



INTRODUCTION TO  
OLI Studio  
V11.5



think simulation



getting the  
chemistry right

## Introduction to OLI Studio

© 1997-2023 OLI Systems, Inc.

The enclosed materials are provided to the lessees, selected individuals and agents of OLI Systems, Inc. The material may not be duplicated or otherwise provided to any entity without the expressed permission of OLI Systems, Inc.

Version: OLI Studio V11.5

## Contact Information

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

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

Other useful links and resources are:

OLI Systems Portal – How to create and account: <https://info.olisystems.com/portal-instructions>

Product Downloads: <http://downloads.olisystems.com/>

OLI Systems YouTube Channel: <https://www.youtube.com/OLISystems>

OLI Systems Wiki page: [http://wiki.olisystems.com/wiki/Main\\_Page](http://wiki.olisystems.com/wiki/Main_Page)

## Disclaimer

This manual was produced using the OLI Studio 11.5.1 build 5 (11.5.1.5). As time progresses, new data and refinements to existing data sets can result in values that you obtain being slightly different than what is presented in this manual. This is a natural progress and cannot be avoided. When large systematic changes to the software occur, this manual will be updated.

# Table of Contents

<b>ABOUT THIS MANUAL</b> .....	<b>7</b>
<b>OLI STUDIO COMPONENTS</b> .....	<b>7</b>
Stream Analyzer .....	7
Corrosion Analyzer .....	7
EVS Analyzer .....	8
think simulation   getting the chemistry right.....	8
<b>CHAPTER I – THE OLI STUDIO SOFTWARE USER INTERFACE</b> .....	<b>9</b>
<b>General View of the User Interface</b> .....	<b>9</b>
Menu Bar .....	9
Tool Bar .....	10
Navigator Pane.....	12
Actions Pane .....	13
Plot Template Manager .....	13
Description / Definition Pane .....	14
Summary Pane .....	14
Calculation Status Output.....	15
<b>Thermodynamic Frameworks and their Databases</b> .....	<b>15</b>
Aqueous (AQ) Thermodynamic Framework.....	15
Mixed Solvent Electrolyte (MSE) Thermodynamic Framework.....	16
Mixed Solvent Electrolyte with Soave-Redlich-Kwong Equation of State (MSE-SRK) Thermodynamic Framework.....	17
<b>Component Search</b> .....	<b>18</b>
<b>Names Manager</b> .....	<b>19</b>
<b>Units Manager</b> .....	<b>20</b>
<b>Customize Toolbars</b> .....	<b>22</b>
<b>Calculation Options</b> .....	<b>23</b>
<b>Object Library</b> .....	<b>24</b>
<b>CHAPTER II – OLI STUDIO: STREAM ANALYZER</b> .....	<b>25</b>
<b>Section 1. Single Point Calculations</b> .....	<b>26</b>
Isothermal.....	28

Bubble Point .....	44
Dew Point .....	48
Isochoric (constant volume) .....	52
Vapor Amount and Vapor Fraction .....	55
Set pH .....	58
Precipitation Point .....	61
Composition Point .....	73
Autoclave .....	75
Custom .....	96
Reaction Kinetics .....	101
<b>Section 2. Survey Calculations .....</b>	<b>117</b>
Single Surveys .....	118
Dual Surveys .....	162
<b>Section 3. Water Analysis (Ionic Inputs) .....</b>	<b>178</b>
Basic Terminology .....	179
Entering Data for Water Analysis .....	181
Water Analyses - Reported Elements as Total Ions .....	183
A Basic Water Analysis .....	183
Exploring Reconciliation Options .....	192
<b>Section 4. Hydrocarbons and Pseudocomponents .....</b>	<b>206</b>
Entering a PVT Analysis .....	206
Entering Pseudocomponents to a Stream .....	211
<b>Section 5. Mixers .....</b>	<b>215</b>
Mixing Options (Definitions) .....	216
A Basic Mixer Calculation .....	217
A Titration Experiment .....	220
Cascading Mixers .....	225
<b>Section 6. Chemical Stability Diagrams .....</b>	<b>231</b>
Building a Chemical Diagram .....	232
<b>CHAPTER III – OLI STUDIO: CORROSION ANALYZER .....</b>	<b>241</b>
<b>Section 7. Stability Diagrams .....</b>	<b>242</b>
How to Interpret a Stability Diagram .....	243
How to determine if corrosion in the absence of oxygen is possible? .....	244
Building a Pourbaix Diagram .....	245
Selective Oxidation and Reduction Chemistry .....	252
Modeling the Effects of Hydrogen Sulfide on Corrosion .....	258
Modeling Corrosion at High Temperature .....	260
Modeling the Effects of Complexation on Corrosion .....	266
Modeling the Effect of Oxidizing Inhibitors on Corrosion .....	272
Implications of Stability Diagrams on Cathodic Protection .....	277
<b>Section 8. Introduction to Rates of Corrosion .....</b>	<b>280</b>
A Basic General Corrosion Rate Calculation .....	281
Exploring corrosion rate calculation options .....	287

Gas condensate corrosion.....	305
<b>Section 9. Thermal Aging and Variations in Alloy Composition.....</b>	<b>321</b>
Overview and Basic Terminology.....	321
Thermal Aging and Variations in Alloy Composition .....	323
Thermal Aging and Localized Corrosion of Annealed and Thermally Aged Duplex Alloy 2324 .....	337
<b>CHAPTER IV – OLI STUDIO: EVS ANALYZER .....</b>	<b>345</b>
<b>Section 10. EVS Overview.....</b>	<b>345</b>
Overview and Theoretical Foundation.....	345
Extreme Value Statistics for Predicting Pitting Damage .....	346
<b>CHAPTER V – OLI STUDIO: SCALECHEM .....</b>	<b>371</b>
Why Use OLI Studio: ScaleChem? .....	371
Input Objects .....	371
Calculation Objects.....	373
<b>Section 11. Entering a Brine Analysis in think simulation   getting the chemistry right.....</b>	<b>374</b>
Entering Data for a Brine Analysis .....	374
Brine Analyses - Reporting Elements.....	378
Reconciliation Options in the Brine Analysis - Definitions.....	379
A Basic Brine Analysis.....	380
<b>Section 12. Entering a Gas Analysis in think simulation   getting the chemistry right.....</b>	<b>385</b>
Entering Data for a Gas Analysis .....	385
A Basic Gas Analysis .....	387
<b>Section 13. Entering an Oil Analysis in think simulation   getting the chemistry right.....</b>	<b>390</b>
Entering Data for an Oil Analysis .....	390
Basic Definitions for the Oil Analysis Tool.....	393
Putting together a complete calculation in think simulation   getting the chemistry right .....	397
Overview of Brine, Gas and Oils and Introducing Mixer, and Saturator Objects .....	418
Introducing the Facilities Object .....	436
<b>CHAPTER VI – SCALING INHIBITION .....</b>	<b>441</b>
<b>Introduction .....</b>	<b>441</b>
<b>What is a mineral scale? .....</b>	<b>441</b>
<b>Scale formation - how OLI predicts this induction time? .....</b>	<b>441</b>
V11.5 Nucleation Induction Time model.....	442
Scale Inhibition - how OLI is used to predict treatment?.....	442
Using the Nucleation Model in OLI Studio.....	443
<b>Performing induction time calculations in V11.5.....</b>	<b>443</b>
Setting up the automatic calculation.....	444
Example #1 – Induction times for CaCO <sub>3</sub> , BaSO <sub>4</sub> , and SrSO <sub>4</sub> in a Stream.....	444

Example #2 – Using induction times in a Mixer calculation .....	450
More Induction time options .....	453
<b>CHAPTER VII – NAMING CONVENTIONS IN OLI STUDIO AND DEFINITIONS .....</b>	<b>456</b>
<b>Naming the Phases of Species .....</b>	<b>456</b>
<b>Ionic Strength .....</b>	<b>456</b>
Ionic Strength (molal based or m-based) .....	456
Ionic Strength (mole fraction based or x-based) .....	457
<b>Material Balance Group (MBG) .....</b>	<b>457</b>
<b>Volume vs. Volume at Standard Conditions vs. Standard Liquid Volume.....</b>	<b>458</b>
Volume.....	458
Volume at Standard Conditions.....	458
Standard Liquid Volume .....	459
<b>INDEX .....</b>	<b>459</b>

## About This Manual

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

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

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

## OLI Studio Components

### Stream Analyzer

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

Three different thermodynamic frameworks:

Mixed Solvent Electrolyte (MSE) model (Default)

Aqueous (AQ) model

Mixed Solvent Electrolyte and Soave-Redlich-Kwong (MSE-SRK) model

Thermophysical properties: Stream Analyzer has thermophysical models to predict surface tension, interfacial tension, viscosity, electrical conductivity, thermal conductivity, diffusivity, and osmotic pressure.

Molecular and ionic inflows: Stream Analyzer accepts molecular inflows, typical of a process stream, and ion inflows, typical of a sample water analysis.

### Corrosion Analyzer

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

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

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

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

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

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

Generation of Pourbaix (E vs pH) diagrams

Calculation of general corrosion rates

Localized corrosion susceptibility

Heat treatment effect

Generation of polarization curves plots

## **EVS Analyzer**

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

## **think simulation | getting the chemistry right**

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

Brine, gas and oil analysis

Scaling scenarios

Compatibility testing of brines using the stream mixing function

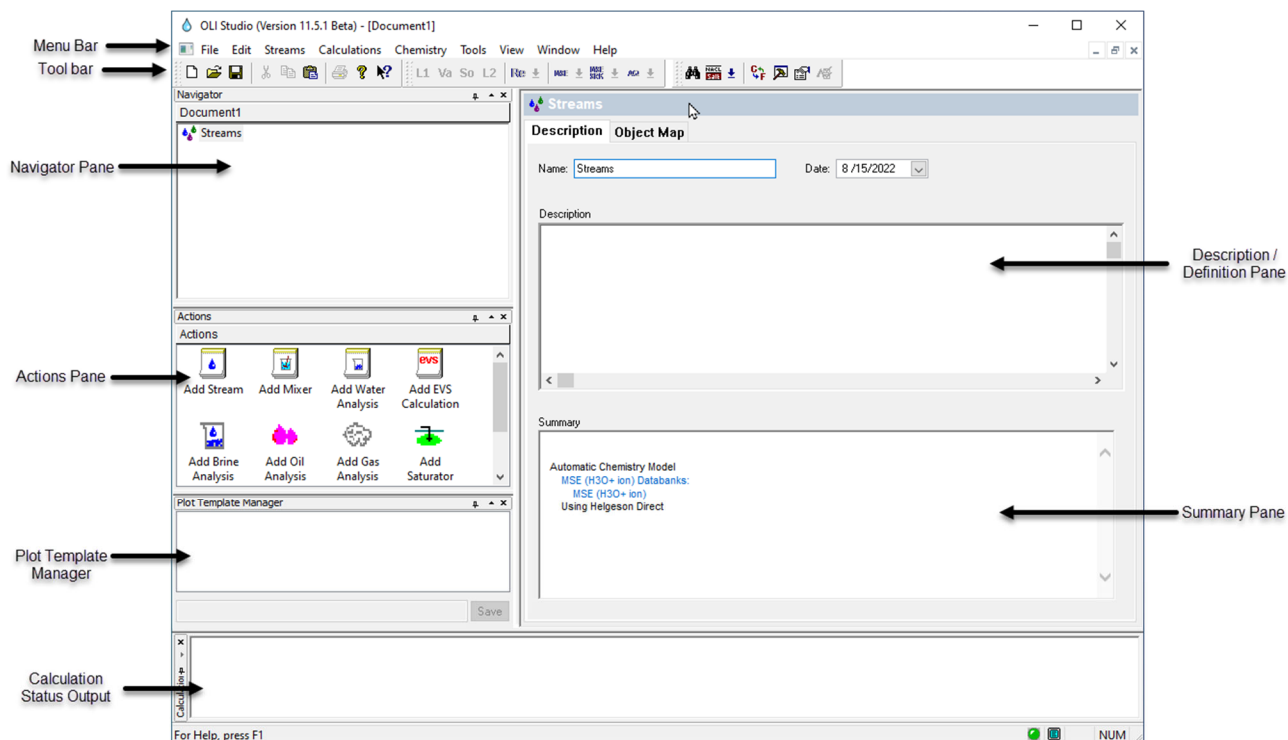
Phase equilibrium calculation for four-phase reservoir saturation, from which as whole fluid reservoir composition is determined

Contour plots to study produced brine properties across a broad temperature and pressure range

# Chapter I – The OLI Studio Software User Interface

## General View of the User Interface

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



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

## Menu Bar

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

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

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

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

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

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

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

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

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

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

## Tool Bar

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



They are laid out in the following order:

Quick access to **File:**



Quick access to **Edit:**



Quick access to **Help:**



Quick access to **Chemistry:**



Quick access to **Tools:**



## Icons in the Chemistry section

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

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

**L1:** Liquid 1 or water-rich phase

**Va:** Vapor phase

**So:** Solid phase

**L2:** Usually organic rich phase and sometimes a critical fluid. It is also referred to as Liquid 2 phase.

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

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

**MSE:** Mixed Solvent Electrolyte databank (Default)

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

**AQ:** Aqueous databank

## Icons in the Tools section

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

**Component search:**



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

**Names manager:**



This tool shows you the name of components in different styles in tables and reports. The style options are: Display name, Formula or OLI Name.

**Units manager:**



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

**Customize toolbars:**



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

**General options:**



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

**Calculation options:**



This tool allows you to include or exclude different types of properties into the calculations.



## Navigator Pane

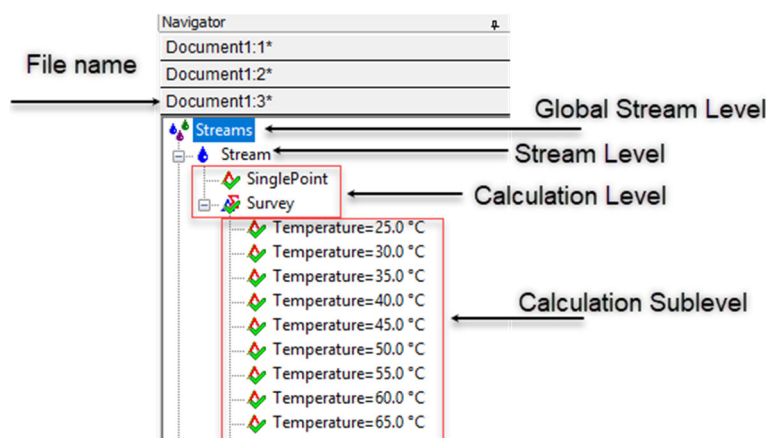
The Navigator Pane (or tree level) contains the list of streams and calculations that are active within a file. This view contains the icons and names of each action in a hierarchical tree. The Description/Definition pane changes depending on the level that is highlighted. A plus sign next to an object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

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

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

**Calculation Level:** Calculation types such as Single point calculations, Survey calculations, etc., are subordinate to streams, and appear in this level. A more detailed explanation of calculation types can be found in [Chapter II](#) of this manual.

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

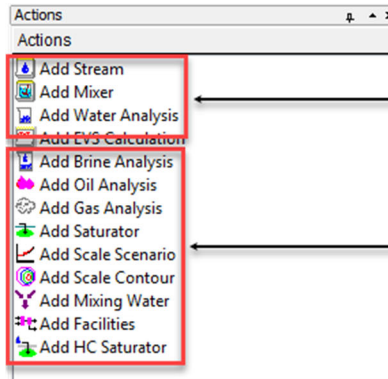


**Note:** A star (\*) next to the file name indicates that the file has not been saved.

## Actions Pane

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

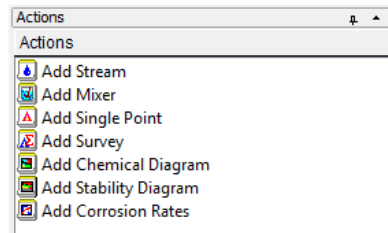
When located at the **Global Stream Level** the following action icons appear on the Actions Pane.



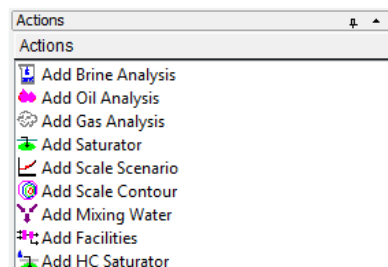
These actions come with Stream and Corrosion Analyzers

These actions come with ScaleChem

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

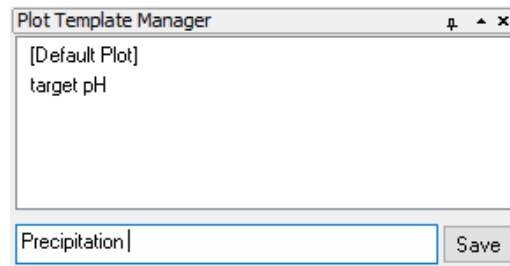


If you select an action item that belongs to think simulation | getting the chemistry right, this action item will be located at the **Stream Level**, and only the following action icons appear on the Actions pane.



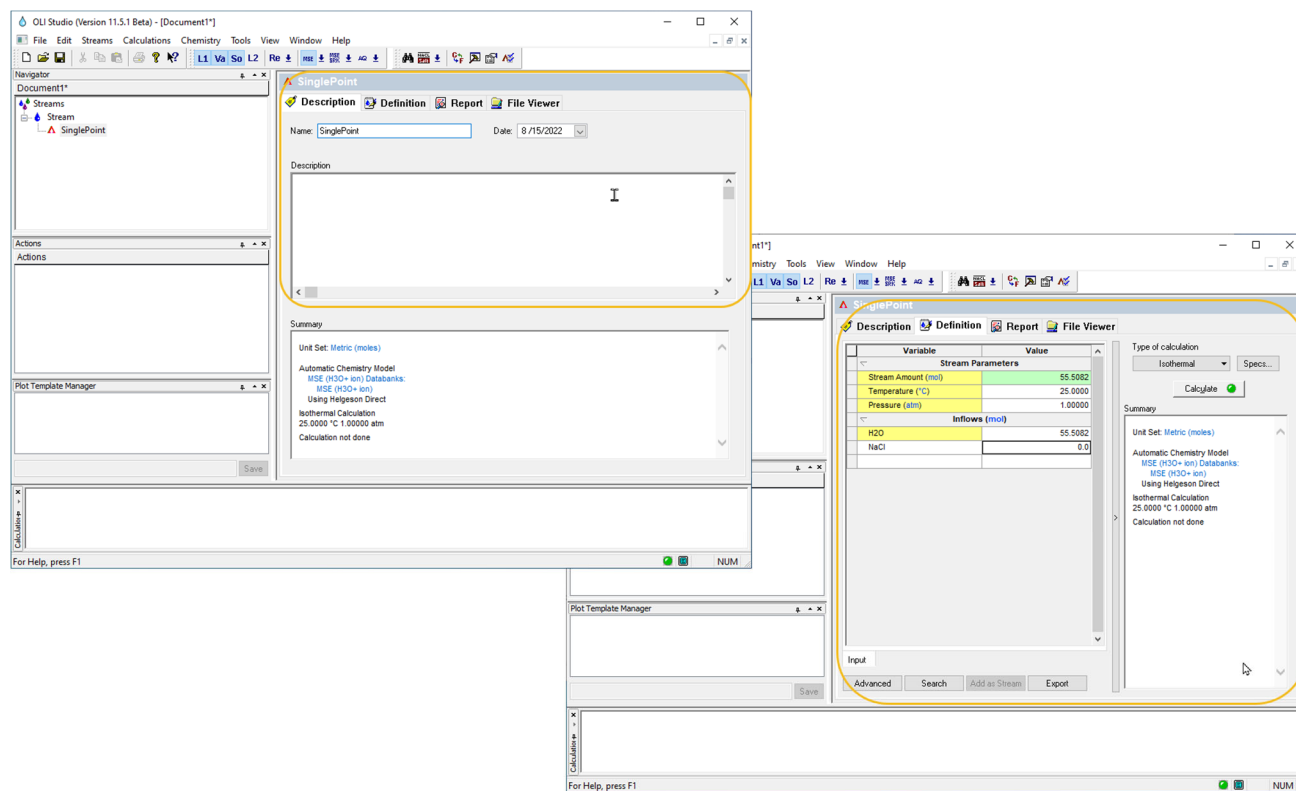
## Plot Template Manager

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



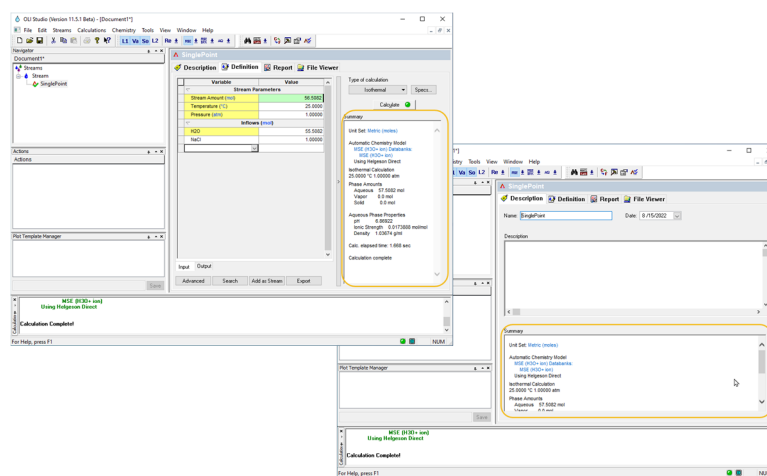
## Description / Definition Pane

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



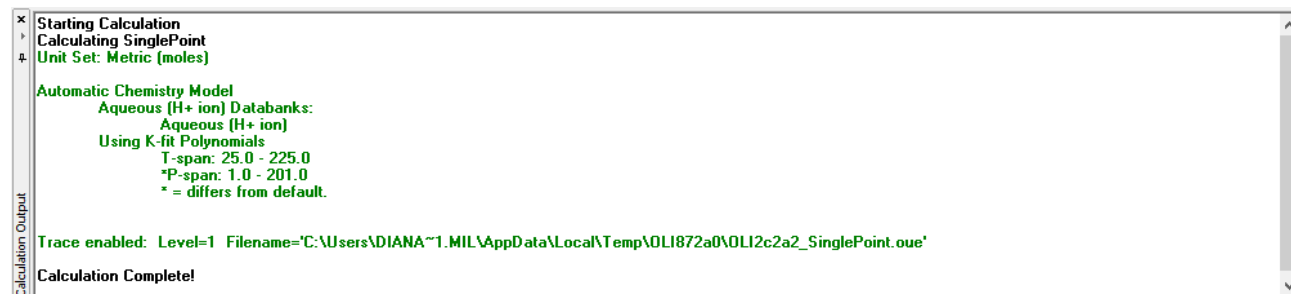
## Summary Pane

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



## Calculation Status Output

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



```
Starting Calculation
Calculating SinglePoint
Unit Set: Metric (moles)

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.

Trace enabled: Level=1 Filename='C:\Users\DIANA~1\MIL\AppData\Local\Temp\OLI872a0\OLI2c2a2_SinglePoint.oue'

Calculation Complete!
```

## Thermodynamic Frameworks and their Databases

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

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

### Aqueous (AQ) Thermodynamic Framework

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

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

The AQ framework utilizes the Bromley-Zemaitis activity model:

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

The model can produce valid results in the following ranges:

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

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

Aqueous (H<sup>+</sup> ion) – Public Database and selected by default

Geochemical (AQ)

Ceramics (AQ)

Corrosion (AQ)

Low Temperature (AQ)

Alloys (AQ)

Ion Exchange (AQ)

Surface Complexation Double Layer Model (AQ)

## Mixed Solvent Electrolyte (MSE) Thermodynamic Framework

A system's thermodynamic properties are calculated from two sources; the first is from the Temperature and Pressure dependent standard-state Gibbs energies (i.e.,  $\bar{G}_i^0(T, P)$ ) 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  $i^{\text{th}}$  species is,  $\bar{G}_i = \bar{G}_i^0 + RT \ln m_i \gamma_i$ , where  $\bar{G}_i^0$  is the standard-state partial Gibbs energy and  $\gamma_i$  is the activity coefficient. This activity coefficient  $\gamma_i$ , is computed using the MSE theory. A comprehensive explanation of the MSE theory is given in Wang et al. [7].

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

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

The model can produce results for the following ranges:

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

The MSE framework contains the following databanks:

MSE (H<sub>3</sub>O<sup>+</sup> ion) – Selected by default

Corrosion (MSE)

Geochemical (MSE)

Urea (MSE)

Surface Complexation Double Layer Model (MSE)

---

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

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

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

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

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

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

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

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


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

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:

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

## Component Search

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

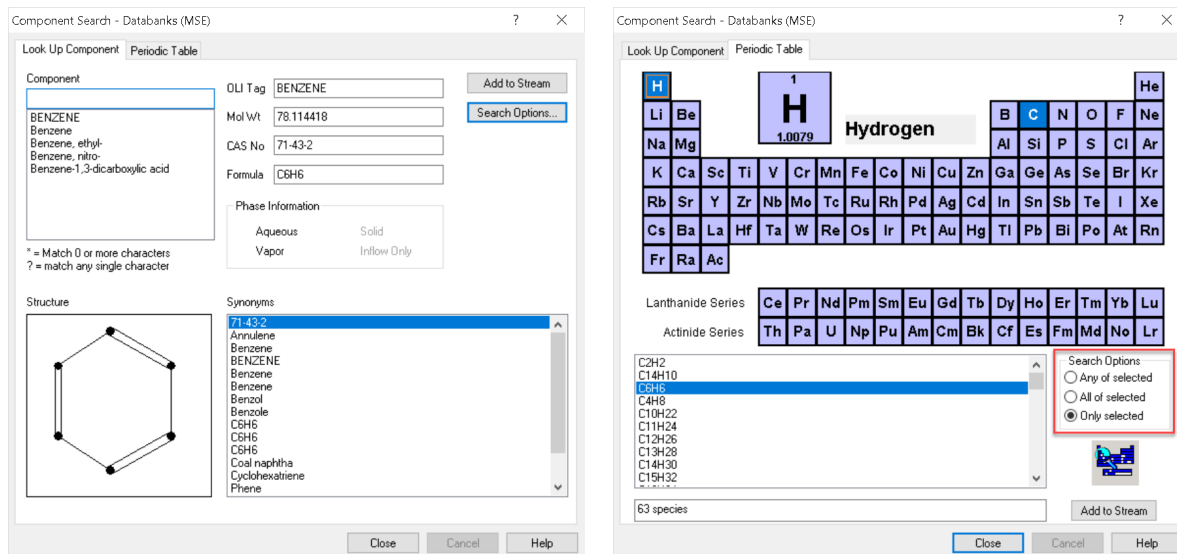
Note: When using the **Component Search** tool, you should be aware that the tool will only show components in the database that you have selected.

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

Any of selected: Will show elements that you have selected

All of selected

Only selected



The image displays two screenshots of the 'Component Search - Databanks (MSE)' window. The left screenshot shows a search for 'BENZENE' with a list of results and a chemical structure. The right screenshot shows a search using the periodic table with search options highlighted.

**Left Screenshot: Search Results for 'BENZENE'**

Component	OLI Tag	Mol Wt	CAS No	Formula
BENZENE	BENZENE	78.114418	71-43-2	C6H6
Benzene				
Benzene, ethyl-				
Benzene, nitro-				
Benzene-1,3-dicarboxylic acid				


**Right Screenshot: Search Options**

Search Options:

- Any of selected
- All of selected
- Only selected

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

## Names Manager

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

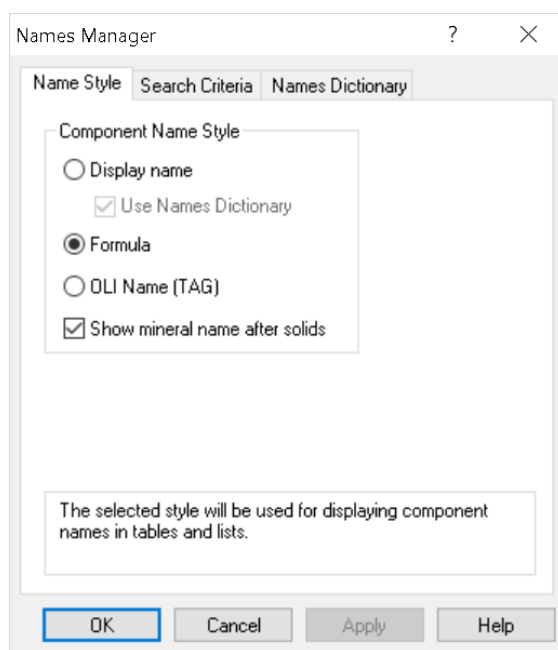
The **Names Manager** option opens a new window where you can select the component name style. There are three different styles:

**Display name:** This is the name that is commonly displayed when a species is entered. This is the default display. For example, Benzene, Cyclohexane, Sodium Chloride

**Formula:** This is the chemical formula name. For example, C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>12</sub>, NaCl

**OLI Name (TAG):** This is the traditional name for the species stored internally in the OLI software. For example: BENZENE, CYCLOHEXAN, NAACL (Note: These names are usually for OLI internal use).

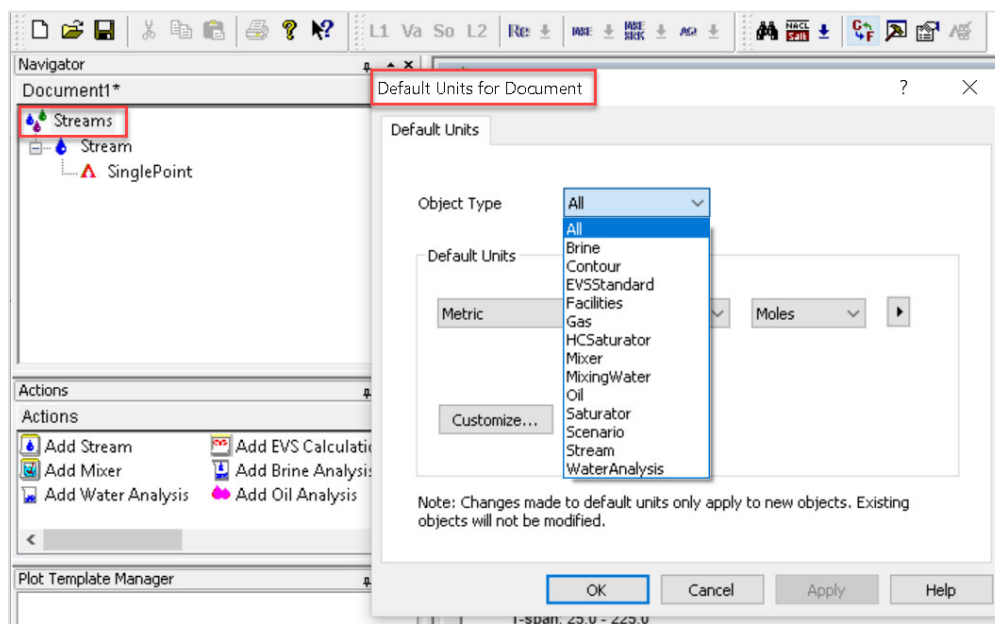
Additionally, you can select if you prefer the mineral name to appear after the solids. For example, NaCl (halite), KCl (sylvite), etc.



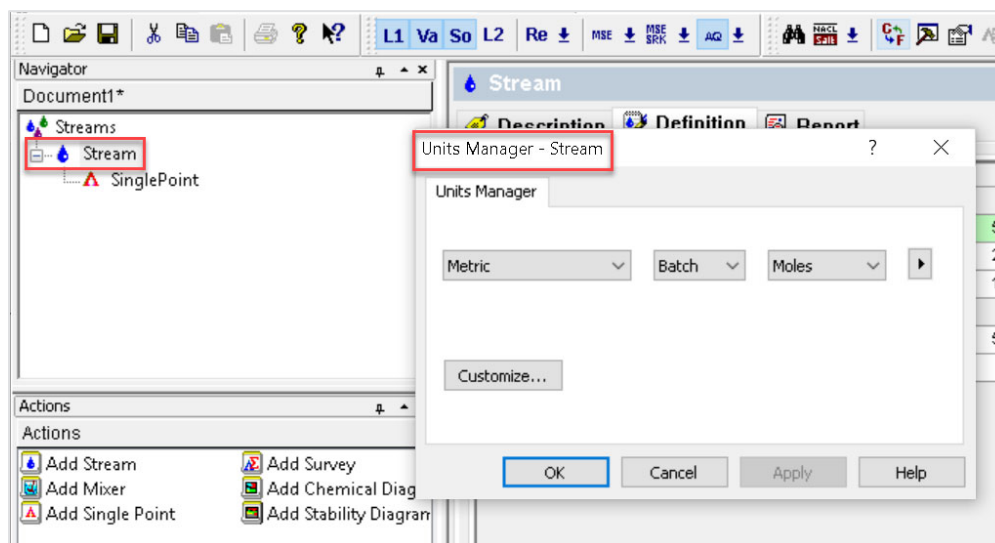
## Units Manager

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

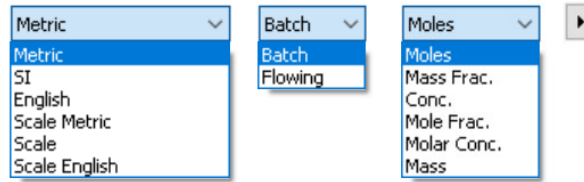
If you are changing units at the Global Stream Level, the **Units Manager** tool will open a new window where you can change the default units for the whole document. You can also select the default units of the different calculation objects.



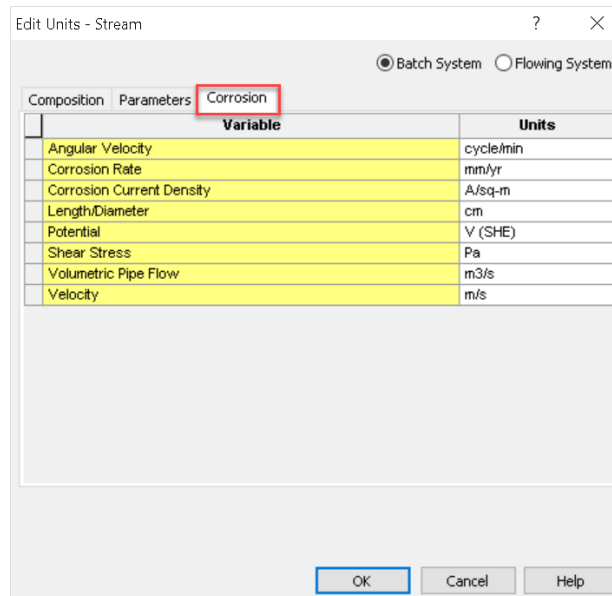
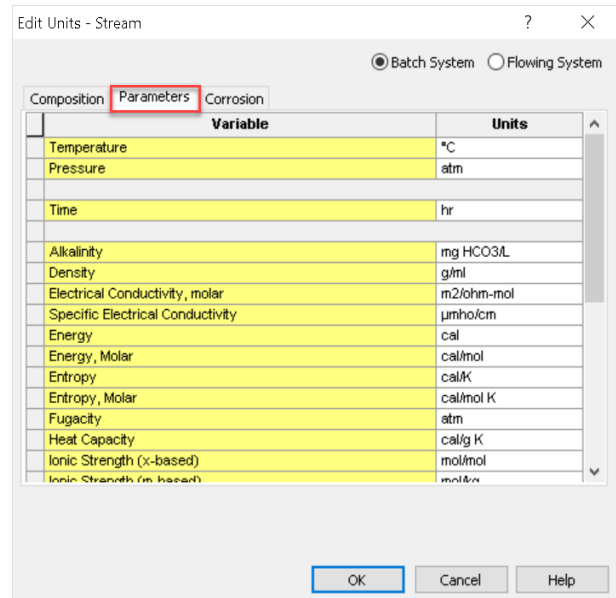
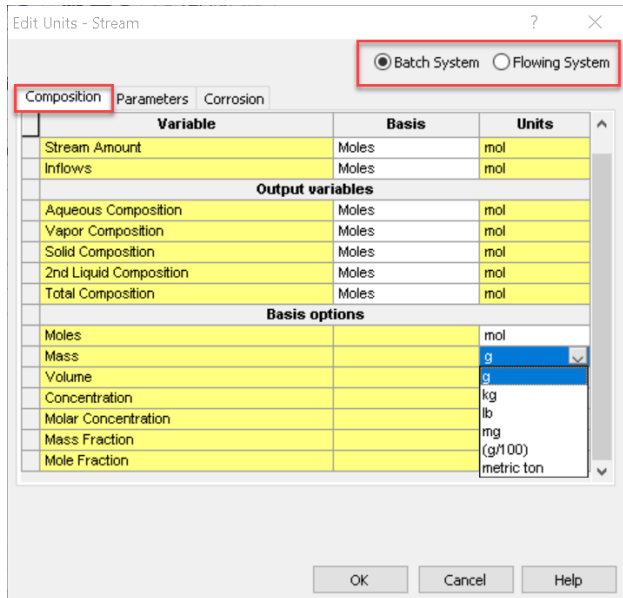
At the Stream Level, the Units Manager tool will open a slightly different window and will change the units only at the Stream Level and Calculation Level.



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




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



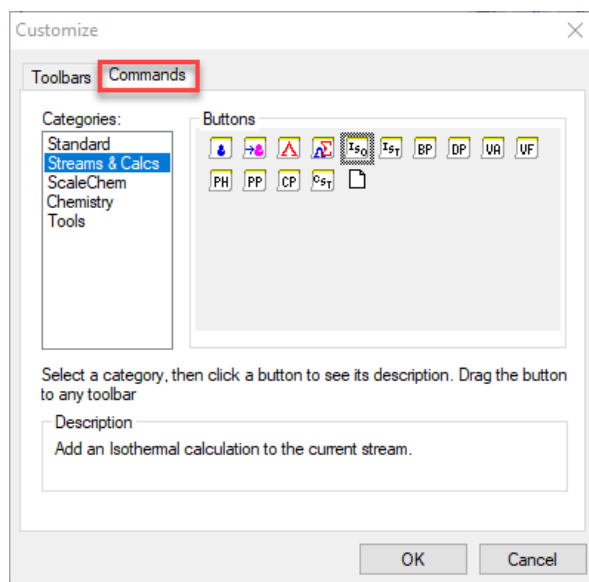
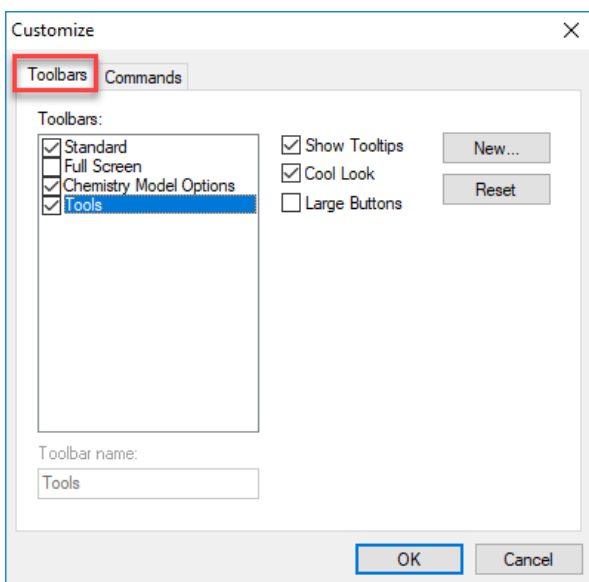
Another option to access the **Units Manager tool** is by clicking on the units highlighted in **blue**. This is a hyperlink to the Units Manager tool, and there you can make changes to the units.

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


## Customize Toolbars

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

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



## Calculation Options

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

### General

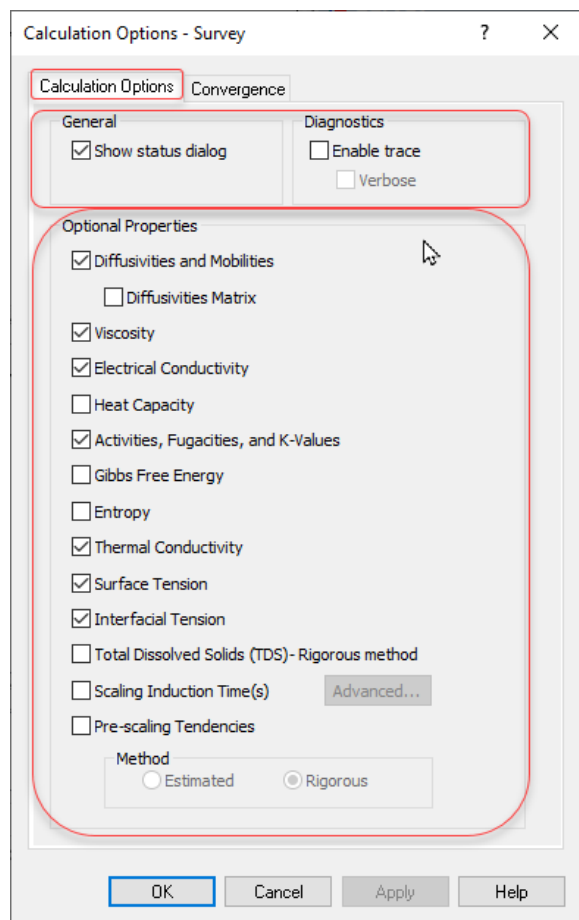
Allows you to disable or enable the status dialog (a popup window that appears after pressing the calculate button)

### Diagnostics

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

### Optional Properties

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

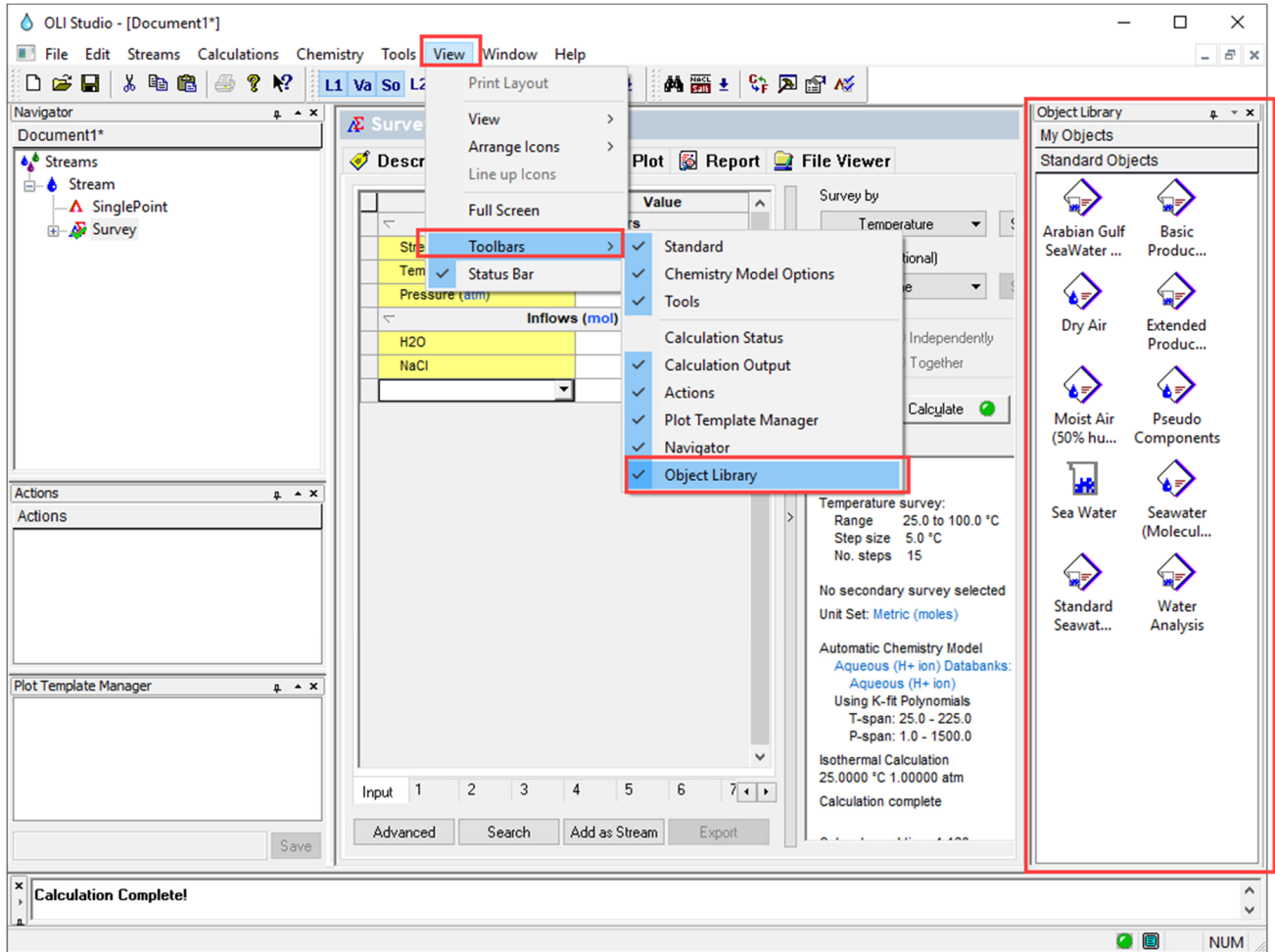


## Object Library

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

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

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



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

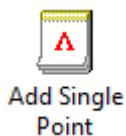
## Chapter II – OLI Studio: Stream Analyzer

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

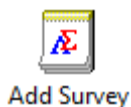
There are five different types of calculations that can be carried out in OLI Studio: Stream Analyzer: Single point, Survey (multiple point), Water Analysis, Mixer, and Chemical Diagram calculations. A brief definition of each type of calculation is given below.



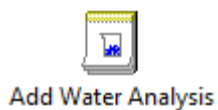
**Add Stream** is used to add a **New Stream** as a molecular input and define a specific chemistry.



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



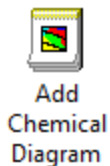
**Survey Calculations** are useful for plotting changes in stream parameters against temperature, pressure, or composition.



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



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

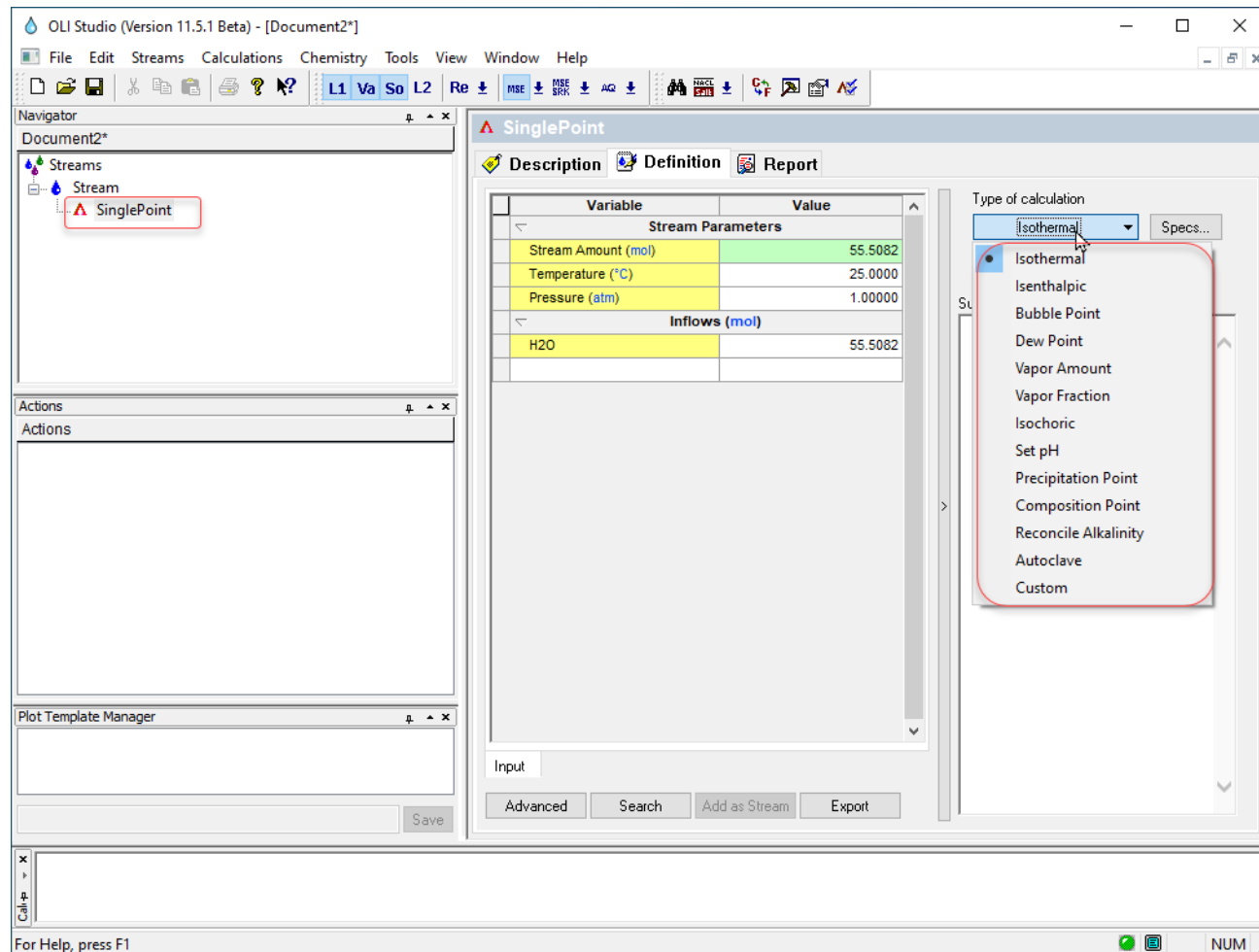


**Chemical Diagram Calculation** allows you to create a stability map for species based on concentration and other parameters such as pH. A contour map is created showing the user where some solids are stable and where others are not.

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

## Section 1. Single Point Calculations

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



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

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

**Bubble Point:** The temperature or pressure is adjusted to reach a condition where a small amount of vapor (bubble) begins to appear (a.k.a. boiling point).

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

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

**Vapor Fraction:** The temperature or pressure is adjusted to produce a user-specified amount of vapor as a fraction of the total quantity of moles in the system.

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

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

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

**Composition Point:** The composition point calculation is used to fix a species value. The software adjusts the flowrate of a species until it reaches the user - specified/fixed species value.

**Reconcile Alkalinity:** The software calculates or reconciles the alkalinity of a solution. There are several reconciliation types within this option: Reconcile pH, Reconcile Alkalinity and pH, and Reconcile Alkalinity, pH and TIC.

**Autoclave:** The software simulates a constant volume vessel (autoclave) in which mass, pressure and temperature are allowed to vary in order to reach a user-specified mole fraction or partial pressure of key gases in the vapor phase.

**Custom:** With the calculations stated so far, variables are predefined. For instance, we must select either temperature or pressure as a variable in the dew point calculation. With Custom single point calculations, we can manipulate a wider variety of variables; for example, you can set up a custom calculation to determine the solubility of a gas in solution.

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

## Isothermal

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

### Example 1: Speciation and its importance for pH calculations

After completing this example, you will learn how to set up an **Isothermal calculation** and will also get a better understanding of the importance of full speciation on the calculation of pH. Let's calculate the pH of a 1 m FeCl<sub>3</sub> solution at 25 °C and 1 atm.

#### Starting the Simulation

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



Let's create a new stream. Click on the **Add Stream** located in the **Action Pane**. When a stream is created only H<sub>2</sub>O is present in the grid. Its cell is yellow because it cannot be removed, it is a permanent inflow.

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

Type **FeCl<sub>3</sub>** in the white cell below H<sub>2</sub>O inflows grid, and press **<Tab>** or **<Enter>**

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

The screenshot shows the OLI Studio interface with the following components:

- Navigator:** Shows a tree view with 'Streams' and 'Stream'.
- Actions Pane:** Lists various actions, with 'Add Stream' highlighted and circled in red (1).
- Definition Tab:** Displays a table with 'Variable' and 'Value' columns. The 'Inflows (mol)' section is expanded, showing H<sub>2</sub>O and FeCl<sub>3</sub> with their respective values. The 'FeCl<sub>3</sub>' cell is circled in red (4).
- Stream Parameters Table:** Shows 'Stream Amount (mol)' as 56.5082, 'Temperature (°C)' as 25.0000, and 'Pressure (atm)' as 1.00000. The 'Stream Amount' cell is circled in red (2).
- Input Section:** Includes buttons for 'Advanced', 'Search', 'Add as Stream', and 'Export'.
- Summary Section:** Shows 'Unit Set: Metric (moles)' and 'Automatic Chemistry Model: MSE (H3O+ ion) Databanks: MSE (H3O+ ion) Using Helgeson Direct'.

Variable	Value
Stream Parameters	
Stream Amount (mol)	56.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H <sub>2</sub> O	55.5082
FeCl <sub>3</sub>	1.00000

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

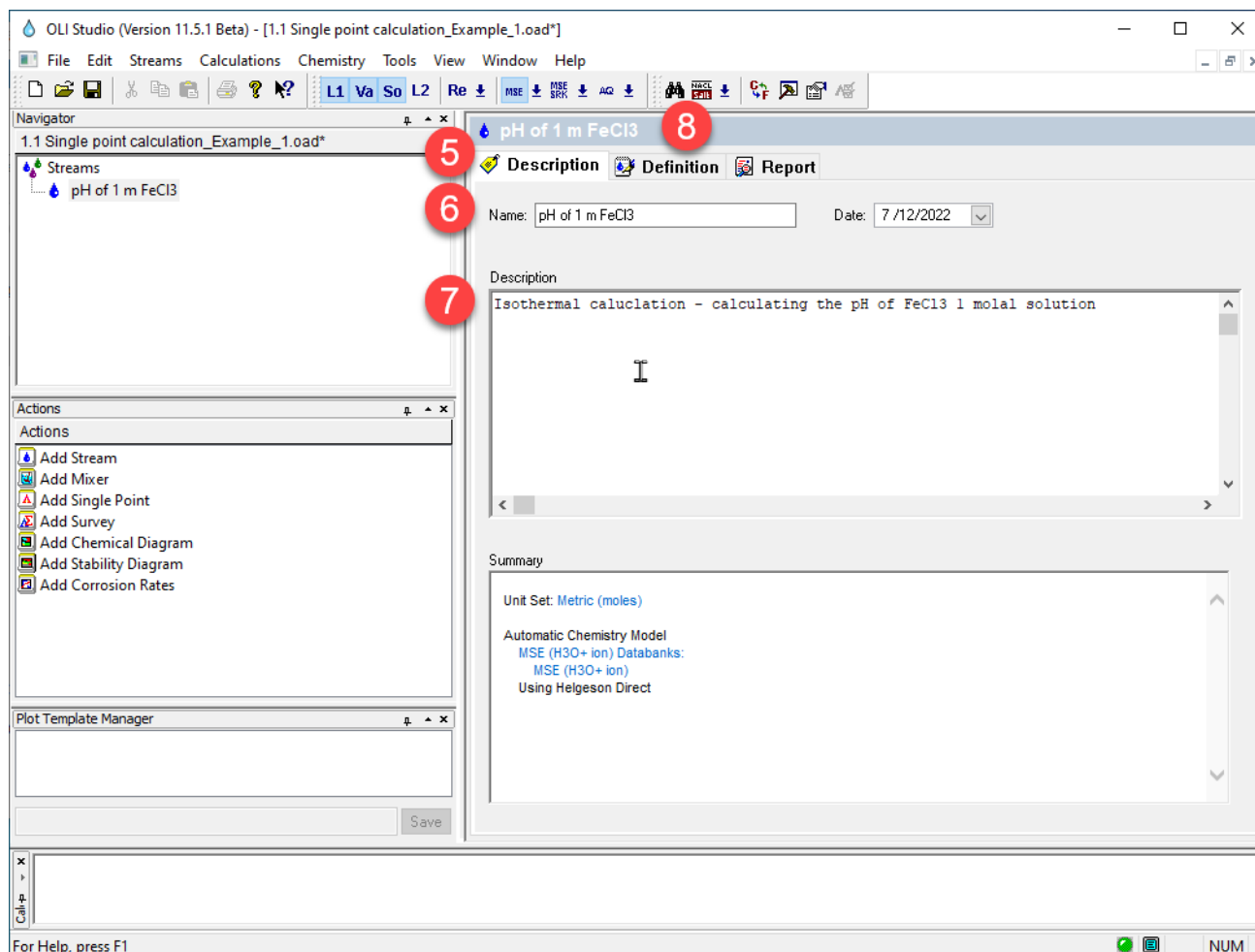
Also, notice that the stream amount will be automatically calculated from the sum of the component inflows. To indicate that the summation has occurred, the grid will highlight the stream amount cell in green.

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

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

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

Go back to the **Definition** Tab



Now, we are ready to perform a calculation

Go to the **Add Calculation** button

Select **Single Point**

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

The screenshot shows the OLI Studio software interface. The main window title is "OLI Studio (Version 11.5.1 Beta) - [1.1 Single point calculation\_Example\_1.oad\*]". The menu bar includes File, Edit, Streams, Calculations, Chemistry, Tools, View, Window, and Help. The toolbar contains various icons for file operations and calculations. The Navigator pane on the left shows a tree view with "Streams" and "pH of 1 m FeCl3". The Actions pane lists several actions, including "Add Single Point". The Plot Template Manager pane is empty. The main workspace displays the "pH of 1 m FeCl3" calculation. The "Description" tab is active, showing a table of variables and values. The "Add Calculation" dropdown menu is open, with "Single Point" selected. The "Input" section at the bottom has buttons for "Advanced", "Search", "Add as Stream", and "Export".


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

Input

Advanced Search Add as Stream Export

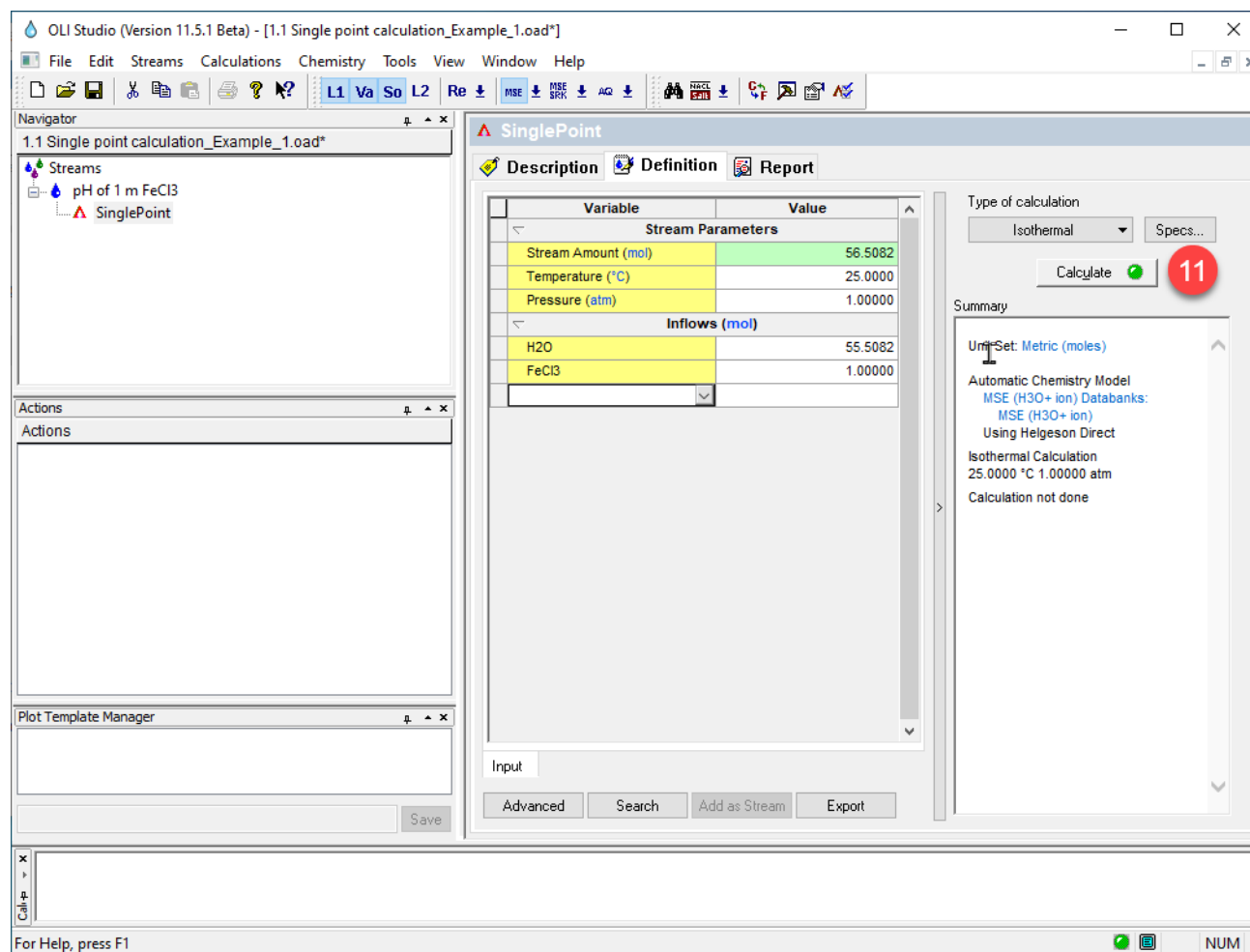
For Help, press F1

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

 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



OLI Studio (Version 11.5.1 Beta) - [1.1 Single point calculation\_Example\_1.oad\*]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator  
1.1 Single point calculation\_Example\_1.oad\*  
Streams  
pH of 1 m FeCl3  
SinglePoint

Actions  
Actions

Plot Template Manager

Save

### SinglePoint

Description Definition Report

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	56.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
H2O	55.5082
FeCl3	1.00000

Input  
Advanced Search Add as Stream Export

Type of calculation  
Isothermal Specs...  
Calculate **11**


Summary  
Unit Set: Metric (moles)  
Automatic Chemistry Model  
MSE (H3O+ ion) Databanks:  
MSE (H3O+ ion)  
Using Helgeson Direct  
Isothermal Calculation  
25.0000 °C 1.00000 atm  
Calculation not done

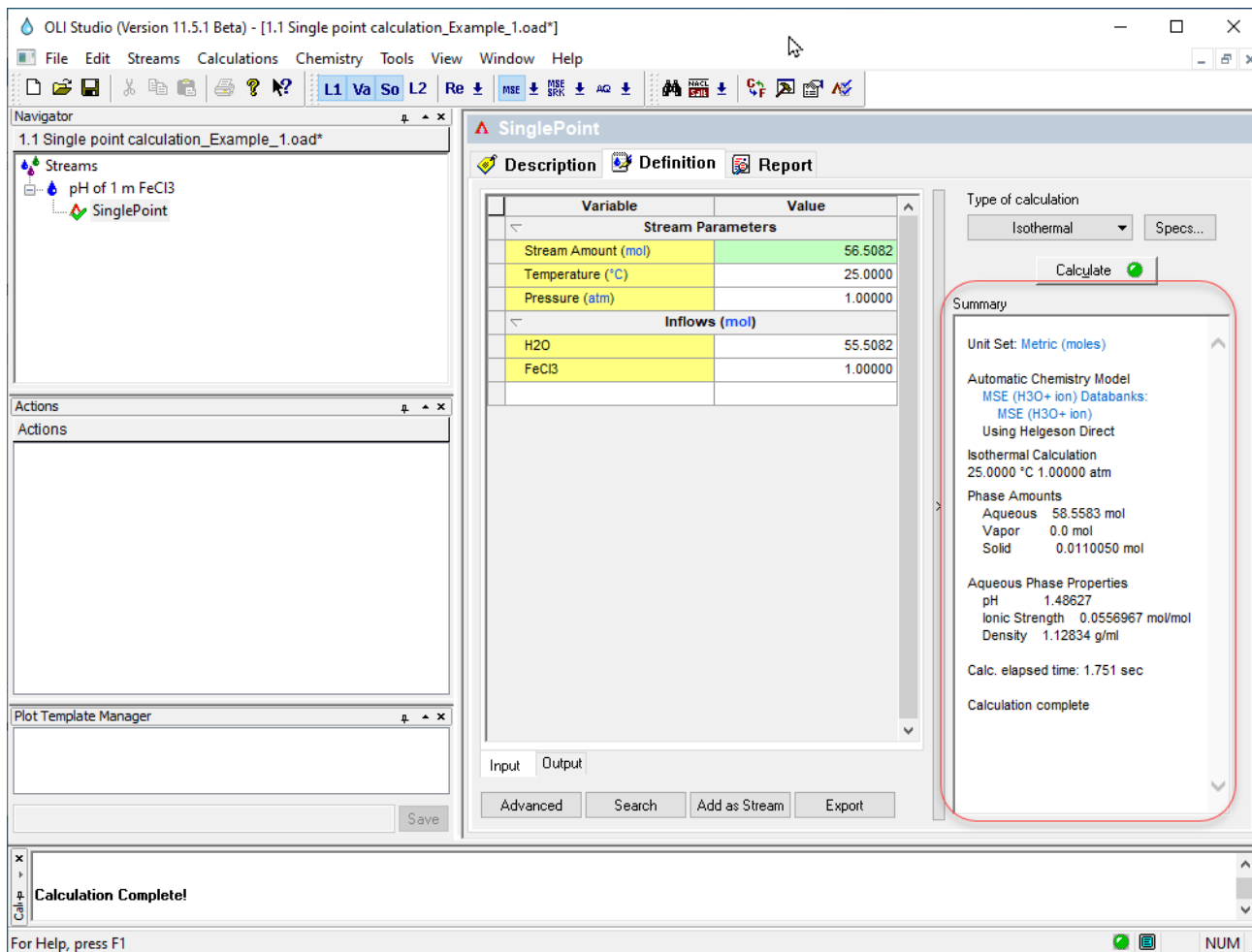
For Help, press F1 NUM

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

The screenshot shows the OLI Studio interface. The 'File' menu is open, and 'Save As...' is highlighted with a red box. A red circle with the number '12' is in the top-left corner. The main window displays a table of stream parameters for 'pH of 1 m FeCl3'. The table has two columns: 'Variable' and 'Value'. The 'Stream Parameters' section includes 'Stream Amount (mol)' (56.5082), 'Temperature (°C)' (25.0000), and 'Pressure (atm)' (1.00000). The 'Inflows (mol)' section includes 'H2O' (55.5082) and 'FeCl3' (1.00000). The right-hand side of the window shows a 'Summary' section with 'Unit Set: Metric (moles)' and 'Automatic Chemistry Model: Aqueous (H+ ion) Databanks: Aqueous (H+ ion)'. The status bar at the bottom reads 'Save the active document with a new name' and 'NUM'.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	56.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
H2O	55.5082
FeCl3	1.00000

When the “**Calculation is complete**” a check mark appears on the calculation object . Now, let us analyze the results of the simulation.



The screenshot shows the OLI Studio interface for a single-point calculation. The main window displays the following data:

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	56.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
H2O	55.5082
FeCl3	1.00000

The Summary box on the right contains the following information:

- Unit Set: Metric (moles)
- Automatic Chemistry Model: MSE (H3O+ ion) Databanks: MSE (H3O+ ion) Using Helgeson Direct
- Isothermal Calculation: 25.0000 °C 1.00000 atm
- Phase Amounts:
  - Aqueous: 58.5583 mol
  - Vapor: 0.0 mol
  - Solid: 0.0110050 mol
- Aqueous Phase Properties:
  - pH: 1.48627
  - Ionic Strength: 0.0556967 mol/mol
  - Density: 1.12834 g/ml
- Calc. elapsed time: 1.751 sec
- Calculation complete

A status bar at the bottom left displays "Calculation Complete!" and "For Help, press F1".

### Analyzing the Results

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

The **pH** is calculated to be approximately **1.49**

Let's analyze the simulation results in more detail

Click on the **Report** Tab

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

OLI Studio (Version 11.5.1 Beta) - [1.1 Single point calculation\_Example\_1.load\*]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator  
1.1 Single point calculation\_Example\_1.load\*  
Streams  
pH of 1 m FeCl3  
SinglePoint

SinglePoint  
Description Definition Report 13  
Jump to: Species Output (True Species) 14  
Customize Export

**Species Output (True Species)**  
Row Filter Applied: Only Non Zero Values  
column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Solid
	mol	mol	mol
H2O	55.4183	55.4183	0.0
Cl-1	2.10599	2.10599	
FeCl+2	0.89331	0.89331	
Fe+3	0.0834103	0.0834103	
H3O+1	0.0449718	0.0449718	
FeOH+2	0.0118615	0.0118615	
Fe(OH)3 (Bernalite)	0.011005		0.011005
FeCl2+1	3.47658e-4	3.47658e-4	
FeO+1	3.00349e-5	3.00349e-5	
Fe2(OH)2+4	1.75659e-5	1.75659e-5	
HCl	3.75364e-9	3.75364e-9	
HFeO2	2.63362e-10	2.63362e-10	
OH-1	5.3521e-13	5.3521e-13	
FeO2-1	3.6281e-18	3.6281e-18	
<b>Total (by phase)</b>	<b>58.5693</b>	<b>58.5583</b>	<b>0.011005</b>

Calculation Complete!

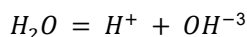
For Help, press F1

Why is the **pH** so low?

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

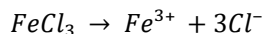
This equilibrium is always present:

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

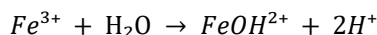


## Speciation Reactions

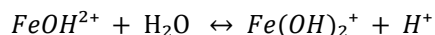
First iron (III) chloride dissociates:



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



Then another water molecule enters into the reaction:



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

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

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

## pH Calculation

The pH is calculated using the following formula:

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

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

---

<sup>3</sup> This hydrolysis reaction is the generic form found in most aquatic textbooks. OLI uses this reaction in the AQ framework. In the MSE framework, a more advanced reaction is used:  $2H_2O=H_3O^+ + OH^-$

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

OLI Studio (Version 11.5.1 Beta) - [1.1 Single point calculation\_Example\_1.oad\*]

File Edit Streams Calculations Chemistry Tools View Window Help

Report Contents

Category

- Report Contents
  - Calculation Summary
  - Stream Inflows
  - Speciation Summary
  - Stream Parameters
  - Total/Phase Flows
  - Scaling Tendencies
  - Scaling Induction Time
  - Species Output
  - Molecular Output
  - Element Balance
  - Species Activity Coefficients
  - Species Fugacities
  - Partial Pressures
  - Species K-Values
  - Species Mobilities
  - Species Self Diffusivities
  - Vapor Phase Diffusivities
  - Gibbs Free Energy of Formation
  - Gibbs Free Energy of Reaction
  - Entropy
  - Entropy - Standard State
  - Reaction Kinetics
  - Redox Equations

Report Contents

To add or remove a section, click the check box. A shaded box means that only part of the component will be printed. To see what's included in a component, click Details.

Sections

- Calculation Summary
- Stream Inflows
- Speciation Summary
- Stream Parameters
- Total/Phase Flows
- Scaling Tendencies
- Scaling Induction Time
- Species Output
- Molecular Output
- Element Balance
- Species Activity Coefficients**
- Species Fugacities
- Partial Pressures
- Species K-Values
- Species Mobilities
- Species Self Diffusivities
- Vapor Phase Diffusivity Matrix
- Gibbs Free Energy of Formation

Up Down Select All Clear All

Description

This section displays the true species activity coefficients.

6 of 23 Sections selected

OK Cancel Apply Help

15

Customize Export

	Liquid-1	Solid
	mol	mol
3	55.4183	0.0
9	2.10599	
1	0.89331	
3	0.0834103	
8	0.0449718	
5	0.0118615	
5		0.011005
4	3.47658e-4	
5	3.00349e-5	
5	1.75659e-5	
9	3.75364e-9	
0	2.63362e-10	
3	5.3521e-13	
8	3.6281e-18	
3	58.5583	0.011005

17

Calculation Complete!

For Help, press F1

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

OLI Studio (Version 11.5.1 Beta) - [1.1 Single point calculation\_Example\_1.load\*]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator: 1.1 Single point calculation\_Example\_1  
Streams: pH of 1 m FeCl3  
SinglePoint

SinglePoint

Description Definition Report

Jump to: Species Activity/Fugacity Coefficients

Species Activity/Fugacity Coefficients

Species	$\gamma$		Fugacity Coefficients
	x-based	m-based	
Cl-1	2.18384	2.06674	
Fe2(OH)2+4	2.69634e-4	2.55176e-4	
FeCl2+1	7.70907	7.2957	
FeCl+2	1.79095	1.69492	
Fe+3	0.132933	0.125805	
FeO2-1	0.706024	0.668167	
FeOH+2	0.162852	0.15412	
FeO+1	0.706024	0.668167	
H2O	0.962773	0.911148	
H3O+1	0.697601	0.660195	
HCl - Liq1	0.825477	0.781214	
HFeO2 - Liq1	0.962773	0.911148	
OH-1	0.556549	0.526706	

Calculation Complete!

For Help, press F1

Thus, the pH is:

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

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

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

$$pH = 1.49$$

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

## Example 2: Calculating the pH of an acetic acid solution

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

### Starting the Simulation

Add a new **Stream**

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

Select the MSE thermodynamic Framework (selected by default)

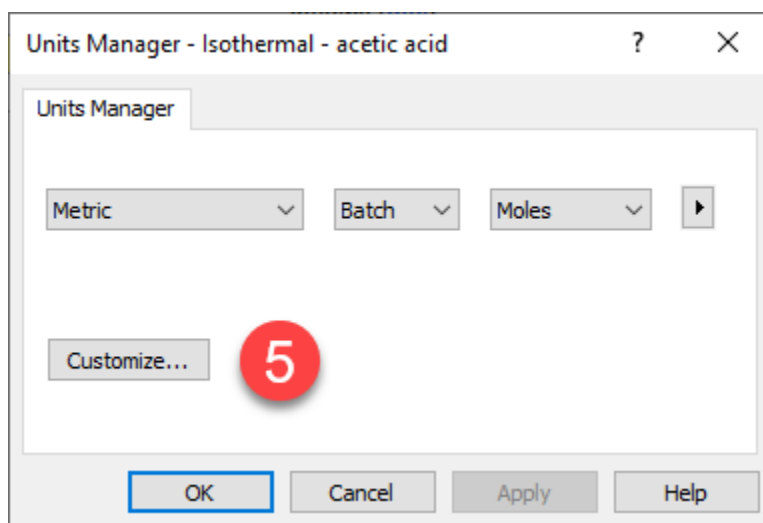
**Click** on the **Units Manager** Icon, and the Units Manager window opens

The screenshot shows the OLI Studio software interface. The main window displays the 'Isothermal - acetic acid' stream definition. The 'Variable' and 'Value' columns are populated with the following data:

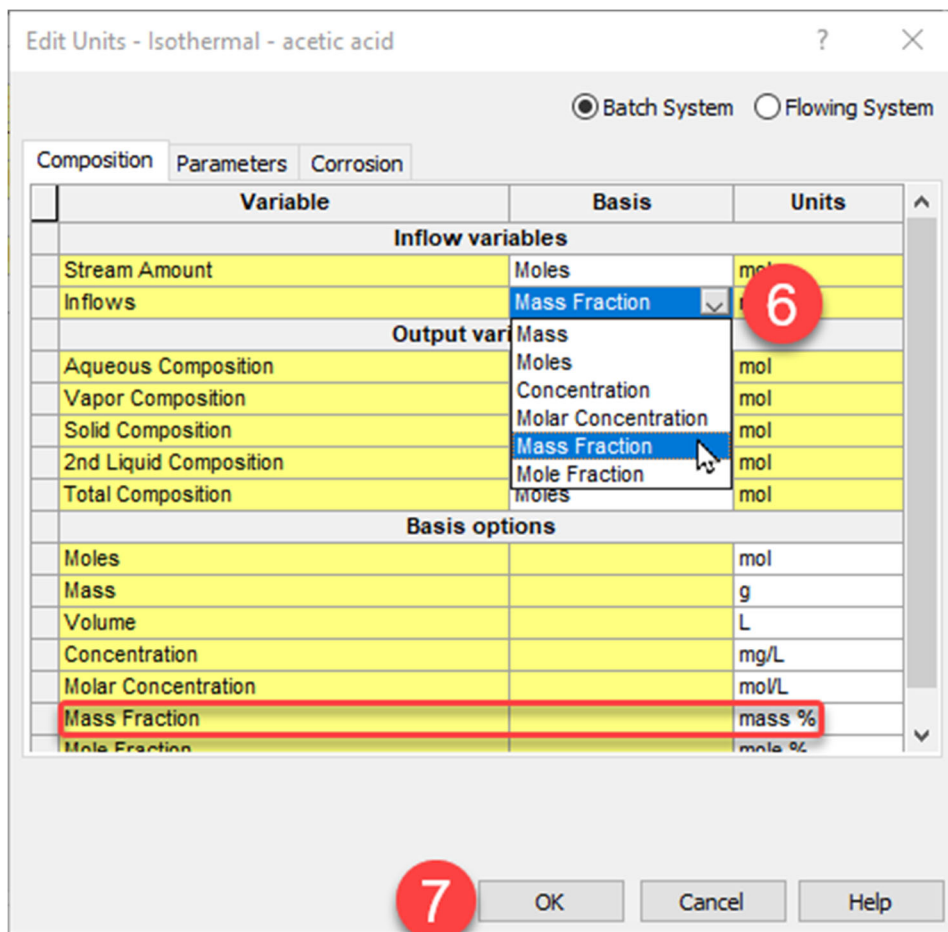
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082

The 'Actions' panel on the left shows the 'Add Stream' option highlighted with a red circle 1. The 'Navigator' on the left shows the 'Isothermal - acetic acid' stream highlighted with a red circle 2. The top toolbar shows the 'MSE' thermodynamic framework selected with a red circle 3, and the 'Units Manager' icon highlighted with a red circle 4.

Click on the **Customize** Button



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



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

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


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

**Go** to the **Add Calculation** button and select **Single Point**. Select the default calculation type – **Isothermal**

**Change** the name to **pH** using the **<F2>** key or by **right-mouse click** on the object and selecting **rename**

**Change** the temperature to **75°C** and pressure to **1 atm**

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

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

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

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

Click on the **Calculate** button

OLI Studio (Version 11.5.1 Beta) - [1.1b Single point calculation\_Example\_2.oad\*]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator

1.1b Single point calculation\_Exam

Streams

- pH of 1 m FeCl3
- SinglePoint
- Isothermal Acetic Acid
- pH **2**

Actions

Actions

Plot Template Manager

Save

pH

Description Definition Report

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C) <b>3</b>	75.0000
Pressure (atm)	1.00000
Inflows (mass %) <b>4</b>	
Water	90.0000
Acetic acid <b>5</b>	10.0000

Type of calculation

Isothermal **1** Specs...

Calculate **6**

Summary

Unit Set: <Custom>

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.

Isothermal Calculation

75.0000 °C 1.00000 atm

Calculation not done

Input

Advanced Search Add as Stream Export

For Help, press F1

NUM

## Analyzing the Results

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

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

**Right-click** on the gray area and select **Sections**

Select **Additional Stream Parameters**

The screenshot shows the OLI Studio interface for a 'pH' calculation. The main window displays a table of results under the 'Description' tab. The table is organized into sections: 'Stream Parameters' (including Stream Amount, Moles (True) - Aqueous, Temperature, and Pressure) and 'Inflows (mass %)' (including Water and Acetic acid). A context menu is open over the gray area below the table, with 'Sections' selected. The 'Additional Stream Parameters' option is highlighted in blue, and a red circle with the number '3' is placed over it. A red circle with the number '1' is placed over the 'Output' mini-tab at the bottom of the grid, and a red circle with the number '2' is placed over the 'Sections' option in the context menu. The status bar at the bottom indicates 'Calculation Complete!' and 'For Help, press F1'.

Variable		
Stream Parameters		
Stream Amount (mol)		
Moles (True) - Aqueous (mol)		
Temperature (°C)		
Pressure (atm)		
Inflows (mass %)		
Water		
Acetic acid		

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

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

The screenshot displays a software interface with three tabs: Description, Definition, and Report. The main window shows a table of variables and their values, categorized into Stream Parameters, Inflows (mass %), and Additional Stream Parameters. The pH value is highlighted in red in the table. To the right, a Summary panel provides details about the calculation, including the unit set, automatic chemistry model, isothermal calculation parameters, phase amounts, and aqueous phase properties. The pH value is also highlighted in red in the summary panel.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.5082
Moles (True) - Liquid-1 (mol)	55.5082
Temperature (°C)	75.0000
Pressure (atm)	1.00000
<b>Inflows (mass %)</b>	
Water	89.9997
Acetic acid	9.99997
<b>Additional Stream Parameters</b>	
Density - Liquid-1 (g/ml)	0.983266
Density - Total (g/ml)	0.983266
Dielectric Constant - Liquid-1	56.7447
Ionic Strength (m-based) - Liquid-1 (mol/kg)	5.61843e-3
Ionic Strength (x-based) - Liquid-1 (mol/mol)	9.79429e-5
pH	2.29495
Standard Liquid Volume - Liquid-1 (L)	1.07368
Total Dissolved Solids (mg/L)	98415.9

Summary

Unit Set: <Custom>

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

Isothermal Calculation  
75.0000 °C 1.00000 atm

Phase Amounts  
Aqueous 1075.27 g

Aqueous Phase Properties  
pH 2.29495  
Ionic Strength 9.79429e-5 mol/mol  
Density 0.983266 g/ml

Calc. elapsed time: 0.766 sec

Calculation complete

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

## Bubble Point

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

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

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

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

#### Starting the Simulation

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

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

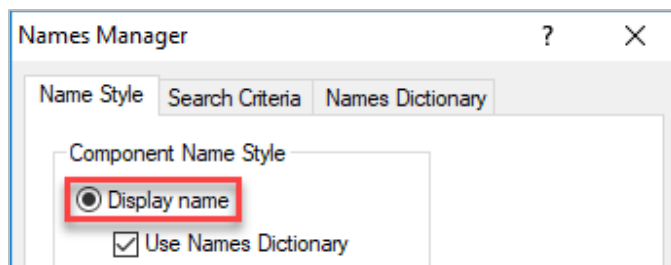
#### Calculating the Bubble Point Temperature (Isobaric)

Add a new **Stream**

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

Select the **MSE** thermodynamic Framework

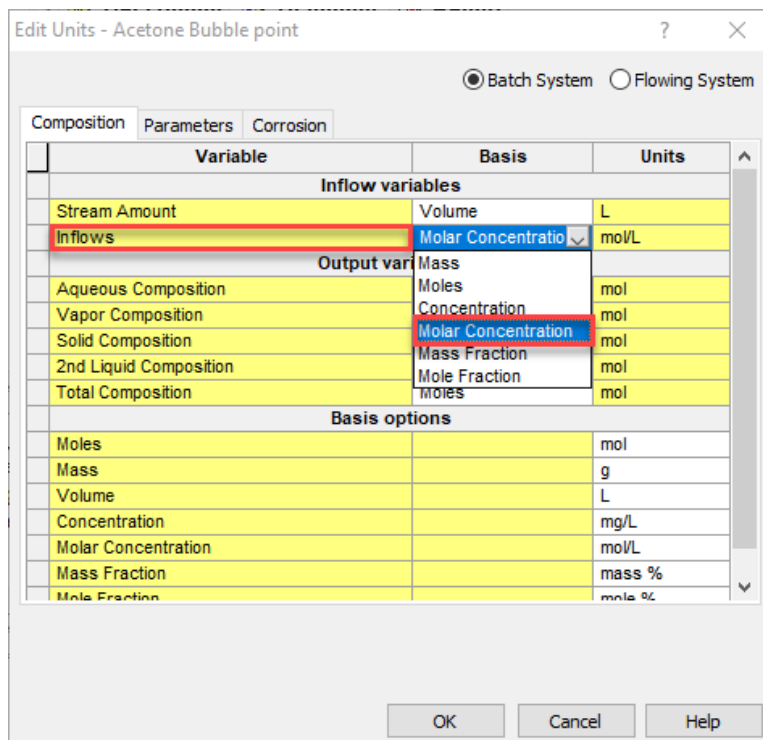
**Click** on the **Names Manager** Icon, and select the **Display Name** option, and click **OK**



Click on the hyperlink [mol](#) next to **Stream Amount**

Variable	Value
<b>Stream Parameters</b>	
Stream Amount ( <a href="#">mol</a> )	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
Water	55.5082

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



Type **Acetone** in the white cell below H2O inflows grid, and press **<Tab>** or hit **<Enter>**, and then enter the value **1.0 mol/L** in the next cell.

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

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

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

A new section appears in the grid, called **Calculation Parameters**. By default, the Temperature Bubble Point calculation is selected. For this calculation leave the default calculation: **Temperature**

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

Variable	Value
Stream Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Calculate	Temperature
Inflows	
Water	Temperature
	Pressure
Acetone	1.00000

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

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

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

## Analyzing the Results

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

Unit Set: <Custom>

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

**Bubble Point Calculation**  
1.00000 atm  
87.4831 °C

**Phase Amounts**  
Aqueous 52.7856 mol  
Vapor 5.27856e-9 mol  
Solid 0.0 mol

**Aqueous Phase Properties**  
pH 6.23325  
Ionic Strength 1.05633e-8 mol/mol  
Density 0.954351 g/ml

Calc. elapsed time: 0.762 sec

Calculation complete

## Calculating the Bubble Point Pressure (Isothermal)

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

Select the Stream named **Acetone Bubble point**

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

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

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

Change the Calculate-Temperature row to **Calculate-Pressure**

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

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

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

### Analyzing the Results

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

The screenshot displays the following information:

- Unit Set: <Custom>
- Automatic Chemistry Model
  - MSE (H3O+ ion) Databanks:
    - MSE (H3O+ ion)
  - Using Helgeson Direct
- Bubble Point Calculation** (highlighted in red)
  - 25.0000 °C
  - 0.0700537 atm
- Phase Amounts** (highlighted in green)
  - Aqueous 52.7856 mol
  - Vapor 5.27856e-9 mol
  - Solid 0.0 mol
- Aqueous Phase Properties
  - pH 6.99771
  - Ionic Strength 1.81463e-9 mol/mol
  - Density 0.990977 g/ml
- Calc. elapsed time: 0.048 sec
- Calculation complete

### Dew Point

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

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

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

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

### Starting the Simulation

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

Dew Point Calculation			
Calculation Settings		Stream Composition and Conditions	
Calculation Type	Single Point Calculation	Stream Amount	Default – 55.5082 moles
Calculation Sub-type	Dew Point	Temperature	120 °C
Stream Name	Sour Natural Gas Dew Point	Pressure	100 atm
Name Style	Display Formula	H2O	Calculated
Unit Set	Metric, Mole Fraction	CO2	1 mole %
Framework	MSE	CH4	95 mole %
		H2S	3 mole %

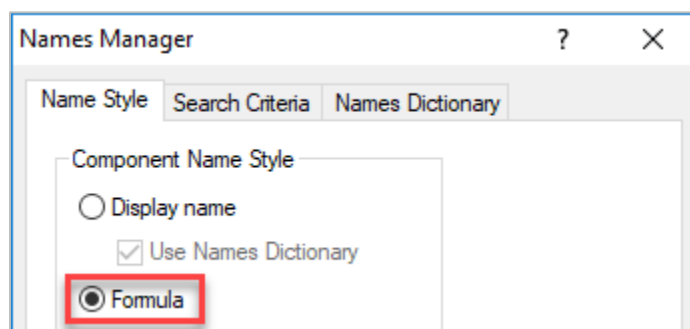
### Calculating the Dew Point Temperature (Isobaric)

Add a new **Stream**

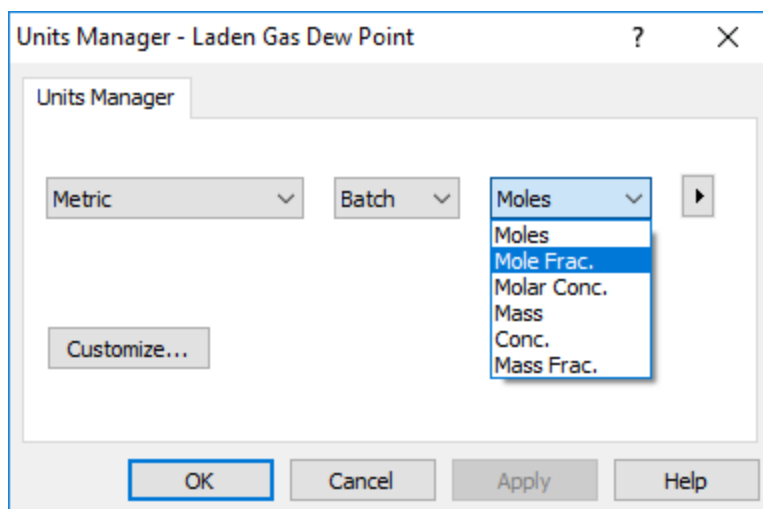
**Click** on the new Stream and press **<F2>** to change the name to *Sour Natural Gas Dew Point*

Select the **MSE** thermodynamic Framework

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



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



Enter the composition of the gas given in the table [above](#)

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

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

Select **Dew point** as Type of Calculation

Keep the Calculate-**Temperature** option

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

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

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

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

## Analyzing the Results

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

### Dew Point Temperature

Unit Set: Metric (mole fraction)

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

**Dew Point Calculation**  
100.000 atm  
91.9154 °C

Phase Amounts  
Aqueous 5.55082e-5 mol  
Vapor 55.5082 mol  
Solid 0.0 mol

Aqueous Phase Properties  
pH 3.77521  
Ionic Strength 3.15475e-6 mol/mol  
Density 0.950536 g/ml

Calc. elapsed time: 0.437 sec

Calculation complete

### Dew Point Pressure

Unit Set: Metric (mole fraction)

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

**Dew Point Calculation**  
120.000 °C  
472.561 atm

Phase Amounts  
Aqueous 1.00000e-6 mol  
Vapor 55.5082 mol  
Solid 0.0 mol

Aqueous Phase Properties  
pH 3.58375  
Ionic Strength 5.08513e-6 mol/mol  
Density 0.953852 g/ml

Calc. elapsed time: 0.043 sec

Calculation complete

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

You can study the composition of the acid gases such as CO<sub>2</sub> and H<sub>2</sub>S 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)**.

Jump to: Species Output (True Species) Customize Export

#### Species Output (True Species)

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

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

**Note:** This image is for the “Dew Point Pressure” calculation

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

## Isochoric (constant volume)

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

$$PV = nRT$$

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

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

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

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

#### Starting the Simulation

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

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

Add a new **Stream**

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

Select the **MSE** (default) thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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

Enter the **gas composition** in the table above

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

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

Select **Isochoric** as Type of Calculation

In the **Calculation Parameters** section set **Total Volume** to **10 L** and **Calculate Pressure**. (To select Pressure, click on the drop-down arrow).

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

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

### Analyzing the Results

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

Description Definition Report

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	154.548
Moles (True) - Liquid-1 (mol)	55.6610
Moles (True) - Vapor (mol)	98.8871
Temperature (°C)	25.0000
<b>Calculation Results (atm)</b>	
Pressure	304.866
<b>Inflows (mol)</b>	
H2O	55.5082
N2	77.0000
O2	21.0000
CO2	1.00000
Ar	0.0400000

Type of calculation: Isochoric Specs...  
 Calculate ✓

**Summary**  
 Unit Set: Metric (moles)  
 Automatic Chemistry Model  
 MSE (H3O+ ion) Databanks:  
 MSE (H3O+ ion)  
 Using Helgeson Direct  
**Isochoric Calculation**  
 25.0000 °C  
 304.866 atm  
**Phase Amounts**  
 Aqueous 55.6610 mol  
 Vapor 98.8871 mol  
 Solid 0.0 mol  
**Aqueous Phase Properties**  
 pH 3.94821  
 Ionic Strength 2.11978e-6 mol/mol  
 Density 1.00310 g/ml  
 Calc. elapsed time: 0.746 sec  
 Calculation complete

Input Output  
 Advanced Search Add as Stream Export

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

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

### Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor
	mol	mol	mol
<b>Mole (True)</b>	154.548	55.6610	98.8871
<b>Mole (App)</b>	154.548	55.6611	98.8871
	<b>g</b>	<b>g</b>	<b>g</b>
<b>Mass</b>	3874.62	1005.05	2869.56
	<b>L</b>	<b>L</b>	<b>L</b>
<b>Volume</b>	10.0001	1.00194	8.99811

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

## Vapor Amount and Vapor Fraction

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

### Example 6: Evaporating a Brine

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

#### Starting the Simulation

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

Vapor Fraction / Vapor Amount Point Calculation			
Calculation Settings		Stream Composition and Conditions	
Calculation Type	Single Point Calculation	Stream Amount	Default - 1 kg
Calculation Sub-type	Vapor Fraction	Temperature	25 °C
Stream Name	Brine Evaporation – Vapor Fraction	Pressure	1 atm
Name Style	Display Formula	H2O	Calculated
Unit Set	Metric, Mass Fraction	NaCl	9 mass %
Framework	MSE	CaSO <sub>4</sub>	1 mass %

#### Calculating the Vapor Fraction Temperature (Isobaric)

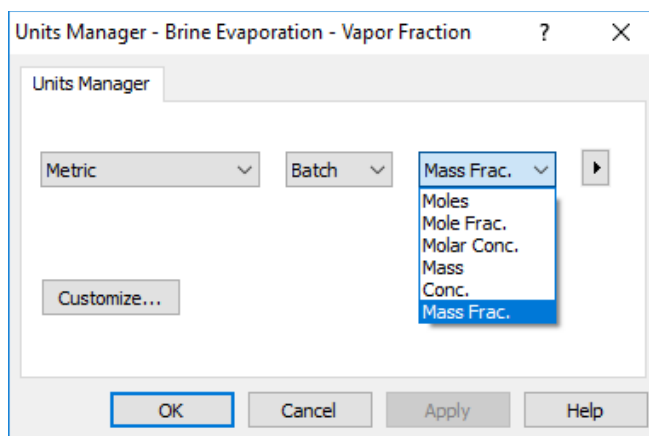
Add a new **Stream**

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

Select the **MSE** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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



Enter the gas composition given in the table [above](#).

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

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

Select **Vapor Fraction** as Type of Calculation

Enter **95** as the **Vapor Fraction** amount.

**Note:** The software will convert the 1 kg to mole units and will put 95% of this in the vapor phase.

Keep the Calculate-**Temperature** option

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

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

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

### Analyzing the Results

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

Unit Set: [Metric \(mass fraction\)](#)

Automatic Chemistry Model  
[MSE \(H3O+ ion\) Databanks:](#)  
[MSE \(H3O+ ion\)](#)  
 Using Helgeson Direct

Vapor Fraction Calculation  
 1.00000 atm  
 108.805 °C

Phase Amounts  
 Aqueous 0.0243143 kg  
 Vapor 0.882612 kg  
 Solid 0.0930728 kg

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

Calc. elapsed time: 0.131 sec

Calculation complete

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

Jump to: Total and Phase Flows (Amounts)

**Total and Phase Flows (Amounts)**  
 column Filter Applied: Only Non Zero Values

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

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

## Set pH

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

### Example 7: Neutralizing Acetic Acid

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

#### Starting the Simulation

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

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

#### Setting the pH

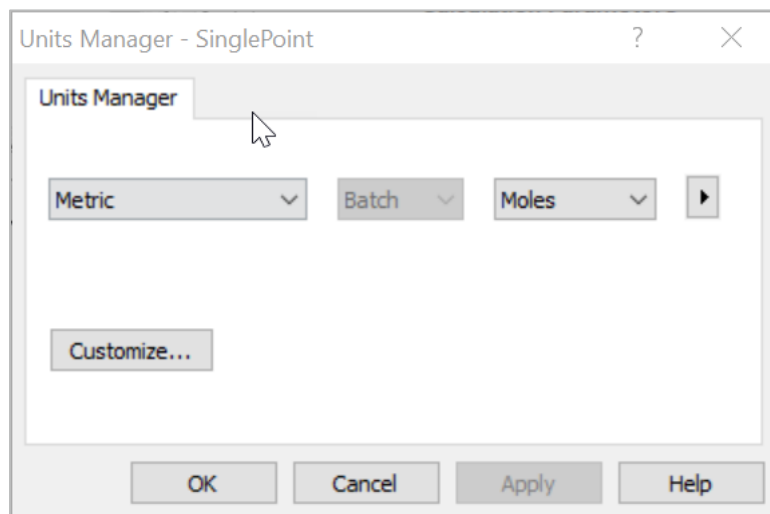
Add a new **Stream**

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

Select the **AQ** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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



Enter **1 mol** of **CH<sub>3</sub>COOH** as an inflow

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

Select **Set pH** as Type of Calculation

Change the **SinglePoint** name to **Neutralizing acetic acid** using the <F2> key

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

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	56.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Parameters</b>	
Target pH	0.0
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
<b>Inflows (mol)</b>	
H2O	55.5082
CH3COOH	1.00000

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

Calculation Options

Category: pH

Select an acid and base to adjust to meet the specified pH.

Use Single Titrant     Hide Related Inflows    **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.

Enter **7** as the **Target pH** value

Use the default titrants: **HCL** and **NAOH**

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

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

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

### Analyzing the Results

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

The screenshot shows the software interface with the 'Definition' tab selected. The main table displays the following data:

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	57.5044
Moles (True) - Liquid-1 (mol)	58.3648
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Results (mol)</b>	
pH titrant added: NaOH	0.996144
<b>Inflows (mol)</b>	
H2O	55.5082
CH3COOH	1.00000
NaOH	0.996144

The 'Summary' box on the right provides the following details:

- Type of calculation: Set pH
- Unit Set: Metric (moles)
- Automatic Chemistry Model: MSE (H3O+ ion) Databanks: MSE (H3O+ ion) Using Helgeson Direct
- Set pH Calculation: 25.0000 °C, 1.00000 atm, Target pH 7.00000, Acid Titrant: HCL, Total: 0.0 mol
- Base Titrant: NaOH, Total: 0.996144 mol, Added: 0.996144 mol
- Phase Amounts: Aqueous 58.3648 mol, Vapor 0.0 mol, Solid 0.0 mol
- Aqueous Phase Properties: pH 7.00000, Ionic Strength 0.0147421 mol/mol, Density 1.03528 g/ml
- Calc. elapsed time: 1.301 sec

At the bottom of the interface, the 'Output' button is highlighted with a red box.

## 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 ( $\text{CaCO}_3$ )

Equilibrium based simulators suffer from a potential problem, that the most stable solid will tend to be included over less stable (meta-stable) solids. Such is the case of calcium carbonate. Calcium Carbonate ( $\text{CaCO}_3$ ) is found in nature in many forms. Two common forms are the more thermodynamically stable solids, **Calcite** and the less stable form **Aragonite**.

In this example, we will compute the solubility of  $\text{CaCO}_3$  as **Calcite** in a solution containing  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ , and  $\text{Cl}^-$  as well as dissolved  $\text{CO}_2$ .

#### 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 $\text{CaCO}_3$ – Precipitation Point	Pressure	1 atm
Name Style	Display Formula	H2O	Calculated
Unit Set	Metric, Mass Fraction (ppm (mass))	CaCl2	10870 ppm (mass)
Framework	MSE	MgCl2	9325 ppm (mass)
		CO2	431 ppm (mass)
		CaCO3	0 ppm(mass)

#### Calculating the Precipitation of Calcite ( $\text{CaCO}_3$ )

Add a new **Stream**

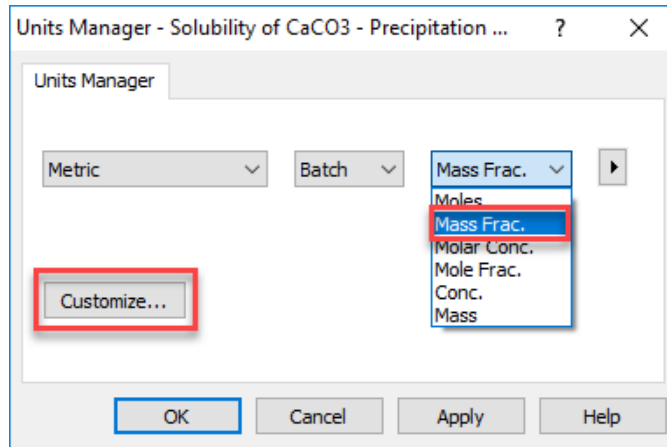
**Click** on the new Stream and press **<F2>** to change the name to *Solubility of  $\text{CaCO}_3$  – Precipitation Point*

Select the **AQ** thermodynamic Framework

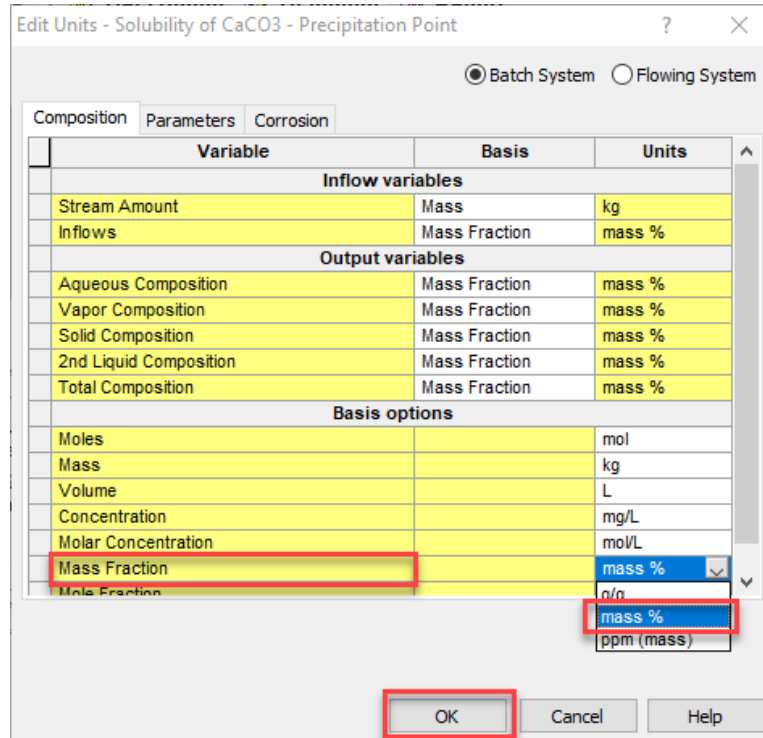
**Click** on the **Names Manager** Icon and select the **Formula** option

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

However, you need to change the units to ppm (mass), to do this **Click** on the **Customize button**.



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



Enter the stream composition given in the table [above](#).

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

Select **Precipitation Point** as Type of Calculation

Change the **SinglePoint** name to **Calcite Precipitation** using the <F2> key

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

The screenshot shows the software interface with the following components:

- Calculation Parameters Grid:**

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (kg)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Parameters</b>	
Precipitant:	<select>
Adjusted inflow:	<select>
<b>Inflows (ppm (mass))</b>	
H2O	9.79374e5
CaCl2	10870.0
MgCl2	9325.00
CO2	431.000
CaCO3	0.0
- Summary Box:**

Unit Set: <Custom>

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

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.

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

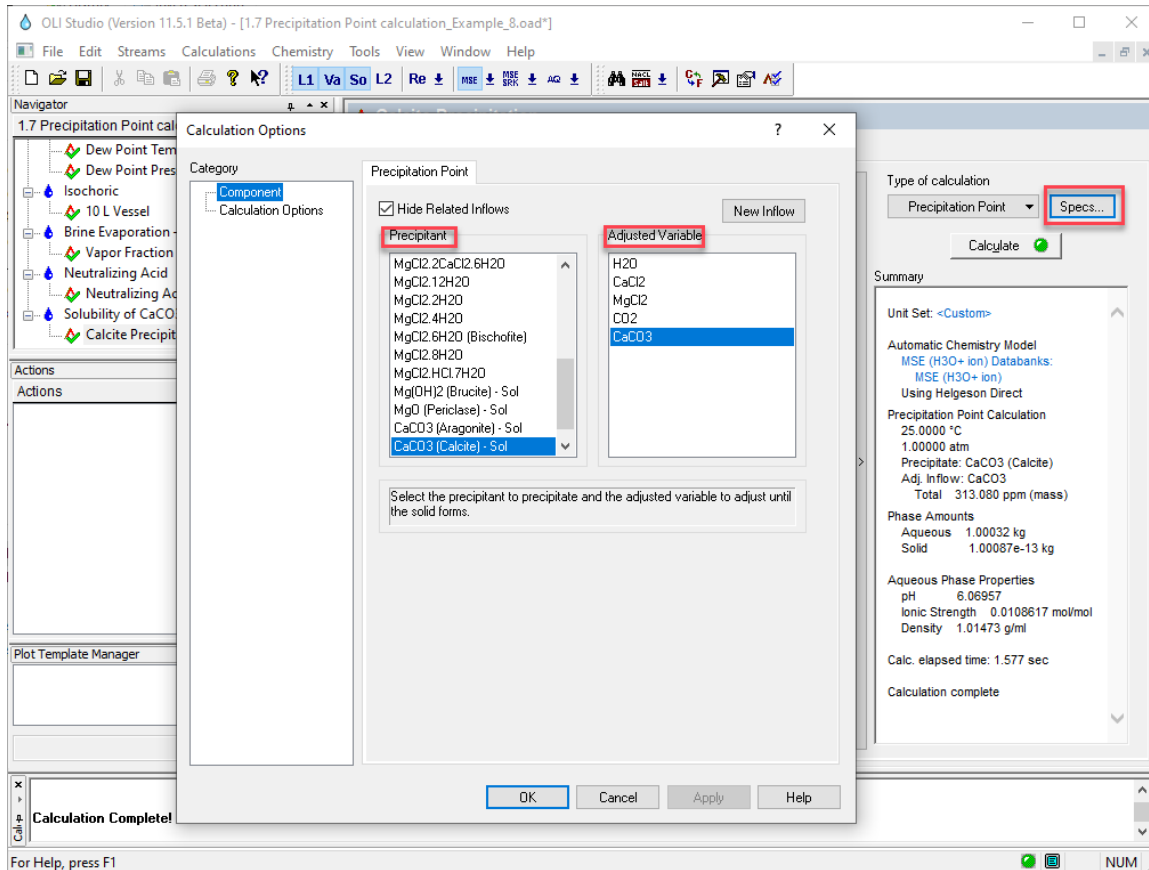
Select **CaCO3** as the **Adjusted Inflow**

Calculation Parameters	
Precipitant:	CaCO3 (Calcite)
Adjusted inflow:	CaCO3
<b>Inflows (ppm (mass))</b>	
H2O	9.79374e5
CaCl2	10870.0
MgCl2	9325.00
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  $1.0 \times 10^{-10}$  times the stream amount.

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

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



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

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

### Analyzing the Results

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

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

Description Definition Report

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (kg)	1.00032
Mass - Liquid-1 (kg)	1.00032
Mass - Solid (kg)	1.00087e-13
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Results (ppm (mass))</b>	
Adjusted Inflow: CaCO3	313.080
<b>Inflows (ppm (mass))</b>	
H2O	9.79064e5
CaCl2	10866.6
MgCl2	9322.05
CO2	430.864
CaCO3	313.080

Type of calculation  
 Precipitation Point

Summary

Unit Set: <Custom>

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

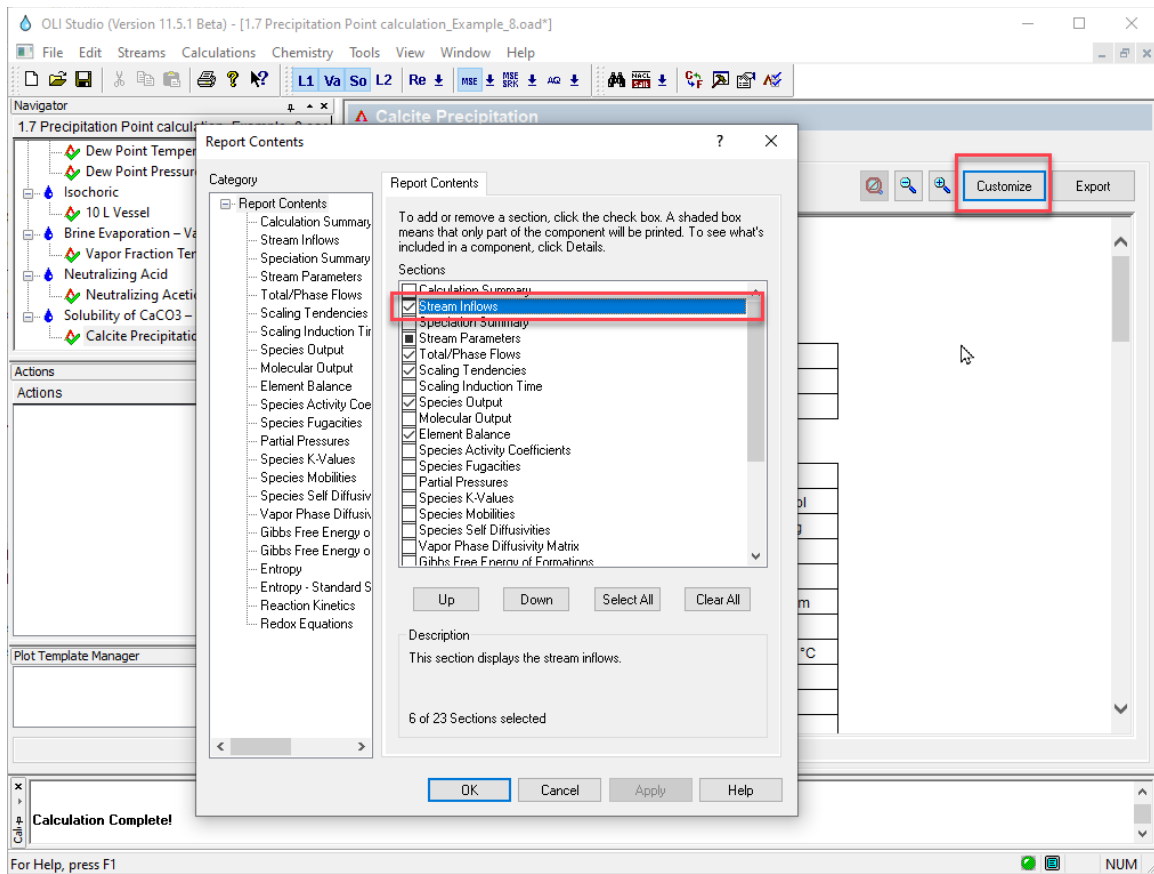
Precipitation Point Calculation  
 25.0000 °C  
 1.00000 atm  
 Precipitate: CaCO3 (Calcite)  
 Adj. Inflow: CaCO3  
 Total 313.080 ppm (mass)

Phase Amounts  
 Aqueous 1.00032 kg  
 Solid 1.00087e-13 kg

Aqueous Phase Properties  
 pH 6.06957  
 Ionic Strength 0.0108617 mol/mol  
 Density 1.01473 g/ml

Calc. elapsed time: 1.577 sec  
 Calculation complete

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



Notice that the concentrations have changed slightly. This is to accommodate the additional 313.1 ppm CaCO<sub>3</sub> needed to meet the calculation specifications.

### Stream Inflows

Row Filter Applied: Only Non Zero Values

Species	Input ppm (mass)	Output ppm (mass)
H2O	9.79374e5	9.79064e5
CaCl2	10870.0	10866.6
MgCl2	9325.00	9322.05
CO2	431.000	430.864
CaCO3	0.0	313.080

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

**Calcite** is the thermodynamically stable phase of calcium carbonate. **Aragonite**, calcite's orthorhombic polymorph, is about 1.5 times more soluble than calcite<sup>4</sup>. At surface conditions, aragonite spontaneously turns into calcite over geologic time, but at higher pressures aragonite, the denser of the two, is the preferred structure.

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

### Starting the Simulation

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

Under the Stream *Solubility of CaCO<sub>3</sub> – Precipitation Point*, **Add a Single Point** calculation

Select **Precipitation Point** as Type of Calculation

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

Select the **CaCO<sub>3</sub> (Calcite)** as the **Precipitant**

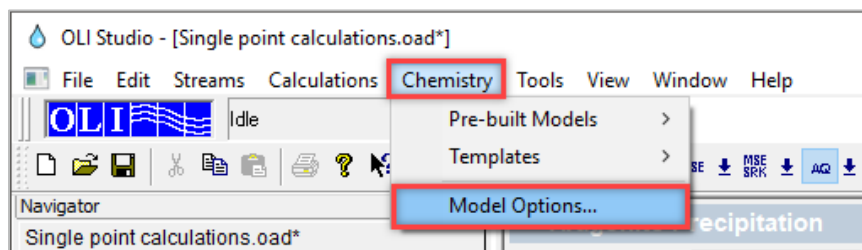
Select **CaCO<sub>3</sub>** as the **Adjusted Inflow**

Calculation Parameters	
Precipitant:	CaCO <sub>3</sub> (Aragonite)
Adjusted Inflow:	CaCO <sub>3</sub>

---

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

Click on **Chemistry > Model Options**

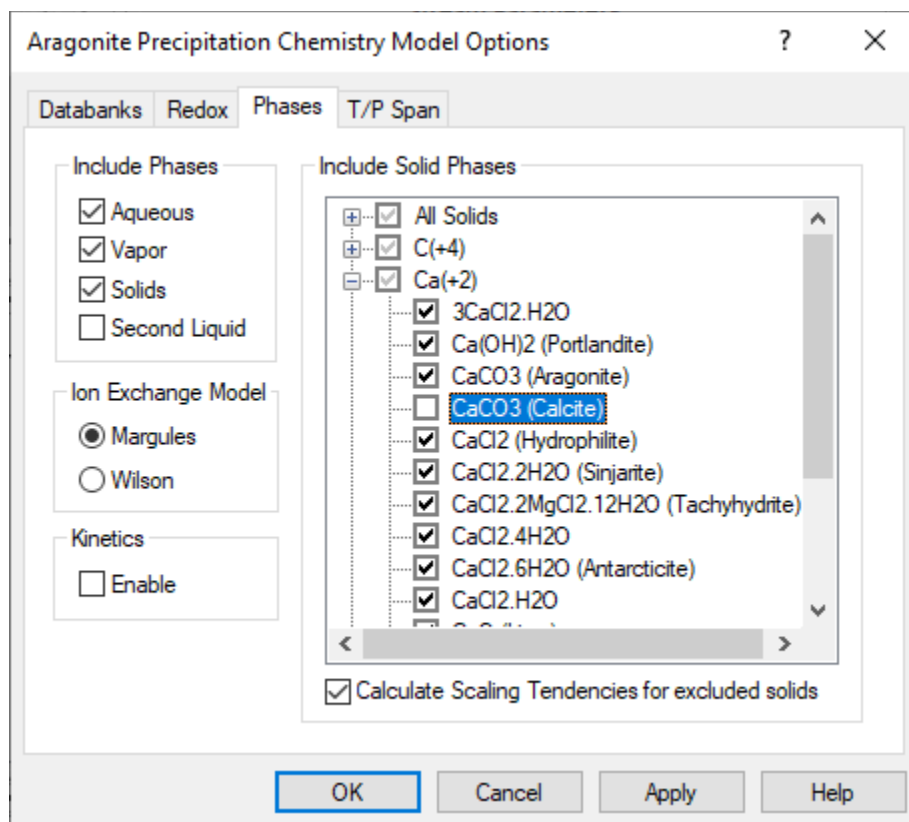


Select the **Phases** tab

**Click** on the “+” next to the Ca(+2) box to display all the calcium containing solids

Scroll down to find CaCO<sub>3</sub> (Calcite) and **uncheck** this solid

Click **OK** continue.



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

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

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

## Analyzing the Results

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

The software calculated that the solubility of  $\text{CaCO}_3$  as Aragonite in the solution under study is around **~353.8 ppm (mass)**. The pH of this solution is ~6.15. You can see that the solubility of Aragonite is higher than the solubility of Calcite (313.1 ppm (mass)).

The screenshot displays a software interface with three tabs: Description, Definition, and Report. The main window is divided into a table on the left and a summary panel on the right.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (kg)	1.00036
Mass - Liquid-1 (kg)	1.00036
Mass - Solid (kg)	1.00087e-13
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Results (ppm (mass))</b>	
Adjusted Inflow: CaCO3	353.836
<b>Inflows (ppm (mass))</b>	
H2O	9.79024e5
CaCl2	10866.1
MgCl2	9321.67
CO2	430.846
CaCO3	353.836

The summary panel on the right contains the following information:

- Type of calculation: Precipitation Point
- Unit Set: <Custom>
- Automatic Chemistry Model: MSE (H3O+ ion) Databanks: MSE (H3O+ ion)
- Excluding 1 solid phase Using Helgeson Direct
- Precipitation Point Calculation: 25.0000 °C, 1.00000 atm
- Precipitate: CaCO3 (Aragonite)
- Adj. Inflow: CaCO3
- Total: 353.836 ppm (mass)
- Phase Amounts: Aqueous 1.00036 kg, Solid 1.00087e-13 kg
- Aqueous Phase Properties: pH 6.14902, Ionic Strength 0.0108837 mol/mol, Density 1.01478 g/ml
- Calc. elapsed time: 1.670 sec
- Calculation complete

At the bottom of the interface, there are buttons for "Input", "Output", "Advanced", "Search", "Add as Stream", and "Export".

## Example 10: Determining the Solubility of Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ )

The third carbonate mineral to mention is **Dolomite**, which is something like calcite with a very high concentration of magnesium in it. Under some conditions there can be much more magnesium added in, and when the amount of magnesium becomes roughly the same as the calcium, the resulting mineral is called Dolomite with the following chemical formula:  $\text{CaMg}(\text{CO}_3)_2$ . The formation of Dolomite is believed to occur in geological time frames.

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

### Starting the Simulation

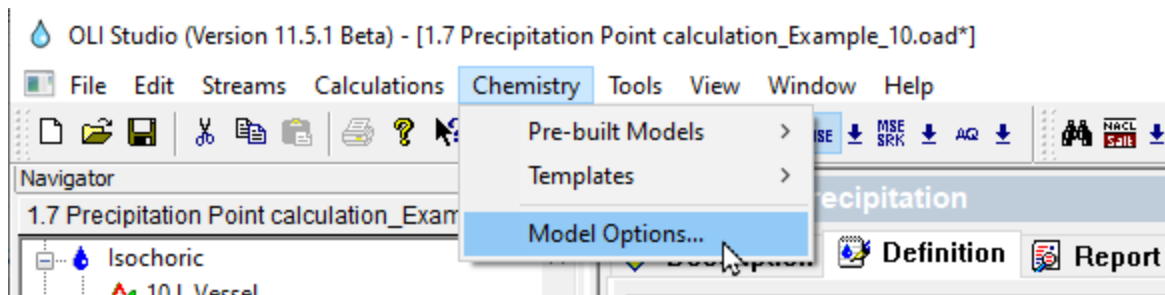
#### Calculating the Precipitation of Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ )

Under the Stream *Solubility of  $\text{CaCO}_3$  – Precipitation Point*, **Add a Single Point** calculation

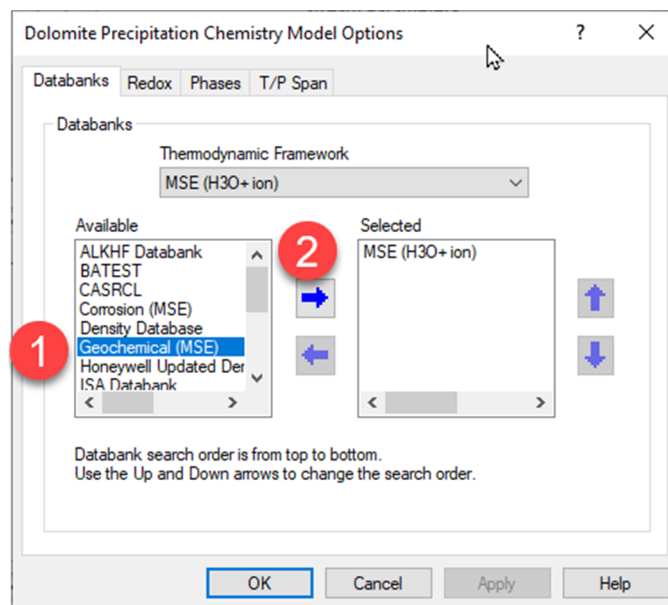
Change the **SinglePoint** name to **Dolomite Precipitation** using the <F2> key

Select **Precipitation Point** as Type of Calculation

Click on **Chemistry > Model Options**



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



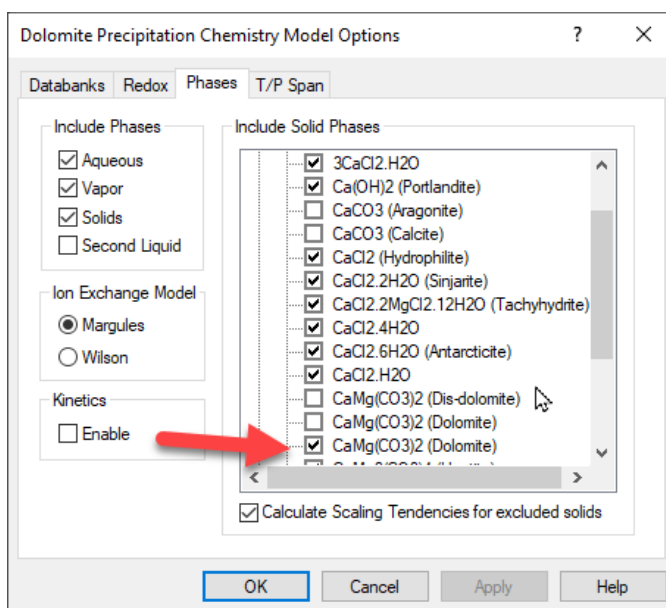
You may have additional or fewer databases depending on previous installations and imported databases. Some are from OLI and some may be private (user) databases.

Select the **Phases** tab

**Click** on the “+” next to the Ca(+2) box to display all the calcium containing solids

Scroll down to find CaCO<sub>3</sub> (Calcite) and CaCO<sub>3</sub> (Aragonite) and **uncheck** these solids. The MSE model also has ordered and disordered dolomite. These also should be unchecked. See the figure below. Make sure to keep the second dolomite species checked.

Click **OK** continue.



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

Select the **CaMg(CO<sub>3</sub>)<sub>2</sub> (Dolomite)** as the **Precipitant**

Select **CaCO<sub>3</sub>** as the **Adjusted Inflow**

Calculation Parameters	
Precipitant:	CaMg(CO <sub>3</sub> ) <sub>2</sub> (Dolomite)
Adjusted Inflow:	CaCO <sub>3</sub>

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

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

## Analyzing the Results

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

The software calculated that the solubility of Dolomite in the solution under study is around **~257.7 ppm (mass)**. The pH of this solution is ~5.95.

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

The screenshot displays a software interface with three tabs: Description, Definition, and Report. The main window is divided into a table on the left and a summary panel on the right.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (kg)	1.00026
Mass - Liquid-1 (kg)	1.00026
Mass - Solid (kg)	1.84402e-13
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Results (ppm (mass))</b>	
Adjusted Inflow: CaCO3	257.706
<b>Inflows (ppm (mass))</b>	
H2O	9.79118e5
CaCl2	10867.2
MgCl2	9322.57
CO2	430.888
CaCO3	257.706

The summary panel on the right shows the following details:

- Type of calculation: Precipitation Point
- Unit Set: <Custom>
- Automatic Chemistry Model: MSE (H3O+ ion) Databanks: Geochemical (MSE) MSE (H3O+ ion)
- Excluding 4 solid phases Using Helgeson Direct
- Precipitation Point Calculation: 25.0000 °C, 1.00000 atm
- Precipitate: CaMg(CO3)2 (Dolomite)
- Adj. Inflow: CaCO3
- Total: 257.706 ppm (mass)
- Phase Amounts: Aqueous 1.00026 kg, Solid 1.84402e-13 kg
- Aqueous Phase Properties: pH 5.95165, Ionic Strength 0.0108318 mol/mol, Density 1.01466 g/ml
- Calc. elapsed time: 1.886 sec
- Calculation complete

Buttons at the bottom include Input, Output, Advanced, Search, Add as Stream, and Export.

## Composition Point

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

### Example 11: Targeting dissolved H<sub>2</sub>S in water below 0.001 m

In this example, you will use the composition point calculation to target the amount of molecular H<sub>2</sub>S 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 °C
Stream Name	Composition Point	Pressure	1 atm
Name Style	Display Formula	H <sub>2</sub> O	55.5082 (default)
Unit Set	Metric, Moles	H <sub>2</sub> S	0 moles
Framework	MSE	Target H <sub>2</sub> S-Aq value	0.001 moles

#### Calculating the Vapor Fraction Temperature (Isobaric)

Add a new **Stream**

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

Select the **MSE** thermodynamic Framework (this is the default)

**Click** on the **Names Manager** Icon and select the **Formula** option

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

Enter the composition of the gas given in the table above

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

Select **Composition Point** as Type of Calculation

Change the *SinglePoint* name to **H<sub>2</sub>S dissolved in water** using the <F2> key

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

Set the **Target H<sub>2</sub>S value** to **0.001** moles

Set the **Adjusted Inflow** to **H<sub>2</sub>S**

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Parameters</b>	
Target Species:	H2S - Liq1
Target H2S Value: (mol)	1.00000e-3
Adjusted Inflow:	H2S
<b>Inflows (mol)</b>	
H2O	55.5082
H2S	0.0

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

### Analyzing the Results

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

The screenshot displays the software interface with three tabs: Description, Definition, and Report. The main window shows a table of variables and values, with the 'Adjusted Inflow: H2S' row highlighted in red. Below the table are buttons for 'Input' and 'Output', with 'Output' also highlighted in red. At the bottom are buttons for 'Advanced', 'Search', 'Add as Stream', and 'Export'.

On the right side, there is a 'Summary' box containing the following information:

- Type of calculation: Composition Point
- Unit Set: Metric (moles)
- Automatic Chemistry Model: MSE (H3O+ ion) Databanks: MSE (H3O+ ion)
- Using Helgeson Direct
- Composition Point Calculation: 25.0000 °C, 1.00000 atm, Target: H2S, Fixed at 1.00000e-3 mol, Adj. Inflow: H2S, Total 1.01049e-3 mol
- Phase Amounts: Aqueous 55.5093 mol, Vapor 0.0 mol, Solid 0.0 mol
- Aqueous Phase Properties (highlighted in red): pH 4.98095, Ionic Strength 1.88927e-7 mol/mol, Density 0.997065 g/ml
- Calc. elapsed time: 1.297 sec
- Calculation complete

According to the calculation, ~0.00101 moles of H<sub>2</sub>S were required to create a solution with 0.001 moles of H<sub>2</sub>S-aq. The pH of this solution is ~**5.0**.

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

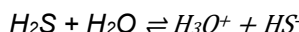
### Species Output (True Species)

Row Filter Applied: Only Non Zero Values

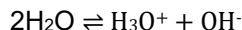
column Filter Applied: Only Non Zero Values

	Total	Liquid-1
	mol	mol
H <sub>2</sub> O	55.5082	55.5082
H <sub>2</sub> S	1.0e-3	1.0e-3
H <sub>3</sub> O <sup>+</sup>	1.04872e-5	1.04872e-5
HS <sup>-</sup>	1.04862e-5	1.04862e-5
OH <sup>-</sup>	9.71758e-10	9.71758e-10
S <sup>-2</sup>	1.01628e-14	1.01628e-14
<b>Total (by phase)</b>	<b>55.5093</b>	<b>55.5093</b>

You can see that the molecular H<sub>2</sub>S is the value that was specified as a target. Notice that the concentration of H<sub>3</sub>O<sup>+</sup> and HS<sup>-</sup> are nearly identical. This is because the following reactions:



H<sub>3</sub>O<sup>+</sup> is slightly higher because a second reaction, the dissociation of water also contributes to the H<sub>3</sub>O<sup>+</sup> formation.



## 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<sub>2</sub>, H<sub>2</sub>S, and chlorides. An autoclave, however, has a constant volume, so it is imperative to know how much material (NaCl solution, CO<sub>2</sub> and H<sub>2</sub>S 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<sub>2</sub> and H<sub>2</sub>S 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**

[Calculating results at ambient conditions](#)

[Increasing the volume of the vessel and its implications](#)

[Increasing the final temperature and its implications](#)

[Increasing the final pressure and its implications](#)

### **Using a Reactive Gas**

[Calculating results at final conditions](#)

[Using a Reactive Gas and a NaOH solution](#)

## Example 12: Using an Inert Gas

### Calculating Results at Ambient Conditions

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

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

We can use the **Ideal Gas Law** to estimate the amount of N<sub>2</sub> needed to fill the headspace:

$$PV = nRT$$
$$1 \text{ atm} \times 1 \text{ L} = n \times 0.082057 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298.15 \text{ K}$$
$$n = 0.040874 \text{ moles}$$

Although this estimate does not consider the H<sub>2</sub>O that is in the 1 L headspace or the amount of N<sub>2</sub> dissolved in water, it is still an easy approach to get a reasonable estimate.

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

### Starting the Simulation

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

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

Add a new **Stream**

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

Select the **MSE-SRK** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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

Enter the **N2** as an **inflow**

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

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

Select **Autoclave** as Type of Calculation

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

Click on the **Specs** button.

The screenshot shows a software interface with a table of variables and a summary panel. The table has two columns: 'Variable' and 'Value'. It is divided into sections: 'Stream Parameters', 'Calculation Parameters', and 'Inflows (mol)'. The 'Calculation Parameters' section is highlighted with a red box. The summary panel on the right shows the 'Type of calculation' set to 'Autoclave' and a 'Specs...' button highlighted with a red box. Below the summary, there is a red error message: 'Volume of vessel is invalid. Use the specs button to select up to 5 gases to consider.'

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

Input

Advanced Search Add as Stream Export

Type of calculation: Autoclave [Specs...]

Calculate [Red]

Summary

Unit Set: Metric (moles)

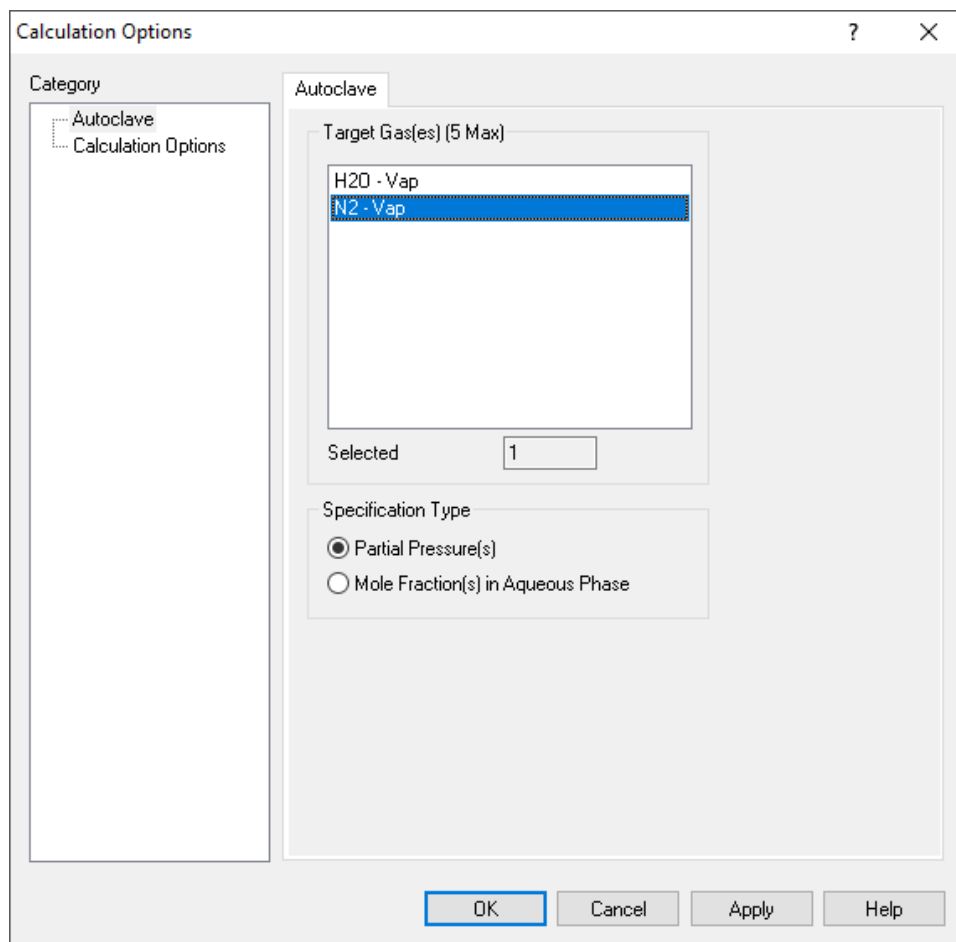
Automatic Chemistry Model  
MSE-SRK (H3O+ ion) Databanks:  
MSE-SRK (H3O+ ion)  
MSE (H3O+ ion)  
Second Liquid phase  
Using Helgeson Direct

Autoclave Calculation  
Specifications:  
Ambient Temperature 25.0000 °C  
Final Temperature 0.0 °C  
Final Pressure  
Vessel Volume 0.0 L

Calculation not done

Volume of vessel is invalid.  
Use the specs button to select up to 5 gases to consider.

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**.



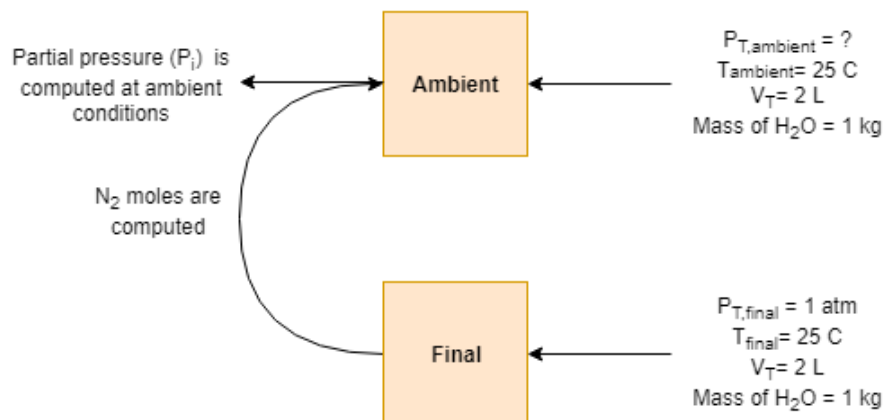
Set the **Final Temperature** to **25°C**, the **Final Pressure** to **1 atm** and the **Vessel Volume** to **2 L**  
 Set the **Compute results at which Conditions** to **Ambient**

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
<b>Calculation Parameters</b>	
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<sub>2</sub>O (55.5082 moles) at an ambient temperature of 25 °C. The partial pressure of N<sub>2</sub> will be calculated at a final temperature, 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<sub>2</sub> needed to create a 1 atm pressure at final conditions. It will then use this N<sub>2</sub> to compute the pressure at ambient conditions. The calculation pathway is shown in the image below.



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

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

### Analyzing the Results

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

The screenshot displays the software interface with the following components:

- Navigation:** Description, Definition, Report, File Viewer.
- Table:** A table with columns for Variable and Value, containing Stream Parameters, Calculation Results, and Inflows.
- Summary Box:** A detailed summary of the calculation results, including unit set, model, and phase amounts.
- Buttons:** Input, Output, Advanced, Search, Add as stream, Export.

Variable	Value
<b>Stream Parameters (mol)</b>	
Stream Amount	55.5483
Moies (True) - Liquid-1 (mol)	55.5076
Moies (True) - Vapor (mol)	0.0407607
<b>Calculation Results</b>	
Ambient Temperature (°C)	25.0000
Ambient Pressure (atm)	0.999983
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	1.99998
Partial Pressure: N2 (atm)	0.968624
Condition that results were computed f	Ambient
<b>Inflows (mol)</b>	
H2O	55.5082
N2	0.0400808

**Summary**

Unit Set: Metric (moles)

Automatic Chemistry Model  
MSE-SRK (H3O+ ion) Databanks:  
MSE-SRK (H3O+ ion)  
MSE (H3O+ ion)

Second Liquid phase  
Using Helgeson Direct

Autoclave Calculation  
Results for ambient conditions:  
Ambient Temperature 25.0000 °C  
Ambient Pressure 0.999983 atm  
Final Temperature 25.0000 °C  
Final Pressure 1.00000 atm  
Vessel Volume 2.00000 L  
N2 0.968624 atm

Phase Amounts  
Aqueous 55.5076 mol  
Vapor 0.0407607 mol  
Solid 0.0 mol  
2nd Liquid 0.0 mol

Aqueous Phase Properties  
pH 6.99756  
Ionic Strength 1.81224e-9 mol/mol  
Density 0.997061 g/ml

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

The amount of N<sub>2</sub> added is 0.0400808 moles, which produces a ~0.9686 atm partial pressure. The computed N<sub>2</sub> inflow compares to the Ideal Gas value of 0.040874 moles, a ~2% deviation.

Let's review the distribution of N<sub>2</sub> in the liquid and vapor phase in the **Report** tab. Scroll down to the last table named **Element Distribution**.

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

### Element Distribution

	Total	Total	Liquid-1	Vapor
	mol	mole %	% of Total	% of Total
H(+1)	111.016	66.6346	99.9977	2.30275e-3
O(-2)	55.5082	33.3173	99.9977	2.30275e-3
N(0)	0.0801616	0.0481148	1.49271	98.5073

These results infer two effects:

As the final pressure ( $P_T$ ) increases, additional N<sub>2</sub> will dissolve in the water, shifting the fraction of nitrogen to the liquid.

As the total autoclave volume ( $V_T$ ) increases relative to the input liquid (which stays constant), additional water will evaporate, shifting the water to the vapor. This case will be shown next.

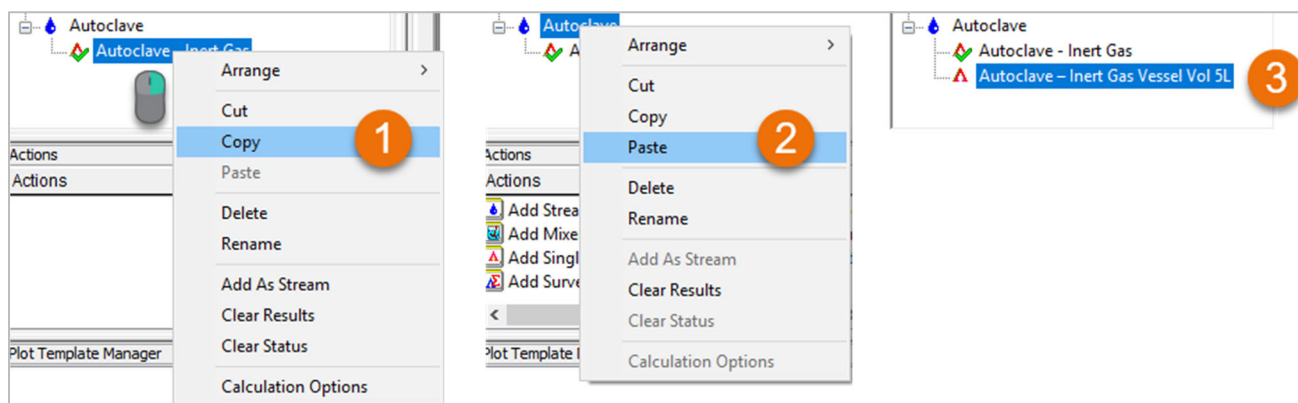
### Increasing the Vessel Volume to 5 L

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

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

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

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



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

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
<b>Calculation Parameters</b>	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	5.00000
Partial Pressure: N2 (atm)	
Compute results at which condition	Ambient
<b>Inflows (mol)</b>	
H2O	55.5082
N2	0.0

Type of calculation: Autoclave [Specs...]  
[Calculate]

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model  
MSE-SRK (H3O+ ion) Databanks:  
MSE-SRK (H3O+ ion)  
MSE (H3O+ ion)  
Second Liquid phase  
Using Helgeson Direct

Autoclave Calculation  
Specifications:  
Ambient Temperature 25.0000 °C  
Final Temperature 25.0000 °C  
Final Pressure 1.00000 atm  
Vessel Volume 5.00000 L  
N2  
Calculation not done

At this point the system is defined as 1 kg H<sub>2</sub>O (55.5082 moles) at an ambient temperature of 25 °C. The partial pressure of N<sub>2</sub> will be calculated at a final temperature, 25 °C and pressure, 1 atm in a 5 L vessel.

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

## Analyzing the Results

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

The screenshot displays a software interface with the following components:

- Navigation Tabs:** Description, Definition, Report, File Viewer.
- Table of Variables and Values:**

Variable	Value
<b>Stream Parameters (mol)</b>	
Stream Amount	55.6671
Moles (True) - Liquid-1 (mol)	55.5037
Moles (True) - Vapor (mol)	0.163414
<b>Calculation Results</b>	
Ambient Temperature (°C)	25.0000
Ambient Pressure (atm)	1.00000
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	5.00004
Partial Pressure: N2 (atm)	0.968642
Condition that results were computed f	Ambient
<b>Inflows (mol)</b>	
H2O	55.5082
N2	0.158888
- Summary Box:**
  - Unit Set: Metric (moles)
  - Automatic Chemistry Model: MSE-SRK (H3O+ ion) Databanks: MSE-SRK (H3O+ ion), MSE (H3O+ ion)
  - Second Liquid phase: Using Helgeson Direct
  - Autoclave Calculation: Results for ambient conditions: Ambient Temperature 25.0000 °C, Ambient Pressure 1.00000 atm, Final Temperature 25.0000 °C, Final Pressure 1.00000 atm, Vessel Volume 5.00000 L, N2 0.968642 atm
  - Phase Amounts: Aqueous 55.5037 mol, Vapor 0.163414 mol, Solid 0.0 mol, 2nd Liquid 0.0 mol
  - Aqueous Phase Properties: pH 6.99756, Ionic Strength 1.81224e-9 mol/mol, Density 0.997061 g/ml
- Buttons:** Calculate, Input, Output, Advanced, Search, Add as Stream, 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<sub>2</sub>O 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<sub>2</sub> required to fill the 4-L headspace is 0.1589 moles; this amount is ~4-times greater than the first case, which is expected for gas with a low water solubility.

### ***Increasing the Final Temperature***

In this example, you will add 1 kg water to a 5 L autoclave and then fill the void (head space) with N<sub>2</sub>. The ambient temperature is 25 °C, and the final conditions will be 1 atm and 100 °C.

The purpose of this example is to raise the H<sub>2</sub>O partial pressure relative to N<sub>2</sub>. In the 5 L case above, the N<sub>2</sub> inflow is 0.1634 moles. As temperature increases, the H<sub>2</sub>O vapor pressure increases, and the amount of N<sub>2</sub> required to fill the vapor void will decrease.

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

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

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

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

	Variable	Value
<	<b>Stream Parameters</b>	
	Stream Amount (mol)	55.5082
	Ambient: Temperature (°C)	25.0000
	Ambient: Pressure (atm)	
<	<b>Calculation Parameters</b>	
	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
<	<b>Inflows (mol)</b>	
	H2O	55.5082
	N2	0.0

At this point the system is defined as 1 kg H<sub>2</sub>O (55.5082 moles) at an ambient temperature of 25 °C. The partial pressure of N<sub>2</sub> will be calculated at a final temperature, 100 °C and pressure, 50 atm in a 5 L vessel.

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

## Analyzing the Results

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

Variable	Value
<b>Stream Parameters (mol)</b>	
Stream Amount	55.5087
Moles (True) - Liquid-1 (mol)	55.5031
Moles (True) - Vapor (mol)	5.54881e-3
<b>Calculation Results</b>	
Ambient Temperature (°C)	25.0000
Ambient Pressure (atm)	0.0339414
Final Temperature (°C)	100.000
Final Pressure (atm)	1.00000
Vessel Volume (L)	5.00091
Partial Pressure: N2 (atm)	2.67276e-3
Condition that results were computed f	Ambient
<b>Inflows (mol)</b>	
H2O	55.5082
N2	4.38602e-4

Input    Output

Advanced    Search    Add as Stream    Export

Type of calculation: Autoclave    Specs...    Calculate

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model  
MSE-SRK (H3O+ ion) Databanks:  
  MSE-SRK (H3O+ ion)  
  MSE (H3O+ ion)  
Second Liquid phase  
Using Helgeson Direct

Autoclave Calculation  
Results for ambient conditions:  
Ambient Temperature 25.0000 °C  
Ambient Pressure 0.0339414 atm  
Final Temperature 100.000 °C  
Final Pressure 1.00000 atm  
Vessel Volume 5.00000 L  
N2 2.67276e-3 atm

Phase Amounts  
Aqueous 55.5031 mol  
Vapor 5.54881e-3 mol  
Solid 0.0 mol  
2nd Liquid 0.0 mol

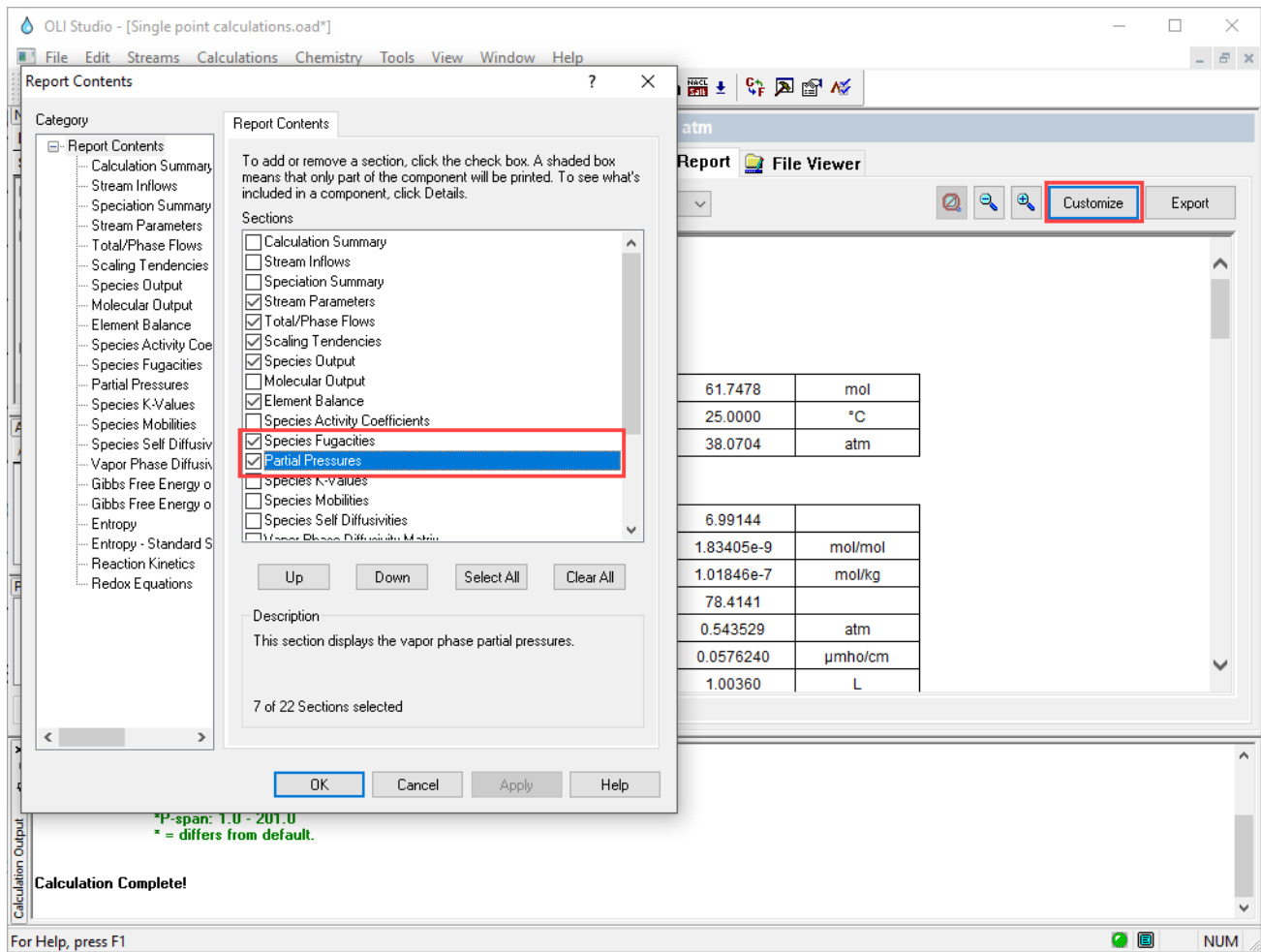
Aqueous Phase Properties  
pH 6.99772  
Ionic Strength 1.81169e-9 mol/mol  
Density 0.997021 g/ml

The amount of N<sub>2</sub> added is very small (~0.0004 moles). This is to be expected, because the vapor pressure of pure water at 100 °C is 1 atm. Therefore, a negligible amount of N<sub>2</sub> is needed to raise the pressure. Notice also that the calculated ambient pressure is 0.0339 atm. The vapor pressure of pure water at 25° C is 0.0313.

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

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

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



Notice that the **Fugacity** and **Partial Pressure** of N<sub>2</sub> are nearly identical. This is expected since at low pressure the fugacity approaches its partial pressure.

### Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.0312529
N2	2.67376e-3

### Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.0312686
N2	2.67276e-3

### Increasing the Final Pressure

In this example, you will add 1 kg water to a 5 L autoclave and then fill the void (head space) with N<sub>2</sub>. The ambient temperature is 25 °C, and the final conditions will be 100 atm and 100 °C.

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

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

**Name it** *Autoclave – Inert Gas Pf=100 atm*

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

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
<b>Calculation Parameters</b>	
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
<b>Inflows (mol)</b>	
H2O	55.5082
N2	0.0

At this point the system is defined as 1 kg H<sub>2</sub>O (55.5082 moles) at an initial temperature of 25 °C. The partial pressure of N<sub>2</sub> will be calculated at a final temperature of 100 °C and a final pressure of 100 atm in a 5 L vessel.

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

## Analyzing the Results

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

The screenshot displays a software interface with a table of variables and values, and a summary box on the right.

Variable	Value
<b>Stream Parameters (mol)</b>	
Stream Amount	67.9053
Moles (True) - Liquid-1 (mol)	55.5441
Moles (True) - Vapor (mol)	12.3611
<b>Calculation Results</b>	
Ambient Temperature (°C)	25.0000
Ambient Pressure (atm)	75.7159
Final Temperature (°C)	100.000
Final Pressure (atm)	100.000
Vessel Volume (L)	5.00000
Partial Pressure: N2 (atm)	75.6782
Condition that results were computed f	Ambient
<b>Inflows (mol)</b>	
H2O	55.5082
N2	12.3970

Summary:

Unit Set: Metric (moles)

Automatic Chemistry Model  
MSE-SRK (H3O+ ion) Databanks:  
MSE-SRK (H3O+ ion)  
MSE (H3O+ ion)  
Second Liquid phase  
Eoson Direct

Autoclave Calculation  
Results for ambient conditions:  
Ambient Temperature 25.0000 °C  
Ambient Pressure 75.7159 atm  
Final Temperature 100.000 °C  
Final Pressure 100.000 atm  
Vessel Volume 5.00000 L  
N2 75.6782 atm

Phase Amounts  
Aqueous 55.5441 mol  
Vapor 12.3611 mol  
Solid 0.0 mol  
2nd Liquid 0.0 mol

Aqueous Phase Properties  
pH 6.98515  
Ionic Strength 1.85714e-9 mol/mol  
Density 1.00012 g/ml

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

According to the calculation, the amount of  $N_2$  in the autoclave is 12.397 moles. This amount of  $N_2$  plus the 55.5082 moles of  $H_2O$  produces a final pressure of 100 atm in a 5 L autoclave at 100 °C.

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

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

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

100 °C and 1 atm

### Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	atm
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	0.0330213
N2	76.0121

### Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	atm
H2O	0.0376589
N2	75.6782

Notice that at low pressures, the partial pressures and fugacities values of both H<sub>2</sub>O and N<sub>2</sub> are nearly identical. At the higher pressure, i.e., 100 atm, the partial pressures and fugacities of H<sub>2</sub>O and N<sub>2</sub> start to differ.

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

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

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

Where,

$\varphi$  is the fugacity coefficient

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

## Example 13: Using Reactive Gases

### Calculating Results at Final Conditions

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

You will then modify the case further by adding NaOH so that additional CO<sub>2</sub> dissolves in water to form bicarbonate.

### Starting the Simulation

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

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

Add a new **Stream**

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

Select the **MSE-SRK** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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

Enter the **CO2 and NaOH** as **inflows**

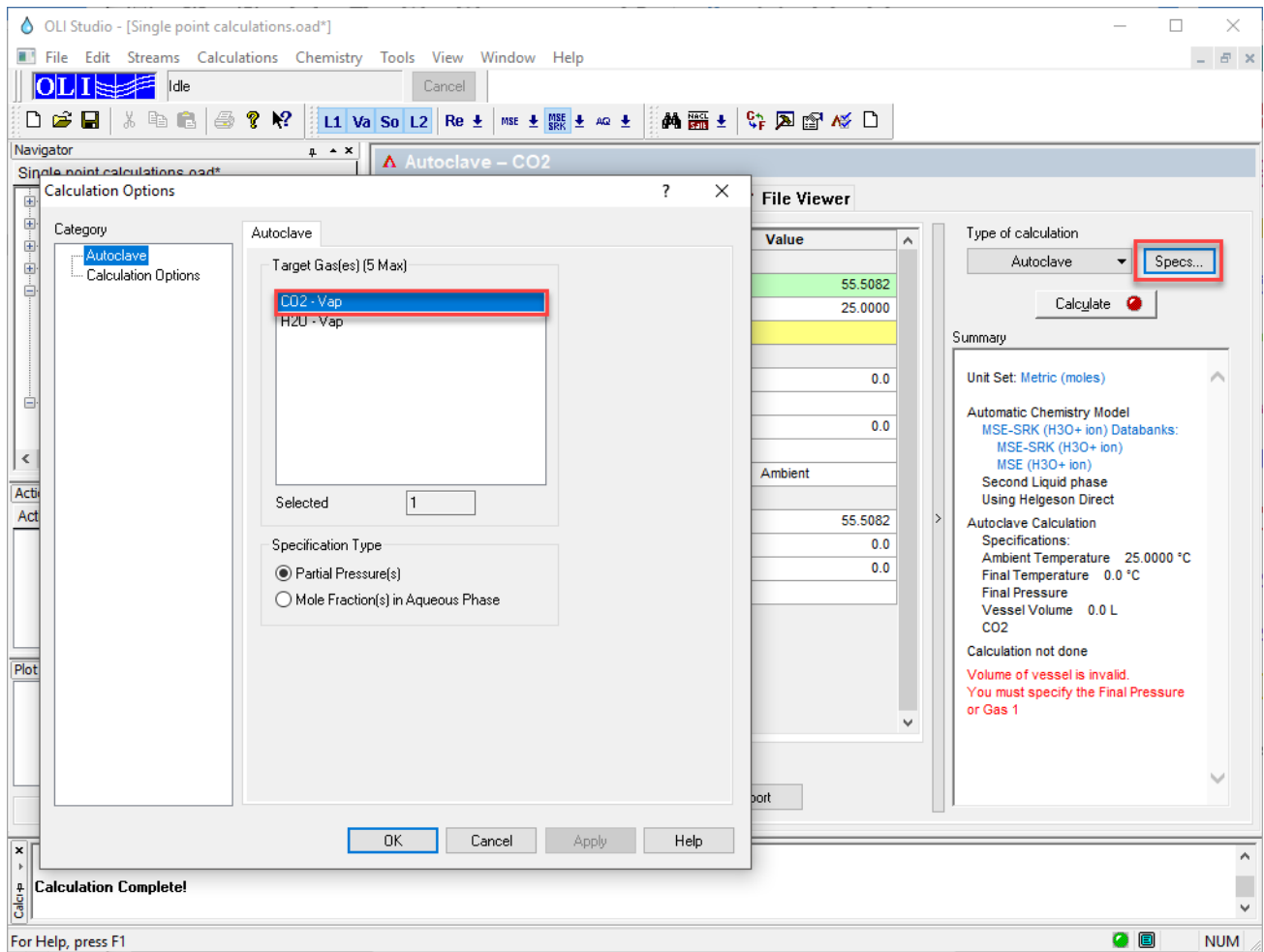
Go to the **Add Calculation** button and select **Single Point** calculation

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

Select **Autoclave** as Type of Calculation

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

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



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

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
<b>Calculation Parameters</b>	
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
<b>Inflows</b>	
H2O	Final
CO2	Ambient
NaOH	0.0
	0.0

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

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

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

### Analyzing the Results

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

The screenshot displays the software interface with the following components:

- Navigation Tabs:** Description, Definition, Report, File Viewer.
- Table:**

Variable	Value
<b>Stream Parameters (mol)</b>	
Stream Amount	55.5808
Moles (True) - Liquid-1 (mol)	55.5397
Moles (True) - Vapor (mol)	0.0409464
<b>Calculation Results</b>	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	2.00001
Partial Pressure: CO <sub>2</sub> (atm)	0.968445
Condition that results were computed for	Final
<b>Inflows (mol)</b>	
H <sub>2</sub> O	55.5082
CO <sub>2</sub>	0.0725227
- Summary Box:**
  - Type of calculation: Autoclave
  - Unit Set: Metric (moles)
  - Automatic Chemistry Model: MSE-SRK (H3O+ ion) Databanks: MSE-SRK (H3O+ ion), MSE (H3O+ ion)
  - Second Liquid phase Using Helgeson Direct
  - Autoclave Calculation Results for final conditions:
    - Ambient Temperature: 25.0000 °C
    - Final Temperature: 25.0000 °C
    - Final Pressure: 1.00000 atm
    - Vessel Volume: 2.00000 L
    - CO<sub>2</sub>: 0.968445 atm
  - Phase Amounts:
    - Aqueous: 55.5397 mol
    - Vapor: 0.0409464 mol
    - Solid: 0.0 mol
    - 2nd Liquid: 0.0 mol
  - Aqueous Phase Properties:
    - pH: 3.91452
    - Ionic Strength: 2.21620e-6 mol/mol
    - Density: 0.997452 g/ml
  - Calc. elapsed time: 5.376 sec.

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

To analyze the CO<sub>2</sub> distribution in more detail, go to the **Report** Tab, and Scroll down until you find the **Element Distribution** table.

### Element Distribution

	Total	Total	Liquid-1	Vapor
	mol	mole %	% of Total	% of Total
H(+1)	111.016	66.5797	99.9977	2.32772e-3
O(-2)	55.6533	33.3768	99.8552	0.144827
C(+4)	0.0725227	0.0434939	45.3215	54.6785

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

### Using Reactive Gas and NaOH solution

In this example, you will further modify the chemistry by adding NaOH so that additional CO<sub>2</sub> dissolves in water to form bicarbonate. This will increase the gas requirement.

#### Starting the Simulation

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

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

**Name it** *Autoclave – CO2 – NaOH*

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

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

At this point the system is defined as 1 kg H<sub>2</sub>O (55.508 moles) and 0.1 moles of NaOH at an ambient temperature of 25 °C. The partial pressure of CO<sub>2</sub> will be calculated at a final temperature, 25 °C and final pressure, 1 atm in a 2 L vessel.

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

#### Analyzing the Results

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

Inflows (mol)	
H2O	55.5082
CO2	0.171600
NaOH	0.100000

The CO<sub>2</sub> inflow is calculated to be 0.1716 moles. This is exactly 0.1 moles more than the calculation with only CO<sub>2</sub> (Example 13-1). The difference results from the acid-base reaction with the 0.1 moles of NaOH.

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

### Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor
	mol	mol	mol
H2O	55.5083	55.507	1.28481e-3
Na+1	0.1	0.1	
HCO3-1	0.0998917	0.0998917	
CO2	0.0716555	0.0320887	0.0395668
CO3-2	5.42505e-5	5.42505e-5	
H3O+1	2.3994e-7	2.3994e-7	
OH-1	6.87229e-8	6.87229e-8	
NaOHCO3-2	2.76574e-14	2.76574e-14	
NaOH	3.90126e-15	3.90126e-15	
<b>Total (by phase)</b>	<b>55.7799</b>	<b>55.7391</b>	<b>0.0408516</b>

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

## Custom

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

### Example 14: Solubility of Oxygen in Water

With a custom calculation, we are going to calculate the solubility of O<sub>2</sub> in water at 25°C and 1 atm.

#### Starting the Simulation

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

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

#### Setting the pH

Add a new **Stream**

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

Select the **MSE** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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

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

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

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

Change the **T** to **30 °C** and **P** to **4 atm**

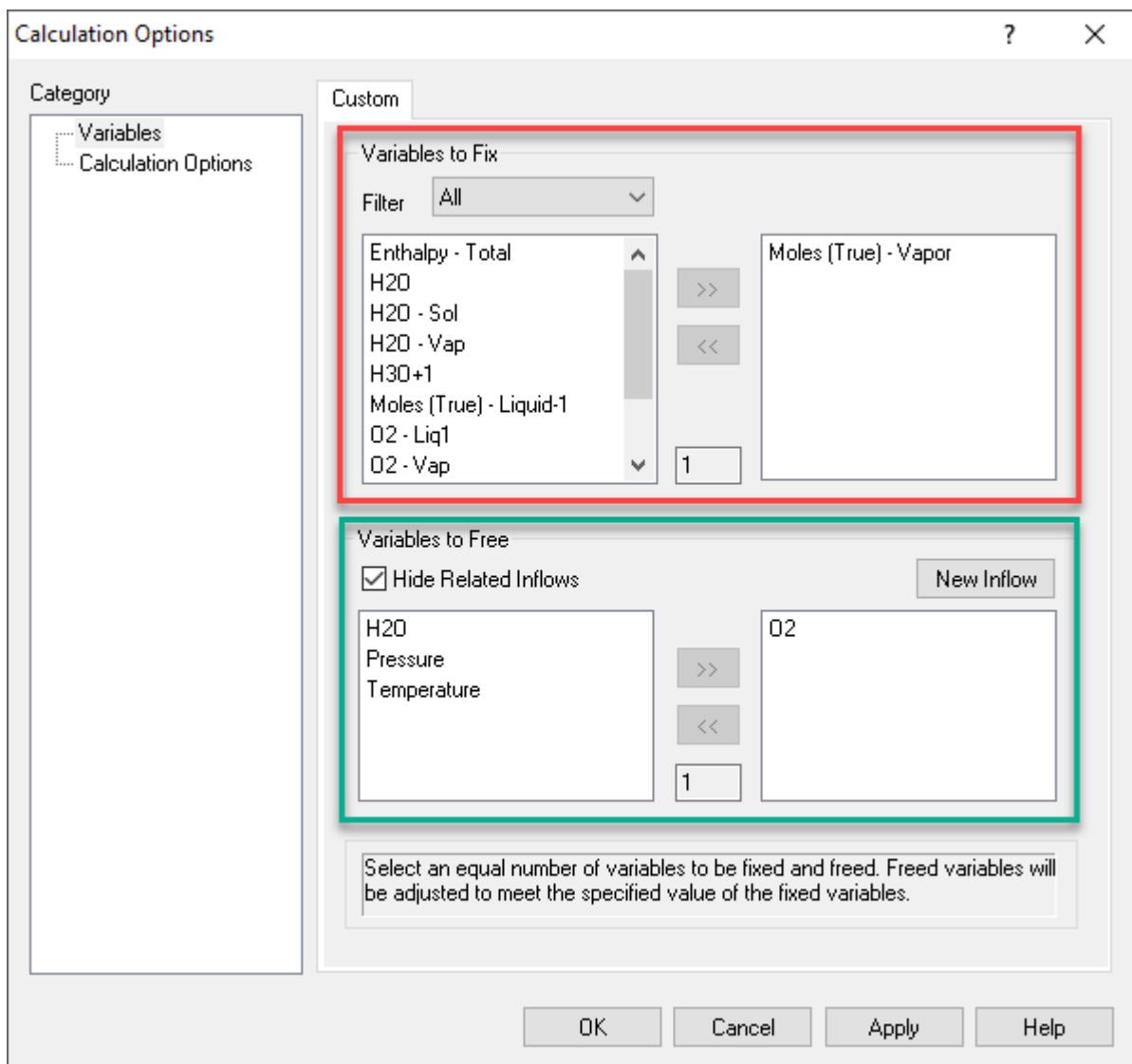
Go to the **Add Calculation** button and select **Single Point** calculation

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

Select **Custom** as Type of Calculation

Select the **Specs** button. This will open the **Calculation Options window**

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



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

This will add a **Calculation Parameters** section, where the Target (Variable to Fix) and the Adjusted Inflow (Variable to Free) are shown. The Target has a brown dot in front of it indicating that the Target: Moles (True) - Vapor is fix value. The Adjusted Inflow value font is green indicating that the software will adjust this value.

The screenshot shows a software interface with a main table and a summary panel on the right.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (kg)	1.00000
Temperature (°C)	30.0000
Pressure (atm)	4.00000
<b>Calculation Parameters</b>	
● Target: Moles (True) - Vapor (mol)	0.0
Adjusted: O2 (ppm (mass))	0.0
<b>Inflows (ppm (mass))</b>	
H2O	1.00000e6
Adjusted: O2	

Summary Panel:

- Type of calculation: Custom
- Calculate button (with a red error icon)
- Unit Set: <Custom>
- Automatic Chemistry Model
  - MSE (H3O+ ion) Databanks: MSE (H3O+ ion)
  - Using Helgeson Direct
- Custom Calculation
  - Fixed variable: Moles (True) - Vapor, target: 0.0 mol
  - Free variable: O2
- Calculation not done
- Moles (True) - Vapor must be greater than 0.0.**

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

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

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

## Analyzing the Results

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

The screenshot displays a software interface with a main table and a summary panel on the right. The table is organized into sections: Stream Parameters, Calculation Results, and Inflows (ppm (mass)). The 'Adjusted: O2' row in the Inflows section is highlighted with a red box. The summary panel on the right contains a 'Custom Calculation' section, also highlighted with a red box, which lists fixed and free variables and their values. Below this, phase amounts and aqueous phase properties are listed.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (kg)	1.00015
Mass - Liquid-1 (kg)	1.00015
Mass - Vapor (kg)	3.18493e-9
Temperature (°C)	30.0000
Pressure (atm)	4.00000
<b>Calculation Results</b>	
Target: Moles (True) - Vapor (mol)	1.00000e-7
<b>Inflows (ppm (mass))</b>	
H2O	9.99854e5
Adjusted: O2	146.938

**Summary**

Unit Set: <Custom>

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

**Custom Calculation**

Fixed variable:  
Moles (True) - Vapor, target:  
1.00000e-7 mol

Free variable:  
O2, total:  
146.938 ppm (mass)

**Phase Amounts**

Aqueous 1.00015 kg  
Vapor 3.18493e-9 kg  
Solid 0.0 kg

**Aqueous Phase Properties**

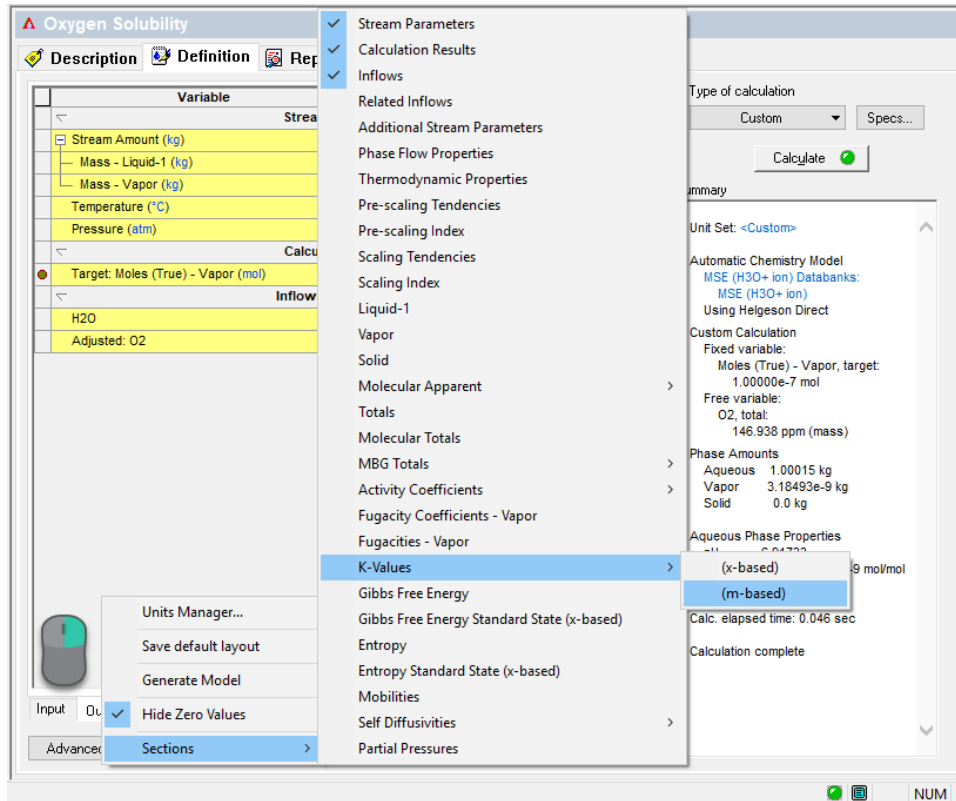
pH 6.91733  
Ionic Strength 2.18165e-9 mol/mol  
Density 0.995710 g/ml

Calc. elapsed time: 1.053 sec  
Calculation complete

At 30°C and 4 atm the solubility of O<sub>2</sub> in water is 146.94 ppm (mass)

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

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



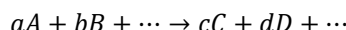
The reciprocal of  $K_{O2VAP}$ :  $O2VAP=O2AQ$  will give you an estimate of the Henry's constant.

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

## Reaction Kinetics

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

For the stoichiometric reaction below:



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 constant between reaction rate and concentration).

The general rate law is generally expressed as:

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

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

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

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

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

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

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

$A$  = Arrhenius frequency factor (*has same units as k*)

$E_a$  = Activation energy ( $\frac{\text{joule}}{\text{gmole}}$ )

$R$  = Universal gas constant ( $8.314 \frac{\text{joule}}{\text{gmole K}}$ )

$T$  = Temperature (K)

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

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

**Non-Standard Rate Law**, referred to as SPEC type within the software.

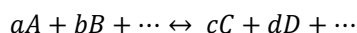
In this section, we will show you how to set up both types of reaction kinetics.

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

## Standard Rate Law

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

For the reaction below:



where:  $a, b, \dots, c, d$  are stoichiometric coefficients

$A, B, \dots$  are reactant species

$C, D, \dots$  are product species

The rate law is of the form:

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

where:

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

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

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

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

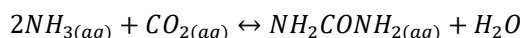
species order coefficients for the forward and reverse reactions if these differ from the stoichiometric coefficients (which are the default).

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

If any of the keywords are not defined, the software assumes a default value for that variable. These default values are assumed to be zero for the reaction rate constants, 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:



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.

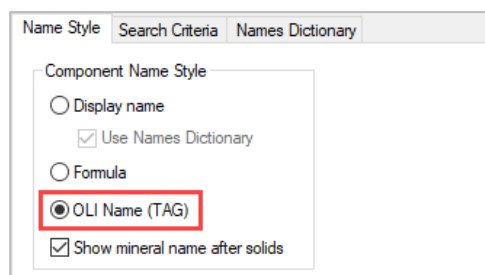
Single Point Calculation with Reaction Kinetics Enabled			
Calculation Settings		Stream Composition and Conditions	
Calculation Type	Single Point Calculation	Stream Amount	Calculated
Calculation Sub-type	Isothermal	Temperature	200 °C
Stream Name	Standard Rxn Kinetics	Pressure	100 atm
Single Point Name	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		

Add a new **Stream**

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

Select the **AQ** thermodynamic Framework

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



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

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

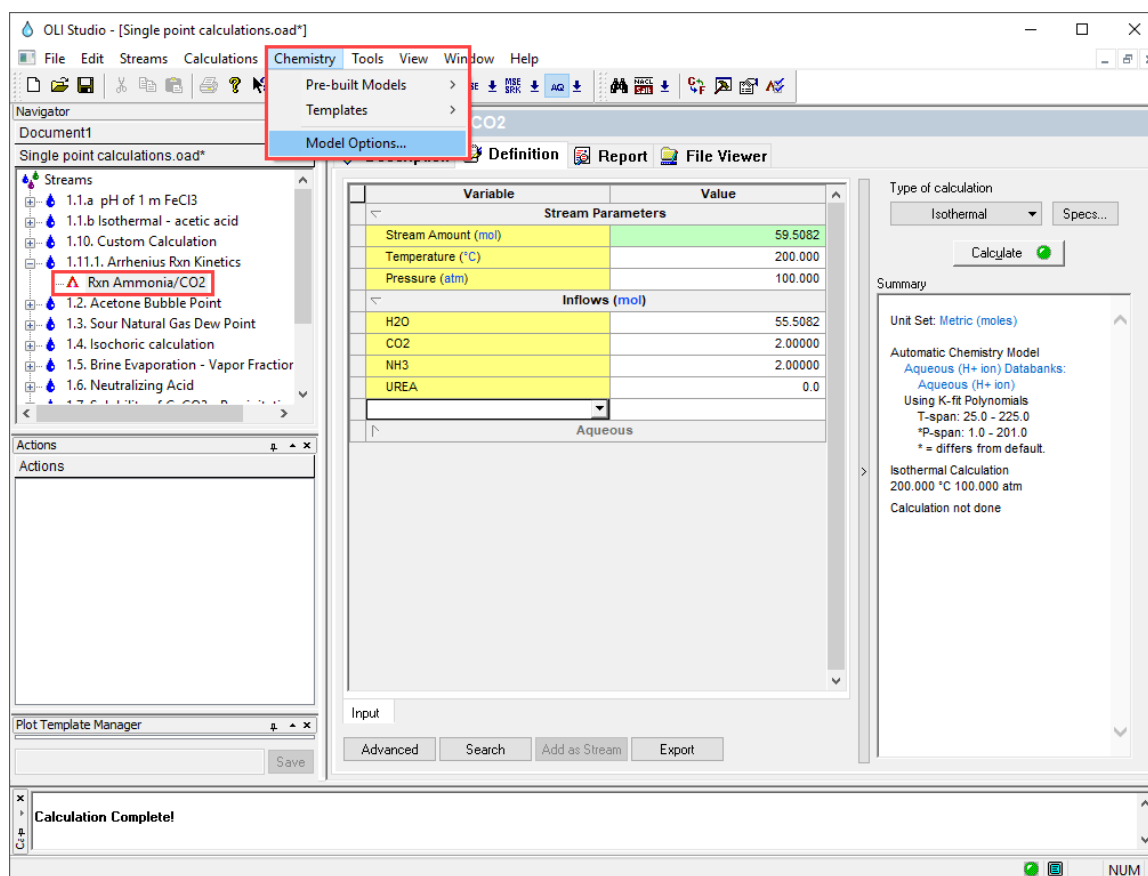
Go to the **Add Calculation** button and select **Single Point** calculation

Select **Isothermal** (default) as Type of Calculation.

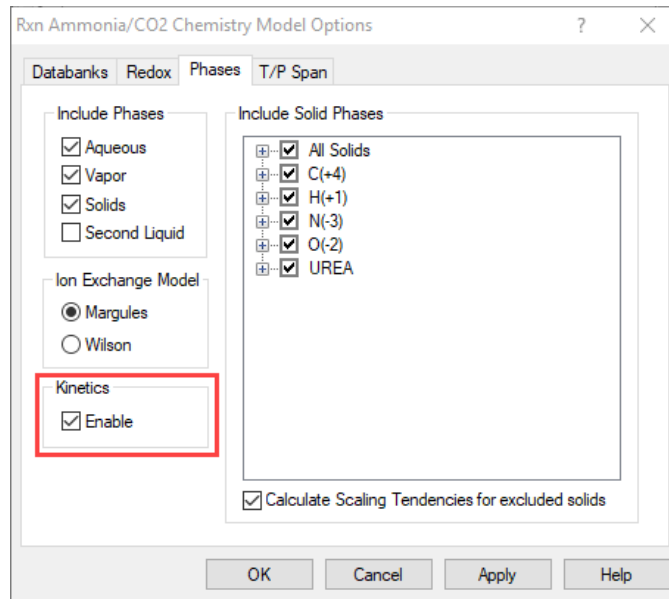
Change the **SinglePoint** name to **Rxn Ammonia/CO2** using the <F2> key

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

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

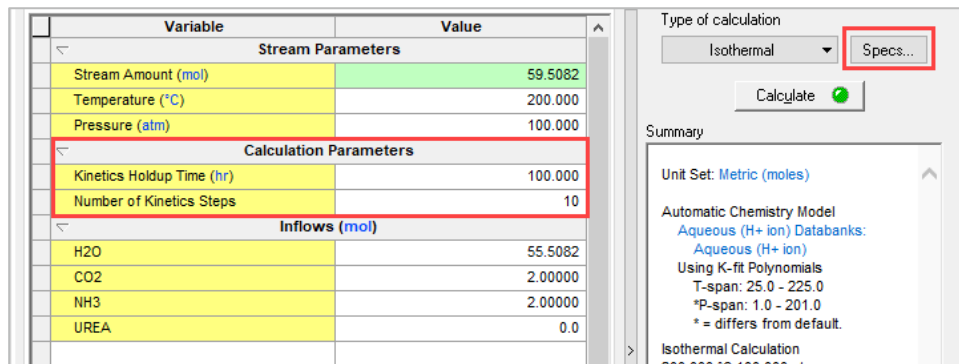


Select the **Phases** tab and check the **Kinetics** box. Then click **OK**.



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

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



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

**Note: Kinetics Holdup Time vs Number of Kinetic Steps**

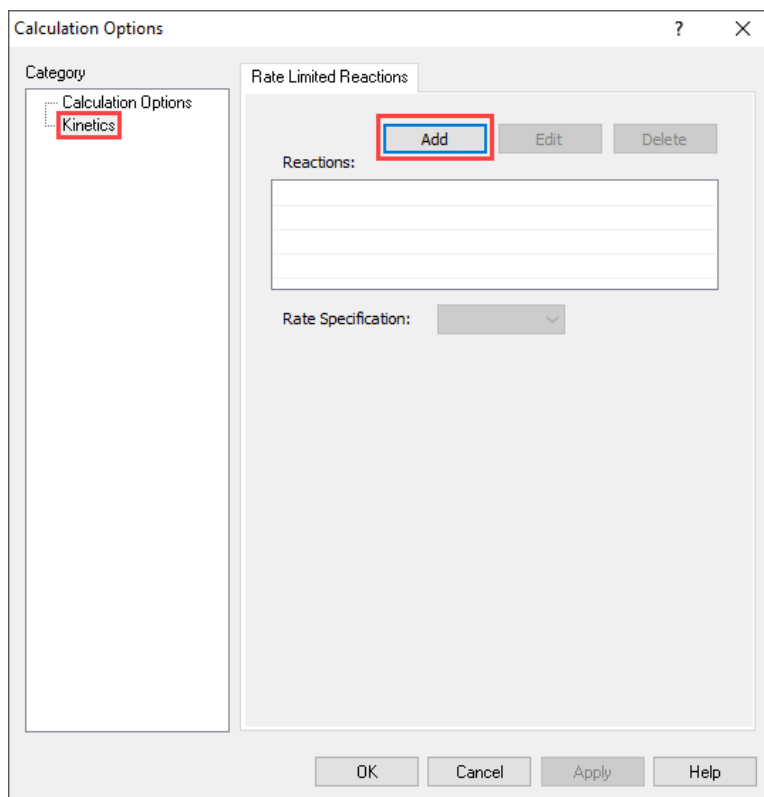
For processes that have reaction kinetics, the software needs to know how the concentration of the reactants (or products) change over time during the reaction, which is given by the **rate law**. It is necessary to divide the total residence time into small steps. Adding more steps decreases the error;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

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

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

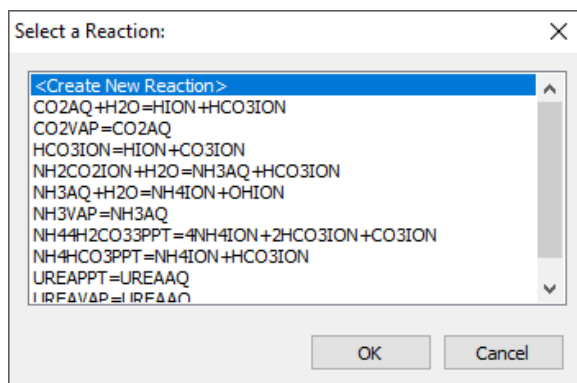
Select **Kinetics** under the Category window

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



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

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



This enables the option to enter a new reaction.

**Type** the following reaction:  $2\text{NH}_3\text{AQ}+\text{CO}_2\text{AQ}=\text{UREAAQ}+\text{H}_2\text{O}$  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.nH<sub>2</sub>O, where n is the hydration number

For an ion: ION

You can find the OLI TAG Name of your specific species using the [Component Search Tool](#).

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

Calculation Options

Category

- Calculation Options
- Kinetics

Rate Limited Reactions

Reactions:

2NH3AQ+CO2AQ=UREAAQ+H2O

Rate Specification: STD

Rate Constants:

Constant	Value
----------	-------

OK Cancel Apply Help

Now, let's start entering the rate constants.

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

$$R = k_f[\text{NH}_3]^2[\text{CO}_2] - kr[\text{NH}_2\text{CONH}_2]$$

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:

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

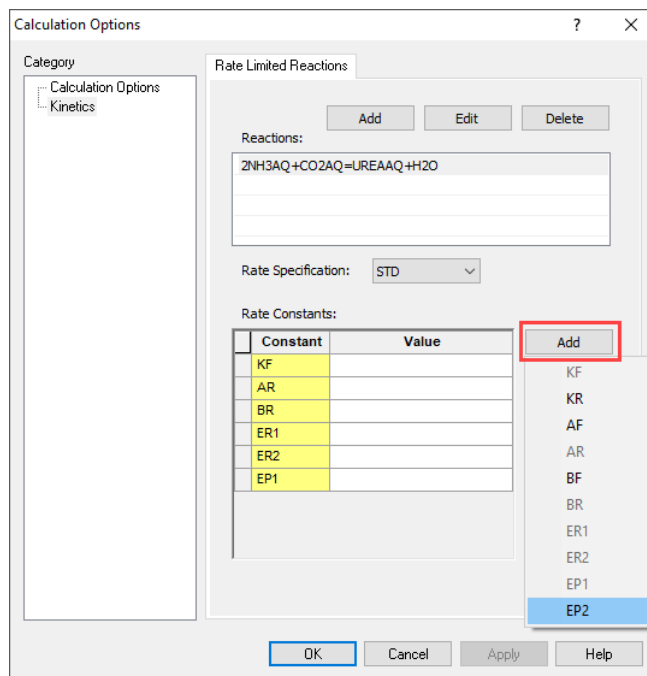
$$KR = 1.2 \times 10^{-10} e^{\frac{-3480.78}{T}}$$

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

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

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

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



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

Calculation Options

Category

- Calculation Options
  - Kinetics

Rate Limited Reactions

Reactions: Add Edit Delete

2NH3AQ+CO2AQ=UREAAQ+H2O

Rate Specification: STD

Rate Constants:

Constant	Value
KF	2000
AR	1.2e-10
BR	3480.78
ER1	2
ER2	1
EP1	1
EP2	0

Add Delete

OK Cancel Apply Help

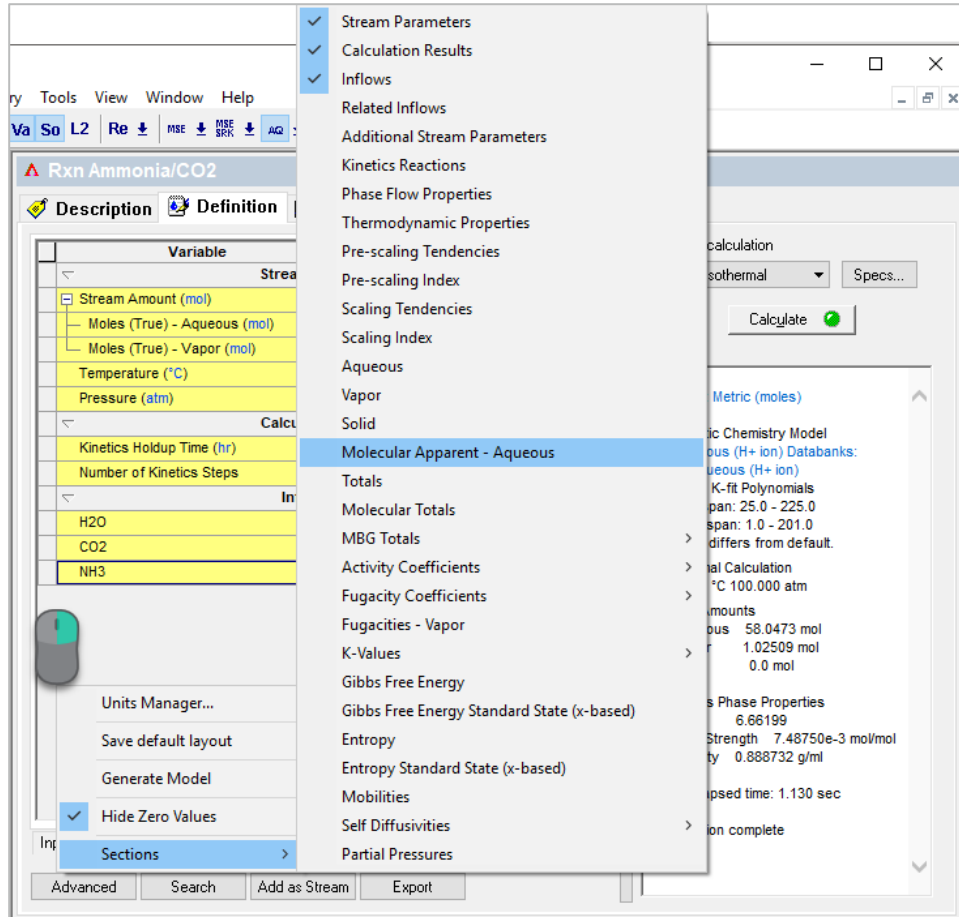
We are ready to perform the calculation. Click on the **Calculate** button or press the **<F9>** key.

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

## Analyzing the Results

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

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



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

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

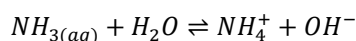
You can make changes on the residence time, reaction conditions or the rate of reaction to maximize the production of urea.

## Non-standard Rate Law

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

### Example 16: Ammonia Hydrolysis

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



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 °C
Stream Name	Non-Standard Rxn Kinetics	Pressure	1 atm
Single Point Name	Ammonia Hydrolysis	Water	55.5082
Name Style	Display OLI Name (TAG)	NH3	0.1 moles
Unit Set	Metric, Moles		
Framework	AQ		
Kinetics	Enabled		

Add a new **Stream**

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

Select the **AQ** thermodynamic Framework

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

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

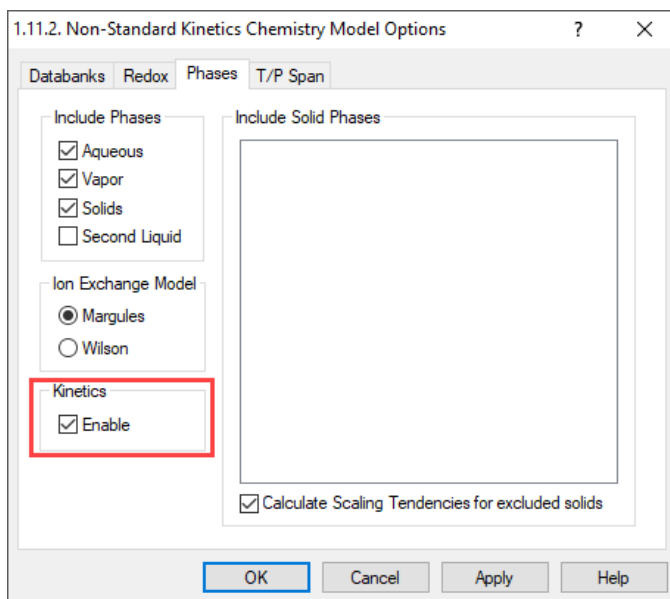
**Enter** the stream composition, temperature and pressure given in the table above.

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

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

Select **Isothermal** (default) as Type of Calculation.

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



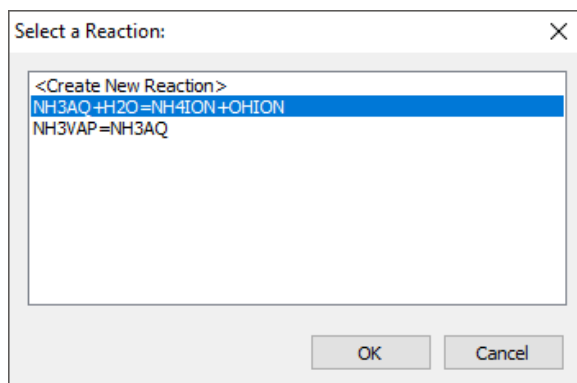
Now, our next step is to define the reaction kinetics.

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

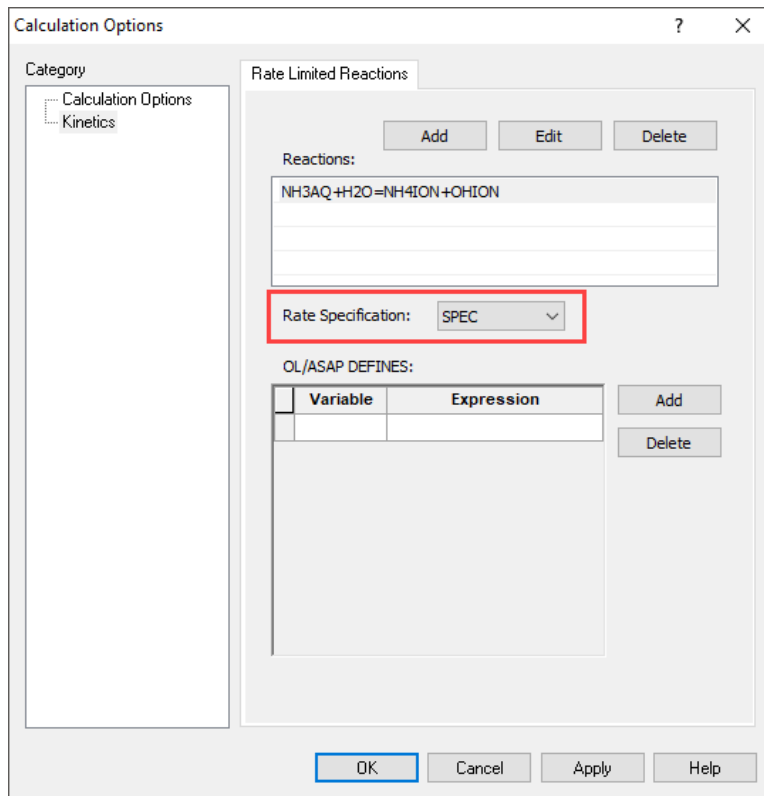
Select **Kinetics** under the Category window

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

**Select** the first reaction:  $\text{NH}_3\text{AQ} + \text{H}_2\text{O} = \text{NH}_4\text{ION} + \text{OHION}$ , and then click **OK**.



Select the SPEC as the Rate Specification.



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

$$Rate_f = k_f \cdot \gamma_{NH_3,aq} [NH_{3,aq}] \cdot \gamma_{H_2O} [H_2O] \quad \text{where } k_f = 3$$

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

Thus, the total rate is given by:

$$Rate = Rate_f - Rate_r$$

$$Rate = k_f \cdot \gamma_{NH_3,aq} [NH_{3,aq}] \cdot \gamma_{H_2O} [H_2O] - k_r \cdot \gamma_{NH_4^+} [NH_4^+] \cdot \gamma_{OH^-} [OH^-]$$

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

We now need to turn these values into "OLI" terms<sup>5</sup>.

---

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

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

Similarly, activity coefficients  $\gamma$  are also taken as the natural log. So,  $\gamma_{\text{OH}^-}$  is written as  $\text{Log}_e \gamma_{\text{OH}^-} = \text{AOHION}$ .

KEQ is the thermodynamic equilibrium constant for the equation. AH2O is special in the Aqueous thermodynamic framework in that it is the variable  $\text{Ln}(a_{\text{H}_2\text{O}})$ .

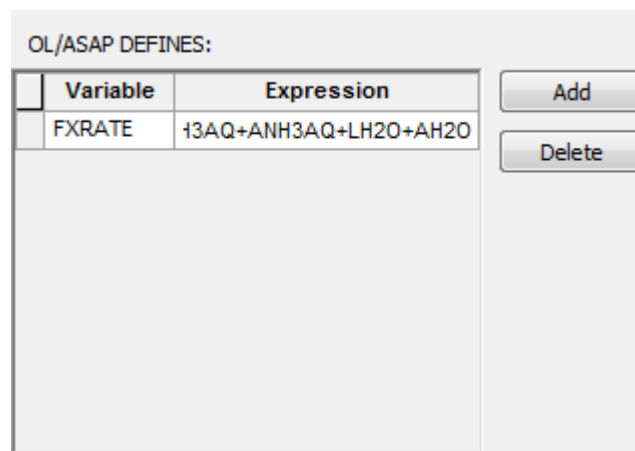
We now need to add these variables to the kinetics window<sup>6</sup>:

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

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

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

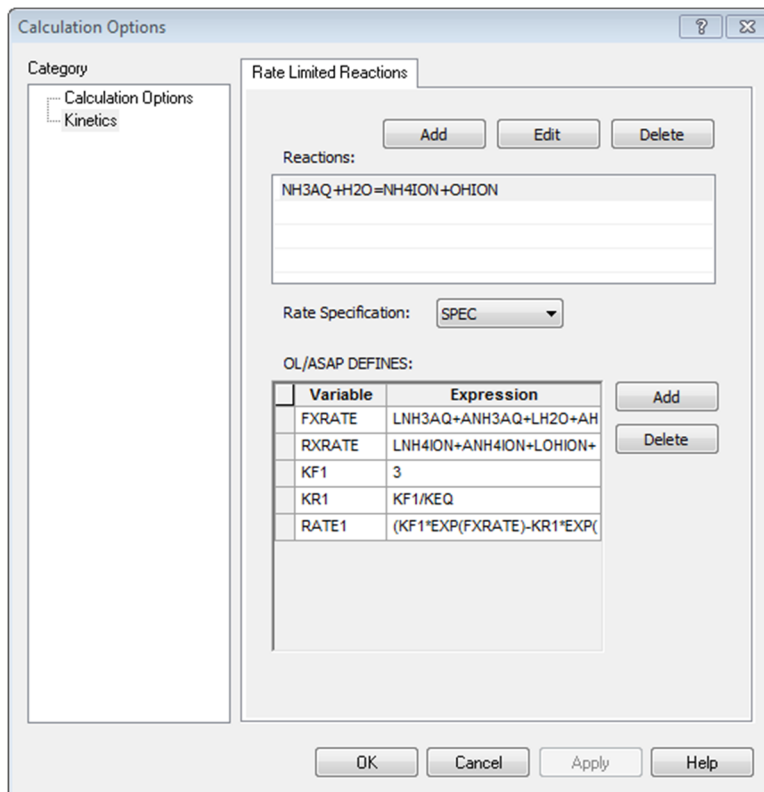
Change the **Kinetics Holdup Time** to **100** hours and the **Number of Kinetic Steps** to **10**.



<sup>6</sup> Copy and paste from this document can make this step easier

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

Complete the remainder of the variables.



The completed equations

Click the **OK** button.

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

Now **Calculate**

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

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.6082
Moles (True) - Aqueous (mol)	55.6082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Results</b>	
Kinetics Holdup Time (hr)	100.000
Number of Kinetics Steps	10
<b>Inflows (mol)</b>	
H2O	55.5082
NH3	0.100000
<b>Aqueous (mol)</b>	
H2O	55.5077
NH3	0.0994574
OHION	5.42587e-4
NH4ION	5.42587e-4
HION	1.97028e-11

Type of calculation: Isothermal  
 Summary:  
 Unit Set: Metric (moles)  
 Automatic Chemistry Model: AQ (H+ ion) Databanks: Public  
 Isothermal Calculation: 25.0000 °C 1.00000 atm  
 Phase Amounts:  
   Aqueous: 55.6082 mol  
   Vapor: 0.0 mol  
   Solid: 0.0 mol  
 Aqueous Phase Properties:  
   pH: 10.7171  
   Ionic Strength: 9.75731e-6 mol/mol  
   Density: 0.996159 g/ml  
 Calc. elapsed time: 0.387 sec  
 Calculation complete

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

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

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

The reaction kinetics have forced the back reaction to be dominant. In the equilibrium case, approximately  $1.3 \times 10^{-3}$  moles of  $\text{NH}_4^+$  have been created. By limiting the forward reactions, we allow the back reaction to take place and that only formed  $5.4 \times 10^{-4}$  moles of  $\text{NH}_4^+$ .

## Section 2. Survey Calculations

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

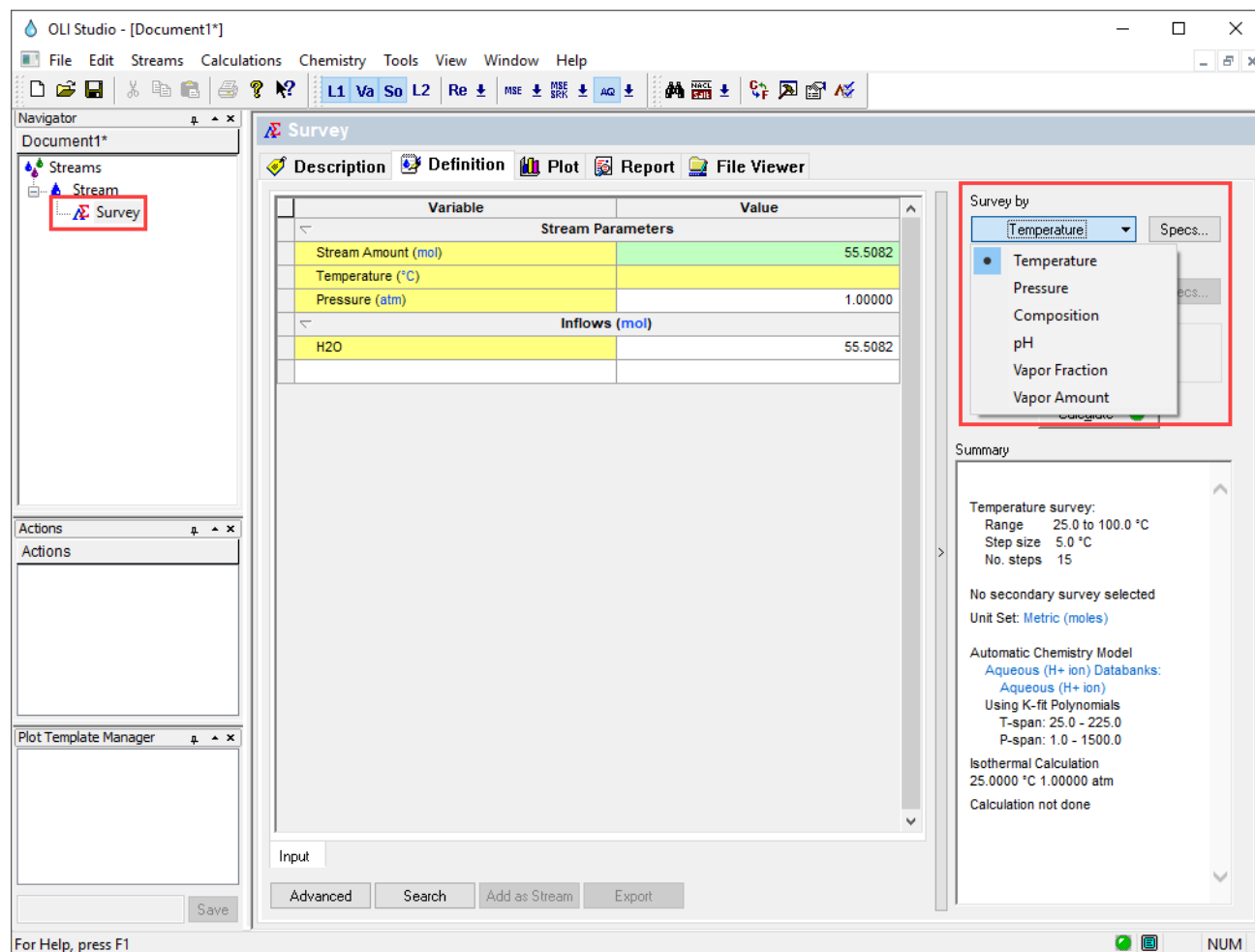
There are three different ways to set up surveys:

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

**Dual Survey:** These calculations allow the user to designate two independent variables.

**Survey by changing the single point calculation type:** By default, the isothermal calculation is selected for survey calculations. If the user wants to study the solubility of a salt in solution, it is possible to change the survey from **Isothermal** to another calculation type like **Precipitation Point**.

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



The screenshot shows the OLI Studio interface for configuring a survey. The 'Survey by' dropdown menu is open, showing the following options:

- Temperature (selected)
- Pressure
- Composition
- pH
- Vapor Fraction
- Vapor Amount

The main window displays a table of variables and values:

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.5082
Temperature (°C)	
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
H2O	55.5082

The summary panel on the right shows the following details:

Temperature survey:  
Range 25.0 to 100.0 °C  
Step size 5.0 °C  
No. steps 15

No secondary survey selected  
Unit Set: Metric (moles)

Automatic Chemistry Model  
Aqueous (H+ ion) Databanks:  
Aqueous (H+ ion)  
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

## Single Surveys

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

### *Example 17: Removal of Nickel from Wastewater*

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

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

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

This example will be divided into three different scenarios:

[Scenario 1: Wastewater without Additives](#)

[Scenario 2: Wastewater with Cyanide Content](#)

[Scenario 3: Wastewater with Sulfide Salts](#)

The power of the Stream Analyzer becomes apparent when we are seeking to study the chemistry of individual streams. For this specific example a Survey by **pH** will be used. We will also be using the **AQ** thermodynamic model instead of the default MSE model.

## Scenario 1: Wastewater without Additives

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

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

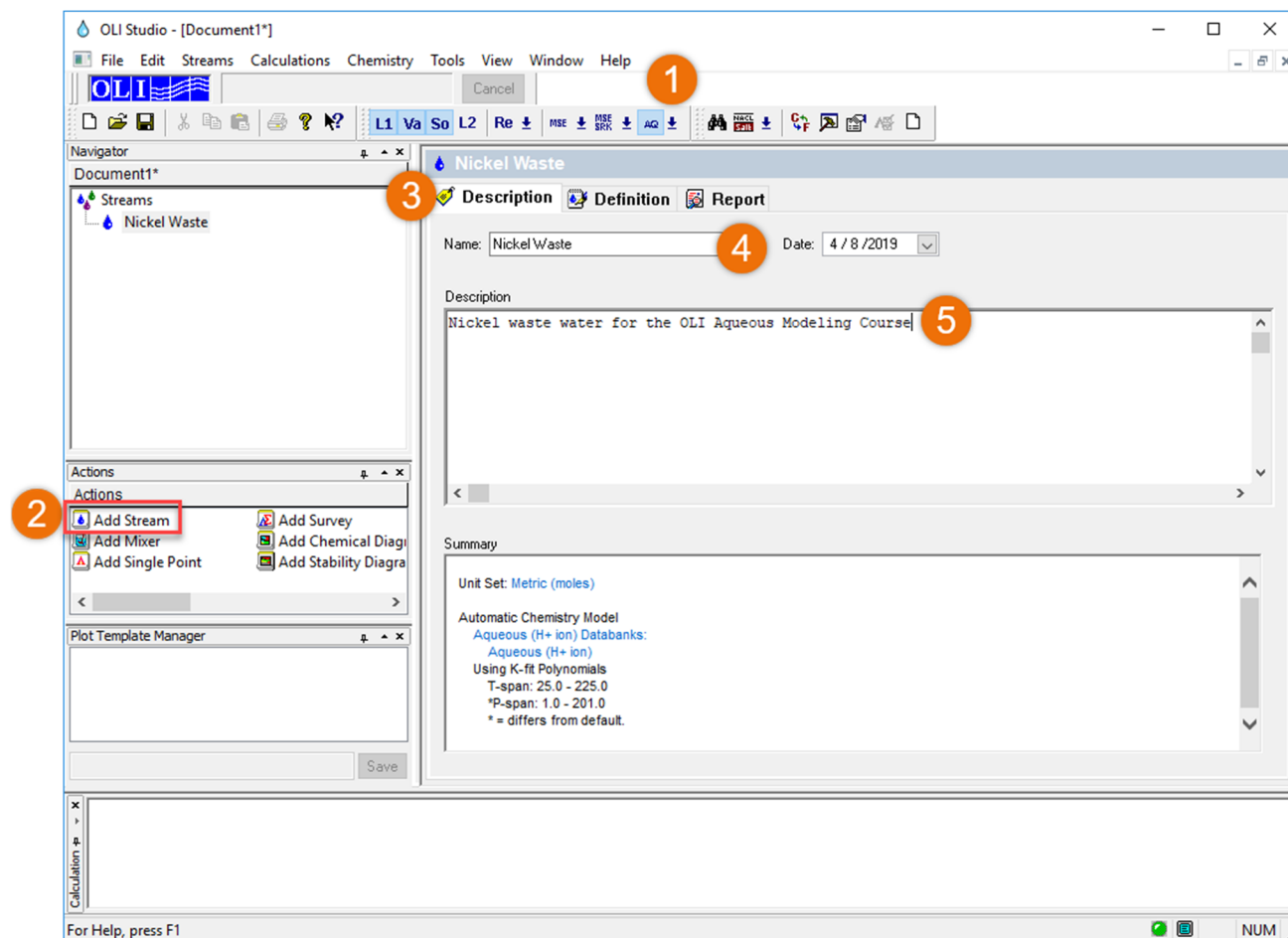
Click on **Add Stream** icon (in the actions panel). This will display the **Definition** window. We should add some descriptive information about this stream, so we can later identify the stream

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

Replace the name **Stream** with the name **Nickel Waste**. It is advisable to change the name of the stream from the default name. You may be entering many streams and will need to sort them out later

Add the following text to the **Description** box: “*Nickel wastewater for the OLI Aqueous Modeling Course*”


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




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

Click in the white box in the grid below the **Inflows** line. Add the formula **Ni(OH)<sub>2</sub>**

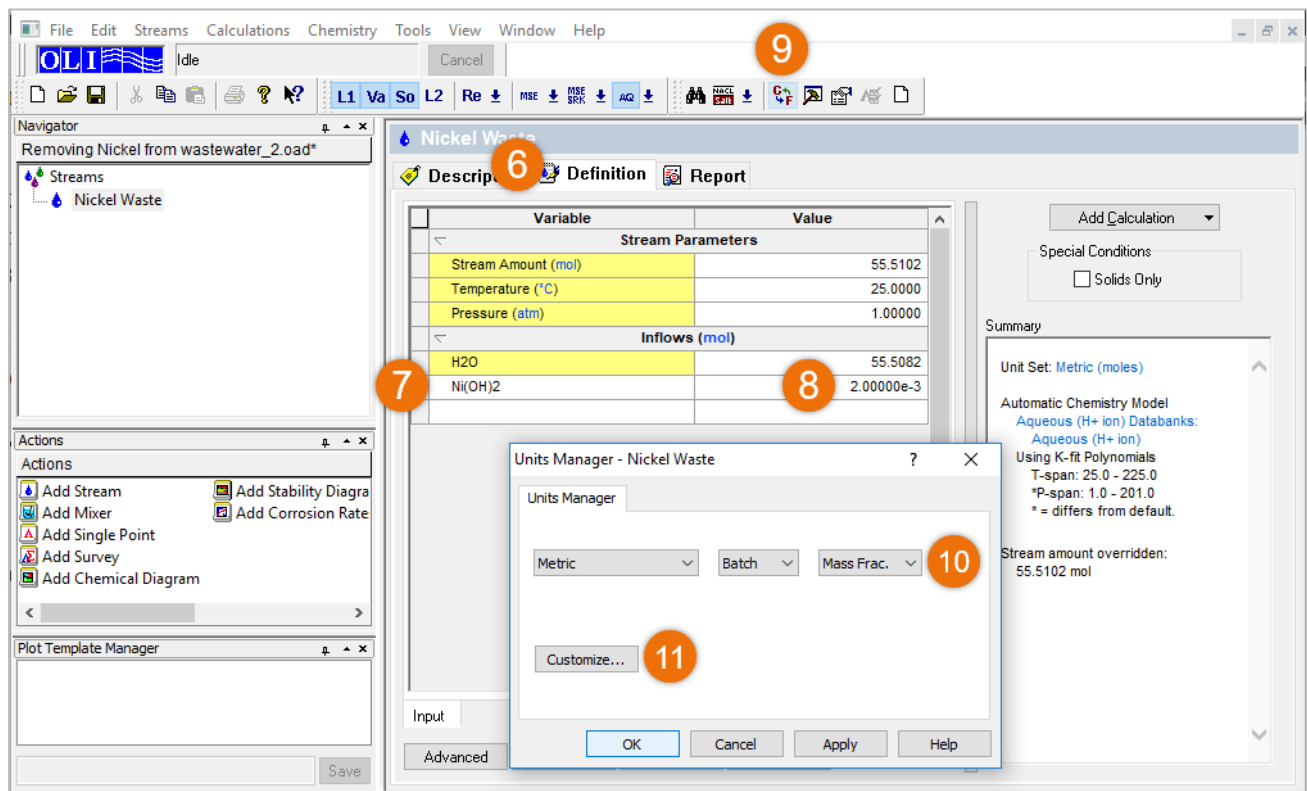
Click in the white box next to the species you just entered and enter the value **0.002**. Press **<Enter>** to update the list

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

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

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

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



The screenshot shows the OLI software interface with the 'Nickel Waste' stream definition window open. The 'Definition' tab is selected, showing a table of variables and values. The 'Inflows (mol)' section is expanded, showing H2O and Ni(OH)<sub>2</sub> with their respective values. The 'Units Manager - Nickel Waste' dialog box is open, showing the 'Metric' unit set and the 'Mass Frac.' unit selected. The 'Customize...' button is highlighted.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH) <sub>2</sub>	2.00000e-3

Units Manager - Nickel Waste

Units Manager

Metric Batch Mass Frac.

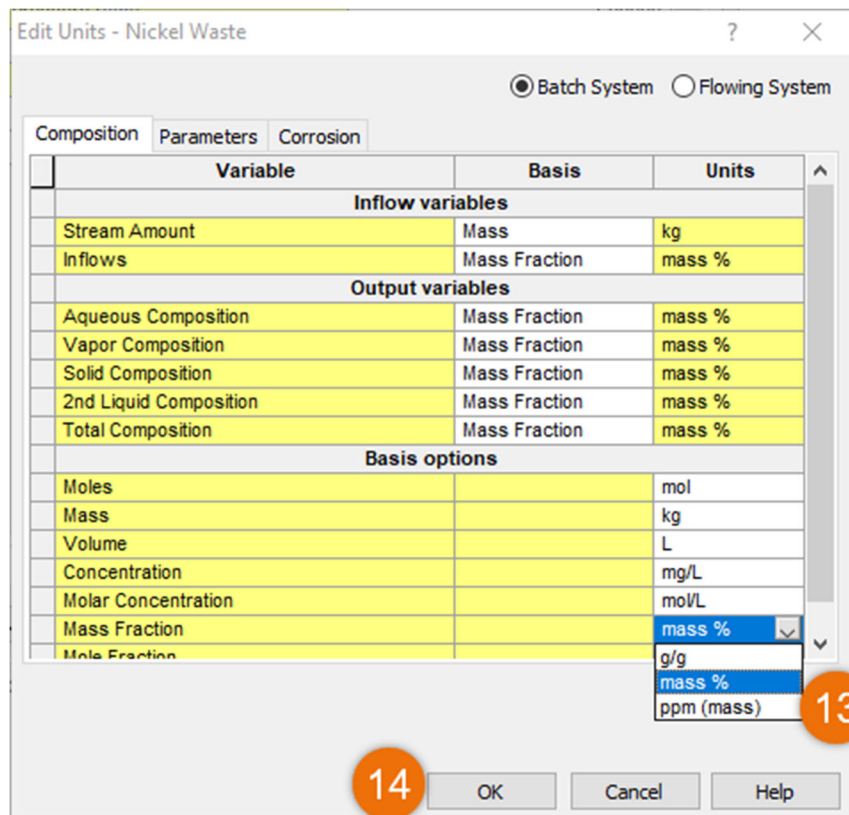
Customize...

OK Cancel Apply Help

Make sure you are on the Composition tab

Change the Mass Fraction Units to ppm (mass)

Click OK



Our primary interest in this application is finding the optimum pH for nickel removal. To create a plot of  $\text{Ni}^{+2}$  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.

Click on the **Add Calculation** button

Select **Survey**

The screenshot shows the 'Nickel Waste' stream information in a software application. The interface is divided into several sections:

- Navigator:** Located on the left, it shows a tree view with 'Streams' and 'Nickel Waste' (highlighted with a red box and a red circle with the number 1).
- Actions:** Below the Navigator, it lists various actions such as 'Add Stream', 'Add Mixer', 'Add Single Point', 'Add Survey', 'Add Chemical Diagram', 'Add Stability Diagram', and 'Add Corrosion Rates'.
- Plot Template Manager:** Located below the Actions panel, it is currently empty.
- Nickel Waste Stream Information:** The main central area displays a table with the following data:

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (kg)	1.00019
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Inflows (ppm (mass))</b>	
H2O	9.99815e5
Ni(OH)2	185.335
- Right-hand Panel:** Contains a dropdown menu labeled 'Add Calculation' (highlighted with a red circle with the number 2). The dropdown menu is open, showing options: 'Single Point', 'Survey' (highlighted with a red circle with the number 3), 'Chemical Diagram', 'Stability Diagram', and 'Corrosion Rates'. Below the menu, there is a 'Summary' section with text: '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', and '\* = differs from default.'

You can now add descriptive information about this calculation.

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

Enter a **Description: Base pH survey without additives**.

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

Click on the **Definition** tab to do the survey calculation.

Click on the **Survey by** button

Select **pH**

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

OLI Studio (Version 11.5.1 Beta) - [2.1 - pH Survey - Example\_17.oad]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator: 2.1 - pH Survey - Example\_17.oad

Streams: Nickel Waste, Base Survey

Base Survey

Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Calculation Type	Set pH
Target pH	
Use Single Titrant	No
pH Acid Titrant	HCl
pH Base Titrant	NaOH
Inflows (ppm (mass))	
H2O	9.99815e5
Ni(OH)2	185.335

Survey by: pH

Summary:

pH survey:  
Acid - HCLIN  
Base - NAOHIN  
Range 0.0 to 14.0  
Step size 1.0  
No. steps 14

No secondary survey selected  
Unit Set: <Custom>

Automatic Chemistry Model  
Aqueous (H+ ion) Databanks:  
Aqueous (H+ ion)  
Using K-fit Polynomials  
T-span: 25.0 - 225.0  
P-span: 1.0 - 1500.0

Set pH Calculation  
25.0000 °C  
1.00000 atm  
Target pH 0.0  
Acid Titrant:  
Base Titrant:

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

Select **File**

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

Click on the **Calculate** button

The screenshot shows the OLI Studio interface for a simulation titled "[Removing Nickel from wastewater\_2.oad]". The File menu is open, and the "Save As..." option is highlighted with a red circle labeled "10". The main window displays a table of parameters for a pH survey. The table is divided into sections: Stream Parameters, Calculation Parameters, and Inflows (ppm (mass)).

Variable	Value
<b>Stream Parameters</b>	
Amount (kg)	1.00019
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Parameters</b>	
pH	
Single Titrant	No
Acid Titrant	HCL
Base Titrant	NAOH
<b>Inflows (ppm (mass))</b>	
2	9.99815e5
	185.335

On the right side of the interface, the "Calculate" button is highlighted with a red circle labeled "11". Below the table, there are buttons for "Advanced", "Search", "Add as Stream", and "Export". The bottom right corner shows a "Summary" section with details about the pH survey, including the acid and base used, range, step size, and number of steps.

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.

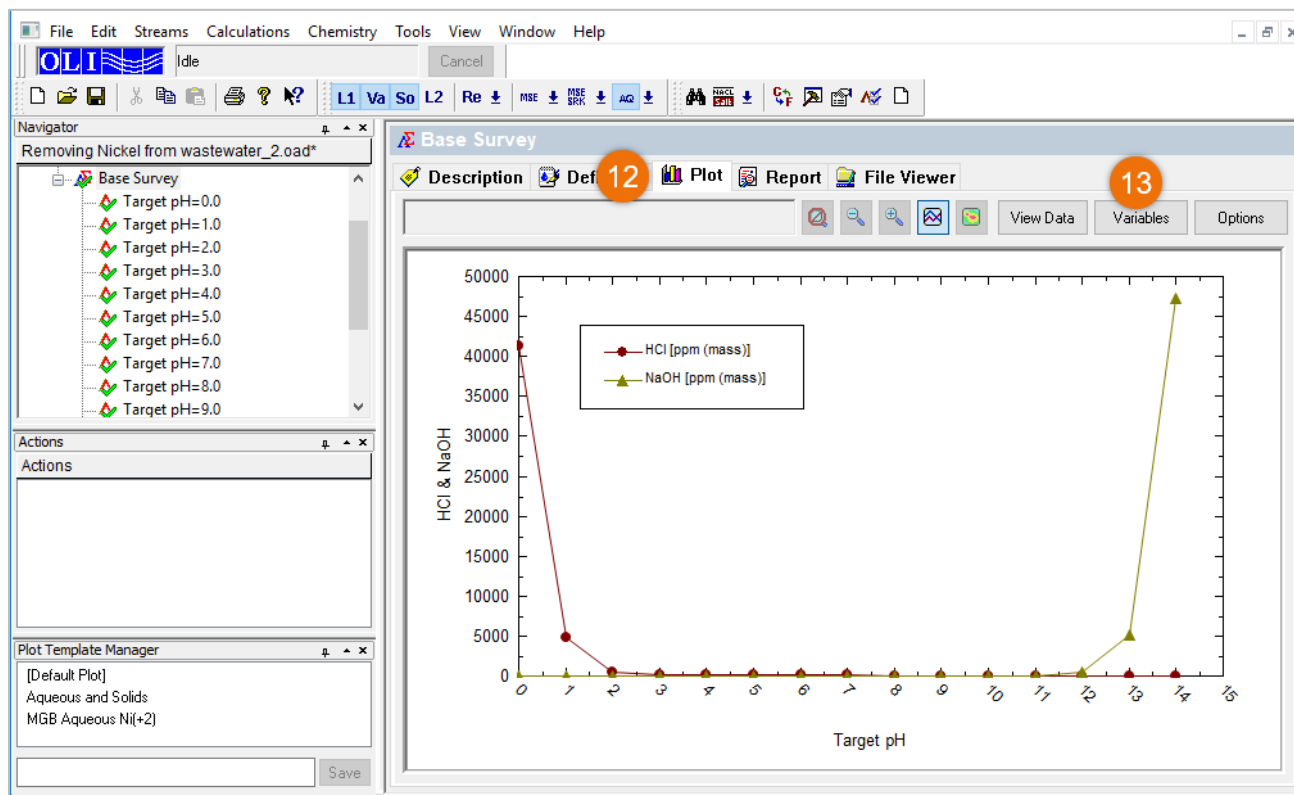
The screenshot shows the OLI software interface with the following components:

- Navigator:** A tree view showing the project structure. The 'Base Survey' folder is expanded, and a red box highlights a list of target pH values: Target pH=0.0, Target pH=1.0, Target pH=2.0, Target pH=3.0, Target pH=4.0, Target pH=5.0, Target pH=6.0, Target pH=7.0, Target pH=8.0, and Target pH=9.0.
- Base Survey Window:**
  - Description:** Stream Parameters (Stream Amount: 1.00019 kg, Temperature: 25.0000 °C, Pressure: 1.00000 atm).
  - Calculation Parameters:** Target pH (selected), Use Single Titrant (No), pH Acid Titrant (HCl), pH Base Titrant (NaOH).
  - Inflows (ppm (mass)):** H2O (9.99815e5), Ni(OH)2 (185.335), HCl (0.0), NaOH (0.0).
- Summary Window:**
  - Survey by: pH
  - Then by (optional): None
  - Vary:  Independently,  Together
  - Calculate:
  - Summary: pH survey: Acid - HCl, Base - NaOH, Range 0.0 to 14.0, Step size 1.0, No. steps 14.
  - No secondary survey selected
  - Unit Set: <Custom>
  - Automatic Chemistry Model: Aqueous (H+ ion) Databanks: Aqueous (H+ ion)
- Calculation Window:** A red box highlights the text 'Calculation Complete!'.

We can now obtain some graphical results.

Click on the **Plot** tab

Click on the **Variables** button

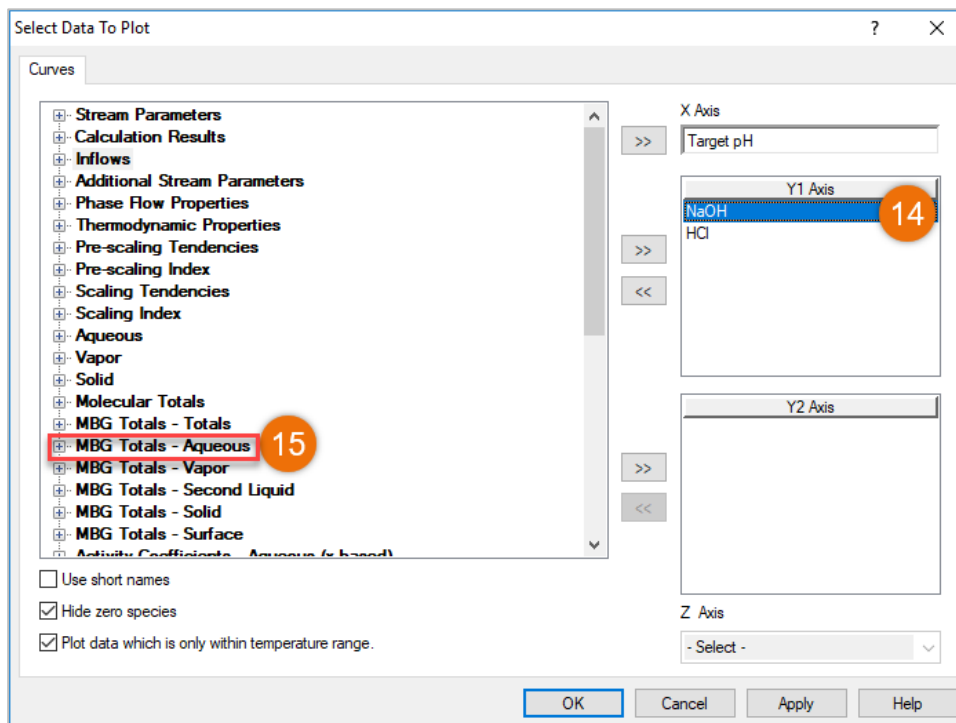


This will open a new window. The **NaOH** and **HCl** variables in the Y-Axis box should be displayed.

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

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

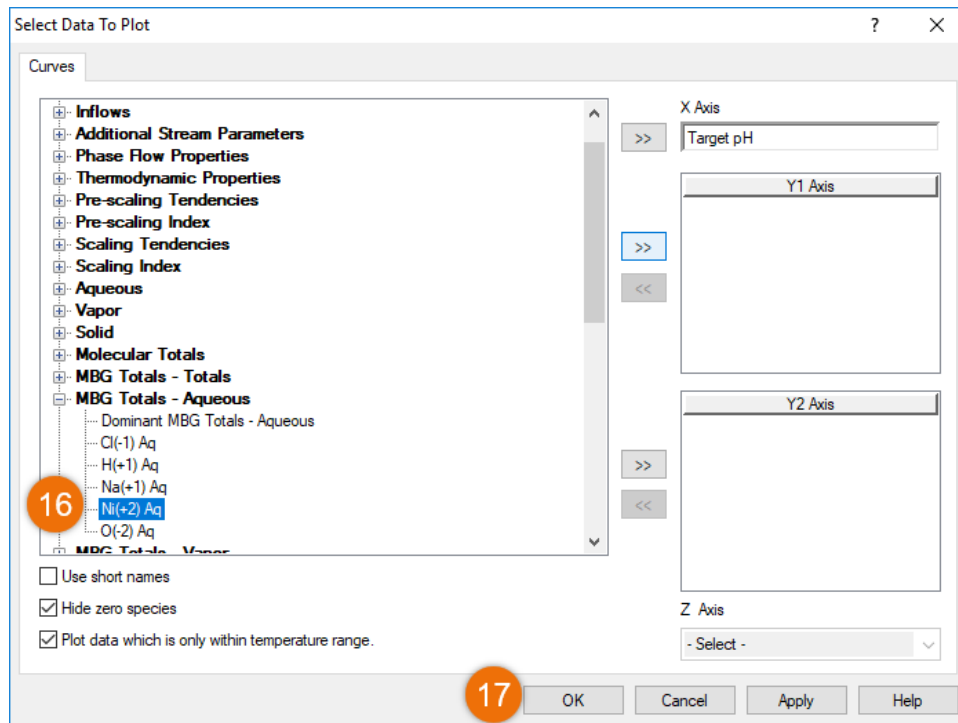
**Note: MGB** is an abbreviation for Material Balance Groups. The **MGB** variable is a sum of all the species for that material in the phase requested.



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

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

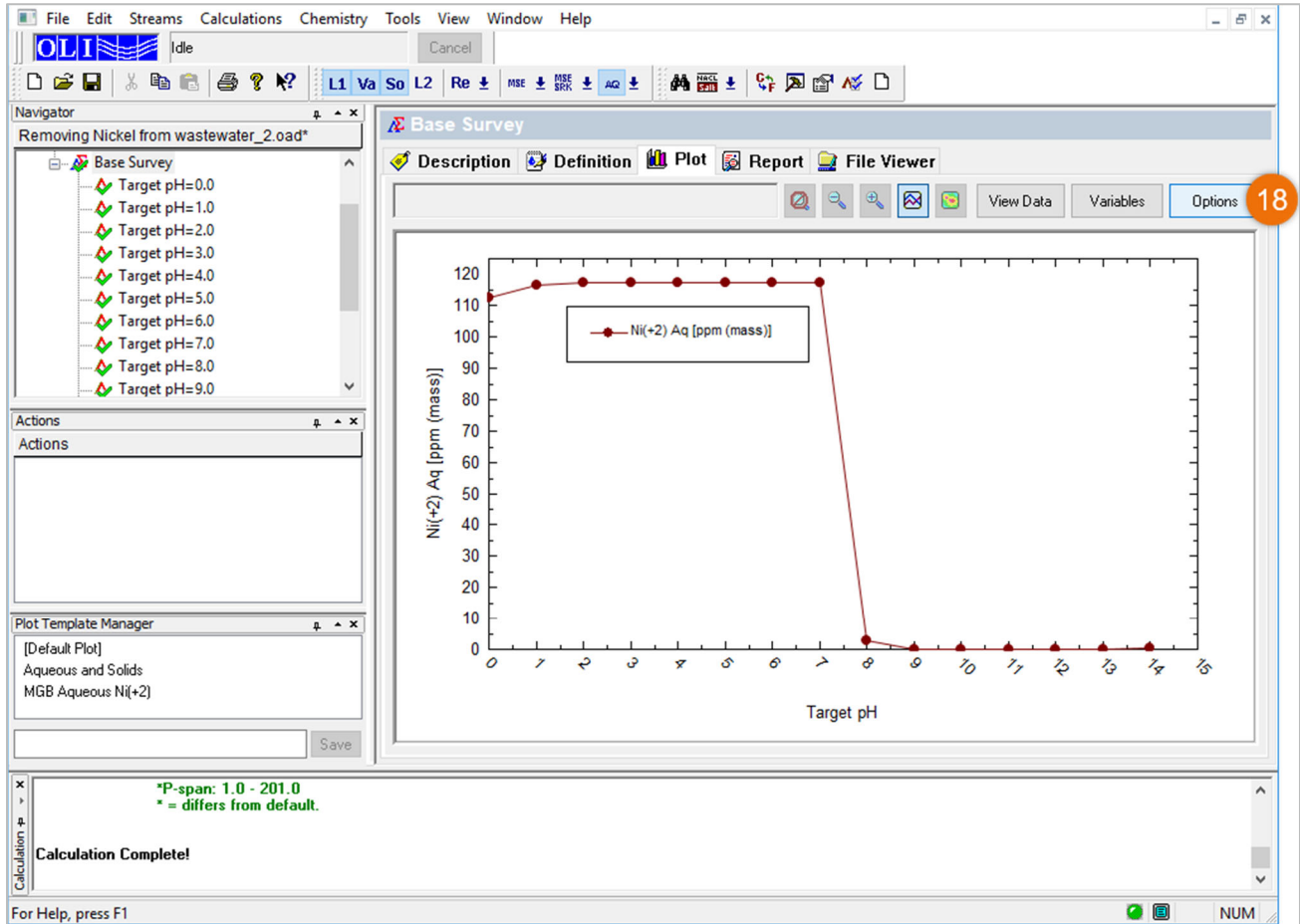
Click on the OK button.



You will see the new plot.

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

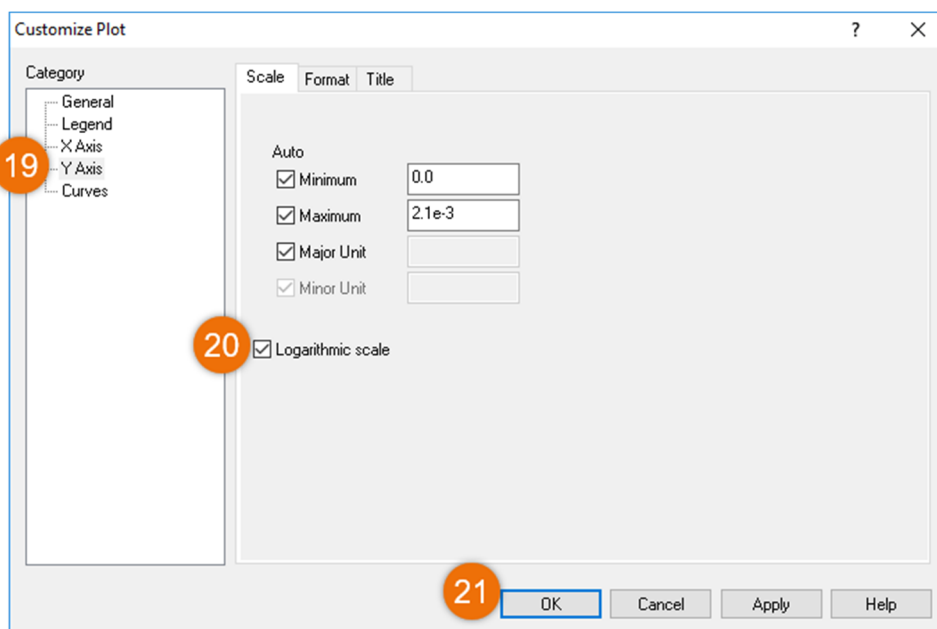
Above the plot window locate and select the **Options** button. This opens a new window.



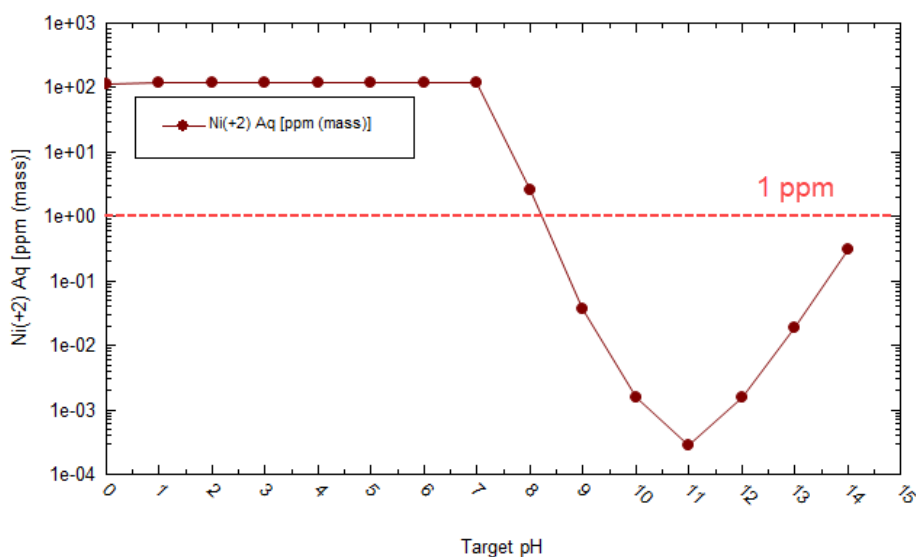
Select **Y-Axis** from the Category List

**Check** the Logarithmic Scale Box

**Click** on the **OK** box



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

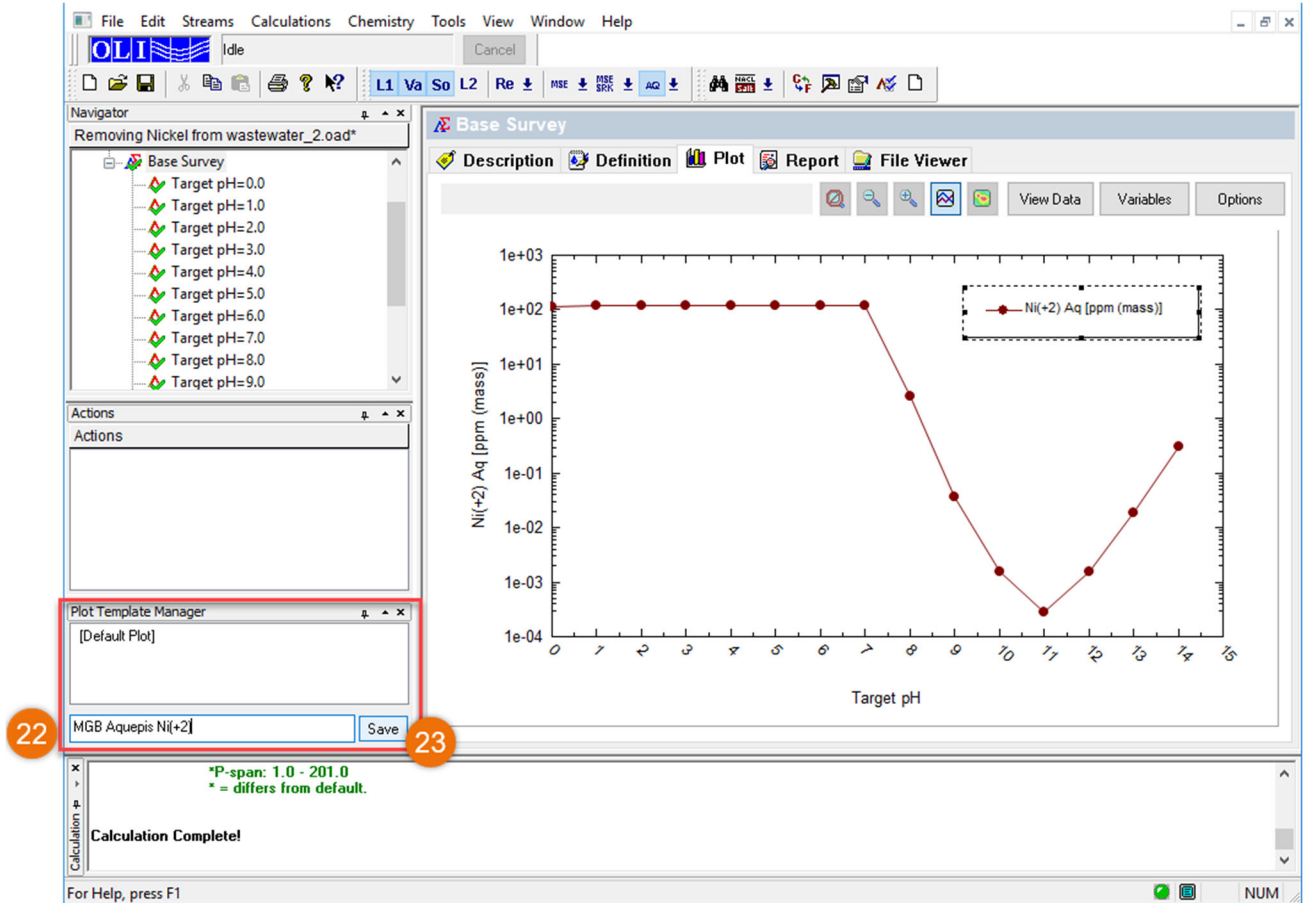


**Note:** The red line was put as a reference. it was not plot with the software.

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

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

Click **Save**

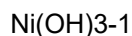
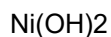


Now there will be two plots on that list now. The first is the default plot, and the second is **MBG Aqueous Ni(+2)**. You are now able to see these plot conditions for any other analyzer object in this case when you add survey for that object.

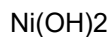
What else is important in this solution?

Click once more on the **Variables** button

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



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

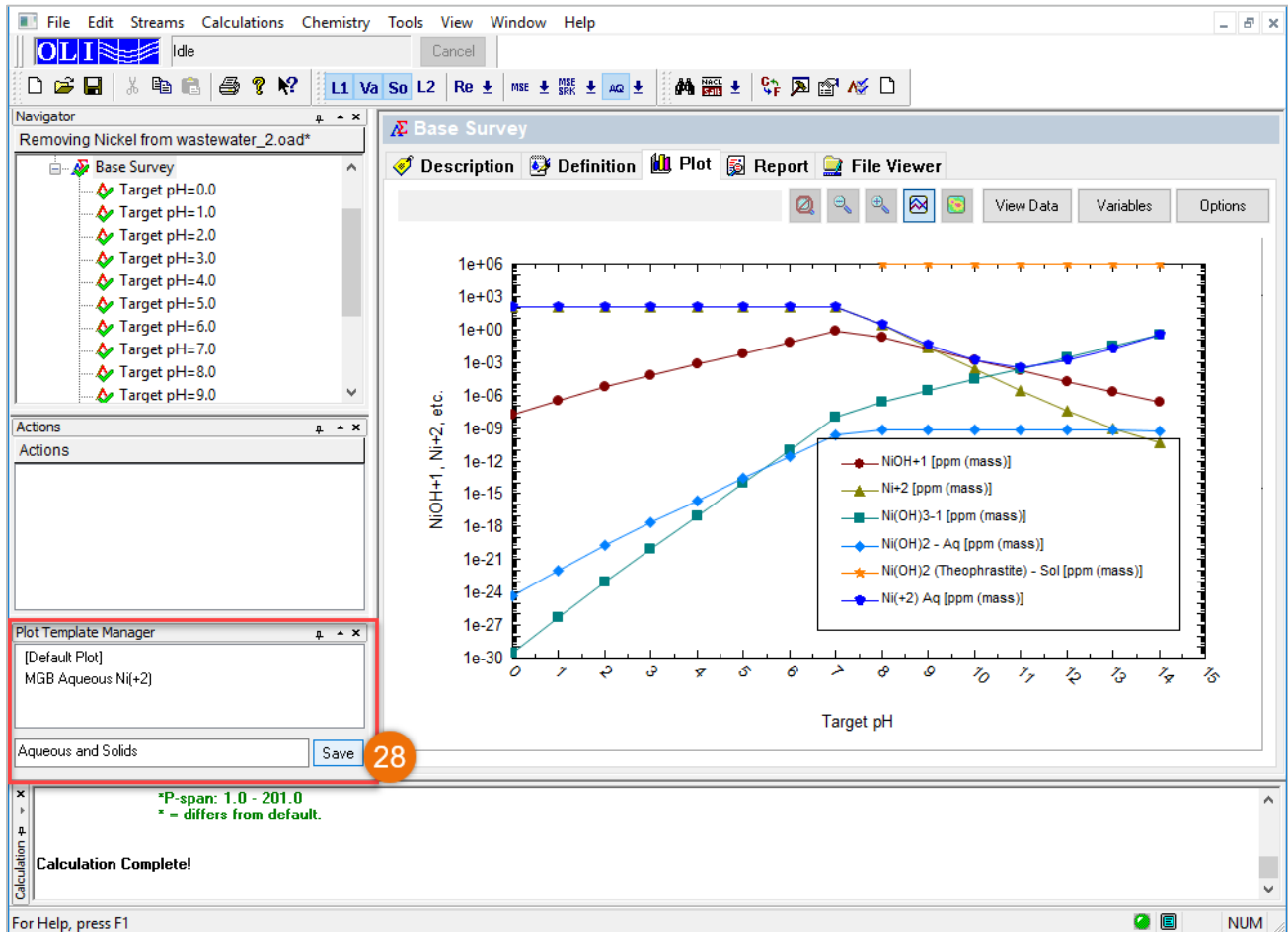


**Click** on the **OK** button when done

The screenshot shows the OLI software interface. The main window is titled "Base Survey" and has a "Variables" button circled in orange with the number 24. A "Select Data To Plot" dialog box is open, showing a list of species under "Aqueous" and "Vapor" categories. The "Vapor" category is selected, and the "Solid" sub-category is highlighted with an orange circle 26. The "Y1 Axis" list contains NiOH+1, Ni+2, Ni(OH)3-1, Ni(OH)2 - Aq, Ni(OH)2 (Theophrastite) - Sol, and Ni(+2) Aq. The "X Axis" is set to "Target pH". The "Y2 Axis" is empty. The "Z Axis" is set to "- Select -". The "OK" button is circled in orange with the number 27. A plot on the right shows a curve of Ni(+2) Aq [ppm (mass)] vs Target pH, with an orange circle 25 near the plot area.

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)<sub>2</sub>-Solid at pH values greater than 7.0 with a maximum near pH=11.

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



## Scenario 2: Wastewater with Cyanide Content

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

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

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

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

**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

The screenshot shows the Stream Analyzer software interface. The main window displays the configuration for the 'Nickel Waste' stream. The 'Inflows (ppm (mass))' table is visible, showing H2O at 9.99815e5 and Ni(OH)2 at 185.335. The 'Actions' pane in the bottom left corner is open, and the 'Add Survey' option is highlighted with a red circle and the number 2. The 'Navigator' pane on the left shows the 'Nickel Waste' stream selected with a red circle and the number 1. The 'Summary' pane on the right shows the unit set as '<Custom>' and the automatic chemistry model settings.

Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00019
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (ppm (mass))	
H2O	9.99815e5
Ni(OH)2	185.335

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

Name: **Waste Survey with CN**

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

Click on the **Definition** Tab

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

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

Click on the **Calculate** button.

The screenshot shows the software interface for configuring a survey. The 'Description' tab is active, displaying the survey name 'Waste Survey with CN' and the description 'pH survey with both Nickel and CN'. The 'Definition' tab is also visible, showing a table of variables and values. The 'Survey by' dropdown is set to 'pH', and the 'Calculate' button is highlighted. The 'Summary' panel shows the survey parameters and the automatic chemistry model.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (kg)	1.00019
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Parameters</b>	
Target pH	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NaOH
<b>Inflows (ppm (mass))</b>	
H2O	9.99325e5
Ni(OH)2	185.335
NaCN	490.000

Survey by: pH

Then by (optional): None

Vary:  Independently  Together

Calculate

Summary:

pH survey:  
Acid - HCLIN  
Base - NaOH  
Range 0.0 to 14.0  
Step size 1.0  
No. steps 14

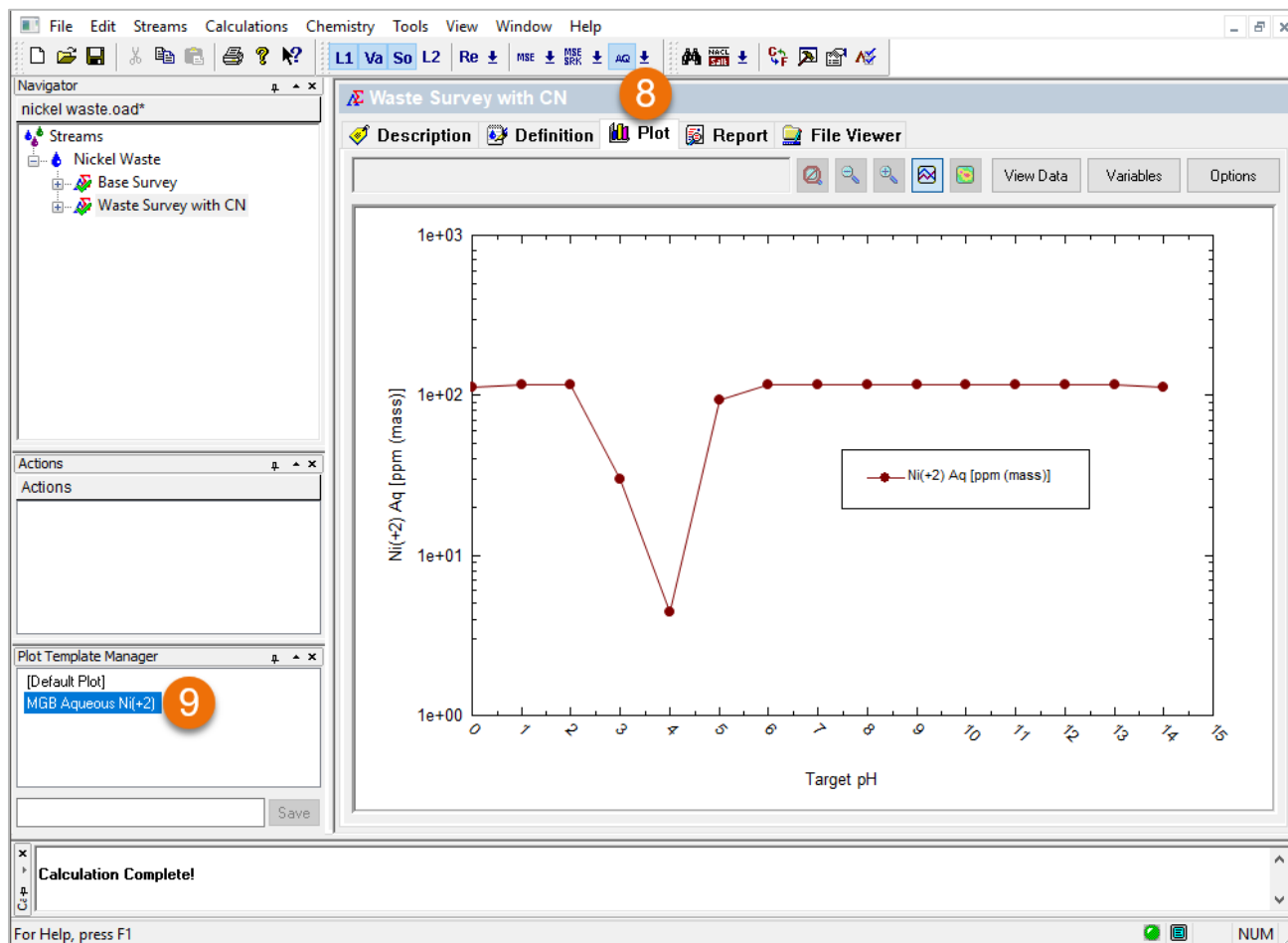
No secondary survey selected  
Unit Set: <Custom>

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.  
Set pH Calculation

Let's review the results.

Click on the **Plot** tab

Go to the **Plot Template Manager** tool, and click on MGB Aqueous Ni(+2)



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

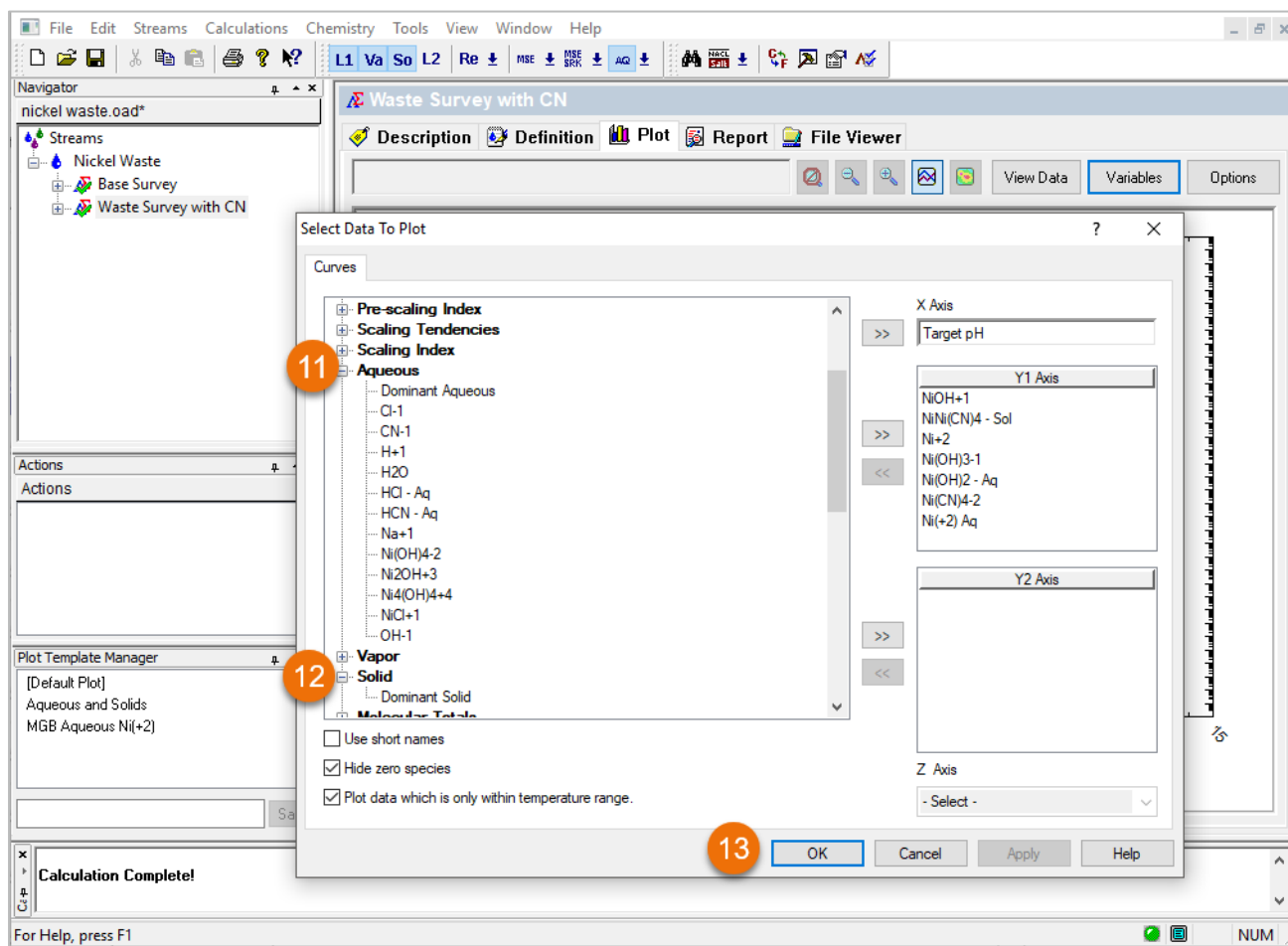
Let's analyze why this is happening. We can now modify the plot to display more variables. Select the **Aqueous and Solids** plot saved in the **Plot Template Manager**.

Click on **Variables**

**Add** the following new **Aqueous** species: Ni(CN)<sub>4</sub><sup>-2</sup>

**Add** the following new **Solid** species: NiNi(CN)<sub>4</sub>-Solid

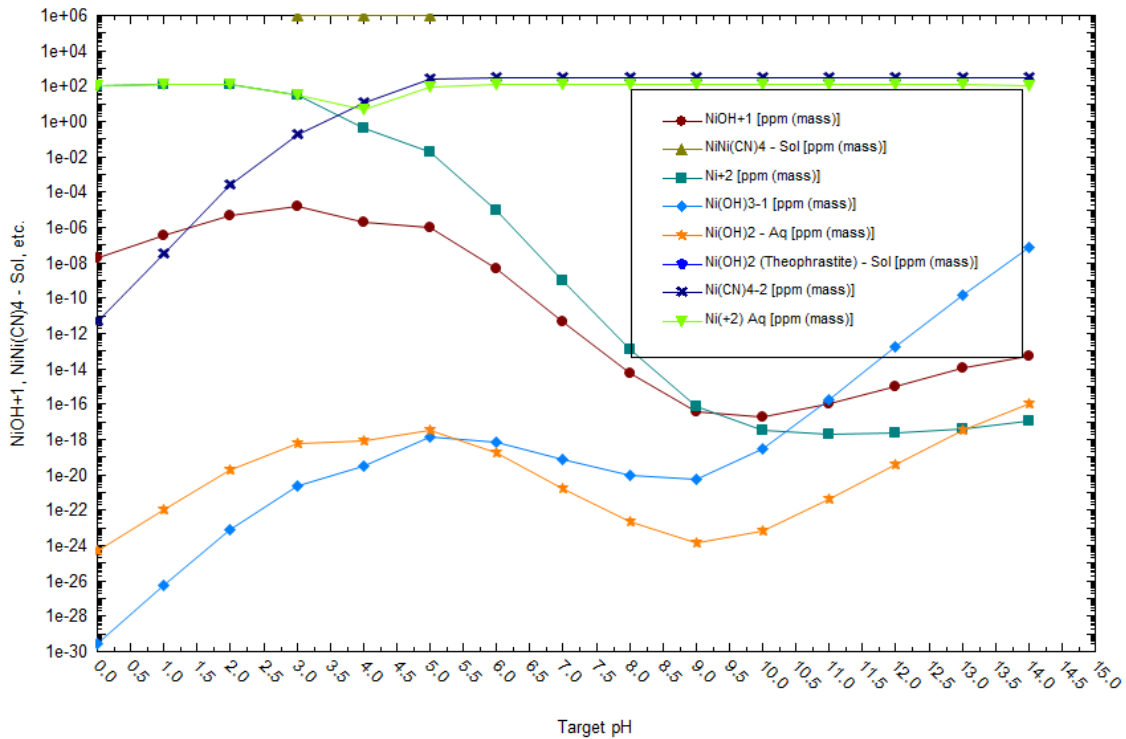
**Click OK**



Let's analyze the results.

The culprit is the  $\text{Ni}(\text{CN})_4^{2-}$  complex of nickel and cyanide. Basically, the plot of the total Ni in solution and the  $\text{Ni}(\text{CN})_4^{2-}$  complex overlap over the interval  $\text{pH}=5$  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  $\text{NiNi}(\text{CN})_4$  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 many metal sulfide salts are highly insoluble.

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

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

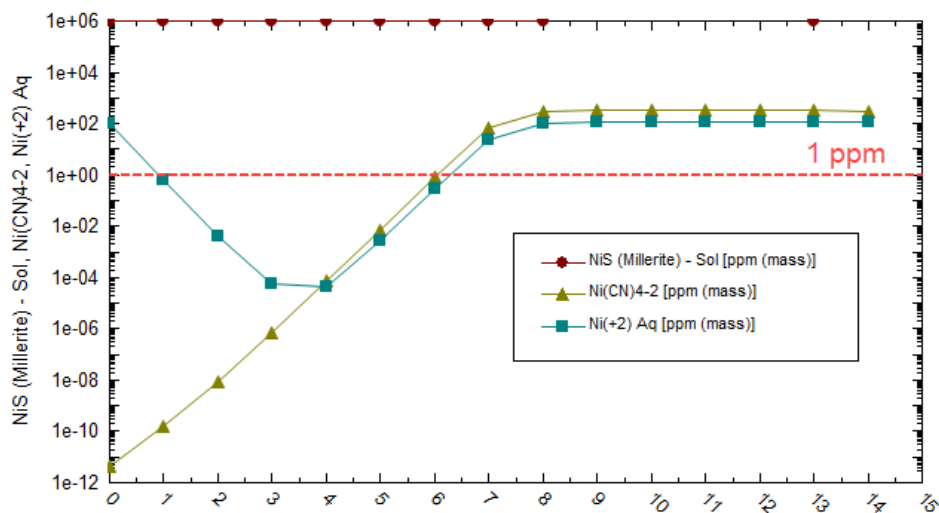
Add **340 ppm** of **H2S**

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

**Aqueous Species:**  $\text{Ni}(\text{CN})_4^{2-}$

**Aqueous Species:** Ni+2

## Solid Species: NiS-Solid



The results reflect a "power struggle" between the  $\text{Ni}(\text{CN})_4^{2-}$  which is holding the nickel in solution and the NiS solid which clearly has a greater tendency to form than the  $\text{Ni}(\text{CN})_4$  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  $\text{Ni}(\text{CN})_4^{2-}$  and not the cation  $(\text{Ni}^{+2})$  as the conventional wisdom might dictate.

## Temperature Survey

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

### *Example 18: Studying a Four-phase mixture and its Partitioning*

The purpose of this first example is to present the basic Temperature survey. You will study how a four-phase mixture partitions with temperature. The system composition will be basic, containing one primary phase component, H<sub>2</sub>O (liquid), CH<sub>4</sub> (gas), Decane (organic), and NaCl (solid). Each component will partition each of the other three phases.

### *Starting the Simulation*

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

Temperature Survey Calculation			
Calculation Settings		Stream Composition and Conditions	
Calculation Type	Survey	Stream Amount	Calculated
Stream Name	Temperature Survey	Temperature Range	25-100 °C (Default)
Survey Name	4-Phase Partitioning	Step Size	Increment by 5 °C (Default)
Name Style	Display Formula	Pressure	1 atm
Unit Set	Metric, Moles	H <sub>2</sub> O	50 moles
Framework	MSE-SRK	CH <sub>4</sub>	10 moles
		C <sub>10</sub> H <sub>22</sub>	10 moles
		NaCl	10 moles

Add a new **Stream**

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

Select the **MSE-SRK** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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

Enter the composition of the stream given in the table above

Go to the **Add Calculation** button and select **Survey** calculation

Change the **Survey** name to **4-Phase Partitioning** using the **<F2>** key

Select **Temperature** as Type of Survey - Default

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

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	80.0000
Temperature (°C)	
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
H2O	50.0000
CH4	10.0000
C10H22	10.0000
NaCl	10.0000

Survey by: Temperature **Specs...**

Then by (optional): None **Specs...**

Vary:  Independently  Together

**Calculate**

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

The **Step Size** can be given as **Increments** or **Number of Steps**. By default, in the Temperature Survey the **Step Size** by 5 increments is selected. Leave the default values. Then click **OK**.

Survey Options

Category: Var. 1 - Temperature

Survey Range

Temperature Range Unit: °C

Selected Range: 25.0 to 100.0 in 15 steps of 5.0

Linear  Log  Point List

**End Points**

Start: 25.0000

End: 100.0000

**Step Size**

Increment: 5.00000  } Select one, the other is calculated

Number Steps: 15  }

**These are the default values**

**OK** Cancel Apply Help

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

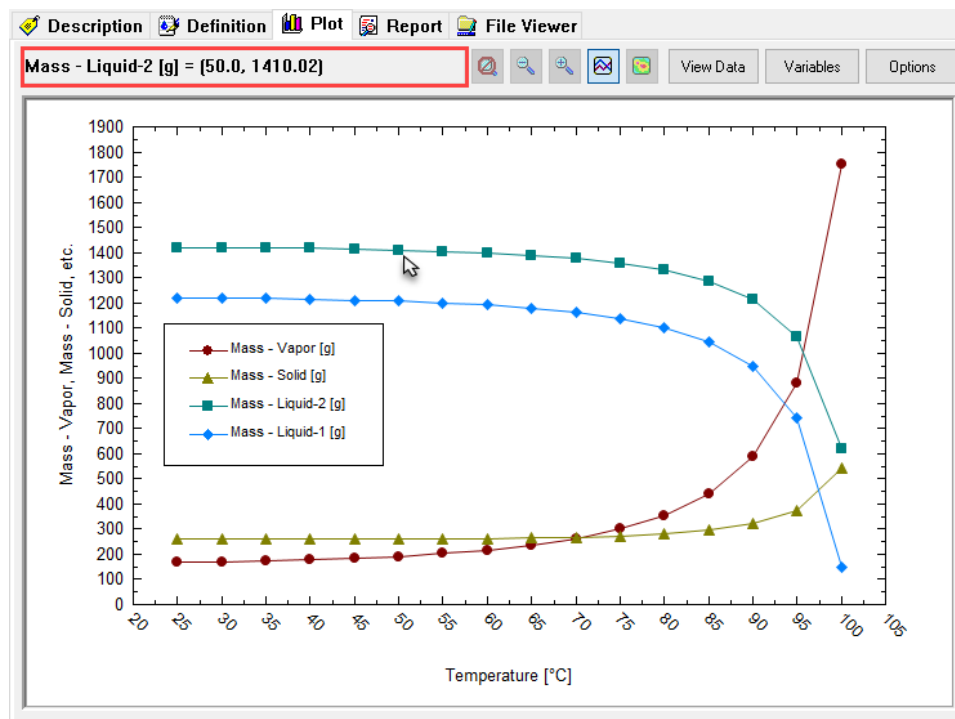
It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

## Analyzing the Results

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

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

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



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

## Pressure Survey

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

### Example 19: Dissolution of CO<sub>2</sub> in water as a Function of Pressure

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

In this example, the dissolution of CO<sub>2</sub> in water (which is a direct reflection of VLE) will be studied as a function of pressure.

#### Starting the Simulation

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

Pressure Survey Calculation			
Calculation Settings		Stream Composition and Conditions	
Calculation Type	Survey	Stream Amount	Calculated
Stream Name	Pressure Survey	Pressure Range	5-100 atm
Survey Name	CO <sub>2</sub> dissolved in water	Step Size	Increment by 5 atm
Name Style	Display Formula	Temperature	25 °C
Unit Set	Metric, Moles	H <sub>2</sub> O	55.5082 moles
Framework	MSE-SRK	CO <sub>2</sub>	10 moles

Add a new **Stream**

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

Select the **MSE-SRK** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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

Enter the composition of the stream given in the table above

Go to the **Add Calculation** button and select **Survey** calculation

Change the **Survey** name to **CO<sub>2</sub> dissolved in water** using the **<F2>** key

Select **Pressure** as Type of Survey

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

The screenshot displays the 'Survey Options Window' in a software interface. On the left, a table lists 'Stream Parameters' and 'Inflows (mol)'. The 'Stream Parameters' table has columns for 'Variable' and 'Value'. The 'Inflows (mol)' table lists components and their values. On the right, the 'Survey by' dropdown is set to 'Pressure', and the 'Specs...' button is highlighted with a red box. Below it, the 'Then by (optional)' dropdown is set to 'None', and the 'Vary' section has radio buttons for 'Independently' and 'Together'.


Variable	Value
Stream Parameters	
Stream Amount (mol)	65.5082
Temperature (°C)	25.0000
Pressure (atm)	
Inflows (mol)	
H <sub>2</sub> O	55.5082
CO <sub>2</sub>	10.0000

The default pressure range is from 1-10 atm with an increment of 1 atm. Change the **Pressure Range** to 5-100 atm. Set the **Step Size** to **5 atm** increments. Then click **OK**.

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

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

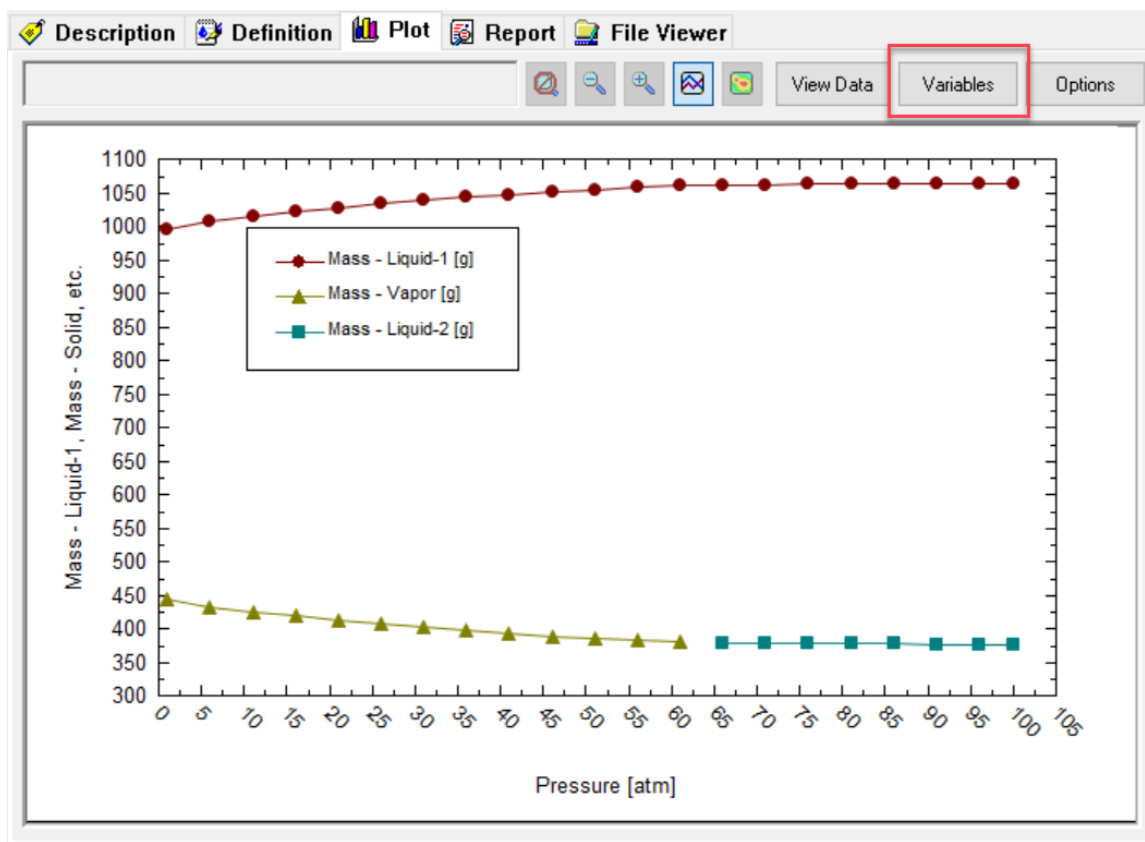
### Analyzing the Results

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

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

We are interested in the solubility of CO<sub>2</sub> in water, i.e. in the Liquid-1 phase. We can change the default plot to show the molecular CO<sub>2</sub> dissolved in water (CO<sub>2</sub>-Liq1).

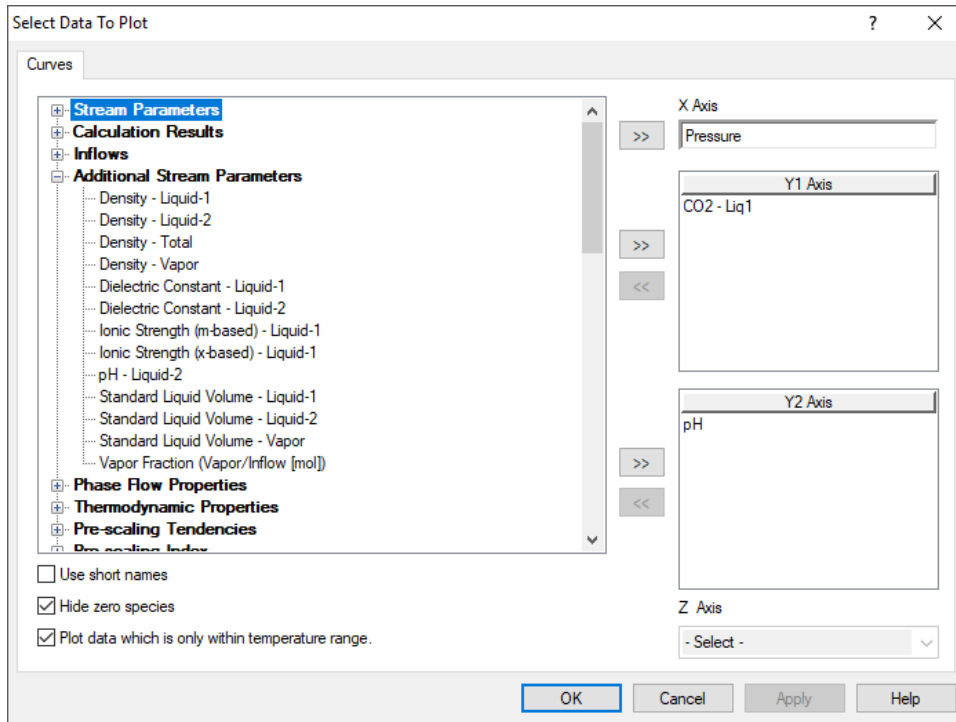
Click on the **Variables** button. This will open the **Select Data to Plot** window.



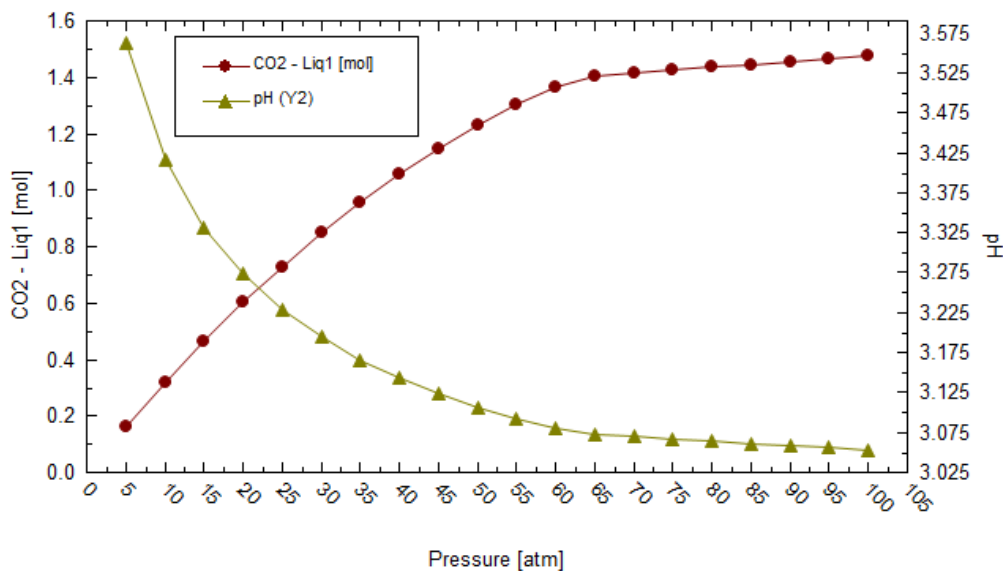
**Double click** or use the **<<** button to remove the **Phase Amount** variables.

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

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

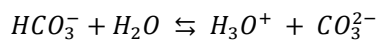
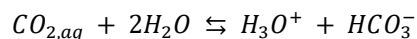
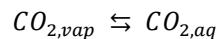


The default plot now shows the selected variables: The dissolved CO<sub>2</sub> in the water (Liquid-1 Phase) in the Y1 Axis, and the pH in the Y2 Axis. Both variables are presented as a function of pressure.



The dissolved CO<sub>2</sub> in solution increases as the pressure increases. When the pressure goes above 65 atm, the dissolved CO<sub>2</sub> 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:



Thus, as the amount of CO<sub>2</sub> 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<sub>2</sub> in solution.

## Composition Survey

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

### *Example 20: Dissolution of Calcite (CaCO<sub>3</sub>) as a function of CO<sub>2</sub>*

Calcite is a scale that forms very easily in the production of oil and gas. It is known that adding CO<sub>2</sub> to water dissolves Calcite. Likewise, removing CO<sub>2</sub> from water precipitates calcite. In this example, you are going to evaluate the effect of different CO<sub>2</sub> concentrations on the dissolution of Calcite.

### *Starting the Simulation*

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

Composition Survey Calculation			
Calculation Settings		Stream Composition and Conditions	
Calculation Type	Survey	Stream Amount	Calculated
Stream Name	Composition Survey	Temperature	25 °C
Survey Name	Calcite Dissolution	Pressure	75 atm
Name Style	Display Formula	H <sub>2</sub> O	55.5082 moles
Unit Set	Metric, Moles	CaCO <sub>3</sub>	0.05 moles
Framework	MSE	CO <sub>2</sub> concentration range	0 - 1 moles
		Step Size	Increment by 0.05 moles

Add a new **Stream**

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

Select the **MSE** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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

Enter the composition of the stream given in the table above

Go to the **Add Calculation** button and select **Survey** calculation

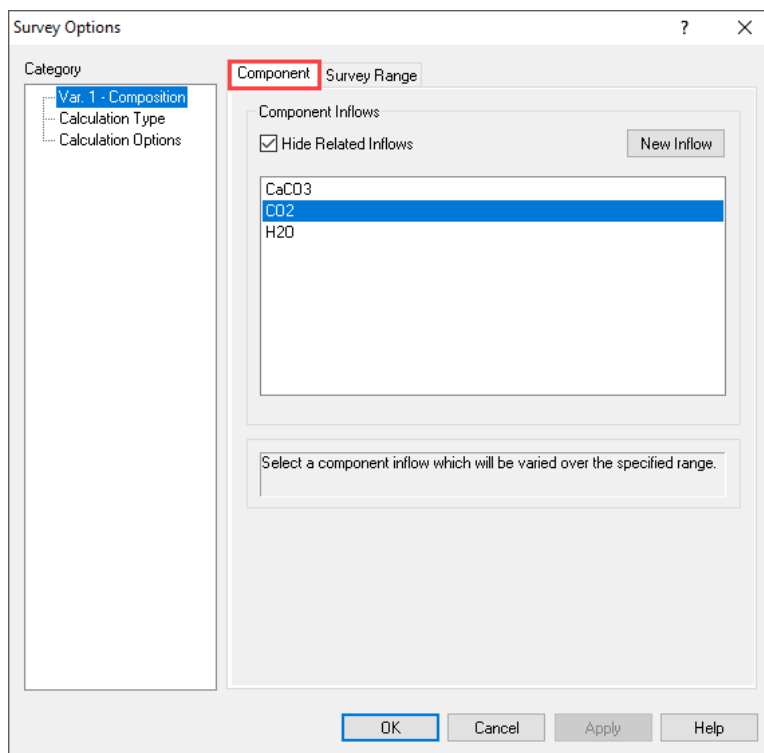
Change the **Survey** name to **Calcite Dissolution** using the **<F2>** key

Select **Composition** as Type of Survey.

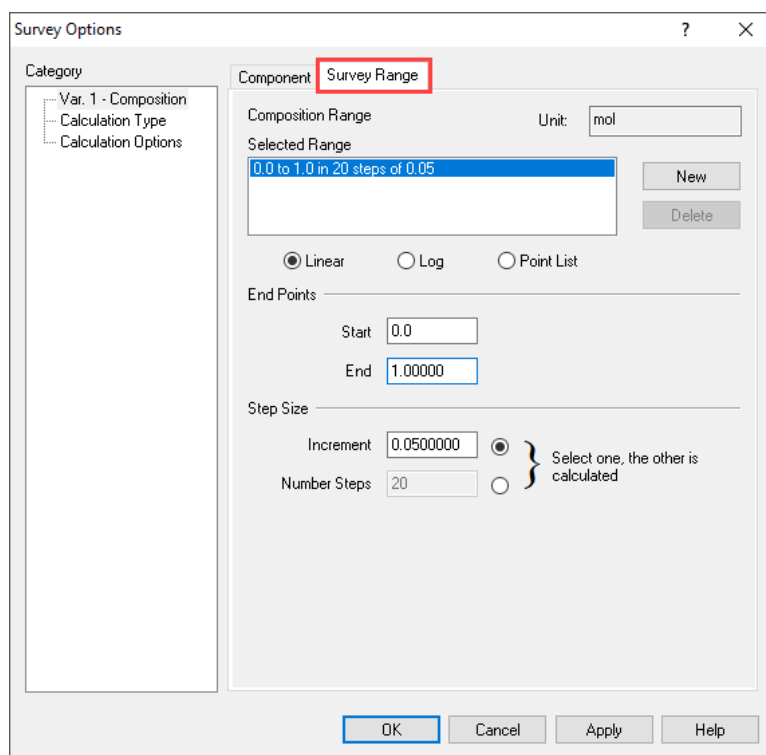
**Note:** In the summary box a message in red appears: **'Component not selected for composition survey variable'**. This means that we need to select the component that we want to vary. In this example CO<sub>2</sub>.

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

Under the **Component** tab, select CO2




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**.



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

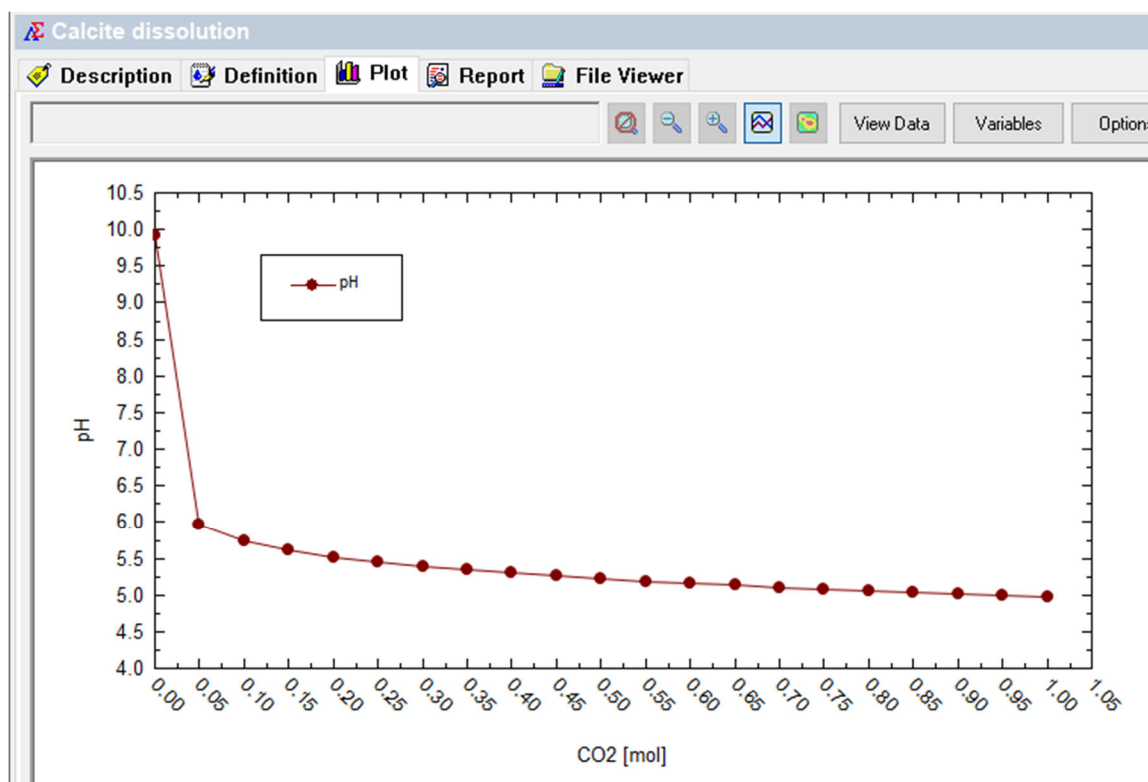
It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save under the same file that we created before named as *Survey Calculations*.

### Analyzing the Results

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

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

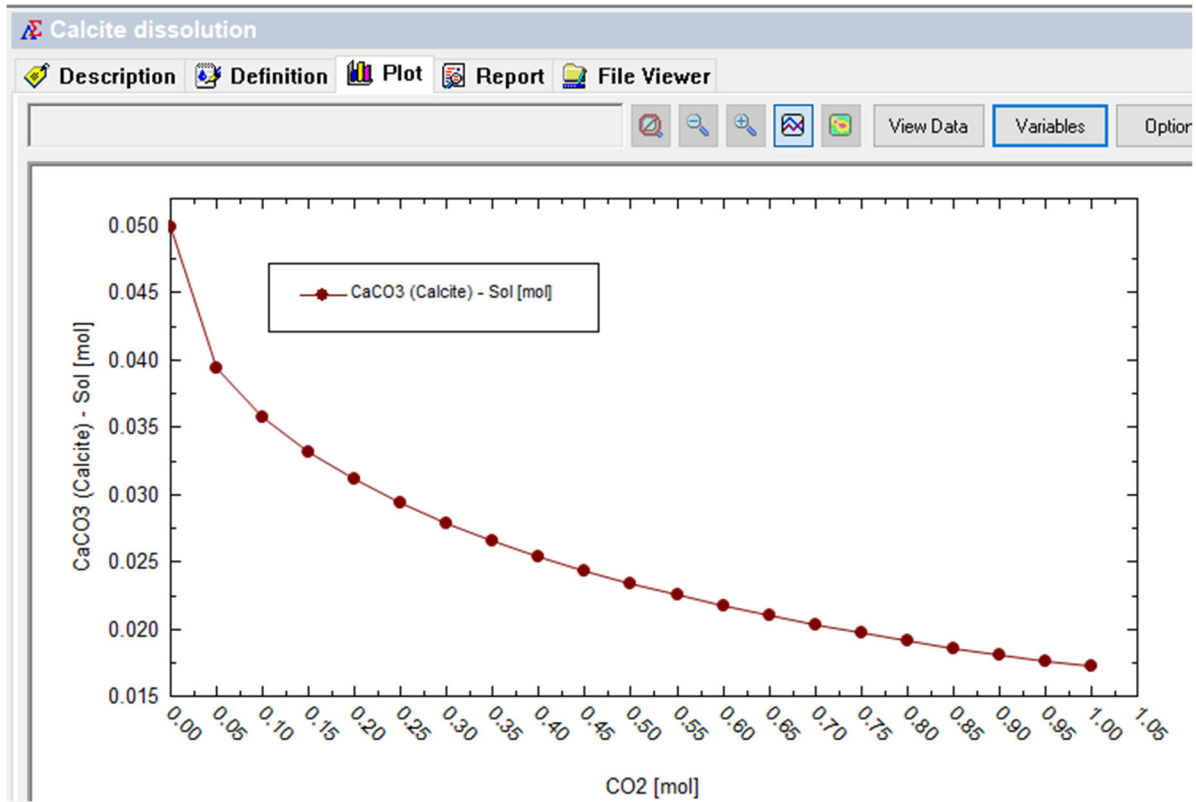
Click on the **Variables** button. This will open the **Select Data to Plot** window.



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

Look for **Solid** section and click on the  $\oplus$  box to show all the available variables. **Select CaCO<sub>3</sub> (Calcite) – Sol** and put it in the Y1 Axis using the >> button. Click **OK**.

The default plot now shows the selected variable: CaCO<sub>3</sub> (Calcite) – Sol as a function of CO<sub>2</sub>.



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

## pH Survey

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

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

In this survey calculation, a 0.001 molal CO<sub>2</sub> solution is titrated with HCl and NaOH. Instead of defining the amount of acid/base to add, the pH will be specified, and the software will compute the amounts of HCl and NaOH needed.

#### *Starting the Simulation*

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

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

Add a new **Stream**

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

Select the **AQ** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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

**Enter** the composition of the stream given in the table above

Go to the **Add Calculation** button and select **Survey** calculation

Select **pH** as Type of Survey

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

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

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

In the **pH Titrants** tab, leave the default pH Titrants: **HCl** and **NaOH**

pH Titrants Survey Range

Select an acid and base to adjust to meet the specified pH.

Use Single Titrant  Hide Related Inflows

Acid	Base
CO2	CO2
H2O	H2O
HCL	NAOH

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

pH Titrants Survey Range

Target pH Range Unit:

Selected Range

4.0 to 12.0 in 80 steps of 0.1

Linear  Log  Point List

End Points

Start

End

Step Size


Increment   } Select one, the other is calculated

Number Steps

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


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

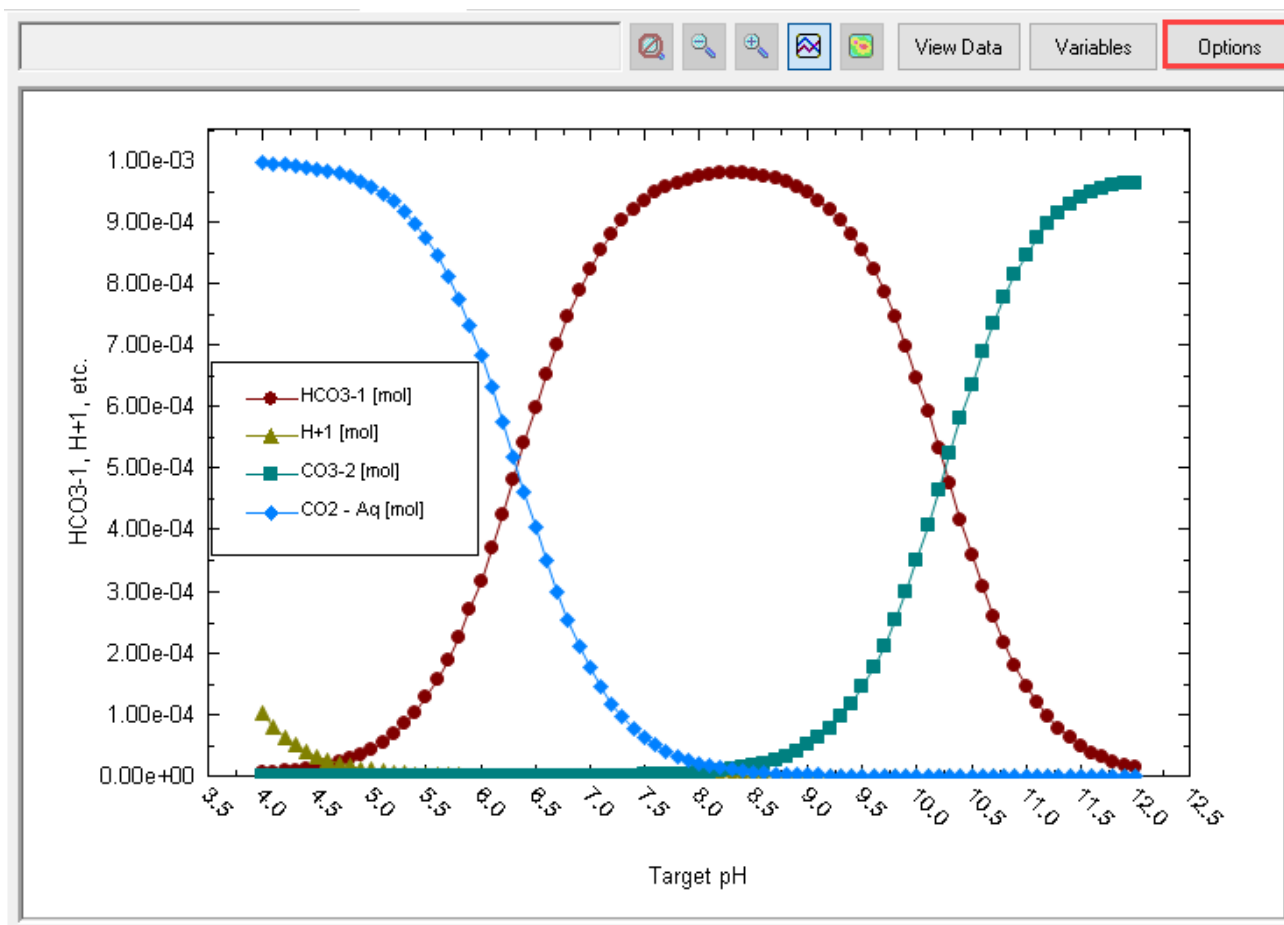
## Analyzing the Results

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

Click on the **Variables** button

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

Look for **Aqueous** section and click on the  box to show all the available species. **Select** the following species: CO<sub>2</sub>-Aq, HCO<sub>3</sub><sup>-1</sup>, CO<sub>3</sub><sup>-2</sup>, and H<sup>+</sup> and put them in the Y1 Axis using the >> button or by double clicking. When you are done, click **OK**.

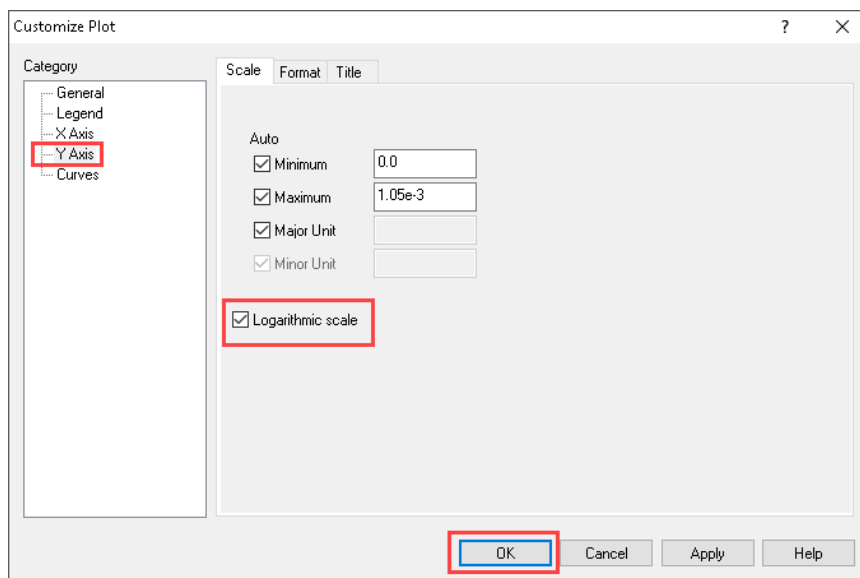


You can also present this plot on a semi-log scale.

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

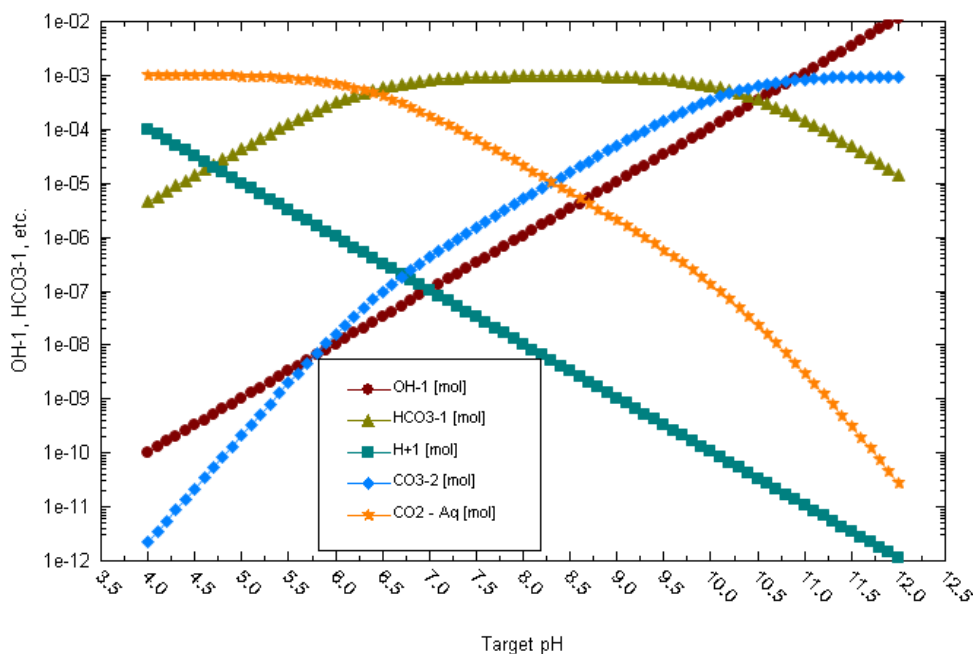
Select **Y Axis** in the Category window

**Check** the Logarithmic scale box, and then click **OK**.

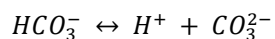
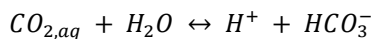


Before analyzing the plot, let's add the OH<sup>-</sup> species.

Click on the **Variables** button, look for OH<sup>-</sup> 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, CO<sub>2</sub>-Aq dominates the system, and notice how the HCO<sub>3</sub><sup>-</sup> slope is 1 and the CO<sub>3</sub><sup>2-</sup> slope is 2. Likewise, in the pH region where CO<sub>3</sub><sup>2-</sup> dominates (high pH), the HCO<sub>3</sub><sup>-</sup> slope is -1 and the CO<sub>2</sub>-Aq slope is -2. These  $\frac{\text{mole}}{\text{pH}}$  slopes are based on the number of H<sup>+</sup> ions added or removed in the chemical reactions. See reactions below.



Note the pH where the CO<sub>2</sub>-Aq and HCO<sub>3</sub><sup>-</sup> lines intersect (pH~6.3), and where the HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> 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 HCO<sub>3</sub><sup>-</sup> to CO<sub>3</sub><sup>2-</sup>, a portion of the NaOH remains as free base, OH<sup>-</sup>. This fraction increases at higher pH values, and its concentration is reflected in the calculated pH. A similar pattern is seen at pH below ~3 for HCl and H<sup>+</sup>.

## Vapor Fraction / Vapor Amount Survey

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

### Example 22: Seawater Evaporation

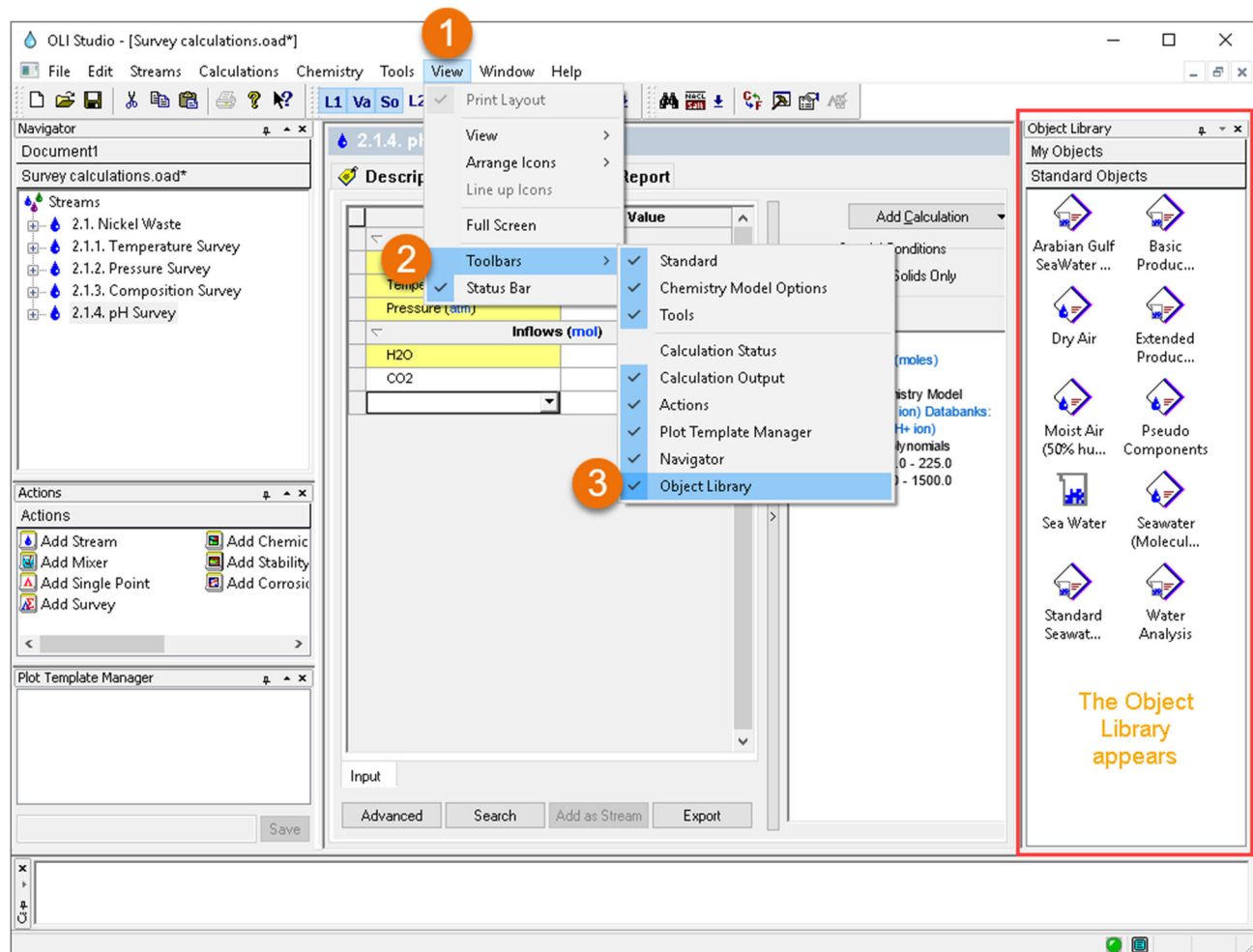
Seawater contains a variety of salts, and when seawater evaporates, these solids are left behind. The most abundant salt in seawater is sodium chloride (NaCl) which is commonly referred to by its mineral name halite.

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

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

### Starting the Simulation


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

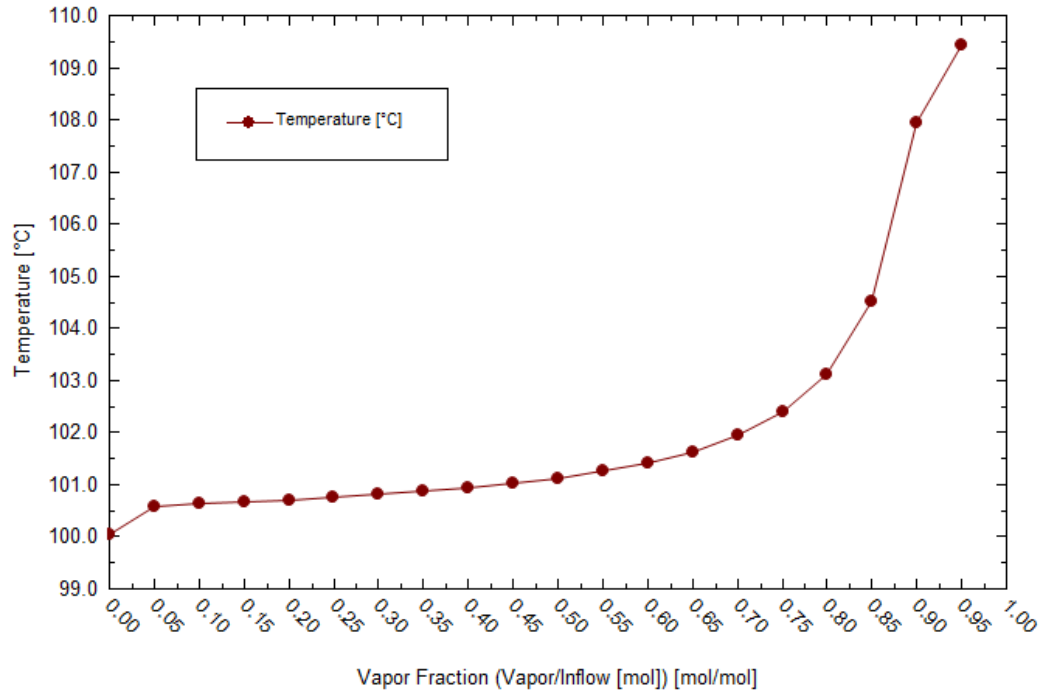






## Analyzing the Results

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.



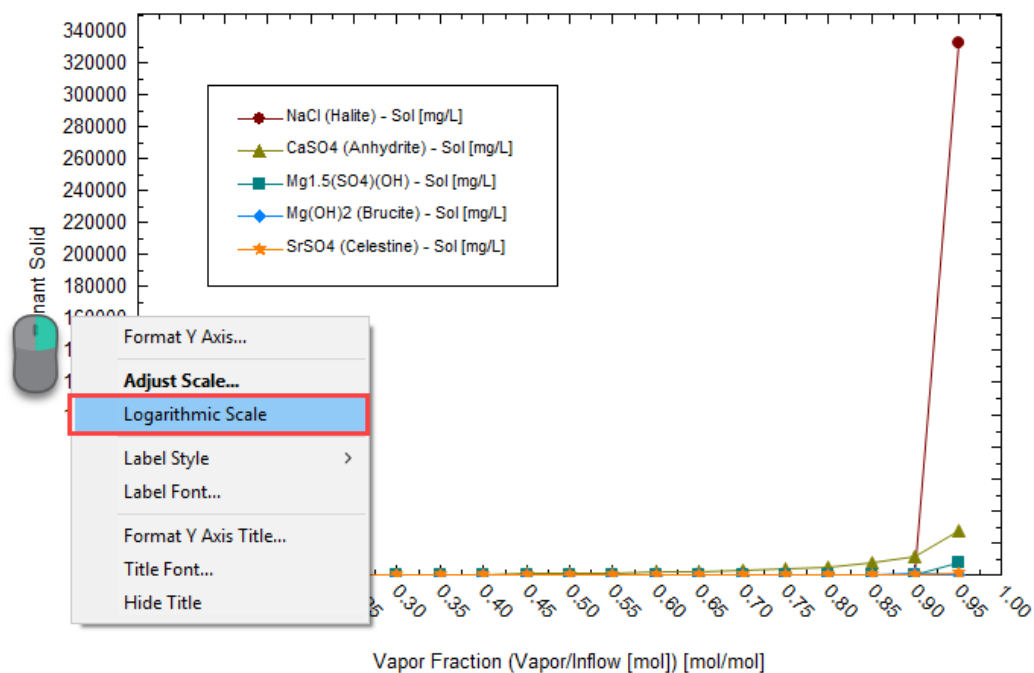
We are also interested to know which solid phases precipitate as the water evaporates.

Click on the **Variables** button

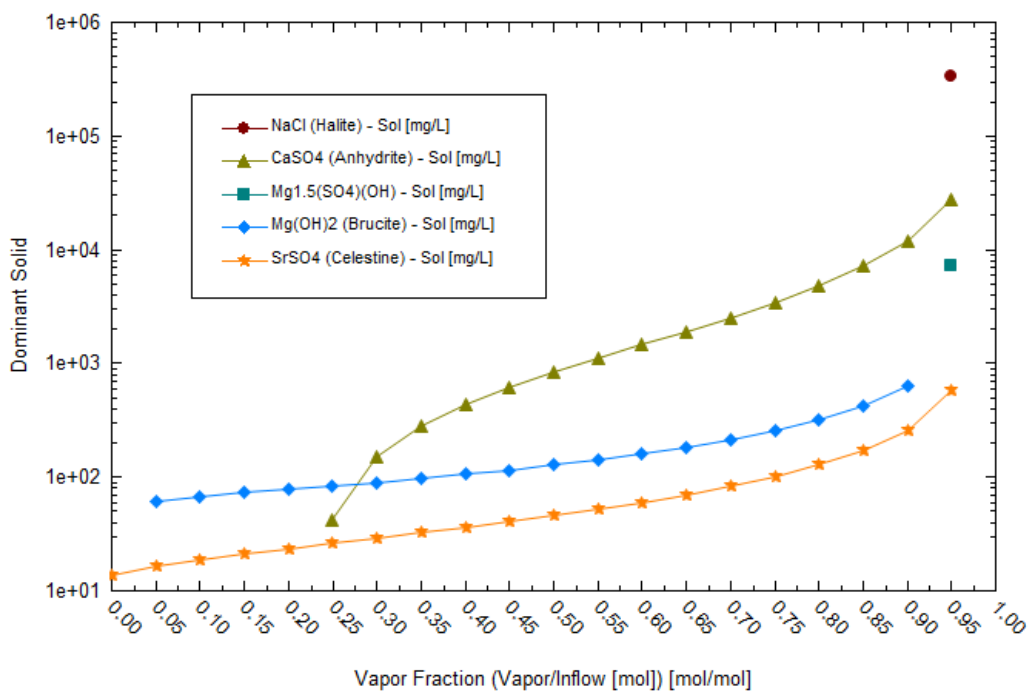
Remove **Temperature** from the Y1 axis (double click or use the << button)

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

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



Plot in semilogarithmic scale



As the water evaporates  $\text{CaSO}_4$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{SrSO}_4$  salts precipitate at all temperatures.  $\text{NaCl}$  and a  $\text{Mg}/\text{SO}_4/\text{OH}$  double salt starts to precipitate at 95% vapor fraction.

## Dual Surveys

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

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

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

The interface shows a table of variables and a configuration panel for dual surveys.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.5082
Temperature (°C)	
Pressure (atm)	
<b>Inflows (mol)</b>	
H2O	55.5082

**Survey Configuration:**

- Survey by: Temperature
- Then by (optional): Pressure
- Vary:  Independently,  Together
- Calculate:

**Summary:**

- Temperature survey:
  - Range: 25.0 to 100.0 °C
  - Step size: 5.0 °C
  - No. steps: 15
- Pressure survey:
  - Range: 1.0 to 10.0 atm
  - Step size: 1.0 atm
  - No. steps: 9
- Primary and secondary survey variables move independently
- Total points: 160
- Unit Set: Metric (moles)
- Automatic Chemistry Model: Aqueous (H+ ion) Databanks

## Temperature and Pressure Survey

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

### *Example 23: Dissolution of CO<sub>2</sub> in water as a Function of Temperature and Pressure*

In Example 19, the dissolution of CO<sub>2</sub> 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<sub>2</sub> dissolution.

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

### *Starting the Simulation*

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

Temperature and Pressure Survey Calculation			
Calculation Settings		Stream Composition and Conditions	
Calculation Type	Survey	Stream Amount	Calculated
Stream Name	T/P Survey	Pressure Range	5-100 atm
Survey Name	CO <sub>2</sub> 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
		H <sub>2</sub> O	55.5082 moles
		CO <sub>2</sub>	10 moles

Add a new **Stream**

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

Select the **MSE-SRK** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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

Enter the composition of the stream given in the table above

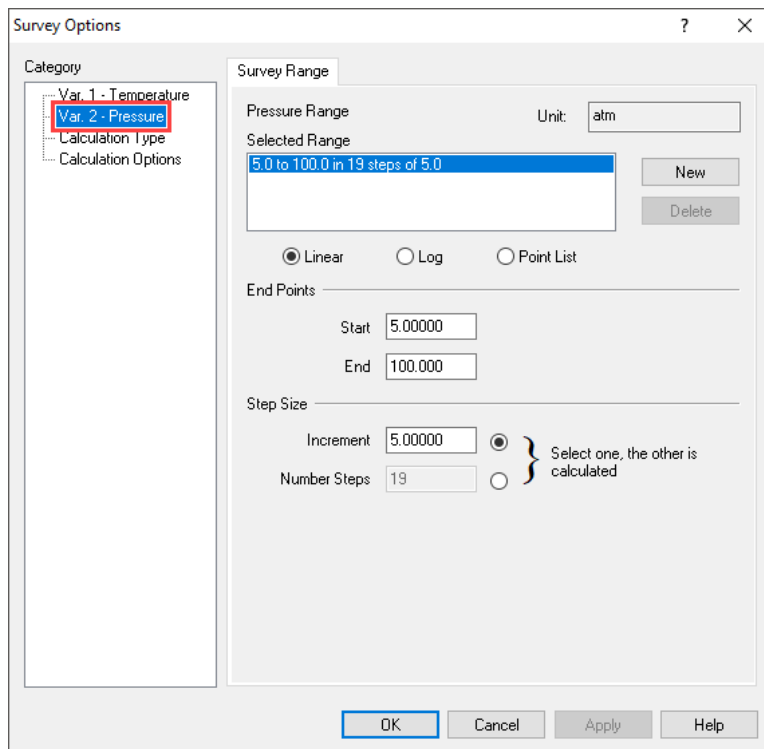
Go to the **Add Calculation** button and select **Survey** calculation

Change the **Survey** name to **CO<sub>2</sub> dissolution T/P** using the **<F2>** key

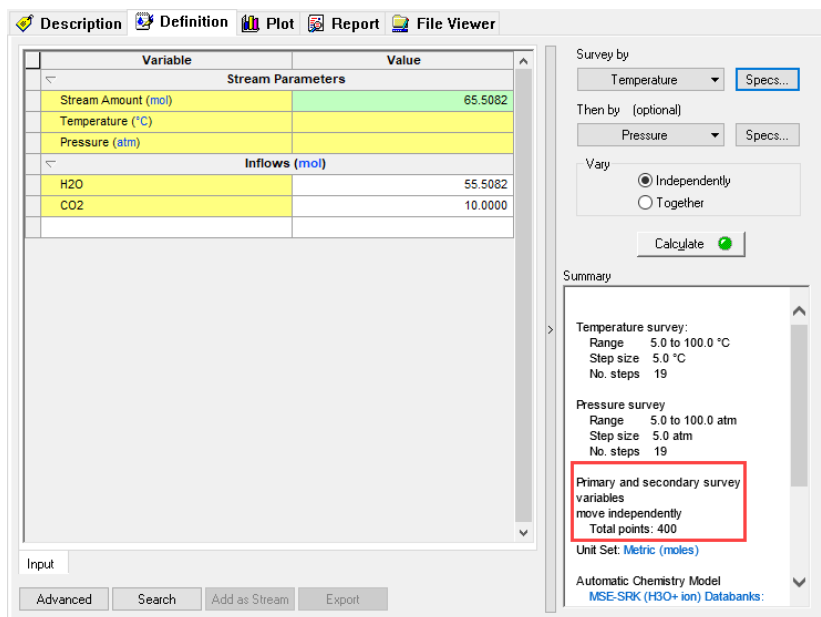
Select **Temperature** and then by **Pressure**

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

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




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



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

### Analyzing the Results

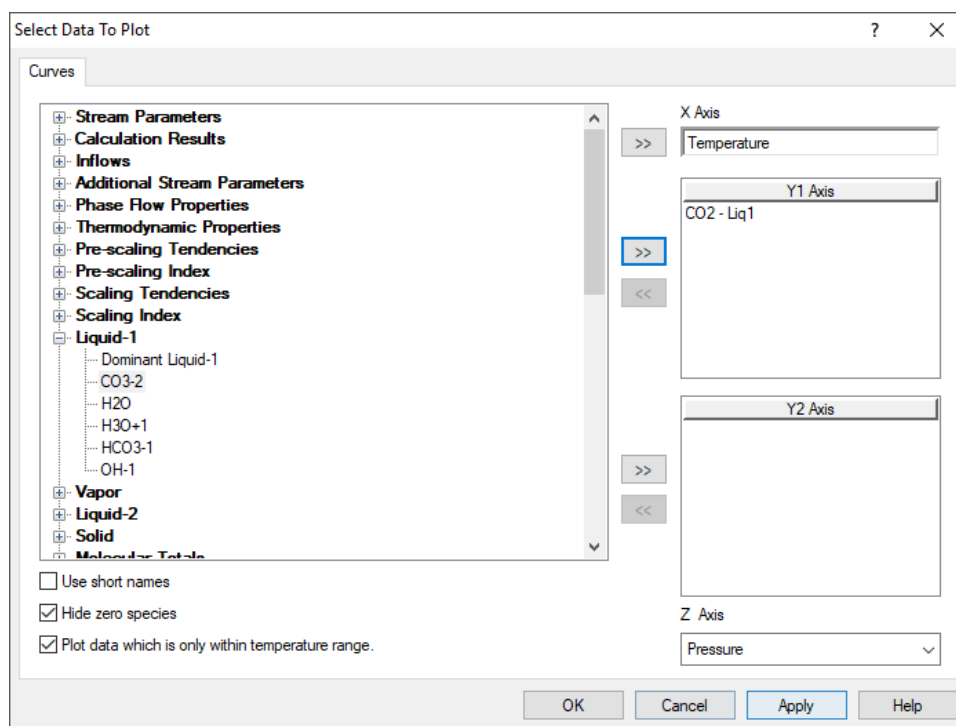
Click on the **Plot** tab (  **Plot** ). The default plot is the phase amounts in grams of Liquid-1 (Aqueous Phase), Liquid-2 (Organic Phase), Solid and Vapor.

We are interested in the solubility of CO<sub>2</sub> in water, i.e., in the Liquid-1 phase. We can change the default plot to show the molecular CO<sub>2</sub> dissolved in water (CO<sub>2</sub>-Liq1).

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

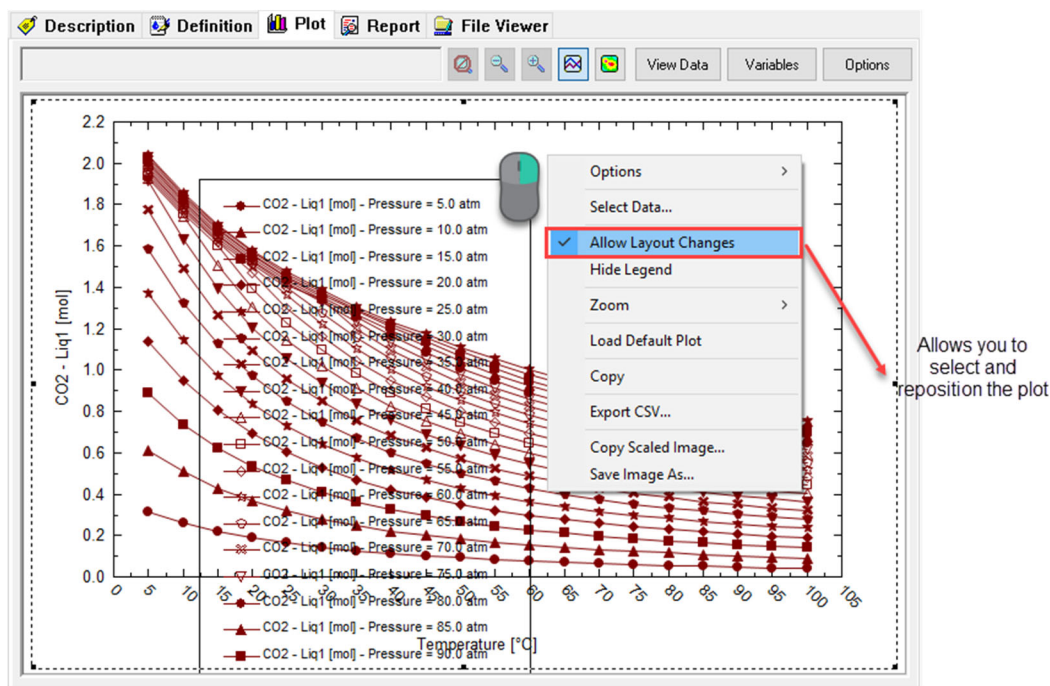
**Double click** or use the << button to remove the **Phase Amount** variables.

Look for **Liquid-1** and click on the  box to show all the available variables. **Select** CO<sub>2</sub>-Liq1 and put it in the Y1 Axis using the >> button. Then click **OK**.

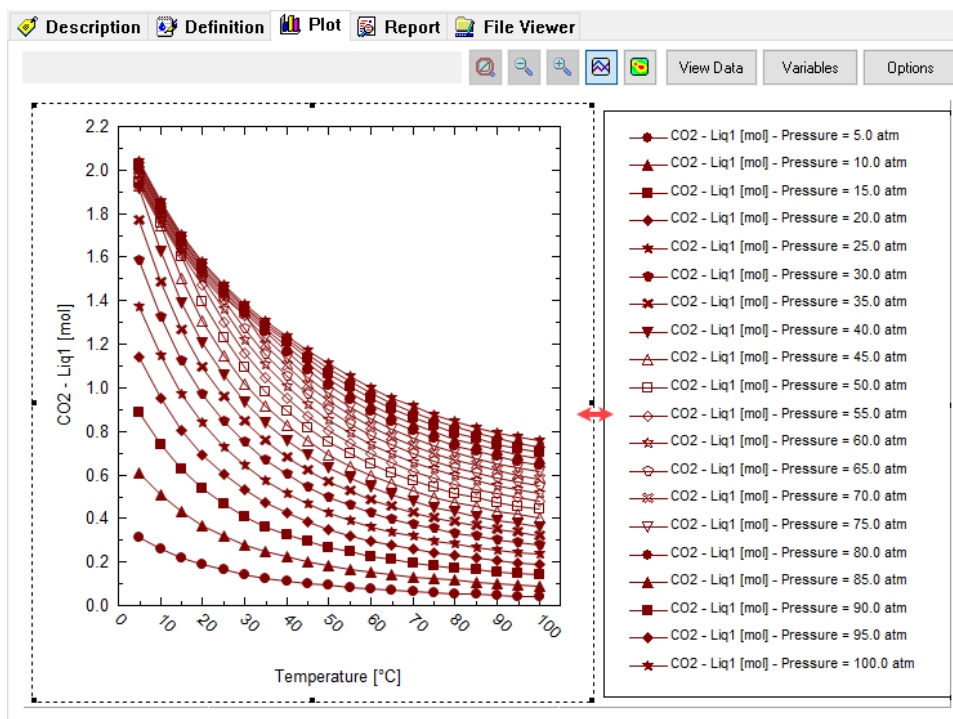


The default plot now is showing the dissolved CO<sub>2</sub> in the water (Liquid-1 Phase) in the Y1 Axis as function of pressure. Unfortunately, the legend is covering the plot.

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



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

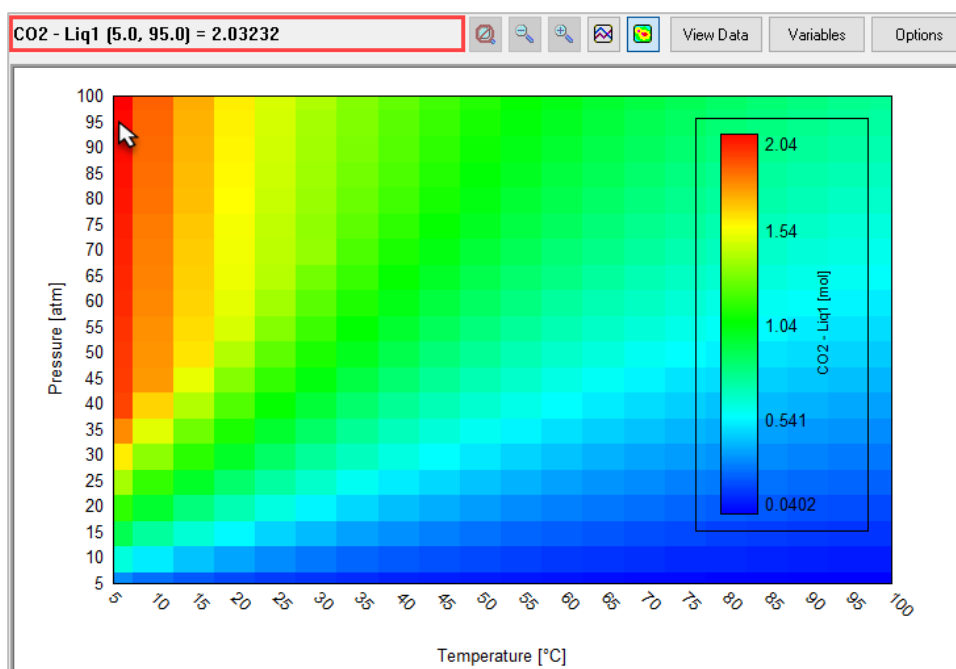


As the temperature increases (at a fixed pressure) the solubility of CO<sub>2</sub> decreases. This is to be expected since at higher temperatures it is easy to overcome the vapor pressure and CO<sub>2</sub> is released as gas. As the pressure increases (at a fixed temperature) the solubility of CO<sub>2</sub> in solution increases.

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

The resulting plot is now a pixelated color plot showing the moles of molecular CO<sub>2</sub> dissolved in the Liquid-1 (Aqueous) phase, at each T and P value.

The number of moles of CO<sub>2</sub> is characterized by a different color that is shown in the legend (maximum value is given in red, and minimum value is given in blue). You can mouse over any location in the plot and the moles of CO<sub>2</sub> dissolved in the Liquid-1 phase at each T and P value will be shown in the left corner box.

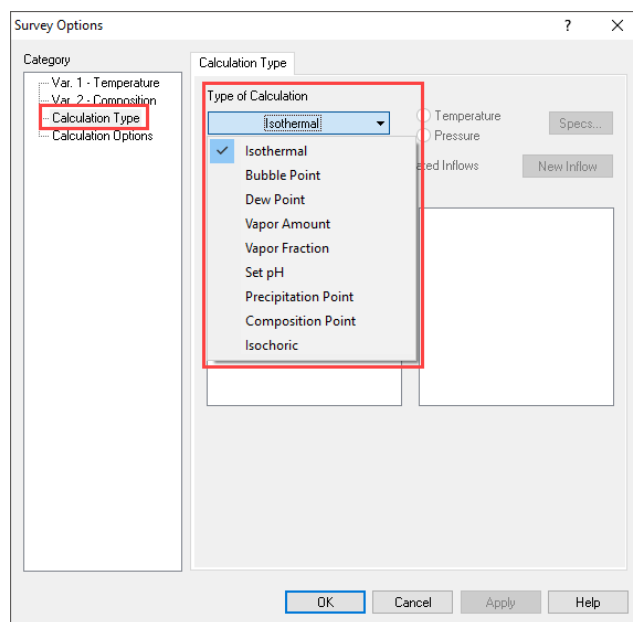


**Note:** The legend scale can also be optimized by either right-mouse-clicking on the Legend and selecting **Options>Plot Options>Contour** or clicking on the **Options** button in the upper right and selecting **Contour**. Both open to the Contour options window, where the color and range can be modified.

In the contour plot, you can see the effect of both Temperature (x-axis) and Pressure (y-axis) on the solubility of CO<sub>2</sub> in water. Higher solubilities are obtained at high pressures and low temperatures, while lower solubilities are obtained at high temperatures and low pressures.

## Survey by changing the single point calculation type

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



## Temperature Survey with a Precipitation Point Calculation

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

### *Example 24: Solubility of Halite as a Function of Temperature*

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

#### *Starting the Simulation*

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

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

Add a new **Stream**

Click on the new Stream and press <F2> to change the name to *Halite Solubility vs T and P*

Select the **MSE** thermodynamic Framework

Click on the **Names Manager** Icon and select the **Formula** option

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

Enter the composition of the stream given in the table above

Go to the **Add Calculation** button and select **Survey** calculation

Change the **Survey** name to *Halite Solubility vs T* using the <F2> key

Select **Temperature** as the type of survey

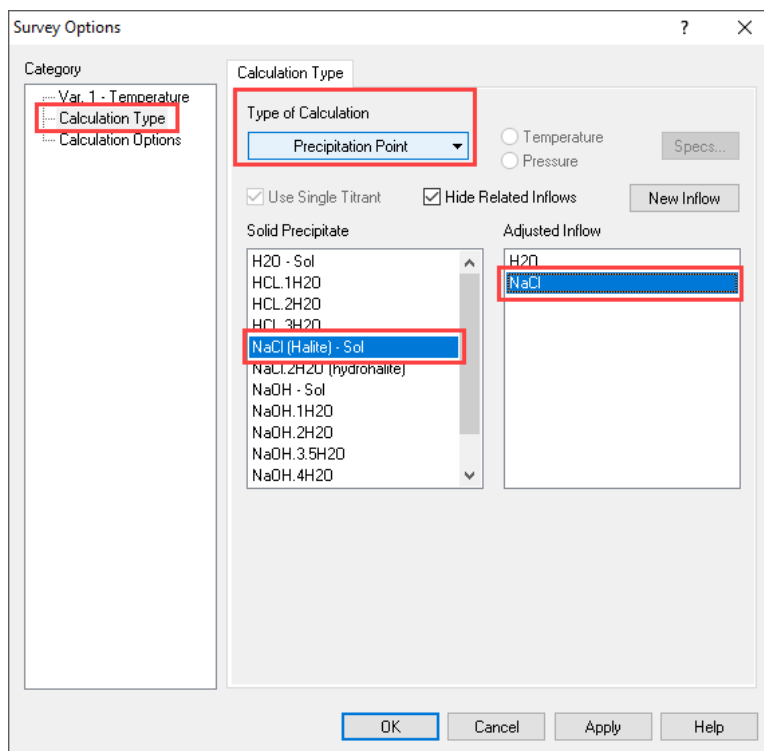
Click on the **Temperature Specs** button. This will open the **Survey Options Window**

Change the **Temperature Range** to 0-100 °C. Set the **Step Size** to 5 °C increments.

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

Under Type of Calculation Change the Default Isothermal to **Precipitation Point** (use the drop-down arrow)

Select **NaCl (Halite)-Sol** as the **Solid Precipitate** and **NaCl** as the **Adjusted Inflow**. Then click **OK**.




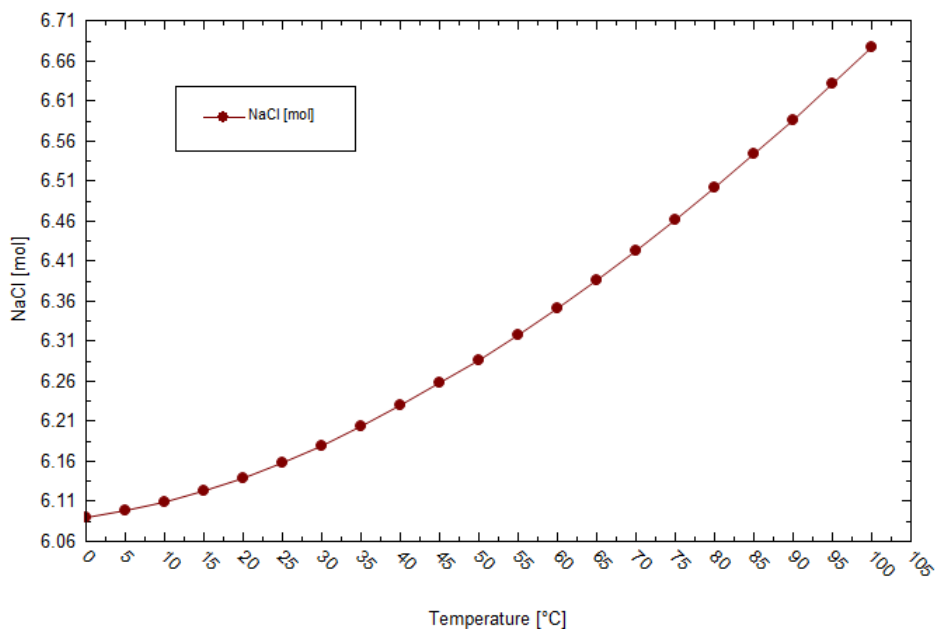
The **Calculation Parameters** section is now shown in the Definition Tab, highlighting the Precipitant (NaCl (Halite)) and the Adjusted Inflow (NaCl).

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

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

### Analyzing the Results

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



Halite solubility increases slightly with temperature, from 6.16 moles/1kg H<sub>2</sub>O at 25°C to 6.68 moles/1kg H<sub>2</sub>O at 100°C.

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

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

#### Starting the Simulation

Under the **Solubility vs T** stream add a new Survey (see Stream information in Example 24)

Change the **Survey** name to **Halite Solubility vs T and P** using the <F2> key

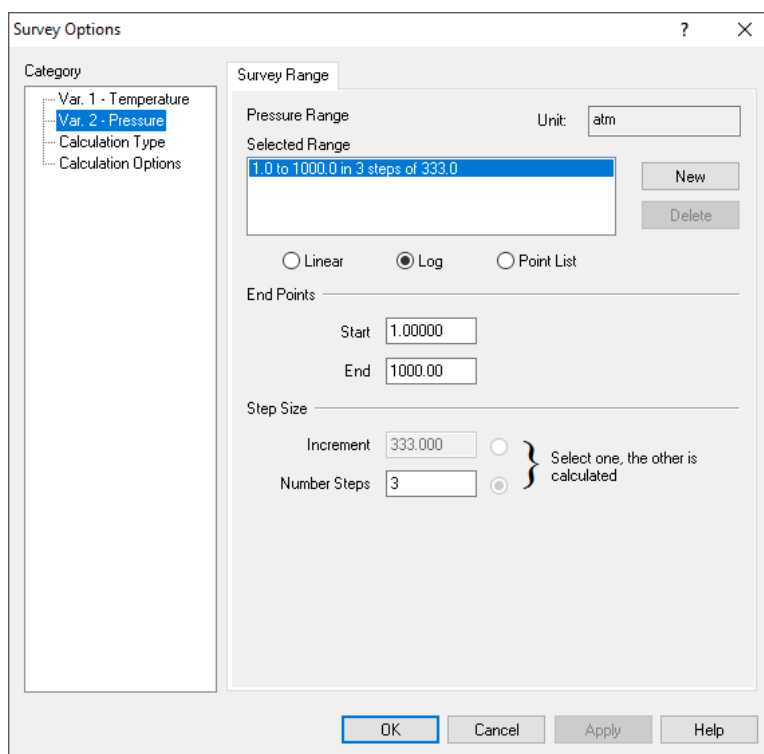
Select Survey by **Temperature** and then by **Pressure** (This is a dual survey)

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

Change the **Temperature Range** to 0-100 °C. Set the **Step Size** to 5 °C increments.

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

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



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


Under Type of Calculation Change the Default Isothermal to **Precipitation Point** (use the drop-down arrow)

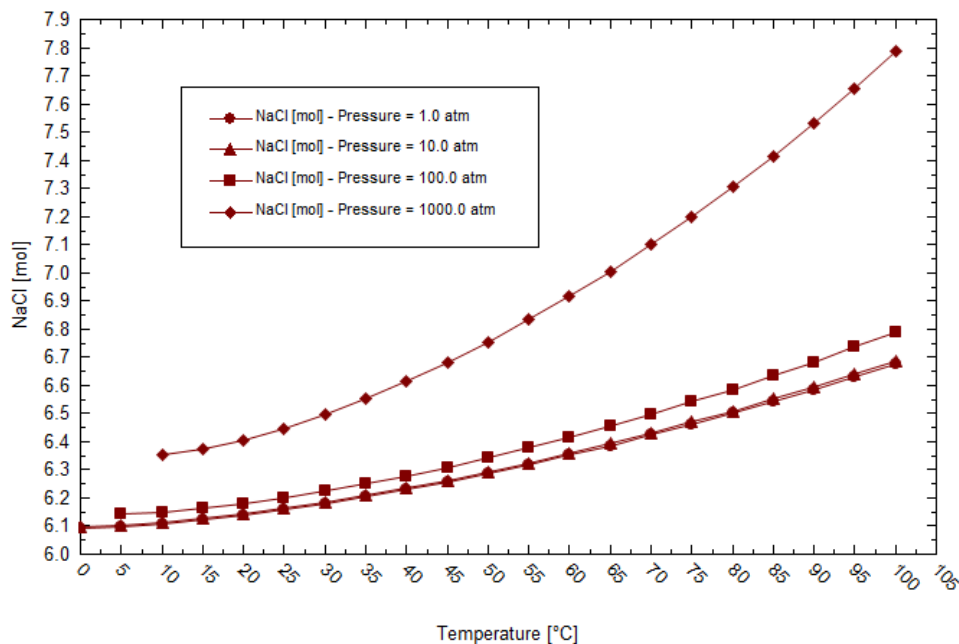
Select **NaCl (Halite)-Sol** as the **Solid Precipitate** and **NaCl** as the **Adjusted Inflow**. Then click **OK**.

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

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

## Analyzing the Results

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



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

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

Return to the **Definition Tab**

Click on the **Temperature Specs** button.

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

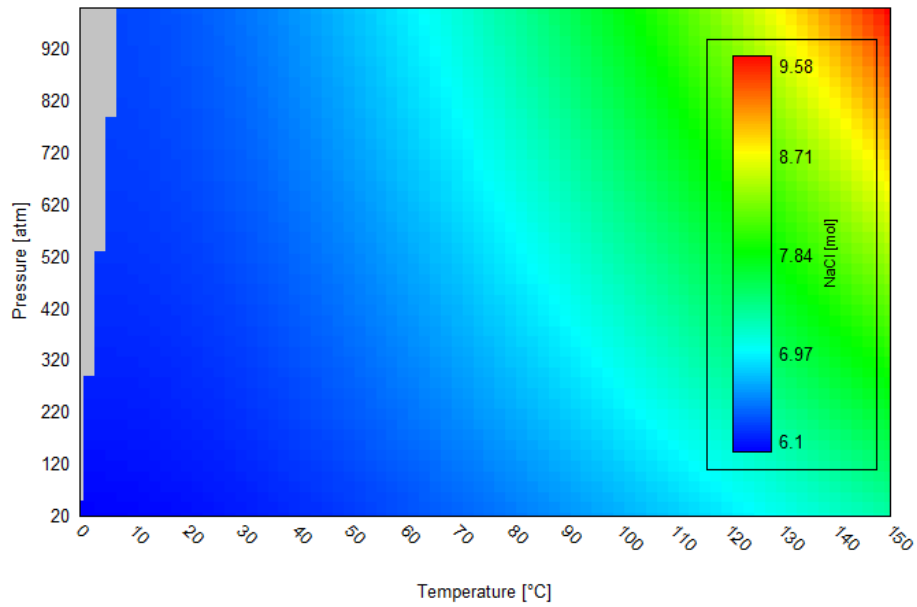
Click on **Var. 2 – Pressure**, in the Category Window to define the Pressure Range.

Change the survey to **Linear** scale, change the **Pressure Range** from 20 to 1000 atm, and set the **Step Size** to **20 atm** increments. Then click **OK**.

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

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

Click on the **Plot** tab and change the Plot to contour (  ).



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

## Composition Survey with a Bubble and Dew Point Calculation

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

### Example 26: Ethanol-Water Azeotrope

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

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

### Starting the Simulation

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

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

### Calculating the Bubble Point

Add a new **Stream**

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

Select the **MSE** thermodynamic Framework

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

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

Enter the composition of the stream given in the table above

Go to the **Add Calculation** button and select **Survey** calculation

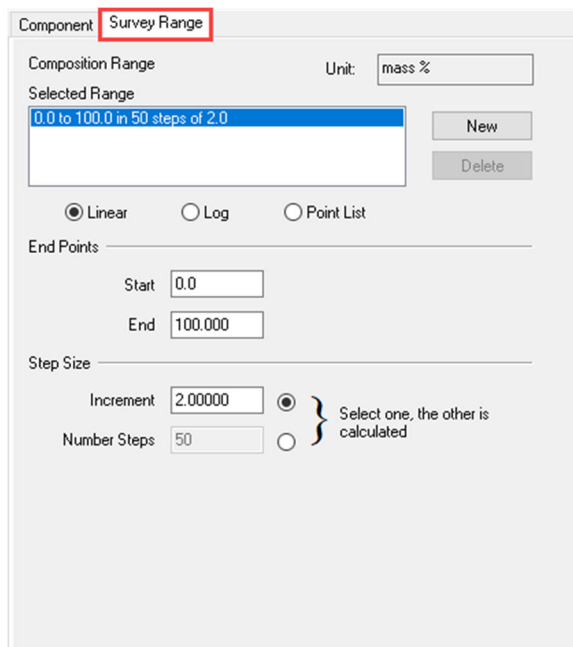
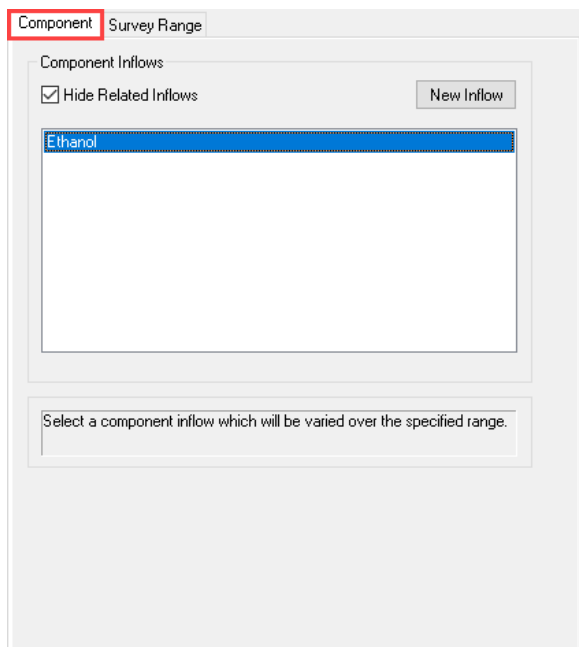
Select **Composition** as the type of survey

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

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

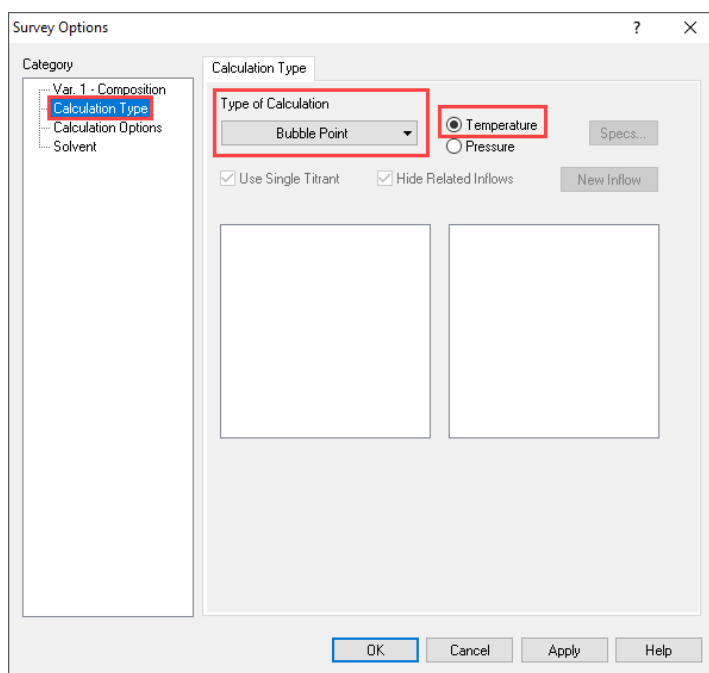
Under the **Component** tab, select **Ethanol**

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



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


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

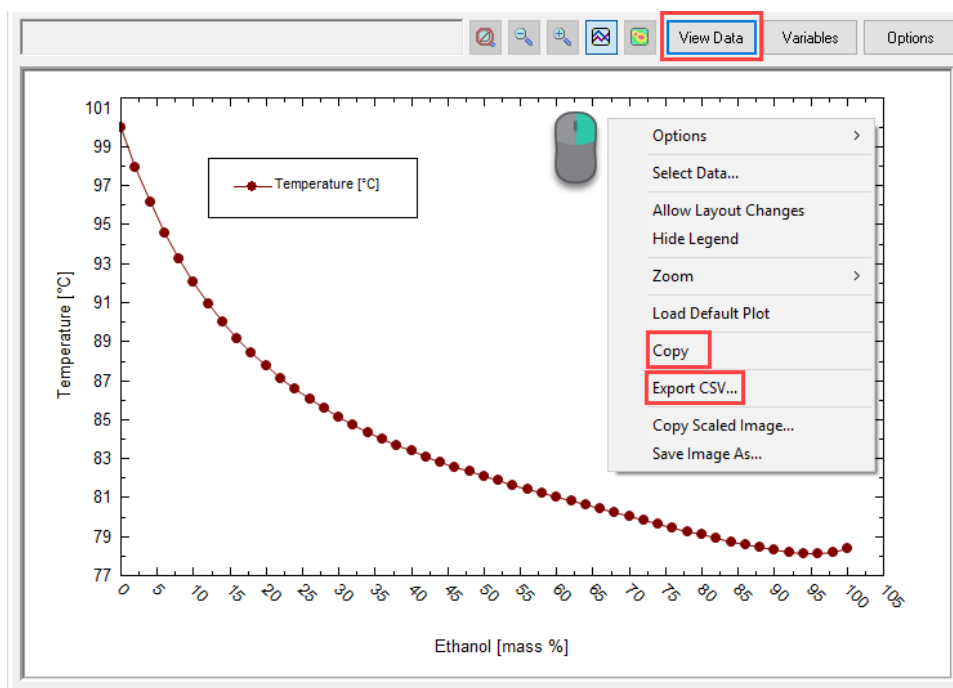


We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key.

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

### Analyzing the Results

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



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

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

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

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

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

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

### *Calculating the Dew Point*

Return to the **Definition tab**

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

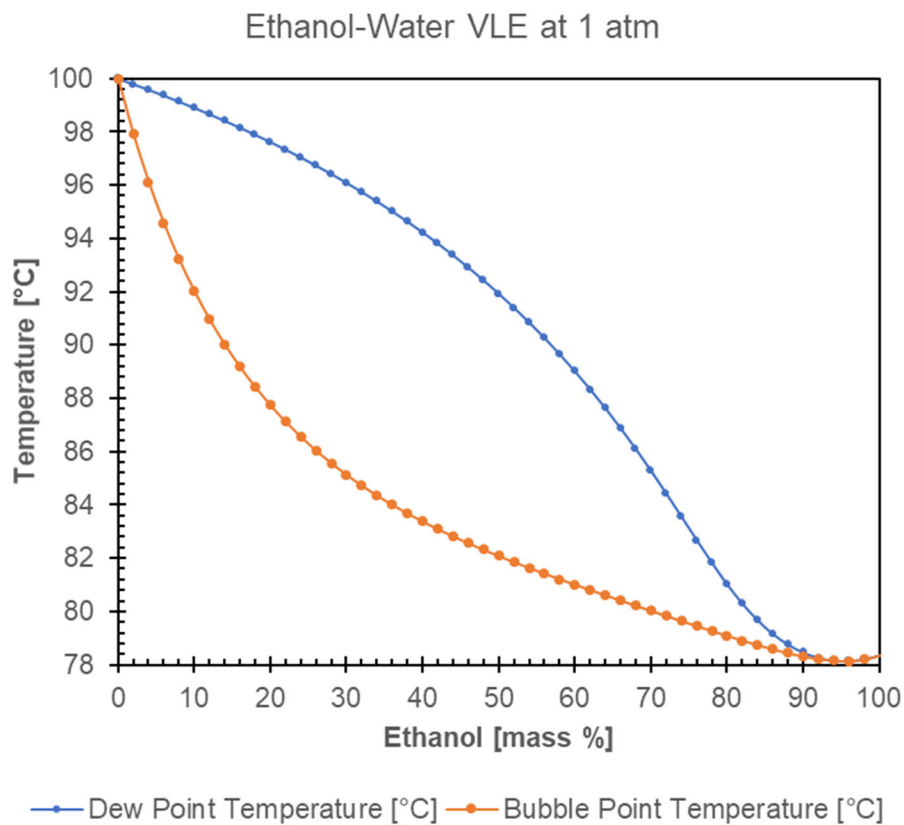
Click on **Calculation Type**, in the Category Window to define the Type of Calculation

Change the calculation type to **Dew Point** (use the drop-down arrow). Then click **OK**.

**Recalculate**, and click on the **Plot tab**

Right click and **Copy** the data, then open your preferred plotting tool and **Paste** the data

**Plot** the two temperature curves vs mass% of ethanol and format as needed



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

## Section 3. Water Analysis (Ionic Inputs)

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

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

The screenshot displays the OLI Studio interface for Water Analysis. The main window is titled "WaterAnalysis" and contains a table with two columns: "Variable" and "Value". The table is organized into several sections:

- Analysis Parameters:**
  - Stream Amount (L): 1.00000
  - Temperature (°C): 25.0000
  - Pressure (atm): 1.00000
- Recorded Properties:**
  - Total Dissolved Solids (mg/L): 0.0
  - Measured pH: 0.0
  - Measured Alkalinity (mg HCO<sub>3</sub>/L): 0.0
  - Density (g/ml): 0.0
  - Specific Electrical Conductivity (µmho/cm): 0.0
- Neutrals (mg/L):**
  - H<sub>2</sub>O: 0.0
  - CO<sub>2</sub>: 0.0
  - H<sub>2</sub>S: 0.0
  - SiO<sub>2</sub>: 0.0
  - B(OH)<sub>3</sub>: 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

On the right side of the interface, there is a "Template Manager" section with a dropdown menu set to "Standard" and a "Save as..." button. Below that is a "Summary" section with the following text:

Unit Set: Metric (mass concentration)  
Automatic Chemistry Model  
Aqueous (H+ ion) Databanks:  
Aqueous (H+ ion)  
Using K-fit Polynomials  
T-span: 25.0 - 225.0  
P-span: 1.0 - 1500.0

At the bottom of the interface, there are "Measured" and "Advanced" tabs, and a "Save" button. The status bar at the very bottom reads "For Help, press F1" and "NUM".

## 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.

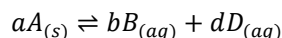
## Scaling

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):



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.

$$IAP = (a_B)_{actual}^b \cdot (a_D)_{actual}^d$$

### 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 ( $K_{sp}$ ).

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

Scaling tendencies are essentially saturation ratios. Thus, if

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

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

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

Thus, if

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

### ***Pre-scaling Tendency and Scale Index***

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

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

### ***Difference between Post-scale and Pre-scale***

**Pre-Scale:** The saturation ratio before solids precipitate.

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

Another way to interpret these two definitions is:

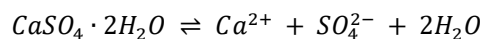
**Pre-Scale** represents the condition before any solids are allowed to form. This is a non-equilibrium condition and can be viewed as the condition where *time* = 0.

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

### **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:



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

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

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

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

$$a_{H_2O} = 0.9997$$

### Calculating the IAP

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

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

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

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

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

### 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

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

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

$$SI \approx -0.231$$

## Entering Data for Water Analysis

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

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

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

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

Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	0.0
Measured Alkalinity (mg HCO <sub>3</sub> /L)	0.0
Measured TIC (mol C/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (µmho/cm)	0.0

The concentration of Neutrals, Total Ions, 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)	
H <sub>2</sub> O	
CO <sub>2</sub>	0.0
H <sub>2</sub> S	0.0
SiO <sub>2</sub>	0.0
B(OH) <sub>3</sub>	0.0
Total Ions (mg/L)	
P as PO <sub>4</sub> -3	0.0
Si as SiO <sub>2</sub>	0.0
B as B(OH) <sub>3</sub>	0.0
Cations (mg/L)	
Na+1	0.0
K+1	0.0
Ca+2	0.0
Mg+2	0.0
Sr+2	0.0
Ba+2	0.0
Fe+2	0.0
Anions (mg/L)	
Cl-1	0.0
SO <sub>4</sub> -2	0.0
HCO <sub>3</sub> -1	0.0
HS-1	0.0
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> -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(+)	CUION
SYN Cu(++)	CUION
SYN Cu(+1)	CUION
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>**.

Neutrals (mg/L)	
H2O	
CO2	0.0
H2S	0.0
SiO2	0.0
B(OH)3	0.0
X OLI	0.0

## Water Analyses - Reported Elements as Total Ions

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

### Converting element concentration to species for Brine or Water Analysis

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

## A Basic Water Analysis

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

## Example 28: Ground Water Analysis

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

### Starting the Simulation

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

Ground Water Analysis					
Analysis Parameters/Settings			Recorded Properties		
Stream Amount	1 L (Default)		Total Dissolved Solids	Not recorded	
Temperature	25 °C		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				
Analysis Name	Basic Water Analysis				
Composition					
Neutrals (mg/L)		Cations (mg/L)		Anions (mg/L)	
CO2	150	Na+1	1060	Cl-1	3896
H2S	15	K+1	50	SO4-2	54
NH3	5	Ca+2	773		
		Mg+2	177		
		Sr+2	0.18		
		Ba+2	0.46		
		Fe+2	62.1		
		Mn+2	2.80		
		Al+3	0.74		

### Setting the Water Analysis

Add a **Water Analysis**

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

Select the **MSE** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

**Click** on the **Units Manager** Icon, and select Metric, Batch, Concentration (it may be defined by default)

Under the **Analysis** Tab, enter the Analysis Parameters, Recorded properties, and composition of the water given in the table above.

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

OLI Studio (Version 11.5.1 Beta) - [3. Water Analysis - Example\_28.oad]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator: 3. Water Analysis - Example\_28.oad

- Streams
  - Basic Water Analysis
    - Reconcile

Basic Water Analysis

Description Analysis Report

Variable	Value
<b>Analysis Parameters</b>	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Recorded Properties</b>	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.70000
Measured Alkalinity (mg HCO <sub>3</sub> /L)	0.0
Measured TIC (mol Cl/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (µmho/cm)	0.0
<b>Neutrals (mg/L)</b>	
H <sub>2</sub> O	
CO <sub>2</sub>	150.000
H <sub>2</sub> S	15.0000
SiO <sub>2</sub>	0.0
B(OH) <sub>3</sub>	0.0
NH <sub>3</sub>	5.00000
<b>Total Ions (mg/L)</b>	
P as PO <sub>4</sub> -3	0.0
Si as SiO <sub>2</sub>	0.0
B as B(OH) <sub>3</sub>	0.0
<b>Cations (mg/L)</b>	
Na+1	1060.00
K+1	50.0000
Ca+2	773.000
Mg+2	177.000
Sr+2	0.180000
Ba+2	0.460000
Fe+2	62.1000
Mn+2	2.80000
Al+3	0.740000
<b>Anions (mg/L)</b>	
Cl-1	3896.00
SO <sub>4</sub> -2	54.0000
HCO <sub>3</sub> -1	0.0
HS-1	0.0
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> -1	0.0

Measured  
Advanced

Actions: Add Reconciliation, Add Water Analysis

Plot Template Manager

Summary: Unit Set: Metric (mass concentration), Automatic Chemistry Model, MSE (H<sub>3</sub>O+ ion) Databanks, MSE (H<sub>3</sub>O+ ion), Using Helgeson Direct

For Help, press F1

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

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

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

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

Select the **No Reconcile** option

The screenshot shows the OLI Studio interface with the 'Reconcile' dialog box open. The 'Reconciliation' tab is active, and the 'No Reconcile' option is selected. The 'Calculate Alkalinity' checkbox is present but unchecked. The main window displays a table of chemical species and their concentrations.

Variable	Value
<b>Analysis Parameters</b>	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Recorded Properties</b>	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.70000
Measured Alkalinity (mg HCO <sub>3</sub> /L)	0.0
Measured TIC (mol C/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (µmho/cm)	0.0
<b>Neutrals (mg/L)</b>	
H <sub>2</sub> O	
CO <sub>2</sub>	150.000
H <sub>2</sub> S	15.0000
SiO <sub>2</sub>	0.0
B(OH) <sub>3</sub>	0.0
NH <sub>3</sub>	5.00000
<b>Total Ions (mg/L)</b>	
P as PO <sub>4</sub> -3	0.0
Si as SiO <sub>2</sub>	0.0
B as B(OH) <sub>3</sub>	0.0
<b>Cations (mg/L)</b>	
Na+1	1060.00
K+1	50.0000
Ca+2	773.000
Mg+2	177.000
Sr+2	0.180000
Ba+2	0.460000
Fe+2	62.1000
Mn+2	2.80000
Al+3	0.740000
<b>Anions (mg/L)</b>	
Cl-1	3896.00
SO <sub>4</sub> -2	54.0000
HCO <sub>3</sub> -1	0.0
HS-1	0.0
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> -1	0.0

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

## Analyzing the Results

### Viewing the Summary Box

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

Neutrals (mg/L)	
H2O	
CO2	150.000
H2S	15.0000
SiO2	0.0
B(OH)3	0.0
NH3	5.00000

Total Ions (mg/L)	
P as PO4-3	0.0
Si as SiO2	0.0
B as B(OH)3	0.0

Cations (mg/L)	
Na+1	1060.00
K+1	50.0000
Ca+2	773.000
Mg+2	177.000
Sr+2	0.180000
Ba+2	0.460000
Fe+2	62.1000
Mn+2	2.80000
Al+3	0.740000

Summary	
Unit Set: Metric (mass concentration)	
Automatic Chemistry Model	
MSE (H3O+ ion) Databanks:	
MSE (H3O+ ion)	
Using Helgeson Direct	
Dominant Ion Charge Balance (eq/L):	
Cation Charge:	0.102945 eq/L
Anion Charge:	-0.111016 eq/L
Imbalance:	-8.07170e-3 eq/L
185.568 mg/L of Na+1 is needed to balance.	
Isothermal Calculation	
25.0000 °C 1.00000 atm	
Phase Amounts	
Aqueous	1001.98 g
Solid	0.0116370 g
Aqueous Phase Properties	
pH	4.49376
Ionic Strength	2.49913e-3 mol/mol
Density	1.00198 g/ml
Calc. elapsed time: 18.727 sec	
Calculation complete	

**Charge Balance information**

**Calculation Type**

**Phase Amounts**

**Aqueous Properties**

The top section contains the **charge balance information** showing the total equivalent charge (positive and negative), and the charge imbalance. This example has a negative imbalance of  $-8.072 \times 10^{-3}$  eq/L, indicating that more cations are needed in solution in order to reach electroneutrality. The software calculates that 185.568 mg/L of Na<sup>+</sup> are needed to balance the solution. The software adds this amount of Na<sup>+</sup> 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 reconciled. In other words, the software has converted the **ionic inflows** into a **molecular stream**.

Variable	Value
<b>Analysis Parameters</b>	
Stream Amount (L)	1.00000
Volume - Liquid-1 (L)	1.00000
Volume - Solid (cm <sup>3</sup> )	2.40298e-3
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Molecular Totals (mg/L)</b>	
AlCl <sub>3</sub>	3.61208
Al(OH) <sub>3</sub>	0.0262829
BaCl <sub>2</sub>	0.631654
BaSO <sub>4</sub>	0.0738067
CaCl <sub>2</sub>	2092.78
CaO	24.1565
CO <sub>2</sub>	150.000
FeCl <sub>2</sub>	124.399
FeS	11.4757
H <sub>2</sub> O	9.95556e5
H <sub>2</sub> S	10.5511
KCl	95.3381
MgCl <sub>2</sub>	693.368
MnCl <sub>2</sub>	6.41382
NaCl	3166.36
NH <sub>3</sub>	4.99999
SO <sub>3</sub>	44.9809
SrCl <sub>2</sub>	0.325663

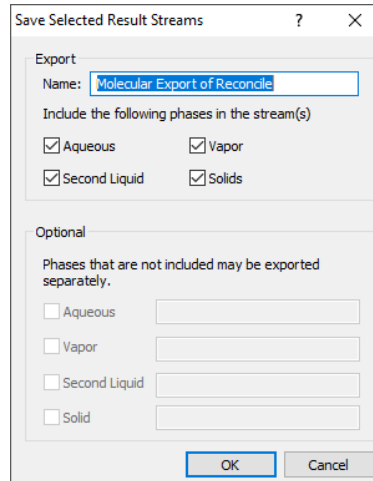
**Note:** The software generates molecular concentrations based on two priorities. The first priority is to create the least number of molecular inflows. This example contains eighteen inflows (plus H<sub>2</sub>O not shown). The second priority is to create the least number of total moles. Moles are not shown here, since the units are mg/l. The moles are shown in the Report tab.

You can use this molecular form as a new Stream in OLI Studio, by using the **Add as Stream** button, or it can be exported to a separate software like OLI Flowsheet: ESP , Aspen Plus, UniSim Design, or other simulators.

## Converting the Ionic Inflows into a Molecular Stream

For practice, let's add this Molecular Basis as a Stream into the Navigator Panel.

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



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

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

OLI Studio - [Water Analysis Calculations.oad]

File Edit Streams Calculations Chemistry Tools View Window Help

L1 Va So L2 Re MSE MSE EXP. AQ

Navigator  
Document1  
Water Analysis Calculations.oad  
Streams  
Basic Water Analysis  
Reconcile  
Molecular Export of Reconcile

Actions  
Add Stream Add Stabl  
Add Mixer Add Corn  
Add Single Point  
Add Survey  
Add Chemical Diagram

Plot Template Manager

Molecular Export of Reconcile

Description Definition Report

Variable	Value
Stream Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mg/L)	
H2O	
CO2	150.000
H2S	10.5511
NH3	4.99999
AlCl3	3.61208
BaCl2	0.631654
CaCl2	2092.78
CaO	24.1565
FeCl2	124.399
KCl	95.3381
MgCl2	693.368
MnCl2	6.41382
NaCl	3166.36
SO3	44.9809
SrCl2	0.325663
BaSO4	0.0738067
FeS	11.4757
Al(OH)3	0.0282829

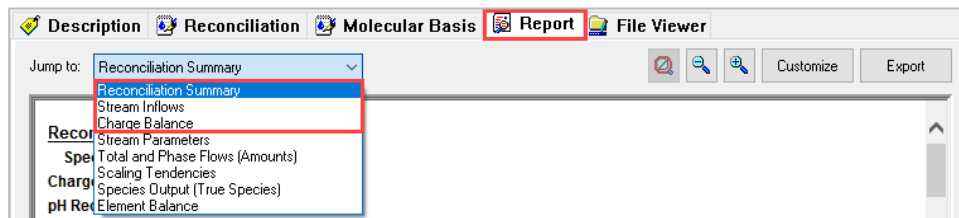
Input

Advanced Search Add as Stream Export

Summary  
Unit Set: Metric (mass concentration)  
Automatic Chemistry Model  
MSE (H3O+ Ion) Databanks:  
MSE (H3O+ Ion)  
Using Helgeson Direct

## Viewing the Report Tab

The **Report** tab is slightly different from the Single Point report described in Section 1. This Report contains three additional tables, all of which are located at the top. These tables are the Reconciliation Summary, Stream Inflows, and Charge Balance.



The **Reconciliation Summary** table confirms the specifications for the reconciliation such as the charge balance method and the reconciliation type (these concepts will be discussed in more detail later in the manual). Additionally, shows the conditions at which the calculation was run, in this case 25°C and 1 atm. And finally, shows a comparison between the measured and calculated properties, in this case it shows the measured vs calculated pH.

### Reconciliation Summary

#### Specification

Charge Balance Method Dominant Ion

pH Reconciliation Type No reconciliation

	Measured	Calculated
Temperature, °C	25.0000	
Pressure, atm	1.00000	
pH	6.70000	4.49376
Density, g/ml		1.00198
Water, mg/L		9.95555e5

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

### Stream Inflows

Row Filter Applied: Only Non Zero Values

Species	Input mg/L	Output mg/L
H2O	1.00000e6	9.95555e5
Na+1	1060.00	
K+1	50.0000	
Ca+2	773.000	
Mg+2	177.000	
Sr+2	0.180000	
Ba+2	0.460000	
Fe+2	62.1000	
Cl-1	3896.00	
SO4-2	54.0000	
CO2	150.000	150.000
H2S	15.0000	15.0000
NH3	5.00000	4.99999
Mn+2	2.80000	
Al+3	0.740000	

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

Charge Balance

Cation Charge: 0.102945 eq/L  
 Anion Charge: -0.111016 eq/L  
 Imbalance: -8.07170e-3 eq/L  
 Adjusted Species: Na+1

Charged Species	Input	Balanced	Difference
	mg/L	mg/L	%
Na+1	1060.00	1245.57	17.51
K+1	50.0000	50.0000	
Ca+2	773.000	773.000	
Mg+2	177.000	177.000	
Sr+2	0.180000	0.180000	
Ba+2	0.460000	0.460000	
Fe+2	62.1000	62.1000	
Mn+2	2.80000	2.80000	
Al+3	0.740000	0.740000	
Cl-1	3896.00	3896.00	
SO4-2	54.0000	54.0000	
HCO3-1	0.0	0.0	
HS-1	0.0	0.0	
C2H3O2-1	0.0	0.0	

## 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](#)).

**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.

**Reconcile pH/Alkalinity:** The software will run an electroneutrality, pH and alkalinity reconciliation. This type of reconciliation will match your recorded pH and alkalinity values. Additionally, the software will compute the water properties such as density, electrical conductivity, etc. The pH of the solution is automatically adjusted by the software by adding either HCl or NaOH or you may select your preferred acids and bases to adjust the pH. The **Alkalinity** is automatically adjusted by the software, using **CO<sub>2</sub>** as the **alkalinity titrant**, **H<sub>2</sub>SO<sub>4</sub>** as the **alkalinity pH** titrant and **4.5** as the **alkalinity end point pH**.

**Reconcile pH/Alkalinity/TIC:** The software will run an electroneutrality, pH, alkalinity and Total Inorganic Carbon (TIC) reconciliation. This type of reconciliation will match your recorded pH, alkalinity and TIC values. Additionally, the software will compute the water properties such as density, electrical conductivity, etc. The **TIC** is automatically calculated by the software, using **CO<sub>2</sub>** as the titrant, **H<sub>2</sub>SO<sub>4</sub>** as the alkalinity pH titrant and 4.5 as the end point pH. The (total) Alkalinity is adjusted by the software by adjusting the acetate concentration (organic acids) to match the target Alkalinity. The Alkalinity is adjusted by adding or removing **acetic acid**. In this calculation, you cannot change the CO<sub>2</sub> or Acetic Acid for the alkalinity adjustment, these are fixed by the software.

Additionally, there is the option to Calculate Alkalinity:  Calculate Alkalinity. It is important to note, that this is only an alkalinity calculation based on the concentration entered, it is not an alkalinity reconciliation.

We will explore the different types of reconciliation and introduce the different specification options according to the reconciliation type.

In this section we will create a new file. We will run a basic water analysis, from which the various reconciliation options will be explored.

## Example 29: Water Analysis – No Reconcile Option

In this example we will calculate the **pH** and different properties of a Produced Water sample based upon its measured composition at 1 atm and 25 °C.

### Starting the Simulation

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

Water Analysis – Reconcile Options					
Analysis Parameters/Settings			Recorded Properties		
Stream Amount	1 L (Default)		Total Dissolved Solids	36500 mg/L	
Temperature	25 °C		Measured pH	7.8	
Pressure	1 atm		Measured Alkalinity	160 mg HCO <sub>3</sub> /L	
Name Style	Display Formula		Density	1.013	
Unit Set	Metric, Batch, Concentration		Specific Electrical Conductivity	Not recorded	
Framework	MSE				
Calculation Type	Water Analysis				
Stream Name	Water Analysis – Reconcile Options				
Composition					
Neutrals (mg/L)		Cations (mg/L)		Anions (mg/L)	
SiO <sub>2</sub>	16	Na <sup>+1</sup>	10000	Cl <sup>-1</sup>	19000
		Ca <sup>+2</sup>	500	SO <sub>4</sub> <sup>-2</sup>	2700
		Mg <sup>+2</sup>	1200	HCO <sub>3</sub> <sup>-1</sup>	142
		Sr <sup>+2</sup>	200	AsO <sub>4</sub> <sup>-3</sup>	12
		Ba <sup>+2</sup>	5	CHO <sub>2</sub> <sup>-1</sup>	20
		Fe <sup>+2</sup>	5	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-1</sup>	50

### Calculating the pH

#### Setting the Water Analysis

#### Add a **Water Analysis**

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

Select the **MSE** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

**Click** on the **Units Manager** Icon, and select Metric, Batch, Concentration (it may be defined by default)

Under the **Analysis** Tab, enter the Analysis Parameters, Recorded properties, and Composition of the water given in the table above.

Go to the **Add Reconciliation** button of the top right corner or select **Add Reconciliation** from the Actions Panel, and name it **No Reconcile**.

Select the **No Reconcile** option (selected by default)

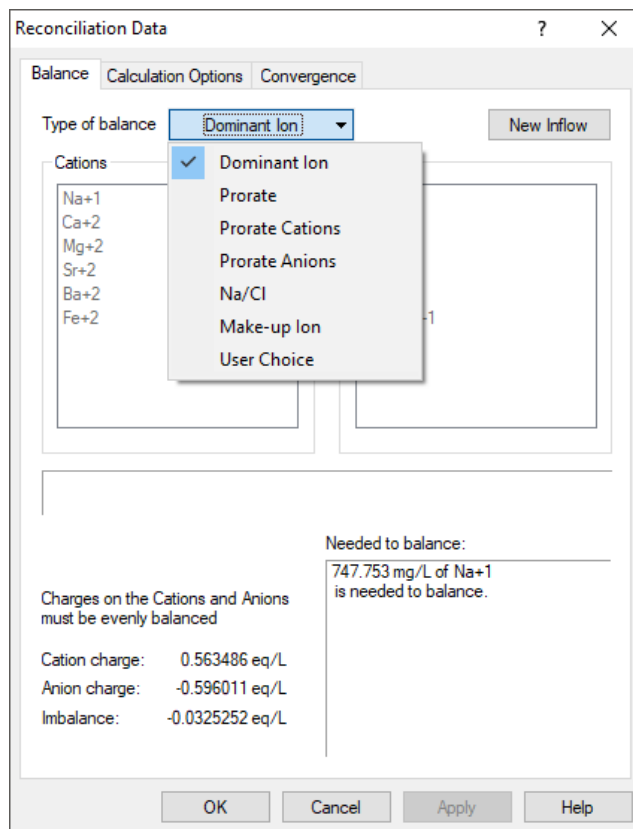
The screenshot displays a software interface for chemical reconciliation. The main window is divided into several sections:

- Navigation Tabs:** Description, Reconciliation (active), Molecular Basis, Report.
- Table:** A table with columns 'Variable' and 'Value'. It is organized into several categories:
  - Analysis Parameters:** Stream Amount (L) 1.00000, Temperature (°C) 25.0000, Pressure (atm) 1.00000.
  - Recorded Properties:** Total Dissolved Solids (mg/L) 0.0, Measured pH 7.80000, Measured Alkalinity (mg HCO<sub>3</sub>/L) 160.000, Measured TIC (mol Cl/L) 0.0, Density (g/ml) 1.01300, Specific Electrical Conductivity (µm) 0.0.
  - Neutrals (mg/L):** H<sub>2</sub>O, CO<sub>2</sub> (0.0), H<sub>2</sub>S (0.0), SiO<sub>2</sub> (16.0000), B(OH)<sub>3</sub> (0.0).
  - Total Ions (mg/L):** P as PO<sub>4</sub>-3 (0.0), Si as SiO<sub>2</sub> (0.0), B as B(OH)<sub>3</sub> (0.0).
  - Cations (mg/L):** Na+1 (10000.0), K+1 (0.0), Ca+2 (500.000), Mg+2 (1200.00), Sr+2 (200.000), Ba+2 (5.00000), Fe+2 (5.00000).
  - Anions (mg/L):** Cl-1 (19000.0), SO<sub>4</sub>-2 (2700.00), HCO<sub>3</sub>-1 (142.000), HS-1 (0.0), C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>-1 (50.00000), HCOO-1 (20.00000), AsO<sub>4</sub>-3 (12.00000).
- Reconciliation Panel (Right):**
  - Buttons: Specs...
  - Section: Reconcile
  - Options:
    - No Reconcile (highlighted with a red box)
    - Reconcile pH
    - Reconcile pH/Alkalinity
    - Reconcile pH/Alkalinity/TIC
  - Calculate Alkalinity
  - Calculate button with a green checkmark.
- Summary Panel (Bottom Right):**
  - Unit Set: Metric (mass concentration)
  - Automatic Chemistry Model
  - MSE (H<sub>3</sub>O+ ion) Databanks: MSE (H<sub>3</sub>O+ ion)
  - Using Helgeson Direct
  - Dominant Ion Charge Balance (eq/L):
    - Cation Charge: 0.563486 eq/L
    - Anion Charge: -0.596011 eq/L
    - Imbalance: -0.0325252 eq/L
  - 747.753 mg/L of Na+1 is needed to balance.
  - Isothermal Calculation: 25.0000 °C 1.00000 atm
  - Calculation not done
- Buttons:** Measured, Advanced, Search, Add as Stream, Export.

**Note:** In the **No reconcile** option, the software runs an electroneutrality reconciliation. The **type of balance** for reconciling electroneutrality is the **Dominant Ion** method. You can select different types of balance for electroneutrality by clicking on the **Specs** button.

### Types of Balance for Electroneutrality

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



There are 7 different Types of Balance:

**Dominant Ion:** This is the default method. The largest counter ion is used to adjust the electroneutrality. In our example, 747.753 mg/L of Na+1 are added since there is an excess of negative charge (see the above image).

**Prorate:** This option keeps the relative amount of the counter ions (for this example, the cations) the same and are adjusted up or down equally until reaching electroneutrality.

**Prorate Cations:** All cations are adjusted up or down equally

**Prorate Anions:** All anions are adjusted up or down equally

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

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

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

Keep the default option, **Dominant Ion**, as the balance type then press **OK**

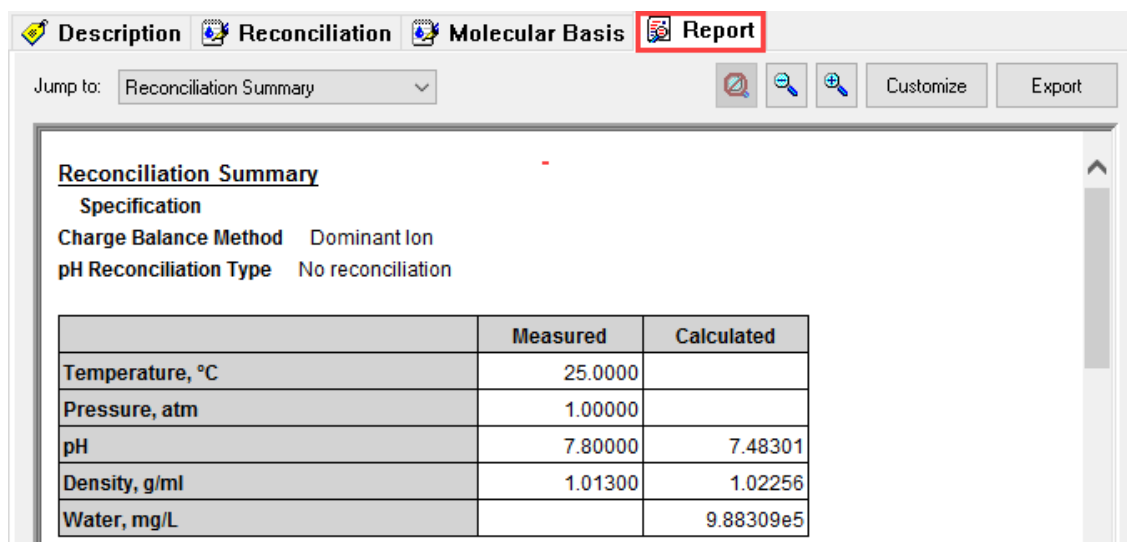
Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

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

### Analyzing the Results

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

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



The screenshot shows the software interface with the **Report** tab selected. The **Reconciliation Summary** table is displayed, showing measured and calculated values for various parameters. The table is as follows:

	Measured	Calculated
Temperature, °C	25.0000	
Pressure, atm	1.00000	
pH	7.80000	7.48301
Density, g/ml	1.01300	1.02256
Water, mg/L		9.88309e5

The calculated pH and density are different to the measured values. The software only used the concentration data to calculate these properties.

### Example 30: Water Analysis – pH Reconcile Option

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

#### Starting the Simulation

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

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

The default units, names and framework have been previously defined

Select the **Reconcile pH** option

Variable	Value
<b>Analysis Parameters</b>	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Recorded Properties</b>	
Total Dissolved Solids (mg/L)	0.0
Measured pH	7.80000
Measured Alkalinity (mg HCO <sub>3</sub> /L)	160.000
Measured TIC (mol C/L)	0.0
Density (g/ml)	1.01300
Specific Electrical Conductivity (µmh)	0.0
<b>Calculation Parameters</b>	
Use Single pH Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
<b>Neutrals (mg/L)</b>	
H <sub>2</sub> O	
CO <sub>2</sub>	0.0
H <sub>2</sub> S	0.0
SiO <sub>2</sub>	16.0000
B(OH) <sub>3</sub>	0.0
<b>Total Ions (mg/L)</b>	
P as PO <sub>4</sub> -3	0.0
Si as SiO <sub>2</sub>	0.0
B as B(OH) <sub>3</sub>	0.0

Reconciliation

Reconcile

No Reconcile

Reconcile pH

Reconcile pH/Alkalinity

Reconcile pH/Alkalinity/TIC

Calculate Alkalinity

Calculate

Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model

MSE (H<sub>3</sub>O<sup>+</sup> ion) Databanks:

MSE (H<sub>3</sub>O<sup>+</sup> ion)

Using Helgeson Direct

Dominant Ion Charge Balance (eq/L):

Cation Charge: 0.563486 eq/L

Anion Charge: -0.596011 eq/L

Imbalance: -0.0325252 eq/L

747.753 mg/L of Na+1 is needed to balance.

Set pH Calculation

Measured pH: 7.80000

pH Titrants:

Acid: HCl

Base: NaOH

Calculation not done

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

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

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

## Analyzing the Results

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

The screenshot shows a software interface with four tabs: Description, Reconciliation, Molecular Basis, and Report. The Report tab is selected and highlighted with a red box. Below the tabs is a 'Jump to:' dropdown menu set to 'Reconciliation Summary'. To the right of the dropdown are three icons (a red circle with a slash, a magnifying glass, and a plus sign) and two buttons labeled 'Customize' and 'Export'. The main content area displays the 'Reconciliation Summary' section, which includes a 'Specification' area with 'Charge Balance Method' set to 'Dominant Ion' and 'pH Reconciliation Type' set to 'Reconcile pH'. Below this is a table with three columns: 'Measured' and 'Calculated'. The table contains the following data:

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

\* Calculated value indicates added or removed amount.

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

## Calculating Alkalinity

Now we will instruct the software to calculate Alkalinity.

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

The screenshot displays the software interface with the **Reconciliation** tab selected. The **Calculate Alkalinity** checkbox is checked. The **Reconcile** options are:  No Reconcile,  Reconcile pH,  Reconcile pH/Alkalinity, and  Reconcile pH/Alkalinity/TIC. The **Summary** section shows the following information:

Unit Set: Metric (mass concentration)  
Automatic Chemistry Model  
MSE (H3O+ ion) Databanks:  
MSE (H3O+ ion)  
Using Helgeson Direct  
Dominant Ion Charge Balance (eq/L):  
Cation Charge: 0.563486 eq/L  
Anion Charge: -0.596011 eq/L  
Imbalance: -0.0325252 eq/L  
747.753 mg/L of Na+1 is needed to balance.  
Set pH Calculation  
Measured pH: 7.80000  
pH Titrants:  
Acid: HCl  
Base: NaOH  
Calculation not done

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  $\text{H}_2\text{SO}_4$  (selected by default) until the pH reduces to 4.5. The software then converts the amount of additional  $\text{H}_2\text{SO}_4$  into the alkalinity value.

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

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

## Analyzing the Results

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

### Reconciliation Summary

#### Specification

Charge Balance Method    Dominant Ion

pH Reconciliation Type    Reconcile pH

Alkalinity pH Titrant:    H2SO4

	Measured	Calculated
Temperature, °C	25.0000	
Pressure, atm	1.00000	
pH	7.80000	7.80000
pH Titrant Acid: HCl, mg/L *	0.0	
pH Titrant Base: NaOH, mg/L *	0.0	44.6585
Alkalinity, mg HCO <sub>3</sub> /L	160.000	249.667
Density, g/ml	1.01300	1.02249
Water, mg/L		9.88319e5

\* Calculated value indicates added or removed amount.

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

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

## Example 31: Water Analysis – Reconcile pH/Alkalinity Option

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

### Starting the Simulation

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

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

The default units, names and framework have been previously defined

Select the **Reconcile pH/Alkalinity** option

The screenshot displays the software interface with the 'Reconciliation' tab selected. The main table is divided into several sections:

- Analysis Parameters:**

Variable	Value
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
- Recorded Properties:**

Variable	Value
Total Dissolved Solids (mg/L)	0.0
Measured pH	7.80000
Measured Alkalinity (mg HCO <sub>3</sub> /L)	160.000
Measured TIC (mol C/L)	0.0
Density (g/ml)	1.01300
Specific Electrical Conductivity (µmho/cm)	0.0
- Calculation Parameters:**

Variable	Value
Alkalinity Titrant	CO <sub>2</sub>
Alkalinity pH Titrant	H <sub>2</sub> SO <sub>4</sub>
Alkalinity End Point pH	4.50000
Use Single pH Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
- Neutrals (mg/L):**

Variable	Value
H <sub>2</sub> O	
CO <sub>2</sub>	0.0
H <sub>2</sub> S	0.0
SiO <sub>2</sub>	16.0000
B(OH) <sub>3</sub>	0.0
- Total Ions (mg/L):** (Section header, no data rows visible)

At the bottom of the table, there are buttons for 'Advanced', 'Search', 'Add as Stream', and 'Export'. The 'Measured' tab is selected.

On the right side, the 'Reconciliation' panel shows the 'Reconcile' options: 'No Reconcile', 'Reconcile pH', 'Reconcile pH/Alkalinity' (selected), and 'Reconcile pH/Alkalinity/TIC'. There is also a 'Calculate Alkalinity' checkbox and a 'Calculate' button.

The 'Summary' panel shows the following information:

- Unit Set: Metric (mass concentration)
- Automatic Chemistry Model: MSE (H<sub>3</sub>O<sup>+</sup> ion) Databanks: MSE (H<sub>3</sub>O<sup>+</sup> ion) Using Helgeson Direct
- Dominant Ion Charge Balance (eq/L):
- Reconcile pH Alkalinity Calculation:
  - Alkalinity: 160.000 mg HCO<sub>3</sub>/L
  - Titration End Pt: 4.50000
  - Alkalinity Titrant: CO<sub>2</sub>
  - Alkalinity pH Titrant: H<sub>2</sub>SO<sub>4</sub>
- pH Reconciliation:
  - Measured pH: 7.80000
  - pH Titrants:
    - Acid: HCL
    - Base: NaOH
- Calculation not done

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).

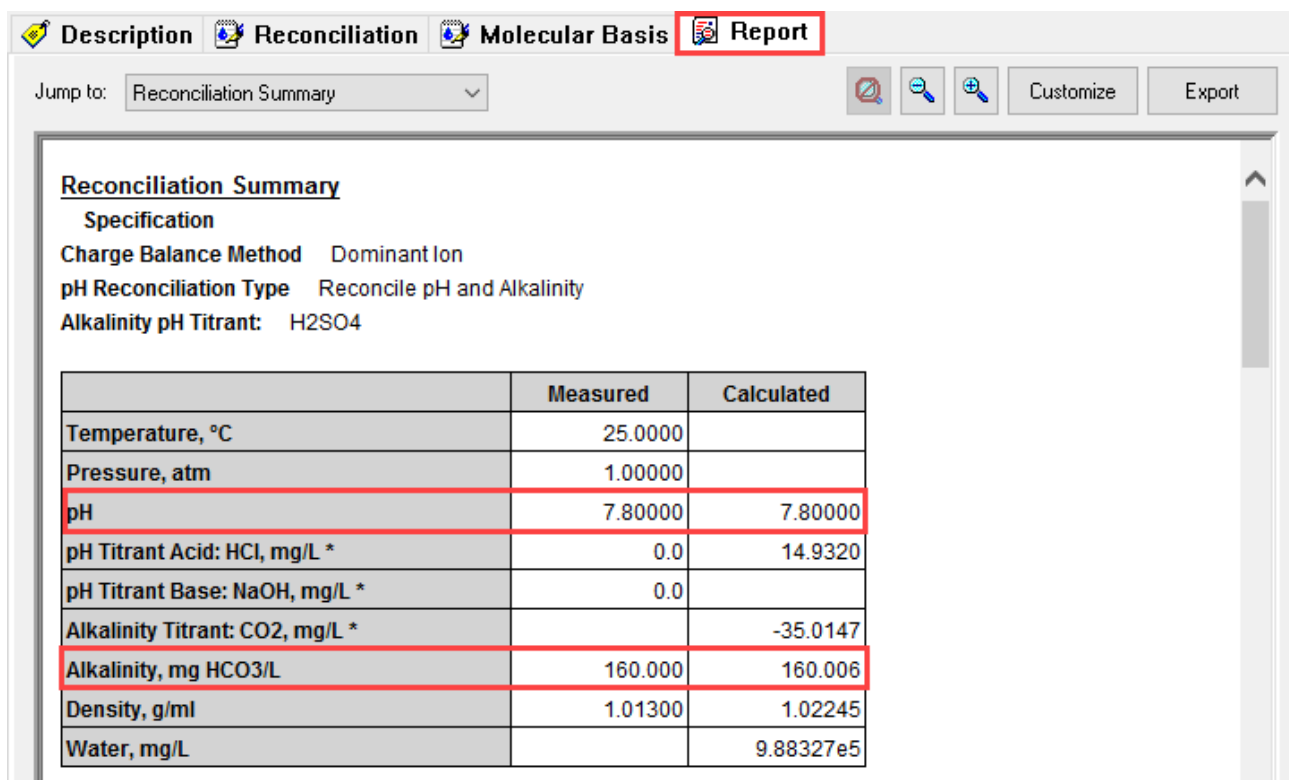
To match the measured alkalinity value, the software added a **Calculation Parameters** section which indicates the alkalinity titrant and the pH titrant used to adjust the alkalinity. CO<sub>2</sub> is used by default as the alkalinity titrant. This is similar to an *alkalinity* single point calculation.

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

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

### Analyzing the Results

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



The screenshot shows the software interface with the **Report** tab selected. The **Reconciliation Summary** table is displayed, showing measured and calculated values for various parameters. The table is as follows:

	Measured	Calculated
Temperature, °C	25.0000	
Pressure, atm	1.00000	
pH	7.80000	7.80000
pH Titrant Acid: HCl, mg/L *	0.0	14.9320
pH Titrant Base: NaOH, mg/L *	0.0	
Alkalinity Titrant: CO <sub>2</sub> , mg/L *		-35.0147
Alkalinity, mg HCO <sub>3</sub> /L	160.000	160.006
Density, g/ml	1.01300	1.02245
Water, mg/L		9.88327e5

The measured and calculated pH and alkalinity values are the same. The software added 14.9320 mg/L of HCl to match the experimentally measured pH and removed 35.0147 mg/L of CO<sub>2</sub> to match the experimentally measured alkalinity value.

## Calculating Pre-scaling Tendencies

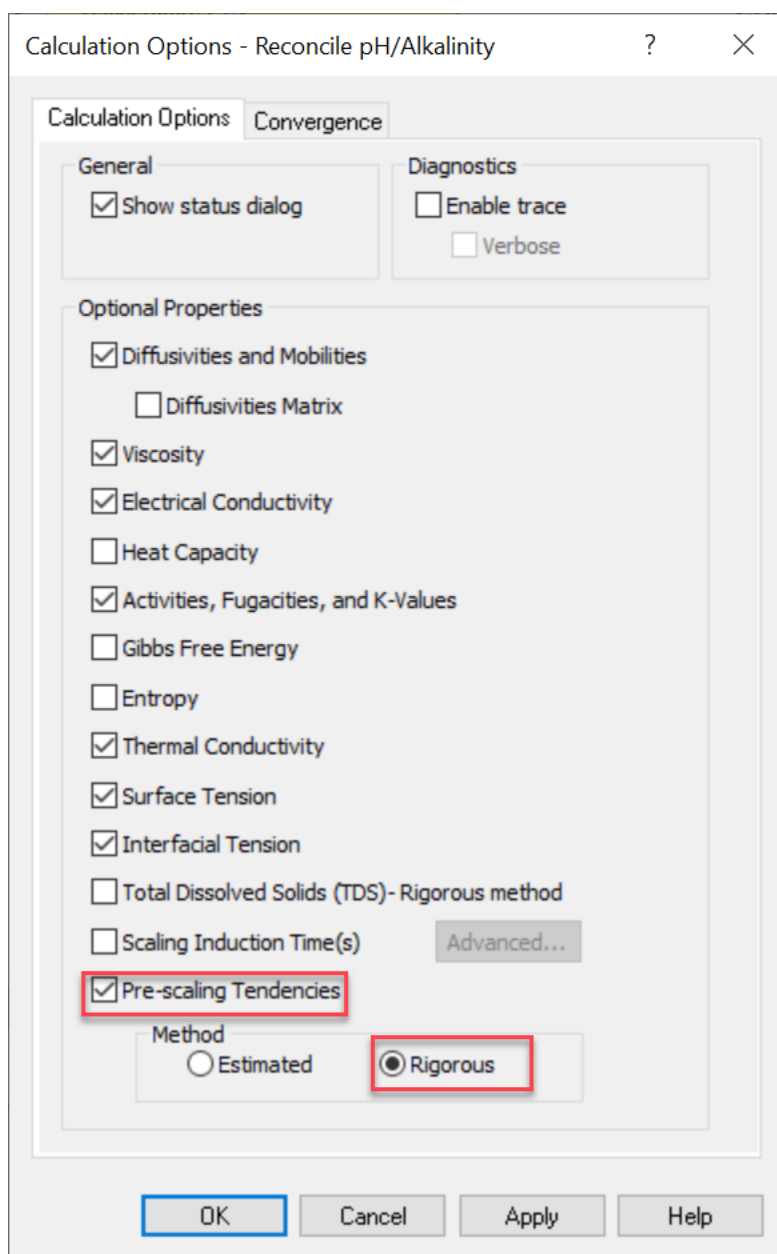
Now we will instruct the software to calculate Pre-scaling tendencies. In OLI Studio: Stream Analyzer, Pre-scaling tendencies are turned OFF by default. We need to enable this option.

### Setting the Water Analysis

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

Click on the **Calculation Options** icon . This will open the Calculation Options window.

Check the **Pre-scaling Tendencies** box and select the **Rigorous method**. Then click **OK**.

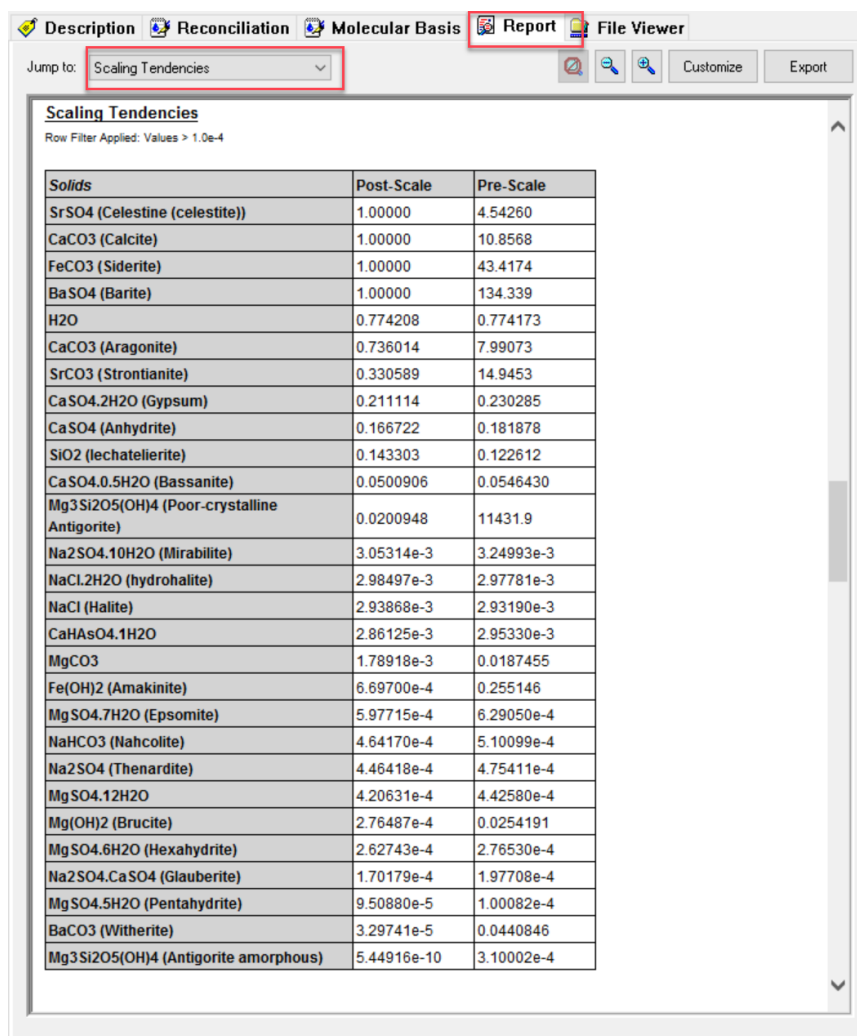


Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

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

## Analyzing the Results

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



Jump to: Scaling Tendencies

Scaling Tendencies  
Row Filter Applied: Values > 1.0e-4

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

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

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

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

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

## Section 4. Hydrocarbons and Pseudocomponents

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

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

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

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

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

The second is to enter the pseudocomponent data directly and using the same thermodynamic methods to predict the component properties.

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

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

### Entering a PVT Analysis

#### Example 32: Creating an Assay

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

#### *Starting the Simulation*

Add a new **Stream**

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

Select the **MSE-SRK** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

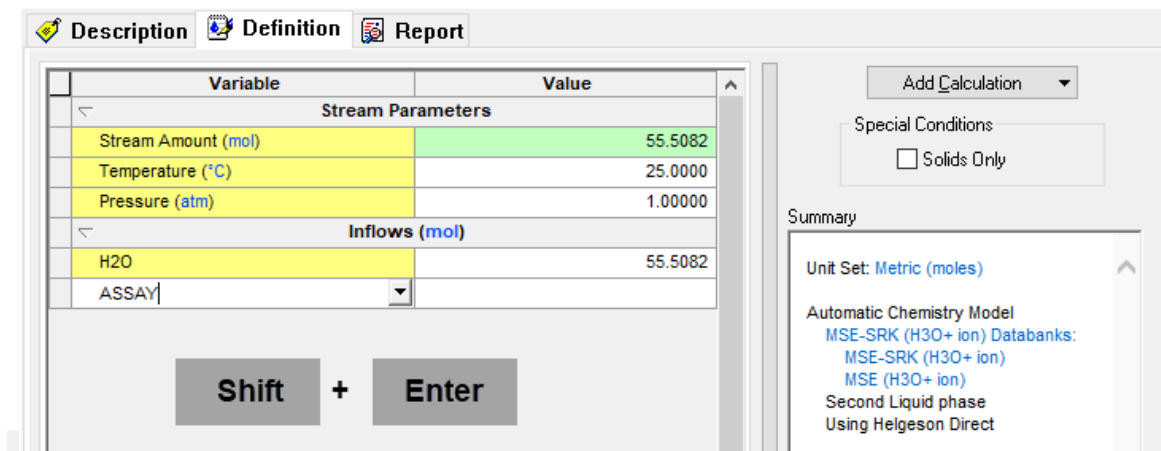
**Click** on the **Units Manager** Icon, and select Metric, Batch, Moles

**Enter** the conditions of the Stream T= 25 °C and 1 atm

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

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

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

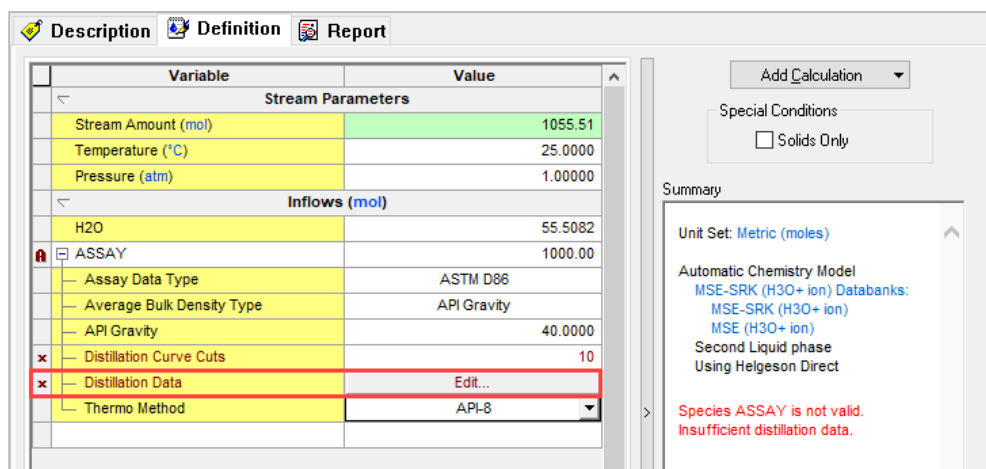


**Note:** After typing the name of your Assay, immediately press Shift + Enter command keys together.

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

Assay Information			
Calculation Settings		Distillation Data	
Assay amount	1000 moles	<b>Volume %</b>	<b>Temperature, °C</b>
Assay Data Type	ASTM D86	1	20
Average Bulk Density Type	API Gravity	5	30
API Gravity	40	10	50
Distillation Curve Cuts	10	20	60
Distillation Data	See next two columns	40	80
Thermo Method	API-8	60	120
		80	150
		90	180
		95	200
		99	220
		100	240

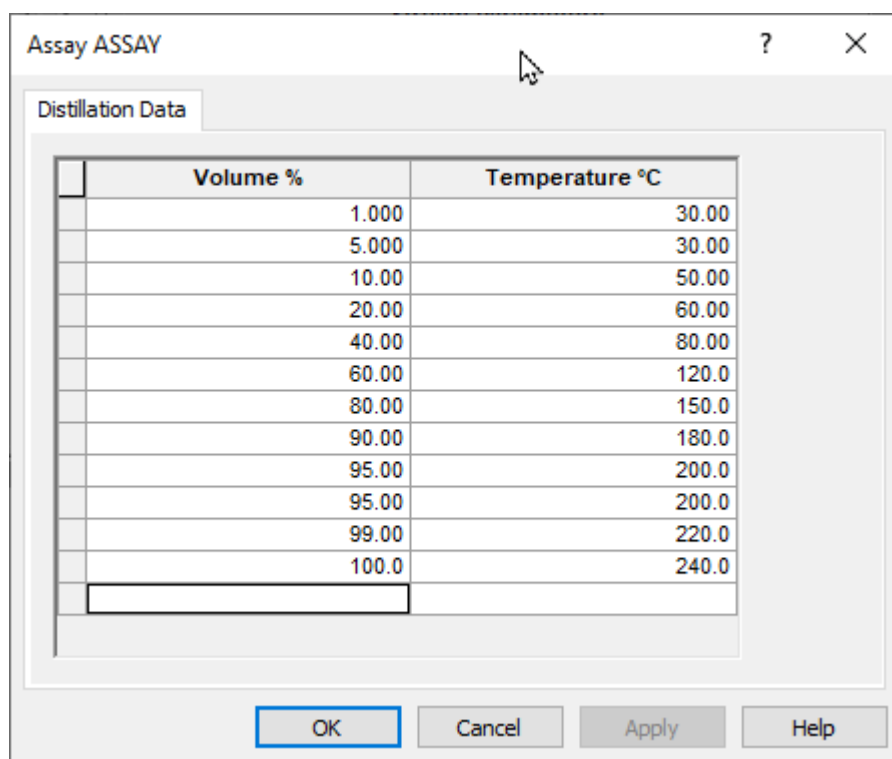
Your screen should look like the image below:



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

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

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



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

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

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

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

It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Save the calculations of this section under the name *Hydrocarbons and Pseudocomponents*.

## Analyzing the Results

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

Click on the **Output Tab**

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

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

The screenshot displays the software interface with the **Output** tab selected. The main window shows a table with columns for **Variable** and **Value**. The table is organized into sections: **Stream Parameters**, **Inflows (mol)**, and a list of **Assay** pseudocomponents. The **ASSAY\_243K** row is expanded, showing sub-properties like **Thermo Method**, **Normal Boiling Point (°C)**, **Specific Gravity**, and **Molecular Weight**. The right-hand panel shows the **Summary** of the calculation, including the **Unit Set** (Metric (moles)), the **Automatic Chemistry Model** (MSE-SRK (H3O+ ion) Databanks), and the **Phase Amounts** (Aqueous: 55.0810 mol, Vapor: 0.0 mol, Solid: 0.0 mol, 2nd Liquid: 1000.43 mol). The **Calculation complete** message is visible at the bottom of the summary panel.

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	1055.51
Moies (True) - Liquid-1 (mol)	55.0810
Moies (True) - Liquid-2 (mol)	1000.43
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
H2O	55.5082
P ASSAY_243K	87.6615
Thermo Method	API-8
Normal Boiling Point (°C)	-30.2796
Specific Gravity	0.717259
Molecular Weight	47.1866
P + ASSAY_278K	82.2275
P + ASSAY_307K	200.849
P + ASSAY_337K	173.140
P + ASSAY_370K	109.658
P + ASSAY_403K	131.728
P + ASSAY_431K	110.846
P + ASSAY_464K	57.0493
P + ASSAY_496K	35.2169
P + ASSAY_524K	11.6247

Input **Output**

Advanced Search Add as Stream Export

Type of calculation: Isothermal [Specs...]  
Calculate [OK]

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model  
MSE-SRK (H3O+ ion) Databanks:  
MSE-SRK (H3O+ ion)  
MSE (H3O+ ion)  
Second Liquid phase  
Using Helgeson Direct

Isothermal Calculation  
25.0000 °C 1.00000 atm

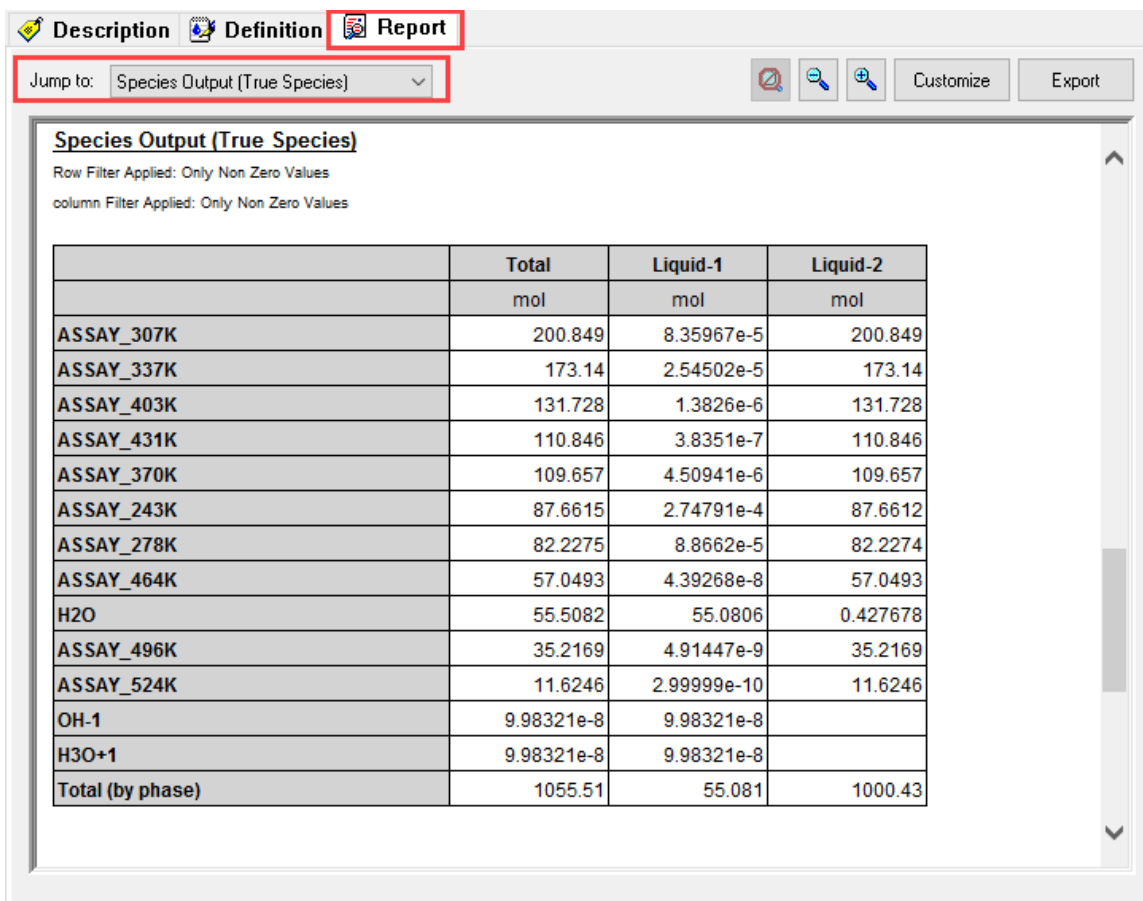
Phase Amounts  
Aqueous 55.0810 mol  
Vapor 0.0 mol  
Solid 0.0 mol  
2nd Liquid 1000.43 mol

Aqueous Phase Properties  
pH 6.99753  
Ionic Strength 1.81246e-9 mol/mol  
Density 0.997043 g/ml

Calc. elapsed time: 1.137 sec  
Calculation complete

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.



Jump to: Species Output (True Species)

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

	Total	Liquid-1	Liquid-2
	mol	mol	mol
ASSAY_307K	200.849	8.35967e-5	200.849
ASSAY_337K	173.14	2.54502e-5	173.14
ASSAY_403K	131.728	1.3826e-6	131.728
ASSAY_431K	110.846	3.8351e-7	110.846
ASSAY_370K	109.657	4.50941e-6	109.657
ASSAY_243K	87.6615	2.74791e-4	87.6612
ASSAY_278K	82.2275	8.8662e-5	82.2274
ASSAY_464K	57.0493	4.39268e-8	57.0493
H2O	55.5082	55.0806	0.427678
ASSAY_496K	35.2169	4.91447e-9	35.2169
ASSAY_524K	11.6246	2.99999e-10	11.6246
OH-1	9.98321e-8	9.98321e-8	
H3O+1	9.98321e-8	9.98321e-8	
<b>Total (by phase)</b>	<b>1055.51</b>	<b>55.081</b>	<b>1000.43</b>

## Entering Pseudocomponents to a Stream

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

### Example 33: Creating Pseudocomponents

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

#### Starting the Simulation

Add a new **Stream**

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

Select the **MSE-SRK** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

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

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

**Change** H2O from the default value to 20 moles

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

In the inflows grid, in the white cell below H2O, type PC1 and then press **<Ctrl + Enter>**

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

The screenshot shows the 'Definition' tab of the software. The main window displays a table with 'Variable' and 'Value' columns. Under 'Stream Parameters', 'Stream Amount (mol)' is 20.0000, 'Temperature (°C)' is 15.0000, and 'Pressure (atm)' is 1.00000. Under 'Inflows (mol)', 'H2O' is 20.0000 and 'PC1' is in a dropdown menu. A large 'Ctrl + Enter' button is overlaid on the bottom of the table. On the right, there is a 'Special Conditions' section with a 'Solids Only' checkbox and a 'Summary' section showing 'Unit Set: Metric (moles)' and 'Automatic Chemistry Model' details including 'MSE-SRK (H3O+ ion) Databanks' and 'Using Helgeson Direct'.

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

Repeat step 8 four more time with the following names: PC2, PC3, PC4 and PC5. Use the information provided in the table below to complete the grid. The molecular weight will be calculated by the software. In general, only two of the three parameters need be entered.

Pseudocomponents Information					
Pseudocomponent name	PC1	PC2	PC3	PC4	PC5
Inflow (moles)	100	200	250	250	180
Thermo Method	API-8	API-8	API-8	API-8	API-8
Boiling Point (°C)	33	60	100	140	190
Specific Gravity	0.72	0.76	0.8	0.85	0.9

Your screen should look like the image below:

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	1000.00
Temperature (°C)	15.0000
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
H2O	20.0000
<b>P</b> PC1	100.000
— Thermo Method	API-8
— Normal Boiling Point (°C)	33.0000
— Specific Gravity	0.720000
— Molecular Weight	
+ Calculated Properties	
<b>P</b> PC2	200.000
— Thermo Method	API-8
— Normal Boiling Point (°C)	60.0000
— Specific Gravity	0.760000
— Molecular Weight	
+ Calculated Properties	
<b>P</b> PC3	250.000
— Thermo Method	API-8
— Normal Boiling Point (°C)	100.000
— Specific Gravity	0.800000
— Molecular Weight	
+ Calculated Properties	
<b>P</b> PC4	250.000
— Thermo Method	API-8
— Normal Boiling Point (°C)	140.000
— Specific Gravity	0.850000
— Molecular Weight	
+ Calculated Properties	
<b>P</b> PC5	180.000
— Thermo Method	API-8
— Normal Boiling Point (°C)	190.000
— Specific Gravity	0.900000
— Molecular Weight	
+ Calculated Properties	

Unit Set: Metric (moles)

Automatic Chemistry Model  
MSE-SRK (H3O+ ion) Databanks:  
MSE-SRK (H3O+ ion)  
MSE (H3O+ ion)  
Second Liquid phase  
Using Helgeson Direct

Input

Advanced Search Add as Stream Export

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.

Description		Definition	Report
Variable	Value		
Stream Parameters			
Stream Amount (mol)	1000.00		
Temperature (°C)	15.0000		
Pressure (atm)	1.00000		
Inflows (mol)			
H2O	20.0000		
PC1	100.000		
Thermo Method	API-8		
Normal Boiling Point (°C)	33.0000		
Specific Gravity	0.720000		
Molecular Weight			
Calculated Properties			
Calc:Molecular Weight	70.3287		
Calc:Specific Gravity	0.720000		
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		
Calc:Rackett	0.277609		
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		

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

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

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

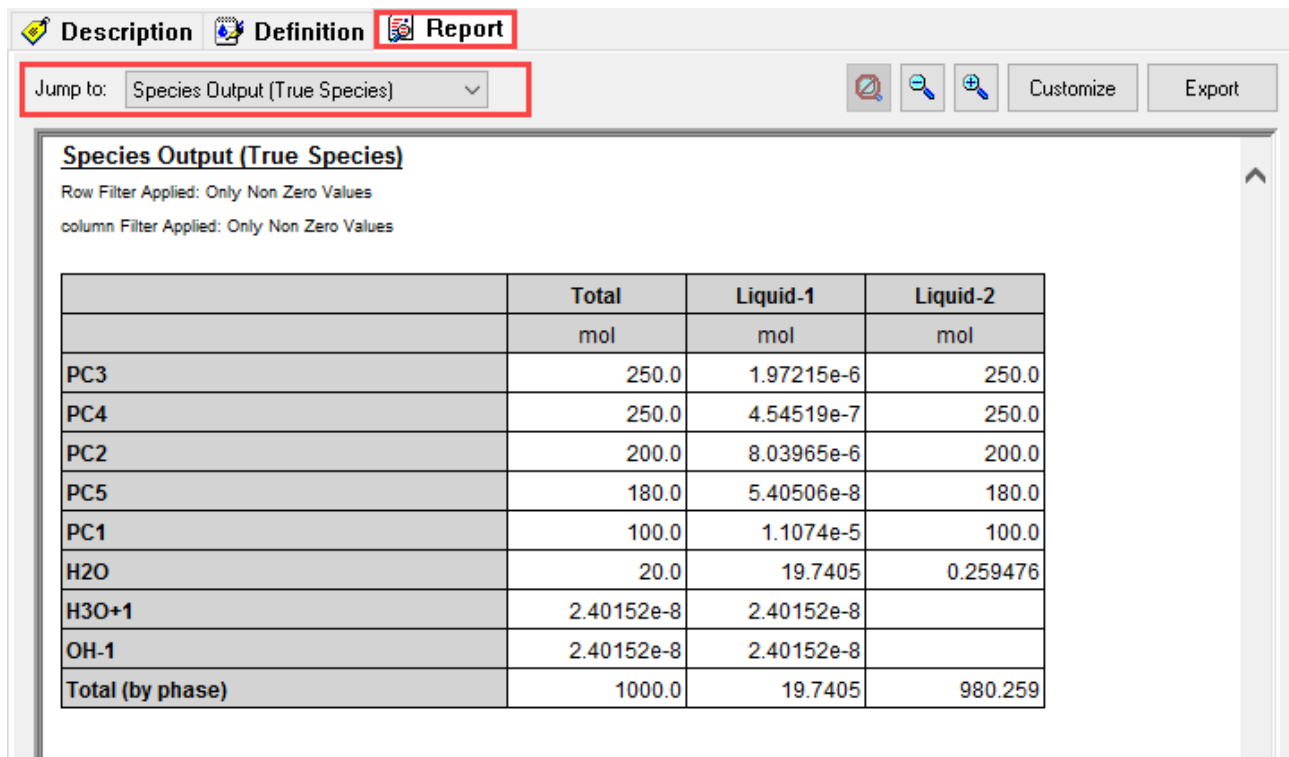
**Click** on the **Calculate** button or press the <F9> key to run the simulation

It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. Save the calculations of this section under the name *Hydrocarbons and Pseudocomponents*.

## Analyzing the Results

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

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

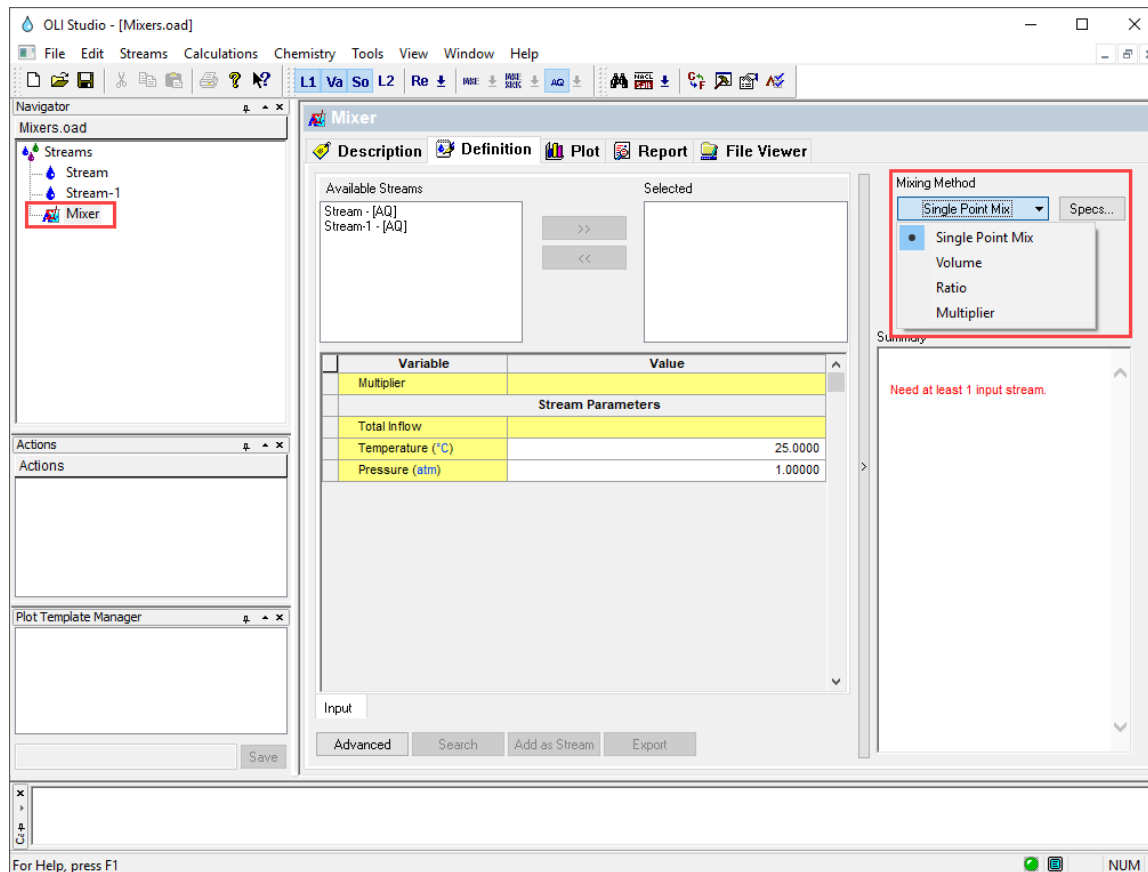


The screenshot shows a software interface with three tabs: 'Description', 'Definition', and 'Report'. The 'Report' tab is selected and highlighted with a red box. Below the tabs, there is a 'Jump to:' dropdown menu with 'Species Output (True Species)' selected, also highlighted with a red box. To the right of the dropdown are icons for zooming and buttons for 'Customize' and 'Export'. Below this is a table titled 'Species Output (True Species)'. The table has a row filter 'Only Non Zero Values' and a column filter 'Only Non Zero Values'. The table has four columns: 'Total', 'Liquid-1', and 'Liquid-2', all with units in 'mol'. The rows are: PC3, PC4, PC2, PC5, PC1, H2O, H3O+1, OH-1, and Total (by phase).

	Total	Liquid-1	Liquid-2
	mol	mol	mol
PC3	250.0	1.97215e-6	250.0
PC4	250.0	4.54519e-7	250.0
PC2	200.0	8.03965e-6	200.0
PC5	180.0	5.40506e-8	180.0
PC1	100.0	1.1074e-5	100.0
H2O	20.0	19.7405	0.259476
H3O+1	2.40152e-8	2.40152e-8	
OH-1	2.40152e-8	2.40152e-8	
Total (by phase)	1000.0	19.7405	980.259

## Section 5. Mixers

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



In this section, you will learn how to set up a **Mixer** and differentiate the different mixing options to get the most out of your simulation results.

## Mixing Options (Definitions)

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

### Single Point Mix

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

### Volume

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

Stream 1	Stream 2
1 L	1 L
1 L	2 L
...	...
1 L	n L

### Ratio

In the ratio mixing type, both streams change at the same time. For example, stream will be 100% and Stream will be 0%, then Stream 1 will be 90% and Stream 2 will be 10%, and so on, until it reaches Stream 1 0% and Stream 2 100%.

Stream 1	Stream 2
100 %	0 %
90 %	10%
...	...
0 %	100 %

### Multiplier

In this mixing option, one stream stays constant, while the other stream changes using a multiplier. The range of the multiplier values is given by the user.

Stream 1	Stream 2
1	Stream 2 × 0
1	Stream 2 × 1
...	...
1	Stream 2 × n

## A Basic Mixer Calculation

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

### Example 34: Calculating the Heat of Mixing

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

#### Starting the Simulation

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

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

Basic Mixing Calculation			
1 <sup>st</sup> Stream		2 <sup>nd</sup> Stream	
Stream Name	Ca(OH) <sub>2</sub>	Stream Name	HCl
Name Style	Display Formula	Name Style	Display Formula
Unit Set	Metric, Batch, Mass Frac.	Unit Set	Metric, Batch, Mass Frac.
Framework	MSE	Framework	MSE
Stream Amount	1 kg	Stream Amount	1 kg
Temperature	25 °C	Temperature	25 °C
Pressure	1 atm	Pressure	1 atm
H <sub>2</sub> O	Calculated	H <sub>2</sub> O	Calculated
Ca(OH) <sub>2</sub>	10 mass%	HCl	10 mass%

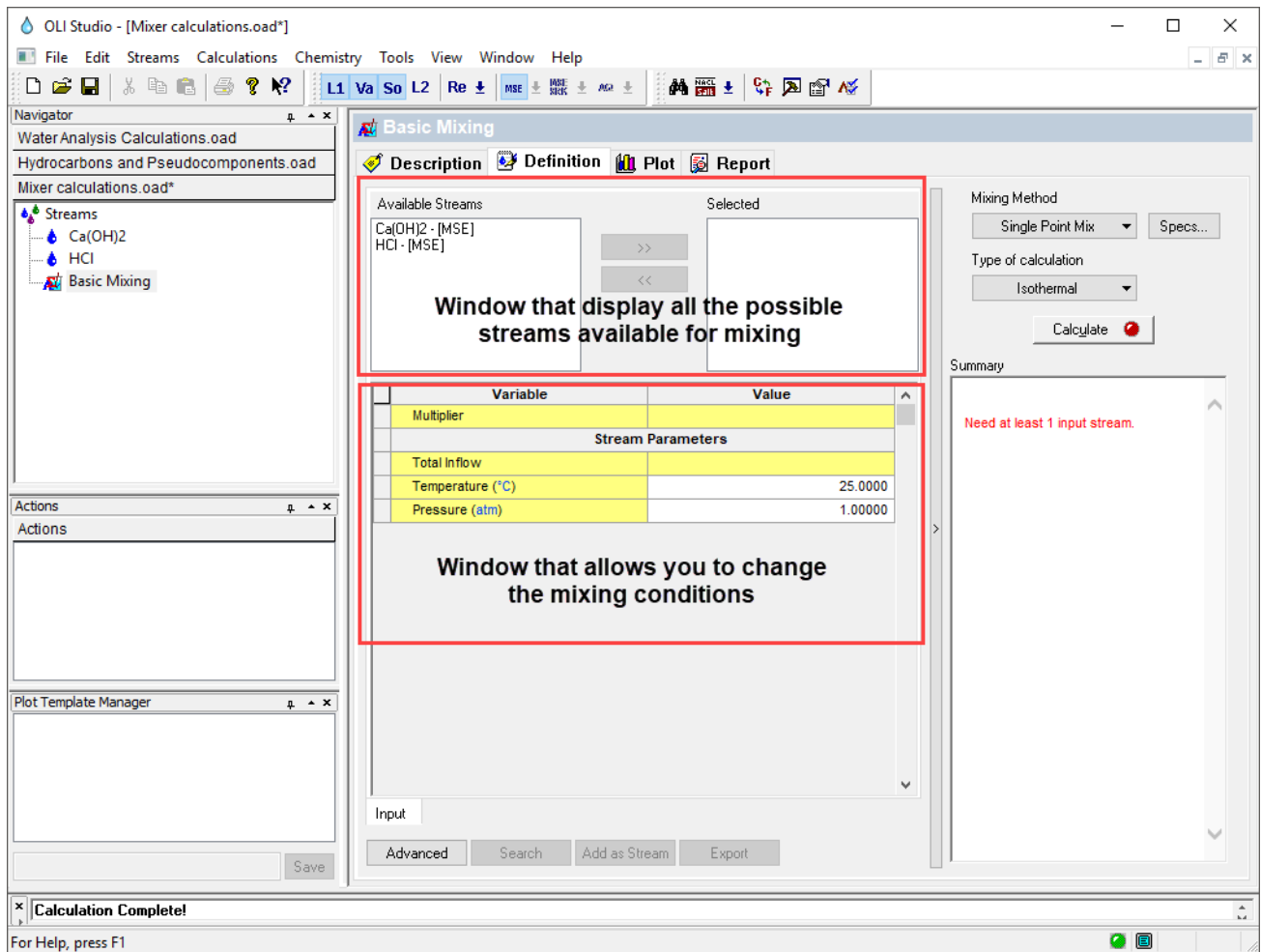
After creating the streams, **Add a Mixer**. The Mixer object can be accessed from the Menu Bar by selecting Calculations > **Add Mixer** or by selecting the **Add Mixer** in the Actions Pane.

Press <F2> to rename the mixer to *Basic Mixing*

Notice that the display layout for the Mixer tool is slightly different. There are two different windows (see image below).

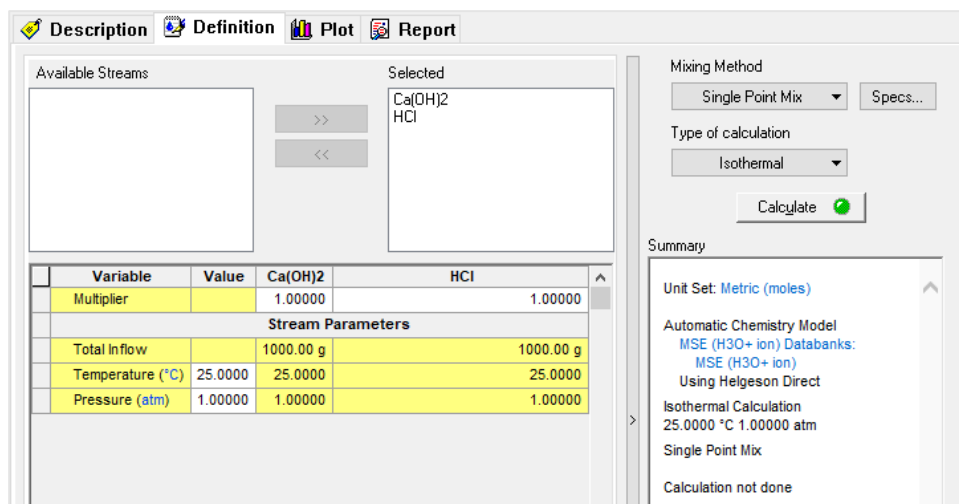
The first window displays all possible streams available for the mix calculation. There is no limit to the number of streams to be mixed.

The second window allows you to change the mixing conditions, e.g., temperature, and pressure of the mixing.



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

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



Also notice that the default calculation is the **Single Point Mix** Method at **Isothermal** conditions. In this example, we want to calculate the heat of mixing and the final temperature of the mixture. Thus, an adiabatic calculation is required to see this effect.

Click on the **Type of Calculation** button and select the **Adiabatic** calculation option

**Note:** Once the streams for the mixing have been selected, notice that the multipliers of both streams: Ca(OH)<sub>2</sub> 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.

The screenshot shows a software interface with a toolbar at the top containing 'Description', 'Definition', 'Plot', and 'Report'. Below the toolbar, there are two panes: 'Available Streams' (empty) and 'Selected' (containing 'Ca(OH)2' and 'HCl'). A table below these panes is highlighted with a red border and contains the following data:

Variable	Value	Ca(OH)2	HCl
Multiplier		1.00000	1.00000
Stream Parameters			
Total Inflow		1000.00 g	1000.00 g
Temperature (°C)	25.0000	25.0000	25.0000
Pressure (atm)	1.00000	1.00000	1.00000

At the bottom of the interface, there are buttons for 'Advanced', 'Search', 'Add as Stream', and 'Export'. On the right side, there is a 'Summary' box with the following content:

Mixing Method: Single Point Mix (dropdown), Specs... (button)  
Type of calculation: Adiabatic (dropdown)  
Calculate (button with green checkmark)

Summary:  
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

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

It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it and name it as *Mixer Calculations*.

### Analyzing the Results

Review the Summary Box. After mixing these two streams, the temperature increased from 25 °C to approximately ~48.65 °C at a constant pressure of 1 atm. This indicates that the enthalpy (or heat) of mixing is exothermic.

## A Titration Experiment

In this example, you will explore the volume mixing option to recreate a titration experiment. As we go through the example, different functionalities, reporting and plotting for the *Mixer tool* will be introduced.

### Example 35: HF Titration with CaCl<sub>2</sub>

In this example, first, we will create two new streams, a 0.1 m HF solution, and a 0.1 m CaCl<sub>2</sub> 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 CaCl<sub>2</sub> 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 CaCl<sub>2</sub> solution. Note that we have switched thermodynamic frameworks to the **AQ** framework. Please make sure that this framework is selected for both streams in this example.

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

Titration Calculation			
1 <sup>st</sup> Stream		2 <sup>nd</sup> Stream	
Stream Name	0.1 m HF	Stream Name	0.1 m CaCl <sub>2</sub>
Name Style	Display Formula	Name Style	Display Formula
Unit Set	Metric, Batch, Moles	Unit Set	Metric, Batch, Moles
Framework	AQ	Framework	AQ
Stream Amount	Calculated	Stream Amount	Calculated
Temperature	30 °C	Temperature	30 °C
Pressure	1 atm	Pressure	1 atm
H <sub>2</sub> O	55.5082 moles	H <sub>2</sub> O	55.5082 moles
HF	0.1 moles	CaCl <sub>2</sub>	0.1 moles

#### Calculating the pH of the individual streams

Add a **Single Point – Isothermal** calculation for each stream

**Change** the name to **pH 0.1 m HF** and **pH 0.1 m CaCl<sub>2</sub>** respectively using the <F2> key

**Calculate** the isothermal calculation for each stream

**Check** the pH values of the individual streams in the **Summary Box**

Results – pH of the individual streams

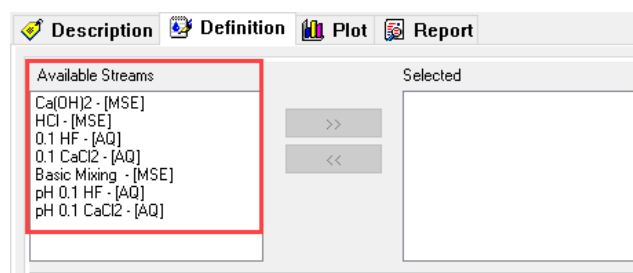
pH 0.1 m HF	pH 0.1 m CaCl <sub>2</sub>
2.13	6.82

## Calculating the pH of the Mixture

After creating the streams, **Add a Mixer**. The Mixer object can be accessed from the Menu Bar by selecting Calculations > **Add Mixer** or by selecting the **Add Mixer** in the Actions Pane.

Press <F2> to rename the mixer to *Titration*

**Note:** Notice that the Available Streams window is showing all the available streams for the mixing calculation. Also notice that this window is showing both: *Streams* and *Single Point calculations*. Additionally, in front of the name of the available streams, the thermodynamic framework appears within brackets, e.g., AQ, MSE or MSE-SRK. This is important because in order to carry out mixing calculations, the selected streams need to use the same thermodynamic framework.



**Select** the 0.1 HF – [AQ] stream. Use the >> button to move it to the **Selected** window

**Select** the 0.1 CaCl2 stream. Use the >> button to move it to the **Selected** window

Select **Single Point Mix** as the Mixing Method and **Isothermal** as the Type of Calculation

**Leave** the default values for the multipliers (1.0) and **change** the temperature at which the mixture takes place to 30 °C.

Variable	Value	0.1 HF	0.1 CaCl2
Multiplier		1.00000	1.00000
Stream Parameters			
Total Inflow		55.6082 mol	55.6082 mol
Temperature (°C)	30.0000	30.0000	30.0000
Pressure (atm)	1.00000	1.00000	1.00000

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model  
Aqueous (H+ ion) Databanks:  
Aqueous (H+ ion)  
Using K-fit Polynomials  
T-span: 25.0 - 225.0  
P-span: 1.0 - 1500.0

Isothermal Calculation  
30.0000 °C 1.00000 atm  
Single Point Mix  
Calculation not done

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

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

**Check** the pH values of the individual streams in the **Summary Box**

Results – pH of the individual streams

The resultant pH is 1.44. How can this be? An acid stream (the HF stream had a pH of approximately 2.13) and a nominally basic stream (the CaCl<sub>2</sub> stream had a pH of 6.82) are mixed and the pH is outside the value of either stream.

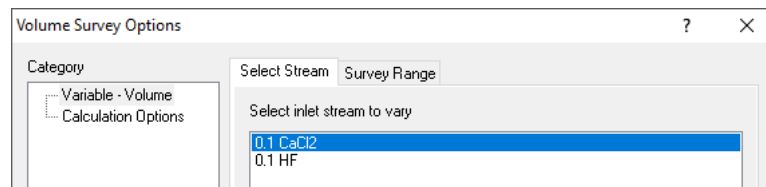
We will continue using Stream Analyzer to further examine the chemistry in more detail. We will titrate the HF stream with CaCl<sub>2</sub>.

*Titration of HF with CaCl<sub>2</sub>*

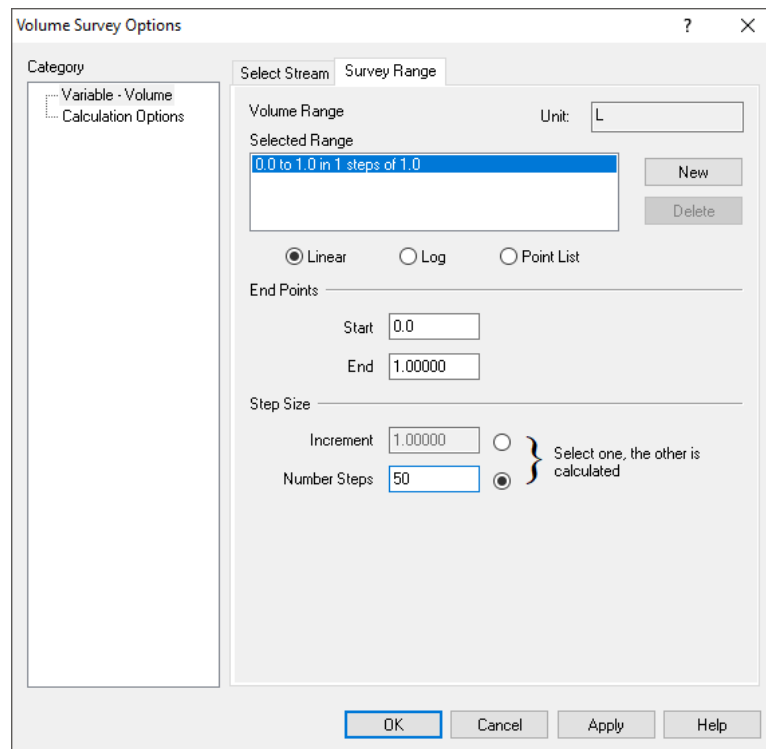
**Change the Single Point Mix as the Mixing Method to the Volume option.**

**Note:** You will receive a warning message: **Need 1 stream selected as the variable stream (Specs...)**

**Click** on the **Specs** button. This will open a new window indicating you to select the Stream to vary  
In the **Select Stream** tab **Select** the 0.1m CaCl<sub>2</sub> stream



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



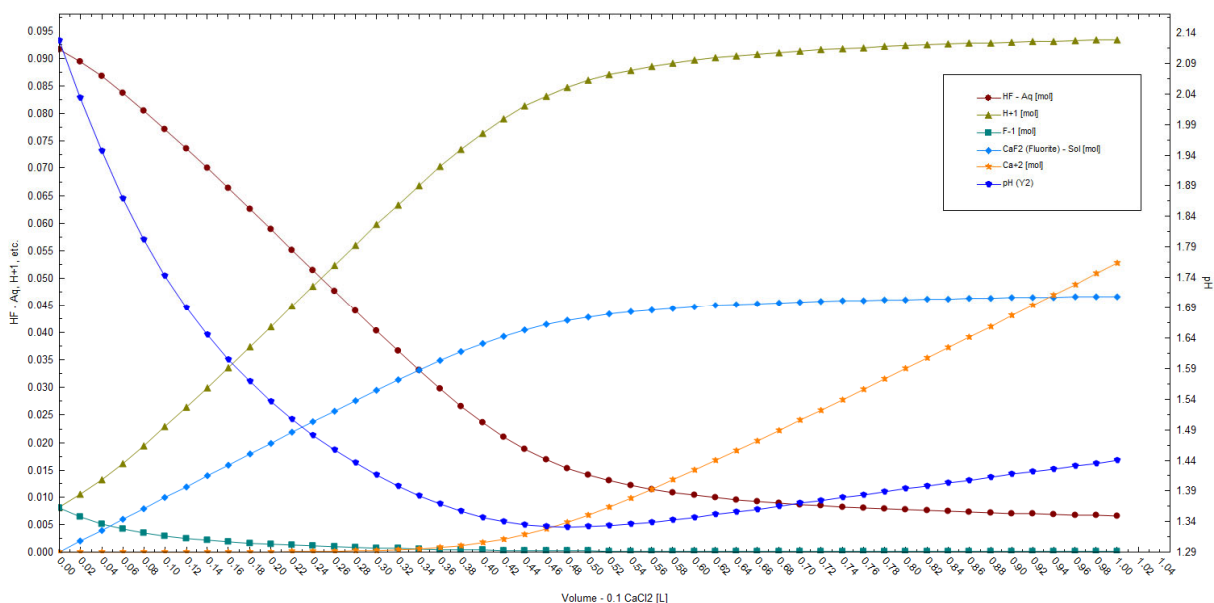
Now, we are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key  
 It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save under the same file that we created before named as *Mixer Calculations*.

### Titration Results and Plotting

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

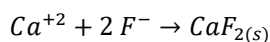
**Click** on the **Variables** button and expand the **Aqueous** section. **Select** and put the following species in the **Y1 axis** using the **>>** button: HF-Aq, H+1, F-1, Ca+2. Expand the **Solid** section and **select** CaF2(s).

Next, expand the **Additional Parameters** Section and **Select** **pH**. Put it in the **Y2 Axis** using the **>>** button. Then click **OK**.

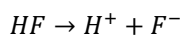


As you can see, adding  $\text{CaCl}_2$  to this solution lowers the pH to values as low as 1.33. The pH does begin to slowly increase after 0.48 L of  $\text{CaCl}_2$  have been added.

Why the unusual pH behavior? You can see that a small amount of  $\text{Ca}^{+2}$  in solution, causes the formation of the solid  $\text{CaF}_2$ . This effectively removes  $\text{F}^-$  from solution according to the following equation:



As we add more  $\text{CaCl}_2$  in solution, more  $\text{CaF}_2$  is formed. As a result, the molecular HF decreases, because it dissociates in order to maintain the equilibrium, by producing more  $\text{F}^-$  ions. This shifts the following equilibrium to the right:

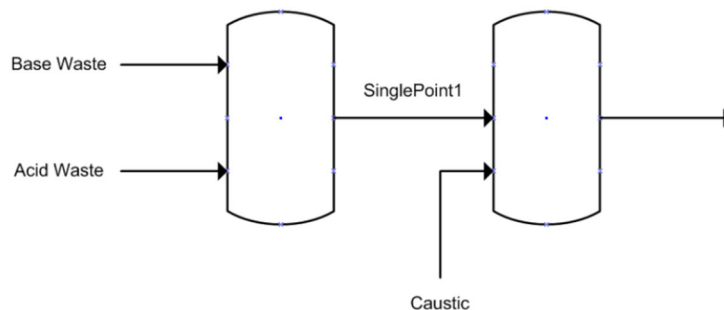


This causes an increase of  $H^+$  in solution, and as a result a decrease in the pH. At some point, at around 0.48 L of 0.1 m  $CaCl_2$ , the solid reaches a steady value, indicating that the solid has reached its saturation (maximum formation) value.

## Cascading Mixers

### Example 36: Cascading Mixers

In this example, we will mix two streams, one basic and one acidic, and mix them together under adiabatic conditions. The output of this mixer will then be used as the input to a second mixer where a new caustic stream is added. The schematic in the figure below illustrates the layout.

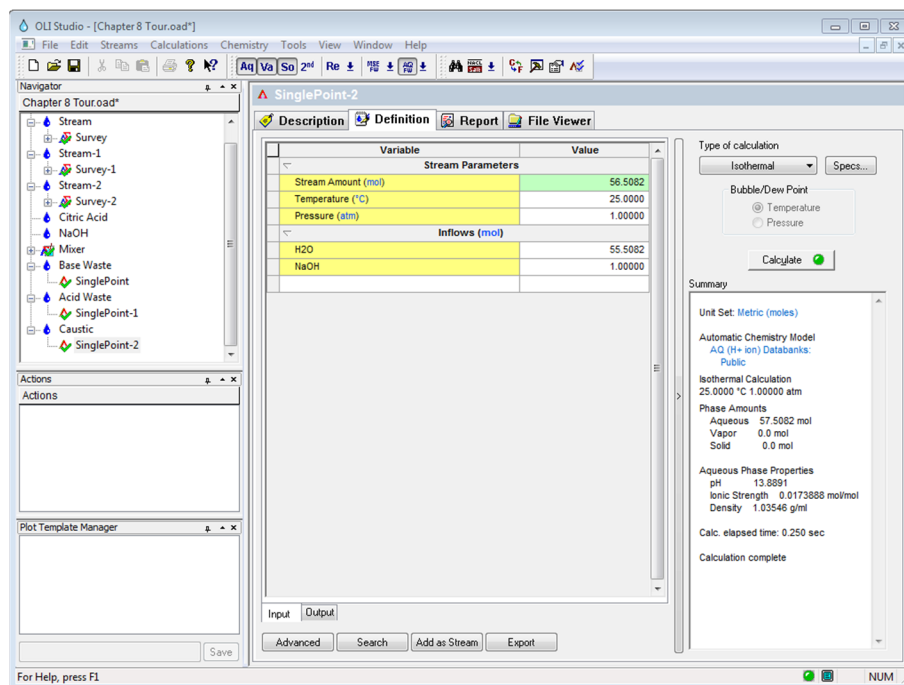


For this example, we need to create three streams. You have already done this in other examples, so we will only give you the input data (for all streams, we will use the AQ – default – thermodynamic framework)

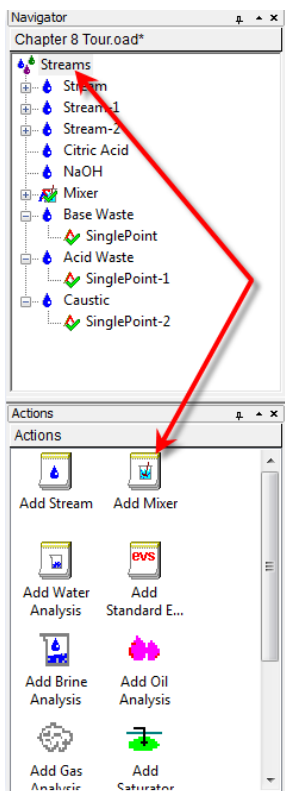
Cascading Mixer Stream Data

Parameter	Value	Units
Stream Name	Base Waste	
Temperature	25.0	°C
Pressure	1.0	Atmospheres
Stream Amount	55.5082 (Default)	Mole
H <sub>2</sub> O	55.5082	Mole
CO <sub>2</sub>	0.1	Mole
NH <sub>3</sub>	0.01	Mole
SO <sub>2</sub>	0.01	Mole
Stream Name	Acid Waste	
Temperature	25.0	°C
Pressure	1.0	Atmospheres
H <sub>2</sub> O	55.5082	Mole
HCl	0.1	Mole
H <sub>2</sub> SO <sub>4</sub>	1.0	Mole
Stream Name	Caustic	
Temperature	25.0	°C
Pressure	1.0	Atmospheres
H <sub>2</sub> O	55.5082	Mole
NaOH	1.0	Mole

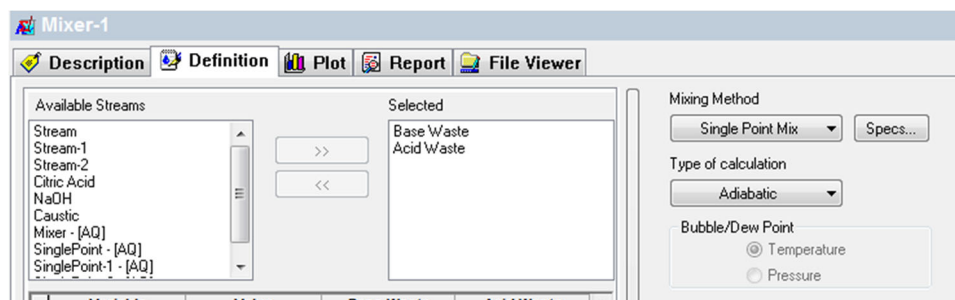
To test that our streams are representing their respective names, perform a single point isothermal flash on each stream. When you are done you should have a window that looks like the image below.



Now we are ready to begin. Click on the “Streams” at the top of the tree-view in the left-hand window and then select Add Mixer from the actions panel.

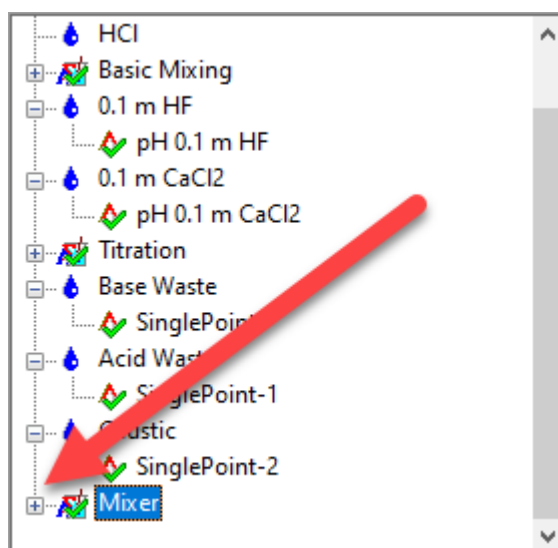


We can now add the “Base Waste” and “Acid Waste” stream as we have done in previous examples. The only difference here is that we are selecting an **Adiabatic** calculation instead of the default isothermal calculation.

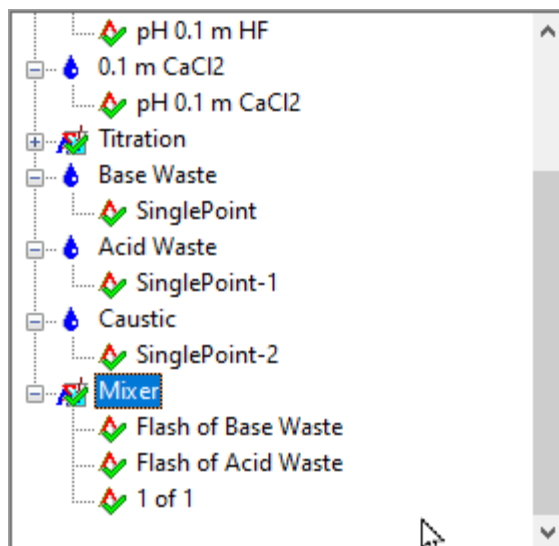


Let's calculate this mixer. Click the Calculate button. If everything is set up correctly the resultant mixed pH should be approximately 0.3.

In the stream tree-view panel, locate your mixer and click the "+" sign.

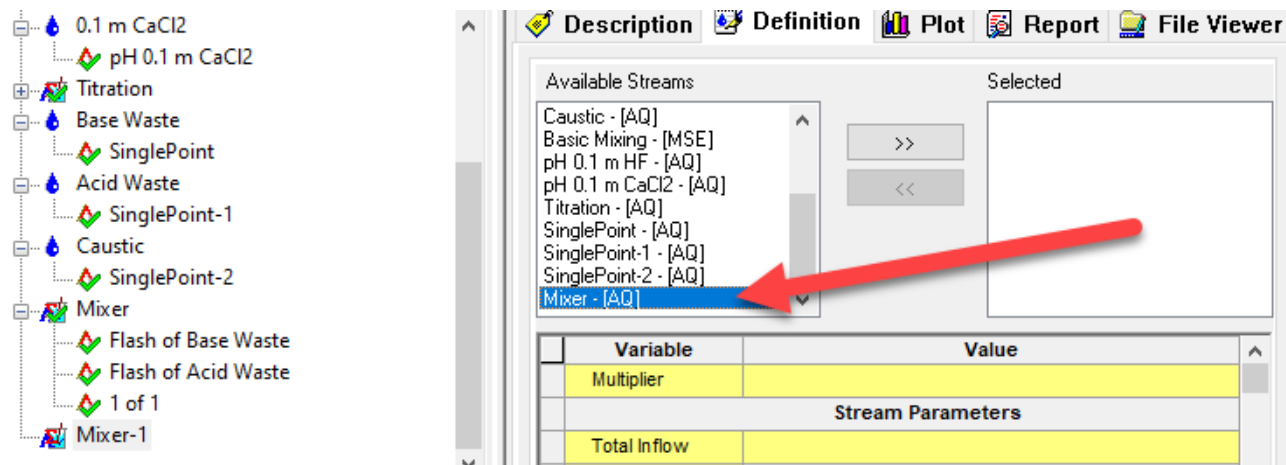


Click the "+" sign to expand the tree.



You can see that the program has performed an equilibrium calculation on each of our input streams as well as calculated the mixer. The results of the mixer are stored in the object "1 of 1".

We will now add a second mixer from the actions panel.



When we add a subsequent mixer, we will see all our previous objects still displayed. It is possible to reuse a stream that we already used (this is not possible in OLI's other simulators such as OLI Flowsheet: ESP.) We want to connect the output from our first mixer (Mixer) to the inlet of the **Caustic** stream. Click the object

**Mixer -(AQ).**

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

Variable	Value	Mixer	Caustic
Multiplier		1.00000	1.00000
<b>Stream Parameters</b>			
Total Inflow		113.236 mol	56.5082 mol
Temperature (°C)	25.0000	25.0000	25.0000
Pressure (atm)	1.00000	1.00000	1.00000

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

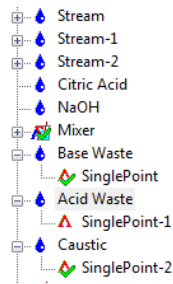
The resultant pH should be approximately 1.0. We want to increase this value. Change the **Multiplier** value for Caustic Stream from 1.0 to 2.4

Variable	Value	Mixer-1	Caustic
Multiplier		1.00000	2.40000
<b>Stream Parameters</b>			
Total Inflow		113.236 mol	56.5082 mol
Temperature (°C)	25.0000	25.0000	25.0000
Pressure (atm)	1.00000	1.00000	1.00000

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

The real value of the cascading mixer is the quick ability to re-calculate the objects if we want to change something. Let's add some diethanolamine to the series of calculations. Click the **Acid Waste** stream (not the single point calculation below it) and add the component DEXH<sup>7</sup> to the grid with a value of 10.0 moles.

<sup>7</sup> This is the OLI Tag name for diethanolamine, which is easier to type if you know the name.



Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	66.6082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
Water	55.5082
Hydrogen chloride	0.100000
Sulfuric(VI) acid	1.00000
DEXH	10.0000

Return to the last mixer you created (Mixer-1 in our example) and then reduce the **Caustic Multiplier back to 1.0**

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

**Mixer-2**

Available Streams: Stream, Stream-1, Stream-2, Citric Acid, NaOH, Base Waste, Acid Waste, Mixer - [AQ], SinglePoint - [AQ]

Selected: Mixer-1, Caustic

Variable	Value	Mixer-1	Caustic
Multiplier		1.00000	1.00000
<b>Stream Parameters</b>			
Total Inflow		123.236 mol	56.5082 mol
Temperature	25.0000	25.0000	25.0000
Pressure (at)	1.00000	1.00000	1.00000

Mixing Method: Single Point Mix

Type of calculation: Isothermal

Calculate

Summary:

Unit Set: Metric (moles)

Automatic Chemistry Model  
AQ (H+ ion) Databanks: Public

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

Calculation complete

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”<sup>8</sup>.

Stream Analyzer has the capability of building chemical stability diagrams by using the *Chemical Diagram tool* that allows to study the precipitation of species as function of ion concentration and other parameters such as pH. In this section we will explore with different examples how to set up cases to use the Chemical Diagram tool.

The screenshot displays the OLI Studio interface for creating a chemical stability diagram. The main workspace shows a table with the following data:

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

The right-hand panel is configured with the following settings:

- Type of diagram: Species vs. Species (dropdown)
- Species vs. Species (dropdown)
- Solids Yield (selected)
- Unit Set: Metric (moles)
- Automatic Chemistry Model: Aqueous (H+ ion) Databanks
- Using K-fit Polynomials: T-span: 25.0 - 225.0, P-span: 1.0 - 1500.0
- Stability diagram: vs. Specify an X variable component for this diagram type.
- Specify at least 1 Y variable component for this diagram type.
- Calculation not done

The status bar at the bottom indicates "Calculation Complete!".

<sup>8</sup> Santucci, R.J., McMahon, M.E. and Scully, J.R., 2018. Utilization of chemical stability diagrams for improved understanding of electrochemical systems: evolution of solution chemistry towards equilibrium. *npj Materials Degradation*, 2(1), p. 1.

## Building a Chemical Diagram

In this section, first we will go through the steps of building a basic chemical diagram, and then we will explore how the concentration of species and other variables such as temperature and pressure have a significant influence on the stability of chemical species.

### Example 37: $\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3 - \text{K}_3\text{PO}_4$ Chemical Diagram

For this example, we are going to reproduce the work found in the following paper: *Andelman, T., Tan, M. C., & Riman, R. (2010). Thermochemical engineering of hydrothermal crystallization processes. Materials Research Innovations, 14(1), 9-15. <https://doi.org/10.1179/143307510X12599329343123>.*

#### Starting the Simulation

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

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

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

#### Add a new Stream

**Click** on the new Stream and press <F2> to change the name to *Chemical Diagrams*

Select the **AQ** thermodynamic Framework

**Click** on the **Names Manager** Icon and select the **Formula** option

**Click** on the **Units Manager** Icon, and select Metric, Batch, Moles

Enter the composition of the stream given in the table above. Notice that the concentrations of  $\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3$  and  $\text{K}_3\text{PO}_4$  are held at a 1:1 molal ratio.

Go to the **Add Calculation** button and select **Chemical Diagram** calculation or by selecting the **Chemical Diagram** icon in the Actions Pane

Select **Species vs Species** as Type of Diagram – Default

Change the **Chemical Diagram** name to **Lanthanum/Phosphate** using the <F2> key

OLI Studio (Version 11.5.1 Beta) - [6.1 Chemical Diagrams - Example\_37.oad\*]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator: 6.1 Chemical Diagrams - Example\_37.oad\*

- Streams
- Chemical Diagrams
- Lanthanum/Phosphate

Actions: Actions

Plot Template Manager

Save

For Help, press F1

NUM

**Lanthanum/Phosphate**

Description Definition Chemical Diagram Report File Viewer

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.7082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Inflows (mol)</b>	
H2O	55.5082
La[C2H3O2]3	0.100000
K3PO4	0.100000
HNO3	0.0
NaOH	0.0

Input: Advanced Search Add as Stream Export

Type of diagram: Species vs. Species **Specs...**

Calculate

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model: Aqueous (H+ ion) Databases: Aqueous (H+ ion)

Using K-fit Polynomials

T-span: 25.0 - 225.0

P-span: 1.0 - 1500.0

Stability diagram: vs

Only one redox system can be selected for display in Species vs Species diagrams.

Specify an X variable component for this diagram type.

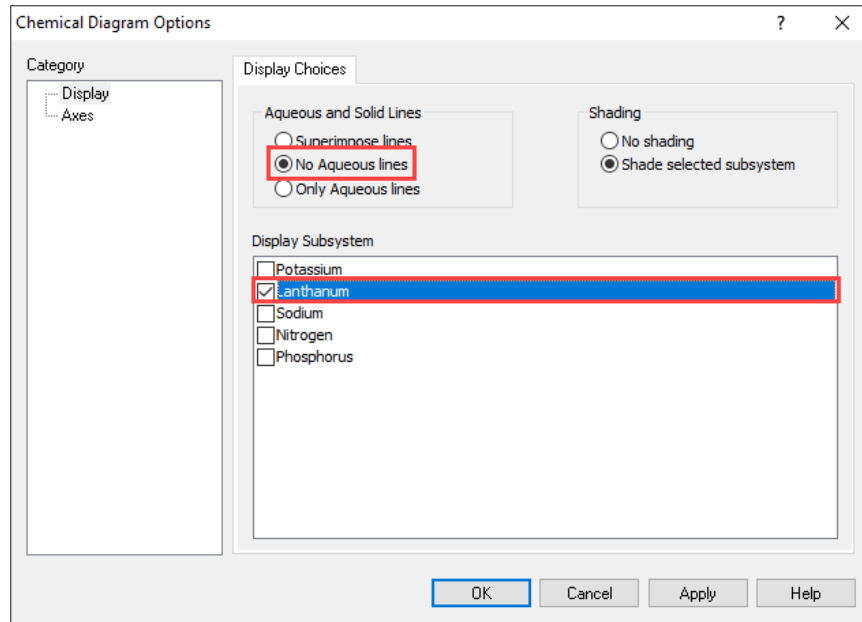
Specify at least 1 Y variable component for this diagram type.

Calculation not done

*Notice that the calculation is not ready*

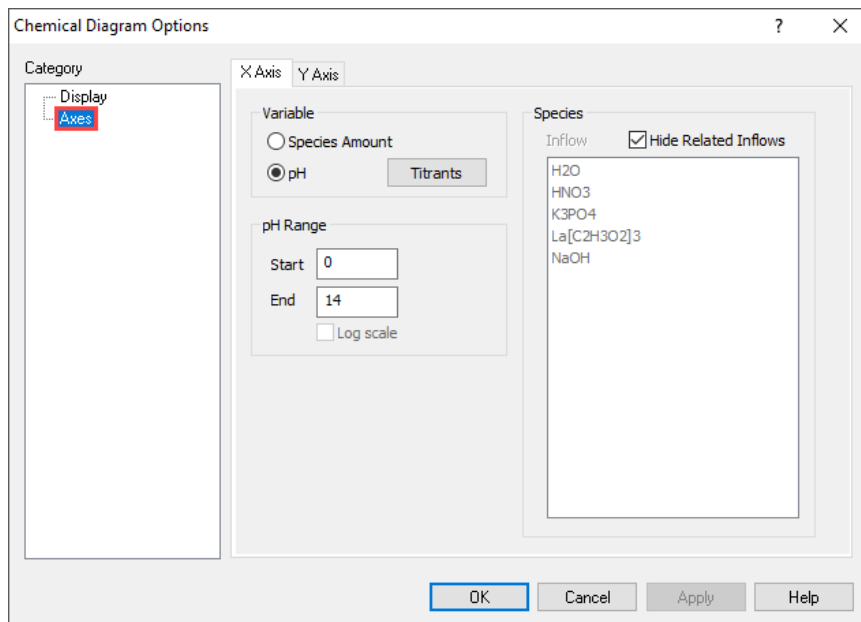
Click on the **Specs** button. This will open the **Chemical Diagram Options** window

In the **Display Choices** tab, select the **No Aqueous lines** button and check the box for **Lanthanum** as the subsystems to display



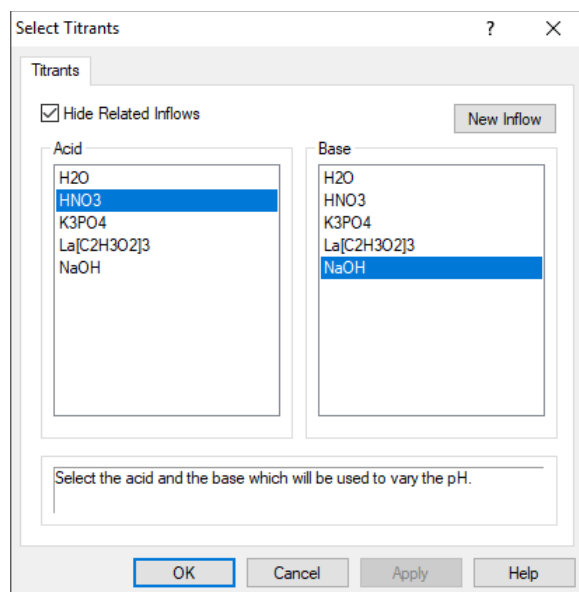
Click on the **Axes** category. The dialog changes to display the **X Axis** tab.

In the **Variable** section select the **pH** option. Leave the default **pH Range**: 0-14. This also enables the **Titration** button.



Click on the **Titration** button. Select **HNO<sub>3</sub>** 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.



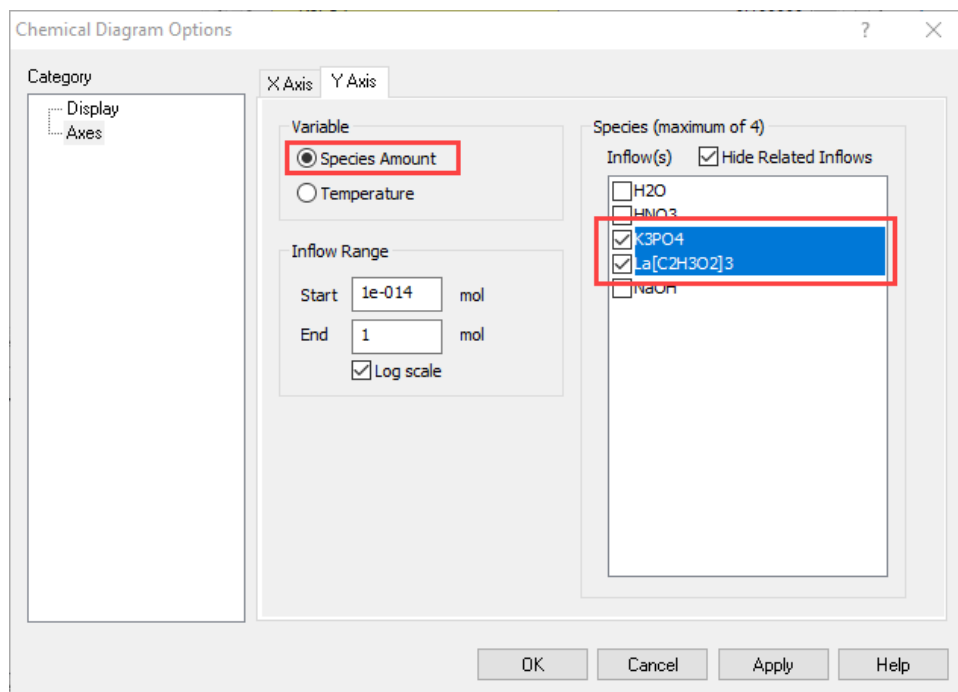
Select the **Y Axis** tab. Select the **Species Amount** button as the variable to change

Select La[C2H3O2]3 and K3PO4 species

For the Inflow Range keep the default range: from 1E-14 to 1.0 moles on a log scale.

**Note:** This means we will have initially 1.0E-14 moles of  $\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3$  and 1.0E-14 moles of  $\text{K}_3\text{PO}_4$  increasing equally until we have 1.0 moles of each.


Click **OK**



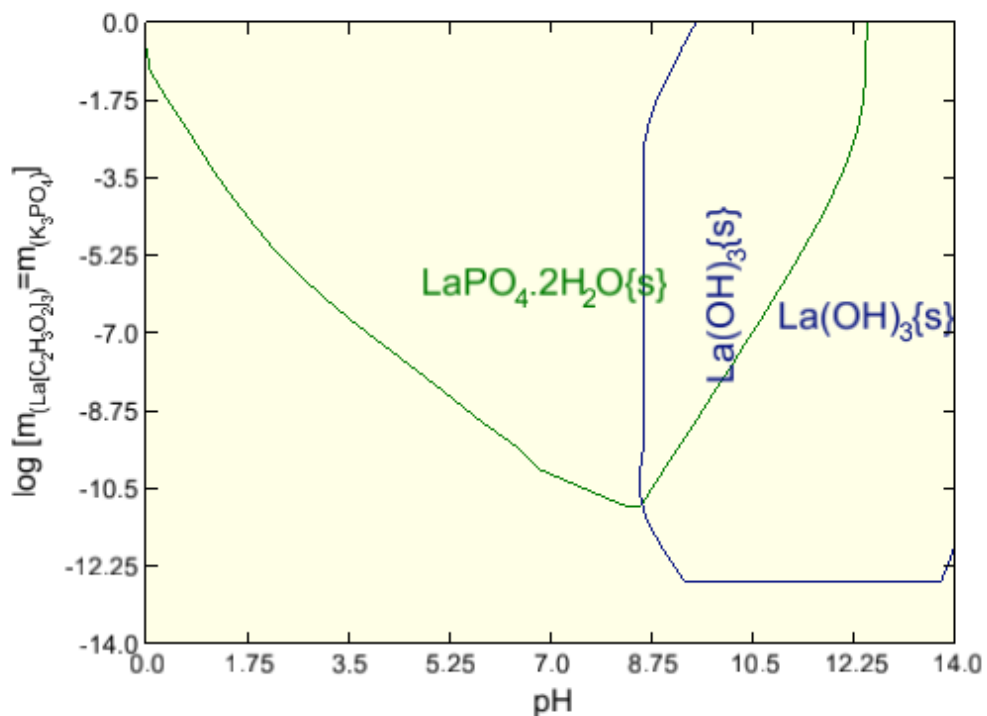
We are ready to perform the calculation. **Click** on the **Calculate** button or press the **<F9>** key

It is time to **save** your file (**File >Save as...**) or using the **save** icon in the tool bar. You can save it and name it *Chemical Diagrams*.

### Analyzing the Results

Click on the **Chemical Diagram** tab (  **Chemical Diagram** ). This tab displays the Species vs pH diagram for the Lanthanum species.

The X axis of the diagram is pH, varied by adding HCl or NaOH, and the Y axis variable is the concentrations of  $\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3$  and  $\text{K}_3\text{PO}_4$ , 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  $\text{OH}^-$  ions are present,  $\text{La}(\text{OH})_3$  begins to form. The pH range in which  $\text{La}(\text{OH})_3$  forms is the right bounded region in the diagram. The area below the lines is where only aqueous species exist.



## Example 38: Adding 50% Lanthanum Acetate

In this second example we will add 50% more to the lanthanum acetate species and see the effect of this increase in concentration on the chemical diagram.

### Starting the Simulation

**Copy** the *Lanthanum/Phosphate* chemical diagram calculated in the Example 37:  $\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3 - \text{K}_3\text{PO}_4$  Chemical Diagram, and **paste** it under the *Chemical Diagrams* stream.

**Change** the name to *Lanthanum 50% increase* using the <F2> key

**Change** the Lanthanum Acetate amount to 0.15 moles

The screenshot shows the OLI Studio interface for a chemical diagram titled "Lanthanum 50% increase". The main window displays a table of variables and values, categorized into Stream Parameters, Calculation Parameters, and Inflows (mol). The "Inflows (mol)" section is highlighted, showing the following data:

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.7582
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Parameters</b>	
Use Single Titrant	No
pH Acid Titrant	HNO3
pH Base Titrant	NaOH
<b>Inflows (mol)</b>	
H2O	55.5082
La[C2H3O2]3	0.150000
K3PO4	0.100000
HNO3	0.0
NaOH	0.0

The right-hand panel shows a "Summary" section with the following details:


- Unit Set: Metric (moles)
- Automatic Chemistry Model: Aqueous (H+ ion) Databanks: Aqueous (H+ ion)
- Using K-fit Polynomials
- T-span: 25.0 - 225.0
- P-span: 1.0 - 1500.0
- Stability diagram: La[C2H3O2]3 vs pH
- User-selected titrants: Acid: HNO3, Base: NaOH
- Range on La[C2H3O2]3: 1.00000e-14 to 1.00000 mol
- Range on pH: 0.0 to 14.0000
- Subsystems: Lanthanum
- Calculation complete

The "Calculate" button is highlighted with a green checkmark. A status bar at the bottom indicates "Calculation Complete!".

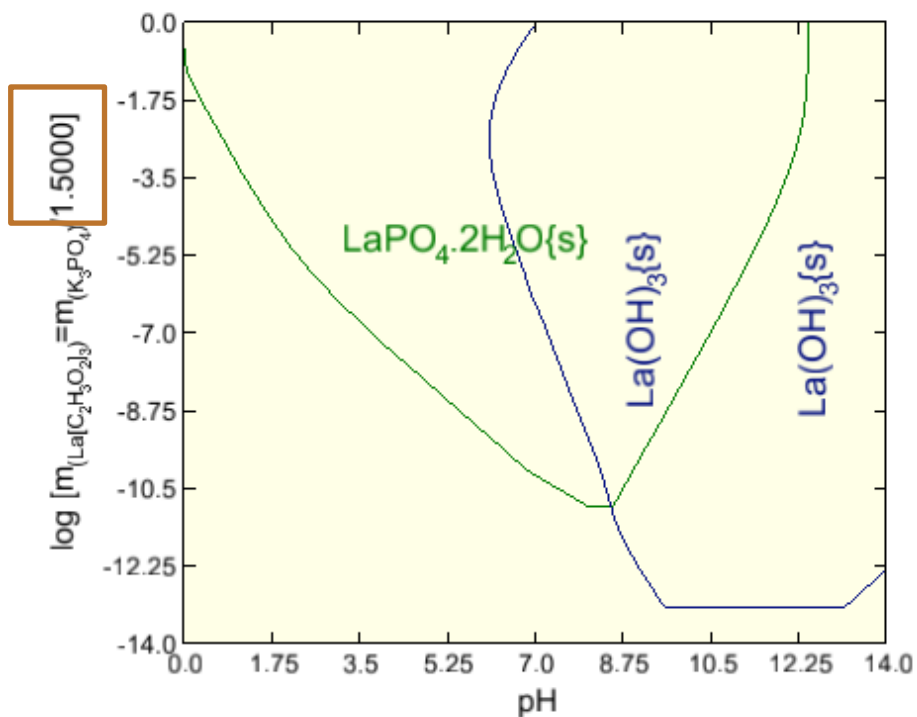
We are ready to perform the calculation. **Click** on the **Calculate** button or press the <F9> key

It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar.

### Analyzing the Results

Click on the **Chemical Diagram** tab (  **Chemical Diagram** ). 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  $\text{La(OH)}_3$  over a wider range of pH.



## Example 39: Changing temperature and pressure

In this third example we will use the original amount of the lanthanum acetate species and see the effect of this increase in temperature and pressure on the chemical diagram.

### Starting the Simulation

**Copy** the *Lanthanum/Phosphate* chemical diagram calculated in the Example 37: La(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>3</sub> – K<sub>3</sub>PO<sub>4</sub> Chemical Diagram, and **paste** it under the *Chemical Diagrams* stream.

**Change** the name to *Lanthanum HTHP* using the <F2> key

**Change** the temperature to 200 °C and the pressure to 25 atmospheres

OLI Studio - [Chemical Diagrams.oad\*]

File Edit Streams Calculations Chemistry Tools View Window Help

Streams

- Chemical Diagrams
  - Lanthanum/Phosphate
  - Lanthanum 50% increase
  - Lanthanum HTHP

Actions

Plot Template Manager

Save

### Lanthanum HTHP

Description Definition Chemical Diagram Report

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	55.7082
Temperature (°C)	200.000
Pressure (atm)	25.0000
<b>Calculation Parameters</b>	
Use Single Titrant	No
pH Acid Titrant	HNO <sub>3</sub>
pH Base Titrant	NaOH
<b>Inflows (mol)</b>	
H <sub>2</sub> O	55.5082
La[C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ] <sub>3</sub>	0.100000
K <sub>3</sub> PO <sub>4</sub>	0.100000
HNO <sub>3</sub>	0.0
NaOH	0.0

Input

Advanced Search Add as Stream Export

Type of diagram: Species vs. Species

Calculate

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model

Aqueous (H+ ion) Databanks:

- Aqueous (H+ ion)

Using K-fit Polynomials

T-span: 25.0 - 225.0

P-span: 1.0 - 1500.0

Stability diagram: La[C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>]<sub>3</sub> vs pH

Auto-selected titrants

Acid: HNO<sub>3</sub>

Base: NaOH

Range on La[C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>]<sub>3</sub>:

1.00000e-14 to 1.00000 mol

Range on pH:

0.0 to 14.0000

Subsystems

- Lanthanum

Calculation not done


Calculation Complete!

For Help, press F1

We are ready to perform the calculation. **Click** on the **Calculate** button or press the <F9> key

It is time to **save** your file (**File > Save as...**) or using the **save** icon in the tool bar.

## Analyzing the Results

Click on the **Chemical Diagram** tab (  **Chemical Diagram** ). This figure shows the stability diagram for  $\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3$  and  $\text{K}_3\text{PO}_4$  over a range of pH values at  $200^\circ\text{C}$  and  $25\text{ atm}$ . Under these conditions, there is a decrease in the pH range over which  $\text{LaPO}_4$  is the stable product. This is because as temperature increases, the insoluble rare earth hydroxides  $[\text{RE}(\text{OH})_3]$  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  $\text{La}(\text{OH})_3$  will form.

