form.

	Temperature	Corrosion Rate	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.

- 3. Click on the Localized Corr. Rate tab (Localized Corr.). This tab displays a plot showing the results of three different calculated data:
 - Corrosion Potential (red dot)
 - Repassivation Potential (yellow triangle)
 - Maximum Pit Current Density (blue square)

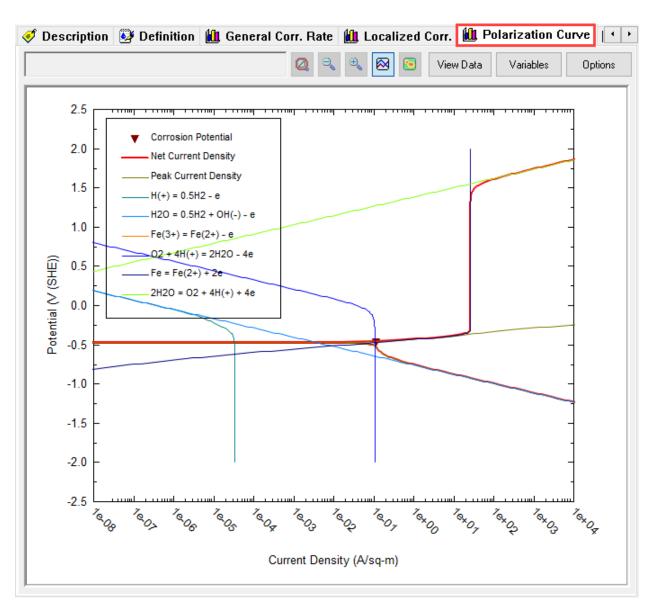


4. Click on the View Data button to see the results in tabulated form.

	Temperature	Corrosion Potential	Repassivation Potential	Maximum Pit Current Density
	°C V (SHE)		V (SHE)	A/sq-m
1	25.0000	-0.472418	-0.481902	0.0144636

Notice that in this case, the corrosion potential has a higher value than the repassivation potential. This indicates that carbon steel at 25 °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.

5. Now, click on the **Polarization Curve** tab (**Polarization Curve**). This tab displays a plot showing the calculated polarization curve of carbon steel.



The net polarization curve is given by the red curve. This red curve is obtained by adding up all the currents of the half reactions at a given potential. The corrosion potential is calculated by applying the mixed potential theory, and it is represented by this red triangle. Once the corrosion potential is obtained, the corrosion current density also is computed and subsequently the corrosion rate.

8.2. Exploring corrosion rate calculation options

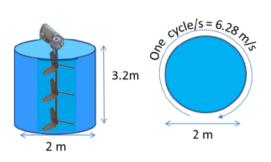
Example 51: Corrosion in a Water-Filled Carbon Steel Tank

In the following example you are going to study the corrosion rate of a carbon steel tank with a volume of 10 m³ tank (3.2 cm high and 200 cm in diameter) that is filled to the top with water. The tank's wall thickness is 1.27 cm.

These are the operation conditions:

- 1. Sometimes the water in the tank remains static (mixer off), closed to the atmosphere
- 2. Some other times the tank is fully mixed (complete agitation)
- 3. The tank when operating has a variable speed mixer with a rotation speed between 0 and 12,000 rpm
- 4. At other times, the tank is open to the atmosphere. The effects of O₂, CO₂ 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					
Calculati	on Settings	ngs Stream Composition and Conditions			
Stream Name CR vs flow		Stream Amount	10000 L		
Calculation Type	Corrosion Rates	Temperature	25 ℃		
Name Style	Display Name	Pressure	1 atm		
Unit Set	Metric, Batch, Concentration	Water	Calculated		
Framework	AQ				
Contact surface Carbon Steel G10100 (generic)					

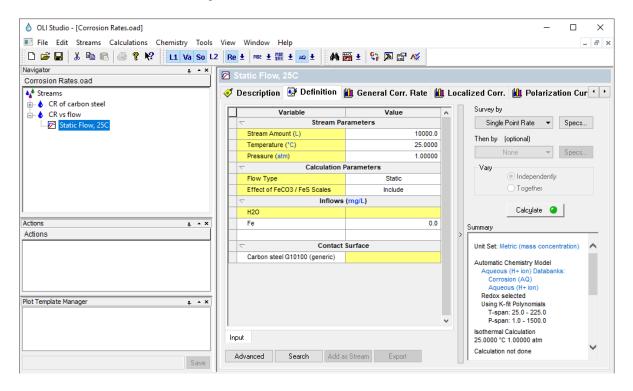
- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to CR vs flow
- 3. Select the **AQ** thermodynamic Framework
- 4. Click on the Names Manager Icon, and select the Display Name option, and click OK
- 5. Click on the Units Manager Icon, and select the Metric, Batch, Conc. option, and click OK

Units Manager - (CR vs flow				?	×
Units Manager						
Metric	~	Batch	\sim	Conc.	~	•

In the Definition tab, notice that the units of the Stream Amount changed from moles (mol) to liters (L).

- 6. Enter the composition, temperature and pressure of the stream given in the table above
- 7. Go to the Add Calculation button and select Corrosion Rates calculation or by selecting the Add Corrosion Rates icon in the Actions Pane.
- 8. Change the *Rates* name to *Static Flow, 25C* using the <F2> key.
- 9. Leave the default Flow Type as Static
- 10. Leave the default alloy Carbon steel G10100 (generic) as the contact surface
- 11. Go to the Survey by option and select Single Point Rate. This option will allow you to calculate the corrosion rate at the temperature and pressure specified.

Your screen should look like the image below.



- 12. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key.
- 13. It is time to save your file (File >Save as...) or using the save icon in the tool bar. You can save it under the same file created in the previous example named Corrosion Rates.

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	
				Single Point Rate 🔻 Specs	
Stream Amount (L)	10000.0			Then by (optional)	
Volume - Aqueous (L)	10000.0				
Temperature (°C)	25.0000			None 🔻 Specs	
Pressure (atm)	1.00000			Vary	
Corrosion	Values			 Independently 	
Repassivation Potential (V (SHE))	99.9000			 Together 	
Corrosion Rate (mm/yr)	7.12696e-3				
Corrosion Potential (V (SHE))	-0.552268			Calc <u>u</u> late 🥝	
Corrosion Current Density (A/sq-	6.14631e-3		S.	ummary	
Inflows (mg/L)			uninary	
H2O	9.96987e5			Unit Set: Metric (mass concentration)	
Contact S	Surface				
Carbon steel G10100 (generic)				Automatic Chemistry Model Aqueous (H+ ion) Databanks:	
				Corrosion (AQ)	
				Aqueous (H+ ion)	
				Redox selected Using K-fit Polynomials	
				T-span: 25.0 - 225.0	
		\mathbf{v}		P-span: 1.0 - 1500.0	
				Isothermal Calculation	
ut 1 N				25.0000 °C 1.00000 atm	

The corrosion rate is 7.13e-3 mm/yr. This is a negligible rate, since the thickness of the tank is ~12.7 mm, then corroding half the wall thickness would take about 900 years.

Second operation condition: Turbulent flow, tank closed to the atmosphere at ambient conditions

- 1. Under the stream '*CR vs Flow*' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane
- 2. Change the *Rates* name to *Turbulent Flow, 25C* using the <F2> key.
- 3. Change the default Flow Type to Complete Agitation
- 4. Leave the default alloy Carbon steel G10100 (generic) as the contact surface
- 5. Go to the Survey by option and select Single Point Rate.

Your screen should look like the image below.

Navigator # * X	Turbulent Flow. 25C	
Corrosion Rates.oad*		
🍓 Streams	🛷 Description 😼 Definition 🛍 General Corr. Rate	🛍 Localized Corr. 🛍 Polarization Cur 💶
🗄 🗄 CR of carbon steel		Survey by
🗄 👌 CR vs flow	Variable Value	∧ Survey by
Static Flow 25C	Stream Parameters	Single Point Rate 🔻 Specs
🗉 🗖 Turbulent Flow, 25C	Stream Amount (L) 10000	0 Then by (optional)
	Temperature (°C) 25.00	0
	Pressure (atm) 1.000	0 None Specs
	Calculation Parameters	Vary
	Flow Type Complete Agitation	 Independently
	Effect of FeCO3 / FeS Scales Include	 Together
	Inflows (mg/L)	
	H2O	Calculate 🥝
Actions	Fe O	0 Summary
Actions		> Summary
	Contact Surface	Unit Set: Metric (mass concentration)
	Carbon steel G10100 (generic)	
		Automatic Chemistry Model

Click on the output tab labeled **1** (next to the input tab), and check the results located in the **Corrosion Values** tab.

		Single Point Rate 🔻 Specs
10000.0		Then by (optional)
10000.0		
25.0000		None 🔻 Specs
1.00000		Vary
n Values		 Independently
99.9000		 Together
0.0196420		
-0.535169		Calc <u>u</u> late 🥝
0.0169394		Summary
(mg/L)	>	Summary
9.96987e5		Unit Set: Metric (mass concentration)
Surface		
		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
	*	
		Isothermal Calculation
	10000.0 10000.0 25.0000 1.00000 N Values 99.9000 0.0196420 -0.535169 0.0169394 (mg/L)	10000.0 10000.0 25.0000 1.00000 n Values 99.9000 0.0196420 0.0169394 (mg/L) 9.96987e5

The corrosion rate increased 0.0196 mm/year, still a relatively low value.

Third operation condition: Varying flow, tank closed to the atmosphere at ambient conditions

- 1. Under the stream '*CR vs Flow*' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane
- 2. Change the *Rates* name to *Varying Flow, 25C* using the <F2> key
- 3. Go to the Survey by button and select Rotating Disk
- 4. Under the Calculation Parameters grid. change the Disk Diameter to 200 cm

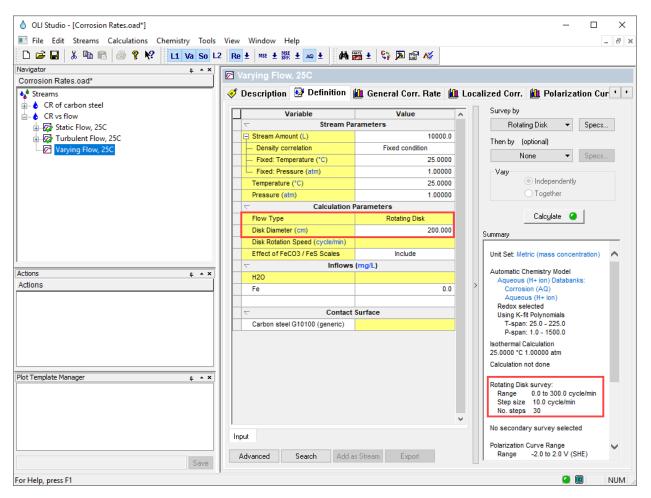
Note: At this point the vertical dimensions of the tank are unimportant. We will assume that the tank can be modeled like a rotating cylinder. The propeller rotates at 1200 rpm, although it is not expected that the wall velocity will approach this value, and so a lower value will be used (we still want it to be high enough to see the effects of shear).

- 5. The next step is to set the speed of the mixer. Go to the **Specs** button next to the **Rotating Disk** option
- 6. Change the Disk Rotation Speed Range from 0 to 300 cycles/min with an increment of 10 cycles/min. Then click **OK**.

Category	Survey Range
Var. 1 - Disk Rotation Speed Polarization Curve Calculation Type Calculation Options	Disk Rotation Speed Range Unit: cycle/min Selected Range 0.0 to 300.0 in 30 steps of 10.0 New
	Linear O Log O Point List End Points
	Start 0.0
	End 300.000
	Step Size
	Increment 10.0000 Select one, the other is
	Number Steps 30 O S calculated

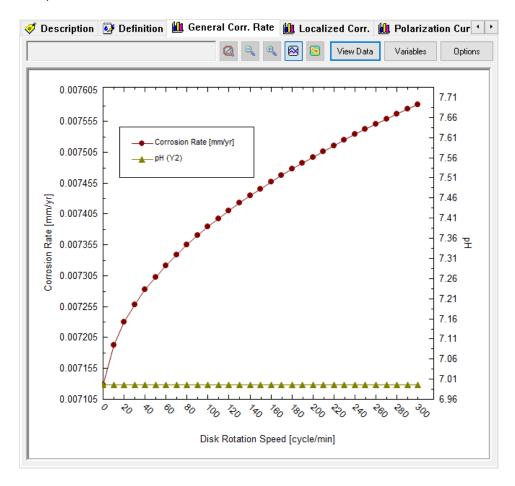
7. Leave the default alloy Carbon steel G10100 (generic) as the contact surface

Your screen should look like the image below.



- 8. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 9. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

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.

- 1. Under the stream '*CR vs Flow*' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane
- 2. Change the *Rates* name to *Static Flow, O2* using the <F2> key
- 3. Add Oxygen (O2) to the inflow grid
- 4. Leave the default Flow Type as Static

- 5. Go to the Survey by button and select Composition
- 6. Change the Disk Diameter to 200 cm
- 7. The next step is the concentration range of oxygen. Go to the **Specs** button next to the **Composition** option. This will open a new window.
- 8. Under **component** select (click on) O2. Then select the **Survey Range** tab and enter the Survey Range as follows: Log Scale, Start=1e-6, End=10, Steps=10. Then click **OK**.

Composition Rates Calculation	?	×	Composition Rates Calculation	? ×
Category Var. 1 - Composition Polarization Curve Calculation Type Calculation Options	Component Survey Range Component Inflows Component Inflows Pide Related Inflows New In Fe 02 Select a component inflow which will be varied over the specified re		Category Var. 1 · Composition Polarization Curve Calculation Options Calculation Options Calculation Options Category Category Composition Range Selected Range Composition Ra	ng O Point List
	OK Cancel Apply	Help	ОК	Cancel Apply Help

9. Leave the default alloy Carbon steel G10100 (generic) as the contact surface

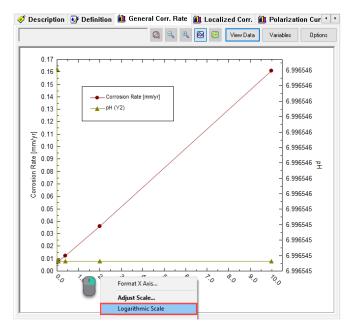
Your screen should look like the image below.

🍓 Streams	< Description 🔯 Definition 🚻	General Corr. Rate 🛍 Loca	alized Corr. 🛍 Polarization Cur 💶
CR of carbon steel	Variable	Value	Survey by
i	Stream Param		Composition - Specs
E CR vs flow	E Stream Amount (L)	10000.0	Composition + Specs
Static Flow, 25C	Density correlation	Fixed condition	Then by (optional)
Turbulent Flow, 25C	Fixed: Temperature (°C)	25.0000	None 👻 Specs
Varying Flow, 25C	Fixed: Pressure (atm)	1.00000	Mani
Static Flow, O2			Vary Independently
	Temperature (°C)	25.0000	
	Pressure (atm)	1.00000	
	Calculation Para		Calculate 🥝
	Flow Type	Static	
	Effect of FeCO3 / FeS Scales	Include	Summary
	☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐		
	H2O		Unit Set: Metric (mass concentration)
Actions	Fe	0.0	Automatic Chemistry Model
Actions + *	02		Aqueous (H+ ion) Databanks:
Actions		>	Corrosion (AQ)
	Contact Surface		Aqueous (H+ ion) Redox selected
	Carbon steel G10100 (generic)		Using K-fit Polynomials
			T-span: 25.0 - 225.0
			P-span: 1.0 - 1500.0
			Isothermal Calculation 25.0000 °C 1.00000 atm
			Calculation not done
Plot Template Manager 📮 🔺 🗙			Composition survey:
			02
			Range 1.0e-6 to 10.0 mg/L
			Logarithmic Scale No. steps 10
	I	*	NO. STEPS TO

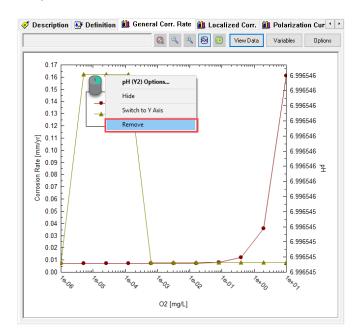
- 10. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 11. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

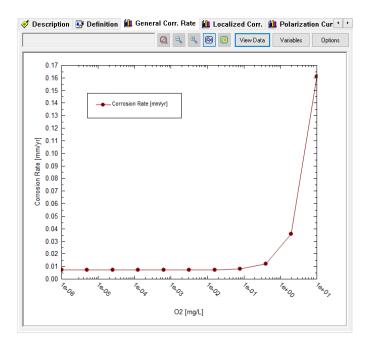
Click on the **General Corr. Rate** tab (M General Corr. Rate). This tab displays a plot showing the results of corrosion rate and pH.

1. Right-mouse click on the X-axis and change it to Logarithmic Scale



2. Right-mouse click on the pH curve and select Remove





The resulting plot shows the impact of oxygen on the corrosion rate. Corrosion increases by a factor of 20 once the concentration increases beyond 100 μ g/l. Aerated water contains approximately 8 mg/l O₂. Corrosion on the tank wall is 0.16 mm/yr. At this rate, 50% of the 12.3 mm wall will be dissolved in 40 years.

Fifth operation condition: Static flow, tank open to the atmosphere (aerated with O_2 and CO_2) at ambient conditions

The atmosphere contains ~400 ppmV CO₂. At this concentration 0.6 mg/l CO₂ is dissolved in water as molecular CO₂, this CO₂ 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 CO₂ on corrosion is two-fold, as two separate reactions occur at the metal surface:

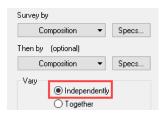
$$H^+ + e^- \leftrightarrow \frac{1}{2}H_2$$

 $HCO_3^- + e^- = \frac{1}{2}H_2 + CO_3^{-2}$

To test the CO₂ impact, you will recalculate the corrosion rate using two CO₂ concentrations: 0 and 0.6 ppm.

- I. Under the stream '*CR vs Flow*' add new corrosion rate calculation. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane
- II. Change the *Rates* name to *Static Flow, O2 and CO2* using the <F2> key
- III. Add Oxygen (O2) and carbon dioxide (CO2) to the inflow grid
- IV. Leave the default Flow Type as Static

V. Go to the *Survey by* button and select Survey by **Composition** and then by **Composition** (as shown below)



- VI. The next step is the concentration range of oxygen and carbon dioxide. Go to the **Specs** button next to the **Composition** option. This will open a new window.
- VII. Under the **Category** section, make sure to select **Var. 1** -Composition. Go to the **Component** tab, and select O2

Composition Rates Calculatio	n	?	×
Calegory	Component Survey Range Component Inflows If the Related Inflows CD2 If the Related Inflows CD2 If the Related Inflows Select a component inflow which will be varied over the state over	New Inflow	
	OK Cancel Apply	Help)

VIII. Then select the **Survey Range** tab and enter the Survey Range as follows: Log Scale, Start=1e-6, End=10, Steps=10. Then click **OK**.

Composition Rates Calculation		?	×
Category	Component Survey Range		
- Var. 1 - Composition - Var. 2 - Composition - Polarization Curve - Calculation Type - Calculation Options	Composition Range Unit mg/L Selected Range 1 De 6 to 10.0 in 10 steps of 1.0	New Delete	
	C Linear ● Log ○ Point List End Points Start 1.00000e-6 End 10.0000 Step Size Increment 1.00000 ○ Number Steps 10 ○ Select one, the calculated	other is	_
	OK Cancel Apply	Help	

IX. Under the **Category** section, select **Var. 2 -Composition**. Go to the **Component** tab, and select CO2

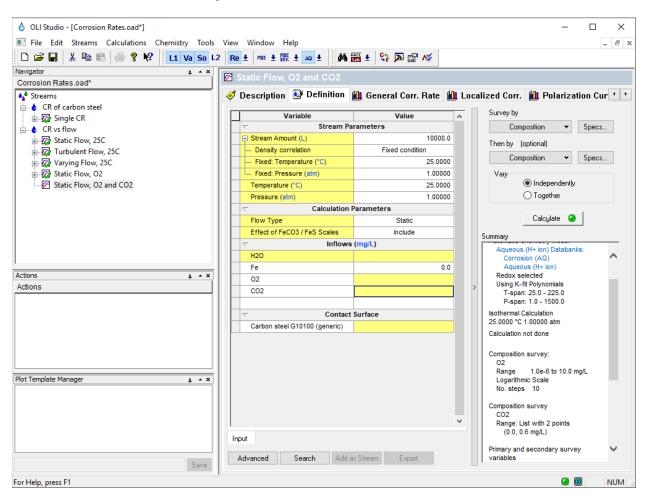
Composition Rates Calculation	n		?	×
Category	Component	Survey Range		
Var. 1 - Composition Var. 2 - Composition – Polarization Curve – Calculation Type – Calculation Options	Compone ✓ Hide CO2 Fe O2	component inflow which will be varied over the	New Inflow	
		OK Cancel App	oly Help	

X. Then select the **Survey Range** tab. Select the Point List option. Create two point with values of 0 and 0.6 mg/L. Then click **OK**.

Composition Rates Calculation		?	×
Category -Var. 1 - Composition - Var. 2 - Composition - Polarization Curve - Calculation Type - Calculation Options	Component Survey Range Composition Range Unit mg/L Selected Range Paint List: 0.0 to 0.0	New	
	O Linear O Log Point List 1 0.0 2 0.6	Add Point Remove Pts	
	OK Cancel Apply	Help	

XI. Leave the default alloy Carbon steel G10100 (generic) as the contact surface

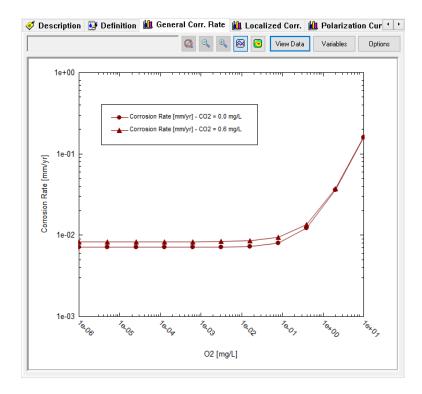
Your screen should look like the image below.



- 12. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 13. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

Click on the **General Corr. Rate** tab (M General Corr. Rate). This tab displays a plot showing the results of corrosion rate and pH.

- 1. Right-mouse click on the X-axis and change it to Logarithmic Scale
- 2. Right-mouse click on the Y-axis and change it to Logarithmic Scale
- 3. Right-mouse click on the pH curve and select Remove Series

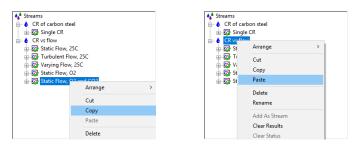


The effects of CO₂ are small, particularly in relation to the oxygen effects. The Corrosion rates at low O₂ content are about 0.0071 mm/yr with no CO₂ and 0.0083 mm/yr with 0.6 mg/l CO₂; a small difference between two small rates. At 10 mg/l O₂ the corrosion rate is 0.16 mm/y and it is the same with and without CO₂. Thus, CO₂ has no effect on corrosion at high O₂ concentrations meaning that the surface is corroded by oxygen and small concentrations of CO₂ 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

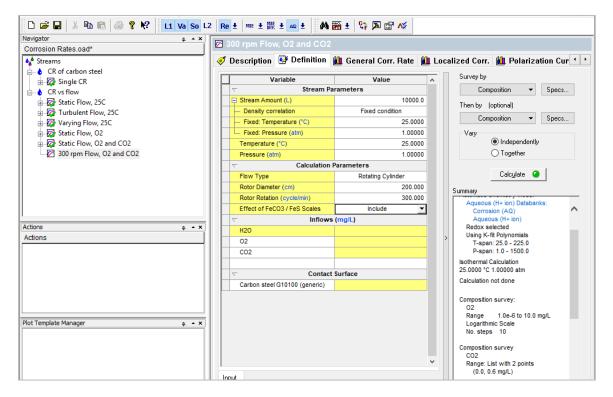
Lastly, you will look at the effects of shear rates on the tank in contact with CO₂ and O₂.

1. **Copy** (right-mouse click or Ctrl+C) *'Static Flow, O2 and CO2'* corrosion calculation, and **paste** (right-mouse click or Ctrl+V)under the stream *'CR vs Flow'*



- 2. Change the Static Flow, O2 and CO2-1 name to 300 rpm flow, O2 and CO2 using the <F2> key
- 3. Add Oxygen (O2) and carbon dioxide (CO2) to the inflow grid
- 4. Change the Flow Type from **Static** to **Rotating Cylinder**
- 5. Set the Rotor Diameter to 200 cm
- 6. Set the Rotor Rotation to 300 cycles/min
- 7. Leave the default alloy Carbon steel G10100 (generic) as the contact surface

Your screen should look like the image below.



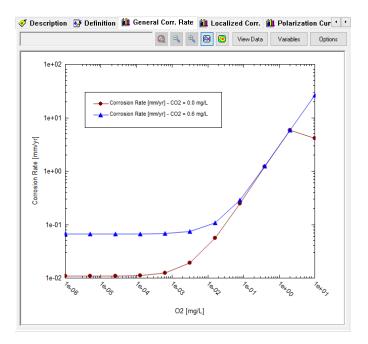
- 8. We are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 9. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

Click on the **General Corr. Rate** tab (M General Corr. Rate). This tab displays a plot showing the results of corrosion rate and pH.

- 1. Right-mouse click on the X-axis and change it to Logarithmic Scale
- 2. Right-mouse click on the Y-axis and change it to Logarithmic Scale
- 3. Right-mouse click on the pH curve and select Remove Series
- 4. Double click on the CO2=0.6 mg/L. This will open a new window. Change the color to blue.

Curve Properties	?	×
Curves		
Corrosion Rate [mm/yr] - CO2 = 0.0 mg/L Corrosion Rate [mm/yr] - CO2 = 0.6 mg/L		
Auto Legend Text		_
Corrosion Rate [mm/yr] - CO2 = 0.6 mg/L		
✓ Auto Line Style ✓ Auto Line Weight ✓ Auto Color ✓		
Auto Symbol Auto Scaling Factor Hidden		
OK Cancel Apply	He	elp

The plot should look like the image below.



The 0.6 mg/L CO₂ curve shifted to higher values at low O₂ concentrations compared to no CO₂ presence. Now, when comparing the corrosion rate for the 0.6 mg/L CO₂ 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 O₂ concentrations (right side of the plot) is also pronounced. Corrosion is still dominated by O₂ attack, but the rate is now over 10 mm/year, about 100x greater than the static conditions.

8.3. Gas condensate corrosion

Example 52: Condensed overhead gas and mitigation strategies

An alkanolamine gas sweetening plant has corrosion problems in the condensed overhead gas.

Diethanolamine is used to neutralize an acid gas containing carbon dioxide (CO_2) and hydrogen sulfide (H_2S) . The diethanolamine is regenerated and the acid gases are driven off in a stripper. The off gas from this stripper is saturated with water vapor. As these gases cool, they will condense. This condensate can be very corrosive. The plant's service life can be shortened considerably due to these condensed acid gases.

In this example, you will calculate the gas dew point temperature, remove the condensed aqueous phase and perform a Corrosion Rate calculation with the condensed water. Lastly, you will consider mitigation strategies for the pipes.

You are introducing *fluid velocity* and *liquid condensation* into the calculation. The software uses a diffusion layer model to compute mass transfer to and from corroding surfaces. Higher rates produce thinner layers, resulting in faster mass transfer rates, and thus higher corrosion rates. The liquid condensation point is straightforward; it calculates the temperature (or pressure) where the first liquid drop forms.

Starting the Simulation

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

	Corrosion Rate Cal	culation	
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

- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to Gas Condensate
- 3. Select the AQ thermodynamic Framework
- 4. Click on the Names Manager Icon and select the Formula option
- 5. Click on the Units Manager Icon, and select Metric, Batch, Mole Fraction
- 6. Enter the composition, temperature and pressure of the stream given in the table above
- 7. Go to the **Add Calculation** button and select **Corrosion Rates** calculation or by selecting the **Add Corrosion Rates** icon in the Actions Pane.
- 8. Go to the Survey by option and select Single Point Rate. Change the name to Gas Cond. Dew Point.

- 9. Change the Flow Type from Static to Pipe Flow.
- 10. Specify the Pipe Diameter = 10 cm and the Pipe Flow Velocity = 2 m/s.
- 11. Leave the default alloy Carbon steel G10100 (generic) as the contact surface

OLI Studio - [Corrosion Rates.oad*]			- 0 ×
File Edit Streams Calculations Chemistry Tools	View Window Help		_ 8 ×
🗅 🚅 🖬 👗 🖻 🛍 🎒 🦿 🤻 📘 L1 Va So L2	2 Re ± MSE ± MSE ± 40 ± 64	🎬 🛨 💱 🔎 😭 🎸	
Navigator	🖉 Rates		
Document1			
Corrosion Rates.oad*	🥵 Definition 🚻 General Corr.	Rate 🛍 Localized Corr.	🛍 Polarization Curve 📓 Report 🚺 🕨
🍫 Streams	Variable	Value	Survey by
CR of carbon steel	Stream Pa		Single Point Rate 🔻 Specs
in	Stream Amount (mol)	1.00000e5	
Gas Condensate	Temperature (°C)	38.0000	Then by (optional)
	Pressure (atm)	1.20000	None 💌 Specs
	Calculation	Parameters	Vary
	Calculate	Temperature	 Independently
	Flow Type	Pipe Flow	 Together
	Pipe Diameter (cm)	10.0000	
	Pipe Flow Velocity (m/s)	2.00000	Calculate 🥥
	Effect of FeCO3 / FeS Scales	Include	Summary
	□		
	H2O	5.42000	Unit Set: Metric (mole fraction)
Actions	C02	77.4000	Automatic Chemistry Model
Actions	N2	0.0200000	Aqueous (H+ ion) Databanks:
	H2S	16.6000	Corrosion (AQ) Aqueous (H+ ion)
	CH4 C2H6	0.500000	Redox selected
	C3H8	0.0300000	Using K-fit Polynomials T-span: 25.0 - 225.0
	Fe	0.0300000	P-span: 1.0 - 1500.0
	10	0.0	Dew Point Calculation
	Contact	Surface	1.20000 atm 37.5851 °C
	Carbon steel G10100 (generic)		Calculation complete
Plot Template Manager			Calculation complete
			Single Point
			No secondary survey selected
			Polarization Curve Range
	Input 1		Range -2.0 to 2.0 V (SHE)
	Input 1		Step size 0.01 V (SHE) No. steps 400
	Advanced Search Add a	as Stream Export	•
Save			
For Help, press F1			Image:

Your screen should look like the image below.

Now that the gas condensate stream is created, the next task is to isolate the condensed water at the dew point temperature.

- 12. Click on the Specs button. This will open a new window
- 13. Under the **Category** section, select **Calculation Type**
- 14. Change the Type of Calculation from Isothermal to **Dew Point.** Make sure that radio button for temperature is selected since we are going to calculate the Dew Point temperature for this example. Then click **OK**.
- 15. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 16. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates*.

- 1. Click on the General Corr. Rate tab (M General Corr. Rate).
- 2. 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.

- 3. Click on the **Polarization Curve** tab (Polarization Curve). Before interpreting this plot, we will format it for easy viewing.
- 4. Click on the **Options** button. This will open a new window.



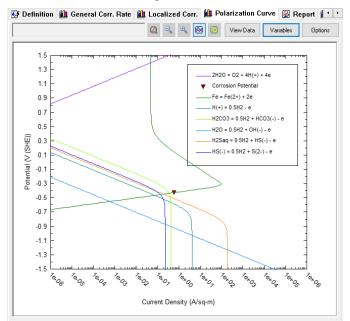
- 5. Under the Category section select X axis. Change the Minimum to 1e-6 and Maximum to 1e6.
- 6. Now, select Y axis. Change the Minimum to -1.5 and Maximum to 1.5. Then click OK.
- 7. Click on the Variables button. This will open a new window.

🛍 Po	arization C	urve	월 R	eport	••
8 💿	View Data	Var	iables	Op	otions

8. Remove the following variables by unchecking them. See image below. Then **Click OK.**

Select Data To Plot	?	×
Survey Points & Reactions		
Half-Reactions		
$\begin{array}{l} 2H20 = 02 + 4H(+) + 4e \\ \hline Corrosion Potential \\ \hline Fe = Fe(2+) + 2e \\ \hline Fe(3+) = Fe(2+) + e \\ H(+) = 0.5H2 - e \\ H2C03 = 0.5H2 + HC03(+) - e \\ H20 = 0.5H2 + 0H(-) - e \\ H25aq = 0.5H2 + HS(-) - e \\ H25aq = 0.5H2 + S(-) - e \\ HS(-) = 0.5H2 + S(-) - e \\ HS(+) $		
Clear all reactions Select all reactions		
OK Cancel App	oly	Help

9. Your polarization curve should look like the image below.



You can click and drag the legend of the polarization curve to your desired position.

This is a measured potential vs. current density plot. The anodic portion (green curve) is the carbon steel. There are cathodic reactions. The sum of the cathodic currents adds up to the anode curve at a single point: The corrosion potential (represented by the inverted red triangle \checkmark) 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/m².

Notice that the cathodic reaction that contributes the most to corrosion is H_2CO_3 (light green line). The next contributors are H_2S (orange line) and HS^{-1} (blue line) equally. After that is H^+ (turquoise line). Water reduction (light blue line), contributes the least to corrosion.

Mitigation Strategies

There are several mitigating solutions to this corrosion problem.

One is adding insulation to prevent temperature drops. The dew point is very close to the overhead gas temperature so this may not be a suitable option. Adding heat to keep the temperature above the dew point is usually considered along with insulation.

Changing the chemistry to change the partial oxidation and reduction processes is also an option.

Changing alloys could mitigate the corrosion problems as well.

We will explore the change of chemistry and change of alloys for this example.

Adjusting the solution chemistry

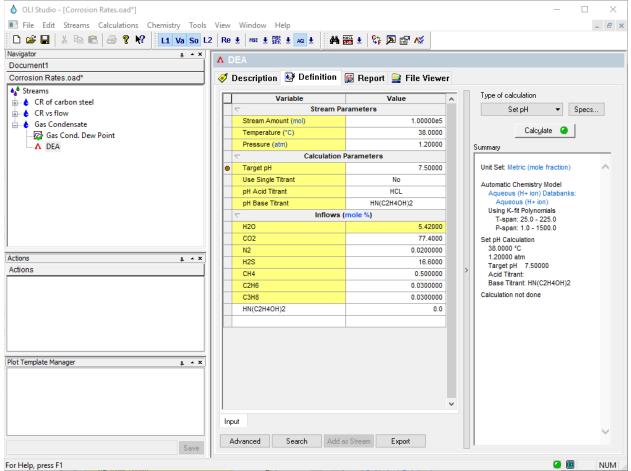
The condensate pH is approximately 3.9. We can try to add a base to increase the pH. In this section, we will add Diethanolamine to raise the pH to 7.5.

Single Point– Set pH Calculation

- 1. Click on the '*Gas Condensate*' stream and go to the Add Calculation button and select Single Point calculation or by selecting the Add Single Point icon in the Actions Pane.
- 2. Change the name to **DEA** using the **<F2>** key.
- 3. Add DEA in the inflows grid. (It should have changed to the formula name: HN(C2H4OH)2
- 4. Go to the Type of Calculation option and select Set pH
- 5. Change the Target pH to 7.5
- 6. Click on the drop-down arrow for the pH Base Titrant and select DEA (or HN(C2H4OH)2)

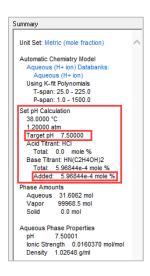
We have set up the calculation to adjust the amount of DEA to match the target value of pH=7.5.

Your screen should look like the image below.



- 7. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 8. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

1. Check the summary box to analyze the results.



The pH is set to 7.5 and the inflow of DEA to the total gas is approximately 5.97e-4 mole%.

The DEA concentration in the condensing water and the amount remaining in the vapor phase can both be viewed in the Report tab.

2. Click on the Report Tab and go to the Total and Phase Flows and Species Output tables

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	
ОН-1	6.55471e-10	2.07387e-6	
H+1	2.47871e-11	7.8425e-8	
Total (by phase)	100.0	100.0	100.0

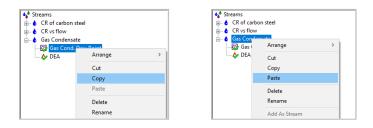
Total and Phase Flows (Amounts) column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mol	mol	mol
Mole (True)	1.00000e5	31.6062	99968.5
Mole (App)	1.00001e5	32.0477	99968.5
	g	g	g
Mass	4.08064e6	642.188	4.08000e6
	L	L	L
Volume	2.11456e6	0.625619	2.11456e6

Recalculating the corrosion rate with DEA

We now can recalculate the corrosion rate with DEA in the stream. This represents some DEA entrained in the vapor phase as the gas leaves the regenerator.

1. Copy 'Gas Cond. Dew Point' corrosion calculation, and paste it under the stream 'Gas Condensate'



- 2. Change the name to **Gas Cond. Dew Point DEA** using the **<F2>** key
- 3. Add DEA to the inflows gird and give it the value computed in the set pH calculation. (DEA =5.96844e-4 mole%)
- 4. Leave the default alloy Carbon steel G10100 (generic) as the contact surface

Your screen should look like the image below.

OLI Studio - [Corrosion Rates.oad*]			– 🗆 X
File Edit Streams Calculations Chemistry Tools	· · · · · · · · · · · · · · · · · · ·		_ & ×
🗅 🗃 🖬 👗 🖻 💼 🍜 🤋 🎌 🛛 💶 Va So L2	Re 🛨 MSE 🛨 SRK 🛨 🗛 🛨 🏘	🎬 🛨 💱 🔎 😭 🌾	
Navigator a *	Gas Cond. Dew Point DEA		
Document1			
Corrosion Rates.oad*	🦪 Description 🛃 Definition	🛍 General Corr. Rate 📶 Loc	alized Corr. 🛍 Polarization Cur 🚹 🕐
🍫 Streams	Variable	Value	Survey by
🕀 🔥 CR of carbon steel	Stream Pa		Single Point Rate 👻 Specs
E CR vs flow	Stream Amount (mol)	1.0000e5	
Gas Condensate	Temperature (°C)	38.0000	Then by (optional)
DEA	Pressure (atm)	1.20000	None 👻 Specs
Gas Cond. Dew Point DEA	Calculation	Parameters	Vary
	Calculate	Temperature	 Independently
	Flow Type	Pipe Flow	 Together
	Pipe Diameter (cm)	10.0000	
	Pipe Flow Velocity (m/s)	2.00000	Calculate 🥝
	Effect of FeCO3 / FeS Scales	Include	Summary
	☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐	(mole %)	
	H2O	5.41940	Unit Set: Metric (mole fraction)
Actions	C02	77.4000	Automatic Chemistry Model
Actions a Actions	N2	0.0200000	Aqueous (H+ ion) Databanks:
Actions	H2S	16.6000	Corrosion (AQ) Aqueous (H+ ion)
	CH4	0.500000	Redox selected
	C2H6	0.0300000	Using K-fit Polynomials
	C3H8	0.0300000	T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0
	HN(C2H4OH)2	5.96844e-4	Dew Point Calculation
	Fe	0.0	1.20000 atm
	Contact	Surface	Calculation not done
Plot Template Manager a. 🔺 🗙	Carbon steel G10100 (generic)	Junace	Olivety Delet
	carbon steer or to roo (generic)		Single Point No secondary survey selected
		J	Polarization Curve Range Range -2.0 to 2.0 V (SHE)
	1		Step size 0.01 V (SHE)
	Input		No. steps 400
	Advanced Search Add a	as Stream Export	Metal: Iron/Mild steel
Save	Add data	and a state of the	P
For Help, press F1			Image: State of the state of

- 9. Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key
- 10. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

- 1. Click on the General Corr. Rate tab (🛍 General Corr. Rate).
- 2. Click on the View Data button to see the results in tabulated form.

	Temperature	Corrosion Rate	pН
	°C	mm/yr	
1	33.5105	1.10650	7.59719

Notice that the corrosion rate has decreased from 0.7 mm/year to 0.48 mm year. The pH is 7.6, and it remained similar to the target value of 7.5. Based on these results neutralizing the pH had a partial effect on corrosion reduction.

Changing the Alloy

Since treating the acid gas with a base is probably not a good idea for metal hydroxides, perhaps we can change the alloy. We will add a new corrosion rates calculation and test different alloys.

13%Cr Stainless Steel

- 1. Copy 'Gas Cond. Dew Point DEA' corrosion calculation, and paste it under the stream 'Gas Condensate'
- 2. Change the name to Gas Cond. 13%Cr using the <F2> key.

Notice that in the inflows, copying and pasting does not bring the DEA and its composition to this corrosion calculation. The reason why is because the DEA was added at the corrosion rate calculation level, and not at the stream level.

3. Change the contact surface to 13%Cr stainless steel

Your screen should look like the image below.

🗅 🗃 🖬 👗 🛍 📸 🍜 🎖 💦 🚹 Va So L2	Re	🛨 MSE ± MSE ± 🗛 ± 🚧	🎬 🛃 💱 🔊 😭 🌾		
Navigator # * X		Gas Cond. %13Cr			
Document1					
Corrosion Rates.oad*	1	Description 📑 Definition	🛍 General Corr. Rate 🛔	Loc	alized Corr. 🛍 Polarization Cur 💶
♦ Streams					Survey by
🛓 👌 CR of carbon steel		Variable	Value	^	
庄 🗄 CR vs flow					Single Point Rate 🔻 Specs
🖶 👌 Gas Condensate		Stream Amount (mol)	1.00000e5		Then by (optional)
🗄 📈 Gas Cond. Dew Point	0	Temperature (°C)	38.0000		None V Specs
🎸 DEA	•	Pressure (atm)	1.20000		None • specs
🖅 🐼 Gas Cond. Dew Point DEA		Calculation I	Parameters		Vary
Gas Cond. %13Cr		Calculate	Temperature		 Independently
		Flow Type	Pipe Flow		 Together
		Pipe Diameter (cm)	10.0000		
		Pipe Flow Velocity (m/s)	2.00000		Calculate 🥝
		Thermal Aging Temperature (°C)	399.000		Summary
		Thermal Aging Time (hr)	0.0		
		Inflows (mole %)		Unit Set: Metric (mole fraction)
1		H20	5.42000		
Actions a *		C02	77.4000		Automatic Chemistry Model Aqueous (H+ ion) Databanks:
Actions		N2	0.0200000	>	Corrosion (AQ)
		H2S	16.6000		Aqueous (H+ ion)
		CH4	0.500000		Redox selected Using K-fit Polynomials
		C2H6	0.0300000		T-span: 25.0 - 225.0
		СЗН8	0.0300000		P-span: 1.0 - 1500.0
		Fe	0.0		Dew Point Calculation 1.20000 atm
			Surface		Calculation not done
Plot Template Manager		Fe(86.850)Cr(13.000)C(0.150)			Single Point

- 4. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 5. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

- i. Click on the **Report** tab to see the results. (You may need to use the ◀► buttons to move the tabs and find the Report tab).
- ii. Go to the Calculated Rates table

mp to: Calculation Summary	\checkmark	Q	a Customize	Export
Calculated Rates				~
Corrosion Rate	0.0622463	mm/yr		
Corrosion Rate Corrosion Potential	0.0622463	mm/yr V (SHE)		

The corrosion rate of 13%Cr is one order of magnitude lower when compared to the corrosion rate for Carbon Steel, i.e. at 0.06 mm/year for 13%Cr vs 0.7 mm/year for Carbon Steel. This is consistent with the use of 13% Cr to protect against CO₂ corrosion.

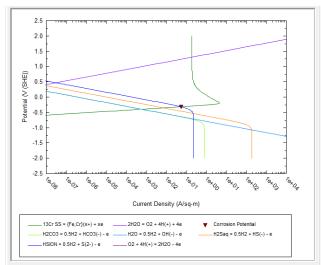
- iii. Click on the **Polarization Curve** tab (Mental Polarization Curve).
- iv. Click on the **Variables** button. This will open a new window.

l	🗓 Po	larization C	urve	👼 Re	eport	••
8	E	View Data	Var	iables	Op	otions

v. Remove the following variables by unchecking them. See image below. Then Click OK.

ect Data To Plot		?	×
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 + HS(-) - e			
Net Current Density			
02 + 4H(+) = 2H2O - 4e			
Peak Current Density			
Clear all reactions Select all reactions			
OK Cancel	Apply	He	lp

vi. The polarization curve (after some layout modifications) should look like the image below.



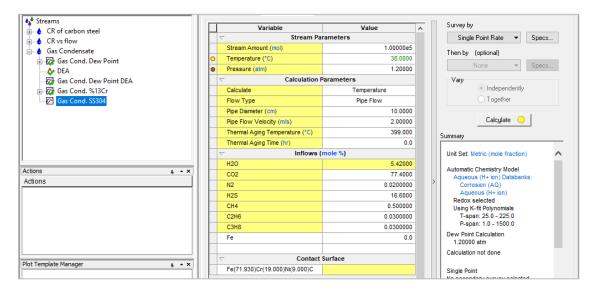
The layout of the plot was changed for easy reading. To change layout, you can right click on any part of the plot and select the option *Alloy Layout Changes* to modify the appearance of your plot.

The corrosion potential of 13%Cr is -0.31 V vs SHE and the corresponding corrosion current i_{corr} =0.06 A/m². The i_{corr} for Carbon Steel was 0.61 A/m², this means that 13%Cr is 10x more resistant to corrosion under the same conditions.

Stainless Steel 304

- 1. Copy 'Gas Cond. Dew Point DEA' corrosion calculation, and paste it under the stream 'Gas Condensate'
- 2. Change the name to Gas Cond. SS304 using the <F2> key
- 3. Change the contact surface to Stainless Steel 304

Your screen should look like the image below.



- 4. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 5. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous example named *Corrosion Rates.*

- 1. Click on the **Report** tab to see the results. (You may need to use the **◄**► buttons to move the tabs and find the Report tab).
- 2. Go to the Calculated Rates table

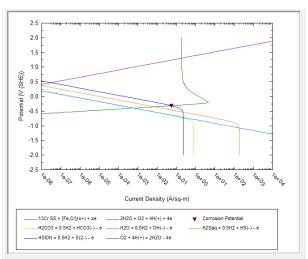
Corrosion Rate	3.57108e-3	mm/yr
Corrosion Potential	-0.172583	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	3.29499e-3	A/sq-m

The corrosion rate of 304 SS is now 0.0036 mm/year. This is a negligible value.

- 3. Click on the **Polarization Curve** tab (Mental Polarization Curve).
- 4. Click on the Variables button. This will open a new window.
- 5. Remove the following variables by unchecking them. See image below. Then Click OK.

lect Data To Plot		ſ	×
Survey Points & Reactions			
Half-Reactions			
2H2O = O2 + 4H(+) + 4e			
Corrosion Potential			
Fe(3+) = Fe(2+) - e			
H(+) = 0.5H2 - e			
H2CO3 = 0.5H2 + HCO3(·) - e			
$H2O = 0.5H2 + OH(\cdot) - e$			
H2Saq = 0.5H2 + HS(-) - e			
Net Current Density			
O2 + 4H(+) = 2H2O - 4e			
Peak Current Density			
S30400 = {Fe,Cr,Ni}(x+) + xe			
Clear all reactions Select all reactions			
Cicar dii redociona Soloci dii redociona			
OK Cancel	Apply	He	h

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/m². With this low corrosion current density, sour gas regeneration can be remedied using a higher-grade alloy such as SS304.

Section 9. Thermal Aging and Variations in Alloy Composition

9.1. Overview and Basic Terminology

Localized corrosion of engineering alloys is a complex function of metallurgical factors and environmental conditions. Among metallurgical factors, effects of thermal instabilities are of interest for assessing the performance and expected service life of industrial components fabricated from nominally corrosion-resistant stainless steels and nickel-base alloys.

Fabrication processes such as heat treatment and welding are known to introduce microstructural changes that may affect both the mechanical and corrosion performance of an alloy. In particular, thermal instability of stainless steels and nickel-base alloys may lead to the formation of complex metal carbides of the type M_3C_2 , M_7C_3 , M_6C , or $M_{23}C_6$ in which the metallic component M represents Cr, Mo, W, and Fe. The carbide is chromium- or molybdenum-rich depending on the carbide type, which in turn depends on the alloy composition and temperature. Also, various chromium-rich intermetallic phases can form in many alloys. Precipitation of such phases may occur at temperatures ranging from 500 to 900 °C depending on alloy composition. Formation of grain boundary carbides often results in the depletion of chromium and, possibly, molybdenum in the vicinity of the grain boundary because of the slow diffusion of substitutional elements such as chromium relative to the interstitial carbon.

Similarly, the corrosion resistance of welded components may be affected by the segregation of alloying elements and precipitation of intermetallic phases, carbides or nitrides in the solidified weld and unmixed zones as well as the precipitation of carbides and other phases in the heat-affected zone adjacent to the weld.

Sensitization of Fe-Ni-Cr-Mo alloys and its effects on intergranular attack and intergranular stress corrosion cracking is the most directly observed effect of Cr depletion. It may result in intergranular attack and intergranular stress corrosion cracking. Localized corrosion can be also affected by Cr and Mo depletion.

Corrosion Analyzer contains the following technology that can help address these issues:

- A grain boundary microchemistry model for predicting the chromium and molybdenum depletion in the vicinity of grain boundaries as a result of carbide formation;
- An electrochemical model for calculating the repassivation potential of Fe-Ni-Cr-Mo-W alloys as a function
 of alloy composition and environmental conditions including temperature and concentrations of aqueous
 solution species;
- A procedure for calculating the observable repassivation potential that corresponds to macroscopic localized corrosion by applying the electrochemical model to the depletion profiles and performing suitable integration.

More details about this technology are described by Anderko et al. (2008), Tormoen et al. (2009), Anderko et al. (2009), and Sridhar et al. (2009).

Alloy Chemistry

Simulations can be performed, in general, for alloys that belong to the Fe-Ni-Cr-Mo-W-N-C family (i.e., for stainless steels and nickel-base alloys).

Depletion profiles in the vicinity of grain boundaries and depletion parameters can be obtained for austenitic alloys (including stainless steels and Ni-base alloys). Also, the effect of Cr and Mo depletion on localized

corrosion can be calculated. This effect can be examined using the repassivation potential, which provides a threshold potential for the stabilization of localized corrosion (Anderko et al., 2009).

For other alloys from the Fe-Ni-Cr-Mo-W-N-C family, the repassivation potential can be calculated if the alloy composition is known. This also includes experimental alloys and separate phases that may be formed as a result of various forms of heat treatment (Sridhar et al., 2009).

Calculation types

Thermal aging is an additional phenomenon that can be simulated within the framework of corrosion kinetics. All calculations types and, in particular, survey types, that are supported for corrosion kinetics are also supported in conjunction with the study of thermal aging.

If it is desired to make calculations on a thermally aged sample, the thermal aging temperature and time need to be specified in the **Calc Parameters** section in the **Definition** tab. The default values are 399 °C for the thermal aging temperature and 0.0 hours for the thermal aging time. If either of these default values is used, no thermal aging effects will be predicted. Thus, by default, Corrosion Analyzer performs calculations on samples that have not been thermally aged.

Thermal Aging Temperature Survey

This calculation makes it possible to vary the thermal aging temperature within a certain range. A fixed value of thermal aging time is assumed as specified by the user. Typically, the temperatures for which thermal aging effects can be observed range from ~500 °C to ~900 °C, with the effects being most pronounced in the middle of this range.

Thermal Aging Time Survey

This calculation can be used to examine the effect of aging time at a fixed thermal aging temperature.

Output Specific to Thermal Aging

The following output can be generated:

- Chromium and molybdenum depletion profiles, i.e., the variation of Cr and Mo concentration within the grain as a function of grain boundary.
- The depletion parameter, which provides compact information on the extent to which the depletion process reduces the grain boundary concentration below a certain critical value of, which can be defined by well-known criteria for maintaining passivity (e.g. $x_{Cr}^* = 0.11 \text{ or } 0.12$). 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.

9.2. Thermal Aging and Variations in Alloy Composition

We will show examples of simulating the effects of thermal aging on Fe-Ni-Cr-Mo-W-C-N alloys (i.e., stainless steels and nickel-base alloys). Specifically, we will show how to predict:

- 1. Chromium and molybdenum depletion profiles in the vicinity of grain boundaries, which result from heat treatment of austenitic alloys;
- 2. Depletion parameters for sensitized austenitic alloys, which provide an indicator of whether the alloy is susceptible to intergranular corrosion.
- 3. Effect of thermal aging on the repassivation potential of austenitic alloys, which provides a threshold condition for localized corrosion (pitting or crevice corrosion).
- 4. The repassivation potential of alloys with compositional variations that may or may not result from thermal aging. This facility can also be used for bulk alloys that are not in the database or to hypothetical or experimental alloys as long as they belong to the Fe-Ni-Cr-Mo-W-C-N family. An example will be given for a duplex alloy, either annealed or thermally treated.

Example 53: Thermal aging of alloy 600

We will be studying the behavior of thermally aged alloy 600 in a dilute aqueous solution of sodium chloride, and will simulate how the time of thermal aging affects alloy 600 at a fixed thermal aging temperature of 700°C.

Starting the Simulation

Thermal Aging Calculation

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

Thermal Aging Calculation				
Calculatio	on 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			

- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to *Thermal Aging*
- 3. Select the AQ thermodynamic Framework (selected by default)
- 4. Click on the Units Manager Icon and select Metric, Batch, Moles
- 5. Click on the Names Manager Icon and select Display Name

- 6. Enter the stream composition and conditions specified in the table above
- 7. Go to the Add Calculation button and select Corrosion Rates

Note: Even though the thermal aging simulation facilities do not predict corrosion rates per se, they belong to the category of corrosion kinetics and, therefore, they are included in the Corrosion Rates section of the Corrosion Analyzer.

- 8. Select the Survey by Thermal Aging Time
- Change the name from *Rates* to *Alloy 600* using the <F2> key or by right-mouse click on the object and select rename
- 10. Select Alloy 600 from the Contact Surface grid
- 11. In the **Calculation Parameters** grid, change the default value for the **Thermal Aging Temperature** to 700°C.

Note that the default value for the **Thermal Aging Temperature** is 399 °C, which is a low value so that, in the default case, no effects of thermal aging are being calculated.

Your screen should look like the image below.

OLI Studio - [Corrosion Rates.oad*]			– 🗆 X
	hamistary Table View Window Ulaba		
File Edit Streams Calculations C			_ F ×
🗋 🗅 🚔 🖬 👗 🐘 💼 🥌 🤶 🎗 😢	L1 Va So L2 Re ± MSE ± MSE ± AQ ±	👬 🎬 ± 💱 🔎 😭 🔏	
Navigator 👖 🔺 🗙	Alloy 600		
Corrosion Rates.oad*		49	
♦ Streams	Sene Description 🔮 Definition 📶 Gene	eral Corr. Rate 📶 Localized Corr.	🛍 Polarization Curve 📓 Report 🕚
CR of carbon steel	Variable	Value A	Survey by
Gas Condensate	Stream Par	ameters	Thermal Aging Time 🔻 Specs
Eccalized Corrosion	Stream Amount (mol)	55.5482	Then by (optional)
🗄 🗄 Thermal Aging	Temperature (°C)	60.0000	
Alloy 600	Pressure (atm)	1.00000	None 🔻 Specs
	Calculation P		Vary
	Flow Type	Static	Independently
	Thermal Aging Temperature (°C)	700.000	O Together
	Thermal Aging Time (hr)	(Calculate 🥝
	Water Inflows	(mol) 55.5082	
	Sodium chloride	0.040000	Summary
A share	Nickel	0.040000	Unit Set: Metric (moles)
Actions 4 • ×		0.0	
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
		~	Thermal Aging Time survey: Range 0.0 to 10.0 hr
	Input		Step size 2.0 hr
			No. steps 5
Save	Advanced Search Add as Stream	Export	
For Help, press F1	1		

12. Now we need to specify the Thermal Aging Time range. **Click** on the **Specs** button. This will open a new window.

13. Under the **Survey Range** tab, change the range for Thermal Aging Time from 0 to 22 hours with an increment of 4.4 hours (of 5 steps).

Rates Calculation		?	\times
Category	Survey Range		
- Var. 1 - Thermal Aging Time - Polarization Curve - Thermal Aging - Calculation Type - Calculation Options	Themal Aging Time Range Unit: hr Selected Range 100 to 22.0 in 5 steps of 4.4	New Delete	
	Clinear Clog Point List Start Clog Clog		_
	Step Size Increment 440000 Select one, the calculated calculated	other is	
< >>	OK Cancel Apply	Help	

14. Under the **Category** section, select the **Thermal Aging** option.

Category Thermal Aging Var. 1. Thermal Aging Erp Directly from Correlation: • No Yes Calculation Durie Alloy Composition wt%: • No Yes Calculation Options Fe (8.534) Cr 15.408 Ni (75.032) Mo+W (0) C 0.026 N (0) Catolide Stoichiomety: • Fe (0) Cr (7 7) Ni (0) • Catolide Thermochemistry: A (405130) B (-25.765) Cr Diffusion Coefficient: D0 (4.4016e-006) Q (-243000)
Mo, W Diffusion Coefficient: D0 0 Q 0 Cr Sensitization Threshold wt%; 11 Grain Size: 123 Revert to Default

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

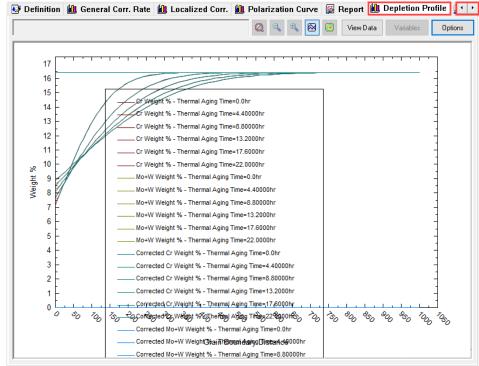
Also, you can indicate whether the repassivation potential (E_{rp}) should be calculated directly from the correlation developed by Anderko et al. (2008), which expresses E_{rp} as a function of alloy composition or not. If it is not calculated directly, then the repassivation potential is calculated 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.

15. For now, we will accept the default settings. Click OK.

- 16. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 17. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous section named *Corrosion Rates*.

Analyzing the Results

Click on the **Depletion Profile** tab (^{▲ Depletion Profile}). If you don't see it in your screen, use the <> buttons to move the tabs.



Note: Since alloy 600 does not contain any molybdenum, the molybdenum curves will always be equal to zero.

This plot will show the concentrations of chromium and molybdenum within a grain as a function of the distance from the grain boundary (in μ 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.

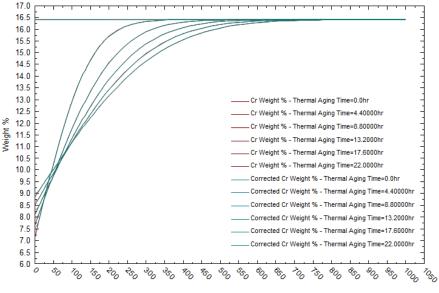
Let's customize the plot

- 2. Click on the **Options** button. This will open a new window.
- 3. Since alloy 600 does not contain Mo or W, eliminate the Mo+W curves. To do this, go to the **Category** section and select the **Curves** option
- 4. Highlight the Mo+W weight % curves by pressing the Shift key and the down key (**Shift +** ↓). After highlighting these curves, check the **Hidden** button.

Customize Plot		?	×
Category General - Legend - Y Axis - Y Axis - Curves	Curves Curves Cr Weight 2: Thermal Aging Time=17.6000hr Cr Weight 2: Thermal Aging Time=22.0000hr Mo-W Weight 2: Thermal Aging Time=2.0000hr Mo-W Weight 2: Thermal Aging Time=3.2000hr Mo-W Weight 2: Thermal Aging Time=12.2000hr Mo-W Weight 2: Thermal Aging Time=2.2000hr Mo-W Weight		
	OK Cancel Apply	Н	elp

5. After hiding the Mo+W weight % curves, do the same for the Corrected Mo+W weight % curves. Then click **OK**.

The plot should look like the image below.



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

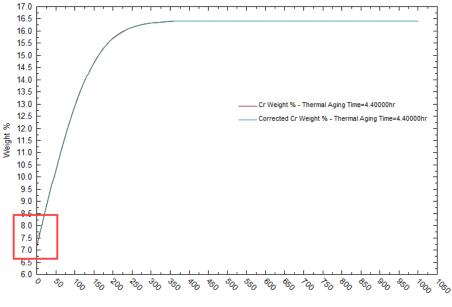
Now, let's focus on the differences between the uncorrected and corrected depletion profiles. To have a clear picture of the difference between them, we will analyze the depletion profiles results obtained at 4.4 hours of thermal aging.

- 6. Click on the Options button, and select the Curves category
- 7. Highlight all curves except the ones labeled as:

Cr Weight % - Thermal Aging Time = 4.40000 hr, and Corrected Cr Weight % - Thermal Aging Time = 4.40000 hr

Check the Hidden box, then click OK.

Your plot should look that the image below.



Grain Boundary Distance

In the obtained plot, you can see the difference between the two curves for small distances from the grain boundary (roughly below 30 μ 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.

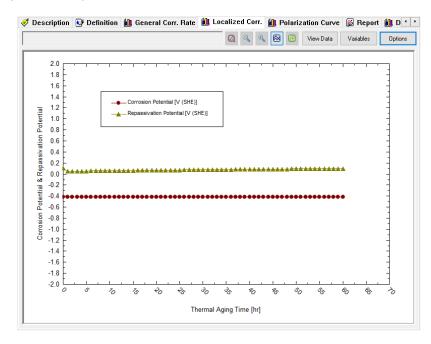
- 1. Copy the Alloy 600 corrosion calculation, and then paste it under the Thermal Aging Stream
- 2. Rename the new calculation as Alloy 600 Cr depletion
- 3. Go back to the **Definition** tab and click the **Specs** button
- 4. In the **Var.1 Thermal Aging Time** category, change the Survey Range as follows: **Start**=0 hours, **End**= 60 hours with an **Increment**= 1 hour. Then click **OK**.

Your screen should look like the image below

A 01101 17 10 1 10 11					
OLI Studio - [Corrosion Rates.oad*]					
🗈 File Edit Streams Calculations Chemistry Tools View Window Help 🗧 🖻					
🗋 🗅 🚅 🖬 🖌 🍋 💼 📾 🍘 🎖 🕨	L1 Va So L2 Re ± MSE ± SRK ± AQ AQ AQ A	🛨 🛛 🚧 🚟 🛨 💱 🔉 😭 📈			
Navigator # * X	Alloy 600-Cr depletion				
Corrosion Rates.oad*					
Streams	🔊 Description 🔮 Definition 🛍 General	Corr. Rate 📶 Localized Corr. 📶 Pol	arization Curve 📓 Report 🛄 D 💶		
	Variable	Value	Survey by		
🕀 💧 Gas Condensate	Stream Para	ameters	Thermal Aging Time 🔻 Specs		
🗄 🔥 Localized Corrosion	Stream Amount (mol)	55.5482	Then by (optional)		
🖃 👌 Thermal Aging	Temperature (°C)	60.0000			
	Pressure (atm)	1.00000	None 💌 Specs		
Alloy 600-Cr depletion	Calculation Pa	arameters	Vary		
	Flow Type	Static	 Independently 		
	Thermal Aging Temperature (°C)	700.000	 Together 		
	Thermal Aging Time (hr)				
		· · ·	Calc <u>u</u> late 🥥		
	Water	55.5082	Summary		
	Sodium chloride	0.0400000			
< >			Unit Set: Metric (moles)		
Actions a + ×	Contact S	urface	Automatic Chemistry Model		
Actions	Alloy 600		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		
			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		
	1	Ŷ	No secondary survey selected		
	Input				
	Advanced County Address?	Turat	Thermal Aging Temperature: 700.000		
Save	Advanced Search Add as Stream	Export			
For Help, press F1					

- 5. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 6. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous section named *Corrosion Rates.*

1. Click on the Localized Corr. tab (Localized Corr.). By default, this tab will show a plot of the corrosion potential and repassivation potential.

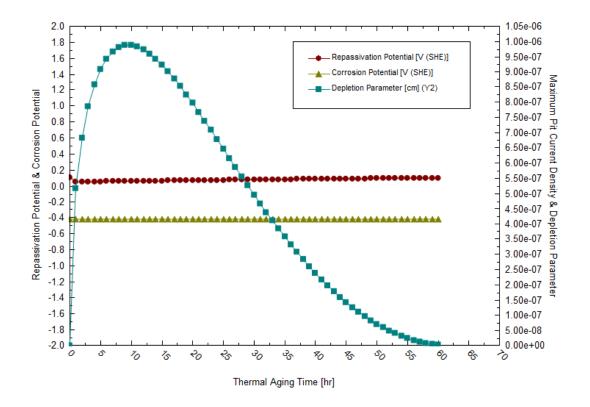


Let's add a new parameter to the plot: The **Depletion Parameter**.

- 2. Click on the Variables button. This will open a new window.
- 3. Look for the **Corrosion Values** section, click on the '+' icon, and select the **Depletion Parameter** option. Click on the >> button that belongs the **Y2 Axis**. This action will place the new variable under the Y2 Axis. Then click **OK**.

elect Data To Plot	? ×
Curves	
Survey Variables Stream Parameters Corrosion Values Comsion Current Density Comsion Rate Depletion Parameter	X Axis Thermal Aging Time Y1 Axis Repassivation Potential Corrosion Potential
Additional Stream Parameters Phase Row Properties Thermodynamic Properties Pre-scaling Tendencies Pre-scaling Index Scaling Index Scaling Index	Y2 Avis
Aqueous Aqueous Solid Molecular Totals MBG Totals - Totals	Maximum Pit Current Density
☐ Use short names ☑ Hide zero species	Z Axis
Plot data which is only within temperature range.	- Select - V
	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				
Calculatio	on 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			

- 1. Under the Thermal Aging stream add a new calculation rate. Go to the Add Calculation button and select Corrosion Rates or select the Add Corrosion Rates icon in the Actions panel
- Change the name from Rates to Alloy 825 using the <F2> key or by right-mouse click on the object and select rename
- 3. Select the Survey by Thermal Aging Temperature option
- 4. Change the stream composition and conditions to the specified values in the table above
- 5. Select Alloy 825 from the Contact Surface grid
- 6. In the Calculation Parameters grid, change the default value for the Thermal Aging Time to 15 hours

Note that the default value for the **Thermal Aging Temperature** is 0 hours, which means that no thermal aging is considered by default.

Your screen should look like the image below

Navigator a 🔺 🗙	Alloy 825		
Corrosion Rates.oad*	Alloy 625		
🍓 Streams	< Description 🔮 Definition 🛍 General Co	orr. Rate 🛍 Localized Corr. 🛍 Polari	zation Curve 📓 Report 🛍 D 💶
🗄 🗄 CR of carbon steel			Survey by
🛓 🗄 CR vs flow	Variable	Value	
🗄 🗄 Gas Condensate	Stream Param		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 👻 Specs
🖶 🐼 Alloy 600-Cr depletion	Calculation Para	imeters	Vary
Alloy 825	Flow Type	Static	 Independently
	Thermal Aging Temperature (°C)		 Together
	Thermal Aging Time (hr)	15.0000	
< >	√ Inflows (m	iol)	Calculate 🥝
1	Water	55.5082	Summary
Actions	Sodium chloride	2.84600e-3	
Actions	Nickel	0.0	Unit Set: Metric (moles)
			Automatia Chamistra Madal
	Contact Surf	face	Automatic Chemistry Model Aqueous (H+ ion) Databanks:
	Alloy 825	>	Corrosion (AQ)
			Aqueous (H+ ion)

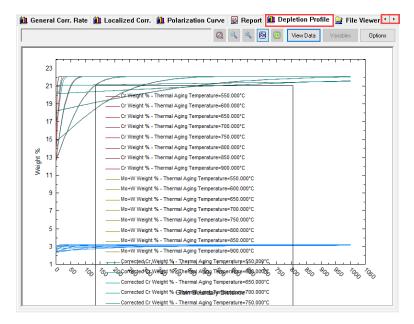
- 18. Now we need to specify the Thermal Aging Temperature range. **Click** on the **Specs** button. This will open a new window.
- 19. Under the **Survey Range** tab, change the range for **Thermal Aging Temperature** from 550 to 900 °C with increments of 50 °C. We will keep the other parameters at their default values. Click **OK**.

Rates Calculation	? ×
Category Var. 1 - Thermal Aging Tempe Polarization Curve Thermal Aging Calculation Type Calculation Options	Survey Range Thermal Aging Temperature Range Unit: C Selected Range Selected Range Selected Range Delete
	Linear OLog Point List Ind Points Start 550.000 End 900.000 Step Size Increment 50.0000 Number Steps 7 O Select one, the other is calculated
< >>	OK Cancel Apply Help

- 20. We are now ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 21. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous section named *Corrosion Rates.*

Click on the Depletion Profile tab (^{the Depletion Profile}). If you don't see it in your screen, use the ◄► buttons to move the tabs.

Since alloy 825 contains Mo in addition to Cr, you will see the depletion profiles for both Cr and Mo.

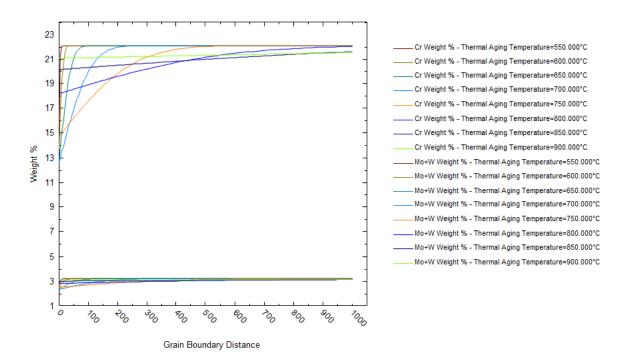


For clarity, let's customize the plot by removing the corrected depletion profiles and leaving only the uncorrected (or directly calculated) ones.

2. Click on the **Options** button, and select the **Curves** category, highlight the Corrected curves and check the hidden box. Then click **OK**.

Customize Plot		?	×
Category General Legend X Axis Curves	Curves 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=500.000°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 Temperat		^ •
	Auto Line Style Auto Line Weight Auto Color Auto Symbol Auto Scaling Factor None 4]
	OK Cancel Apply	H	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.

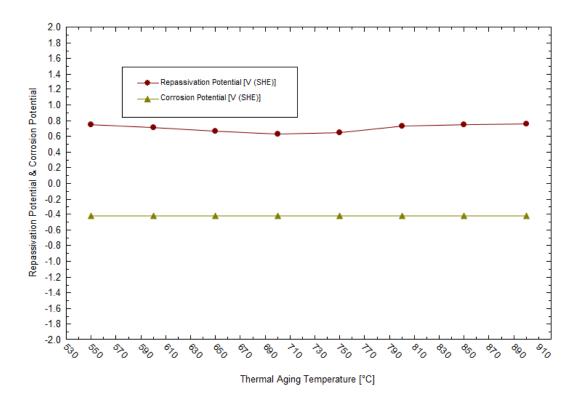
As shown in the plot above, the depletion profile is very narrow at the lowest temperature, i.e., 550 °C. On the other hand, it becomes flat at high temperatures and it has a high minimum. The high minimum value is particularly important because it indicates that the local depletion of Cr and Mo is much 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

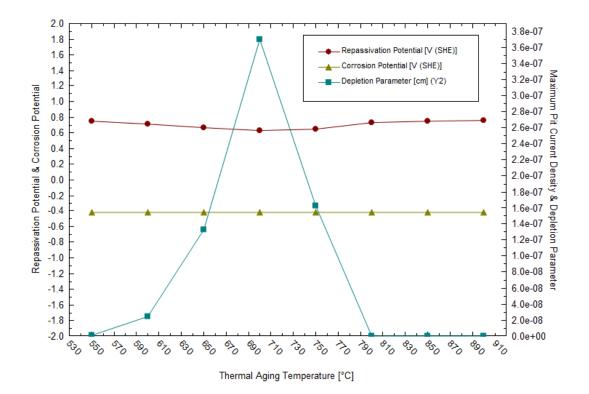
3. Click on the **Localized Corr.** tab (Localized Corr.). By default, this tab will show a plot of the corrosion potential and repassivation potential.



Let's add a new parameter to the plot: The Depletion Parameter.

4. Click on the Variables button. This will open a new window.

Look for the **Corrosion Values** section, click on the '+' icon, and select the **Depletion Parameter** option. Click on the >> button that belongs the **Y2 Axis**. This action will place the new variable under the Y2 Axis. Then click **OK**.



It is evident that both the depletion parameter and repassivation potential show their extreme values at intermediate temperatures of thermal aging. In the case of the depletion parameter, it is a maximum and, in the case of the repassivation potential, it is a minimum. This is in agreement with experimental data (Anderko et al., 2009). Non-zero values of the depletion parameter indicate the possibility of intergranular corrosion. A depression in the repassivation potential indicates an increased tendency for localized corrosion.

9.3. Thermal Aging and Localized Corrosion of Annealed and Thermally Aged Duplex Alloy 2324

In the previous examples, we used the Corrosion Analyzer's capabilities to predict the Cr and Mo depletion profiles for austenitic stainless steels and nickel-base alloys. However, we are not limited to such calculations.

We can also use the Corrosion Analyzer to predict the localized corrosion behavior of other alloys and other phases, including those that are not stored in the database. This facility is based on a generalized correlation for predicting the repassivation potential of Fe-Ni-Cr-Mo-W-N alloys as a function of alloy composition (Anderko et al., 2008). This correlation can be applied to both bulk alloys that are not in the database and to phases that may result from thermal aging.

In this section, we will go through two simulations:

- First, we will predict the tendency for localized corrosion for the duplex alloy 2324 in an aerated chloride solution. Alloy 2324 (a.k.a. AISI 329) is not in the database, so the repassivation potential will be calculated from the generalized correlation (Anderko et al., 2008). The corrosion potential will be calculated for a similar alloy because the corrosion potential does not differ much for many Fe-Cr-Ni-Mo alloys in the passive state in neutral solutions.
- Second, we will predict the localized corrosion tendency for alloy 2324 after thermal aging. Thermal aging of duplex steels in the temperature range of 900°C to 600°C leads to the formation of various phases χ, σ, M₂₃C₆-type carbide, and secondary austenite (γ₂). The secondary austenite phase is primarily responsible for the increased tendency of the alloy for localized corrosion. This is due to a very significant depletion of chromium in the secondary austenite over relatively wide spatial areas (Sridhar et al., 2009). Since the composition of the secondary austenite cannot be predicted at present, we will use experimental microstructural data (Sridhar et al., 2009) in conjunction with the generalized correlation for the repassivation potential.

Example 55: Prediction of Localized Corrosion for Alloy 2324 Before Thermal Aging in an Aerated NaCl Solution

Starting the Simulation

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

Thermal Aging Calculation			
Calculation Settings		Stream Composition and Conditions	
Stream Name	Thermal Aging – Alloy 2324	Stream Amount	Calculated
Calculation Type	Corrosion Rates	Temperature	60 °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

- 1. Add a new Stream
- 2. Click on the new Stream and press <F2> to change the name to Thermal Aging Alloy 2324
- 3. Select the AQ thermodynamic Framework (selected by default)
- 4. Click on the Units Manager Icon and select Metric, Batch, Moles
- 5. Click on the Names Manager Icon and select Display Name
- 6. Enter the stream composition and conditions specified in the table above
- 7. Go to the Add Calculation button and select Corrosion Rates
- 8. Select the Survey by Composition
- 9. Change the name from *Rates* to *Alloy 2324 before aging* using the <F2> key or by right-mouse click on the object and select rename

Since alloy 2324 is not available in the database, we will select stainless steel 316 as the contact surface. This will ensure that the predicted corrosion potential is very similar to that for alloy 2324.

10. Select Stainless Steel 316 from the Contact Surface grid

Unlike in the previous examples, do not make any changes in the **Calc Parameters** section. We will not make Cr depletion calculations; rather, we will be specifying the **compositions of the phases**.

Your screen should look like the image below.

OLI Studio - [Corrosion Rates.oad*]			- 🗆 X
File Edit Streams Calculations	s Chemistry Tools View Window Help		_ <i>8</i> ×
D 🚅 🖬 👗 🖻 🛍 🥚 💡 I	L1 Va So L2 Re ± MSE ± SEK ± AQ	🗄 🚧 🎬 🛨 💱 🔊 😭 🛷	
Navigator # * X	Alloy 2324 -before aging	<u></u>	
Corrosion Rates.oad*	C D		
Streams	< Description 🛃 Definition 🛍 Genera	I Corr. Hate 🛄 Localized Corr. 🛄 I	Polarization Curve 😥 Report 📶 🚺
CR vs flow	Variable	Value	Survey by
Gas Condensate	Stream Para	ameters	Composition - Specs
Localized Corrosion	Stream Amount (mol)	55.6082	Then by (optional)
🗄 💧 Thermal Aging	Temperature (°C)	60.0000	
🛓 👌 Thermal Aging -Alloy 2324	Pressure (atm)	1.00000	None Specs
Alloy 2324 -before aging	Calculation Pa	arameters	Vary
	Flow Type	Static	 Independently
	Thermal Aging Temperature (°C)	399.000	Together
	Thermal Aging Time (hr)	0.0	
		· ·	Calc <u>u</u> late 🥝
	Water	55.5082	Summary
	Sodium chloride	0.0	
	Oxygen	0.0200000	Unit Set: Metric (moles)
Actions <u>a</u> • ×	Nitrogen	0.0800000	Automatic Chemistry Model
Actions	Iron	0.0	Aqueous (H+ ion) Databanks:
			Corrosion (AQ) Aqueous (H+ ion)
	Contact S	urface	Redox selected
	Stainless steel 316		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 & ×			
			Composition survey: No Inflow selected
			No secondary survey selected
	1		Thermal Aging Temperature: 399.000
	Input		°C Thermal Asian Times 0.0 hr
	Advanced Search Add as Stream	Export	Thermal Aging Time: 0.0 hr
Save			
For Help, press F1			Image:

We will be running a composition survey to see how the concentration of NaCl affects the propensity for localized corrosion.

- 11. We need to specify the NaCl concentration range. Click on the Specs button. This will open a new window.
- 12. Under the Component tab select Sodium Chloride

Composition Rates Calculation	on	?	\times
Category Var: 1 - Composition - Polarization Curve - Themal Aging - Calculation Type - Calculation Options	Component Survey Range Component Inflows Inform Nitrogen Oxygen Sodium Chloride Water Select a component inflow which will be varied over	New Inflow	
	OK Cancel /	Apply He	lp .

13. Click on the **Survey Range** tab and change the concentration range as follows: Start=0.001 moles, End=6 moles, and number of steps=20. Then, click on the Log radio button.

Composition Rates Calculatio	n	?	×
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 0.239395	New Delete	
	C Linear ● Log O Point List End Points Start 1.00000e-4 End 6.00000 Step Size Increment 0.299995 O Select one, to Number Steps 20 ⊙ Select one, to	ne other is	
	OK Cancel Apply	Help	

14. Under the **Category** section, select the **Thermal Aging** option. The screen will be populated with default parameters for type 316 stainless steel.

In the following steps we are going to enter the alloy 2324 composition and use the repassivation potential (E_{rp}) correlation (embedded in the software) to calculate the E_{rp} of the alloy. This is necessary because no

parameters for alloy 2324 are stored in the databank and we have to rely exclusively on the correlation to predict the repassivation potential.

- 15. First, click on the Yes button next to "Erp directly from correlation:"
- 16. Then, enter the composition of alloy 2324 by replacing the default values for alloy 316.

Enter the following composition of alloy 2324:

Element	Composition (wt%)
Fe	67.245*
Cr	25.4
Ni	5.75
Mo+W	1.5
С	0.025
N	0.08

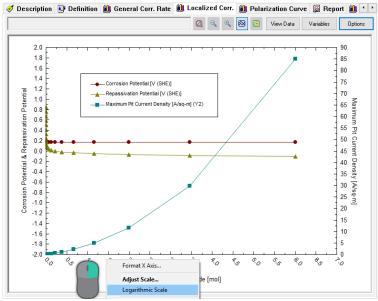
*which is the balance that includes many minor elements

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	on	?
Category	Thermal Aging	
Var. 1 - Composition – Polarization Curve – Thermal Aging – Calculation Type – Calculation Options	Erp Directly from Correlation: 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: C 0.025 N 0.08	
	Fe 0 Cr 19.74 Ni 0 Mo+W 3.26 C 6 N 0	_
	Catbide Thermochemistry: A 41221 B -966 Cr Diffusion Coefficient: D0 0.00016818 Q -289000	
	Mo, W Diffusion Coefficient: D0 7.93e-005 Q -274000	
	Cr Sensitization Threshold wt%: 12 Grain Size: 100 Revert to Default	
	OK Cancel Apply	Help

- 17. Click **OK** to accept the changes
- 18. We are now ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 19. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it under the same file created in the previous section named *Corrosion Rates.*

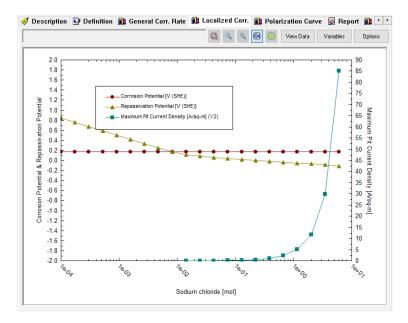
1. Click on the **Localized Corr.** tab (Localized Corr.). By default, this tab will show a plot of the corrosion and repassivation potentials as a function of NaCl concentration. In the Y2 axis the Maximum Pit Current Density is also plotted.



To visualize the results better, change the horizontal axis to a logarithmic scale.

2. Right-mouse click on the X Axis and select Logarithmic Scale

The plot should look like the image below.



These results indicate that alloy 2324 is susceptible to localized corrosion in aerated solutions when the chloride concentration exceeds \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.

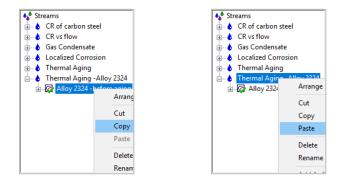
Example 56: Prediction of Localized Corrosion for Alloy 2324 After Thermal Aging

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-increase tendency for localized corrosion. We will use this experimental data to approximate the localized corrosion tendency of alloy 2324.

Starting the Simulation

1. Copy the Alloy 2324-before aging calculation and paste it under the Thermal Aging – Alloy 2324 stream



- Rename the calculation as Alloy 2324 after aging by using the <F2> key or by right-mouse click on the object and select rename
- 3. Click on the **Specs** button. This will open a new window.
- 4. Under the **Category** section, select the **Thermal Aging** option. The screen will be populated with default parameters for type 316 stainless steel.
- 5. Click on the **Yes** button next to "*Erp directly from correlation:*" because we will be running calculations for a completely new phase
- 6. Then, enter the composition of the secondary austenite phase by replacing the default values for alloy 316.

Note: we are using experimental data obtained for alloy 2205 for illustration purposes). For more details how these compositions were determined, see the paper of Sridhar et al. (2009).

Enter the following composition:

Element	Composition (wt%)
Fe	80.774*
Cr	12.512
Ni	5.134
Mo+W	1.399
С	0.017
N	0.164

*which is the balance that includes many minor elements

The remaining parameters in the Thermal Aging screen can remain the same because we will not be using them in this example (i.e., we will not be calculating any depletion profiles). After entering the values, the screen should look like the image below.

Composition Rates Calculation	n ?	×
Composition Rates Calculation Category	n ? Thermal Aging Erp Directly from Correlation: No • Yes Alloy Composition wt%; Fe 90.774 C 12.512 Ni 5.314 Mo+W 1.339 C 0.017 N 0.164 Carbide Stoichiomety: Fe 0 C 13.74 Ni 0 Mo+W 3.26 C 6 N 0 0 Carbide Thermochemistry: A 11221 B 966 960 Cr Diffusion Coefficient: D0 0.00016818 Q 289000 90.000 Mo, W Diffusion Coefficient: D0 7.33e-005 Q 274000 Cr Sensitization Threshold wt%; 12 Grain Size: 100	×
	OK Cancel Apply He	۱p

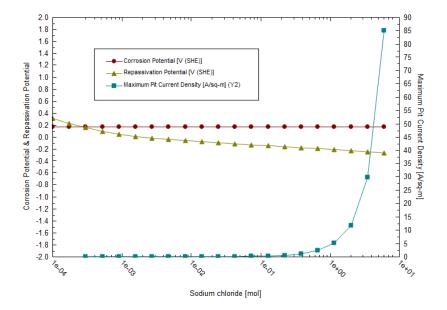
- 7. Click **OK** to accept the changes
- 8. We are now ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 9. It is time to save your file (File >Save as...) or using the save icon in the tool bar. You can save it under

1. Click on the **Localized Corr.** tab (Localized Corr.). By default, this tab will show a plot of the corrosion and repassivation potentials as a function of NaCl concentration. In the Y2 axis the Maximum Pit Current Density is also plotted.

To visualize the results better, change the horizontal axis to a logarithmic scale.

2. Right-mouse click on the X Axis and select Logarithmic Scale

The plot should look like the image below.



The obtained plot shows that the repassivation potential is much lower than that for bulk alloy 2324. Because of the strong depression of the repassivation potential, the corrosion potential exceeds the repassivation potential at chloride concentrations of ~0.0007 m. Thus, localized corrosion is predicted to be possible at concentrations above 0.0007 m. This indicates a very strong increase in the propensity for localized corrosion compared with bulk alloy 2324, for which the predicted threshold is ~0.3 m.

In general, you can use this facility to predict the repassivation potential for any alloys, including unknown and experimental ones, as long as they belong to the Fe-Ni-Cr-Mo-W-N-C family.

Section 10. Extreme Value Statistics (EVS)

10.1. Overview and Theoretical Foundation

Engineering systems may have a large number of pits and corroded areas of varying degree of severity. The first perforation, whose time and location will be a matter of probability, may cause the failure of the construction. Accordingly, the probability of such failure must be known as accurately as possible.

Extreme value statistics (EVS) is one of the most powerful statistical techniques that have been used extensively to extrapolate damage (maximum pit depth) from small samples in the laboratory to larger area samples in the field (see, for example, Eldridge G. 1957, Shibata T. et al. 1988, Kowaka et al. 1994). Thus, it was shown (Shibata T. et al. 1988) that probability of failure of a construction, P_f, i.e. the probability that at least one pit reaches the critical dimension, d, (for example wall thickness) in the system with area S is described by the equation:

$$P_f = 1 - \exp\left\{-\frac{\exp\left[-d - \left(u + \alpha \ln\frac{S}{s}\right)\right]}{\alpha}\right\}$$
(1)

where location parameter, u, and scale parameter, α , are measured by using small samples with constant area, s. Equation (1) is to extrapolate corrosion damage from a small reference area, such as a coupon to a larger operation area, S. This is the classical use of Extreme Value Statistics.

Experimental studies demonstrate that both the shape and location parameters are time dependent. However, those dependencies must be established empirically and since no theory contained within classical EVS is available for the functional forms of u(t) and $\alpha(t)$, 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 α 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 a₁, a₂, and a₃ are readily determined by calibration from short term data in order to predict damage over the longer time. Namely, equations (2) are used now by OLI software for predicting damage in corroding systems. It must be noted that a different (power) form of such dependencies has been used by Laycock et al. 1990.

Input and Output Specific to EVS

For applying this technique the user has to provide a set of experimental data (x_i , t_i , s_i), i = 1, 2, ..., N, where x_i is the depth of the deepest pit over area s_i , of a metal exposed to corrosion attack. The separate area, s_i , could be distinct coupons from a designed experiment or random samples at various times from different locations in the system. Experiments must be performed for at least two different times.

The output of the code yields the probability of failure as a function of time for a large system with area S. The code also allows the user to answers on several engineering questions, for example, what service life, t, will have the pipe with the width, d, and length L in order to ensure acceptable performance (probability of failure, P_f).

Advantages and Disadvantages of EVS

The advantage of this approach is self-evident. The prediction of corrosion damage for long times will be done by using experimental data for short times without requiring the explicit determination of any information about the kinetic parameters of the system. However, such approach has evident disadvantages, as follows:

- The results of the analysis cannot be transferred for predicting corrosion damage to other systems (for example pipelines) due to the different technological and environmental conditions that generally exist. The results cannot be used for predicting damage in the same system if technological and environmental conditions change.
- 2. We can expect that when the depth of the pit increases some critical value, the nucleation of cracks can occur. It is clear that a purely statistical method cannot predict such a transition. This method also cannot predict any catastrophic event.
- 3. This method cannot be used for design of new constriction, because it relies upon calibration upon a preexisting system.

10.2. Extreme Value Statistics for Predicting Pitting Damage

We will show examples of applications of Extreme Value Statistics for predicting pitting damage. Specifically, we will show how to predict:

- 1. The depth of the deepest pit in the engineering structure or laboratory systems as a function of time and the surface area of the system
- 2. Probability of failure for a given penetration depth and the area of the system as a function of observation time
- 3. Probability of failure for a given observation time and the area of the system as a function of penetration depth
- 4. Probability of failure for a given penetration depth and observation time as a function of the area of the system

Foundations of Extreme Value Statistics can be found in the following references: (Aziz, 1956, Kowaka et al. 1994, Laycock et al. 1990, Engelhardt and Macdonald, 2004).

Example 57: Corrosion of Aluminum Alloy in Tap Water

In this example, we will consider the classical data for pitting corrosion (Aziz, 1956). In this paper, we can find particularly the experimental data for the maximum pit depths developed on Alcan 2S-O coupons with area s≈129 cm² immersed in Kingston tape water at 25 °C. The experimental data is summarized in the table below.

Maximum pit depth (in µm) developed on Alcan 2S-O coupons with immersed in Kingston tape water for different observation times. Area of all coupons is s≈129 cm²

Coupon #	One Week	One Month	Three Months	Six Month	One Year
	7 days	30 days	90 days	180 days	365 days
1	180	460	480	620	640
2	266	500	578	620	680
3	290	510	610	620	700
4	306	580	610	680	760
5	334	580	610	680	800
6	340	640	660	720	810
7	340	654	690	740	820
8	410	680	718	740	840
9	410	692	760	760	840
10	545	692	798	760	900

Calculating the Depth of the Deepest Pit

Starting the Simulation

1. Add a new EVS calculation. Select the Add EVS Calculation icon in the Actions Pane

Actions	
🚺 Add Stream	
🗷 Add Mixer	
🗔 Add Water Analysis	
😬 Add EVS Calculation	
🔛 Add Brine Analysis	

- 2. Click on the new EVS calculation and press <F2> to change the name to EVS-Aluminum samples. Notice that the default calculation is the *Pit Depth Prediction*.
- 3. All samples have a constant area s = 129 cm². Under the **Calculation Parameters** grid, enter 129 cm² for the **Surface Area** and **Default Value** cells.

OLI Studio - [EVS.oad]			– 🗆 X
	ions Chemistry Tools View Window Help		_ <i>8</i> ×
	1.2	🛤 🎬 🛃 💱 🔊 😭 🌾	
Navigator + ×			
Document1	¢v _{\$} EVS		
EVS.oad	< Description 🧕 Definition 🛍 Plot 👼 R	eport	
🎻 Streams	Description	Pit Depth (µm) Area (sq-cm)	
^{Ev} s EVS-Aluminum samples	Calculation Para		Pit Depth Prediction 👻 Specs
	Surface Area	129.000	
	Experiment Start (day)	0	Calculate 🥥
	Default Value	129.000	Summary
	Sample Group 01 (day)	7172.14	Summary
			EVS Calculation Type: Pit Depth Prediction
			Calculation Parameter(s): Surface Area 129.000 sq-cm
			Experiment Start: 01/01/2000
< >			Range 0.0 to 365.0 day Step size 5.0 day
Actions # * *			No. steps 73
Actions			> Default Area Value: 129.000
Plot Template Manager + ×	Add Group		~
For Help, press F1	,		

There are experimental data sets for 5 different periods of time. This means that we need to enter 5 different sample groups.

- 4. By default, **Sample group 01** is created. Click on the <u>...</u> button to edit this field. This will open a new window.
- 5. Change the title to One Week, enter the number 7 for the number of elapsed days, and check the box 'Include for Calculation'. Then click OK.

EVS Sample Group Info Editor	?	×
Title:		
One Week		
Elapsed: (day)		
7		
Included for Calculation		
OK Cancel		

6. Enter the **Pit Depth** data (second column) obtained for 1 week

Description	Pit Depth (µm)	Area (sq-cm)			
Calculation Parameters					
Surface Area					
C Experiment Start (day)	0				
Default Value		129.000			
✓ One Week (day)	7.0				
1	180.000	129.000			
2	266.000	129.000			
3	290.000	129.000			
4	306.000	129.000			
5	334.000	129.000			
6	340.000	129.000			
7	340.000	129.000			
8	410.000	129.000			
9	410.000	129.000			
10	545.000	129.000			

Now we need to add 4 more groups.

- 7. Click on the Add Group button (located at the bottom of the window). This will open a new window.
- 8. Change the title to One Month, enter the number 30 for the number of elapsed days, and check the box 'Include for Calculation'. Then click OK.
- 9. Enter the **Pit Depth** data (second column) obtained for 1 month.
- 10. Click on the **Add Group** button, and repeat the same procedure for one month, three months, six months and one year.

	Description	Pit Depth (µm)	Area (sq-cm)
	One Month (day)	30.0	
	1	460.000	129.000
	2	500.000	129.000
	3	510.000	129.000
	4	580.000	129.000
	5	580.000	129.000
	6	640.000	129.000
	7	654.000	129.000
	8	680.000	129.000
	9	692.000	129.000
his group	10	692.000	129.000
n-checking			
ormation is not	Three Months (day)	89.9999	
he calculation	1	480.000	129.000
e calculation	2	578.000	129.000
	3	610.000	129.000
	4	610.000	129.000
	5	610.000	129.000
	6	660.000	129.000
	7	690.000	129.000
	8	718.000	129.000
	9	760.000	129.000
	10	798.000	129.000
	Six Months (day)	180.0	
	1	620.000	129.000
	2	620.000	129.000
	3	620.000	129.000
	4	680.000	129.000
	5	680.000	129.000
	6	720.000	129.000
	7	740.000	129.000
	8	740.000	129.000
	9	760.000	129.000
	10	760.000	129.000
	Cone Year (day)	365.0	
		640.000	129.000
	2	680.000	129.000
	3	700.000	129.000
	4	760.000	129.000
	5	800.000	129.000

Note the following:

- Here, for the description of different experiments we simply used the number of the corresponding row in Table 1. However, this description can be done in an arbitrary form.
- For each group, the order of samples relative depth can be arbitrary (not necessary in ascending order as in Table 1)
- If coupons have different areas each area must be specified in the column Area
- Radio button Elapsed means the time after corrosion attack is used in calculations and namely this time is used usually in scientific publication. However, it is possible to use also Actual Time of the experiments.

At this point, the experimental data has been entered. Now we need define the period of time for which we want to do the prediction of failure due to pitting.

- 11. Click on the Specs button. This will open a new window.
- 12. Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 days, End=365 days, and number of steps=50. Then click **OK**

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	
● Linear ◯ Log ◯ Point List		
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:

- I. The first case will include the experimental data for 1 week and 1 month short term experiments
- II. The second case will include all the experimental data long term experiments

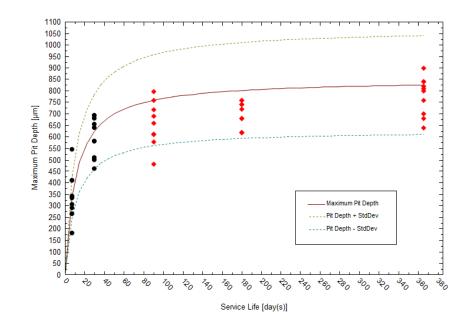
Predicting the Worst Pit Depth for 1 year of service life using short term experiments (Experimental Data for 1 week and 1 month)

Description	Pit Depth (µm)	Area (sq-cm)
Calculation Pa	rameters	
Surface Area		129.00
Experiment Start (day)	0	
Default Value		129.00
Cone Week (day)	7.0	
1	180.000	129.00
2	266.000	129.00
3	290.000	129.00
4	306.000	129.00
5	334.000	129.00
6	340.000	129.00
7	340.000	129.00
8	410.000	129.00
9	410.000	129.00
10	545.000	129.00
Circ One Month (day)	30.0	
	460.000	129.00
2	500.000	129.00
2 3		129.00
4	510.000	129.00
5	580.000	129.00
6	640.000	129.00
-	654.000	129.00
8	680.000	129.00
9	692.000	129.00
9 10	692.000	129.00
10	092.000	129.00
Three Months (day)	89.9999	
1	480.000	129.00
2	578.000	129.00
3	610.000	129.00
4	610.000	129.00
5	610.000	129.00
6	660.000	129.00
7	690.000	129.00
8	718.000	129.00
9	760.000	129.00
10	798.000	129.00
Six Months (day)	180.0	
1	620.000	129.00

13. Check the boxes for 1 week and 1 month only to include them into the calculations

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

It is important to note that only data for short term experiments (for 1 week and 1 month) are shown as black circles in the plot. The additional data are shown as red diamonds, only for demonstrating the accuracy of prediction.



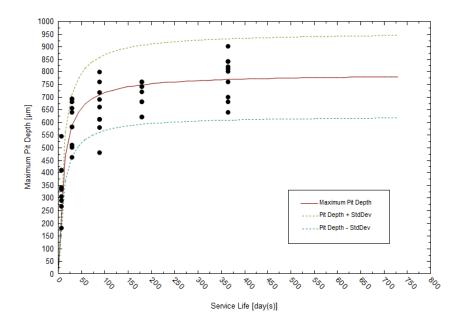
17. Click on the Report tab, and to the Calculation Results table.

The predicted depth of the deepest pit at 365 days is $610.43\mu m \le 825.373\mu m \le 1040.31\mu m$ (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)

- 18. The accuracy of prediction increases when additional group of experiments are included into consideration. For this case we are going to add the experimental data for 3 months, 6 months and 1 year.
- 19. Go back to the Definition tab
- 20. Include (check) the experimental data for 3 months, 6 months and 1 year
- 21. Click on the Specs button. This will open a new window
- 22. Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 days, End=730 days, and number of steps=50. Then click **OK**
- 23. Then **Click** on the **Calculate** button or press the **<F9>** key

24. Click on the Plot tab (1 Plot).



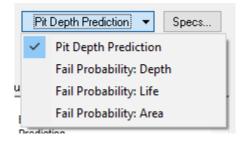
25. Click on the Report tab, and to the Calculation Results table.

The predicted depth of the deepest pit at 730 days (1 year) is 617.57 μ m \leq 780.873 μ m \leq 944.18 μ 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 m² have to have in order to ensure acceptable performance (probability of failure P_f< 5% at design service life, t_s =5 years?

Starting the Simulation

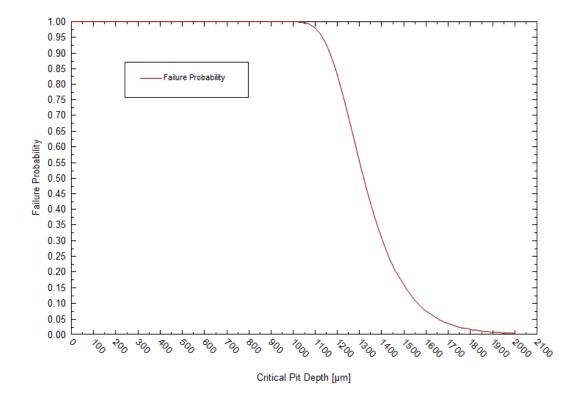
- 1. Use the data enter in the example above. Change the Calculation Type to Fail Probability: Depth
- 2. Under the **Calculation Parameters** grid, enter 1 m² for the **Surface Area** and 5 years for the **Service Life**. Change units by clicking on the **blue** hyperlinks.
- 3. Make sure all data sets are selected (checked)

Your screen should look like the image below.

Navigator д ▲ × Document1	L1 Va S	So L2 Re ± Mase ± see ± ∧a robability	🛓 👫 🚟 ± 👫 (
EVS.oad	🦪 Description	n 🥺 Definition 📶 Plot 📓	Report		
Streams		Description	Pit Depth (µm)	Area (sq-m) 🔺	
EVS-Aluminum samples		Calculation Pa	rameters		Fail Probability: Depth 👻 Specs
EVS-Fail Probability	Surface Area			1.00000	
	Service Life ()	/r)		5.00000	Calculate 🥝
	$\overline{\nabla}$	Experiment Start (yr)	0		
	Default Value			0.0129000	Summary
		One Week (yr)	0.0191781		EVS Calculation Type: Failure
	1		180.000	0.0129000	Probability - Critical Depth Based
	2		266.000	0.0129000	Calculation Parameter(s):
	3		290.000	0.0129000	Surface Area 1.00000 sq-m
	4		306.000	0.0129000	Service Life 5.00000 yr
	5		334.000	0.0129000	Experiment Start: 01/01/2000
< >	6		340.000	0.0129000	Experiment start. On on 2000
	7		340.000	0.0129000	Range 0.0 to 2000.0 µm
Actions # * ×	8		410.000	0.0129000	Step size 10.0 µm No. steps 200
Actions	9		410.000	0.0129000	> 10.0000 200
	10		545.000	0.0129000	Default Area Value: 129.000
		One Month (yr)	0.0821918		
	1		460.000	0.0129000	
	2		500.000	0.0129000	
	3		510.000	0.0129000	
	4		580.000	0.0129000	
Plot Template Manager 🛛 🖡 🔺 🗙	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	0.04200000	/

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

6. Click on the Plot tab (Plot). You will see a plot of predicted probability of failure



7. Click on the **Report** tab, and to the **Calculation Results** table.

We can conclude that the acceptable pipe wall width is reached at d > 1950 μ 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 μm with area S=10 m² in order to ensure acceptable performance i.e. probability of failure, P_f< 5 %? Starting the Simulation

- 1. Change the Calculation Type to Fail Probability: Life
- Under the Calculation Parameters grid, enter 10 m² for the Surface Area and 1850 μm for the Critical Pit Depth. Change units by clicking on the blue hyperlinks (If needed).

For this calculation we need to specify the period of time at which we want to bound the calculation.

- 3. Click on the **Specs** button. This will open a new window.
- 4. Change the **Service Life** range as follows: Start=0 years, End=3 years and Increments=0.2 years. Then click **OK**.

EVS Calculation Options	?	Х
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 O Scalculated		
OK Cancel Apply	Hel	p

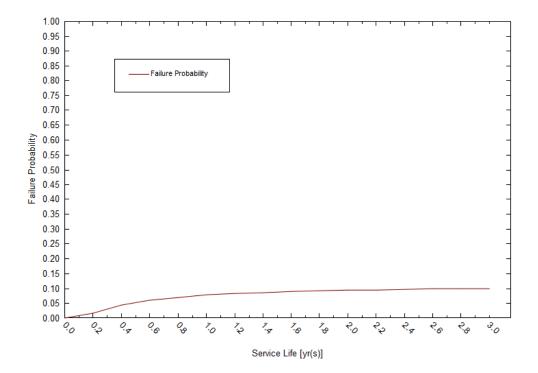
Your screen should look like the image below.

< Description 🛃 Definition 🛍 Plot 📓 Report

	Description	Pit Depth (µm)	Area (<mark>sq-m</mark>)
		Parameters	
Surface Ar			10.0000
Critical Pit Depth 1850.00			
$\overline{\nabla}$	Experiment Start (yr)	0	
Default Val	Je		0.0129000
$\overline{\mathbf{v}}$	One Week (yr)	0.0191781	
1		180.000	0.0129000
2		266.000	0.0129000
3		290.000	0.0129000
4		306.000	0.0129000
5		334.000	0.0129000
6		340.000	0.0129000
7		340.000	0.0129000
8		410.000	0.0129000
9		410.000	0.0129000
10		545.000	0.0129000
	One Month (yr)	0.0821918	
1		460.000	0.0129000
2		500.000	0.0129000
3		510.000	0.0129000
4		580.000	0.0129000
5		580.000	0.0129000
6		640.000	0.0129000
7		654.000	0.0129000
8		680.000	0.0129000
9		692.000	0.0129000
40		000.000	0.0400000

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

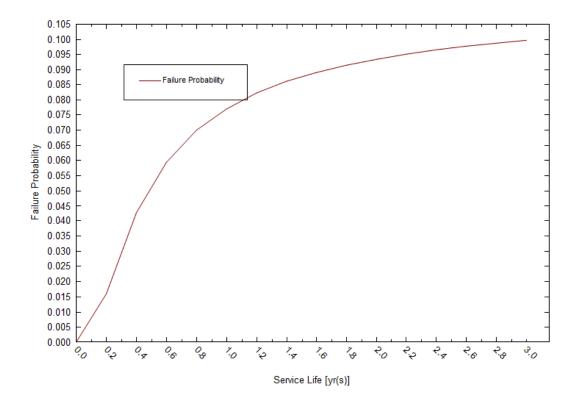
7. Click on the **Plot** tab (Plot). You will see a plot of predicted probability of failure. We need to modify the plot to see the results in more detail.



- 8. **Double click** on the **Y axis**. This will open a new window.
- 9. Check the boxes Minimum and Maximum. Then click OK.

Y Axis - Properties			?	×
Scale				
Auto				
Minimum 0.0				
Maximum 1.0				
Major Unit				
Minor Unit				
Logarithmic scale				
OK Cancel	Арр	ly	Help)

The plot should look like the image below



The maximum probability of failure seems to be at around 10%.

10. Click on the Report tab, and to the Calculation Results table.

We can conclude that the lifetime of this pipe before failing is <0.6 years.

Fail Probability: Area

Finally, let's do the the calculation of Probability of failure for a given penetration depth and service time as a function of the area of the system.

We are going to answer the following question:

 What area, S, can have the aluminum pipe with the width, d=2000 μm and service life t=5 years in order to ensure acceptable performance i.e. probability of failure, P_f < 5 %?

Starting the Simulation

- 1. Change the Calculation Type to Fail Probability: Area
- Under the Calculation Parameters grid, enter 2000 μm for Critical Pit Depth and 5 years for the Service Life. Change units by clicking on the blue hyperlinks (If needed).

For this calculation we need to specify the surface area range that we want to survey.

- 3. Click on the **Specs** button. This will open a new window.
- 4. Change the **Surface Area** range as follows: Start=0 sq-m, End=100 sq-m and Number of steps=50. Then click **OK**.

EVS Calculation Options	?	\times
Survey Range		
Failure Probability - Surface Area Based Unit: sq-m		
Selected Range		
0.0 to 100.0 in 50 steps of 2.0	New	
	Delete	:
● Linear ○ Log ○ Point List		
End Points		- 1
Start 0.0		
End 100.000		
Step Size		-
Increment 2.00000 O 🔪 Selectione. th	ne other is	
Number Steps 50		
OK Cancel Apply	He	łp

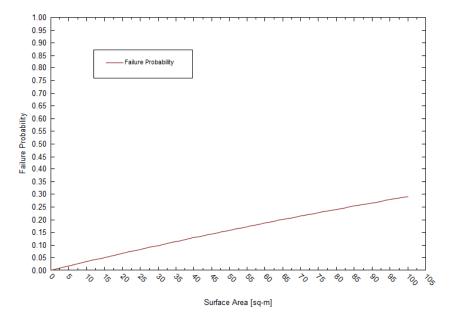
Your screen should look like the image below.

Description	Pit Depth (µm)	Area (<mark>sq-m</mark>)
	tion Parameters	
Critical Pit Depth	2000.00	
Service Life (yr)		5.0000
Experiment Start (yr)	0	
Default Value		0.012900
✓ One Week (yr)	0.0191781	
1	180.000	0.012900
2	266.000	0.012900
3	290.000	0.012900
4	306.000	0.012900
5	334.000	0.012900
6	340.000	0.012900
7	340.000	0.012900
8	410.000	0.012900
9	410.000	0.012900
10	545.000	0.012900
Cone Month (yr)	0.0821918	
1	460.000	0.012900
2	500.000	0.012900
3	510.000	0.012900
4	580.000	0.012900
5	580.000	0.012900
6	640.000	0.012900
7	654.000	0.012900
8	680.000	0.012900
9	692.000	0.012900
40	000.000	0.040000

🛷 Description 🔯 Definition 🛍 Plot 📓 Report

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

7. Click on the **Plot** tab (Plot). You will see a plot of predicted probability of failure. We need to modify the plot to see the results in more detail.



The maximum probability of failure seems to be at around 30%.

8. Click on the **Report** tab, and to the **Calculation Results** table.

We can conclude that acceptable performance is reached at <14 m².

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

1. 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	

- 2. Click on the new EVS calculation and press <F2> to change the name to EVS-Pipeline samples. Notice that the default calculation is the *Pit Depth Prediction*.
- 3. Under the Calculation Parameters grid, enter 1 cm² for the Surface Area and Default Value cells.

Note: Because the area of the pipelines metal was not changed with time the information about this area is not needed for extrapolation of corrosion damage in time.

4. Since the data is in hours, click on the blue hyperlink **day** and change it to hours (**hr**) (for both: The **Experiment Start** and the **Sample Group**.

Your screen should look like the image below:

OLI Studio - [EVS.oad*]		- 🗆 X
📧 File Edit Streams Calculati	_ & ×	
🗋 🗅 🚅 🔛 🖌 🖻 🛍 🥌 🕯	N? 🛛 L1 Va So L2 🛛 Re ± 🕅 🕸 ± 🖓 ± 🗛 ± 🛛 👫 🎬 ± 💱 🔎 🕋 📈	
Navigator + × × Document1 EVS.oad*	 EVS-Pipeline samples Description	
• Streams 	Description Pit Depth (µm) Area (sq-cm) Calculation Parameters	Pit Depth Prediction 🔻 Specs
EVS-Pipeline samples	Surface Area 1.00000 C Experiment Start (hr) 0	Calculate 🥥
	Default Value 1.00000 ▽ I Sample Group 01 (hr) 1.72174e5	Summary
		EVS Calculation Type: Pit Depth A

There are experimental data sets for 8 different periods of time. This means that we need to enter 8 different sample groups.

- 5. By default, **Sample group 01** is created. Click on the <u>m</u> button to edit this field. This will open a new window.
- 6. Leave the default name as Sample Group 01, enter the number 1440 for the number of elapsed hours, and check the box 'Include for Calculation'

EVS Sample Group Info Editor	?	×
Title:		
Sample Group 01		
Elapsed: (hr)		
1440.0		
Included for Calculation		
OK Cancel		

7. Enter the **Pit Depth** data (second column) obtained for 1440 hours.

Description 🧕 Definit	n 🛍 Plot 📓 Report	
Description	Pit Depth (mm)	Area (sq-cm)
Cal	lation Parameters	
Surface Area		1.00000
C Experiment Start	r) 0	
Default Value		1.00000
Sample Group 01	r) 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.

8. Click on the Add Group button (located at the bottom of the window. This will open a new window.

- 9. Leave the default name as Sample Group 02, enter the number 5040 for the number of elapsed hours, and check the box 'Include for Calculation'. Then click OK.
- 10. Enter the **Pit Depth** data (second column) obtained for 5040 hours.
- 11. Click on the **Add Group** button, and repeat the same procedure for 5760, 8959, 12624, 17688, 28032 and 28272 hours.

Once you have entered all the experimental data, your screen should look like the image below.

L2 Re≇ ± Maar ± Maar ± Ana ± EVS-Pipeline-Pit Depth Pred			
Description 🧾 Definition 🛍			
Description	Pit Depth (mm)	Area (sq-cm)	<u> </u>
Sample Group 01 (hr)	1440.0		Pit Depth Prediction 👻 Specs
1	0.100000	1.00000	
3 4	0.300000	1.00000	Calculate 🥥
	0.400000	1.00000	Summary
5	0.900000	1.00000	
6	0.300000	1.00000	EVS Calculation Type: Pit Depth
Sample Group 02 (hr)	5040.0		Prediction
2	0.490000	1.00000	Calculation Parameter(s):
3	1.60000	1.00000	Surface Area 1.00000 sq-cm
<u> </u>	1.0000	1.00000	Experiment Start: 01/01/2000
Sample Group 03 (hr)	5760.0		
5	1.57000	1.00000	Range 0.0 to 87600.0 hr Step size 1752.0 hr
6	1.20000	1.00000	No. steps 50
			Default Area Value: 1.00000
Sample Group 04 (hr)	8959.0		Default Area value. 1.00000
1	1.40000	1.00000	
2	1.95000	1.00000	
3	1.80000	1.00000	
4	1.60000	1.00000	
5	2.10000	1.00000	
6	1.40000	1.00000	>
Sample Group 05 (hr)	12624.0		
1	1.70000	1.00000	
2	2.10000	1.00000	
4	1.65000	1.00000	
5	2.21000	1.00000	
6	1.40000	1.00000	
Sample Group 06 (hr)	17688.0		
1	1.90000	1.00000	
2	2.08000	1.00000	
4	1.88000	1.00000	
5	2.40000	1.00000	
6	1.55000	1.00000	
Sample Group 07 (hr)	28032.0		
5	2.40000	1.00000	
6	1.71000	1.00000	
Sample Group 08 (hr)	28272.0		
(I)	20212.0		×

Make sure that all the groups are selected (checked) to be considered for the calculation.

At this point, the experimental data has been entered. Now we need define the period of time for which we want to do the prediction of failure due to pitting.

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

13. Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 hours, End=30000 hours, and Increment=2000 hours. Then click **OK**

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	
End Points		- 1
Start 0.0		
End 30000.0		
Step Size		-
Increment 2000.00 💿 🔪 Select one, th	ne other is	
Number Steps 15 O Scalculated		
OK Cancel Apply	He	lp

Before running the calculation, we are going to study two different cases:

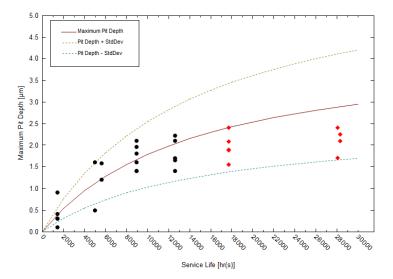
- I. The first case will include the experimental data from groups 01 to 05
- II. The second case will include all the experimental data from groups 01 to 08

Calculation including Groups 01 to 05

- 14. Check the boxes for Group 01 to 05
- 15. We are now ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 16. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Save it under the same file that we previously created as *EVS calculations*.

Analyzing the results

17. Click on the **Plot** tab (\square **Plot**). You will see a plot of the predicted mean value of the depth of the deepest pit, x_m and the plots of values $x_m - \sigma$ and $x_m + \sigma$, where σ is the standard deviation of x_m .



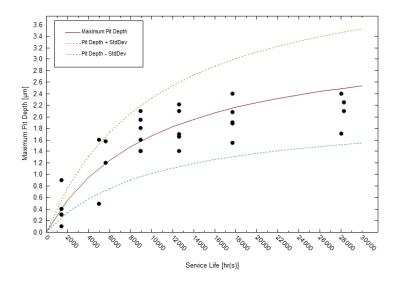
As previously noted, only the points in black mean that were used for predicting propagation of corrosion damage. The red diamonds mean that were not taken into account for the calculation and are shown only for demonstrating the accuracy of prediction.

Calculation including Groups 01 to 08

- 18. Check the boxes for Group 01 to 08
- 19. We are now ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 20. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Save it under the same file that we previously created as *EVS calculations*.

Analyzing the results

21. Click on the Plot tab (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.

22. Click on the Report tab, and to the Calculation Results table.

You can see here that at 30,000 hours the maximum pit depth predicted is 1.55 μ m ≤2.54 μ m ≤3.53 μ 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 cm², depth in μ m

Calculation the Depth of the Deepest Pit

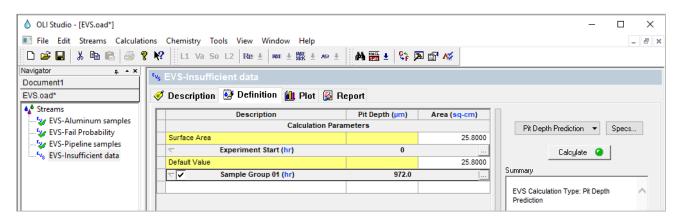
Starting the Simulation

1. 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	

- 2. Click on the new EVS calculation and press <F2> to change the name to EVS-Insufficient Data. Notice that the default calculation is the *Pit Depth Prediction*.
- 3. Under the Calculation Parameters grid, enter 25.8 cm² for the Surface Area and Default Value cells.
- 4. Since the data is in hours, click on the blue hyperlink **day** and change it to hours (**hr**) (for both: The **Experiment Start** and the **Sample Group**.

Your screen should look like the image below:



There are experimental data sets for 9 different periods of time. This means that we need to enter 9 different sample groups.

- 5. By default, **Sample group 01** is created. Click on the <u>m</u> button to edit this field. This will open a new window.
- 6. Leave the default name as Sample Group 01, enter the number 40.5 for the number of elapsed hours, and check the box 'Include for Calculation'

EVS Sample Group Info Editor	?	×
Title:		
Sample Group 01		
Elapsed: (hr)		
40.5		
Included for Calculation		
OK Cancel		

7. Enter the **Pit Depth** data (second column) obtained for 40.5 hours.

Now we need to add 8 more groups.

- 8. Click on the Add Group button (located at the bottom of the window. This will open a new window.
- 9. Leave the default name as Sample Group 02, enter the number 144.17 for the number of elapsed hours, and check the box 'Include for Calculation'. Then click OK.
- 10. Enter the **Pit Depth** data (second column) obtained for 144.17 hours.
- 11. Click on the **Add Group** button, and repeat the same procedure for the rest of the experimental data (groups)

Once you have entered all the experimental data, your screen should look like the image below.

avigator a • ×	🐝 EVS-Insu				
Jocumenti					
VS.oad	🤣 Descript	ion 🥸 Definition 🛍 Plot	😥 Report		
V Streams		Description	Pit Depth (µm)	Area (sq-cm)	
- Se EVS-Fail Probability			Parameters		Pit Depth Prediction 👻 Specs
	Surface Ar			25.8000	
EVS-Insufficient data	7	Experiment Start (hr)	0		Calcylate 🥥
	Default Val		40.5	25.8000	Summary
	V	Sample Group 01 (hr)			
	1		775.000	25.8000	EVS Calculation Type: Pt Depth
	~~	Sample Group 02 (hr)	144.17		Prediction
	1	Sample Group 02 (m)	1326.00	25.8000	Calculation Parameter(s):
	2		1176.00	25.8000	Surface Area 25.8000 sq-cm
			1110.00	23.0000	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		20.000
	1		912.000	25.8000	
	2		1173.00	25.8000	
	~~	Sample Group 05 (hr)	331.0		
ctions a + ×	1		1361.00	25.8000	
ctions	2		1534.00	25.8000	>
		Sample Group 06 (hr)	378.5		
	1		1613.00	25.8000	
	2		1641.00	25.8000	
		Secondar Conversion (California	453.25		
		Sample Group 07 (hr)	463.25	25.8000	
	2		2024.00	25.8000	
	-		2024.00	23.0000	
	~~	Sample Group 08 (hr)	477.0		
	1		1722.00	25.8000	
ot Template Manager a 🔺 🗙	2		1798.00	25.8000	
	3		1496.00	25.8000	
		Sample Group 09 (hr)	528.0		
	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.

- 12. Click on the Specs button. This will open a new window.
- 13. Under the **Survey Range** tab, enter the range for **Pit Depth Prediction** as follows: Start=0 hours, End=580 hours, and number of steps=50 hours. Then click **OK**

EVS Calculation Options	;				?		×
Survey Range							
Pit Depth Prediction Ra	ange		Unit:	hr			ר
Selected Range							
0.0 to 580.0 in 50 step	os of 11.6				Ne	ew	
					Del	lete	
Linear			int List				
End Points							_
Start [0.0						
End	580.000						
Step Size							-
Increment	11.6000	0	Selec	ct one, th	ne other i	is	
Number Steps	50) •	calcu	ulated			
OH	(Cancel		Apply		Help	

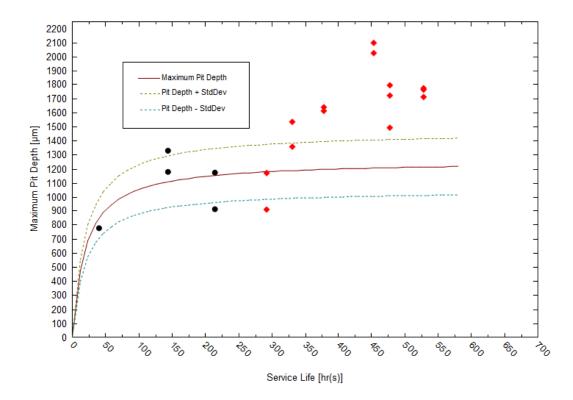
Before running the calculation, we are going to study two different cases:

- I. The first case will include the experimental data from groups 01 to 03
- II. The second case will include all the experimental data from groups 01 to 09

Calculation including Groups 01 to 03

- 14. **Check** the boxes for Group 01 to 03
- 15. We are now ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 16. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Save it under the same file that we previously created as *EVS calculations*.

17. Click on the Plot tab (M Plot).

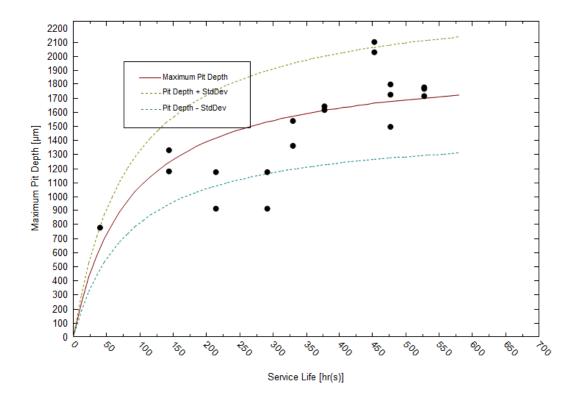


We see that in this case the prediction cannot be considered satisfactory. The reason is that for the first, second, and third observation times the observed mean value of deepest pit decreases. Obviously, such behavior of maximum pit depth has no physical foundation. Generally speaking, such situation 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

- 18. Check the boxes for Group 01 to 09
- 19. We are now ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 20. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Save it under the same file that we previously created as *EVS calculations*.

21. Click on the Plot tab (10 Plot).



The plot above show how the predicted results improved with increasing number of subsequent inspections.

The plot above also shows that the results of approximation of the full set of available experimental data from Laycock et al. 1990) can be reasonably approximated by using EVS approach.

Additionally, these results show that insufficient number of coupons (measurements at given observation times) can be compensated by increasing numbers of observation at different times.

22. Click on the Report tab, and to the Calculation Results table.

You can see here that at 580 hours the maximum pit depth predicted is 1309.93 μ m ≤ 1724.09 μ m ≤1724.09 μ m.

Chapter IV –OLI Studio. : ScaleChem

ScaleChem 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. OLI Studio: ScaleChem 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. OLI Studio. : ScaleChem 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.

OLI Studio: ScaleChem can be used to calculate scaling at one or more user specified temperatures and pressures. Other calculation options include the ability to mix waters at user specified ratios to find compatible waters, and the ability to saturate a water with respect to one or more solids to simulate reservoir conditions.

There are different types of inputs and calculations objects that can be used in OLI Studio: ScaleChem. 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 OLI Studio: ScaleChem software: Brine Analysis, Oil Analysis and Gas Analysis.



OLI Studio: ScaleChem refers to all waters and aqueous samples as brines. This option is added by double clicking on the **Add Brine Analysis.** A brine can be a surface water, an injection water, a formation water, a production water or any other type of aqueous fluid you can create. Brine compositions are entered in terms of ionic concentrations. In addition, the brine pH, total inorganic carbon and alkalinity can also be specified.



Add Oil Analysis allows you to enter an oil (non-aqueous phase). The oil sample may consist of pure component hydrocarbons (e.g., alkanes), distillation data, pseudocomponent or all three.



Add Gas

Analysis

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 (CH₄) 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 OLI Studio: ScaleChem: 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 during production.



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 these 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 OLI Studio: ScaleChem

11.1. Entering Data for a Brine Analysis

To add a **Brine Analysis**, go to the toolbar menu and click on **Streams > ScaleChem > Add Brine**, or by selecting the **Add Brine Analysis** icon in the Actions Pane.

Streams	Calculati	ons	Chemis	stry	Tools	View	Windo
Add	Stream			Va	So L2	Re	± MRE
Add	New Ana		;				
Scale	Chem		>		Add C	il	1
					Add G	as	
nalysis oncile		Na	me: Stre		Add B	rine	

Actions	
🖲 Add Stream	
🛃 Add Mixer	
🖬 Add Water Analysis	
Add EVS Calculation	
🛓 Add Brine Analysis	
👄 Add Oil Analysis	
le Add Gas Analysis	
📥 Add Saturator	
Add Scale Scenario	
🔞 Add Scale Contour	
¥ Add Mixing Water	
* Add Facilities	
1	

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
Ĕ	Catior	ns (mg/L)		Units
Data Entry	Na+1	0.0	0.0	mg/L
Га	K+1	0.0	0.0	Display
	Ca+2	0.0	0.0	Formula
2	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
		is (mg/L)		Standard \sim
	CI-1	0.0	0.0	Save as
	S04-2	0.0	0.0	Suve usin
	HC03-1	0.0	0.0	
	HS-1	0.0	0.0	Balance Options
	C2H3O2-1	0.0	0.0	Туре
				Dominant Ion
		als (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**, simple type the species either using the formula name or its name, as has been shown in the previous sections.

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

	Variable	Value	Balanced	Entry Options
	Cation	ns (mg/L)		Units
	Na+1	0.0	0.0	mg/L v
	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
	Cu	\sim		remplate Manager
ł	Display Name	OLIN	lame	▲ Standard ∨
	▲ Cs+1	CSIO	N	Save as
		CSIO	N	
	styn Cu(+)	CUIIC	DN .	
	sin Cu(++)	CUIO	N	Balance Options
ŀ	S™Cu(+1)	CUIIC	N	Туре
ŀ	\$W(Cu(+2)	CUIO	N	♥ Dominant Ion ∨
ľ	C02	0.0	0.0	
	H2S	0.0	0.0	
	Si02	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 **>**.

	Neutrals (mg/L)	
C02	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.

Ś	De	scr	iption	2	Des	ign	5	Rep	ort					
	Data Entry		Calculate Brine Properties Using: Concentration Data Only Gas-Phase CO2 Content (mole% Measured pH and Alkalinity							%) Calc <u>u</u> late G				
	Reconcile		 Measured pH Only Measured pH, Alkalinity, TIC Calculate Alkalinity 											
	Sec		Properties						ľ	Measured	Calculated			
	Ľ		Temperature (°C)							25.0000				
			Pressure (atm)							1.00000				
			pН							0.0				
			Alkalinity (mg HCO3/L)						0.0					
			Density		· · ·					0.0				
			Elec Co	nd, s	pecific	c (µmh	io/cm	1)		0.0				
			Total Di	ssolv	ed So	lids (n				0.0				
								ompo	sition A	Adjustments				
			Charge	Bala	nce Ur	nknow	/n.							

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	
Density (g/ml)	0.0	
Elec 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 Alkalinity¹⁰, 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.

 $^{^{10}}$ 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 (HCO₃). OLI Studio: ScaleChem can reconcile on a measured alkalinity by adjusting the solution composition.

If you don't have a measured property value, let's say for example, the Specific Electrical Conductivity, just leave it blank.

The yellow cells, under the **Calculated** column, will contain calculated values by the software and will be shown once the simulation is run.

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

There are 5 different types of **Reconciliation Options**:

- a) Concentration Data Only
- b) Gas-phase CO2 content (mole%)
- c) Measured pH and Alkalinity
- d) Measured pH Only
- e) Measured pH, Alkalinity, TIC

Additionally, there is the option to calculate the alkalinity value by checking the **Calculate Alkalinity** box.

Calculate Brine Properties Using:			
Concentration Data Only	Specs	Calc <u>u</u> late	0
◯ Gas-Phase CO2 Content (mole%)			
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.

11.2. Brine Analyses - Reporting Elements

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

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)
S, Sulfur	Sulfate or Sulfide	HS-1 or SO4-2 (cannot tell from total S only)	S (mg/l) × 1.03 for HS-1 (mg/l) or S (mg/l) × 3.0 for SO4-2 (mg/l)

Converting element concentration to species for Brine Analysis

11.3. 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. (See electroneutrality options).
- 2. Gas-phase CO2 content (mole%): Frequently it is simpler and more stable to measure the gas-phase CO₂ 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. OLI Studio: ScaleChem performs a CO₂ 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 CO₂ is adjusted to match a saturated gas composition.
- **3. Measured pH Only:** Many brines analyses report a measured pH. This pH may or may not match the pH calculated by the software. The cause may be an incomplete and/or inaccurate brine description. The software will run both an electroneutrality and pH reconciliation. This type of reconciliation will match your recorded pH. Additionally, the software will compute the water properties such as, density, electrical conductivity, etc. The pH of the solution is automatically adjusted by the software by adding either HCl or NaOH, or you may select your preferred acids and bases to adjust the pH.
- 4. Measured pH and Alkalinity: The purpose of the Measured pH and Alkalinity reconciliations is to match the computed pH and alkalinity values with those you measured. The software will run an electroneutrality, pH and alkalinity reconciliation. Additionally, the software will compute the water properties such as density, electrical conductivity, etc. The pH of the solution is automatically adjusted by the software by adding either HCI or NaOH or you may select your preferred acids and bases to adjust the pH. The Alkalinity is automatically calculated by the software, using CO₂ as the alkalinity titrant, H₂SO₄ as the alkalinity pH titrant and 4.5 as the alkalinity end point pH. You can also change a different alkalinity titrant if you prefer.
- 5. Measured pH, Alkalinity, TIC: The purpose of this reconciliation is to match the measured pH, alkalinity and the total inorganic carbon (TIC). The software adjusts the acetate concentration (organic acids) to match the target TIC. The TIC is adjusted by adding or removing acetic acid. The alkalinity is adjusted using CO₂ as the alkalinity titrant, H₂SO₄ as the alkalinity pH titrant and 4.5 as the alkalinity end point pH. You cannot however change the CO₂ 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.

11.4. A Basic Brine Analysis

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

Example 60: Basic Brine Analysis

In this example, we will input dissolved species concentrations and other measured properties into a **Brine Analysis** object to model a hypothetical water sample. Will calculate the **pH** and **scaling tendency** of a brine sample based upon its measured composition at 1 atm and 25 °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										
Cations (mg/L)		Anions (mg/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

1. Add a **Brine Analysis.** Go to the toolbar menu and click on **Streams > ScaleChem > Add Brine**, or by selecting the **Add Brine Analysis** icon in the Actions Pane

reams	Calculations C	hannista	Tools View Windo	Add Stream
Add	Stream New Analysis		a So L2 Re ± Mate	Add Water Analysis Add EVS Calculation Add Brine Analysis
Scale Ilysis Icile	Chem	> < Stre	Add Oil Add Gas Add Brine	 Add Gas Analysis ★ Add Saturator ✓ Add Scale Scenario Ø Add Scale Contour
				Add Mixing Water

- 2. Click on the new Brine and press <F2> to change the name to Brine Analysis
- 3. Select the **AQ** thermodynamic Framework (default)
- 4. Click on the Names Manager Icon and select the Formula option (default)
- 5. Click on the Units Manager Icon, and select Metric, Concentration (default)

6. Under the **Design** Tab, enter the **Cation, Anion,** and **Neutrals** composition given in the table above. Your screen should look like the image below:

Variable	Value	Balanced	Entry Options	Summary
Cations (n	ng/L)		Units	Unit Set: Metric (mass concentration)
Na+1 K+1 Ca+2 Mg+2 Sr+2 Ba+2 Fe+2 Anions (n	20400.0 400.000 3800.00 830.000 15.0000 0.700000 10.0000 ng/L)	20400.0 400.000 3800.00 830.000 15.0000 0.700000 10.0000	mg/L ✓ Display Formula ✓ Show Non-zero Only Show Balanced Column Template Manager	Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion) No Solid phase(s) Using K-fit Polynomials T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0 Stream Parameters: Temperature (*C) 25.0000 Pressure (atm) 1.00000
CI-1	37000.0	38949.0	Standard	Stream amount (L) 1.00000
S04-2	2200.00	2200.00	Save as	Dominant Ion Charge Balance
HC03-1	720.000	720.000		(eq/L):
HS-1	0.0	0.0	Balance Options	 Cation Charge 1.15621
C2H3O2-1	0.0	0.0	Туре	Anion Charge -1.10124
Neutrals (mg/L)			Dominant Ion 🗸 🗸	Imbalance 0.0549756 Ion(s) needed to balance (mg/L):
CO2	150.000	150.000	Dominant Ion Prorate Cation	CI-1 1949.049
H2S	15.0000	15.0000	Prorate Anion	Concentration Data Only.
Si02	0.0	0.0	Makeup Ion	
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:

- Dominant Ion: This is the default method. The largest counter ion is used to adjust the electroneutrality. In our example,1949.049 mg/L of CI-1 are added since there is an excess of positive charge (see the above image).
- 2) Prorate Cations: All cations are adjusted up or down equally
- 3) **Prorate Anions**: All anions are adjusted up or down equally
- 4) **Make-up Ion**: This option allows for a single ion species to be adjusted. User selects an ion to increase or decrease.
- 5) Under the **Design** Tab, enter the **Cation, Anion,** and **Neutrals** composition given in the table above.
- 7. Select **Dominant Ion** as balance option
- 8. Click on the **Reconcile** (vertical blue tab)

Notice that there that five different types of reconciliation are available in in the upper left corner of the window (see image below). Also, you can see the **Calculate Alkalinity box** (Calculate Alkalinity) option, which allows you to compute the alkalinity, based on the concentration entered.

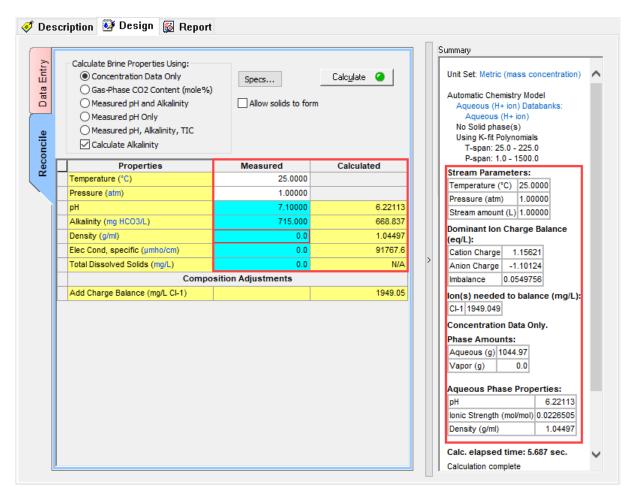
- 9. Select the Concentration Data Only option. This option means that the software will compute the water properties based on the current concentration of neutral, cations, and anions species. The calculation will not use the measured pH, or the measured alkalinity entered (if any).
- 10. Enter the **measured properties**: pH = 7.1 and Alkalinity = 715 as mg HCO3/L

🛷 De	scription 遂 Design 📓 Report			
Data Entry	Calculate Brine Properties Using: Concentration Data Only Gas-Phase CO2 Content (mole%) Measured pH and Alkalinity	Specs	Calc <u>u</u> late 🥥	Summary Unit Set: Metric (mass concentration)
Reconcile	 Measured pH Only Measured pH, Alkalinity, TIC Calculate Alkalinity 			Aqueous (H+ ion) Databanks: Aqueous (H+ ion) No Solid phase(s) Using K-fit Polynomials T-span: 25.0 - 225.0 P-span: 1.0 - 1500.0
Re	Properties	Measured	Calculated	Stream Parameters:
	Temperature (°C)	25.0000		Temperature (°C) 25.0000
	Pressure (atm)	1.00000		Pressure (atm) 1.00000
	рН	7.10000		Stream amount (L) 1.00000
	Alkalinity (mg HCO3/L)	715.000		Dominant Ion Charge Balance
	Density (g/ml)	0.0		(eq/L):
	Elec Cond, specific (µmho/cm)	0.0		Cation Charge 1.15621
	Total Dissolved Solids (mg/L)	0.0		Anion Charge -1.10124
	Compos	sition Adjustments		Imbalance 0.0549756
	Add Charge Balance (mg/L CI-1)			Ion(s) needed to balance (mg/L):
		· · · · · · · · · · · · · · · · · · ·		CI-1 1949.049
				Concentration Data Only.
				concentration bata only.
				×

- 11. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 12. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Create a new file and name it: *ScaleChem Analysis Calculations*.

Analyzing the Results

Once the calculation is done, the **Calculated** column displays the results obtained based on the concentrations entered in the **Data Entry** tab. Notice that the calculated results are pH=6.22 and Alkalinity=669 mg HCO3-1/L vs the measured values of pH=7.1 and Alkalinity=715 mg HCO3-1/L.



To the right you can see the results summarized in the Summary Box.

The top section contains the **Stream Parameters** information. In this example, the software performed the calculation at 25 °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 6.22. The density of this solution is 1.04497 g/ml. Remember, for this example the software used only the concentration of neutrals, cations and anions in solution to do a reconciliation.

1. Click on the **Report** tab, and scroll down to the **Pre and Post Scaling Tendencies** table.

Scale Mineral	Pre-scaling	Pre-index	Post-scaling	Post-index
BaSO4 (Barite)	9.44533	0.975217	9.44533	0.975217
CaCO3 (Calcite)	2.44082	0.387535	2.44082	0.387535
CaSO4.2H2O (Gypsum)	0.938902	-0.0273798	0.938902	-0.0273798
CaSO4 (Anhydrite)	0.740543	-0.130450	0.740543	-0.130450
FeCO3 (Siderite)	0.178450	-0.748484	0.178450	-0.748484
FeS (Pyrrhotite)	500.789	2.69966	500.789	2.69966
KCI (Sylvite)	6.72458e-4	-3.17233	6.72458e-4	-3.17233
FeS (Mackinawite)	8.54999	0.931965	8.54999	0.931965
NaCl (Halite)	0.0122161	-1.91307	0.0122161	-1.91307
SrCO3 (Strontianite)	0.0290888	-1.53627	0.0290888	-1.53627
SrSO4 (Celestine)	0.203964	-0.690447	0.203964	-0.690447

Pre and Post Scaling Tendencies

From this table, you can see that Barite, Calcite, Pyrrhotite and Mackinawite solids have been predicted to be supersaturated.

For more detailed information about scaling tendencies you can go to Scaling section in page 174.

2. Scroll down to the Brine Composition table

Brine Composition							
Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)		
K(+1)	400.000	CI(-1)	38949.0	CO2	158.990		
Na(+1)	20400.0	HCO3- (*)	707.535	H2S	14.9948		
Ba(+2)	0.700000	SO4-2	2203.08				
Ca(+2)	3800.00						
Fe(+2)	10.0000						
Mg(+2)	830.000						
Sr(+2)	15.0000						

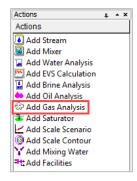
This table shows the composition of the brine after the reconciliation (calculation) has taken place.

Section 12. Entering a Gas Analysis in OLI Studio: ScaleChem

12.1. Entering Data for a Gas Analysis

To add a **Gas Analysis**, go to the toolbar menu and click on **Streams > ScaleChem > Add Gas**, or by selecting the **Add Gas Analysis** icon in the Actions Pane.

Stre	ams	Calculat	tions	Chemi	stry	Tools	View	Windo
Add Stream Add New Ana				Va	So L2	Re	± MBE	
		alysis		;				
	Scal	eChem		>		Add C	il	
nalysis		Na	me: Str		Add G Add B			



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	Entry Options
		Subtotal: 0.0/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)	Units
	H20	0.0	0.0	mole %
	N2	0.0	0.0	Display
	C02	0.0	0.0	Formula
	H2S	0.0	0.0	Show Non-zero Only
	CH4	0.0	100.000	Show Normalized Colum
	C2H6	0.0	0.0	Show Normalized Colum
	СЗН8	0.0	0.0	Template Manager
	i-C4H10	0.0	0.0	Standard
	n-C4H10	0.0	0.0	Standard
	i-C5H12	0.0	0.0	Save as
	C5H12 C6H14	0.0	0.0	
		0.0	0.0	Normalize Options
╟		~		Makeup
				(lancap
				Group Manager
				Use Groups Add

We will start in the **Data Entry** (red) sub-tab. Here you enter the concentration of a pure-component hydrocarbon gas, in **mole** % units. The standard list of component extents to C6 alkanes.

If there is a component that is not present in the prepopulated grid, simply click on the white grid and type the species of interest, using the formula name or its name, as has been shown in the previous sections. Let's say for example, you want to add Isooctane. Type isooctane or i-C8H18 in the white cell to add it to the list.

There is also the option of using the drop-down arrow, that allows you to search for the specific components you want to add.

Subtotal: 100.000/100.000 (mole %) 0.0 0.0 0.0 100.00 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	0 mole % 0 Display 0 Formula 0 Show Non-zero Only 0 Show Normalized Colun 0 Template Manager	
0.0 100.00 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	0 Display 0 Formula 0 Show Non-zero Only 0 Show Normalized Colun 0 Template Manager	
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	Jispary Jispary Jispary Formula Show Non-zero Only Show Normalized Colum Template Manager	
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	0 Formula 0 Show Non-zero Only 0 Show Normalized Colum 0 Template Manager	
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	0 0 Show Non-zero Only 0 Show Normalized Colum 0 Template Manager	
0.0 0.0 0.0 0.0 0.0 0.0	Contraction of the second seco	
0.0 0. 0.0 0.	0 Template Manager	
0.0 0.	remplate Manager	
0.0 0.		
	0 Standard	
0.0 0.	0 Save as	
0.0 0.	0	
0.0 0.		
0.0 0.		
OLI Name	Makeup	
ISOBUTANE	Group Manager	
IPENTAN		
MEPNTAN224		
IOD2EL		
IBUTYLAMN		
	0.0 0.0 0.0 0. OLI Name ISOBUTANE IPENTAN MEPNTAN224 IODZEL	

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
	H2O	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 Colu
	СЗН8	0.0	0.0	Template Manager
	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	0.0	0.0	Normalize Options
	OLI	0.0	0.0	Makeup
				Group Manager

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 atm).

🤊 De	scr	ription	🚱 Design 🚱 Definition 📓 Report		
Inflows	F	H20	Component	Normalized Subtotal: 100.000/100.000 (mole %) 0.0	Calculate G
Reconcile		CH4		100.000	Conditions Value Temperature (*C) 15.5556 Pressure (atm) 1.00231
					Show Non-zero Only

12.2. A Basic Gas Analysis

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

Example 61: Basic Gas Analysis

The Gas Analysis object provides a quick way to enter a pure-component hydrocarbon gas.

Setting the Gas Analysis

1. Add a Gas Analysis. Go to the toolbar menu and click on Streams > ScaleChem > Add Gas, or by selecting the Add Brine Analysis icon in the Actions Pane



- 2. Click on the new Gas and press **<F2>** to change the name to Gas Analysis
- 3. Select the **AQ** thermodynamic Framework (default)
- 4. Click on the Names Manager Icon and select the Formula option (default)
- 5. Click on the Units Manager Icon, and select Metric, Concentration (default)
- 6. Under the **Inflows** Tab, enter the gas composition given in the table below

Gas	Analysis 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:

🛷 Description 🔮 Design 🐼 Definition 📓 Report

Component	Value	Normalized	Entry Options
	Subtotal: 100.000/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)	Units
H2O	1.80000	1.80000	mole %
N2	3.00000	3.00000	Display
C02	1.50000	1.50000	Formula ~
H2S	0.500000	0.500000	
CH4 CH4	65.5000	65.5000	Show Non-zero Only
C2H6	14.0000	14.0000	Show Normalized Column
СЗН8	8.00000	8.00000	Template Manager
i-C4H10	1.00000	1.00000	-
n-C4H10	3.00000	3.00000	Standard V
i-C5H12	0.500000	0.500000	Save as
C5H12	0.700000	0.700000	
C6H14	0.500000	0.500000	
			Normalize Options
			Makeup ~
			Group Manager
			Use Groups Add

Note: There are several options to the right of the data entered.

- 1) **Entry options:** Here you can select the prefer units, and display name. You also have the options to show the non-zero values only sometimes the composition of species is zero and show normalized (yellow) column this option is useful when the values don't add up to 100 mole%.
- Template manager: Here you can select the standard (default) template or the extended template which includes hydrocarbons with longer chains. You can also create and save your own template for future use.
- 3) **Normalize options:** When your analysis does not add up 100 mole% you can select between two options: Make-up and Prorate. For the Make-up option, the default gas used is CH4.
- 7. Click on the **Reconcile** (vertical blue tab). The reconciliation calculation will be calculated at 15.556 C and 1.00231 atm (standard conditions).

🦪 Description	🛃 Design	Definition	反 Report
---------------	----------	------------	----------

ŝ	Component	Normalized	Reconciled Gas	Calculate 🥝
Inflows		Subtotal: 100.000/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)	
르	H2O	1.80000	1.75645	Condition
_	N2	3.00000	3.00133	Conditions Value
e	C02	1.50000	1.50066	Temperature (°C) 15.5556
Reconcile	H2S	0.500000	0.500221	Pressure (atm) 1.0023
20	CH4	65.5000	65.5290	
ž	C2H6	14.0000	14.0062	1
	C3H8	8.0000	8.00355	
	i-C4H10	1.00000	1.00044	Show Non-zero Only
	n-C4H10	3.00000	3.00133	Show Non-zero Only
	i-C5H12	0.500000	0.500222	
	C5H12	0.700000	0.700310	
	C6H14	0.500000	0.500222	

- 8. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 9. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Create a new file and name it: *ScaleChem Analysis Calculations*.

Analyzing the Results

Once the calculation is done, the Reconciled Gas column displays the results at equilibrium conditions.

Component Normalized Reconciled Gas Calcylate M20 Subtotal: 100.0001/00.000 (mole %) Subtotal: 100.0001/00.000 (mole %) Condition N2 3.0000 3.0000 3.0000 Condition N2 0.02 1.5000 1.5000 Condition H2S 0.0001/00.000 (mole %) Temperature (°C) Pressure (atm) H2S 0.500000 0.500200 Pressure (atm)	Value 15.5556	Unit Set: Metric (mole fraction) Automatic Chemistry Model
N2 3.0000 3.00133 Conditions		Automatic Chemistry Model
N2 3.0000 3.0133 Conditions C02 1.50000 1.50060 Temperature (°C) H2S 0.500000 0.50021 Pressure (atm)		Automatic Chemistry Model
CO2 1.5000 Temperature (°C) H2S 0.50000 0.50021 Pressure (atm)	15.5556	Aqueous (H+ ion) Databanks:
H2S 0.500000 0.500221 Pressure (atm)		Aqueous (H+ ion)
	1.00231	Second Liquid phase
CH4 65.500 65.5290		Using K-fit Polynomials T-span: 25.0 - 225.0
C246 14.0000 14.0062		P-span: 1.0 - 1500.0
C3H8 8.00000 8.0355		Stream Parameters:
LC4H10 0.00000 0.00044		Temperature (°C) 15.5556
n-C4H10 3.00000 3.00130 Show Non-zero Only		Pressure (atm) 1.00231
LeSH12 0.50000 0.50022		Makeup Normalization: CH4.
C5H12 0.50000 0.50000 0.50000 0.50000 0.50000 0.500000		Equilibrium Calculation.
	1	Phase Amounts:
C6H14 0.500202 0.500222		Aqueous (mol) 0.0443282
		Vapor (mol) 99.9557
		Solid (mol) 0.0
		2nd Liquid (mol) 0.0
		End Eddid (mor) 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.

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.

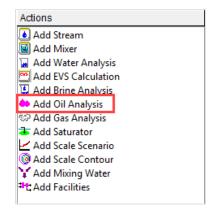
3. Click on the **Report** tab. Here you will see a more complete representation of the results at equilibrium.

Section 13. Entering an Oil Analysis in OLI Studio: ScaleChem

13.1. Entering Data for an Oil Analysis

To add an **Oil Analysis**, go to the toolbar menu and click on **Streams** > **ScaleChem** > **Add Oil**, or by selecting the **Add Oil Analysis** icon in the Actions Pane.

Streams	Calculat	tions	Chem	istry	Tools	View	Windo
Ac	ld Stream			Va	So L2	Re	± MBE
Ac	ld New An	alysis					
Sc	ScaleChem		>		Add Oil		
				_	Add G	as	
Analysis concile		Na	me: Si	TE	Add B	rine	



You will see four different tabs for this analysis. The **Description**, **Design**, **Definition** and **Report** tab.

The oil analysis opens in the **Design** tab, which has 4 different sub-tabs: **Combined**, **Pseudocomponents**, **Assay** and **Reconcile**.

In the **Combined** (red) sub-tab, pure components (organic and inorganic) are entered. If there is a component that is not present in the prepopulated grid, simply click on the white grid and type the species of interest, using the formula name or its name, as has been shown in the previous sections. Let's say for example, you want to add Isooctane. Type isooctane or i-C8H18 in the white cell to add it to the list.

Also, you can use the **show non-zero only** option to hide all the zero values – since they are not needed.

Descr	iption 🛃 Design 📓 Report			
	Component	Value	Normalized	Entry Options
ombined	n-C4H10	0.0	0.0	Units
Ē	i-C5H12	0.0	0.0	mole %
3	C5H12	0.0	0.0	Display
	C6H14	0.0	0.0	Formula ~
	C7H16	0.0	0.0	
	i-C8H18	0.0	0.0	Show Non-zero Only
	n-C8H18	0.0	0.0	Show Normalized Column
	C9H20	0.0	0.0	Template Manager
	C10H22	0.0	0.0	
	C11H24	0.0	0.0	Standard v
	C12H26	0.0	0.0	Save as
	C13H28	0.0	0.0	ouve donn
	C14H30	0.0	0.0	
	C15H32	0.0	0.0	Normalize Options
2 -	C16H34	0.0	0.0	Prorate v
	C17H36	0.0	0.0	
	C18H38	0.0	0.0	
	C19H40	0.0	0.0	
	C20H42	0.0	0.0	
	C21H44	0.0	0.0	
	C22H46	0.0	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	
	C40H82	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.

Combined	Component	Molecular Weight	Nomal Boiling Point (°C)	Specific Gravity	Thermo Method	Value (mole %)
onents	<enter a="" name=""></enter>					
Pseudocompo						
Pse						

In the **Assay** (red) sub-tab, distillation curves can be entered. The Assay screen contains three data entry grids: Component, Entry Options and Distillation Data.

	Component	t mole %			Di	stillation Data	Grid		
	<enter a="" name=""></enter>			Vo	ume%			Temperature (°C)	
5	Entry Options								
	Type A	STM D86 \vee							
g	Thermo Method A	PI-8 🗸							
oner	Density 0.00 Sp	pecific Gravity 🛛 🗸							
duo	No, of Cuts	0							
Pseudocomponents	Display Ass	say Cuts							
	Entry O	ptions							
Assay	Assay Properties	Mole %	Mol Wt.	NBP (°C)	Sp Gr	Cr Temp (°C)	Cr Pres (atm)	Cr Vol (L/mol)	Acentric Facto

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 Option	s		
Туре		ASTM D86	\sim
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 Method	API-8 V
Density 34.00	API-8 API-5
No. of Cuts	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 thee 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. OLI Studio: ScaleChem 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 374-377.

Distillation Data Grid: In this section the distillation data is entered.

And in the **Reconcile** tab, is where the equilibrium calculations are performed.

The **Reconcile** sub-tab is used to calculate the properties of the gas at the temperature and pressure conditions specified. By default, the values of temperature, and pressure are 60 °F (15.56°C) and 14.7 psia (1 atm).

1	Des	cription 😻 Design 🛃 Definition 📓 Report		
	ŝ	Component	Normalized	Calculate 🥝
	Inflows		Subtotal: 100.000/100.000 (mole %)	Condition
	-	H20	0.0	Conditiona Valua
		CH4	100.000	Temperature (°C) 15.5556
	cile			Pressure (atm) 1.00231
	Reconcile			
	Sec			
	-			
				Show Non-zero Only

13.2. Basic Definitions for the Oil Analysis Tool

13.2.1. Hydrocarbon Petroleum Fractions

Frequently a hydrocarbon analysis is the only data available for entry into the software. This analysis is usually a distillation curve where the volume distilled as a function of temperature of a petroleum fraction has been analyzed. This information must be turned into a vapor, organic and aqueous component for use in the simulator.

ASTM D86

Used for light and medium petroleum products and is carried out at atmospheric pressure. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline.

ASTM D1160

Used for heavier petroleum products and is often carried out under vacuum. Sometimes as low as 1 mm Hg. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline.

ASTM D2887

Uses gas chromatography to produce the distillation curve and is applicable to a wide range of petroleum products. The results are always reported on a volume percent basis. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline

True Boiling Point (TBP)

These curves, in practice, are difficult to obtain. The other methods are usually used instead.

13.2.2. Thermodynamic Methods (pseudo-components and petroleum fractions)

The methods used within OLI to calculate the critical temperature and pressure are the API, Cavett and Lee-Kesler methods.

API Method

Uses the specific gravity to estimate the critical parameters. The specific gravity, if not entered, can be estimated from the API gravity or the Watson K. The boiling points are taken from the assay data. API version 5 (API-5) and API version 8 (API-8) are currently supported.

The API method is selected by the user. Tc, Pc, and Vc are calculated as follows:

$$T_c = 24.2787 \times T_b^{0.58848} \times SG^{0.3596}$$

$$\ln P_c = \frac{3.12281\rho + 9}{T_b^{2.3125} SG^{2.3201}} \text{ if } T_b < 1000 \text{ °F}$$

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 Δ is multiplied by f:

$$f = \left(T_c - \frac{536.67}{T_c - T_b}\right)^{0.38}$$

If Tc>593 R,

$$\Delta = \left(\frac{(0.98907 \times SG)(\Delta - 592.4439)}{MW}\right)^{0.5}$$

Cavett

This method uses the API gravity method to determine the critical properties. The API gravity, if not entered can be estimated from the actual specific gravity or the Watson K. The boiling points for the pseudo-components are taken from the assay.

If the Cavett method is chosen by the user, Tc, Pc and Vc are calculated as follows:

$$\begin{split} T_c &= 768.0712 + 1.7133693 \times T_b - 0.0010834 \times T_b^2 - 0.008921258 \times T_b \times API + (3.8890584\rho - 7) \\ &+ T_b^3 \times 5.309492\rho - 6 \times T_b^2 \times API + 3.27116\rho - 8 \times (T_b \times API)^2 \end{split}$$

$$\begin{split} log P_c &= 2.829046 + 0.0009412 \times T_b - 3.047475\rho - 5 \times T_b^2 - 2.087611\rho - 5 \times API \times T_b + 1.5184103\rho - 9 \times T_b^3 \\ &+ 1.1047809\rho - 8 \times API \times T_b^2 - 4.82716\rho - 8 \times API^2 \times T_b + 1.3949619\rho - 10 \times (API \times T_b)^2 \end{split}$$

$$V_c = \frac{Z_c \times T_c \times 10.73}{P_c}$$

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 Δ is multiplied by f:

$$f = \left(T_c - \frac{536.67}{T_c - T_b}\right)^{0.38}$$

If Tc>593 R,

$$\Delta = \left(\frac{(0.98907 \times SG)(\Delta - 592.4439)}{MW}\right)^{0.5}$$

Lee-Kesler

This method uses the Watson K and the specific gravity (which can be estimated via the Watson K) to determine the critical parameters.

If the Lee-Kesler method is selected by the user, Tc, Pc, and Vc are calculated as follows:

$$\begin{split} T_c &= 341.7 + \frac{811}{SG} + (0.4244 + 0.1174\,SG) \times T_b + (0.4669 - 3.2623\,SG) + \frac{100,000}{T_b} \\ &\ln P_c = 8.3634 - \frac{0.566}{SG} - \left(0.24244 + \frac{2.2898}{SG} + \frac{0.11857}{SG^2}\right) \times 0.001 \times T_b \\ &+ \left(1.4685 + \frac{3.648}{SG} + \frac{0.47127}{SG^2}\right) \times \left|\rho - 7 \times T_b^2 - \left(0.42019 + \frac{1.6977}{SG^2}\right)\right| \rho - 10 \times T_b^3 \\ &V_c = \frac{Z_c \times T_c \times 10.73}{P_c} \end{split}$$

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 Δ is multiplied by f:

$$f = \left(T_c - \frac{536.67}{T_c - T_b}\right)^{0.38}$$

If Tc>593 R,

$$\Delta = \left(\frac{(0.98907 \times SG)(\Delta - 592.4439)}{MW}\right)^{0.5}$$

13.2.3. Average Bulk Density

Specific Gravity

Unitless, relative to pure water (H₂O) at 15 °C which has a density of 1.0 g/mL

API Gravity

Degrees API (°API). This is calculated via the following equation:

$$API(60F) = \left(\frac{141.5}{s.\,g.\,(60F)}\right) - 131.5$$

where, SG is the specific gravity at 60 °F.

Watson K

The Watson K has no units but is calculated via:

$$K = \left(\frac{NBP^{1/3}}{SG}\right)$$

where NBP is the normal Boiling point.

13.3. A Basic Gas Analysis

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

Example 62: Basic Gas Analysis

The Gas Analysis object provides a quick way to enter a pure-component hydrocarbon gas.

Setting the Gas Analysis

10. Add a Gas Analysis. Go to the toolbar menu and click on Streams > ScaleChem > Add Gas, or by selecting the Add Brine Analysis icon in the Actions Pane

	Actions
	🖲 Add Stream
	國 Add Mixer
Streams Calculations Chemistry Tools View Windo	🚂 Add Water Analysis
Add Stream Val Sol L2 Re 👱 🗰	Add EVS Calculation
Add New Analysis	🔛 Add Brine Analysis
	🎃 Add Oil Analysis
ScaleChem > Add Oil	Add Gas Analysis
Add Gas	📥 Add Saturator
Analysis Add Brine -	🗹 Add Scale Scenario
oncile Name: Stre	Add Scale Contour
	Y Add Mixing Water
	**t: Add Facilities

- 11. Click on the new Gas and press **<F2>** to change the name to Gas Analysis
- 12. Select the **AQ** thermodynamic Framework (default)
- 13. Click on the Names Manager lcon and select the Formula option (default)
- 14. Click on the Units Manager Icon, and select Metric, Concentration (default)
- 15. Under the **Inflows** Tab, enter the gas composition given in the table below

Gas Analy	Gas Analysis Composition					
Formula	Component Name	Mole %				
H2O	Water	1.80				
N2	Nitrogen	3.00				
CO2	Carbon Dioxide	1.50				
H2S	Hydrogen Sulfide	0.50				
CH4	Methane	65.5				
C2H6	Ethane	14.0				
C3H8	Propane	8.00				
i-C4H10	Isobutane	1.00				
n-C4H10	n-Butane	3.00				
i-C5H12	Isopentane	0.50				
C5H12	n-Pentane	0.70				
C6H14	n-Hexane	0.50				

Your screen should look like the image below:

Component	Value	Normalized	Entry Options
	Subtotal: 100.000/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)	Units
H20	1.80000	1.80000	mole %
N2	3.00000	3.00000	Display
C02	1.50000	1.50000	Formula
H2S	0.500000	0.500000	
CH4	65.5000	65.5000	Show Non-zero Only
C2H6	14.0000	14.0000	Show Normalized Colur
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
			Group Manager
			Use Groups Add

Note: There are several options to the right of the data entered.

- 4) **Entry options:** Here you can select the prefer units, and display name. You also have the options to show the non-zero values only sometimes the composition of species is zero and show normalized (yellow) column this option is useful when the values don't add up to 100 mole%.
- 5) **Template manager:** Here you can select the standard (default) template or the extended template which includes hydrocarbons with longer chains. You can also create and save your own template for future use.
- 6) **Normalize options:** When your analysis does not add up 100 mole% you can select between two options: Make-up and Prorate. For the Make-up option, the default gas used is CH4.
- 16. Click on the **Reconcile** (vertical blue tab). The reconciliation calculation will be calculated at 15.556 C and 1.00231 atm (standard conditions).

H21		Subtotal: 100.000/100.000 (mole %) 1.80000	Subtotal: 100.000/100.000 (mole %) 1.75645	Condition
		1.80000	1 75645	Condition
N2				Conditions Malus
	1	3.00000	3.00133	Conditions Value Temperature (°C) 15.555
CO H2: CH)2	1.50000	1.50066	Pressure (atm) 1.0023
H2	2S	0.500000	0.500221	Pressure (am) 1.0023
CH	14	65.5000	65.5290	
C2	2H6	14.0000	14.0062	1
C3	3H8	8.00000	8.00355	
i-C	C4H10	1.00000	1.00044	Show Non-zero Only
n-C	C4H10	3.00000	3.00133	Show Non-zero Only
i-C	C5H12	0.500000	0.500222	
C5	5H12	0.700000	0.700310	
C6	5H14	0.500000	0.500222	

- 17. Now, we are ready to perform the calculation. Click on the Calculate button or press the <F9> key
- 18. It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Create a new file and name it: *ScaleChem Analysis Calculations*.

Analyzing the Results

Once the calculation is done, the Reconciled Gas column displays the results at equilibrium conditions.

١г	Component	Normalized	Reconciled Gas	Calcylate 🥥		1
		Subtotal: 100.000/100.000 (mole %)	Subtotal: 100.000/100.000 (mole %)		Unit Set: Metric (mole fraction)	
	H2O	1.80000	1.75645	Condition	Automatic Chemistry Model	
1	N2	3.00000	3.00133	Conditions Value	Aqueous (H+ ion) Databanks:	
ľ	C02	1.50000	1.50066	Temperature (°C) 15.5556	Aqueous (H+ ion)	
ľ	H2S	0.500000	0.500221	Pressure (atm) 1.00231	Second Liquid phase Using K-fit Polynomials	
ľ	CH4	65.5000	65.5290		T-span: 25.0 - 225.0	
ŀ	C2H6	14.0000	14.0062	J	P-span: 1.0 - 1500.0	
ŀ	СЗНВ	8.00000	8.00355		Stream Parameters:	
ì ľ	i-C4H10	1.00000	1.00044		Temperature (°C) 15.5556	
	n-C4H10	3.00000	3.00133	Show Non-zero Only	Pressure (atm) 1.00231	
	i-C5H12	0.500000	0.500222		Makeup Normalization: CH4.	
	C5H12	0.700000	0.700310		> Equilibrium Calculation.	
	C6H14	0.500000	0.500222		Phase Amounts:	
					Aqueous (mol) 0.0443282	
Iľ					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 the

The **Phase amounts** section shows the distribution of species in the different phases. This analysis contains two phases: aqueous and vapor.

The **Aqueous Phase Properties** information shows the computed pH, ionic strength, and density of the solution.

4. Click on the **Report** tab.

Here you will see a more complete representation of the results at equilibrium.

13.4. Putting together a complete calculation in ScaleChem

Now that we have defined some terms, we are now ready to begin entering the information required to run a calculation. In this calculation we will be entering the concentrations of a single brine.

Task 1 – Create a Brine Analysis

In this tour we will show the main interface of a Brine Analysis, followed by an example of a brine (water analysis) and calculate its scale tendency. Let's begin. Steps for the simulation will be given with bullet points.

1. Add Brine Analysis from Actions Panel.

.
Add Brine
Analysis

2. Click on the description Tab. If the *Description* tab is not currently displayed, click on the tab.

🗽 Brine		
🦪 Description	🛃 Design	<u>§</u> 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				
Cations	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

1	2	Variable	Value	Balanced	Entry Options
1	Data Entry	Cations (ng/L)		Units
1	a	Na+1	36000.0	36116.0	mg/L ~
1	Dat	K+1	300.000	300.000	Display
1	2	Ca+2	600.000	600.000	
1		Mg+2	150.000	150.000	Formula ~
	cile	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
		Anions (r	ng/L)		Standard 🗸
		CI-1	57000.0	57000.0	
		S04-2	250.000	250.000	Save as
	2	HC03-1	600.000	600.000	
		HS-1	0.0	0.0	Balance Options
		C2H3O2-1	0.0	0.0	Type
					Dominant Ion V
		Neutrals (mg/L)		Dominant Ion
		C02	0.0	0.0	
		H2S	0.0	0.0	
		SiO2	0.0	0.0	
		B(OH)3	0.0	0.0	

3. 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.

4. Select the Show **non-zero only** box

	Variable	Value	Balanced	Entry Options
Data Entry	Cation	s (mg/L)		Units
a	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
L CO	Ba+2	5.00000	5.00000	Show Balanced Column
Å.				
	Anions (mg/L)			Template Manager
	CI-1	57000.0	57000.0	Standard 🗸
	S04-2	250.000	250.000	
	HC03-1	600.000	600.000	Save as
	Neutrals (mg/L)		Balance Options	
				Туре
				Dominant Ion V

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	Cations	s (mg/L)	
a	Na+1	36000.0	36116.0
Dat	K+1 13	300.000	300.000
	Ca+2	600.000	600.000
	Mg+2	150.000	150.000
Reconcile	Sr+2	80.0000	80.0000
	Ba+2	5.00000	5.00000
å			
	Anions	(mg/L)	
	CI-1	57000.0	57000.0
	S04-2	250.000	250.000
	HCO3-1	600.000	600.000
	Neutral	s (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.

E	alance Options	
	Туре	
	Dominant Ion 👻 🔻	
	Dominant Ion	ŀ
	Prorate Cation	l
	Prorate Anion	l
	Makeup Ion	l

5. Select **Dominant Ion** balance option type.

You can review the Dominant Ion Charge and Ions needed to balance in the tables presented in the Summary Box.

ummary					
Unit Set: Metric (mass concentration)					
Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion) No Solid phase(s) Custom K-fit P-span					
Stream Paran	nete	ers:			
Temperature (°C)	25.0000			
Pressure (atm))	1.00000			
Stream amount	t (L)	1.00000			
Dominant Ion (eq/L):			ance		
Cation Charge		1.61776			
Anion Charge	_ ·	1.62280			
Imbalance	-5.0	4367e-3			
lon(s) needed	d to	balance	(mg/L):		
Na+1 115.954					
Concentration	n Da	ta Only.			

The summary box shows additional detail about the brine's chemistry and balance option. The stream parameters table shows default values. The Dominant Ion Charge Balance shows the total cations or anions, and the total imbalance.

Now is time to enter the measured property data in the *Reconcile Tab.*

- 6. Select Concentration Data Only Option
- 7. Check the Calculate Alkalinity box
- 8. Enter the measured pH (7.67), density (1.064 g/mL) and TDS (96280 mg/L)
- 9. Leave the *Allow solids to form* unchecked.

We will leave the **Allow solids to form** unchecked because generally the industry uses acid to preserve water samples, which prevent solids to form. Acidified samples contain the unprecipitated ion concentration, which is what we entered into the brine. In this step, we will eliminate solids because allowing solids to form would change the brine's composition significantly.

Reconcile Data Entry	Calculate Brine Properties Using: O Concentration Data Only Gas-Phase CO2 Content (mole%) Measured pH and Alkalinity Measured pH Only Calculate Alkalinity	Specs Calculate G			
<u>.</u>	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			
	Co	mposition Adjustments			
	Add Charge Balance (mg/L Na+1)				

10. Select the **Calculate** button or press the **<F9>** key

Reconcile Data Entry	Calculate Brine Properties Using: Oconcentration Data Only Gas-Phase CO2 Content (mole%) Measured pH and Alkalinity Measured pH Only Calculate Alkalinity	Specs	Calculate 🥥
8	Properties	Measured	Calculated
	Temperature (°C)	25.0000	
	Pressure (atm)	1.00000	
	рН	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
	Com	position Adjustments	
	Add Charge Balance (mg/L Na+1)		115.954

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 Properties:				
pH	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	ated 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.

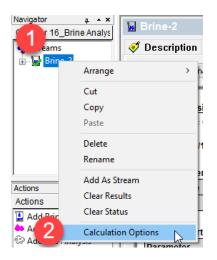
np to: Brine Analysis Dat	а	~			Customize Export
Pre and Post Scaling T	endencies	<			_
Scale Mineral	Pre-scaling	Pre-index	Post-scaling	Post-index	
BaCO3 (Witherite)	7.09380e-4	-3.14912	7.09380e-4	-3.14912	
BaSO4 (Barite)	6.22755	0.794317	6.22755	0.794317	
CaCO3 (Calcite)	6.35375	0.803030	6.35375	0.803030	
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	h				
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:

11. Right click on the brine analysis icon

12. Select Calculation Options



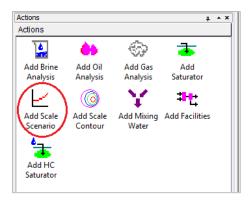
13. Enable Pre-scaling Tendencies

Calculation Options - Brine-2	?	×
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 Elyrgy		
Entropy		
Thermal Conductivity		
Surface Tension		
✓ Interfacial Tension		
Pre-scaling Tendencies Method O Estimated O Rigorous		
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.

🦪 De	scription 🧕 Design	🛍 Plot 📓 Report	🚊 File Viewer
_			
sts	Туре	Name	Flow
Inlets	<select></select>		
Conditions			
diti			
Co			
σ			
Solid	Detail Info of Selected Inlet		
("	Compone	ent	Value (mol/hr)

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 OLI Studio: ScaleChem 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 Ca	Iculations C	Chemistry Tools View W	ndow Help			- 8 ×
		Cancel				
🗅 🚅 🖬 🛛 🕹 🛍 🗍	a 🖇 😽	Aq Va So 2 nd Re ±		🛗 ± 🤤 🔊 😭 🌾		
Navigator # * × Chapter 16 Brine Analysis*	🛃 Brine	Scale Scenario				
♦ Streams	I Desc	ription 🤒 Design 🚻	Plot 📓 Report 🚊 F	ile Viewer		
🗄 🙀 Brine-2						
Brine Scale Scenario	L to L	Туре	Name	Flow	Calculate 🥥	
	nlets	<select></select>				
					Calculate Alkalinity	
					Summary	
	onditions				Unit Set: Scale Metric	^
	Cond				Automatic Chemistry Model	
					Aqueous (H+ ion) Databanks: Aqueous (H+ ion)	
					Custom K-fit P-span	
	0	Detail Info of Selected Inlet Nam	e		At least one inlet should be selected	L.
Actions a + ×	Sec. 1	Component	Va	lue (mol/hr)	Selected Solids:	
Actions 4 X					No Solid Selected.	
					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)

ets	Туре	Name	Flow
Inlets	<select></select>		
	Whole Fluid		
su			
Conditions			
ŏ			
	1		
Solid	Detail Info of Selected Inlet I		
(°)	Compone	nt Va	lue (mol/hr)

6. Select Brine from the drop-down menu in the Name column.

🦪 Des	cription	🥸 Design	🛍 Plot 髮 Report 🚊 Fi	le Viewer
ţs		Туре	Name	Flow
Inlets	Brine		-	
	<select< th=""><th>></th><th>Brine [AQ]</th><th></th></select<>	>	Brine [AQ]	
			6	

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)

	Des	scri	iption	>	Desig	jn 📶	l, Plot	<u> </u> Rej	port 🧯	👔 File Viewer	
Í	Inlets	Ρ	<enter th="" <=""><th>locat</th><th>Locatio</th><th></th><th>•</th><th>Temper</th><th>ature (</th><th>Pressure (bar)</th><th>Drop Solid</th></enter>	locat	Locatio		•	Temper	ature (Pressure (bar)	Drop Solid
	-	6	-2.1101								
2	Conditions			2							
	Solid		Auto Ste iteps:	р 5	Go	Sort T		'oom € ⊖	0		

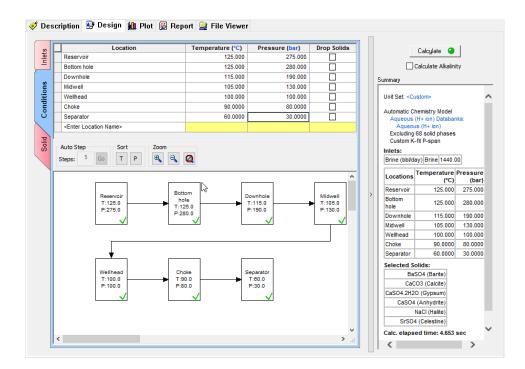
The *Conditions* section is where we enter points along the production scheme. The first column is Location. We can use the dropdown menu in each row to select a location or type in our own location name.

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** box both show the locations in the order that we entered. This screen has options for zooming, auto steps, sorting by temperature or pressure, and dropping solids at particular conditions.



The graphical view clearly shows the five locations and their Temperature and pressure conditions.

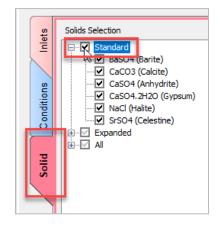
The Drop Solids checkbox column at the very end of the grid is designed to help the users decide if they want to carry forward solids from certain locations or not.

Solid Tab

- 10. Select the Solid Tab
- 11. Make sure that the solid button in the menu bar is selected.



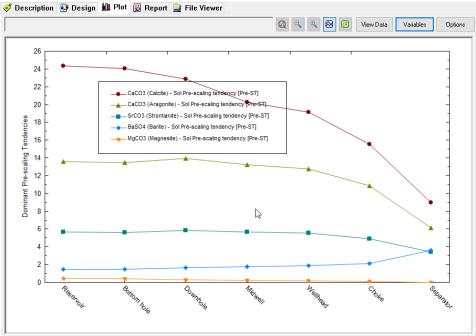
12. Select the Standard checkbox



13. Press the Calculate button of select the <F9> key

14. Select the Plot Tab

You can customize which curves are visible by selecting the Variables button.



15. Select the View Data button

Ø	Θ	⊕_	\boxtimes	S	View Data	Variables	Options

The *View Data* button shows the pre-scaling tendency at each location. We can copy the results of this table to a program like Excel by selecting the top left cell then selecting <Ctrl>+<C> on the keyboard.

Task 3 – Create a Gas Analysis

1. Double click on the Add Gas Analysis object in the Actions Panel

kctions					
Actions					
•	🖬 🖉		evs	}	
Add Stream	Add Mixer	Add Water Analysis	Add EVS Calculation	Add Brine Analysis	
- 45	 Image: A mail Image: A	3		0	
Add Oil Analysis	Add Gas Analysis	Add Saturator	Add Scale Scenario	Add Scale Contour	
- Y 1	#t	*			
Add Mixing Water	Add Facilities	Add HC Saturator			

This adds a Gas object to the Navigator panel.

2. Select the **Description** tab, then rename the object Gas Analysis.

Navigator 🛛 🖡 🔺 🗙	🗇 Gas Analysis
Chapter 16_Brine Analysis*	Sar Gas Analysis
🍫 Streams	< < Description 🛃 Design 🛃 Defin
Brine Brine Scale Scenario Gas Analysis	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 of the two below, depending on the Names view you select.

	Component	Value	Normalized	Entry Options
		Subtotal: 100.0	Subtotal: 100.000/	Units
Г	H2O	1.80000	1.80000	mole %
Г	N2	3.00000	3.00000	Display
	CO2	1.50000	1.50000	Formula
	H2S	0.500000	0.500000	
	CH4	65.5000	65.5000	Show Non-zero Only
	C2H6	14.0000	14.0000	Show Normalized Col
	C3H8	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

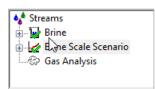
This is the extent of the gas entry step. There are modifications that can be part of the gas analysis entry step (in the Reconcile Tab), but in this case, they are not considered. Now that the gas is entered, the scale scenario considered in Task-2 will be recomputed.

Inflows	Γ	Component		Reconciled Ga	Calc <u>u</u> late	•	Summary	
ê	L		Subtotal: 10	Subtotal: 100.0	Condition		Unit Set: Metric (mole fraction)
-		H2O	1.80000	1.75645			Automatic Chemistry Model	
		N2	3.00000	3.00133	Saturate With	None 🔻	Aqueous (H+ ion) Databan	KS:
Ð	Г	C02	1.50000	1.50066	Conditions	Value	Aqueous (H+ ion)	
Keconcile		H2S	0.500000	0.500221	Temperature (°C)	15.5556	Second Liquid phase Custom K-fit P-span	
20		CH4	65.5000	65.5290	Pressure (atm)	1.00231	Stream Parameters:	
ř	F	C2H6	14.0000	14.0062			Temperature (°C) 15.5556	
	F	C3H8	8.00000	8.00355			Pressure (atm) 1.00231	
	F	i-C4H10	1.00000	1.00044			Makeup Normalization: CH4.	
	F	n-C4H10	3.00000	3.00133	Show Non-zero Only		Equilibrium Calculation.	
	F	i-C5H12	0.500000	0.500222			Phase Amounts:	
	F	C5H12	0.700000	0.700310			Aqueous (mol) 0.0443276	
	F	C6H14	0.500000	0.500222			> Vapor (mol) 99.9557	
	F				2		Solid (mol) 0.0	
	F				~		2nd Liquid (mol) 0.0	
							Aqueous Phase Propertie	s:
							pH 4.	.75178
							Ionic Strength (mol/mol) 3.20	691e-7
							Density (g/ml) 0.9	99257

Task 4 – Recalculate Scale Scenario with Gas

The gas analysis will be added to the Scale Scenario so that it is considered during the scale evaluation.

1. Select the Brine Scale Scenario icon in the navigator panel



- 2. Select the Design Tab (horizontal tab) if not automatically sent there
- 3. Select the Inlets tab (vertical) if not automatically sent there
- 4. In the Type Column Add Gas

ŝ	Туре	Name	Flow
Inlets	Brine (bbl/day)	Brine	1400.00
(=	Gas (std E3m3/day)	•	
	Brine		
	Whole Fluid		
itions	Gas	N	
¦≓	-	N.	

5. In the Name column select Gas Analysis

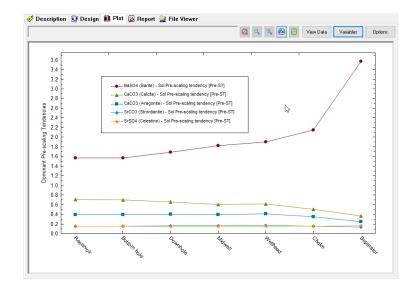
ŝ	Туре	Name	Flow
Inlet	Brine (bbl/day)	Brine	1400.00
-	Gas (std E3m3/day)	•	
$\left \right\rangle$	<select></select>	Gas Analysis	

6. Enter a flowrate of 250 std E3m3/day in the flow cell

6			
Inlets	Brine (bbl/day)	Brine	1400.00
	Gas (std E3m3/day)	Gas Analysis	250.000
	<select></select>		

7. Calculate (Press <F9>)

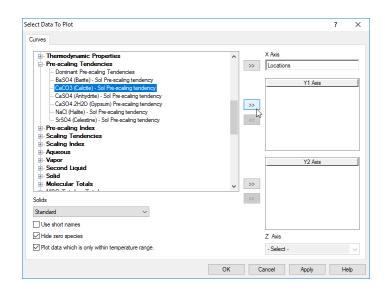
8. Select Plot Tab



- 9. Select Variables button
- 10. Remove all the variables from the Y1 Axis and the Y2 axis by double-clicking on the variables (this removes then from the list). Alternatively, highlight each variable and click on the double-arrow.

You will replace the existing variables with the calcite pre-scaling tendency.

- 11. Expand the Pre-scaling Tendencies button by clicking the + sign
- 12. Double-click on the CaCO3 (Calcite) variable to move it to the Y1 Axis
- 13. Expand the Additional Stream Parameters and add pH to the Y2 axis
- 14. Click <u>OK</u>



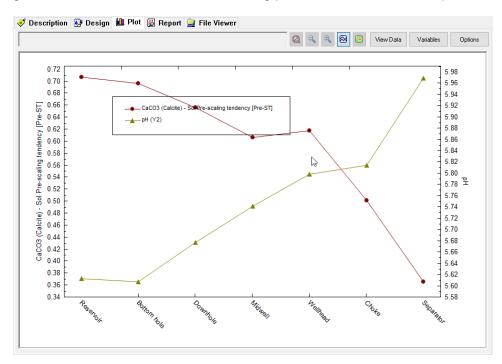
If you are in the *View Data* view, then the table should be similar to the one below.

	Locations	CaCO3 (Calcite) - Sol Pre-sali ng tendenc y	рН
		Pre-ST	
1	Reservoir	0.705312	5.61211
2	Bottom hole	0.694891	5.60661
3	Downhole	0.655192	5.67654
4	Midwell	0.604697	5.74096
5	Wellhead	0.616784	5.79768
6	Choke	0.500689	5.81369
7	Separator	1.24448	6.14419

Calcite is sub-saturated (S<1) at all locations, except the separator.

15. Select the View plot button

The decreasing calcite saturation trend and the increasing pH is easier to see from the plot view.



Task 5 – Creating a Saturator Object

You will use the *Saturator* object to set the reservoir minerals at equilibrium with the produced fluid. It is reasonable, in some cases, to saturate the produced fluid with common evaporite and secondary minerals like CaCO3, CaSO4.H2O, FeCO3, and NaCI. This is based on the assumption that as the reservoir fluid flows through the rock pores, there is sufficient time to interact with the surface minerals. This is based on a second assumption that the vertical column of liquid and gas are in complete equilibrium and that the saturating minerals are distributed throughout the reservoir matrix, such that complete water-mineral contact is possible.

In this case we are going to simulate a particular oil & gas well: ABC. This well produces from calcite-cemented sandstone. Barite is also present in minor quantities in the rock matrix. You will, therefore, create a reservoir called ABC Reservoir and saturate the Brine (previously calculated) with calcite and barite. You will then recalculate the Brine Scale Scenario.

1. Add a Saturator Object

Actions **μ ▲ ×** Actions 4 **W** ۵ evs 1 Add Stream Add Mixer Add Water Add EVS Add Brine Calculation Analysis Analysis \odot 3 \bigcirc 66 ŀ Add Oil Add Gas Add Add Scale Add Scale Analysis Scenario Saturato Analysis Contour <mark>₽</mark>ቲ **ہ** Add HC Add Mixina Add Facilities Water Saturato

2. Select the **Description** Tab to rename the Object **Reservoir**

Navigator # * *	🗈 Reservoir			
Chapter 16_Scale Scenario with 8	- Reservoir			
褖 Streams	🦪 Description	🥺 Design	题 Report	🧕 F
🖶 🙀 Brine				
	Name: Reservoir			
🗄 🚽 💋 Brine Scale Scenario	Name: Neservoir			D
🛓 🧼 Gas Analysis				
Reservoir				

3. Select the Design Tab

🎺 De	scri	ption 🥸 Design 👔	🖥 Report 📄 File Viev	ver			
	_						
Inlets		Туре	Name	Flov	v	Calc <u>u</u> late 🥥	
Ξ		<select></select>				Calculate Alkalinity	
T						Summary	
Solid						Unit Set: Scale Metric	
						Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion) Custom K-fit P-span	
	┢	Con Temperature (°C)	ditions	Value		At least one inlet should be selected for Reservoir	
		Pressure (bar)				Selected Solids:	
	De	tail Info of Selected Inlet Na	ame			Calculation not done	
		Compone	nt	Value (mol/hr)			
\triangleright							

The Saturator has two vertical tabs: Inlets and Solid.

In the **Inlets** Tab the Fluids are entered in the top grid and the Conditions are entered in the bottom grid.

Solids are selected and saturated in the Solid Tab.

- 4. Enter the Brine calculated in Task 1
- 5. Enter the Gas calculated in Task 3

6. Enter the Reservoir conditions: 125 C and 275 bar in the conditions section.

ä	Туре	Name	Flow		Calc <u>u</u> late 🥝	
Inlets	Brine (m3/day)	Brine		200.000	Calculate Alkalinity	
	Gas (std E3m3/day)	Gas Analysis		250.000		
	<select></select>				Summary	_
					Unit Set: Scale Metric	1
					Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion)	
					Second Liquid phase	
		onditions	Value		Excluding 83 solid phases	
	Temperature (°C)			125.000	Custom K-fit P-span	
	Pressure (bar)			275.000	Inlets: Brine (m3/day) Brine 200.00	
	Detail Info of Selected Inlet Nar	ne			Gas (std Gas E3m3/day) Analysis 250.00	
	Compor	ant	Value (mole %)			

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
CaCO3 (Calcite)	CaCO3
<select solid=""></select>	

At this point, the Calculate button is green indicating that the specifications are complete.

- 11. Calculate (or press the <F9> key)
- 12. Click the Report tab

The Saturator Report tab contains several tables: Saturation Details, Inlet Summary, Stream/Phase Properties, Pre and Post Scaling Tendencies, Brine Composition, Gas Composition, and if selected an inlet summary.

• Scroll down to the Pre and Post Scaling Tendencies Table

Pre and Post Scalir	ng Tendencies						
Formula	Mineral	Excess Solute	Excess Solute	Pre-Scale	Pre-Scale	Post-Scale	Post-Scale
		mg/L	lb/1000bbl	S, ST	SI, Index	S, ST	SI, Index
CaSO4.2H2O	Gypsum	0.0	0.0	0.0179366	-1.74626	0.0179365	-1.74626
SrSO4	Celestine	0.0	0.0	0.148191	-0.829178	0.148191	-0.829178
SrCO3	Strontianite			0.209852	-0.678087	0.209852	-0.678087
BaSO4	Barite	2.64658e-5	9.27644e-6	1.00000	1.82534e-6	1.00000	0.0
CaSO4	Anhydrite	0.0	0.0	0.0934633	-1.02936	0.0934633	-1.02936
CaCO3	Calcite	1.13495e-5	3.97806e-6	1.00000	-4.81593e-8	1.00000	0.0
Mg(OH)2	Brucite	T		4.98480e-4	-3.30235	4.98479e-4	-3.30235
NaCl	Halite	0.0	0.0	0.0245553	-1.60985	0.0245553	-1.60985
KCI	Sylvite			2.14382e-4	-3.66881	2.14382e-4	-3.66881

of of the

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).

Des and Dest Casting Tandanaia

The Max scale column shows that trace amounts of BaSO4 and CaCO3 are present in the water. These exceedingly small values (in the parts-per-trillion range) are the specifications or targets for the calculation. The software sets these target solid concentrations and then adjusts up or down, the BaSO4 and CaCO3 inflows until it reaches these targets. These part-per-trillion values may look arbitrary, but in fact the values are equivalent to 1e-10 moles of solid/kg water.

Notice also, that the pre-scale tendency for BaSO4 and CaCO3 are set to 1.0, by saturation definition. That is, these are not calculated, they are defined. The remaining scale tendencies are computed.

Task 6 – Recalculate the Scale Scenario with the Saturated Reservoir

Considerable time is spent creating what is hoped to be a more representative brine. The Brine is reconciled for charge balance, and where needed, alkalinity and pH; the gas is saturated with water as needed (though not done in this case), and lastly the fluids are set to equilibrium with important reservoir minerals. It is only after these steps are complete, and that there is confidence that the assumptions and calculations are representative of the process, that a final scaling calculation is run.

The **Reservoir** calculation contains the representative fluid. It is, therefore, the output of this calculation that will be used in all subsequent calculations. To access this output, a new Type of fluid, Whole Fluid is defined. The Whole Fluid type represents 100% of the contents of a previous calculation, regardless of phase.

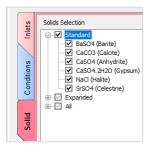
You will use the Whole Fluid from the Reservoir to rerun the scaling calculations.

- 1. Select Brine Scale Scenario in the Navigator Pane and rename it Reservoir Scale Scenario
- 2. Select the Design tab
- 3. In the *Inlets* tab in the Type column delete the Brine and Gas from the Type column
- 4. Add Whole Fluid
- 5. In the **Name** column select **Reservoir**
- 6. In the Flow column select < Automatic>

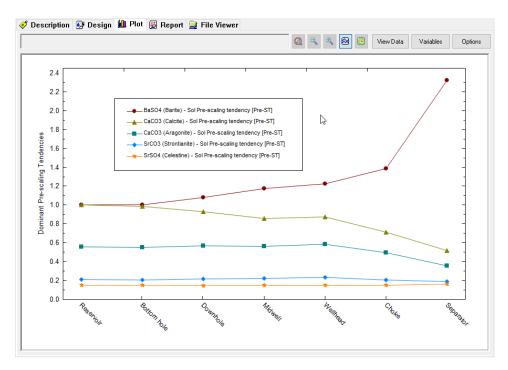
🍼 Des	cription	🥸 Design	🛍 Plot	巓 Report	📄 File	Viewer
		Туре		Name		Flow
Inlets	_	luid (m3/day)	Reservoir	Name		Automatic> 💌
=	<select></select>	•				

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.

7. Go to the Solid tab and make sure that the Standard box is checked



- 8. Calculate (Press <F9>)
- 9. Select Plot tab and select View Plot



The Saturator is a tool for normalizing the thermodynamics of a reservoir system. The purpose of this calculation is to apply the constraint of solid-liquid equilibrium on a system to create a specific compositional starting point.

The basis of this calculation is that water in the pores of a rock matrix is at equilibrium with the mineral surface. Some questions to consider are whether it is reasonable to assume that a reservoir gas, oil, water, and rock

are in equilibrium. Furthermore, we should also consider over what vertical and radial distance we can make this claim.

Regardless of the inconsistencies, the industry widely accepts this approach. It is up to the analyst to decide if the Saturator produces a more representative fluid than the original data.

Task 7 – Add a Contour Diagram

An alternative to the *Scale Scenario* calculation is the *Contour Diagram*. The conditions defined in the Scale Scenario are specific to production locations, and generally no more than ten are entered. By comparison, the conditions defined in the Contour Diagram are a range of temperatures and pressures. The object then computes a matrix of temperature and pressure conditions and creates a presentation-quality contour diagram.

- 1. Add Scale Contour
- 2. Rename the Object Contour Reservoir

Navigator	Ontour Res	servoir		
streams	🛷 Description	🥺 Design	🛍 Plot	
Brine Brine Reconciled-Brine Reservoir Scale Scenario Gas Analysis	Name: Contour Re	servoir		
🖶 🎝 Reservoir	Description			_

- 3. Select the **Design** Tab
- 4. Select the Inlets (vertical) tab
- 5. Select the bottom right corner of the 1st cell in the Inlet grid and choose *Whole Fluid*
- 6. Select *Reservoir* in the 2nd column
- 7. Keep the **<***Automatic***>** flow rate option in the 3rd column

Desc	ription 🧕 Design 🛍 Plot	🛯 🚅 File Viewer	
Inlets	Туре	Name	Flow

8. Click Conditions (vertical) tab

The minimum and maximum conditions are at the Separator 60C, 30 bar and Reservoir 125C, 275 bar. These are the start and end range of the study. To create a reasonable number of calculations (~300) and to keep the matrix somewhat symmetric, we will use increments of 2 C and 10 bar.

- 9. Change the Start to 60
- 10. Change the End to 125
- 11. Select the Increment radio button
- 12. Enter 5 as the increment
- 13. Uncheck the Log box (if it is checked)

- 14. In the Pressure Range box, change the Start to 30
- 15. Change the End to 275
- 16. Select the Increment radio button (uncheck the Log box first)
- 17. Change the Increment to 10

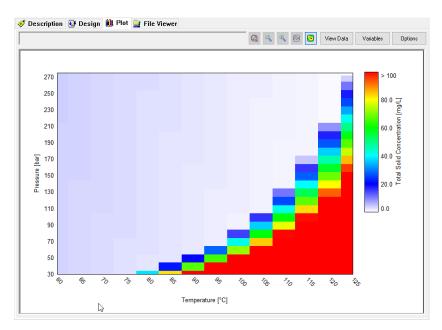
() Con	tour Re	servoir							
🦪 Des	scription	🔮 Des	ign	🛍 Plot	<u> </u> F	ile Viewe	r		
Inlets		emperature	Rang	e			°C		~
Conditions		Start End		60.0 125.0		Incre Number Number	ement ber Steps		5.0 13
		essure Ran	ge				bar		~
Solid		Start End		30.0 275.0		 Incre Numl 	ement ber Steps		10.0 25
								AF.	

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

10. Select the Solid Tab

- 11. Check the Standard box
- 12. Calculate. The calculation should take less than 10 min to be complete
- 13. When calculation is done, go to the Plot tab



The default plot is the total solids forming. The color scale represents a different numerical range. The red cells indicate heavier solid precipitation, and the faint purple-white in the center and left of the screen indicate that little to no scale forms. The upper right corner is the Reservoir conditions (125C and 275 bar). The lower left represents Separator conditions (60C and 30 bar). At both points, minimal solids are computed to form. The fluid traveling through the piping traverses this plot as temperature and pressure decreases. Layering production conditions (e.g., early to late life) over this plot provides an indication as to whether production will be at risk now or in the future. For example, if the pressure decline is significant (e.g., 60 bar), then the fluid will be unstable at the higher temperatures (bottom of well).

13.5. Overview of Brine, Gas and Oils and Introducing Mixer, and Saturator Objects

Other calculation options include the ability to mix waters at user specified ratios to find compatible waters, and the ability to saturate a water with respect to one or more solids to simulate reservoir conditions.

This chapter will cover the same calculation objects using fewer instructions and will introduce *Mixing, Saturator* and *Facility* Calculations. Its purpose is to reinforce what was learned in the previous chapter and to promote the anticipating of next steps when using the interface.

Task 1 – Add a Brine

- 1. Add a Brine Analysis from the Action Panel
- 2. Rename the Brine in the Description Tab, and name it WTXWTR

Navigator	4 • ×		
Document1*			
🐶 Streams		< Description 🧕 Design	G
WTXWTR		Name: WTXWTR	-
		Description	
		West Texas Water Supply	

3. 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 Supp		
Species Na ⁺ Ca ⁺² Mg ⁺² Fe ⁺² Cl ⁻¹ SO ₄ ⁻² HCO ₃ ⁻ HS ⁻¹	3074 910 249 0.77 4474 2960 439	ntration mg/L mg/L mg/L mg/L mg/L mg/L mg/L	
HS-	146.2	mg/L	

- 4. Check the Show non-zero Only box (under Entry Options)
- 5. Go to the Reconcile (vertical) tab
- 6. Select the measured pH and alkalinity Option
- 7. Enter the following conditions (change units if necessary)
 - To change units just click on the hyperlink next to the variable that you want to change.

_	-	L
	Temperature (°F)	I
	Pressure (ps	

Temperature	77 F
Pressure	14.7 psia
pН	7.98
Alkalinity end Point pH	439 mg/L as HCO3-
Titration pH	4.5
Density	(will be estimated)

		/TR ription 🔯 Design 🙀 Repo	rt 📴 File Viewer		Summary
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	Calc <u>u</u> late 🥥	Unit Set: <custom> Automatic Chemistry Model Aqueous (H+ ion) Databanks: Aqueous (H+ ion) No Solid phase(s) Custom K-fit P-span</custom>
ŏ		Properties	Measured	Calculated	Stream Parameters:
Sec		Temperature (°F)	77.0000	Galoalated	Temperature (°F) 77.0000
Ţ.,	F	Pressure (psia)	14.7000		Pressure (psia) 14.7000
\backslash	F	pH	7.98000		Stream amount (L) 1.00000
		Alkalinity (mg HCO3/L)	439.000		Dominant Ion Charge Balance (eg/L):
	F	Alkalinity End Point pH	4.50000		Cation Charge 0.199639
	F	Density (g/ml)	0.0		Anion Charge -0.199436
		Elec Cond, specific (µmho/cm)	0.0	0.0 Imbalance	
		Total Dissolved Solids (mg/L)	0.0		Ion(s) needed to balance (mg/L):
		Compo	sition Adjustments		CI-1 7.195
		Added titrant (mg/L)			Measured pH and Alkalinity.
		Add Charge Balance (mg/L CI-1)			

8. Click the Calculate Button

Task 2 – Add a Second Brine

- 1. Add a Brine Analysis
- 2. Enter the composition given below in the *Data Entry* (vertical) Tab

<u>~</u> []	Variable	Value	Balance	 Entry Options 	
	Catior	ns (mg/L)		Units	
	Na+1	20400.0	20400.0	mg/L	`
	K+1	402.000	402.000	Display	
	Ca+2	3800.00	3800.00		
	Mg+2	829.000	829.000	Formula	`
	Sr+2	15.2000	15.2000	Show Non-zero O	nly
	Ba+2	0.70000	0.70000	Show Balanced Co	olumn
2	Fe+2	9.50000	9.50000	Taurala ta Managana	
				Template Manager	
	Anior	ns (mg/L)		Standard	~
	CI-1	37000.0	38934.7	Course of	
	SO4-2	2200.00	2200.00	Save as	
	HCO3-1	0.0	0.0		
	B(OH)4-1	4.00000	4.00000	Balance Options	
	HS-1	0.0	0.0	Type	
	C2H3O2-1	715.000	715.000	Dominant Ion	`
		-		Dominiant Ion	
	Neutra	als (mg/L)			
	CO2	0.0	0.0		
	H2S	0.0	0.0	v	

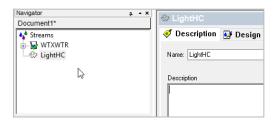
- 3. Go to Reconcile tab
- 4. Select *pH* and Alkalinity calculation type, and enter the information provided in the figure below.

le Data Entry	Calculate Brine Properties Using: Concentration Data Only Gas-Phase CO2 Content (mole Measured pH and Alkalinity Measured pH Only Calculate Alkalinity	%)	Calc <u>u</u> late 🥥
Reconcile	Properties	Measured	Calculated
œ́	Temperature (°C)	25.0000	
	Pressure (atm)	1.00000	
	pH	7.10000	
	Alkalinity (mg HCO3/L)	715.000	
	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	
	Compos	sition Adjustments	
	Added titrant (mg/L)		
	Add Charge Balance (mg/L CI-1)		

5. Click the Calculate button

Task 3 – Add a Gas

- 1. From the Actions Panel click on Add Gas Analysis
- 2. Input the name in the **Description** tab. Name it LightHC



- 3. Go to the **Design** Tab and enter the following composition in the **Inflows** (vertical) tab
- 4. Enter the following composition:

Component	Composition
Carbon dioxide (CO2)	10 mole %
Water (H2O)	15 mole %

1	Des	cri	iption	🔮 Design	🥸 Defi	nition 🛛 🛐	Report 🚊 Fil	e Viewer
0		_						
	S		Co	omponent	Value	Normalize	-	
	Inflows				Subtotal:	Subtotal:	Units	
	Ξ		۲ <u>۲</u>	120	15.0000	15.000	mole %	~
				12	0.0	0	Display	
			<u> </u>	02	10.0000	10.000	Formula	~
	ij j		H ا	125	0.0	0		
	Reconcile		()	CH4	0.0	75.000	Show Non-z	· · · · ·
				2H6	0.0	0	Show Norma	alized Column
				C3H8	0.0	0	Template Manad	ner
			i i	-C4H10	0.0	0		,
			r 🗌	-C4H10	0.0	0	Standard	\sim
			i	-C5H12	0.0	0	Save	as
				C5H12	0.0	0		
				C6H14	0.0	0	l	
							Normalize Optio	ns
							Makeup	\sim
							Course Manager	
							Group Manager	
				2			Use Groups	Add

OLI Studio: ScaleChem will assume that all of the hydrocarbon gas is methane (CH4). So, in this case the software normalizes the gas adding 75 mole% of CH4.

5. Go to the *Reconcile* (vertical) Tab

IΓ	Component	Normali	Reconcile	Calculate	0
		Subtota	Subtotal:		
	H2O	15.0000	1.75794	Condition	
ľ	C02	10.0000	11.5567	Saturate With	None 🔻
	CH4	75.0000	86.6854	Conditions	Value
				Temperature (°C)	15.5556
				Pressure (atm)	1.00231

- 6. Leave the default conditions for Temperature and Pressure
- 7. Calculate

Task 4 – Add an Oil

- 1. From the Actions Panel click Add Oil Analysis.
- 2. Enter the name in the **Description** Tab. Name it OIL-1

Navigator	₽	* X	🐸 OIL-1
Document1*			
💠 Streams			< Description 🔮 Design 📓 Report
			Name: OIL-1
	\square		Description

3. Go to the **Design** tab

- a. This tab is divided into:
 - i. Combined Tab: Here pure components (organic and inorganic) are entered.
 - ii. Pseudocomponent Tab
 - iii. Assay Tab: Here distillation curves are entered.
 - iv. Reconcile Tab

For this example, we will enter pure component and pseudocomponent data.

- 4. Go to the **Combined** tab
- 5. Enter the following composition:

Methane (CH4)	20.53mole %
Hexane (C6H14)	8.595mole %
CO2	6.09mole %

Note: You will have to scroll down to find the CO2 entry.

Г	Component	Value	Normalized	Entry Options Summary	
8	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 I AQ (H+ ion) Databa	
5	C6H14	8.59500	24.4072	Formula Public	TING. S
	C02	6.09000	17.2938	Second Liquid phas Sow Non-zero Only Custom K-fit P-spar	
				Show Normalized Column Stream Parameters Temperature (*C) 15.	
n acri					0000
				Standard Prorate Normalization. Normalized Summa	ry (mole %):
					100.000
				Pseudocomponents:	0.0
fpeer				Normalize Options Assay:	0.0
				Prorate Equilibrium Calculat	tion.

6. Go to the **Pseudocomponent** tab

Combined	Component	Molecular Weight	Nomal Boiling Point (°C)	Specific Gravity	Thermo Method	Value (mole %)
5 [<enter a="" na<="" td=""><td></td><td></td><td></td><td></td><td></td></enter>					
Reconcile Assay Pseudocom	g					

7. Add the following pseudocomponents:

Name	MW (g/mol)	nBP (F)	Thermo Method	Value mole %
PC1	98.43	100.21	API	27.57
PC2	170.34	216.32	API	29.35
PC3	282.55	343.78	API	7.19
PC4	506.0	645.00	API	0.68

The completed input looks like this:

Combined	Component	Molecular Weight	Nomal Boiling Point (°F)	Specific Gravity	Thermo Method	Value (mole %)
Col	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	7.19000
ö	PC4	506.000	645.000		API-8	0.680000
3	<enter a="" na<="" td=""><td>3</td><td></td><td></td><td></td><td></td></enter>	3				

8. Go to the *Reconcile* (vertical) tab

Here you will see how well the pseudocomponent will predict the phase behavior of the hydrocarbon sample.

- 9. In the Condition option (below calculate button) enter T=204 F and P=1 atm.
- 10. Click on the Add boiling point curve (red square shown)

	Component	Normalized	Calculate 🥝
	Inflows	Subtotal: 35.2132/	Unit Set: <custom></custom>
	H2O	0.0	Condition
Combined	CH4	20.5290	Saturate With None Automatic Chemistry Model Aqueous (H+ ion) Databanks;
۱I ⁻	C6H14	8.59457	Aqueous (H+ ion)
	C02	6.08970	Conditions Value Second Liquid phase Temperature (*F) 204.000 Custom K-fit p-span
5			
ê i	Pseudocompo	Subtotal: 64.7868/	Pressure (psia) 14.6960 Stream Parameters:
Pseudocom	PC1	27,5686	Temperature (°F) 204.000
<u>ר</u>	PC2	29.3485	Pressure (psia) 14.6960
	PC3	7.18964	Show Non-zero Only Prorate Normalization.
	PC4	0.679966	Boiling Point Curve Normalized Summary (mole %):
	PC4	0.679900	Add boiling point curve
Assay			Pseudocomponents: 64.7000
¥			Assay: 0.0
-1			Equilibrium Calculation.
e l		A.	
Ē		-0	
Reconcile			
ຂໍ			

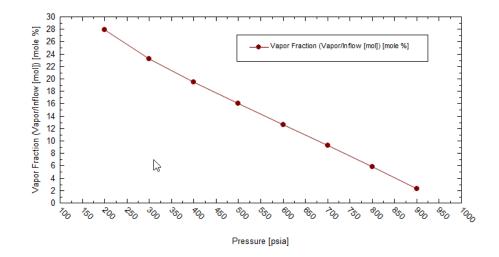
11. A new calculation appears in the navigation panel below OIL1 Object.

🕈 Streams	
WTXWTR	
🗄 🦁 LightHC	
- de OIL-1	
A Boiling	
-	
NO	
13	

- 12. This is a survey by Pressure. Click on the specs button and specify the conditions below. Change pressure units if necessary.
 - Survey by
 Pressure
 Then by (optional)
 None
 Specs...
- 13. Enter a pressure range:

Start	200 psia
End	2000 psia
Decrement	100 psia

- 14. Click the **Calculate** button.
- 15. Click on the plot tab, you will see the following graph: You could adjust the parameters by clicking on curves.



If the curve does not meet expectations, you will have to adjust the mole percentages or the pseudocomponent properties. This is a manual iterative approach. You can see the actual data by clicking the View data button.

	Pressure	Vapor Fraction (Vapor/Inflow [mol])
	psia	mole %
1	200.000	27.8711
2	300.000	23.1977
3	400.000	19.4660
4	500.000	16.0216
5	600.000	12.6532
6	700.000	9.26672
7	800.000	5.80919
8	900.000	2.24433
9	1000.00	
10	1100.00	
11	1200.00	
12	1300.00	
13	1400.00	
14	1500.00	
15	1600.00	
16	1700.00	
17	1800.00	
18	1900.00	
19	2000.00	

Frequently the hydrocarbon is saturated with water. We will simulate this part.

16. Go back to OIL-1 in the Action panel



17. Click on the **Design** tab

18. Click on the Saturate with drop down. Select H2O

	C	omponent	N	ormalized		Calc <u>u</u> late 🥝
Pe		Inflows	Subt	otal: 35.2132/		Condition
ē	H2O			0.0		
Combined	CH4			20.5290	S	Saturate With None
Ĭ	C6H	14		8.59457	Ē	Conditio Vone
È	C02			6.08970		Temperature H2O
Pseudocom					-E	Pressure (psia) 14.696
P	Pse	udocompo	Subt	otal: 64.7868/		
Pse	PC1			27.5686		
	PC2			29.3485		Show Non-zero Only
	PC3			7.18964	_	- ,
	PC4			0.679966		Boiling Point Curve
say						Add boiling point curve
Assay						
Reconcile						

- In the Conditions option use T= 77 F and 14.7 psia.
 Note: The software requires an initial "Guess" for the concentration of the water.
- 20. Click on the Calculate button.

When done, the software will create a *Reconciled OIL-1* in the Navigator pane.

The Brine, Gas and Oil that we already calculated will be used for the upcoming Mixer, Saturator and Facilities Calculations.

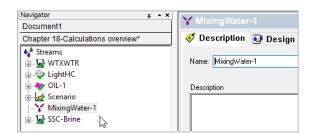
Task 5 – Adding a Mixer Calculation

The Mixer calculation determines if two waters (brines) can be mixed. Frequently the mixing of two waters will cause precipitates to form which were not present in original brines. This can lead to the plugging of a formation when an injection water is mixed with the natural fluids in the formation.

1. From the Actions Panel, click on the Add Mixing Water logo.



2. After double clicking the logo, you will the object in the Navigation Panel.



- 3. Click on the **Design** tab to enter more information.
- 4. Select your Brines, Gas and Oil s as shown in the figure below. Enter the indicated brine flow rate of 1000 bbl/day, gas flow of 230 stdMft3/day and oil flow of 7 bbl/day.

Note: To change units on brine, oil and gas, click on the hyperlinked (**blue**) units inside of the bracket next to Inlets First Brine, Second Brine etc. This is under the column heading Type.

🦪 Desa	cription 🥸 Design 🛍 Plot	😼 Report 🚊 File Vi
Inlets	Type	
Ξ	First Brine (bbl/day)	WTXWTR
	Second Brine (bbl/day)	SSC_Brine
	Gas (std E3m3/day)	Light-HC
Suc	Oil (bbl/day)	OIL-1
nditions	<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	? ×
	stem () Flowing System
Variable	Units
Brine Quantity	bbl/day 🚽
Oil Quantity	bbl/day
Gas Quantity	std Mft3/day
Whole Fluid Quantity	m3/day
OK C	Cancel Help

The final Mixer with inflows entered should look like the image below:

L	Туре	Name	Flow			Cal	c <u>u</u> late 🥝		
	First Brine (bbl/day)	WTXWTR		1000.00		Calo	ulate Alkalin	itv	
	Second Brine (bbl/day)	SSC-Brine				_		,	
	Gas (std Mft3/day)	LightHC		230.000		Summary			
	Oil (bbl/day)	OIL-1		7.00000		Unit Set: <custon< td=""><td>n></td><td></td><td></td></custon<>	n>		
						Automatic Chemi Aqueous (H+ i		nks:	
	L Con	ditions	Value			Aqueous (H Second Liquid Excluding 116	+ ion) phase		
۱ŀ	Temperature (°F)	antons	Value	100.000		Custom K-fit P			
	Pressure (psia)								
				200.000		Inlets:			
	riccoure (point)			200.000	>	Brine (bbl/day)	WTXWTR		
	etail Info of Selected Inlet Nam	-		200.000	>			1000.00	
		-	Value (mg/L)	200.000	>	Brine (bbl/day)	SSC- Brine	1000.00	
	etail Info of Selected Inlet Nam	-	Value (mg/L)	200.000	>	Brine (bbl/day) Brine (bbl/day) Gas (std	SSC- Brine LightHC	1000.00	
	etail Info of Selected Inlet Nam	-	Value (mg/L)	200.000	>	Brine (bbl/day) Brine (bbl/day) Gas (std Mft3/day)	SSC- Brine LightHC	1000.00 230.000	
	etail Info of Selected Inlet Nam	-	Value (mg/L)	200.000	>	Brine (bbl/day) Brine (bbl/day) Gas (std Mft3/day) Oil (bbl/day) Brine Ratio: WTXWTR SSC-	SSC- Brine LightHC OIL-1 Brine	1000.00 230.000	
	etail Info of Selected Inlet Nam	-	Value (mg/L)	200.000	>	Brine (bbl/day) Brine (bbl/day) Gas (std Mft3/day) Oil (bbl/day) Brine Ratio: WTXWTR SSC- 1.00000	SSC- Brine LightHC OIL-1 Brine 0.0	1000.00 230.000	
	etail Info of Selected Inlet Nam	-	Value (mg/L)		>	Brine (bbl/day) Brine (bbl/day) Brine (bbl/day) Gas (std Mft3/day) Oil (bbl/day) Brine Ratio: WTXWTR SSC- 1.00000 0.800000	SSC- Brine LightHC OIL-1 Brine 0.0 00000	1000.00 230.000	
	etail Info of Selected Inlet Nam	-	Value (mg/L)	200.000	>	Brine (bbl/day) Brine (bbl/day) Brine (bbl/day) Gas (std Mft3/day) Oil (bbl/day) Brine Ratio: WTXWTR SSC- 1.00000 0.800000 0.20 0.600000 0.44	SSC- Brine LightHC OIL-1 Brine 0.0	1000.00 230.000	

5. Go to the *Conditions* tab.

In this example, we are mixing the brines at 100 F and 200 psia. The first brine specified (WTXWTR) is the one we compare to when evaluating the ratios. In this case we start out with all brine WTXWTR and none of the SSC_Brine and end up with none of brine WTXWTR and all of the SSC_Brine.

6. Leave the default values

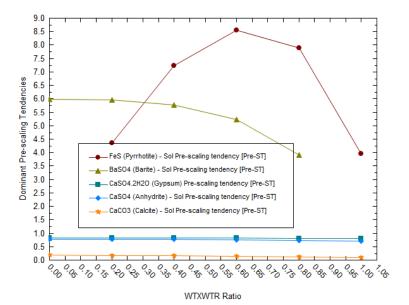
Mixing Water-1 Description 🐼 Design 🛍 Plot 🐼 Report 🚘 File Viewer						
s	Select Type	Enter Values				
Inlets	Ratio 🔻	WTXWTR	SSC_Brine			
		1.00000	0.0			
	Total flow: 1000.00 bbl/day	0.800000	0.200000			
<u>.</u>	Steps: 5 Auto Step	0.600000	0.400000			
đ	Ани зтер	0.400000	0.600000			
Conditions		0.200000	0.80000			
Ľ		0.0	1.00000			
Solid						
ŭ						

7. Go to the Solid tab

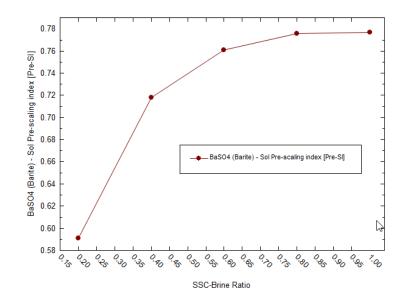
For this calculation we are only selecting a few of the possible solids. Mark a check box next to desired solids (BaSO4, CaCO3, CaSO4.2H2O, NaCl).

	ng Water-1 scription 🐼 Design 🛍 Plot
Solid Conditions Inlets	Solids Selection Standard Garden BaSO4 (Barite) Gardo3 (Calcite) Gardo3 (Calcite) Gardo4 (Anhydrite) Gardo4 (Anhydrite) Gardo4 (Anhydrite) Gardo4 (Calcite) Gardo4 (Celestine) G

- 8. Click on the Calculate button.
- 9. Click on the **Plot** tab.



To study the effects better go to the variables button and eliminate other solids precipitated by the << arrow. Keep only one solid (in this case BaSO4). The ratio is relative to the first brine specified. This means at a ratio of 0.0 (all the first brine and none of the second) we have no BaSO4 scaling. As we add the second brine, the amount of BaSO4 increases. These waters are perhaps incompatible.



Task 5 – Adding a Saturator Calculation

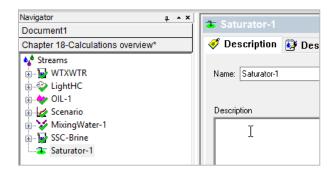
Water and gas samples at the surface are not necessarily representative of conditions in the reservoir. The processing of the samples may involve significant changes in the chemistry.

The Saturate option (often referred to as "Saturate at reservoir conditions") allows the user to "Back-calculate" the conditions downhole.

1. Select Add Saturator from the Actions Panel.



2. Rename the object in the descriptions tab. Name it Saturator-1



- 3. Go to Design tab
- 4. And go to Inlets (vertical) tab

We will select objects that we have already defined.

5. Enter a Brine flow of 1000 bbl/day

- 6. Enter a Gas flow of 230 std Mft3/day
- 7. Enter T=77 F and P=14.7 psia
- 8. Set these units as custom units for all new objects in Units manager.



Units Manager - Saturator-1	? ×
Units Manager	
<custom> ~ ~</custom>	~
Customize	
OK Cancel Ap	ply Help

The window should look like the image below.

🦪 Des	cription 🥸 Design 👔	Report 🚊 File Viewer	
Inlets	Туре	Name	Flow
Ē	Brine (bbl/day)	SSC-Brine	1000.00
	Gas (Mft3/day)	LightHC	230.000
Solid	<select></select>		
	Temperature (°F)	ditions	Value 77.0000
	Pressure (psia) Detail Info of Selected Inlet Nam	e	14.7000
	Componer	nt	Value (mole %)

- 9. Go to Solid (vertical) tab
- 10. Check the Standard box

We need to select solids inflow to vary for Saturator1. Under the table *Select Inflows to Vary*, choose the solid to vary from the dropdown list.

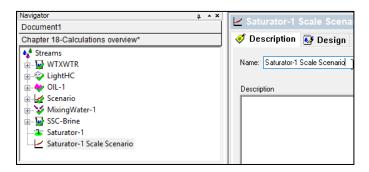
11. Select BaSO4 (solid) and hit enter. Automatically the inflow to vary BaSO4 will appear.

🦪 D	escription	🛃 Design	髮 Report	📄 File Vie	wer	
Solid Inlets	27		Standard BaSO4 (Barit CaCO3 (Calk CaSO4 (Anh CaSO4,2H2 FeCO3 (Side NaCl (Halite) SrSO4 (Cele: Expanded All	ite) ydrite) O (Gypsum) rite)		
	Rese	ervoir Mineral Satu	to saturate		Inflow to your	1
			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		
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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
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For Help, press F1		🥥 🗉	NUM

12. Name the new Scale Scenario as Saturator-1 Scale Scenario under the Description tab.



- 13. Go to the Design Tab
- 14. Under the Inlets (vertical) tab, select Brine under the Type column
- 15. Make sure to select Saturator-1, as is shown in the picture below:

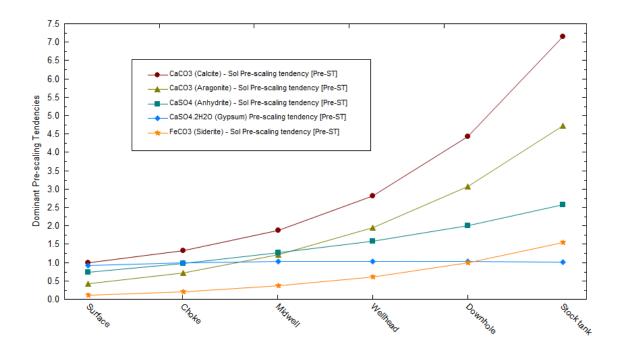
	Des	cr	iption 🔮 Design <u>(11</u> Pla	t 📓 Report 🚊 File Viewer	
Í	Inlets		Туре	Name	Flow
	nle		Brine	•	
5	-		<select></select>	WTXWTR [AQ]	
	0			Saturator-1 [AQ]	

Flow will be automatically controlled. Locations can be input under the *Conditions* tab.

16. Go to *Conditions* (vertical) tab, and enter the information provided in the figure below:

s I	Location	Temperature (°F)	Pressure (psia)	Drop Solids
Inlets	Surface	77.0000	14.7000	
-	Choke	101.000	71.7600	
	Midwell	126.200	128.820	
Suc	Wellhead	150.800	185.880	
Ĕ	Downhole	175.400	242.940	
Conditions	Stock tank	200.000	300.000	
ŭ	<enter location="" name=""></enter>			
Solid Solid	Auto Step Sort Zoom		lidwell	Wellhead
	Steps: 5 Go T P Q	10ke 01.0	tidwell 126.2 :128.8	Wellhead • T:150.8 P:185.9

- 17. Go to **Solid** tab and check the Standard box
- 18. Click the Calculate Button
- 19. Go to Plot tab



After the calculation is complete, the plot for scale scenario shows that other solids are appearing.

20. Go to the Report tab, and look for Pre and Post Scaling Tendencies

Pre and Post Scaling Tendencies

Formula	Mineral	Excess Solute	Excess Solute	Pre-Scale	Pre-Scale	Post-Scale	Post-Scale
		mg/L	lb/1000bbl	S, ST	SI, Index	S, ST	SI, Index
CaSO4.2H2O	Gypsum	0.0	0.0	0.928262	-0.0323294	0.928262	-0.0323294
FeCO3	Siderite	0.0	0.0	0.114350	-0.941763	0.114350	-0.941763
SrSO4	Celestine	0.0	0.0	0.203747	-0.690908	0.203747	-0.690908
SrCO3	Strontianite			0.0120481	-1.91908	0.0120481	-1.91908
BaSO4	Barite	0.0	0.0	1.00000	-2.23307e-11	1.00000	0.0
CaSO4	Anhydrite	0.0	0.0	0.731753	-0.135635	0.731753	-0.135635
CaCO3	Calcite	0.0	0.0	1.00000	-1.46285e-11	1.00000	0.0
NaCl	Halite	0.0	0.0	0.0121174	-1.91659	0.0121174	-1.91659
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.

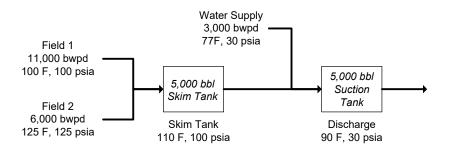
Post-Scale: The saturation ratio AFTER solids precipitate (if solids are selected).

S, ST – Saturation, Scale Tendency: The ratio of the concentration (activity) to its solubility (S=1).

SI - Scale Index: Log(S).

13.6. Introducing the Facilities Object

This section presents a new calculation object: *Facilities*. The Facilities is a simplified process simulator; it mixes and separates. OLI Studio: ScaleChem 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
C			
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:

- 1. Open a new Window for Simulation
- 2. Create the above brines: Field 1, Field 2 and Water Supply
- 3. Use the Add Brine Analysis object as you have done before to create them.

The Data Entry Windows should look like this:

-				_						_					
4	Variable Cations (r	Value	Balanced	^	È	Н	Variable	Value	Balanced	^	Entry	Н	Variable K+1	Value 0.0	Balanced 0.
+		38209.0	00070 4		Entry	H	K+1	0.0	0.0		5	H		910.000	910.00
ŀ	Na+1		38370.4		Data		Ca+2	4480.00	4480.00		Data	H	Ca+2		
_	K+1	0.0	0.0		ă		Mg+2	1191.00	1191.00		Ĩ	H	Mg+2	249.000	249.00
	Ca+2	6600.00	6600.00				Sr+2	0.0	0.0				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		Reconcile		Fe+2	6.60000	6.60000		econcile		Fe+2	0.770000	0.77000
	Ba+2	0.0	0.0		8						5		6		
	Fe+2	120.000	120.000		e e		Anions (La L		Anions	(mg/L)	
							CI-1	51134.0	51257.9				CI-1	4474.00	4637.9
	Anions (n	ng/L)					SO4-2	1840.00	1840.00				S04-2	2960.00	2960.0
Г	CI-1	73150.0	73150.0				HC03-1	677.000	677.000				HCO3-1	439.000	439.00
t	S04-2	2453.00	2453.00				HS-1	146.200	146.200			H	HS-1	0.0	0.
t	HCO3-1	421.000	421.000				C2H3O2-1	0.0	0.0			H	C2H3O2-1	0.0	0.
t	HS-1	244.000	244.000									H			
t	C2H3O2-1	0.0	0.0				Neutrals					H	Neutrals	(mg/L)	
H							CO2	0.0	0.0			H	C02	0.0	0.0
h	Neutrals (ma/L)					H2S	0.0	0.0			H	H2S	0.0	0,0
H	C02	0.0	0.0				SiO2	0.0	0.0			H	Si02	0.0	0
r	H2S	0.0	0.0				B(OH)3	0.0	0.0			H	B(OH)3	0.0	0.
	Si02	0.0	0.0							¥			D(OII)S	-	0.

- 4. Reconcile these three brines for measured pH and alkalinity.
- 5. Make sure that the *Allow solids to form* box is uncheck at the bottom of the reconciliation options for all the brines.

Desc	cription 🥸 Design 📓 Report 🚊	🥻 File Viewer	
ie Data Entry	Calculate Brine Properties Using: Concentration Data Only Gas-Phase CO2 Content (mole%) Measured pH and Alkalinity Measured pH Only Calculate Alkalinity	Specs	Calculate 🥥
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
	Add carbonate (mg/L CO2)		-238.440
	Add Charge Balance (mg/L Na+1)		161.374

6. Select Add Facilities from the Action Panel.



7. Go to the Description Tab and rename the object as Facilities-1

₩: Facilities					
🦪 Description	📑 Design	🛍 Plot	🔯 Report	📄 File Vi	ewer
Name: Facilities-1			Date:	6 /21/2016	

The facilities calculation is based upon transferring information between calculations through nodes. These nodes can be thought of as pseudo brines and gases. These pseudo brines are not stored as individual brine rather they are used internally in the calculation. The concentration and flow rates for these nodes can be viewed in the output.

- 8. Go to the **Design** tab
- 9. Go to the Inflow Specs (vertical tab)

Within Inflow Specs, we can add Nodes via Node input options. There will be one default node added.

10. Double click on the node name (where it says: Node 1) and type "Skim Tank".

₱₽ Fac	ilit	ies-1					
🛷 De	sci	ription 🧕 Design	🛍 Plot 📓 Repor	rt 📄 File Viewe	r		
Inflow Specs	[Skim Tank	+		A III		Calculate Calculate Alkalinity Summary Unit Set: Scale Metric
Solid					Ŧ		Automatic Chemistry Model AQ (H+ ion) Databanks: Public Custom K-fit P-span Some node(s) do not have inlet. Node(s):
		lode Input Current Node: Skim Tank Add Delete		• • @	►]	>	Skim Tank: No inlet Selected Solids: No Solid Selected.
		Con Temperature (°C)	ditions	Value	15.0		Calculation not done
	E	Pressure (bar)		1	.01325		
		Type <select></select>	Name	Flow			

11. Enter the name, description, conditions, and streams for the Skim Tank shown in the table below:

	Flow	Temperature, F	Pressure, psia
Field 1	11000 bbl/day	100	100
Field 2	6000 bbl/day	125	125
Water Supply	3000 bbl/day	77	30
Skim Tank	5000 bbl/day	110	100
Suction Tank	5000 bbl/day	90	30

12. Make sure to select drop solids checkbox at the Skim Tank node.

When complete, your screen should look like this.

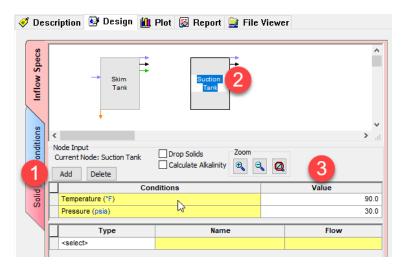
Conditions Inflow Specs	Skim Tank Node Input Current Node: Skim Tank	Drop Solids LaSalculate Alkalinity	* * *
ပိ	Add Delete Co	nditions	Value
	Temperature (°F)		110.0
Solid	Pressure (psia)		100.0
	Туре	Name	Flow
	Brine (bbl/day)	Field 1	11000.0
	Brine (bbl/day)	Field 2	6000.00
	<select></select>		

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.

- 13. Click on the Add button to add a second Node
- 14. Change the name of the node to Suction Tank
- 15. Change the conditions of this node to 90 F and 30 psia.

When complete your screen should look like the image below:



When a brine is calculated in a facilities calculation, we have the option of allowing any produced solids to be considered (that is they traveled along with the brine) or to *eliminate* them as they precipitate out. We will eliminate the solids in this case. The orange downward arrow from Skim Tank indicate dropped solids.

We are also adding the Water Supply to this tank.

- 16. In the Type column and first row select *Brine from*. In the Name column select *Skim Tank*. The *Flow* is calculated (since it comes from the Skim Tank).
- 17. In the Type column and second row select *Brine*. In the Name column select *Water Supply*. Enter 3000 bbl/day in the Flow column.

٨ Inflow Specs Skim ction Tank Tank Conditions 2 < Node Input Drop Solids Zoom Name: Suction Tank Calculate Alkalinity € ⊖ 0 Add Delete Value Conditions Solid Temperature (°F) 90.0 30.0 Pressure (psia) Туре Name Flow Brine from (bbl/day) Skim Tank Calculated Brine (bbl/day) Water Supply 3000.00 <select>

When complete the screen should look like the image below.

- 18. Click on the Calculate button, or press <Ctrl+F9>
- 19. Go to the **<u>Report</u>** tab, and check for the Pre-scaling Tendencies and Scaling Tendencies
- 20. See the Results

Pre-Scaling Tendencies Column Filter Applied: Values > 1.0e-4 Temperature Filter Applied: Active TRange Only.

Nodes	CaCO3 (Aragonite)	CaCO3 (Calcite)	CaSO4.2H2O (Gypsum)	CaSO4 (Anhydrite)	FeCO3 (Siderite)	Fe(OH)2 (Amakinite)
Temp Range °C	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
Skim Tank	5.20710	8.91186	1.24207	1.39847	0.165109	3.48775e-4
Suction Tank	4.83533	9.86145	1.18226	1.09089	0.147451	1.58132e-4

Nodes	FeS (Pyrrhotite)	FeS (Mackinawite)	MgCO3.3H2O (Nesquehonite)	MgCO3 (Magnesite)	Mg(OH)2 (Brucite)	MgSO4.7H2O (Epsomite)
Temp Range °C	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
Skim Tank	41958.3	906.834	4.47209e-3	9.15709e-3	1.05810e-3	1.11430e-3
Suction Tank	41552.1	781.107	3.37396e-3	4.74809e-3	3.15204e-4	1.21290e-3

Based on these results, it is clear to see that the software predicts the formation of several solids in this process. Solids with a Pre-Scaling Tendency > 1 are predicted to form.

Index

Adiabatic, 215, 223				
Alkalinity, 387, 395, 451, 452	Depletion Profile, 317, 336			
Alloy Chemistry, 316	Dew Point, 26, 47, 457			
Anions, 391	Dolomite, 67			
API Gravity, 386	Dominant lons, 393			
Aragonite, 59	Electroneutrality, 191, 421			
Assay, 382, 383	Entropy, 513			
ASTM, 382	Equation of State, 15			
ASTM D1160, 382	Equilibrium Constant, 108, 111, 388 Extreme Value Statistics EVS, 348, 350			
ASTM D2887, 382				
Average Bulk Density, 386				
Brines, 387, 401, 429, 430, 433, 441, 442, 443, 457	Facility Calculation, 441			
	Gases, 391, 401, 407, 430, 443, 457			
Bubble Point, 25	Heat Capacity, 513 hydrocarbon, 426 Hydrocarbon, 407			
Calcium Carbonate, 59				
Calculation Types, 317				
Cascading Mixers, 220	Isenthalpic, 25 Isochoric, 26 Isothermal, 25, 37, 225			
Cavett, 201, 383				
CO ₂ Fraction in Gas, 387				
Composition Point, 26	<i>Lee-Kesler</i> , 384 Make Up Ion, 393 Mixed Solvent Electrolyte			
Composition Survey, 218, 340				
Contour Plot, 159, 163, 486, 490				
Corrosion, 256, 261, 266, 316, 317, 329, 339, 350, 367	MSE, 15 Mixer, 220, 222, 225, 227, 429, 433, 513			
density, 201, 386, 390, 394, 396, 421, 461				
Depletion Parameters, 316				

Oxidation, 248, 249, 252, 253, 255 Selective Redox, 252 Passivation, 257, 261, 262, 266 Single Point Calculation, 513 Petroleum Fractions, 209 Soave Redlich Kwong SRK, 15 pH, 26, 33, 37, 56, 119, 120, 121, 128, 131, 132, 133, 136, 137, 218, 219, 224, 226, 227, 233, 255, 257, 263, 265, 268, 270, 272, 387, 390, 391, 394, 395, 396, 421, Solubility Product 441, 442, 448, 451, 452, 453, 456, 501, 502, 503, 513 KSP, 387, 388 Pit Depth, 348, 350, 377 Speciation, 132, 216, 451, 453, 454, 459 Precipitation Point, 26 Stability Diagram, 258 Pressure Survey, 141, 159, 486 Temperature Survey, 121, 468, 515, 529 Proration Cation, 393 Thermal Aging Temperature Survey, 317 Pseudo-components, 383 Thermal Aging Time Survey, 317 Reaction Kinetics, 97 Thermodynamic Framework, 111, 220 Redox, 252 Tree View, 120, 132, 225 Reduction, 241, 248, 255, 268, 270 **True Boiling Point** Report Tab, 454, 515 TBP, 382 Saturate Calculations, 435 Vapor Amount, 26 **Scaling Tendencies** Vapor Fraction, 26 ST, 459 Watson K, 382, 383, 384, 386 Scaling Tendency, 176, 387