



INTRODUCTION TO

OLI Studio

9.6

think simulation

getting the
chemistry right

Introduction to OLI Studio

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Version: OLI Studio 9.6

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

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- OLI Systems Wiki page: http://wiki.olisystems.com/wiki/Main_Page

Disclaimer

This manual was produced using the OLI Studio / OLI Analyzer 9.6. build 2 (9.6.2). 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.

Chapter 1 Introduction

The OLI Studio

The OLI Studio is freeform electrolyte simulation software. With this software, a client can define chemistry and process pathways without predefined recipes that produce specific results. The OLI Studio is a software suite containing several modules including, Stream Analyzer, Corrosion Analyzer, and Studio ScaleChem. A client's license determines which modules are enabled within the OLI Studio.

The Training Manual

This training manual is designed by Aqueous Process Simulations, Inc. (AQSim) to highlight OLI Studio: Stream Analyzer and Corrosion Analyzer features and functions. AQSim has a separate training manual for OLI Studio: ScaleChem.

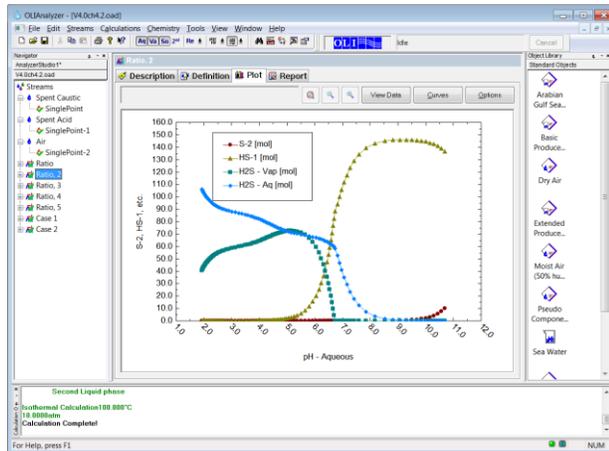
The manual provides general concepts, theory, explanations of chemical principles, and various calculations. Certain chapters have follow-up examples, which are designed to reinforce concepts learned within the chapter. The subsequent chapters have real world applications of the software. The manual is self-guided but is also used to accompany trainings provided by AQSim.

OLI Studio Components

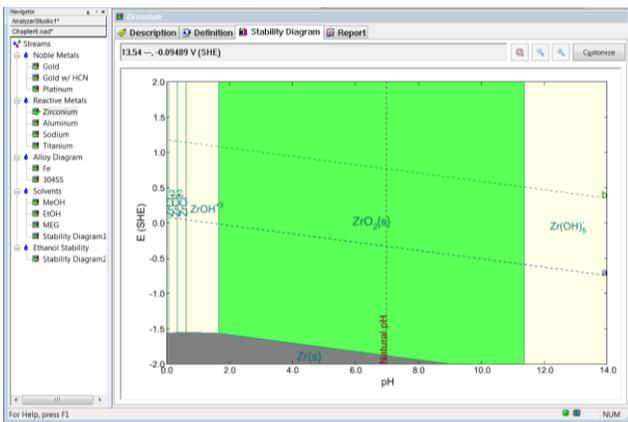
Stream Analyzer

Stream Analyzer is standalone software. It requires no additional components to run basic calculations. It is the main interface of the OLI Studio, highlights of which include:

- Thermodynamic Frameworks
- Phase Selection and Manipulation
- Names Manager and Units Manager
- Calculation Objects
- Plotting, Reporting, Customization tools; Water Analysis charge and pH reconciliation



Corrosion Analyzer



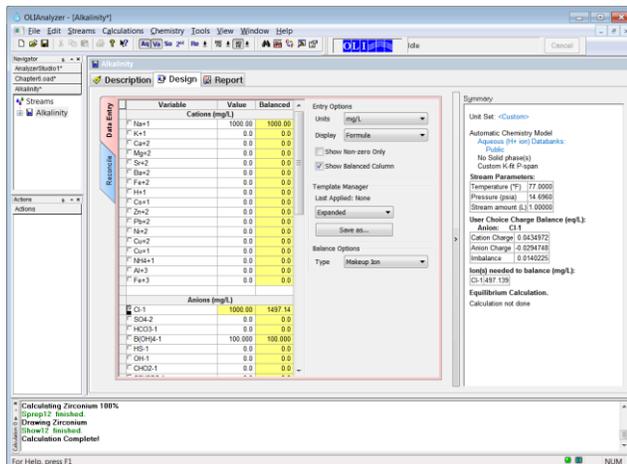
Corrosion Analyzer is a module within the OLI Studio. A separate license enables this module. Highlights include:

- EH-pH Stability (Pourbaix) Diagrams
- Species Phase Diagrams
- Polarization Diagrams
- General Corrosion Rates
- Local Corrosion Rates
- Extreme Value Statistics (a module within Corrosion Analyzer)

Studio ScaleChem

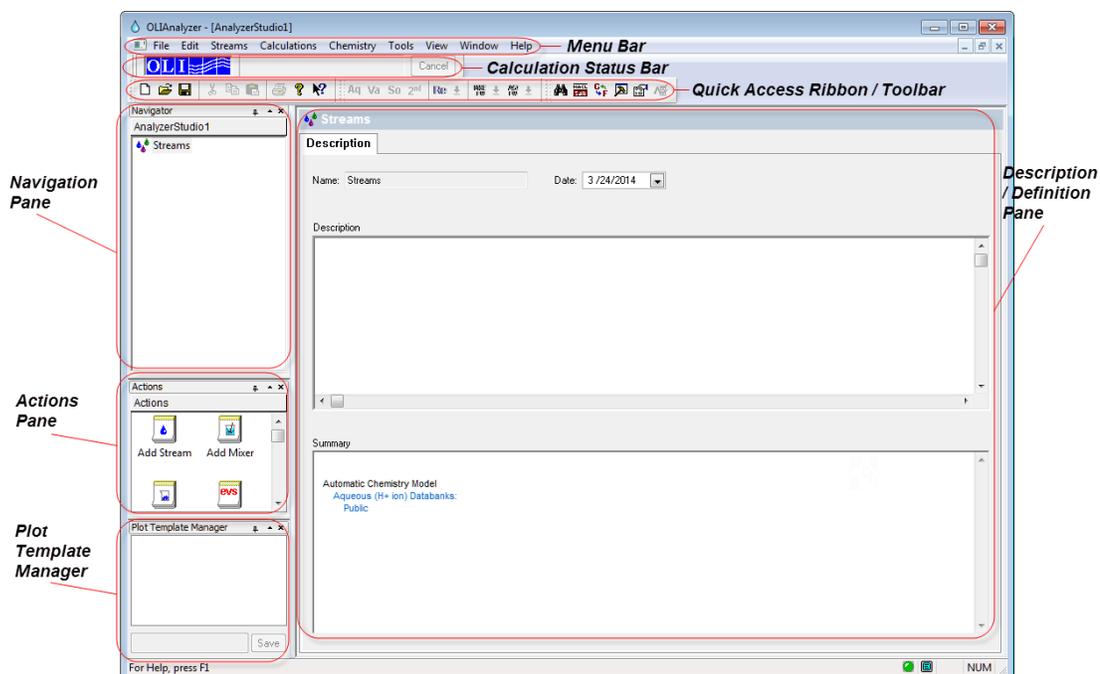
ScaleChem was OLI Systems' standalone, upstream software. This software is now a component within the OLI Studio. Studio ScaleChem can perform the following operations within both OLI thermodynamic frameworks (Mixed Solvent Electrolytes and Aqueous) and special databases:

- Brine, Hydrocarbon, Oil Analyses
- Scaling Scenarios
- Mixer and Saturator Calculations
- Facilities
- Contour Diagrams



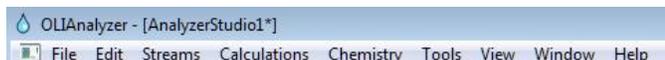
OLI Studio Interface

The OLI Studio modules share a common interface. Clients can hide or show many of the sections described below. For instance, clients can remove the Calculation Status bar or Template Manager or add or remove tools from the Quick Access Ribbon (Toolbar).



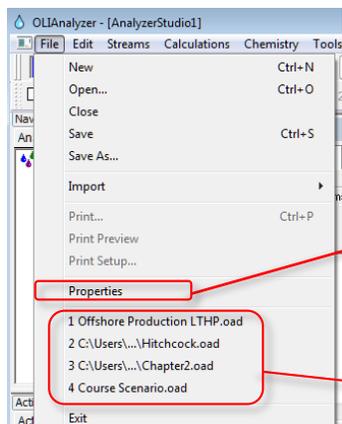
The Navigator Pane displays streams and calculation objects in a branched hierarchy. Below this is the Action Pane, which lists all the objects of Studio modules enabled by a client's OLI license. The Calculation Status and Output bars are on by default but can be hidden. Clients will mostly work in the Description / Definition area, which is contextual - changing depending on which object a client is working on.

Menu Bar



Notable features within the menu bar are explained below. View, Window, Help are options

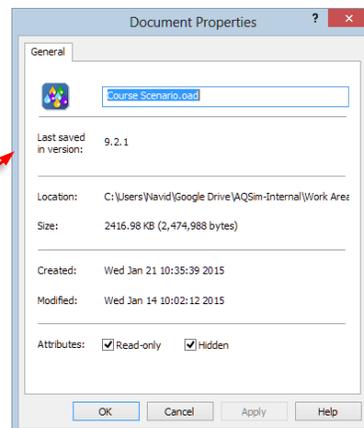
File



This File menu contains standard options like New, Save, Print, etc.

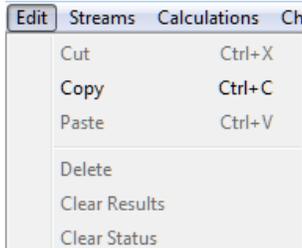
Properties opens a box that shows file type, location, size, the date, build and version number of the last save.

The most recently worked on streams will also be shown.



Edit

Certain streams can be copied and pasted within the Navigator using the Edit menu or right-mouse click options.



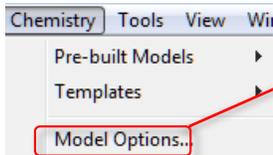
The Edit menu also has the following actions of note:

Clear Results – Removes all calculation output

Clear Status – Stops or removes a calculation

Chemistry

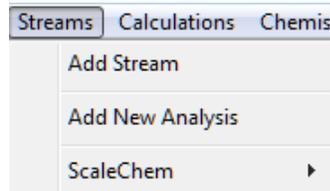
Clients can adjust the chemistry of the software in this menu



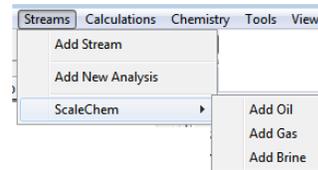
Pre-built Models lets clients create a single, specialized model and port it to or from other application files.

Templates allows clients to make a series of standard input component sets e.g. a standard seawater

Streams

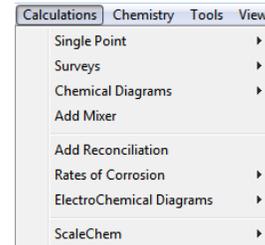


The Streams menu contains actions that can also be performed using the Actions Pane. These actions are Add Stream, Add Analysis, and ScaleChem, which has its own sub-menu.



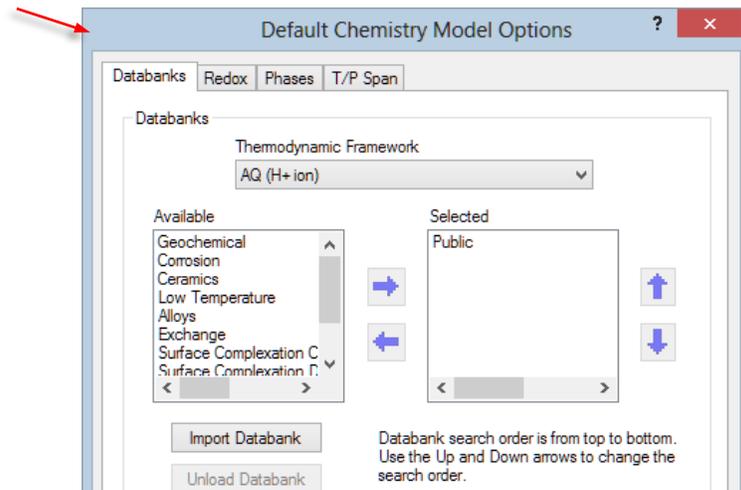
Calculations

The Calculations menu contains all the calculations found in the Actions pane, as well as more specific calculation types.



For instance, the Single Point calculation option opens into a submenu for the 10 single point calculations available in the software.

Selecting **Model Options** opens a submenu with that allows clients to make advanced changes to the chemistry of the software.



Thermodynamic Framework –To select either the Aqueous or MSE (Mixed Solvent Electrolyte) Framework

Databases – To select an installed database

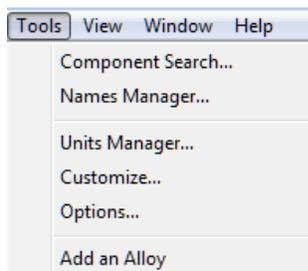
Redox – To toggle on/off oxidation-reduction reactions

Phases– To toggle on/off phases or solids can be selected as well.

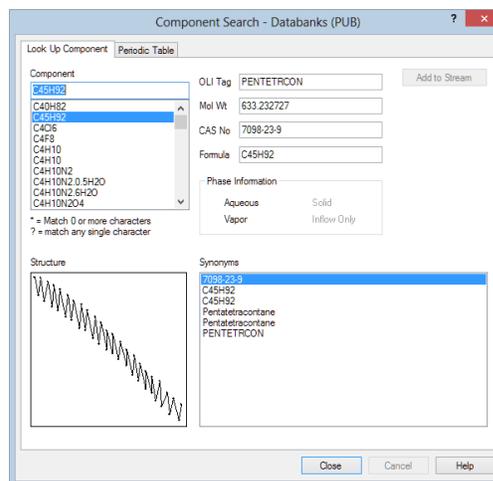
T/P Span – To change Temperature and Pressure maximums

Tools

This menu item contains several features.



Component Search allows clients search for species in the OLI database.

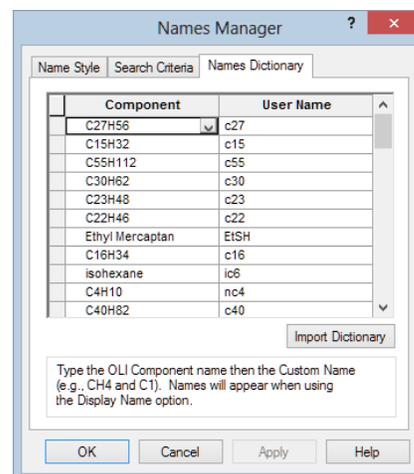
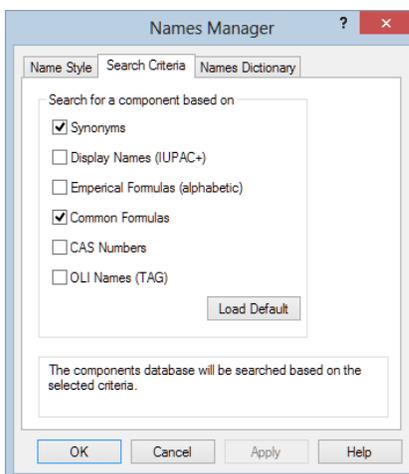
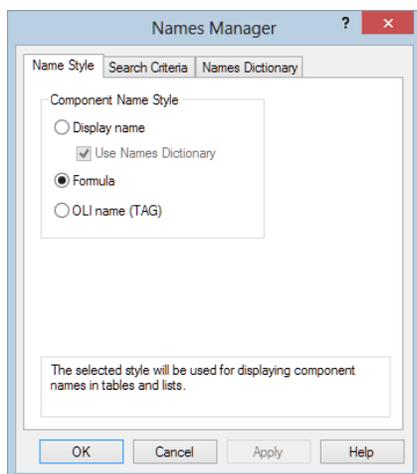


Names Manager

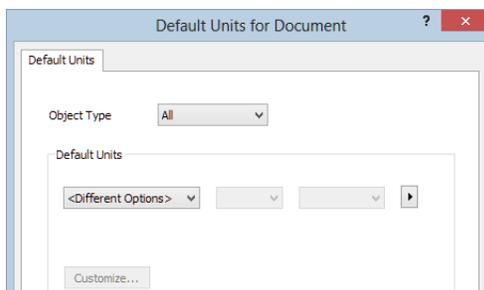
Names Style: clients select how to view chemical names i.e. by Formula, Display Name or the OLI convention (TAG names).

Search Criteria: clients determine how the software searches for components. The default option is to search by all available names.

Names Dictionary: clients can rename components with this tab or import dictionaries used by OLI software.



Units Manager allows clients to modify units.



Toolbar (Quick Access Ribbon)

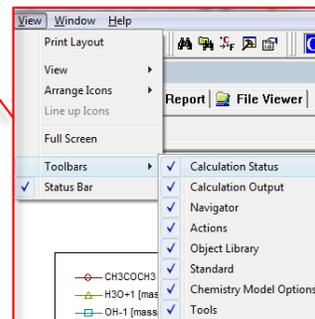


The Quick Access Ribbon or toolbar sits below the menu bar Menu Bar. Tools within the ribbon can be added or removed or repositioned (the Calculation Status Bar can also be hidden or moved).



To move a set of tools, clients can drag the left side of a set of tools.

The ribbon can also be customized by selecting View from the Menu bar, then selecting Toolbars. Key tools are described below:



Phases Turn on/off specific phases i.e. if So (solid) is turned off, then no solid phases form



Redox Turn on/off Oxidation-Reduction and select redox subsystems



Chemistry Model Options Select the Aqueous or Mixed Solvent Electrolyte thermodynamic framework.



Component Search Add inflows to the calculation



Names Manager Changes the style of names i.e. Display, Formula, OLI Tag names



Units Manager Changes units



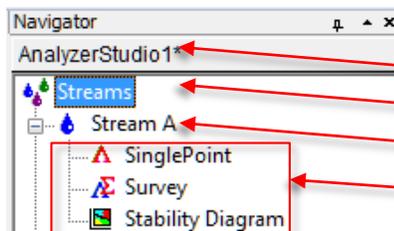
Customize window Customize the window appearance



Tools Options Shortcut Adjusts default software settings

Navigation 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 substreams or branches. There are three main levels here.

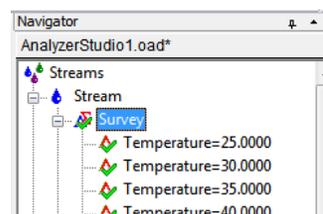


Filename A star next to a filename indicates that it has not been saved

Global Streams Level Provides the broadest view of Navigator objects

Stream Level Chemistry is entered at this level.

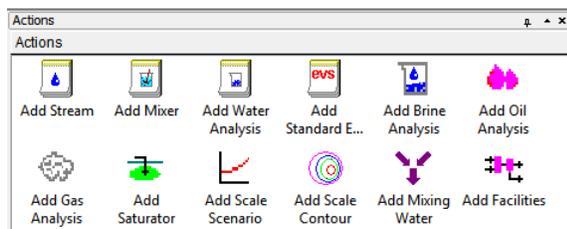
Calculation Level Most calculations (except mixing blocks) are subordinate to streams and appear as substreams. Certain streams (i.e. ScaleChem objects) have embedded calculations.



Calculation sublevel Some calculations have their own substreams. These substreams can be added to the Global level using the Add as Stream function.

Action 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.



After adding an item from the action pane, the action appears as a “stream” in the Navigator menu. Depending on the item selected, additional actions may appear in the actions pane. Items can also be selected from the menu bar.

Calculation Types

Once a client selects or highlights an object, object-specific calculations become available in the Actions bar. Stream and Water Analysis objects each have a specific set of calculations. The calculation available within a Water Analysis object is called a Reconciliation. Available Stream calculations are:

Single Point calculations  **SinglePoint2** compute the properties for a stream at one set of conditions. Clients choose from isothermal, dew point, bubble point, precipitation point, or custom.

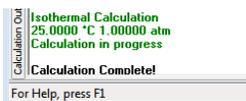
Multiple Point or Survey calculations  **Survey3** are a series of single-point calculations in which independent variables such as temperature adjusts with each calculation (e.g., a temperature survey). Up to two variables can be adjusted simultaneously, and a third can be fixed (e.g., pH or bubble point pressure/temperature). There are several examples of multiple point calculations in the TOT manual.

Chemical or Stability Diagrams,  **Chemical Diagram4** also known as real-solution Pourbaix diagrams, plot the phase stability region across a two-independent-variable range. An example would be Calcite stability when a pH and CO2 vary.

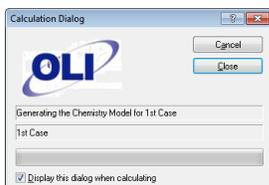
Corrosion Rate calculations  **Rates6** compute the general and localized corrosion rates of metals and alloys. They contain both single- and multiple-point calculations

Calculation Status Screens

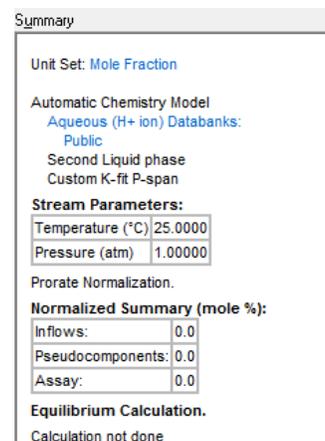
The **Calculation Output Window** shows progress, errors, temporary file locations, and other data.



The **Calculation Status Dialog** shows an estimate of the remaining calculation time.



The **Summary Window** shows inputs, calculation outputs, warnings, and has hyperlinks to the Units and Framework managers. This window varies with object.



Chapter 2 Single Point Calculations

Introduction

Training of OLI Studio: Stream Analyzer begins with the Single Point Calculation. It is the software's simplest set of calculations. There are thirteen single-point calculation types, and elements of each are presented in this chapter.

The key elements of training include entering molecular inflows in the Stream object, adding a single point object and selecting one of the calculation options. Through each example, subtle changes are presented so that additional features and functions are learned. These feature/functions enhance the software flexibility, enabling certain system states to be modeled.

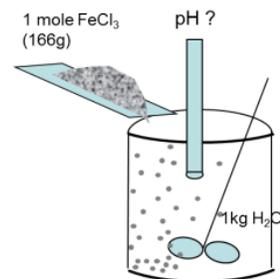
The single point calculations are listed below.

2.1 Isothermal	2
2.2 Bubble Point.....	11
2.3 Dew Point.....	15
2.4 Vapor Fraction and Amount.....	19
2.5 Isochoric (Constant Volume) calculations.....	23
2.6 Set pH.....	26
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2.1 Isothermal

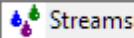
Overview

The default and most basic single point calculation is **Isothermal**. The software computes solution properties based on a known composition, and condition. You will create a 1.0 molal solution of FeCl_3 at 25°C and 1 atm and calculate the solution properties.



- ✓ Launch the software



The Software opens with a new file named Document1. The Navigation panel contains a single Streams object - . This global Streams object is used to fix the default settings of the file, like the names, units, and thermodynamic framework.

- ✓ Click Add Stream icon in the Actions pane. Or, select Streams > Add Stream from the Menu



A new stream object appears in the Navigator panel below the global Streams object. The object has the generic name "Stream." The stream name is changed using the <F2> key, or by selecting the Description tab, or by right-mouse-clicking on the object and selecting rename.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature ($^\circ\text{C}$)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082

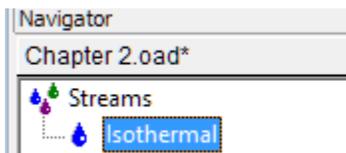
The software switches to the Definition tab. This tab contains the grid in which the solution composition is defined (added). The grid is divided into two Stream Parameters and Inflows.

This Stream Parameters section contains three rows, Stream Amount, temperature, and pressure. The default settings are 1 kg at 25°C and 1 atm. The inflows category contains the molecular components that make up the system. When a stream is created only H_2O is present in the grid. Its cell is yellow because it cannot be removed, it is a permanent inflow.

Starting the work

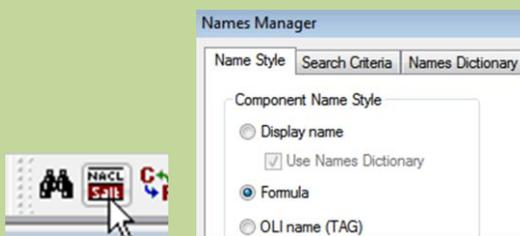
Before starting a working file for this chapter...

- ✓ Save the file (File > Save As...) and type an appropriate name (e.g. *Chapter 2*)
- ✓ Select the stream in the Navigator then press <F2> and rename it 'Isothermal'



Changing how components and species appear. The Names Manager is used to change the text in the grid. It can be formulas (e.g. H₂O) or display names (e.g. water).

- ✓ Select the **Names Manager** in the toolbar then select **Formula**



The software has two chemical frameworks. The Aqueous Framework (AQFW) which is the default and the Mixed Solvent Electrolytes Framework (MSEFW). We will use the MSEFW for this example.

- ✓ Select the MSE Framework (MSE FW) button in the toolbar



The grid formats and the thermodynamic setting changes are complete. The object is ready for study.

- ✓ Type **FeCl₃** in the white cell below H₂O Inflows of the grid
- ✓ Press <Tab> or <Enter>

Pressing the Enter or Tab keys advances the cursor to the next selectable cell.

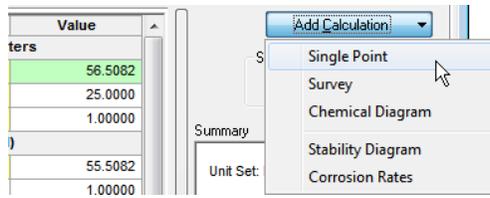
- ✓ Enter a value of 1.0 mole

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

Adding a Single Point Calculation

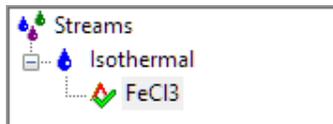
The next step is to perform the calculation. Calculations are run in a Calculation object that sits under a Stream object. There are several calculation objects, and this chapter focuses on the Single Point.

- ✓ Click on the Add Calculation dropdown menu and select Single Point



The Single Point object is a unit of the Stream and will contain the stream inflows, formats, and specifications.

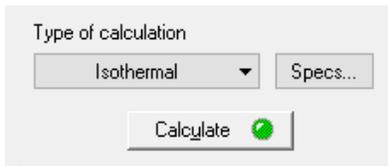
- ✓ Label the calculation object FeCl3



The overall format of a calculation object is similar to the Stream object, with some differences. First, there are more yellow cells on the grid. This is the chemistry added at the Stream level and it cannot be removed at this level (though the amount can be changed).

Inflows (mol)	
H2O	55.5082
FeCl3	1.00000

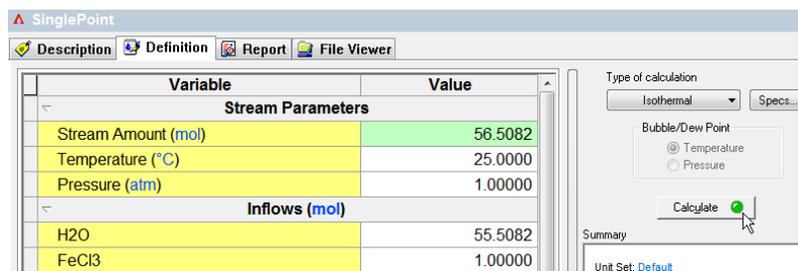
Second, the upper right section (the calculation section) contains a calculate button and multiple calculation types.



The calculation button has three colors:

- Red - insufficient specifications for a calculation
- Yellow - Incomplete specifications but calculation can continue
- Green – Completed specifications, the calculation is ready

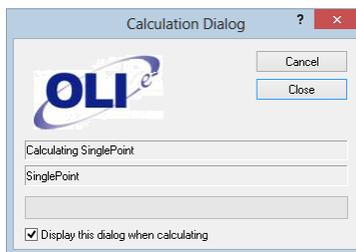
The default calculation type is Isothermal. An isothermal calculation is defined having the temperature, pressure, and total composition known. The total system energy, phase behavior and speciation are computed.



The calculate button is green, and object is ready to calculate.

- ✓ Click the Calculate button (you can also press the <F9> key)

A Calculation Dialog box appears during the calculation. It displays the calculation's progress. Single-point isothermal calculations compute very fast. This calculation dialog is more important when multiple point calculations are run.

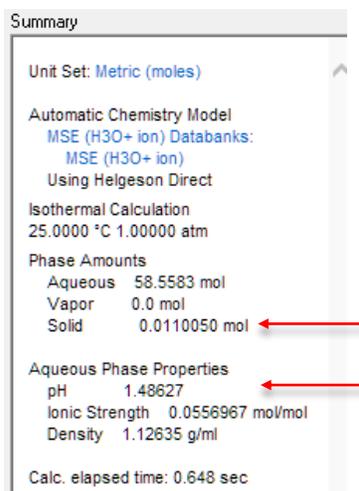


When finished, the box reads "Calculation Complete" then the window closes. There is now a check mark on completed calculation object.  SinglePoint .

Viewing the Results

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

- ✓ Find the pH and the amount of solid that formed



The pH should be about 1.5, and there is about 0.01 moles of solid present. The complete set of results are in the Report tab.

- ✓ Click the Report tab



- ✓ Scroll down to the Stream Parameters table

This table contains the thermophysical properties for each phase that forms in a calculation. The top table is for Liquid 1 (the water phase), and the properties include pH, salinity (ionic strength), dielectric constant, viscosity and other measurable properties.

Liquid 1 Properties

pH	1.48627	
Ionic Strength (x-based)	0.0556967	mol/mol
Ionic Strength (m-based)	3.26679	mol/kg
Dielectric Constant	63.2146	
Osmotic Pressure	129.216	atm
Specific Electrical Conductivity	2.28671e5	µmho/cm
Viscosity, absolute	1.64261	cP
Thermal Conductivity	492.192	cal/hr m °C
Surface Tension	0.0747997	N/m
Standard Liquid Volume	1.04076	L
Volume, Std. Conditions	1.03079	L

The next table is the Solids Properties There is less data computed for the solid phases. This is in part because there can be multiple phases, and this information is presented in other sections.

Solid Properties

Standard Liquid Volume	-2.05640e-5	L
------------------------	-------------	---

The next table down should be the thermodynamic properties. This include density and enthalpy for each phase and for the Total system. The Total Density is the bulk density.

Thermodynamic Properties

	Unit	Total	Liquid-1	Solid
Density	g/ml	1.12711	1.12635	3.40023
Enthalpy	cal	-3.91546e6	-3.91324e6	-2215.34

✓ Scroll down to the Scaling Tendency table

This table contains the thermodynamic saturation of potential minerals. If the value is 1.0, then the solid phase is present and in equilibrium with the water. If the value is below 1, then the solid phase is subsaturated.

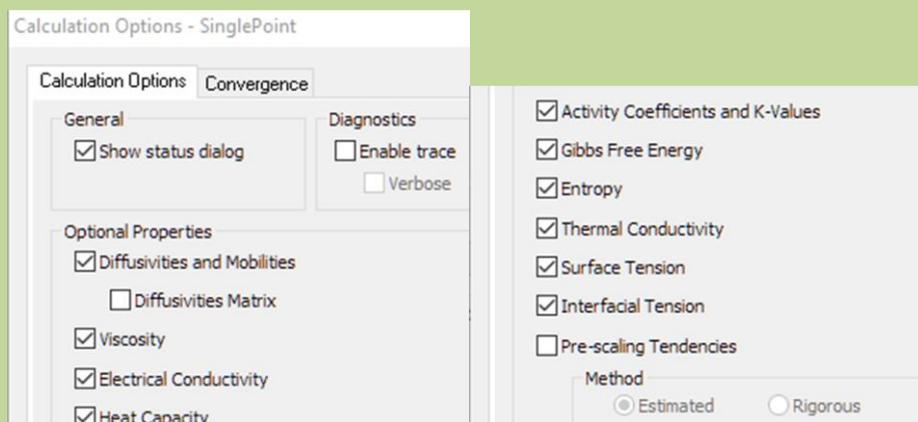
Scaling Tendencies

Row Filter Applied: Values > 1.0e-4

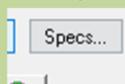
Solids	Post-Scale
Fe(OH)3 (Bernalite)	1.00000
H2O	0.718055
FeCl3.10H2O	1.41516e-4

It is common for the user to prefer the Pre-Scale tendency (also called Saturation Ratio). The pre-scale tendency is the value BEFORE solids precipitate, and represents the driving force for precipitation or dissolution. The pre-Scale Tendency, is an optional property that can be selected in the Calculation Options window.

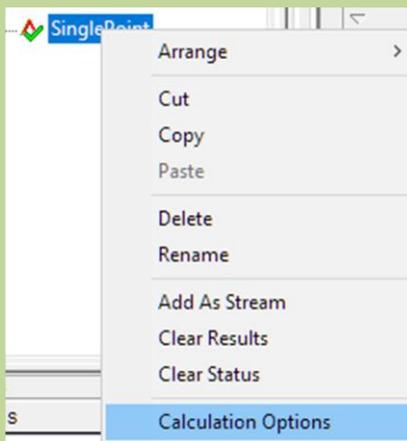
Calculation Options – Not all properties are computed by default. There are additional properties available, including heat capacity, entropy, Gibbs energy, etc. These properties are off by default but can be turned on in the calculation options window.



This can be accessed in a few ways, including the specs button in the toolbar , the Specs.



Button above the calculation button - , or by right-mouse-clicking on the Single Point Calculation and selecting Calculation options



- ✓ Scroll down to the Species Output (True Species) table
- ✓ Review the Solid column first

The software computes that 0.011 moles $\text{Fe}(\text{OH})_3$ solid has formed and is in equilibrium with the ~ 1.5 pH solution. The remaining 0.89 moles of iron added is dissolved in water as various aqueous complexes, such as iron chlorides and hydroxides.

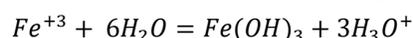
Species Output (True Species)

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

The low pH computed results from iron's reaction with water. Dissolved iron-hydroxide complexes and solid Fe(OH)₃ sequesters OH⁻¹, results from H₂O hydrolysis (splitting) according to the following example:



The **0.011** moles of Fe(OH)₃ precipitate generates **0.033 moles H₃O⁺**. This is about 3/4th the total H₃O⁺¹ in solution (0.45 mol). The remaining H₃O⁺¹ is produced from the 0.012 moles FeOH⁺².

By definition, $pH = -\log a_{H_3O^{+1}}$, where $a_{H_3O^{+1}}$ is the activity of the hydronium ion. An approximation is using the hydronium concentration:

$$pH \cong -\log_{10}(H_3O^{+1}) = 1.35$$

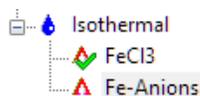
This value is close to the computed value of 1.45, the difference being the hydronium ion activity coefficients that is not part of the approximation.

The software computes nine total iron-containing species, each coordinate a different number of water, hydroxide, and chloride. A more detailed explanation of iron speciation is provided in the appendix of this manual or in various aquatic chemistry textbooks.

Recalculating using different iron-containing inflows

The mixture FeCl₃-H₂O produces a low pH. The chloride ion is the conjugate of the strong acid HCl, and it does not interact with H₃O⁺ until the pH is very low (negative values). If instead of using the conjugate of a strong acid, a weak acid conjugate like phosphate, acetate, borate, are used, then a different pH would be computed. This is because these anions have a greater affinity for H₃O⁺, and reducing its overall activity (thus raising pH).

- ✓ Return to the Isothermal stream in the Navigator
- ✓ Add a new single point calculation and label it Fe-Anions



- ✓ Click on the Fe-Anions object (if not already in focus)

- ✓ Enter FePO₄.2H₂O in the grid cell below FeCl₃
- ✓ Enter a value of 1 mole and set the FeCl₃ inflow to zero

Inflows (mol)	
H ₂ O	55.5082
FeCl ₃	0.0
FePO ₄ .2H ₂ O	1.00000

Notice that the FePO₄.2H₂O cell is white. This is because it was added at the calculation level, and not the stream level. This inflow will be local to this calculation only and will not be transferred to other objects added to this stream.

- ✓ Calculate (or press the <F9> key)
- ✓ View the pH and solids in the summary section

```

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

Isothermal Calculation
25.0000 °C 1.00000 atm

Phase Amounts
Aqueous 55.5083 mol
Vapor 0.0 mol
Solid 0.999998 mol

Aqueous Phase Properties
pH 3.05312
  
```

The pH is about 3; 1.5pH units higher than the FeCl₃ case. This is because the H₃O⁺ concentration is ~1/10^{1.5} the concentration. Move to the report and review the Species Output table.

	Total	Liquid-1	Solid
	mol	mol	mol
H ₂ O	55.5063	55.5063	0.0
FePO ₄ .2H ₂ O (Phosphosiderite)	0.998962	0.0	0.998962
Fe(OH) ₃ (Bernalite)	1.03555e-3	0.0	1.03555e-3
H ₂ PO ₄ -1	9.18999e-4	9.18999e-4	0.0
H ₃ O ⁺	9.15466e-4	9.15466e-4	0.0
H ₃ PO ₄	1.18447e-4	1.18447e-4	0.0
FeOH+2	1.28079e-6	1.28079e-6	0.0
FeO+1	4.6812e-7	4.6812e-7	0.0
Fe+3	2.15425e-7	2.15425e-7	0.0
HPO ₄ -2	7.15566e-8	7.15566e-8	0.0

The table is quite long but most species are at low amounts and can be ignored. The species with the highest amount is the solid, FePO₄.2H₂O; 99.8% of it precipitated. This solid phase is identical to the inflow and so there is essentially no reaction/hydrolysis of water. However, the next highest amount is Fe(OH)₃ solid (0.00104 moles), and this phase creates three equivalents of H₃O⁺ as in the FeCl₃ calculation above. The H₃O⁺ amount is not 3 x 0.00104 moles, because the PO₄⁻³ that did not precipitate reacted with the acid to form H₂PO₄⁻¹ and H₃PO₄. Thus PO₄⁻³, acts as a pH buffer, and “absorbs” the acid that is generated from the formation of Fe(OH)₃ solid phase.

- ✓ Save the file by selecting the save button in the tools ribbon 

Follow-up Example #1 – Find the pH of Selected Solutions

The table below contains common industrial chemicals. We want to determine the pH when 1 mole/kg of each component is added to water (1 mole in 55.508 moles H₂O).

The following steps outline one method of approaching this application.

- ✓ Create a new stream, label it Example #1
- ✓ Add the first component, HCl and set the inflow to 1 mole
- ✓ Add a single point isothermal calculation, calculate and then note the pH
- ✓ Create a new stream or type over HCl with the second component, H₂SO₄
- ✓ Confirm that the flow is still 1.0 mole and calculate
- ✓ Type over H₂SO₄ with H₃PO₄ and calculate
- ✓ Continue until each component below is tested

Follow-up Example #1 – Find the pH of Selected Solutions			
<i>Acid Chemicals</i>	<i>pH @25C and 1 atm</i>	<i>Base Chemicals</i>	<i>pH @ 25C and 1 atm</i>
HCl		NaOH	
H ₂ SO ₄		Ca(OH) ₂	
H ₃ PO ₄		Mg(OH) ₂	
HF		NH ₃	
B(OH) ₃		CaCO ₃	
Citric Acid		Na ₂ CO ₃	

Some questions to consider:

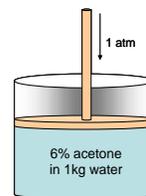
- Are there any unexpected results?
- Why is the pH of HF much higher than HCl (and also HBr and HI)?
- Boric acid's, B(OH)₃, chemical formula resembles a base, why is it acidic?
- Why is there such a pH difference between Mg(OH)₂ and Ca(OH)₂?
- The same question can be posed about the difference between Na₂CO₃ and CaCO₃.

2.2 Bubble Point

Overview

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.

The OLI Studio calculates this phenomenon using a calculation type called **Bubble Point**. Since the OLI does not assume an air phase, the confining pressure acts like a plunger on a liquid's surface. The pressure the plunger exerts is the pressure entered in the grid.



Pressure (atm)	1.00000
----------------	---------

You will compute the Bubble Point of a 6% acetone solution by changing temperature (isobaric) and then pressure (isothermal).

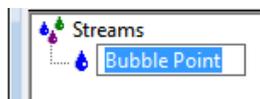
Starting the work

- ✓ Add a new stream  Add Stream

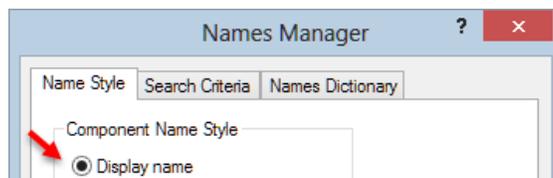
Use the inputs and parameters from the table below to create the stream's composition. Most examples in this manual use similar tables. Certain default categories, such as the names, style and units set will require further adjustments, which will be described below.

2.2 Bubble Point Stream Composition			
Stream Name:	Bubble Point	Stream Amount	1 kg
Names Style	Display Name	Temperature	25C
Units Set	Metric, mass fraction	Pressure	1 atm
Framework	MSE (mixed solvent)	Water	94 mass%
		Acetone	6 mass%

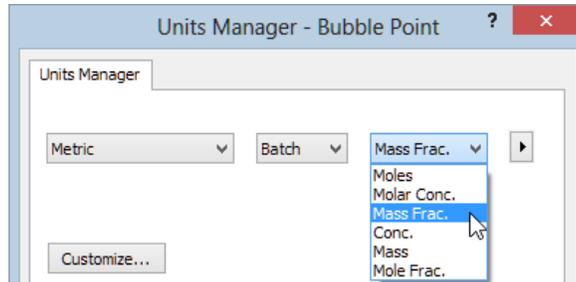
- ✓ Rename the stream **Bubble Point**, by click on the object and pressing <F2>, or click on the Description tab and enter the name there.



- ✓ Select the Names Manager button in the toolbar 
- ✓ Select the Display Name radio button



- ✓ Select the Units Manager button in the toolbar 
- ✓ Select Mass Frac from the third dropdown list

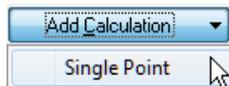


- ✓ Select the MSE button in the toolbar
- ✓ Select the Definition tab
- ✓ Enter Acetone in the Inflows cell below Water
- ✓ Change the Acetone mass % to 6 (the water value automatically adjusts)

Inflows (mass %)	
Water	94.0000
Acetone	6.00000

Calculate the Bubble Point Temperature (isobaric)

- ✓ Use the Add Calculation dropdown menu to add a Single Point Calculation

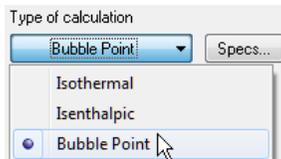


A new calculation object appears under the Bubble Point stream

- ✓ Label the stream **Acetone BPT** (BPT=bubble point temperature)



- ✓ Select Bubble Point as the calculation type



A Calculation Parameters section appears in the grid. This section contains single option – the calculation variable, temperature or pressure to be changed. Temperature is the default setting.

Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Calculate	Temperature
Inflows (mass %)	
Water	94.0000
Acetone	6.00000

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”.

- ✓ Calculate or press the <F9> key
- ✓ Review the Summary

```

Automatic Chemistry Model
MSE (H3O+ ion) Databanks:
MSE (H3O+ ion)
Using Helgeson Direct
Bubble Point Calculation
1.00000 atm
87.2555 °C ←
Phase Amounts
Aqueous 0.999999 kg
Vapor 1.77944e-10 kg
Solid 0.0 kg
  
```

The temperature at the bubble point is computed to be 87.26°C at 1 atm. Notice the vapor amount, 1.78e-10 kg out of a total 1 kg. This is by design, and is explained as follows:

- 1) This stream is 1 kg.

Stream Amount (kg)	1.00000
--------------------	---------

The software converts the 1 kg stream amount to apparent moles (this value can be found in the report)

- 2) The software then sets the amount of vapor at 1/10^{10th} the moles of the Stream Amount (top row of grid)

Mole (App)	53.2108	53.2108	5.32108e-9
------------	---------	---------	------------

- 3) Lastly, it varies the temperature until this amount of vapor mole is reached. This computed temperature reported as the bubble point temperature.

The software uses this same phase appearance technique for dew point and precipitation point calculations.

Pressure at Bubble Point

This next calculation computes the bubble point pressure for the same stream. This is a simple switch.

- ✓ Change the Calculate-Temperature row to Calculate Pressure

● Temperature (°C)	25.0000
● Pressure (atm)	1.00000
◀ Calculation Parameters	
Calculate	Pressure

The yellow buttons to the left of the Temperature and Pressure rows switch, and now the 1.000 atm pressure is green; the initial guess. The 25 C temperature is fixed.

- ✓ Calculate (or press the <F9> key)
- ✓ Review the Summary

```

Automatic Chemistry Model
MSE (H3O+ ion) Databanks:
MSE (H3O+ ion)
Using Helgeson Direct
Bubble Point Calculation
25.0000 °C
0.0708948 atm ←
Phase Amounts
Aqueous 0.999999 kg
Vapor 2.16616e-10 kg

```

The bubble point pressure is **0.07089** atm. Notice that the vapor mass differs. It is 2.17×10^{-10} kg in this case compared to 1.8×10^{-10} kg in the bubble point temperature case. The identical number of moles of vapor is present in both cases. The reason this occurred is because the vapor composition changed. In the bubble point temperature case, the fraction of acetone in the vapor is 66.9%. In the bubble point pressure case, the acetone fraction in the vapor is 80.8%. Since acetone weighs 58.1 g/mol vs water at 18 g/mol the mass of vapor weighs more at the 25 C case than at the 87 C case.

Follow-up Example #2a – Boiling Points of Common Organics/Inorganics

Use the approach presented above to compute the boiling point temperature of the following solutions at 1 atm pressure. The abbreviated instructions are as follows:

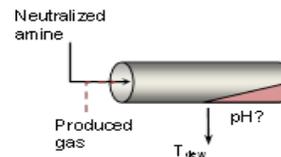
- ✓ Add a new stream
- ✓ Change the units to Metric, mass fraction
- ✓ Enter the component and give it a value of 6 mass %
- ✓ Add a Single-Point, Bubble-Point calculation and select the temperature button
- ✓ Calculate then record the temperature
- ✓ Add another stream with the next component, and so on

<i>Follow-up Example #2a – Boiling Points of Common Organics/Inorganics</i>			
<i>Organic at 6 mass%</i>	<i>Boiling Point at 1atm</i>	<i>Inorganic at 6 mass</i>	<i>Boiling Point at 1atm</i>
Methanol		HCl	
Formaldehyde		NaCl	
Acetic Acid		CaCl ₂	
Ethylene Glycol		FeCl ₃	

2.3 Dew Point

Overview

The purpose of this next example is to review the Dew Point calculation, and the properties and phase compositions computed by it. The case is a sour natural gas (contains H₂S) and the temperature at which this gas will condense, and potentially corrode the existing equipment. The **Dew Point** calculation computes the initial condensation point of a stream. This point is defined as when 1/10⁶ of the existing system (or 1 mole whichever is smaller) is in a liquid phase.



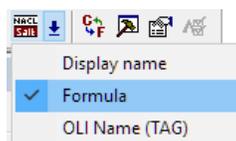
The sour gas source is a dolomite reservoir in which sulfates have been reduced to form H₂S. This sour gas can create potential process and safety problems, and understanding its state is important to the engineer.

The stream to be modeled contains 3% CO₂ and 1% H₂S. It is a fairly acidic gas.

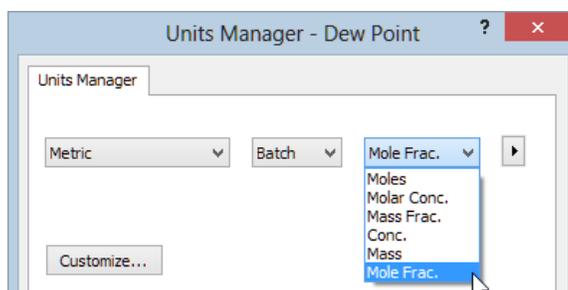
2.3 Dew Point Stream Composition			
Stream Name	Dew Point	Temperature	120 C
Units Set	Metric-Batch-Mole Fraction	Pressure	100 atm
Names Style	Formula	H2O	(calculated)
Framework	Aqueous (H+)	CH4	94 mole %
Stream Amount	1e6	CO2	3 mole %
		H2S	1 mole %

Starting the work

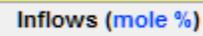
- ✓ Add a new stream  **Add Stream** and name it '**Dew Point**'
- ✓ Click on the down-arrow adjacent to the Names Manager button  (in the toolbar) and select the Formula view



- ✓ Select the Units Manager button in the toolbar  and change the basis to Mole Frac.

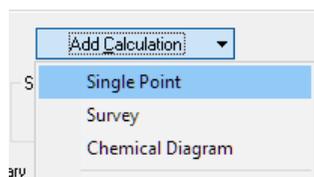


- ✓ Press OK to return to the Definition grid

The Inflows should now be in mole % units. 

- ✓ Enter the data in the table above, starting with the Stream Amount (1.0e6 mol), Temperature (120C), and Pressure (100 atm). Next add the inflows (94% CH₄, 3% CO₂ and 1% H₂S)

- ✓ Select Single Point from the Add Calculation dropdown list



- ✓ Select Dew Point as the Type of Calculation

Variable	Value
Stream Parameters	
Stream Amount (mol)	1.0000e6
Temperature (°C)	120.000
Pressure (atm)	100.000
Calculation Parameters	
Calculate	Temperature
Inflows (mole %)	
H2O	2.00000
CH4	94.0000
CO2	3.00000
H2S	1.00000

You will keep the Temperature radio button selected.

- ✓ Calculate (or the <F9> key)
- ✓ Review the Summary box and note the temperature
- ✓ Select the Pressure radio button recalculate

Calculation Parameters	
Calculate	Pressure

- ✓ Review the Summary box and note the pressure

Summary	Summary
Unit Set: Metric (mole fraction)	Unit Set: Metric (mole fraction)
Automatic Chemistry Model AQ (H+ ion) Databanks: Public	Automatic Chemistry Model AQ (H+ ion) Databanks: Public
Dew Point Calculation 100.000 atm 113.481 °C ←	Dew Point Calculation 120.000 °C 130.004 atm ←
Phase Amounts Aqueous 1.00000 mol Vapor 9.99999e5 mol Solid 0.0 mol	Phase Amounts Aqueous 1.00000e-4 mol Vapor 1.00000e6 mol Solid 0.0 mol
Aqueous Phase Properties pH 3.88927 Ionic Strength 2.35733e-6 mol/mol Density 0.952526 g/ml	Aqueous Phase Properties pH 3.85843 Ionic Strength 2.53172e-6 mol/mol Density 0.948443 g/ml

The aqueous phase is small relative to the total system size as seen in the Phase Amounts list of the Summary. OLI Studio computes the dew point by fixing the aqueous mass at a small value and adjusts the temperature or pressure accordingly until that amount of liquid is obtained.

The calculated temperature is 113.5°C. The dew point pressure is 129.8 atm. These conditions create potential corrosion problems. How would we mitigate them?

- ✓ Click on the Report tab (do this AFTER you switch to Calculate-Pressure)
- ✓ Scroll down to the Species output table

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

Column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mole %	mole %	mole %
CH4	94.0	0.164183	94.0
CO2	3.0	0.0506417	3.0
H2O	2.0	99.7388	2.0
H2S	1.0	0.0459017	1.0
H+1	2.53172e-14	2.53172e-4	0.0
HCO3-1	1.30227e-14	1.30227e-4	0.0
HS-1	1.2293e-14	1.2293e-4	0.0

The aqueous phase composition is shown in the center column. The dissolved CH₄, CO₂ and H₂S are 0.164, 0.051 and 0.046 mole %, respectively. The gas-phase CO₂ is three-times H₂S, yet their aqueous concentrations are roughly the same. This is because H₂S solubility in water is about three times greater than CO₂ at these conditions.

Follow-up Example #3 – Dew Point pH of Acid Gases

You will test the impact of acid gases and organic acids on dew point pH. You will enter the following gas compositions and calculate the dew point temperature and condensate pH. The pressure is 70 atm and the initial temperature is 120°C. Use mole fraction units for this example.

Follow-up Example #3 – Dew Point pH of Acid Gases						
Name	FE#3	FE#3-1	FE#3-2	FE#3-3	FE#3-4	FE#3-5
Inflow (mol %)						
H2O	1.5	1.5	1.5	1.5	1.5	1.5
CO2	0	.01	.1	0	0	0
H2S	0	0	0	.01	.1	0
Acetic Acid	0	0	0	0	0	.0001
Methane	98.5	98.49	98.4	98.49	98.4	98.4999
Dew Point Temp?	96.8384					
Dew Point pH?	6.14237					

One way of approaching this example is with following procedure:

- ✓ Add a new stream ✓ Open the Units Manager and select Metric-Batch-Mole Frac.
- ✓ Change the temperature to 120C and the pressure to 70
- ✓ Enter CO₂, H₂S, Acetic Acid, and Methane as the Inflows
- ✓ Keep the mole% values empty
- ✓ Add a Single Point calculation
- ✓ Select the Dew Point type and keep the Temperature radio button selected
- ✓ Right-mouse click on the stream and select Copy



- ✓ Right-mouse click on the Global Stream object  and select Paste
- ✓ Paste the stream five times so that you have a total of six duplicate streams
- ✓ At the stream level of each new object, change the inflows to match the composition values (mole%) of the corresponding row from the table above (H₂O computes automatically)
- ✓ Select each of the calculation sub-streams and press the calculate button
- ✓ Determine the dew point temperature and the dew point (condensate) pH

The acidity of certain gas components is a function of ionization constants and water solubility.

- ✓ Compare the streams named, “FE#3 -1” and “FE#3 -3” (the 0.01 CO₂ and 0.01 H₂S streams)
- ✓ View the species output table in the report tab of each stream

In the 0.01 H₂S stream (FE#3-3), the condensed water H₂S concentration is 3.34e⁻⁴ mol%. In the 0.01 CO₂ stream (FE#3 -1), The CO₂ concentration is 1.10e⁻⁴ mol%, one-third that of H₂S. However, since CO₂ is slightly more acidic at this temperature, pK_a (CO₂) =6.34 vs. pK_a (H₂S) =6.98, the pH values are roughly the same.

As for the acetic acid stream, at 1e⁻⁴ mole% (1ppmV), its concentration in water is 7.64e⁻³ mol%. This is 23 and 70 times higher than H₂S and CO₂, respectively. Coupled with a stronger acidity (pK_a(HAc)=4.94), it creates a much lower solution pH.

2.4 Vapor Fraction and Amount

Overview

The Vapor Fraction and Vapor Amount calculations are identical in nature to the Bubble Point calculation of Section 2.2, except that instead of the software defining the vapor amount at $1/10^{10}$ the total stream amount, the user defines the vapor size in either mole fraction units (Vapor Fraction) or mole units (Vapor Amount).

You will evaporate boiler feed water (BFW) up to 95 % (a vapor fraction calculation). The feed water composition has been created from a water analysis (see chapter 4) and the molecular flow is being used. To assist the user in recognizing the BFW composition, a second table displaying the concentrations are also shown. Seawater will be created using an already-prepared calculation object, plus the Add as Stream function.

Starting the work

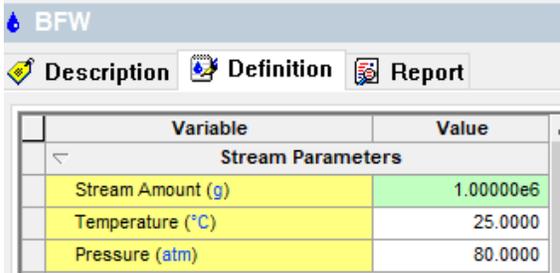
The table below contains the BFW composition in molecular form. These molecular flows do not represent any specific phases, rather they are the elements (and oxidation states) that are part of this stream. The stream is 1,000 kg in amount.

BFW molecular inflow in grams			
Inflow	Grams	Inflow	Grams
H2O	994869	MgO	0.160
SiO2	44.77	Na2O	1207.3
CaO	0.0674	NaCl	2985.9
CO2	857.45	SO3	12.41
K2O	23.86		

- ✓ Create a new stream and label it BFW
- ✓ Set the framework to MSE FW - 
- ✓ Open the Units Manager and set the units to Metric-Batch-Mass


- ✓ Set the pressure to 80 atm
- ✓ Enter the inflows above

When finished, the grid should look like the one below.



Inflows (g)	
H2O	9.94869e5
SiO2	44.7700
CaO	0.0674000
CO2	857.450
K2O	23.8600
MGO	0.160000
NA2O	1207.30
NaCl	2985.90
SO3	12.4100

This set of molecular inflows is based on the following water analysis. This analysis is studied in a later chapter.

Neutrals (ppm (mass))	
H2O	9.94918e5
SiO2	44.7754
Cations (ppm (mass))	
Ca+2	0.0481456
Mg+2	0.0962913
K+1	19.8119
Na+1	2070.32
Anions (ppm (mass))	
CO3-2	1169.23
Cl-1	1759.76
SO4-2	14.8890
OH-1	3.37020

Evaporate BFW to 75%

- ✓ Add a single-point calculation
- ✓ Set the calculation type to Vapor Fraction
- ✓ Set the fraction to 75%. Be sure that the pressure is 80 atm.

Variable	Value
Stream Parameters	
Stream Amount (g)	1.00000e6
Temperature (°C)	25.0000
Pressure (atm)	80.0000
Calculation Parameters	
Vapor Fraction (Vapor/Inflow [mol]) (mole)	75.0000
Calculate	Temperature

The software will convert the 1000 kg to mole units, and will put 75% of this in the vapor phase. It then changes the temperature until that vapor amount is reached.

- ✓ Calculate
- ✓ Review the summary section

Summary	
Unit Set: Metric (mass)	
Automatic Chemistry Model	
MSE (H3O+ ion) Databanks:	
MSE (H3O+ ion)	
Using Helgeson Direct	
Vapor Fraction Calculation	
80.0000 atm	
296.833 °C	
Phase Amounts	
Aqueous	2.52358e5 g
Vapor	7.47642e5 g
Solid	0.430506 g
Aqueous Phase Properties	
pH	9.70832
Ionic Strength	6.36341e-3 mol/l
Density	0.750113 g/ml

The phase amounts are 74.8% in the vapor and 25.2% in the water phase. This is slightly different from the 75% set point, and this is because the set point is in moles and the summary is in mass. This will be seen next.

- ✓ Select the Report tab and scroll down to the Total and Phase flow table

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor	Solid
	mol	mol	mol	mol
Mole (True)	55382.5	13896.5	41486.0	4.56828e-3
Mole (App)	55314.6	13828.6	41486.0	4.56828e-3
	g	g	g	g
Mass	1.00000e6	2.52358e5	7.47642e5	0.430506
	L	L	L	cm3
Volume	18344.4	336.426	18008.0	0.167540

The Apparent moles (second row) are the molecular representation of the system. There is a total of 55314.6 apparent moles in this system, of this exactly 75%, or 41486 moles is set to vapor.

- ✓ Scroll down to the Scaling Tendencies table

Two solids, brucite and pectolite are computed to be present, as their scale tendency is 1.0.

Scaling Tendencies

Row Filter Applied: Values > 1.0e-4

Solids	Post-Scale
Mg(OH)2 (Brucite)	1.00000
NaCa2Si3O8(OH) (Pectolite)	1.00000
...	...

The amount that precipitated is in the Species Output table.

- ✓ Scroll down to the Species Output table and look for the phases in the Solid column.

The brucite mass is 0.23 g pectolite mass is 0.2 g. The remaining composition is less important since the main concern with boiler feed water is solids formation.

Species
Mg(OH)2 (Brucite)	0.231507	0.0	0.0	0.231507
NaCa2Si3O8(OH) (Pectolite)	0.198999	0.0	0.0	0.198999

- ✓ Scroll up to the Stream Parameters table and note the final temperature

The equilibrium temperature at 75% evaporation is 296.8 C.

Stream Amount	1.00000e6	g
Temperature	296.833	°C
Pressure	80.0000	atm

Conditions at 90% evaporation

- ✓ Recalculate the case at 90% evaporation and note the system temperature and the solids that formed

The temperature is computed to be 297.95 C, which is about 1 C higher than the 75% evaporation state. The reason for the increase is the increased water salinity which changes the vapor pressure of the liquid.

Mixture Properties

Stream Amount	1.00000e6	g
Temperature	297.952	°C
Pressure	80.0000	atm

Brucite and Pectolite remain the key minerals, and their mass changed very little. This indicates that these minerals probably precipitated much earlier in the evaporation step.

Mg(OH)2 (Brucite)	0.231514	0.0	0.0	0.231514
NaCa2Si3O8(OH) (Pectolite)	0.19956	0.0	0.0	0.19956

Conditions at 1% and 99% evaporation

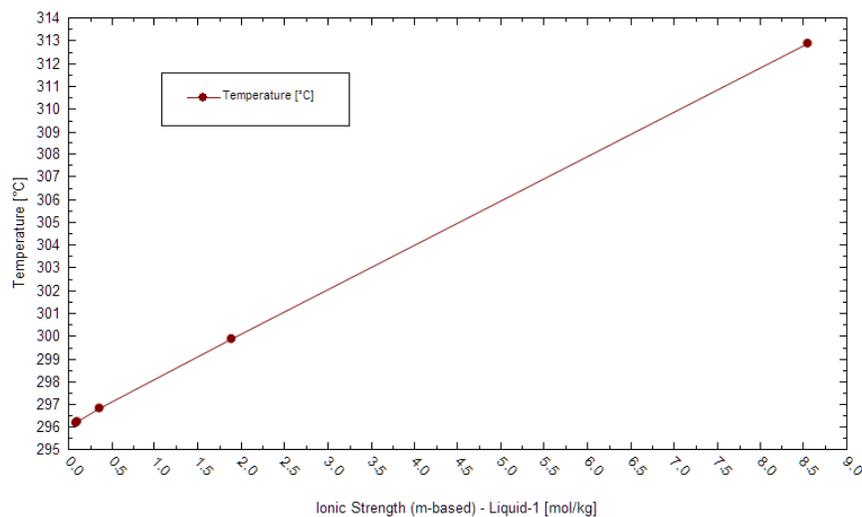
Calculate this system twice more, at 1% and 99 % evaporation. The purpose of this is two-fold, to calculate the temperature rise across the boiling range and to see if the two minerals are forming at low fractions of vapor.

- ✓ Recalculate the case at 1% evaporation and note the system temperature and the solids that formed
- ✓ Calculate again at 99%
- ✓ Tabulate the results, temperature, solids, and ionic strength (molal-based)

There is a significant temperature increase above 95% evaporation, and is due to the significant ionic strength (salinity) change.

Evaporation	Temperature, C	Ionic strength (molal)	Mg(OH)2, (Brucite), g	NaCa2Si3O8 (Pectolite), g	CaCO3 (Calcite), g	Na2CO3 (Natrite), g
1%	296.17	0.091	0.231	0.168		
10%	296.22	0.099	0.231	0.180		
75%	296.83	0.36	0.232	0.199		
95%	299.87	1.9	0.232	0.200		
99%	312.89	8.5			0.094	1178

The plot below is the boiling temperature relative to the ionic strength. The temperature-ionic strength relationship is fairly linear. It took until about 95% evaporation before a significant change in the salinity, and therefore temperature, was observed.



At 1% evaporation, the same brucite and pectolite minerals form with similar mass. Thus, these solids are not a function of the evaporation process. At 99% evaporation, CaCO₃ and Na₂CO₃ are computed to form instead of the brucite and pectolite.

2.5 Isochoric (Constant Volume) calculations

Overview

The Isochoric calculation sets 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 $P=nRT/V$. If temperature is the free variable, then $T=Pv/nR$; and for a given volume, pressure, and gas moles, temperature can be obtained. Likewise for P and V , depending on what two variables, P , V , and T are defined.

Also, since the final state is computed, the system enthalpy is also computed. Thus, the total system state is computed simultaneously, provided that three of the five variables, P , V , T , H , or n are held constant.

You will run a series of gas-phase calculations, in which the system mass and volume are defined

Starting the work

The table below contains the stream composition.

- ✓ Add a new stream and label it Isochoric
- ✓ Add the following components: N₂, O₂, CO₂ and Ar
- ✓ Set their compositions to 77, 21, 1, and 0.04 mol, respectively.

Description Definition Report		
Variable	Value	
Stream Parameters		
Stream Amount (mol)	154.548	
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
Inflows (mol)		
H ₂ O	55.5082	
N ₂	77.0000	
O ₂	21.0000	
CO ₂	1.00000	
AR	0.0400000	

This composition represents 1 kg water in about 100 moles of air.

- ✓ Add a single point calculation and change it to Isochoric

Variable	Value	
Stream Parameters		
Stream Amount (mol)	154.548	
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	

Type of calculation: Isochoric

Calculate

- ✓ Change the Calculate to Pressure and the total volume to 10 L

Calculation Parameters	
Calculate	Pressure
Total Volume (L)	10.0000

- ✓ Calculate

According to the calculation, 305 atm pressure is needed to compress the 154.548 moles of gas and liquid into a 10-liter volume at 25C.

- ✓ Go to the Report tab and view the Total and Phase Flow table

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

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

The system is 10 L as defined (within the $1/10^6$ tolerance). The water phase makes up slightly less than 1 L and the balance is vapor. At this pressure, about 2 moles of water condenses, and it has a pH of 3.8.

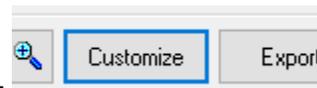
- ✓ Redo the calculation using the volume of 1000 L

The total pressure is now 2.45 atm, and the pH is 4.71.

There is an interesting difference in this calculation. The higher pressure increased the CO₂ partial pressure, and so the pH decreased to 3.8. At the lower pressure, the pH is higher. You can confirm this in the report. There are two report variables, Gas-phase partial pressure and fugacity.

- ✓ Click on the Report tab

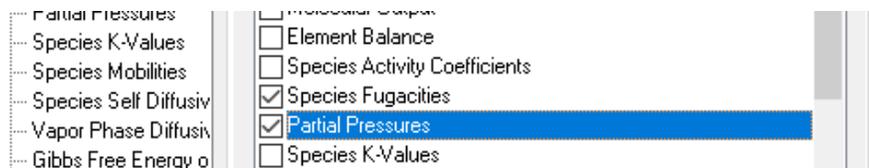
- ✓ Click the Customize button in the upper right of the window -



- ✓ Press the Clear All button in the center right to deselect All the tables -



- ✓ Next, click on the Species Fugacity and Partial Pressure boxes



This selects the two tables, Species Fugacities and Partial pressure. The Center part of this window is for selecting tables. The left part of the window is for formatting the tables.

The two images below are for the 10L and 1000 L case.

Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	atm
AR	0.115869
CO2	1.61757
H2O	0.0389791
N2	260.615
O2	60.5881

Species Fugacities

Row Filter Applied: Only Non Zero Values

Species	atm
AR	9.77637e-4
CO2	0.0242646
H2O	0.0314245
N2	1.88468
O2	0.513319

Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	atm
AR	0.123345
CO2	2.97764
H2O	0.0649713
N2	237.74
O2	64.7698

Partial Pressures

Row Filter Applied: Only Non Zero Values

Species	atm
AR	9.79094e-4
CO2	0.024458
H2O	0.0316359
N2	1.88479
O2	0.514026

Figure 1 - Calculated fugacities and partial pressures for the 10 L (left) and 1000 L (right) isochoric calculation. The total pressure for the 10 L calculation is about 300 atm. The total pressure for the 1000 L case is about 2.5 atm

- ✓ Return to the Definition tab and recalculate at 10 L.
- ✓ Click on the report and view these fugacities

The two tables above are the computed gas-component values. The lower table, Partial pressure is an indication of how much pressure is in the gas phase (N₂ is 237 atm and 1.9 atm for the two cases). Notice for the CO₂, that the partial pressure and fugacity differ by about 33% (1.6 atm vs 3 atm). This is not so in the 1000 L calculation; the partial pressure and fugacity are nearly identical. H₂O deviates in by about 50%.

The cause of this deviation is the *non-ideal effects of high pressures on gas molecules as they are forced closer together*. At low pressures, gas molecules are too far apart to interact. As pressure increases, the average distance between two molecules decrease, until at short range, intermolecular attractive forces begin to impact the molecular properties. The impact of this effect is quantified in the fugacity term. Notice that fugacity and partial pressure have the same units, atm. Thus, when reviewing these two tables, the partial pressure is the idealized gas property extrapolated effects at higher pressures and in the absence of intermolecular forces. The fugacity is the real gas property at this pressure. The non-ideal effect of pressure is therefore encapsulated in the relationship, $\phi = \frac{\text{fugacity}}{\text{Partial Pressure}}$ where $\phi =$ *fugacity coefficient*, At low pressures, a gas molecule's (g) fugacity approaches its partial pressure $f_g \rightarrow P_g$ or $\phi = 1$.

2.6 Set pH

Overview

The **Set pH** calculation is a useful tool in analyzing or designing a process. It allows one 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.

You will fix the pH of water containing carbonates, to see the speciation and buffering that carbonates provide to natural water. The system will contain three components, CO₂, HCl and NaOH. The CO₂ will be the solution's pH buffer, and HCl / NaOH are the strong acid and base to adjust the pH.

Starting the work

2.6a - Basic pH calculation

The solution will be 1 kg water (default) with 0.001 moles CO₂. The pH will then be adjusted to 4.3, 8.3, and 10.3. These are key pH values in a carbonate system when at ambient conditions.

2.5a - Basic pH Calculation					
Stream Name	Carbonate Buffer	Stream Amount	(calculated)	Inflows (mol)	
Name Style	Formula	Temperature	25 °C	CO ₂	0.001
Framework	Aqueous	Pressure	1 atm	NaOH	0
Units Set	Default (moles)			HCl	0

- ✓ Add a new stream  **Add Stream** and label it 'Carbonate Buffer'  **Carbonate Buffer**
- ✓ Enter the inflows from the above table
- ✓ Add a Single Point calculation
- ✓ Change the type to Set pH

Type of calculation

Set pH ▾ Specs...

Calculate 

The Calculation Parameters category appears on the grid. It contains four rows, the target pH, and three titrant specifications.

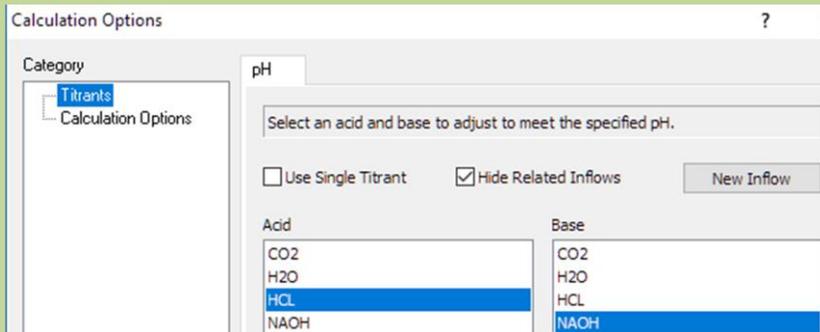
Calculation Parameters	
Target pH	4.30000
Use Single Titrant	No ▾
pH Acid Titrant	HCL
pH Base Titrant	NAOH

Set pH to 4.3

- ✓ Enter 4.3 in the Target pH cell in the grid

The default titrants are HCl and NaOH (common) and so no additional settings/specifications are required except to set the pH.

Specs window – The set pH calculation can also be specified in the Specs window.



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.

- ✓ Calculate
- ✓ Change the view to the Output tab and look at the amount of HCL added

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5093
Moles (True) - Aqueous (mol)	55.5093
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Results (mol)	
pH titrant added: HCL	4.14819e-5
Inflows (mol)	
H2O	55.5082
CO2	1.00000e-3
HCL	4.14819e-5

About 4×10^{-5} moles HCL is added to reach 4.3. The pH of 0.001 mole CO₂ is about 4.6 (not calculated) and there is no bicarbonate alkalinity in the water. Thus, very little acid is needed to reduce the pH to 4.3 because there are no species in the water to accept the H⁺ added.

- ✓ Click the Report tab and scroll down to the Species Output (True Species) table

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous
	mol	mol
H2O	55.5082	55.5082
CO2	9.90947e-4	9.90947e-4
H+1	5.05349e-5	5.05349e-5
Cl-1	4.14819e-5	4.14819e-5
HCO3-1	9.05278e-6	9.05278e-6
OH-1	2.0427e-10	2.0427e-10
CO3-2	8.70938e-12	8.70938e-12
HCl	1.22156e-15	1.22156e-15
Total (by phase)	55.5093	55.5093

Species Output at 4.3 pH

This table contains the computed species in mole units, the amount of each species in water. The CO₂ amount is 9.91e⁻⁴ moles; 99.1% the CO₂ added is this form. The HCO₃⁻¹ amount, is 9.05e⁻⁶ moles; 0.9% of the CO₂ added. The free H⁺ amount is 5.05e⁻⁵ moles, greater than the HCO₃⁻¹ amount.

The ~4.3 pH is an accepted endpoint for bicarbonate alkalinity, because 99% of all the carbonate is in the CO₂⁰ state and the H⁺ amount is greater than the available HCO₃⁻¹. Thus, adding more H⁺ does not change this. The following equilibrium equation illustrates this:

$$K_{A1} = \frac{H^+ * HCO_3^-}{CO_2^0 * H_2O} = 10^{-6.3} (@25C)$$

If the pH endpoint of 4.3, and we assume that the water activity is 1.0, then:

$$\frac{K_{A1}}{H^+} = \frac{10^{-6.3}}{10^{-4.3}} = \frac{HCO_3^-}{CO_2^0 * 1} = \frac{1}{100}$$

Thus, at a pH of 4.3, the HCO₃⁻¹ content is 1% of the CO₂⁰ content.

Set pH to 8.3

- ✓ Select the Definition tab
- ✓ Change the Target pH cell to 8.3

Calculation Parameters	
pH - Aqueous	8.30000

- ✓ Calculate then view the Species Output (True Species) table in the Report tab

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

Column Filter Applied: Only Non Zero Values

	Total	Aqueous
	mol	mol
H2O	55.5083	55.5083
Na+1	1.0006e-3	1.0006e-3
HCO3-1	9.7801e-4	9.7801e-4
CO2	1.04094e-5	1.04094e-5
CO3-2	1.02335e-5	1.02335e-5
OH-1	2.09942e-6	2.09942e-6
NaHCO3 (Nahcolite)	1.31542e-6	1.31542e-6
NaCO3-1	3.12102e-8	3.12102e-8
H+1	5.19401e-9	5.19401e-9
Total (by phase)	55.5103	55.5103

Species Output at 8.3 pH

At 8.3 pH, the HCO₃⁻¹ content is 97.8% of the total carbonate, CO₂⁰ is 1.05%, and CO₃⁻² is 1.02%. (ignore the small amount of NaHCO₃⁰ ion-pair for now). Therefore, the 8.3 pH relationship with HCO₃ is the same as the 4.3 pH relationship with CO₂, aq. The accepted endpoint for CO₃⁻² titration to HCO₃⁻¹ or CO₂ titration to HCO₃⁻¹ is 8.3 pH. From compositional relationship described in the first part of this paragraph, we can see why this pH is used.

Set pH to 10.3

- ✓ Select the Definition tab
- ✓ Change the Target pH cell to 10.3

Calculation Parameters	
Target pH	10.3000
Use Single Titrant	No
pH Acid Titrant	HCl
pH Base Titrant	NaOH

- ✓ Calculate then view the Species Output (True Species) table in the Report tab

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous
	mol	mol
H2O	55.5088	55.5088
Na+1	1.73464e-3	1.73464e-3
CO3-2	5.22242e-4	5.22242e-4
HCO3-1	4.74069e-4	4.74069e-4
OH-1	2.13512e-4	2.13512e-4
NaCO3-1	2.57186e-6	2.57186e-6
NaHCO3 (Nahcolite)	1.06808e-6	1.06808e-6
CO2	4.95924e-8	4.95924e-8
H+1	5.28206e-11	5.28206e-11
Total (by phase)	55.5117	55.5117

At 10.3 pH, the CO_3^{2-} and HCO_3^{-1} amounts are roughly equal. The following equations illustrate why. The equilibrium constant for the $\text{HCO}_3^{-1} - \text{CO}_3^{2-}$ reaction is $10^{-10.3}$ at standard conditions.

$$K_{A2} = \frac{H^+ * CO_3^{-2}}{HCO_3^{-1}} = 10^{-10.3} (@25\text{ C}, 1\text{ atm})$$

Therefore, at 10.3 pH, the $\text{CO}_3^{2-}:\text{HCO}_3^{-1}$ ratio is 1.

$$\frac{K_{A2}}{H^+} = \frac{10^{-10.3}}{10^{-10.3}} = \frac{CO_3^{-2}}{HCO_3^{-1}} = 1$$

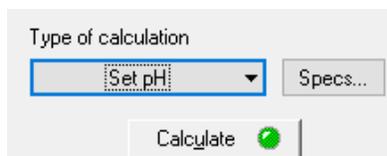
At 12.3 pH the HCO_3^{-1} conversion to CO_3^{2-} is 99% complete, effectively the endpoint of HCO_3^{-1} conversion. This however, is difficult to titrate because at 12 pH the OH^{-1} concentration is about 0.01 mol/kg and so adding NaOH to convert HCO_3^{-1} also produces free OH^{-1} ions. You can test this relationship pH and confirm it is the case.

2.6b – Neutralizing acetic acid

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

2.5c Neutralizing Acetic Acid			
Name:	Neutralize Acid	Temperature	25 C
Names Style	Formula	Pressure	1 atm
Framework	Aqueous (H+)	H2O	55.5082
Unit Set	Default (moles)	CH3COOH	1

- ✓ Add a new stream  Add Stream and name it 'Neutralize Acid' 
- ✓ Enter the stream specifications from the above table
- ✓ Add a Single Point calculation and change the Calculation type to Set pH



- ✓ Enter 7.0 as the Target pH in the Calculation Parameters grid section

The acid and base titrants default to HCl and NaOH, and therefore these components do not need to be added.

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

- ✓ Calculate
- ✓ View the summary and confirm the amount of NaOH or HCl added

```

Summary
Set pH Calculation
25.0000 °C
1.00000 atm
pH - Aqueous 7.00000
Acid Titrant: HCl
  Total: 0.0 mol
Base Titrant: NaOH
  Total: 0.997023 mol
  Added: 0.997023 mol

Phase Amounts
Aqueous 58.3044 mol
Vapor 0.0 mol
Solid 0.0 mol
  
```

About 0.997 mole of NaOH is needed to neutralize 1 mole of acetic acid.

- ✓ Click on the report and review the Species Output table

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

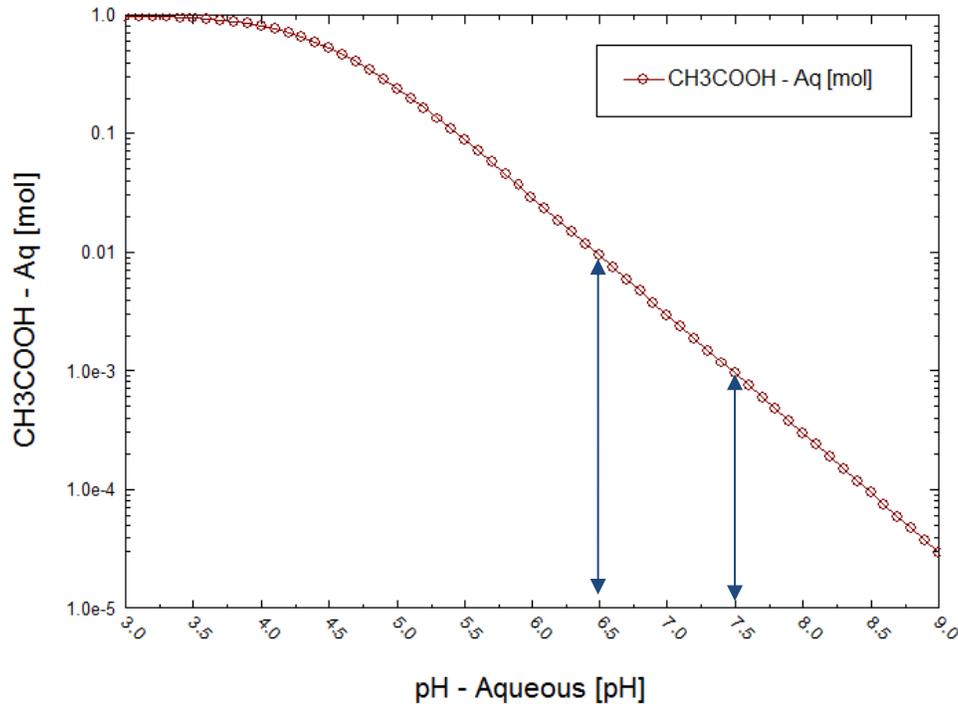
	Total	Aqueous
	mol	mol
H2O	56.5053	56.5053
C2H3O2-1	0.799096	0.799096
Na+1	0.799096	0.799096
Na[C2H3O2]	0.197926	0.197926
CH3COOH	2.97719e-3	2.97719e-3

At 7pH, nearly all the acetic acid is deprotonated and exists as either acetate-1 and NaAc⁰ (ion pair). There is 0.297% of the acetic acid (CH3COOH) not neutralized. This is because as a weak acid, there is

attractive bonding between the H^+ and Ac^{-1} such that at 7pH not all the H^+ is removed. This again is shown in the explanation below

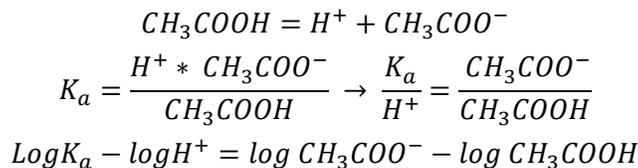
Explanation

The assumption that 7pH is neutral is not entirely accurate. Neutralizing an acid or base, especially weaker acids and bases, is an asymptotically vanishing relationship. The plot below is the remaining acetic acid (CH_3COOH) content in water as pH increases. The starting amount is 1 mole. At 3pH, the system has about 1 mole of acetic acid (~100% of added). At 9pH, the acetic acid amount is $3e^{-5}$ moles.



For practical purposes, an acid is neutralized when 99% is converted to the anion. This condition exists at 6.5pH for acetic acid (it is 99.9% neutralized at 7.5pH). Thus, the 7 pH setpoint effectively neutralizes acetic acid, but it does not remove it entirely.

To see why the content changes minutely when the pH changed by one, review the following chemical reaction:



The value K_a is a constant, and at higher pH, CH_3COO^- is a constant relative to CH_3COOH (nearly all of it is converted). Also, the term $-\text{log}(H^+)$ is essentially, pH. Therefore, we can write this as:

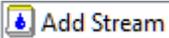
$$pH = -\text{log} CH_3COOH + \text{Constant}$$

When plotted on a semi-log plot, this creates the straight line with a slope of -1.0 (shown above). Therefore, at the high pH when CH_3COO^- is nearly constant, the content of acetic acid decreases logarithmically with pH. There is more to this discussion, but let us leave it there for now.

Follow-up Example #6 – Acidity and Basicity of Various Mixtures

Let us look at other acids and bases. We will add these components to a stream with 55.508 moles (or 1 kg) of H_2O . Then we will neutralize the solution to 7 pH using NaOH or HCl and note how much of either was used for neutralization.

Follow-up Example #6 – Acidity and Basicity of Various Mixtures			
1 mole Acid in 1Kg (55.508 moles) stream	NaOH added to achieve 7pH	1 mole Base in 1 Kg (55.508 moles) stream	HCl added to achieve 7pH
HCl		KOH	
H_2SO_4	2 mol	NH_4OH	
H_3PO_4		CaOH_2	2 mol
HF		Na_2CO_3	
Formic Acid		Na_3PO_4	
Citric Acid		$\text{Na}_2\text{B}_4\text{O}_7$	
FeCl_3		ZnOH_2	

- ✓ Add a new stream 

We can approach this problem in several ways. We can add a stream for each of the components then proceed with the steps below. We can add all of the components at once then go back and zero the component's values out then add a value to the next component. Or we can complete the remaining steps below, then copy and paste the stream, replacing one component with the next

- ✓ Enter an acid or base from the table above then enter either NaOH or HCl
- ✓ Give the acid or base a value of 1 mol
- ✓ Add a Single Point calculation then change the type to Set pH



- ✓ Enter 7.0 as the Target pH in the Calculation Parameters grid section
- ✓ Click the Specs... button
- ✓ Select the appropriate titrants

The instructor can help guide you which titrants to select.

- ✓ Press OK and Calculate
- ✓ Record the amount of base or acid added to the solution

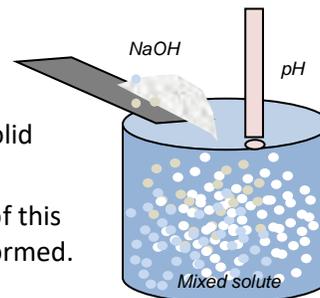
A question that often arises is why FeCl_3 behaved like a strong acid. We confirmed in the first section of this chapter that this component is in fact a weak Lewis acid.

2.7 Precipitation Point

Overview

A precipitation point calculation computes the amount of material held in solution at given conditions. This is also called a solubility calculation. The purpose of this calculation type is to find the solubility envelope of a particular solid phase. A common example, is the solubility of a mineral like NaCl in pure water.

The software computes this solubility envelope by forcing a very small amount of this solid to exist. It then adjusts an inflow up or down until that amount of solid is formed.

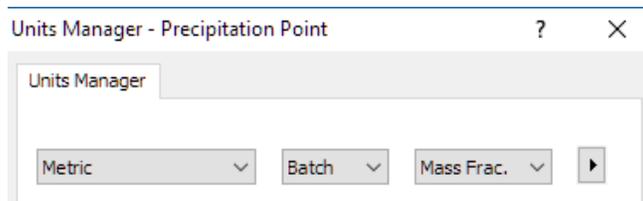


Starting the work

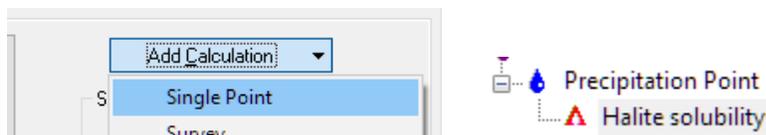
Basic NaCl solubility calculation

In this first example, you will instruct the software to compute NaCl solubility in pure water at 25C. The number of steps required to compute this are few, making this an ideal example to test the tool's capabilities.

- ✓ Add a Stream and label it Precipitation Point
- ✓ Open the Units Manager window and set the units to Metric-Batch-Mass Fraction



- ✓ Add NaCl to the grid below water
- ✓ Add a Single Point Calculation and label it Halite Solubility



This manual will always refer to the solid phase that forms by its mineral name. This is because there are a number of solid phases with the same composition but with different properties. This is because they form different minerals – graphite / diamond (both C) is an example of this, as is calcite / aragonite (both CaCO_3).

- ✓ Change the calculation type to Precipitation Point

A category called Calculation Parameters appears on the grid. Set both the Adjusted Inflow and Precipitant to NaCl. Notice that the precipitant includes the mineral name, to confirm that this is the crystal form being studied.

Calculation Parameters	
Adjusted Inflow:	NaCl
Precipitant:	NaCl (Halite)
Inflows (mass %)	
H2O	100.000
NaCl	0.0

- ✓ Calculate and review the data in the Summary

According to the software, NaCl has a solubility of 26.4 wt% in water. Notice the small amount of solid that formed, 0.03µg. This is the target or specification point on which the software converged the calculation.

Summary

<p>Unit Set: Metric (mass fraction)</p> <p>Automatic Chemistry Model AQ (H+ ion) Databanks: Public</p> <p>Precipitation Point Calculation 25.0000 °C 1.00000 atm</p>	<p>Precipitate: NaCl (Halite) Adj. Inflow: NaCl Total 26.4437 mass %</p> <p>Phase Amounts Aqueous 1.35950 kg Vapor 0.0 kg Solid 3.24407e-8 kg</p>
--	--

✓ Next, click on the Output tab at the bottom of the grid -

Input
Output

	Variable	Value
Stream Parameters		
[-]	Stream Amount (kg)	1.35950
[-]	Mass - Aqueous (kg)	1.35950
[-]	Mass - Solid (kg)	3.24407e-8
	Temperature (°C)	25.0000
	Pressure (atm)	1.00000
Calculation Results (mass %)		
	Adjusted Inflow: NaCl	26.4437
Inflows (mass %)		
	H2O	73.5563
	NaCl	26.4437

This screen contains the final composition. Notice that the stream amount is now 1.36 kg, and not the initial 1 kg. this is because 360 grams NaCl was added to saturate it in the 1 kg of starting water. The final solution is 73.6% H2O and 26.4% NaCl.

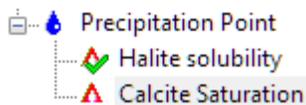
Saturating a salt water solution with calcite

In this next example, you will compute the amount of NaOH needed to saturate calcite in a water containing Ca²⁺, Mg²⁺, Cl⁻, and CO₂. You will add NaOH to raise the pH. This converts CO₂ to CO₃⁻², which will cause calcite to precipitate.

The calculation specifications are provided in the table below.

2.4 Precipitation Point Stream Composition			
Stream Name:	CaCO3 Precipitation	H2O	Calculated (ppm (mass))
Units	ppm (mass) Flowing	CaCl2	10870
Names Style	Formula	MgCl2	9325
Framework	Aqueous (H+)	CO2	431
Temperature	25C	NaOH	0
Pressure	1 atm		

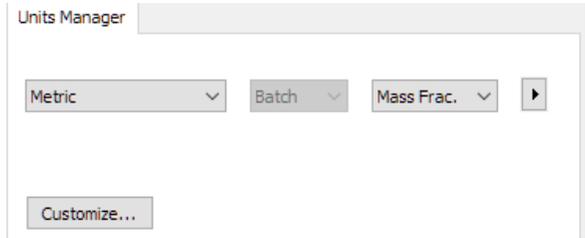
- ✓ Add a new single point calculation to the existing Precipitation point stream



- ✓ Name it Calcite Saturation

You will modify the existing units to change the mass fraction units from Mass% to ppm (mass)

- ✓ Select the Units Manager button in the toolbar 
- ✓ Click on the Customize button



- ✓ Change the Mass fraction Basis Option from Mass% to ppm (mass)

Molar Concentration		mol/L
Mass Fraction		ppm (mass)
Mole Fraction		mole %

- ✓ Close the Units editor window.
- ✓ Enter the composition from the table above

Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (ppm (mass))	
H2O	9.79374e5
NACL	0.0
CACL2	10870.0
MGCL2	9325.00
CO2	431.000
NAOH	0.0

- ✓ Change the Calculation type to Precipitation Point



The calculate button is red. There is red text in the Summary box with instructions that additional specifications are needed before the calculation can continue.

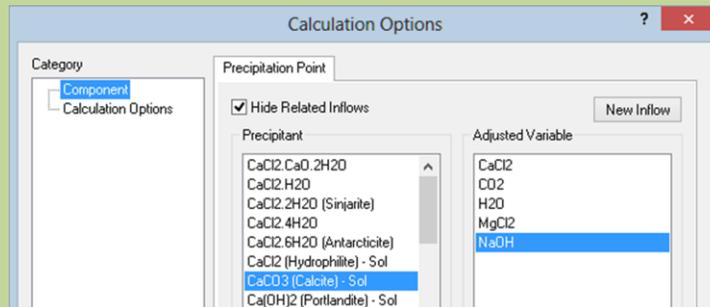
Calculation not done
 Please select a target solid.
 Please select a variable to adjust.

These specifications are defined in the Calculation Parameters grid section

- ✓ Change the Adjusted Flow to NaOH
- ✓ Change the Precipitant to CaCO3 (Calcite)

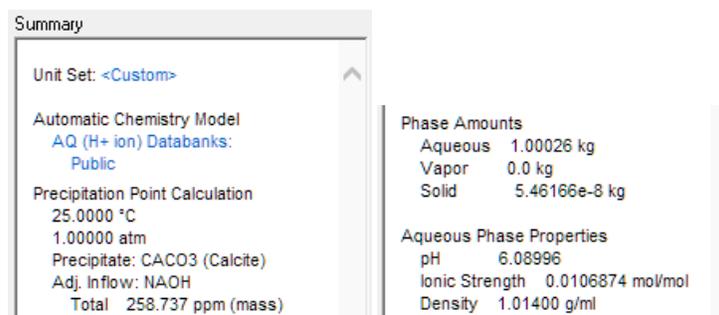
Calculation Parameters	
Adjusted Inflow:	NAOH
Precipitant:	CACO3 (Calcite)

Specs window – The precipitation point parameters can also be set within the Specs window. Each calculation has a set of specifications. The specifications for precipitation point are the Precipitant and Adjusted Variable.



The Precipitant refers to the independent variable – in this calculation, the phase selected is given as mole amount of $1/10^8$ the total system moles. The Adjusted Variable is the variable to be changed by the software until the target mole amount is achieved.

- ✓ Calculate
- ✓ Review the Summary window



The software calculated that ~259 ppm NaOH raises the pH to 6.09 which is sufficient to precipitate calcite. The final composition can be confirmed in the Output tab

Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00026
Mass - Aqueous (kg)	1.00026
Mass - Solid (kg)	5.46166e-8
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Results (ppm (mass))	
Adjusted Inflow: NaOH	258.737
Inflows (ppm (mass))	
H2O	9.79121e5
CaCl2	10867.2
MgCl2	9322.59
CO2	430.889
NaOH	258.737

It can also be observed in the Report tab

- ✓ Select the Report tab and look at the Stream Inflows section (top of report)

Stream Inflows

Row Filter Applied: Only Non Zero Values

	Input	Output
Species	ppm (mass)	ppm (mass)
H2O	9.79374e5	9.79121e5
CACL2	10870.0	10867.2
MGCL2	9325.00	9322.59
CO2	431.000	430.889
NAOH	0.0	258.737

Notice that the concentrations have changed slightly. This is to accommodate the additional 259 ppm NaOH needed to meet the calculation specifications.

Follow-up Example #4 – Solubility of Pure Components in Water

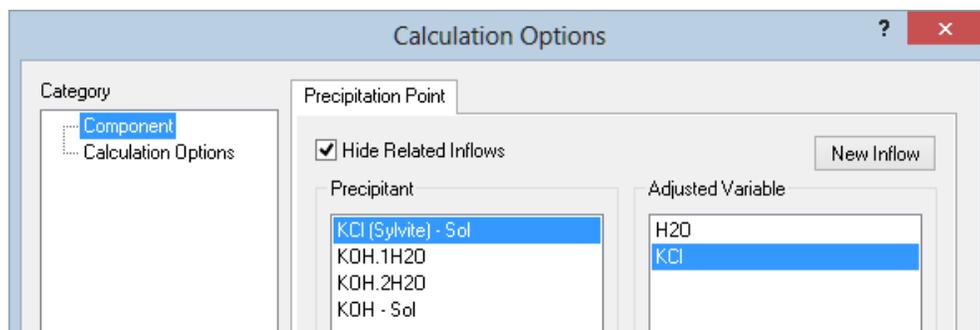
You will run a series of precipitation point calculations to determine the solubility of the following minerals. Do the calculation three times, at 25° C and 95° C and again at 95° C and 1 mole NaCl.

Follow-up Example #4 – Solubility of Pure Components in Water			
Material	Solubility		
	@25°C	@95°C	@95°C & 1 mol NaCl
KCl			
BaSO4			
CaCO3			
ZnOH2			
Ag2O			
Hg			

- ✓ Add a new stream
- ✓ Add KCl as an inflow but do not give it a value yet
- ✓ Add a Single Point calculation then change the type to Precipitation Point



- ✓ Select the Specs button
- ✓ Highlight KCl in the precipitant column and in the adjusted variable column



- ✓ Press OK to close the window
- ✓ Change the units to ppm(mass) flowing

- ✓ Press calculate and record the mass (or moles) of KCl that precipitated
- ✓ Change the temperature to 95°C, recalculate, and record the KCl moles
- ✓ Keep the temperature at 95°C, add 58350 ppm (1 mol) of NaCl then recalculate

In this particular case, we can add NaCl at the Calculation level or at the Stream level.

- ✓ Repeat the above steps for each of the other components from the table above but in the Calculation Options window, select that component as the Precipitant and Adjusted Variable

Note that the inflow may not be the precipitate. For instance, the transition metals will probably precipitate as oxides not in the form they were entered.

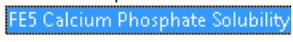
Follow-up Example #5 – Calcium Phosphate Solubility

The phases created by precipitation point calculations are important to note. If nature were at equilibrium, then only the most stable solids would exist. Since nature is not at equilibrium, it is possible for unstable solids to exist. They exist because of kinetic and inhibition factors.

Such is the case with the solids of calcium phosphate and calcium carbonate. Calcite can form four different solid phases while calcium phosphate can form seven. These solid phrases are listed below, from most to least stable:

<i>Solids Phases Formed from Calcite and Calcium Phosphate</i>	
Calcium Carbonates (polymorphs of CaCO ₃)	Calcium Phosphates (different Ca:P ratios)
Calcite	Hydroxyapatite [Ca ₅ (OH)(PO ₄) ₃]
Aragonite	TriCalcium Phosphate [Ca ₃ (PO ₄) ₂]
Vaterite	Octacalcium Phosphate [Ca ₄ HPO ₄ (PO ₄) ₂ ·2.5H ₂ O]
Ikaite	Calcium Hydrogen Phosphate [CaHPO ₄]
	Calcium Hydrogen Phosphate dehydrate [CaHPO ₄ ·2H ₂ O]
	Calcium dihydrogen Phosphate [Ca(H ₂ PO ₄) ₂]

Calcium phosphate has interesting chemistry. Many solids can form from the simple system, CaO-P₂O₅-H₂O. We will look at this system in the following example. We will add CaHPO₄ to water and precipitate a list of solids. We do this by “turning off” all solids, except the target solid. We then run a precipitation point calculation and document the CaHPO₄ concentration needed to form the solid.

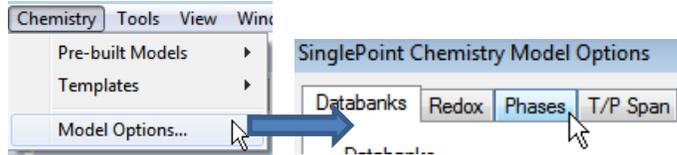
- ✓ Add a new stream  Add Stream
- ✓ Name it 'FE5 Calcium Phosphate Solubility' 
- ✓ Select the MSE button in the toolbar  ✓ Change the units to ppm (mass) Flowing
- ✓ Add CaHPO₄ as an inflow

Variable	Value
Stream Parameters	
Stream Amount (kg/hr)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (ppm (mass))	
H ₂ O	1.00000e6
CaHPO ₄	0.0

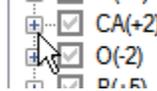
- ✓ Add a Single Point calculation then change the type to Precipitation Point



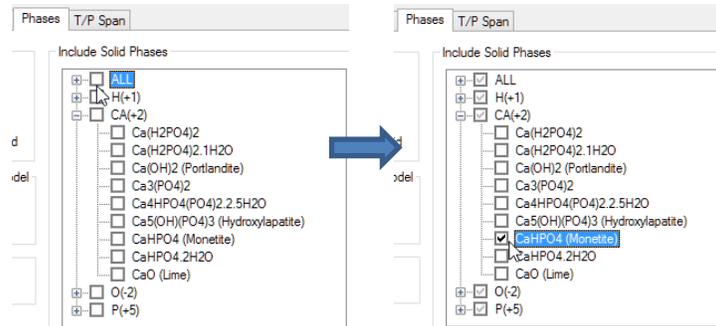
- ✓ From the menu bar, select Chemistry > Model Options > Phases



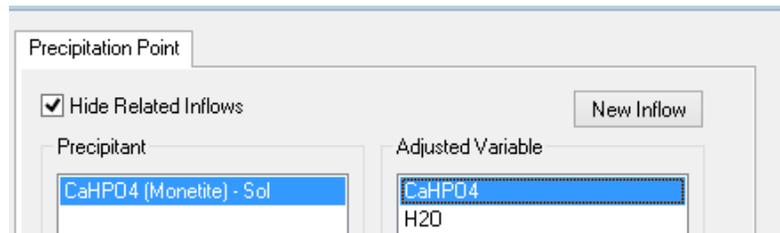
- ✓ * In the phases tab, expand the CA(+2) category



- ✓ * First uncheck the ALL button, then check the box next to CaHPO4 (Monetite)



- ✓ * Press OK then select the Specs... button.
- ✓ * Select CaHPO4 - Sol as the Precipitant and select CaHPO4 as the Adjusted Variable



- ✓ * Press OK
- ✓ * Calculate and record the CaHPO4 mass added

Variable	Value
Stream Parameters	
Stream Amount (kg/hr)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Precipitant: CaHPO4	
Adjusted Variable: CaHPO4	
Inflows (ppm (mass))	
H2O	1.00000e6
Adjusted Variable: CaHPO4	0.0

Type of calculation: Precipitation Point

Bubble/Dew Point: Temperature Pressure

Calculate

Summary

Precipitation Point Calculation
 25.0000 °C
 1.00000 atm
 Precipitate: CaHPO4
 Adj. Inflow: CaHPO4
 Total: **64.0088 ppm (mass)**

Repeat the starred steps but select the following species in the Phases tab instead of CaHPO_4 . The instructor will discuss what happens when we select $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

Solid to precipitate	Amount of CaHPO_4 added (mass)
CaHPO_4	64.0088
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	
$\text{Ca}_4\text{HPO}_4(\text{PO}_4)_2 \cdot 2.5\text{H}_2\text{O}$	
$\text{Ca}_3(\text{PO}_4)_2$	
$\text{Ca}_5(\text{OH})(\text{PO}_4)_3$	
$\text{Ca}(\text{H}_2\text{PO}_4)_2$	

2.8 Composition Point

Overview

The composition point calculation is used to fix a species value. If for example, the target amount of molecular H₂S in water is to be set at 0.001 moles in 1 kg water, then this is the calculation tool that would be used.

Presently, Version 9.5 (the time of this publication), allows only mole units for composition targets. Therefore, the examples provided here are based on these units.

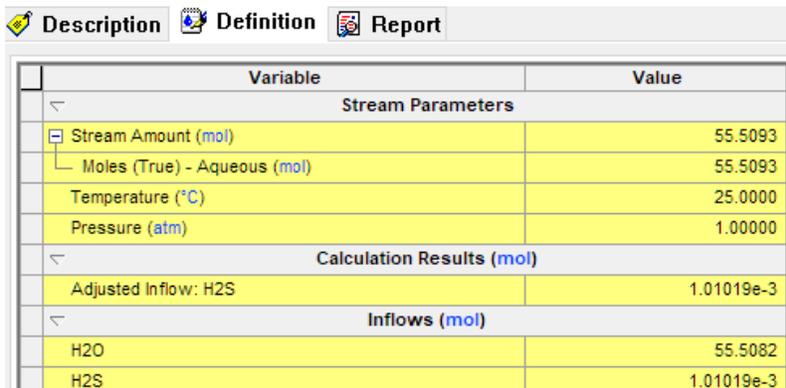
Starting the work

2.8a - H₂S, aq composition point

- ✓ Create a new stream and name it Composition Point
- ✓ Add a single point calculation and name it **H₂S, aq**
- ✓ Add H₂S to the grid
- ✓ change the calculation type to Composition Point

The Calculation Parameters section appears in the grid. It contains three rows, the Target species, the adjusted inflow and the target value.

- ✓ Set the Target species to H₂S-aq
- ✓ Set the Target Value to 0.001 mole (that is 0.001 mol/kg water or 32 mg/kg)
- ✓ Set the Adjusted Inflow to H₂S
- ✓ Calculate
- ✓ Click on the Output tab at the bottom of the grid to view the calculated composition



The screenshot shows a software interface with three tabs: Description, Definition, and Report. The Report tab is active, displaying a table with two columns: Variable and Value. The table is organized into sections: Stream Parameters, Calculation Results (mol), and Inflows (mol).

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5093
Moles (True) - Aqueous (mol)	55.5093
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Results (mol)	
Adjusted Inflow: H ₂ S	1.01019e-3
Inflows (mol)	
H ₂ O	55.5082
H ₂ S	1.01019e-3

According to the software, 0.00101 moles H₂S was required to create a solution with 0.001 moles of H₂S aq. The additional 0.00001 moles is the amount that converted to HS⁻1 at equilibrium. The pH is 5.0 (look at the Summary section).

Target: H2S
 Fixed at 1.00000e-3 mol
 Adj. Inflow: H2S
 Total 1.01019e-3 mol

Phase Amounts
 Aqueous 55.5093 mol
 Vapor 0.0 mol
 Solid 0.0 mol

Aqueous Phase Properties
 pH 4.99328

This is $\sim 1e^{-5}$ moles H^+ , which is consistent with the additional H2S.

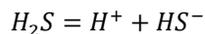
- ✓ Click the Report tab and view the Species output

Species Output (True Species)

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

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

The molecular H₂S is $1e^{-3}$ moles as specified in the calculation. Notice that the H^+ and HS^- concentrations are nearly identical. This is because the following reaction takes place:

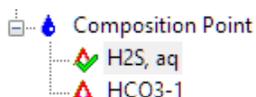


One mole of H₂S creates one mole each of H^+ and HS^- . H^+ is slightly higher, because a second reaction $H_2O = H^+ + OH^-$ also contributes to H^+ formation.

2.8b - HCO₃⁻¹ composition point

The purpose of this example is to explore carbonate speciation and its relationship with pH. In this case, you will start with a fixed amount of CO₂ and then add NaOH to convert it to HCO₃⁻¹ and CO₃⁻². You will monitor both the speciation of CO₃⁻², HCO₃⁻¹, and CO₂, aq, and the pH.

- ✓ Add another single point calculation to the Composition point stream
- ✓ and name it **HCO₃⁻¹**



- ✓ Add CO₂ and give it a value of 0.001 mol
Add NaOH to the grid
- ✓ change the calculation type to Composition Point
- ✓ Set the Adjusted Inflow to NaOH
- ✓ Set the Target species to HCO₃⁻¹

- ✓ Set the Target Value to 0.0005 mole

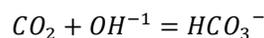
This converts 50% of the CO₂ added to HCO₃⁻¹.

Description		Definition		Report	
Variable				Value	
Stream Parameters					
Stream Amount (mol)				55.5092	
Temperature (°C)				25.0000	
Pressure (atm)				1.00000	
Calculation Parameters					
Adjusted Inflow:				NaOH	
Target Species:				HCO3-1	
Target HCO3-1 Value: (mol)				5.00000e-4	
Inflows (mol)					
H2O				55.5082	
CO2				1.00000e-3	
NaOH				0.0	

- ✓ Calculate
- ✓ Click on the Output tab at the bottom of the grid to view the calculated composition

Calculation Results (mol)			
Adjusted Inflow: NaOH		4.99995e-4	
Inflows (mol)			
H2O		55.5082	
CO2		1.00000e-3	
NaOH		4.99995e-4	

As expected, 0.0005 moles NaOH is required to create 0.0005 moles HCO₃⁻¹, simply because acid base reactions are stoichiometric, and this is a 1:1 reaction.



- ✓ Click on the report. View the pH,.

Aqueous Properties

pH	6.33201	
Ionic Strength (y based)	0.01074e-6	mol/mol

The computed pH, in which 50% of the CO₂ is converted HCO₃⁻¹ is 6.3 (image below). This is the same value as pK_{a1} (log acid dissociation constant of CO_{2,aq}).

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous
	mol	mol
H2O	55.5082	55.5082
HCO3-1	4.99998e-4	4.99998e-4
Na+1	4.99652e-4	4.99652e-4
CO2	4.99605e-4	4.99605e-4

The following equilibrium reaction is written in log space to show the relationship between pH and pK_{a1}.

$$K_{A1} = \frac{H^+ * HCO_3^-}{CO_2^0 * H_2O} = 10^{-6.3} (@25C)$$

$$\text{Log}K_{a1} - \log\{H^+\} + \log\{H_2O\} = \log\{HCO_3^-\} - \log\{CO_2\}$$

The curly brackets represent the activity of the species. Since this is a water solvent, $\{H_2O\}$ is set to 1 by definition. Also, pH is defined in this model as: $-\log\{H^+\}$. Thus, the relationship is simplified and replacing log Ka1 with log(-6.3).

$$-6.3 + pH = \log\{HCO_3^-\} - \log\{CO_2\}$$

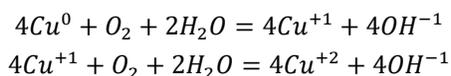
At 6.3 pH, the activities of HCO3 and CO2 would be the same. This is what is seen in the results.

One note. The term “activities” is introduced above. This is required because the variable, $\log\{H_2O\}$ is not presented in this equation concentration unit, and if it were, the K_{a1} value would have a different value. This may be new to the reader. Activities will be discussed in later sections and chapters. For now, if it is confusing, consider the solvent to not be in concentration units, and when developing equilibrium equations where the solvent is included, it can be set to 1, as a first assumption.

2.8C – Oxidizing Copper

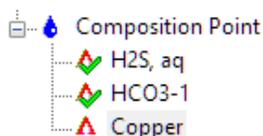
This will be the first opportunity to use Oxidation-Reduction (REDOX) reactions. It is OLI’s experience that REDOX reactions are considered arcane by non-chemists. We hope to provide some simplifying explanation here. Additional discussion is found in the Pourbaix Diagram chapters.

The example here is copper oxidation. Copper metal is stable in water (i.e. will not react), when air (oxygen) is not present. When O_2 is present, copper donates electrons to the oxygen. This converts copper to an ion which dissolves in water, and the oxygen converts to OH^- ions. Energy is released in the reaction which is why it occurs. The reaction is below. In fact, there are two sequential reactions because copper can donate one or two electrons and form $Cu(+1)$ or $Cu(+2)$, depending on the availability of oxygen.

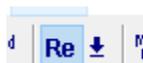


These are also considered general corrosion reactions, where the corrosion label infers the rate at which these reactions will proceed.

- ✓ Add a single point calculation to the Composition point stream
- ✓ Name it **Copper**



- ✓ Add Cu and give it a value of 0.001 mol
- ✓ Add O2 to the grid
- ✓ Turn on REDOX reactions using the Re button in the toolbar



Notice the text in the Summary section “Redox selected”. This ensures that oxidation-reduction reactions will be considered. There are additional settings for redox, but they won’t be used in this example.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5092
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Cu	1.00000e-3
O2	0.0

Type of calculation: Isothermal [Specs...]

Calculate [OK]

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model

AQ (H+ ion) Databanks: Public

Redox selected

- ✓ Calculate,
- ✓ Look at the Summary section for the ORP value (bottom)

Aqueous Phase Properties	
pH	6.99670
Ionic Strength	1.81599e-9 mol/mol
Density	0.996845 g/ml
ORP	-0.158506 V (SHE)

The value is -0.159 volt (SHE)¹. As will be shown in this example, this value is slightly reducing; the system is relatively abundant in electron availability. You will look at this several times in this case.

- ✓ Open the Report and scroll down to the element balance table
- ✓ Compare the amounts of Cu(0), Cu(+1) and Cu(+2)

Virtually all the copper is present as a metal. There are negligible amounts of Cu(+1) and Cu(+2).

Element Balance

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Solid
	mol	mol	mol
H(+1)	111.016	111.016	0.0
Cu(+2)	1.4455e-17	1.4455e-17	0.0
O(-2)	55.5082	55.5082	0.0
H	3.64123e-12	3.64123e-12	0.0
O(0)	3.68927e-69	3.68927e-69	0.0
Cu(+1)	3.6412e-12	3.6412e-12	0.0
Cu(0)	1.0e-3	0.0	1.0e-3

What we can conclude at this point is that elemental copper (copper metal) is present in the water, and the ORP of the water is -0.159 V (SHE). The slight negative ORP (at 25C and 7pH water) means that the

¹ The ORP, or Oxidation-Reduction potential is a voltage scale used to measure the availability of electrons in a system. A low ORP (e.g., -2V, SHE), represents high electron availability. These available electrons are not “free”, but rather held by materials like iron or copper metal. A high ORP (e.g., +2V, SHE), represents a low electron availability, or rather a high availability of *electron vacancies*. Molecules like O₂, contain electron vacancies. If electron-rich iron is in contact with electron-poor O₂, electrons transfer from the iron to oxygen, and energy is released.

The calculated ORP is therefore the relative scale of electron abundance. A low ORP means that there is more iron than O₂. A high ORP means the reverse. The scale’s reference point is the Standard Hydrogen Electrode, SHE. This ORP is also pH and temperature dependent, and so the scale is not a simple, linear relationship.

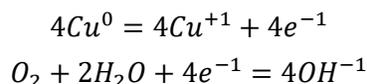
existing system is slightly reducing. (It is important to include the reference scale (i.e., SHE) when reporting ORP, since there are many reference scales (probes) used.)

Redo the calculation using the Composition Point Calculation Type

- ✓ Change the calculation type to Composition Point
- ✓ Set the Adjusted Inflow to O2
- ✓ Set the Target species to Cu (Copper) - Sol
- ✓ Set the Target Value to 0.0005 mole

Calculation Parameters	
Adjusted Inflow:	O2
Target Species:	Cu (Copper) - Sol
Target Cu (Copper) Value: (mol)	5.00000e-4

The software will compute how much O2 is needed, for 50% of the copper to react away. Elemental copper (electron donor) and oxygen (electron acceptor) are the electron transfer elements, as seen in the two expressions.



If 50% or $5e^{-4}$ moles of copper is to react away, the according to the above reactions, one-fourth, or $1.25e^{-4}$ moles O₂ will be needed.

- ✓ Calculate
- ✓ Select the Output tab at the bottom of the grid

According to the calculation, $1.25e^{-4}$ moles O₂ is required; consistent with the above equations.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5094
Moles (True) - Aqueous (mol)	55.5082
Moles (True) - Solid (mol)	7.49997e-4
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Results (mol)	
Adjusted Inflow: O2	1.25000e-4
Inflows (mol)	
H2O	55.5082
Cu	1.00000e-3
O2	1.25000e-4

- ✓ Click on the Report tab and scroll down to the Element balance table

One-half of the elemental copper has reacted to form Cu(+1), in agreement with the first reaction. There is a small amount of Cu(+2), but it again is negligible compared to the Cu(0) and Cu(+1) amounts.

Element Balance

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Solid
	mol	mol	mol
H(+1)	111.016	111.016	0.0
Cu(+2)	5.08212e-11	5.08212e-11	0.0
O(-2)	55.5085	55.5082	2.49997e-4
H	9.67616e-19	9.67616e-19	0.0
O(0)	5.22431e-56	5.22431e-56	0.0
Cu(+1)	5.0e-4	6.82512e-9	4.99993e-4
Cu(0)	5.0e-4	0.0	5.0e-4

It is possible that copper could have donated two electrons and not one to oxygen. In that case twice as much O₂ would have been required. Instead, only one electron was transferred from copper. This relates back to the ORP.

- ✓ Return to the Definition tab
- ✓ Look at the ORP value

Aqueous Phase Properties	
pH	7.01161
Ionic Strength	1.88032e-9 mol/mol
Density	0.996845 g/ml
ORP	0.0351125 V (SHE)

The ORP is higher, 0.035 V (SHE), meaning that the system is more oxidizing than the previous case. However, there is still elemental copper present, meaning that there are additional electrons to donate.

Recalculate using a target value of 1e-6 moles Cu

- ✓ Change the Target Cu amount to 1e-6

A final elemental copper amount of 1e⁻⁶ moles means that 99.9%, or 9.99e⁻⁴ of the copper will have reacted away. This should therefore mean that about 2.4975e⁻⁴ moles O₂ is required to convert Cu(0) to Cu(+1).

- ✓ Calculate

Instead of using the Report tables, you will interpret the results using the Grid, since this is a convenient way to view the information.

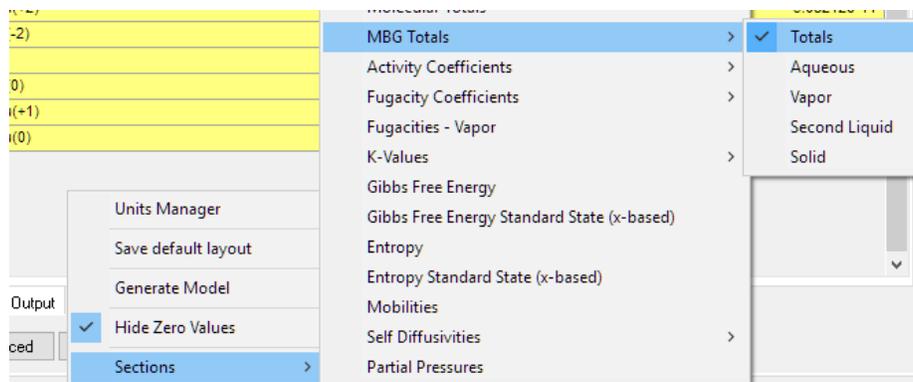
- ✓ Select the Output tab at the bottom of the grid -



The calculated O₂ amount is 2.4975e⁻⁴ moles, which is exactly the stoichiometric value of converting Cu(0) to Cu(+1).

Calculation Results (mol)	
Adjusted Inflow: O2	2.49750e-4

- ✓ Right mouse-click on the grid and Select Sections>MBG Totals>Totals



The output grid now displays the MBG Totals. This is the Element Balance Table of the report, specifically the first column of that table.

MBG Totals - Totals (mol)	
H(+1)	111.016
Cu(+2)	5.08212e-11
O(-2)	55.5087
H	9.67616e-19
O(0)	5.22431e-56
Cu(+1)	9.99000e-4
Cu(0)	1.00000e-6

The remaining elemental copper is the targeted value of $1e^{-6}$ moles. The remaining O_2 is virtually zero, at $5.22e^{-56}$ moles (about one mole per earth).

Since there is still excess copper metal (albeit small) and no remaining oxygen, the system is still slightly reducing. Look at the ORP value to see what this slightly reducing condition is.

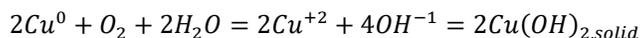
- ✓ Review the summary section to find the ORP

Aqueous Phase Properties
 pH 7.01161
 Ionic Strength 1.88032e-9 mol/mol
 Density 0.996845 g/ml
 ORP 0.0351125 V (SHE)

Recalculate using a different Target, Cu(OH)₂.

In this calculation, you will add sufficient O_2 so that two electrons are donated by elemental copper to produce $Cu(+2)$.

Here the catch: $Cu(+2)$ is insoluble, and so the conversion reaction shown above is followed by a precipitation reaction.



Therefore, you need to find the appropriate target species to make the calculation do what you want.

The Composition Point calculation has certain limitations. The only target variables are solids, vapor species or dissolved liquid species. If the goal is to convert $Cu(0)$ to $Cu(+2)$, then it's a matter of finding a variable that will capture this transition. The only variable in this case is $Cu(OH)_2$, solid. $Cu(OH)_2$ is insoluble at neutral pH. Therefore, nearly all the $Cu(0)$ that gets converted to $Cu(+2)$ will be in the form of $Cu(OH)_2$. If the pH was low, where significant Cu^{+2} dissolves, then we could not use this target. Thus, it's important to understand what the limitations of this (and other) calculations are.

- ✓ Click on the Definition tab and change the target species to $Cu(OH)_2$ (Spertinite) – Sol

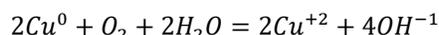
- ✓ Set the value to 5e-4 moles

Calculation Parameters	
Adjusted Inflow:	O2
Target Species:	Cu(OH)2 (Spertinite) - Sol
Target Cu(OH)2 (Spertinite) Value: (mol)	5.00000e-4

- ✓ Calculate
- ✓ Click on the Output tab
- ✓ View the Oxygen requirements

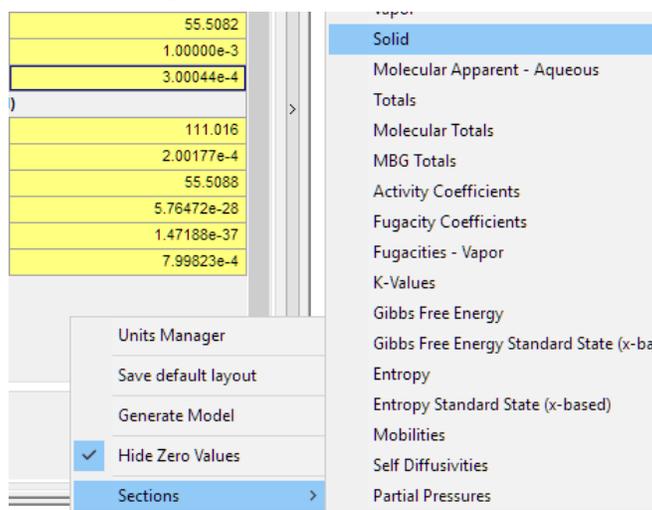
Calculation Results (mol)	
Adjusted Inflow: O2	3.75044e-4

If 5e⁻⁴ moles of Cu(0) is converted to Cu(+2), then according to the reaction below, 2.5e⁻⁴ moles O₂ is needed.



However, 3.75e⁻⁴ moles is required, or 1.25e⁻⁴ moles of additional O₂ was added. This difference is an opportunity to introduce another grid section, the Solids list.

- ✓ Right-mouse-click on the grid and select Sections>Solid



The grid now shows the Solids present in the output. There is no longer any elemental copper present. All is converted to Cu(+1) and Cu(+2). The additional 1.25e⁻⁴ moles O₂ required was to convert Cu(0) to Cu(+1).

Solid (mol)	
Cu2O (Cuprite)	2.49911e-4
Cu(OH)2 (Spertinite)	5.00000e-4

What this means, albeit not obvious, is that Cu(0) and Cu(+2) does no coexist at these conditions. Cu(0) and Cu(1) coexist, as do Cu(1) and Cu(2) as shown above.

- ✓ Look at the MBG Totals section

MBG Totals - Totals (mol)	
H(+1)	111.016
Cu(+2)	5.00177e-4
O(-2)	55.5090
H	5.76469e-28
O(0)	1.47187e-37
Cu(+1)	4.99823e-4

The total amount of Cu(+2) is $5.002e^{-4}$ moles. That $0.002e^{-4}$ moles additional Cu(+2) is the amount dissolved in the water. This is small relative to the solid phase, which is why Cu(OH)₂, solid could be used as a surrogate to compute the conversion of Cu(0) to Cu(+2).

The oxygen content is still very low, $\sim 10^{-37}$, and there is no longer any Cu(0) present. So, this is neither a reducing or an oxidizing system. The ORP for this calculation is 0.27 V SHE

Aqueous Phase Properties

pH 7.55944
 Ionic Strength 9.59770e-9 mol/mol
 Density 0.996845 g/ml
 ORP 0.275572 V (SHE)

2.9 Reconcile Alkalinity

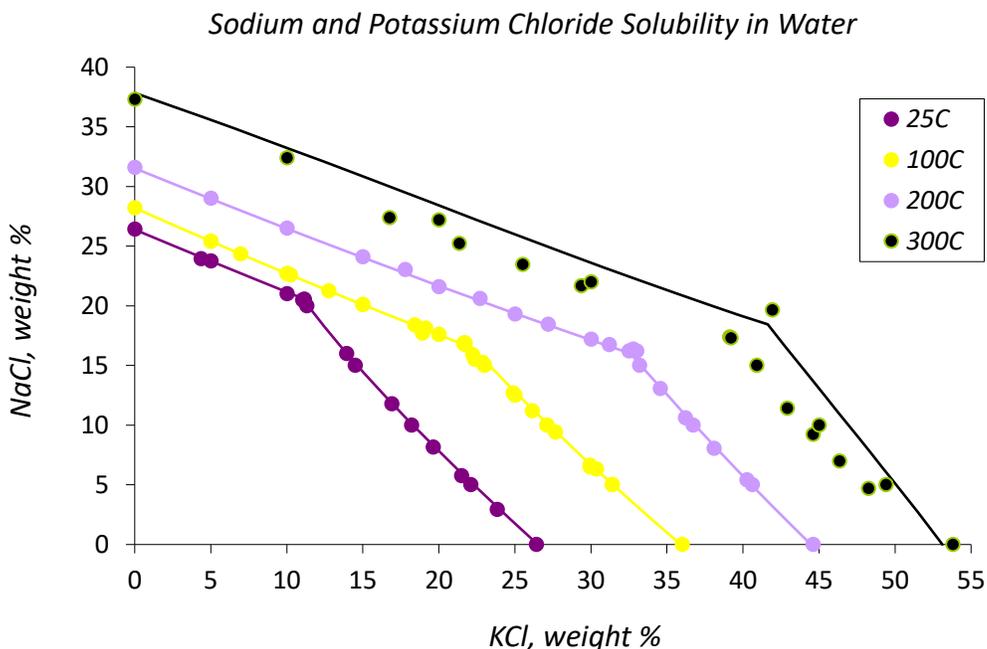
2.10 Custom Calculations

Overview

With the calculations that we have seen so far, variables are predefined. For instance, we must select either temperature or pressure as a variable in the dew point calculation and we have to set select pH as the variable for set pH calculation. On the other hand, we can select from a wider variety of variables using the **Custom** single point calculation.

For this calculation, we select which variables to fix or to free. We can select variables related to composition or fluid properties (e.g. pH, vapor fraction) as fixed or independent, while setting other variables as free or dependent (e.g. temperature, pressure).

With a custom calculation, it is possible to calculate the precipitation point of NaCl and KCl in H₂O at known temperatures. The precipitation point is where both NaCl and KCl solids coexist in solution, as represented in the figure below. NaCl and KCl coexist at the point where the two lines converge.



When setting up a custom calculation for data like this, we would define the following variables:

<i>NaCl and KCl Solubility Custom Calculation Defined</i>		
Fixed Variable	Value	Adjustable Variable
KCl (s)	1e-6 moles	KCl
NaCl (s)	1e-6 moles	NaCl

The value, $1e^{-6}$ moles, represents the mass of each solid in solution, i.e., the first crystallite of KCl and NaCl. Respectively, they amount to 79 kg and 58 kg of KCl and NaCl solid. Any number can be used, as long as it is small relative to the solution mass. We could also use $1e^{-7}$ moles.

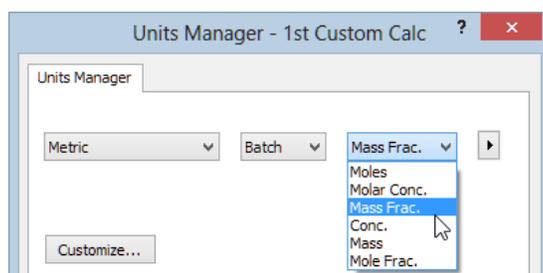
In this section, we will work on three cases that involve custom calculations. The purpose of these examples is to demonstrate a few of the many possible applications of the custom calculation.

2.10a First Custom Calculation

In the first example, we will run the calculation described above, which is to calculate the precipitation point of NaCl and KCl in H₂O at known temperatures.

2.10a First Custom Calculation			
Name:	1st Custom Calc	Temperature	25 C
Units Set	Mass fraction	Pressure	1 atm
Names Style	Formula	H2O	100 mass %
Framework	MSE	NaCl	0.0
Stream Amount	calculated	KCl	0.0

- ✓ Add a new stream  Add Stream and name it '1st Custom Calc' 
- ✓ Select the MSE button in the toolbar 
- ✓ Select the Units Manager button in the toolbar 
- ✓ Select Mass Frac. from the third dropdown list



- ✓ Press OK then enter NaCl and KCl as inflows

Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00000
Temperature (°C)	25.00000
Pressure (atm)	1.00000
Inflows (mass %)	
H2O	100.000
NaCl	0.0
KCl	0.0

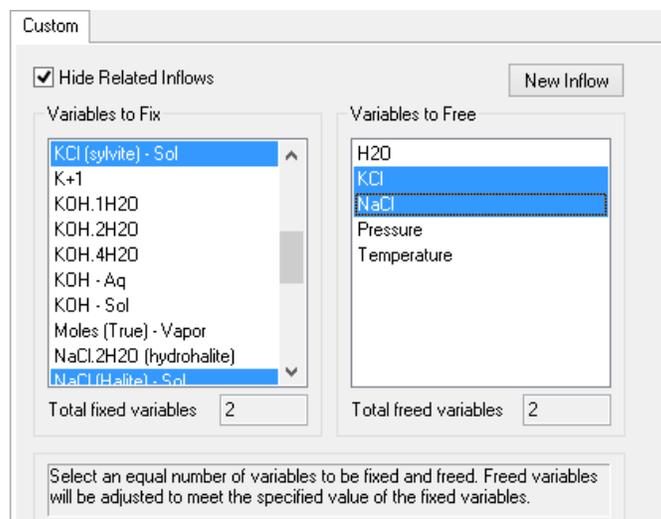
- ✓ Add a Single Point calculation then change the type to Custom



Custom calculations require us to designate which variables to fix and which to free. Since we must add additional parameters, the Calculate button is red for now.

- ✓ Select the "Specs..." button
- ✓ Highlight the following Fix and Free variables

2.10a Calculation Options	
Fix:	Free
KCl (Sol)	KCl
NaCl (Sol)	NaCl



Note, the total number fixed and the total number of freed variables are two each, as reported in the field towards the bottom of the Calculation Option window.

- ✓ Press OK

After pressing OK, the Definition tab displays a new field called Calculation Parameters.

Calculation Parameters	
Target 1: KCl (sylvite) (mol)	0.0
Target 2: NaCl (Halite) (mol)	0.0
Variable 1: KCl (mass %)	0.0
Variable 2: NaCl (mass %)	0.0

The values for the two freed variables are colored green. Green-colored values will be computed by the software but are also adjustable parameters. We will keep these blank.

Notice the Calculate button is red, which indicates that we have to add additional information.

- ✓ Enter the following for the two Target variables in the

2.10a Calculation Parameters	
Target 1: KCl	1e-6
Target 2: NaCl	1e-6

After entering the Target variables, the calculate button will turn green.

- ✓ Calculate or press the <F9> key then review the summary box

Summary	
Custom Calculation	
Fixed variables:	
KCl, target:	1.00000e-6 mol
NaCl, target:	1.00000e-6 mol
Free variables:	
KCl, total:	10.7777 mass %
NaCl, total:	20.8209 mass %
Phase Amounts	
Aqueous	1.46196 kg
Vapor	0.0 kg
Solid	1.32994e-7 kg
Aqueous Phase Properties	
pH	6.54365
Ionic Strength	0.104372 mol/mol
Density	1.23880 g/ml

Without entering initial inflows for KCl or NaCl, the custom calculation determined the specific masses the system would need to create the desired fluid properties of $1e-6$ mol KCl and NaCl. To reach these targets, the system would need 11 mass % of KCl and 21 mass % of NaCl, as shown in the Summary box.

Now we will see what happens when we run the calculation at a higher temperature. What are some predictions for the masses?

- ✓ Change the temperature to 100C

Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00000
Temperature (°C)	100.000
Pressure (atm)	1.00000

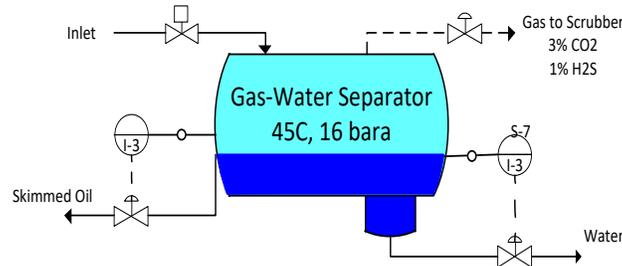
- ✓ Select the Calculate button
- ✓ Review the Summary

Summary	
Custom Calculation	
Fixed variables:	
KCl, target:	1.00000e-6 mol
NaCl, target:	1.00000e-6 mol
Free variables:	
KCl, total:	21.8491 mass %
NaCl, total:	16.4682 mass %
Phase Amounts	
Aqueous	1.62120 kg
Vapor	0.0 kg
Solid	1.32994e-7 kg
Aqueous Phase Properties	
pH	5.81576
Ionic Strength	0.125690 mol/mol
Density	1.24212 g/ml

How much mass of KCl and NaCl does the calculation require to meet the $1e-6$ mol targets?

2.10b Second Custom Calculation – Fixing the Gas composition

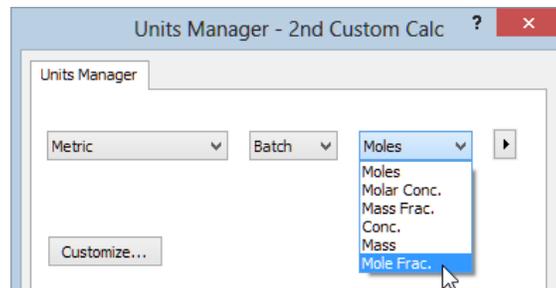
This case examines a gas separator that contains two outlets: gas and water. The gas contains H₂S and CO₂, both of which affect H₂O. We want to understand this effect.



The custom calculation is the simplest way to model the effects of the gas on the water. We will create a scenario where the gas-phase CO₂ and H₂S partial pressures are fixed. To do this, we will need a gas and water phase. The total mass is unimportant because we want to evaluate the equilibrium condition.

2.10b Second Custom Calculation			
Name:	2 nd Custom Calc	Inflows	Mole%
Units Set	Mole fraction	H2O	100
Names Style	Formula	CO2	0
Framework	MSE	H2S	0
Temperature	45C	CH4	0
Pressure	15.7908 atm (16 bar)		

- ✓ Add a new stream Add Stream and name it '2nd Custom Calc'
- ✓ Select the MSE button in the toolbar
- ✓ Select the Units Manager button in the toolbar
- ✓ Use the third dropdown menu to select Mole Frac. Units then press OK



- ✓ Enter the Stream Parameters (45C and 15.7908 atm) and inflows (CO₂, H₂S, and CH₄)

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	45.0000
Pressure (atm)	15.7908
Inflows (mole %)	
H2O	100.000
CO2	0.0
H2S	0.0
CH4	0.0

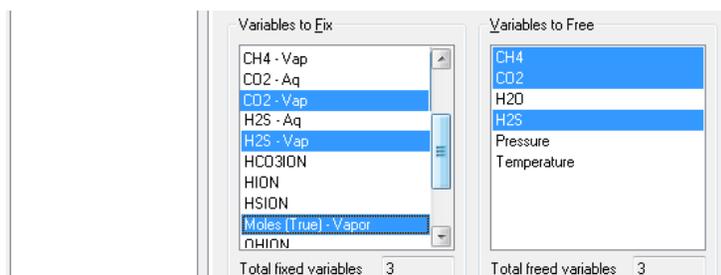
- ✓ Add a Single Point calculation then change the type to Custom



- ✓ Select the Specs button

2.10b Specs ... Calculation Options	
<i>Fix:</i>	<i>Free</i>
CO2 (vap)	CH4
H2S (vap)	CO2
Moles (True) Vapor	H2S

- ✓ Highlight the Fix and Free variables as per the table above



- ✓ Press OK then in the Calculation Parameters grid, enter these Targets

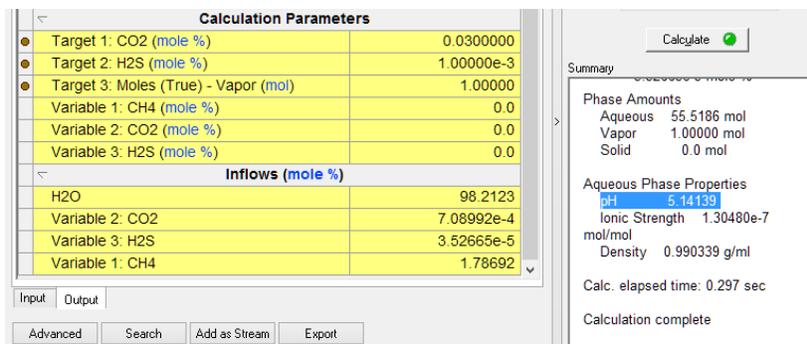
2.10b Calculation Parameters	
<i>Target 1: CO2</i>	.03
<i>Target 2: H2S</i>	1e-3
<i>Target 3: Moles (True)</i>	1

Calculation Parameters	
Target 1: CO2 (mole %)	0.0300000
Target 2: H2S (mole %)	1.00000e-3
Target 3: Moles (True) - Vapor (mol)	1.00000
Variable 1: CH4 (mole %)	0.0
Variable 2: CO2 (mole %)	0.0
Variable 3: H2S (mole %)	0.0

- ✓ Press <F9> or the Calculate button

We will view the results of the calculation with the Output tab.

- ✓ Select the Output tab below the Definition grid



The system needs 7.09×10^{-4} mole% CO₂, 3.52×10^{-5} mole% H₂S, and 1.79 mole% CH₄ to meet specified targets. This composition results in a 5.15 pH water phase, according to the Summary.

- ✓ Save the file

2.10c Third Custom Calculation – Gypsum and Anhydrite

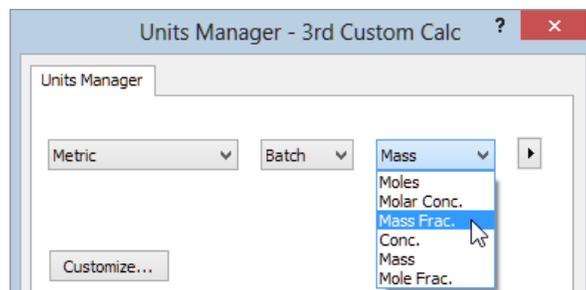
This example considers the eutectic temperature between gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4).

Hydrates are solids containing chemically bonded water. An interesting example is FeCl_3 , which has five unique hydrated phases, whose stability is a function of temperature. As temperature increases, water dislodges, and hydration decreases. Once a certain temperature is reached, the solid dehydrates.

In our case, the system has only one hydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and one dehydrated solid, CaSO_4 . The two solids meet at a single temperature where both are present. We want to determine this temperature.

2.10c Third Custom Calculation			
Name:	3rd Custom Calc	Temperature	25 C
Units Set	Mass fraction	Pressure	1 atm
Names Style	Formula	H2O	100
Framework	MSE	CaSO4	0

- ✓ Add a new stream  Add Stream and name it '3rd Custom Calc' 
- ✓ Select the MSE button in the toolbar 
- ✓ Select the Units Manager button in the toolbar 
- ✓ Select Mass Frac. From the third dropdown list



- ✓ Press OK
- ✓ Enter CaSO_4 as an inflow

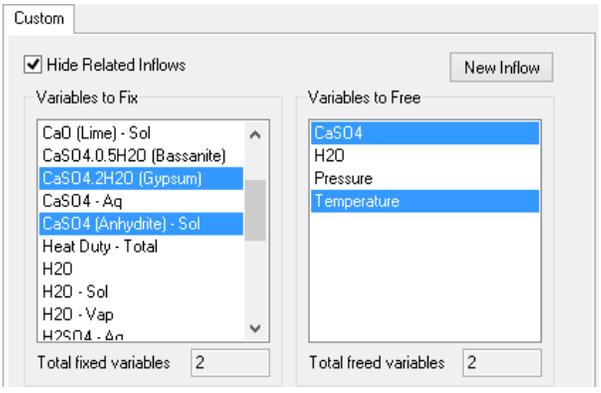
Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mass %)	
H2O	100.000
CaSO4	0.0

- ✓ Add a Single Point calculation then change the type to Custom



- ✓ Select the "Specs..." button
- ✓ Highlight the Fix and Free variables from the table below

2.10c Specs ... Calculation Options	
Fix:	Free
CaSO4.2H2O	CaSO4
CaSO4 – Sol	Temperature



- ✓ Press OK
- ✓ Enter the following Target values

2.10c Calculation Parameters	
CaSO4.2H2O	1e-6
CaSO4 (s)	1e-6

Calculation Parameters	
● Target 1: CaSO4.2H2O (Gypsum) (mol)	1.00000e-6
● Target 2: CaSO4 (Anhydrite) (mol)	1.00000e-6
Variable 1: CaSO4 (mass %)	0.0
● Variable 2: Temperature (°C)	0.0

- ✓ Press <F9> or the Calculate button
- ✓ Select the Output tab below the Definition grid

Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00211
Variable 2: Temperature (°C)	40.0727
Pressure (atm)	1.00000
Calculation Parameters	
● Target 1: CaSO4.2H2O (Gypsum) (mol)	1.00000e-6
● Target 2: CaSO4 (Anhydrite) (mol)	1.00000e-6
Variable 1: CaSO4 (mass %)	0.0
● Variable 2: Temperature (°C)	0.0
Inflows (mass %)	
H2O	99.7899
Variable 1: CaSO4	0.210139

Summary

Custom Calculation

Fixed variables:

- CaSO4.2H2O (Gypsum), target: 1.00000e-6 mol
- CaSO4 (Anhydrite), target: 1.00000e-6 mol

Free variables:

- CaSO4, total: 0.210139 mass %
- Temperature, calculated: 40.0727 °C

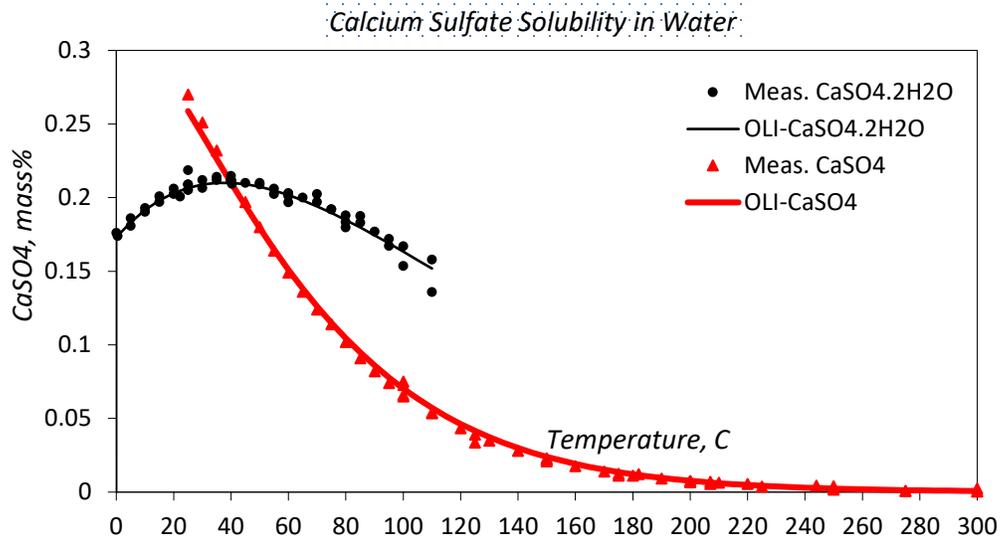
Phase Amounts

- Aqueous 1.00210 kg
- Vapor 0.0 kg
- Solid 3.08314e-7 kg

Aqueous Phase Properties

- pH 6.81840
- Ionic Strength 6.94090e-4 mol/mol
- Density 0.994271 g/ml

The temperature where both solids are at saturation simultaneously is about 40°C and 0.2109 mass% CaSO_4 . We can see where this transition occurs at the inflection in the follow plot:



2.11 REDOX (REDuction/OXidation) Basics

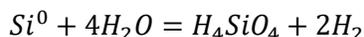
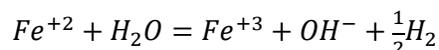
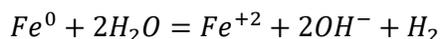
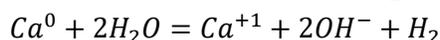
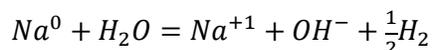
Overview

REDOX is an OLI Studio option that activates a critical mechanism in electrolyte chemistry. All elements possess the ability to gain (reduction) or release (oxidation) electrons. When oxidation occurs, elements increase their oxidation state. When reduction occurs, the element decreases its oxidation state. The software's REDOX option allows us to modify the oxidation state of a system so that we can better represent an actual process.



The REDOX option button in the OLI Studio menu bar.

In this chapter, we will calculate five oxidation-reduction reactions, which are shown below:



Basic REDOX calculation

In this example, we will prepare several samples to see how energy is released when metals are added to water. Then we will compare the amount of energy released as the element changes from group and period on the Periodic Table.

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	** 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
*Lanthanoids	* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb				
**Actinoids	** 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No				

- ✓ Add a new stream Add Stream and rename it 'REDOX Reactions'
- ✓ Enter the inflows from the table below

2.11 - Basic REDOX Calculation					
Stream Name	Redox Reaction	Stream Amount	(calculated)	Inflows (mol)	
Name Style	Formula	Temperature	25 °C	H2O	55.508
Framework	Aqueous	Pressure	1 atm	Na	0
Units Set	Default (moles)			Ca	0
Settings	REDOX ON			Fe	0
				Si	0.
				Au	0

- ✓ Turn the REDOX calculations button 
- ✓ Select the down arrow next to REDOX then place a check next to all the components



- ✓ Add a Single Point calculation and confirm the type of Calculation is Isothermal



- ✓ Calculate then select the Report tab and note the total enthalpy in the Stream Parameters section (incorrectly labeled Heat Duty in some versions of the software).

Enthalpy	cal	-3.79193e6
----------	-----	------------

- ✓ Add 1 mole Na and recalculate. ✓ Record the total enthalpy

Enthalpy	cal	-3.79193e6
----------	-----	------------

- ✓ Deselect Sodium in the REDOX menu then press <F9> to recalculate.



- ✓ Record the Total Enthalpy

Enthalpy	cal	-3.79193e6	-3.79193e6
----------	-----	------------	------------

The difference between REDOX on and off when Na is added is about 43 kcal. This is an example (albeit incomplete) of the energy released when Na element reacts with water to produce Na⁺, OH⁻, and H₂.

- ✓ Recalculate the case with Na REDOX on, and review the Species Output Table

The reaction products result in one mole of Na⁺, one mole OH⁻, and 0.5 moles H₂. This is consistent with the overall redox reaction between Na and H₂O shown above.

	Total	Aqueous	Vapor
	mol	mol	mol
H2O	54.508	54.4924	0.0156048
H+1	2.24116e-14	2.24116e-14	0.0
OH-1	1.0	1.0	0.0
H2	0.5	5.59324e-4	0.499441
O2	4.00578e-84	7.20085e-87	3.99858e-84
Na+1	1.0	1.0	0.0
Total (by phase)	57.008	56.493	0.515045

Species output with REDOX on and 1 mole of sodium

- ✓ Select the Definition grid and zero the Na value and change the Ca value to 1 mole
- ✓ Calculate
- ✓ Document the Total Enthalpy and the species output

Enthalpy	cal	-3.89066e6
----------	-----	------------

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
H2O	53.508	53.4756	0.0324095	0.0
H+1	4.78297e-13	4.78297e-13	0.0	0.0
OH-1	0.0293985	0.0293985	0.0	0.0
H2	1.0	7.25388e-4	0.999275	0.0
O2	8.63998e-84	1.00737e-86	8.62991e-84	0.0
Ca+2	0.013169	0.013169	0.0	0.0
CaOH+1	3.06039e-3	3.06039e-3	0.0	0.0
Ca(OH)2 (Portlandite)	0.983771	0.0	0.0	0.983771
Total (by phase)	55.5374	53.5219	1.03168	0.983771

Species output with REDOX on and 1 mole of calcium

The Total Enthalpy change from pure water (and calcium) is about 100 kcal. We can deselect the Ca redox and confirm that the total enthalpy is -3.79195e6 cal. The species output table shows that the 1 mole of calcium converted to Ca^{+2} , H_2 , and OH^- . In this example, the oxidized calcium reacted with OH^- to produce lime ($\text{Ca}(\text{OH})_2$)

- ✓ Recalculate the case using 1 mole of Fe and zero moles of Ca

Enthalpy	cal	-3.79157e6	-3.65309e6
----------	-----	------------	------------

Elemental Fe oxidized into Fe^{+2} and Fe^{+3} . Nearly all the iron is as Fe^{+3} and has precipitated to $\text{Fe}(\text{OH})_3$. These dissolved ions reacted with H_2O to form various aquo- groups.

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
H2O	53.508	53.4756	0.0324342	0.0
H+1	5.14755e-10	5.14755e-10	0.0	0.0
OH-1	1.85252e-5	1.85252e-5	0.0	0.0
Fe2(OH)2+4	2.26791e-44	2.26791e-44	0.0	0.0
Fe+3	3.47052e-28	3.47052e-28	0.0	0.0
Fe(OH)2+1	1.52852e-16	1.52852e-16	0.0	0.0
Fe(OH)3	2.18457e-12	2.18457e-12	0.0	0.0
Fe(OH)4-1	1.04812e-12	1.04812e-12	0.0	0.0
FeOH+2	4.11111e-21	4.11111e-21	0.0	0.0
Fe+2	6.39656e-6	6.39656e-6	0.0	0.0
FeOH+1	5.73184e-6	5.73184e-6	0.0	0.0
FeO	8.71307e-8	8.71307e-8	0.0	0.0
H2	1.0	7.32508e-4	0.999267	0.0
HFeO2-1	2.63054e-10	2.63054e-10	0.0	0.0
O2	8.65353e-84	1.01885e-86	8.64334e-84	0.0
Fe(OH)2 (Amakinite)	0.999988	0.0	0.0	0.999988
Total (by phase)	55.508	53.4763	1.0317	0.999988

Species output with REDOX on and 1 mole of iron

- ✓ Recalculate the case using 1 mole Si and zero moles of Fe

Enthalpy	cal	-3.87005e6	-3.65126e6
----------	-----	------------	------------

Elemental silicon oxidized into Si^{+4} . Nearly all of it has precipitated to SiO_2 . The remaining Si^{+4} reacts with H_2O to form the oxy-acid, H_4SiO_4 . This acid dissociates to $\text{H}_3\text{SiO}_4^{-1}$ and $\text{H}_2\text{SiO}_4^{-2}$. It also dehydrates to form SiO_2 , which is how it is reported below.

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
H2O	53.508	53.4431	0.0648922	0.0
H+1	5.1378e-7	5.1378e-7	0.0	0.0
OH-1	1.83501e-8	1.83501e-8	0.0	0.0
H2	2.0	7.32067e-4	1.99927	0.0
O2	1.73032e-83	1.01824e-86	1.7293e-83	0.0
H2SiO4-2	7.35062e-14	7.35062e-14	0.0	0.0
H3SiO4-1	4.9543e-7	4.9543e-7	0.0	0.0
SiO2	1.0	1.83494e-3	0.0	0.998165
Total (by phase)	56.508	53.4457	2.06416	0.998165

Species output with REDOX on and 1 mole of silicon

- ✓ Calculate the case one last time using 1 mole of Au (gold) instead of Si

Enthalpy	cal	-3.79193e6
----------	-----	------------

Virtually all the Au remains as the metal. Oxidization in water to Au^{+1} and Au^{+3} is negligible. Based on the table below, there are 10^{-32} moles Au^{+1} in water or about 1 atom in about 40 kilotons water. This is because gold does not oxidize in water. Hence, why gold is a “noble” metal.

	Total	Aqueous	Solid
	mol	mol	mol
H2O	55.508	55.508	0.0
H+1	1.008e-7	1.008e-7	0.0
OH-1	1.008e-7	1.008e-7	0.0
Au+3	2.61421e-79	2.61421e-79	0.0
Au(OH)3	3.00377e-56	3.00377e-56	0.0
Au(OH)4-1	1.18729e-60	1.18729e-60	0.0
Au(OH)5-2	5.45478e-67	5.45478e-67	0.0
Au+1	4.59621e-32	4.59621e-32	0.0
H2	7.98394e-17	7.98394e-17	0.0
O2	9.59198e-61	9.59198e-61	0.0
Au (Gold)	1.0	0.0	1.0
Total (by phase)	56.508	55.508	1.0

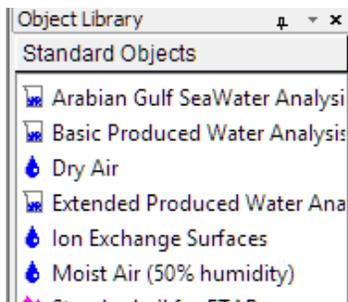
Species output with REDOX on and 1 mole of gold

2.12 Air – Using Air in Analyzer Calculations

Overview

Open system calculations require air. Calculations require air for several reasons. For instance, the focus can be N_2 as an incompressible gas, O_2 for oxidation/corrosion, or CO_2 acid-base reactions. Regardless, adding air to a calculation is an integral part of many OLI Studio applications.

While the software does not have a separate component called “air,” the OLI Studio does allow different ways to add an air stream. One approach is to select from a set of commonly used chemistries called Standard Objects. The objects library includes two air streams: a dry air and a moist air.



Adding these streams to the calculation is simple. We simply have to select the object in the Objects panel then drag it to the Navigator panel. Once dragged to the Navigator panel, these objects become like any other stream. They can be used in mixers or as base streams for calculations.

The alternative to using pre-designed streams is to add the air components to existing streams.

Inflows (mol)	
H2O	55.5082
NaCl	0.0
CaCl2	0.0
BaSO4	0.0
N2	0.0
O2	0.0
Ar	0.0
CO2	0.0

A limitation to this approach is that we would have to know the exact compositions **and** amounts. We would have to add the correct fraction of each gas component. This amount has to be enough so that the vapor components do not dissolve and change the final gas fraction but not too much that the liquid water evaporates.

These are among the limits of using “closed-system” software to model open systems.

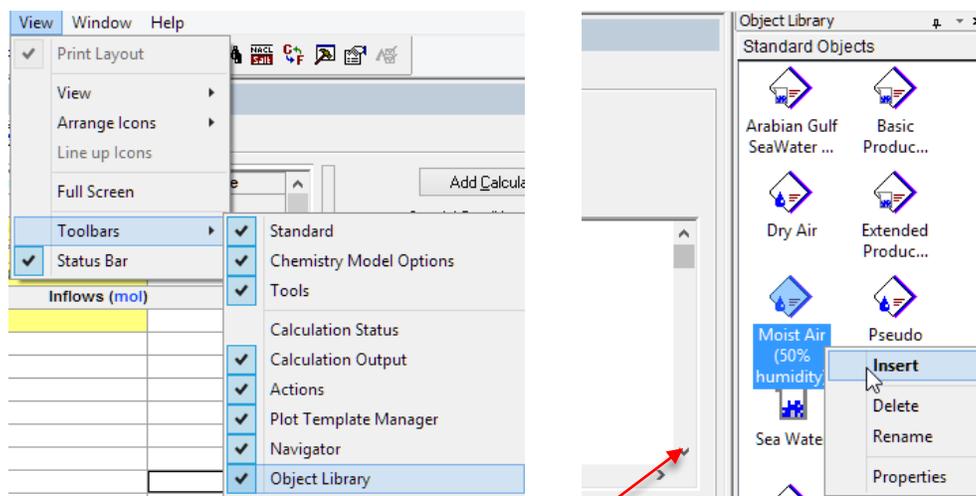
The following examples are ways to get around the problem of using closed-system calculations to model open systems.

2.12a – Using the Air Stream in a Mixer

The first example is the simplest. It involves mixing two streams using a Mixer block. The mixer block has not been presented yet (it is presented in a later chapter), but it is needed here. Therefore, we will keep the application simple. You will mix air with calcite-water and see how the seawater pH changes when in contact with atmospheric CO_2 .

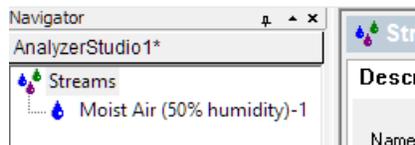
- ✓ From the menu bar, select File > New then save the file with an appropriate name

- ✓ Open the Object Library: Click on View>Toolbars>Object Library



- ✓ When the Object Library opens, drag the Moist Air object to add it to the Navigator panel

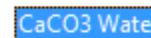
The Navigator now has the inserted object. We can view this object's composition in the Definition grid.



The Stream Amount is only 1 mole. The CO₂ is 360 ppmV, lower than the current atmospheric value of 400 ppm, but we can change this as we want. At present, there is a total of 0.00036 moles CO₂ in this stream (1 mole * 0.036%). This Air is a fixed-mass stream.

Variable	Value
Stream Parameters	
Stream Amount (mol)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mole %)	
H2O	1.66400
N2	76.8000
O2	20.6000
Ar	0.900000
CO2	0.0360000

- ✓ Add a new stream  Add Stream and rename it 'CaCO3'Water'
- ✓ Add CaCO₃ as an Inflow give it a value of 0.001 moles



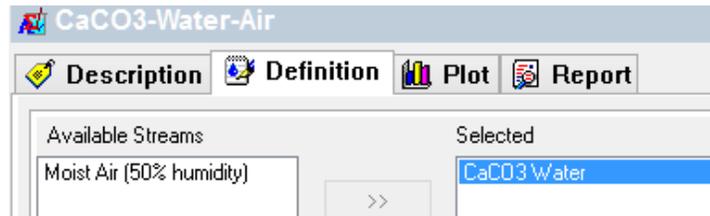
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5092
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
CaCO3	1.00000e-3

The purpose of this stream is to provide a base reaction for the acid gas in the air. The CaCO_3 value of 0.001 moles is sufficient to saturate calcite in the water. When the CaCO_3 -water reacts with atmospheric CO_2 , calcite will dissolve, to the extent that CO_2 is available (remember OLI calculations are closed systems so the moles of CO_2 added to the calculation will be fixed).

- ✓ Create a mixer, by clicking on Add Mixer from the Action panel -  Add Mixer

We will revisit the Mixer object in further detail in Chapter 5.

- ✓ Label it CaCO_3 -Water-Air -  CaCO_3 -Water-Air
- ✓ Double click the CaCO_3 -Water in the Available Streams window to add to the Selected field



- ✓ Calculate then view the Report tab

A 10 pH at ambient conditions is expected when pure calcite is in equilibrium with water. You can confirm that CaCO_3 solid is present by scrolling down to the scale tendency table.

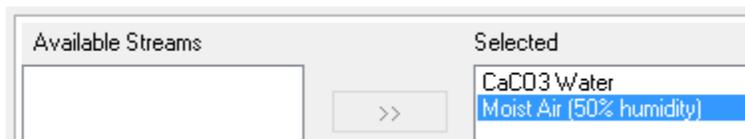
Mixture Properties

StrAmt	55.5092	mol
Temp	25.0000	°C
Pres	1.00000	atm

Aqueous Properties

pH	9.86447	
----	---------	--

- ✓ Return to the Definition tab.
- ✓ Add the Moist Air to the Selected field



The details of the mixer are not taught here, but what we created is a mixer that will bring in 55.5092 moles of CaCO_3 -water and 1 mole of Air.

- ✓ Calculate and view the pH and also the PCO_2

Temp	25.0000	°C
Pres	1.00000	atm

Aqueous Properties

pH	8.59953	
Ionic Strength (x based)	1.55806e-5	mol/mol

- ✓ Scroll down to the Species Output table

Notice that the vapor-phase CO₂ moles is 8.7e⁻⁵ moles, and the total vapor is 1.01 moles. Now the P_{CO₂} is 87 ppmV instead of 360 ppmV. CO₂ dissolved into the water and reacted with CO₃⁻² to form HCO₃⁻¹. The reaction is complete, but now the CO₂ is no longer at atmospheric values.

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
H2O	55.5246	55.4927	0.0319386	0.0
H+1	2.59901e-9	2.59901e-9	0.0	0.0
OH-1	4.17381e-6	4.17381e-6	0.0	0.0
CaCO3	7.14661e-4	1.93157e-5	0.0	6.95346e-4
CaHCO3+1	1.60214e-6	1.60214e-6	0.0	0.0
Ca+2	2.83719e-4	2.83719e-4	0.0	0.0
CaOH+1	1.76453e-8	1.76453e-8	0.0	0.0
CO2	9.00957e-5	2.90464e-6	8.71911e-5	0.0
CO3-2	1.12455e-5	1.12455e-5	0.0	0.0
HCO3-1	5.42395e-4	5.42395e-4	0.0	0.0
Ar	9.0e-3	1.22378e-5	8.98776e-3	0.0
N2	0.768	4.9171e-4	0.767508	0.0
O2	0.206	2.55725e-4	0.205744	0.0
Total (by phase)	56.5093	55.4943	1.01427	6.95346e-4

Mixer species output with Moist Air

- ✓ Return to the definition tab and change the Moist Air Multiplier to 10

Variable	Value	CaCO3-Water	Moist Air (50% humi
Multiplier		1.00000	10.0000

This changes the Moist Air inflow to 10 moles.

- ✓ Calculate, and look at the pH and vapor-phase CO₂ then the Species Output table

Aqueous Properties

pH	8.23424	
Ionic Strength (x-based)	2.36610e-5	mol/mol

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
H2O	55.6742	55.3545	0.319681	0.0
H+1	6.05642e-9	6.05642e-9	0.0	0.0
OH-1	1.80886e-6	1.80886e-6	0.0	0.0
CaCO3	5.63509e-4	1.92666e-5	0.0	5.44242e-4
CaHCO3+1	3.73329e-6	3.73329e-6	0.0	0.0
Ca+2	4.32747e-4	4.32747e-4	0.0	0.0
CaOH+1	1.13473e-8	1.13473e-8	0.0	0.0
CO2	3.17312e-3	1.04993e-5	3.16262e-3	0.0
CO3-2	7.79959e-6	7.79959e-6	0.0	0.0
HCO3-1	8.51836e-4	8.51836e-4	0.0	0.0
Ar	0.09	1.22103e-5	0.0899878	0.0
N2	7.68	4.90288e-4	7.67951	0.0
O2	2.06	2.55123e-4	2.05974	0.0
Total (by phase)	65.5093	55.3566	10.1521	5.44242e-4

Mixer species output with 10x Moist Air

The pH is closer to what we know fresh water lakes to be at, 8.3 pH. Also note that the CO₂ vapor is 3.16e⁻³ moles (divided by 10.15 vapor moles) or 311 ppmV. This is closer to the atmospheric value.

Raising the Air amount more will increase the P_{CO_2} closer to its target value, however it will never be the exact amount simply because a certain amount of CO_2 will dissolve. Adding too much, however, will dehydrate the water.

- ✓ Return to the Definition tab
- ✓ Change the Moist Air multiplier to 1000

Now there will be 1000 moles of air in contact with 55.5 moles of liquid. At atmospheric conditions, 31 moles H_2O will be present in the air. Half of this is 15.5 moles H_2O is part of the 50% moist air. The other 15.5 moles will evaporate from the water. Confirm this by calculating.

Variable	Value	CaCO3-Water	Moist Air (50% humi
Multiplier		1.00000	1000.00
Stream Parameters			
Total Inflow		55.5092 mol	1000.00 mol

- ✓ Calculate and review the Total and Phase Flow table

We started with 1L (1kg) of water. Now the volume is 0.726 L (724 grams). Therefore, one-fourth of the liquid water has evaporated. This concentrates all the dissolved components in the water phase, which changes the calculation.

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
Mole (True)	1055.51	40.1775	1015.33	6.55071e-4
Mole (App)	1055.51	40.1779	1015.33	6.55071e-4
	g	g	g	g
Mass	29781.3	723.855	29057.4	0.0655643
	L	L	L	cm3
Volume	24836.3	0.726102	24835.6	0.0241918

Mixer species Total and Phase Flows with 1000x Moist Air

To fix this problem you would need to saturate the air with water and add slightly excess CO_2 to the air so that when the air and water reach equilibrium, the P_{CO_2} remains at the original value of 360 ppmV (or now 400 ppmV).

2.12b – Using Makeup CO_2 and H_2O Streams with the Mixer

There are options to correct this, and it involves manually editing the air stream composition, or adding separate CO_2 and H_2O makeup streams

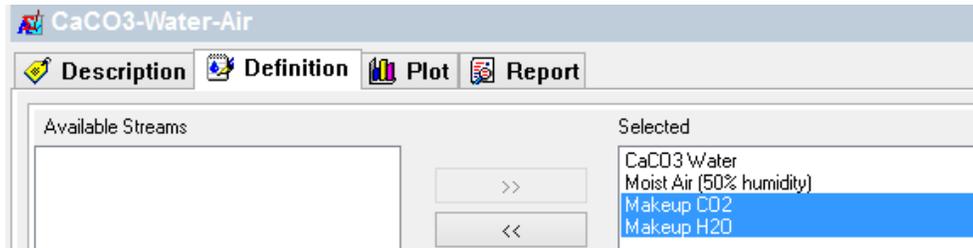
- ✓ Create a new stream – label it 'Makeup H2O' -  Makeup H2O
- ✓ Change the H2O moles to 1, to make it easier to remember

Inflows (mol)	
H2O	1.00000

- ✓ Create another stream – label it "Makeup CO_2 " -  Makeup CO_2
- ✓ Add CO_2 to the inflow and set the value to 0.001 mole
- ✓ Set H2O to zero

Inflows (mol)	
H2O	0.0
CO2	1.00000e-3

- ✓ Return to the CaCO₃-Water-Air mixer
- ✓ Add the Makeup H₂O and Makeup CO₂ to the Selected Stream



- ✓ We know that we are missing 15 moles H₂O, so change the multiplier for H₂O to 15.
- ✓ We do not know how much CO₂ is needed, so keep this multiplier at 1 for now

Variable	Value	CaCO ₃ -Water	Moist Air (50%)	Makeup H ₂ O	Makeup CO ₂
Multiplier		1.00000	1000.00	15.0000	1.00000
Stream Parameters					
Total Inflow		55.5092 mol	1000.00 mol	15.0000 mol	1.00000e-3 mol

- ✓ Calculate and view the Liquid water amount and the vapor-CO₂ amount of the Species Output table

The Total Aqueous phase is 55.18 (close to the original 55.51 moles), which is good enough. Furthermore, the vapor-CO₂ is 0.36 moles in 1000 moles, which is conveniently 360 ppmV .

Species Output (True Species)

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

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
H ₂ O	87.1478	55.1758	31.972	0.0
H+1	6.58319e-9	6.58319e-9	0.0	0.0
OH-1	1.65625e-6	1.65625e-6	0.0	0.0
CaCO ₃	5.45119e-4	1.92043e-5	0.0	5.25915e-4
CaHCO ₃ +1	4.05798e-6	4.05798e-6	0.0	0.0
Ca+2	4.50812e-4	4.50812e-4	0.0	0.0
CaOH+1	1.08208e-8	1.08208e-8	0.0	0.0
CO ₂	0.360554	1.19291e-5	0.360542	0.0
CO ₃ -2	7.49209e-6	7.49209e-6	0.0	0.0
HCO ₃ -1	8.89059e-4	8.89059e-4	0.0	0.0
Ar	9.0	1.2171e-5	8.99999	0.0
N ₂	768.0	4.88673e-4	768.0	0.0
O ₂	206.0	2.54298e-4	206.0	0.0
Total (by phase)	1070.51	55.178	1015.33	5.25915e-4

Mixer species output table with Makeup H₂O and CO₂

We can modify the multipliers for makeup CO₂ and H₂O to make it exact if needed. This method, however, requires manual iteration because it is not an automatic approach.

2.12c - Using Air Components in a Stream

**Please note that this section may not work in certain versions of the software.*

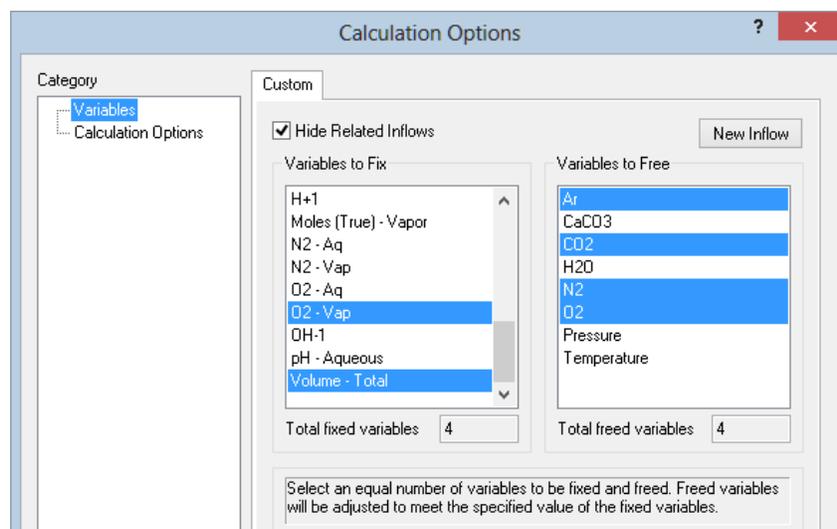
The alternative to using an Air stream is to add each air component to a work stream. This has some advantages over the mixer object in that we have direct control over the air components. The drawback is that we will not be able to distinguish between the air and liquid masses because they would represent a total mass.

We can compute air space using the custom calculation. This calculation will let us fix the vapor fraction components to the atmospheric values. There is one complication, and that deals with setting a gas volume. It is not possible to set all the gas phase components, since the gas-phase composition will change as H₂O evaporates (with temperature). Thus, the best way to compute a gas phase is to fix n=2 of the gas phase components and to fix the total volume. In this case n=5, including H₂O, N₂, O₂, Ar, and CO₂. Note that H₂O cannot be fixed, because it is liquid. N₂ cannot be fixed because the mole fraction of the gas needs to be 100%. Furthermore, without knowing H₂O, N₂ cannot be set.

Therefore, the best way to model a system like this is using the following fix-free table. The values used are for air composition. The Total Volume of 2L is arbitrary, and could have been any value, but since we do not want to evaporate too much water, a 1L headspace is sufficient.

Fix	Fix Value	Free
Ar - Vap	.90%	Ar
CO2 - Vap	.04%	CO2
O2 - Vap	20%	O2
Volume-Total	2 L	N2

- ✓ Click on the CaCO₃-Water stream
- ✓ Add a single point calculation
- ✓ Enter the components N₂, O₂, Ar, and CO₂ into the grid
- ✓ Change the calculation type to Custom
- ✓ Click on the Specs button and select the variables on the Variables to Fix and Variables to Free fields as defined in the above table



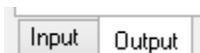
Make sure that the Total fixed and Total Free variables are 4.

- ✓ Press OK to close the window

- ✓ Enter the Fix Values into the Calculation Parameters section (values are in the above table)

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5092
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Target 1: Ar (mole %)	0.900000
Target 2: CO2 (mole %)	0.0400000
Target 3: O2 (mole %)	20.0000
Target 4: Volume - Total (L)	2.00000
Variable 1: Ar (mol)	0.0
Variable 2: CO2 (mol)	0.0
Variable 3: N2 (mol)	0.0
Variable 4: O2 (mol)	0.0
Inflows (mol)	
H2O	55.5082
CaCO3	1.00000e-3
Variable 3: N2	
Variable 4: O2	
Variable 1: Ar	
Variable 2: CO2	

- ✓ Calculate and view the Output tab (bottom of the grid) -



We can see the input amount of each gas component. This amount creates a 2L system of gas and liquid.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5500
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Target 1: Ar (mole %)	0.900000
Target 2: CO2 (mole %)	0.0400000
Target 3: O2 (mole %)	20.0000
Target 4: Volume - Total (L)	2.00000
Variable 1: Ar (mol)	0.0
Variable 2: CO2 (mol)	0.0
Variable 3: N2 (mol)	0.0
Variable 4: O2 (mol)	0.0
Inflows (mol)	
H2O	55.5082
CaCO3	1.00000e-3
Variable 3: N2	0.0314283
Variable 4: O2	8.40249e-3
Variable 1: Ar	3.79196e-4
Variable 2: CO2	4.97555e-4

- ✓ Move to the Report tab and view the pH and Species Output

Aqueous Properties

pH	8.16310	
Ionic Strength (v-based)	2.57284e-5	mol/mol

It is difficult to see the vapor fractions using mole units, and we can change them to be more relevant.

- ✓ Click on the Units manager tab -



Metric Batch Moles

- ✓ Click on Customize button -

Customize...

- ✓ Change vapor composition to mole fraction then press OK twice to return to the Report tab

Aqueous Composition	Moles	mol
Vapor Composition	Mole Fraction	mole %
Solid Composition	Moles	mol

- ✓ We will need to refresh the Report screen by clicking off the Report and then back on.

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mol	mole %	mol
CaCO3	5.2343e-4	1.93193e-5	0.0	5.04111e-4
CaHCO3+1	4.41714e-6	4.41714e-6	0.0	0.0
Ca+2	4.72142e-4	4.72142e-4	0.0	0.0
CaOH+1	1.04565e-8	1.04565e-8	0.0	0.0
CO2	2.98186e-5	1.3518e-5	0.04	0.0
CO3-2	7.28792e-6	7.28792e-6	0.0	0.0
H2O	55.5078	55.5065	3.14892	0.0
HCO3-1	9.32601e-4	9.32601e-4	0.0	0.0
H+1	7.16588e-9	7.16588e-9	0.0	0.0
OH-1	1.54234e-6	1.54234e-6	0.0	0.0
N2	0.0314283	4.93359e-4	75.9111	0.0
O2	8.40249e-3	2.52178e-4	20.0	0.0
Ar	3.79196e-4	1.24315e-5	0.9	0.0
Total (by phase)	55.55	55.5087	100.0	5.04111e-4

We can see that the CO₂, H₂O, O₂ and Ar values that you entered into the Calculation Parameters section of the grid. Now we have a liquid phase in contact with air, and the amount of air is no longer a factor in the calculation.

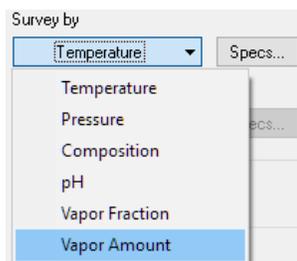
- ✓ Save the file

Chapter 3 Survey Calculations – Single Surveys

Introduction

Survey calculations are single point calculations strung together in series. They are also referred to as multiple point calculations. These calculations allow the user to designate as independent, one or two variables. The resulting plots are then used to interpret the calculation results.

The independent survey variables are listed below:



This chapter contains instructions on how to perform the following survey calculations

3.1 Temperature survey and Pressure survey of a four-phase mixture.....	2
3.2 Composition survey –NH ₃ -HAc-H ₂ O.....	6
3.3 pH Survey – CO ₂ -NaOH-H ₂ O	8
3.4 pH Survey – Transition Metals.....	12
3.5 Vapor Fraction survey – Seawater evaporation	18

3.1 Temperature survey and Pressure survey of a four-phase mixture

The purpose of this first example is to present the basic Temperature and Pressure survey. The system composition will be basic, containing one primary phase component, H₂O, CH₄, Decane, and CaCO₃. Each component will partition each of the other three phases.

Getting started

- ✓ Create a new Stream and label it **Phase vs Conditions**
- ✓ Set the framework to MSE - 
- ✓ Add CH₄, C₁₀H₂₂, and CaCO₃ to the grid
- ✓ Set the H₂O to 50 moles
- ✓ Set the remaining inflows to 10 moles

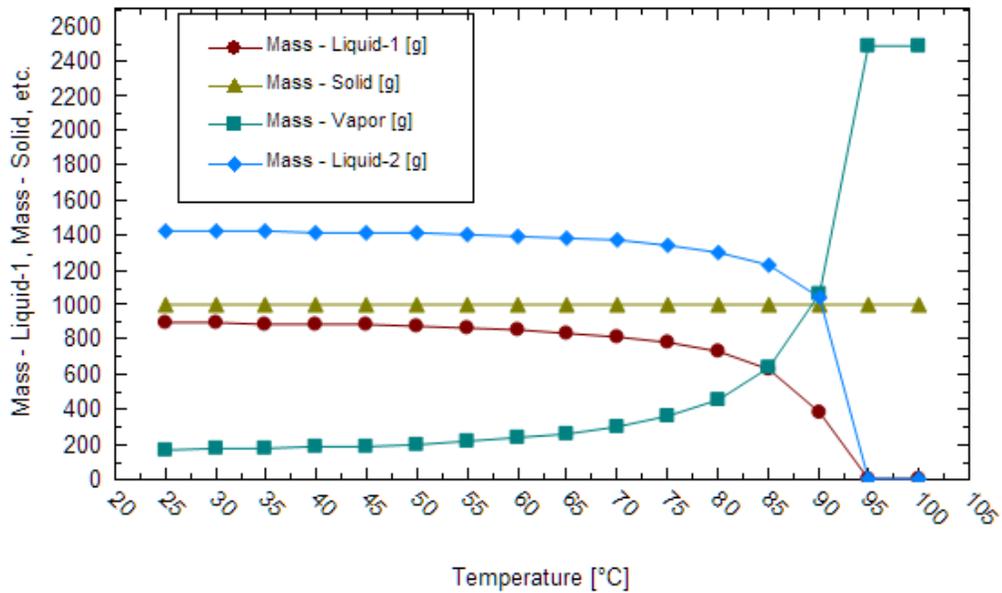
	Variable	Value
<	Stream Parameters	
	Stream Amount (mol)	80.0000
	Temperature (°C)	25.0000
	Pressure (atm)	1.00000
<	Inflows (mol)	
	H ₂ O	50.0000
	CH ₄	10.0000
	C ₁₀ H ₂₂	10.0000
	CaCO ₃	10.0000

Temperature Survey

- ✓ Add a Survey calculation and label it Temperature Survey
- ✓ Calculate

The default plot is a temperature survey from 25 to 100 C by 5 C increments.

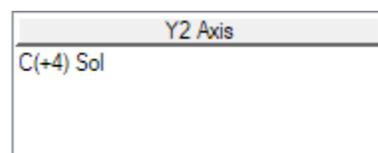
- ✓ Click on the Plot tab



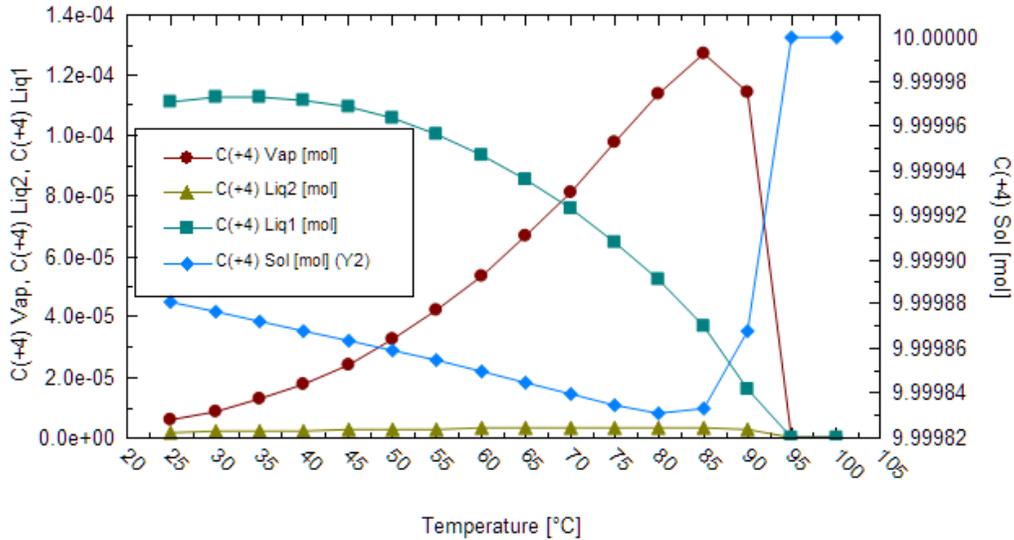
The default plot is the phase amounts. The above plot shows that as temperature increases, the mass of liquid-1 (aqueous) and liquid-2 (organic) decreases, evaporating to the vapor phase. The solid phase mass remains constant.



- ✓ Click on the Variables button in the upper right of the plot -
- ✓ Delete all the variables from the Y1 axis (double click on each or highlight them and remove with the double arrow)
- ✓ Expand the MBG Totals – Liquid-1 section
 - Add C(+4) Liq-1 to the Y1 axis
- ✓ Expand the MBG Totals – Vapor section
 - Add C(+4) Vap to the Y1 axis
- ✓ Expand the MBG Totals – Liquid-2 section
 - Add C(+4) Liq-2 to the Y1 axis
- ✓ Expand the MBG Totals – Solid section
 - Add C(+4) Sol to the Y2 axis



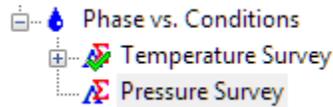
- ✓ Close the window and view the plot.



The inorganic carbon, C(+4) is present in the three mobile phases up to 90 C. Above this temperature the system evaporates entirely and nearly all the carbon transfers to the solid phase.

Pressure Survey

- ✓ Return to the Phase vs Conditions stream and add a new survey
- ✓ Name it Pressure Survey



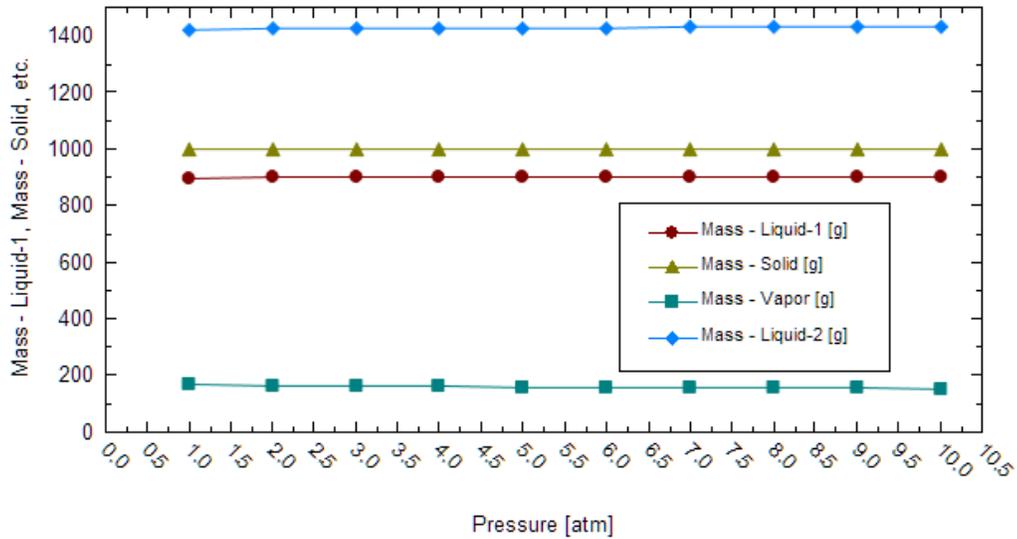
- ✓ Change the Survey by from Temperature to Pressure



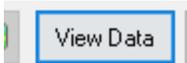
The default pressure setting is 1 to 10 atm by 1 atm increments. You will use these settings for this calculation.

- ✓ Calculate and click on the Plot tab

The plot is unremarkable; each curve is a flat line. This is because, in part, the y-axis range is wide, 0 to 1400 g. Instead of reviewing the data in this form, the alternative is to look at the actual data.



✓ Click on the View data button in the upper right of the plot -



	Pressure	Mass - Liquid-1	Mass - Solid	Mass - Vapor	Mass - Liquid-2
	atm	g	g	g	g
1	1.00000	894.865	1000.86	168.155	1421.05
2	2.00000	897.852	1000.86	162.907	1423.31
3	3.00000	898.840	1000.86	160.585	1424.65
4	4.00000	899.341	1000.86	158.977	1425.75
5	5.00000	899.648	1000.86	157.651	1426.77
6	6.00000	899.859	1000.86	156.467	1427.75
7	7.00000	900.016	1000.86	155.362	1428.69
8	8.00000	900.138	1000.86	154.309	1429.63
9	9.00000	900.237	1000.86	153.288	1430.55
10	10.0000	900.320	1000.86	152.291	1431.46

This results view can be more usable for some scenarios. According to the results there is no change in the solid mass, and there are small changes, up to 16 grams, in the other three phases.

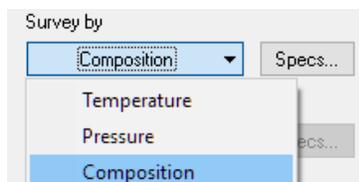
3.2 Composition survey –NH₃-HAc-H₂O

Getting started

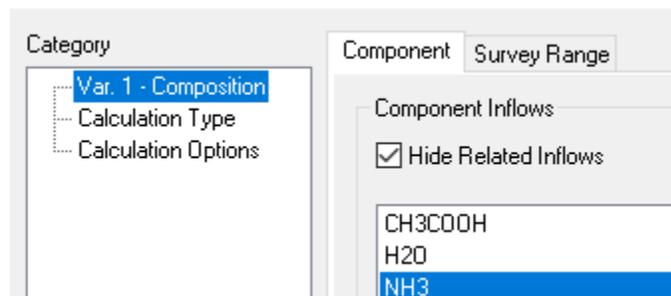
- ✓ Add a stream and label it **pH vs. Concentration**
- ✓ Add acetic acid to the grid and enter a 0.5 mole value
- ✓ Add NH₃ to the grid

Inflows (mol)	
H ₂ O	55.5082
CH ₃ COOH	0.500000
NH ₃	0.0

- ✓ Add a Survey calculation and label it Acetic Acid-NH₃
- ✓ Change the calculation type to Composition

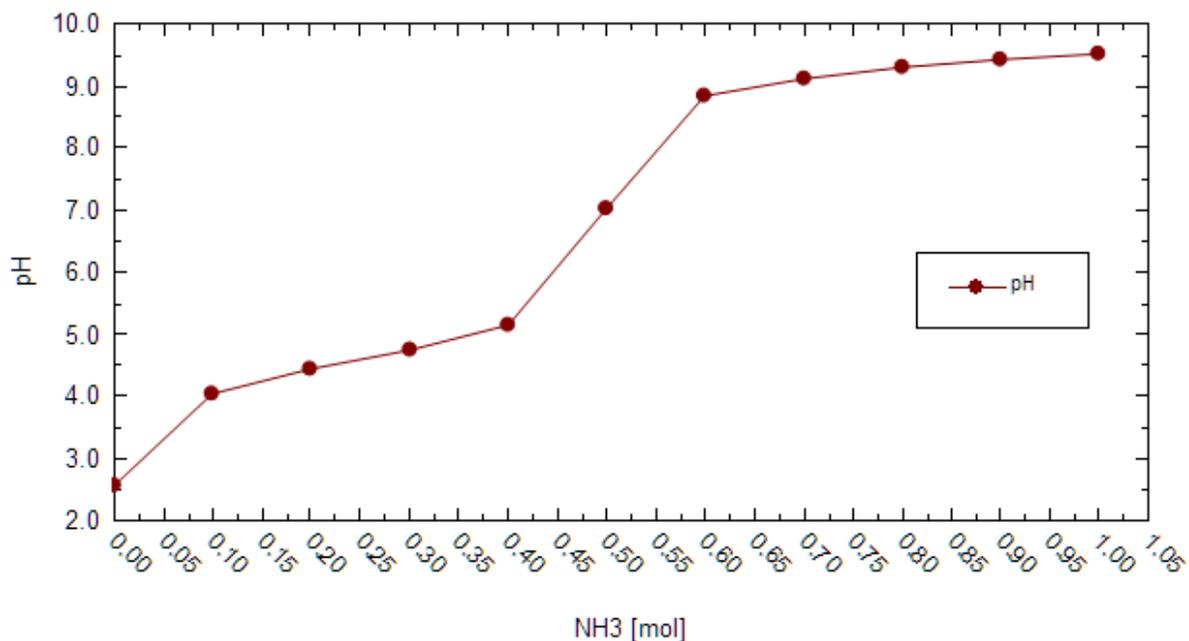


- ✓ Click on the Specs... button and highlight NH₃



- ✓ Close the window and Calculate
- ✓ View the plot

The resulting plot is a typical acid-base titration curve. The base composition is 0.5 m Acetic acid. NH₃ is added at 0.1 m increments up to 1 m. The inflection point for the titration is at 0.5 m, which is expected. Here, the independent variable is the molecular composition, and the dependent variable is the pH.



This composition survey differs from a standard laboratory titration in a significant way. This titration is pure NH_3 . By comparison, a laboratory titration would use a base titrant with a known strength e.g. 1 N. Also, size of the water sample is not considered in this calculation. The stream amount is 56.0082 moles, and this is because of the H_2O and HAc inflows. By comparison, the water sample of unknown or incomplete composition is added to the titration apparatus (e.g., 100 ml or 100 g of water sample) and the titration is performed on this.

A different approach to doing an acid-base titration/calculation is shown in the next case.

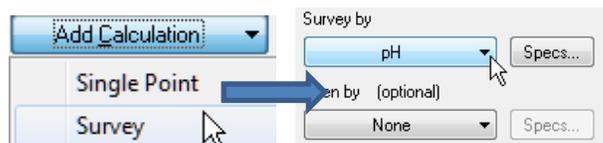
3.3 pH Survey – CO₂-NaOH-H₂O

This case is a follow-up to the previous case, and to the set-pH calculation performed in Chapter 2. In this survey calculation, a 1 molal CO₂ solution is titrated with HCl and NaOH. Instead of defining the amount of acid/base to add (as in the above case) the pH will be specified and the software will compute the amounts of HCl and NaOH needed.

Getting started

3.3 Bicarbonate Titration Composition					
Stream Name	Bicarbonate Titration	Stream Amount	Calculated	Inflows	
Name Style	Formula	Temperature	25 °C	CO ₂	0.001
Framework	Aqueous+	Pressure	1 atm		
Units Set	Default (moles)				

- ✓ Add a new stream  **Add Stream** and name it **Bicarbonate Titration** 
- ✓ Enter the inflows from the table above
- ✓ Add a Survey calculation and name it **Titrate CO₂**, and select Survey by pH.



The calculation can be run without modification. The default titrants are HCl and NaOH, and there is a default pH range: 0 to 14 by 1 pH.

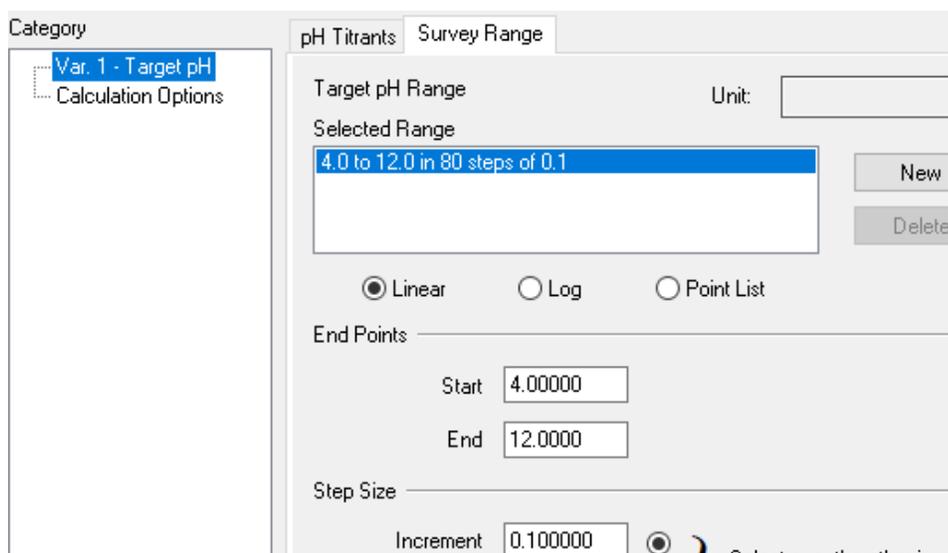
This pH range however is too broad for the carbonate system, in which most of the speciation occurs between pH=4 and 12.

- ✓ Click the Specs... button
- ✓ Select the Survey Range tab

- ✓ Change the Start, End, and Increment values using data from the table below

3.3 Survey Options	
Start	4
End	12
Increment	0.1

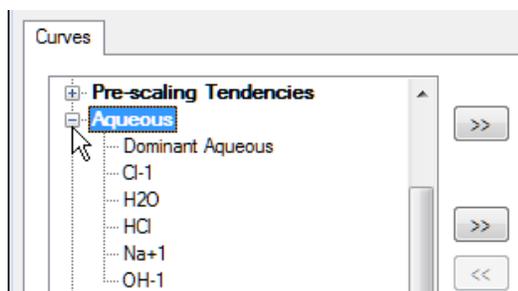
This will produce a survey with 81 points



- ✓ Press OK to exit the window
- ✓ Press the <F9> key or select the Calculate button
- ✓ Select the Plot tab

The default pH plot is the amount of acid and base titrant used. This is not the target variable and you will change it to display the carbonate-containing species.

- ✓ Select the Variables button
 - Click on the header to highlight all the variables then press the << button
- ✓ Expand the **Aqueous** Section on the left-side of the window



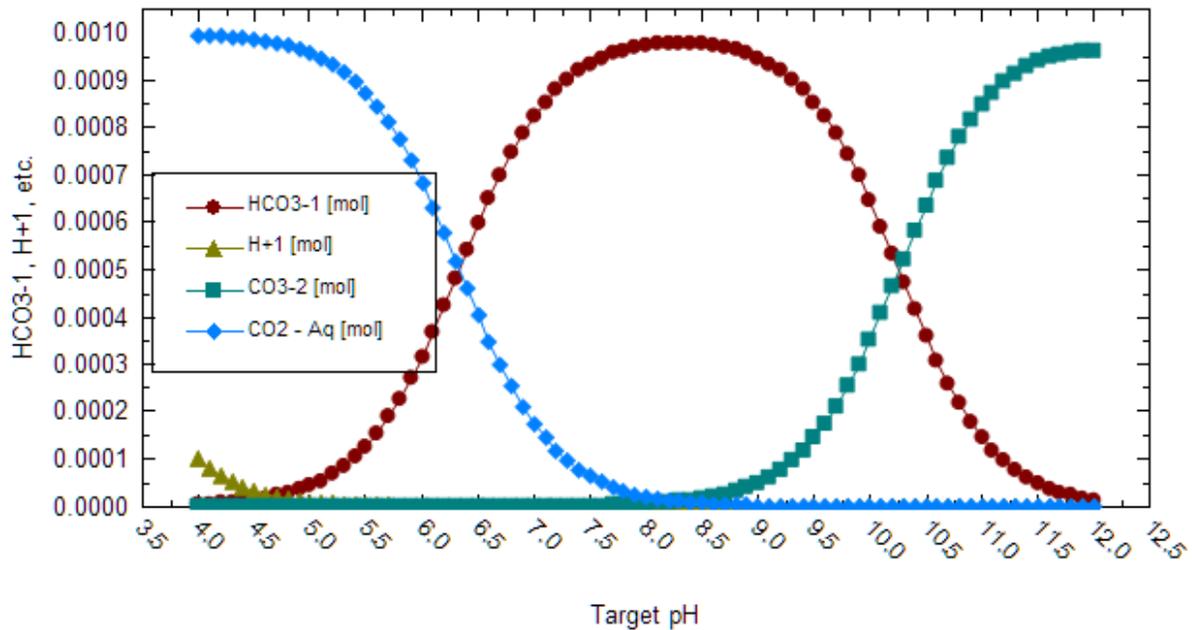
- ✓ Add the CO₂, HCO₃⁻¹, CO₃⁻², and H⁺ to the Y1 Axis window

The window should look like the image below.



✓ Press OK to close the window and view the plot

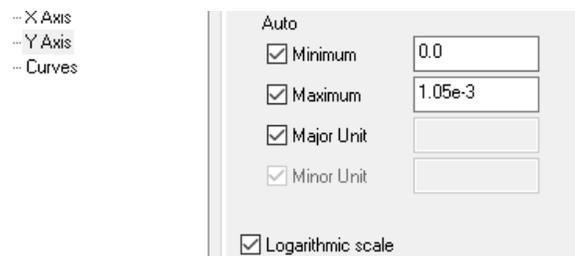
The plot below is a typical acid-base speciation plot displaying the important carbonate species. At low pH, CO_2, aq is the dominant species, as pH increases it converts to HCO_3^{-1} which is the dominant species at ~ 8.3 pH. At higher pH, ~ 12 the CO_3^{-2} species dominates.



You will next review the plot on a semi-log scale.

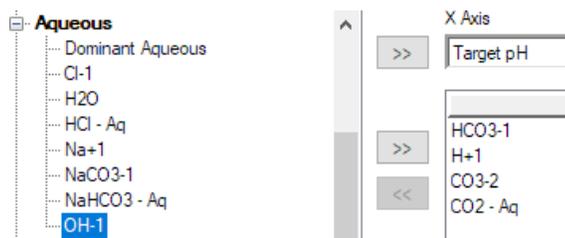
- ✓ Select the Options button 
- ✓ Select Y Axis in the Category window
- ✓ Click on the Logarithmic scale box

The window should look like the following.



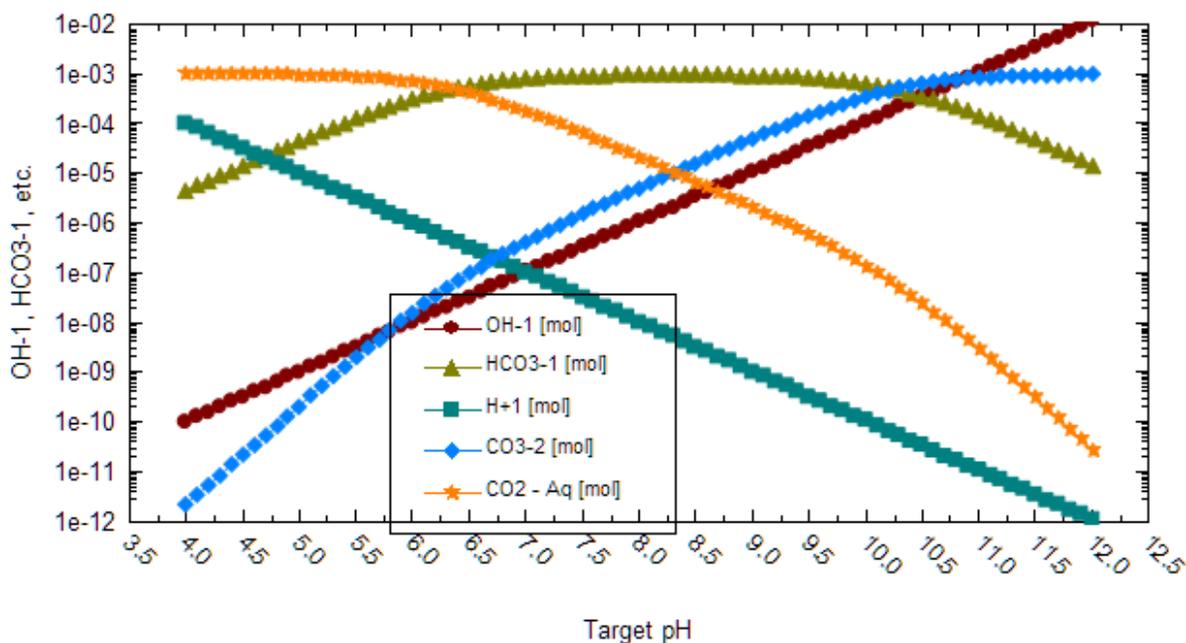
✓ Press OK to close the window

- ✓ Before viewing the plot, add the OH-1 species to the plot
 - Click the Variables window, expand the Aqueous category and add OH-1



- ✓ Close the Variables window and view the plot

This is a busy but useful plot. It contains the acid-base products for the Carbonate and water system. The H^+ and OH^{-1} curves are linear, and have a $\frac{mole}{pH}$ slope of -1 and 1, respectively. Note also between 6 and 10 pH, where HCO_3^{-1} dominates the speciation, the CO_2 and CO_3^{-2} $\frac{mole}{pH}$ slopes are also -1 and 1.



At lower pH, where CO_2 dominates the system, the HCO_3^{-1} slope is 1 and the CO_3^{-2} slope is 2. Likewise, in the pH region where CO_3^{-2} dominates, the HCO_3^{-1} slope is -1 and the CO_2, aq slope is -2. These $\frac{mole}{pH}$ slopes are based on the number of H^+ ions added or removed in that chemical reaction.

Note the pH where the CO_2, aq and HCO_3^{-1} lines intersect ($pH \cong 6.3$), and where the HCO_3^{-1} and CO_3^{-2} lines intersect ($pH \cong 10.3$). These pH values are the same as the pK_a values (the equilibrium equations for that reaction).

- ✓ Look at the curves above 11 pH

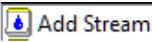
As NaOH is added to convert HCO_3^{-} to CO_3^{-2} , a portion of the NaOH remains as free base, OH^{-1} . This fraction increases at higher pH's, and its concentration is reflected in the calculated pH. A similar pattern is seen at pH below ~ 3 for HCl and H^+ . This increasing H^+ is the pH.

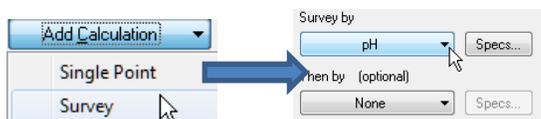
3.4 pH Survey – Transition Metals

We just computed the pH curve of a weak protic- or Bronsted-Lowry acid. We will now look at the titration curve of a Lewis acid. The acidity of Lewis acids results from the donation of electrons from another molecule to the acid. Transition metals are typical Lewis acids; they react with H₂O to form metal-hydroxide complexes. This reaction splits or hydrolyzes the water, resulting in released H⁺. In this example, we will follow the reactions between nickel and H₂O, and see how the reactions change as acidity changes.

Getting started

3.4 Nickel Speciation Composition					
Stream Name	Nickel Speciation	Stream Amount	Calculated	Inflows (mol)	
Name Style	Formula	Temperature	25 °C	NiOH2	0.02
Framework	Aqueous+	Pressure	1 atm		
Units Set	Default (moles)				

- ✓ Add a new stream  and rename it 'Nickel Speciation' - 
- ✓ Enter the Inflows from the table above
- ✓ Add a Survey calculation then change the type to pH



- ✓ Click the Specs button

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5282
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Target pH	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Inflows (mol)	
H2O	55.5082
Ni(OH)2	0.0200000

Survey by: pH
Then by (optional): None
Vary: Independently Together
Calculate 

Summary
pH survey:
Acid - HCLIN
Base - NAOHIN
Range 0.0 to 14.0
Step size 0.25
No. steps 56

- ✓ Select the Survey Range tab
- ✓ Change the Start, End, and Increment values using the table below

3.4 Survey Options	
Start	0
End	14
Increment	0.25

The survey will contain 56 individual calculations.

Selected Range
 0.0 to 14.0 in 56 steps of 0.25

New
 Delete

Linear Log Point List

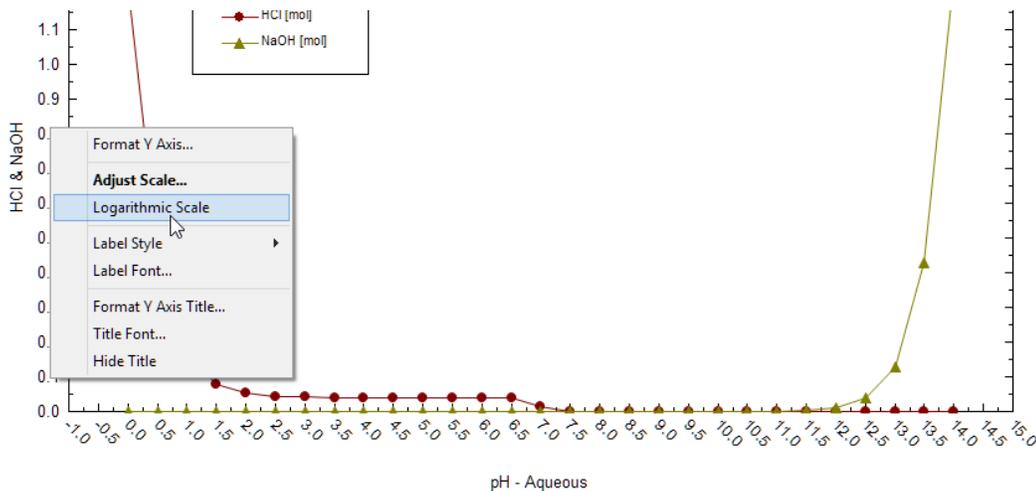
End Points
 Start: 0.0
 End: 14.0000

Step Size
 Increment: 0.250000 } Select one, the other is calculated
 Number Steps: 56

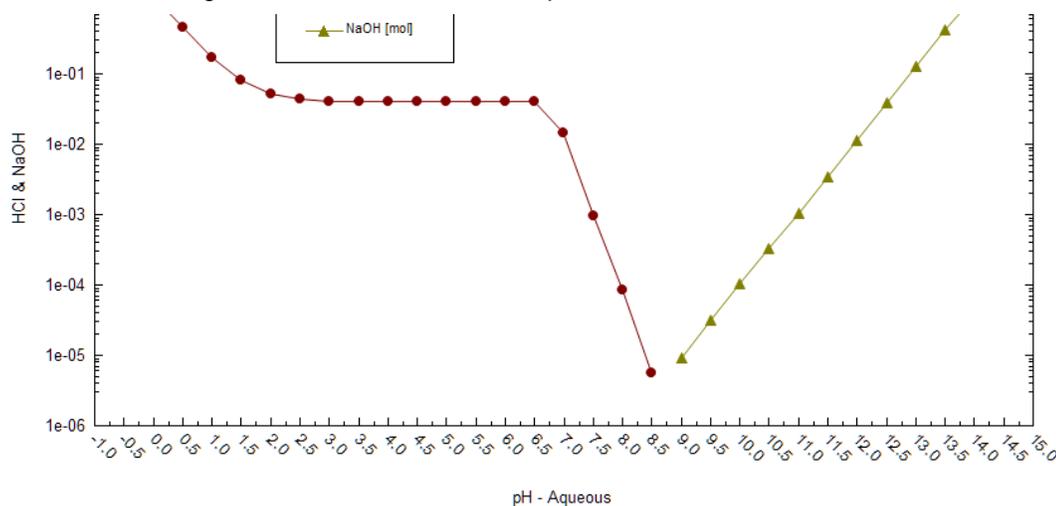
- ✓ Press OK
- ✓ Calculate then select the Plot tab

For this and many other calculations, the y-axis values extend over a very large range of numbers. The default linear axis may not capture all the required details, so we will switch to a logarithmic scale.

- ✓ Right-mouse click a number along the Y-Axis



- ✓ Select the Logarithmic Scale and view the plot



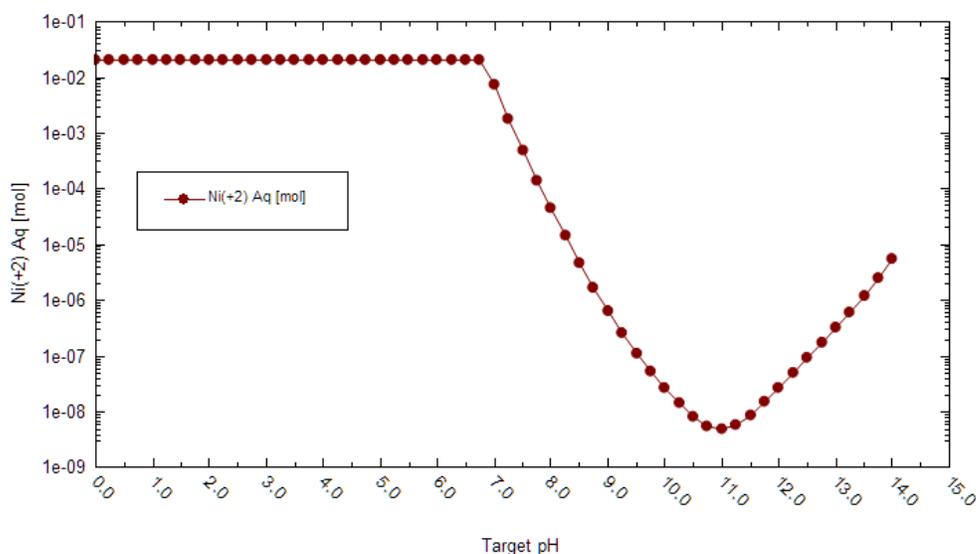
The next step is to change the viewing variables. This case focuses on nickel speciation vs. pH. Therefore, the focus variables will be the total dissolved nickel and the nickel species/complexes.

- ✓ Click the Variables button
- ✓ Remove all variables from the Y1 axis
- ✓ Expand the **MBG Aqueous Totals** category
- ✓ Add Ni(+2) to the Y1 Axis



MBG is an abbreviation for Material Balance Groups and shows the species' sum in a phase. The curve below is the sum of all dissolved nickel species.

- ✓ Press OK then view the plot

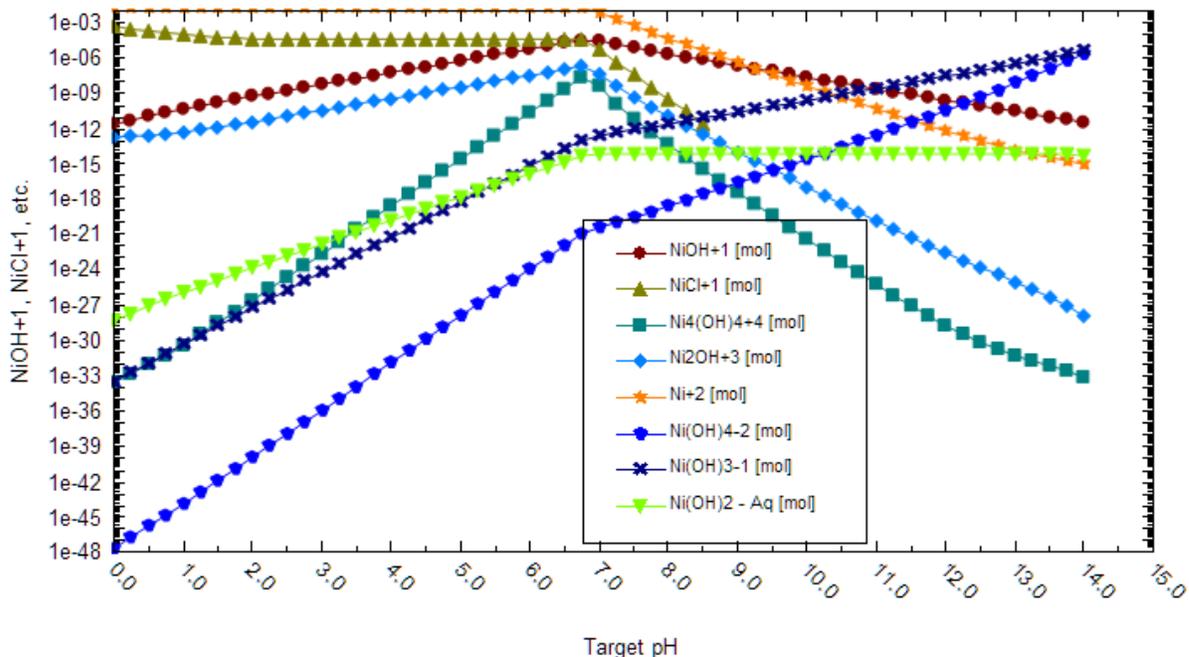


Total dissolved nickel decreases by about six orders-of-magnitude between 7 and 11 pH. The cause is the formation of an insoluble Ni(OH)₂ solid phase.

- ✓ Open the variables window again and expand the Aqueous category
- ✓ Add the Ni-containing species to the Y1 Axis.

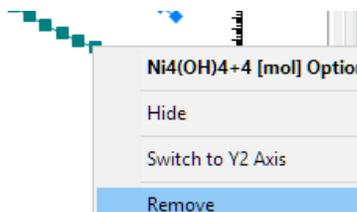
Aqueous Category		Y1 Axis
	Ni(OH) ₂	
	Ni(OH) ₃₋₁	
	Ni(OH) ₄₋₂	
	Ni ⁺²	
	Ni ₂ OH ₃	
	Ni ₄ (OH) ₄₊₁	
	NiCl ⁺	
	NiOH ₁	

- ✓ Press OK when done

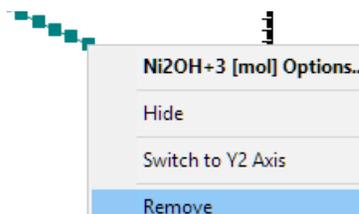


The y-axis scale is 45-orders of magnitude in concentration. Several of these species do not exceed 10^{-6} mol/kg water, and can be removed without compromising the interpretation. Removing variables is accomplishable from the plot view, by using the Right-Mouse-Click option.

- ✓ Right-mouse-click anywhere along the $\text{Ni}_4(\text{OH})_4+4$ curve – select Remove

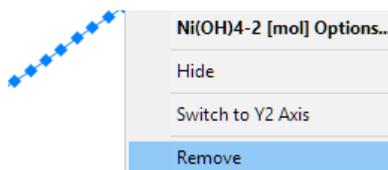


- ✓ Right-mouse-click anywhere along the $\text{Ni}_2\text{OH}+3$ curve – select Remove



The $\text{Ni}(\text{OH})_4-2$ species covers nearly 40-orders of magnitude concentration between 0 and 14 pH. It is important at very high pH, but is largely irrelevant at neutral pH, and so it will be removed.

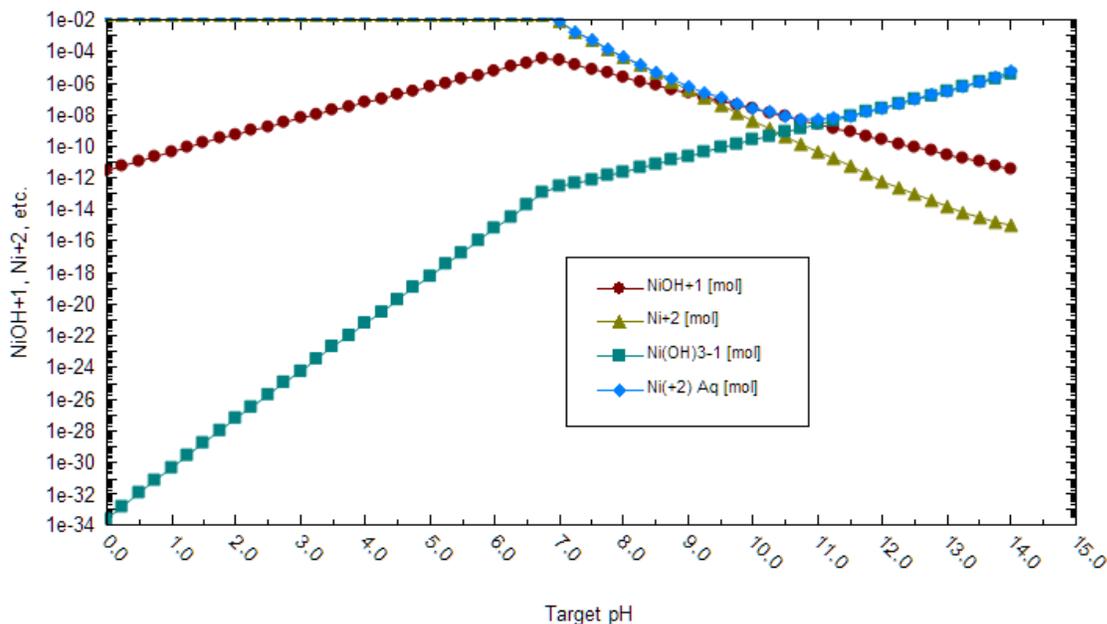
- ✓ Right-mouse-click anywhere along the $\text{Ni}(\text{OH})_4-2$ curve – select Remove



Lastly, the $\text{NiCl}+1$ and the $\text{Ni}(\text{OH})_2,\text{aq}$ species are also of limited significance within the pH region where they are important. $\text{NiCl}+1$ is present at low pH, as HCl is added to reduce the pH. However, it is small relative to the $\text{Ni}+2$ species, by about four-orders of magnitude. The $\text{Ni}(\text{OH})_2$ phase is also several order-of-magnitude less abundant than the several species at the moderate pH.

- ✓ Remove the $\text{NiCl}+1$ and the $\text{Ni}(\text{OH})_2,\text{aq}$ species from the plot

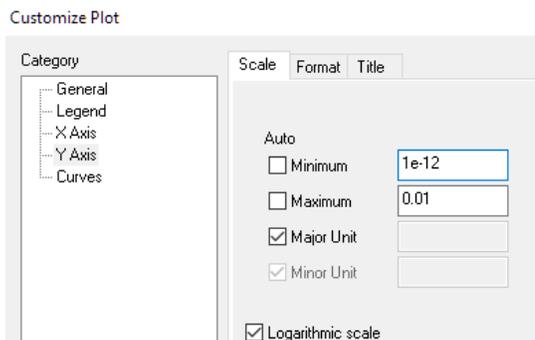
The remaining plot contains three aqueous species plus the total dissolved nickel. Each of the dissolved species parallel the total dissolve nickel curve in certain pH ranges. It is the stability of these species in fact that set the nickel solubility in water.



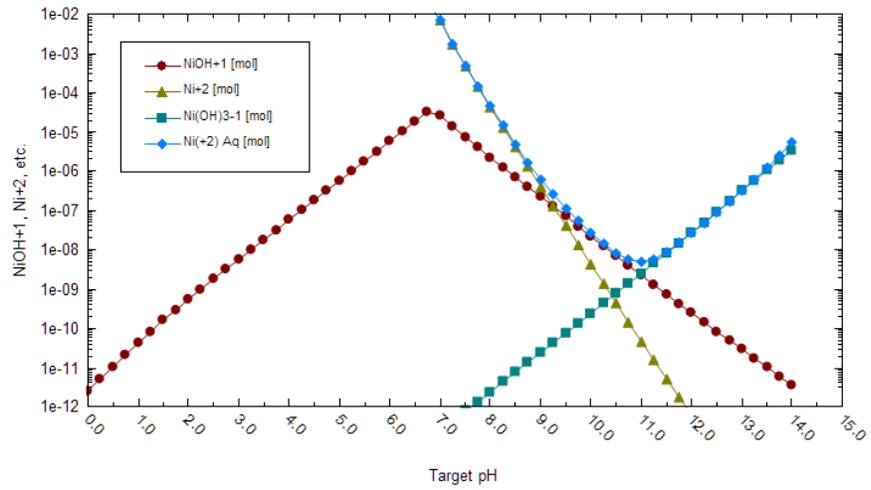
Below 9 pH, the dominant species is $\text{Ni}+2$. Its stability in water defines the overall nickel solubility in this region. Between 9 and 11 pH, the $\text{NiOH}+1$ species dominates, and it is this species that defines the total dissolved nickel. Lastly, the $\text{Ni}(\text{OH})_3-1$ species controls nickel solubility above 11 pH.

It is possible to focus on the upper region of the plot so that the y-axis scale is smaller. This is done in the Options window.

- ✓ Select the Options button 
- ✓ Click the Y Axis category and change the minimum value to $1\text{e-}12$



- ✓ Press OK to view the plot



The values of the final four variables in the dominant concentration region can now be viewed more clearly.

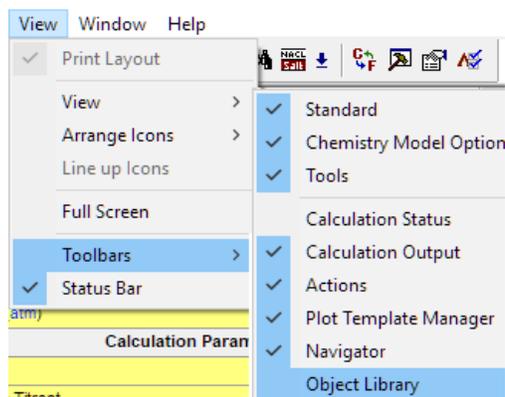
3.5 Vapor Fraction survey – Seawater evaporation

This next application is as interesting for the chemistry it computes as it is for the capability of the tool. It is a vapor fraction survey calculation. The purpose of this calculation type is to set a specific fraction of the stream to the vapor phase, and compute the temperature or pressure required to achieve that state. This application was explained in Chapter 2, as a single point, but now it will be done as a survey.

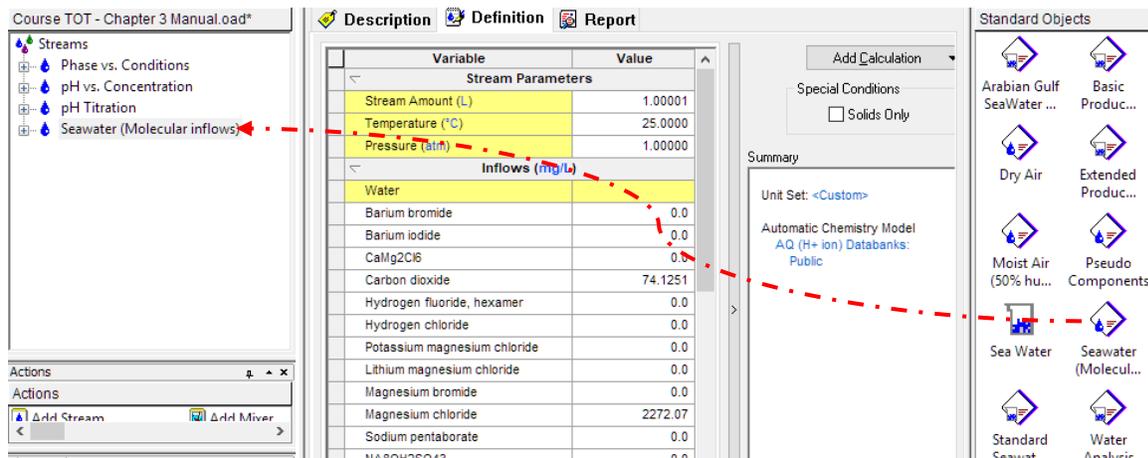
You will evaporate seawater to dryness and look at the solids that form. What is interesting is the number of phases that can be produced when seawater evaporates, giving you a sense of how certain natural systems build up sediment of a particular nature.

Getting started

- ✓ Open the Object Library window – from the menu, View>toolbar>Object Library



- ✓ Drag the Seawater (Molecular inflows) stream to the navigation panel (drag it to either the top-level stream or in the white-space below the other streams and calculation objects).



- ✓ Add a Survey calculation
- ✓ Change the calculation type to Vapor Fraction
- ✓ Click on the Specs... button
 - change the survey End to 0.95
 - Change the increment to 0.05

Category

Var. 1 - Vapor Fraction (Vapo
Calculation Type
Calculation Options

Survey Range

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

Selected Range
0.0 to 0.95 in 19 steps of 0.05

New
Delete

Linear Log Point List

End Points

Start 0.0

End 0.950000

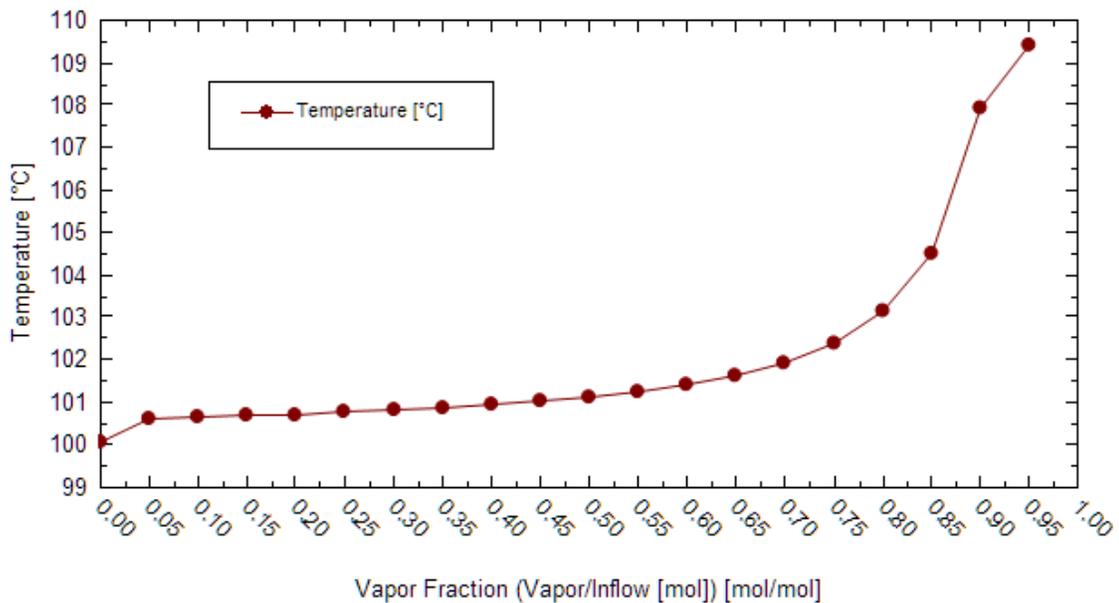
Step Size

Increment 0.0500000 } Select one, the other is calculated

Number Steps 19

- ✓ Calculate
- ✓ View the plot

The default Vapor Fraction plot is the dependent variable, Temperature. It shows that seawater boils initially at 100 C, and at near complete evaporation (95%) the temperature is 109.4 C.

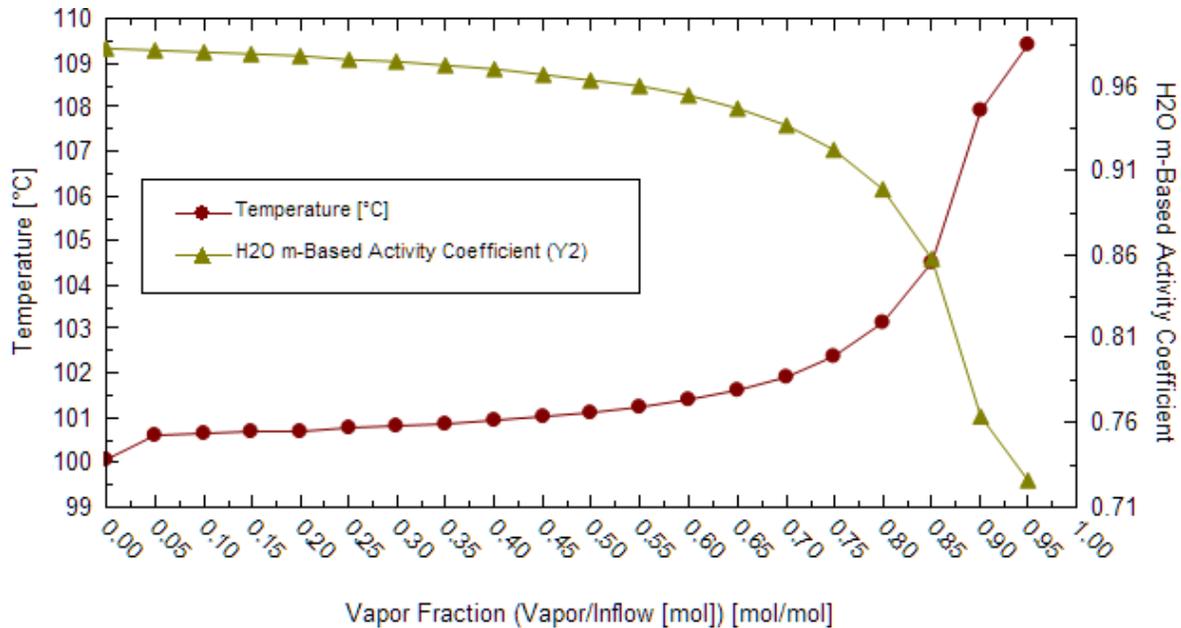


The reason for the boiling point rise, is the salinity effects on the water (water activity). As more ions fill the intermolecular spaces between the water solvent, the charges attract the negative or positive region of the water molecule, holding it tighter in the liquid phase. This effect on the boiling point is seen in the water activity property.

- ✓ Click on the Variables button.
- ✓ Expand the Activity Coefficients – Aqueous (m-based) category
- ✓ Add H2O to the Y2 axis

Y2 Axis
H2O m-Based Activity Coefficient

✓ Close the window and view the plot

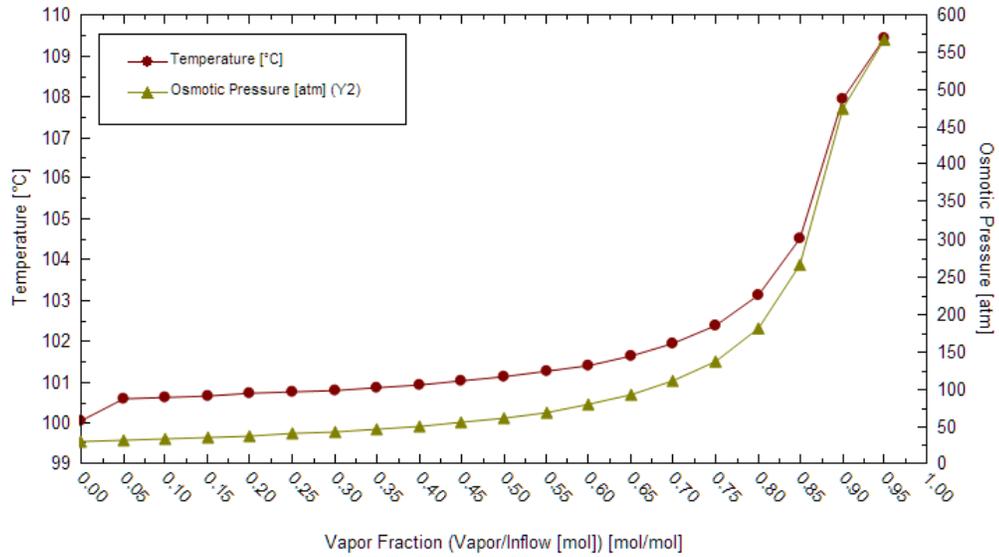


The boiling temperature and the water activity curves are mirror images, which is not coincidental. At standard pressure, 100% of pure water boils at 100 C, there is no vapor-fraction curve (a pure component has a single boiling point).

Dissolved ions like salts have the net effect of expanding the boiling point range from a single point to a curve. Ions interfere with the inter-molecular attractive and repulsive forces that exist in pure water. These disrupted and modified forces in turn change water's properties, like boiling point. The impact is concentration-dependent. The twenty points in the plot above are the water boiling point at different salt concentrations. As the vapor fraction increase, the salt concentration in the remaining water increases. This increase in dissolved salt causes the increase in boiling point temperature.

Another variable, labeled Osmotic pressure (Π) is also related to the water activity and boiling point rise.

- ✓ Reopen the Variables window.
- ✓ Remove the Activity coefficient from the Y2 axis
- ✓ Expand the Thermodynamic Properties category and add Osmotic Pressure to the Y2 Axis



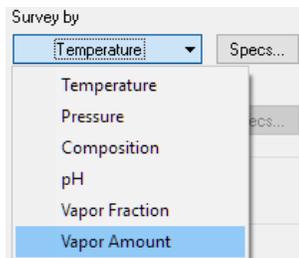
A similar relationship is seen between boiling point temperature and osmotic pressure. Osmotic Pressure is computed from the dissolved ion concentration, and so this plot is also not coincidental. This variable is commonly reported when evaluating or designing the performance of reverse osmosis membranes. This osmotic pressure is essentially the pump pressure required on the saline side of the membrane to force water through the membrane to the pure water side.

Chapter 3 Survey Calculations

Introduction

Survey calculations are single point calculations strung together in series. They are also referred to as multiple point calculations. These calculations allow the user to designate as independent either one or two variables. The resulting plots are then used to interpret the calculation results.

The independent survey variables are listed below:



This chapter contains instructions on how to perform the following survey calculations

3b.1 Temperature and Pressure Survey	2
3b.2 pH and Composition Survey – Ni(OH) ₂ -NaCN-H ₂ O (strong complexation).....	7
3b.3 Vapor Fraction-Pressure survey – Dead Sea water	11

3b.1 Temperature-Pressure Survey

In this example, 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 a few ways.

This example is

Getting Started

- ✓ Create a new Stream, and name it Dual Survey
- ✓ Change the units to Metric-Batch-Mass
- ✓ Add NH3 and N2 to the grid
- ✓ Add a Survey Calculation and name it NH3-N2-H2O T/P Survey
- ✓ Enter the following composition

H2O	1000	g
NH3	10	g
N2	100	g

- ✓ Change the Then by survey type from None to Pressure

Survey by
Temperature ▼ Specs...

Then by (optional)
Pressure ▼ Specs...

- ✓ Calculate

The default temperature survey is 25 to 100 C by 5 C increments. Likewise, the default Pressure survey is 1 to 10 atm by 1 atm increments. This produces a 160-point matrix.

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

- ✓ View Plot

The default plot is the mass of four potential phases. This is not the plot that will be useful to review.

- ✓ Click on the Variables button and remove the Y1 Axis variables
- ✓ Expand the Vapor category and add NH3 to the Y1 Axis

Vapor

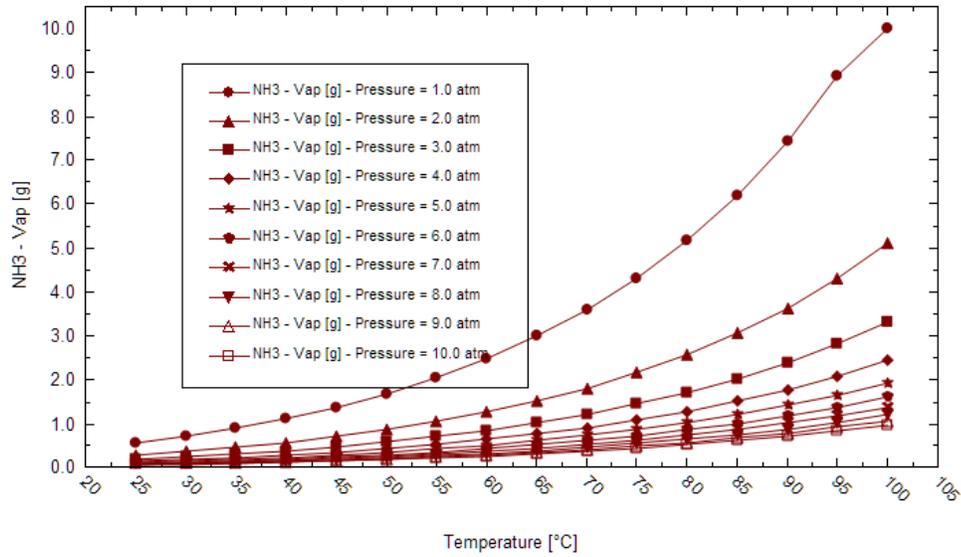
- Dominant Vapor
- H2O - Vap
- NH3 - Vap

Solid

Y1 Axis

NH3 - Vap

The resulting plot is the NH₃ mass partitioned to the vapor phase. It can be expected, that at lower pressures and higher temperatures more NH₃ is vaporized. At 1 atm and 100 C, all 10 g of NH₃ is vaporized. (it is also certain that all the H₂O is vaporized, and this can be checked as well).



- ✓ Return to the Definition tab
- ✓ Open the first Specs... window
- ✓ Change the Start to 0 C and the increment to 2 C

End Points

Start

End

Step Size

Increment } Select one, the other is calculated

Number Steps

- ✓ Click on the Var. 2 Pressure Category

Category

- Var. 1 - Temperature
- Var. 2 - Pressure**
- Calculation Type
- Calculation Options

- ✓ Change the increment to 0.2 atm

End Points

Start

End

Step Size

Increment } Select one, the other is calculated

Number Steps

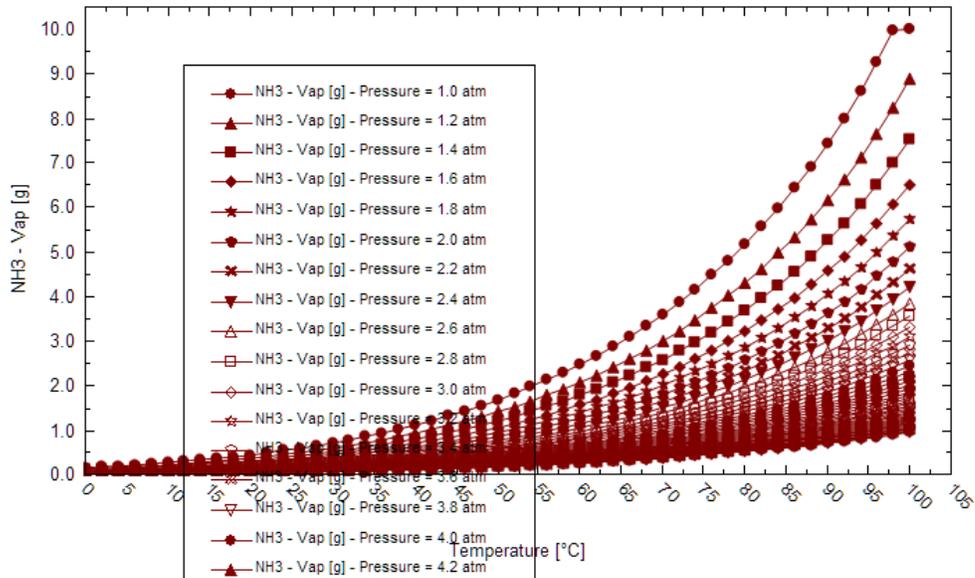
- ✓ Calculate

There are now 2346 calculation points.

Primary and secondary survey variables
move independently
Total points: 2346

- ✓ View the Plot

There are now forty-six curves on the plot, and if you attempt to resize the Legend, it will cover the complete plot area.

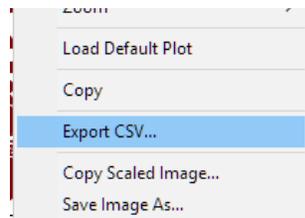


This amount of data may be important and so reducing the total number of points may be a diminishing compromise. Therefore, alternative viewing and data options are embedded into the plot. You will look at three options here.

These next options require that a spreadsheet tool exist in your computer.

Save as CSV

- ✓ Right-mouse-click on the Plot. Select Export CSV..



- ✓ Save the file and open it in a spreadsheet software

	A	B	C	D	E	F	G	H
1	Temperat	NH3 - Vap	NH3 - V					
2	0	0.153101	0.127889	0.109846	0.096295	0.085744	0.077296	0.0703
3	2	0.171879	0.143587	0.123336	0.108124	0.096279	0.086794	0.0790
4	4	0.192581	0.160896	0.138212	0.121117	0.107897	0.097269	0.0885
5	6	0.215361	0.179946	0.154585	0.135529	0.120688	0.108801	0.0990
6	8	0.240383	0.200873	0.172574	0.151308	0.134742	0.121474	0.1106
7	10	0.267817	0.223823	0.192304	0.168614	0.150159	0.135375	0.1232
8	12	0.297846	0.248947	0.213907	0.187565	0.167041	0.150598	0.137
9	14	0.330661	0.276407	0.23752	0.208281	0.185497	0.167242	0.1522
10	16	0.366461	0.306371	0.26329	0.230892	0.205641	0.185409	0.1688
11	18	0.405456	0.339015	0.291368	0.25553	0.227594	0.205207	0.1868

Copy-Paste from plot

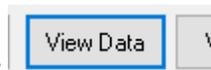
- ✓ Click on the plot area
- ✓ Press Control-C (standard Windows copy)
- ✓ Open a spreadsheet (or word document)
- ✓ Press Control-V

As with the CSV export, the copy-paste from plot option transfers a data matrix to the receiving software.

	A	B	C
1	Temperat	NH3 - Vap	NH3 -
2	0	0.153101	0.127
3	2	0.171879	0.143
4	4	0.192581	0.160
5	6	0.215361	0.179
6	8	0.240383	0.200
7	10	0.267817	0.223
8	12	0.297846	0.248

Viewing and copying from the View Data table

- ✓ Click on the View Data button in the upper right of the plot -



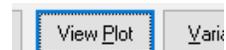
The table shown is the Array form of the data. This table contains 2346 rows, sorted by Pressure and then Temperature. This table can be copied entirely, by clicking on the upper-left gray cell, or by clicking on specific columns and rows and then using the Copy function.

	Temperature	Pressure	NH3 - Vap
	°C	atm	g
1	0.0	1.00000	0.153101
2	2.00000	1.00000	0.171879
3	4.00000	1.00000	0.192581
4	6.00000	1.00000	0.215361
5	8.00000	1.00000	0.240383
6	10.0000	1.00000	0.267817
7	12.0000	1.00000	0.297846

	Temperature	Pressure	NH3 - Vap
	°C	atm	g
1	0.0	1.00000	0.153101
2	2.00000	1.00000	0.171879
3	4.00000	1.00000	0.192581
4	6.00000	1.00000	0.215361
5	8.00000	1.00000	0.240383
6	10.0000	1.00000	0.267817
7	12.0000	1.00000	0.297846

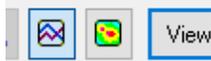
Viewing a (Pixilated) Contour diagram

- ✓ Return to the plot by clicking on the View Plot button in the upper right -

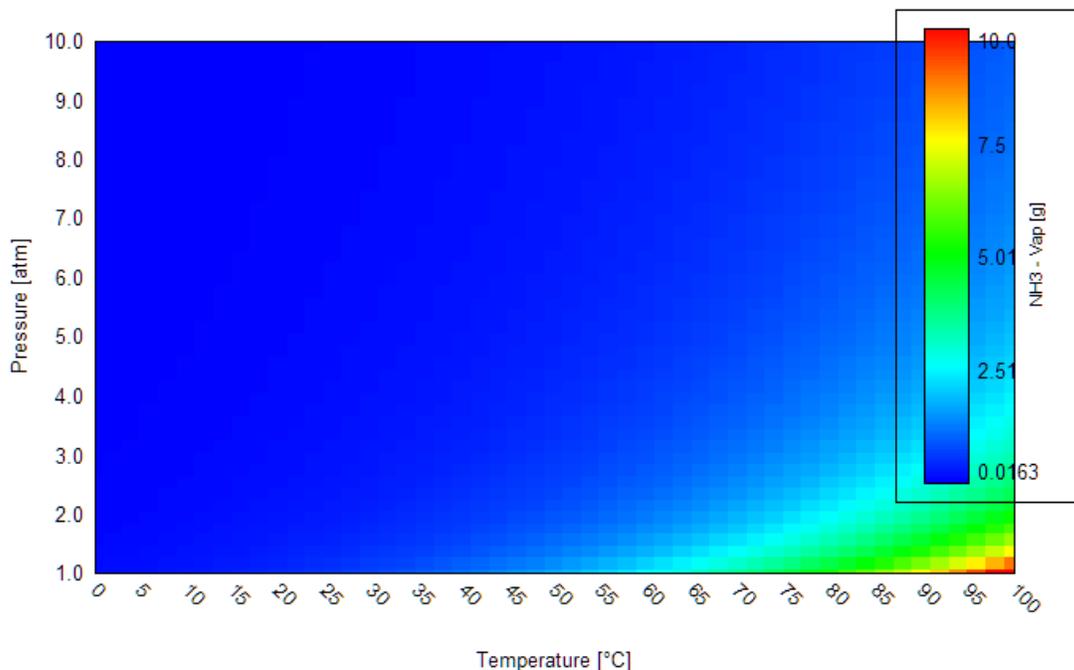


Switching to the plot is not necessary but it makes the plot easier for initial users.

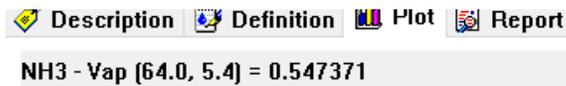
✓ Click on the colored Contour button adjacent to the View Data (or View Plot) button -



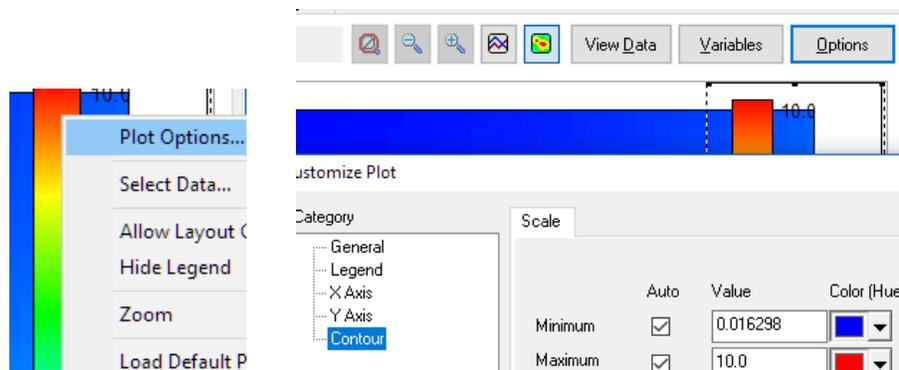
The resulting plot is now a pixelated color plot showing the NH₃ vapor mass at each T and P value. The amount is characterized by a different color that is shown in the legend.



You can mouse over any location in the plot and the value will be shown in the marquee.



The legend scale can also be optimized by either right-mouse-clicking on the Legend and selecting Plot Options 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.



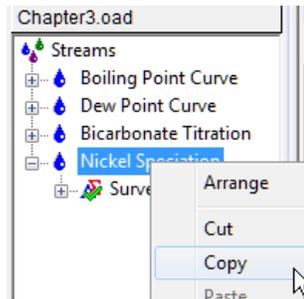
With respect to the calculation results, 10 g NH₃ is in the system. This 10 g is in the vapor phase at 1 atm and 100 C. Mouse over the lowermost right point to confirm this. Most of the plot is shaded blue, which is less than 1 g NH₃ in the vapor.

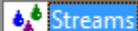
3b.2 pH-Composition Survey – Ni(OH)₂-NaCN-H₂O (strong complexation)

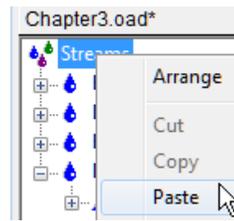
Overview

In this example, we will add a complexing factor, cyanide, to the previous survey and stream. Cyanide is a strong electron donor and therefore competes with H₂O to complex with transition metals. We want to know how much cyanide the system can take before we look for alternative separation methods.

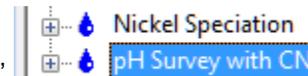
- ✓ In the Navigator pane, right-mouse click the Nickel Speciation stream
- ✓ Select copy from the drop-down list



- ✓ Right mouse click the Global Streams icon  then select paste



- ✓ Change the name of the new stream to 'pH Survey with CN'
- ✓ Select the Definition tab
- ✓ In the Inflows grid, enter HCN

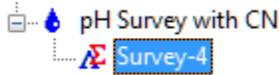


HCN is a convenient way for us to add cyanide. We could have also used NaCN.

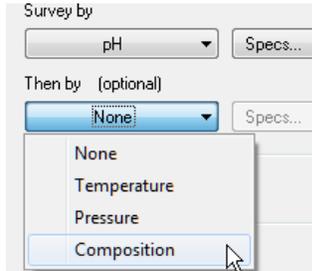
pH Survey with CN		
Description	Definition	Report
Variable	Value	
Stream Parameters		
Stream Amount (mol)	55.5282	
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
Inflows (mol)		
H ₂ O	55.5082	
Ni(OH) ₂	0.0200000	
NaOH	0.0	
HCl	0.0	
HCN	0.0	

When we copied the stream, we also copied the survey. Since the first survey calculation in this example uses most of the same parameters as the previous survey, we will not need to add a new survey.

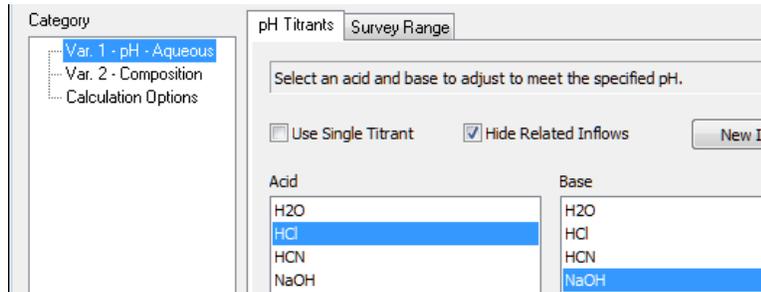
- ✓ In the Navigator, select the survey for the pH Survey with CN stream



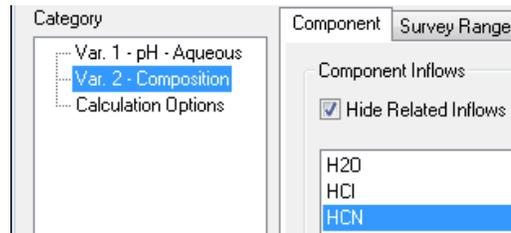
- ✓ On the top right of the Definition tab, use the Then by dropdown list to select Composition



- ✓ Select the top Specs button
- ✓ Select Var. 1 – pH and make sure the acid is HCl and the base is NaOH

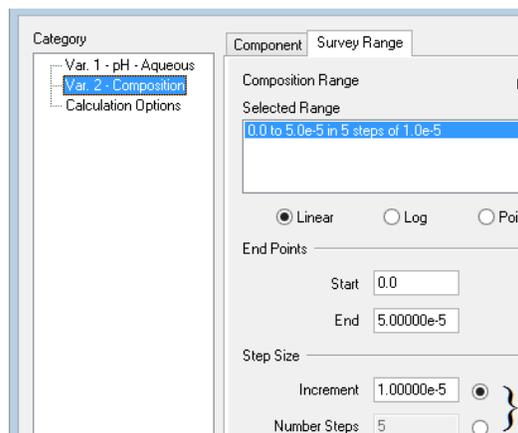


- ✓ Select Var. 2 – Composition and highlight HCN in the Component List

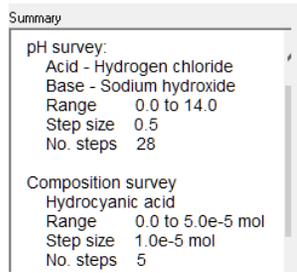


- ✓ Select the Survey Range tab change the end points according to the following:

3.5 Var. 2 Survey Range	
Start	0.0
End	5e-5
Increment	1e-5



- ✓ Press OK to then Calculate
- ✓ View the Summary box

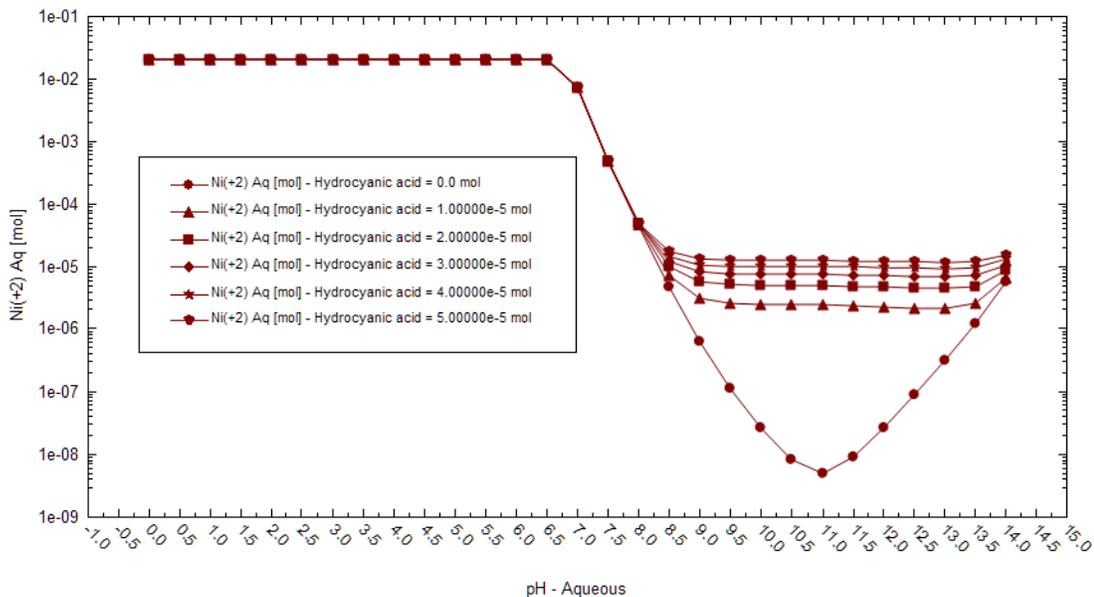


The Summary indicates that the survey will have 28 pH calculations with 5 composition calculations each, for 174 single-point calculations.

- ✓ Select the Plot tab
- ✓ Right-mouse click a point along the Y1 Axis then select the Logarithmic Scale
- ✓ Select the Variables button
- ✓ Select the Y1 Axis header to highlight all the variables then press the << button
- ✓ Expand the **MBG Aqueous Totals** category and double-click NI+2 to add it to the Y1 axis



- ✓ Press OK when finished then save the file



The plot contains six curves, one for each HCN concentration. We can see the original MBG Aqueous nickel curve when HCN is at 0.0 mol. The other curves show the HCN impact on nickel solubility. The Ni²⁺ content is 4.9e-5 mol at 8pH or about 10,000 times higher than the minimum concentration in the absence of cyanide. Since the atomic weight of nickel is 58670mg/mol, the minimum solubility is 2.42 mg/kg (or ppm). Even when CN⁻¹ is at a low concentration of 10ppm, the system is unable to maintain the soluble Ni requirements. Why is this?

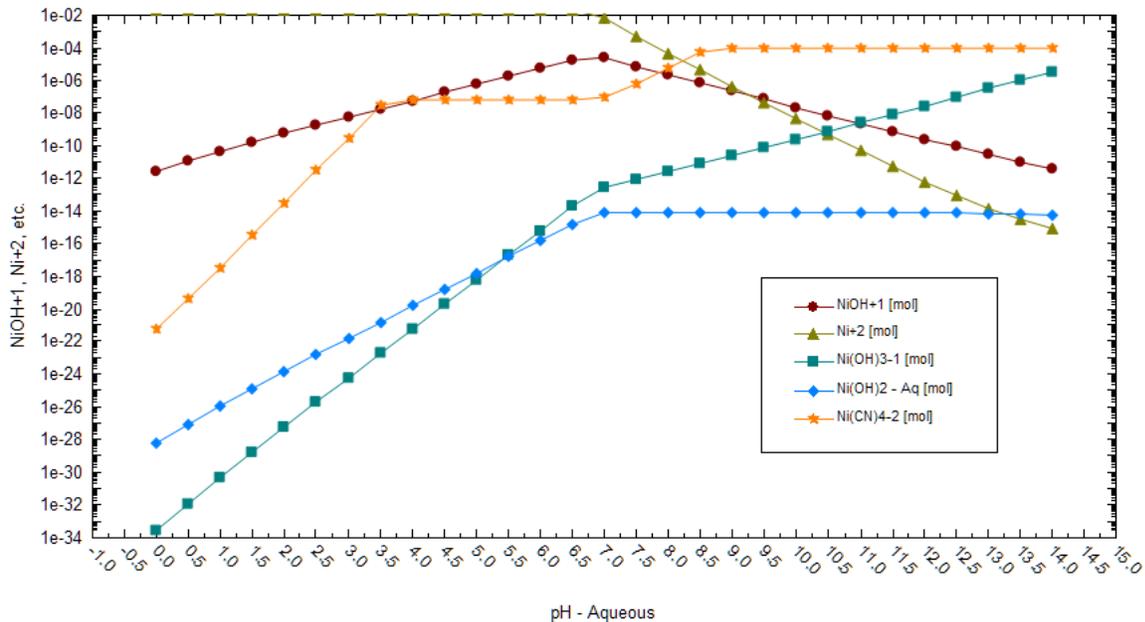
Optional Steps

The following steps are optional:

- ✓ Copy and paste the pH Survey with CN stream
- ✓ Change the HCN concentration from 0.0 to 3.7e-4 mol
- ✓ In the Navigator panel, expand the stream then select the survey
- ✓ Change the survey Then by option from Composition to None
- ✓ Press <F9> to calculate then select the Plot tab then the Curves button
- ✓ Select the Y1 Axis header to highlight all the variables then press the << button
- ✓ Expand the **Aqueous** category then add the following components to the Y1 Axis

Ni(OH)2	Ni(OH)3-1	Ni(CN)4-2	Ni+2	NiOH+1
---------	-----------	-----------	------	--------

- ✓ Press OK then right mouse click on the Y1 Axis and select the Logarithmic Scale



Considerations

In the presence of CN^{-1} and above 7.5 pH, the dominant aqueous species is $\text{Ni}(\text{CN})_4^{-2}$. This very stable complex increases overall Ni solubility by 10,000 times. Given this stability, we can estimate Ni solubility by knowing how much CN we add. The atomic weight of Ni is 58.67; the CN formula weight is 26.02. The complex $\text{Ni}(\text{CN})_4^{-2}$ is comprised of 58.67 g Ni and 104.08 g CN. That means for every 10ppm CN in solution, up to 5.64ppm Ni dissolves. If CN concentrations exceed a few ppm, the plant will never be able to maintain Ni content below 1 ppm. Let us assume that 10ppm CN is entering the stream and there is no way to stop it. We will need some new ideas to remove nickel to below 1ppm.

3b.3 Vapor Fraction-Pressure survey – Dead Sea water

The purpose of this example is to show how boiling / evaporating water from brines at different temperatures can affect the product solids that form. Dead Sea water is a hypersaline solution of sodium, potassium, magnesium, chloride and bromide. These elements form temperature-dependent double-salt and hydrated solids. As a result, evaporating Dead Sea water at low temperature (under a vacuum) will produce a different set of minerals than evaporation at atmospheric pressure.

Getting Started

The table below is the Dead Sea water composition in molecular form. These molecular inflows do not represent any specific phases. Rather these combinations of elements at their specific oxidation are an efficient way to create a system composition.

Dead Sea water					
Stream Name	Dead Sea Water	H2O	890.27	KCl	14.59
Name Style	Formula	SiO2	0.02	MgCl2	172.36
Framework	MSE (H3O+)	B2O3	0.158	NaBr	6.82
Units Set	Metric-Batch-Mass	CaCl2	47.49	NaCl	95.27
Temperature	40 °C	CaO	0.066	SO3	0.067
		CO2	0.034	CaCO3	0.0086

- ✓ Create a new Stream object and name it Dead Sea Water
- ✓ Enter the composition from the table

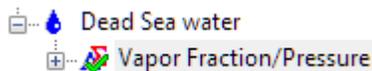
When completed, the grid should look like the image below.

Variable	Value
Stream Parameters	
Stream Amount (g)	1227.15
Temperature (°C)	40.0000
Pressure (atm)	1.00000

Inflows (g)	
H2O	890.270
SiO2	0.0200000
B2O3	0.158000
CaCl2	47.4900
CaO	0.0660000
CO2	0.0340000
KCl	14.5900
MgCl2	172.360
NaBr	6.82000
NaCl	95.2700
SO3	0.0670000
CaCO3	8.60000e-3

The next step is to create the Vapor Fraction survey with the secondary Pressure survey. The following are the specifications that will be used

- ✓ Add a Survey calculation and label it Vapor Fraction / Pressure



- ✓ Change the First Survey option to Vapor Fraction
- ✓ Set the Then by (Optional) to Pressure

Survey by

Vapor Fraction ▾ Specs...

Then by (optional)

Pressure ▾ Specs...

Vary

Independently

Together

- ✓ Click on the first Specs... button
- ✓ Change the Start vapor fraction to 5 %
- ✓ Set the increments to 5 %

End Points

Start 5.00000

End 100.000

Step Size

Increment 5.00000 } Select one, the other is calculated

Number Steps 19

- ✓ Click on the Var.2 – Pressure category

Category

Var. 1 - Vapor Fraction (Vapo

Var. 2 - Pressure

Calculation Type

Calculation Options

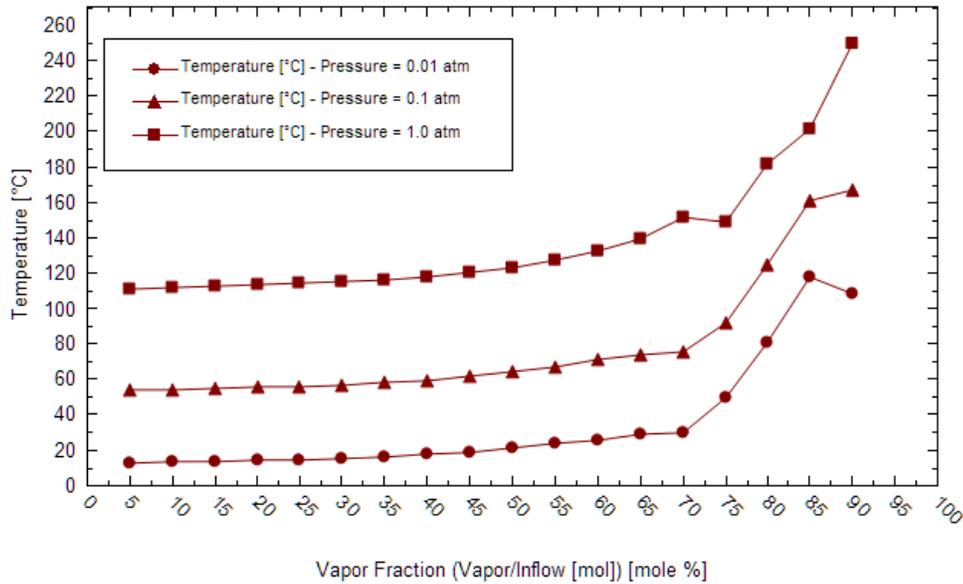
- ✓ Select the Point List radio button
- ✓ Add two points to the grid
- ✓ Enter pressures of 0.01, 0.1, and 1 atm

Linear Log Point List

	Value
1	0.0100000
2	0.100000
3	1.00000

- ✓ Close the Specs window and Calculate
- ✓ Click the Plot tab

The plot below is the default Temperature curves as the vapor fraction of the sample increases. Each curve represents a different pressure condition. The top curve is the atmospheric pressure condition, and the software computes that the boiling temperature range is between 110 and 250 C. The bottom curve is the low pressure (0.01 atm) condition and the boiling temperature range here is between 13 and 120 C. Note that the curves start at the 5 % vapor fraction that was selected. The curves end however at 90% vapor fraction and not the 100 % that was set.



The reason that the 95% and 100% condition failed is because the Dead Sea brine is only 92% water. The rest is salt. Therefore, these vapor fractions were not feasible. Note also, that the software computed a temperature reduction from 85% to 90% for the low-pressure conditions. Changes like this sometimes reflect the technical limits of the software or thermodynamic database and are worth questioning further before conclusions are drawn.

- ✓ Return to the Definition tab
- ✓ Change the Vapor fraction to end at 90%

End Points

Start

End

Step Size

Increment } Select one, the other is calculated

Number Steps

- ✓ Recalculate

Studying the solids forming

- ✓ Click on the Plot tab

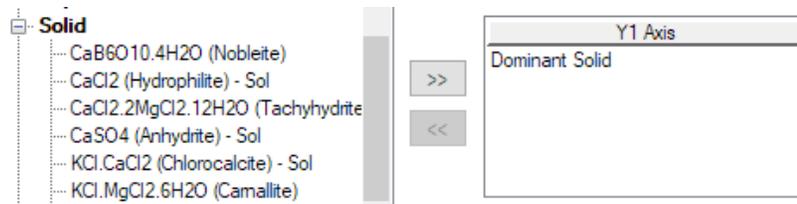
- ✓ Open the Variables window (Click on the Variables button) -



- ✓ Remove the Temperature from the Y1 Axis
- ✓ Expand the Solids section

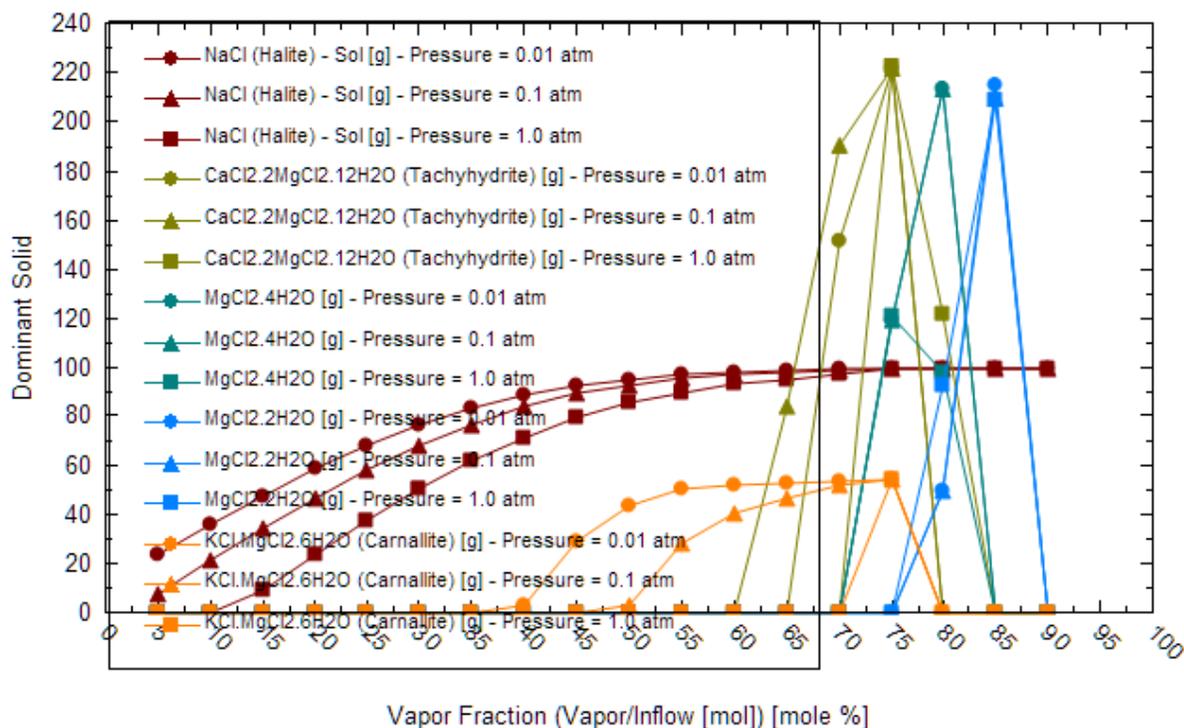
There are about fifteen solids computed to be stable during the evaporation study. This is too many to add at once, given that three pressure surveys are run. Therefore, the approach is to look at the most significant solids and then focus in on specific solids.

- ✓ Add the Dominant Solids to the Y1 Axis field

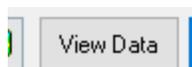


✓ Close the window and view the plot

The Dominant Solids plot displays the five most significant solids in the survey calculation. These are NaCl, $\text{CaCl}_2 \cdot \text{MgCl}_2 \cdot \text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. There are fifteen curves in total three for each phase. Since this plot is too confusing to review, the Data Table will be used instead.



✓ Click on the View Data button -



The table contains a multi-column solids list sorted by temperature and pressure. At lowest pressures, the five dominant solids are the five phases listed above. Halite is present in all calculations. The other phases however, are present only at specific evaporation fractions (or at specific temperatures). Carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, is computed to form between 40 and 75% vapor fraction at 0.1 atm. This phase is computed to form at 75% vapor fraction only when the pressure is 1 atm.

	Vapor Fraction (Vapor/Inflow [mol])	Pressure	NaCl (Halite) - Sol	CaCl ₂ .2MgCl ₂ .12H ₂ O (Tachyhydrite)	MgCl ₂ .4H ₂ O	MgCl ₂ .6H ₂ O (Bischofite)	KCl.MgCl ₂ .6H ₂ O (Carnallite)
	mole %	atm	g	g	g	g	g
1	5.00000	0.0100000	23.5223	0.0	0.0	0.0	0.0
2	10.0000	0.0100000	36.0541	0.0	0.0	0.0	0.0
3	15.0000	0.0100000	47.7702	0.0	0.0	0.0	0.0
4	20.0000	0.0100000	58.5154	0.0	0.0	0.0	0.0
5	25.0000	0.0100000	68.1240	0.0	0.0	0.0	0.0
6	30.0000	0.0100000	76.4367	0.0	0.0	0.0	0.0
7	35.0000	0.0100000	83.3286	0.0	0.0	0.0	0.0
8	40.0000	0.0100000	88.6417	0.0	0.0	0.0	3.04088
9	45.0000	0.0100000	92.1360	0.0	0.0	0.0	28.8026
10	50.0000	0.0100000	94.9833	0.0	0.0	0.0	43.7703
11	55.0000	0.0100000	96.8978	0.0	0.0	0.0	50.3255
12	60.0000	0.0100000	97.8448	0.0	0.0	100.316	52.0170
13	65.0000	0.0100000	98.5681	0.0	0.0	234.330	52.8047
14	70.0000	0.0100000	99.0109	150.978	0.0	176.381	53.8617
15	75.0000	0.0100000	99.1437	221.772	118.942	2.67251	54.2961
16	80.0000	0.0100000	99.1437	0.0	213.522	0.0	0.0
17	85.0000	0.0100000	99.1437	0.0	0.0	0.0	0.0
18	90.0000	0.0100000	99.1437	0.0	0.0	0.0	0.0
19	5.00000	0.100000	7.42856	0.0	0.0	0.0	0.0

- ✓ Open the Variables window and remove the Dominant solids
- ✓ Plot all the MgCl₂-containing solids. There should be six of them.



- ✓ View the Data

At 0.01 atm, 1.965 g of MgCl₂-containing solids form. At 1 atm, this amount is 0.967 g. The primary difference is MgCl₂.6H₂O, where at 0.01 atm, 0.514 g is computed to form and 0 g forms at 1 atm.

Additional interpretation can be done with this data. If you are interested, consider looking at the water (H₂O) activity, the remaining amounts of dissolved element (element balance table), the cation-anion complexes that form (Speciation table), and the gas-phase components (Speciation table).

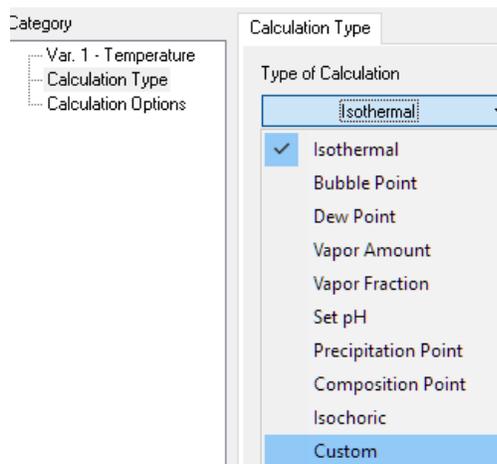
Chapter 3 c. Survey Calculations with embedded single points

Introduction

This chapter contains several survey calculations that contain an embedded single point calculation.

3c.1 Solubility vs. Temperature	3
3c.2 Composition Survey with Bubble Point: Acetone-H ₂ O	11
3c.2 Composition Survey with Dew Point: Ethanol:H ₂ O.....	16
3.4a Temperature & Pressure Surveys	Error! Bookmark not defined.

The first two sections of this chapter presented single and dual surveys. In addition to adjusting these survey variables, a user can select one of several single point calculations embedded within the survey. The embedded single point calculations include



- Isothermal – default
- Bubble, Dew Point, Vapor Amount and Fraction – This is used when a specific fraction/amount of material is in the vapor. It is not used when the Vapor Fraction/Amount survey is selected
- Set pH – the user fixes the pH at a single value throughout the survey. This is not used with pH Survey

- Precipitation point – the user can model for example a solid solubility vs temperature or composition
- Composition Point – A user can fix the aqueous or vapor composition of a specific species as the survey is run
- Isochoric – A user can fix the total volume of the system at a single value during the survey.
- Custom – A user can fix one or more variables and free an equal number of variables within the survey.

3c.1 Solubility vs. Temperature

A very common application is calculating the solubility of a solid as temperature and pressure vary. This is a thermodynamic solubility phase diagram, and when presented in two- and three-dimensional plot, provides insight into the physical- chemical properties of a solid phase. Several examples will be run, to provide general insight into the behavior of many solid phase types.

- ✓ Create a new file
- ✓ Save the file with a name such as “Chapter 3c” (and save often)
- ✓ Add a new stream and name it ‘Mineral Solubility’
- ✓ Change the framework to MSE

Add nothing to the Inflows grid (all will be added in the individual surveys)

Getting Started - Halite

Halite solubility vs. Temperature

- ✓ Add a Survey calculation and name it Halite
- ✓ Add NaCl to the grid
- ✓ Select the Specs button
- ✓ Set the temperature range from 0 to 100 C by 5 C increments

End Points

Start

End

Step Size

Increment } Select one, the other is calculated

Number Steps

- ✓ Select the Calculation Type category

Category

- Var. 1 - Temperature
- Calculation Type**
- Calculation Options

Calculation Type

Type of Calculation

Precipitation Point Temperature Pressure

Use Single Titrant Hide Related Inflows

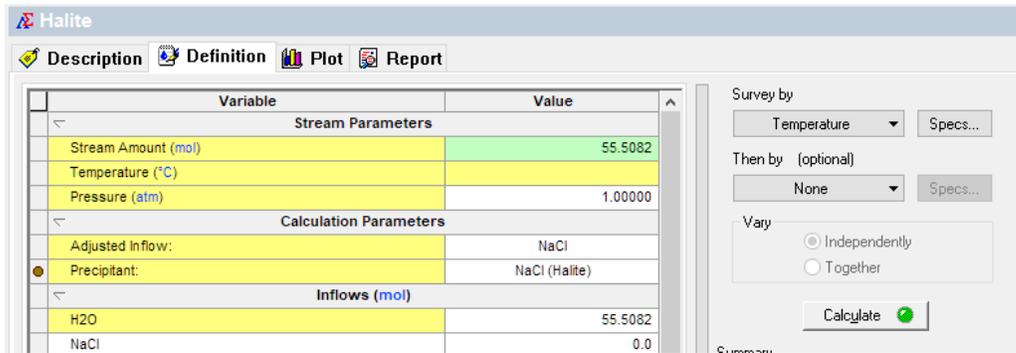
Solid Precipitate

- NaCl (Halite) - Sol**
- NaOH - Sol
- NaCl - Sol

Adjusted Inflow

- H2O
- NaCl**

- ✓ Change the Type of Calculation to Precipitation Point
- ✓ Select Halite for the solid and NaCl for the Adjusted.
- ✓ Close the window

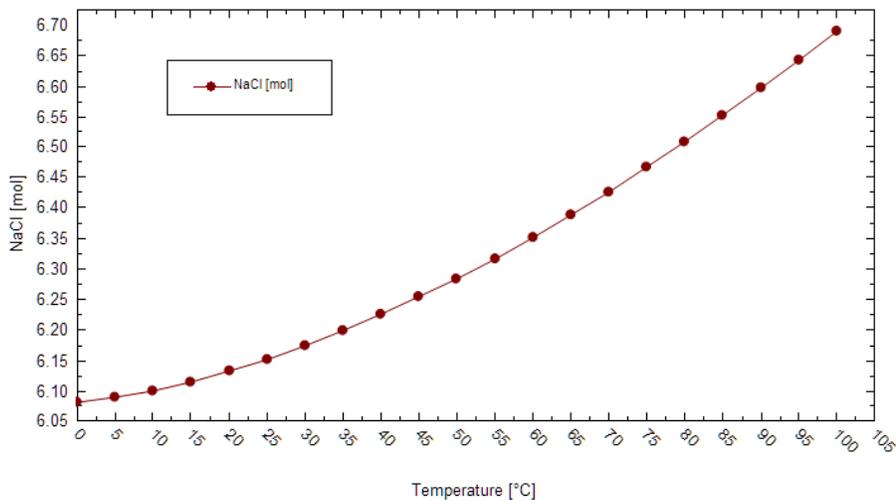


The screen should look like the one above. There are a few points to note. First, the Inflow, NaCl does not mean that halite is being added. Rather, NaCl inflow is the efficient way of adding Na(+1) and Cl(-1) to the system. Only the solid phase, Halite, is defined.

Secondly, depending upon the version you use, the main screen may contain the options to change the calculation type selection and the solid phase, the inflow selections.

- ✓ Calculate
- ✓ Click on the Plot tab

The default plot is the dependent variable, the amount of NaCl add to 1 kg of H2O before halite precipitates. This variable is called NaCl (Inflow). The default units are moles.



Halite solubility increases slightly with temperature, about 10%. This relative increase is small compared to other minerals, however, the overall soluble amount is high, at 6.1 to 6.7 moles/kg H2O.

Halite solubility vs. 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.

- ✓ Return to the Definition tab
- ✓ Change the Then By (optional) calculation to Pressure
- ✓ Click on the second Specs... button
- ✓ Change the scale to Log, the End pressure to 500 (atm) and the Steps to 3

Linear Log Point List

End Points

Start

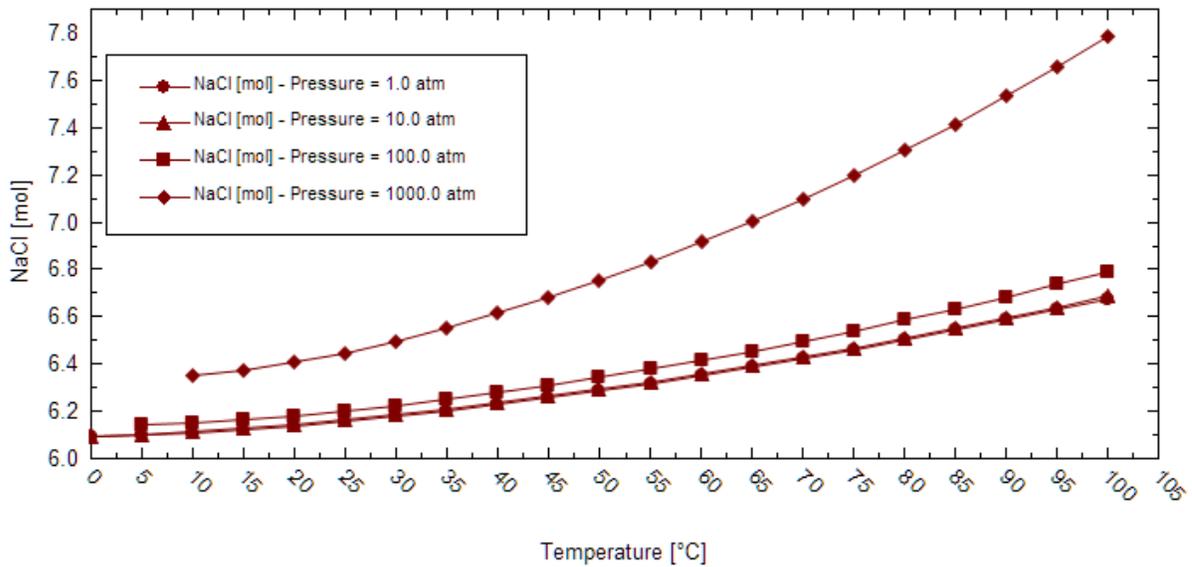
End

Step Size

Increment } Select one, the other is calculated

Number Steps }

- ✓ Calculate
- ✓ Review the plot



The effect of pressure is significant between 100 and 1000 atm relative to the effects between 1 and 100 atm. The range between the 0 C, 1 atm condition (6.1 moles/kg) and the 100 C, 1000 atm condition (7.8 moles/kg) is about 28%.

Halite Solubility using Contour Diagram

This last procedure will include several hundred points to create a surface or contour plot of its solubility.

- ✓ Return to the Definition tab
- ✓ Click on the Specs... button
- ✓ Change the maximum temperature to 150 C and change the increments to 2 (75 steps)

End Points

Start

End

Step Size

Increment } Select one, the other calculated

Number Steps }

- ✓ Click on the Var. 2 - Pressure category | Var. 2 - Pressure

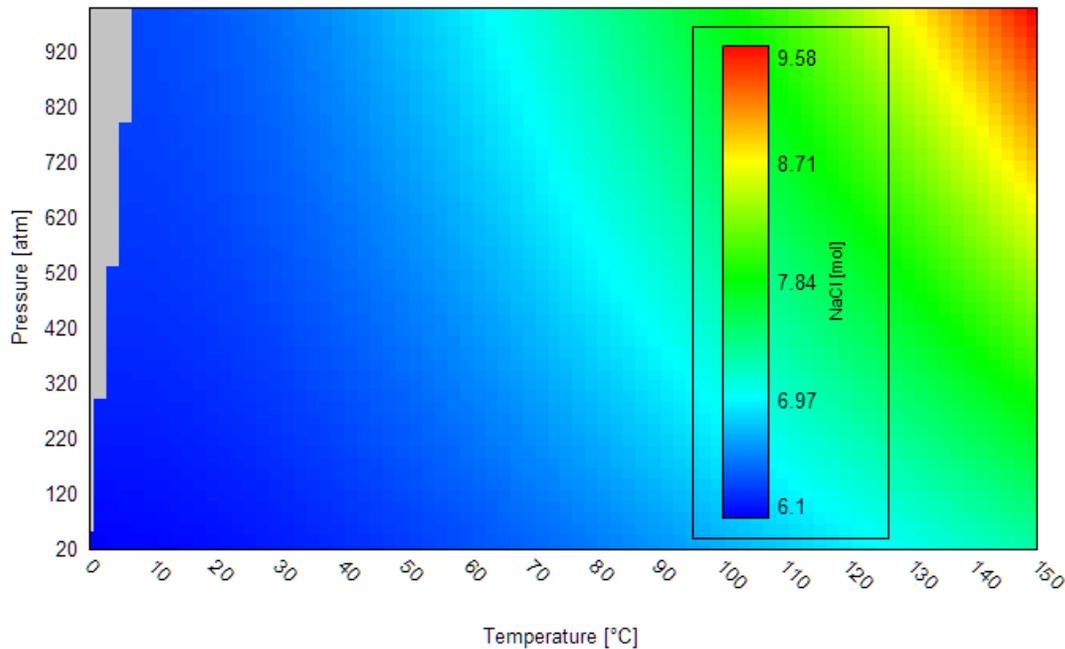
- ✓ Change the survey to Linear, the start to 20 atm and the increments to 20 atm (49 points)

This produces a matrix of 75 steps x 49 steps for a total of 76 temperature and 50 pressure points, or 3800 points in total. This calculation will take a few minutes to compute.

- ✓ Click on the Plot tab
- ✓ Click on the Variables button, remove the existing variables
- ✓ Expand the Inflows category and add NaCl (inflow) to the Y1 axis. Close the window



- ✓ Change the plot type 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.

Zabuyelite (Li_2CO_3)

Solubility vs. Temperature and Pressure

Li_2CO_3 is an important intermediate chemical in the lithium battery manufacturing process. Lithium is obtained from salt flats and lakes in what is called the Lithium Triangle of the Andes. These lakes contain Li^+ concentrations that are high relative to other surface waters. Lithium is recovered through a series of evaporation and precipitation processes and the product transported from the mining region is Li_2CO_3 . The purpose of this example is to compute this mineral's solubility.

- ✓ Add a new Survey calculation to the Mineral Solubility stream
- ✓ Name the survey Zabuyelite (Li_2CO_3)
- ✓ Add Li_2CO_3 to the inflow grid

Calculation Parameters	
Adjusted Inflow:	Li_2CO_3
Precipitant:	Li_2CO_3 (Zabuyelite)
Inflows (mol)	
H_2O	55.5082
Li_2CO_3	0.0

- ✓ Open the Specs window and change the Temperature Specifications to start at 0 C and end at 100 C by 5 C increments.
- ✓ Click on the Calculation Type Category and change the type from Isothermal to Precipitation Point
- ✓ Select Zabuyelite as the solid and Li_2CO_3 as the inflow

End Points

Start:

End:

Step Size

Increment: } Select one, the other is calculated

Number Steps:

Type of Calculation

Precipitation Point Temperature

Pressure

Use Single Titrant Hide Related Inflows

Solid Precipitate

Adjusted Inflow

You will modify the units before calculating

- ✓ Click on the (mol) hyperlink in the Inflows grid category - Inflows (mol)
- ✓ Change the Inflows basis to Mass Fraction -

Inflow variables		
Stream Amount	Moles	mol
Inflows	Mass Fraction	mass %

- ✓ Change the Aqueous and Total Composition basis to Mass Fraction -

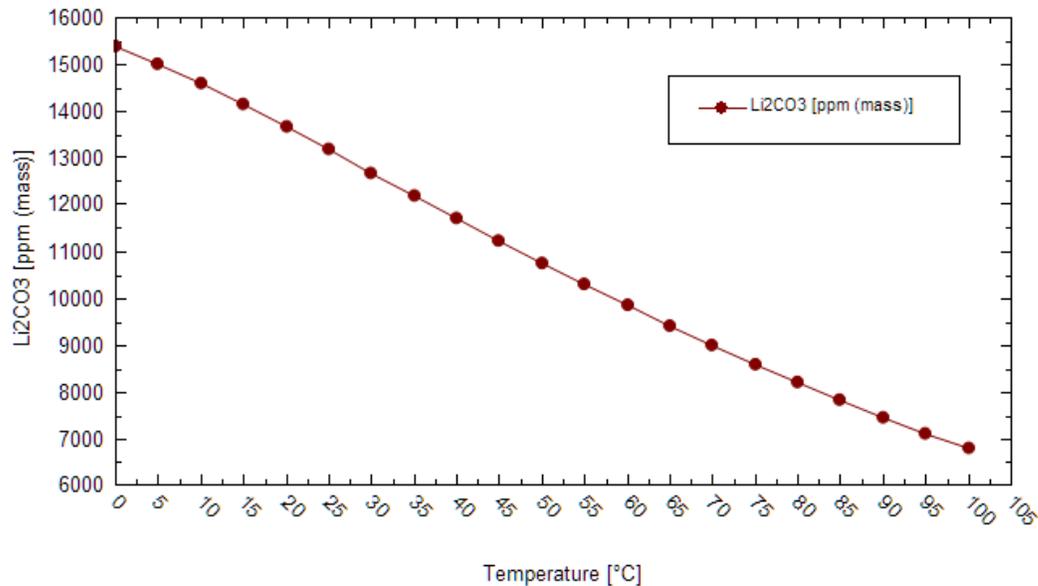
Output variables		
Aqueous Composition	Mass Fraction	mass %
Vapor Composition	Moles	mol
Solid Composition	Moles	mol
2nd Liquid Composition	Moles	mol
Total Composition	Mass Fraction	mass %

- ✓ Change the Mass fraction units from mass% to ppm (mass)

Molar Concentration	mol/L
Mass Fraction	ppm (mass)
Mole Fraction	mole %

- ✓ Calculate and view the plot

Zabuyelite solubility is computed to decrease by a factor of about 2.5x as temperature increases from 0 to 100 C.



Extending the Lithium removal using a second Composition survey

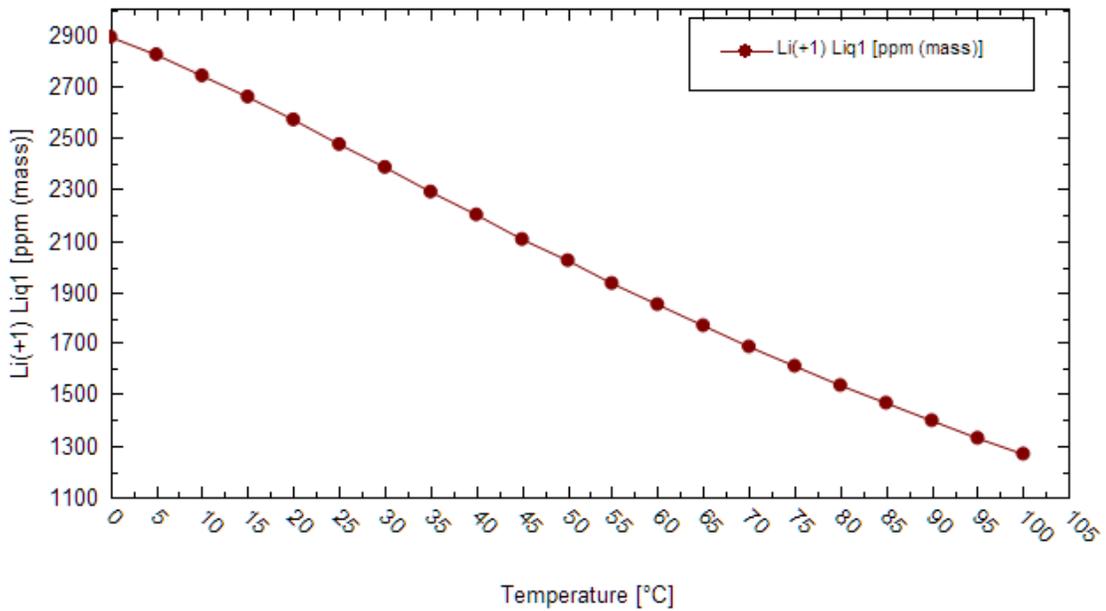
The simulation above is the normal solubility of Li₂CO₃ in pure water. This would not be an optimal way to recover lithium. A more efficient method to increase lithium yield is to increase the dissolved CO₃⁻² concentration relative to Li⁺¹. This can be done by adding Na₂CO₃ or another carbonate source.

You will start by first displaying the dissolved Li⁺¹ concentration and then make the inflow change

- ✓ Open the Variables window and remove the existing Y1 Axis variable
- ✓ Expand the MBG Total – Liquid-1 category and add Li+1 to the Y1 Axis



The resulting plot is the dissolved lithium ion (separate from the carbonate). Its concentration is 2900 ppm at 0 C and 1300 ppm at 100 C.



- ✓ Return to the Definition tab

H2O	1.00000e6
Li2CO3	0.0
Na2CO3	

- ✓ Add Na2CO3 to the inflow Grid -

Survey by
 Temperature ▼ Specs...
 Then by (optional)
 Composition ▼ Specs...

- ✓ Change the second (Optional) survey to Composition
- ✓
- ✓ Click on the 2nd Specs... button

Component Inflows
 Hide Related Inflows New Inflow

Li2CO3
Na2CO3

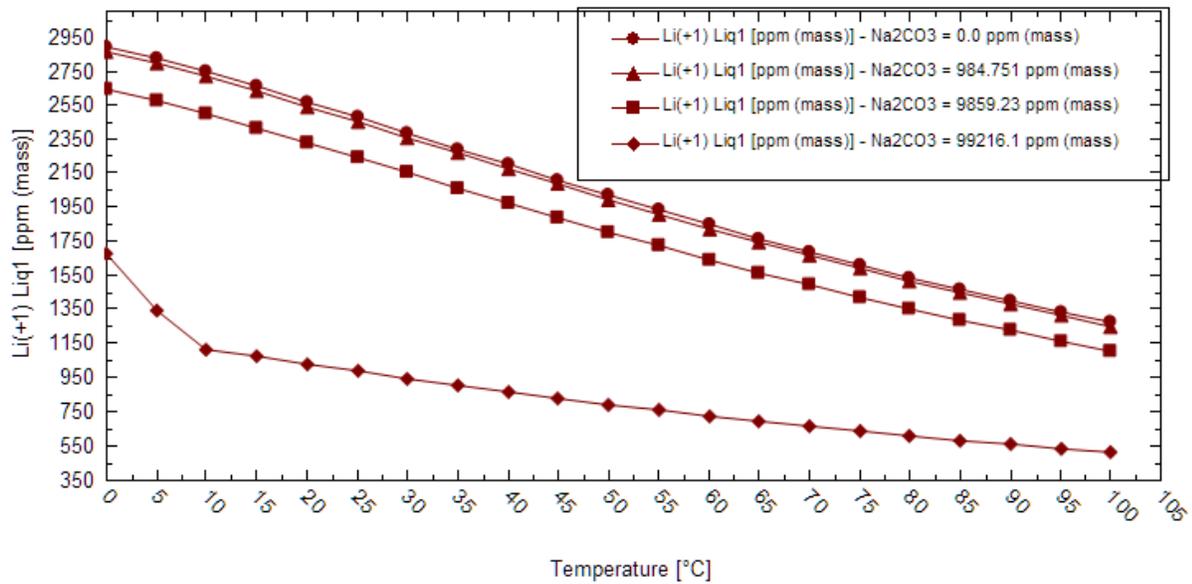
- ✓ Select Na2CO3 as the Inflow -
- ✓ Click on the Survey Range button and change the survey to Point List
- ✓ Add the following concentrations, 0, 1000, 10000, and 100000 ppm

Linear
 Log
 Point List

	Value
1	0.0
2	1000.00
3	10000.0
4	1.00000e5

- ✓ Close the window and calculate
- ✓ View the plot

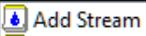
Based on the calculations, the amount of Li^{+1} remaining in the water phase can be decreased by up to 50% if the process fluid is high in CO_3^{2-} . There is a limit to the amount of Na_2CO_3 that can be added, because at low temperature, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ precipitates (the kink in the curve at 0 to 10 C).

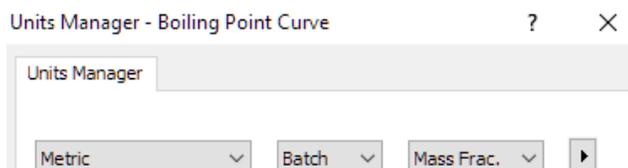


3c.2 Composition Survey with Bubble Point: Acetone-H₂O

The next task is to explore the boiling point of water when miscible organics are added to it. The organics are common materials, acetone, ethylene glycol and methylamine.

Getting started

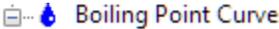
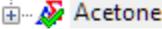
- ✓ Add a new stream 
- ✓ Select the <F2> key or Description tab to rename it 'Boiling Point Curve'
- ✓ Select the Names Manager in the toolbar  and switch to Display Name
- ✓ Select the MSE button in the toolbar 
- ✓ Select the Units Manager button in the toolbar  and change it to Mass Frac



- ✓ Press OK then return to the Definition tab
- ✓ Enter Acetone, MEG, and methylamine to the Inflows grid

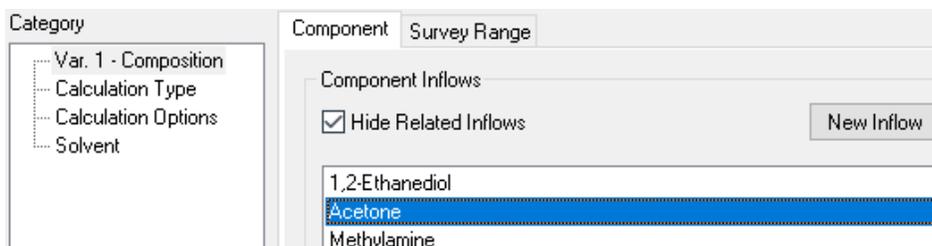
Inflows (mass %)	
Water	100.000
Acetone	0.0
1,2-Ethanediol	0.0
Methylamine	0.0

Acetone-Water curve

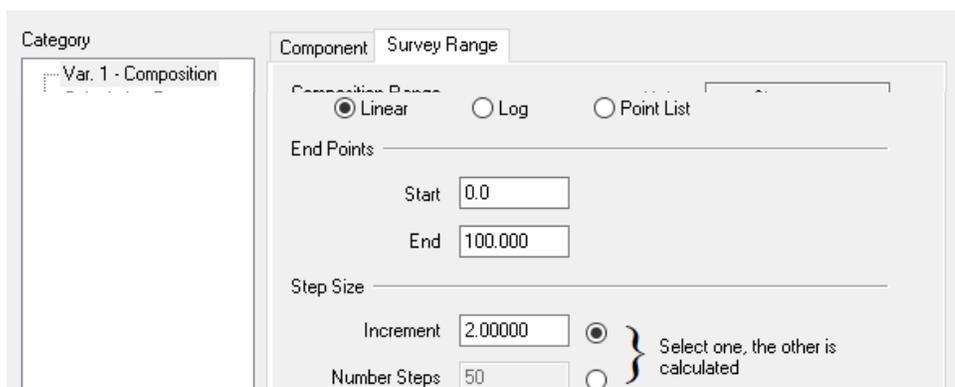
- ✓ Add a Survey calculation and name it Acetone -  
- ✓ Change Survey to Composition - 

The calculation button is red, which indicates that the survey needs more specifications.

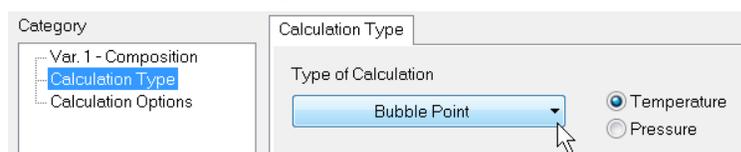
- ✓ Click the Specs ... button on the top right
- ✓ Select Acetone from the Component list



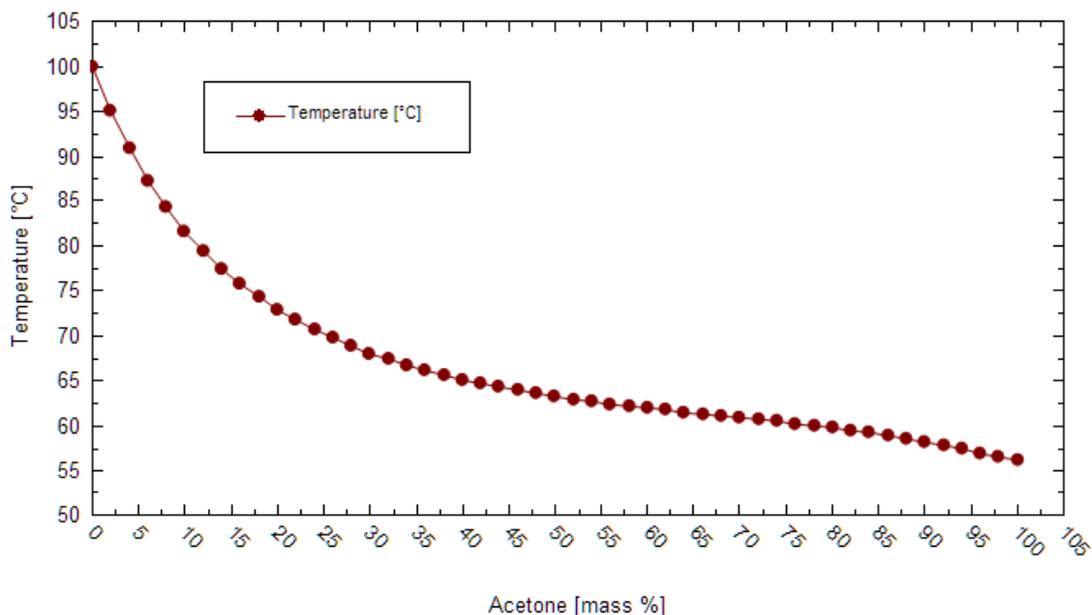
- ✓ Click on the Survey Range tab, then enter the following values: Start 0, End 100, Increments 2



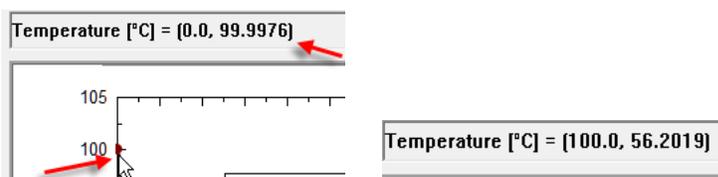
- ✓ Select the Calculation Type category, then change the calculation to Bubble Point



- ✓ Press OK to and Calculate or press the <F9> key
- ✓ Select the Plot tab



The pure component boiling points are the far left and far right points on the curve. Mouse over these points to identify the values. H₂O is 100 C and acetone is 56.2 C at 1 atm.

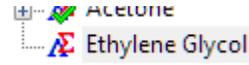


The water boiling point decreases as the acetone fraction increases (far left of the plot). Likewise, the acetone boiling point increases as the water content increases (far right of the plot). The curve would be a

straight line at ideal conditions. However, because of the disruption of molecular interactions cause by mixing the two components, it is a non-linear curve.

MEG-H2O Boiling

- ✓ Add a Survey calculation and name it Ethylene Glycol -
- ✓ Change Survey to Composition



Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mass %)	
Water	94.0000
Acetone	6.00000

Survey by
Composition Specs...

Then by (optional)
None Specs...

Vary
 Independently
 Together

Calculate ●

The calculation button is red, which indicates that the survey needs more specifications.

- ✓ Click the Specs ... button on the top right
- ✓ Select 1,2-Ethanediol (ethylene glycol) in the Component list

Category

- Var. 1 - Composition
- Calculation Type
- Calculation Options
- Solvent

Component Survey Range

Component Inflows

Hide Related Inflows

1,2-Ethanediol

- ✓ Click on the Survey Range tab, then enter the following values: Start 0, End 100, Increments 2

Category

- Var. 1 - Composition

Component Survey Range

Composition Basis
 Linear Log Point List

End Points

Start

End

Step Size

Increment } Select one, the other is calculated

Number Steps

- ✓ Select the Calculation Type category, then change the calculation to Bubble Point

Category

- Var. 1 - Composition
- Calculation Type
- Calculation Options

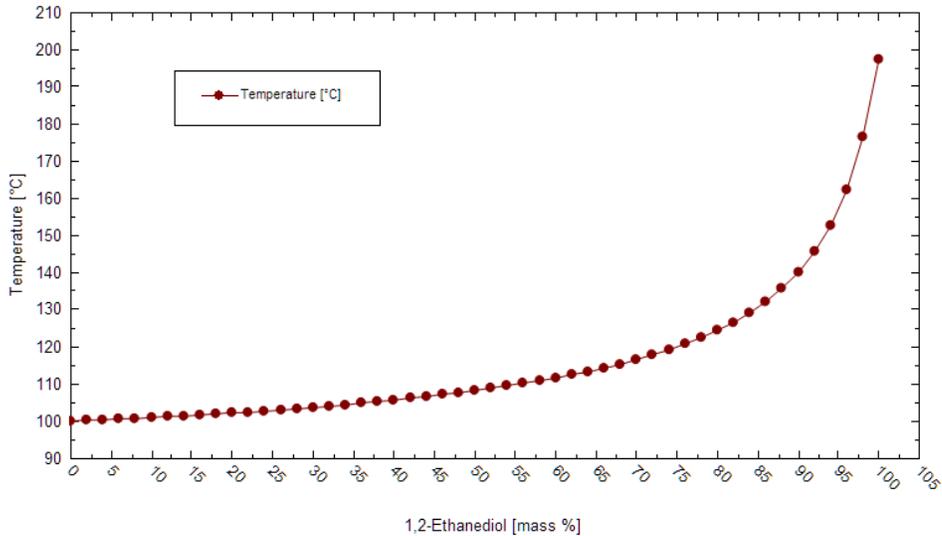
Calculation Type

Type of Calculation

Bubble Point

Temperature
 Pressure

- ✓ Press OK to and Calculate or press the <F9> key
- ✓ Select the Plot tab

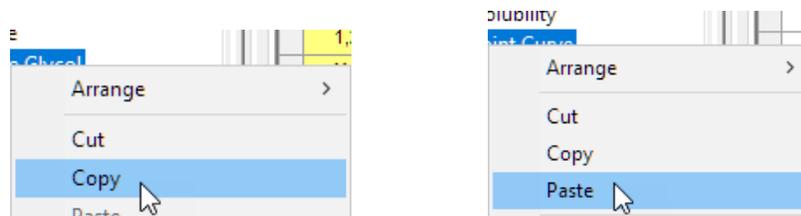


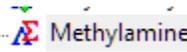
Ethylene glycol has a higher boiling point than water, and therefore the curve is a mirror image of the acetone water plot.

Methylamine-H₂O boiling Point

Instead of creating and formatting a new survey, you will use the copy-paste shortcut programmed in the software.

- ✓ Right-mouse-click on the Ethylene Glycol survey and select Copy
- ✓ Right-mouse-click on the Boiling Point Curve stream and select Paste

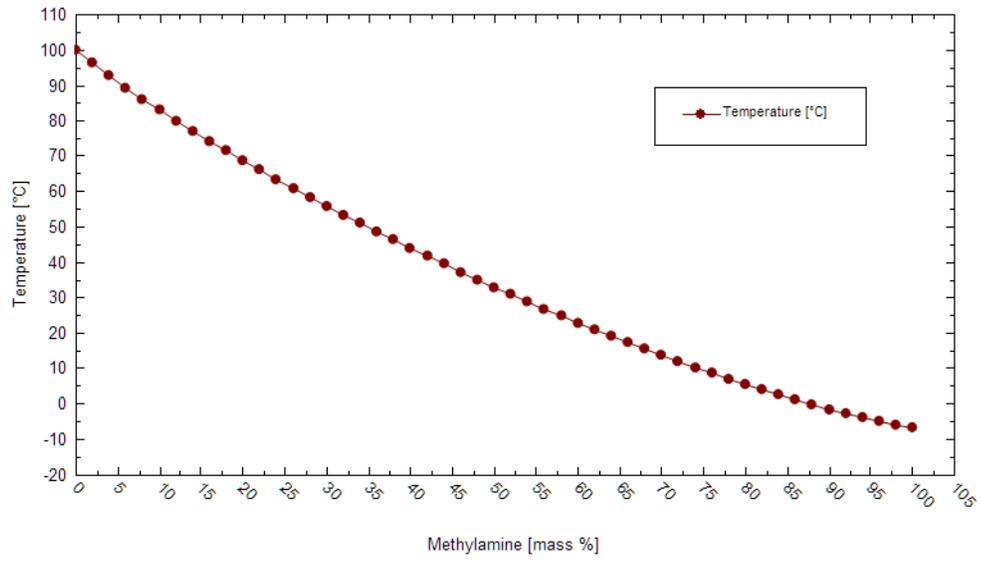


- ✓ Rename the new survey Methylamine - 
- ✓ Open the Specs... window and change the Component inflow to Methylamine



- ✓ Close the Specs... window and calculate.

The resulting plot is a fairly linear curve that extends from 100 C (pure water) to -7 C (pure methylamine). This is an example of a miscible solution of two components with a wide boiling point difference.



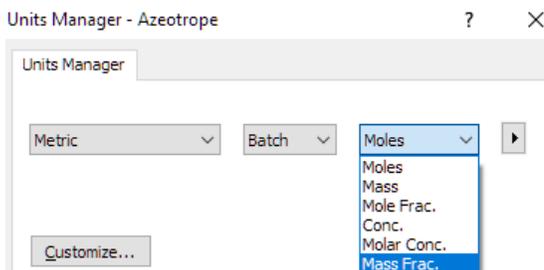
3c.3 Composition Survey: Azeotrope

This case is similar to the previous case. A dew point and bubble point calculation will be run using ethanol and water. The two data sets will then be transferred to a spreadsheet where the curves are plotted together to locate the azeotrope.

You will need a spreadsheet software to complete this case

Getting Started

- ✓ Add a new stream  Add Stream and label it Azeotrope
- ✓ Select the Names Manager  and switch to Display Name
- ✓ Select the MSE button 
- ✓ Set the Units  to Mass Frac



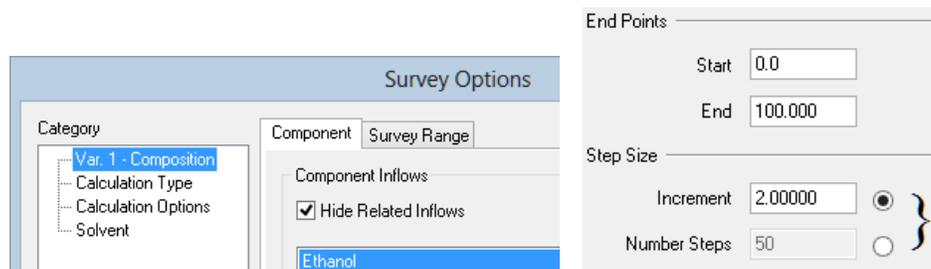
- ✓ Enter the following components, Ethanol, HCl, and HF

Inflows (mass %)	
Water	100.000
Ethanol	0.0
Hydrogen chloride	0.0
Hydrogen fluoride	0.0

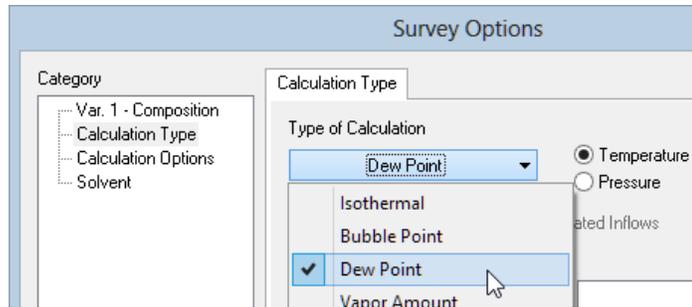
- ✓ Add a Survey calculation and name it EtOH Azeotrope - 
- ✓ Change the Calculation type to Composition

Calculating the Ethanol-Water dew point

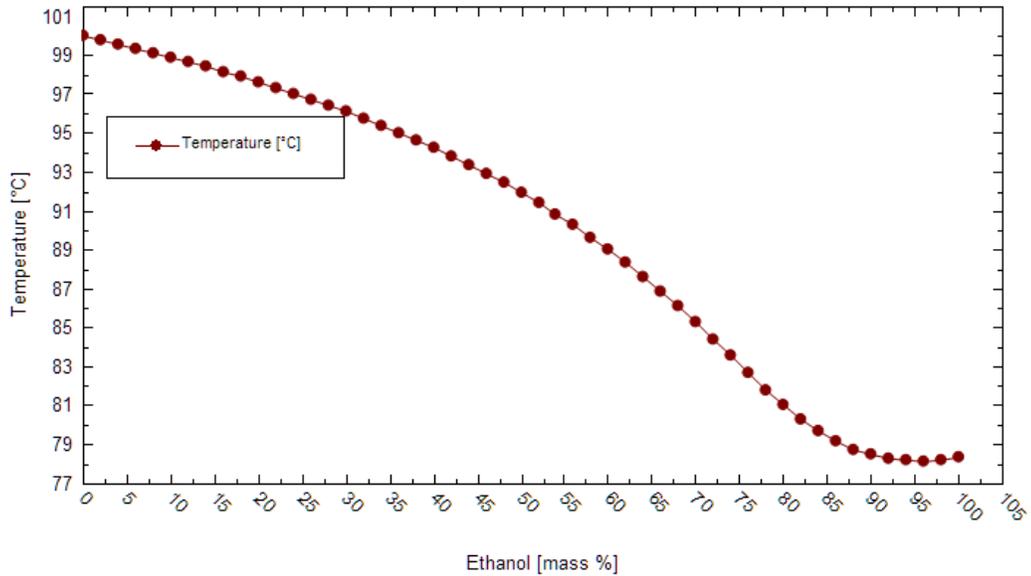
- ✓ Select the Specs... button
- ✓ Select Ethanol from the list in the Component Tab and enter the Start, End, and Increments of 0, 100, and 2 %



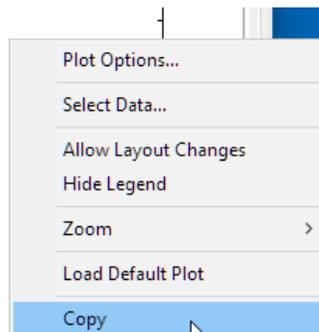
- ✓ Click the Calculation Type Category and change from isothermal to Dew Point



- ✓ Press OK and Calculate
- ✓ Select the Plot tab



- ✓ Right-mouse-click on the white region of the plot to open the Drop-Down menu
- ✓ Select Copy

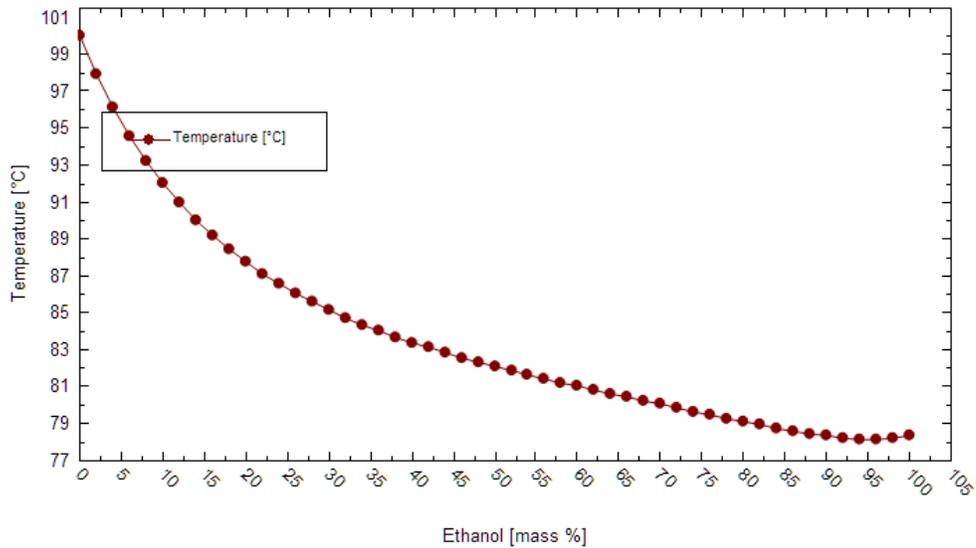


- ✓ Open the Spreadsheet software and paste the data

Calculating the Ethanol-Water bubble point

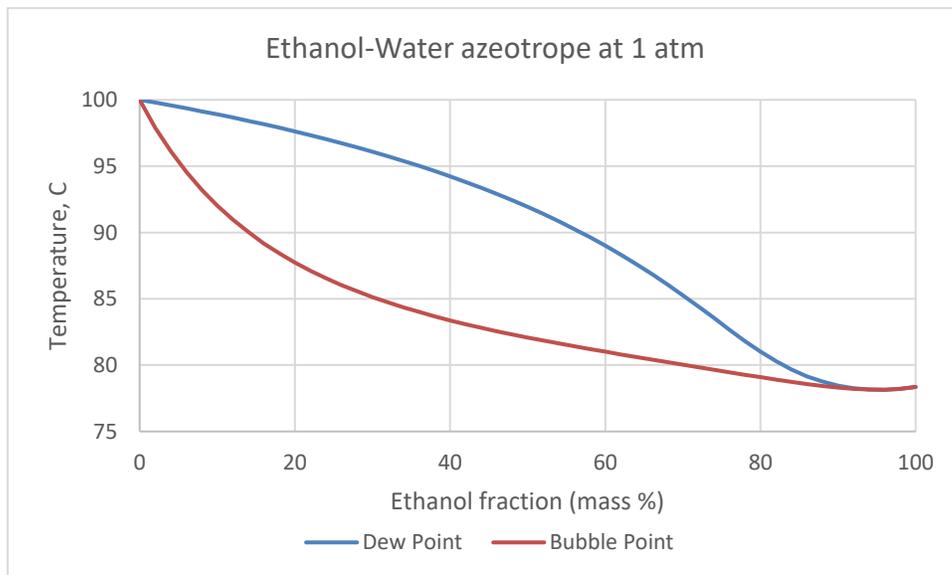
- ✓ Return to the Definition tab
- ✓ Open the Specs... window and select the Calculation Type category
- ✓ Change the calculation to Bubble Point

- ✓ Recalculate
- ✓ Click on the Plot tab



- ✓ Copy this data to the spreadsheet
- ✓ Plot the two temperature curves and format the plot as needed

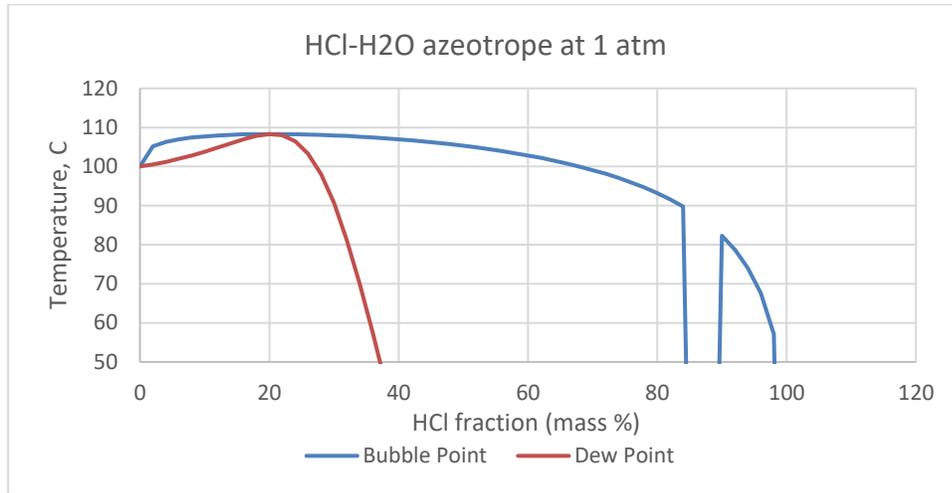
The Azeotrope occurs at about 95% ethanol where the two curves intersect.



HCl-H₂O Azeotrope

- ✓ Repeat the above procedure and use HCl as the adjustable component
- ✓ Instead of creating a new survey, make a copy of the Ethanol Azeotrope survey and modify that
- ✓ Bring the data to the spreadsheet and plot

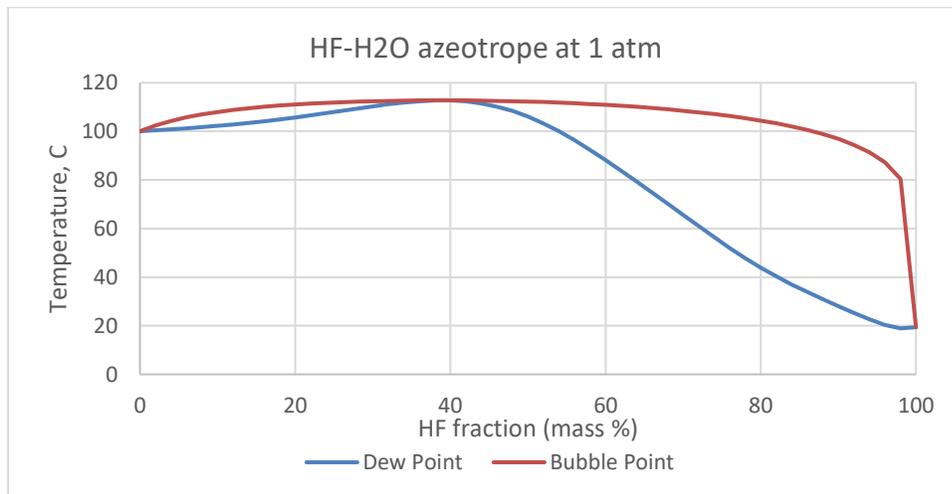
The azeotrope occurs at 21% HCl, and the two curves should intersect at this point. It is likely that there are multiple calculation failures at the high HCl fractions. Non-aqueous solutions can be difficult to converge, and this problem is compounded by HCl's volatility at high purity.



HF-H2O Azeotrope

- ✓ Repeat the above procedure and replace HF as the adjustable component

- ✓ Bring the data to a spreadsheet and plot



The azeotrope is computed to exist at 40 C at 1 atm. Below and above this temperature, there is composition separation between the dew point and bubble point for the same temperature.

- ✓ Save the file

3c.4 Custom Calculation in a Survey

The Custom calculation option used in Chapter 2 enables users to fix one or more variables and then adjust other variables in turn. In this case, the custom calculation will be used within an H₂S-H₂O composition survey. The H₂S concentration will be increased from 0 to 10,000 mg/l. At the same time the amount of NaOH required to neutralize the pH to 7 will be computed, and lastly the bubble point pressure of the mixture will be calculated.

Getting Started

- ✓ Add a new stream and label it H₂S-H₂O System

- ✓ Change the framework to MSE - 

- ✓ Change the units to Metric-batch-conc - Metric Batch Conc.

Inflows (mg/L)	
H ₂ O	
H ₂ S	0.0
NaOH	0.0

- ✓ Enter H₂S and NaOH to the grid -
- ✓ Add a survey calculation and label it 0 to 10,000 mg/l H₂S
- ✓ Set the Calculation type to Composition
- ✓ Enable Custom calculations by selecting the Tools menu at the top of the page, and choose Options. At the bottom of the new dialog box, check the option under Advanced to “Enable custom calculation within survey.”
- ✓ Open the Specs... window
- ✓ Highlight H₂S and set the range: 0 to 10000 by 500 mg/l –

H₂S

NaOH

End Points

Start

End

Step Size

Increment } Select one, the calculated

Number Steps

- ✓ Click on the Calculation Type category
- ✓ Change the type to Custom

Category

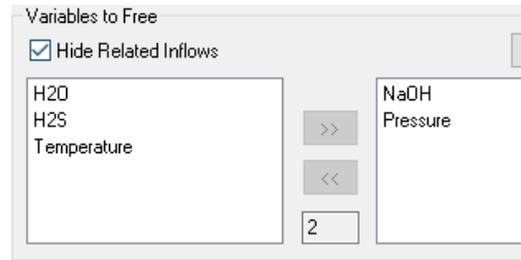
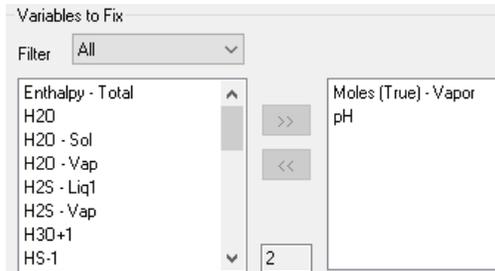
- Var. 1 - Composition
- Calculation Type
- Calculation Options
- Calculation

Calculation Type

Type of Calculation

Custom Temperature Pressure Specs...

- ✓ Click on the Specs... button
- ✓ Fix two variables: pH and Moles (True) – Vapor
- ✓ Free two variables: NaOH and Pressure
- ✓ Close the windows and return to the Definition tab

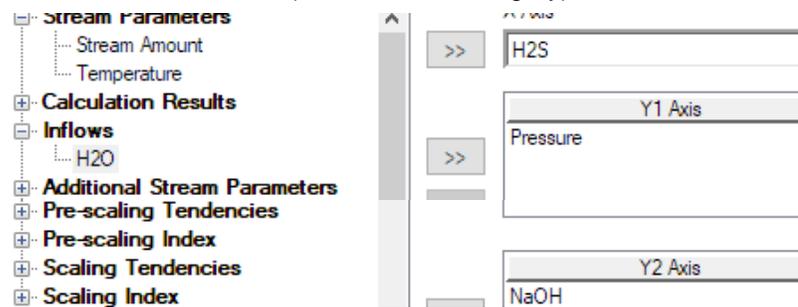


A new grid section appears, Calculation parameters. It contains four rows, one for each of the fix and free variables just selected.

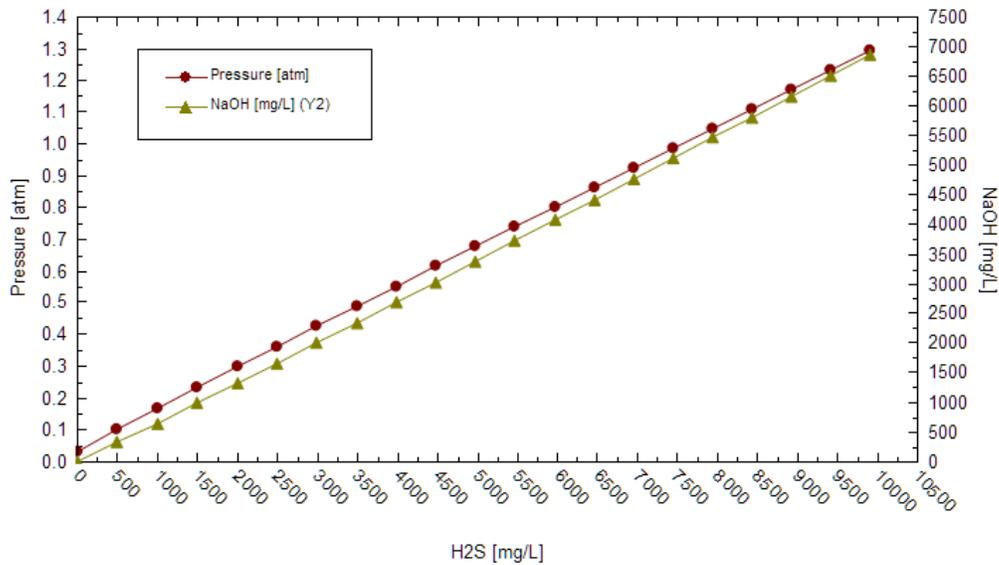
- ✓ Set the Target: Moles (True) Vapor to 1e-6
- ✓ Set the Target: pH to 7

Calculation Parameters	
● Target: Moles (True) - Vapor (mol)	1.00000e-6
● Target: pH	7.00000
○ Adjusted: NaOH (mg/L)	0.0
○ Adjusted: Pressure (atm)	0.0

- ✓ Calculate
- ✓ Click on the Plot tab
- ✓ Change the variables.
 - Add to Y1 axis - Pressure (in Stream Parameters category)
 - Add to Y2 axis - NaOH (in the Inflows category)

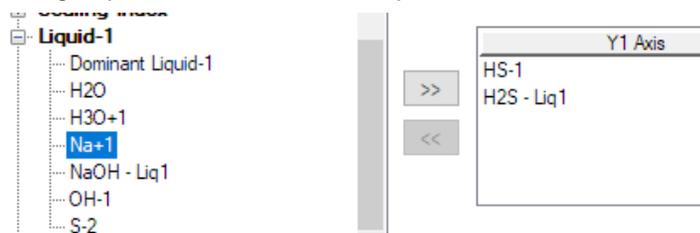


The resulting plot is somewhat unremarkable containing two straight lines. The bubble point at 7 pH is computed to increase from 0.031 atm (pure water vapor pressure) to 1.3 atm at 10,000 ppm H₂S (total).

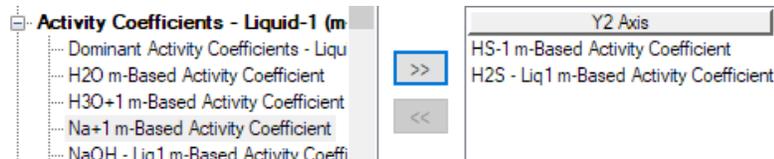


The amount of NaOH added starts at zero (pure water has a 7 pH) up to 6860 mg/l NaOH at 10,000 mg/l H2S. The maximum amount of material added is 16,860 mg/l or about 1.7%.

- ✓ Remove the existing variables
- ✓ Add the following Liquid-1 variables, H2S, Liq 1 and HS-1 to the Y1 axis



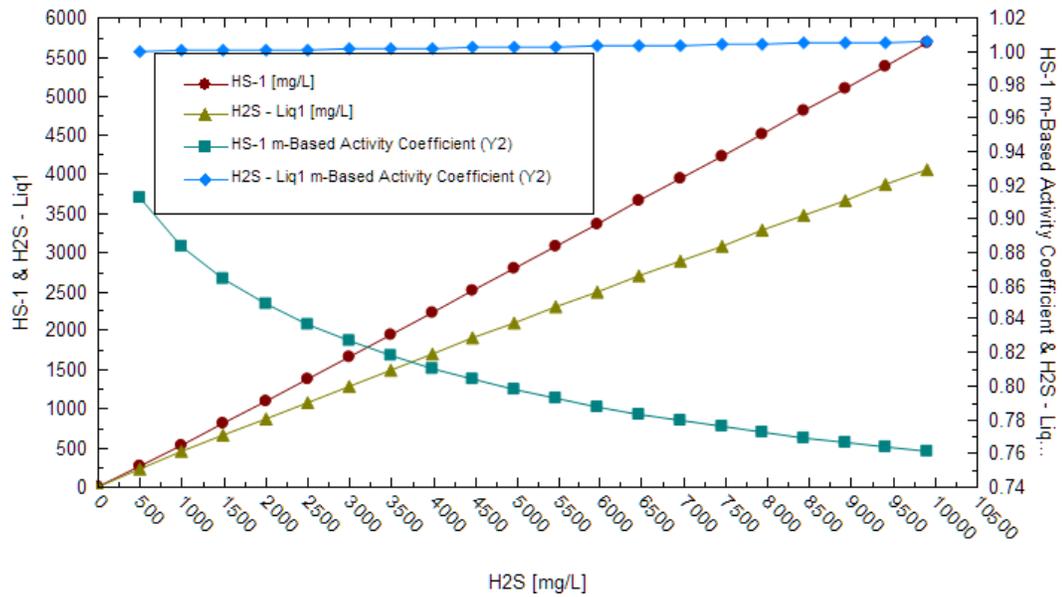
- ✓ Add the following Activity coefficient Liquid-1 (m-based) variables, H2S, Liq 1 and HS-1 to the Y2 axis



- ✓ Close and view the plot

The interpretation of this plot is as follows. As H₂S is added, the HS⁻¹ concentration increases faster than the H₂S concentration. This is despite the fixed pH of 7, which when using a simple concentration relationship should fix the HS⁻¹/H₂S concentration ratio (the brackets represent concentrations).

$$\frac{K_{A,H2S}}{[H^+]} \approx \frac{[HS^{-1}]}{[H_2S]} \approx \text{constant at constant pH and } T$$



The Y2 axis of curves explain the reason for this disparity. As H₂S and the neutralizing NaOH is added, the salinity increases. This increased salinity affects the behavior of all species, but mostly the charged ions. As a result, the activity coefficient for HS-1 decreases, while the H₂S activity coefficient remains constant. This effect is the difference between the two concentrations at each point.

3c.5 – Iron Oxidation

This case presents another bubble point pressure scenario, in which elemental iron is added to water. The Fe and H₂O react spontaneously, producing H₂ gas. This gas exerts a vapor pressure and the vapor pressure value is computed using the Bubble Point calculation. Oxygen is added using a composition survey. It will also react with iron and does so preferentially to water (more energy is released). Therefore, as more O₂ is added, less H₂S is produced, which has the net effect of lowering the vapor pressure. Eventually the iron is consumed, and any excess O₂ added exerts a vapor pressure which is again computed by the software.

Getting Started

- ✓ Add a stream and label it Iron Oxidation

- ✓ Change the framework to MSE - 

Inflows (mol)	
H2O	55.5082
Fe	0.0
O2	0.0

- ✓ Add Fe and O₂ to the grid -

- ✓ Turn on Redox by clicking on the Re button - 

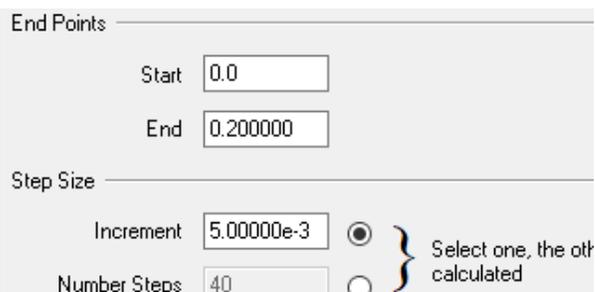
- ✓ Add a Survey calculation and label it O₂ titration

- ✓ Set the iron amount to 0.1 mole

- ✓ Change the calculation to Composition

- ✓ Open the Specs... Select O₂ as the component to vary

- ✓ Set the range: Start = 0, End = 0.2, Increment = 0.005 moles



End Points

Start

End

Step Size

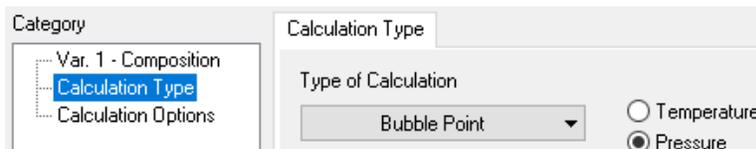
Increment } Select one, the other calculated

Number Steps



Fe
H2O
O2

- ✓ Change the Calculation type from Isothermal to Bubble Point and select Pressure as the calculated variable



Category

- Var. 1 - Composition
- Calculation Type
- Calculation Options

Calculation Type

Type of Calculation

Bubble Point

Temperature

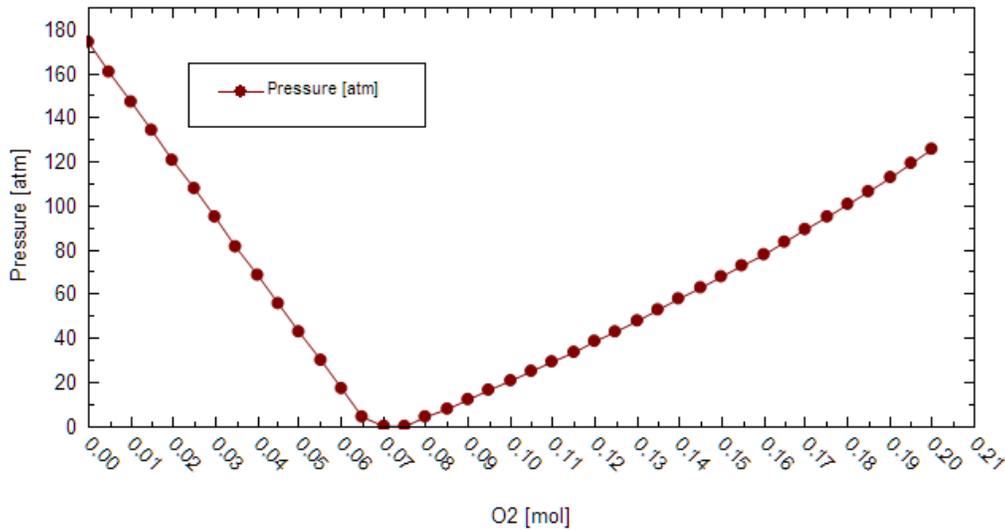
Pressure

The grid should now look like the following. The 0.1 mole Fe, will produce 0.1 mole H₂ in pure water, and this H₂ will exert a vapor pressure. The total pressure will be adjusted to match this exerted vapor pressure.

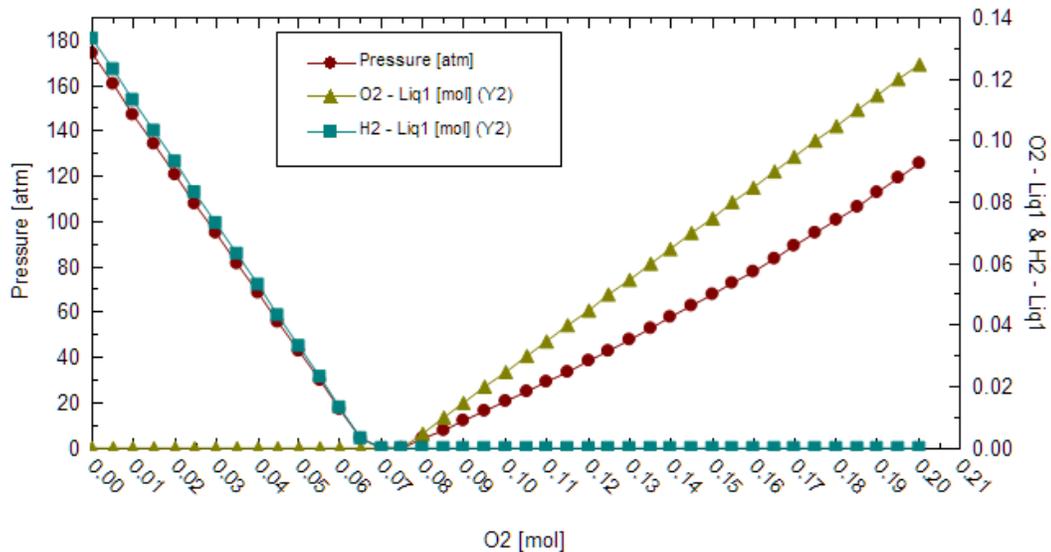
Calculation Parameters	
Calculate	Pressure
Inflows (mol)	
H2O	55.5082
Fe	0.100000
O2	

- ✓ Calculate and view the plot

The default plot is Pressure, since this is the dependent/adjustable variable. The V-shape is evidence of the initial existence of dissolved H_2 , its reduction and eventual elimination as O_2 is added, and finally the excess O_2 after the iron is completely oxidized.



- ✓ Open the Variables window.
- ✓ Expand the Liquid-1 category and add H2 and O2 to the Y2 axis

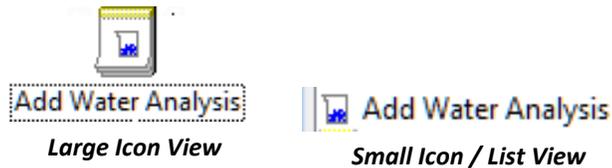


The resulting plot contains the dissolved H_2 and O_2 amounts. These curves follow the outline of the bubble point pressure curve.

Chapter 4 Water & Oil Analyses

Introduction

In this chapter, we will learn how to enter cations and anions using the OLI Studio: Stream Analyzer object called *Water Analysis*. We can add a water analysis from the Menu bar by selecting Streams > Add Analysis or by selecting its icon from the Actions pane:



Using this object, we will learn about automatic and manual alkalinity measurements, create a PVT analysis, and input customized data or pseudocomponent properties into a stream.

Calculation List

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4.1 Entering Data into a Water Analysis

Background

OLI Studio: Stream Analyzer was developed to accept two input types, molecular and ionic inflows. Chapters 2 and 3 focused on molecular inflows and this chapter will focus on ionic inflows.

Species	Concentration (mg/L)
SiO2	25.0000
Cations (mg/L)	
Na+1	10000.0
K+1	350.000
Ca+2	2000.00
Mg+2	800.000
Sr+2	300.000
Ba+2	150.000
Anions (mg/L)	
Cl-1	21000.0

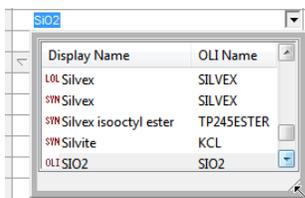
A populated Water Analysis screen

The OLI database contains on average seven synonyms for each species. This provides flexibility on how any species name is added to the grid. For example, the ions Na^+ and CH_3COO^- can be added in the following ways:

Cation (e.g., sodium)			Anions (e.g., acetate)		
Na+	NAION	Natrium ion(+1)	C2H3O2-	C2H3O2-1	C2H3O2(1-)
Na+1	Sodium ion		C2H3O2(-)	Acetate ion(-1)	
Na(+)	Natrium ion		C2H3O2(-1)	ACETATEION	

In total, the database has approximately 2,000 ions (and 15,000 synonyms). Therefore, just about any species of importance can be added.

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.



The database dropdown box

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.

SiO2	16.0000
X AQSIm	0.0

Mistaken identity

4.2a Creating a High Calcium/Barium Water

Sections 4.2a and 4.2a are part of the same project. You will create two water analyses and then perform a reconciliation calculation on each. These two waters are mixed in the next chapter.

The water in this section is high in divalent cations, calcium and barium, and low in their precipitating anions, HCO_3^{-1} and SO_4^{-2} . This water is purely hypothetical, and is created to extend the concept of water incompatibility.

The table below shows the water composition. The stream volume is 1 L, the temperature is 25 C, and the sample is at 1 atm pressure.

4.2a – High Calcium/Barium Water Composition							
Analysis Parameters		Neutrals mg/L		Cations mg/L		Anions mg/L	
Default		SiO2	25	Na+1	10000	Cl-1	21000
Recorded Properties				K+1	350	Br-1	150
Total Dissolved Solids (mg/L)	35000			Ca+2	2000	HCO3-1	26
pH	6.3			Mg+2	800	SO4-2	0.5
Density (g/ml)	1.025			Sr+2	300		
				Ba+2	150		

- ✓ Create a new file. Save it as “Water Analysis Mixer” or another name to recall later.

You will use this file in the next chapter, and so be certain to save the data once completed.

- ✓ Add a new Water Analysis to the file  Add Water Analysis
- ✓ Name it “High Calcium/Barium”



- ✓ Enter the Recorded properties, pH, alkalinity, etc. from the above table
- ✓ Enter the composition including the neutrals, cations, and anions

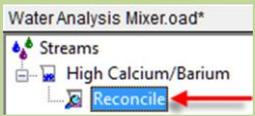
Make sure to include the charge symbols + or - while entering the data.

The screen should look like the one below. Be certain that there are no red x’s in the neutrals section. This would indicate that a species was not recognized.

Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	35000.0
Measured pH	6.30000
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	1.02500
Specific Electrical Conductivity (µmho/cm)	0.0

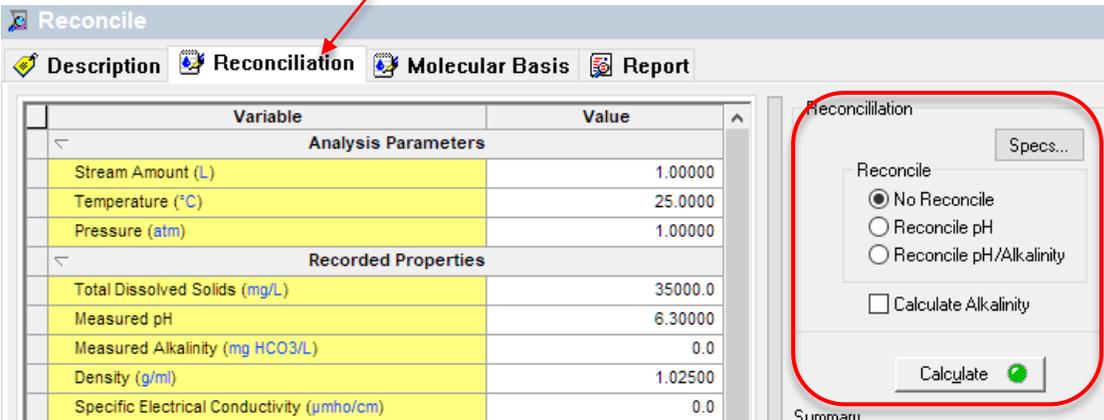
Neutrals (mg/L)	
H2O	
SiO2	25.0000
Cations (mg/L)	
Na+1	10000.0
K+1	350.000
Ca+2	2000.00
Mg+2	800.000
Sr+2	300.000
Ba+2	150.000
Anions (mg/L)	
Cl-1	21000.0
Br-1	150.000
HCO3-1	26.0000
SO4-2	0.500000

- ✓ Select Add Reconciliation from the Actions pane or the top right of the screen
- ✓ Name the stream – Reconciled Ca/Ba



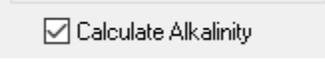
After selecting *Add Reconciliation*, the Navigator panel displays a substream called *Reconcile* as a branch to the initial water analysis object. We can change the reconcile substream name in the *Description* tab or by pressing the <F2> key.

The software opens to a tab called *Reconciliation*, which has a grid that looks the same as the initial grid.



The upper-right calculation section contains three ways to adjust the calculated fluid properties. These options will be discussed in detail throughout this chapter.

The default calculation is No reconcile. This option means that the software will compute the water properties based on the current concentration of cations, anions, and molecular species. The calculation will not use the measured pH or the measured alkalinity.

- ✓ Click on the Calculate Alkalinity button - 
- ✓ Press the <F9> key or click the Calculate button

Contents of the Summary Section

- ✓ View the Summary section

The *Summary* section contains several pieces of information. The top section contains the charge balance information showing the total equivalent charge (positive and negative), and the charge imbalance.

Below the charge balances, the *Summary* panel displays the calculation type the software used. In our 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 *Summary* also contains the Phase Amounts. This particular analysis contains a single water phase. The last section is the computed pH, ionic strength, and density. The measured pH is 6.30 and the computed pH is 6.99.

This case has a positive imbalance of **0.0239** equivalents of positive charge, which corresponds to 848.9 mg/L of Cl⁻. The software adds this amount of chloride to the water. We can see this by selecting the *calculated* tab at the bottom of the grid.

Neutrals (mg/L)	
H2O	
SiO2	25.0000

Cations (mg/L)	
Na+1	10000.0
K+1	350.000
Ca+2	2000.00
Mg+2	800.000
Sr+2	300.000
Ba+2	150.000

Anions (mg/L)	
Cl-1	21000.0
Br-1	150.000
HCO3-1	26.0000
SO4-2	0.500000

Summary

Unit Set: Concentration

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

Dominant Ion Charge Balance (eq/L):
Cation Charge: 0.618592 eq/L
Anion Charge: -0.594647 eq/L
Imbalance: 0.0239445 eq/L

Charge Balance Information
848.906 mg/L of Cl-1 is needed to balance.

Isothermal Calculation **Calculation Type**
25.0000 °C 1.00000 atm

Phase Amounts **Phase Amounts**
Aqueous 1022.72 g
Vapor 0.0 g
Solid 0.0 g

Aqueous Phase Properties **Properties**
pH 6.99524
Ionic Strength 0.0126052 mol/mol
Density 1.02272 g/ml

Calc. elapsed time: 4.488 sec

Viewing the Molecular Basis Tab

- ✓ Click 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 that the water analysis created.



This molecular form can be exported to a standard OLI Studio stream, or it can be exported to separate software like Flowsheet: ESP, Aspen Plus¹, UniSim Design², or other simulators.

This molecular representation is one of many molecular configurations that the software can devise. The configurations may differ depending on the order in which the ions were entered. For example, the top row shows **BaCl2 - 227.448 mg/l**. Barium and chloride could also be added as Ba(OH)₂ and HCl at their respective concentrations. Two alternative configurations are shown below:

¹ Aspen Technologies, Cambridge MA.

² Honeywell Corporation, Calgary AB

Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Molecular Totals (mg/L)	
BaCl2	181.998
BaO	33.4656
CaCl2	5538.40
CO2	18.7530
H2O	9.87070e5
KBr	223.397
KCl	527.416
MgCl2	3133.87
NaCl	25421.1
SiO2	25.0000
SO3	0.416725
SrCl2	542.773

Molecular Basis – Configuration 1

Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Molecular Totals (mg/L)	
BaCl2	227.448
CaCl2	5538.40
CO2	18.7530
H2O	9.87070e5
KCl	667.368
MgBr2	172.813
MgCl2	3044.51
NaCl	25421.1
SiO2	25.0000
SO3	0.416725
SrCl2	508.174
SrO	22.6159

Molecular Basis – Configuration 2

The software generates molecular concentrations based on two priorities. The first priority is to create the least number of molecular inflows. This example contains twelve inflows (plus H₂O not shown). The second priority is that the least number of total moles be created. Moles are not shown here, since the units are mg/l. The moles are shown in the report tab.

Viewing the Report Tab

- ✓ Click on the Report tab



The Report tab is slightly different from the Single Point report described in Chapter 2. 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 selected calculation type, conditions, and any calculated property that needs to be compared to a measured property. This calculation was run at 25C and 1 atm. The two measured properties shown are pH and density.

Reconciliation Summary

Specification
 Charge Balance Method Dominant Ion
 pH Reconciliation Type No reconciliation

	Measured	Calculated	Difference
			%
Temperature, °C	25.0000		
Pressure, atm	1.00000		
pH	6.30000	6.99524	11.04
Density, g/ml	1.02500	1.02272	-0.22
Water, mg/L	1.00000e6	9.87066e5	

The Stream Inflows table represents what we entered in the initial water analysis grid.

Stream Inflows

Row Filter Applied: Only Non Zero Values

Species	mg/L
H2O	9.87066e5
Na+1	10000.0
K+1	350.000
Ca+2	2000.00
Mg+2	800.000
Sr+2	300.000
Ba+2	150.000
Cl-1	21848.9
Br-1	150.000
HCO3-1	26.0000
SO4-2	0.500000
SiO2	25.0000

The Charge Balance table contains the concentrations entered and the final balanced values. In this case only the chloride concentration was changed. This table is provided because when the prorating balance is selected, several concentrations are changed.

Charge Balance

Cation Charge: 0.618592 eq/L
Anion Charge: -0.594647 eq/L
Imbalance: 0.0239445 eq/L
Adjusted Species: Cl-1

Charged Species	Input	Balanced	Difference
	mg/L	mg/L	%
Na+1	10000.0	10000.0	
K+1	350.000	350.000	
Ca+2	2000.00	2000.00	
Mg+2	800.000	800.000	
Sr+2	300.000	300.000	
Ba+2	150.000	150.000	
Cl-1	21000.0	21848.9	4.04
Br-1	150.000	150.000	
HCO3-1	26.0000	26.0000	
SO4-2	0.500000	0.500000	

The remaining tables in the Report tab are the same as those found in the Single Point calculation report.

- ✓ Save the file

4.2b Creating a High Bicarbonate/Sulfate Water

The water analysis in this case contains a high concentration of sulfate and bicarbonate and low concentrations of divalent cations. It is incompatible with the first water (solids will precipitate) which is its purpose. As with the first water, this water is hypothetical.

- ✓ Add a new Water Analysis  **Add Water Analysis** and name it 'High Bicarb/Sulfate'
- ✓ Use the table below to complete the Water Analysis's composition:

4.2b – High Bicarbonate/Sulfate Water Composition							
Analysis Parameters		Neutrals mg/L		Cations mg/L		Anions mg/L	
Default		SiO2	10	Na+1	23000	Cl-1	35000
Recorded Properties				K+1	200	SO4-2	2000
TDS (mg/L)	61000			Ca+2	25	HCO3-1	950
pH	7.8			Mg+2	15		
Alkalinity (mg/l HCO3)	900			Sr+2	10		
Density (g/ml)	1.042			Ba+2	.05		

The screen will look like the one below:

Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	61000.0
Measured pH	7.80000
Measured Alkalinity (mg HCO3/L)	900.000
Density (g/ml)	1.04200
Specific Electrical Conductivity (µmho/cm)	0.0
Neutrals (mg/L)	
H2O	
SiO2	10.0000
Cations (mg/L)	
Na+1	23000.0
K+1	200.000
Ca+2	25.0000
Mg+2	15.0000
Sr+2	10.0000
Ba+2	0.0500000
Anions (mg/L)	
Cl-1	35000.0
SO4-2	2000.00
HCO3-1	950.000

Actions

- ✓ Add a Reconciliation object from the Actions panel  **Add Reconciliation**

Before proceeding, you will enable an important calculation option for this case.

- ✓ Click on the Calculation Options button in the Toolbar ribbon 
- ✓ Check the box for Pre-scaling Tendencies, and keep the Estimated method. Press OK



- ✓ Calculate (or press the <F9> key)

The calculated pH is 7.6 and the density is 1.04 g/ml. There are no solids forming in this sample; the Solids Amount is zero g. Additional information on the solids scaling tendencies is in the Report.

Neutrals (mg/L)	
H2O	9.77650e5
SiO2	10.0000
Cations (mg/L)	
Na+1	23831.5
K+1	200.000
Ca+2	25.0000
Mg+2	15.0000
Sr+2	10.0000
Ba+2	0.0500000
Anions (mg/L)	
Cl-1	35000.0
SO4-2	2000.00
HCO3-1	950.000

Summary	
Automatic Chemistry Model	
Aqueous (+/- ion) Databanks:	
Public	
Dominant Ion Charge Balance (eq/L):	
Cation Charge:	1.00826 eq/L
Anion Charge:	-1.04443 eq/L
Imbalance:	-0.0361685 eq/L
831.512 mg/L of Na+1 is needed to balance.	
Isothermal Calculation	
25.0000 °C 1.00000 atm	
Phase Amounts	
Aqueous	1039.69 g
Vapor	0.0 g
Solid	0.0 g
Aqueous Phase Properties	
pH	7.63323
Ionic Strength	0.0185024 mol/mol
Density	1.03969 g/ml

- ✓ Click on the Report tab and scroll down to the Scaling Tendencies table

This table should contain two columns, the Post-Scale and Pre-Scale tendencies. The column names are not optimal, and will be modified in future versions. These columns represent the saturation ratio of each potential solid phase.

Scaling Tendencies

Row Filter Applied: Values > 1.0e-4

Solids	Post-Scale	Pre-Scale
CaCO3 (Calcite)	0.752846	0.752846
BaSO4 (Barite)	0.743728	0.743728
CaCO3 (Aragonite)	0.316103	0.316103

The first column is the saturation ratio (or scaling tendency) after all potential solids come to equilibrium. This is the true equilibrium condition (time=∞). The second column is the pre-scale tendency and 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 equals 0.

In this case, the pre- and post-scale tendency values are the same, because no solids are at risk of forming – A solid is at risk of forming when the scale tendency value is greater than 1.0.

- ✓ Save the file then close it by selecting File > Close

4.3 Exploring Reconciliation Options

This section starts a new file. It includes a basic water analysis, from which the various reconciliation options can be studied.

- ✓ Create a new file and save it with a name that can distinguish it from the file created for the first two cases.

Setting up a New Water Analysis

4.3 – Water Analysis Composition							
Analysis Parameters		Neutrals mg/L		Cations mg/L		Anions mg/L	
Default		SiO2	16	Na+1	10000	Cl-1	19000
Recorded Properties				Ca+2	500	SO4-2	2700
TDS (mg/L)	36500			Mg+2	1200	HCO3-1	145
pH	7.8			Sr+2	200	AsO4-3	12
Alkalinity (mg/l HCO3)	160			Ba+2	5	CHO2-1	20
Density (g/ml)	1.013			Fe+2	5	C2H3O2-1	50

- ✓ Add a new Water Analysis  and name it “4.3 WaterAnalysis”
- ✓ Use the table above to input the water analysis’s composition

Despite zero values, HCl, a strong acid, and NaOH, a strong base, will adjust the pH for our first calculation.

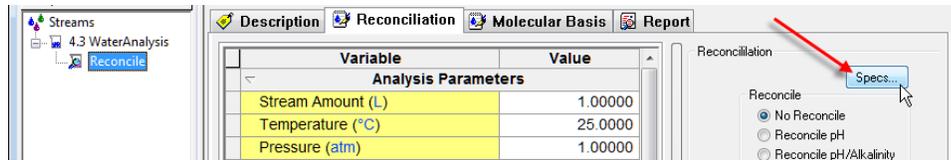
Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	36500.0
Measured pH	7.80000
Measured Alkalinity (mg HCO3/L)	160.000
Density (g/ml)	1.01300
Specific Electrical Conductivity (µmho/cm)	0.0
Neutrals (mg/L)	
H2O	
SiO2	16.0000
Cations (mg/L)	
Na+1	10000.0
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
SO4-2	2700.00
HCO3-1	145.000
AsO4-3	12.0000
HCOO-1	20.0000
C2H3O2-1	50.0000

Reconciliation #1 – Reconcile sample with a fixed pH and solids allowed to form

- ✓ Select Add Reconciliation and name it Reconcile #1
- ✓ Turn on the Pre-Scale Tendencies using the Calculation Options window

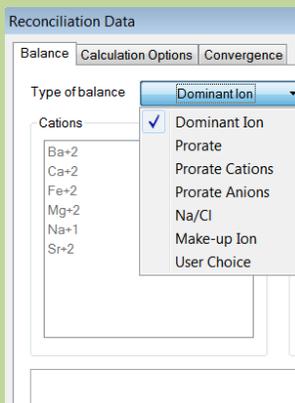


- ✓ Click the Specs button



Selecting the Specs button opens the Reconciliation Data menu. We do not have to adjust the reconciliation specifications yet but will look at some of the options available.

Reconciliation Data options – Types of Balance



Dominant Ion – The highest species concentration of the deficient charge is added. In our example, Na^+ ion is added since there is excess negative charge.

Prorate - An equal portion of every deficient ion is added.

Prorate Cations – All cations are adjusted up or down equally

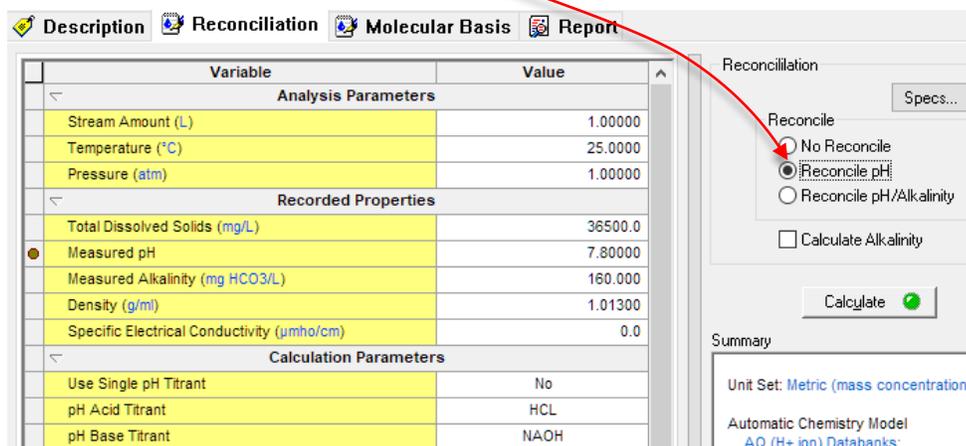
Prorate Anions – All anions are adjusted up or down equally

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 – User selects an ion to increase or decrease. There is no software check to ensure that sufficient concentration exists to decrease

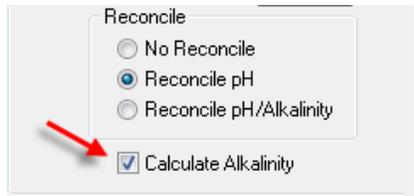
User Choice – Analyzer determines if an anion or cation is needed to balance the solution and the user chooses the specific ion.

- ✓ Keep the default option, Dominant Ion, as the balance type then press OK
- ✓ Click on the Reconcile pH radio button



You will next instruct the software to calculate alkalinity. Calculating the alkalinity requires a second calculation. After completing the reconciliation, the software adds H_2SO_4 (or another acid) until the pH reduces to 4.5. The software then converts the amount of additional acid to alkalinity.

- ✓ Check the Calculate Alkalinity box



- ✓ Press the <F9> key or the Calculate button
- ✓ View the Summary

Although the Report tab, which we will look at later, has more detail, the Summary shows several important points about the reconciliation:

- | | |
|---|---|
| <ol style="list-style-type: none"> 1) The software added 748.9 mg/l Na+ to balance the charge 2) To fix the pH at 7.8, the software added 58.6 mg/l NaOH 3) The calculated alkalinity is 260.8 mg/l as HCO₃/L 4) The reconciliation predicts that 0.49 g of solids will form | <p>Dominant Ion Charge Balance (eq/L):
 Cation Charge: 0.563486 eq/L
 Anion Charge: -0.596060 eq/L
 Imbalance: -0.0325744 eq/L</p> <p>748.883 mg/L of Na+1 is needed to balance.</p> <p>Set pH Calculation
 Measured pH: 7.80000
 pH Titrants:
 Acid: HCl
 Base: NaOH
 Added: 58.6172 mg/L</p> <p>Alkalinity: 260.831 mg HCO₃/L</p> <p>Phase Amounts
 Aqueous 1021.87 g
 Vapor 0.0 g
 Solid 0.491681 g</p> |
|---|---|

- ✓ Click the Report Tab
- ✓ Scroll down to the Scaling Tendencies Table

Scaling tendencies are essentially saturation ratios. When the scaling tendency for a species is 1.0, it indicates that this species is in equilibrium with water. In other words, the species is in the solid phase. A scaling tendency below 1.0 indicates sub-saturation and that the solid phase will not form.

Scaling Tendencies

Row Filter Applied: Values > 1.0e-4

Solids	Post-Scale	Pre-Scale
SrSO ₄ (Celestine)	1.00000	5.42046
CaCO ₃ (Calcite)	1.00000	34.1980
BaSO ₄ (Barite)	1.00000	164.202
FeCO ₃ (Siderite)	0.494154	7.79291
CaCO ₃ (Aragonite)	0.419878	14.3589

The table shows the presence of three solids SrSO₄, CaCO₃, and BaSO₄. What the table does not show are the amounts of each solid. To see solid mass, we will review a different table within the Report tab.

- ✓ Scroll down to the Species Output (True Species) table

The Species Output list is extensive and is sorted by concentration. You can filter this list to focus on the phases of interest. In this case it is the solid phase column.

- ✓ Click on the Species Output (True Species) heading (it is hyperlinked)

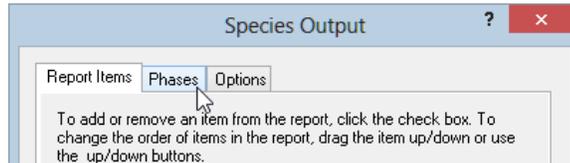
[Species Output \(True Species\)](#)

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

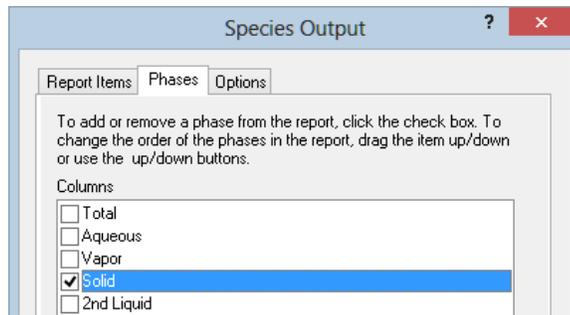
	Total	Aqueous	Solid
--	-------	---------	-------

The hyperlink opens to a customization menu. Most tables have similar options. We can customize tables by clicking their headers or by selecting the Customize button and selecting the table from the Category list.

- ✓ Click the Phases tab



- ✓ Uncheck all the boxes, except for the Solids phase



- ✓ Press OK
- ✓ Scroll down to the Species Output table

The table, now contains the concentrations of predicted solids.

[Species Output \(True Species\)](#)

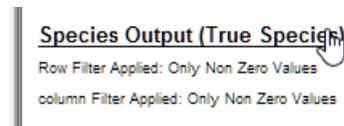
Row Filter Applied: Only Non Zero Values
column Filter Applied: Only Non Zero Values

	Solid
	mg/L
SrSO4 (Celestine)	337.99
CaCO3 (Calcite)	145.248
BaSO4 (Barite)	8.44299
Total (by phase)	491.681

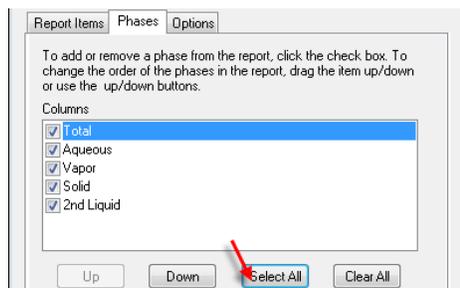
Two of the solids, SrSO₄ and BaSO₄ are salts of a strong acid, H₂SO₄. This means that these solids are not pH-sensitive and the predicted masses will be the same regardless of the water sample's pH. By comparison, the 145 mg/l CaCO₃ solid is pH-sensitive. If a different pH is set, then the CaCO₃ mass will change.

The next task is to study the water composition, and so the complete Species Output table will be reviewed. To eliminate unneeded rows, the table will be filtered to show only values greater than 8 mg/l

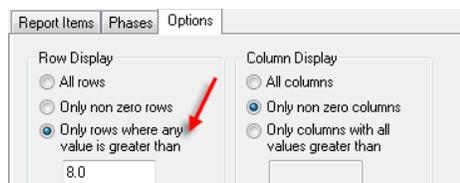
- ✓ Click the header for the Species Output (True Species) header



- ✓ Click the Phases tab
- ✓ Click the Select All button



- ✓ Click the Options tab
- ✓ Select the button for “Only rows where any value is greater than”
- ✓ Enter a value of 8.0 to show species only greater than 8.0 mg/l



- ✓ Press OK then scroll down to the Species Output (True Species) table

We will focus on the dissolved carbonate species, CaCO_3^0 , MgHCO_3^+ , NaHCO_3^0 , and HCO_3^{-1} . Carbonates are part of all natural waters because CO_2 is a key atmospheric component and calcite mineral is a component of many rocks. Carbonates are also critical pH buffering species in surface waters, rivers, lakes, and oceans.

Species Output (True Species)

Row Filter Applied: Values > 8.0
 column Filter Applied: Only Non Zero Values

	Total	Aqueous	Solid
	mg/L	mg/L	mg/L
H2O	9.87593e5	9.87732e5	0.0
Cl-1	18997.3	19000.0	0.0
Na+1	10571.8	10573.3	0.0
SO4-2	1456.18	1456.39	0.0
Mg+2	1137.92	1138.08	0.0
NaSO4-1	1045.07	1045.22	0.0
Ca+2	429.972	430.033	0.0
SrSO4 (Celestine)	344.025	6.08309	337.99
MgSO4	243.864	243.898	0.0
CaCO3 (Calcite)	146.92	1.69316	145.248
Sr+2	35.7366	35.7416	0.0
C2H3O2-1	34.6179	34.6228	0.0
CaSO4 (Anhydrite)	31.4034	31.4078	0.0
HCO3-1	31.1573	31.1617	0.0
MgHCO3+1	19.971	19.9738	0.0
Mg[C2H3O2]+1	13.5767	13.5786	0.0
HAsO4-2	12.0854	12.0871	0.0
SiO2 (Lechatelierite)	11.8788	11.8805	0.0
HCOO-1	11.5153	11.5169	0.0
NaHCO3 (Nahcolite)	10.2068	10.2083	0.0
BaSO4 (Barite)	8.4418	0.0	8.44299
Total (by phase)	1.02222e6	1.02188e6	491.681

The measured or initial HCO_3^{-1} concentration was 145 mg/l. After reconciliation, only 31 mg/l exists as the dissolved species because the rest has precipitated or complexed: 1.7 mg/l CaCO_3^0 , 20.0 mg/l MgHCO_3^+ , 10.2 mg/l NaHCO_3^0 , 31.1 mg/l HCO_3^{-1} , and 145.1 mg/l CaCO_3 (s).

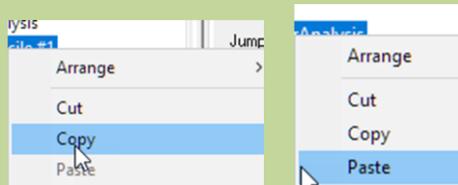
- ✓ Save the file

Reconciliation #2 – Reconcile sample with a fixed pH and solids not allowed to form

The goal of this next calculation step is to see how the chemistry changes when solids are prevented from forming. Such a scenario would exist if the solids are supersaturated by for example, addition of a scale inhibitor. We will assume the pH is correct but that the solids are supersaturated and metastable.

Before proceeding, it may help to organize the Navigator Pane. The following steps are optional.

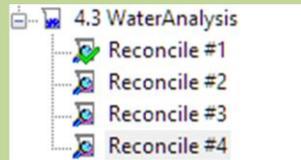
- ✓ Right-mouse click on the Reconcile #1 object and select Copy
- ✓ Right-mouse click the 4.3 WaterAnalysis stream, then select Paste



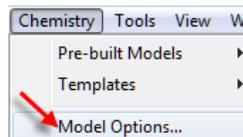
- ✓ Repeat this step two more times

The 4.3 WaterAnalysis should now have four reconcile objects.

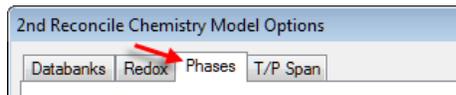
- ✓ Rename each Reconcile #1, Reconcile #2, Reconcile #3, and Reconcile #4



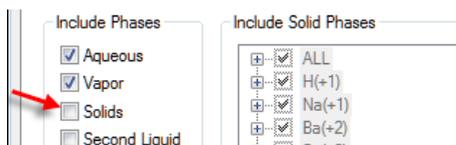
- ✓ Click on Reconcile #2
- ✓ From the menu bar, select Chemistry > Model Options



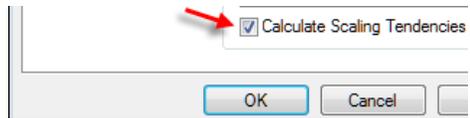
- ✓ Select the Phases tab



- ✓ Remove the check from the Solids box in the Include Phases field



- ✓ Make sure that the Calculate Scaling Tendencies box is checked



- ✓ Press OK

The steps above show the longer way to turn off solid formation. A quicker way is to deselect the Solid phases button in the toolbar. 

- ✓ Press the <F9> key or the Calculate button
- ✓ Select the Report tab
- ✓ Scroll down to the Scaling Tendencies table

Scaling Tendencies

Row Filter Applied: Values > 1.0e-4

Solids	Post-Scale
BaSO4 (Barite)	164.184
SrSO4 (Celestine)	5.41572
CaCO3 (Calcite)	2.86583
FeCO3 (Siderite)	1.22065
CaCO3 (Aragonite)	1.20939
CaSO4.2H2O (Gypsum)	0.247714

The software predicts five solids have saturation ratios greater than 1.0. This means that all five solid phases can potentially form at time equals 0:00. What actually forms will depend on nucleation rates, crystal growth rates, and thermodynamic equilibrium (i.e., minimum free energy conditions). When we turned solids off, we also turned these factors off so they are reflected in the scaling tendencies table. However, this table provides technologists who deal with solids buildup, such as, fouling, scaling, crystallization, etc., with an indication of the thermodynamic driving force for each phase to form.

- ✓ Select the Reconciliation Tab and review the Summary

Dominant Ion Charge Balance (eq/L):
 Cation Charge: 0.563486 eq/L
 Anion Charge: -0.596060 eq/L
 Imbalance: -0.0325744 eq/L

748.883 mg/L of Na+1
 is needed to balance.

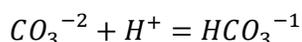
Set pH Calculation
 Measured pH: 7.80000
 pH Titrants:
 Acid: HCl
 Base: NaOH
 Added: 2.54827 mg/L

Alkalinity: 175.288 mg HCO3/L

Phase Amounts
 Aqueous 1022.25 g
 Vapor 0.0 g

Aqueous Phase Properties
 pH 7.80000
 Ionic Strength 0.0117531 mol/mol
 Density 1.02225 g/ml

In the previous calculation, the software added 58.7 mg/l of NaOH to set the pH to 7.8. In this calculation, the software added 2.6 mg/l of NaOH. The reason is calcite was not allowed to precipitate, and therefore CO₃⁻² remained in solution. Since CO₃⁻² is a weak base – it pairs with H⁺ ions to form HCO₃⁻¹:



This reduces the H⁺ concentration and increases pH. Therefore, less NaOH is needed to meet the 7.8 pH. Another effect of eliminating solids is the carbonate speciation.

- ✓ Select the Report tab
- ✓ Scroll down to the Species Output (True Species) table

The table will maintain the customization of showing only species above 8.0 mg/l that we made earlier.

Species Output (True Species)

Row Filter Applied: Values > 8.0
column Filter Applied: Only Non Zero Values

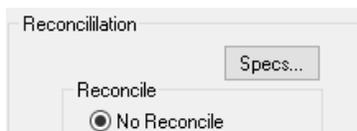
	Total	Aqueous
	mg/L	mg/L
H2O	9.87647e5	9.87647e5
Cl-1	18999.8	18999.8
Na+1	10525.1	10525.1
SO4-2	1561.66	1561.66
Mg+2	1126.96	1126.96
NaSO4-1	1105.22	1105.22
Ca+2	484.273	484.273
MgSO4	254.512	254.512
Sr+2	183.637	183.637
HCO3-1	80.1949	80.1949
MgHCO3+1	50.5783	50.5783
CaSO4	37.1481	37.1481
C2H3O2-1	34.5298	34.5298
SrSO4	32.9187	32.9187
NaHCO3	26.0689	26.0689

The carbonate concentrations are 80 mg/l HCO₃⁻¹, 51 mg/l MgHCO₃⁺¹, and 26 mg/l NaHCO₃⁰. The concentrations increased by a factor of approximately 2.5 when comparing with the previous concentrations.

Reconciliation #3 – Reconcile sample without fixed pH and solids not allowed

Next, we will see what the pH would be if NaOH is not added

- ✓ Select the Reconcile #3 object and click on the Reconciliation tab
- ✓ Make sure solids are turned off or deselect the Solid phase box in the toolbar 



- ✓ Select No Reconcile -
- ✓ Calculate then review the pH in the Summary box

The calculated pH is 7.63. Since this pH is close to the measured pH of 7.8, it prompts the question of whether the water sample's pH was measured before any solids formed.

Aqueous Phase Properties
 pH 7.63160
 Ionic Strength 0.0117533 mol/mol
 Density 1.02225 g/ml

Reconciliation #4 – Reconcile sample without fixing pH and solids allowed to form

The question to be asked in this final example is: what would the pH be if the solids were allowed to form?

- ✓ Select Reconcile #4; and click on the Reconciliation Tab
- ✓ Select No Reconcile



- ✓ Select Chemistry > Model Options > Phases to turn Solids back on or select the Solid button in the Quick Access Ribbon



- ✓ Press <F9> to calculate then Review the pH in the Summary box

Dominant Ion Charge Balance (eq/L):	
Cation Charge:	0.563486 eq/L
Anion Charge:	-0.596060 eq/L
Imbalance:	-0.0325744 eq/L
748.883 mg/L of Na+1 is needed to balance.	
Alkalinity Calculation	
25.0000 °C 1.00000 atm	
Alkalinity: 171.379 mg HCO3/L	
Phase Amounts	
Aqueous	1021.94 g
Vapor	0.0 g
Solid	0.355010 g
Aqueous Phase Properties	
pH	7.35418
Ionic Strength	0.0116562 mol/mol
Density	1.02194 g/ml

The pH is 7.35, lower than the measured value. Adding the 58.6 mg/l NaOH (in Reconcile #1) will increase this pH to the reported value of 7.8.

- ✓ Save the file

Summary

The preceding calculations are examples of how the measured properties, in this case pH, can vary based on reconciliation settings. For instance, if carbonates are predicted to form, then allowing or disallowing solid formation will affect the calculated results.

By comparison, if the pH is forced to a measured value (7.8 in this example), then acid or base will be added. Adding such components changes the stream composition. The software added 58 mg/l NaOH in the first calculation, which increased the Na⁺ concentration by ~35 mg/l Na⁺. Although this concentration is small relative to the initial Na⁺ concentration of 10,000 mg/l, the additional species added or removed may not always be so insignificant.

4.4 Automatically Reconcile for Alkalinity

Water analyses often involve alkalinity measurements. An alkalinity measurement determines the amount of acid a water sample can absorb before its pH drops below 4.5. The 4.5 value, widely regarded as the buffer capacity, represents the endpoint between the reaction of bicarbonate and free acid at 25 °C.

While the alkalinity measurement has a historical legacy, it is not applicable in every situation. This is because alkalinity is a measurement of all ions that will buffer a solution such as phosphate, borate, organic acids, etc. and not just carbonates and bicarbonates. However, alkalinity is still reported in bicarbonate units, as is the case within the OLI Studio. Therefore, we need to rethink our interpretation of this value.

For this example, we will work with the previous water analysis. We will convert the HCO_3^- concentration to an alkalinity. We will then see how this changes the speciation and scale tendencies of the system

- ✓ Return to the 4.3 WaterAnalysis stream and select Add Reconciliation

It may be helpful to rename the new reconciliation object to 'Reconcile #5'

- ✓ Select the Reconcile pH/ Alkalinity button

This reconciliation option opens a new grid section called Calculation Parameters

- ✓ Change the Measured Alkalinity-Aqueous quantity from 0.0 to 145 mg/L

The screenshot shows the '4.3 WaterAnalysis' stream with five reconciliation objects. The 'Reconcile #5' object is selected, opening a grid with 'Variable' and 'Value' columns. The grid is divided into 'Recorded Properties' and 'Calculation Parameters' sections. The 'Recorded Properties' section includes Total Dissolved Solids (36500.0 mg/L), Measured pH (7.80000), Measured Alkalinity (160.000 mg HCO3/L), Density (1.01300 g/ml), and Specific Electrical Conductivity (0.0 μmho/cm). The 'Calculation Parameters' section includes Alkalinity Titrant (CO2), Alkalinity pH Titrant (H2SO4), Alkalinity End Point pH (4.50000), Use Single pH Titrant (No), pH Acid Titrant (HCL), and pH Base Titrant (NAOH). To the right, the 'Reconciliation' control panel shows 'Reconcile' options: 'No Reconcile', 'Reconcile pH', and 'Reconcile pH/Alkalinity' (selected). There is also a 'Calculate Alkalinity' checkbox and a 'Calculate' button.

- ✓ Calculate then review the Summary

The screenshot shows the 'Summary' window with two main sections. The 'Alkalinity Calculation' section displays: Measured Alkalinity: 145.005 mg HCO3/L, Titration End Pt: 4.50000, Alkalinity Titrant: CO2, Removed: 44.1916 mg/L, Alkalinity pH Titrant: H2SO4, pH Reconciliation: Measured pH: 7.80000, pH Titrants: Acid: HCl, Added: 17.3433 mg/L, Base: NaOH. The 'Phase Amounts' section displays: Aqueous: 1021.90 g, Vapor: 0.0 g, Solid: 0.397795 g. The 'Aqueous Phase Properties' section displays: pH: 7.80000, Ionic Strength: 0.0116485 mol/mol, Density: 1.02190 g/ml.

The results differ from previous calculations. To achieve a 7.8 pH and 145 mg/l alkalinity, the software removes 44 mg/l CO₂ (1.0 mmol/l) and adds 17 mg/l HCl (0.475 mmol/l). Removing 44 mg/l CO₂, reduced the dissolved carbonic acid concentration by 1 mmol/l. This reduces total dissolved carbonate AND increases the pH. To counteract the higher pH, the software adds 0.475 mmol/l H⁺ (as HCl).

Summary

The software has a pathway that allows us to use measured pH and alkalinity values in water analyses.

4.5 Manually Reconcile for pH & Alkalinity

In the previous case, the software automatically reconciled for alkalinity by adjusting the carbonate inflow until the calculated alkalinity equaled the measured alkalinity. It also automatically adjusted the pH by adjusting NaOH/HCl.

In this example, the pH is adjusted manually. You will adjust the HCO_3^- concentration until the calculated value matches the measured value. You will also adjust the H^+ or the OH^- concentration until the pH is matched properly. This is an iterative process, and may take several steps. The manual reconciliation enables more user control over the chemistry.

- ✓ Return to the 4.3 WaterAnalysis stream and select Add a new Reconciliation
- ✓ Name it Reconcile #6
- ✓ Add H^+ to the Cations grid
- ✓ Add OH^- to the Anions grid
- ✓ Add CO_2 to the Neutral grid
- ✓ Check the Calculate Alkalinity box
- ✓ Calculate then review the Summary box

The pH is 7.35 and the alkalinity is 171.369 mg/l as HCO_3^- , the same as the previous calculation. You will change some or all of the following concentrations, CO_2 , HCO_3^- , OH^- , and/or H^+ until the pH is 7.8 and the alkalinity is 160 mg/l as HCO_3^- . We will set it manually by adjusting the HCO_3^- concentration and either the H^+ or the OH^- concentrations.

The difference between the Calculated and Measured alkalinity is ~12 mg/l, and the difference between the measured and calculated pH is -0.45. Therefore, you will start by reducing the HCO_3^- by 25 mg/l and by adding about 15 mg/l OH^- .

- ✓ Reduce the HCO_3^- value in the anion grid from 145 mg/l to 133 mg/l.
- ✓ Increase the OH^- from 0 to 15 mg/l

HCO3-1	133.000
AsO4-3	12.0000
HCOO-1	20.0000
C2H3O2-1	50.0000
OH-1	15.0000

- ✓ Calculate
- ✓ View the Summary section, specifically the calculated Alkalinity and pH

Alkalinity Calculation
 25.0000 °C 1.00000 atm
 Alkalinity: 213.725 mg HCO3/L

Phase Amounts
 Aqueous 1021.89 g
 Vapor 0.0 g
 Solid 0.436196 g

Aqueous Phase Properties
 pH 7.63418

The Alkalinity increased to 214 mg/l, and the pH to 7.63. The OH⁻¹ added had two effects. It increased the pH, and it also increased alkalinity. For every 17 mg/l OH⁻ added, the alkalinity increases by 61 mg/l HCO3⁻¹. The following simplified equation for alkalinity illustrates this effect.

$$\text{Alkalinity} = \text{HCO}_3^{-1} + \text{CO}_3^{-2} + \text{OH}^{-} - \text{H}^{+} + \text{others} \dots$$

We really don't know how much OH⁻ or HCO3⁻¹ to add or remove, so you will take another guess.

- ✓ Keep the OH⁻ concentration at 15 mg/l and reduce the HCO3⁻¹ to 80 mg/l.
- ✓ Calculate and review the Summary

Anions (mg/L)	
Cl-1	19000.0
SO4-2	2700.00
HCO3-1	80.0000
AsO4-3	12.0000
HCOO-1	20.0000
C2H3O2-1	50.0000
OH-1	15.0000

Alkalinity Calculation
 25.0000 °C 1.00000 atm
 Alkalinity: 163.025 mg HCO3/L

Phase Amounts
 Aqueous 1021.86 g
 Vapor 0.0 g
 Solid 0.428692 g

Aqueous Phase Properties
 pH 8.06757
 Ionic Strength 0.01163
 Density 1.02186 g/ml

The pH increased to 8.1 and the alkalinity 163 mg/l is near the target value. The next step should be a lower OH⁻¹ concentration with a higher HCO3⁻¹. Since the mass ratio of OH⁻¹ to HCO3⁻¹ is 17 mg to 61 mg, every mg OH⁻¹ removed requires 3.6 mg/l HCO3⁻¹ be added to maintain alkalinity. Before adding any more HCO3⁻¹ however, we can drop the alkalinity to 160 by reducing OH⁻¹ by 1 mg/l

- ✓ Reduce the OH⁻¹ concentration to 14 mg/l
- ✓ Calculate

Anions (mg/L)	
Cl-1	19000.0
SO4-2	2700.00
HCO3-1	80.0000
AsO4-3	12.0000
HCOO-1	20.0000
C2H3O2-1	50.0000
OH-1	14.0000

Alkalinity Calculation
 25.0000 °C 1.00000 atm
 Alkalinity: 159.436 mg HCO3/L

Phase Amounts
 Aqueous 1021.87 g
 Vapor 0.0 g
 Solid 0.423640 g

Aqueous Phase Properties
 pH 8.01999

The pH is now 8.02 and the alkalinity is 159 mg/l as HCO₃⁻¹. These numbers are closer to the target values. Perhaps a little less OH and more HCO₃ will achieve the desired target.

- ✓ Increase the HCO₃-1 concentration to 88 mg/l and reduce the OH-1 to 12
- ✓ Calculate

Anions (mg/L)	
Cl-1	19000.0
SO4-2	2700.00
HCO3-1	88.0000
AsO4-3	12.0000
HCOO-1	20.0000
C2H3O2-1	50.0000
OH-1	12.0000

Alkalinity Calculation
 25.0000 °C 1.00000 atm
 Alkalinity: 159.913 mg HCO₃/L

Phase Amounts
 Aqueous 1021.88 g
 Vapor 0.0 g
 Solid 0.414596 g

Aqueous Phase Properties
 pH 7.85928

The alkalinity is now at 160 mg/l as HCO₃⁻¹, and the pH dropped slightly to 7.86. At this point, the results are close to the target values, and probably close enough to continue on to the next task.

- ✓ If you like, complete the manual adjustment to reduce the error further.

Summary

This case study presents a method to set the pH and alkalinity by manually adjusting inflow compositions. It is much more labor intensive than the automatic method, but it has the advantage of enabling the user to manipulate what they want and not relying on the automatic calculation.

Follow-up Example #1 – Arabian Gulf Seawater Analyses

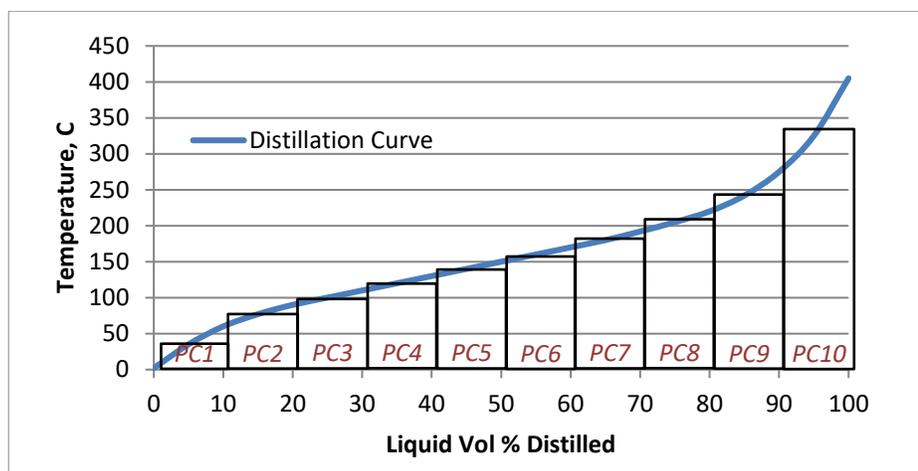
This example reinforces the concepts from the earlier sections. We will run this example using two different water analyses. The first one is seawater from the Middle East. The other is a groundwater with a unique composition. We will build the two samples and perform two reconciliations on each: a basic equilibrium, then a pH reconciliation. We want to keep track of the amount of additive required to achieve the set pH and also track the solid content in each reconciliation.

Name	<i>Middle East Seawater</i>	<i>6,000 M Well</i>
Stream Amount (L)	1	1
Temperature (°C)	30	15
Pressure (atm)	1	1
Recorded Properties		
TDS(mg/L)	42,528	211,197
pH	8.2	4.6
Density(g/ml)	1.029	1.09
Conductivity(mho/m)	5	
Neutrals		
H2O	Calculated	Calculated
B(OH)3	31	43
SiO2	2	300
Cations (mg/L)		
Li+	0.25	
Na+	13,440	55,895
K+	485	9,730
Ca+2	520	17,163
Mg+2	1,765	473
Sr+2	1	121
Ba+2	0.08	630
Fe+2	0.008	469
Pb+2		3.6
Zn+2		1.3
Anions (mg/L)		
F-	1.5	3.1
Cl-	24,050	126,700
SO4-2	3,380	9.2
HCO3-1	165	1.1
CO3-2	88	---
Basic Equilibrium Reconciliation		
Amount of additives to set pH:		
Amount of total solid phase:		
pH Reconciliation		
Amount of additives to set pH:		
Amount of total solid phase:		

4.6 Crude Oils

Crudes oils are complex groups of organic molecules containing, perhaps, thousands of pure components. 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 workaround is to create pseudocomponents.

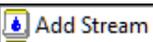
The properties of a crude oil are characterized by its distillation curve. The complete boiling point range is a progression of molecular weights, densities, solubilities, viscosities, and other molecular properties. It is reasonable for low boiling point molecules to be low molecular weight, low density, low viscosity, and more soluble in water. This boiling point curves can be sliced into temperature ranges, and well-accepted characterization methods are used to create pseudocomponents. These pseudocomponents when combined represent the aggregate properties of the whole oil. Below is an example of a distillation curve that is segmented into 10 pseudocomponents.



4.7 Entering a PVT Analysis

You will create a simple PVT analysis using the data from the table below. This is done by creating an Assay Editor within the inflow grid.

4.6 Crude Oil Analysis Composition			
Stream Name	Crude Oil	Assay Data Type	ASTM D86
Unit Set	Default	Average Bulk Density Type	API Gravity
H2O	55 mol	API Gravity	40
Inflow name	ASSAY	Distillation Cuts	10
Inflow amount (mol)	1000	Distillation Data	(see table below)
		Thermo Method	API-8

- ✓ Add a new stream  and change the name to 'Crude Oil' 
- ✓ Select the 2nd Liquid phase button in the toolbar



- ✓ In the Inflows Grid, type ASSAY then press **Shift + Enter**

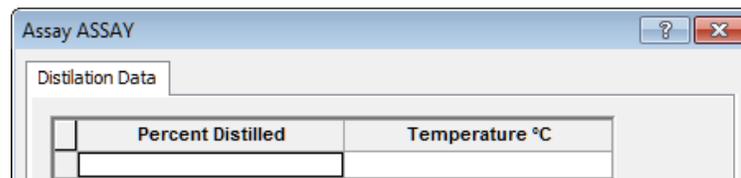
The <Shift + Enter> action instructs the software to create an Assay rather than look for a species or pure component from the database. The sub-grid menu that opens is straightforward.

- ✓ Use the table above to complete the initial grid

	Variable	Value
Stream Parameters		
	Stream Amount (mol)	1055.51
	Temperature (°C)	25.0000
	Pressure (atm)	1.00000
Inflows (mol)		
	H2O	55.5082
	ASSAY	1000.00
	— Assay Data Type	ASTM D86
	— Average Bulk Density Type	API Gravity
	— API Gravity	40.0000
	— Distillation Curve Cuts	10
	— Distillation Data	<input type="button" value="Edit..."/>
	— Thermo Method	API-8

- ✓ Click the Edit button in the Distillation Data

This opens a new menu.



- ✓ Enter the following data from the following table

ASSAY Distillation Data	
Percent Distilled	Temperature, °C
1	20
5	30
10	50
20	60
40	80
60	120
80	150
90	180
95	200
99	220
100	240

Pressing the <Tab> or <Enter> key advances to the next empty cell.

Percent Distilled	Temperature °C
1.000	20.00
5.000	30.00
10.00	50.00
20.00	60.00
40.00	80.00
60.00	120.0
80.00	150.0
90.00	180.0
95.00	200.0
99.00	220.0
100.0	240.0

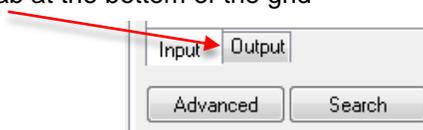
- ✓ Press OK when done
- ✓ Add a Single Point calculation and keep the type as Isothermal



- ✓ Press the <F9> key or the Calculate button

We will review the results in the Output tab.

- ✓ Click the Output tab at the bottom of the grid



The Output grid shows 10 pseudocomponents, corresponding to each distillation cut of the crude.

Inflows (mol)		
	H2O	55.5082
P	+ ASSAY_243K	87.6615
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

The name of each cut is the combination of the oil name (ASSAY) plus its boiling point in Kelvin. The + sign adjacent to each Assay is a sub table containing the critical properties of each cut.

- ✓ Expand the first pseudocomponent by clicking on the + button adjacent to ASSAY_243K

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

The grid expands to show the pseudocomponent properties boiling point, density, and molecular weight. Also shown is the thermodynamic method used to create the properties.

- ✓ Click on the Report tab and scroll down to Species Output

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

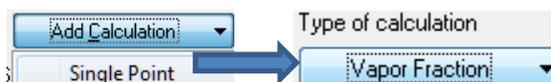
	Total	Aqueous	2nd Liquid
	mol	mol	mol
ASSAY_307K	200.849	7.92146e-5	200.849
ASSAY_337K	173.14	2.38856e-5	173.14
ASSAY_403K	131.728	1.35223e-6	131.728
ASSAY_431K	110.846	3.90166e-7	110.846
ASSAY_370K	109.658	4.2682e-6	109.657
ASSAY_243K	87.6615	2.78888e-4	87.6612
ASSAY_278K	82.2275	8.60183e-5	82.2274
ASSAY_464K	57.0493	4.80476e-8	57.0493
H2O	55.5082	55.076	0.432201
ASSAY_496K	35.217	6.27641e-9	35.2169
ASSAY_524K	11.6247	4.30204e-10	11.6246
H+1	1.00016e-7	1.00016e-7	0.0
OH-1	1.00016e-7	1.00016e-7	0.0
Total (by phase)	1055.51	55.0765	1000.43

The pseudocomponents are distributed between the aqueous and second liquid. The aqueous solubility decreases with each increasing boiling point. The computed range is over five orders of magnitude.

We will now look at the vapor associated with the assay using the Vapor Fraction calculation. This single-point calculation distributes the mass (in terms of moles) evenly across the vapor and liquid phases.

- ✓ Return to the Crude Oil object

- ✓ Add a Single Point calculation and set the calculation to type to Vapor Fraction



- ✓ Change the framework to MSE
- ✓ Make the Vapor Fraction value 50 mol%

	Variable	Value
Stream Parameters		
	Stream Amount (mol)	1055.51
	Temperature (°C)	25.0000
	Pressure (atm)	1.00000
Calculation Parameters		
	Vapor Fraction (Vapor/Inflow [mol]) (mole %)	50.0000
	Calculate	Temperature
Inflows (mol)		
	H2O	55.5082
	ASSAY	1000.00

- ✓ Calculate then view the Summary

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
 AQ (H+ ion) Databanks:
 Public
 Second Liquid phase

Vapor Fraction Calculation
 1.00000 atm
 75.5232 °C

Phase Amounts
 Aqueous 0.0 mol
 Vapor 527.754 mol
 Solid 0.0 mol
 2nd Liquid 527.754 mol

- ✓ Select the Report tab and scroll to the Total and Phase Flows (Amounts) table

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Vapor	2nd Liquid
	mol	mol	mol
Mole (True)	1055.51	527.754	527.754
Mole (App)	1055.51	527.754	527.754
	g	g	g
Mass	91589.1	34388.6	57200.4
	L	L	L
Volume	14896.4	14824.3	72.1604

- ✓ Scroll down to the Species Output table

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Vapor	2nd Liquid
	mol	mol	mol
ASSAY_307K	200.849	152.252	48.5968
ASSAY_337K	173.14	99.7572	73.3825
ASSAY_403K	131.728	19.8074	111.921
ASSAY_431K	110.846	7.38536	103.461
ASSAY_370K	109.658	36.9317	72.7258
ASSAY_243K	87.6615	83.1548	4.50666
ASSAY_278K	82.2275	71.9182	10.3093
ASSAY_464K	57.0493	1.24392	55.8054
H2O	55.5082	55.039	0.469279
ASSAY_496K	35.217	0.238298	34.9787
ASSAY_524K	11.6247	0.0260148	11.5986
Total (by phase)	1055.51	527.754	527.754

Follow-up Example # 2

The OLI Studio computes the critical properties of pseudocomponents using one of the three models discussed above. To see this data, we will need to open a temporary file generated by the software using Notepad or a similar program. To determine the name of the file, we will have to enable the File Viewer plug-in and select Trace File from the drop-down menu. A more detailed procedure is provided in the appendix. For now, the instructor will walk through this process.

Below is the formatted text that shows the critical generated properties of a pseudocomponent. This is a snapshot of a particular case so your data may not be the same. Our interest is to look at the available variables.

<i>Name: Assay_301K</i>					
General Information		Vapor Level		Aqueous Level	
IDNO	9001	ACEN	1.652281E-01	HREF	-1.187195E+05
FORM	C4H8	TCRI	4.943862E+02	GRES	-1.754773E+05
CHEM	C4H8	PCRI	5.677158E+06	SREF	2.406714E+02
MOLW	58.3910	VCRI	2.255796E-04	CPRE	1.485803E+01
MATC	8800	BOIL	3.012723E+02	VREF	0.000000E+00
STOI	1.0	CP	-1.305125E+01 3.066628E-01 -3.051758E-03 - 1.318545E-04 -3.885781E-15	HKF	0.0 0.0 0.0 0.0 - 3.412494E+02 1.724216E+06 - 1.968107E+06
		HREF	-1.261644E+05	ZRAC	2.732220E-01
		GRES	-1.963413E+05		
		SREF	3.103500E+02		
		CPRE	6.665928E+01		
		EQUA	PVTCu_294KVAP= PVTCu_294KAQ		

The General Information category describes the created pseudocomponent(s). In this case, it is a C4H8 molecule with a 58 amu molecular weight. The MATC is a material code identified by the software and STOI is the stoichiometry of this material (1 moles of 8800 or 1 mole of C4H8). The thermodynamic properties for the vapor and aqueous species are as shown above. Critical temperature (TCRI) is 494K (221°C) and critical pressure (PCRI) is 5.67e6 Pa (~56 atm). See the end of the chapter for a more detailed explanation of each term in the generated critical properties file.

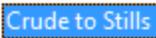
Our task now is to regenerate these pseudocomponents using the Lee Kessler and the Cavett models.

How do the results differ?

4.8 Entering Pseudocomponents to a Stream

Many clients have their own PVT analysis models with pseudocomponent properties. Clients can enter this information using OLI Studio: Stream Analyzer’s pseudocomponent entry option, which is the focus of this section. We will enter three properties - boiling point, molecular weight, and density. The software will use one of four thermodynamic models – API-8, API-5, Cavett or Kessler-Lee – to calculate critical properties.

4.7 Crude to Stills Composition							
Stream Name	Crude to Stills	Pseudocomponent	PC1	PC2	PC3	PC4	PC5
Stream Amount	(calculated)	Inflow (mol)	100	200	250	250	180
Temperature	15C	Thermo Method	API-8	API-8	API-8	API-8	API-8
Pressure	1 atm	Boiling Point (C)	33°C	60	100	140	190
H2O	20 mol	Specific Gravity	0.72	0.76	0.8	0.85	0.9

- ✓ Add a new stream  and change the name to 'Crude to Stills' 
- ✓ Select the 2nd Liquid phase button in the toolbar



- ✓ Change the Temperature to 15 C
- ✓ Change the H2O inflows 20 moles
- ✓ In the Inflows grid, enter the name 'PC1' in a blank cell then press <Ctrl+Enter>

The CTRL-Enter action instructs the software to create a pseudocomponent rather than look for a species.

- ✓ Repeat the previous step four more times with the following names PC2, PC3, PC4, and PC5
- ✓ Use the table above to complete the details for each pseudocomponent

The screen will look like the one below

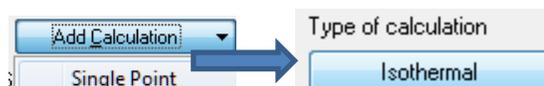
The screenshot displays the OLI Studio interface. On the left, a table lists variables and their values for five pseudocomponents (PC1-PC5) and H2O. On the right, a summary panel shows calculation settings and results.

Variable	Value
H2O	20.0000
PC1	100.000
Thermo Method	API-8
Normal Boiling Point (°C)	33.0000
Specific Gravity	0.720000
Molecular Weight	
Calculated Properties	
PC2	200.000
Thermo Method	API-8
Normal Boiling Point (°C)	60.0000
Specific Gravity	0.760000
Molecular Weight	
Calculated Properties	
PC3	250.000
Thermo Method	API-8
Normal Boiling Point (°C)	100.000
Specific Gravity	0.800000
Molecular Weight	
Calculated Properties	
PC4	250.000
Thermo Method	API-8
Normal Boiling Point (°C)	140.000
Specific Gravity	0.850000
Molecular Weight	
Calculated Properties	
PC5	180.000
Thermo Method	API-8
Normal Boiling Point (°C)	190.000
Specific Gravity	0.900000

Summary Panel:

- Type of calculation: Isothermal
- Bubble/Dew Point: Temperature, Pressure
- Calculate:
- Unit Set: Metric (moles)
- Automatic Chemistry Model: AQ (H+ ion) Databanks: Public
- Second Liquid phase
- Isothermal Calculation: 15.0000 °C 1.00000 atm
- Phase Amounts:
 - Aqueous: 19.7387 mol
 - Vapor: 0.0 mol
 - Solid: 0.0 mol
 - 2nd Liquid: 980.261 mol
- Aqueous Phase Properties:
 - pH: 7.16798
 - Ionic Strength: 1.22403e-9 mol/mol
 - Density: 0.999220 g/ml
- Calc. elapsed time: 0.579 sec

- ✓ Add a Single Point calculation and keep the type as Isothermal



- ✓ Calculate
- ✓ Select the Report tab then scroll down to the Species Output table

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	2nd Liquid
	mol	mol	mol
PC4	250.0	4.5228e-7	250.0
PC3	250.0	1.82695e-6	250.0
PC2	200.0	7.27511e-6	200.0
PC5	180.0	5.38264e-8	180.0
PC1	100.0	9.92525e-6	100.0
H2O	20.0	19.7387	0.261272
H+1	2.41608e-8	2.41608e-8	0.0
OH-1	2.41608e-8	2.41608e-8	0.0
Total (by phase)	1000.0	19.7387	980.261

As with the PVT analysis, below are critical properties that were created for the pseudocomponents. Here is what the first pseudocomponents look like. Compare your results and see if they differ:

General Information		Vapor Level		Aqueous Level	
IDNO	9001	ACEN	1.971444E-01	HREF	-1.161440E+05
FORM	C5H4	TCRI	4.869634E+02	GRES	9.132121E+03
CHEM	C5H4	PCRI	4.693782E+06	SREF	2.396181E+02
MOLW	70.3287	VCRI	2.710277E-04	CPRE	2.462721E+02
MATC	8501	BOIL	3.061500E+02	VREF	0.000000E+00
STOI	1.0	CP	-1.018304E+02	HKF	0.0 0.0 0.0 0.0
			8.012371E-01		3.812119E+01 -
			2.297224E+06		2.436481E+04 -
			-7.714722E-04		2.426621E+03
			3.384218E-07		
		HREF	-1.284117E+05	ZRAC	2.928183E-01
		GRES	-9.686262E+03		
		SREF	3.438813E+02		
		CPRE	1.033026E+02		
		EQUA	PC1VAP=PC1AQ		

Follow-up Example #3

As a last follow-up, we will run a whole fluid calculation. We will assume that the case in question is a gas-condensate-black oil fluid being produced from a newly developed field. The field produces 50,000 bbl/day oil and 3MM of gas. We have a whole fluid analysis that includes pure component data, a PVT curve and pseudocomponents. In addition, the new well produces 1000 bbl/day of brine. This is what the data looks like. This is an actual sample, so do not be surprised if it takes you a long time to work on this.

Water Analysis		Whole Fluid Analysis				Flow Rates	
pH	4.7	Pure Component	Mole %	Pseudocomponents		Water	100 bwpd
Density	1.01	H2O	...	PC1 (mole%)	10.6	Oil/Gas	1000 bopd (1314 kgmol)
Calc type	pH only	N2	0.32	NBP, C	270		
Neutrals	ppm	CO2	0.106	MW	212		
SiO2	12.7	H2S	0.001				
B(OH)3	38.3	C1	51.5	PC2 (mole%)	8.4		
Cations	ppm	C2	3.0	NBP, C	340		
Na+	2700	C3	2.5	MW	282		
K+	30	iC4	1.5				
Mg+2	169	nC4	1.5	PC3 (mole%)	5.1		
Ca+2	3200	iC5	1.10	NBP, C	400		
Sr+2	7.9	nC5	1.0	MW	350		
Ba+2	6.6	C6	1.0				
Mn+	1.1	C7	1.1	PC4 (mole%)	3.1		
Zn+	1.8	C8	1.1	NBP, C	450		
Fe+3	28	C9	0.8	MW	420		
Anions	ppm	C10	0.9				
Cl-	10150	Balance	Mole%	PC5 (mole%)	2.4		
HCO3-1	46	PC1	12.6	NBP, C	520		
SO4-2	13	PC2	8.4	MW	560		
		PC3	5.1				
		PC4	3.1				
		PC5	2.4				

Chapter 5 Mixers

Introduction

In this chapter, we will look at how Stream Analyzer mixes two or more streams. The object is called *Mixer* and you will familiarize yourselves with its three mixing options, Multiplier, Ratio, and Volume. It should be noted that in previous software versions, the Multiplier option was called Ratio and the Ratio option was labeled Proportion. If you are familiar with Versions 4 and earlier, you will note this difference.

We will also mix two incompatible waters using the *Water Analysis* objects that were created in Chapter 4. Lastly, we will perform a titration experiment using the Mixer feature. As in previous chapters, these lessons are designed around real-world situations.

The *Mixer* object or block can be accessed from the Menu Bar by selecting Calculations > Add Mixer or by selecting the Add Mixer in the Actions Pane as shown below:



The *Mixer* should not be confused with the Studio ScaleChem object called *Mixing Water*:



Calculation List

5.1 Mixing Two Incompatible Waters.....	2
5.2 Simple Mixer Calculation	8
5.3 Neutralizing Two Streams.....	12
5.4 Creating a Titration Curve.....	23

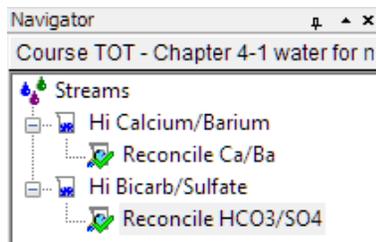
5.1 Mixing Two Incompatible Waters

Overview

This case was begun in Chapter 4, where two water analyses, High Ca/Ba and High HCO₃/SO₄ were created. These waters will be mixed in this case. The potential solid phases are Ca⁺², Sr⁺², and Ba⁺² forms of SO₄⁻² and CO₃⁻². The exact phase that forms depends on the mixing fraction of each water.

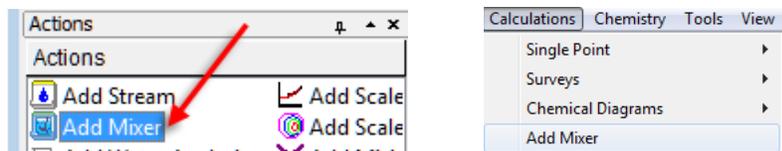
Procedure

- ✓ Open the file that contains the 'High Calcium/Barium' and the 'High Bicarb/Sulfate' analyses

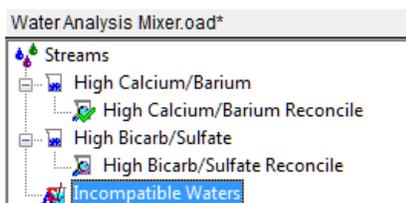


Each object should have a distinct label. This will be important in the next step

- ✓ Add a new Mixer from the Actions Pane or from the menu bar Calculations > Add Mixer



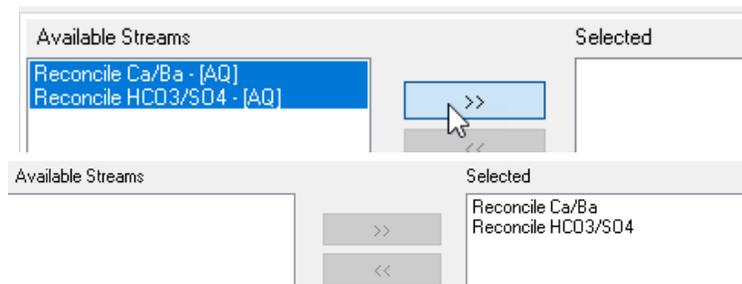
- ✓ Rename the mixer 'Incompatible Waters'



- ✓ Select the Definition tab of the new mixer

There should be two streams in the Available field, Reconcile Ca/Ba and Reconcile HCO₃/SO₄. These are the two Reconcile objects. By comparison the Water Analysis objects are not present, because no charge balance or calculation was done at that level.

- ✓ Highlight both streams and add them to the Selected section.



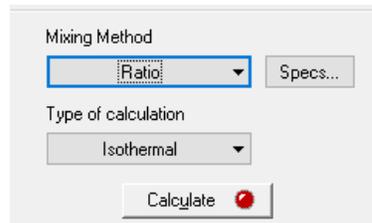
The grid should now look like the one below. Two streams are in the mixer. Each has an inflow of 1 L. Their inflow conditions are 25 C and 1 atm. These flows and conditions cannot be edited because they are set in that reconcile object.

The Current Mixer conditions (the value column) is 25 C and 1 atm. These conditions can be adjusted.

Variable	Value	Reconcile Ca/Ba	Reconcile HCO3/SO4
Multiplier		1.00000	1.00000
Stream Parameters			
Total Inflow		1.00000 L	1.00000 L
Temperature (°C)	25.0000	25.0000	25.0000
Pressure (atm)	1.00000	1.00000	1.00000

The top row is the multiplier. This row is used to multiply up or down, the stream inflow. The default values is 1, and so each stream enters the mixer at 1 L. These multipliers can also be modified using the Mixing Method option in the upper right of the mixer

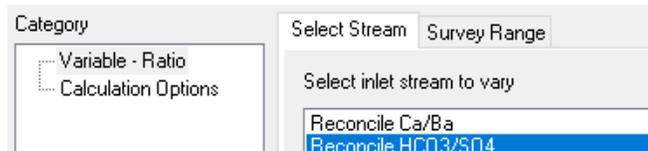
- ✓ Select Ratio as the Mixing Method



The Ratio option mixes between 0% and 100 % of one stream to the other. The first calculation contain 0% of Stream A and 100% of Stream B. The last calculation contains 100% of Stream A and 0% of Stream B.

The calculation button is red. A stream needs to be selected as being *adjusted* relative to the other. In fact, both streams are adjusted;

- ✓ Click on the Specs... button
- ✓ Highlight the 'High Bicarb/Sulfate Reconcile' stream



- ✓ Click on the Survey Range tab

The default setting is to start at 0 fraction of Reconcile HCO3/SO4 and end at a 1 fraction of this stream. The increments are 0.1.

- ✓ Click on the Calculation Options Category
- ✓ Check the Pre-scaling Tendency box if not already selected



- ✓ Press OK to close the Specs Window

The Multiplier cell for the Reconcile HCO3/SO4 is now yellow, it is no longer editable, since it will be adjusted automatically by the Ratio selection. The Reconcile Ca/Ba multiplier is still adjustable, but this has

the net effect of changing the total amount of flow to the system, and not just this stream, since the mixing is still based on fraction.

- ✓ Calculate
- ✓ Select the Plot tab



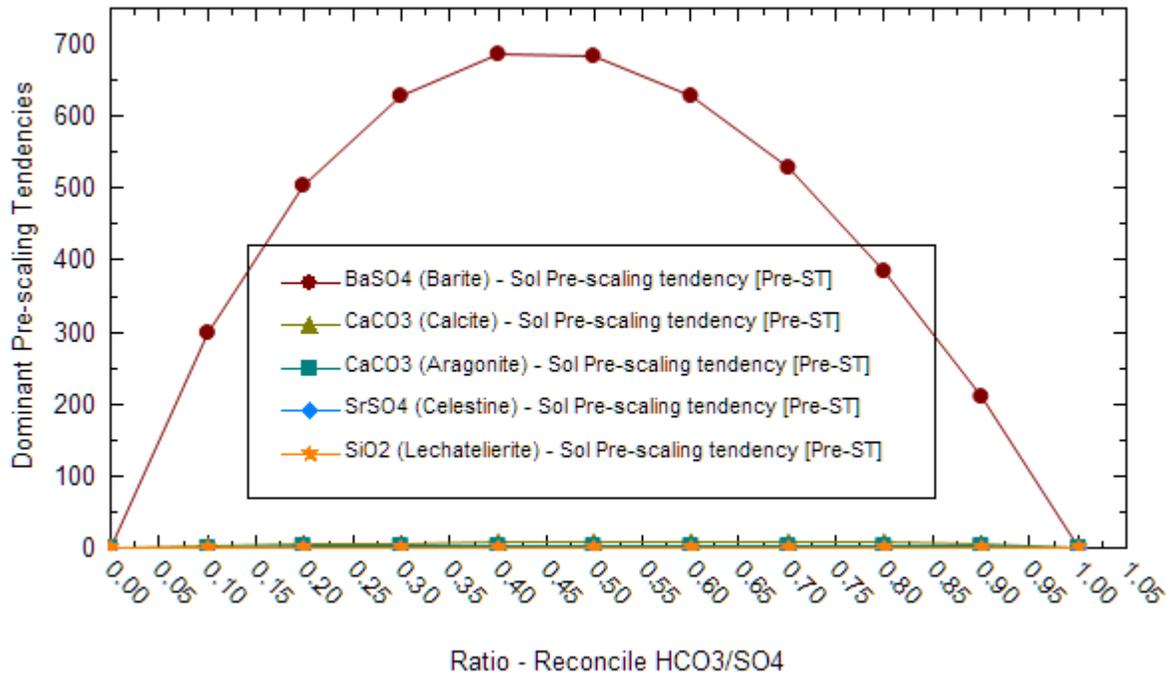
The plot will be blank, because there is no default variable set. You will select variables next.

- ✓ Select the Variables button
- ✓ Remove any variables from the Y1 Axis
- ✓ Expand the **Pre-Scaling Tendencies** category
- ✓ Double-click Dominant Pre-Scaling Tendencies to add it to the Y1 Axis



- ✓ Press OK and view the plot

The resulting plot is a typical fluid incompatibility. The two waters when mixed equally are predicted to reach maximum supersaturation with barite. Notice that other curves are present, but their shape cannot be seen because of the high barite value.

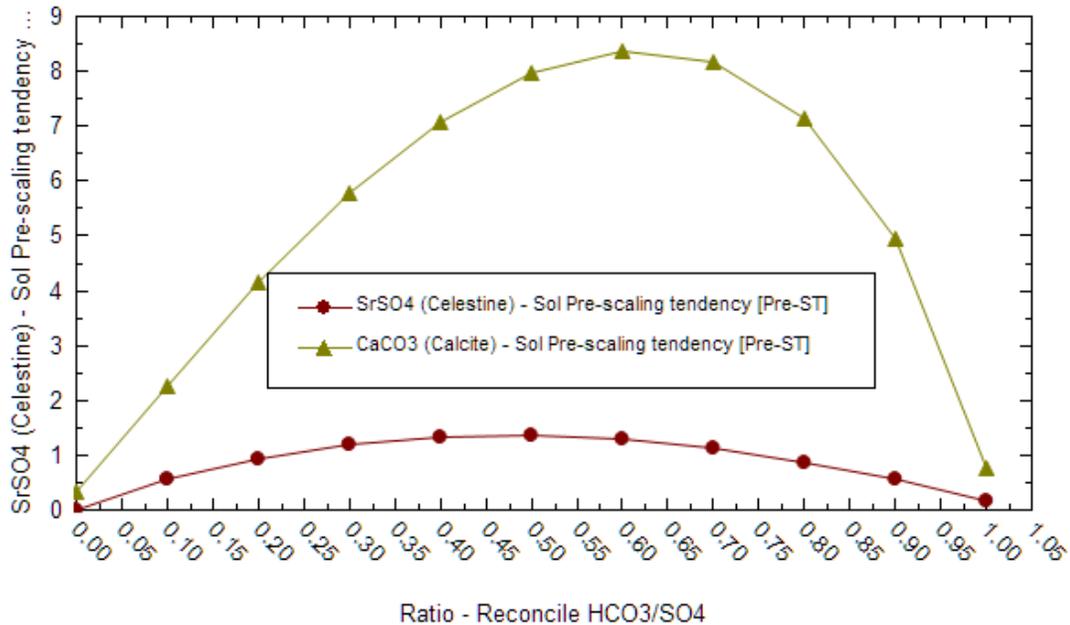


- ✓ Select the Curves button
- ✓ Double-click Dominant Pre-Scaling Tendencies to remove it from the Y1 Axis
- ✓ Expand the **Pre-Scaling Tendency** category
- ✓ Add CaCO3 (Calcite) and SrSO4 to the Y-Axis



- ✓ Press OK and view the plot

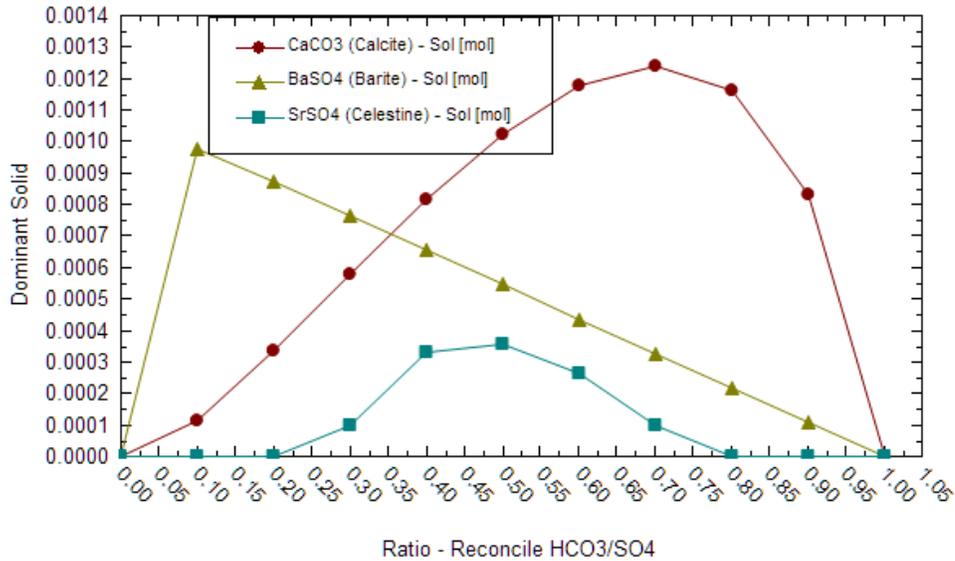
These two phases display the characteristic bell-shapes, meaning that the two waters are also incompatible with respect to these phases. The mixing ratios where the solids reach maximum risk are different.



- ✓ Select the Curves button
- ✓ Select the Y1 Axis header then select the << button to remove all the variables
- ✓ Expand the **Solid** category and double-click Dominant Solid to add it to the Y1 Axis

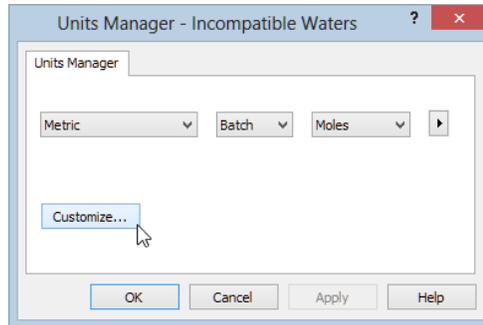


- ✓ Press OK and view the plot



The maximum scale mass occurs at 3 different ratios, 5% for BaSO₄, 50% for SrSO₄, and 75% for CaCO₃. The units are in moles, which is useful when looking at absolute values. In this case, however, concentration units will be more useful.

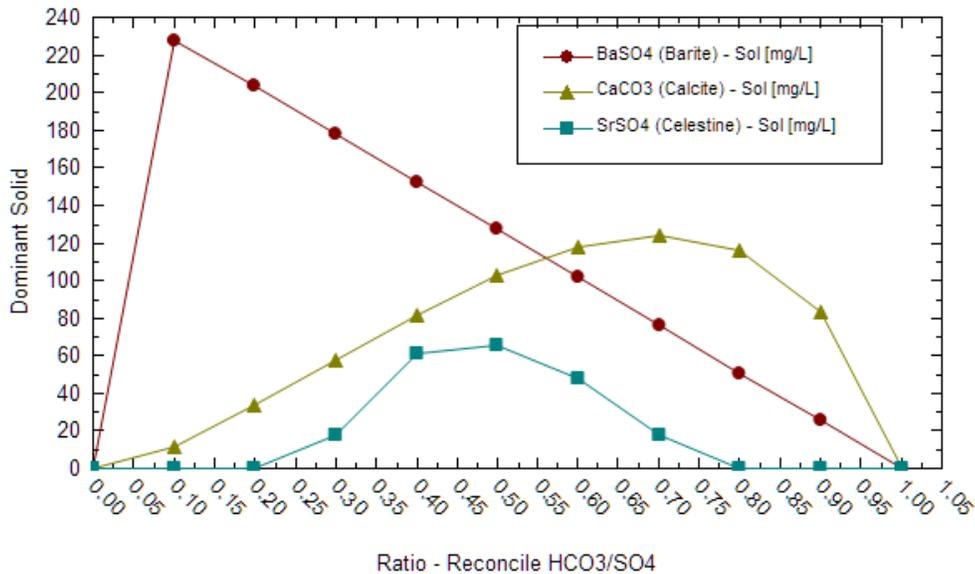
- ✓ Select the Units Manager button in the toolbar 
- ✓ Select the Customize button



- ✓ Change the Solids Composition row from Moles to Concentration

Units Manager - Incompatible Waters			
Units Manager			
Metric	Batch	Moles	▶
Customize...			
OK Cancel Apply Help			
<input checked="" type="radio"/> Batch System <input type="radio"/> Flow System			
Composition Parameters Corrosion			
Variable	Basis	U	
Stream Amount	Moles	mol	
Inflows	Moles	mol	
Aqueous Composition			
Vapor Composition	Moles	mol	
Solid Composition*	Concentration	mg/L	
2nd Liquid Composition	Moles	mol	
Total Composition	Moles	mol	

- ✓ Press OK twice to close the Units windows
- ✓ Refresh the plot by clicking a different tab (for example click on the Definition tab) then click back on the Plot tab



The curves have similar shapes, but now the high formula weight of BaSO₄ makes this curve more pronounced. The ratio where the barite amount is at maximum is at 5% of the High Bicarb/Sulfate stream. We can see this comparing the Ba⁺² and SO₄⁻² concentrations in their respective waters (view the table below). The amount of Ba⁺² and SO₄⁻² in the two waters are 0.00109 and 0.0208 moles/kg respectively. They therefore are equivalent in moles, when the High Calcium/Barium water is 19.1 times greater than the High Bicarb/Sulfate water.

<i>Barium and Sulfate concentrations</i>			
	mg/l	Molal	Mole Ratio
High Calcium/Barium	150 mg/l Ba ⁺²	0.00109	1
High Bicarb./Sulfate	2000 mg/l SO ₄ ⁻²	0.0208	19.1

Likewise, the calcium to carbonate molar ratio in the two waters is 3.2 moles Ca⁺² to 1 mole CO₃⁻². Therefore, the maximum mas should occur at $\frac{3.2}{3.2+1} = 76\%$ of the High Bicarb/Sulfate water.

<i>Calcium and Carbonate concentrations</i>			
	mg/l	Molal	Mole Ratio
High Calcium/Barium	2000 mg/l Ca ⁺²	0.0499	3.20
High Bicarb./Sulfate	950 mg/l CO ₃ ⁻²	0.0156	1

Lastly, the strontium to sulfate molar ratio is 1 to 6.12, which, of using the same logic would result in maximum SrSO₄ mass forming at $\frac{6.12}{6.12+1} = 86\%$ of the High Calcium/Barium water. However, it instead occurs at 50% mixture. A question to consider: why does this happen?

<i>Strontium and Sulfate concentrations</i>			
	mg/l	Molal	Mole Ratio
High Calcium/Barium	300 mg/l Sr ⁺²	0.0034	1
High Bicarb./Sulfate	200 mg/l SO ₄ ⁻²	0.0208	6.12

✓ Save the file

Summary

This case is an example of how we can test the incompatibility of two waters using the ratio mixing option.

5.2 Simple Mixer Calculation

Overview

This is a simple two-step calculation. First, we will create two new streams, 0.1 HF and 0.1 CaCl₂. We will perform a single point calculation on each. Then, we will mix them in equal amounts. Our goal is to determine the new mixture's pH.

- ✓ Select File > New then select File > Save As ... and enter 'Chapter 5' as the name

1 st Stream		2 nd Stream	
Name	0.1 HF	Name	0.1 CaCl ₂
Unit Set	Default	Unit Set	Default
Names Style	Formula	Names Set	Formula
Framework	Aqueous	Framework	Aqueous
Temperature	30 C	Temperature	30 C
Pressure	1 atm	Pressure	1 atm
H ₂ O	calculated	H ₂ O	calculated
HF	0.1 mol	CaCl ₂	0.1 mol

- ✓ Add two new streams with the compositions from the table above

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Temperature (°C)	30.0000
Pressure (atm)	1.00000
Inflows (mol)	
H ₂ O	55.5082
HF	0.100000

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Temperature (°C)	30.0000
Pressure (atm)	1.00000
Inflows (mol)	
H ₂ O	55.5082
CaCl ₂	0.100000

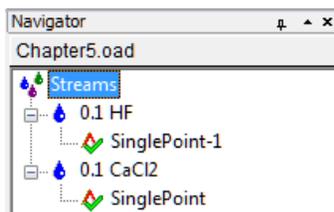
- ✓ Add a single point, isothermal calculation on each stream



- ✓ Calculate

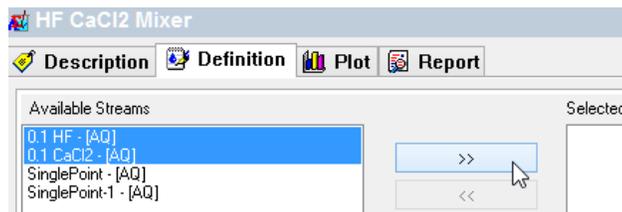
The Navigator contains the two streams and their single point calculations. We can now mix the streams.

- ✓ Highlight the Global Streams icon in the Navigator



- ✓ Add a new Mixer Add Mixer
- ✓ Press the <F2> key to rename the mixer 'HF CaCl₂ Mixer'
- ✓ Select the mixer's Definition tab

- ✓ Highlight 0.1 HF and 0.1 CaCl₂ in the Available Streams column
- ✓ Click the double arrows >> to move them to the Selected column



- ✓ Select Single Point Mix as the Mixing Method
- ✓ Select Isothermal as the Type of Calculation

Variable	Value	0.1 CaCl ₂	0.1 HF
Multiplier		1.00000	1.00000
Stream Parameters			
Total Inflow		55.6082 mol	55.6082 mol
Temperature (°C)	25.0000	30.0000	30.0000
Pressure (atm)	1.00000	1.00000	1.00000

- ✓ Press the <F9> key or select the Calculate button
- ✓ Select the Report tab then scroll down to the
- ✓ In the Report tab, scroll down to the Stream Parameters section

Stream Parameters

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

Mixture Properties

StrAmt	111.216	mol
Temp	25.0000	°C
Pres	1.00000	atm

Aqueous Properties

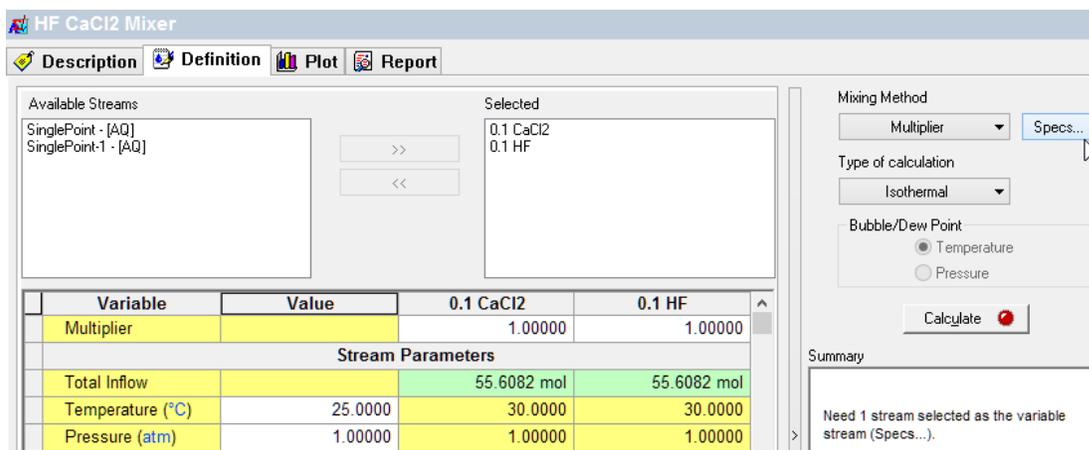
pH	1.43676	---
Ionic Strength (x-based)	2.27328e-3	mol/mol
Ionic Strength (m-based)	0.126587	mol/kg
Osmotic Pressure	3.73060	atm
Elec Cond, specific	2.35949	mho/m
Elec Cond, molar	0.0237004	m ² /ohm-mol
Viscosity, absolute	0.901901	cP
Viscosity, relative	1.01255	---
Standard Liquid Volume	2.01174	L
Volume, Std. Conditions	2.00895	L

The pH is 1.44. Does this seem like unusual pH behavior? Mixing an acid and a base should result in a neutralized solution. In this case, the pH is lower than the starting streams.

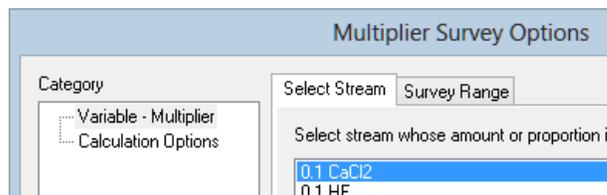
Mixer Changes

- ✓ Select the Definition tab

- ✓ Change the Mixing Method from Single Point Mix to Multiplier



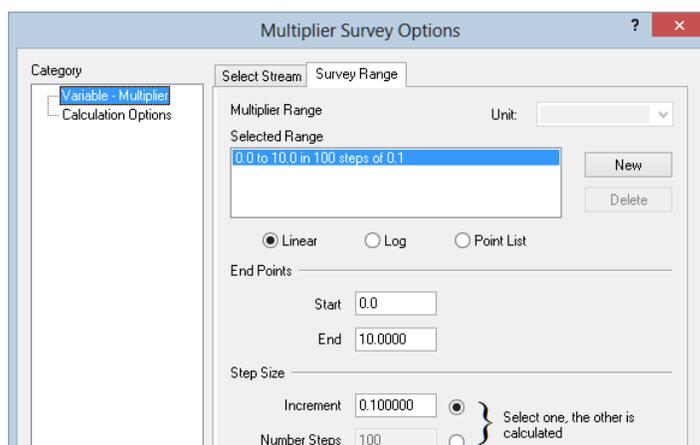
- ✓ Click the Specs button
- ✓ In the Category field, select Variable-Multiplier
- ✓ Select 0.1 CaCl2 in the Selected Stream field



- ✓ Select the Survey Range tab

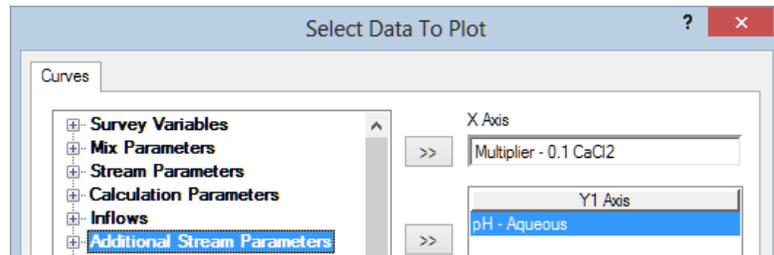
<i>HF CaCl2 Mixer Survey Range</i>	
Start	0
End	10
Increment	0.1

- ✓ Change the survey range according to the table above

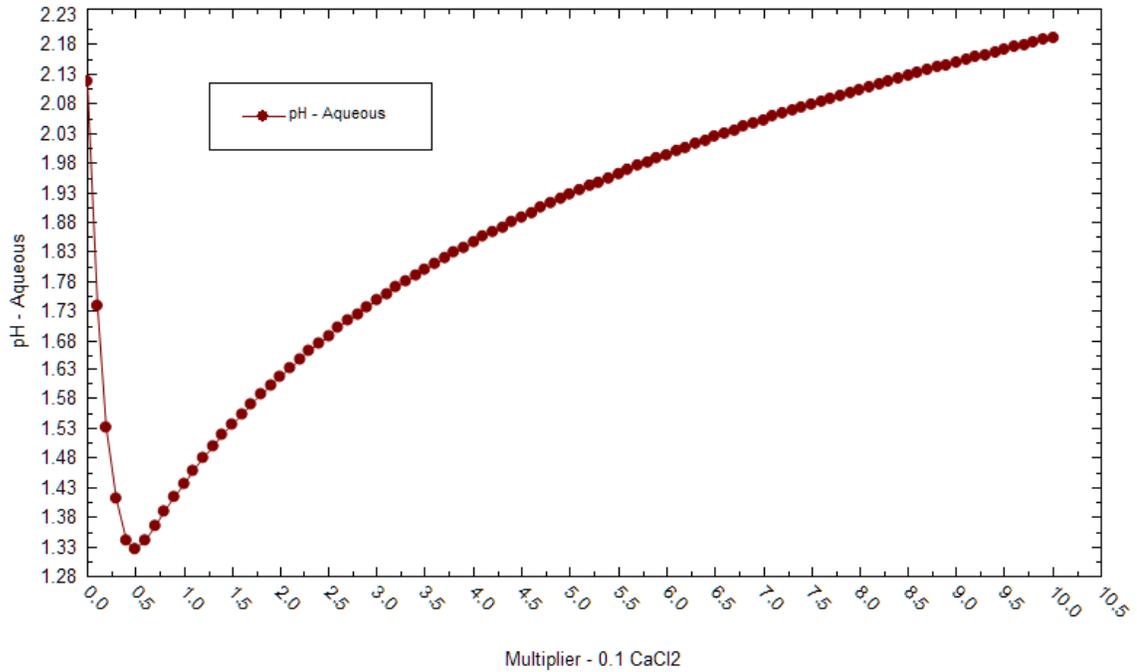


- ✓ Press OK then Calculate
- ✓ Select the Plot tab then select the Curves button
- ✓ Press the Y1 Axis header then the << button to remove any variables

- ✓ Expand the **Additional Stream Parameters** category then double click pH Aqueous



- ✓ Press OK to view the plot



What does this plot indicate about the pH?

- ✓ Save the file

5.3 Neutralizing Two Streams

In this section, we will learn more about the Volume, Ratio, and Multiplier mixing methods. We will create two refinery wastewaters, a spent caustic, and a spent sulfuric acid. A third stream will contain air. We will mix the streams and study their speciation.

- ✓ Create three new streams
- ✓ Set to formula view or Name view, depending on ease of use
- ✓ Set all streams to Aqueous Framework
- ✓ Change the Units Manager based on the settings provided for each stream

5.3 Spent Caustic	
Name	Spent Caustic
Units	Metric Mass Frac
Amount	1000 kg
Temp	50 C
Pressure	1 atm
H2O (mass%)	balance
NaOH	0.9
Methyl mercaptan	0.2
NaCl	0.2
H2S	0.5
Phenol	0.2
Naphthenic acid	0.15
NH4Cl	0.07

Spent Caustic	
Description Definition Report	
Variable	Value
Stream Parameters	
Stream Amount (kg)	1000.00
Temperature (°C)	50.0000
Pressure (atm)	1.00000
Inflows (mass %)	
Water	97.7800
Sodium hydroxide	0.900000
Methanethiol	0.200000
Sodium chloride	0.200000
Hydrogen sulfide	0.500000
Phenol	0.200000
Cyclohexanecarboxylic acid	0.150000
Ammonium chloride	0.0700000

Summary	
Unit Set:	Metric (mass fraction)
Automatic Chemistry Model	Aqueous (H+ ion) Databank: Public
Isothermal Calculation	50.0000 °C 1.00000 atm
Phase Amounts	Aqueous 999.999 kg Vapor 0.0 kg Solid 0.0 kg
Aqueous Phase Properties	pH 10.6926 Ionic Strength 4.89335e-3 mol/mol Density 1.00155 g/ml

5.3 Spent Acid	
Name	Spent Acid
Units	Metric, Mass Frac
Amount	1500 kg
Temp	42 C
Pressure	1 atm
H2O (mass%)	balance
H2SO4	1.5
Na2SO4	0.5
Na2S2O3	0.3
Lauric acid	5.2

Spent Acid	
Description Definition Report	
Variable	Value
Stream Parameters	
Stream Amount (kg)	1500.00
Temperature (°C)	42.0000
Pressure (atm)	1.00000
Inflows (mass %)	
Water	92.5000
Sulfuric(VI) acid	1.50000
Sodium sulfate	0.500000
Sodium thiosulfate	0.300000
Lauric acid	5.20000

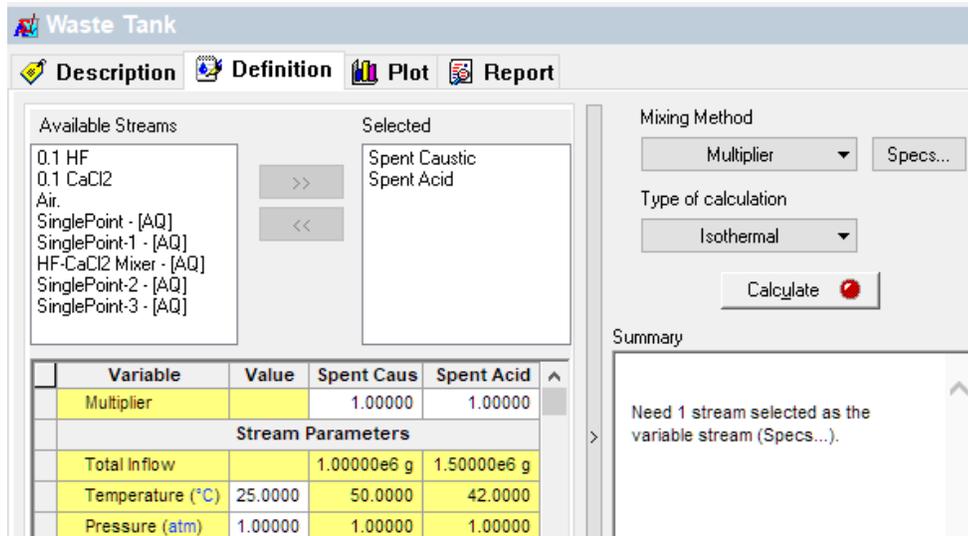
Summary	
Unit Set:	Metric (mass fraction)
Automatic Chemistry Model	Aqueous (H+ ion) Databank: Public
Isothermal Calculation	42.0000 °C 1.00000 atm
Phase Amounts	Aqueous 1500.00 kg Vapor 0.0 kg Solid 0.0 kg
Aqueous Phase Properties	pH 0.918347 Ionic Strength 5.88721e-3 mol/mol Density 1.05491 g/ml

5.3 Air*	
Name	Air
Units	Metric Mole Frac
Amount	3500 mol
Temp	25 C
Pressure	1 atm
H2O (mole%)	balance
N2	76.85
O2	20 %
CO2	0.04 %

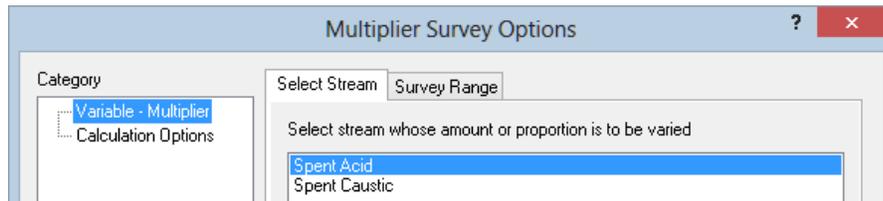
Air.	
Description Definition Report	
Variable	Value
Stream Parameters	
Stream Amount (mol)	3500.00
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mole %)	
H2O	3.11000
N2	76.8500
O2	20.0000
CO2	0.0400000

Summary	
Unit Set:	Metric (mole fraction)
Automatic Chemistry Model	AQ (H+ ion) Databank: Public
Isothermal Calculation	25.0000 °C 1.00000 atm
Phase Amounts	Aqueous 0.0 mol Vapor 3500.00 mol Solid 0.0 mol

- ✓ Add a new Mixer  Add Mixer and rename it 'Waste Tank'  Waste Tank
- ✓ Add the Spent Caustic and Spent Acid to the Selected field
- ✓ Select Multiplier as the Mixing Method



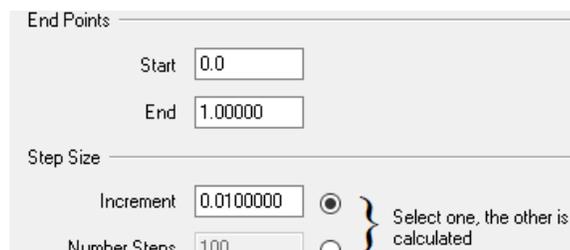
- ✓ Click the Specs button
- ✓ Select Spent Acid as the adjustable stream



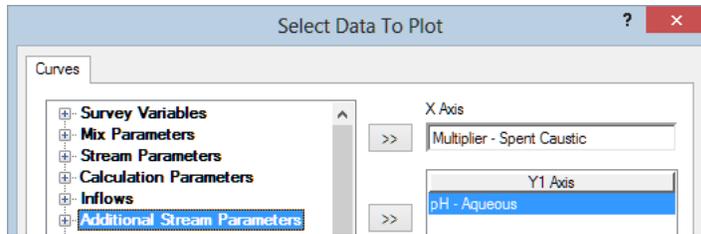
- ✓ Select the Survey Range tab

<i>Multiplier survey range</i>	
Start	0
End	1
Increment	0.01

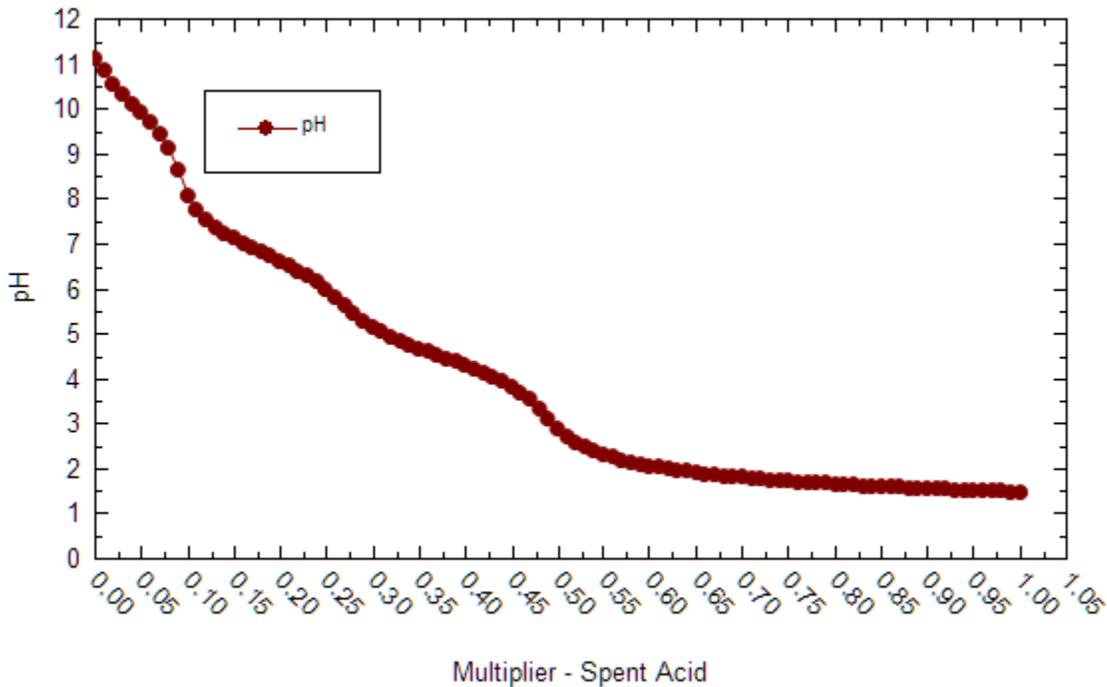
- ✓ Change the survey range according to the table above



- ✓ Close the window and Calculate
- ✓ Select the Plot tab then select the Curves button
- ✓ Press the Y1 Axis header then the << button to remove any variables
- ✓ Expand the **Additional Stream Parameters** category then double click pH Aqueous

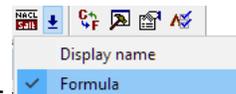


✓ Press OK then view the plot



The steep slope (inflection points) are at about 7.3 pH, 5.1 pH, and 2.9 pH. These pH values are the ends of the buffering regions created by the the weak acids and bases in the two waters. The pH buffering regions are at the shallow sloped areas.

There are a number of variables to review in a multicomponent mixing calculation like this, and several plots will be studied herein. Remember to clear any variables before proceeding. Click the top double arrow buttons to add or removes curves to or from the X Axis. Click the bottom double arrow buttons to add or remove curves to or from the Y2 Axis.



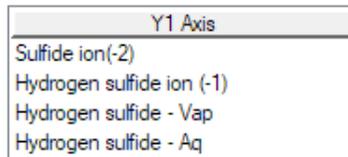
✓ Change the Names manager so that it displays Formula View -

You will want to toggle among names view as you study the various chemical systems, inorganics are generally easier to interpret in Formula view.

H₂S speciation during mixing

- ✓ Select the Curves button
- ✓ Change the plot variables to the following

Category	Curve	Axis
Aqueous	HS-1, H ₂ S, S-2	Y1 Axis
Vapor	H ₂ S	Y1 Axis

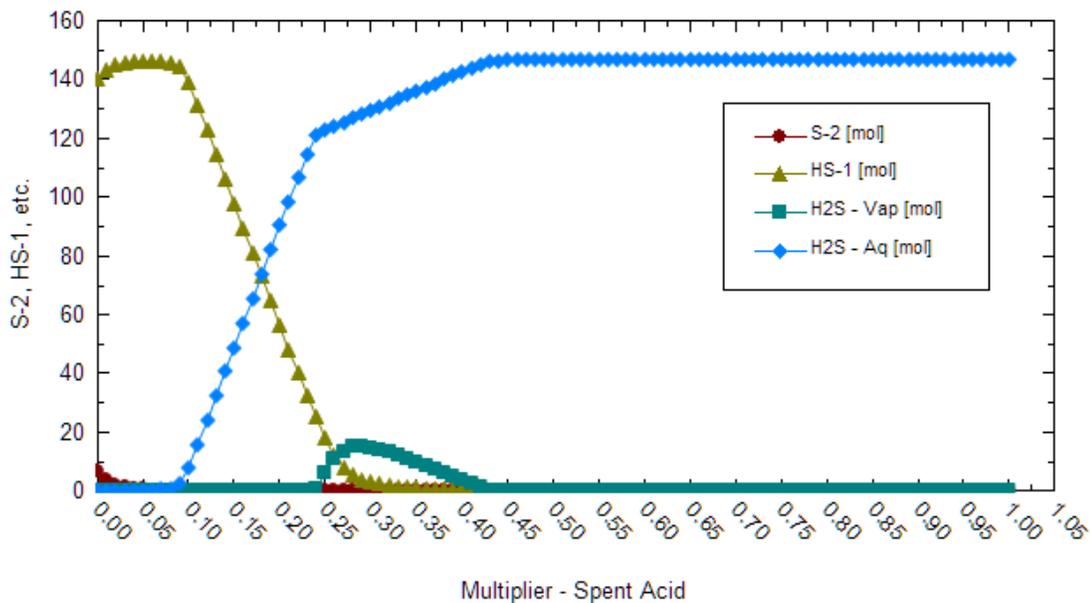


or



- ✓ Press OK and view the plot

As Spent Acid is added to Spent Caustic, the sulfide speciation shifts to molecular H₂S. At about 0.25 Multiplier of the spent acid, an H₂S bubble forms as the nearly all the sulfide present in the system is converted to H₂S. This H₂S vapor is present until about 0.43 multiplier. The shallow decline of the H₂S vapor is the result of dilution as more liquid is added. Eventually the overall H₂S concentration reduces enough to where the vapor phase collapses under the 1 atm confining pressure.



This can be confirmed by plotting the total dissolved sulfur using concentration units.

- ✓ Open the Units Manager and select the Customize button.
- ✓ Set the Aqueous composition to Concentration

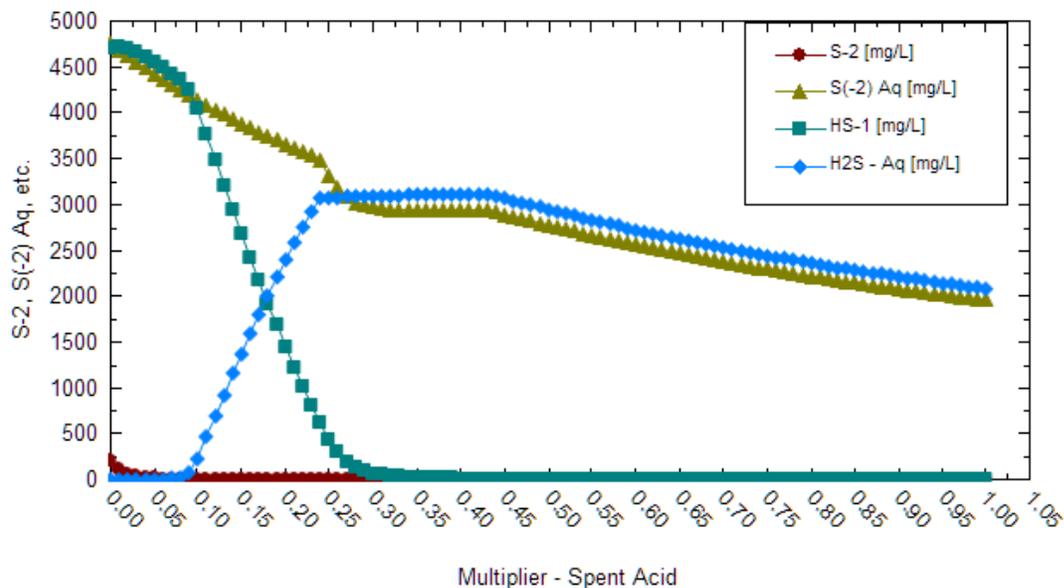


- ✓ Open the Variables window. Expand the MBG Totals - Aqueous category
- ✓ Add S-2 to the Y1 Axis
- ✓ Remove the H₂S Vap from the Y1 Axis



- ✓ Close the window and view the plot

The updated plot shows all the aqueous concentration



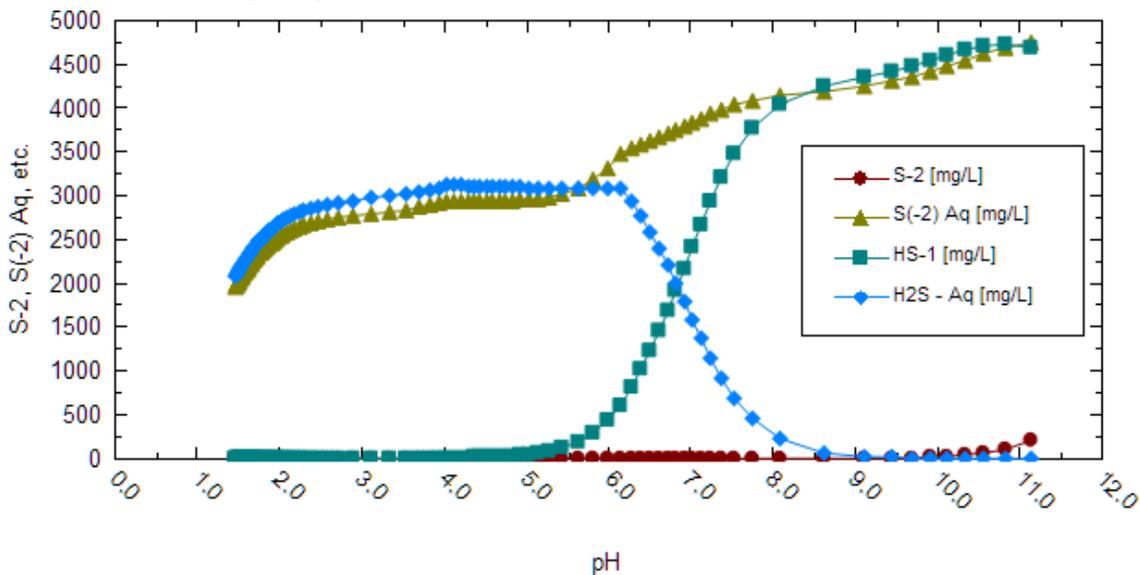
The amber triangles is the total dissolved sulfide. Its value is 4755 mg/l in the ~1000 L spent caustic that is present in the mixer. As the Spent acid is added, the total dissolved H₂S decreases linearly. At 0.25 multiplier, which is about 400 L, there is a sharp concentration drop as H₂S partitions to the vapor phase. Eventually sufficient liquid is added at 0.45 multiplier (~650 L) to where the H₂S redissolves and continues to decrease in concentration as the total mixer volume increases. Once all the spent acid is added, the final volume is about 2400 L, and so the total dissolved H₂S decreases to about 1960 mg/l.

It is also possible to study the results using pH as the x-axis, rather than the Spent Acid Multiplier.

- ✓ Open the Variables window and change the x-axis to pH



The HS-H₂S curves cross at about 6.6 pH. This is the maximum pH-buffering region for the reaction: $HS^{-1} + H^{+} = H_{2}S(aq)$.

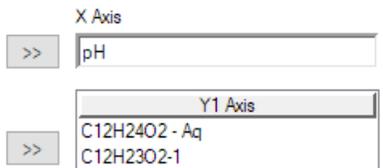


The dissolved H₂S-aq curve increases steadily from 9 to 6 pH, after which it levels abruptly. This is because any additional H₂S that is created as the pH decreases partitions to the vapor phase.

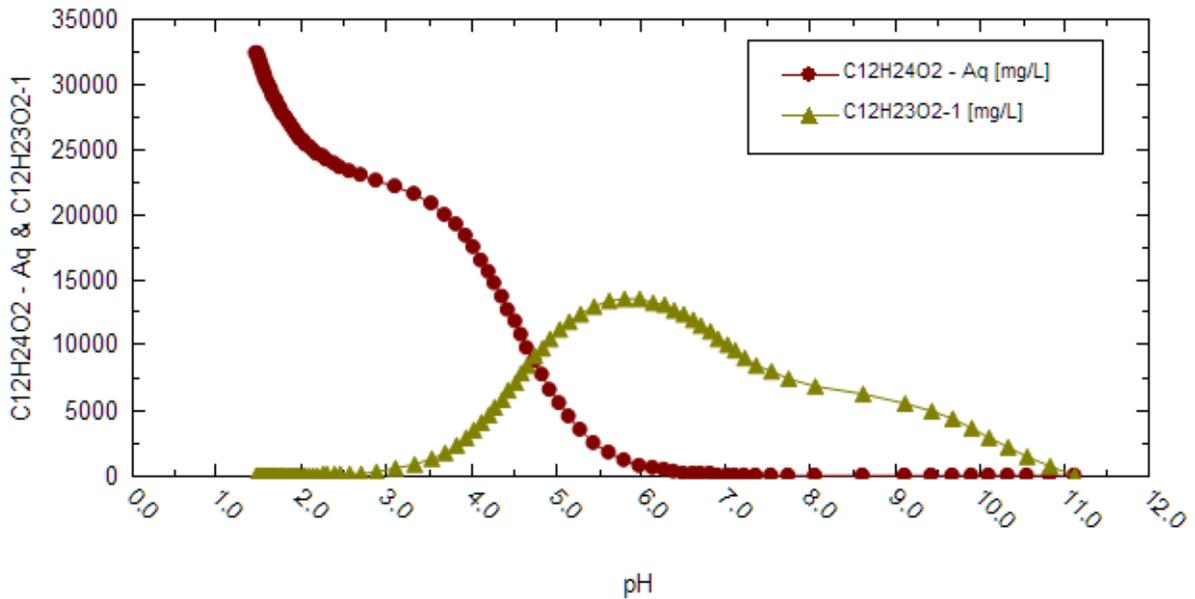
Organic acid speciation during mixing

- ✓ Select the Curves button and change the plot variables to the following

Category	Curve	Axis
Additional Stream Parameters	pH Aqueous	X Axis
Aqueous	C12H23O2-1, C12H24O2	Y1 Axis



- ✓ Press OK and view the plot

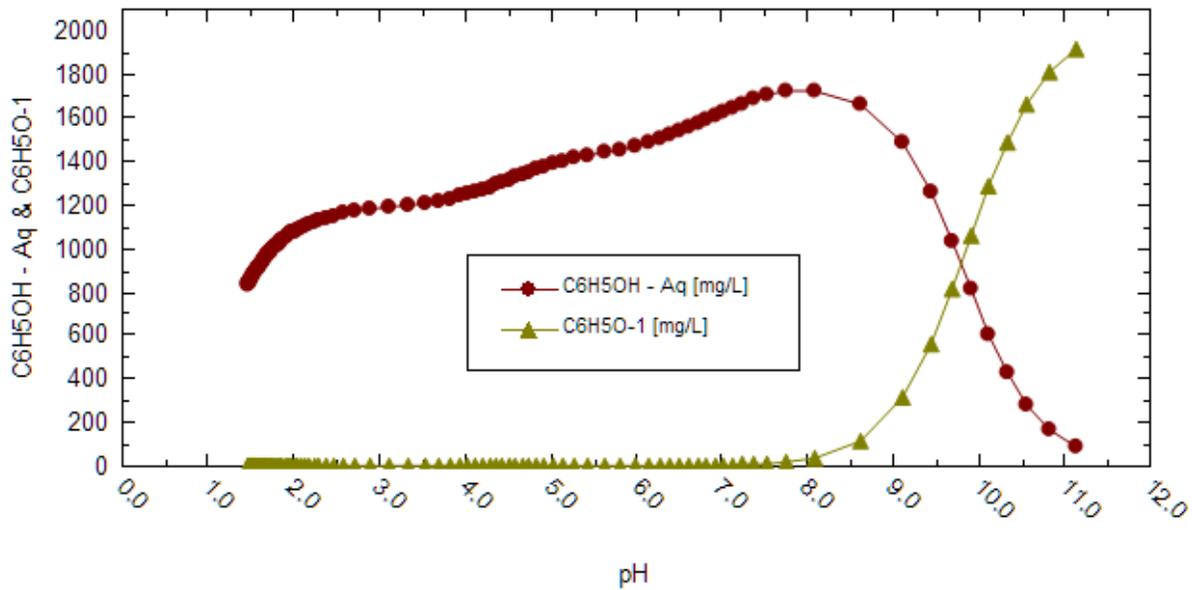


Lauric acid (C₁₂H₂₄O₂ (aq)) – also known by its more formal name dodecanoic acid – comes in with the Spent Acid. As pH decreases, the concentration increases. Note that the crossover occurs at 4.6 pH.

Phenol speciation during mixing

- ✓ Select the Curves button and change plot variables to the following then press OK

Category	Curve	Axis
Additional Stream Parameters	pH Aqueous	X Axis
Aqueous	C6H5O-1, C6H5OH	Y1 Axis

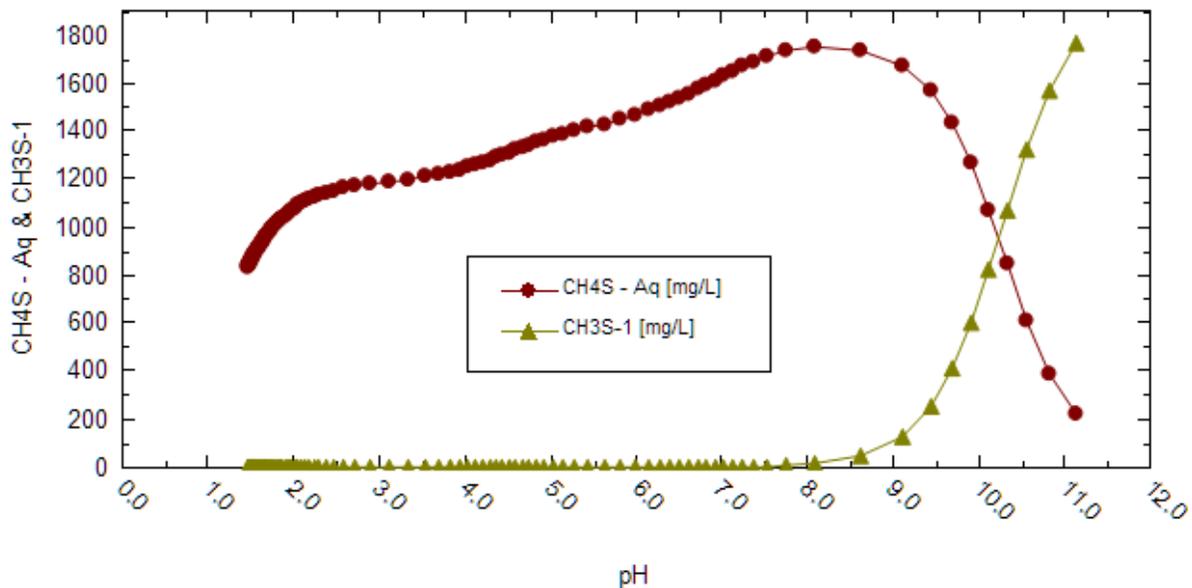


The phenol-phenolate crossover occurs at a high pH of 9.39. Thus, as the spent acid mixes with the spent caustic, this reaction will create the buffering at high pH.

Methyl mercaptan speciation during mixing

- ✓ Select the Curves button and change plot variables to the following then press OK

Category	Curve	Axis
Additional Stream Parameters	pH Aqueous	X Axis
Aqueous	CH3S-1, CH4S	Y1 Axis
Vapor	CH4S	Y1 Axis



The Mercaptan reaction $CH_3S^{-1} + H^+ = CH_3SH (aq)$ also occurs at a high pH of 10. This will be the first H^+ adsorption reaction that occurs when the spent acid mixes. These curves cross at different pH levels. The crossing points are called equivalence points and are where buffering is the greatest.

Next Step – H2S Safety

The next step in this case is to review the H₂S aqueous-vapor partitioning. The existence of an H₂S vapor below 6 pH is a safety hazard. Therefore, the properties of the mixture will be investigated further. The first calculation will be to determine the vapor pressure of the mixture. The confining pressure is 1 atm, the default value. Now however, the software will compute what the confining pressure needs to be so that no vapor forms

Pressurized system

The first calculation is consistent with what is already computed, except in this next step the vapor pressure of the mix will be computed.

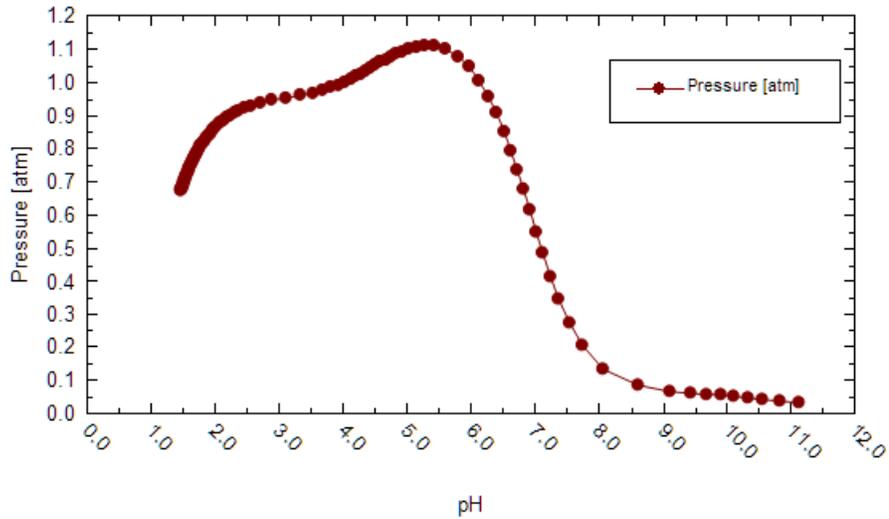
- ✓ Select the Definitions tab
- ✓ Change the Type of Calculation to Bubble Point
- ✓ Change the Calculate cell from Temperature to Pressure

The screenshot shows the 'Waste Tank' software interface. The 'Definition' tab is active. The 'Available Streams' list includes 0.1 HF, 0.1 CaCl₂, Air, SinglePoint-1 - [AQ], HF-CaCl₂ Mixer - [AQ], SinglePoint-2 - [AQ], and SinglePoint-3 - [AQ]. The 'Selected' list contains Spent Caustic and Spent Acid. The 'Mixing Method' is set to 'Multiplier'. The 'Type of calculation' is set to 'Bubble Point'. The 'Calculate' button is highlighted with a green checkmark. A red arrow points to the 'Calculate' dropdown menu, which is currently set to 'Pressure'.

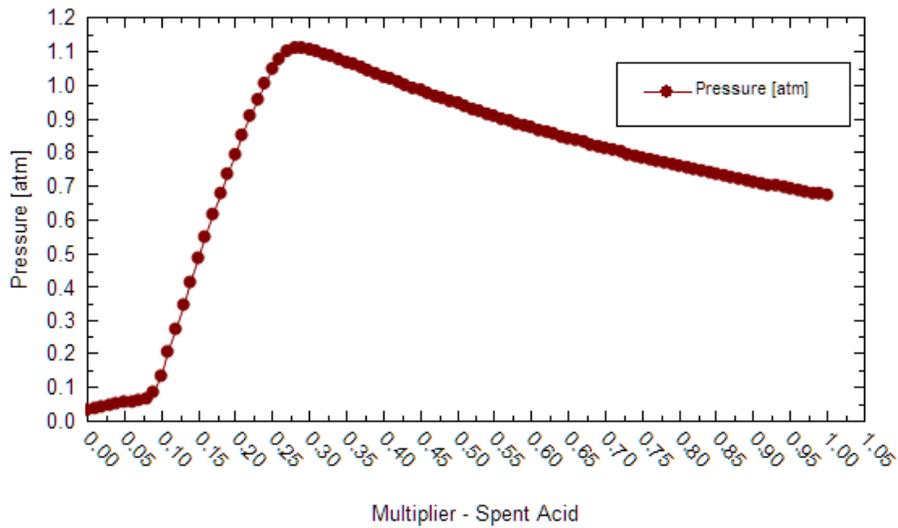
Variable	Value	Spent Causti	Spent Acid
Multiplier		1.00000	<Varied>
Stream Parameters			
Total Inflow		1.00000e6 g	0.0 g
Temperature (°C)	25.0000	50.0000	42.0000
Pressure (atm)	1.00000	1.00000	1.00000
Calculation Parameters			
Calculate	Pressure		

- ✓ Calculate
- ✓ Plot the Total pressure (Stream Parameters category) on the Y1 axis against either the pH, which is the default, or gains the Waste Acid multiplier (Survey Variables)

The resulting plots show that the maximum confining pressure is about 1.1 atm. At 5.5 pH or at about 0.28 multiplier (~400 l) the H₂S vapor pressure reaches a maximum. Thus, according to this calculation, the mixing tank will need to be closed with at least a 1.2 atm positive pressure to eliminate degassing.



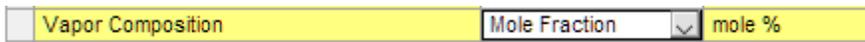
Or



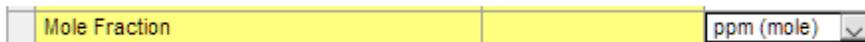
Case 2 – Atmospheric system

The purpose of this example is to estimate the amount of H₂S in the nearby air if the tank is open to the atmosphere. The Air stream amount is 3500 moles. This occupies a volume of 85.6 m³. This is an arbitrary value, and represents the airspace 5 m high above a tank with a radius of 2.3 m.

- ✓ Return to the Definitions tab
- ✓ Start by editing the units – Change the Vapor Composition from moles to mole fraction



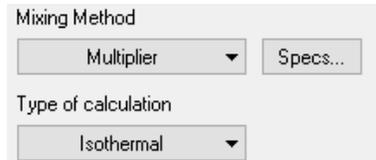
- ✓ Next, change the Mole fraction units from mole % to ppm (mole)



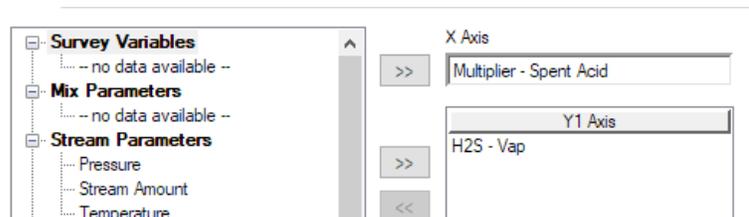
- ✓ Add Air to add it to the Selected column



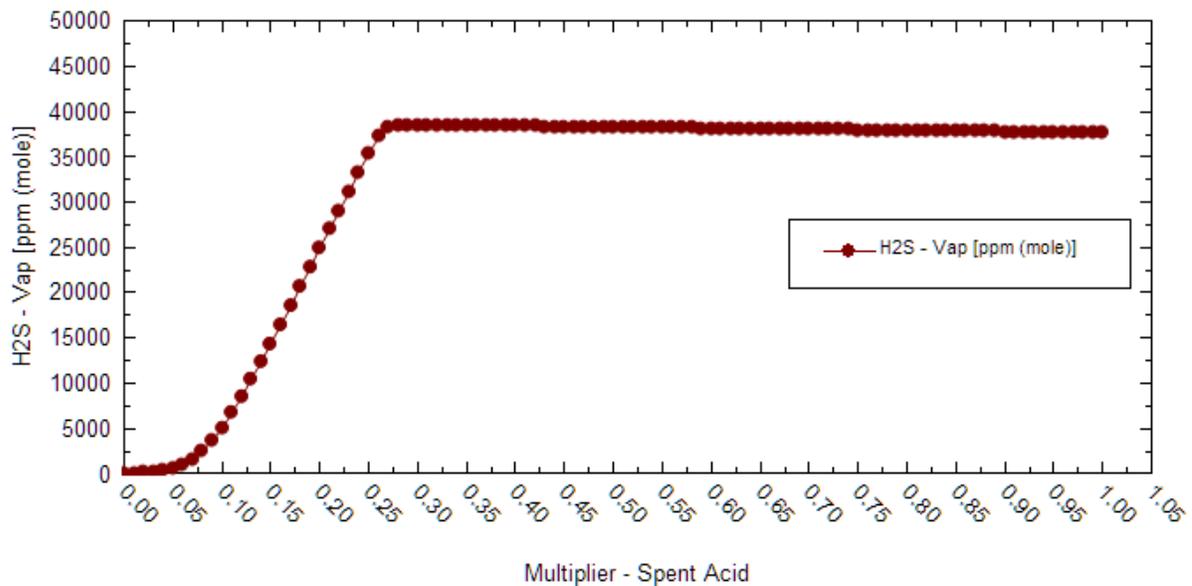
- ✓ Change the Type of Calculation back to Isothermal



- ✓ Calculate
- ✓ Select the Plot tab and change the plot variables
 - Change the x-axis to Multiplier – Spent Acid (Survey Variables category)
 - Change the y1 axis to H2S – vapor



- ✓ Press Ok and view the plot



Air, or a headspace, is now present in all mixing points, and not only when H2S form the headspace. As a result, H2S is in the air and the fraction increases as the Spent acid amount increases. It reaches a maximum value of ~38000 ppmV at the 0.25 multiplier and remains relatively constant thereafter. Thus virtually any mixture of these two waste stream when open to the atmosphere will present an H2S safety hazard.

Summary

The mixing results are secondary to the objective of comparing the different mixing scenarios. The list below summarizes the mix types.

Multiplier Survey – This survey calculation adjusts the inflow mass of the selected stream only. Its mass is multiplied by the multiplier value.

$$\text{Stream Mass} * \text{Multiplier} = \text{Total Inflow Mass}$$

The second (third, fourth, etc.) stream inflows are kept constant.

Volume Survey – This survey calculation adjusts the inflow volume while keeping the other stream volumes constant.

Ratio Survey – The Ratio survey calculation adjusts both inflow streams using the following rule

$$\begin{aligned} \text{Selected Stream Mass} * \text{Ratio} &= \text{Inflow Mass} \\ \text{Sum of Other Stream Masses} * (1 - \text{Ratio}) &= \text{Other Mass} \end{aligned}$$

In this survey calculation, the overall inflow mass is kept constant.

5.4 Creating a Titration Curve

Overview

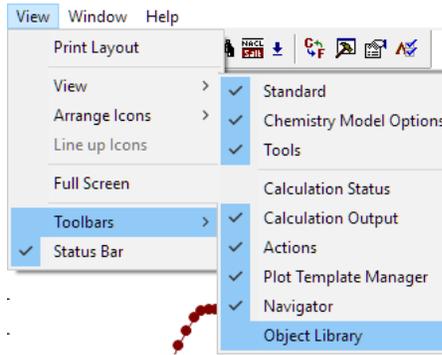
A titration curve shows the mixing of two reagents, typically an acid and base. The software can mix two or more reagent streams and model typical acid-base or other potentiometric titrations. In this example, we will titrate seawater down to 4.5 pH to compute its alkalinity.

Getting started

Adding the seawater analysis

There are several Seawater objects installed with the software. They are found in the Object library with several other standard streams. So, instead of starting from a laboratory analysis, you will add the Seawater object from the library to the Navigator pane.

- ✓ Open the Object Library if it is not opened at the right of the screen
 - Click on View-Toolbars-Object Library (from the menu)

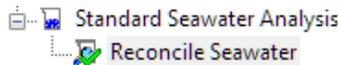


- ✓ Drag the Standard Seawater Analysis object to the Navigator Panel



Seawater is at the bottom of the Object Library. When you drag it to the Navigator panel, drag to the top-most Streams or to below the last object in the panel.

- ✓ Add a Reconciliation object and name it Reconciled Seawater



- ✓ Calculate

Adding the 1N H2SO4 reagent

- ✓ Add a new stream and give it a name, 1 N H2SO4 (1ml) -  1N H2SO4 (1ml)
- ✓ Change the units to Metric-Batch-Molar Conc

- ✓ Change the Stream amount to 0.001 L (1ml)
- ✓ Add H2SO4 to the grid and enter a value of 0.5 mol/l

Variable	Value
Stream Parameters	
Stream Amount (L)	1.00000e-3
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol/L)	
H2O	
H2SO4	0.500000

Adding the titration apparatus

- ✓ Add a new Mixer  **Add Mixer** and rename it 'Titration Apparatus'  **Titration Apparatus**
- ✓ Add the Reconciled Seawater and 1N H2SO4 to the Selected section

Selected
 Reconcile Seawater
 1N H2SO4

- ✓ Select Multiplier as the Mixing Method
- ✓ Open the Specs button and 1N H2SO4 as the Adjusted stream

Select Stream

Select inlet stream to vary

- ✓ Set the Survey: Start at 0, end at 10 (ml) with increments of 0.1 (ml).

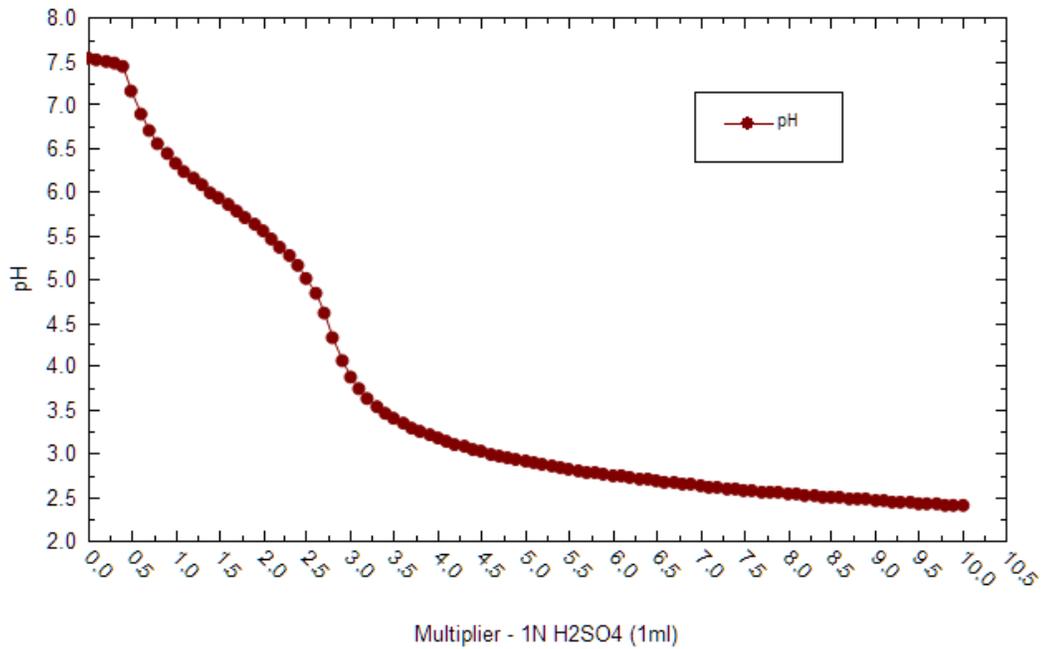
End Points
 Start
 End

Step Size
 Increment } Sele
 Number Steps calc

- ✓ Calculate
- ✓ Click on the Plot tab and plot the pH in the Y1 axis



The resulting pH titration curve is the standard approach for measuring total alkalinity. The alkalinity endpoint is 4.5 pH, and the corresponding H2SO4 multiplier is 2.8, or 2.8 ml.



The conversion from ml H2SO4 to mg/l Alkalinity as HCO₃⁻¹ is straight forward:

$$\text{Alkalinity as } HCO_3^{-1} \left(\frac{mg}{l} \right) = \frac{\text{vol } H_2SO_4 \text{ (ml)} * N \text{ } H_2SO_4 \left(\frac{eq}{l} \right)}{\text{vol Sample (ml)} * 61000 \left(\frac{mg}{eq} \right)}$$

$$\text{Alkalinity as } HCO_3^{-1} \left(\frac{mg}{l} \right) = \frac{2.8 \text{ (ml)} * 1 \left(\frac{eq}{l} \right)}{1000 \text{ (ml)} * 61000 \left(\frac{mg}{eq} \right)} = 170.8 \frac{mg}{l} \text{ as } HCO_3^{-1}$$

Diagram Construction

Pourbaix diagrams are composed of the following sections:

- X-axis, with a range of 0 to 14 pH.



Figure 2 - The x-axis of the stability diagram is pH. pH is modified by adding an acid (HCl) or base (NaOH) to the fluid

- Y-axis, with a range of -2 to 2 Volts. The voltage references the Standard Hydrogen Electrode and its value is 0 volts (axis shown below is tilted 90°).

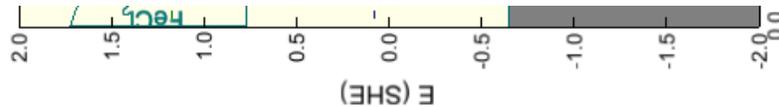


Figure 3 - The y-axis of the stability diagram is the Electrochemical Potential (E, SHE). The SHE term refers to the Standard Hydrogen electrode. E is adjusted using a potentiometer.

- A calculated bulk solution pH shown as a vertical red line (shown below tilted 90°).

Natural pH -----

Figure 4 - The initial or natural pH line of the water sample. This is the water's computed pH before it is adjusted using with acid or base (x-axis above) to create the diagram.

- A calculated bulk solution electrochemical potential (red circle).



Figure 5 - The circle represents the initial electrochemical potential of the water phase. This is the value before being adjusted using the potentiometer (y-axis above).

- A gray shaded area that represents the base metal stability region. Elemental iron, Fe⁰ is the base metal in the above plot. It is stable when the electrochemical potential is below -0.66V, and when the pH is between 0 to 14.

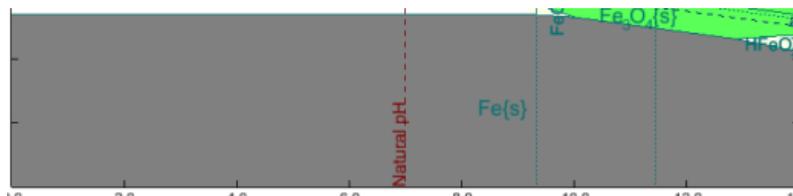


Figure 6 - The gray shaded area of the plot is the pH and E region in which the base metal (e.g., carbon steel) is stable, i.e., it will not corrode.

- A Green-shaded area that represents any solid phase produced by oxidation of the metal. In the above plot, the shaded areas are solid phases of Fe⁺² and Fe⁺³, which are the oxidation products of Fe⁰. The phases include Fe₂O₃ (Hematite) which is stable at high E_H conditions and moderate to high pH and Fe₃O₄ (magnetite), which is stable between 9 and 14 pH and moderate E_H.

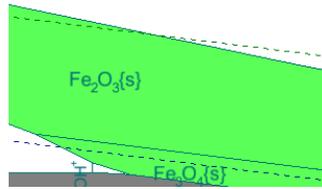


Figure 7 - The green-shaded area of the plot is the pH and E region in which a solid-phase corrosion product forms. In some cases, these corrosion products protect the metal from further corrosion, or its presence reduces the corrosion rate.

- A negative-sloped line, labeled “a.”

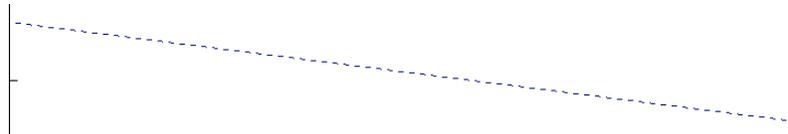


Figure 8 - The water reduction line. Below this line, water reacts to form H_2 (gas) and OH^- ions. Water is unstable below this line.

This line represents the water reduction reaction: $2H_2O + 2e^- = H_2 + 2OH^-$. If E_H/pH conditions are below this line, then water decomposes to form H_2 gas and the pH is increasing. If the reducing agent is an external source (i.e., an electrical current) and not a chemical species, then the E_H remains constant and the solution pH migrates rightwards. If the reducing source is a metal or other consumable, then the pH migrates right and the E_H slowly migrates upwards until all the material is consumed. At this point the E_H/pH point should be along or slightly below the “a” line, depending on the soluble H_2 concentration. The actual location depends on the final pH.

- A negative sloped-line, labeled “b.”

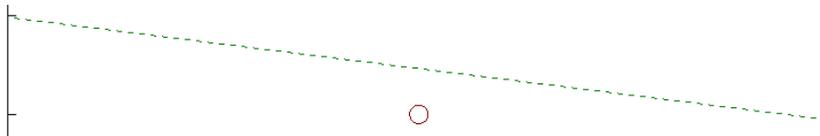


Figure 9 - The water oxidation line. Above this line, water reacts to form O_2 (gas) and H^+ ions. Water is unstable above this line.

This line represents the water oxidation reaction: $2H_2O = O_2 + 2H^+ + 2e^-$. If E_H/pH conditions are above this line, then water decomposes to O_2 , and the pH is decreasing simultaneously.

If an oxidant like $NaClO_4$ is added to the liquid the reaction products are O_2 , $NaCl$, and H^+ . The new equilibrium point will have a higher E_H and a lower pH.

- The white areas represent E_H -pH conditions where no solid phase is stable. These are areas where the material will dissolve and form no solid-phase corrosion product.

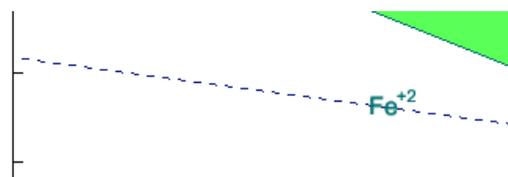


Figure 10 - The white region of the stability diagram is the pH and E region in which no potentially protective solid phase can form. The iron that corrodes does not precipitate.

If kinetics are not limiting, then we can infer that the white region of the plot is where Fe will corrode and not be protected by any solid-phase film.

Boundary lines

Vertical lines are the changes in acid base chemistry that are independent of E_H

- Dashed vertical lines represent transitions between dominant dissolved (e.g., $\text{Fe}(\text{OH})_2^+$ to $\text{Fe}(\text{OH})_3^0$, not show in above plot).

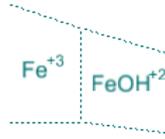


Figure 11 - the dashed, vertical dotted lines are the transition lines for the dissolved ions.

- Solid vertical line represent solid-phase boundary within the same oxidation state (e.g., Fe^{+3} to $\text{Fe}(\text{OH})_3$ at 2.5pH).

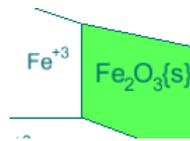


Figure 12 - The solid, vertical lines are the solid-liquid boundaries for metals (e.g., iron) with the same oxidation state. Solid Fe_2O_3 forms if the pH is above this line.

- Horizontal lines are the changes in oxidation state that are independent of pH.
 - Dashed horizontal lines are oxidation state boundaries of dissolved species (e.g., Fe^{+2} to Fe^{+3} between 0 and 2 pH).

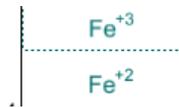


Figure 13 - Dashed, horizontal lines are the boundaries between oxidation states of the metal. Fe^{+2} is converted by oxidation to Fe^{+3} as the water's E moves above the line.

- Solid horizontal lines are oxidation state boundaries of solid phases (e.g. Fe_0 to Fe^{2+} at -0.66V when below pH 6)



Figure 14 - Solid lines separating gray areas is the boundary between a stable metal and a corroding metal. below this line, the metal is stable. Above this line, the metal is at risk of corroding.

- Sloped lines are changes in both oxidation state and acid base chemistry
 - Sloped, dashed lines are oxidation/pH boundaries between dissolved species of different oxidation states (e.g., Fe^{+3} to FeO_4^{-2} between 0 and 2 pH or Fe^{+2} to $\text{Fe}(\text{OH})_3^0$ above 5 pH). Multiple lines are shown below.

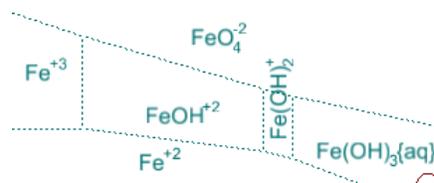


Figure 15 - Sloped, dashed lines are similar to the vertical dashed lines in that they represent transitions from one species or oxidation states to the ext, but in these cases, the transition varies with pH AND with E.

- Sloped solid lines are solid-phase boundaries that are pH and EH dependent (e.g., Fe^{+2} to Fe_2O_3 between 2 and 6 pH).

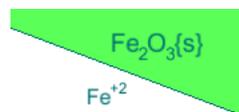


Figure 16 - Sloped lines between the green shaded areas and the white area are the solubility boundaries. The difference in this case is that the solubility is a function of both pH AND E.

In the more general case, the lines slope, since both E and $[\text{H}^+]$ or $[\text{OH}^-]$ affect the Redox process.

Titriments

The x-axis value is varied using a strong acid, HCl and a strong base, NaOH. They are used because sodium and chloride ions do not form strong complexes with many dissolved species nor do they precipitate at low concentrations.

Passive films

Passivity results when certain metals and alloys form very thin, oxidized, protective films on their surfaces in corrosive solutions. Most commercially available corrosion resistant alloys depend on passive films for their resistance. For instance, Fe_3O_4 is a passivating film that forms on iron surfaces in oxidizing aqueous environments. This film dramatically reduces the corrosion rate by acting as a transport barrier. It acts as an electric insulator, slowing the rate of electrons transfer from the metal to the water. It also blocks reaction sites on the surface preventing further corrosion. Jones (1996) observed that the corrosion rate is reduced substantially by the forming films even when there is no visible evidence of the film.

Limitations

Some limitations of stability diagrams include:

- These diagrams provide no information on corrosion kinetics
- The diagrams are for a specific temperature and pressure.
- In areas where a stability diagram shows oxides to be thermodynamically stable, these oxides are not necessarily of a protective (passivating) nature.
- Dealloying cannot be predicted from the diagram alone.
- Everywhere on the plot, the activity of the Fe^{+2} and Fe^{+3} species are fixed at 10^{-6} . In concentration units, this is ~56 ppb of the free Fe^{+2} and Fe^{+3} ion. It also means that Total Fe concentration is not constant, since in some EH/pH conditions, Fe^{+2} may represent a very small fraction of the total Fe in solution.

Water Stability

The base layer of a Pourbaix diagram is the water stability lines. Water-stability lines are found on all diagrams computed by the OLI software. On top of this layer are the metal stability regions described in the previous section.

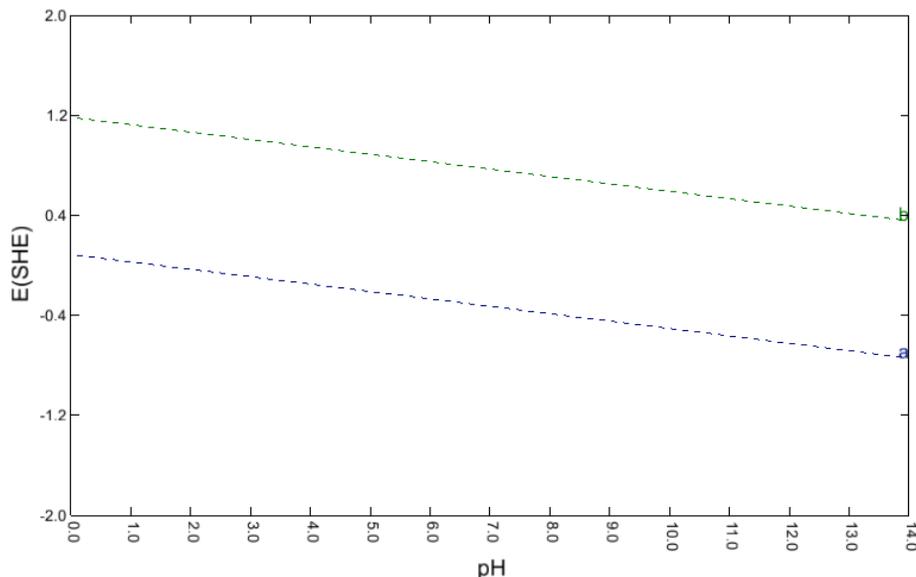


Figure 17 - First layer of the Pourbaix diagram.

As described above, the *b-line* in the diagram is the water stability boundary under high oxidizing conditions. Above this line, H_2O decomposes into O_2 gas and H^+ ions. This does not happen in natural waters, because strong oxidants are required (i.e., bleaches or some other laboratory created chemical). Thus, anything above the *b-line* can generally be ignored when reviewing these plots.

Also described above is the *a-line*, the water-stability boundary under reducing conditions. Below this line, water decomposes into H_2 gas and OH^- ions. This reaction is common in natural waters, and is the key reaction in the corrosion process. A strong reducing agent is required to make this reaction occur. In production operations, the reducing agent is metallic Fe, Cr, and Ni in steels. Therefore, the area around the *a-line* (both above and below) is important to production chemistry.

Stability of Naturally Occurring Waters

Naturally occurring waters tend to lie within a pH range of four to nine. Well-aerated natural waters near the surface contain enough dissolved oxygen to get close to the reduction of water to O_2 . Eutrophic lake water contains sufficient dissolved organic matter to approach closely the Hydrogen reduction line. Ocean waters are relatively basic and may be oxidizing if saturated in O_2 or reducing if saturated in organic matter (i.e. in stagnant lagoons, etc.). Fresh waters are considerably more acidic (because of dissolved carbon dioxide), but they can be oxidizing if saturated in oxygen, or reducing if too much organic matter is present. This acidity is greatly enhanced in bogs and organic laden soils due to high humic acid content. (Humic acids are complex organic acids occurring in the soil and in bituminous substances formed by the decomposition of dead vegetable matter). The following figure shows the oxidation/reduction ability of several waters.

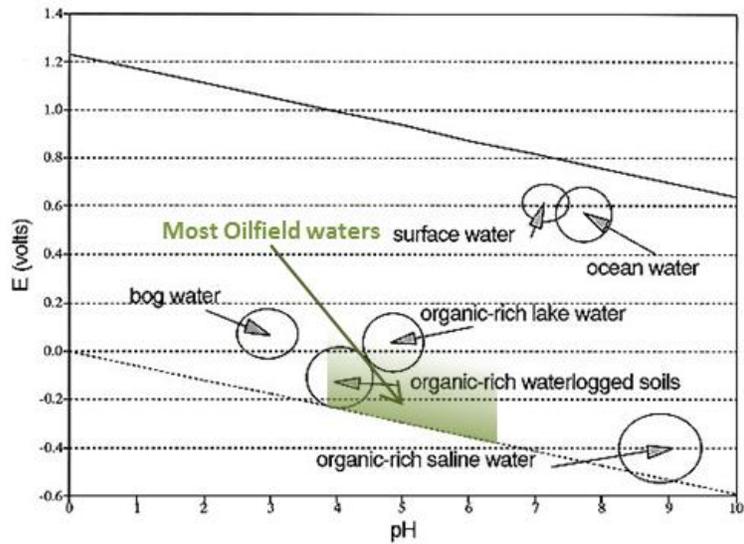


Figure 18 - Oxidation/Reduction potentials and pH ranges of several natural waters (Morgan, 1993)

Stability Diagrams

The diagram below represents the thermodynamic condition that exists when the Block 0/14 combined gas is in contact with carbon steel at 4C and 200 bar. It also represents conditions where a condensed water is present, and the CO₂ and H₂S gas concentrations are 2.5 mol% and 5500ppmV, respectively.

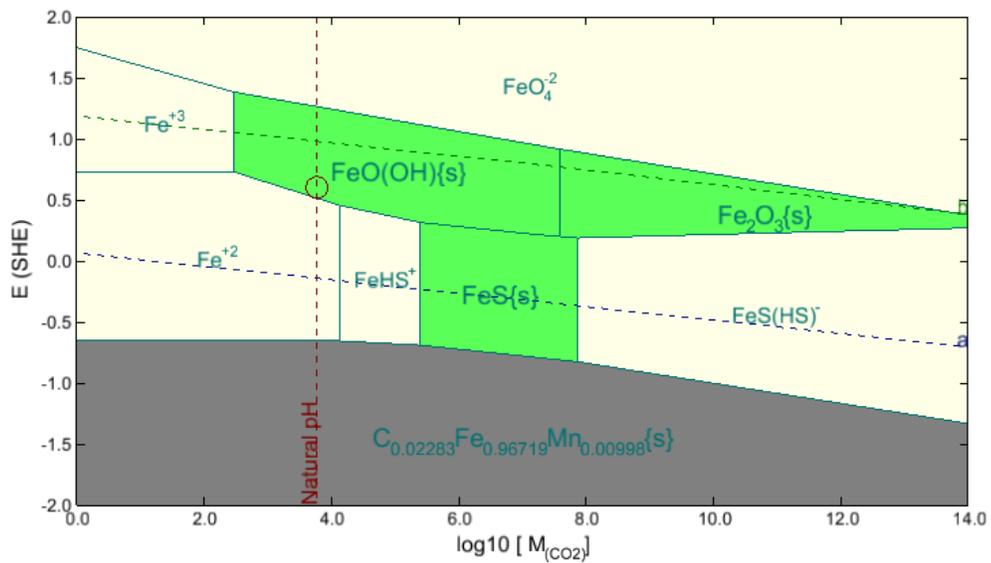


Figure 19 - A complete Pourbaix Diagram. The Diagram works like a map, in which pH and E are the coordinate. The map then shows where the metal or solid corrosion products are stable. The circle displays where the pH and E coordinates for the water being tested.

The above diagram works like a map, containing three layers.

Water Stability lines

The water stability lines described in the previous section can be considered as the first layer of a diagram. It shows the region within the plot where water is stable. Since water is the conducting material that enables the corrosion process to exist, the region between the a- and b-line is the target area.

pH and EH of the Existing Water

The next layer is the vertical line and circle which represent pH and oxidation/reduction potential of the bulk water.

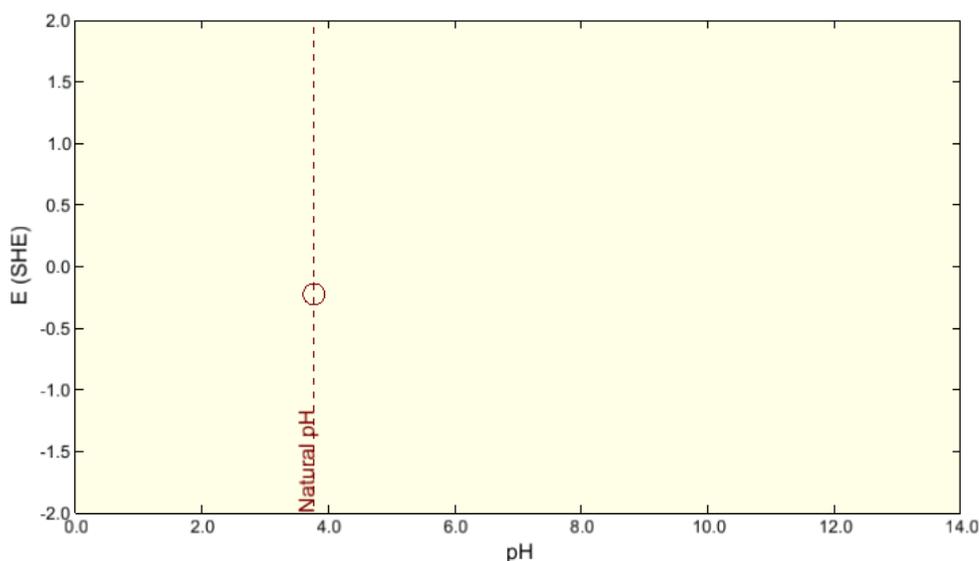


Figure 20 - The Pourbaix Diagram showing the natural pH and E of the water only.

In the above plot, the dotted red line and circle intersect at ~ 3.9 pH and ~ 0.6 V (SHE)

Iron (Steel) Stability

The last layer is the stability regions of the solid phases. Carbon steel is used in the figure below. The gray area represents the region where the carbon steel is stable. Note that the gray region never intersects the a-line (water reduction line). This is because carbon steel and water cannot co-exist at equilibrium. Either 100% of the carbon steel corrodes or 10% of the H_2O reduces to H_2 gas. The green area represents the region where the iron corrosion products are stable. When carbon steel corrodes in H_2S -containing water, FeS film forms as long as the pH near the surface is between 5 and 8. The white areas are regions where no solid is present.

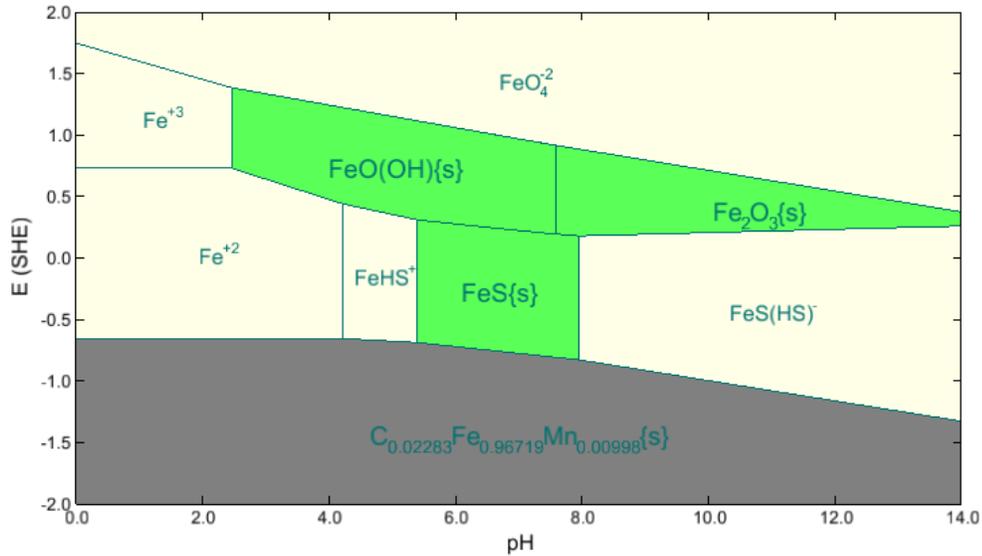


Figure 21 - The Pourbaix diagram in which the solid phases are shown.

The default concentration of the dissolved iron in solution is ~56 ppb, or essentially, a low concentration that represents the initial condensed water phase. This is representative of the above plot.

Combining Each Overlay to Interpret Pipeline Results

The stability plot below is the Block 0/14 combined gas on carbon steel pipe at 4C and 200 bar. The gas contains 2.5% CO₂ and 5500 ppm H₂S. The condensed water that forms on the steel contains no salts or dissolved iron. It contains dissolved gases only.

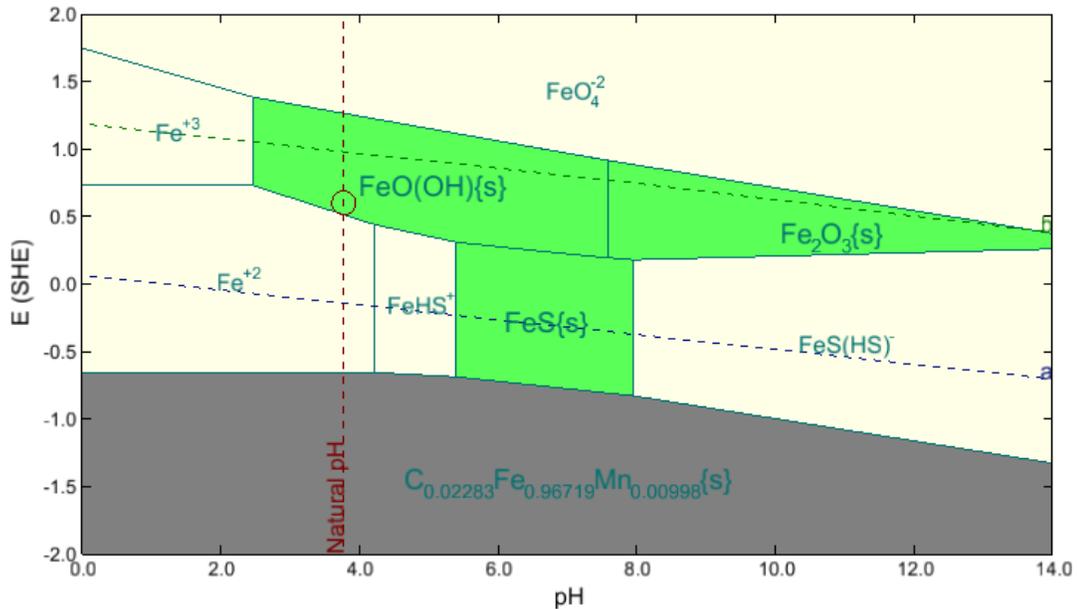


Figure 22 - The Pourbaix diagram in which the natural pH/E of the water, the stable solid phases, and the important dissolved species are shown.

The red circle sits on the solid phase FeO(OH). It is a corrosion product, a form of rust. Thus, the condensed water as it sits on the bare metal will corrode it and form this phase.

Continuing Contact Between Condensed Water and Pipe

As corrosion proceeds, there is buildup of the reaction products: H_2 , OH^- (actually loss of H^+), and Fe^{+2} . The H_2 buildup has the effect of lowering the circle towards the *a*-line and shifting the natural pH to the right (higher pH). Furthermore, the Fe^{+2} concentration increase in the near surface water making corrosion oxides and scales likelier.

The next plot is a snapshot of the water-metal contact sometime later in the corrosion process as the concentration of corrosion products at the liquid-solid boundary increase: H_2 is 1ppB, Fe^{+2} concentration is 6ppm, and 1ppm H^+ ion is consumed.

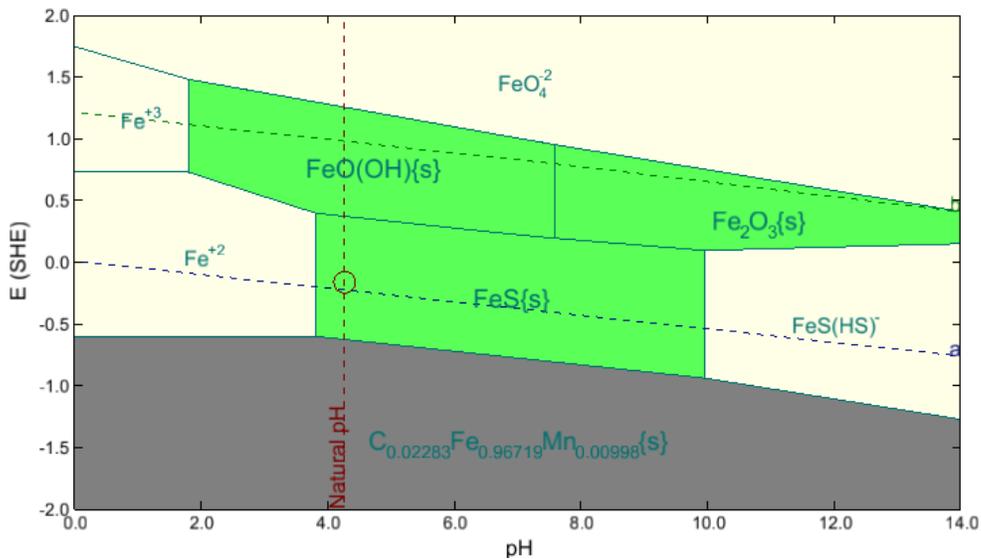


Figure 23 - A Pourbaix diagram of a water in which dissolved Fe^{+2} has increased through corrosion. the increasing Fe^{+2} concentration increases the saturation of FeS (solid). Thus the pH/E region where FeS solids can form is larger than the plot above.

The resulting plot shows that the green phase boundaries increased because Fe^{+2} concentration increased. In addition, the higher H_2 concentration reduced the E-value to $\sim -1V$, or just above the *a*-line. Lastly, the consumption of H^+ increased the pH to ~ 4.2 . The combination of all three reactions produces a system in which the steel surface can now be protected by an FeS film.

Chapter 6b Applications of Stability Diagrams

Introduction

In this chapter, we will practice using the OLI Studio: Corrosion Analyzer objects on practical examples.

Sections

6.1 Alchemy: Creating Precious Metals from Electrons	2
6.2 Temperature effects on Iron Stability	8
6.3 Composition effects on iron stability.....	13
6.4 Why Rust Forms & Why Stainless Steel is Stainless	17
6.5 Iron Stability in Multiple Solvents.....	23

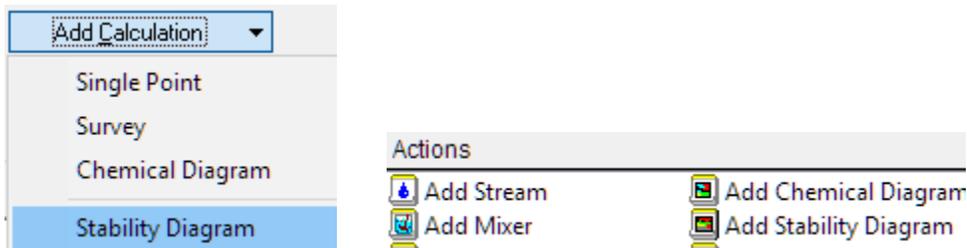
6.1 Alchemy: Creating Precious Metals from Electrons

We will first see how to use OLI Studio: Corrosion Analyzer to create a gold stability diagram.

- ✓ Start a new file then give it a unique name
- ✓ Add a new stream  Add Stream and rename it 'Noble Metals' 

Gold Stability Diagram

- ✓ Add a Stability Diagram from the Action panel or the  Add Stability Diagram



- ✓ Name the object 'Gold' 
- ✓ Type Au in the new grid section labeled Contact Surface



Make sure to enter Au or Gold to the contact surface grid (the software will automatically add it to the neutrals grid). The calculation will not proceed until a contact surface is selected.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Inflows (mol)	
H2O	55.5082
Au	0.0
Contact Surface (mol)	
Au	

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model

AQ (H+ ion) Databanks:

- Corrosion
- Public
- Redox selected

Stability diagram: E vs pH

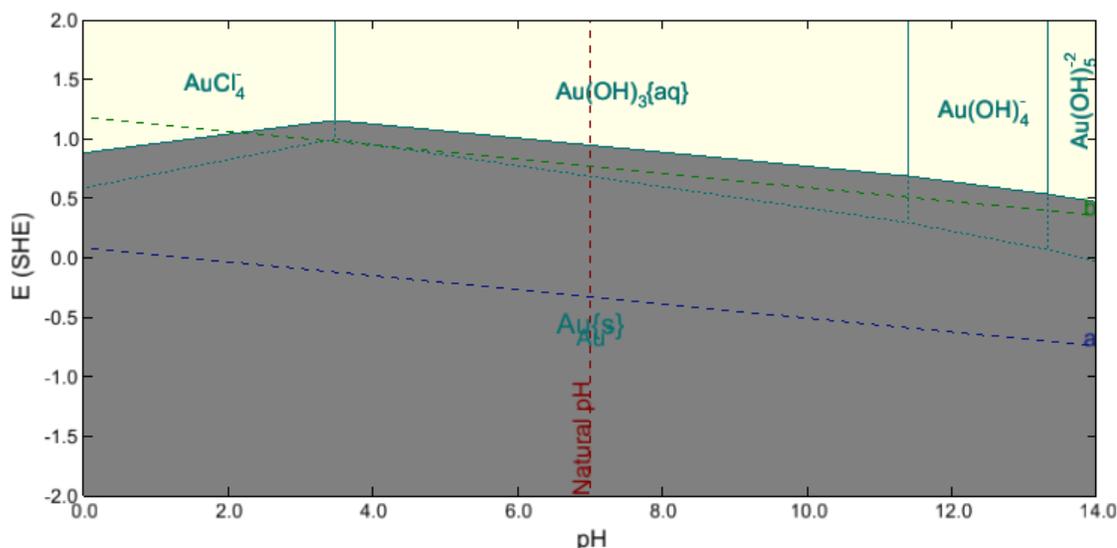
User-selected titrants

Acid:

Base:

- ✓ Calculate (press the <F9> key)
- ✓ Select the Stability Diagram tab

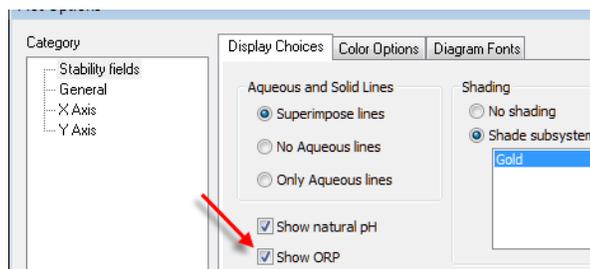
The plot contains all gray shading with some white areas at high EH. The gray shading is the gold stability region. It is here where gold is stable (it does not corrode or dissolve). The white region is where elemental gold is unstable and is present as Au(+3).



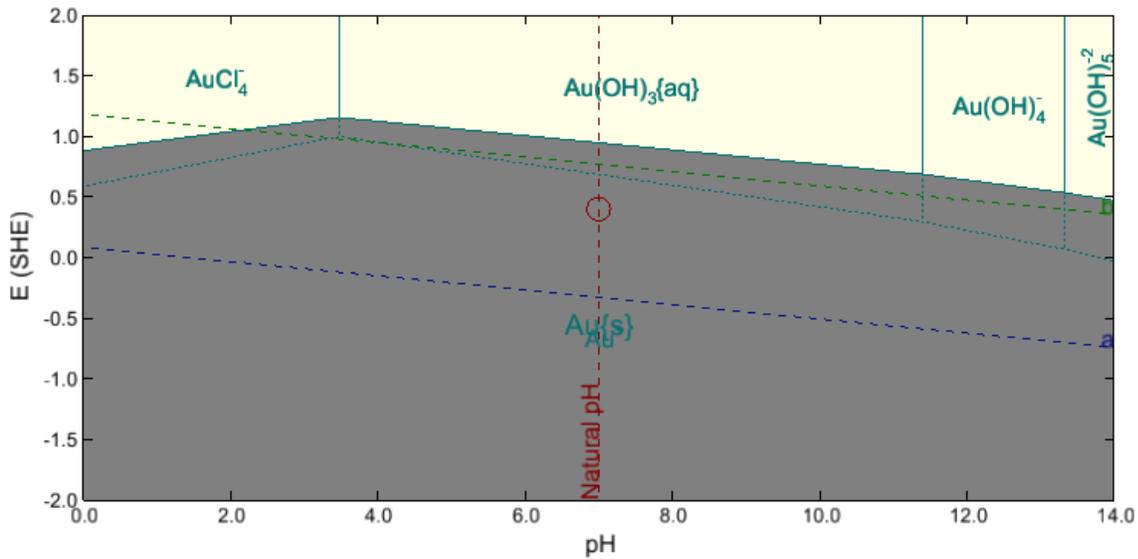
According to the plot, elemental gold is stable between 0 and 14 pH and up to between 0.7 and 1.2 V (SHE). Underneath the gold stability fields are the water stability lines. Water is represented by two sloped lines, labeled a and b. the b-line is the water oxidation line. The upper boundary of Au is above the b-line at all pH's except 1 and below. This means that water will oxidize to O₂ before Au oxidizes to Au⁺³ unless the pH is less than 1. In this pH region, water is stable where gold decomposes.

This is why gold does not dissolve or corrode. Its stability makes it, among other metals (which we will see later) popular in electronic and medical applications.

- ✓ Select the Customize button to the top right of the diagram  
- ✓ Select the Show ORP box



- ✓ Press OK

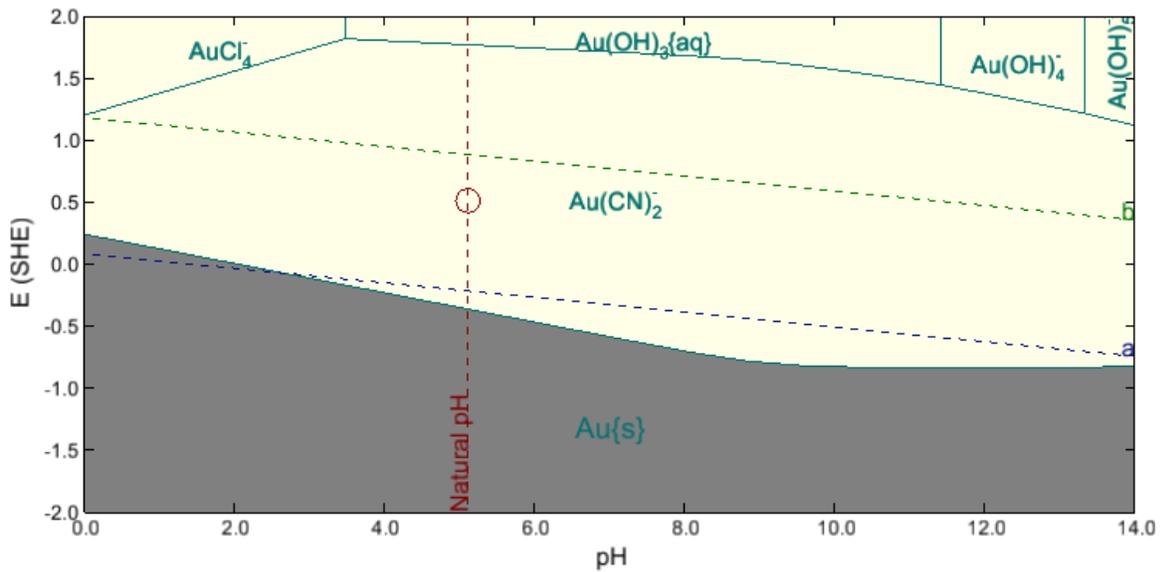


If gold does not corrode in water, then a suitable chemical approach is required to dissolve gold so that it can be processed. The approach is to add cyanide to water. Cyanide destabilizes gold to form a soluble $\text{Au}(\text{CN})_2^-$ complex in water.

- ✓ Select the Definition tab
- ✓ Add HCN to the Neutrals grid and enter a value of 0.1 mol

Neutrals (mol)	
H2O	55.5082
pH Acid Titrant: HCl	0.0
pH Base Titrant: NaOH	0.0
Au	0.0
HCN	0.100000

- ✓ Press <F9> to calculate
- ✓ Click the Stability Diagram



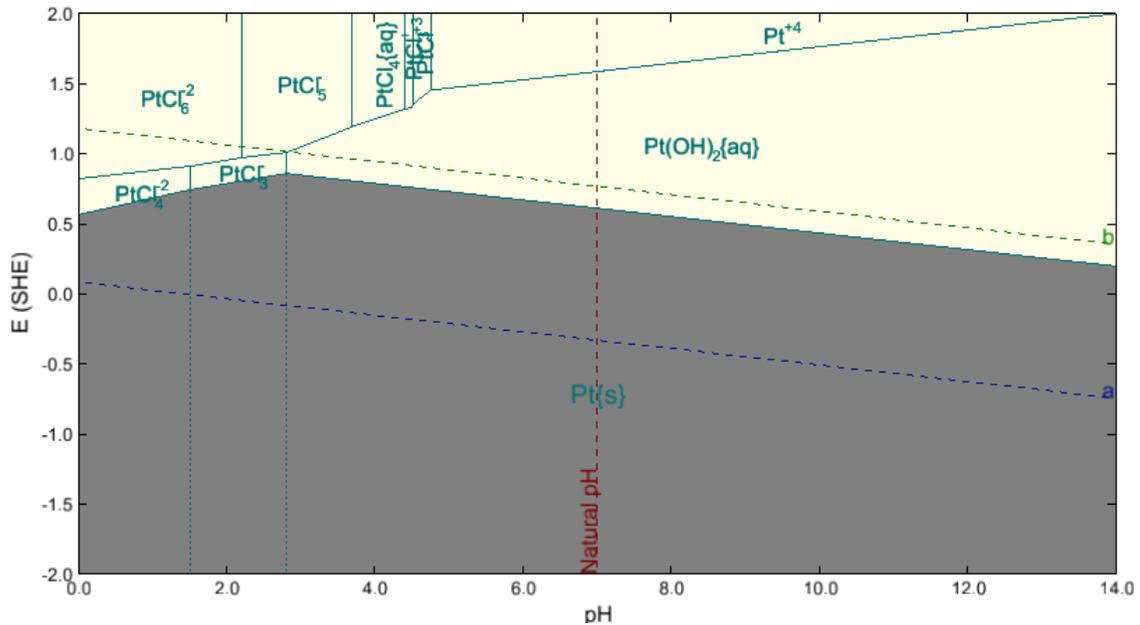
The diagram shows that the 0.1 m CN-1 cause elemental gold to become unstable, and the Au(CN)2-1 complex dominates the system over all pH's and at low and high electrochemical potentials. Now, Au(CN)2 is stable over all regions where water is stable, meaning that gold can now be processed in water at a variety of conditions.

Platinum Stability Diagram

- ✓ Select the Noble Metals stream
- ✓ Add a Stability Diagram  Add Stability Diagram and name it 'Platinum' 
- ✓ Add Pt to the Contact Surface grid

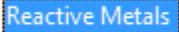


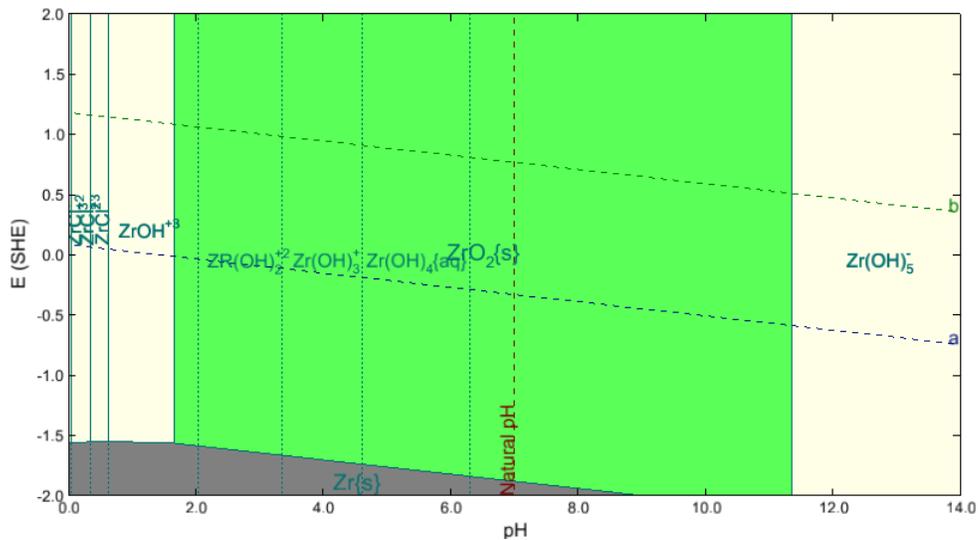
- ✓ Calculate or press the <F9> key
- ✓ Select the Stability Diagram tab



Platinum is also stable at wide pH ranges, and at moderate oxidizing conditions. Only under strong oxidizing and acidic (HCl) conditions, does platinum corrode forming a dissolved PtCl_x, and Pt(OH)₂ complexes.

Zirconium Stability Diagram

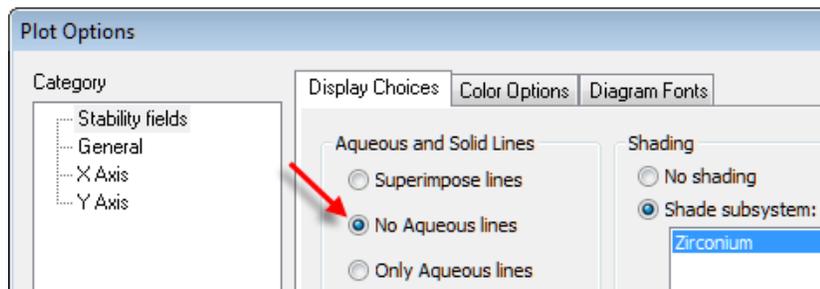
- ✓ Add a new stream  Add Stream and rename it 'Reactive Metals' 
- ✓ Add a Stability Diagram  Add Stability Diagram and rename it 'Zirconium' 
- ✓ Type Zr or Zirconium in the Contact Surface
- ✓ Calculate then click the Stability Diagram tab



Zirconium metal is highly reactive and unstable under natural conditions. It reacts with water to form zircon, ZrO_2 and H_2 .

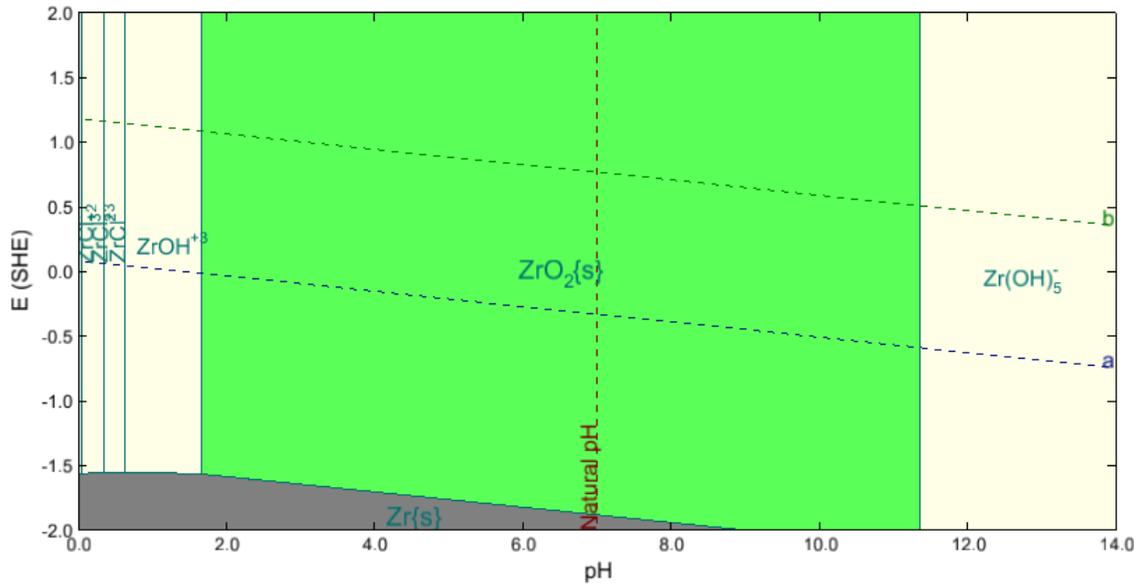
The stability diagram calculates both the dominant solid phase and aqueous species. The dotted lines represent the stability boundaries for each dominant aqueous species. At high pH, >6.2 , $Zr(OH)_5^-$ is the dominant aqueous phase. Between 4.5 and 6.2, $Zr(OH)_4^0$ dominates. Between 3.3 and 4.5, $Zr(OH)_3^+$ dominates, etc. To see this better, we will create a pH survey plot and view the speciation for a fixed $Zr(OH)_4$ concentration. The aqueous lines are useful, but sometimes confuse the plot with too much information. They can be removed.

- ✓ Select the Customize button 
- ✓ In the Plot Options menu, select the button next to No Aqueous Lines



The Appendix explains other plot options for the stability diagram.

- ✓ Press OK and view the diagram



✓ Save the file

Follow-up Examples

Create three new stability diagram calculations within the current Reactive Metals stream. Compute the stability diagrams for the following metals: Aluminum, Sodium, and Titanium

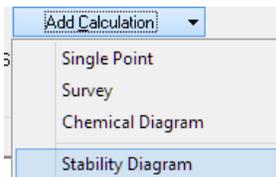
6.2 Temperature effects on Iron Stability

In this section, you will create Stability Diagrams of iron at different temperatures. The goal is to view the temperature effects on iron stability. These results will give us an idea of how boilers, heat exchangers, and other surfaces behave.

Fe diagram vs temperature and phosphate

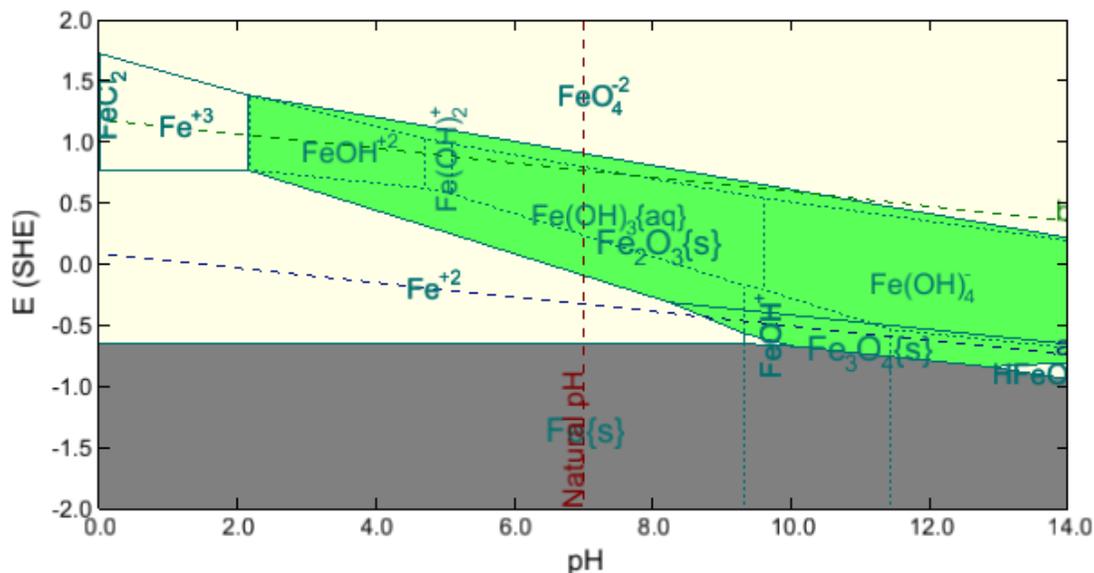
Add a new stream  Add Stream and rename it 'Fe Diagram'  Fe Diagram

- ✓ Add a Stability Diagram calculation



- ✓ Type Fe or iron into the Inflows grid
- ✓ Calculate and view the Stability Diagram (tab)

The diagram is an overlay of Fe phase stability on H₂O stability (this is described in detail in Chapter 6a). Elemental iron (gray section) is stable from -2 to -0.67 V (SHE). It is in fact also stable at much more negative voltages, but this is where the calculation started. At a potential greater than -0.67 V, Fe⁰ oxidizes to Fe⁺². If the pH is above 10, the boundary is at a lower potential for example, -0.93V at 14 pH.



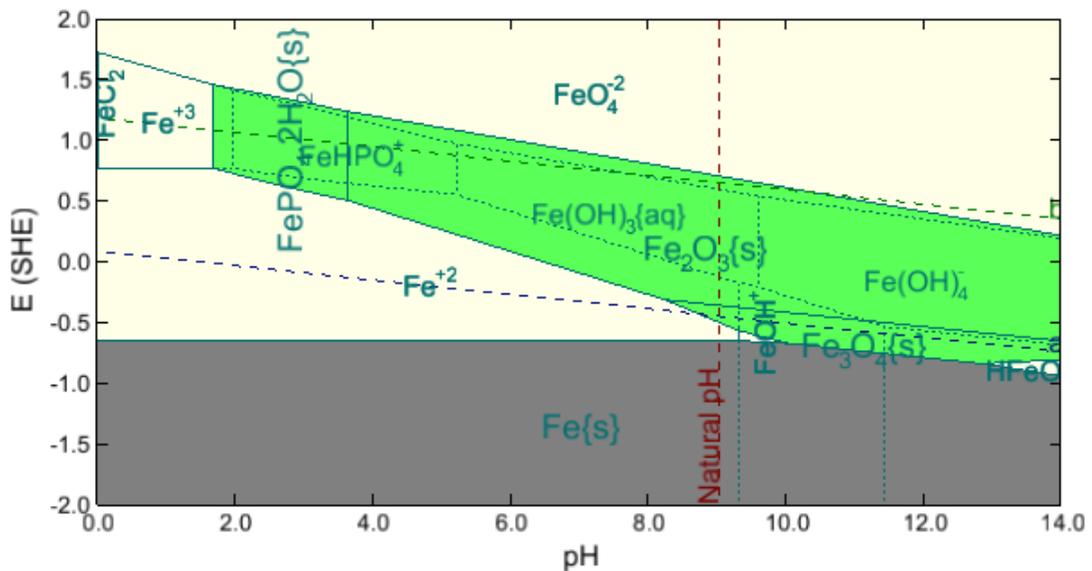
The software computes that Fe₃O₄ (magnetite) is stable between a pH of ~8.3 and 14. This is a well-known *Passive Film* that protects the iron surface from active corrosion. At higher potentials, the software computes Fe₂O₃ (hematite). Hematite is the dehydrated form of Fe(OH)₃ and FeOOH, two forms of rust. These phases provide less corrosion protection the iron surface than the magnetite.

Also shown on the diagram in lighter letters and dashed lines, are the dominant iron-containing, dissolved species in the electrolyte solution (in this case water). The species with the largest range is Fe⁺² (this is the white section of the plot on the left side). The software computes stability for this species from -0.67 V to 0.75V, at low pH, and vanishes at about 10 pH. Fe⁺² is the iron corrosion product. Within the white region

where Fe^{+2} dominates, no protective films are computed to form. Thus, active corrosion of the iron surface is predicted if the pH is between 0 and 8. The actual corrosion rate cannot be predicted from this plot, nor can the pH of the water film (diffusion layer) in contact with the iron surface. Therefore, the pH range of 0 to 8 is a guideline and not a direct prediction.

- ✓ Return to the Definition tab
- ✓ Add Na_2HPO_4 to the inflow list and add 0.001 moles (95 mg/l total phosphate)
- ✓ Calculate and view the stability diagram

Adding the alkaline buffer, Na_2HPO_4 , influences the diagram in several ways. First, it raises the solution pH from 7 to 9. The raised pH places the electrolyte phase in a region where Fe_3O_4 is stable as the iron surface corrodes. The software computes a new phase, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, exists at a lower pH. This phase is more stable than Fe_2O_3 below a 3.7 pH, and its stability extends to 1.5 pH. Lastly, the FeHPO_4^{+1} complex is computed to be the dominant species between 2.5 and 5 pH (see dotted-line trapezoid surrounding the FeHPO_4^{+1} name).

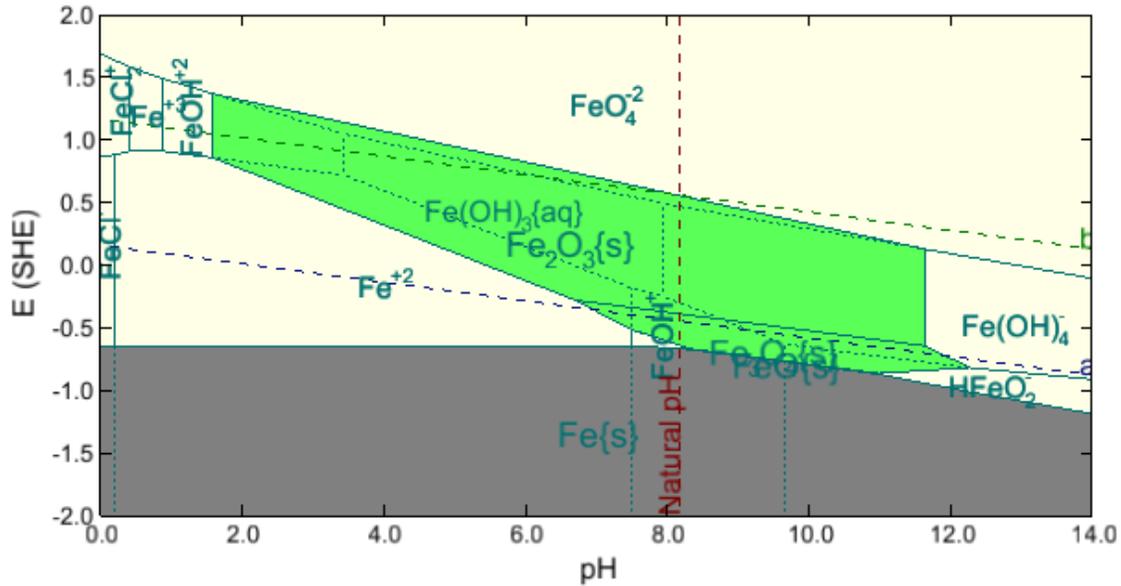


Protecting iron surfaces with phosphate is a known application, often used in automobile rust-proofing.

- ✓ Change the total pressure to 30 atm and the temperature to 100C
- ✓ Calculate and view the Stability Diagram (tab)

The diagram boundaries have shifted to the left. Note for example that the natural pH of the liquid is ~8 instead of 9. This is due in part, to the thermal effects on water's ionization constant. (Pure water has a pH of 6.1 100C compared to 7.0 at 25C).

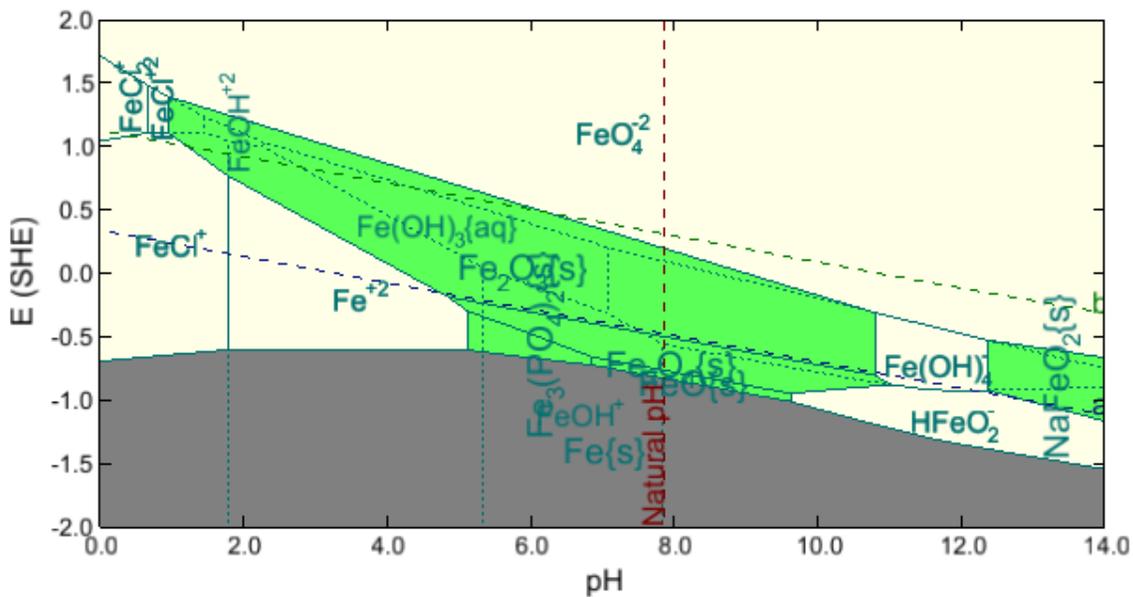
The Fe_3O_4 passive film is now computed to be stable between 7 and 12 ph. The phosphate-buffered water has a pH, which will enable the Fe_3O_4 to be stable when formed.



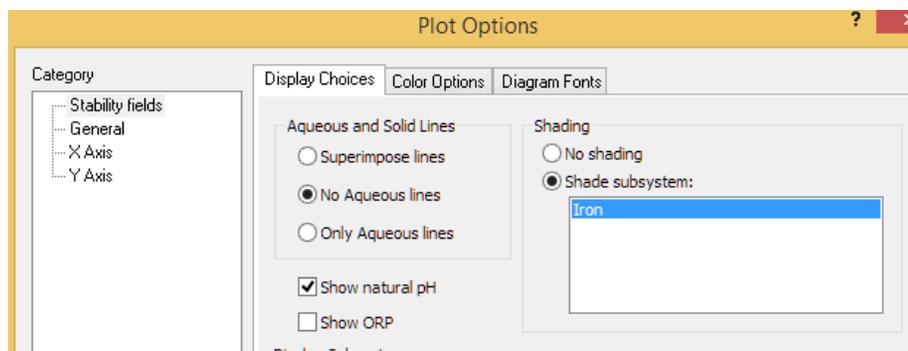
Note the changes to the diagram. First, FeCl_x^- aqueous complexes are computed to exist and be the dominant iron-containing species at a low pH. Also, an FeO phase, the anhydrous form of Fe(OH)_2 , is computed to exist at alkaline pH. This phase is harder to see and is just behind the Fe_3O_4 text.

- ✓ Change the temperature to 250C
- ✓ Change the pressure to 60 atm
- ✓ Calculate and view the Stability Diagram (tab)

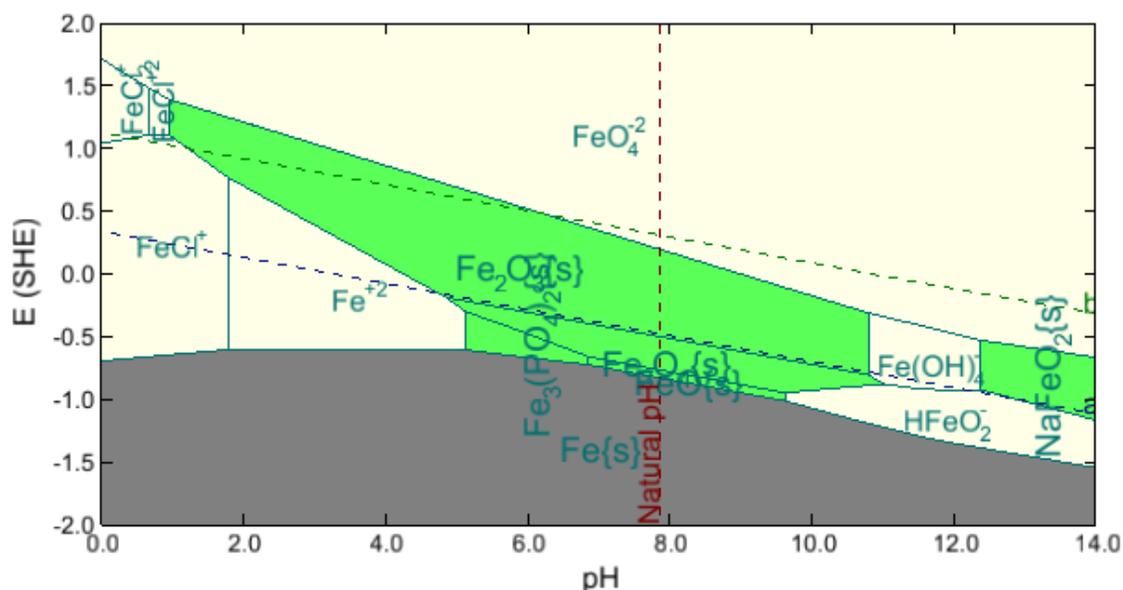
The resulting plot contains more text and it is difficult to read. Therefore, we will remove the Dominant Aqueous layer from the plot and study the solid phase layer first.



- ✓ Click on the Customize button in the upper left of the diagram
- ✓ Click on the No Aqueous lines Radio button then close the window.



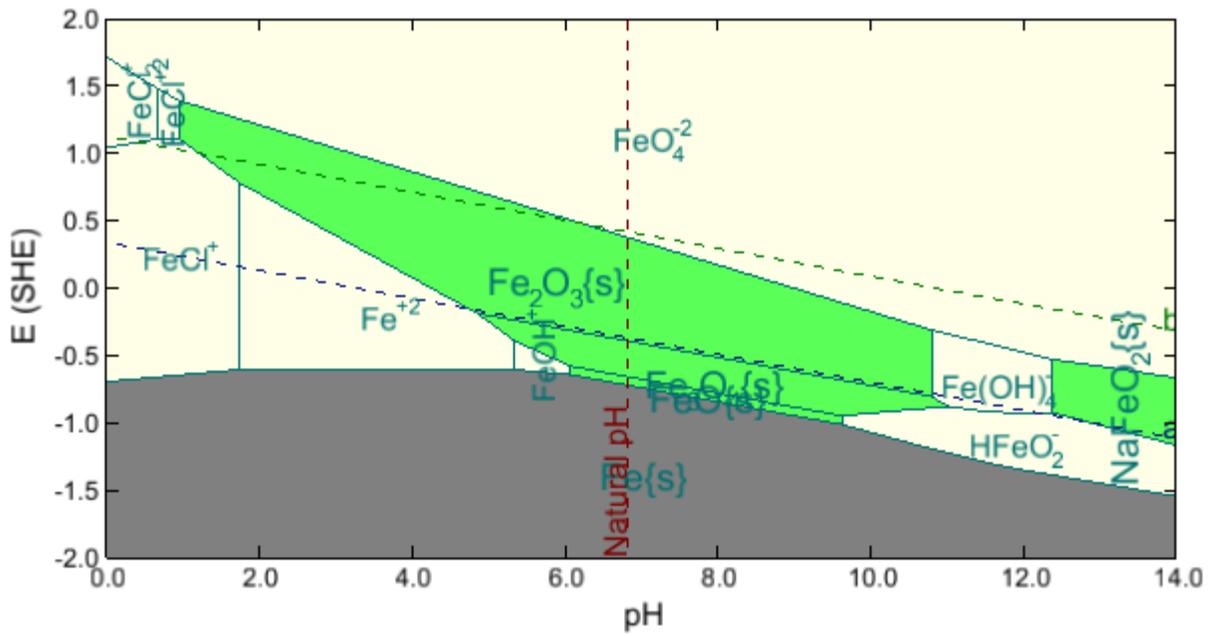
The diagram now displays five corrosion phases, Fe_2O_3 , Fe_3O_4 , FeO , $\text{Fe}_3(\text{PO}_4)_2$, and NaFeO_2 . Thermodynamically, this iron should be protected from corrosion when put into service at 250 C, because the Fe_3O_4 phase is computed to be stable, in the water that is present in this system.



The concentration of phosphate in this water is 95 mg/l and this would be the continuous concentration added. If the phosphate concentration were 5 mg/l, then the Na_2HPO_4 inflow would be 5.5×10^{-5} moles.

- ✓ Change the Na_2HPO_4 inflow to 5.5×10^{-5} moles
- ✓ Calculate and review the diagram

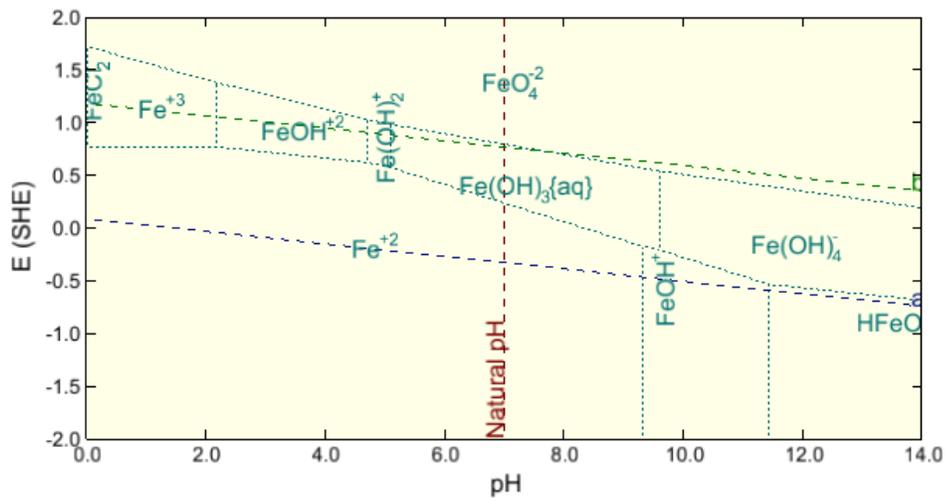
The resulting diagram containing 5 mg/l total phosphate differs from the higher phosphate in that the $\text{Fe}_3(\text{PO}_4)_2$ phase is no longer stable. The buffered pH remains in the magnetite stable region, which would be an indication that at this concentration of phosphate buffer, the system will still be protected from corrosion.



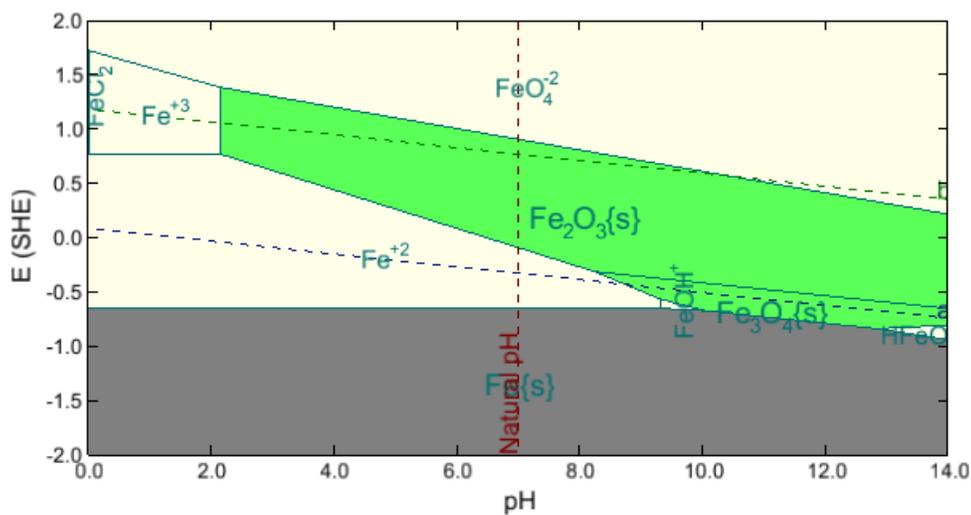
6.3 Composition effects on iron stability

The composition effects on a Pourbaix (stability) diagram impact the dissolved species and the phases that form. To understand how this occurs, it is necessary to know how these diagrams are developed. In each of these calculations, you **have not** entered a concentration for the contact surface. That is because the contact surface and its corroding ion are pre-set by the software.

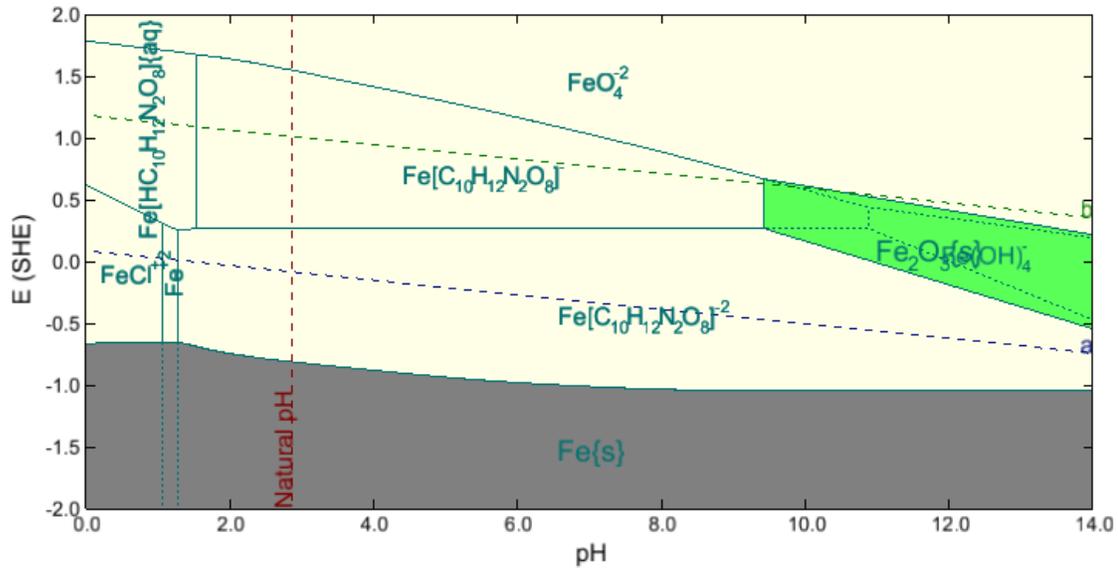
Setting the species activities affects the calculation in the following ways. First, it means that the total concentration of the focus element, e.g., total dissolved iron, is not constant across the plot area. This is because the activity of the key species, Fe^{+2} and Fe^{+3} are held constant at $1e^{-6}$, about 56 ppB at ideal activity.



Another affect is on the solid-liquid and solid-solid boundary lines. The activity of the solid phases are set to 1 (ideal). Setting the pure solid phase activity to unity thermodynamically correct, and is not a simplification. It nonetheless simplifies the plot lines.



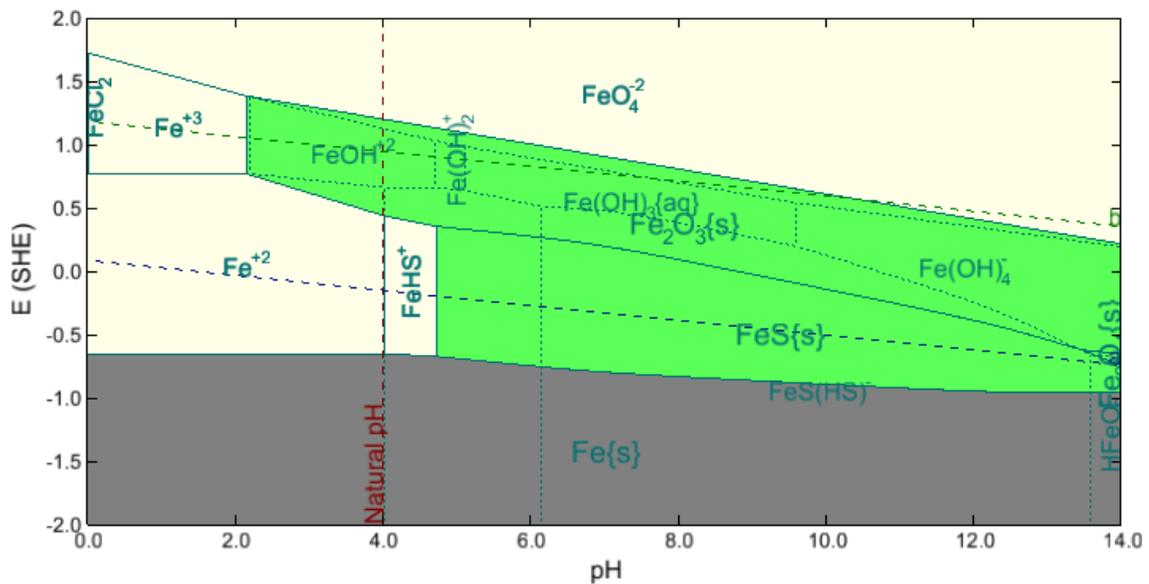
The chelant, EDTA⁴⁻ forms a strong complex with Fe²⁺ and with Fe³⁺. This complex caused the stability of each solid phase to decrease. There is now a greater electrical potential difference between H₂O reduction and Fe oxidation: the energy released from the corrosion reaction is now greater than the case with no EDTA.

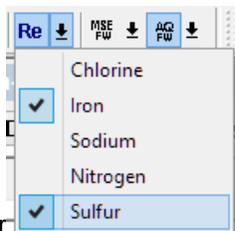


Both cases of adding NH₃ and EDTA results in the formation of strong aqueous complexes with Fe²⁺ and Fe³⁺. This results in the elemental iron surface of being less stable in water and also the reduction in the stability of any protective film. Both cases would result in active corrosion.

- ✓ Remove the EDTA value and add 0.1 mole H₂S
- ✓ Calculate and view the plot

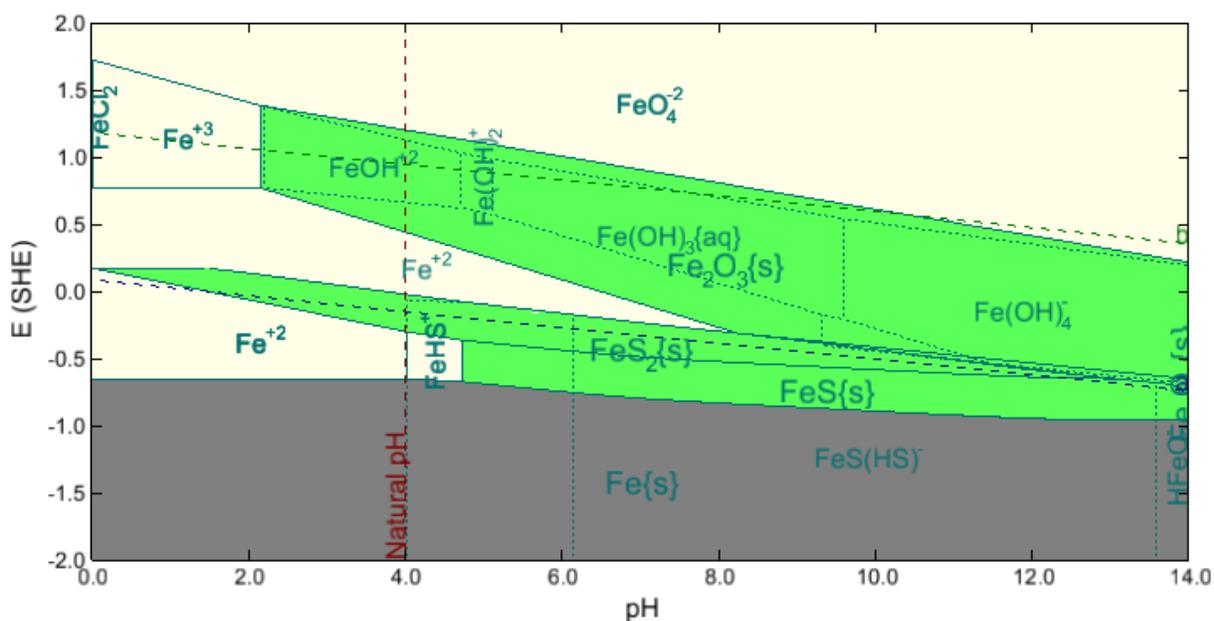
The H₂S (S²⁻) forms a relatively insoluble precipitate with Fe²⁺. This precipitate has the potential to cover the metal surface and enhance the pH region where iron is protected from the water.





- ✓ Click on the down arrow in the Redox button and select Sulfur
- ✓ Recalculate

Sulfur is OFF by default in redox calculations. When it is turned on, the software will compute H₂S oxidation S(0) and higher sulfur oxidation states. The plot now shows that FeS₂ (marcasite or pyrite) form at the electrochemical potentials around the water reduction line. Therefore, during the corrosion process, some of H₂S will oxidize to elemental sulfur. This sulfur reacts with Fe⁺² and S⁻² to form the insoluble precipitate.



6.4 Why Rust Forms & Why Stainless Steel is Stainless

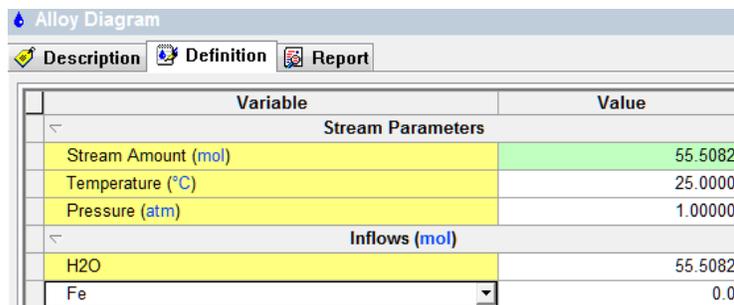
In this section, we will use Stability Diagrams to visualize and answer the two age-old questions.

Why Rust Forms

The previous case presented the iron stability regions, and also the regions where the products of iron oxidation forms. Iron (Fe^0) is thermodynamically unstable in water it reacts spontaneously to form Fe^{+2} and H_2 . When O_2 is present, it oxidizes further to Fe^{+3} .

Iron oxidation products include $\text{FeO}(\text{OH})$, Fe_2O_3 , and Fe_3O_4 . Under atmospheric conditions, the oxide is most likely FeOOH , a form of rust, the crystalline nature of which makes it a poor protective layer. Thus corrosion continues through the layer that forms. When Fe^0 is alloyed with Ni^0 and Cr^0 , different surface precipitates accumulate, including Ni_3O_4 , NiFe_2O_4 , and Cr_2O_3 . These oxides are more impervious and once formed, these precipitates protect surfaces from further corrosion. We will see from the following example that that Fe^0 is inherently unstable in water. This instability is captured using a relatively simple diagram called an EH-pH diagram.

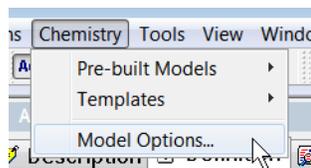
- ✓ Add a new stream  Add Stream and rename it 'Alloy Diagram'  Alloy Diagram
- ✓ Enter Fe in the inflow grid



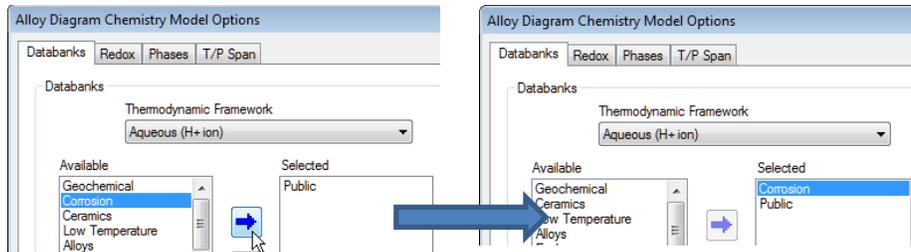
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Fe	0.0

The procedure is to run a series of equilibrium calculations to determine the stability of the different iron oxide phases. The phase, $\text{FeO}(\text{OH})$, is thermodynamically less stable relative to other iron oxides. By comparison, a more thermodynamically stable phase is hematite (Fe_2O_3). The software allows phase inclusion/exclusion through the chemistry model. The following calculations will explore this phase stability.

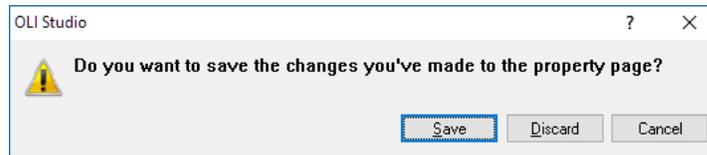
- ✓ Select Chemistry > Model Options from the menu



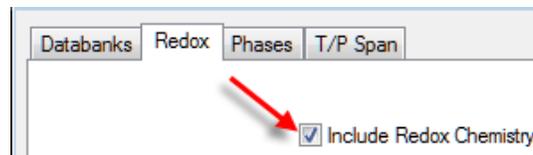
- ✓ Move Corrosion from the Available databanks to Selected Databanks



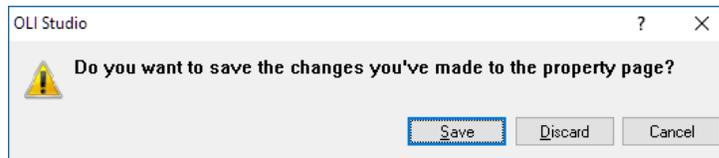
- ✓ Select the Redox tab and select save when prompted



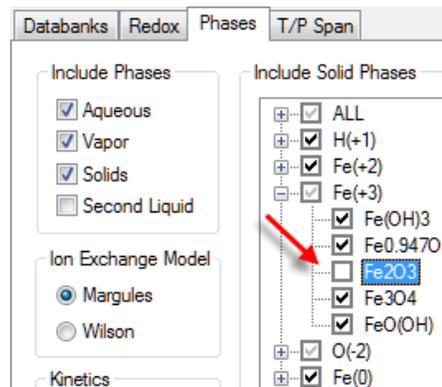
- ✓ In the Redox tab, place a check next to Include Redox Chemistry



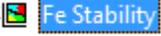
- ✓ Select the Phases tab and select save when prompted



- ✓ Expand the Fe(+3), then uncheck Fe₂O₃



Hematite / FeO(OH) has now been removed as a potential solid. Therefore, the next stable solid forms.

- ✓ Press OK
- ✓ Add a Stability Diagram  Add Stability Diagram and rename it 'Fe Stability' 
- ✓ Type Fe in the Contact Surface

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Inflows (mol)	
H2O	55.5082
Fe	0.0
Contact Surface (mol)	
Fe	

- ✓ Press <F9> to calculate then select the Stability Diagram tab
- ✓ Click on the Customize button and select the No Aqueous lines radio button

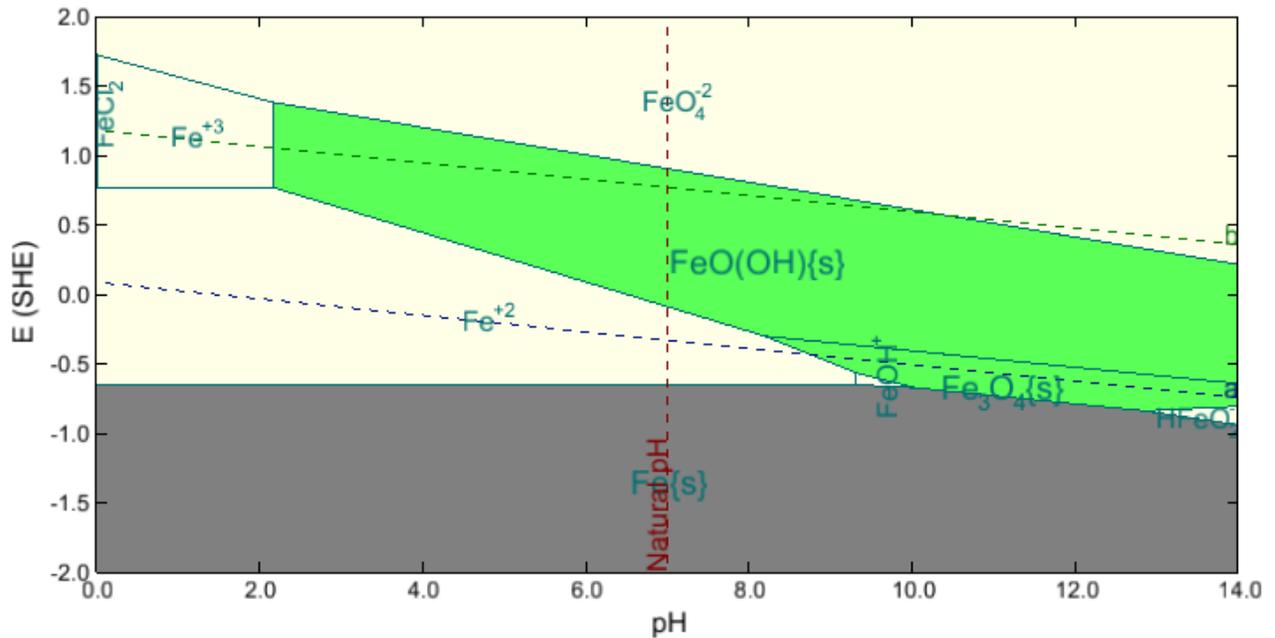
Aqueous and Solid Lines

Superimpose lines

No Aqueous lines

Only Aqueous lines

The plot shows the iron stability similar to previous plots, except that the FeO(OH) phase is now the dominant phase for Fe⁺³.

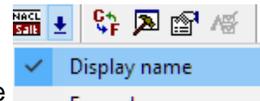


The complete plot is represented as follows:

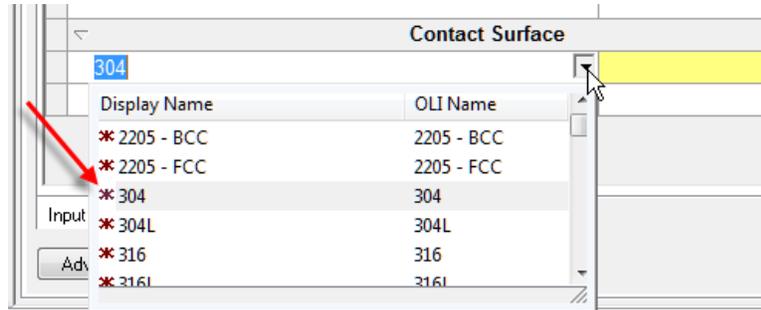
- The gray area is the region where elemental iron is stable. Iron is stable over all pH ranges when EH is below -0.6 V (SHE).
- The green area are the oxidized iron phases. Two phases are present in this calculation: *magnetite* (Fe_3O_4) at 8 and 14 pH and *goethite* ($FeOOH$) at 3 to 14 pH when Fe is in the Fe⁺³ oxidation state.
- This white region is where no iron phases are present. This is the active corrosion region.

Stainless Steel

- ✓ Click back on the Alloy Diagrams stream



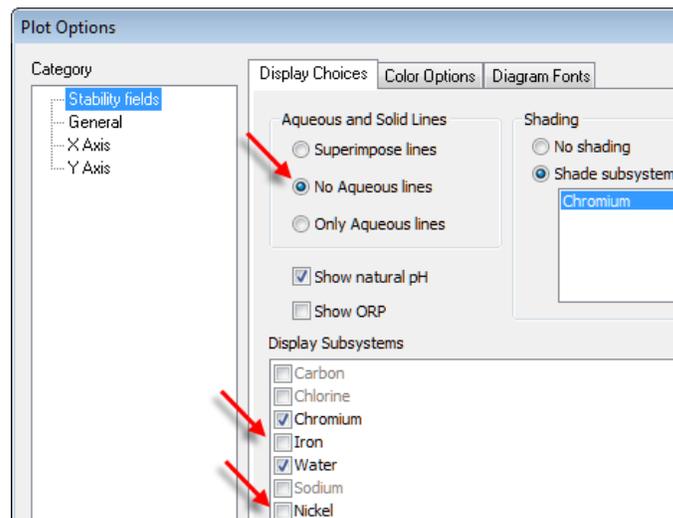
- ✓ Change the Names Manager to Display name
- ✓ Add a new Stability Diagram and name it '304 Stainless Steel'
- ✓ Click on the bottom right corner of the empty grid in Contact Surface section and select 304



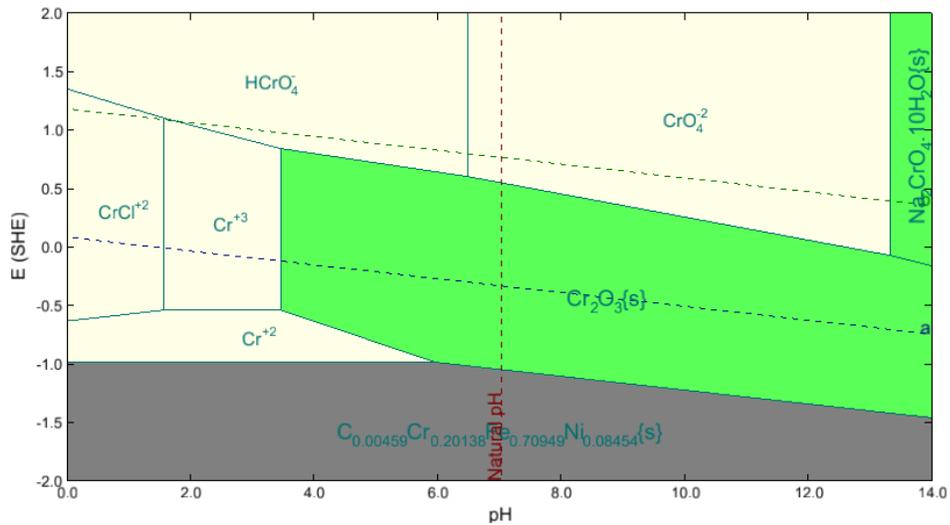
- ✓ Press <F9> to calculate
- ✓ Select the Stability Diagram tab

The initial stability diagram contains several lines and equations. We will clean this up.

- ✓ Select the Customize button
- ✓ Select No Aqueous line
- ✓ Uncheck Nickel and Iron in the Display box

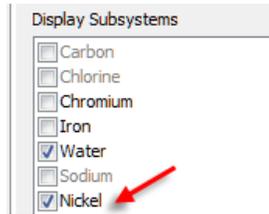


- ✓ Press OK

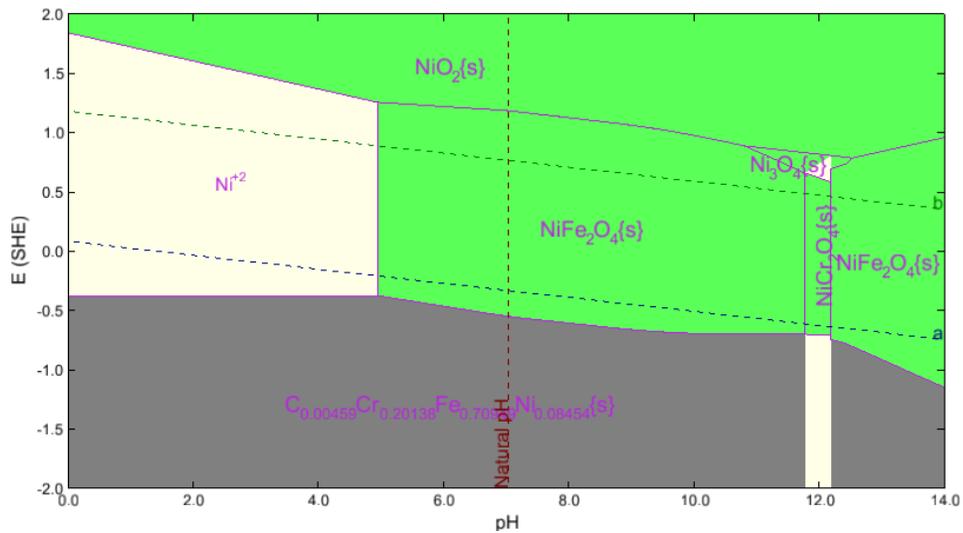


The large green wedge in the middle of the plot is the Cr_2O_3 stability zone. As Cr^0 reacts with water Cr_2O_3 precipitates (forming a protective layer on the steel surface). The phase stable between 4 to 14 pH, providing acid protection.

- ✓ Click the Customize button
- ✓ Uncheck Chromium and select Nickel then press OK



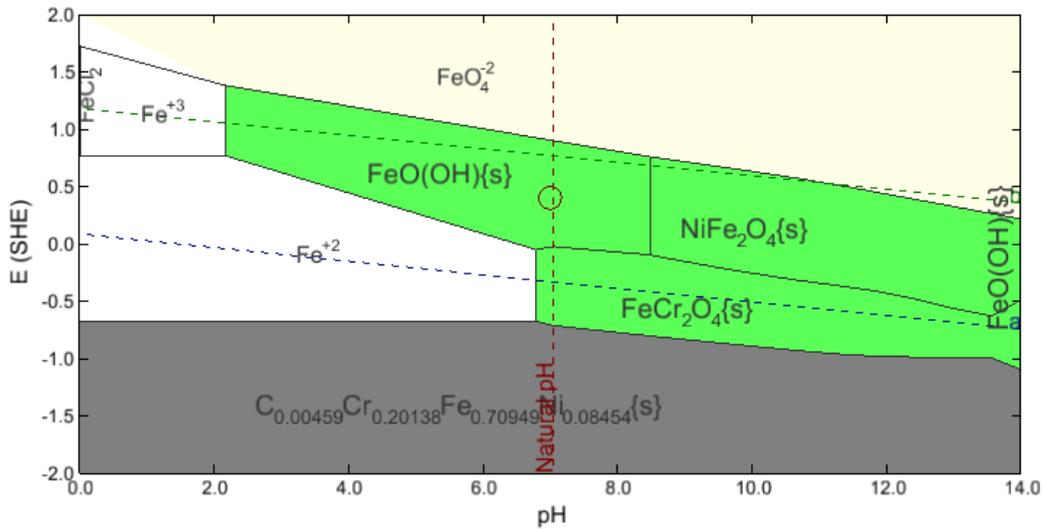
The mixed metal oxide, NiFe_2O_4 is computed to be stable between 5 and 14 pH and up to oxidation states where water is unstable.



- ✓ Click the Customize button and change the display subsystem (metal) to Iron.

- Display Subsystems
- Carbon
 - Chlorine
 - Chromium
 - Iron
 - Water

The iron oxide phase that forms is different from carbon steel. Here, two mixed metal oxides, NiFe_2O_4 and FeCr_2O_4 form. These phases are similar in structure to Fe_3O_4 , the film that forms and protects carbon steel from corrosion at neutral pH.



The Cr_2O_3 and NiFe_2O_4 phases that form from the reaction between stainless steel and water are the key contributors to this alloy's stability, and protects the surface from further attack.

6.5 Iron Stability in Multiple Solvents

This is an interesting case because it extends concept of metal stability in electrolytes. This case will investigate the thermodynamic stability of iron in methanol, ethanol, and ethylene glycol. By changing the solvent, the OH⁻ species is eliminated under acidic conditions, and therefore, the oxides observed in the water phase do not exist.

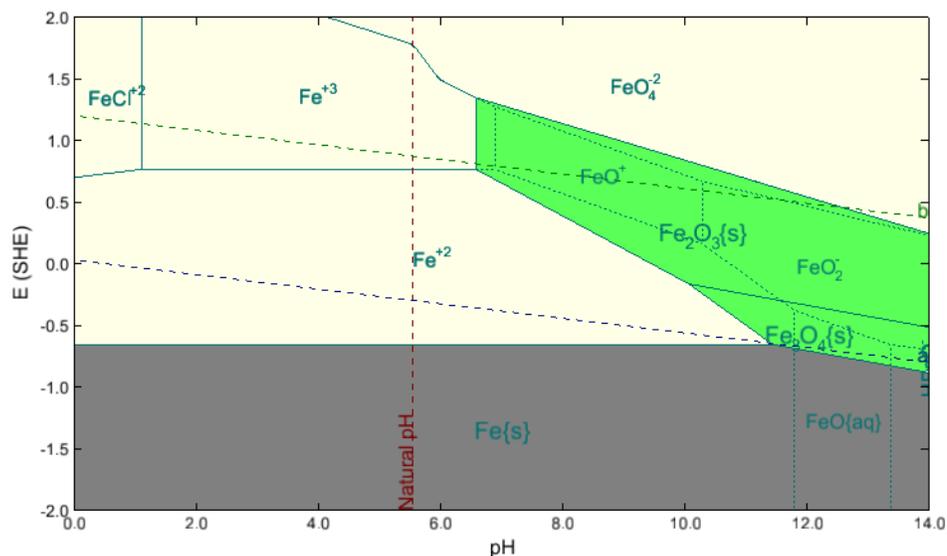
- ✓ Add a new stream  Add Stream and rename it 'Solvents' 
- ✓ Select the MSE button in the toolbar 
- ✓ In the Inflows section, set the Water value to 0
- ✓ Add the following species in the Inflows grid: methanol, ethanol, and ethylene glycol

Solvents	
Description Definition Report	
Variable	Value
Stream Parameters	
Stream Amount (mol)	0.0
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
Water	0.0
Methanol	0.0
Ethanol	0.0
1,2-Ethanediol	0.0

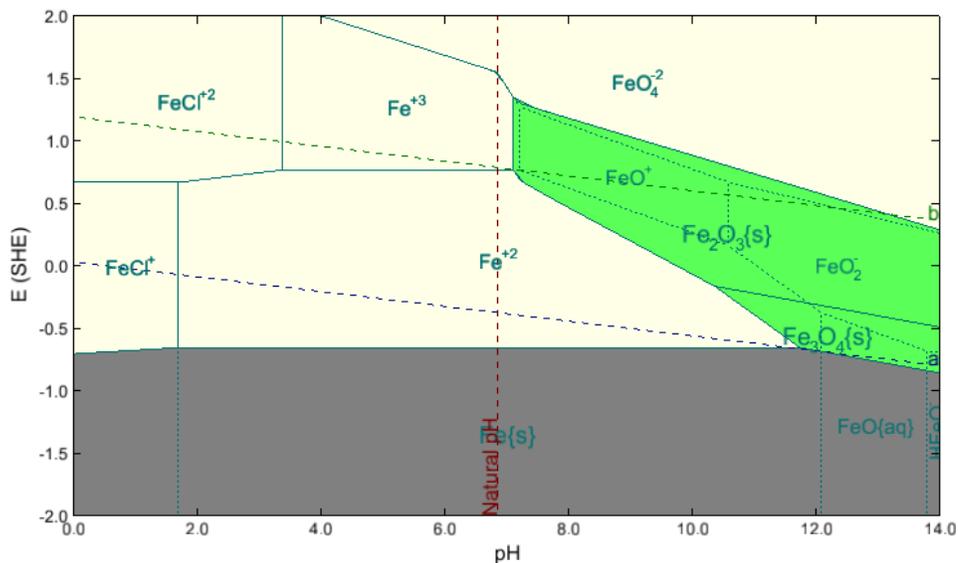
- ✓ Add a Stability Diagram  Add Stability Diagram and rename it 'MeOH' 
- ✓ Set the Methanol inflow to 100 moles
- ✓ Enter Iron as the Contact Surface

MeOH	
Description Definition Stability Diagram Report	
Variable	Value
Stream Parameters	
Stream Amount (mol)	100.000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	Hydrogen chloride
pH Base Titrant	Sodium hydroxide
Inflows (mol)	
Water	1.00000e-10
Methanol	100.000
Ethanol	0.0
1,2-Ethanediol	0.0
Iron	0.0
Hydrogen chloride	0.0
Sodium hydroxide	0.0
Contact Surface (mol)	
Iron	

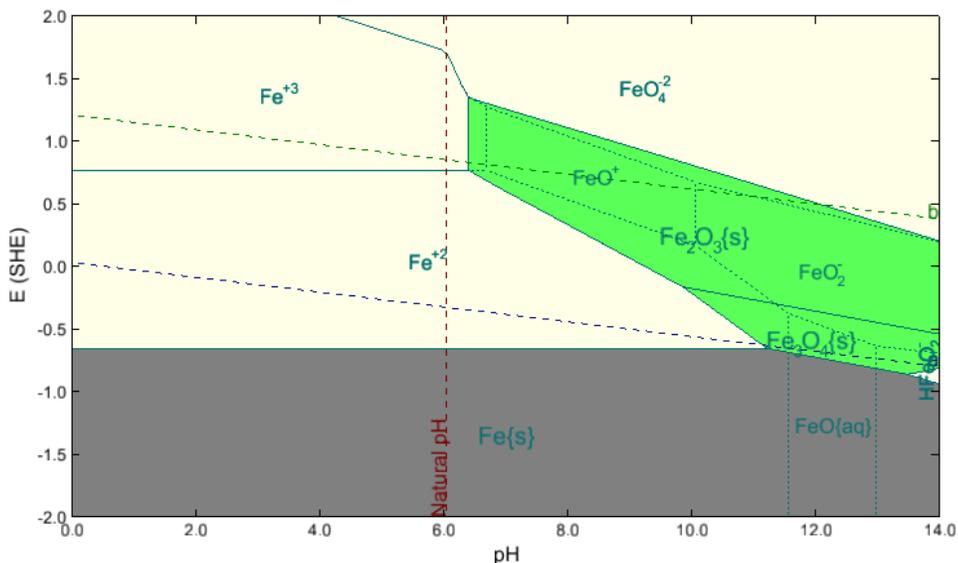
- ✓ Calculate or press the <F9> key then select the Stability Diagram tab



- ✓ Add another Stability Diagram and rename it 'EtOH' 
- ✓ Select the Definition tab and change the Ethanol rate to 100 moles
- ✓ Add Iron as a contact surface
- ✓ Calculate or press the <F9> key then select the Stability Diagram tab



- ✓ Add another Stability Diagram and rename it 'MEG' 
- ✓ Select the MEG diagram
- ✓ Select Description tab, change the Ethylene Glycol (1,2-Ethanediol) rate to 100 moles
- ✓ Add Iron as a contact surface
- ✓ Calculate or press the <F9> key then select the Stability Diagram tab



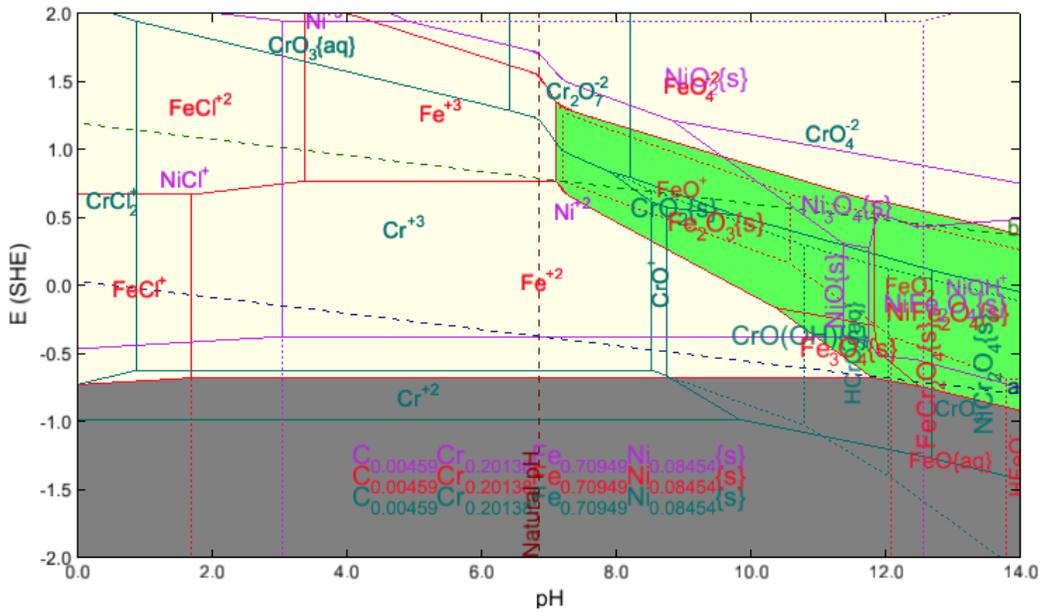
- ✓ Add new stream Add Stream and rename it 'Ethanol Stability'
- ✓ Select the MSE button in the toolbar
- ✓ In the Inflows section, set the Water value to 0
- ✓ Enter Ethanol as an inflow with 100 moles

Ethanol Stability	
Description Definition Report	
Variable	Value
Stream Parameters	
Stream Amount (mol)	100.000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
Water	0.0
Ethanol	100.000

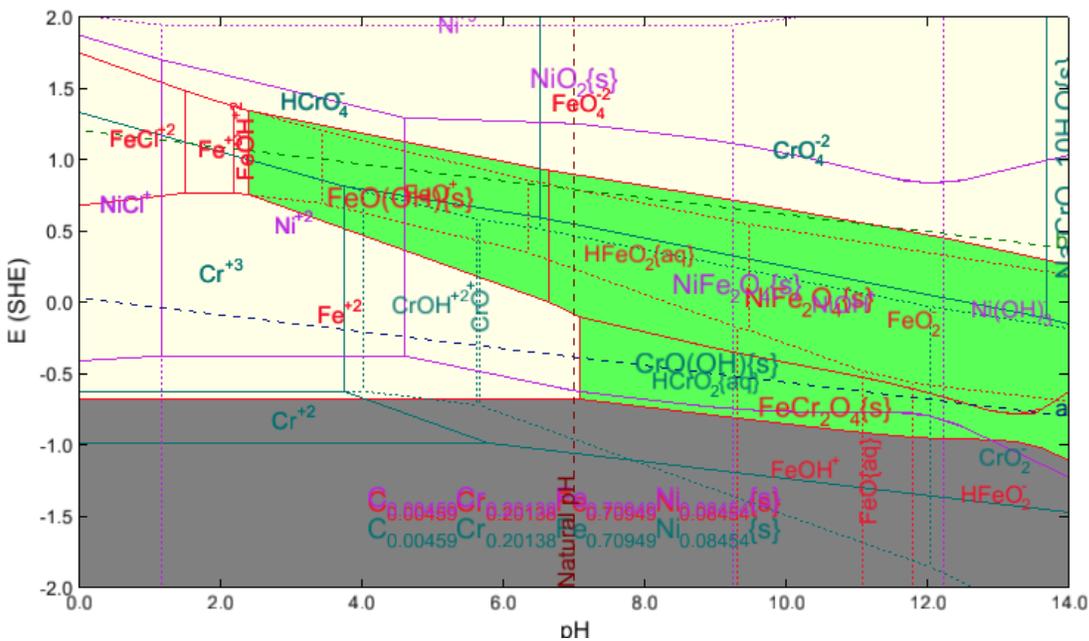
- ✓ Add a Stability Diagram Add Stability Diagram and rename it 'EtOH Stability'
- ✓ Select 304 as the contact surface

Neutrals (mol)	
Water	0.0
Ethanol	100.000
pH Acid Titrant: Hydrogen chloride	0.0
pH Base Titrant: Sodium hydroxide	0.0
304	0.0
Contact Surface	
304	

- ✓ Calculate or press the <F9> key then select the Stability Diagram tab

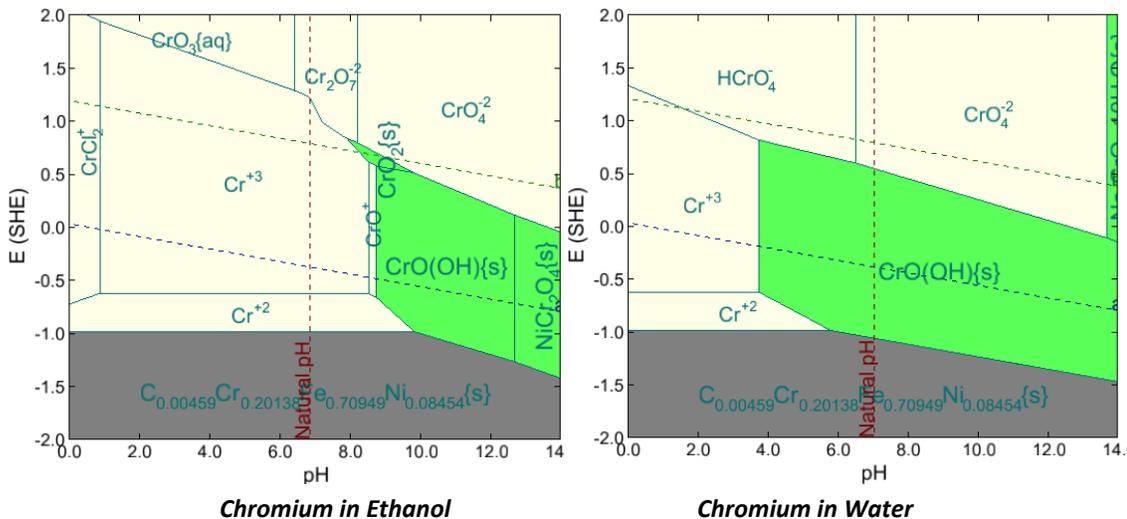


- ✓ Add a second Stability Diagram and name it 'Stability in H2O'
- ✓ 
- ✓ Select the stability diagram's Definition tab
- ✓ Change the Ethanol value to 0 moles and change the Water value to 100 moles
- ✓ Enter 304 as the Contact Surface grid
- ✓ Calculate or press the <F9> key then select the Stability Diagram tab

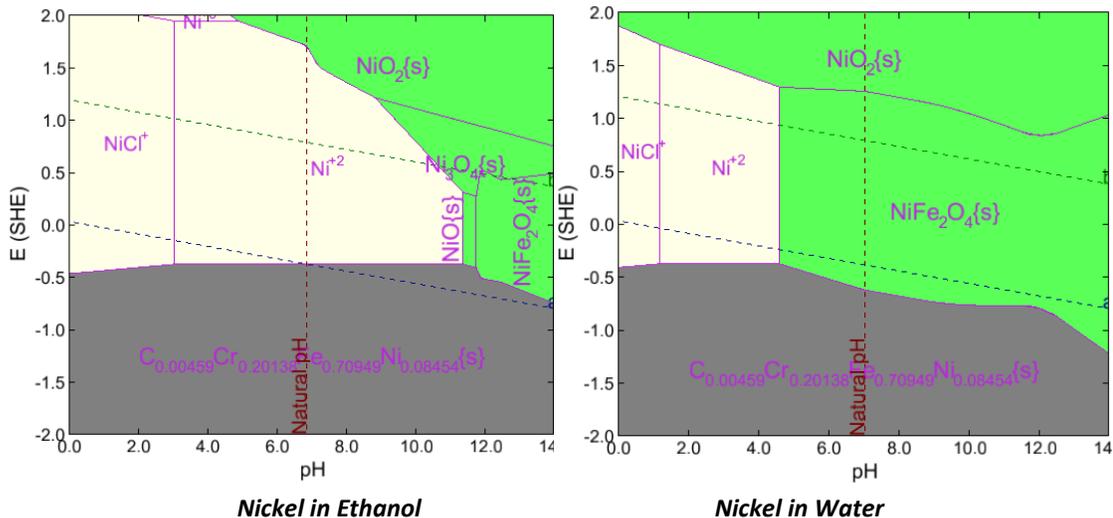


You will review the Ni, Cr, and Fe sub-systems in Ethanol and compare them to the water solvent. Through the analysis, the key difference will be the existence of the oxide film above 7 pH. Above this pH, NaOH is added to raise the pH. This is the source of OH-1 and O-2 which converts to the metal oxides and hydroxides.

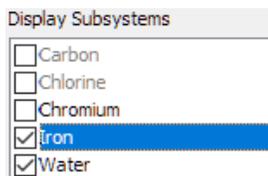
✓ Set both diagrams to display the Cr subsystem

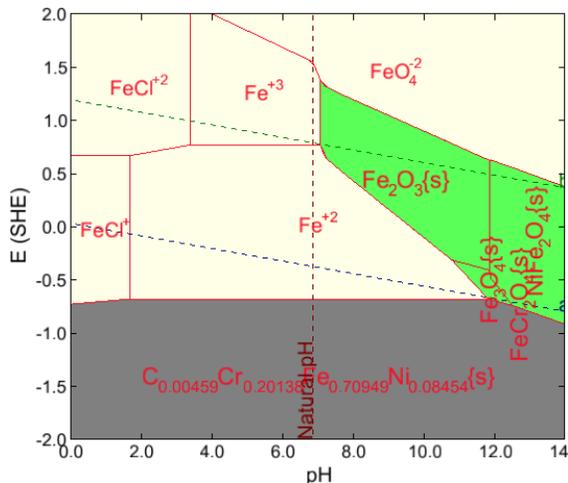


✓ Set both diagrams to display the Ni subsystem

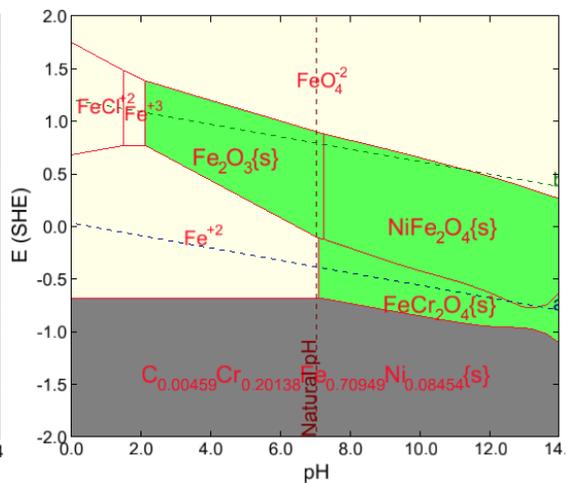


✓ Set both diagrams to display the Fe subsystem





Iron in Ethanol



Iron in Water

Chapter 7a- Interpreting Polarization Curves

Overview

The polarization plot is a useful tool that displays in a single diagram why a material is corroding. It illustrates the chemical reasons for corrosion and quantifies the impact of each corroding material. In this particular system, the main causes of corrosion would be H^+ (acid) corrosion, CO_2 corrosion, H_2S corrosion, H_2O corrosion, and some remote O_2 corrosion. The polarization plot shows what the contribution of each potential corrodant is to the corrosion of a given surface.

Polarization Curves Plots

The Purpose of the Polarization Plot

The purpose of creating the polarization curve is to determine how fast the metal/alloy will give up electrons and how fast the dissolved species will accept them. It shows what species are responsible for corrosion and what amount these species contribute to corrosion. Polarization curves are a replacement of the experimental procedure of determining corrosion rates. The benefit of using polarization curves, among other things, is to perform a hypothetical experiment in a system that would be difficult to do in the laboratory or would be very expensive. What the user gets out of polarization diagrams is an understanding of why a material is corroding and what species are contributing to the corrosion process.

Polarization Diagram Layout

The diagram below is a simplified polarization plot. The plot contains a positive-sloped **anode curve**, one or more negative-sloped **cathode curves**, and a **corrosion potential triangle**, which indicates the steady-state corrosion rate. The y-axis reflects the **electrochemical potential**, and the x-axis describes the **electron current density**.

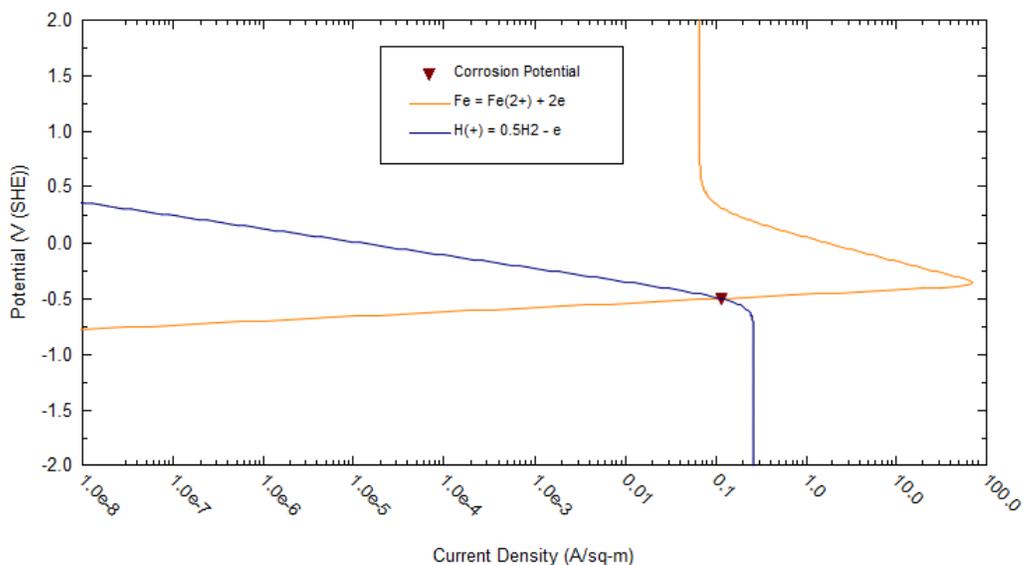
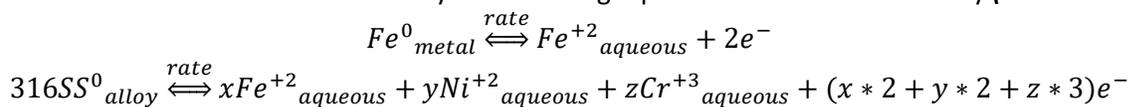


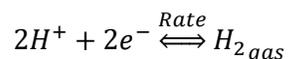
Figure 1 - Simplified Polarization Curve showing the Fe⁺² oxidation curve, the H⁺ reduction curve, and the corrosion potential triangle (steady-state corrosion rate). This diagram represents the corrosion of a 10cm carbon steel (G10100) diameter pipe by a 5pH solution at 25C/1atm. The solution also contains 55 µg Fe⁺² and 61 µg HCO₃⁻ and flows through the pipe at 2 m/s.

The corrosion reaction can be described by the following equations for a metal and alloy (**anode curve**):

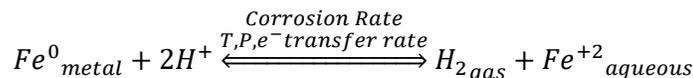


The corroding atoms release electrons ($2e^-$). The above reactions are called **half-reactions**, because the electrons are part of the equation.

The electrons released by the metal combine with electron-accepting species, dissolved in water, and adjacent to the metal surface. An example of this is the half-reaction for H⁺, which is converted to H₂ gas (**cathode curve**).



These reactions are combined to form a **complete REDOX reaction**¹, because electrons are consumed in the reaction. The 2e⁻ cancel each other out and the resulting equation takes the form of a generic corrosion reaction:



We should keep in mind two rules about corrosion that cannot be broken:

- 1) For corrosion to occur, both *electron-producing (anode)* and *electron-accepting (cathode)* reactions must be present.
- 2) The number of electrons produced must equal the number of electrons accepted (**corrosion potential triangle**):

$$\sum e^-_{released} = \sum e^-_{consumed}$$

The combination of these two rules plus the **complete REDOX reaction**, like the one above, is the observed corrosion rate. This rate depends on the concentrations, or activities, of the reactants (Fe, H⁺), the products (H₂, Fe⁺²), conditions (T, P), and the base electron transfer rate. The corrosion rate observed in the field is the time-averaged rate defined in the above equation and quantified in the diagram.

What then does the polarization curve try to accomplish? The purpose of the polarization curve plot, and the experiment that is performed in the laboratory to create it, is to put values on these reactions and to uncover any side reactions that may occur during corrosion.

The X- and Y-Axes

The two axes on the plot are the **electrochemical potential** and the **current density**. These terms appear arcane but in fact are straightforward concepts. What makes these terms confusing is that they represent a procedure that takes place in a laboratory, and so the reader would need some kind of experience with this experiment. Therefore, to explain the x- and y-axes, we will explain the experiment.

Experimental Setup

We start with a water solution at a constant temperature, salinity, and pH. The solution also contains a constant concentration of the corroding species, such as dissolved CO₂ and H₂S. This water represents the corroding solution. The solution is created with a bubbler, such as the one shown in the diagram below.

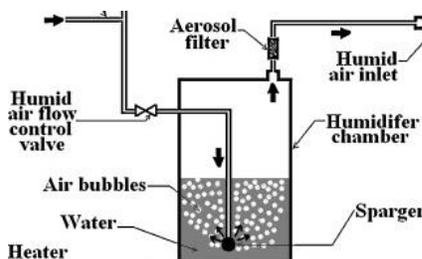


Figure 2 – An experimental solution kept at a constant composition of dissolved gasses.

Source: Science Direct <http://qoo.qi/m9jUR>

A piece of metal (e.g. carbon steel) is added to this water. This metal is polished, shaped like a cylinder, and has a known surface area, such as 1cm². The metal is generally attached to a motor that rotates it a given rpm. This metal represents the corroding surface. This metal is called the **active electrode**, or **anode**.

If the metal contacts the water, an uncontrolled corrosion reaction will begin. However, we do not want this to happen because we want to know what controls the reaction.

¹ The English words *oxidation* and *reduction* do not have a physical significance. These terms originally described two specific reactions; $2Fe^0 + \frac{3}{2}O_2 = Fe_2O_3$ (oxidation- oxygen being added to metal) and $Fe_2O_3 + heat = 2Fe^0 + \frac{3}{2}O_2$ (reduction in the mass of solid). In modern vernacular, oxidation and reduction (or REDOX) are both general terms that describe reactions in which electrons are transferred.

What is done instead is the following:

- 1) The metal is attached to a wire that is connected to a potentiostat, an electrical apparatus that provides a voltage.
 - 2) A second wire leaves the potentiostat and is attached to a non-reactive, carbon electrode. This electrode is called the **counter electrode**.
 - 3) A third wire is attached to a reference electrode. This electrode is used to set the reference voltage.
- All electrodes are kept in the same water.
The diagram showing this system is below.

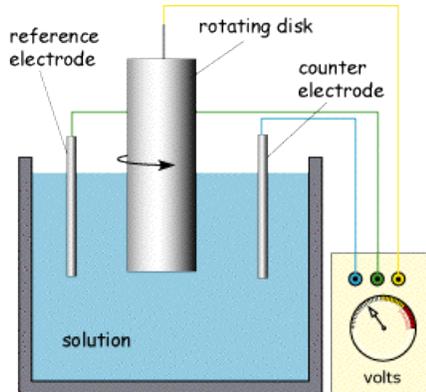


Figure 3 – A potentiostat attached to a rotating metal and two electrodes.

Source: Center for Research in Electrochemical Science and Technology: <http://goo.gl/4t1AF>

- 4) The operator sets the voltage output of the potentiostat to very negative values (e.g., -2V) and scans up to high values (e.g., +2V).

As the voltage scans upwards, the operator reads the electric current produced as electrons flow from the rotating disk metal to the counter electrode. This is reflected in the x-axis.

The resulting plot is the electrochemical polarization curve.

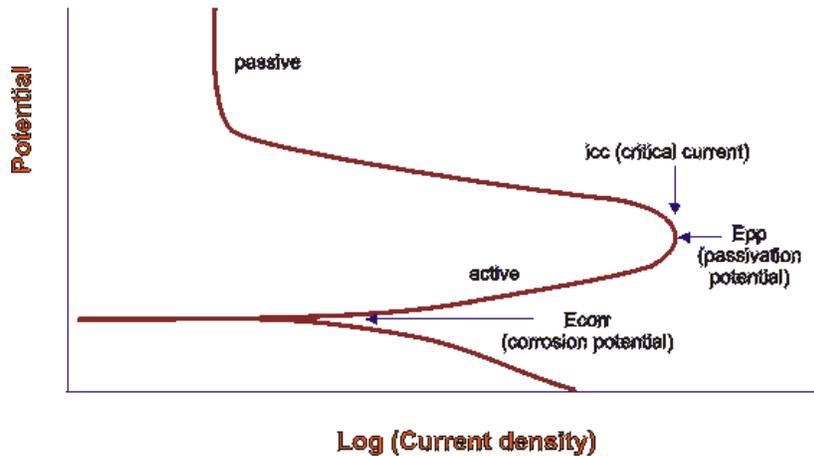


Figure 4 – The experimental results are reported in a plot of the electrochemical potential over current density. This is a polarization diagram for a passivable system with active, passive and transpassive regions.

Source: NACE Resource Center <http://goo.gl/yqaZE>

First Layer of the Diagram: Corrosion Potential or Steady-State General Corrosion Rate

The first layer displays the **corrosion rate** (x-axis) and the corresponding **electrochemical potential** of the solution at the metal surface (y-axis). The triangle in the plot below is at the coordinates of -0.5 V and $4.47 \frac{\mu A}{cm^2}$. This means that the water-metal interface has a **corrosion potential** of -0.5 V, and the rate at which electrons leave the surface is $4.47 \frac{\mu A}{cm^2}$.

An explanation of the two axes and their practical significance is provided in the next section.

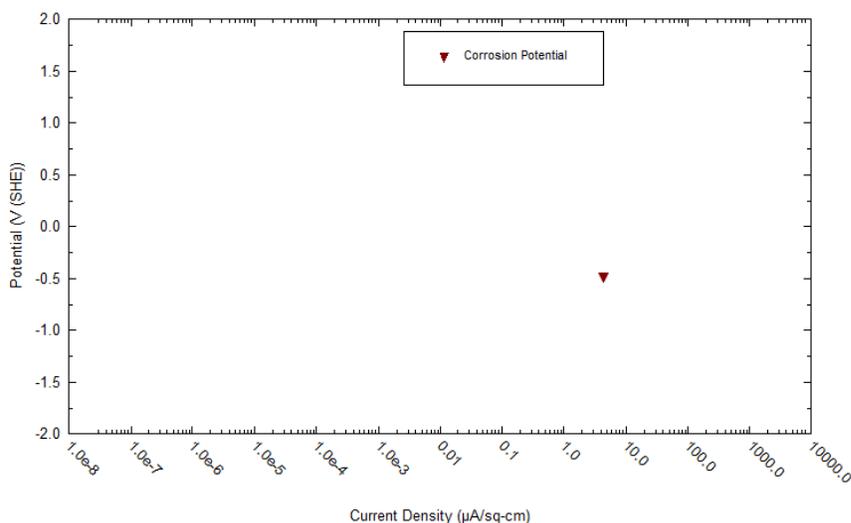


Figure 5 – The first layer contains the corrosion potential triangle. This corrosion potential represents the steady-state flux of electrons from the corroding metal (or alloy) into the corroding solution. This triangle represents how fast general corrosion occurs. The Corrosion Density units are A/m², which can be converted into grams metal/alloy corroded per m².

X-Axis: Current Density ($\mu A/cm^2$)

The **current density** is the flux of electrons leaving the corroding surface and entering the liquid. The current density units are *Amperes/area* ($e^-/s\text{-area}$), which are units of flux.

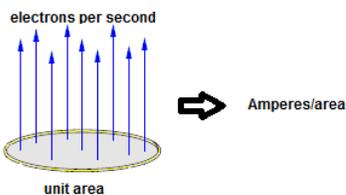


Figure 6 – A flux of electrons leaving a corroding surface (unit area) and entering the liquid.

The current density is converted to the corrosion rate using a standard equation:

$$\text{Corrosion Rate (mpy)} = \text{Current Density} \left(\frac{\mu A}{cm^2} \right) * \frac{0.1288 \left(\frac{mpy \cdot g}{\mu A \cdot cm} \right)}{\text{alloy density} \left(\frac{g}{cm^3} \right)} * \frac{AW \left(\frac{g}{mole} \right)}{n \left(\frac{equivalents}{mole} \right)^2}$$

For the above scenario, the corrosion rate is computed to be 2.0 mpy.

$$\text{Corrosion Rate (mpy)} = \text{Current Density} \left(\frac{\mu A}{cm^2} \right) * \frac{0.1288 \left(\frac{mpy \cdot g}{\mu A \cdot cm} \right)}{7.85 \left(\frac{g}{cm^3} \right)} * \frac{55.85 \left(\frac{g}{mole} \right)}{2 \left(\frac{equivalents}{mole} \right)} = 4.47 \left(\frac{\mu A}{cm^2} \right) * 0.458 = 2.0 \text{ mpy}$$

² Derived from the text, the *Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements*. ASTM Publication G 102 – 89. K is the conversion constant that is based on the units used in the equation. “n” is the number of electrons in each corroding metal atom, AW is the atomic weight of the metal.

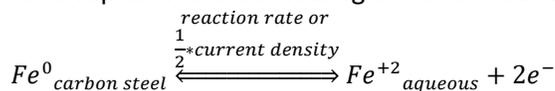
Y-Axis: Electrochemical Potential

The **electrochemical potential** is the energy state that exists in the system. Its units are volts. When volts are combined with electron flux, the units become energy (joules=volts*coulombs). The electrochemical potential axis will have greater meaning when we review the second and third layers of the diagram.

The electrochemical potential of water is a property of the water composition. For instance, O₂-saturated, 7pH water at 25C has an electrochemical potential of 0.8 V.

Second Layer of the Diagram: Rate at Which the Surface Corrodes

The second layer is the anode curve. The anode is the metal surface that corrodes, or chemically speaking, releases electrons. The anode curve represents the following corrosion reaction:



The anode curve shown below indicates how many electrons flow from the surface for a given electrochemical potential value. As you review this plot, use the y-axis as the fixed or known variable and the x-axis as the value that is calculated or measured.

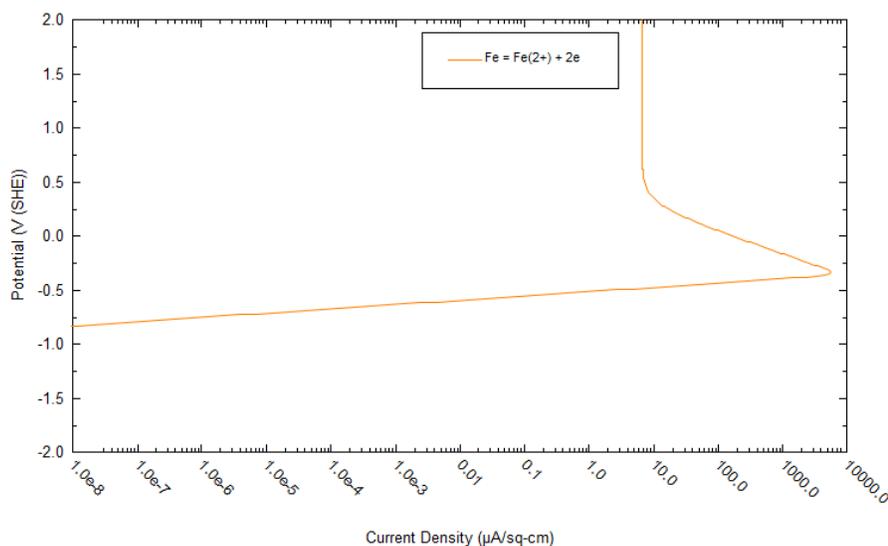


Figure 7 – The second layer of the diagram describes the rate at which the surface corrodes. The yellow line describes how many electrons flow from the surface at a given electrochemical potential. The y-axis here is the fixed or known variable and the x-axis is the value that is calculated or measured.

When the electrochemical potential (y-axis) is at -0.86 volts, the x-axis value of the anode curve is $1e^{-8} \frac{\mu A}{cm^2}$ (see far left of plot). This converts to a corrosion rate of $4.58e^{-9}$ mpy, which is a negligible corrosion rate:

$$\text{Corrosion Rate (mpy)} = 1e^{-8} \left(\frac{\mu A}{cm^2} \right) * 0.458 = 4.58 \times 10^{-9} \text{ mpy}$$

As the potential increases to -0.35V, the anode line increases to $6000 \frac{\mu A}{cm^2}$, which converts to a corrosion of 4580 mpy, which is an extremely high corrosion rate:

$$\text{Corrosion Rate (mpy)} = 6000 \left(\frac{\mu A}{cm^2} \right) * 0.458 = 4,580 \text{ mpy}$$

At a potential of +1V, the anode curve shifts back to the left and becomes vertical. Its x-axis coordinate is $6.7 \frac{\mu A}{cm^2}$, which is a corrosion rate of 3.1 mpy, which is a moderate corrosion rate:

$$\text{Corrosion Rate (mpy)} = 6.7 \left(\frac{\mu A}{cm^2} \right) * 0.458 = 3.1 \text{ mpy}$$

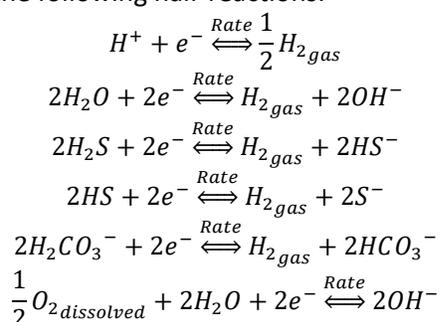
Relating to Real Systems

In a real system, if the electrochemical potential at the water/steel interface is -0.78V, the corrosion rate would be negligible. Such a scenario would exist if electrons were being pumped into the system from an external source, like with an Mg, Al, or Zn sacrificial anode or an impressed cathodic protection device.

As the electrochemical potential increases, or moves up the y-axis, the availability of electrons decreases. Consequently, the rate of the corrosion reaction equations accelerates. In other words, more electrons will leave the metal surface, which creates a positive slope. Thus, the current density and therefore corrosion rate increase. In a real system, this would exist when the system has a high concentration of dissolved species that attract electrons (e.g., O₂).

Third Layer: Rate at Which the Solution Accepts Electrons from the Corroding Surface

The third layer contains the cathode curves. Physically, the cathode lines are the corrodants, O₂, HCl, H₂S, CO₂, etc. They are represented by the following half-reactions.



These curves have negative slopes because as the potential decreases, more electrons are available. Consequently, the rate at which the reactants in the above equations accept electrons increases. The plot below contains the five cathode half reactions shown above.

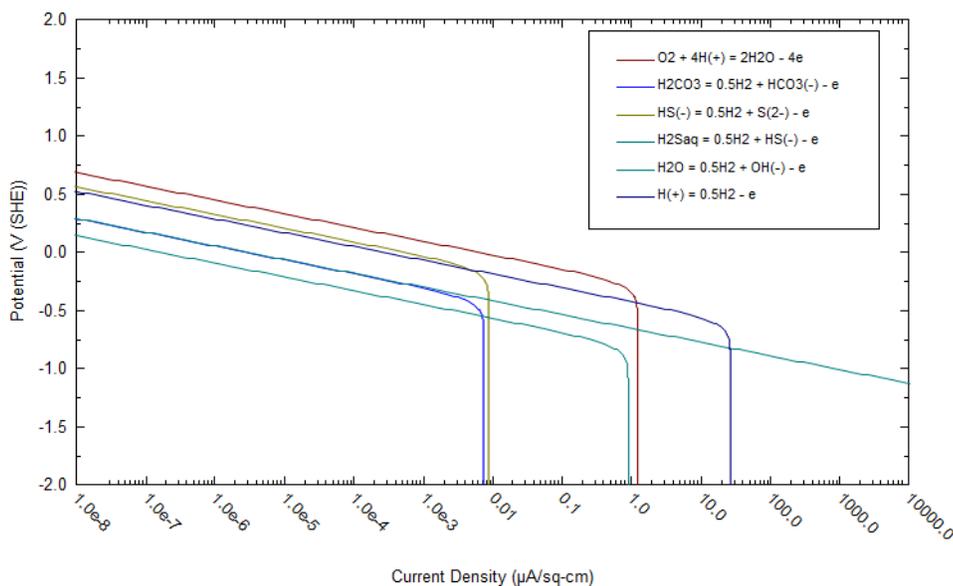


Figure 8 –The third layer of the diagram shows 7 total curves. All but one (H₂O), suddenly drops below a particular electrochemical potential. These curves become vertical because there is an insufficient concentration of the species at the surface to accept electrons at a faster rate. H₂O is available in abundance.

Note that each curve has the same negative slope. This is because as the potential decreases, the reactants in the above equations accept electrons at an equal and faster rate. Note that all the curves except H₂O

become vertical below a particular electrochemical potential. When this happens, it means that there is an insufficient concentration of the species at the surface to accept electrons at a faster rate. The H₂O curve continues with the negative slope because H₂O is the solvent and available in abundance.

Combining the Curves to Create the Complete Diagram

When the three layers are combined, the resulting plot is generated. It shows the contributions of all the cathodes accepting electrons as compared to the anode donating electrons. Recall that the following condition must be true:

$$\sum e^{-} \text{ released by anode} = \sum e^{-} \text{ consumed by cathode}$$

The point where this reaction is satisfied is the inverted red triangle. This point then becomes the instantaneous corrosion rate or current density (x-axis), and the electrochemical potential existing at the corroding surface (y-axis).

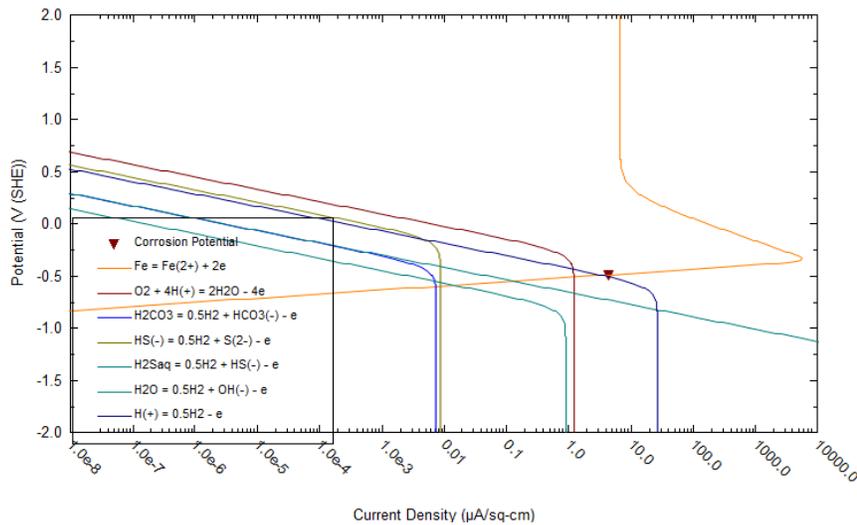


Figure 9 – Complete Polarization curve showing all the cathodic and anodic curves and the previous three layers.

One of the important aspects of this plot is that it quantifies the contribution of each cathodic reaction. Here is how it works. The liquid-surface interface will have a single instantaneous corrosion potential. The y-axis is the value associated with the inverted triangle. If you draw a horizontal line from the triangle to the y-axis, you will cross the cathode curves. The diagram below is a zoomed-in version of the plot above and centers on the sections where the cathode reactions cross the liquid-surface electrochemical potential.

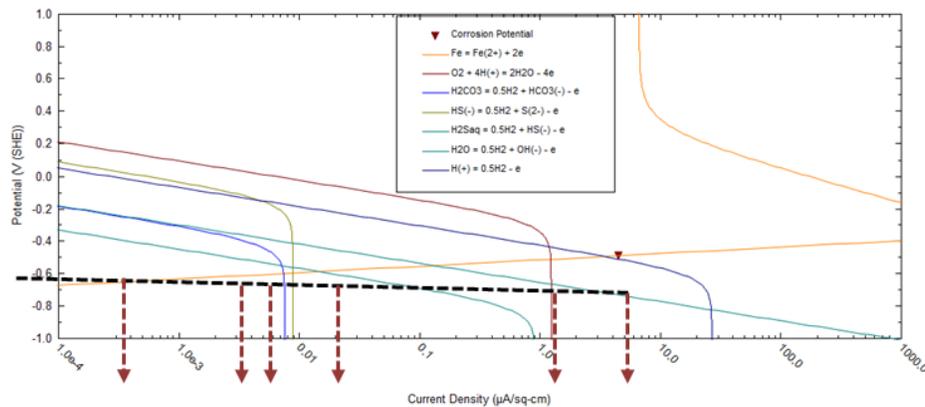


Figure 10 – The completed polarization diagram with drawn in lines (illustration software). The dashed horizontal lines represent the electrochemical potential of the liquid-surface interface. The dashed vertical lines represent the intersection points for each cathode curve. The x-axis point where the intersections occur is the rate at which these species accept electrons.

The dashed horizontal line is the electrochemical potential of the liquid-surface interface. As we move from right-to-left across the dashed line, the cathode curves intersect. The dashed, red vertical arrows are the intersection points for each cathode curve with this line. The x-axis point where these curve intersect is the rate at which these species are accepting electrons. **This is their individual contribution to corrosion.** We can see that the curve that accepts the most electrons (farthest to the right) is the blue H+ ion.

This is the dominant corrodant in this system. It intersects the x-axis at $\sim 3.7 \frac{\mu A}{cm^2}$.

The next important is the vertical O2 line, which intersects the horizontal line at $1 \frac{\mu A}{cm^2}$.

The third most important corrodant is the aqua H2O line, which intersects at $0.03 \frac{\mu A}{cm^2}$.

Therefore, we can conclude that there are two important corrodants, H+, which is responsible for ~80% of the corrosion rate, O2 is responsible for ~20%, and the remaining corrodants contribute 1% or less to corrosion. The table below contains this cross-reference list of corrodants.

Table 1 – A description of corrodants with their current densities, corrosion rates, and corrosion contribution percentage.			
Cathode Curve	Current density ($\frac{\mu A}{cm^2}$)	Corrosion Rate (mpy)	Contribution to corrosion (%)
H+	3.2	1.46	72
O2	1.2	0.55	27
H2O	0.04	0.02	0.9
HS-	0.009	0.004	0.2
H2CO3	0.006	0.003	0.15
H2S	0.001	0.0005	0.02
Total	4.47	2.04	100

Notice that the O2 and HS- lines cross the horizontal Electrochemical Potential line with a vertical slope. These species are diffusion limited, meaning that they cannot accept more electrons because they cannot get to the surface fast enough. If the fluid were flowing faster, creating a thinner diffusion layer, then these vertical lines would be shifted to the right, and these species would accept more electrons (contribute more to corrosion).

Summary

Generating a polarization curve on a computer has two purposes. The first is to predict the general corrosion rate of a material under process conditions. The second is to determine what chemistry is causing the corrosion and, when there are multiple corrodants, the contribution of each corrodant to the total corrosion rate.

The polarization plot also computes when the material surface may be in an area of passivation, i.e. when a surface oxide film has formed and protects the surface for accelerated corrosion (the vertical section of the anode curve).

Lastly, the plot shows the effects of flow rate on the corrosion rate. By plotting the cathodic reactions and showing where they bend to a vertical slope the user can see how the flow rate (and therefore diffusion layer thickness) affects overall corrosion.

Chapter 7b Polarization Curve Applications

Introduction

In this chapter, we will continue to explore features of the OLI Studio: Corrosion Analyzer specifically looking at corrosion rates and polarization curves with practical examples.

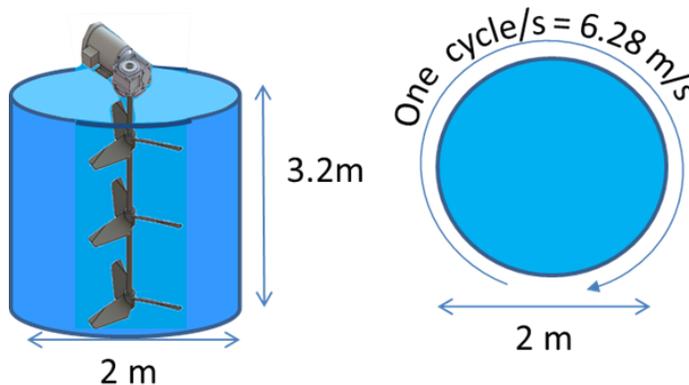
Sections

7b.1 Corrosion in a Water-Filled Carbon Steel Tank	2
7b.2 Corrosion in a Pipe Carrying Acids.....	10
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7b.5 Gas Condensate Corrosion	24

7b.1 Corrosion in a Water-Filled Carbon Steel Tank

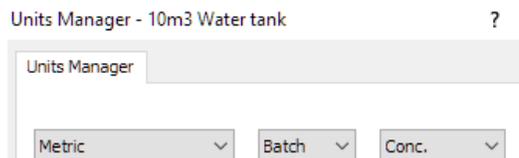
Overview

This case is a 10m³ tank (3.2m high and 2m in diameter) that is filled to the top with water. The tank has a variable speed mixer with a rotation speed between 0 and 12,000 rpm. The tank is static at times (mixer off) and is fully mixed at other times. At certain instances, the tank is sealed and there is no air ingress. At other times, the tank is open to the atmosphere. Each interval will be studied to compute the corrosion risk.



Getting started

- ✓ Create a new file and give it a name such as "Chapter 7"
- ✓ Add a new stream,  Add Stream and rename it '10m3 Water Tank'  10m3 Water Tank
- ✓ Open the Units Manager  then use the Quick List button to select Metric, concentration

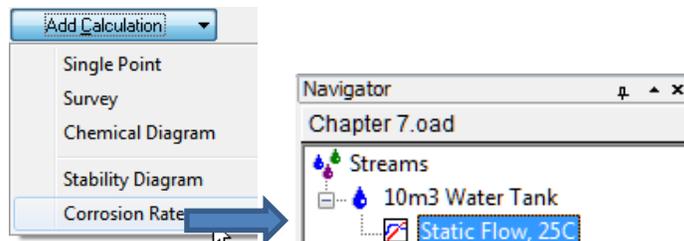


- ✓ Press OK
- ✓ Change the Stream Amount to 10,000.00 L (or 10m3)

Pure water, static flow, closed to the atmosphere, ambient conditions

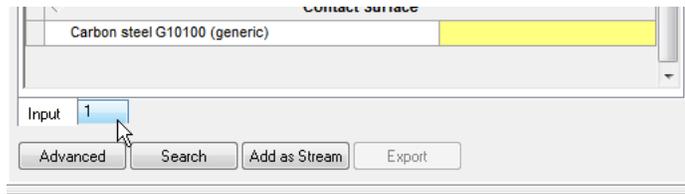
This requires no data entry, only the mouse.

- ✓ Add a Corrosion Rates calculation, label it 'Static Flow, 25C'

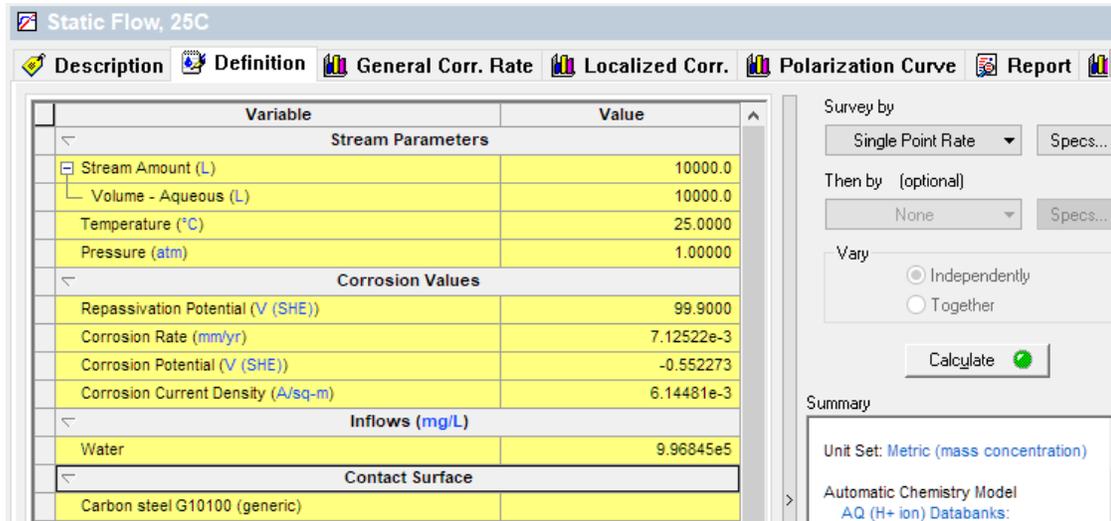


- ✓ Press the <F9> key or select Calculate

- ✓ Click on the “1” tab at the bottom of the grid

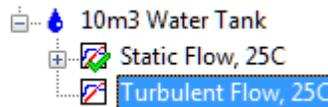


The Corrosion Rate is 7.1×10^{-3} mm/yr. This is a negligible rate, for if the tank wall's thickness is $\frac{1}{2}$ inch (~12.7 mm) then corroding half the wall thickness would take about 900 years.

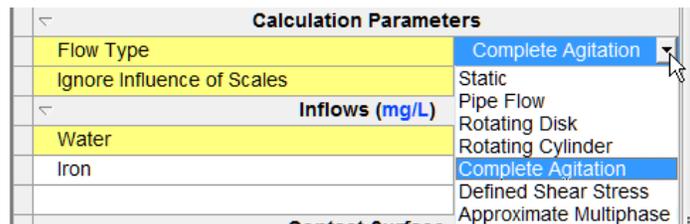


Pure water, turbulent flow, closed to the atmosphere, ambient conditions

- ✓ Add a new Corrosion Rates and rename it 'Turbulent Flow, 25C'



- ✓ Select on the Static cell in the Flow Type and change to Complete Agitation



- ✓ Calculate
- ✓ Select the “1” tab at the bottom of the grid

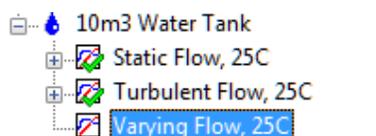
Variable	Value
Stream Parameters	
Stream Amount (L)	10000.0
Volume - Aqueous (L)	10000.0
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Corrosion Values	
Repassivation Potential (V (SHE))	99.9000
Corrosion Rate (mm/yr)	0.0196379
Corrosion Potential (V (SHE))	-0.535173
Corrosion Current Density (A/sq-m)	0.0169358
Inflows (mg/L)	
Water	9.96845e5
Contact Surface	
Carbon steel G10100 (generic)	

The corrosion rate increased 0.019 mm/yr, still a relatively low value.

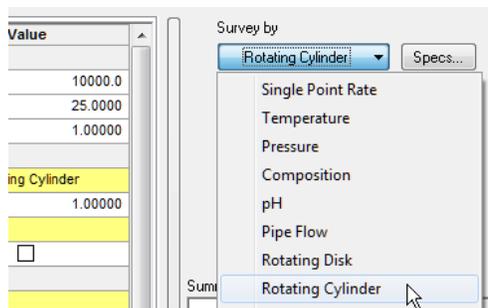
Pure water, varying flow, closed to the atmosphere, ambient conditions

The next step is to compute the flow across the tank wall. The software contains four flow types, Pipe, Disk, Cylinder, and Shear Stress. The best option is probably the Rotating Cylinder, which would be the tank moving relative to the water.

- ✓ Add a new Corrosion Rates and rename it 'Varying Flow, 25C'



- ✓ Change the Survey by to Rotating Cylinder



- ✓ Change the Rotor diameter to 200 cm

Calculation Parameters	
Flow Type	Rotating Cylinder
Rotor Diameter (cm)	200.000

The vertical dimensions of the tank are unimportant. We will assume that the tank can be modeled like a rotating cylinder. The propeller rotates at 1200 rpm, although it is not expected that the wall velocity w will approach this value, and so a lower value will be used (we still want it to be high enough to see the effects of shear). The next step is to set the speed of the mixer.

- ✓ Select the Specs button.

Varying Flow, 25C Survey Range	
Start	0
End	300
Increment	10

- ✓ In Var1 – Rotator Rotation category, change the Survey Range according to the table above

End Points

Start

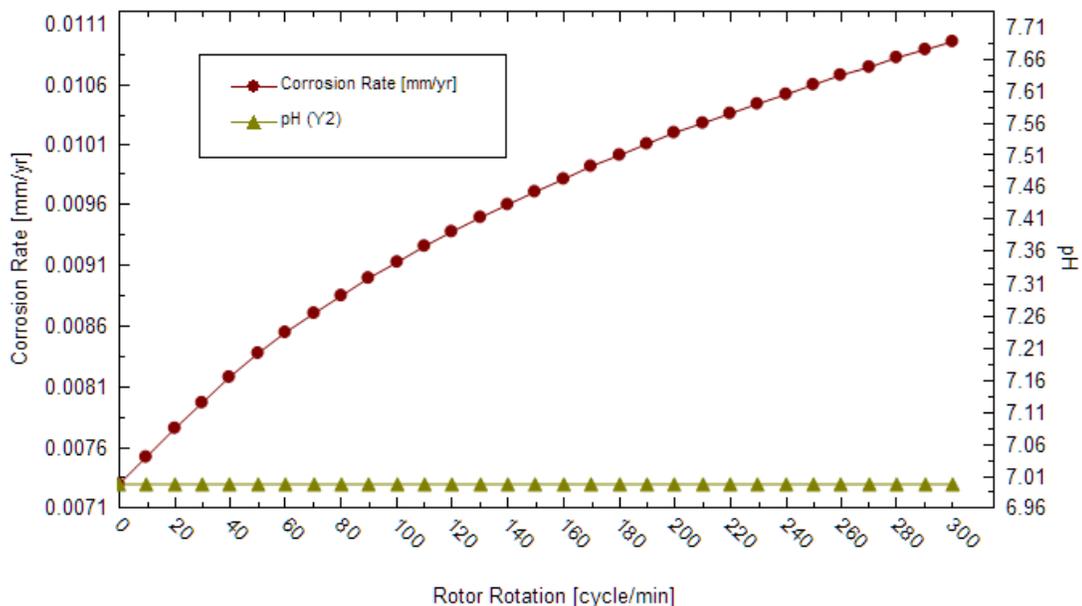
End

Step Size

Increment } Select one, the other calculated

Number Steps

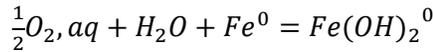
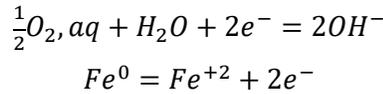
- ✓ Press OK then Calculate
- ✓ Select the General Corr. Rate tab then select the Curves button
- ✓ Double-click pH-Aqueous in the Y2 Axis to remove it
- ✓ Press OK then view the plot



The corrosion rate is computed to increase as the bulk liquid velocity increases from 0 to 300 rpm near the wall surface. The reason is straightforward; The higher velocity reduces the static water film thickness on the metal surface. This **Diffusion Layer** film limits the mass transfer of corrosion products and bulk chemicals to and from the surface. As the liquid velocity (and therefore shear force) increases, the film thickness decreases, and the concentration gradient increase. This increases the flux of materials to and from the surface, which increase corrosion rates.

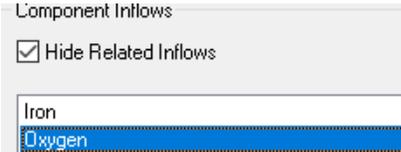
Pure water, static flow, aerated (O₂ only), ambient conditions

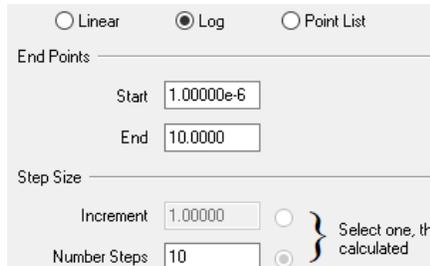
Open steel tanks are in contact with oxygen in the air and in some cases atmospheric salts. Oxygen accelerates corrosion through the reaction:



The chlorides in the salt will also affect the surfaces ability to inhibit the corrosion reaction.

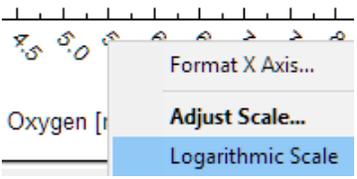
- ✓ Add a Corrosion Rate  **Add Corrosion Rates** and label it 'O2 Effects'  **O2 Effects**
- ✓ Add Oxygen (O₂) to the inflow grid -

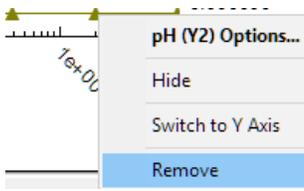
- ✓ Change the Survey to Composition 
 - Survey by
 - Composition
 - Specs...
- ✓ Select the Specs ... button and Select Oxygen as the inflow 
 - Component Inflows
 - Hide Related Inflows
 - Iron
 - Oxygen
- ✓ Select the Survey Range as follows, Log Scale, Start=1e-6, End=10, Steps=10



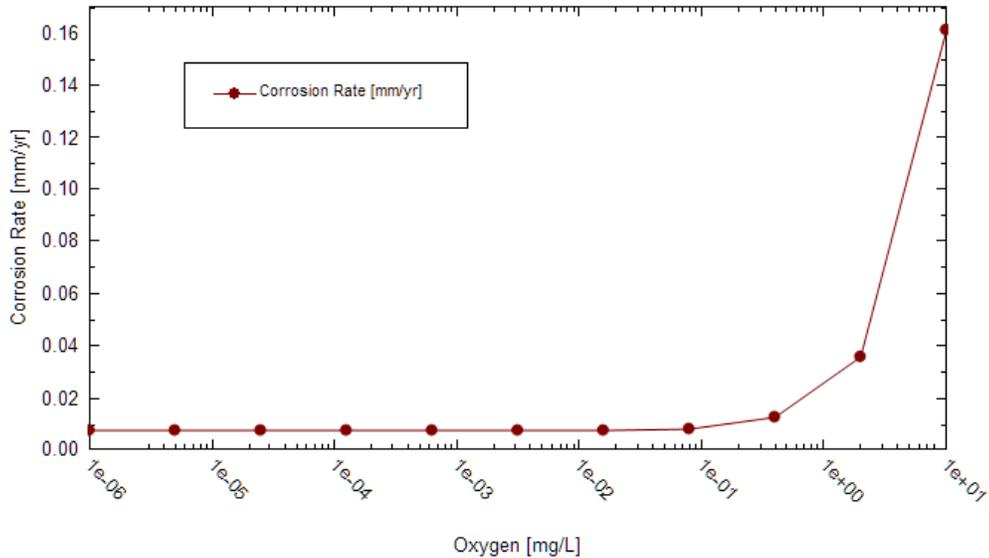
Linear Log Point List
 End Points
 Start: 1.00000e-6
 End: 10.0000
 Step Size
 Increment: 1.00000 } Select one, th
 Number Steps: 10 calculated

- ✓ Press OK then Calculate
- ✓ Select the General Corr. Rate tab

- ✓ Right-mouse click the X Axis and change to Logarithmic Scale - 
 - Format X Axis...
 - Adjust Scale...
 - Logarithmic Scale

- ✓ Right-mouse-click on the pH curve and select Remove 
 - pH (Y2) Options...
 - Hide
 - Switch to Y Axis
 - Remove

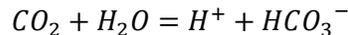
The resulting plot shows the impact of oxygen on the corrosion rate. Corrosion increases by a factor of 20 once the concentration increases beyond 100 µg/l. Aerated water contains approximately 8 mg/l O₂. Corrosion on the tank wall is 0.16 mm/yr. At this rate, 50% of the 12.3 mm wall will be dissolved in 40 years.



Air also contains carbon dioxide, which will corrode steel. Its impact is studied in the next calculation.

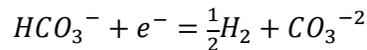
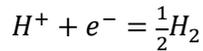
Pure water, static flow, aerated (O₂, CO₂), ambient conditions

The atmosphere contains ~400 ppmV CO₂. At this concentration 0.6 mg/l CO₂ is dissolved in water as molecular CO₂, this CO₂ hydrolyzes (splits) water to form the following reactants.



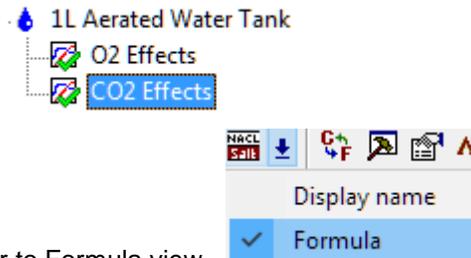
The resulting pH is about 5.6 at ambient conditions.

The impact of CO₂ on corrosion is two-fold, as two separate reactions occur at the metal surface

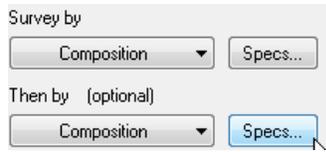


To test the CO₂ impact, you will recalculate the corrosion rate using two CO₂ concentrations: 0 and 0.6 ppm.

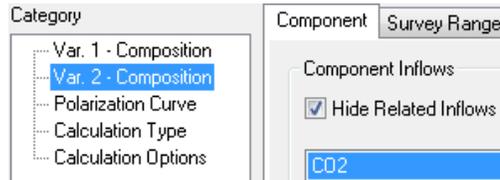
- ✓ Copy the existing O2 effects calculation and paste it back to the 10 m3 Water Tank stream.
 - Right-mouse click on the calculation and select Copy
 - Right-mouse click the 10 m3 Aerated Water Tank, and select Paste
- ✓ Rename the duplicated object 'CO2 Effects'



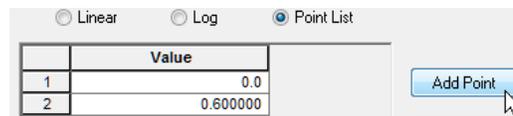
- ✓ Change the Names Manager to Formula view -
- ✓ Add O2 and CO2 to the Inflow grid (the O2 may not have copied over)
- ✓ Change the Then By (optional) option from None to Composition



- ✓ Select the lower Specs button
- ✓ Select CO₂ as the inflow -

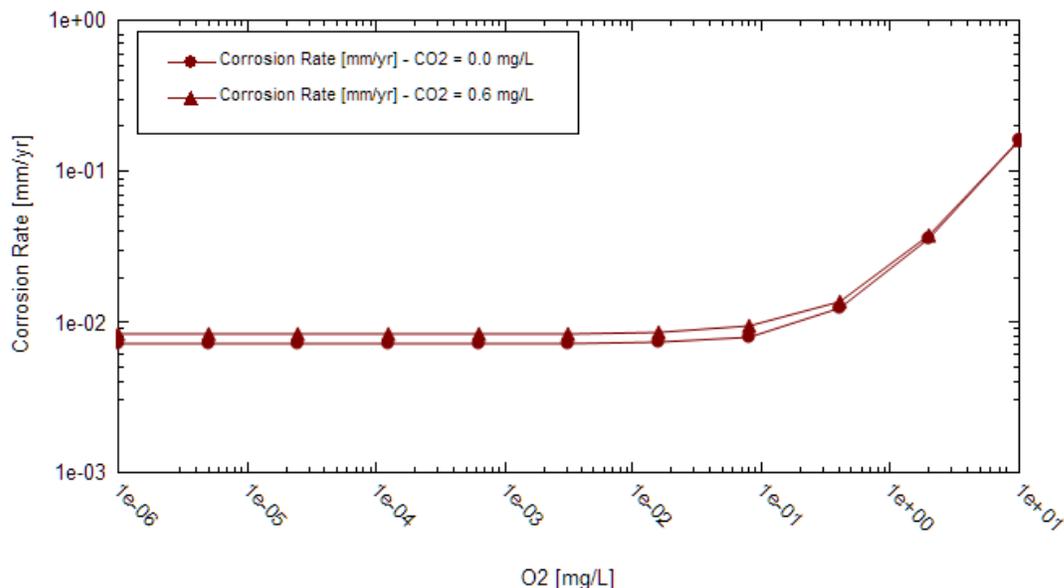


- ✓ Click on the Survey Range button and check the Point List button
- ✓ Create two points, with values of 0 and 0.6 mg/l



- ✓ Close the window and Calculate
- ✓ Select the General Corr. Rate tab
- ✓ Change the X and Y axes to log scale
- ✓ Remove the pH curve (right-mouse-click and remove series)
- ✓ Select the Curves button and remove any variable in the Y2 Axis then press OK

The effects of CO₂ are small, particularly in relation to the oxygen effects. The Corrosion rates at low O₂ content is about 0.0071 mm/yr with no CO₂ and 0.0083 mm/yr with 0.6 mg/l CO₂; a small difference between two small rates. At 10 mg/l O₂ the corrosion rate is 0.16 mm/y and it is the same with and without CO₂. Thus, CO₂ has no effect on corrosion at high O₂ concentrations meaning that the surface is corroded by oxygen and small concentrations of CO₂ does not change this rate.



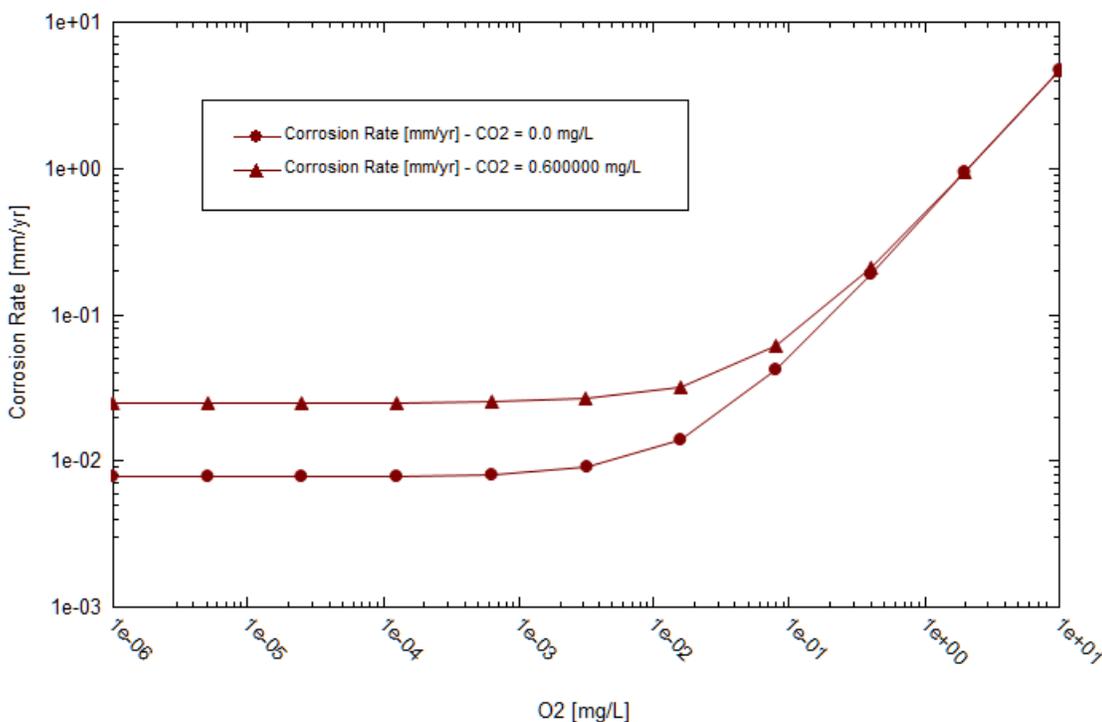
Pure water, 300 cycles/min flow, aerated (O₂, CO₂), ambient conditions

Lastly, you will look at the effects of shear rates on the tank in contact with CO₂ and O₂.

- ✓ Select the Definition tab
- ✓ Change the Flow type from Static to Rotating Cylinder
- ✓ Set the Rotor Diameter to 200 cm
- ✓ Set the Rotor Rotation to 300 cycles/minute

Calculation Parameters	
Flow Type	Rotating Cylinder
Rotor Diameter (cm)	200.000
Rotor Rotation (cycle/min)	300.000
Effect of FeCO ₃ / FeS Scales	Include

- ✓ Calculate then select the General Corr. Rate tab to review the plot



The 0.6 mg/l CO₂ curves shifted at low O₂ concentrations. The rate is 0.048 mm/yr compared to 0.008 mm/yr at static conditions. The effect of shear at high O₂ concentrations (right side of the plot) is also pronounced. Corrosion is still dominated by O₂ attack, but the rate is now over 10 mm/yr. about 100x greater than the static conditions.

- ✓ Save the file

7b.2 Corrosion in a Pipe Carrying Acids

Some of the more common commercial acids include muriatic acid (20% HCl), Aqua Regia (25% HNO₃:75% HCl), Battery Acid (30% H₂SO₄), commercial grade nitric acid (68% HNO₃), and fuming HCl (37%).

In this example, the metallurgy within a vacuum HCl tower will be studied at HCl production. Fuming HCl is purified from feedstock through distillation. The HCl-H₂O mixture however, forms an Azeotrope at 20% HCl and 110C. Consequently, multiple distillation sequences are needed to achieve the 37% mixture. In this case, the conditions within the first tower are investigated. Here the feedstock is at vacuum pressures (0.3 atm).

Vacuum HCL Tower			
Stage	T, C	HCl %	H2O %
1	78.1	25	75
2	77.6	24	76
3	77	23	77
4	76.3	22	78
5	75.4	21	79
6	74.4	20	80
7	73.6	20	80
8	72.8	19	81
9	68.7	12	88

Carbon steel tower

- ✓ Add a new stream  Add Stream ; rename it 'Vacuum HCl Tower' 
- ✓ Open the Units Manager  then use the Quick List button to select Metric, Flowing, Mass Fraction

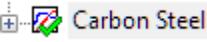
- ✓ Set the Stream Amount to 12500 kg/hr

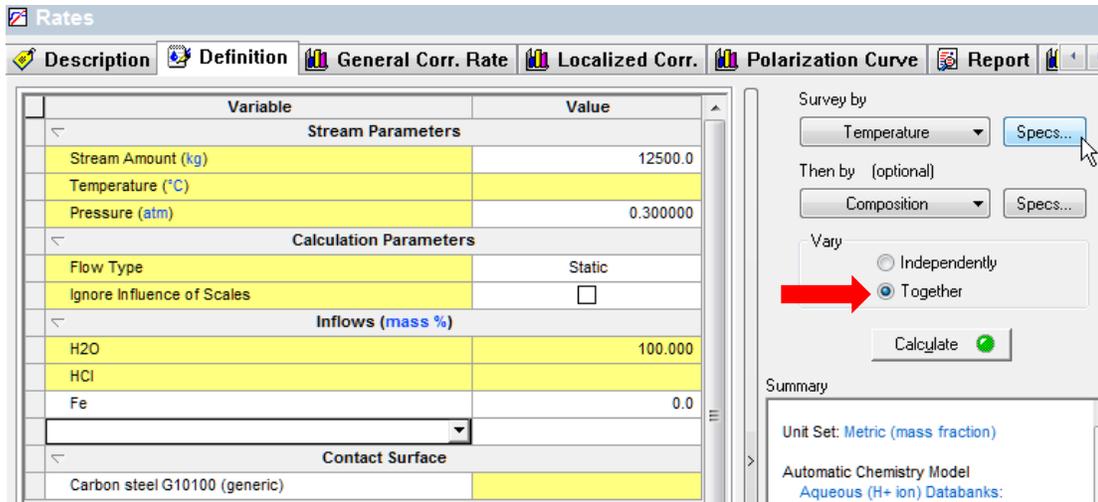
The Stream Amount does not have to be changed, but to keep this stream consistent with the process, the conditions and compositions will be included.

- ✓ Change the pressure to 0.3 atm

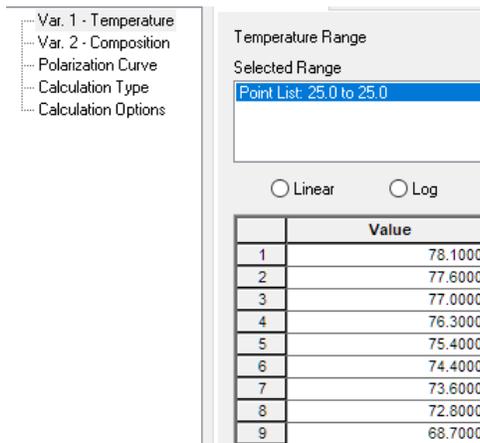
This is the tower pressure, which in fact decreases from 0.3 to 0.25 atm (bottom to top of tower).

However, it is not practical to adjust the pressure when changing temperature and HCl% content, so we will leave the value at the tower bottom pressure

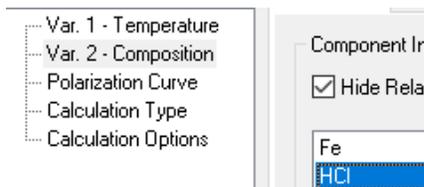
- ✓ In the Inflows grid, enter HCl
- ✓ Add a Corrosion Rate calculation and name it Carbon Steel - 
- ✓ Change the Survey by to Temperature
- ✓ Change the Then by (optional) to Composition
- ✓ **Select the Together button just above the Calculate button**
- ✓ Select the top Specs button



- ✓ Click the Point List button
- ✓ Create nine points and enter the temperatures from the table above



- ✓ Click on the Var. 2 Composition Category and select HCl as the inflow to be adjusted



- ✓ Click the Survey Range tab and click on the Point List button
- ✓ Add eight more points to the list and enter the %HCl values from the table above

Var. 2 - Composition
Polarization Curve
Calculation Type
Calculation Options

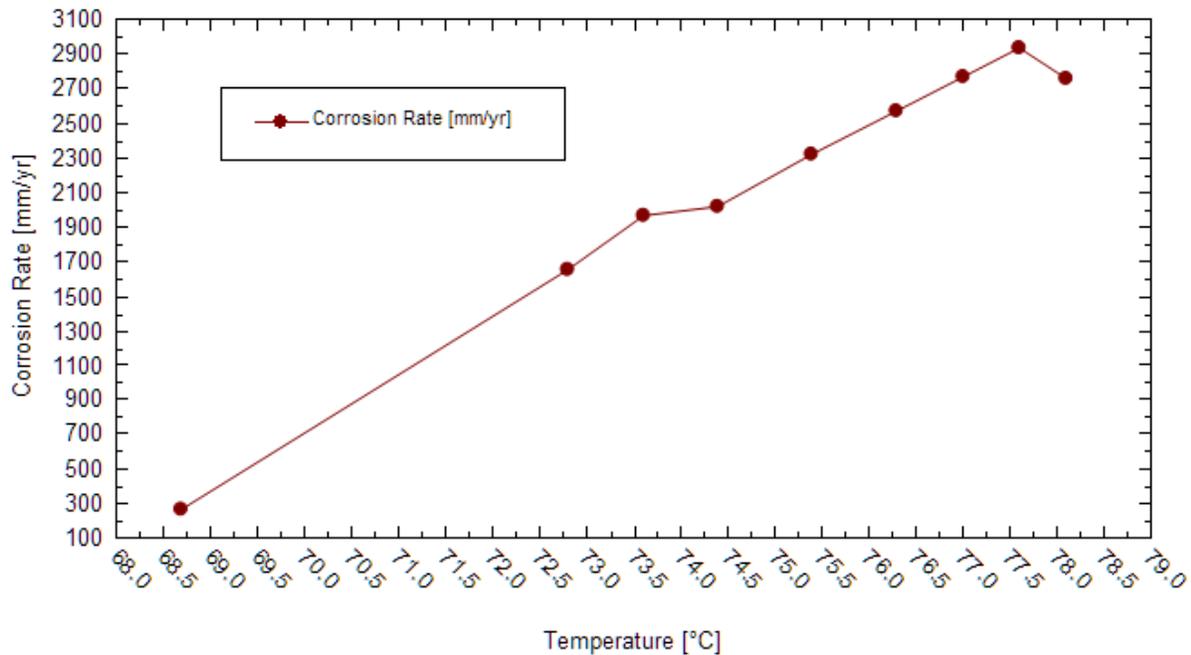
Composition Range
Selected Range
Point List: 0.0 to 0.0

Linear Log

	Value
1	25.0000
2	24.0000
3	23.0000
4	22.0000
5	21.0000
6	20.0000
7	20.0000
8	19.0000
9	12.0000

- ✓ Press OK then Calculate
- ✓ Select General Corr. Tab
- ✓ Remove the pH curve – Right-mouse-click and select Remove

Corrosion rates increase from 270 mm/yr at the top of the tower to 2760 mm/yr at the bottom. At these rates, the 1" thick (254 mm) carbon steel plate at the tower bottom will dissolve in about 30 hours!



Another material of construction is needed. We will test these out now.

316 stainless steel tower

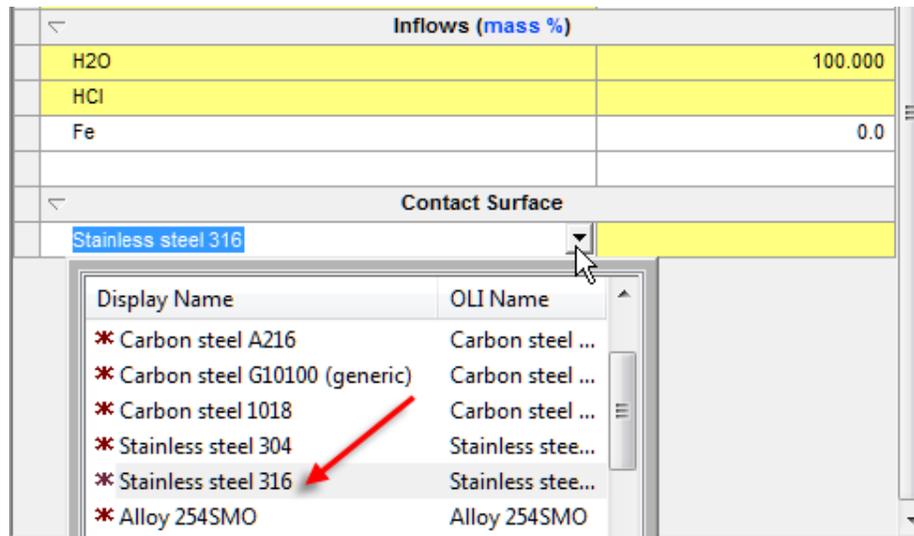
- ✓ Copy the Carbon Steel corrosion calculation and paste it twice to the Vacuum HCl Tower

Vacuum HCl Tower

- Carbon Steel
- Stainless Steel 316
- Carbon Steel ?

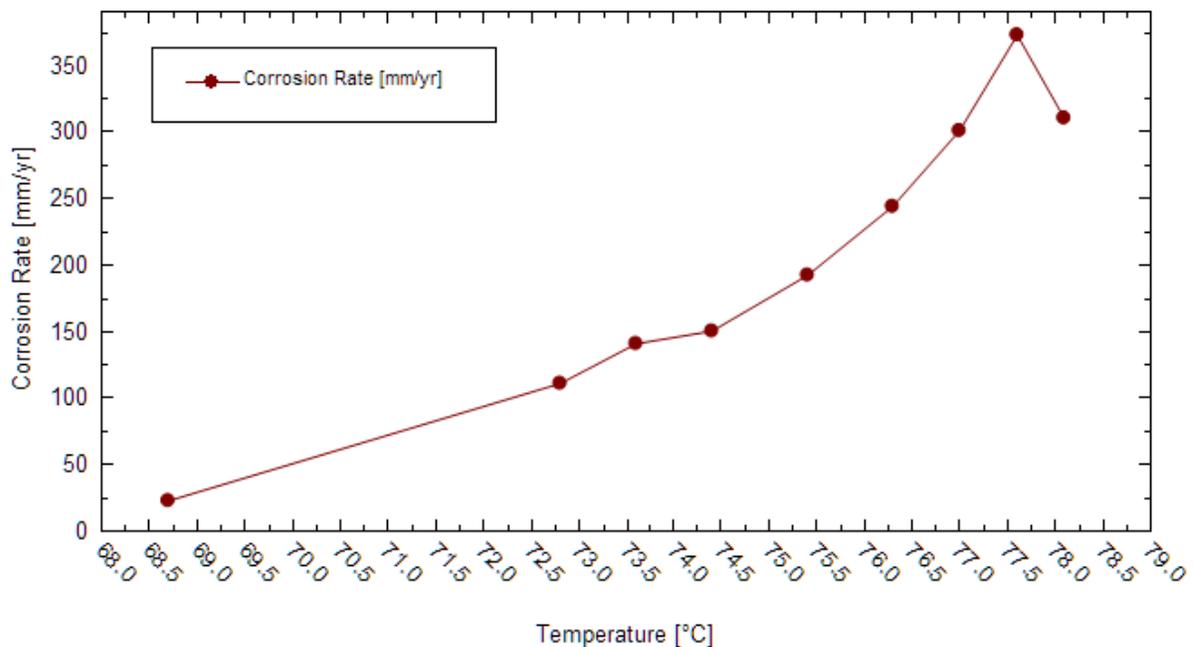
- ✓ Name the new calculation Stainless Steel 316 -

- ✓ Change the Contact Surface to Stainless Steel 316



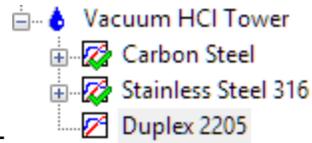
- ✓ Calculate then select the General Corr. Tab
- ✓ Remove the pH

The Corrosion rates for 316 stainless are about 10 times lower than carbon steel. The rates vary from 22 at the tower top to 310 mm/yr at its bottom. This is still a very high value, as a 254 mm wall at the tower bottom would dissolve in nine months.

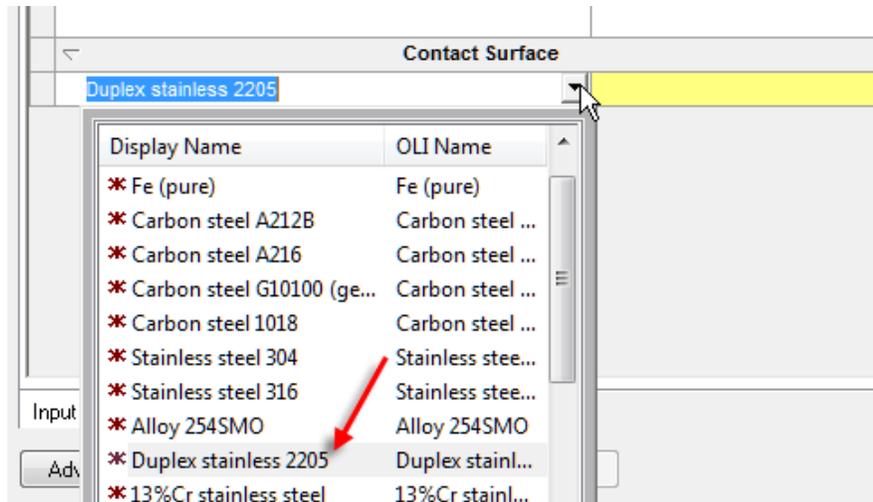


Corrosion using a Duplex Stainless 2205 (high chrome)

- ✓ Rename the third calculation object Duplex 2205 (copied)

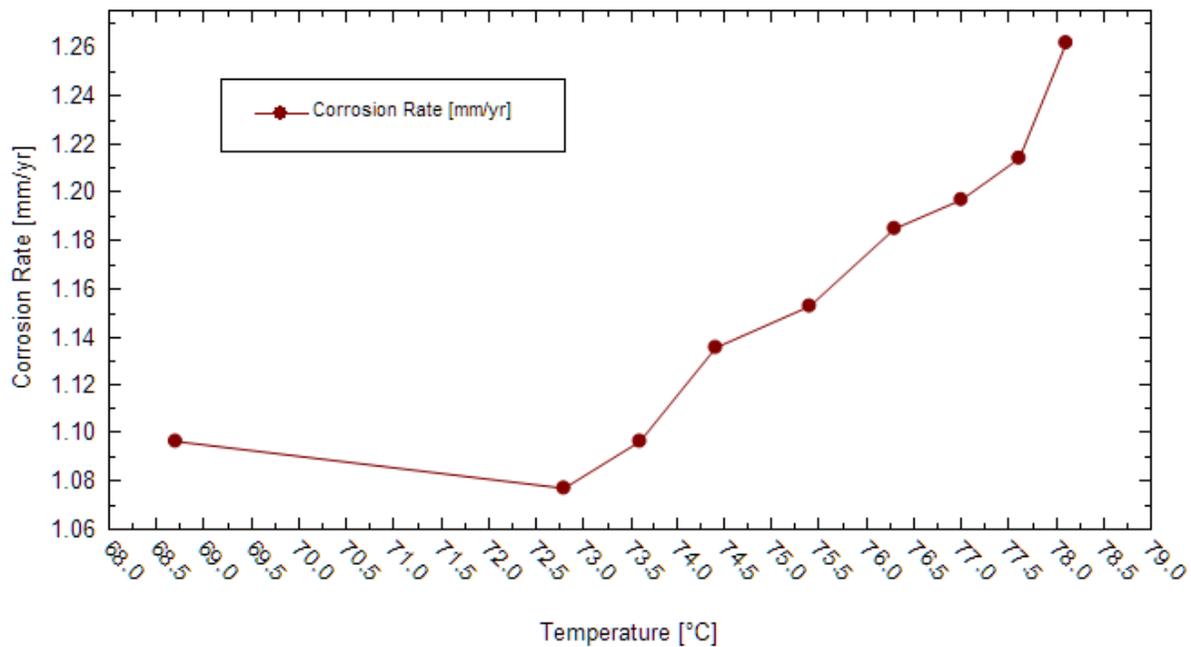


- ✓ Change the Contact Surface to Duplex Stainless 2205 -



- ✓ Calculate then select the General Corr. Tab

Corrosion rates are considerably smaller, one-thousandth the rates observed with carbon steel and up to 100 times less than 316 stainless.



At these rates, which are roughly the same across the tower (1.1 to 1.26 mm/yr), a 25 mm duplex steel wall will lose one-half its wall thickness in 20 years.

7b.3 Corrosivity of Soda Pop

In this example, you will compute the corrosion rate of soda on an aluminum can. Aluminum cans are internally coated with an epoxy resin to prevent corrosion.¹ In this exercise, you will compute the corrosion rate without this coating. Below are some properties for various soda brands. These soda products contain phosphoric or citric acid and its pressure is carbonation (CO₂), this produces a low pH.

You will create soda properties by adding H₃PO₄ to lower pH and CO₂ to raise the bubble point pressure. You will then compute the corrosivity of this liquid on aluminum. You can alternatively test the effects of citric acid on corrosivity, and figure out how much tooth enamel (calcium fluorphosphate) will dissolve in 12 ounces (355 ml) of soda.

7b.3 Corrosivity of Soda Pop			
Soda ²	pH	Pressure, atm	Corrosion Rate
Coke	2.53	4.7@23C ³	
Diet Coke	3.29		
Pepsi	2.53	2.7@16C ⁴ .	
Diet Pepsi	3.03		
Dr. Pepper	3.17	3.0 @50F ⁵	
RC Cola	2.39		
Mountain Dew	3.23		
Diet Mountain Dew	3.37		
7-up	3.20	3.2 @4C ⁶	
Sprite	3.71		
Mug Root Beer	4.04		

The first step is to calculate the amount of acid (CO₂ and H₃PO₄) in the soda. This is done using the Custom calculation. The second step is to run the Corrosion Rate calculation using the calculated amount of CO₂ and H₃PO₄. You will need to manually enter the CO₂ and H₃PO₄ calculated in the first step into the second step calculation.

Calculate the amount of H₃PO₄ and CO₂ in the soda

The Custom calculation will be used to fix the soda pH and the can pressure (specifications) and adjust the amount of CO₂ and H₃PO₄ needed to meet these specifications. With Coke for example, the pH is set to 2.525 and the pressure to 4.7 atm.

The custom calculation works slightly different from other single-point calculations. Custom calculation specifications require an entered value. For example, the standard Bubble Point calculation fixes the vapor amount at 1e⁻¹⁰ the total stream amount. In the Custom calculation, the user needs to enter this value. You will enter a small amount (e.g, 1e⁻⁶ moles). This ensures that a vapor is present, which will allow the calculation to continue.

The instructions below are for the Coke example.

- ✓ Add a new stream  Add Stream ; name it 'Coke'  
- ✓ Open the Units Manager  then use the Quick List button to select Metric, concentration

¹ http://en.wikipedia.org/wiki/Beverage_can

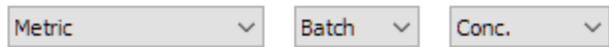
² <http://quittingsoda.com/post/the-acidity-ph-of-soda-pop>

³ <http://hypertextbook.com/facts/2000/SeemaMeraj.shtml>

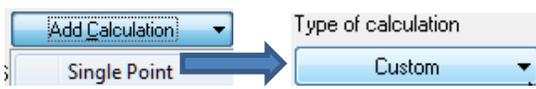
⁴ [ibid](#)

⁵ <http://goo.gl/pzk4G4>

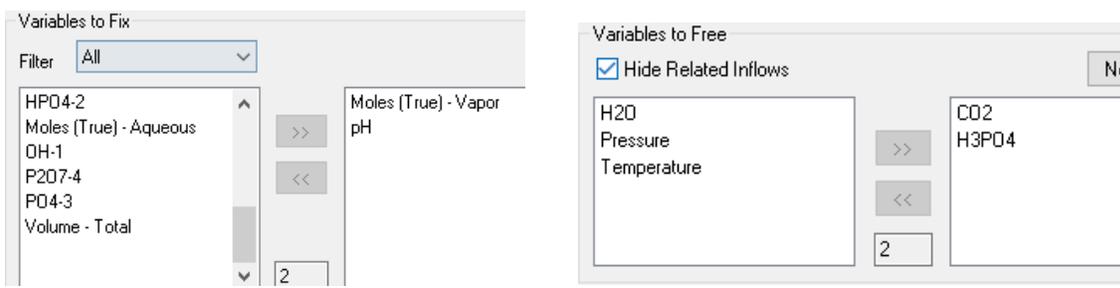
⁶ *38F is estimate, report states "refrigerated"



- ✓ Add H3PO4 and CO2 to the grid
- ✓ Change the Stream amount to 0.355 L (12 ounces)
- ✓ Change the temperature to 23C
- ✓ Change the pressure to 4.7 atm
- ✓ Add a Single Point calculation then change the type to Custom



- ✓ Select the Specs button
- ✓ Open the Specs window
- ✓ In the Variables to Fix column, select Moles (True)-Vapor and pH
- ✓ In the Variables to Free column, select CO2 and H3PO4



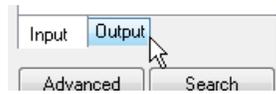
- ✓ Press OK

The Calculation Parameters Section of the grid is active and it contains four rows, two target specifications and two adjustable variables. The Target specifications require values. The adjustable variables can benefit from adding initial guesses, since it can speed up the calculation. You will add initial guesses in this case.

- ✓ Add the following Values to the Calculation Parameters Section

7b.3 Calculation Parameters	
Target 1: Moles - Vapor	1e-4
Target 2: pH – Aqueous	2.525
Variable 1: CO2 (mg/l)	100
Variable 2: H3PO4 (mg/l)	100

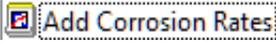
- ✓ Calculate
- ✓ Click on the Output tab at the bottom of the grid



Variable	Value
Stream Parameters	
Stream Amount (L)	0.355000
Temperature (°C)	23.0000
Pressure (atm)	4.70000
Calculation Parameters	
Target 1: Moles (True) - Vapor (mol)	1.00000e-4
Target 2: pH - Aqueous	2.52500
Variable 1: CO2 (mg/L)	100.000
Variable 2: H3PO4 (mg/L)	100.000
Inflows (mg/L)	
H2O	9.90727e5
Variable 2: H3PO4	430.981
Variable 1: CO2	7076.78

The software computed that to achieve this pH and can pressure, this beverage contains **431** mg/l H₃PO₄ and **7077** mg/l CO₂ (if these were the only two ingredients in the product).

Calculate the Soda corrosion rate on Aluminum

- ✓ Return to the Coke stream
- ✓ Add a Corrosion Rate calculation 
- ✓ In the Inflows grid, enter H3PO4 with a **431** mg/l value
- ✓ In the Inflows grid, enter CO2 with a **7077** mg/l value
- ✓ Change the Contact Surface to Aluminum 1100

Calculation Parameters	
Flow Type	Static
Inflows (mg/L)	
H2O	
H3PO4	431.000
CO2	7077.00
Al	0.0
Contact Surface	
Aluminum 1100	

- ✓ Calculate then select the “1” tab at the bottom of the grid to view the results

Corrosion Values	
Repassivation Potential (V (SHE))	99.9000
Corrosion Rate (mm/yr)	0.0302820
Corrosion Potential (V (SHE))	-0.781090
Current Density (µA/sq-cm)	2.79164
Depletion Parameter (cm)	0.0

The calculated corrosion rate on the aluminum can wall is 0.03 mm/yr (30µm/yr). According to Wikipedia, the can wall thickness is ~80 µm⁷. If we assume this is correct, then a coke will dissolve in less than three years. Thankfully, the epoxy coating keeps the beverage from tasting like aluminum.

⁷ http://en.wikipedia.org/wiki/Beverage_can, they provide no citation.

7b.4 Corrosion of Steel Pilings in Seawater

Steel pilings are driven into seawater beds to retain soil, control erosion, provide wave breaks, docks, supports the weight of piers, etc. However, the combination of salt and oxygen corrodes, and the sand in waves erodes the steel. We are interested in studying the effects of seawater and oxygen on general corrosion.



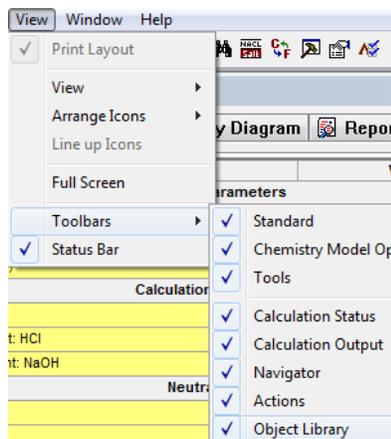
Figure 1 - Photo from <http://www.gimrock.com/images/Ocean%20Ave%20Demo4.jpg>, showing sheet piles driven into sediments during construction of a bridge in Palm Beach Fl.

The purpose of this case is to compute the corrosion of these steel pilings as a function of depth. Steel exposed to the surface is in contact with oxygen. Steel within the seabed sediments will not, and the lack of flow should also impact overall corrosion. Therefore, the output of this calculation is a corrosion profile. Its accuracy will depend on the software ability to include key corrosion factors.

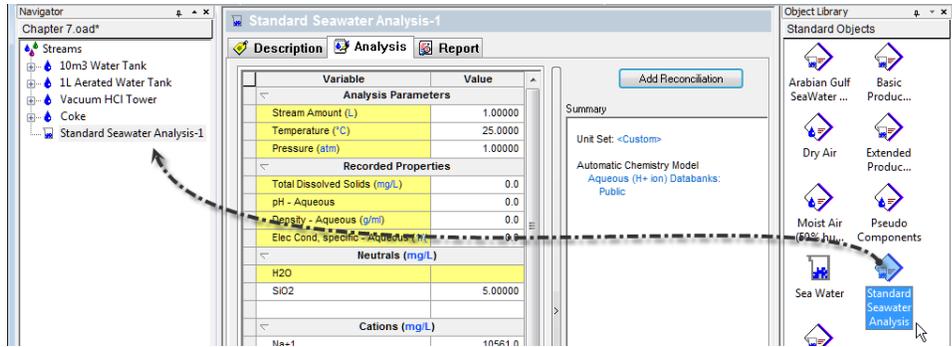
The two conditions tested will be cold, anoxic conditions under static flow (below sediment) and warm, aerated conditions with some flow (surface conditions).

Getting started

- ✓ Open the Object Library by clicking on View>Toolbars>Object Library



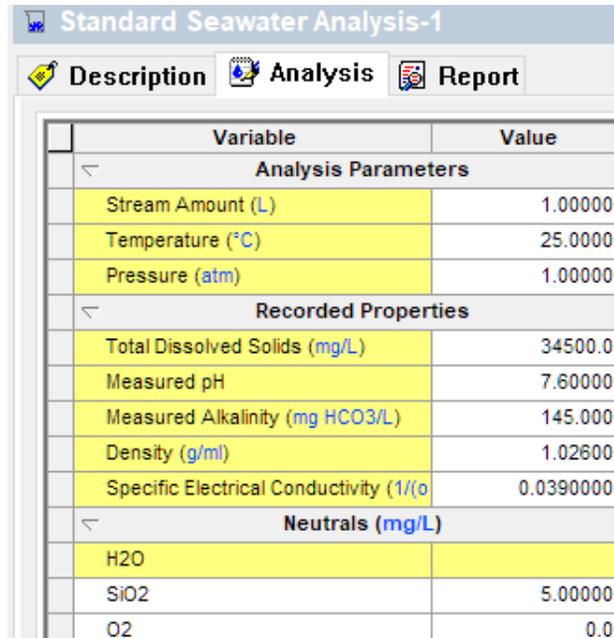
- ✓ Drag the Standard Seawater Analysis object to the Navigation Pane



- ✓ Add O2 to the list of Neutrals and enter a value of 8 mg/l

The concentration of oxygen at the surface of seawater is about 8 mg/l. As depth increases, the concentration decreases because O₂ is consumed faster than it can be replenished.

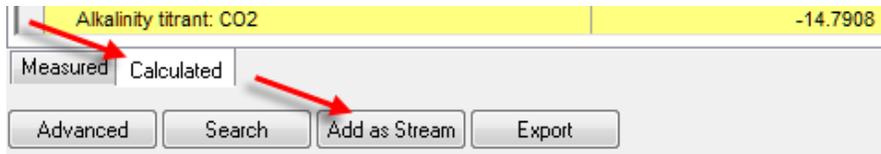
- ✓ Add HCl and NaOH to the Neutrals list



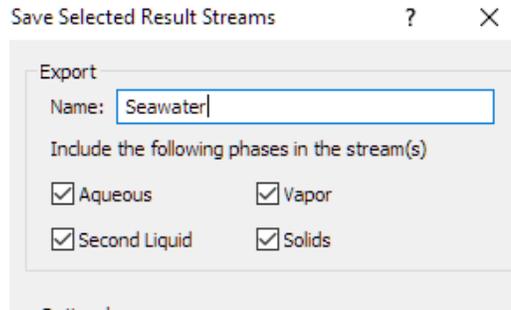
- ✓ Enter the following values into the Recorded Properties section

7b.4 Recorded Properties		
Total Dissolved Solids	34500	mg/l
pH	7.6	
Alkalinity	145	mg/l HCO ₃
Density	1.026	g/ml
Conductivity @25C	0.039	1/ohm-cm

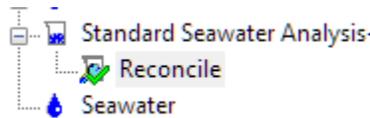
- ✓ Add a Reconciliation calculation
- ✓ Select Reconcile pH/Alkalinity
- ✓ Calculate
- ✓ Select the Calculated tab at the bottom
- ✓ Select the Add as Stream at the bottom



- ✓ Name the Exported stream Seawater and press OK



This creates a new stream called Seawater. This stream contains the molecular composition of the analysis we reconciled. Converting the water analysis to a stream format makes available the standard calculation objects, like Single Point, Survey, Corrosion Rates.



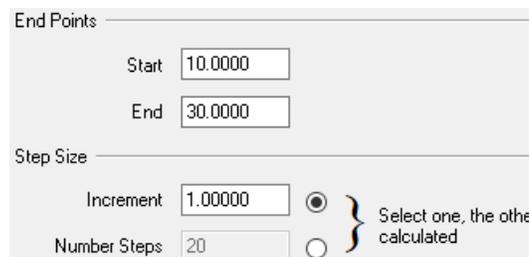
Corrosion between 10 and 30 C and in static flow

The first scenario is to compute the general corrosion rate as temperature changes. Seawater temperature varies with location (near shore, offshore), depth, latitude, and season. In our case, we are interested in near-shore water, perhaps 10 meters deep, where the water temperature range is 10 to 30 C.

- ✓ Add a Corrosion Rate Calculation  **Add Corrosion Rates** to this new stream

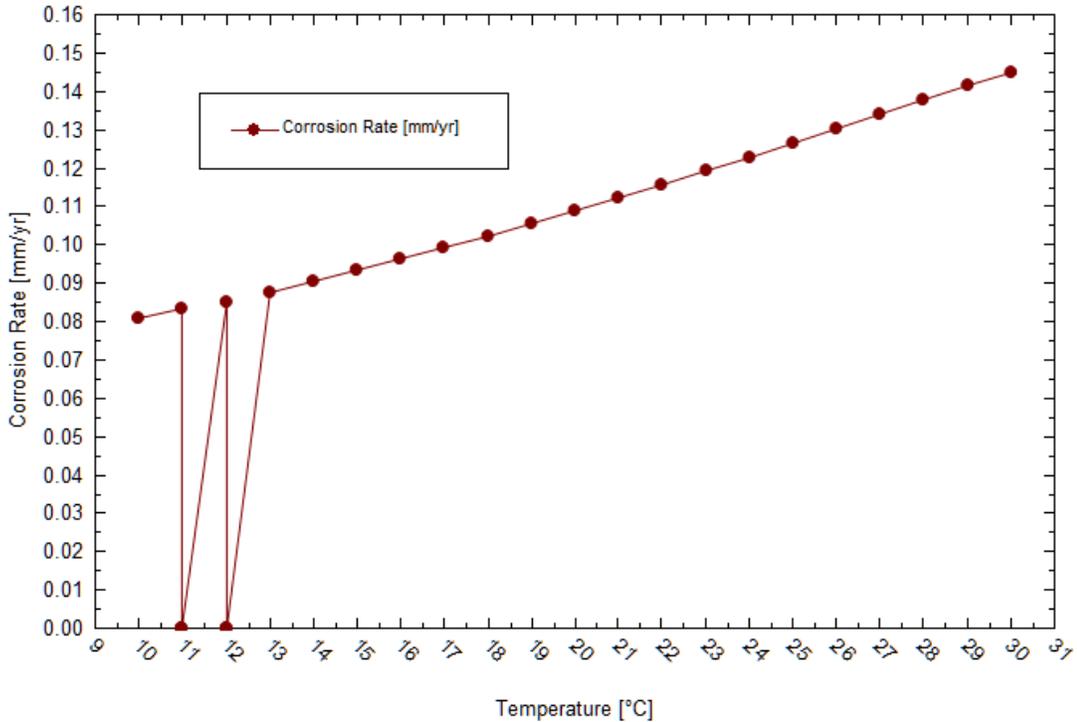


- ✓ Change the Survey by to Temperature
- ✓ Open the Specs window and set the Start=10, End=30, and Increment=1 C



- ✓
- ✓ Press OK and Calculate
- ✓ Select the General Corr. Rate tab then the Curves button
- ✓ Remove the pH from the plot using the right-mouse-click option.

The corrosion rates vary range from 0.080 to 0.140 mm/yr under static conditions. Notice that a few of the calculations failed (the zero values). Calculation failures occur at time, and when it does, ignore the values if we can as long as it does not detract from the interpretation. With respect to the corrosion rate, a steel pilings 12.7 mm thick will last up to 80 years (50% wall loss).



Corrosion between 10 and 30C in liquid flowing

If the water is flowing, then the situation is different. Modeling waves moving against the pilings is not simple, and there is no Flow Type (flow model) in the software that mimics it. We can attempt a guess.

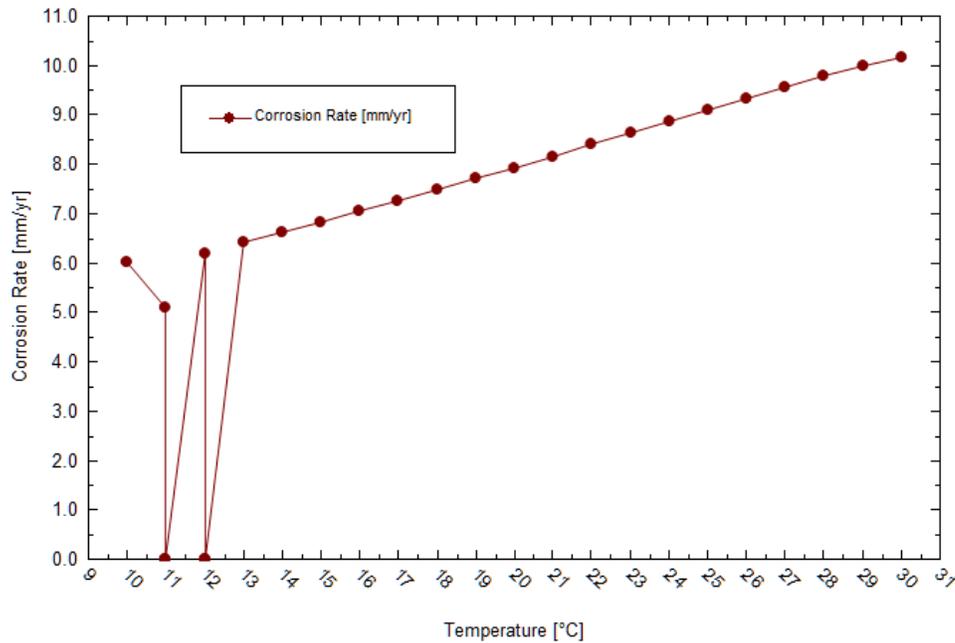
We assume that the water flows across the surface at a rate at which a person walks, ~5 km/hr. This is about 1.5 m/s. Next, we need to consider the shape of the surface. The software does not have a flat plate, but perhaps a pipe with a large diameter would suffice. We can try several diameters, 1,000 or 10,000 meters for example (the arc would approach a flat plate).

- ✓ Return to the Definition tab
- ✓ Change the flow type to Pipe Flow
- ✓ Change the Pipe Diameter units to meters



- ✓ Set the pipe diameter to 10000 meters
- ✓ Change the Pipe Flow Velocity to 1.5 m/s
- ✓ Calculate and View the Plot

The corrosion rate increases by a factor of 10x, decreasing the piling life to about 8-10 years.



Compare to Field Data⁸

An NBS monograph written in 1977 provides some reference for our evaluation. The adjacent plot contains the wall loss on unlined steel pilings driven into the soil. A portion of the pipe is exposed to wave action, tide changes, sand movement, and quiescent pore waters.

The mean seawater salinity is 26.8 ppt, lower than the 34.5 g/l value used in our calculation. In addition, the mean seawater temperature is 14.4C

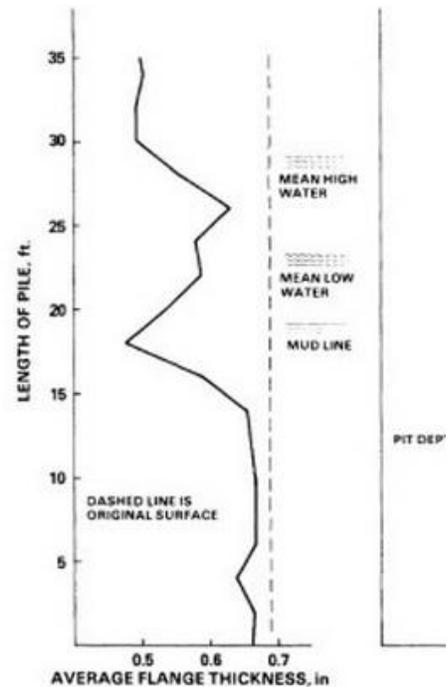
The piles are 30' long (9.1m) and 0.7" (18mm) thick. They were driven into the sand to 19 ft. The wall loss occurs on two sides of the pilings. Therefore the wall loss is effectively double the corrosion rate.

The pilings were exposed to this environment for six years. They were inspected annually using electrochemical and visual methods. They were removed after six years for inspection.

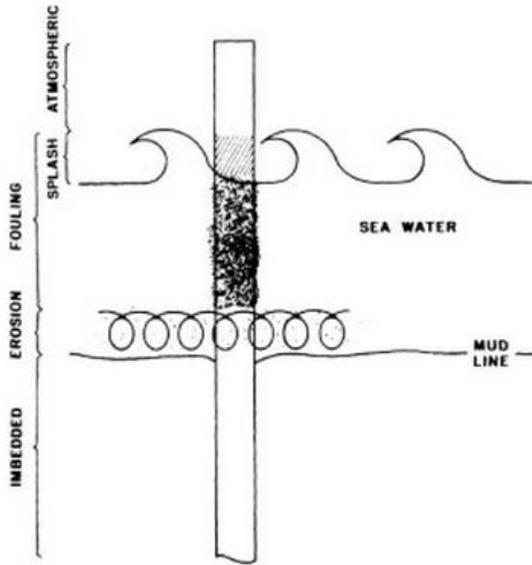
The authors reported several distinct corrosion sections, from below the mud line to the splash and atmospheric section (adjacent plot). The highest corrosion was above the Mean High water, where corrosion rates were between 8 to 12 mpy.

Below the high water mark, the corrosion was between 4 and 8 mpy on average. At the Mudline, which is the erosion zone, the rate averaged 9 mpy, and shifted because of the shifting mud-line elevation.

1A BARE CARBON STEEL



⁸ Escalante, E.; Iverson, W. P.; Gerhold, W. F.; Sanderson, B. T. & Alumbaugh. 1977. *Corrosion and Protection of Steel Piles in a Natural Seawater Environment*. Washington D.C.. UNT Digital Library. <http://digital.library.unt.edu/ark:/67531/metadc13190/>.



Below the mud line (<15ft) the corrosion rate decreased to 1-3 mpy, and some of the observed corrosion was pitting.

The adjacent diagram shows the environmental impact of seawater, wave action, and sand movement on the piling. We can only model the chemical aspect of corrosion, so when we compare numbers, it is important to recognize this.

Comparing Values

We ran two corrosion rate calculations, one at static conditions and one in which we considered movement across a flat surface. The corrosion rate for both at 14C (the average seawater temperature in the above paper) is 0.09 mm/yr at static conditions and 1 mm/yr under flowing conditions.

Location	Reported rate, mpy (mm/yr)	Computed Rate, mpy (mm/yr) [flow type]
Mean High water (Splash-Atmosphere)	8 to 12 mpy (0.2 to 0.3 mm/yr)	
Mean Low water	4 to 8 mpy (0.1 to 0.2 mm/yr)	40 mpy (1 mm/yr) [flowing]
Mudline	9 mpy (0.23 mm/yr)	
Mud, sand	1 to 3 mpy (0.025 to 0.075 mm/yr)	3.6 mpy (0.09 mm/yr) [static]

Fluid is static and the pore water is isolated from the bulk seawater. Pore water properties will change as corrosion progresses. For example, higher Fe^{+2} and pH are reaction products. In addition, the concentrations of corrodants cannot be replenished. They should therefore decrease. As a result, the wall loss is about 0.03" (0.8mm) over the six-year life. The annual corrosion rate is:

$$0.8mm * \frac{1}{2 \text{ sides}} * \frac{1}{6 \text{ yrs}} = 0.066 \frac{mm}{yr}$$

This value is similar to the static conditions computed above, but that may be entirely coincidental.

The high wall loss at the mud line is associated erosion, which cannot be modeled by the software. Within the Mean Low Water section (~23 ft) seawater is constantly present. The wall loss is approximately 0.1" (2.54mm) over the six-year time span. This is a rate of 0.21 mm/yr. Above the surf line in the Splash and Atmospheric section, the wall loss is 0.2" (5.5mm), which converts to a corrosion rate of 0.5 mm/yr.

7b.5 Gas Condensate Corrosion

Overview

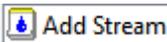
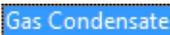
An alkanolamine gas sweetening plant has corrosion problems in the condensed overhead gas. Diethanolamine is used to neutralize an acid gas containing carbon dioxide and hydrogen sulfide. The diethanolamine is regenerated and the acid gases are driven off in a stripper. The off gas from this stripper is saturated with water vapor. As these gases cool, they will condense. This condensate can be very corrosive. The plant's service life can be shortened considerably due to these condensed acid gases. In this example, you will calculate the gas dew point temperature, remove the condensed aqueous phase and perform a Corrosion Rate calculation with the condensed water. Lastly, you will consider mitigation strategies for the pipes.

You are introducing *fluid velocity* and *liquid condensation* into the calculation. The software uses a diffusion layer model to compute mass transfer to and from corroding surfaces. Higher rates produce thinner layers, resulting in faster mass transfer rates, and thus higher corrosion rates. The liquid condensation point is straightforward; it calculates the temperature (or pressure) where the first liquid drop forms.

Gas Condensate

Start by creating a gas condensate stream. Note that the units are mole fraction. When using these units, the water's mole percentage is automatically calculated from the sum of the other inflow components. You may see error messages if your inflows' concentrations cause the water mole percentages to be negative.

7b.5 Gas Condensate Corrosion			
Name	Gas Condensate	H2O	Calculated (mole %)
Names Style	Formula	CO2	77.4
Units	Metric, mole fraction	N2	0.02
Stream Amount	1 e5 mol (100 kgmol)	H2S	16.6
Temperature	38C	CH4	0.50
Pressure	1.2 atm	C2H6	0.03
		C3H8	0.03

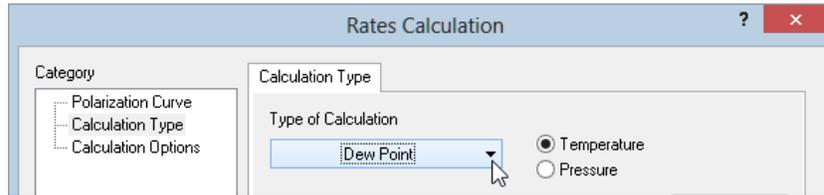
- ✓ Add a new stream ; name it 'Gas Condensate' 
- ✓ Change the Units Manager to Metric, batch, mole fraction

- ✓ Use the table above to complete the stream's composition

Now that the gas condensate stream is created, the next task is to isolate the condensed water at the dew point temperature.

- ✓ Add a Corrosion Rate calculation
- ✓ Name it CSG10100
- ✓ Set the Flow Type to Pipe Flow with Pipe Diameter=10cm, Pipe Flow Velocity=2 m/s
- ✓ Use the default contact surface of carbon steel G10100
- ✓ Keep the default Survey by of Single Point
- ✓ Select the Specs button

- ✓ Select the Calculation Type category
- ✓ Change the calculation type to Dew Point.



- ✓ Press OK

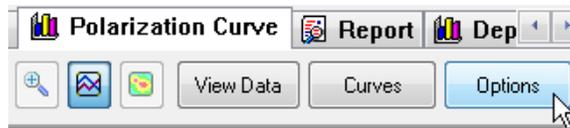
Variable	Value
Stream Parameters	
Stream Amount (mol)	1.00000e5
Temperature (°C)	25.0000
Pressure (atm)	1.20000
Calculation Parameters	
Calculate	Temperature
Flow Type	Pipe Flow
Pipe Diameter (cm)	10.0000
Pipe Flow Velocity (m/s)	2.00000
Effect of FeCO ₃ / FeS Scales	Include
Inflows (mole %)	
H ₂ O	5.42000
CO ₂	77.4000
N ₂	0.0200000
H ₂ S	16.6000
CH ₄	0.500000
C ₂ H ₆	0.0300000
C ₃ H ₈	0.0300000

- ✓ Calculate then select the select the Polarization Curve tab



Before interpreting this plot, it will be formatted for easier viewing.

- ✓ Click the Options button to change the axis minimum and maximums



- ✓ Select the X-Axis category
- ✓ Check to see that the X Axis minimum is 1e-6 and the max is 1e6
- ✓ Change the Y Axis minimum to -1.5 and the max to 1.5

X Axis
Y Axis
Curves

Auto

Minimum 1.0e-6

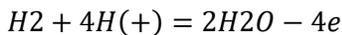
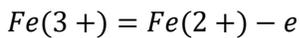
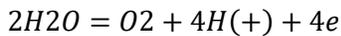
Maximum 1.0e6

Major Unit

Minor Unit

Logarithmic scale

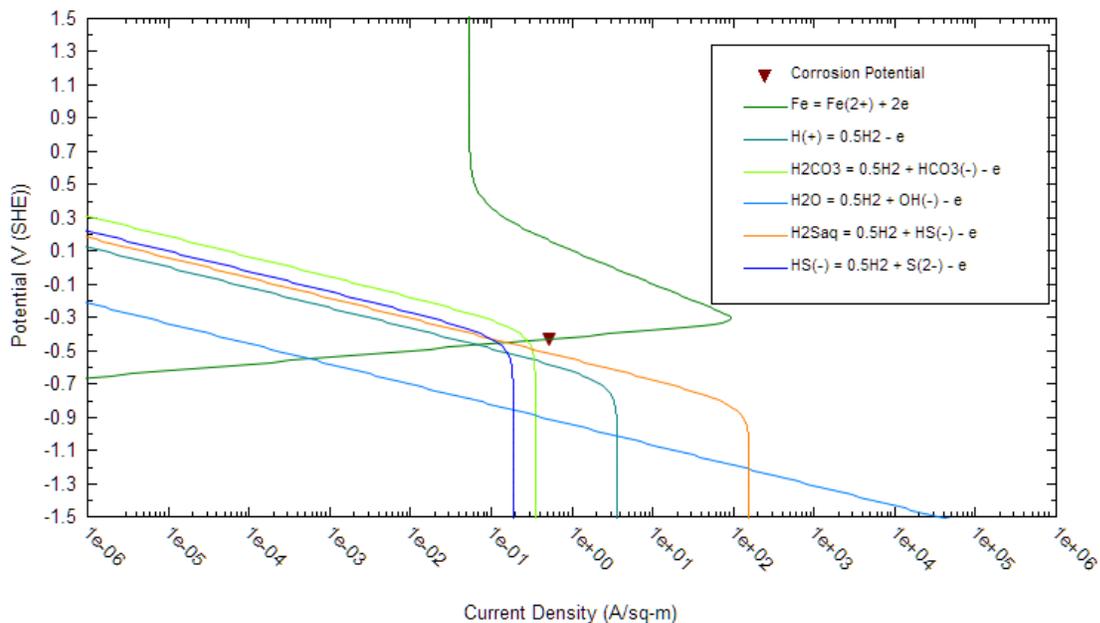
- ✓ Press OK
- ✓ Click on the Variables button
- ✓ Remove following variables by unchecking them



Peak Current Density

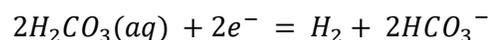
Net Current Density

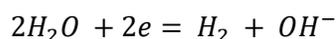
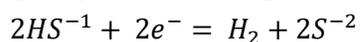
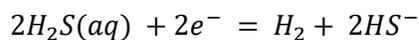
- ✓ Press OK view the plot



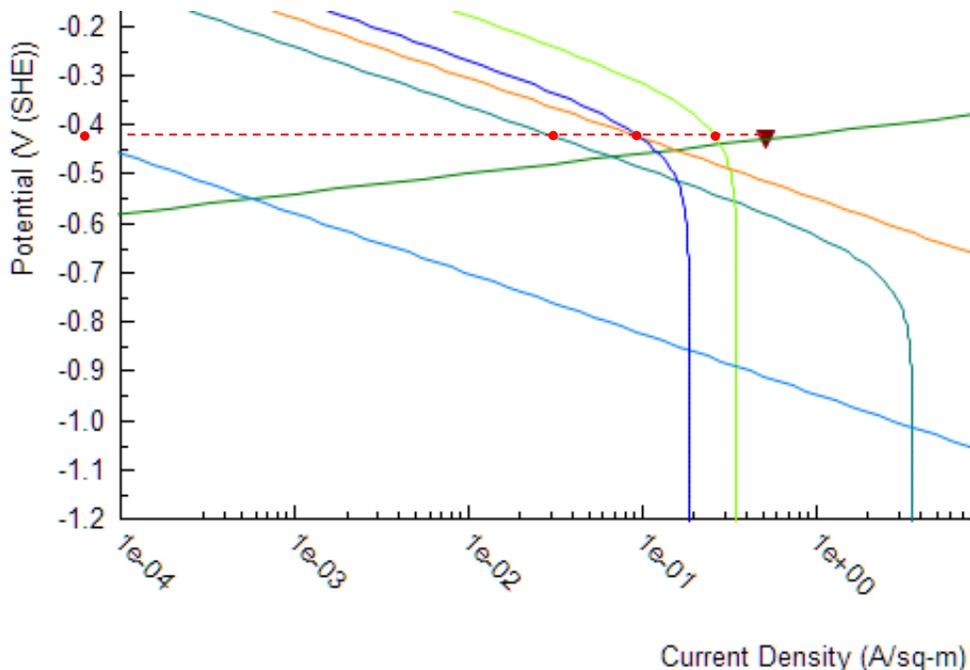
This is a measured potential vs. current density plot. It shows the flux of electrons moving from the metal or to the corrodant as the electrochemical potential changes. The two sets of curves have increasing slopes or decreasing slopes. The increasing slopes is the metal (anode) and decreasing is the corrodent (cathode). The anode is the carbon steel. There are several cathodes, H^+ , H_2CO_3 , H_2S , HS^{-1} . The sum of the cathode curves adds up to the anode curve at a single point. This point is the inverted triangle. At this point the release of electrons from the metal equals the consumption of the electrons by the cathodes.

The cathodic reaction that contributes the most to corrosion is H_2CO_3 . Its line nearest to the triangle when a horizontal line is drawn from the triangle to the Y-axis (see plot below). The next contributors are H_2S and HS^{-1} , equally. After that is H^+ .





Water reduction contributes the least to corrosion.



✓ Click the Report Tab and scroll down to the Calculated Rates and Stream Parameters tables

The contribution of each corrodent contributes to the final corrosion rate and that steady-state rate is linked to a specific electrochemical potential. Both are shown in the report as the Rate and Potential.

Calculated Rates

Corrosion Rate	0.704799	mm/yr
Corrosion Potential	-0.427501	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	0.607821	A/sq-m

The corrosion rate is approximately 0.70 mm/yr. The dew point is 37.6 °C, and the dew point pH is 3.9.

Mixture Properties

Stream Amount	1.00000e5	mol
Temperature	37.5872	°C
Pressure	1.20000	atm

Aqueous Properties

pH	3.92733	
----	---------	--

Mitigation

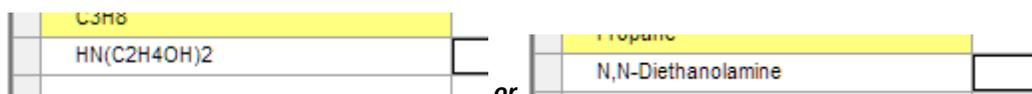
We have several mitigating solutions to this corrosion problem. One is adding insulation to prevent temperature drops. The dew point is very close to the overhead gas temperature so this may not be a

suitable option. Adding heat to keep the temperature above the dew point is usually considered along with insulation. Changing the chemistry to change the partial oxidation and reduction processes is also an option. Furthermore, changing alloys could mitigate the corrosion problem.

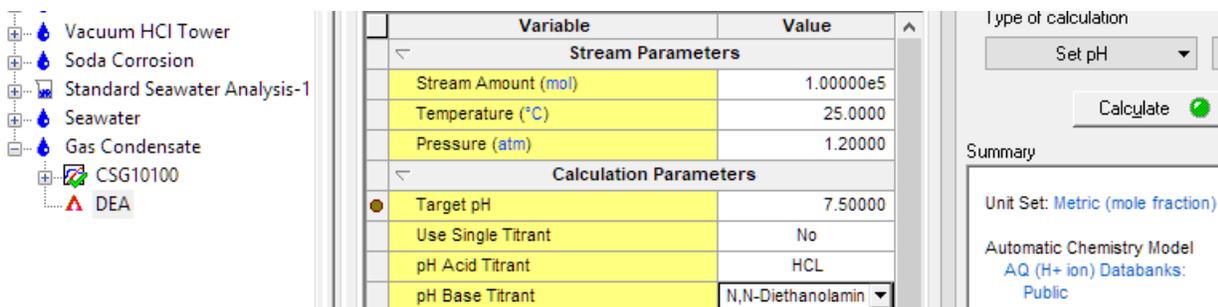
Adjusting the solution chemistry

The condensate pH is approximately 3.9. We can try to add a base to increase the pH. In this section, we will add Diethanolamine to raise the pH to 7.5.

- ✓ Click on the Gas Condensate stream
- ✓ Add a Single Point calculation  Add Single Point then rename it DEA 
- ✓ Type DEA in the first available inflow cell



- ✓ Select Set pH from the Type of calculation
- ✓ Enter 7.5 or pH
- ✓ Click on the dropdown arrow for the pH Base Titrant and select DEA (or the corresponding name that appears: N,N-Diethanolamine or HN(C2H4OH)2).



Variable	Value
Stream Parameters	
Stream Amount (mol)	1.00000e5
Temperature (°C)	25.0000
Pressure (atm)	1.20000
Calculation Parameters	
Target pH	7.50000
Use Single Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	N,N-Diethanolamin

Type of calculation: Set pH

Calculate 

Summary

Unit Set: Metric (mole fraction)

Automatic Chemistry Model
 AQ (H+ ion) Databanks:
 Public

The program is now set up to adjust the amount of DEA to match a target value of pH = 7.5.

- ✓ Calculate
- ✓ Review the Summary box

```

Set pH Calculation
38.0000 °C
1.20000 atm
Target pH 7.50000
Acid Titrant: HCl
Total: 0.0 mole %
Base Titrant: HN(C2H4OH)2
Total: 6.05698e-4 mole %
Added: 6.05698e-4 mole %

Phase Amounts
Aqueous 32.1151 mol
Vapor 99968.0 mol
Solid 0.0 mol

Aqueous Phase Properties
pH 7.50001
  
```

The pH is set to 7.5 and the inflow of DEA to the total gas is approximately 6.1e-4 mole %. The DEA concentration in the condensing water and the amount remaining in the vapor phase can both be viewed in the report section.

- ✓ Click on the Report tab and view the Total & Phase Flows and Species Output and tables

Species Output (True Species)

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

	Total	Aqueous	Vapor
	mole %	mole %	mole %
H2O	5.41961	96.686	5.39027
H+1	2.5208e-11	7.84264e-8	0.0
OH-1	6.65999e-10	2.07203e-6	0.0
NH2(C2H4OH)2(+1)	5.11007e-4	1.58983	0.0
HN(C2H4OH)2	2.5489e-5	0.0777442	5.00417e-7
C2H6	0.03	9.0821e-7	0.0300096
C3H8	0.03	7.06078e-7	0.0300096
CH4	0.499999	1.37048e-5	0.50016
CO2	77.3994	0.0416883	77.4243
CO3-2	3.92625e-6	0.0122152	0.0
C5H10NO4-1	6.97173e-5	0.216902	0.0
H2S	16.5999	0.0271338	16.6052
HCO3-1	3.74845e-4	1.16621	0.0
HS-1	5.85836e-5	0.182263	0.0
N2	0.02	2.56684e-7	0.0200064
S-2	3.99833e-9	1.24395e-5	0.0
Total (by phase)	100.0	100.0	100.0

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mol	mol	mol
Mole (True)	1.00000e5	32.1424	99968.0
Mole (App)	1.00001e5	32.5909	99968.0
	g	g	g
Mass	4.08064e6	652.995	4.07999e6
	L	L	L
Volume	2.11454e6	0.636284	2.11454e6

- ✓ Change the units to whatever is easiest to interpret

The units might be different, so use whichever are easiest to interpret. To achieve 7.5 pH, the gas-phase DEA needs to be 6.1e-4 mole % or about 15.6 ppm (mass). Since the condensing water mass is extremely small relative to the gas (view the total flow section further up the report), the overall mass is still small. How would the DEA requirements change if the temperature dropped well below the dew point?

Recalculating the Corrosion Rate with DEA

We now can recalculate the corrosion rate with DEA in the stream. This represents some DEA entrained in the vapor phase as the gas leaves the regenerator.

- ✓ Return to the CSG10100 calculation
- ✓ Enter DEA to the grid and give it the value computed in the previous calculation.

Fe	0.0
HN(C2H4OH)2	6.05698e-4

- ✓ Calculate and click on the Report tab to view the rates, dew point temperature, and pH

The corrosion rate has decreased from 0.7 to 0.48 mm/yr. If we run this at static flow, the values reduce from 0.4 to 0.27 mm/yr.

Calculated Rates

Corrosion Rate	1.10237	mm/yr
Corrosion Potential	-0.427350	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	0.950687	A/sq-m

The pH is 7.6, similar to the target value of 7.5. Therefore, neutralizing the pH had a partial effect on corrosion reduction.

Mixture Properties

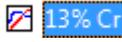
Stream Amount	1.00000e5	mol
Temperature	33.5777	°C
Pressure	1.20000	atm

Aqueous Properties

pH	7.59988	
----	---------	--

Alloys

Since treating the acid gas with a base is probably not a good idea for metal hydroxides, perhaps we can change the alloy. We will add a new corrosion rates calculation and test different alloys.

- ✓ Copy the CSG10100 calculation back into the stream
 - Right-mouse-click on the CSG10100 object and select Copy.
 - Right-mouse-click on the Gas Condensate stream and select Paste
- ✓ Rename it '13% Cr' 
- ✓ In the Contact Surface grid, Select 13%Cr stainless steel
- ✓ Change the flow conditions from Static to Pipe Flow, keeping the other default values

13% Cr

Survey by: Single Point Rate

Then by (optional): None

Vary: Independently Together

Calculate 

Summary

Unit Set: Metric (mole fraction)

Automatic Chemistry Model: AQ (H+ ion) Databanks: Corrosion Public

Redox selected

Dew Point Calculation: 1.20000 atm

Calculation not done

Single Point

Variable	Value
Temperature (°C)	38.0000
Pressure (atm)	1.20000
Calculation Parameters	
Calculate	Temperature
Flow Type	Pipe Flow
Pipe Diameter (cm)	10.0000
Pipe Flow Velocity (m/s)	2.00000
Thermal Aging Temperature (°C)	399.000
Thermal Aging Time (hr)	0.0
Inflows (mole %)	
H2O	5.42000
CO2	77.4000
N2	0.0200000
H2S	16.6000
CH4	0.500000
C2H6	0.0300000
C3H8	0.0300000
Fe	0.0
Contact Surface	
Fe(86.850)Cr(13.000)C(0.150)	

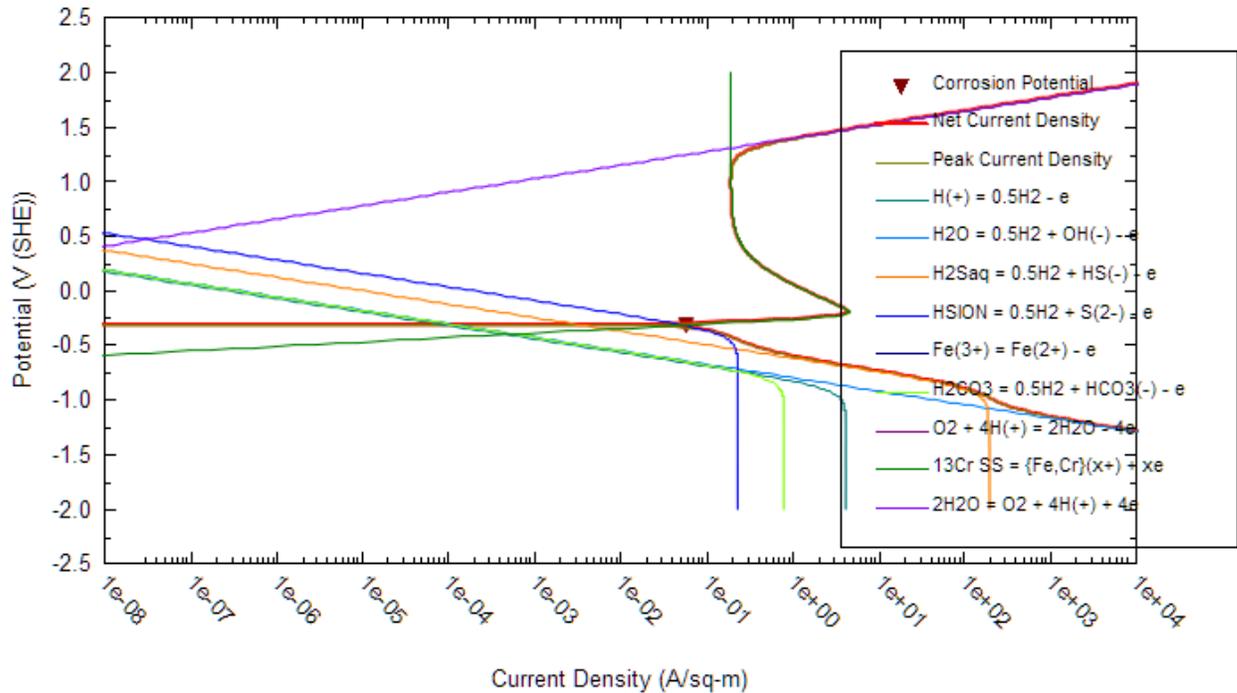
- ✓ Calculate
- ✓ Click on the Report and view the corrosion rates

The corrosion rates are an order of magnitude lower at ~60 um/yr. This is consistent with the use of 13% Cr to protect against CO2 corrosion.

Calculated Rates

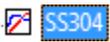
Corrosion Rate	0.0629723	mm/yr
Corrosion Potential	-0.314266	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	0.0566488	A/sq-m

- ✓ Select the Polarization Curve tab



The curve has changed in two ways, first the 13%Cr curve has shifted upwards. It is 0.51 V instead of 0.67 V (a smaller relative driving force to oxidize). Second, because of the anode curve being shifted upwards, the intersection between the anode and cathode reaction (mixed potential) shifted to the left (lower current density).

The next step is to repeat with Stainless Steel 304.

- ✓ Copy the CSG10100 calculation again to create a new corrosion calculation
- ✓ Name it 'SS304' 
- ✓ Calculate

SS304

Description Definition General Corr. Rate Localized Co

Variable	Value
Stream Parameters	
Stream Amount (mol)	1.00000e5
Temperature (°C)	38.0000
Pressure (atm)	1.20000
Calculation Parameters	
Calculate	Temperature
Flow Type	Pipe Flow
Pipe Diameter (cm)	10.0000
Pipe Flow Velocity (m/s)	2.00000
Thermal Aging Temperature (°C)	399.000
Thermal Aging Time (hr)	0.0
Inflows (mole %)	
H2O	5.42000
CO2	77.4000
N2	0.0200000
H2S	16.6000
CH4	0.500000
C2H6	0.0300000
C3H8	0.0300000
Fe	0.0
Contact Surface	
Fe(71.930)Cr(19.000)Ni(9.000)C(0.070)	

- ✓ Click the Report and view the results

The corrosion rate is now ~3um/yr, a negligible value.

Calculated Rates

Corrosion Rate	3.57122e-3	mm/yr
Corrosion Potential	-0.172553	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Corrosion Current Density	3.29512e-3	A/sq-m

- ✓ Click on the Polarization Curve plot

Thus, sour gas regeneration corrosion can be remedied using a higher-grade alloy.

Follow-up example

The effect of double-layer thickness on corrosion rates is evident from the previous case. The sudden change in slopes of the cathodes from slight negative to vertical is the result of the inability of those species to reach the surface at a high enough rate to accept the electrons that the surface is willing to provide it. If we consider the terms associated with diffusion to and from the surface, we can estimate these diffusion properties.

First, we know the maximum rate, or more specifically, flux at which each species is transported to the surface. It is the value in A/m² on the polarization where the vertical line crosses. Using the last plot we created (304SS), the values are $CO_2 = 0.35 \frac{A}{m^2}$, $H^+ = 4.14 \frac{A}{m^2}$ and $H_2S = 190 \frac{A}{m^2}$

✓ Return to the report and find the concentration for these species

Your results may differ: $CO_2 = 1011 ppm \left(\frac{16.3 mmole}{kg} \text{ solution} \right)$, $H^+ = 0.12 ppm \left(0.12 \frac{mmol}{kg} \text{ solution} \right)$ and $H_2S = 521.2 ppm \left(15.33 \frac{mmol}{kg} \text{ solution} \right)$.

The half reactions for the corrodants are $CO_2 + H_2O + e^- = \frac{1}{2} H_2 + HCO_3^-$, $H^+ + e^- = \frac{1}{2} H_2$ and $H_2S + e^- = \frac{1}{2} H_2 + HS$, where e⁻ in this case is one mole of electrons. Remembering, $A = \frac{C}{s} = e^-$

$\frac{C}{s}$ ($A = \text{Ampere}, C = \text{Coulomb}$), we can first calculate the maximum moles of each species that can reach the surface each second. Since each species consumes a single mole of electrons in their reaction, then

resulting flux of species to the surface is $CO_2 = 0.35 \frac{\text{moles}}{m^2 s}$, $H^+ = 4.14 \frac{\text{moles}}{m^2 s}$ and $H_2S = 190 \frac{\text{moles}}{m^2 s}$.

If the system in question is a 1m³ cube filled with this solution, and if we assume a 1 g/cc density then the total moles of each species becomes: $CO_2 = 16.3 \frac{\text{moles}}{m^3} \text{ solution}$, $H^+ = 0.12 \frac{\text{moles}}{m^3} \text{ solution}$ and $H_2S = 15.3 \frac{\text{moles}}{m^3} \text{ solution}$.

Dividing the concentration by its maximum flux yields: $CO_2 = 46.6 \frac{s}{m} = 0.0214 \frac{m}{s}$, $H^+ = 0.029 \frac{s}{m} = 34.5 \frac{m}{s}$ and $H_2S = 0.805 \frac{s}{m} = 12.4 \frac{m}{s}$. Pull the species mobilities from the report: $CO_2 = 2.63e-9 \frac{m^2}{s}$, $H^+ = 1.13e-8 \frac{m^2}{s}$ and $H_2S = 2.45e-9 \frac{m^2}{s}$.

Chapter 8 Refinery Applications

Introduction

This section contains refinery and production applications of the OLI Studio.

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List of amines and amine hydrochlorides in the existing OLI V9.5.2 database

Descriptive name	Chemical formula	OLI Formula	OLI Tag	Cation name	Amine Hydrochloride name	OLI Tag Name for hydrochloride
Alkyl amines						
Methylamine	CH ₃ NH ₂	CH3NH2	MEAMINE	MEAMINEHION	Methylamine hydrochloride	MEAHCL
Dimethylamine	(CH ₃) ₂ NH	C2H7N	DMEA	DMEAHIION	Dimethylamine hydrochloride	DMEAHCCL
Trimethylamine	(CH ₃) ₃ N	C3H9N	TRIMEAMINE	TRIMEAMHION	Trimethylamine hydrochloride	TMEAHCCL
Ethylamine	CH ₃ CH ₂ NH ₂	C2H7N	ETAMINE	ETAMINEHION	Ethylamine hydrochloride	EAHCCL
Diethylamine	CH ₃ CH ₂ NHCH ₂ CH ₃	C4H11N	DIETHYLAMN	DIETHYLHION	Diethylamine hydrochloride	DEAHCCL
Propylamine	CH ₃ (CH ₂) ₂ NH ₂	C3H9N	PROPYLAMN	PROPAMHION	n-Propylamine hydrochloride	PROPAMHCCL
Butylamine	CH ₃ (CH ₂) ₃ NH ₂	C4H11N	BUTYLAMINE	BUTYLAMHION	Butylamine hydrochloride	BUTAMHCCL
2-Butanamine	CH ₃ CH ₂ CH(CH ₃)NH ₂	C4H11N	SECBUTYAMN	SECBUAHION	2-Butylamine hydrochloride	SECBACHCL
Cyclohexylamine	c-(CH ₂) ₅ CHNH ₂	C6H13N	CYCLHEXAMN	CHEXAMNHION	Cyclohexylamine hydrochloride	CHEXACHCL
Ethylenediamine	H ₂ N(CH ₂) ₂ NH ₂	C2H8N2	ENAMN2	ENAMN2HION	Ethylenediamine dihydrochloride	ENAMN2HCCL
Alkanolamines						
Ethanolamine	HO(CH ₂) ₂ NH ₂	NH2C2H4OH	MEXH	MEXH2ION	Ethanolamine hydrochloride	MEXHCCL
Diethanolamine	HO(CH ₂) ₂ NH(CH ₂) ₂ OH	HN(C2H4OH)2	DEXH	DEXH2ION	Diethanolamine hydrochloride	DEXHCCL
Dimethylethanolamine	(CH ₃) ₂ N(CH ₂) ₂ OH	C4H11NO	DMEXH	DMEXH2ION		
Diglycolamine	HO(CH ₂) ₂ O(CH ₂) ₂ NH ₂	NH2C2H4OC2H4OH	DGXH	DGXH2ION		
Dimethylisopropanolamine	HOCH(CH ₃)CH ₂ N(CH ₃) ₂	C5H13NO	DMIPA	DMIPAHION	Dimethylisopropanolamine hydrochloride	DMIPAHCL
Methyldiethanolamine	CH ₃ N(C ₂ H ₄ OH) ₂	C5H13NO2	MDEXH	MDEXH2ION		
Oxygenated amines						
3-Methoxypropylamine	H ₂ N(CH ₂) ₃ OCH ₃	C4H11NO	MOPA	MOPAHION	3-Methoxypropylamine hydrochloride	MOPAHCL
Morpholine	c-(CH ₂) ₂ O(CH ₂) ₂ NH	C4H9NO	MORPHOLN	MORPHHION	Morpholine hydrochloride	MORPHHCCL
N-Methylmorpholine	c-(CH ₂) ₂ O(CH ₂) ₂ NCH ₃	C5H11NO	NMM	NMMHION	N-methylmorpholine hydrochloride	NMMHCCL
N-Ethylmorpholine	c-(CH ₂) ₂ O(CH ₂) ₂ NC ₂ H ₅	C6H13NO	NEM	NEMHION	N-Ethylmorpholine hydrochloride	NEMHCCL

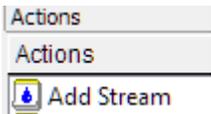
8.1 – NH₄Cl Vapor Solid equilibrium

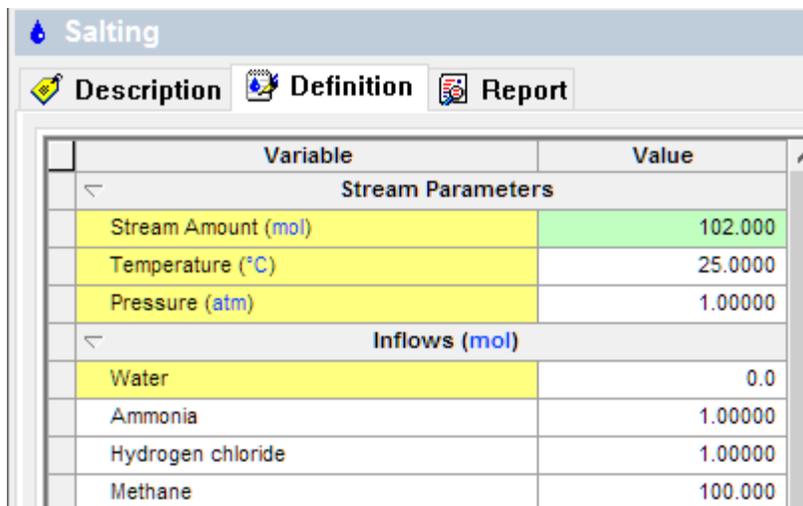
Overview

The following example will illustrate one of the elements associated with overhead corrosion, salting of components from the vapor phase to form a solid. In this simple example, you will precipitate ammonium chloride, NH₄Cl, from a vapor by cooling a gas. This salting mechanism is also called desublimation.

Creating the Process

Add the stream

- ✓ Double-click on the Add Stream object in the Actions Panel - 
- ✓ Name the stream **Salting** – press F2 to edit the name - 
- ✓ Change the thermodynamic framework to MSE. Do this by clicking on the MSE-FW button in the toolbar - 
- ✓ Enter the following components to the grid, NH₃ HCl, and CH₄.
- ✓ Set the NH₃ and HCl values to 1 mole, the CH₄ to 100 moles and the water to zero.



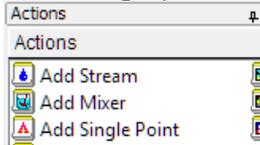
Variable	Value
Stream Parameters	
Stream Amount (mol)	102.000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
Water	0.0
Ammonia	1.00000
Hydrogen chloride	1.00000
Methane	100.000

The reason for adding the methane is to create a vapor phase. The NH₃ and HCl will then represent partial pressures in this methane vapor. In this case NH₃ and HCl are each 1/102 or 0.0098% of the total inflows, and if the calculation is 100% vapor, then their partial pressures will be 0.0098 atm (that the total pressure is 1atm).

Note also, that water (H₂O) is set to zero. This prevents a water phase from condensing and dissolving any NH₄Cl salt that may form. Thus, the only phases possible for these inflows are a vapor and a solid phase.

Calculate conditions at 25 C

- ✓ Add a Single point calculation by double-clicking on Add Single Point in the Action panel.



- ✓ Press the Calculate button.
- ✓ Click on the Report tab to view the results.
- ✓ Scroll down to the Total and Phase Flows (Amounts) table.

The software computed that 1 mole of solid (specifically, 0.999999) and 100 moles of vapor are present. Under these conditions the NH_4Cl solid phase is stable, and nearly all the NH_3 and HCl added is present as a solid phase

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Vapor	Solid
	mol	mol	mol
Mole (True)	101.000	100.000	0.999999
Mole (App)	101.000	100.000	0.999999
	g	g	g
Mass	1657.79	1604.30	53.4915
	L	L	cm3
Volume	2442.45	2442.42	35.0300

- ✓ Scroll down further to the Species Output (True Species) table.

There are four components. The two main phases are methane gas and ammonium chloride solid. There is also NH_3 and HCl in the vapor phase but virtually all of it has precipitated. The remaining amount of NH_3 and HCl in the vapor is small, about $1/10^6$ the total moles added.

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Vapor	Solid
	mol	mol	mol
Methane	100.0	100.0	0.0
Ammonium chloride (Sal ammoniac)	0.999999	0.0	0.999999
Ammonia	9.84203e-7	9.84203e-7	0.0
Hydrogen chloride	9.84203e-7	9.84203e-7	0.0
Total (by phase)	101.0	100.0	0.999999

Thus, at 25C, the fraction of NH_3 and HCl in the vapor phase is 9.84×10^{-7} moles. The total vapor moles is 100. The NH_3 and HCl vapor fraction is 9.84×10^{-9} mol/mol, or $P_{\text{NH}_3}=P_{\text{H}_2\text{S}}=9.84 \times 10^{-9}$ atm when in equilibrium with the solid phase at 25C and 1atm.

Calculate conditions at 250 C

- ✓ Return to the Definition tab.
- ✓ Set the temperature to 250 C.
- ✓ Calculate.
- ✓ Return to the Report tab and scroll down to the Species Output (True Species).

The system is now all vapor and 100% of the NH₃ and HCl are in the gas phase. The partial pressures are 0.098 atm for each.

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

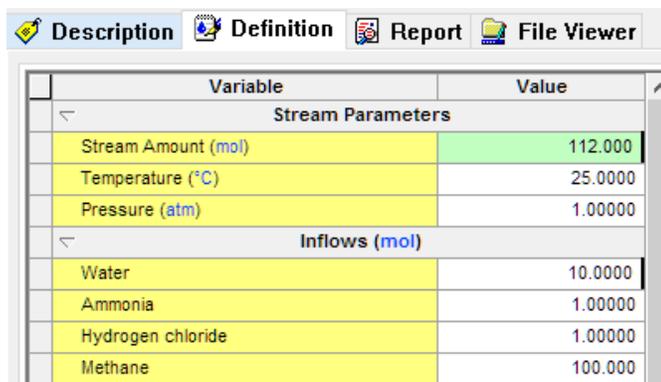
column Filter Applied: Only Non Zero Values

	Total	Vapor
	mol	mol
Methane	100.0	100.0
Ammonia	1.0	1.0
Hydrogen chloride	1.0	1.0
Total (by phase)	102.0	102.0

Thus, we can compute the temperature dependence of NH₄Cl stability. At 25C, NH₃ and HCl have stable partial pressures of $\sim 1e^{-6}$ atm. at 250 C, the stable partial pressures are at least 0.0098 atm. It may be higher, because there is no NH₄Cl solids present. In other words, the NH₃ and HCl partial pressures can increase further before a solid forms. The exact increased amount would need to be computed.

Calculate conditions at 25 C when excess water is present

- ✓ Return to the Definition tab.
- ✓ Set the temperature to 25 C.
- ✓ Enter a water value of 10 moles.



Variable	Value
Stream Parameters	
Stream Amount (mol)	112.000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
Water	10.0000
Ammonia	1.00000
Hydrogen chloride	1.00000
Methane	100.000

- ✓ Calculate.
- ✓ View the Summary section of the screen – note that the Phase Amounts are now Aqueous and Vapor. There is no longer a solid phase.

Phase Amounts
Aqueous 9.50528 mol
Vapor 102.495 mol
Solid 0.0 mol

Note that the pH is low, 3.58. This is for two reasons. First, dissolved NH_3 and HCl is a solution of a weak base and a strong acid. What this means is that the amount of H^+ generated from HCl is greater than the amount of OH^- generated from NH_3 . Consequently, the pH is low: $\text{pH} \approx -\log(\text{H}^+)$.

```
Aqueous Phase Properties
pH      3.57783
Ionic Strength  0.105205 mol/mol
Density  1.08583 g/ml
```

Second, HCl is more soluble than NH_3 in water. Therefore, the H^+ concentration is further increased.

- ✓ Click on the Report tab and view the HCl and NH_3 amounts in the vapor phase.

Ammonia	1.82389e-5	1.8334e-6	1.64055e-5
Ammonium hydroxide	2.19822e-7	2.19822e-7	0.0
Hydrogen chloride	6.24332e-8	4.35439e-10	6.19977e-8

The NH_3 amount in the vapor is 1.64×10^{-5} moles. By comparison, the HCl amount is 6.2×10^{-8} moles, nearly 1000 times less. This is evidence of the solubility difference in water

Calculate conditions at 25 C when limited water is present

- ✓ Change the water value to 3 moles.

Variable	Value
Stream Parameters	
Stream Amount (mol)	105.000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
Water	3.00000
Ammonia	1.00000
Hydrogen chloride	1.00000
Methane	100.000

- ✓ Calculate.
- ✓ View the Summary section of the screen – There are now three phases.

```
Phase Amounts
Aqueous  0.640759 mol
Vapor    102.494 mol
Solid    0.932541 mol
```

- ✓ The pH is also lower, 3.0.

```
Aqueous Phase Properties
pH      3.02542
Ionic Strength  0.105280 mol/mol
Density  1.08587 g/ml
```

The pH is lower because the solution is more concentrated with NH_3 and HCl .

- ✓ Click on the report tab and view the Species Output table

The NH_3 and HCl in the gas, liquid, and solid phase are in equilibrium with each other. The amounts of NH_3 and HCl in the gas phases is 4.6×10^{-6} and 2.2×10^{-7} moles. The total gas amount is 102.5 moles, and thus their

partial pressures is 4.6×10^{-8} and 2.2×10^{-9} atm, respectively. These partial pressures are in equilibrium with the 0.933 moles of NH_4Cl that formed and with the dissolved NH_3 and HCl .

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor	Solid
	mol	mol	mol	mol
Methane	100.0	2.11123e-6	100.0	0.0
Water	3.0	0.505839	2.49416	0.0
Ammonium chloride (Sal ammoniac)	0.932541	0.0	0.0	0.932541
Chloride ion(-1)	0.067459	0.067459	0.0	0.0
Ammonium ion(+1)	0.0674546	0.0674546	0.0	0.0
Ammonia	4.63623e-6	3.46688e-8	4.60156e-6	0.0
Hydronium ion(+1)	4.41888e-6	4.41888e-6	0.0	0.0
Hydrogen chloride	2.21504e-7	1.05152e-10	2.21398e-7	0.0
Ammonium hydroxide	4.15341e-9	4.15341e-9	0.0	0.0
Hydroxide ion(-1)	2.82647e-13	2.82647e-13	0.0	0.0
Total (by phase)	104.067	0.640759	102.494	0.932541

- ✓ Save the file with the name Chapter 8 – Refinery cases

Summary

This is the basis of the amine-hydrochloride salting from the vapor and the subsequent dissolving in water when that phase becomes present.

8.2 – NH4Cl solubility in water vs. temperature

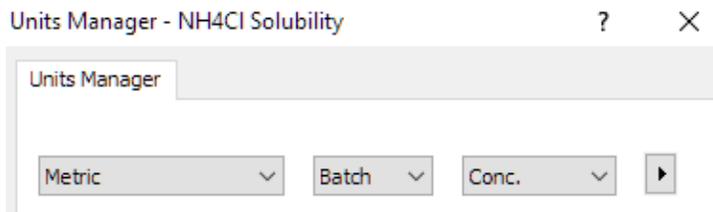
Overview

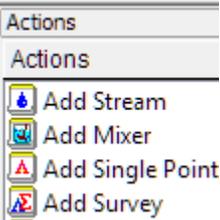
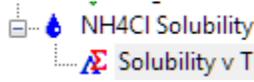
The following example illustrates the temperature effects on amine-hydrochloride solubility and its impact on the salt dew point and the resulting pH.

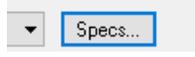
Creating the Process

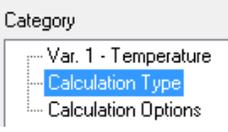
Study NH4Cl solubility in water

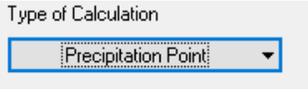
- ✓ Create a new stream and label it NH4Cl Solubility - 
- ✓ Change the framework to MSE - 
- ✓ Add NH4Cl to the inflow grid. Give it no value.
- ✓ Click on the Units Manager button in the Toolbar - 
- ✓ Change the units to Metric – Batch – Concentration



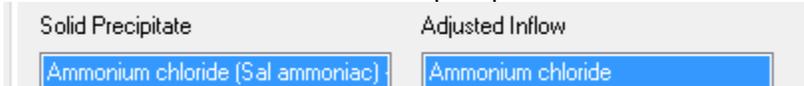
- ✓ Add a Survey calculation 
- ✓ Name it Solubility vs. T - 

- ✓ Click on the Specs button in the upper right - 

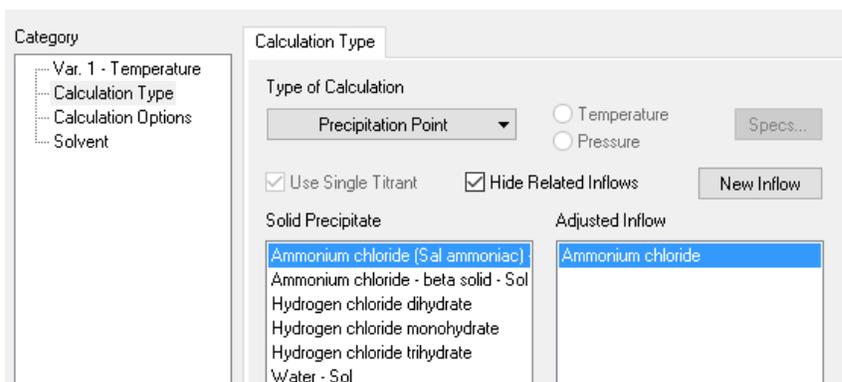
- ✓ Click on the Calculation Type category - 

- ✓ Change the Type of Calculation to Precipitation Point - 

- ✓ Select Sal Ammoniac as the solid to precipitate and ammonium chloride as the material to add -

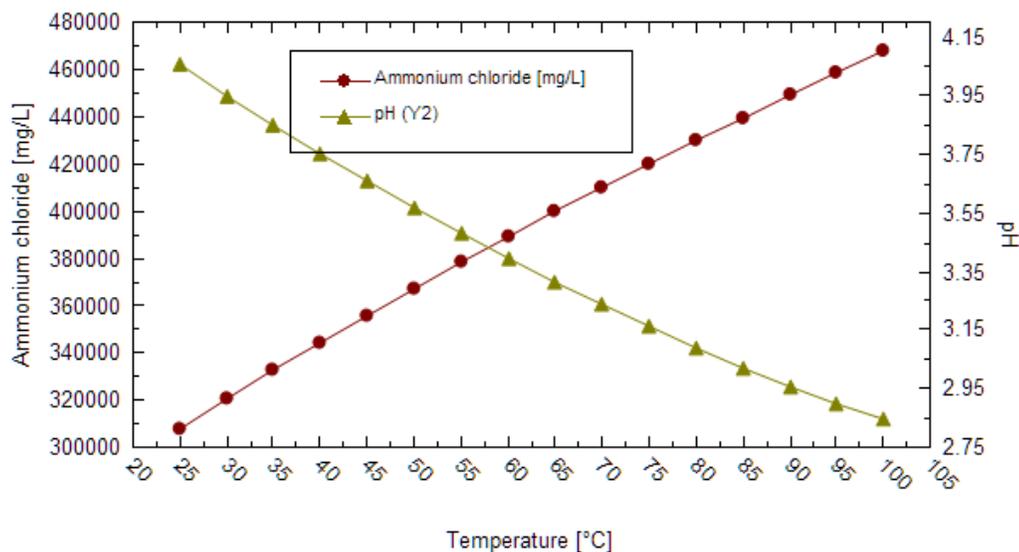


When complete, the screen should look like this:



- ✓ Click OK and calculate.
- ✓ Click on the Plot tab – the plot will be the NH₄Cl solubility.
- ✓ Click on the Variables button and expand the Additional Stream Parameters category.
- ✓ Add the pH to the Y2 axis.

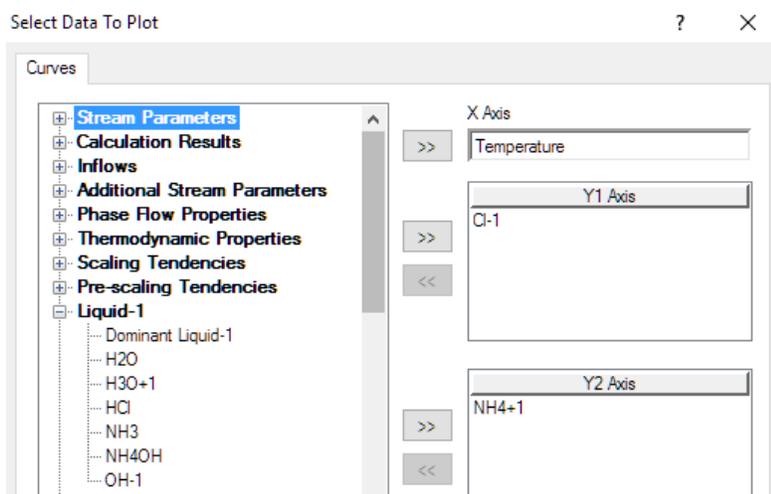
The dissolved NH₄Cl concentrations increases with temperature from 300,000 mg/l at 25C to about 460,000 mg/l at 100C. The pH decreases from 4.1 down to about 2.8 over the same range.



The calculation you ran is called a Precipitation Point. You instructed the software to add sufficient molecular NH₄Cl to the water until a small amount of NH₄Cl solid forms (~20 µg/l). The amount of NH₄Cl added is the saturation concentration, and is what gets plotted.

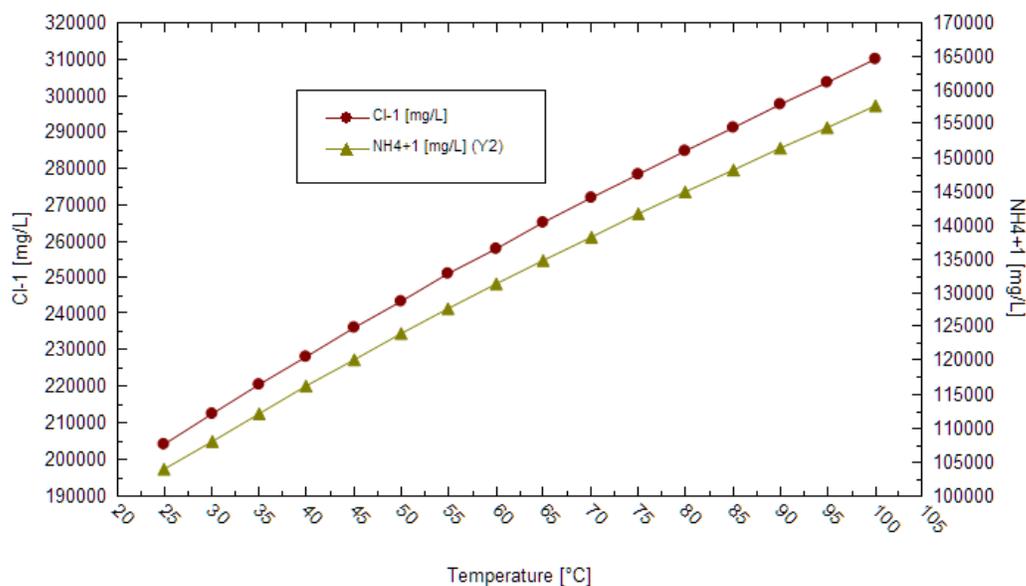
Investigate the water composition more deeply

- ✓ Click on the Variables button to access the Plot Variables
- ✓ Remove everything from the Y1 and Y2 axes
- ✓ Expand the Liquid-1 category
- ✓ Add the Cl-1 to the Y1 axis and NH₄+1 to the Y2 axis



- ✓ Close the window and view the plot

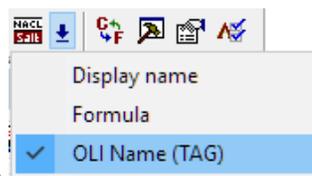
The concentrations of the Cl^{-1} and NH_4^{+1} ions increase proportionally. Because of the mole weight difference ($\text{Cl}^{-1} = 35.45 \text{ g/mole}$ and $\text{NH}_4^{+1} = 18.04 \text{ g/mole}$), the dissolved chloride is about twice the concentration of ammonium.



The plot instructions will stop here, but you are welcome to investigate further the variables that are available to plot.

Try amines important to your process

- ✓ Click back on the Definition tab.



- ✓ Change the Names manager selection to OLI Tag -

- ✓ Enter one of the amine-hydrochlorides from the list on the second page. Add it to the cell below the NH4Cl inflow.

The last column of the Page 8-2 table contains the OLI Tag Name for the amine hydrochloride. This is the most convenient way (fewest letters) to enter the names. So, it is our recommendation that you enter the names this way to minimize potential error.

The amine used in the images below is MEAHCl.

Inflows (mg/L)	
H2O	
NH4CL	0.0
MEAHCL	0.0

- ✓ Change the Adjusted Inflow and Precipitant to match the component you added.

Calculation Parameters	
Adjusted Inflow:	MEAHCL
Precipitant:	MEAHCL

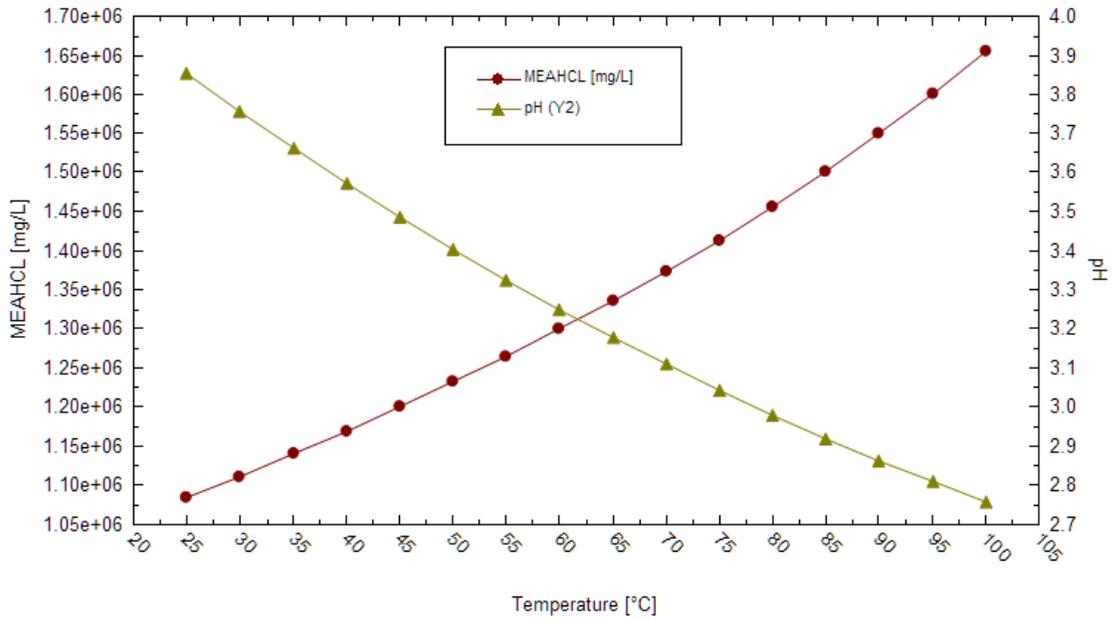
- ✓ Calculate.
- ✓ Click on the Plot.

- ✓ Open the Variables window - 

- ✓ Remove the existing Y1 and Y2 axis variables.
- ✓ Open the Inflows category and move the component you added to the Y1 axis.



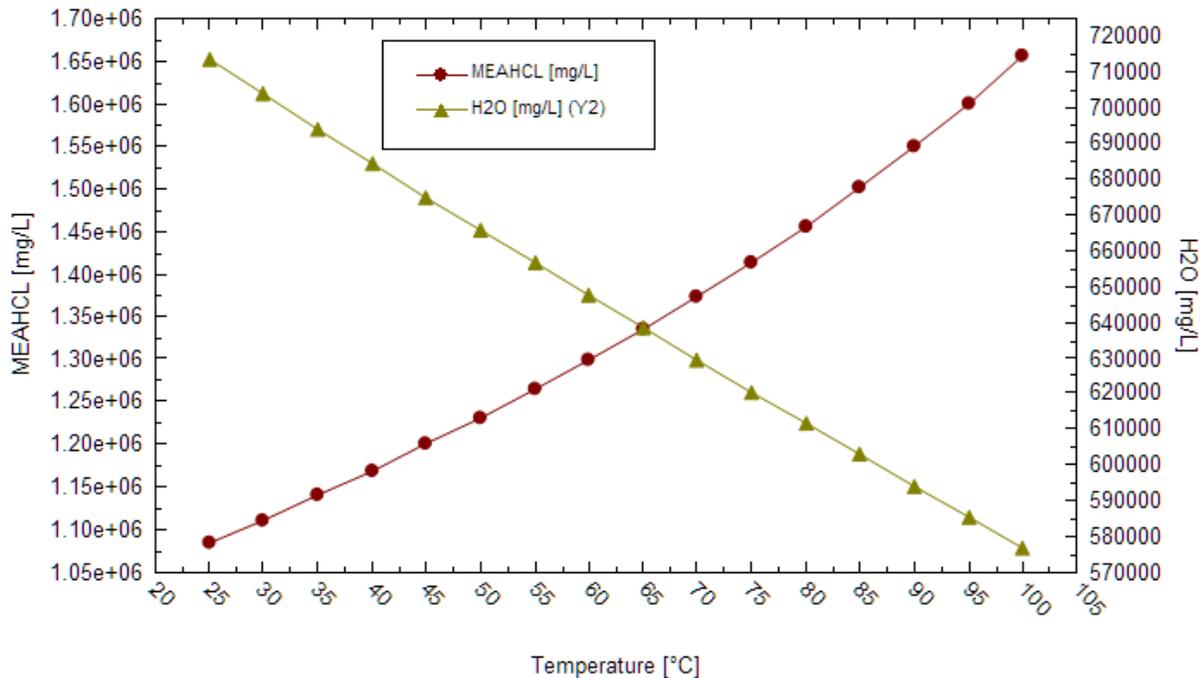
- ✓ Add pH to the Y2 axis if not there. It is found in the Additional Stream Parameters category.
- ✓ Close the window and view the amine-HCl solubility and solution pH.

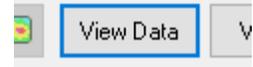


In the example above, MEAHCL solubility in water is between 1.05×10^6 and 1.65×10^6 mg/l. This may seem as unrealistic, initially, however since the density of this fluid is well above 1, it is reasonable to have concentrations above 10^6 mg/l. Confirm this now

- ✓ Return to the Variables window, and remove the pH variable from the Y2 axis
- ✓ Expand the Liquid-1 category and add H2O to the Y2 axis.

The H2O concentration in the liquid decreases from 827,000 mg/l to 478,000 mg/l. At 25C, for example the total mass of MEAHCL and H2O in the liquid is 827000+1470000





- ✓ Click on the View Plot button in the upper right to view the calculated data

At each temperature, the total concentration per liter is the sum of the MEAHCL and H2O. These values approach about 1.8e6 mg/l. That puts the density of the liquid at about 1.8 g/ml.

	Temperature	MEAHCL	H2O
	°C	mg/L	mg/L
1	25.0000	1.08339e6	7.13681e5
2	30.0000	1.11098e6	7.03716e5
3	35.0000	1.13948e6	6.93963e5
4	40.0000	1.16897e6	6.84382e5
5	45.0000	1.19954e6	6.74946e5
6	50.0000	1.23130e6	6.65630e5
7	55.0000	1.26438e6	6.56417e5
8	60.0000	1.29893e6	6.47295e5
9	65.0000	1.33512e6	6.38252e5
10	70.0000	1.37315e6	6.29282e5
11	75.0000	1.41326e6	6.20380e5
12	80.0000	1.45570e6	6.11543e5
13	85.0000	1.50078e6	6.02772e5
14	90.0000	1.54887e6	5.94068e5
15	95.0000	1.60038e6	5.85437e5
16	100.000	1.65582e6	5.76887e5

- ✓ Confirm this. Reopen the Variables list and expand the Additional Stream Parameters category
- ✓ Add the Density, Liquid-1 to the Y1 axis.
- ✓ Close the window and view the results

You can see that the density varies from 1.8 g/l to 2.2 g/l, a fairly dense electrolyte liquid.

	Temperature	MEAHCL	Density - Liquid-1	H2O
	°C	mg/L	g/ml	mg/L
1	25.0000	1.08339e6	1.79708	7.13681e5
2	30.0000	1.11098e6	1.81470	7.03716e5
3	35.0000	1.13948e6	1.83345	6.93963e5
4	40.0000	1.16897e6	1.85335	6.84382e5
5	45.0000	1.19954e6	1.87449	6.74946e5
6	50.0000	1.23130e6	1.89693	6.65630e5
7	55.0000	1.26438e6	1.92080	6.56417e5
8	60.0000	1.29893e6	1.94623	6.47295e5
9	65.0000	1.33512e6	1.97337	6.38252e5
10	70.0000	1.37315e6	2.00244	6.29282e5
11	75.0000	1.41326e6	2.03364	6.20380e5
12	80.0000	1.45570e6	2.06724	6.11543e5
13	85.0000	1.50078e6	2.10355	6.02772e5
14	90.0000	1.54887e6	2.14294	5.94068e5
15	95.0000	1.60038e6	2.18582	5.85437e5
16	100.000	1.65582e6	2.23270	5.76887e5

- ✓ Repeat these step for some of the other amine hydrochlorides.

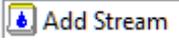
8.3 – NH₄Cl Salting in an Overhead Stream

Overview

The following example uses a 1-kg hydrocarbon gas phase containing NH₃ and HCl to show how the software computes the NH₄Cl precipitation. The dew point temperature of this stream is about 102 C. Above this temperature a dry NH₄Cl solid precipitates. Below this temperature liquid water forms and the NH₄Cl solids that formed dissolve in it. As a result the plots generated from this calculation show a transition from a dry solid to a wet salt (ionic liquid) and eventually to a dilute boot water stream.

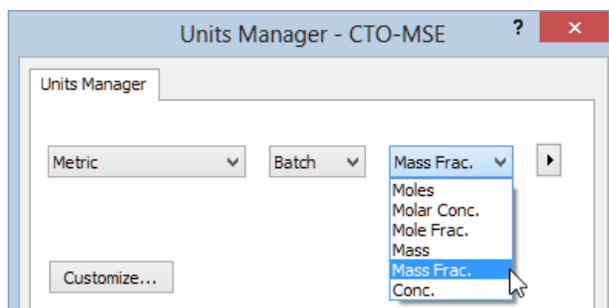
Creating the overhead stream

8.3 NH ₄ Cl Salting in an Overhead Stream					
Stream Name	CTO	Inflow	Mass %	Inflow	Mass %
Names Style	Display	NH ₃	0.001	Hexane	8
Units Set	Mass Fraction	HCl	0.001	Heptane	11
Framework	MSE	Propane	2	Octane	10
Stream Amount (kg)	1	butane	5	Nonane	10
Temperature (°C)	125	Pentane	6	Decane	11
Pressure (atm)	1			Dodecane	13

- ✓ Add a new stream 
- ✓ Rename the stream 'CTO' 
- ✓ In the toolbar, select the 2nd Liquid phase and the MSE button.



- ✓ Select the Units Manager  then use the third dropdown list to select Mass Frac.



- ✓ Press OK.
- ✓ Change the Temperature to 125 C.
- ✓ Enter the components and inflows (mass%) from the table above.
- ✓ Save the file.

Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00000
Temperature (°C)	125.000
Pressure (atm)	1.00000
Inflows (mass %)	
Water	23.9980
Ammonia	1.00000e-3
Hydrogen chloride	1.00000e-3
Propane	2.00000
n-Butane	5.00000
n-Pentane	6.00000
n-Hexane	8.00000
n-Heptane	11.0000
n-Octane	10.0000
n-Nonane	10.0000
n-Decane	11.0000
n-Dodecane	13.0000

Variable	Value
Stream Parameters	
Stream Amount (kg)	1.00000
Temperature (°C)	125.000
Pressure (atm)	1.00000
Inflows (mass %)	
H2O	23.9980
NH3	1.00000e-3
HCl	1.00000e-3
C3H8	2.00000
C4H10	5.00000
C5H12	6.00000
C6H14	8.00000
C7H16	11.0000
C8H18	10.0000
C9H20	10.0000
C10H22	11.0000
C12H26	13.0000

CTO stream with the Formula View and standard Display Name view

- ✓ Add a Survey calculation Add Survey

In this calculation, we will fix the temperature and vary the total system energy. To see what phases form, we will look at a broad temperature range. Later, we will focus on specific production conditions.

- ✓ Press the <F2> key to rename the survey object 'Temperature Survey'

The screen looks identical to the original stream, except the inflow cells are now colored yellow (un-editable) and there is a calculations section in upper right.

The default survey is temperature. The default temperature range is 25 C to 100 C by 5 C increments (see the summary section).

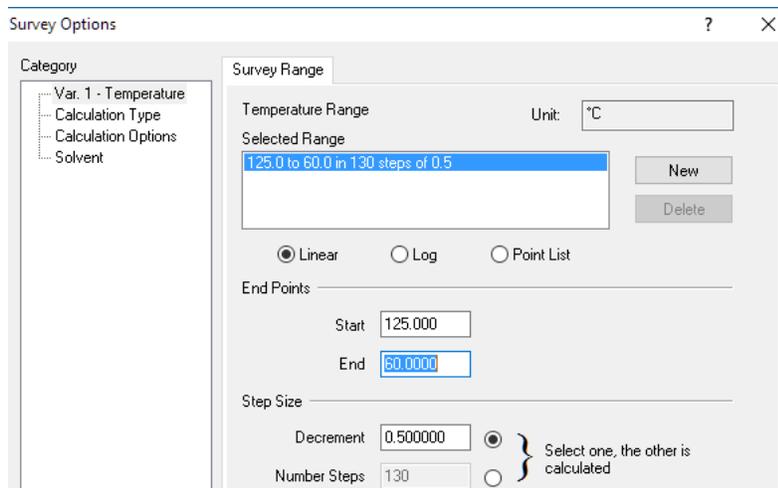
Summary	
Temperature survey:	
Range	25.0 to 100.0 °C
Step size	5.0 °C
No. steps	15

This will be modified to start at 125 C and decrease to 60 C.

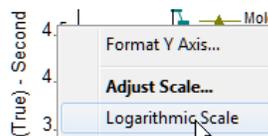
- ✓ Select the Specs button and change the Survey Range to:

Temperature Survey	
Start	125
End	60
Decrement	0.5

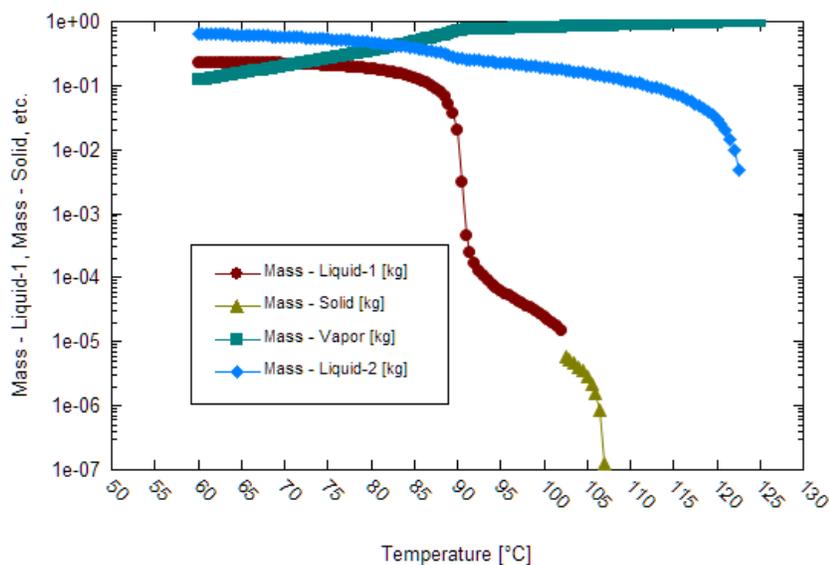
Your window should look like the following:



- ✓ Press OK then Calculate.
- ✓ Select the Plot tab.
- ✓ Right-click on the Y1 Axis and select the Logarithmic scale.



The plot that is produced contains the calculated mass of each phase. Gas is the dominant phase at high temperatures and oil dominates at low temperatures. The water phase increases exponentially over a twenty-degree range (105 C to 85 C).



According to the calculations, a solid phase forms at 107 C and disappears (dissolves into the water) at 102 C. A water phase (Liquid-1) condenses at 102 C forms. As temperature decreases, the water mass increases from $\sim 1.5e-5$ kg (@102 C) to ~ 0.232 kg (@60 C).

The Naphtha phase (Liquid-2) condenses at 122.5 C and increases as temperature decreases. Likewise the gas flow decreases as it cools. You can also view the calculated data instead of the viewing the plot using



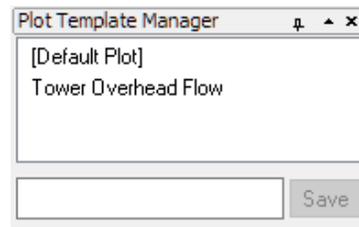
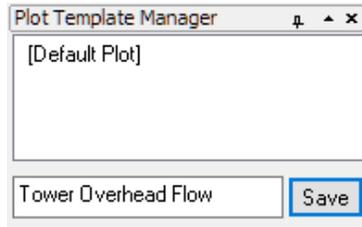
the View Data button.

The solids phase is NH4Cl although it is not obvious from this plot. So we will change the variables.

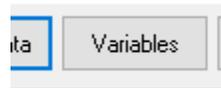
Saving to the Plot Template Manager

Before changing the plot, save the current plot parameters as a template for later use.

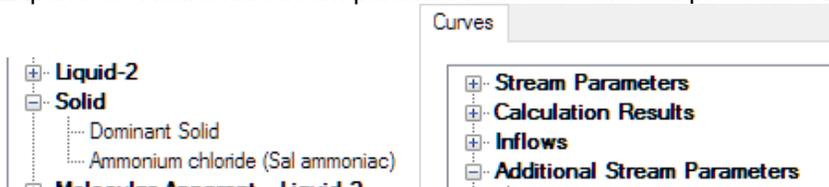
- ✓ Enter the name Tower Overhead Flow in the Plot Template Manager panel (lower left panel) and press the Save button.



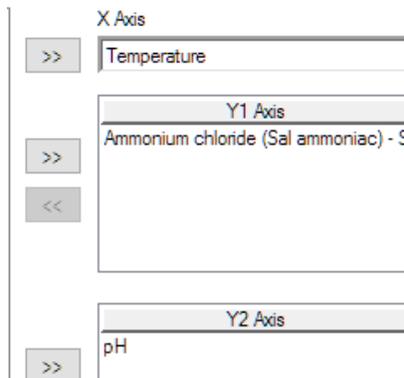
Modifying the plot



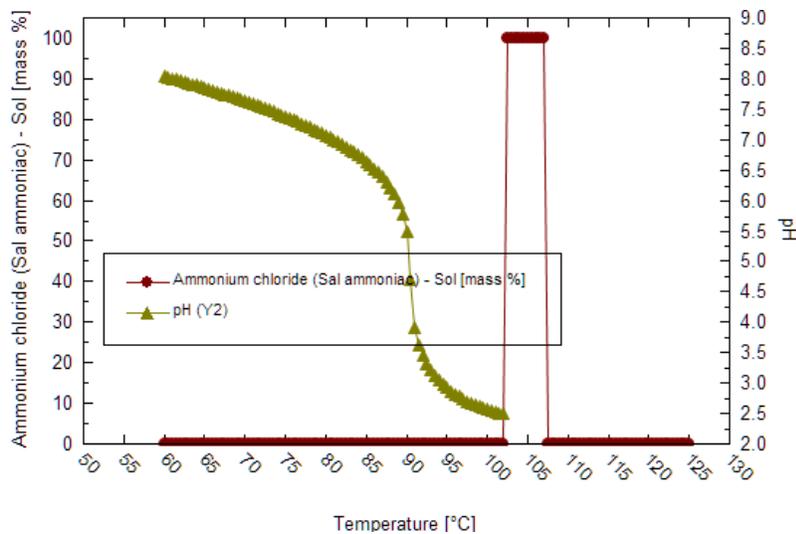
- ✓ Click on the Variables button in the upper right
- ✓ Remove all the variables from the Y1 axis.
- ✓ Expand the Solid category and add Ammonium chloride to the Y1 axis.
- ✓ Expand the Additional stream parameters section and add pH to the Y2 axis.



The Y1 and Y2 fields should look like this:



- ✓ Press OK and view the plot.
- ✓ Change the Y1 axis back to linear by right-mouse-clicking on the axis and selecting Logarithmic Scale (it is checked and this will uncheck it).



The plot isn't that convenient to look at because the solids units are mass%, which is mass% of the total solid mass. To view it with more clarity you will change the Solids units to mass.

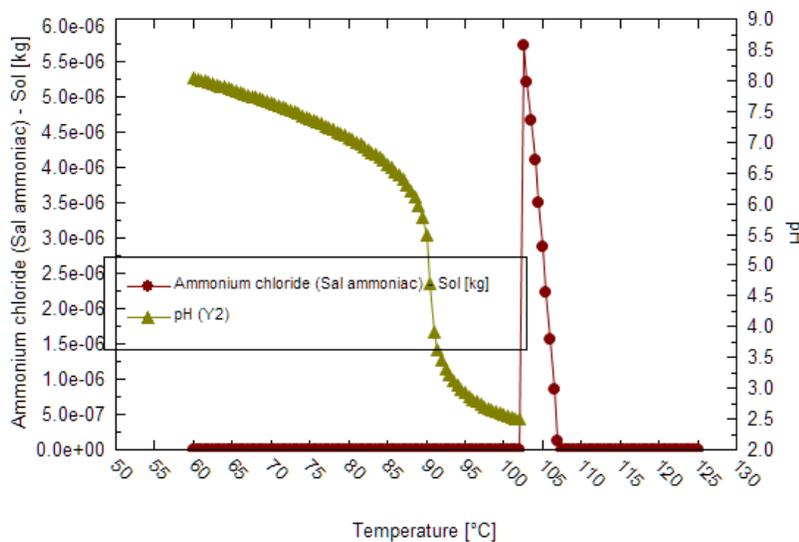
- ✓ Click on the Units Manager button in the Toolbar ribbon - 

Customize...

- ✓ Click on the Customize button
- ✓ Then change the Solids Composition from Mass Fraction to Mass

Vapor Composition	Mass Fraction	mass %
Solid Composition	Mass	kg
2nd Liquid Composition	Mass Fraction	mass %

- ✓ Close the windows to view the plot.
- ✓ Click OFF the Plot (e.g. to Definition) and Click back on again – this is needed to update the plot units.



As temperature decreases the NH_4Cl mass increases until water starts to condense. At this point, the NH_4Cl dissolves into the water phase.

At the water condensation temperature (102 C) the computed water pH is 2.5, acidic. The pH increases slightly to about 4 as the temperature decreases to 91 C. Then it increases sharply below this temperature. The cause of the sharp increase is the exponential increase in water mass which dilutes the dissolved HCl.

✓ Save the file  .

8.4 – Creating an Accumulator Inlet Stream

Overview

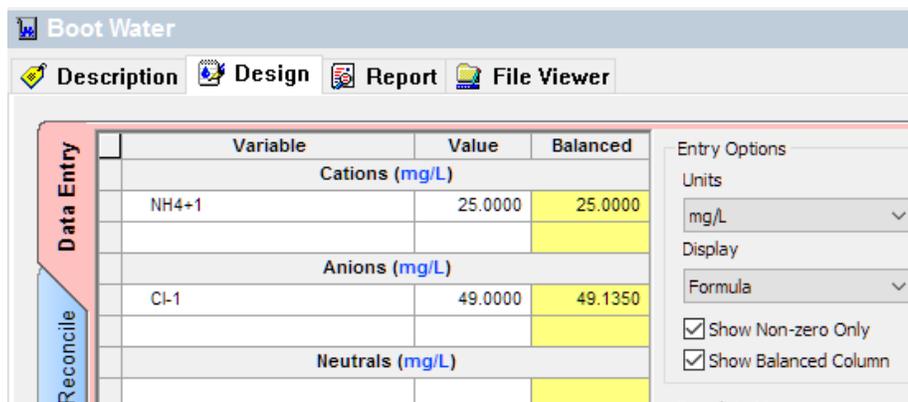
The purpose of this section is to show you how to create the overhead stream. An overhead stream is created by combining the exit streams from the accumulator. These streams include the Naphtha, Off Gas, and Boot Water. The composition and flow rate of each stream is required for this procedure to work.

You will create three analysis objects; a gas, an oil and a water. You will also use the Studio: ScaleChem analysis tools; Add Gas, Add Oil and Add Brine.

Creating the Brine Analysis object – The boot water analysis

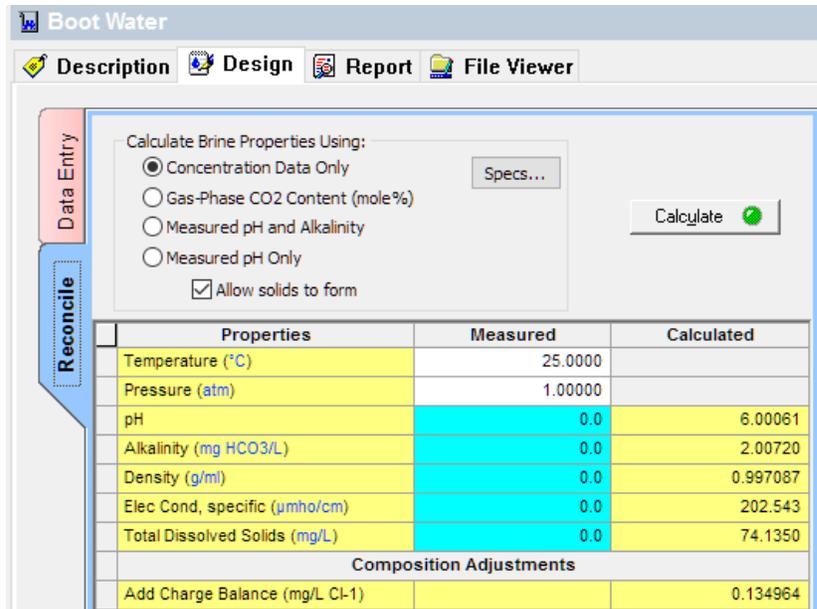
- ✓ Click on the Add Brine Analysis object in the Actions panel -  Add Brine Analysis .
- ✓ Label the object **Boot Water**.
- ✓ Click the MSE framework button  in the menu bar.
- ✓ Select the So and 2nd buttons -  in the menu bar.
- ✓ Type in NH₄⁺ in the first available cation cell and enter a value of 25 mg/l.
- ✓ Enter Cl-1 concentrations of 49 mg/l.
- ✓ Select the Show Non-zero button.

The screen should look like the one below.



Variable	Value	Balanced
Cations (mg/L)		
NH ₄ ⁺	25.0000	25.0000
Anions (mg/L)		
Cl-1	49.0000	49.1350
Neutrals (mg/L)		

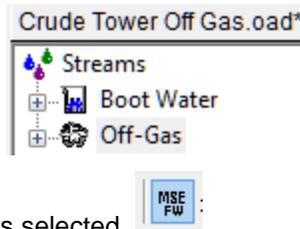
- ✓ Click on the blue Reconcile tab (it's a vertical tab)
- ✓ Click on the Allow Solids to form button
- ✓ Press the Calculate button



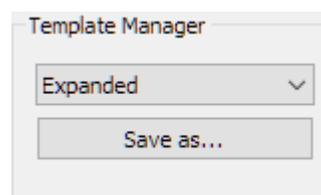
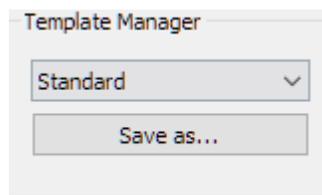
The software computes that this simple ammonium chloride salt solution is slightly acidic.

Adding the Off-Gas analysis

- ✓ Add a new Gas Analysis Add Gas Analysis
- ✓ Rename it 'Off-Gas'.



- ✓ Make sure the MSE button is selected
- ✓ Click on the Standard button in the Template Manager and change to to Expanded.



The Expanded Template contains a larger hydrocarbon list. This eliminates the need to enter all the component names manually. But you will have to add Hydrogen to the bottom of the list.

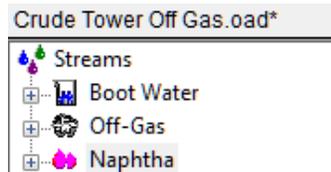
- ✓ Enter the following Off Gas composition:

Gas Composition	(mole %)	Gas Composition	(mole %)
Hydrogen	2.5	Isobutane	9.7
Nitrogen	4.6	n-Butane	16
Carbon dioxide	2.5	Isopentane	5.3
Hydrogen sulfide	0.5	n-Pentane	4.3
Methane	19.4	n-Hexane	3.45
Ethane	12.35	n-Heptane	0.3
Propane	19.	n-Octane	0.1

- ✓ Click on the Reconcile tab and press Calculate.
- ✓ Look to the right of the screen at the Summary table – confirm that the system is 100% vapor.

Adding the Naphtha analysis

- ✓ Add a new Oil Analysis  Add Oil Analysis
- ✓ Rename it 'Naphtha'.



- ✓ Make sure the MSE button is selected.
- ✓ Enter the following Naphtha composition:

Naphtha Composition	(mole %)	Naphtha Composition	(mole %)
Methane	0.12	n-Hexane	17.5
Ethane	0.3	n-Heptane	18.4
Propane	0.78	n-Octane	15.2
Isobutane	2.5	n-Nonane	15.4
n-Butane	1.7	n-Decane	12.2
Isopentane	4.9	Carbon dioxide	0.2
n-Pentane	10.7	Hydrogen sulfide	0.1

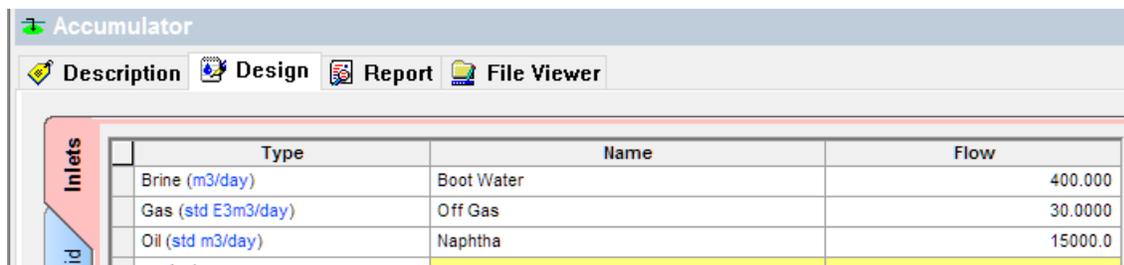
- ✓ Click on the Reconcile tab and press Calculate.
- ✓ Look to the right of the screen at the Summary table – confirm that the system is 100% liquid-2.

Create an Accumulator

- ✓ Add a Saturator object  Add Saturator and rename it 'Accumulator'  Accumulator
- ✓ Add the following boot water, off-gas, and naphtha flows to the Inlets grid:

Phase type	Phase Name	Flow Rate	units
Brine	Boot water	400	m3/day
Gas	Off-gas	30	std E3m3/day
Oil	Naphtha	15000	std m3/day

Your screen should look like the one below.



- ✓ Set the Accumulator conditions to 55 C and 1.7 bar.

Conditions	Value
Temperature (°C)	55.0000
Pressure (bar)	1.70000

- ✓ Calculate.
- ✓ Review the Report.

Phase Properties

Parameter	Liquid-1	Vapor	Liquid-2
pH	4.42117		8.23521
Mass (kg/day)	3.92096e5	68793.4	1.02920e7
Moles (True) (kgmol/day)	21761.9	1470.63	1.00899e5
Density (g/ml)	0.985551	2.97712e-3	0.648925
Specific Electrical Conductivity (µmho/cm)	356.705		4.66408e-12
Ionic Strength (x-based) (mol/mol)	2.61829e-5		9.15889e-18
Ionic Strength (m-based) (mol/kg)	1.45356e-3		2.12610e-13
Viscosity, absolute (cP)	0.504327	9.25709e-3	0.355511
Thermal Conductivity (cal/hr m °C)	555.790	19.8754	99.7637
Volume Units	m3/day	E3m3/day	m3/day
Volume	397.845	23.1074	15860.1
Volume, Std. Conditions Units	m3/day	std E3m3/day	std m3/day
Volume, Std. Conditions	393.300	34.1314	15010.4

According to the calculations, the boot water pH is 4.4 and the calculated gas and liquid volumes are consistent with what was added. Review the phase volumes and compare it to what you added.

Phase	Input volume	Calculated volume	Units
Boot Water	400	393.3	m3/day
Off Gas	30	34.1	Std E3m3/day
Naphtha	15000	15010	Std m3/day

The boot water volume has decreased and the off-gas and naphtha increased. This is the result of water partitioning to the vapor and oil phase. The input H2O for off gas and naphtha is 0%. The computed fraction is shown in the table below. This partitioning contributed to the calculated H2O volume reduction and hydrocarbon volume increase. It is a small, but quantifiable change.

Phase	Input H2O	Calculated H2O	Units
Off Gas	0	9.3	mole%
Naphtha	0	0.24	mole%

By comparison, the hydrocarbon components also partition to the water phase. According to the software calculation the boot water has as much dissolved organics (~32 mg/l), H2S (55 mg/l), and CO2 (as 123 mg/l HCO3-1), as the measured NH4+ and Cl-.

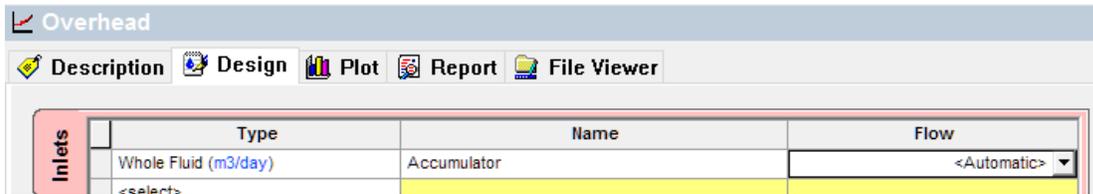
Brine Composition

Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)
NH4+	23.6976	Cl(-1)	49.4011	H2S	54.5688
		HCO3- (*)	122.735	N2	0.615538
				H	0.0537836
				C1	4.47369
				C2	4.56815
				C3	4.62043
				nC4	3.54142
				C6	2.31054

All this is to explain that what may be measured in a standard analysis can be an incomplete representation.

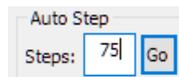
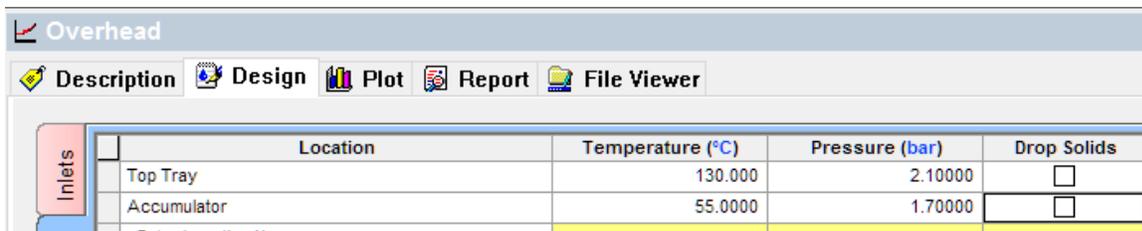
Modeling the overhead cooling process

- ✓ Add a Scale Scenario object and name the object Overhead.
- ✓ Add the Accumulator output to the Overhead as follows:
 - Type=Whole Fluid, Name= Accumulator, and Flow= <Automatic>



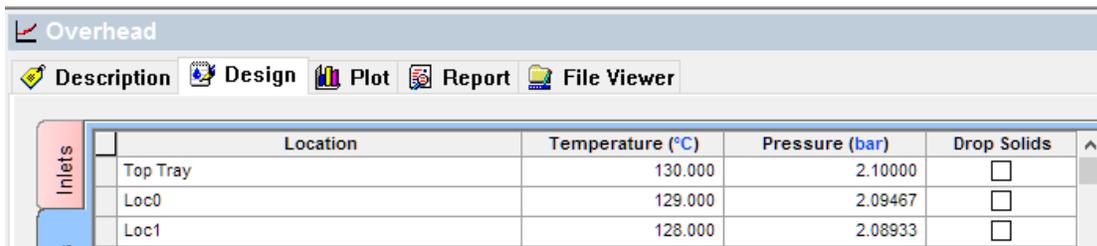
This brings in the output from the Accumulator into the overhead. Essentially, we are modeling the flow in reverse. But, since mass is presumed to be conserved from the top of tower (or from a wash water point) to the accumulator outlet, this is an acceptable approach. In this scenario we assume that there is no wash water and that mass is conserved from the top tray to the accumulator.

- ✓ Click on the Conditions Tab.
- ✓ Label the first condition Top Tray (type this name) and set the conditions to 130 C and 2.1 bar.
- ✓ Label the second condition Accumulator (type this name) and set the conditions to 55 C and 1.7 bar.

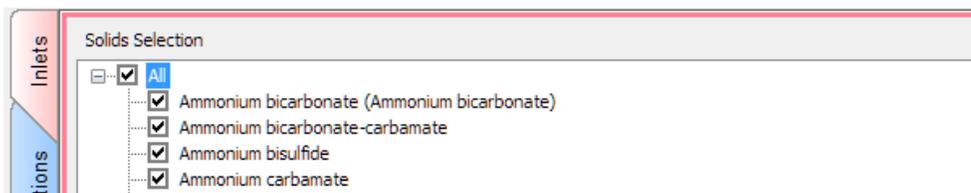


- ✓ Set the Auto Step field to 75 and click on the Go button.

This will put 75 calculations between the two conditions, and set the temperature decrement to 1 C and the pressure decrement to ~0.053 bar.



- ✓ Click on the Solid tab and Check the All box



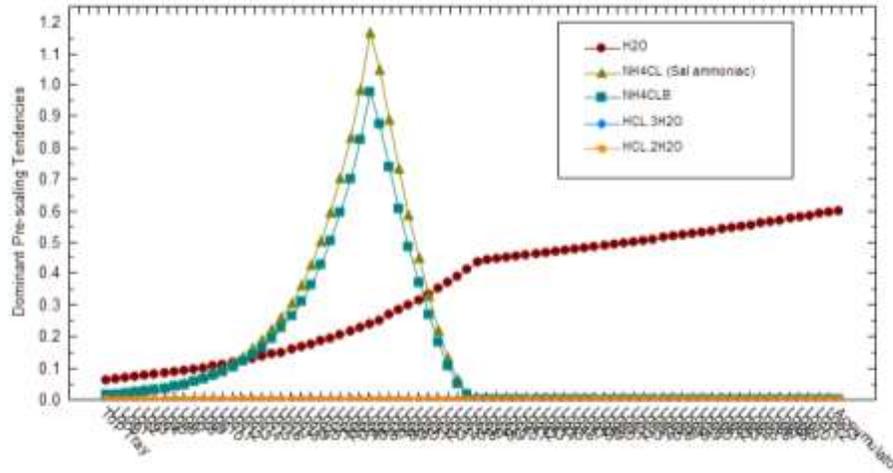
- ✓ Calculate.

The software will now compute the properties at each temperature, and we will look to see how the phase amounts change and if any solids form.

- ✓ Click on the Plot tab.

The default plot is the “Scale Tendencies” of any potential solids. A scale tendency is the driving force for a solid to form. If the value is greater than 1, then the solid can precipitate. If it is below 1, the solid is subsaturated and will not form.

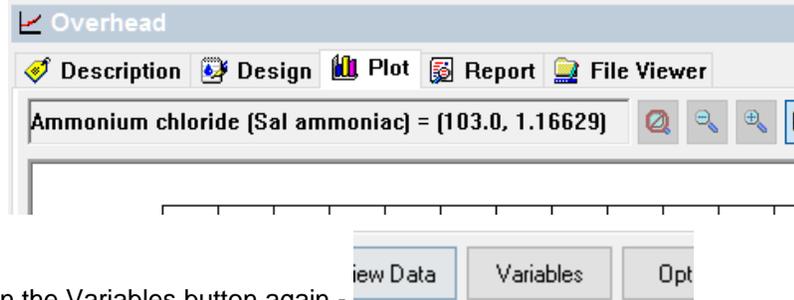
According to these results, one form of NH4Cl is computed to be supersaturated ($S > 1$) and will form, given enough time.



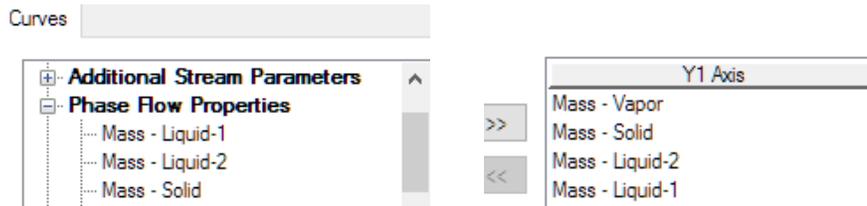
It is impractical to know at what condition the NH4Cl is occurring because the x-axis is the Location name, and they are bunched together. Therefore, we will need to change the X-axis variable to temperature.

- ✓ Click on the Variables tab in the upper right -
- ✓ Expand the Stream Parameters category – the Temperature variable is there -
- ✓ Highlight the Temperature variable and add it to the X-axis using the >> double arrows.
- ✓ Close the window and review the plot.
- ✓ Mouse over the highest point of the NH4Cl curve.

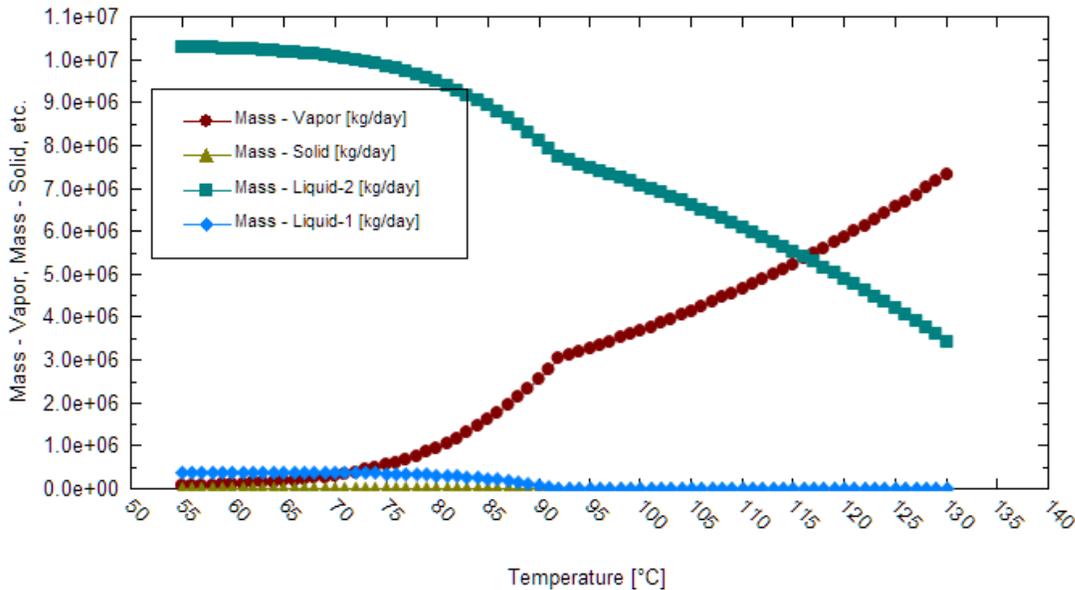
The marquee above the plot will display the point information. The NH4Cl solid has a saturation of 1.17 at 103 C. It is at this temperature that the software predicts that NH4Cl will precipitate.



- ✓ Click on the Variables button again -
- ✓ Delete the existing variable in the Y1 axis by double-clicking on it.
- ✓ Expand the Phase Flow Properties category and select the Mass for all four phases, Liquid-1, Liquid-2, Solid, and Vapor (do not select Total)

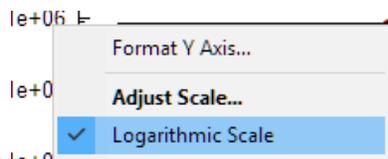


- ✓ Close the window.

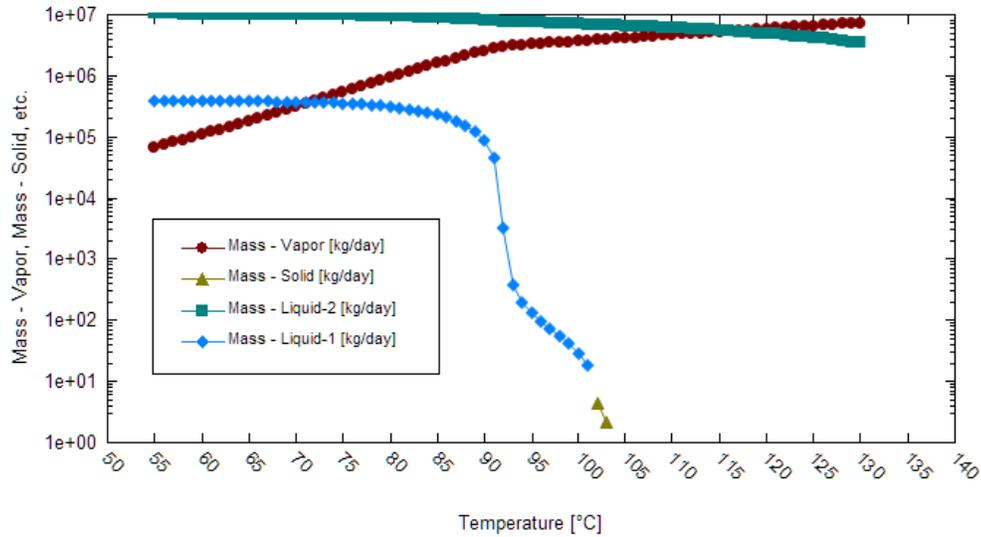


The four phases are shown, however they have different magnitudes. Therefore, the plot is better viewed with a logarithmic Y-axis.

- ✓ Right-mouse-click over the y-axis values (any value, but it must be within that vertical field).



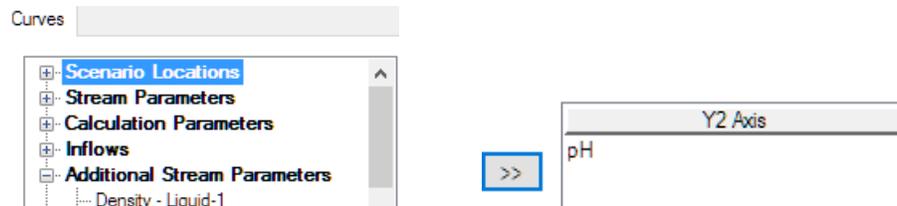
- ✓ Select Logarithmic Scale.



It is now easier to see the progression between the NH₄Cl solids and the water phase. According to the software, the critical temperatures begin at 103 C and end at 92 C. At 91 C, the water volume increases exponentially, essentially flushing the system.

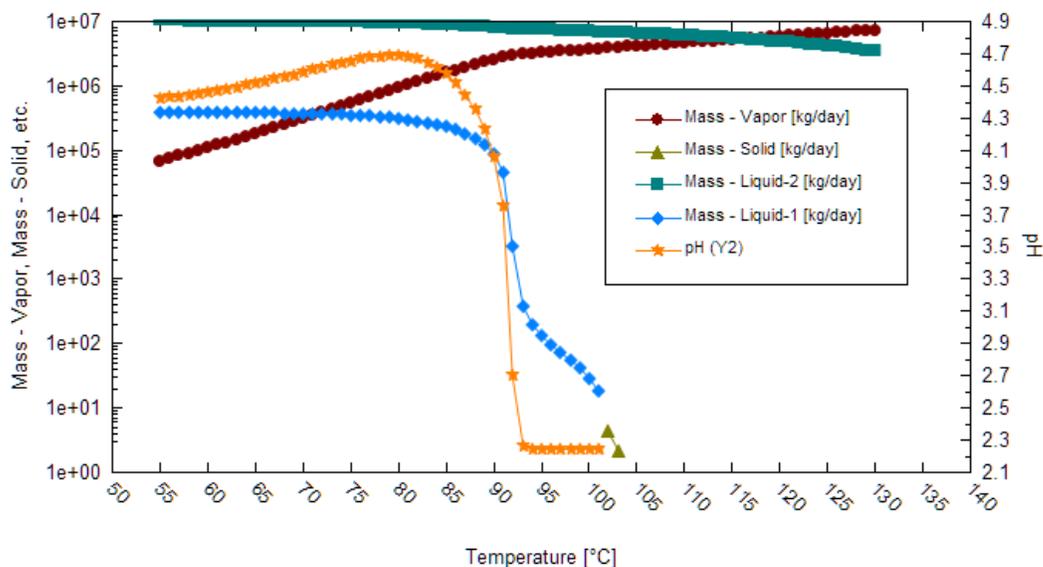
This temperature range is more substantive if the pH is plotted along with it. Therefore, you will plot the pH on the Y-2 axis.

- ✓ Open the Variables window again and expand the Additional Stream Parameters category..
- ✓ Add pH to the Y-2 axis.



- ✓ Close the window and view the plot.

This plot shows that at 103 and 102 C, a dry NH₄Cl solid phase is present. Below 102 C, water condenses and the NH₄Cl solid dissolves.



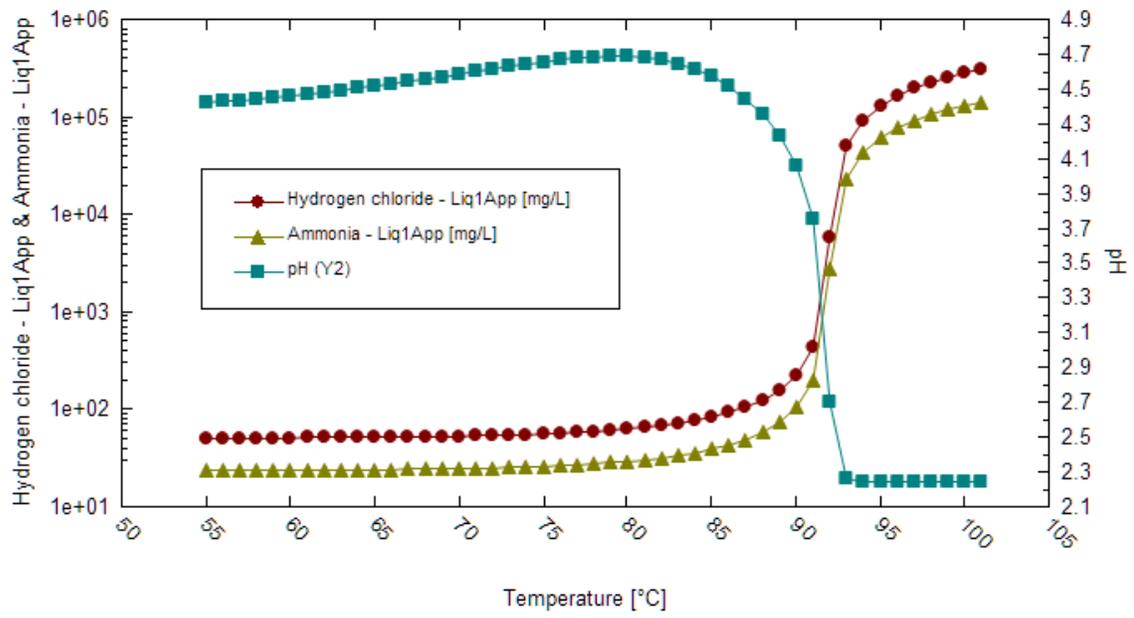
This plot also shows that between 101 C and 93 C the pH is flat at 2.2 and as the temperature drops to 91 C, the pH increases to 3.7. Thus, it is this lower end of this reverse S-shaped curve that is the potential region for aggressive corrosion. Below 92 C, there is substantial condensation, diluting of the dissolved ions, and increasing the pH.

This can be seen again by plotting the dissolved NH₃ and HCl- concentrations.

- ✓ Open the Variables window again.
- ✓ Remove all the variables from the Y-1 axis.
- ✓ Scroll to the bottom of the Category list to the Molecular apparent – Liquid 1.
- ✓ Open it and add NH₃ (ammonia) and HCl (hydrogen chloride) to the Y-1 axis.



The new plot shows that between 103 C and 93 C, the concentrations of NH₃ and HCl are above 100,000 mg/l. When the system cools to 91 C, the concentrations have dropped to about 400 mg/l. Thus, it is this high concentration (saline) and low pH condition between 101 C and 93 C where the water is aggressive to carbon steel.



8.5 – Overhead case using an Assay for Naphtha

Overview

This case uses OLI Studio: ScaleChem objects. The Studio ScaleChem tool was designed to work with upstream oil and gas production. However, we have found that it is useful as a tool for refinery applications as well.

The calculation objects we will use are the *Brine*, *Gas*, and *Oil Analysis* and the *Saturator*. We will start by creating accumulator output analyses (off gas, boot water, and naphtha). We will combine these analyses at their proper flow rates into the saturator object. At that point, we will transfer the results to another Studio ScaleChem object, the *Facilities* calculation, to complete the remaining work.

Available Data

The table below contains the compositions for the three phases we will use in this section. The table shows hydrocarbons as displays names and with their Names Dictionary names (if enabled).

Table 1 - Compositions of Brine (left), Gas (middle), and Oil (right) analyses

Boot water	mg/l	Off Gas	mole%	Naphtha	Values
Cations		Nitrogen	4.5	Name	Naphtha
NH4+	36	Carbon dioxide	1.7	Mole%	100
Anions		Hydrogen sulfide	1.2	Type	ASTM D86
Cl-1	30	Methane	5.7	Thermo	API-8
SO3-2	32	Ethane	6	Density	63
HS-1	6	Propane	22	Density units	API Gravity
HCO3-1	15	Isobutane	12	No. of Cuts	13
Neutrals		n-butane	26	Volume%	Temp. C
Propionic acid	10	Isopentane	8	1	45.8
n-butanoic acid	25	n-pentane	7	5	67.4
Ethylenediamine (ENAMN2)	15	n-hexane	5	10	81.3
2-Dimethylaminoethanol (DMEXH)	15	Hydrogen	0.3	20	102.4
2-Aminoethanol (MEXH)	30	Ethene	0.2	30	119.8
3-Methoxypropylamine (MOPA)	5	Propene	0.15	40	135.4
		Trans-2-butene	0.02	50	151.7
		1-butene	0.04	60	169.5
		Cis-2-butene	0.02	70	188.6
		Isobutylene	0.17	80	209.1
				90	232.5
				95	247.9
				100	255.

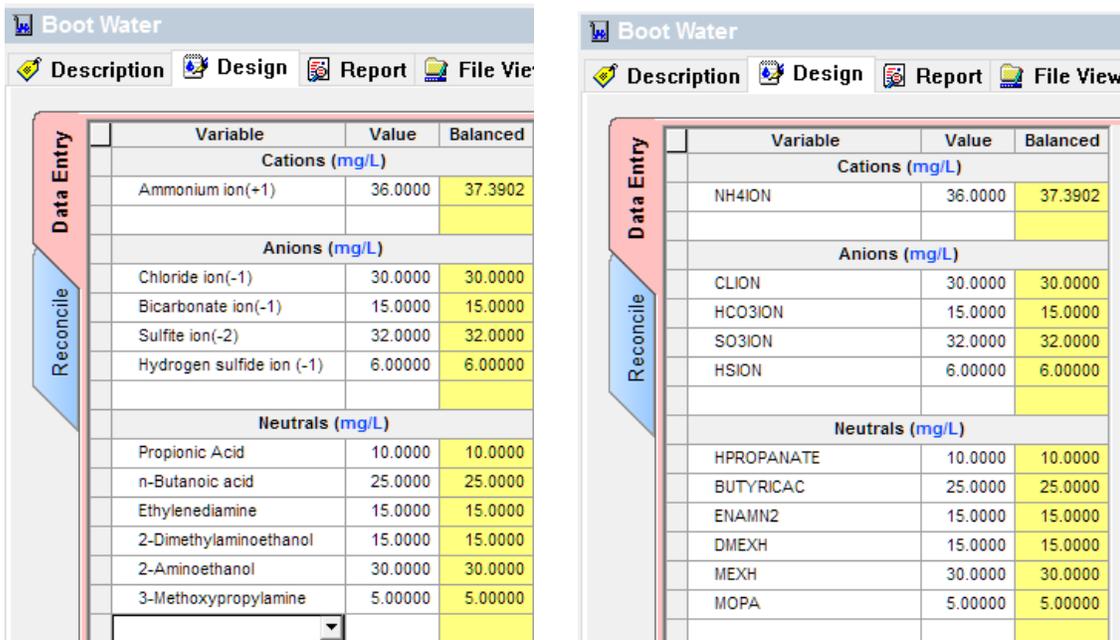
Adding the Boot Water analysis

- ✓ Continue working in the Chapter 8 file or start a new file called 'Crude Tower Off Gas'.
- ✓ Add a new Brine Analysis by selecting the icon  Add Brine Analysis from the Actions pane or from the menu bar Streams > ScaleChem > Add Brine.
- ✓ Rename the brine Boot Water  Boot Water
- ✓ Click the MSE framework button  in the menu bar.

We should not have to select the MSE button again. However, we should check to see it is enabled while adding other objects.

- ✓ Select the So and 2nd buttons -  in the menu bar.
- ✓ Type in NH₄⁺ in the first available cation cell and enter a 36 mg/l value.
- ✓ Enter the remaining anion concentrations (Cl⁻ at 30mg/L, HCO₃⁻ at 15mg/L, SO₃⁻ at 32 mg/L, and HS⁻ at 6 mg/L). You will have to add the SO₃⁻ anion to the list.
- ✓ Add the neutral species and their concentrations from Table 1.
- ✓ Select the Show Non-zero button.

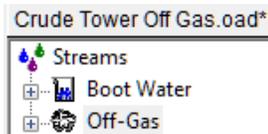
The screen should look like the one below.



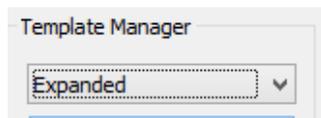
Variable	Value	Balanced
Cations (mg/L)		
Ammonium ion(+1)	36.0000	37.3902
Anions (mg/L)		
Chloride ion(-1)	30.0000	30.0000
Bicarbonate ion(-1)	15.0000	15.0000
Sulfite ion(-2)	32.0000	32.0000
Hydrogen sulfide ion (-1)	6.00000	6.00000
Neutrals (mg/L)		
Propionic Acid	10.0000	10.0000
n-Butanoic acid	25.0000	25.0000
Ethylenediamine	15.0000	15.0000
2-Dimethylaminoethanol	15.0000	15.0000
2-Aminoethanol	30.0000	30.0000
3-Methoxypropylamine	5.00000	5.00000

Adding the Off-Gas analysis

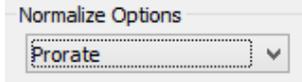
- ✓ Add a new Gas Analysis  Add Gas Analysis
- ✓ Rename it 'Off-Gas'.



- ✓ Make sure the MSE button is selected 
- ✓ In the Design tab, change the Template Manager to Expanded.



- ✓ Select the Normalize Options button and change to Prorate.



- ✓ Change the Display button to Display Name.



- ✓ Enter the Off Gas composition from above.
- ✓ Stop at n-Hexane [nc6].

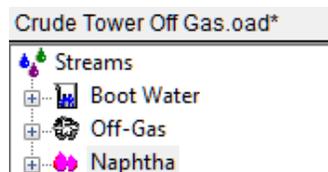
We will need to type in the names of the last seven inflows.

- ✓ Type in the component names from Hydrogen to Isobutylene from Table 1.
- ✓ When finished, select the Show Non-zero Only button.

Component	Value	Normalized
Water	0.0	0.0
Nitrogen	4.50000	4.50000
Carbon dioxide	1.70000	1.70000
Hydrogen sulfide	1.20000	1.20000
<input checked="" type="checkbox"/> Methane	5.70000	5.70000
Ethane	6.00000	6.00000
Ethene	0.200000	0.200000
Propane	22.0000	22.0000
Propene	0.150000	0.150000
n-Butane	26.0000	26.0000
trans-2-Butene	0.0200000	0.0200000
1-Butene	0.0400000	0.0400000
cis-2-Butene	0.0200000	0.0200000
Isobutane	12.0000	12.0000
Isobutylene	0.170000	0.170000
Hydrogen	0.300000	0.300000
n-Pentane	7.00000	7.00000
Isopentane	8.00000	8.00000
n-Hexane	5.00000	5.00000

Adding the Naphtha analysis

- ✓ Add a new Oil Analysis Add Oil Analysis
- ✓ Rename it 'Naphtha'



- ✓ Make sure the MSE button is selected.

In some versions of the OLI Studio: ScaleChem, an inconvenience occurs when switching from the Aqueous to the MSE frameworks. There will be red x's, which are components not recognized in the MSE database. These inflows have to be deleted before proceeding.

- ✓ Select the Combined tab if not already there
- ✓ Select each of the red x's and press the delete key.



	cis-2-Hexene	0.0	0.0
--	--------------	-----	-----

We can now proceed with our work.

- ✓ Select the Assay tab.



- ✓ Enter the name 'ASSAY' in the Component cell and give it a value of 100%.

Component	mole %
ASSAY	100.000

- ✓ Enter the data from Table 1.

The screen should look like the one below:

Component	mole %
NAFTA	100.000

Volume%	Temperature (°)
1.00000	45.8000
5.00000	67.4000
10.0000	81.3000
20.0000	102.400
30.0000	119.800
40.0000	135.400
50.0000	151.700

- ✓ Select the Display Assay Cuts button.

The calculated Assay properties are generated. The data shown in the main table are the critical properties the boiling point, density, and molecular weight for each cut. The name, e.g., NAFTA_254K is constructed from the name you entered plus the normal boiling point in Kelvin.

There are a series of tabs below this table. These tabs contain the thermodynamic properties for each assay cut. We can select any of these tabs to view this data in more detail.

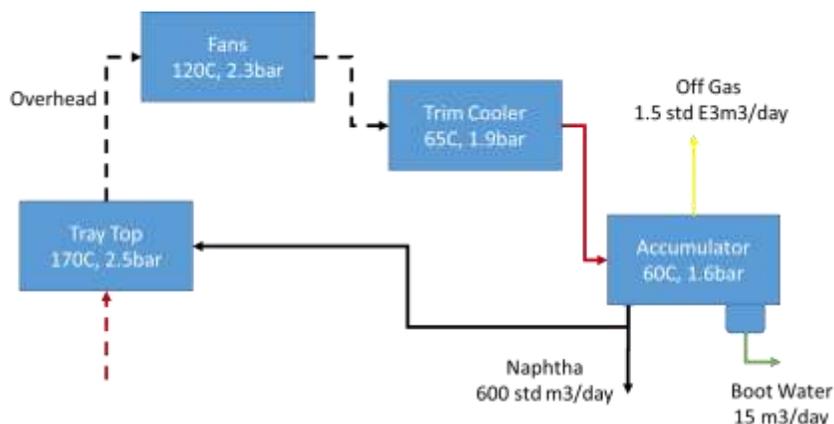
Name	Mol Wt.	NBP (°C)	Sp Gr	Cr Tem	Cr Pres	Cr Vol (Acentric
NAFTA_2	49.7544	-19.0402	0.61638	141.396	46.2857	0.21648	0.163728
NAFTA_2	59.0910	6.20751	0.63616	170.172	40.2103	0.25517	0.195496
NAFTA_3	68.4698	29.6262	0.65346	196.173	36.0269	0.29354	0.225560
NAFTA_3	78.2842	52.3944	0.66944	221.096	32.7745	0.33306	0.255601
NAFTA_3	89.4729	76.5163	0.68559	247.212	29.8970	0.37752	0.288519
NAFTA_3	101.532	100.651	0.70101	273.028	27.4152	0.42503	0.322762
NAFTA_3	113.835	123.569	0.71505	297.200	25.3233	0.47332	0.352213
NAFTA_4	127.674	147.579	0.72920	322.108	23.3452	0.52758	0.389074

Summary | NAFTA_254K | NAFTA_279K | NAFTA_303K | NAFTA_326K | NAFTA_350K

At this point, we should have entered all of the experimental data. Now we will create a representative overhead gas.

The process to model

The simple schematic below is the process to be modeled. The diagram contains the flow rates for each output and the naphtha reflux. The diagram also shows the estimated output temperature and pressure at each process point.



Creating a Saturation object to model the accumulator

The Studio ScaleChem *Saturator* object works effectively as an isothermal mixer. It accepts volumetric flows from multiple inlet streams and generates a single output. This is what the Accumulator represents if it were to be modeled in reverse flow.

- ✓ Add a Saturator object and rename it 'Accumulator'

We will now modify the units.

- ✓ Select the Units Manager object -

- Select the Customize button.
- Select the Parameters tab.
- Change the Pressure units to bar.

Pressure	bar
----------	-----

- Change the time units to day.

Time	day
------	-----

- Select the Inlets tab -
- Change ALL the flows to match the table below:

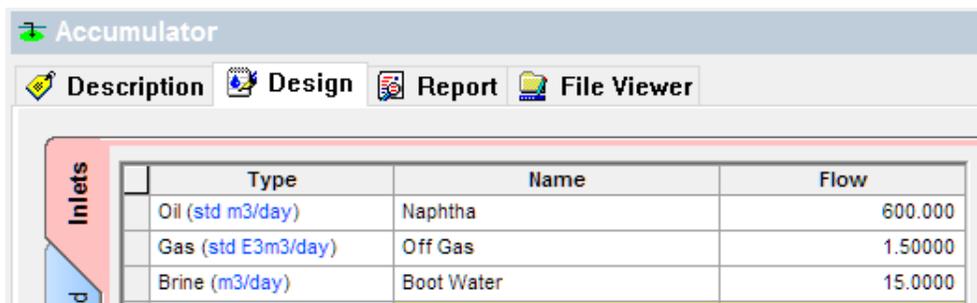
Variable	Units
Brine Quantity	m3/day
Oil Quantity	std m3/day
Gas Quantity	std E3m3/day
Whole Fluid Quantity	m3/day

- ✓ Press OK twice to exit the Units Manager (some clients may have to restart the software to enable the new units).

- ✓ Use the Type, Name, and Flow cells to enter the three outlets as inlets to the accumulator:

Type	Name	Flow	Units
Oil	Naphtha	600	Std m3/day
Gas	Off Gas	1.5	Std E3m3/day
Brine	Boot Water	15	m3/day

The screen should look like the one below:

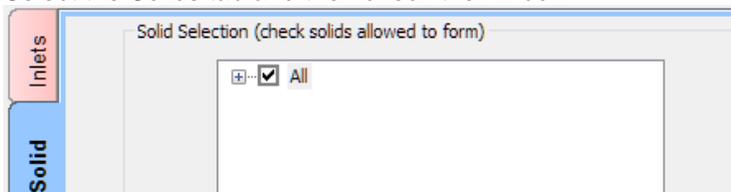


- ✓ Enter the accumulator output conditions of 60 C and 1.6 bar.

Conditions	Value
Temperature (°C)	60.0000
Pressure (bar)	1.60000

We are not creating a custom refinery units set in this chapter. Creating such units would eliminate the constant clicking on the Units Manager button. The instructor can detail how to create custom refinery units after this application.

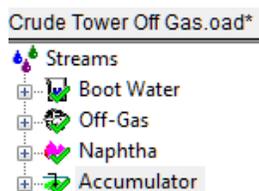
- ✓ Select the Solids tab and then check the All box



- ✓ Press the Calculate button.

The software will first compute reconciliation and other calculations for the Brine, Gas, and Oil analysis objects. Once these objects converge, the Saturator object will calculate.

As each object is calculated, a green check will appear next to its icon in the Navigator pane. This assures that the calculations are complete.



- ✓ Review the Report. The summary and properties should look like the following:

Saturation Summary
Row Filter Applied: Only Non-Zero Values

Accumulator 01/13/2017

Inlets Summary

Type	Name	Flow	Unit
Oil	Naphtha	600.000	std m ³ /day
Gas	Off Gas	1.50000	std E3m ³ /day
Brine	Boil Water	15.0000	m ³ /day

Stream Properties

Stream Amount	1502.00	m ³ /day
Temperature	60.0000	°C
Pressure	1.60000	bar

Phase Properties

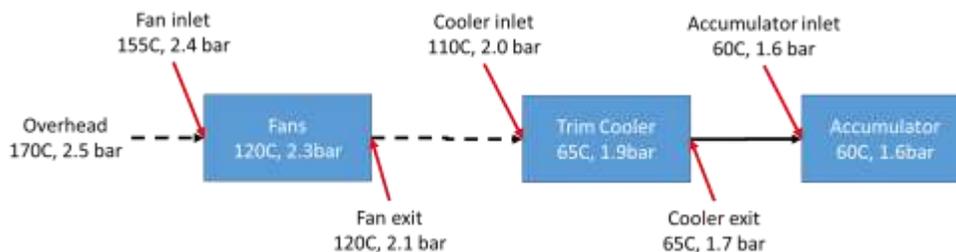
Parameter	Liquid-1	Vapor	Liquid-2
pH	6.85404		10.0155
Mass (kg/day)	14747.4	2695.58	4.37602e5
Moles (True) (kgmol/day)	818.471	52.2998	3674.96
Density (g/ml)	0.983295	3.05372e-3	0.724170
Specific Electrical Conductivity (µmho/cm)	642.908		4.60262e-11
Ionic Strength (x-based) (mol/mol)	5.51903e-5		1.40857e-16
Ionic Strength (m-based) (mol/kg)	3.06433e-3		5.58324e-12
Viscosity, absolute (cP)	0.466807	8.80878e-3	0.563470
Thermal Conductivity (cal/hr m °C)	560.065	18.4269	94.2957
Volume Units	m ³ /day	E3m ³ /day	m ³ /day
Volume	14.9980	0.882718	604.280
Volume, Std. Conditions Units	m ³ /day	std E3m ³ /day	std m ³ /day
Volume, Std. Conditions	14.7896	1.20653	603.085

Notice that in this case, the calculated off-gas volume is different from the value entered. This is in part because of mixing between the vapor and the liquid.

✓ Save the file.

Studying the overhead gas properties across the production line

The mass does not change from the tower overhead to the accumulator in this simple process. Such a simplification enables us to limit the modeling complexity. We will continue with the simulation by using the Facilities object to model different points in the production line. We are now modeling the following section of the process. The temperature and pressures are now annotated on the diagram.



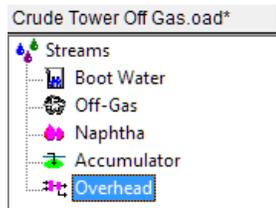
Simulate the cooling using the Facilities Calculation object

The Facilities calculation object is a pseudo-process simulator. This object allows the user to add and separate streams at various process points. This object is ideal for the case we are studying.

The facilities object uses the term *Node* to represent different locations in a process. A node can represent a specific process unit or simply a location along a pipe. Nodes are isothermal calculations. Node Outputs

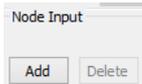
can be set up as a separator, in which each phase moves to a different location, or it can be set so that all phase remain together.

- ✓ Add a Facilities object  **Add Facilities** and label it 'Overhead'.



- ✓ Select the 2nd Liquid button (it may already be checked) - 
- ✓ Confirm that the volumes are in m3 and pressure in bar. If not, the select the Units Manager and choose Scale Metric-Flowing-Conc. If you are using an OLI Studio version below V9.3.2 then you may need to do additional units editing through the Customize window.

We are ready to add the process nodes to the object.

- ✓ Select the Add button to add the first Node - 
- ✓ Double-click the node box change its name to 'Tower Top'.



- ✓ Enter the temperature and pressure of the tower top in the cells provided.

Conditions	Value
Temperature (°C)	170.0
Pressure (bar)	2.5

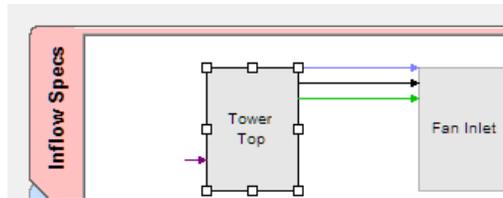
- ✓ Select the Type cell and select Whole Fluid.
- ✓ Select Accumulator [MSE] as the Name.
- ✓ Keep the <Automatic> flow.

The screen should look like the one below:

Type	Name	Flow
Whole Fluid (m3/day)	Accumulator	<Automatic>
<select>		

- ✓ Create a new Node and rename it 'Fan Inlet'.
- ✓ Enter the temperature and pressure of the fan inlet – 155 C and 2.4 bar.
- ✓ Enter the Fan Inlet streams.
 - Select the Type cell and select Whole Fluid From.
 - Select Tower Top as the Name.

This action takes the fluid from the **Tower Top** node and sends it to this node. The screen should now show that the **Tower Top** stream is flowing into the **Fan Inlet**.



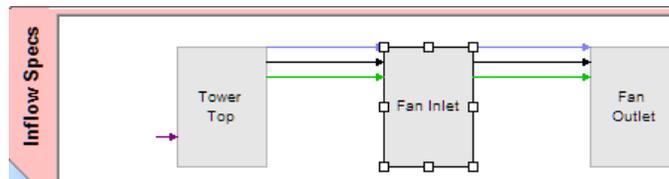
The lower section should look like this. The type is Whole Fluid from and the Name is Tower Top. Notice the units are unimportant here, since the flow rate is defined in the tower top object.

Conditions		Value
Temperature (°C)		155.0
Pressure (bar)		2.4

Type	Name	Flow
Whole Fluid from (m3/day)	Tower Top	Calculated
<select>		

- ✓ Add a new node and rename it 'Fan Outlet'.
- ✓ Enter the conditions 120 C and 2.1 bar.
- ✓ Select Whole Fluid from in the Type Cell and **Fan Inlet** in the Name cell.

The top of the screen should now look like the one below:



The grid section should look like this:

Conditions		Value
Temperature (°C)		120.0
Pressure (bar)		2.1

Type	Name	Flow
Whole Fluid from (m3/day)	Fan Inlet	Calculated
<select>		

- ✓ Repeat the steps for the three remaining nodes, Trim Cooler Inlet, Trim Cooler Outlet, and Accumulator.

This is the screen after the Trim Cooler Inlet is complete:

Conditions		Value
Temperature (°C)		110.0
Pressure (bar)		20.0

Type	Name	Flow
Whole Fluid from (m3/day)	Fan Outlet	Calculated
<select>		

This is the screen after the **Trim Cooler Outlet** is added:

Conditions		Value
Temperature (°C)		65.0
Pressure (bar)		1.7

Type	Name	Flow
Whole Fluid from (m3/day)	Cooler Inlet	Calculated
<select>		

This is the screen after the **Accumulator inlet** is added. Notice that the Separate Gas, Oil, and Solids boxes are checked, and that four arrows exit the node.

Conditions		Value
Temperature (°C)		60.0
Pressure (bar)		1.6

Type	Name	Flow
Whole Fluid from (m3/day)	Cooler Outlet	Calculated
<select>		

- ✓ Select the Solids button. 
- ✓ Select the ALL button, so that any solid that can precipitate will form.



- ✓ Save the file.

We are now ready to calculate.

- ✓ Calculate.
- ✓ View the Report tab.

- ✓ Scroll down the report and view the phase property table, specifically the solids mass.

Some report sections contain a solids column, and others will not. For example, the tables below are for the Fan Inlet location. The software computes 0.32 kg/day of Ethylenediamine-HCl solids at this location.

Calculated Details: Fan Inlet Stream Properties

Stream Amount	42415.1	m ³ /day
Temperature	155.000	°C
Pressure	2.40000	bar

Phase Properties

Parameter	Vapor	Solid	Liquid-2
pH			6.26024
Mass (kg/day)	2.11220e5	0.324481	2.43824e5
Moles (True) (kgmol/day)	2947.53	2.43932e-3	1598.23
Density (g/ml)	5.01808e-3	1.21000	0.754206
Specific Electrical Conductivity (µmho/cm)			
Specific Electrical Conductivity			1.79266e-6
Ionic Strength (x-based) (mol/mol)			
Ionic Strength (x-based)			4.36320e-14
Ionic Strength (m-based) (mol/kg)			
Ionic Strength (m-based)			4.18740e-10
Viscosity, absolute (cP)	9.43655e-3		0.825605
Thermal Conductivity (cal/hr m °C)	26.6223		87.7639
Volume Units	E3m ³ /day	m ³ /day	m ³ /day
Volume	42.0918	2.88166e-4	323.286
Volume, Std. Conditions Units	std E3m ³ /day		std m ³ /day
Volume, Std. Conditions	86.0240		322.885

Pre and Post Scaling Tendencies

Scale Mineral	Max Scale (mg/L)	Pre-scaling	Pre-index	Post-scaling	Post-index
Ethanolamine hydrochloride	0.0	6.75294e-3	-2.16986	0.0	0.0
Ethylenediamine dihydrochloride	0.324481	7.56751	0.878953	0.0	0.0
Ammonium chloride - base solid	0.0	1.73981e-3	-1.50096	0.0	0.0

The Fan outlet report shows that there is a water phase present. Its pH is 3.5 and there are still solids that form; 0.25 kg/day.

Calculated Details: Fan Outlet Stream Properties

Stream Amount	34566.9	m ³ /day
Temperature	120.000	°C
Pressure	2.10000	bar

Phase Properties

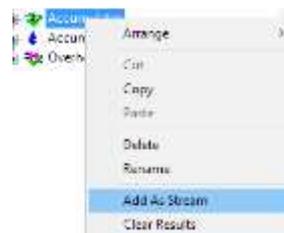
Parameter	Liquid-1	Vapor	Solid	Liquid-2
pH	3.47445			6.62595
Mass (kg/day)	0.606263	1.33112e5	0.254169	3.21931e5
Moles (True) (kgmol/day)	0.0178653	2266.36	1.91074e-3	2279.39
Density (g/ml)	2.62043	3.89957e-3	1.21000	0.745642
Specific Electrical Conductivity (µmho/cm)	6.65928e5			2.91606e-8
Ionic Strength (x-based) (mol/mol)	0.442935			6.70799e-14
Ionic Strength (m-based) (mol/kg)	57.9456			6.42199e-10
Viscosity, absolute (cP)	0.506895	8.08653e-3		0.729279
Thermal Conductivity (cal/hr m °C)	482.942	23.9724		90.4617
Volume Units	m ³ /day	E3m ³ /day	m ³ /day	m ³ /day
Volume	2.31360e-4	34.1351	2.10057e-4	431.751
Volume, Std. Conditions Units	m ³ /day	std E3m ³ /day		std m ³ /day
Volume, Std. Conditions	2.42993e-4	51.4122		431.374

Pre and Post Scaling Tendencies

Scale Mineral	Max Scale (mg/L)	Pre-scaling	Pre-index	Post-scaling	Post-index
Ethanolamine hydrochloride	0.0	0.0753988	-1.12264	0.109352	-0.961173
3-Methoxypropylamine hydrochloride	0.0	6.43803e-4	-3.19125	8.37208e-4	-3.07717
Ethylenediamine dihydrochloride	1.08959e5	1.44433	0.159665	1.00000	0.0
Ammonium chloride - base solid	0.0	0.0194291	-1.71157	0.0249355	-1.60318

Perform the same calculation using a multi-point survey

There is a more intensive way to run this calculation, but additional information is obtained. You will create a stream from the accumulator calculation, and add a Survey calculation to it. Then you will set this survey calculation to perform one hundred calculations and small temperature changes.



- ✓ Right-mouse click on the Accumulator and select Add as Stream.
- ✓ Click on the new stream and change the units to Metric-Flowing-Mass.

Then click on Customize and change the Mass to Kg, the volume to m3, time to day, and pressure to bar.

Variable	Basis	Units
Inflow variables		
Stream Amount	Mass	kg/day
Inflow	Mass	kg/day
Output variables		
Aqueous Composition	Mass	kg/day
Vapor Composition	Mass	kg/day
Solid Composition	Mass	kg/day
2nd Liquid Composition	Mass	kg/day
Total Composition	Mass	kg/day
Basis options		
Moles		mol/day
Mass		kg/day
Volume		m ³ /day
Concentration		mg/L
Molar Concentration		mol/L
Mass Fraction		mass %
Heat Fraction		wt% H ₂ O

Variable	Units
Temperature	°C
Pressure	bar
Time	day
Alkalinity	mg HCO ₃ /L
Density	g/ml
Electrical Conductivity, molar	m ² /ohm-mol
Specific Electrical Conductivity	µmho/cm
Energy	cal/day
Energy, Molar	cal/mol
Entropy	cal/K day
Entropy, Molar	cal/mol K
Fugacity	atm
Heat Capacity	cal/g K
Ionic Strength (x-based)	mol/mol
Ionic Strength (m-based)	mol/m

- ✓ Add a Survey calculation.
- ✓ Change the Then-by survey to Pressure.
- ✓ Click the Together Vary button.

Survey by

Temperature ▼ Specs...

Then by (optional)

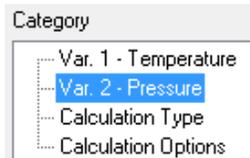
Pressure ▼ Specs...

Vary

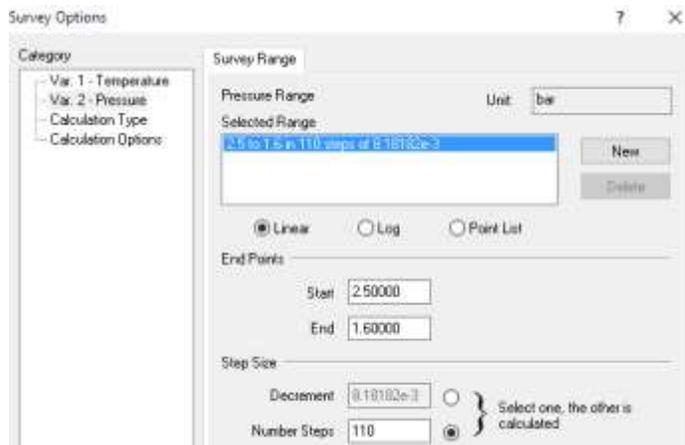
Independently

Together

- ✓ Click on the first Specs button in the upper right.
 - Set the starting temperature at 170 C.
 - Set the end temperature to 60 C.
 - Set the decrement to 1 C.
- ✓ Click on the Pressure category.



- Set the starting Pressure to 2.5 bar.
- Set the end temperature to 1.6 bar.
- Set the number of steps to 110.

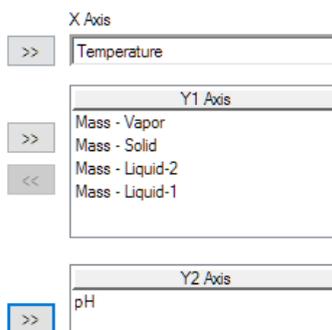


- ✓ Close the window and Calculate.
- ✓ Click on the Plot tab.
- ✓ Change the Y-axis to a log scale. Right-mouse-click on the axis and select Logarithmic Scale.

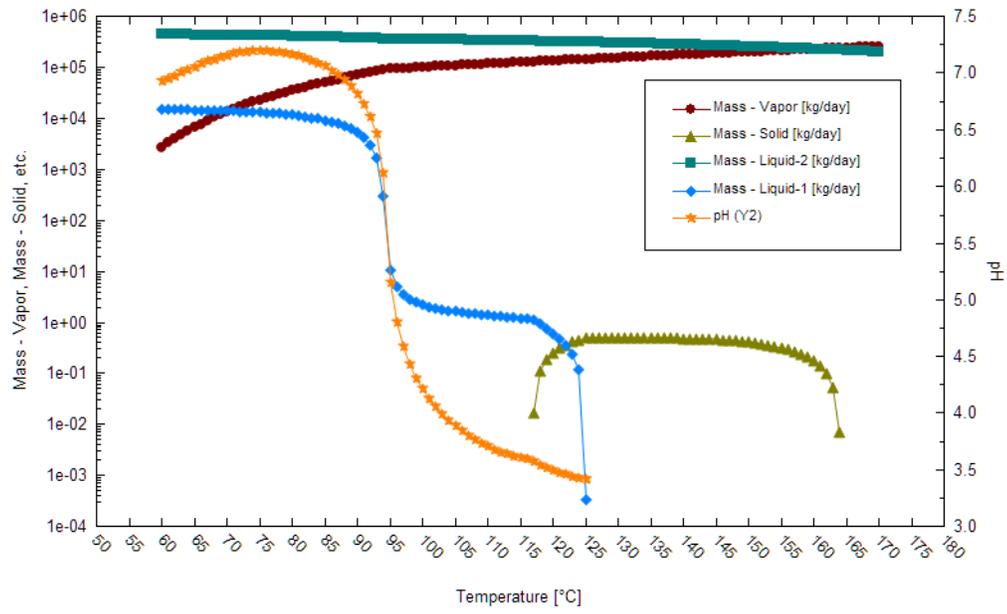


The plot displays the amounts of the four phases. A solid phase (ethylenediamine-HCl) starts forming at 164 C, and continues to 117 C. At 125 C, the water phase forms.

- ✓ Click on the Variables window, expand the Additional Stream Parameters category and add the pH to the Y2-axis.



The pH of the condensing water is about 3.4. Therefore in this case the aggressive corrosion risk would be between 125 C and 100 C, where water is present and the pH is relatively low.



8.6 – Kmetz-Truax curve

Overview

This case uses the Survey object in OLI Studio: Analyzer to study the carbonate, ammonia, sulfide, and polysulfide speciation associated with Alkaline Carbonate Stress Corrosion Cracking, ACSCC.

Information provided by authors reported in NACE 34108¹ are contained in the following table. These are the compositions/conditions where materials are susceptible to ACSCC and also conditions where ACSCC is avoidable. The report was clear that the controlling conditions had not been confirmed in the field.

Author	pH	CO3-2 (ppm)	H2S	Polysulfide (active sulfide)	Temperature, F	E _{Corr} (SCE)
Kmetz and Truax						
	>9	>100				
	8 to 9	>400				
						-500 to -600
Schutt						
	>9	>800	<0.5% (total S)			
		>1200	>0.5% (total S)			
API 581						
	7.6		>50 ppm			
Med risk	7.6 to 8.4	>1000				
Med risk	>9	100 to 500				
High risk	8.4 to 9	>1000				
High risk	9.0	>400				
API RP-571						
	7.6		50 ppm			
	>9	>100				
	8 to 9	>400				
Schutt – Controlling ACSCC						
	>8			25 ppm	<150	
	>8			25-250 ppm	150-230	
	>8			250 ppm	<230	

The plan in this section is to model the speciation of ammonia, sulfide, carbonate, and polysulfide as a function of pH and temperature. These plots were also referred to in the NACE publication and provided as appendices.

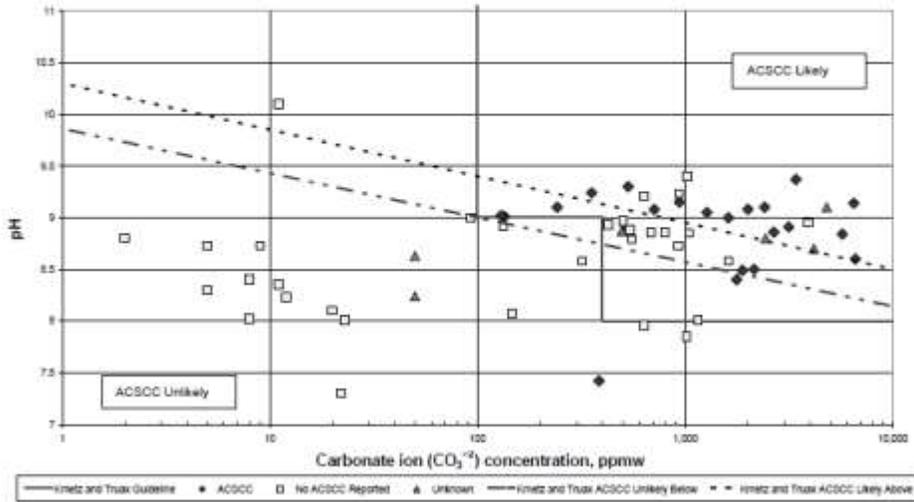
The plot below is a reference to the speciation to be created and its comparison to the reported pH and carbonate associated with ACSCC. The plan is to use speciation to examine this plot more thoroughly.

¹ Review and Survey of Alkaline Carbonate Stress Corrosion Cracking in Refinery Sour Waters. NACE Publication 34108. Task Group 347 Petroleum Refineries, Environmental Cracking: Reviews of Carbonate Stress Corrosion Cracking. (2008).

Appendix C
Proposed Guidelines for ACSCC Susceptibility

This appendix is intended to provide supplementary information only, although it may contain mandatory or recommending language in specifications or procedures that are included as examples of those that have been used successfully. Nothing in this appendix shall be construed as a requirement or recommendation with regard to any future application of this technology.

Figure C1



Kmetz and Truax guidelines that have been proposed to define the region where ACSCC is likely to occur along with the pH and carbonate ion concentration data from CORROSION'90 paper no. 206.⁴

Getting Started

- ✓ Create a new stream – label it Kmetz-Truax curve - [Kmetz-Truax Curve](#)
- ✓ Add the following components, $(\text{NH}_4)_2\text{CO}_3$, CO_2 , H_2S , NH_3 , NaOH , Na_2S_5 .
- ✓ Set the units to Metric – Batch – Mass Fraction. Then select the Customize button to change the Mass Fraction units from mass% to ppm.

Your screen should look like the one below.

Kmetz-Truax Curve		
Description	Definition	Report
Variable	Value	
Stream Parameters		
Stream Amount (kg)	1.00000	
Temperature ($^{\circ}\text{C}$)	25.0000	
Pressure (atm)	1.00000	
Inflows (ppm (mass))		
H ₂ O	1.00000e6	
$(\text{NH}_4)_2\text{CO}_3$	0.0	
CO_2	0.0	
H_2S	0.0	
NH_3	0.0	
NaOH	0.0	
Na_2S_5	0.0	

- ✓ Add a Survey Calculation.
- ✓ Change the First Survey by from Temperature to pH.
- ✓ Set the second pH survey to Composition.

- ✓ Click the Together button in the Vary field.

Survey by
 pH ▾ Specs...

Then by (optional)
 Composition ▾ Specs...

Vary
 Independently
 Together

- ✓ Click on the first Specs. Button.
- ✓ Click on the Use Single Titrant box.
- ✓ Set the titrant to NH3.
- ✓ Click on the Survey Range tab.
- ✓ Set the Survey type to Point List.
- ✓ Add five points and set them to 10, 9.6, 9.2, 8.8, 8.4

pH Titrants Survey Range

Select an inflow to adjust to meet the sp

Use Single Titrant Hide Rela

Titrant

- (NH4)2CO3
- CO2
- H2O
- H2S
- HCLIN
- Na2CO3
- Na2S5
- NaOH
- NH3

pH Titrants Survey Range

Target pH Range Unit:

Selected Range

Point List: 10.0 to 8.4

Linear Log Point List

	Value
1	10.0000
2	9.60000
3	9.20000
4	8.80000
5	8.40000

- ✓ Click on the Var. 2 – Composition category.
- ✓ Set the Component inflow to CO2.
- ✓ Click on the Survey Range tab.
- ✓ Set the Survey type to Point List.
- ✓ Add five points and set them to 2.5, 45, 750, 10000, and 125000.

Component Survey Range

Component Inflows

Hide Related Inflows

- (NH4)2CO3
- CO2
- H2S
- Na2CO3
- Na2S5
- NaOH
- NH3

Component Survey Range

Composition Range Unit:

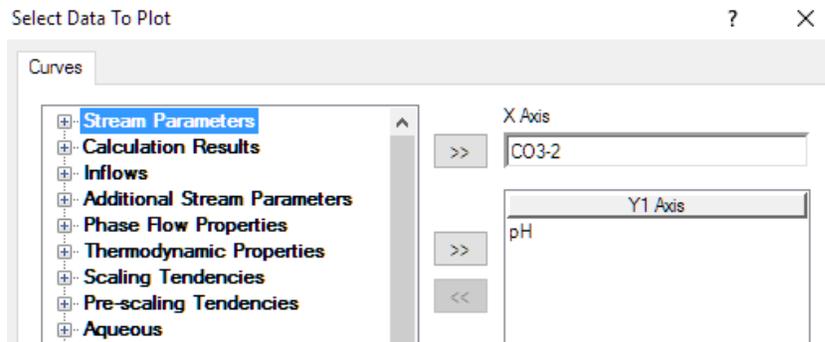
Selected Range

Point List: 2.5 to 1.25e5

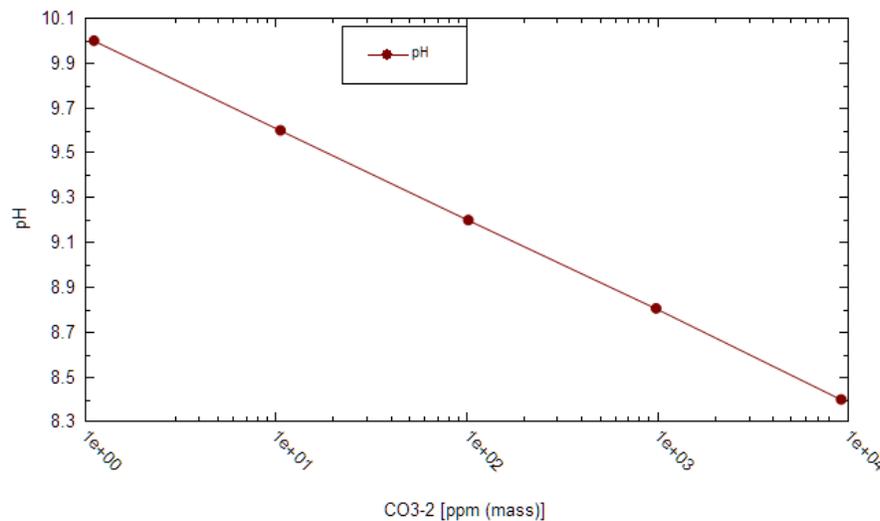
Linear Log Point List

	Value
1	2.50000
2	45.0000
3	750.000
4	10000.0
5	1.25000e5

- ✓ Close the window.
- ✓ Calculate.
- ✓ Click on the Plot tab.
- ✓ Click on the Variables button.
- ✓ Remove the existing variable from the Y1 axis.
- ✓ Expand the Aqueous category and put CO3-2 species on the X-axis.
- ✓ Expand the Additional Stream parameters category and add pH to the Y1 axis.



- ✓ Close the window.
- ✓ Right-mouse-click on the x-axis and change to Logarithmic scale.
- ✓ The plot will look like the following. It is the basic form of the Kmetz-Truax plot displayed above. It is a semi-log plot of pH and carbonate concentration. (Actually it is a Log-Log plot, since pH is a log scale of Hydronium+ activity).

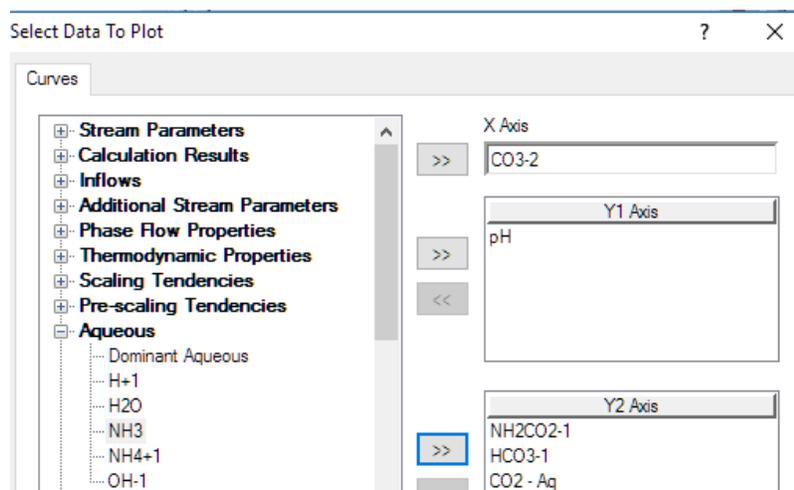


Viewing the dissolved concentrations of carbonate and ammonia

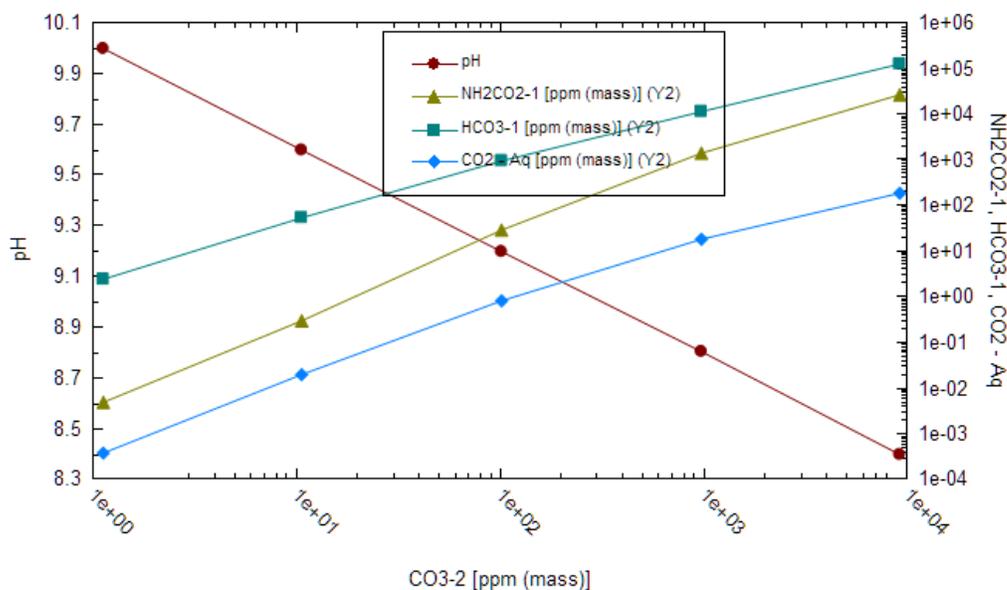
The next step is to overlay the various dissolved species on the plot. You will first overlay the dissolved inorganic carbon species.

- ✓ Open the Variables window.
- ✓ Expand the Aqueous category.

- ✓ Add the following species to the Y2 axis: HCO3-1, CO2, and NH2CO2-1.

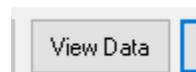


As the CO_3^{-2} concentration increases, and as the pH decreases, the total inorganic carbon concentration must increase, and it does substantially. For example, if the dissolved CO_3^{-2} concentration is measured at 1000 ppm, and the measured pH is 8.8 (fourth symbol on the pH curve), the the dissolved HCO_3^{-1} concentration is approximately 11,000 ppm, roughly 11 times the CO_3^{-2} concentration. Furthermore, if this is part of a Sour Water stripper system, and NH_3 is regulating pH, then the carbamate ion concentration ($\text{NH}_2\text{CO}_2^{-1}$) is computed to be about 900 ppm.



You can see the computed concentrations by selecting the View Data button in the upper right of the plot

- ✓ Click on the View Data button in the upper right of the plot -

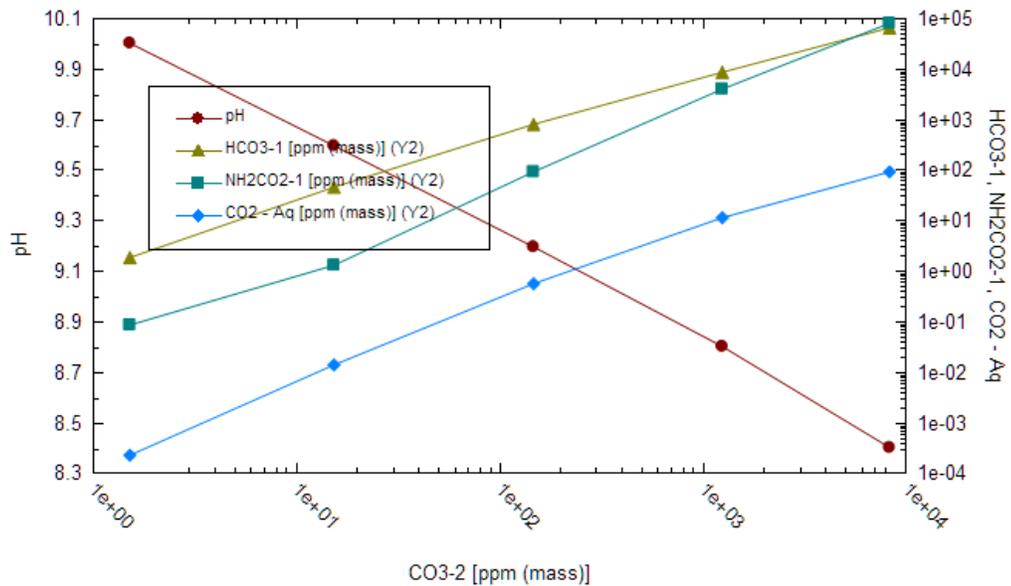


	CO3-2	pH	HCO3-1	NH2CO2-1	CO2 - Aq
	ppm (mass)		ppm (mass)	ppm (mass)	ppm (mass)
1	1.12518	10.0000	2.31655	4.83321e-3	3.61998e-4
2	10.7066	9.60000	51.1798	0.287789	0.0195622
3	102.213	9.20000	906.281	27.4882	0.781822
4	982.209	8.80000	11407.6	1334.90	18.4841
5	9175.15	8.40000	1.25617e5	25837.5	178.121

These are the dissolved inorganic carbon concentrations associated with the Kmetz-Truax boundary between ACSCC and no ACSCC. Please note this is the case at 25C.

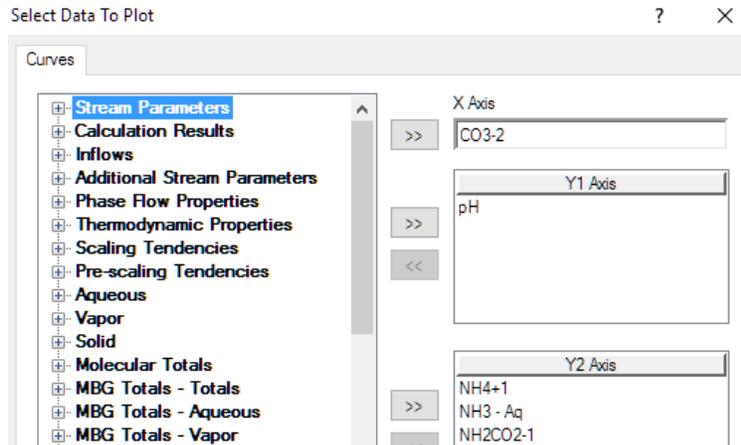
- ✓ Return to the Definition tab and raise the temperature to 60 C and recalculate.

If the pH can be scaled properly (pH is affected by temperature), then this is what the plot and concentrations would look like at the elevated temperature. The carbamate concentration is computed to increase relative to the other species.

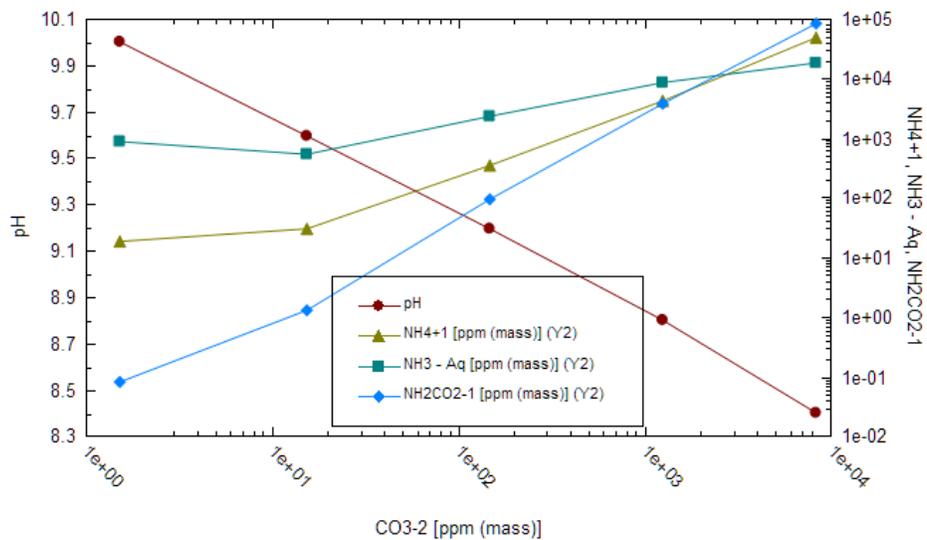


Next you will overlay the ammonium-containing species.

- ✓ Click on the Variables tab.
- ✓ Remove the CO2 and HCO3-1 from the Y2 axis.
- ✓ Add NH3 and NH4+1 to the Y2 axis.



✓ Close the window and view the plot.



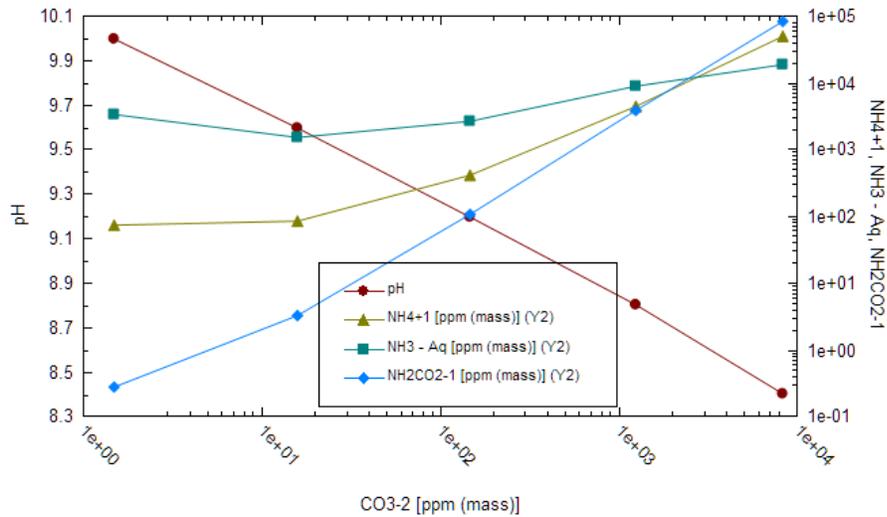
The plot is similar in scale and trend as the inorganic plot. The concentrations of all NH₃-containing species increase as CO₃⁻² increases AND as pH decreases. These are the compositions that are computed to exist *if* the field-measured carbonate is in fact CO₃⁻² and the pH is controlled by NH₃ and no other species.

Adding some H₂S to the system

According to the NACE report 34108, H₂S concentrations above 50 ppm also play a factor. This will be added next. Before doing so, however, recognize that the 50 ppm concentration of H₂S is several orders of magnitude lower than the ammonia and inorganic carbon concentrations for much of this curve.

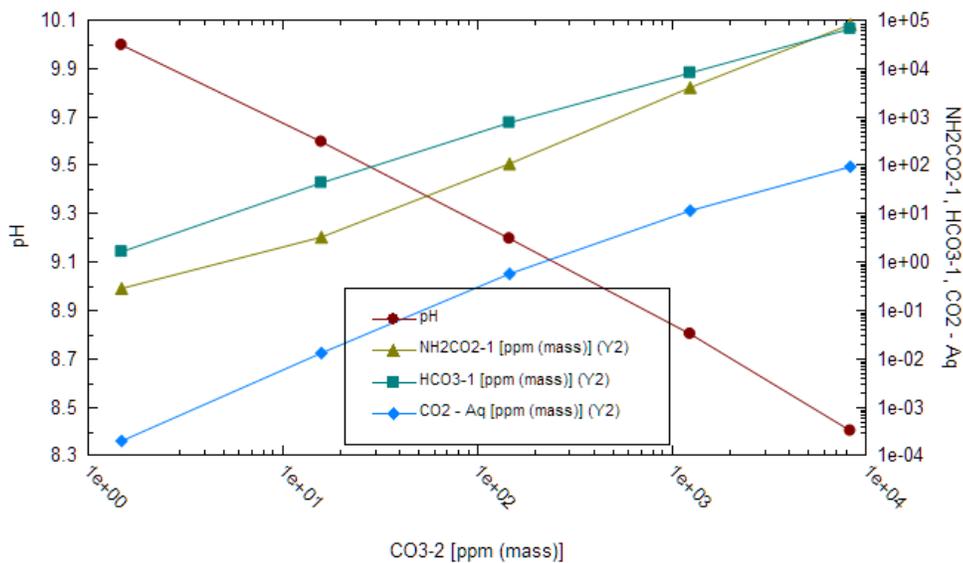
Therefore, we should expect negligible change to the right-side of the plots that were just created.

- ✓ Return to the Definition tab and add 100 ppm H₂S.
- ✓ Calculate.
- ✓ View the existing plot of the dissolved ammonia species.



There is a slight shift in concentration on the far left. This is because additional NH_3 is needed to raise the pH, since adding 100 ppm H_2S adds acid to the system.

- ✓ Change the plot variables.
- ✓ Remove the NH_3 and NH_4+1 from the Y2.
- ✓ Add CO_2 and HCO_3-1 to the Y2 axis.



There appears to be a negligible shift in the curves here as well. Therefore, if these plots accurately represent the solution composition that promotes ACSCC, and if H_2S is involved in ACSCC, then it does not appear to be due to its effect on the bulk solution chemistry.

- ✓ Change the H_2S concentration to 1000 ppm and see how this affects the plot.

Summary

The purpose of this section is to look at the bulk solution chemistry for dissolved carbonates and ammonia when the solution conforms to the Kmetz-Truax Curve. This curve represents an approximate boundary for ACSCC. At higher carbonate concentrations and lower pH, the right-side of the plots studied above, the

concentrations of dissolved carbon and ammonia increase exponentially, reaching concentrations that exceed 10,000 ppm. This again, is true only if the x-axis of the Kmetz-Truax is the dissolved CO₃-2 species (phenolphthalein alkalinity) and that there are no other alkaline species (e.g., OH, mercaptans, etc.) contributing to the x-axis. This is also true, only if the source of alkalinity to raise pH is NH₃, and not NaOH or other alkaline sources. Therefore, because of the uncertainty posited between what you computed and what may exist in the plant, it is advisable to determine the exact nature of the dissolved carbonate measured, and if there are other species of significant in the sour water recirculating in the Stripper pumparound.

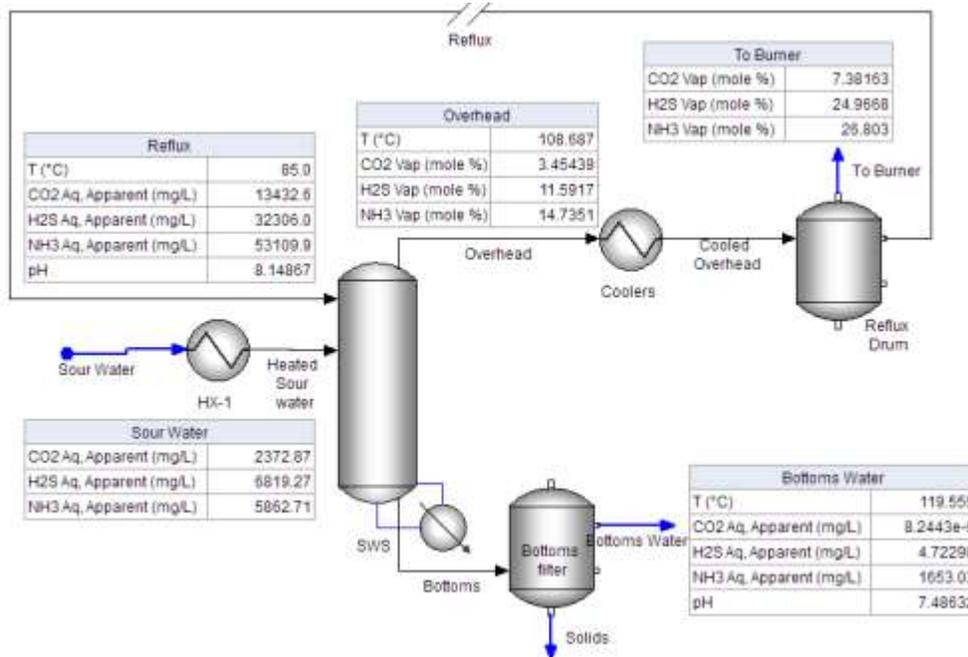
8.7 – Sour Water Chemistry and Corrosion

Overview

There are multiple references to corrosion occurring in equipment processing sour water. The purpose of this case file is to study the chemical composition of the gas and fluid phases flowing through the separation unit. This case will use both the Flowsheet ESP and OLI Studio software. The Flowsheet software will be used to create the stripping process and to compute the composition in each stream and on each column stage. The OLI Studio tool will be used to study the stream composition further, to compute corrosion rates and to test effects of changing compositions and conditions.

Getting Started

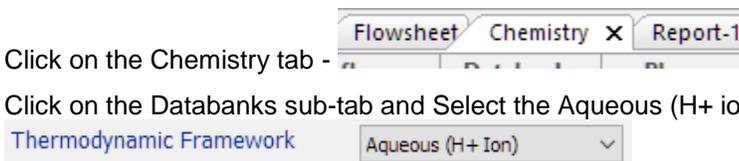
The image below is the process flowsheet that will be studied. It represents a generic stripping column in which heated sour water is injected into the fourteenth stage of a of a twenty-stage tower. Tower overheads are cooled and the liquid reflux returned to the top of the column. The remaining gas exits the process.

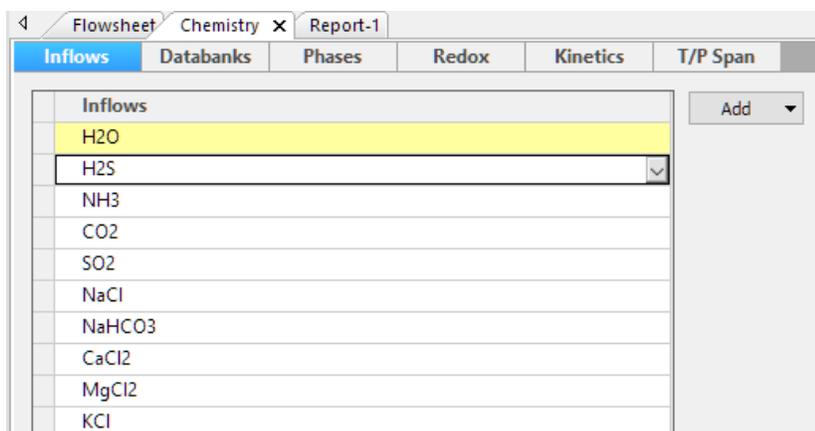


Creating the chemistry model

Start by adding the necessary chemical components to the chemistry model. The components are fairly basic, gases plus salts.

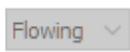
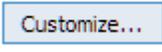
- ✓ Click on the Chemistry tab -
- ✓ Click on the Databanks sub-tab and Select the Aqueous (H+ ion) framework -
- ✓ Click on the Inflows subtab and add the components shown in the screenshot below





You are done with the Chemistry build step. There are no additional changes, such as redox reactions, kinetics, or solids selection.

Setting the Units

- ✓ Click on the Units manager button in the toolbar - 
- ✓ Set the units to Metric-Flowing-Mass -   
- ✓ Click on the Customize button to edit the existing units - 
- ✓ Make the following changes to the units, there are several

Variable	Basis	Units
Inflow variables		
Total Flow	Mass	kg/hr
Inflows	Mass Fraction	ppm (mass)
Output variables		
Aqueous Composition	Concentration	mg/L
Vapor Composition	Mole Fraction	mole %
Solid Composition*	Concentration	mg/L
2nd Liquid Composition	Mole Fraction	mole %
Total Composition	Moles	mol/hr
Basis options		
Moles		mol/hr
Mass		kg/hr
Volume		m ³ /hr
Concentration		mg/L
Molar Concentration		mol/L
Mass Fraction		ppm (mass)
Mole Fraction		mole %

Building the Process

Add the sour water stream

- ✓ Click on the Add Stream button from the toolbar - 
- ✓ Create a stream and label it Sour Water

- ✓ Unclick the Add Stream, button - 
- ✓ Double-click on the new stream you created to enable the name editor and change the name to Sour Water

Next you will enter the Sour water composition in the Properties panel

- ✓ Enter the conditions and compositions shown in the image below. Confirm that your Total flow units are kg/hr and Inflow units are ppm(mass).

Sour Water	
Definition	Calculated
Parameters	
Temperature (°C)	80.0
Pressure (atm)	1.1
Total Flow (kg/hr)	1000.0

Inflows (ppm (mass))	
H2O	9.81e5
H2S	8000.0
NH3	6000.0
CO2	3000.0
SO2	1500.0
NaCl	100.0
NaHCO3	100.0
CaCl2	100.0
MgCl2	100.0
KCl	100.0
Total	1.0e6

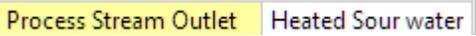
Normalization	
Type	Makeup with Water

- ✓ Set the Normalization to Makeup with Water – in that way the H2O is entered automatically.

Add the Heat exchanger

- ✓ Double-click on the Heat Exchanger icon in the Library to add it to the process



- ✓ Select the Sour as the inlet in the Properties Panel - 
- ✓ Type in the outlet name, Heated Sour Water - 
- ✓ Set the Process Stream Spec. type to Discharge Temp - 
- ✓ Set the Discharge T to 80 C

The Properties panel should look like the one below when finished

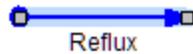
HX-1 Heat Exchanger	
Definition	General
Inlets	
Process Stream Inlet	Sour Water
Utility Stream Inlet	
Outlets	
Process Stream Outlet	Heated Sour water
Utility Stream Outlet	

Process Stream	
Spec. Type	Discharge Tempera...
Discharge Temperature (°C)	80.0
Pressure Spec.	Inlet Pressure

Heat Exchanger	
Flow Geometry	Counter-current

Add a Reflux stream to be used in the Stripper

- ✓ Click on the Add Stream button and create a new stream

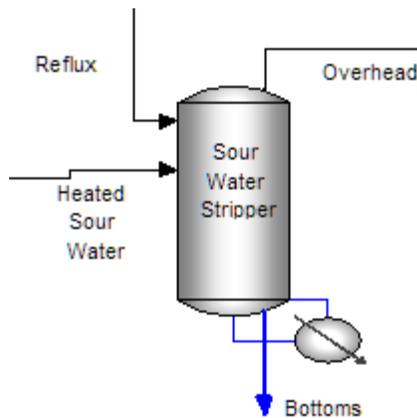


- ✓ Label it Reflux -
- ✓ Enter the following initial guess to the reflux composition

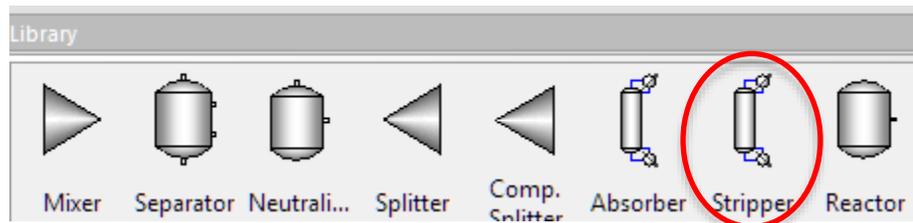
Properties		
Reflux		
Definition	Calculated	General
Parameters		
Temperature (°C)		85.0
Pressure (atm)		1.3
Total Flow (kg/hr)		20.0
Inflows (ppm (mass))		
H2O		9.0e5
H2S		20000.0
NH3		60000.0
CO2		20000.0

This composition is an initial guess, because it will be the outlet of the reflux drum and will become an internal (calculated) stream, once the case is finished.

Add the Stripper column

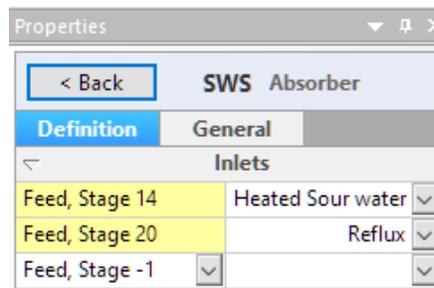


The stripper object contains a number of settings, so make sure that you complete each step.

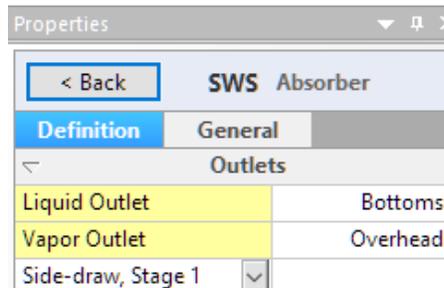


- ✓ Double-click on the Stripper object in the Library panel and add it to the process
- ✓ Name it Sour Water Stripper
- ✓ Move to the Properties panel and make the following changes
- ✓ Set the Calculation method to Equilibrium
- ✓ Set the Number of stages to 20
- ✓ Set Include condenser to No
- ✓ Open the Inlets window
- ✓ Use the down arrows to add the Heated sour water to Stage 14 and the Reflux stream to stage 20

Calculation Method	Equilibrium
Number of Stages	20
Include Condenser	No
Include Reboiler	Yes



- ✓ Click on the Outlets window
- ✓ Enter the name Bottoms to the Liquid Outlet and Overhead to the Vapor Outlet



- ✓ Open the Spec./Controls Editor window
- ✓ Click on the Add button to create a new tower Specification

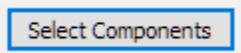
Specification section

- ✓ Select Liquid Composition for Spec. Variable
- ✓ Set the stage # to 1
- ✓ Set the value to 5e-4 mass%. If mass% is not available, then use 5 ppm.

Value	5.0e-4	mass %	Value	5	ppm (mas:)
-------	--------	--------	-------	---	------------

- ✓ Select the component H₂S from the popup window that appears.

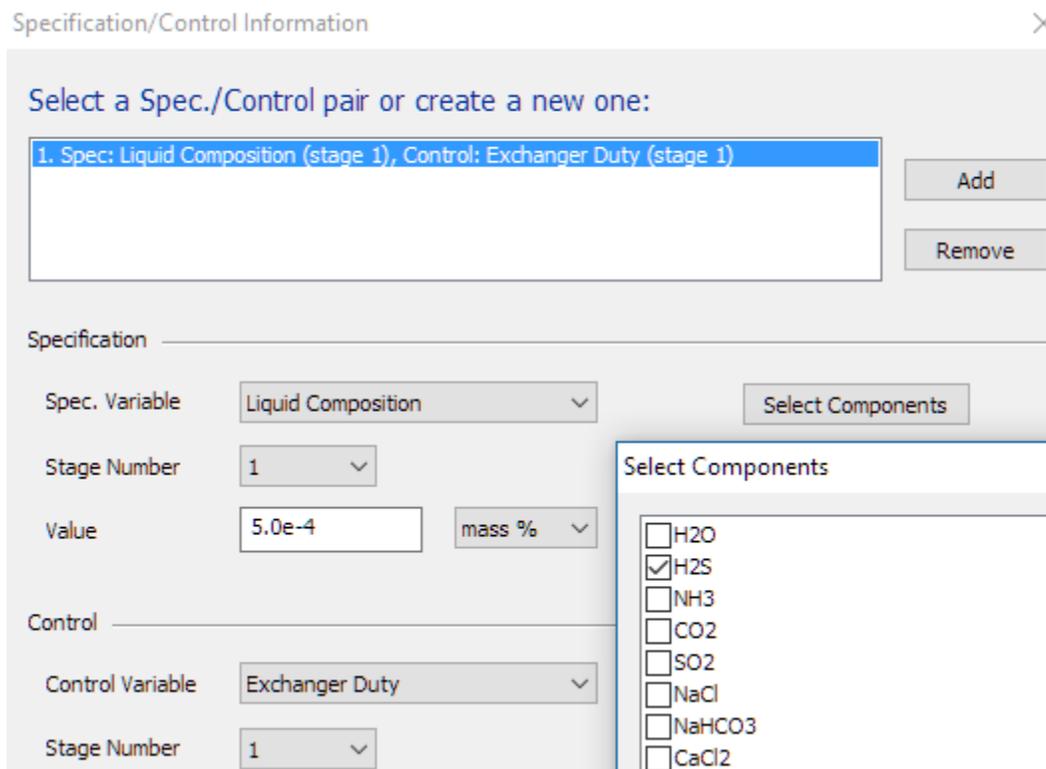
If the component popup window does not appear after pressing Enter, then click on the Select Components button



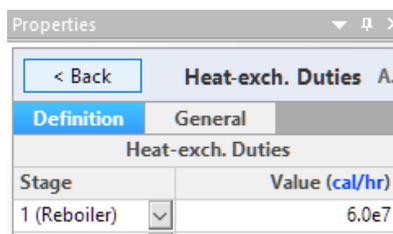
Control section

- ✓ Select Exchanger duty
- ✓ Select Stage 1

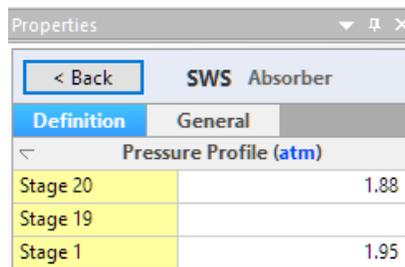
Your windows should look like the one below



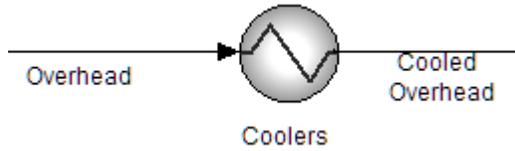
- ✓ Close the Specifications window
- ✓ Click on the Heat Exch. Duties editor button - **Heat Exch. Duties**
- ✓ Set the initial guess for the Stage 1 (Reboiler) heat duty to 6e7 cal/hr



- ✓ Click on the Pressure Profile editor button - **Pressure Profile**
- ✓ Set Stage 20 to 1.88 atm and stage 1 to 1.95 atm



Add the Overhead Coolers



- ✓ Add another Heat Exchanger object and name it Coolers
- ✓ Use the Properties panel to link the Overhead stream to the Process Stream Inlet field
- ✓ Type the name Cooled Overhead in the Process Stream outlet field

Properties

Coolers Heat Exchanger

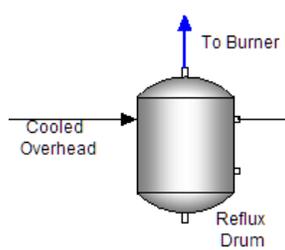
Definition General

Inlets		Outlets	
Process Stream Inlet	Overhead	Process Stream Outlet	Cooled Overhead
Utility Stream Inlet		Utility Stream Outlet	

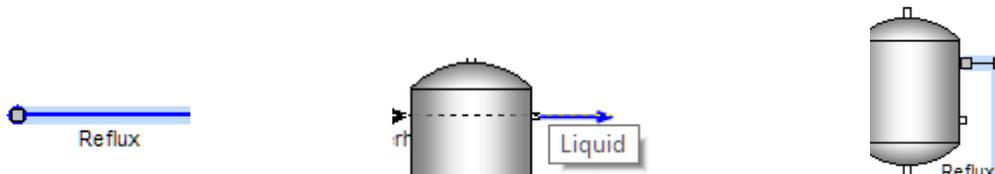
- ✓ Set the Process Stream Spec. Type to Discharge Temperature
- ✓ Set the discharge Temperature to 85C
- ✓ Set the Pressure Spec. to Absolute Pressure
- ✓ Set the Pressure to 1.3 atm

Process Stream	
Spec. Type	Discharge T...
Discharge Temperature (°C)	85.0
Pressure Spec.	Absolute Pre...
Pressure (atm)	1.3

Add the Reflux Drum



- ✓ Add a Separator object to the case and label it Reflux Drum
- ✓ Use the Properties panel to select the Cooled Overhead as the Inlet stream
- ✓ Click on the front-end of the Reflux stream and drag it to the liquid outlet of the Reflux drum



- ✓ Type the name To Burner to the Vapor Outlet

- ✓ Keep the existing Equilibrium Calculation Properties

Outlets		Equilibrium Calculation	
Liquid	Reflux	Calculation Type	Adiabatic
Solids		Pressure Spec.	Min. Inlet Pressure
Vapor	To Burner	Heat Duty (cal/hr)	0.0
Organic		Entrainment	>

At this point, you may want to rearrange the blocks and streams at this time to keep the flowsheet organized.

Adding the Bottoms filter

- ✓ Add another Separator block and label it Bottoms Filter
- ✓ Link the Bottoms stream to the Inlet
- ✓ Create two outlet streams – Bottoms water in the Liquid outlet and Solids in the Solids outlet

Bottoms filter Separator		Outlets															
<table border="1"> <thead> <tr> <th colspan="2">Inlets</th> </tr> </thead> <tbody> <tr> <td>Feed</td> <td>Bottoms</td> </tr> <tr> <td>Feed</td> <td></td> </tr> </tbody> </table>		Inlets		Feed	Bottoms	Feed		<table border="1"> <tbody> <tr> <td>Liquid</td> <td>Bottoms Water</td> </tr> <tr> <td>Solids</td> <td>Solids</td> </tr> <tr> <td>Vapor</td> <td></td> </tr> <tr> <td>Organic</td> <td></td> </tr> </tbody> </table>		Liquid	Bottoms Water	Solids	Solids	Vapor		Organic	
Inlets																	
Feed	Bottoms																
Feed																	
Liquid	Bottoms Water																
Solids	Solids																
Vapor																	
Organic																	

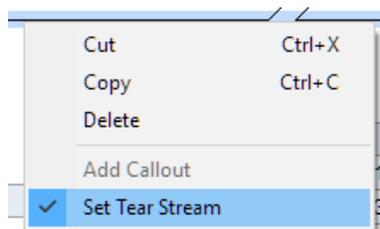
- ✓ Open the Entrainment editor -
- ✓ Set the Liquid to Solid ratio in the Solids stream to 4

Entrainment	
Liquid in Solid (g/g)	4.0
Vapor in Liquid (g/g)	
Aqueous in Organic Liquid (g/g)	
Organic Liquid in Aqueous (g/g)	

This action will add four grams of liquid to every gram of solids that flow. It is essentially a solids slurry containing 80% water.

Set the Reflux stream as the Recycle/Tear Stream

- ✓ Right mouse-click anywhere along the Reflux stream to activate the drop-down menu
- ✓ Select the Set Tear option



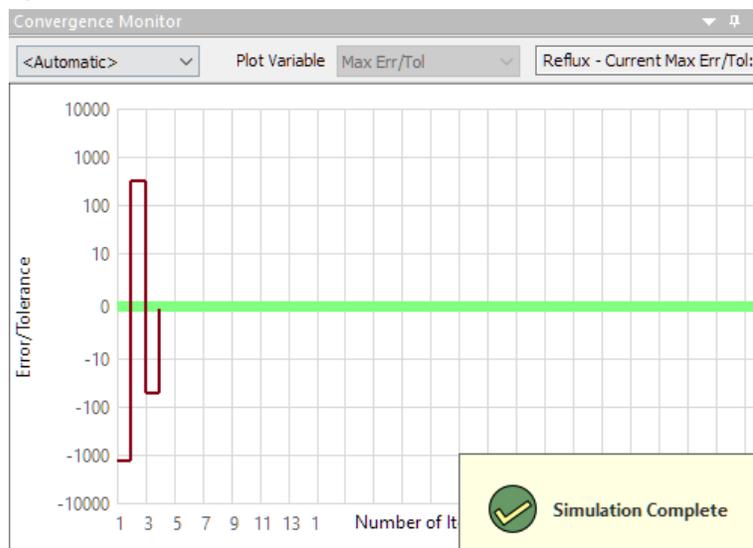
- ✓ Save the file – label it Stripper-Sour Water.

Calculate the case

- ✓ Press the Calculate button -

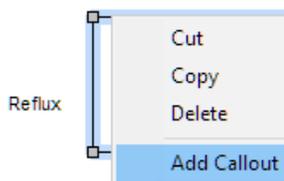
- ✓ View the Convergence monitor. It will provide a quick view of the calculation progress

It may take many iterations before the process converges. The monitor will show if the existing error is decreasing or increasing (calculation unstable).



Reviewing the calculations

- ✓ Right-mouse-click on the Reflux stream and select Add Callout



- ✓ Double-click on the callout table that appears to edit the variables
- ✓ Remove the pressure from the existing variable list
- ✓ Expand the Liquid-1, Apparent field and select CO₂, H₂S, and NH₃

Reflux	
T (°C)	85.0
pH	8.14867
CO ₂ Aq, Apparent (mg/L)	13432.8
H ₂ S Aq, Apparent (mg/L)	32305.9
NH ₃ Aq, Apparent (mg/L)	53110.1

According to the calculation, this is the concentration of sour components in the reflux stream. Use this data plus the pH to evaluate whether corrosion is possible at these conditions.

- ✓ Add other callout tables where you think that corrosion may be a problem in your process and review the composition at these locations.

Summary

The purpose of this example was to create the steady-state conditions within a sour water stripper unit. Once the simulation is converged, the compositions and temperatures at locations within the process can be reviewed so that corrosion can be assessed.

8.8 – HF Regeneration

Chapter 9 Autoclave Calculations

Introduction

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.

In this chapter, you will simulate autoclaves using three general approaches. The first is to use Custom calculation. This calculation type allows you to select variables to fix and to free. The second type is the Autoclave calculation type. This fixes temperature and partial pressures, and calculations initial/final pressures and gas inflow amounts. The third option is using the Mixer set to isochoric. This option calculates temperature or pressure, and the user manually adjust the inflow rate of a given stream.

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9.1 Basic Autoclave #1 – Using Inert Gas

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

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

We can use the Ideal Gas Law to estimate the amount of N₂ needed to fill the headspace:

$$P * V = n * R * T$$

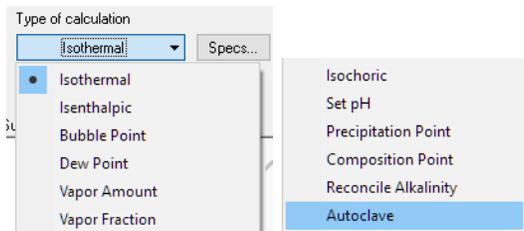
$$1 \text{ atm} * 1 \text{ L} = n * 0.082057 \frac{\text{L-atm}}{\text{K-mol}} * 298.15 \text{ K}$$

$$n = 0.040874 \text{ moles}$$

Although this estimate does not consider the H₂O that is in the 1 L headspace or the amount of N₂ dissolved in water, it is still an easy approach to get a reasonable estimate. You will compare this equation to the results at several points in this case. You will also review the results in greater detail in this case, because part of the goal of this first case it to show where the important variables and properties are that impact an autoclave calculation.

Getting Started

- ✓ Start a new file and give it a name such as **Chapter 9 Autoclaves**
- ✓ Create a new stream and rename it **Basic Autoclave – Inert Gas**
- ✓ Change the framework to MSE
- ✓ Make sure the units are set to Metric-Batch-Moles
- ✓ Add N₂ as an inflow
- ✓ Add a Single Point Calculation then select Autoclave as the calculation type



The basic grid should look like the one below

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation Parameters	
Final Temperature (°C)	0.0
Final Pressure (atm)	
Vessel Volume (L)	0.0
Compute results at which condition	Ambient
Inflows (mol)	
H ₂ O	55.5082
N ₂	0.0

Type of calculation: Autoclave

Calculate

Summary

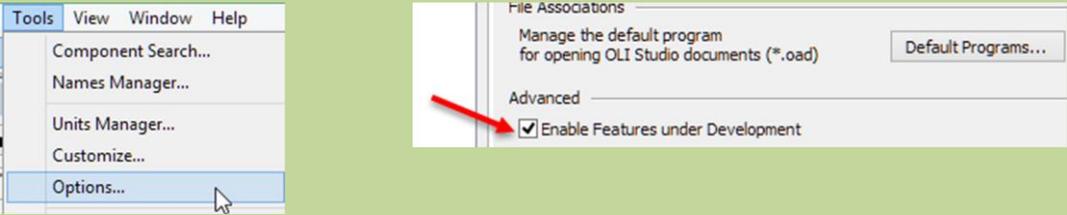
Unit Set: Metric (moles)

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

Autoclave Calculation
Specifications:
Ambient Temperature 25.0000 °C

If you do not see the Autoclave then follow the instructions in the insert below.

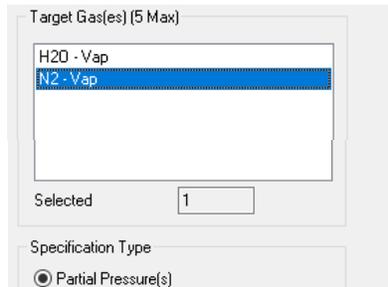
✓ Select Tools > Options ✓ Select the Enable Features box



✓ Press OK.

If Autoclave option does not appear in the single point Calculation Type list, then restart software

- ✓ Click the Specs button
- ✓ Highlight N2 in the gas field then press OK



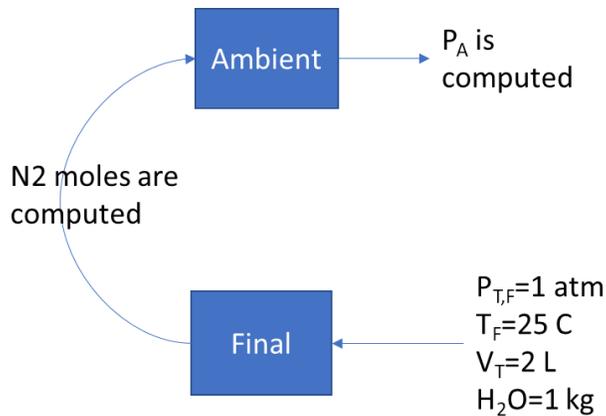
- ✓ Change the Vessel volume to 2 L
- ✓ Change the final temperature to 25 C and Final Pressure to 1 atm

At this point the system contains, 1 kg H2O (55.508 moles), the initial temperature is 25 C and the final temperature and pressure will be 25 C and 1 atm.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation Parameters	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	2.00000
Partial Pressure: N2 (atm)	
Compute results at which condition	Ambient
Inflows (mol)	
H2O	55.5082
N2	0.0

- ✓ Calculate

The software will perform two calculations, one at ambient (initial) conditions and one at final conditions. It will compute the amount (in moles) of N₂ needed to create a 1 atm pressure at final conditions. It will then use this N₂ to compute the pressure at ambient conditions. The calculation pathway image below shows this.



- ✓ View the Summary section

```

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 2.00000 L
N2 0.968638 atm
  
```

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 also identical, and by design, the autoclave calculation uses the identical inflows for ambient and final conditions.

The final N2 partial pressure is computed to be 0.9687 atm.

- ✓ Click on the Output tab -

The amount of N2 added is 0.04007 moles. This produces the 0.9686 atm partial pressure.

Inflows (mol)	
H2O	55.5082
N2	0.0400673

- ✓ Review some of the remaining data

Variable	Value
Stream Parameters (mol)	
Stream Amount	55.5483
Moles (True) - Liquid-1 (mol)	55.5076
Moles (True) - Vapor (mol)	0.0407388
Calculation Results	
Ambient Temperature (°C)	25.0000
Ambient Pressure (atm)	1.00000
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	1.99999
Partial Pressure: N2 (atm)	0.968638
Condition that results were computed for	Ambient

The size of the liquid phase, in moles, is 55.508 and the vapor is 0.407, or a 1364:1 ratio. The volumes are nearly identical: 1 L liquid and 1 L vapor.

- ✓ Click on the Report tab
- ✓ Scroll down to the last table, Element Distribution

The last row is N (molecular nitrogen). The distribution is 98.5% in the vapor and 1.5% in the liquid phase. Conversely, 0.0023% of the water has evaporated (note 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	2.30175e-3
O(-2)	55.5082	33.3173	99.9977	2.30175e-3
N	0.0801347	0.0480986	1.51293	98.4871

These results infer two effects: as the final pressure increases, additional N₂ will dissolve in the water, shifting the fraction of nitrogen to the liquid; As the total autoclave volume increases relative to the input liquid, additional water will evaporate, shifting the water to the vapor. This will be shown next.

Setting the Vessel volume to 5 L and 10,000 L

You will compute this case using larger autoclave volumes. The case above is a 2 L autoclave containing 1 kg (~1 L) water. The moles of liquid is computed to be 55.5076.

- ✓ Click on the Input tab and change the Vessel volume to 5 L

Calculation Parameters	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	5.00000

- ✓ Calculate
- ✓ Click on the Output tab and view the Phase amounts

Stream Amount	55.6671
Moies (True) - Liquid-1 (mol)	55.5037
Moies (True) - Vapor (mol)	0.163374

The moles of liquid is now 55.5037. The reduction of 0.0039 moles is because this amount of H₂O evaporated into the larger headspace.

- ✓ Scroll down to the Inflow grid and view the N₂ inflow

The grid shows the amount of N₂ required to fill the 4-L headspace. The amount is 4-times greater than the first case, which is expected for gas with a low water solubility.

Inflows (mol)	
H ₂ O	55.5082
N ₂	0.158857

- ✓ Return to the Input tab and change the volume to 10000 L.

This creates a 9999 L headspace. The Liquid moles is now 42.69, and the 12.818 mole reduction is evaporation.

Stream Parameters (mol)	
Stream Amount	451.420
Moles (True) - Liquid-1 (mol)	42.6900
Moles (True) - Vapor (mol)	408.730

This phase distribution is important to modeling the autoclave system properly, especially at elevated conditions as will be seen in the next example.

Testing the 5 L case at 1 atm and 100 C final temperature

The purpose of this example is to raise the H₂O partial pressure relative to N₂. In the 5 L case above, the N₂ inflow is 0.1634 moles. As temperature increases, the H₂O vapor pressure increases, and the amount of N₂ required to fill the vapor void will decrease.

- ✓ Change the Final Temperature to 100 C
- ✓ Change the vessel volume to 5 L

Calculation Parameters	
Final Temperature (°C)	100.000
Final Pressure (atm)	1.00000
Vessel Volume (L)	5.00000

- ✓ Calculate
- ✓ View the Output tab and the Summary section

Variable	Value
Stream Parameters (mol)	
Stream Amount	55.5082
Moles (True) - Vapor (mol)	55.5082
Calculation Results	
Ambient Temperature (°C)	25.0000
Ambient Pressure (atm)	0.0312726
Final Temperature (°C)	100.000
Final Pressure (atm)	1.00000
Vessel Volume (L)	43393.5
Condition that results were computed for	Ambient
Inflows (mol)	
H2O	55.5082

Type of calculation: Autoclave

Calculate

Summary

Unit Set: Metric (moles)

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

Autoclave Calculation
Results for ambient conditions:
Ambient Temperature 25.0000 °C
Ambient Pressure 0.0312726 atm
Final Temperature 100.000 °C
Final Pressure 1.00000 atm
Vessel Volume 5.00000 L
N2VAP

The amount of N₂ added is zero (no value is shown). This is to be expected, because the vapor pressure of pure water at 100 C is 1 atm. Therefore, no N₂ is needed to raise the pressure. Notice also that the ambient pressure is 0.0313 atm. This is the vapor pressure of pure water at 25 C. Therefore, the autoclave will have a vacuum pressure at ambient temperatures, and when heated to 100 C will reach atmospheric pressure. This, by the way is the principle of the double-espresso pot in reverse.

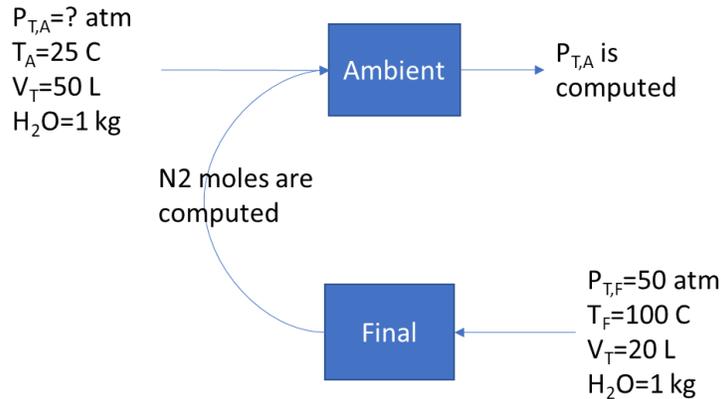


The water is added into the lower chamber. The pot is sealed at ambient pressures and is heated. The water boils and condenses in the upper chamber. When taken off the stove, the lower chamber cools,

producing a vacuum, this vacuum pulls the condensed water through the coffee. The system has two temperatures, two pressures, and one composition.

Testing the 20 L case at 50 atm final pressure and 100 C final temperature

This scenario contains two different sets of T, P conditions. The calculation approach however, is the same: the final T and P are known, and the N₂ inflow amount is computed. This N₂ amount is added to the Ambient calculation, and P_{T,A} is calculated.



- ✓ Change the Final temperature and Pressure to 100 C and 50 atm

Calculation Parameters	
Final Temperature (°C)	100.000
Final Pressure (atm)	50.0000
Vessel Volume (L)	20.0000
Partial Pressure: N2 (atm)	
Compute results at which condition	Ambient

- ✓ Calculate
- ✓ View the Summary section

```

Autoclave Calculation
Results for ambient conditions:
Ambient Temperature  25.0000 °C
Ambient Pressure    38.4373 atm
Final Temperature   100.000 °C
Final Pressure      50.0000 atm
Vessel Volume       20.0000 L
N2 38.4035 atm
    
```

The computed ambient pressure P_{T,A} is 38.437 atm. Of this total, 38.404 atm is N₂ (P_{N2}=38.404) and 0.033 atm is H₂O (P_{H2O}=0.033 atm). Thus, to create a 50 atm final pressure, the autoclave would need to be charged with N₂ at a regulator pressure of 38.437 atm.

- ✓ Click on the Output tab and view the results

Stream Parameters (mol)	
Stream Amount	85.2675
Moles (True) - Liquid-1 (mol)	55.5049
Moles (True) - Vapor (mol)	29.7626
Calculation Results	
Ambient Temperature (°C)	25.0000
Ambient Pressure (atm)	38.4373
Final Temperature (°C)	100.000
Final Pressure (atm)	50.0000
Vessel Volume (L)	20.0000
Partial Pressure: N2 (atm)	38.4035
Condition that results were computed for	Ambient
Inflows (mol)	
H2O	55.5082
N2	29.7592

According to the calculation, the amount of N₂ in the autoclave is 29.759 moles. This amount of N₂ plus the 55.508 moles of H₂O produces a final pressure of 50 atm in a 20 L autoclave at 100 C.

Summary

The purpose of this case was to display the inter-dependence of the two calculations that are part of an autoclave calculation. The further purpose was to show the user where to find the relevant data.

9.2 Basic Autoclave #2 – Using Reactive Gas

You will modify the Case 9.1 approach by using a reactive gas, CO₂, to fill the headspace. You will then modify the case further by adding NaOH so that additional CO₂ dissolves in water to form bicarbonate. This increases the gas requirement

Getting Started

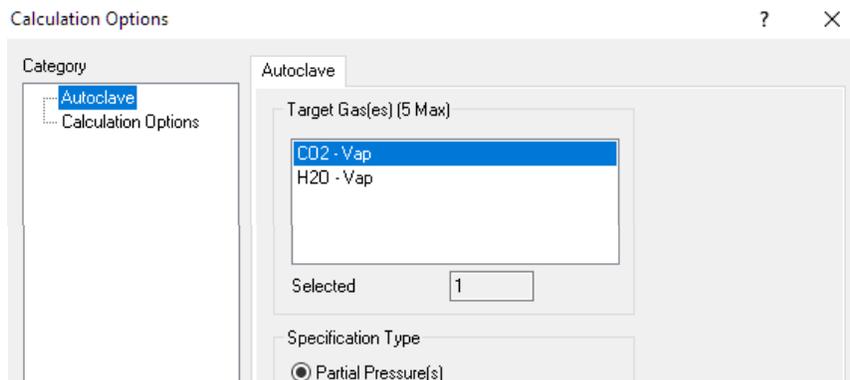
- ✓ Create a new stream and rename it **Basic Autoclave – Reactive Gas**
- ✓ Change the framework to MSE
- ✓ Make sure the units are set to Metric-Batch-Moles
- ✓ Add CO₂ and NaOH to the inflow list

Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
CO2	0.0
NaOH	0.0

Special Conditions
 Solids Only

Summary
Unit Set: Metric (moles)
Automatic Chemistry Model
MSE (H3O+ ion) Databanks:
MSE (H3O+ ion)

- ✓ Add a Single Point Calculation, then select Autoclave as the calculation type
- ✓ Click the Specs button
- ✓ Highlight CO₂ in the gas field, then press OK



- ✓ Set the final temperature to 25 C
- ✓ Set the final Pressure to 1 atm
- ✓ Set the Vessel volume to 2 L
- ✓ Change the Compute results at which condition to Final

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

- ✓ Calculate
- ✓ Click on the Report tab and review the Stream Inflows table

Stream Inflows

Row Filter Applied: Only Non Zero Values

	Input	Output
Species	mol	mol
H2O	55.5082	55.5082
CO2	0.0	0.0724077

This table displays the Input and Output inflows. The 0.072 moles CO₂ added is computed by the software to set the autoclave pressure to 1 atm. For comparison, the same scenario in Section 9.1 required 0.04 mole N₂. The difference is the amount of CO₂ that dissolved in the water. CO₂ is more soluble than N₂ in water.

- ✓ Scroll down to the Element Distribution table

This table contains three rows, H(+), O(-2), and C(+4). These are the elements of H₂O and CO₂.

- ✓ Compare the C(+4) in the liquid and vapor

Element Distribution

	Total	Total	Liquid-1	Vapor
	mol	mole %	% of Total	% of Total
H(+1)	111.016	66.5798	99.9977	2.33021e-3
O(-2)	55.6531	33.3768	99.8553	0.144741
C(+4)	0.0724077	0.043425	45.2687	54.7313

About 45% of the CO₂ dissolved in the water phase. By comparison, 1.5% of the added N₂ dissolved in water at the same condition.

- ✓ Scroll up to the Element Balance table to view the moles C(+4) in each phase.

Element Balance

Row Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor
	mol	mol	mol
H(+1)	111.016	111.014	2.58692e-3
O(-2)	55.6531	55.5725	0.0805529
C(+4)	0.0724077	0.032778	0.0396297

The table below is the comparison between the Ideal Gas law calculation, and the N₂ and CO₂ autoclave calculations.

T	P	Vol _T	Moles Gas in 1L	Moles of N ₂ mixed with 1kg H ₂ O		Moles of CO ₂ mixed with 1kg H ₂ O	
C	atm	L	Ideal Gas Law	Calculated (total)	Calculated (vapor)	Calculated (total)	Calculated (vapor)
25	1	2	0.041	0.040	0.039	0.072	0.040

Testing with 0.1m NaOH

You will repeat the study with NaOH added to the water. NaOH reacts with CO₂ to form HCO₃⁻¹ and CO₃⁻², increasing overall CO₂ solubility.

- ✓ Click on the Input tab
- ✓ Add 0.1 moles NaOH to the input grid

Inflows (mol)	
H2O	55.5082
CO2	0.0
NaOH	0.100000

✓ Calculate

Variable	Value
Stream Parameters (mol)	
Stream Amount	55.7797
Moles (True) - Liquid-1 (mol)	55.7389
Moles (True) - Vapor (mol)	0.0408296
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	2.00002
Partial Pressure: CO2 (atm)	0.968498
Condition that results were computed for	Final
Inflows (mol)	
H2O	55.5082
CO2	0.171450
NaOH	0.100000

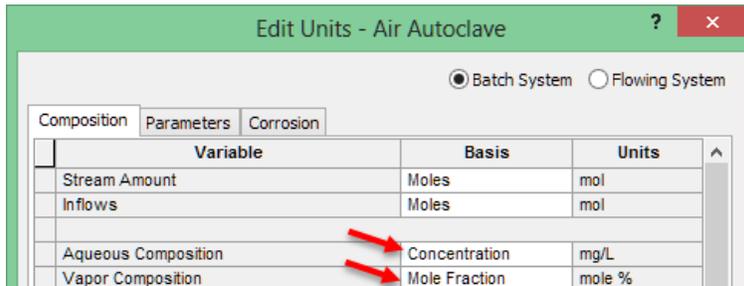
The CO₂ inflow is approximately 0.17 moles. This is 0.1 mole more than the first calculation and results from the acid-base reaction with the 0.1 moles of NaOH.

9.3 Basic Autoclave #3 - Using Air

The previous case represents an example of how to create autoclave and how the results compare to the Ideal Gas Law. In the next case, we will use air. Dry air has a composition of 78.08% N₂, 20.95% O₂, 0.93% Ar, and 0.04% CO₂¹. The composition of H₂O-saturated air is ~3.1% less, or 75.7% N₂, 20.3% CO₂, 0.90% Ar, 0.039% CO₂, and 3.1% H₂O. Since CO₂ is a reactive gas that dissolves in water, this will create a calculation deviation from the ideal gas law.

Getting Started

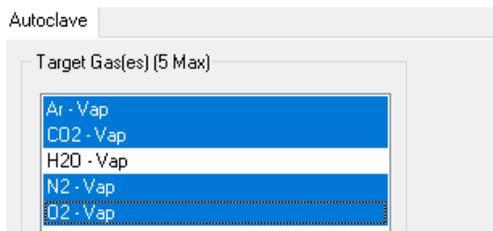
- ✓ Add a new stream and rename it **Air Autoclave**
- ✓ Change the framework to MSE
- ✓ Select the Units Manager button  and make sure the units are Metric-Moles, then:
- ✓ Click the Customize button
- ✓ Change Aqueous Composition to Concentration
- ✓ Change Vapor Composition to Mole Fraction



- ✓ Press the OK button twice to exit the Units Manager
- ✓ In the Inflows grid, add the components N₂, O₂, CO₂, and Ar

Inflows (mol)	
H2O	55.5082
N2	0.0
O2	0.0
CO2	0.0
Ar	0.0

- ✓ Add a Single Point Calculation then change the calculation type to Autoclave
- ✓ Click the Specs button
- ✓ Highlight Ar, CO₂, N₂, and O₂



- ✓ Click OK to exit the window

¹ Taken from http://en.wikipedia.org/wiki/Gas_composition. This is reportedly from the 1997 edition of the CRC handbook. The 0.04% CO₂ is not from this reference, it is obtained from NOAA <http://www.esrl.noaa.gov/gmd/ccgg/trends/>.

- ✓ Change the Vessel Volume to 5 L
- ✓ Change the Final Temperature to 25 C
- ✓ Change the Final Pressure to 1 atm
- ✓ Set the pressures for Ar, CO₂, and O₂ gases to 0.009, 0.00039, and 0.203 atm, respectively

Calculation Parameters	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	5.00000
Partial Pressure: Ar (atm)	9.00000e-3
Partial Pressure: CO2 (atm)	3.90000e-4
Partial Pressure: N2 (atm)	
Partial Pressure: O2 (atm)	0.203000

The N₂ partial pressure is not set. This is because the total pressure and the partial pressures of the other gas components are fixed. One variable must be adjustable and it cannot be P_{H₂O}, because that is a product of the water phase calculation.

$$P_T - P_{Ar} + P_{O_2} + P_{CO_2} + P_{H_2O} = P_{N_2}$$

The values on the left side of the equation are known. The P_{H₂O} is computed from the vapor pressure of liquid water. Therefore, P_{N₂} must be the difference variable.

- ✓ Change the Compute results cell to Final

The purpose of the Compute Results cell is to instruct the software on what results to display in the Report tab. Presently, there is a single report tab and only one set of conditions, Ambient or Final can be displayed (a software limitation).

- ✓ Calculate
- ✓ Click the Output tab below the grid to view the results

The calculated P_{N₂} is 0.756 atm. The P_{H₂O} is not shown, because it was not defined. It can be computed by subtraction of the partial pressures from 1 atm total pressure:

$$P_{H_2O} = 1 - 0.009 - 0.00039 - 0.7562 - 0.203 = 0.314 \text{ atm.}$$

Variable	Value
Stream Parameters (mol)	
Stream Amount	55.6673
Moles (True) - Liquid-1 (mol)	55.5039
Moles (True) - Vapor (mol)	0.163397
Calculation Results	
Ambient Temperature (°C)	25.0000
Ambient Pressure (atm)	1.00000
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	5.00000
Partial Pressure: Ar (atm)	9.00005e-3
Partial Pressure: CO2 (atm)	3.90001e-4
Partial Pressure: N2 (atm)	0.756223
Partial Pressure: O2 (atm)	0.203003
Condition that results were computed for	Ambient

The moles of gas added is shown in the inflows. How these gases are added to the system is not explained in this calculation. However, it can be simply a matter of creating a bottle gas with the four components at the moles (or mole ratios) in the grid below.

Inflows (mol)	
H2O	55.5082
N2	0.124038
O2	0.0334252
CO2	7.93442e-5
Ar	1.48304e-3

$$Total = 0.12404 + 0.03342 + 7.934e^{-5} + 1.483e^{-3} = 0.1590255 \text{ moles}$$

$$\%N_2 = \frac{0.124038}{0.1590255} * 100 = 77.999\%$$

$$\%O_2 = \frac{0.0334252}{0.1590255} * 100 = 21.019\%$$

$$\%Ar = \frac{0.001483}{0.1590255} * 100 = 0.933\%$$

$$\%CO_2 = \frac{7.93442e^{-5}}{0.1590255} * 100 = 0.050\%$$

The above values would be the bottle gas composition that would create an air composition in the autoclave at 1 atm and 25 C. This mixture is also dependent on the headspace to liquid ratio, because each gas has a different solubility in water.

- ✓ Click on the Report tab and review the Stream Inflow, Stream Parameters, Total and Phase Flow, and Species Output tables

The Stream Inflows table shows the same information as the Inflows grid. The H₂O content, 55.508 is the initial amount. The additional material is what the software added to match our specifications.

Stream Inflows

Row Filter Applied: Only Non Zero Values

Species	mol
H2O	55.5082
N2	0.124037
O2	0.0334251
CO2	7.93448e-5
Ar	1.48303e-3

The computed pH is 5.6. This is consistent with rainwater pH.

Liquid 1 Properties

pH	5.61223
----	---------

The total volume is 5 L. The liquid volume is slightly higher than 1 L because the computed volume of the 1 kg H₂O at STP is 1.0029 L. Therefore, the gas is slightly less than 4 L.

	L	L	L
Volume	4.99998	1.00321	3.99677

The vapor and aqueous composition are in the Species Output table. The vapor fractions should be consistent with the defined values for O₂, Ar, and CO₂. The N₂ and H₂O fractions are computed. The dissolved CO₂ is 0.58 mg/l and this value is consistent with surface waters around the globe.

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mol	mg/L	mole %
H2O	55.5082	9.96712e5	3.13836
OH-1	4.14892e-9	7.03366e-5	0.0
H3O+1	2.44702e-6	0.0464017	0.0
N2	0.124037	13.2157	75.6223
O2	0.0334251	8.13609	20.3003
CO2	7.6902e-5	0.578066	0.0390002
CO3-2	4.71141e-11	2.81825e-6	0.0
HCO3-1	2.44278e-6	0.148575	0.0
Ar	1.48303e-3	0.495933	0.900005
Total (by phase)	55.6673	9.96734e5	100.0

Summary

The purpose of this example was to introduce multiple gas components to an autoclave calculation. The software does not limit the number of gases that can be fixed, although this does make the calculation more difficult to converge.

9.4 Basic Autoclave #4 – CO₂/H₂S/CH₄ in seawater

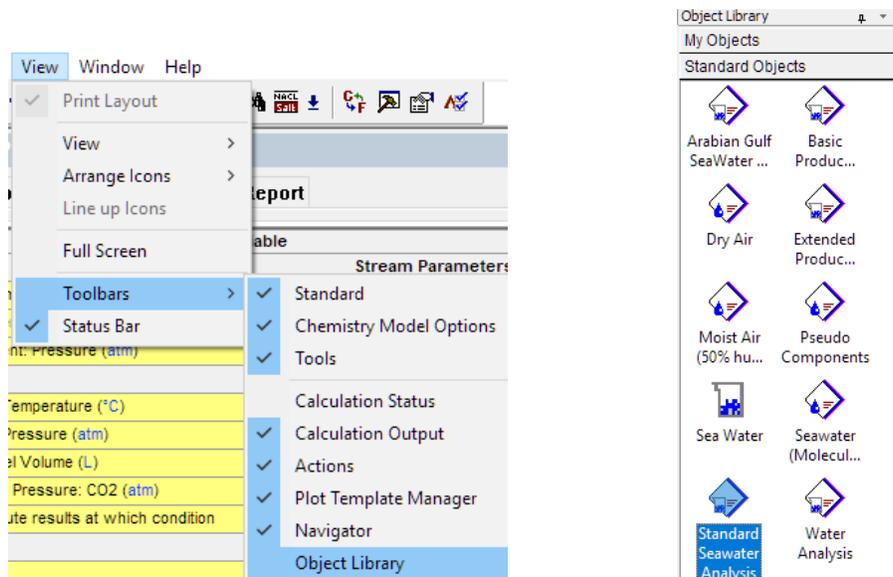
This example will use the standard seawater analysis object to create the brine for the autoclave. Then the gases will be added. The hypothetical is that seawater is being injected into a reservoir, and its reaction with the reservoir gas is being studied.

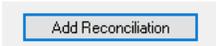
The training purpose of this case is to incorporate several calculation objects into the autoclave study. You will start by bringing in the seawater analysis from the object library, then you will create a new stream from it. Lastly, you will run the autoclave calculation.

Getting Started

Bringing in the Standard Seawater analysis from the Object library and reconciling it

- ✓ Open the Object Library panel using the Menu action: View>Toolbars>Object Library



- ✓ Drag the Standard Seawater Analysis object from the Standard Objects Panel to the Navigator panel
- ✓ Complete the Seawater reconciliation by Adding a Reconciliation object -  - and calculating.

Variable	Value
Density (g/ml)	0.0
Specific Electrical Conductivity (1/(ohm-cm))	0.0
Neutrals (mg/L)	
H2O	
SiO2	5.00000
Cations (mg/L)	
Na+1	10561.0
Mg+2	1272.00
Ca+2	400.000
K+1	380.000
Sr+2	13.0000
Li+1	0.100000
Ba+2	0.0500000
Anions (mg/L)	
Cl-1	18980.0
SO4-2	2648.30
Br-1	65.0000
B(OH)4-1	33.5500
F-1	1.40000
I-1	0.0500000
HCO3-1	144.000

Reconciliation

Reconcile

No Reconcile

Reconcile pH

Reconcile pH/Alkalinity

Calculate Alkalinity

Calculate

Summary

Dominant Ion Charge Balance (eq/L):

Cation Charge: 0.594036 eq/L

Anion Charge: -0.594166 eq/L

Imbalance: -1.30049e-4 eq/L

2.990 mg/L of Na+1 is needed to balance.

Isothermal Calculation

25.0000 °C 1.00000 atm

Phase Amounts

Aqueous 1022.09 g

Vapor 0.0 g

Solid 0.0392764 g

Aqueous Phase Properties

pH 7.53445

Convert the Reconciled Seawater to a Stream object and running the Autoclave calculation

- ✓ Click on the Add as Stream object at the bottom of the grid -
- ✓ Change the Name of the saved stream to 1L Seawater

Save Selected Result Streams

Export

Name: 1 L Seawater

Include the following phases in the stream(s)

Aqueous Vapor

Second Liquid Solids

- ✓ Press OK to create the new Stream -
- ✓ Click on the 1 L Seawater stream
- ✓ Open the Units Manager and change the units to Metric-Batch-Mass

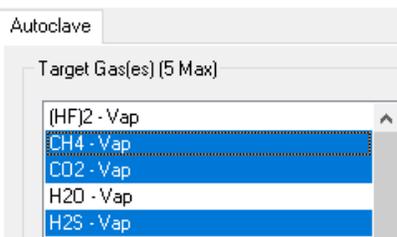
Units Manager

Metric Batch Mass

- ✓ Add H2S and CH4 to the grid (the CO2 is already there)

Variable	Value
Stream Parameters	
Stream Amount (g)	1022.13
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (g)	
H2O	987.659
SiO2	5.00000e-3
B2O3	0.0148130
BaCl2	4.64607e-5
CaCl2	1.06416
CO2	0.0866069
KCl	0.724571
LiCl	6.10784e-4
MgCl2	2.25929
MgF2	2.29552e-3
MgO	1.15145
NaBr	0.0837018
NaCl	26.8072
NaI	5.90579e-5
SO3	2.20721
SrCl2	0.0235202
BaSO4	3.29017e-5
CaCO3	0.0392435
H2S	0.0
CH4	0.0

- ✓ Add a Single Point calculation
- ✓ Change the calculation type to Autoclave
- ✓ Open the Specs window and select CO2, H2S, and CH4



- ✓ Set the Final Temperature to 100 C
- ✓ Set the final pressure to 100 atm
- ✓ Set the vessel volume to 1.5 L
- ✓ Set the CO2 partial pressure to 2 atm
- ✓ Set the H2S partial pressure to 0.1 atm
- ✓ Calculate
- ✓ Click on the Report and scroll down to the Stream Parameters Scaling Tendencies table. Note the pH and saturated solids

According to the calculation, the sweater pH decreases to 4.9 at reservoir conditions (it is 7.5 at the surface).

Aqueous Properties

pH	4.91906	
Ionic Strength (x based)	0.0116852	mol/mol

Also, barite is the only mineral computed to be saturated. The solids amount is small, according to the Phase and Flows table. Its computed to be about 0.04 mg.

Scaling Tendencies

Row Filter Applied: Values > 1.0e-4

<i>Solids</i>	Post-Scale	Pre-Scale
BaSO4 (Barite)	1.00000	

Summary

The purpose of this case was to incorporate several Studio objects into an autoclave study. The key aspect is recognizing that the stream created has a known size, 1 L, and this size needs to fit in the autoclave volume entered. Also, the units needed to be changed to mass, because keeping volume units in the Stream Amount row, causes calculation problems for the autoclave.

9.5 Basic Autoclave #5 - Calculating the Material Needed for a Sour Gas Experiment

A common autoclave application is testing corrosion in a high pressure/temperature gas production well. In such a case, the CO₂ and H₂S partial pressures are known at the HPHT conditions, and the laboratory is required to create an experiment that meets the P_{CO₂} and P_{H₂S} values. Since it is difficult to measure the gas composition at the HPHT testing conditions, we would need to perform gas-phase calculations to predict the amount of CO₂ and H₂S needed for the pressure vessel.

The simulation is a gas well with bottom-hole conditions are 150 C and 400 atm and the CO₂ and H₂S partial pressures are 20 and 1 atm. The carrier gas is a mixture of light hydrocarbons (C1 - C6) plus N₂ and H₂ (for safety reasons, flammable gases, C1 - C6 and H₂, are not used, and N₂ is the only additional gas). The client has a brine analysis, including the laboratory measured pH and alkalinity.

Getting started

The table below contains the water analysis. This is entered in a water analysis object, and sent to a stream where the autoclave calculation is run. It is the same procedure as the previous case, except you will start with a blank water analysis instead of the completed seawater.

Properties		Neutrals, mg/l		Cations, mg/l		Anions, mg/l	
TDS	71500	SiO2	56	Na+1	26570	Cl-1	42800
pH	6.5	B(OH)3	78	K+1	525	SO4-2	84
Alkalinity	490			Ca+2	570	HCO3-1	420
Density	1.04			Mg+2	250	B(OH)4-1	0.0
				Sr+2	41	HS-1	0.0
				Ba+2	16	C2H3O2-1	144
				Fe+2	0.0	CHO2-1	27

- ✓ Add a new Water Analysis from Actions pane icon  Add Water Analysis
- ✓ Name it object **Gas Well Water**
- ✓ Select the MSE framework
- ✓ Change the Stream Amount to 0.5 L
- ✓ Enter the measured properties in the grid
- ✓ Enter the cation-anion data into the grid
- ✓ Select the Add Reconciliation button, then select the Reconcile pH/Alkalinity button

Variable	Value
Analysis Parameters	
Stream Amount (L)	0.500000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	71500.0
Measured pH	6.50000
Measured Alkalinity (mg HCO ₃ /L)	490.000
Density (g/ml)	1.04000
Specific Electrical Conductivity (µmho/cm)	0.0
Calculation Parameters	
Alkalinity Titrant	CO ₂
Alkalinity pH Titrant	H ₂ SO ₄
Alkalinity End Point pH	4.50000
Use Single pH Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Neutrals (mg/L)	
H ₂ O	
SiO ₂	56.0000
B(OH) ₃	78.0000
CO ₂	0.0

Cations (mg/L)	
Na+1	26570.0
K+1	525.000
Ca+2	570.000
Mg+2	250.000
Sr+2	41.0000
Ba+2	16.0000
Fe+2	0.0

Anions (mg/L)	
Cl-1	42800.0
SO ₄ -2	84.0000
HCO ₃ -1	420.000
B(OH) ₄ -1	0.0
HS-1	0.0
C ₂ H ₃ O ₂ -1	144.000
HCOO-1	27.0000

- ✓ Calculate then view the information in the Summary
- ✓ Confirm that the measured pH and Alkalinity values were duplicated by the software

The software added 94.6 mg/l CO₂ and also added 2.2 mg/l HCl to generate the measured pH and alkalinity values.

Summary

Unit Set: **Metric (mass concentrator)**

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

Dominant Ion Charge Balance (eq/L)
Cation Charge: 1.21933 eq/L
Anion Charge: -1.21890 eq/L
Imbalance: 4.31571e-4 eq/L

15.300 mg/L of Cl-1
is needed to balance.

Reconcile pH Alkalinity Calculation
Alkalinity: 490.000 mg HCO₃/L
Titration End Pt: 4.50000
Alkalinity Titrant: CO₂
Added: 94.6307 mg/L
Alkalinity pH Titrant: H₂SO₄
pH Reconciliation:
Measured pH: 6.50000
pH Titrants:
Acid: HCl
Added: 2.19967 mg/L
Base: NaOH

Phase Amounts
Aqueous 523.276 g
Vapor 0.0 g
Solid 0.0123250 g

Aqueous Phase Properties
pH 6.50000
Ionic Strength 0.0220112 mol/m
Density 1.04655 g/ml

The water analysis is completed and is ready to be used in the autoclave

Convert the water analysis to the Autoclave Input water

- ✓ Click on the Add as Stream button on the bottom of the grid and give it a name **Gas Well Autoclave #1** –

Save Selected Result Streams ? ×

Export

Name:

Include the following phases in the stream(s)

Aqueous Vapor

Second Liquid Solids

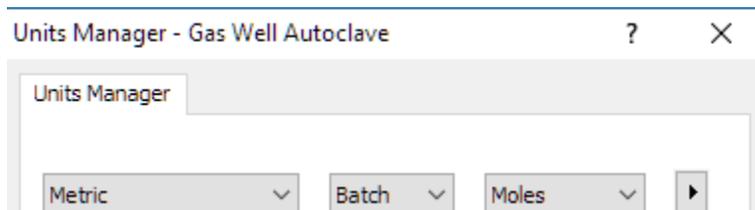
Gas Well Autoclave 1	
Description	
Variable	Value
Stream Parameters	
Stream Amount (L)	0.500003
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mg/L)	
H2O	
SiO2	55.9997
B(OH)3	0.0
CO2	397.562
HCl	0.0

B2O3	43.9108
Ba[C2H3O2]2	2.78201
CaCl2	1114.49
CaO	234.418
K[C2H3O2]	237.215
KCl	820.854
MgCl2	979.330
NaCl	67508.4
Na[HCOO]	40.7883
SO3	61.5534
SrCl2	74.1786
BaSO4	24.6499

- ✓ Add CO2, H2S and N2 to the Inflows grid

The CO₂ will already be there, but by typing it again, the software will place it at the bottom of the grid with the H₂S and N₂. This will make it easier to review the gas inflow after the calculation is completed.

- ✓ Change the units to Metric-Batch-Moles



- ✓ Select the Customize button then make the following changes to the Inflow and composition variables

- ✓ Inflows moles

Inflow variables		
Stream Amount	Mass	g
Inflows	Moles	mol

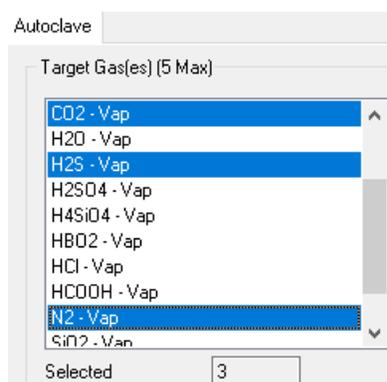
- ✓ Aqueous Composition Concentration
- ✓ Vapor Composition Mole Fraction
- ✓ Solids Composition Concentration
- ✓ 2nd Liquid Composition Mole Fraction

Output variables		
Aqueous Composition	Concentration	mg/L
Vapor Composition	Mole Fraction	mole %
Solid Composition*	Concentration	mg/L
2nd Liquid Composition	Mole Fraction	mole %
Total Composition	Mass	g

You will use Mole units in this case, because it makes it easier to determine the mole fraction of N₂, CO₂, and H₂S needed in the gas phase. The moles of the other water components are not important here, and so the values shown in the grid for these components can be ignored.

- ✓ Add a Single Point > Autoclave calculation
- ✓ Click the Specs button

- ✓ Highlight CO₂, H₂S, and N₂ and then press OK



- ✓ Set the following Calculation Parameters
- ✓ Final Temperature = 150 C
- ✓ Final Pressure = 400 atm
- ✓ Vessel Volume = 1 L
- ✓ CO₂ partial pressure = 20 atm
- ✓ H₂S partial pressure = 1 atm
- ✓ Compute results = Ambient

Calculation Parameters	
Final Temperature (°C)	150.000
Final Pressure (atm)	400.000
Vessel Volume (L)	1.00000
Partial Pressure: CO ₂ (atm)	20.0000
Partial Pressure: H ₂ S (atm)	1.00000
Partial Pressure: N ₂ (atm)	
Compute results at which condition	Ambient

- ✓ Calculate
- ✓ Select the Report tab and view the Input table, specifically the CO₂, H₂S, and N₂ values

Stream Inflows

Row Filter Applied: Only Non Zero Values

	Input	Output
Species	mol	mol
CO ₂	4.51676e-3	0.254726
H ₂ S	0.0	0.0199076
N ₂	0.0	4.15506

Compare the CO₂ output value to the input. The difference is the amount needed to create the 20 atm partial pressure at test conditions. Also, note the pressures that is required at ambient conditions. This is the charging pressure needed to create the 400 atm test pressure.

- ✓ Scroll down to the Properties table

Mixture Properties

Stream Amount	651.376	g
Temperature	25.0000	°C
Pressure	225.851	atm

Liquid 1 Properties

pH	4.93117	
----	---------	--

The Ambient Pressure is 226 atm. This is the gas charging pressure. In other words, after the CO₂, H₂S, and N₂ are added to the autoclave at the amount shown in the above calculation, the final pressure is computed to be 226 atm.

- ✓ Scroll to the Total and Phase flow table

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total g	Liquid-1 g	Vapor g	Solid g
Mass	651.376	526.215	125.149	0.0116293
	L	L	L	cm3
Volume	1.00000	0.501326	0.498672	2.59599e-3

The total volume is 1 L, as designed. The Aqueous volume is slightly larger than 0.5 L due to density changes. There is also 12 mg barite solid present (see Scale Tendency table), but this does not affect the calculations, because the mass is relatively small.

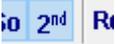
Summary

This case is similar to the previous case, except that more work is done to create the water stream. Also, instead of creating a gas phase and equilibrating the gas with the water as to inlet streams (as done in ScaleChem), the Autoclave calculation is used to create the reservoir fluid.

9.6 Basic Autoclave #6 - Dense-phase liquid in an autoclave

This example is similar to previous cases, except that the pressure is very high, 1000 bar, and the gases added reach a dense-phase state. The purpose of this example is to show that the software works the same, whether the gas added remains as a gas phase or compresses to a supercritical state.

Getting Started

- ✓ Add a new Stream and label it Supercritical gas
- ✓ Turn on the 2nd Liquid Phase - 
- ✓ Set the framework to MSE
- ✓ Open the Units Manager
- ✓ Set the units to Metric-Batch-Mass
- ✓ Customize the Output as follows
- ✓ Vapor Composition = Mole Fraction
- ✓ 2nd Liquid Composition = Mole Fraction

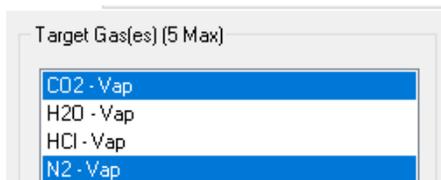
Vapor Composition	Mole Fraction	mole %
Solid Composition	Mass	g
2nd Liquid Composition	Mole Fraction	mole %

- ✓ Add the following inflows to the grid, NaCl, NaHCO₃, N₂, CO₂, and H₂S
- ✓ Set the NaCl to 60 g and the NaHCO₃ to 1 g

Inflows (g)	
H ₂ O	1000.00
NaCl	60.0000
NaHCO ₃	1.00000
N ₂	0.0
CO ₂	0.0

Supercritical CO₂

- ✓ Add a Single Point calculation and label it CO₂ Dense Phase
- ✓ Change the calculation type to Autoclave calculation
- ✓ Open the Specs window and select N₂ and CO₂



- ✓ Enter the following settings
- ✓ Final Temperature = 180 C
- ✓ Final Pressure = 1000 atm
- ✓ Vessel Volume = 1.5 L

- ✓ Partial Pressure CO₂ = 10 atm
- ✓ Compute Results = Final

Variable	Value
Stream Parameters	
Stream Amount (g)	1061.00
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation Parameters	
Final Temperature (°C)	180.000
Final Pressure (atm)	1000.00
Vessel Volume (L)	1.50000
Partial Pressure: CO ₂ (atm)	10.0000
Partial Pressure: N ₂ (atm)	
Compute results at which condition	Final

- ✓ Calculate
- ✓ Click on the Report tab and review the Species Output table

Species Output (True Species)

Row Filter Applied: Values > 1.0e-6

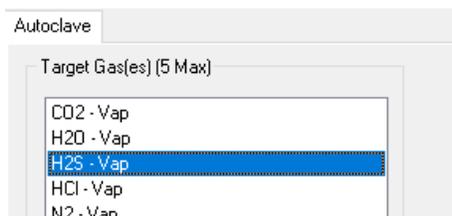
column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Liquid-2
	g	g	mole %
Cl-1	36.3975	36.3975	1.87645e-17
H ₂ O	1000.01	991.521	6.9514
Na+1	23.8761	23.8761	4.29113e-15
OH-1	3.28078e-3	3.28078e-3	1.14106e-17
CO ₂	3.04069	0.0592314	1.00002
CO ₃ -2	0.0169851	0.0169851	2.18202e-11
HCO ₃ -1	0.680014	0.680014	5.90653e-19
H ₃ O+1	2.21572e-6	2.21566e-6	5.19732e-11
NaOH	9.60647e-6	9.58876e-6	6.5341e-9
N ₂	180.962	6.27843	92.0486
Total (by phase)	1244.98	1058.83	100.0

The Liquid-2 column contains the supercritical gas composition. It is dominated by N₂ (92%), H₂O (7%) and CO₂ (1%). There are also low concentrations of dissolved ions (an aspect of the MSE framework) that can be ignored. The 1% CO₂ @1000 atm PT is the 10 atm partial pressure. Therefore, you can see that in this case, the partial pressure as it relates to a dense/liquid phase is also computed.

Supercritical H₂S

- ✓ Add a Single Point calculation and label it H₂S Dense Phase
- ✓ Change to Autoclave calculation
- ✓ Open the Specs window and select H₂S



- ✓ Enter the following settings
- ✓ Final Temperature = 40 C
- ✓ Final Pressure = 100 atm
- ✓ Vessel Volume = 1.5 L
- ✓ Partial Pressure CO2 = 10 atm
- ✓ Compute Results = Final

Calculation Parameters	
Final Temperature (°C)	40.0000
Final Pressure (atm)	100.000
Vessel Volume (L)	1.50000
Partial Pressure: H2S (atm)	
Compute results at which condition	Final

- ✓ Calculate
- ✓ Click on the Report tab and review the Species Output table

The Liquid-2 column is 98.2% H2S, this is the supercritical phase. There is also a small amount of H2O dissolved in this dense phase.

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

Column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Liquid-2
	g	g	mole %
H2O	1000.21	997.365	1.66496
H2S	378.657	60.7621	98.2351
Cl-1	36.3975	36.3969	1.95197e-4
Na+1	23.8761	23.8758	1.53523e-4
CO2	0.521045	0.105076	0.0995447

- ✓ Scroll up to the Thermodynamic Properties table

The densities of each phase is shown. The supercritical H2S is computed to have a density of 0.77 g/cc. the bulk density of the system is 0.96 g/cc (Total)

Thermodynamic Properties

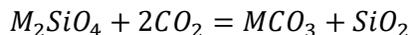
	Unit	Total	Liquid-1	Liquid-2
Density	g/ml	0.960047	1.03389	0.768754
Enthalpy	cal	-3.96999e6	-3.88062e6	-89370.1

Summary

This is a very simple case, with the new aspect being that instead of fixing the pressures in the vapor phase, the dense/critical fluid phase becomes the target phase.

9.7 Basic Autoclave #7 - CO₂ Sequestration

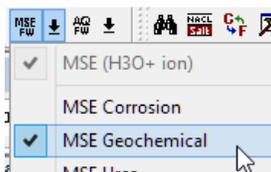
A proposed CO₂ sequestration process is to inject CO₂ gas into rock rich in alkali-silicate minerals. These silicates react with CO₂ in the following way



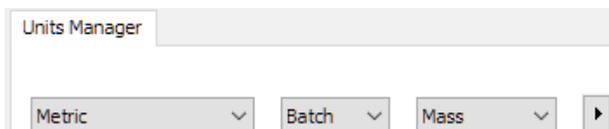
where M is Ca⁺², Mg⁺² or Fe⁺². The rates at which the CO₂ dissolves the silicates and precipitates into carbonates is important to the sequestering process, but it will not be considered in this example.

Getting Started

- ✓ Create a new stream and rename it **CO₂ Sequestration**
- ✓ Change the framework to MSE
- ✓ Add the MSE Geochemical database



- ✓ Open the Units Manager then change the units to Metric-Batch-Mass



- ✓ Add the following inflows and values to the grid:

Inflow	Grams
H ₂ O	950
NaCl	50
Fe ₂ SiO ₄	500
Mg ₂ SiO ₄	500
Ca ₂ SiO ₄	500
CO ₂	

The vessel contains 1 kg of 5% NaCl solution and 1.5 kg of minerals that are found in basalt rock. These minerals will react with CO₂ via the acid-base reaction shown above.

Variable	Value
Stream Parameters	
Stream Amount (g)	2500.00
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (g)	
H ₂ O	950.000
NaCl	50.0000
Fe ₂ SiO ₄	500.000
Mg ₂ SiO ₄	500.000
Ca ₂ SiO ₄	500.000
CO ₂	0.0

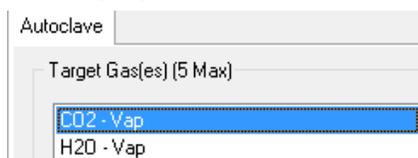
Summary

Unit Set: Metric (mass)

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

- ✓ Add a Single Point Calculation and label it **HP CO₂-Rx reaction**
- ✓ Change the Calculation type to Autoclave

- ✓ Set the Final Temperature to 200 C
- ✓ Set the Final Pressure to 300 atm
- ✓ Set the Vessel volume to 2.0 L
- ✓ Change the “Compute results at which condition” cell to Final
- ✓ Click the Specs button and Highlight CO2



The grid should look like the following.

Variable		Value
Stream Parameters		
Stream Amount (g)		2500.00
Ambient: Temperature (°C)		25.0000
Ambient: Pressure (atm)		
Calculation Parameters		
Final Temperature (°C)		200.000
Final Pressure (atm)		300.000
Vessel Volume (L)		2.00000
Partial Pressure: CO2 (atm)		
Compute results at which condition		Final
Inflows (g)		
H2O		950.000
NaCl		50.0000
Fe2SiO4		500.000
Mg2SiO4		500.000
Ca2SiO4		500.000
CO2		0.0

- ✓ Calculate
- ✓ Click the Output tab and view the Inflows at the bottom of the grid

The composition added to the Autoclave is show in the screenshot below. This composition creates a 2 L mixed-phase system at 200 C and 300 atm.

Inflows (g)	
H2O	950.000
NaCl	50.0000
Fe2SiO4	500.000
Mg2SiO4	500.000
Ca2SiO4	500.000
CO2	862.762

Nearly 900 grams CO₂ is added to this autoclave. Although this does not indicate whether all of it has reacted, since some gas must be present to create the 300 atm pressure

- ✓ Click the Report tab and scroll down to the Element Balance table

The table below is a portion of the element balance. The row C(+4) represents the CO₂. The 235.464 grams carbon in the Total column is the 862.762 grams CO₂ that was added to the grid.

Element Balance

Row Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor	Solid
	g	g	g	g
H(+1)	106.306	105.062	0.374164	0.869639
Na(+1)	19.6687	19.6687	0.0	0.0
Ca(+2)	232.688	2.37934e-3	0.0	232.686
Fe(+2)	274.059	0.166102	0.0	273.893
Mg(+2)	172.752	0.187196	0.0	172.565
O(-2)	2041.24	884.035	51.9441	1105.26
Cl(-1)	30.3313	30.3313	3.27125e-7	0.0
C(+4)	235.464	18.7051	18.3832	198.376
Si(+4)	250.254	0.183569	5.54024e-7	250.071

Of the 235.46 g C(+4) added, 198.376 g (84.3%) reacted to form solids. The rest dissolved in water (8%), or remained unreacted in the vapor (7.8%).

- ✓ Scroll up to the Species Output table and view the Solids column

The table below is the bottom portion of the Species Output table where solid phases are. According to the software, the silicates reacted with CO₂ to form quartz and talc. The metals formed carbonates.

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor	Solid
	g	g	g	g
SiO ₂ (Quartz)	431.308	0.0	0.0	431.308
Mg ₃ Si ₄ O ₁₀ (OH) ₂ (Talc)	163.608	0.0	0.0	163.608
FeCO ₃ (Siderite)	568.2	0.0	0.0	568.2
CaMg(CO ₃) ₂ (Dolomite)	1070.6	0.0	0.0	1070.6
Total (by phase)	3362.76	1058.34	70.7014	2233.72

The above minerals are the phases in the Geochemical database that are computed to be the most thermodynamically stable at these conditions. Since this calculation does not include reaction pathways, the minerals that form, for example dolomite, may not form initially, but rather over time.

- ✓ Lastly, scroll up to the Total and Phase Flows table

The case started with 1500 g of minerals (Fe₂SiO₄, Mg₂SiO₄, and Ca₂SiO₄). The final solid mass is 2233 g. The 733 g is nearly all the sequestered CO₂.

Total and Phase Flows (Amounts)

Column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor	Solid
	g	g	g	g
Mass	3362.76	1058.34	70.7014	2233.72
	L	L	L	cm ³
Volume	2.00002	1.06480	0.196578	738.643

Summary

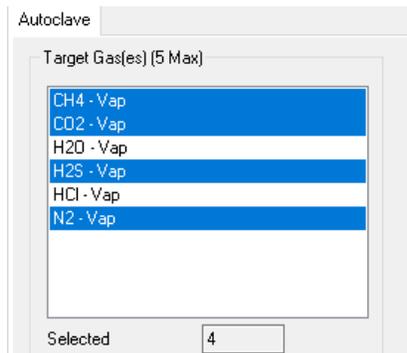
This is an example where the Autoclave tool is used to develop a chemical conversion process. In this case, the main reaction components are the minerals, and the purpose of the autoclave was to reach the proper final pressure using CO₂ as the gas stream.

9.8 Intermediate Autoclave – Calculating the incremental pressures during the charging steps

- ✓ Add a stream and label it **Pressure Charging steps**
- ✓ Add the following components, NaCl, CO₂, H₂S, N₂, and CH₄
- ✓ Change the units to Metric-Batch-Mass
- ✓ Set the H₂O to 450 g and the NaCl to 50 g

Calculate the final state of the autoclave

- ✓ Add a Single Point calculation and label it Final conditions
- ✓ Open the Specs window and select the target gases, CH₄, CO₂, H₂S, and N₂



- ✓ Set the following Calculation Parameters
- ✓ Final Temperature = 100 C
- ✓ Final Pressure = 200 atm
- ✓ Vessel Volume = 1 L
- ✓ PCO₂ = 20 atm
- ✓ PH₂S = 1 atm
- ✓ PN₂ = 10 atm
- ✓ Compute Results = Final

Calculation Parameters	
Final Temperature (°C)	100.000
Final Pressure (atm)	200.000
Vessel Volume (L)	1.00000
Partial Pressure: CO ₂ (atm)	20.0000
Partial Pressure: H ₂ S (atm)	1.00000
Partial Pressure: N ₂ (atm)	10.0000
Partial Pressure: CH ₄ (atm)	
Compute results at which condition	Final

- ✓ Click on the Output tab and view the inflows

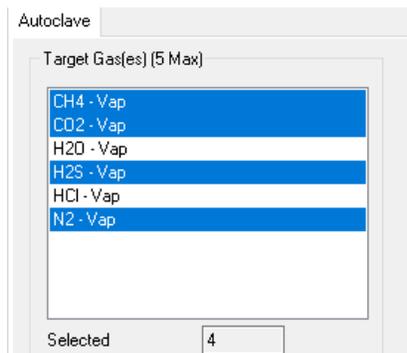
Inflows (g)	
H2O	450.000
NaCl	50.0000
CO2	17.2511
H2S	0.799225
N2	4.87627
CH4	46.8914

- ✓ View the Calculation results and the partial pressures for each component. The PCH4 and PH2O were calculated . The PCH4 is shown here.

Partial Pressure: CO2 (atm)	19.9999
Partial Pressure: H2S (atm)	0.999991
Partial Pressure: N2 (atm)	9.99998
Partial Pressure: CH4 (atm)	167.419

Calculating the pressure steps for the H2S addition

- ✓ Add a new Single Point calculation and label it H2S charging
- ✓ Open the Specs window and select the target gases, H2S



- ✓ Set the following Calculation Parameters
- ✓ Final Temperature = 100 C
- ✓ Final Pressure = 200 atm
- ✓ Vessel Volume = 1 L
- ✓ PCO2 = 20 atm
- ✓ PH2S = 1 atm
- ✓ PN2 = 10 atm
- ✓ Compute Results = Final

Calculation Parameters	
Final Temperature (°C)	100.000
Final Pressure (atm)	200.000
Vessel Volume (L)	1.00000
Partial Pressure: CO2 (atm)	20.0000
Partial Pressure: H2S (atm)	1.00000
Partial Pressure: N2 (atm)	10.0000
Partial Pressure: CH4 (atm)	
Compute results at which condition	Final

9.9 Advanced Autoclave #1 - CO₂ and H₂S in headspace of a 5% NaCl-H₂O solution

The purpose of this example, is to simulate a basic autoclave preparation. The procedure is as follows: 1) place the deaerated water and the test apparatus in the autoclave and seal it, 2) purged the autoclave with N₂ to remove any remain oxygen 3) Add CO₂ and H₂S gases to the prescribed initial pressure, and 4) heat the vessel to test temperature.

The above procedure is seven steps. By comparison, the basic Autoclave tool is a single-step calculation. All materials are entered at one time. Therefore, what is explained in this chapter is how to use the current autoclave and mixer objects to perform properly, each of the above steps. This example will detail each step.

This example uses the following Autoclave settings.

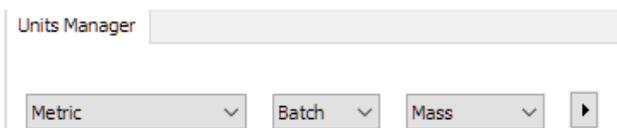
The autoclave is a 1 L vessel filled with 0.5 L of 5% NaCl solution, and a 0.25 L test apparatus. The test temperature is 115 C and the test partial pressures for CO₂ and H₂S are 20 and 0.1 atm, respectively.

You will compute the conditions of the autoclave at each step, compute the amounts of CO₂ and H₂S to be added, and lastly compute the autoclave pressures at ambient and at test conditions.

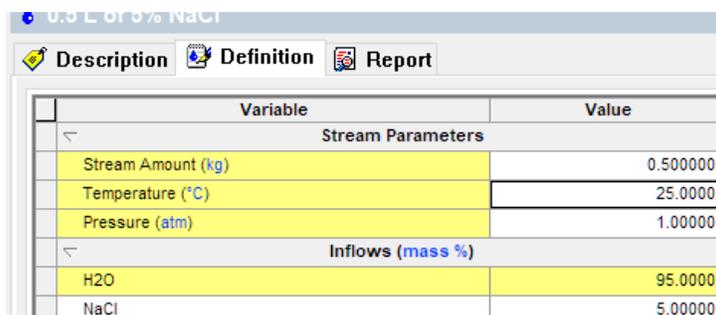
Getting Started

Creating the 0.5 L, 5% NaCl solution

- ✓ Add a new stream and label it 0.5 L of 5% NaCl
- ✓ Change the framework to MSE
- ✓ Change the units to Metric-Batch-Mass



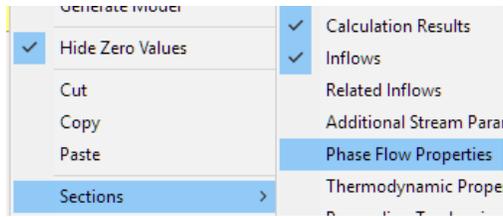
- ✓ Add NaCl to the grid and enter 5 grams
- ✓ Change water to 95 grams
- ✓ Change the stream amount to 0.5 kg (estimate)



The image shows a software window titled "0.5 L of 5% NaCl". It has three tabs: "Description", "Definition", and "Report". The "Description" tab is active, showing a table with two columns: "Variable" and "Value".

Variable	Value
Stream Parameters	
Stream Amount (kg)	0.500000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mass %)	
H2O	95.0000
NaCl	5.00000

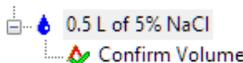
- ✓ Add a single point calculation, and label it **Confirm Volume**
- ✓ Calculate and Click on the Output tab when converged
- ✓ Right-mouse-click on the grid and select Sections>Phase Flow Properties



- ✓ View the liquid volume – it needs to be 0.5 L

Volume - Total (L)	0.484039
Volume - Liquid-1 (L)	0.484039

- ✓ Adjust the Stream amount in the Stream object to make this volume is 0.5 L. The value is 0.5165 kg.



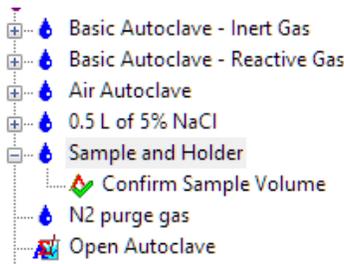
Stream Amount (kg)	0.516500
Temperature (°C)	25.0000
Pressure (atm)	1.00000

It's important that this amount change be done in the Stream object, because this object will be used in the next calculation.

Creating a 0.25 L sample and holder

- ✓ Add a new calculation to the stream and label it 0.25 L Sample/Holder

- ✓ Set the framework to MSE - 
- ✓ Set the units to Metric-Batch-Mass
- ✓ Add C (carbon) to the grid and give it a mass of 750 g
- ✓ Set the water flow to zero



Variable	Value
Stream Parameters	
Stream Amount (g)	750.000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (g)	
H2O	0.0
C	750.000

Aluminum is inert in these calculations because REDOX is not on. Thus, it is a convenient material to occupy the 250 ml volume. The exact amount of Al needed to produce 250 ml still needs to be compute, and this will be done next.

- ✓ Add a single-point calculation and label it Confirm Sample volume
- ✓ Calculate and click on the Output tab
- ✓ Open the Volume section of the grid (Right-mouse-click, Sections>Phase Flow Properties)

The 750 grams C occupies 330.8 ml volume. Therefore, you will adjust this to 676.1 g to produce the 250 ml volume ($250/330.819 \times 750$).

Mass - Solid (g)	750.000
Volume - Total (L)	0.330819
Volume - Solid (cm3)	330.819

- ✓ Change the C value to 566.78 grams in the Sample and Holder stream

Sample and Holder-1
 Confirm Sample Volume

Variable	Value
Stream Parameters	
Stream Amount (g)	566.780
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (g)	
H2O	0.0
C	566.780

- ✓ Return to the calculation object, calculate, and confirm that the volume is 250 ml

Mass - Total (g)	566.780
Mass - Solid (g)	566.780
Volume - Total (L)	0.250002
Volume - Solid (cm3)	250.002

Create the N2 purge gas

During the procedure, N₂ is added to purge any excess O₂. If the autoclave is at 1 atm back pressure, then the pressure in the vessel will be 1 atm, and N₂ (plus some H₂O) occupies the headspace. The software does not have the practical problem of excluding oxygen, but there is still a need to include the N₂ that fill the headspace. Therefore, this N₂ stream is needed for this step.

- ✓ Create a new stream and label it N2 purge gas
- ✓ Set the framework to MSE
- ✓ Add N₂ to the grid, and give it a value of 1 mole
- ✓ Set H₂O to zero

N2 purge gas

Description Definition Report

Variable	Value
Stream Parameters	
Stream Amount (mol)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	0.0
N2	1.00000

Add Calculation

Special Conditions

Solids Only

Summary

Unit Set: Metric (moles)

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

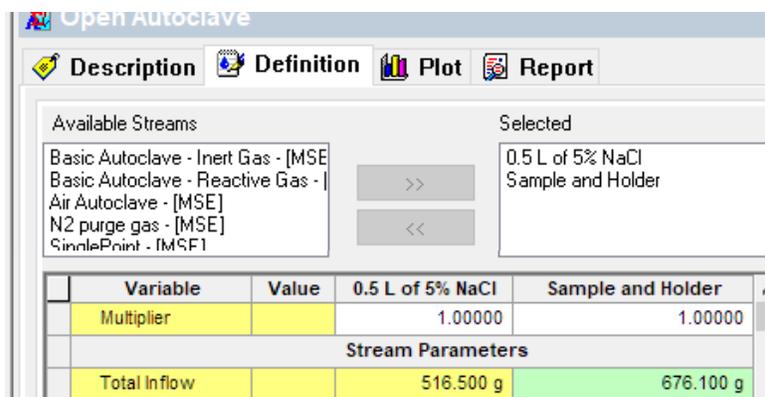
It's not necessary to test volume here, because that will be done once the three streams are mixed. That will be next.

Step #1 - Add the Brine and sample holder to the open autoclave

This next step is performed in a mixer object. The mixers were presented in Chapter 5, and so if there are questions about how this block works, refer to that chapter.

- ✓ Add a Mixer object  Add Mixer and label it **Open Autoclave**
- ✓ Add the following streams to the mixer, **0.5 L of 5% NaCl** and **Sample and Holder**

Notice the Total inflow row. They should show the mass of each stream adjusted in the previous steps.



✓ Click on the Report tab and scroll down to the Total and Phase flow table
Both the liquid and solid volumes should be the expected values, 500 ml liquid and 250 ml solid.

Total and Phase Flows (Amounts)

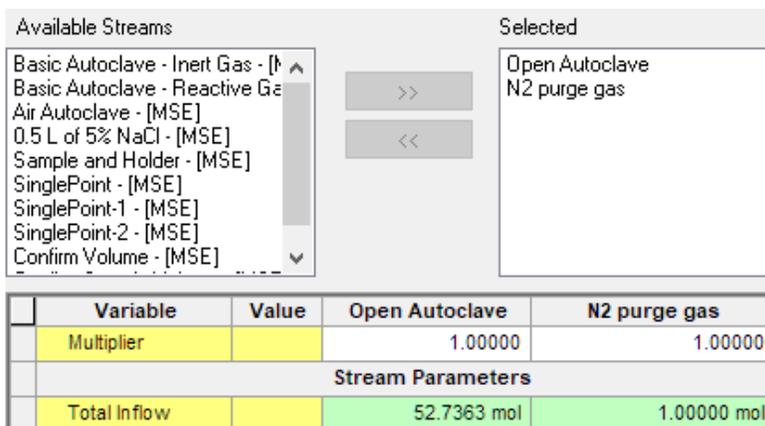
column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Solid
	g	g	g
Mass	1192.60	516.500	676.100
	L	L	cm3
Volume	0.750015	0.500012	250.002

Step #2 - Add N2 purge gas to the closed autoclave

- ✓ Add a new mixer and label it **Closed Autoclave**
- ✓ Add the **Open Autoclave** and **N2 Purge gas** streams to the Selected section

The Total inflows row now shows mole units, because the units in the Open Autoclave object was not modified. This will not affect the next steps.



The next step is to add sufficient N₂ so that it fills the autoclave headspace. The total autoclave volume is 1 L, and 750 ml is occupied by the water and apparatus. Thus, you will manually change the multiplier of the N₂ purge gas, until the total volume is 1 L. This is a manual process, and so this step may take several iterations.

The amount of N₂ needed to fill 250 ml headspace at ambient conditions, can be calculated from the ideal gas equation:

$$n = \frac{PV}{RT} = \frac{1 \text{ atm} * 0.25 \text{ l}}{0.082057 \frac{\text{l} \cdot \text{atm}}{\text{mol} \cdot \text{K}} * 298.15 \text{ K}} = 0.01022 \text{ moles}$$

- ✓ Set the N2 purge gas multiplier to 0.01022

Variable	Value	Open Auto	N2 purge gas
Multiplier		1.00000	0.0102200

- ✓ Calculate
- ✓ Click on the Report tab and view the Total and Phase Flow table

Total and Phase Flows (Amounts)

	Total	Liquid-1	Vapor	Solid
	L	L	L	cm3
Volume	1.00162	0.500192	0.251421	250.002

The autoclave is 1.62 ml too high. Once again, using ideal gas to remove this much from the sample

$$0.01022 - \frac{1 \text{ atm} * 0.00162 \text{ l}}{0.082057 \frac{\text{l} \cdot \text{atm}}{\text{mol} \cdot \text{K}} * 298.15 \text{ K}} = 0.01016 \text{ moles}$$

- ✓ Change the multiplier to 0.01016

Variable	Value	Open Auto	N2 purge gas
Multiplier		1.00000	0.0101600
Stream Parameters			
Total Inflow		52.7363 mol	0.0101600 mol

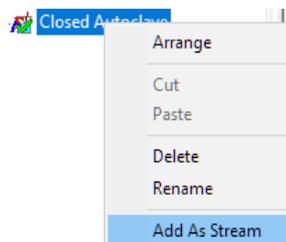
- ✓ Calculate and view the phase flow table in the Report

	L	L	L	cm3
Volume	1.00010	0.500192	0.249907	250.002

Step #3 and #4 – Add the CO₂/H₂S and set the final Autoclave condition

The last two steps are combined into one. First, the mixer output is converted to a stream and then an autoclave calculation computes the amount of CO₂ and H₂S needed.

- ✓ Right-mouse-click on the **Closed Autoclave** mixer object and select Add as Stream

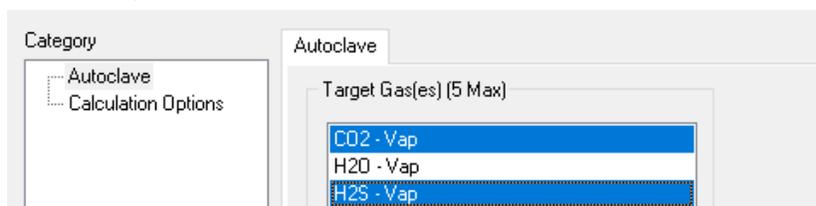


- ✓ Name the stream **Heated Autoclave**
- ✓ Add CO₂ and H₂S to the grid

Inflows (mol)	
H2O	27.2365
NaCl	0.441884
Al	25.0579
N2	0.0101600
CO2	0.0
H2S	0.0

- ✓ Add a Single Point calculation and label it Test Temperature
- ✓ Change the calculation type to Autoclave
- ✓ Open the Specs window and select CO2 and H2S from the Target Gas list

Calculation Options



- ✓ Set the final temperature to 115 C
- ✓ Set the Vessel volume to 1 L
- ✓ Set the CO2 Partial Pressure to 20 atm
- ✓ Set the H2S Partial Pressure to 0.1 atm
- ✓ Set the Compute results to Final

Stream Parameters	
Stream Amount (mol)	52.7464
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation Parameters	
Final Temperature (°C)	115.000
Final Pressure (atm)	
Vessel Volume (L)	1.00000
Partial Pressure: CO2 (atm)	20.0000
Partial Pressure: H2S (atm)	0.100000
Compute results at which condition	Final

- ✓ Calculate
- ✓ Click on the Report tab and view the Stream Parameters table

The software computes that the final pressure is 23.3 atm and the pH is 3.5.

- ✓ Scroll up to the Stream Inflows table

The software computes that to achieve the target partial pressures, 0.220 moles CO₂ and 0.00202 moles H₂S are needed.

The software does not show the Ambient pressure in this view, and the calculation needs to be repeated to see it. For this, the Compute Results needs to be changed Ambient

- ✓ Change the Compute Results to Ambient and calculate
- ✓ View the Summary section to find the ambient pressure

According to the software, the pressure needs to be increase with CO₂ and H₂S to 0.4 atm. The assumption is that a gas bottle will be created with the molar ratio of 0.2197 CO₂ to 0.002023 moles H₂S. This converts to a 99.087% CO₂ and 0.912% H₂S gas composition in the bottle.

Summary

The purpose of this example is to show how several calculation objects are used to model the autoclave charging and test procedure.

9.9 Advanced Autoclave #2 - Manual Autoclave setup using stepwise gas addition

This next example provided by a client, was to simulate the NACE TM-0185-06 standard (internal coatings testing). The procedure called for a stepwise charging of the autoclave with H₂S and CO₂. After each charging step, the autoclave pressure is measured. The targets were the concentrations of dissolved H₂S and CO₂ (molecular only) in the water at test temperatures.

This experimental approach is not covered by the Autoclave calculation because two ambient pressures are needed rather than one. As a result, the mixers are used to mimic the experimental procedure.

The image below is a cartoon of the autoclave apparatus. Water and the coupon apparatus are added to the autoclave and autoclave sealed. N₂ (hydrated) purges the water to remove O₂. The gas release valve is closed and H₂S is added to a specified total pressure. The H₂S valve is closed and CO₂ gas is added to a specified total pressure. The CO₂ valve is closed and the reactor is heated to test temperature. The test pressure is recorded.

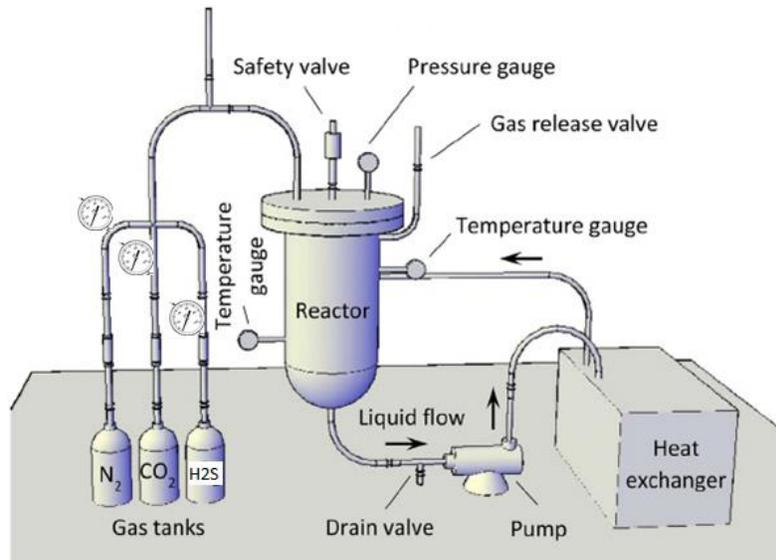


Figure 1 autoclave adapted from : https://www.researchgate.net/figure/285578029_fig1_Fig-1-Schematic-for-immersion-corrosion-testing-in-a-stainless-steel-autoclave-type

You will create five inlet streams, the salt water, headspace gas, apparatus, CO₂ gas, and H₂S gas. These streams will be added to a four mixers lined up in series, with each mixer representing a different procedure step. The table below contains the target specification for the autoclave.

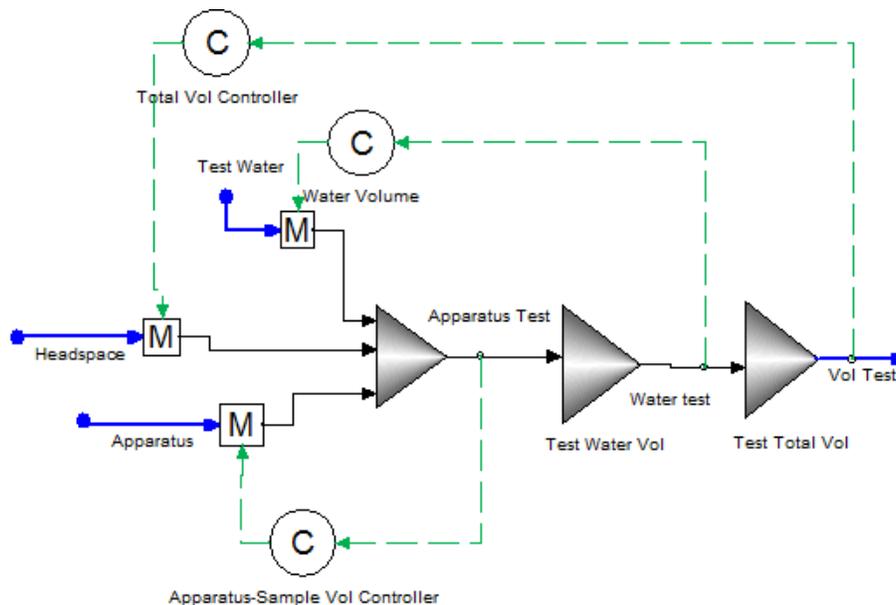
2.3 CO₂ Sequestration Autoclave Setup			
Stream and Autoclave (mixer) Setup		Autoclave Target Specification	
Streams	Salt Water	Vessel Vol	3.6 L
	Sparging N ₂	Final T	260 F
	Apparatus		
	H ₂ S gas		
	CO ₂ gas		
Autoclave (mixer unit)	Autoclave Step 1 (fill and seal)	Dissolved CO ₂	3500 mg/l
	Autoclave Step 2 (Charge with H ₂ S)	Dissolved: H ₂ S	500 mg/l
	Autoclave Step 3 (Charge with CO ₂)		
	Autoclave Step 4 (Heat to test T)		

Explanation

The images below are an indication how this procedure will be performed.

Step 1 - Setting up the autoclave with water, apparatus volume and sparging N₂ in headspace

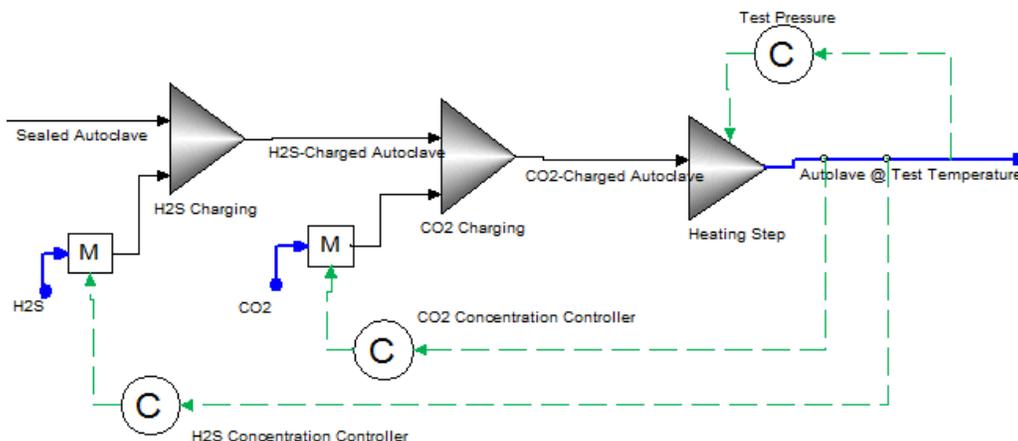
The first image shows the initial charging step. The water, apparatus and headspace make up the total volume in the sealed autoclave at ambient conditions. Controllers, are used to adjust the volume each inflow to match the specified filling volumes and the total autoclave volume. In this example, you will act as the controller by adjusting manually, the amount of each stream.



To accomplish this step, you will create three streams, brine, sparging N₂, and apparatus and add it to a mixer. You will then adjust manually the Multiplier cell in the mixer so that the specified volumes are met.

Step 2 through 4 – Adding H₂S, CO₂, and Raising temperature

The next image contains Steps 2 through 4 in which H₂S and CO₂ are added individually and the amount required is based on the concentrations measured at test temperature. Three controllers adjust; the amount of H₂S, the amount of CO₂, and the final pressure at test temperature.

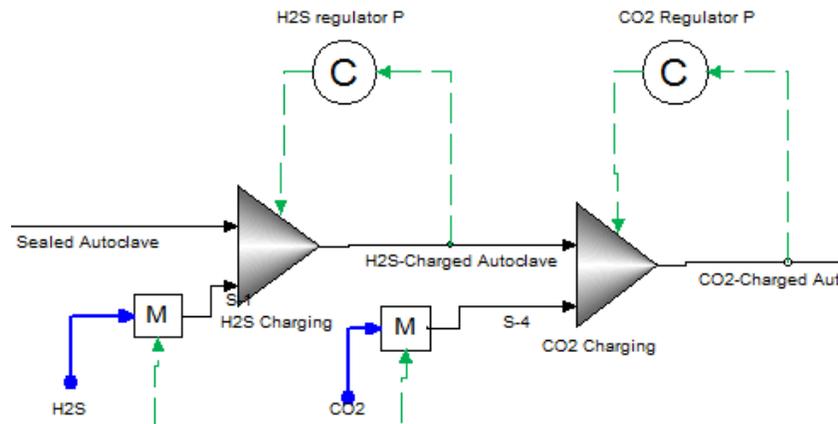


You will create two streams, H₂S and CO₂, and three mixers, H₂S Charging, CO₂ Charging, and Heating Step. You will then manually adjust the H₂S and CO₂ inflows (using the Multiplier cell in the mixers) until their target concentrations in the Heating Step mixer are met. You will simultaneously adjust Pressure in the Heating Step mixer until the total volume matches the total autoclave volume. All three adjustments are interdependent, and thus are made simultaneously.

These three manual adjustments will take multiple iterations (several minutes). Through these adjustments, you will observe the impact of total pressure on CO₂ and H₂S solubility, CO₂ and H₂S mass inflow on total pressure, and CO₂ and H₂S inflow on the solubility on the other gas.

Steps 5 and 6 – calculate the ambient pressure for the H₂S and CO₂ charging steps

The final steps are to calculate the pressures in the H₂S and CO₂ charging steps. you will adjust manually the pressure in the H₂S mixer and the CO₂ mixer until the total volume is 3.6 L. the pressure obtained represents the regulator pressure of the gas tanks that feed H₂S and CO₂ into the autoclave.



You will adjust the pressure in each mixer until the total calculated volume in each match the 3.6L autoclave volume.

Getting started

The table below contains the streams you will create. Note the units.

Brine		N2 (100% humidity@21C)		Apparatus		H2S		CO2	
(grams)		(mole %)		(moles)		(moles)		(moles)	
Stream Amt	1000	Stream Amt	1 (moles)	Stream Amt	1	Stream Amt	1	Stream Amt	1
T, C	21	T, C	21	T, C	21	T, C	21	T, C	21
P, atm	1	P, atm	1	P, atm	1	P, atm	1	P, atm	1
H2O	994.75	H2O	2.46	H2O	0	H2O	0	H2O	0
NaCl	5	N2	97.54	Carbon	1	H2S	1	CO2	1
NaHCO3	0.25			Solids Only box	Check box				

- ✓ Create the streams using the information provided in the above table. Note the units change.
- ✓ Select the MSE framework for ALL the streams

Carbon is used for the Apparatus mass because it will be inert to all chemical reactions in this calculation. Using carbon is not intuitive, rather it is discoverable, and this, plus shortcuts will become routine as you spend time using the software.

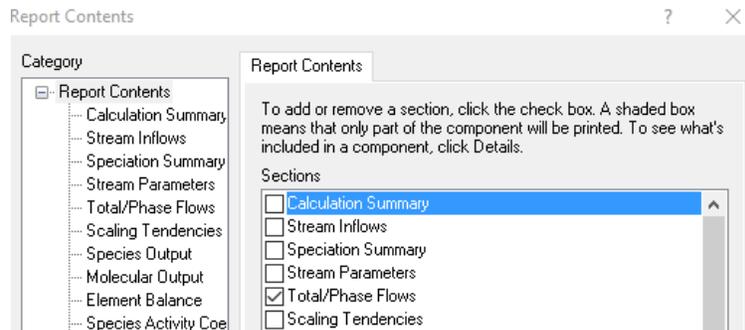
- ✓ Create four mixers, label them Autoclave Step 1 Autoclave Step 2, Autoclave Step 3 and Autoclave Step 4

Use the information in the table below for the input settings

Inlet Streams	Autoclave Step 1	Autoclave Step 2	Autoclave Step 3	Autoclave Step 4
Units	Metric-batch-moles	Metric-batch-moles	Metric-batch-moles	Metric-batch-moles Aqueous = Concentration Vapor = mole fraction
T, F	21	21	21	130
P, atm	1			
Streams	Brine N2 Apparatus	Autoclave Step 1 H2S	Autoclave Step 2 CO2	Autoclave Step 3
Target Spec	Brine = 1 L Apparatus = 500 ml Total Vol = 3.6 L	Total Vol = 3.6L	Total Vol = 3.6 L	CO2 (aq) = 3500 mg/l H2S (aq) = 500 mg/l Total Vol = 3.6 L

Add first Autoclave (Autoclave Step 1)

- ✓ Create the first mixer – label it Autoclave Step 1
- ✓ Add the stream, Brine
- ✓ Calculate
- ✓ Check the total volume in the Report.
- ✓ Modify the Report so that the total volume appears at the top of the report. Select the Customize button in the Report and deselect all tables except for Total/Phase Flows



- ✓ Adjust the Multiplier until the volume is exactly 1.

Variable	Value	Brine
Multiplier		1.00180
Stream Parameters		
Total Inflow		1001.80 g

	Total	Aqueous
	mol	mol
Mole (True)	55.4936	55.4936
Mole (App)	55.4079	55.4079
	g	g
Mass	1001.80	1001.80
	L	L
Volume	0.999982	0.999982

- ✓ Add the Apparatus stream to the mixer and calculate

- ✓ Review the solid volume in the report. Adjust the multiplier until the solids volume is 500 ml

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Solid
	mol	mol	mol
Mole (True)	1128.45	55.4936	1072.96
Mole (App)	1128.37	55.4079	1072.96
	g	g	g
Mass	2074.76	1001.80	1072.96
	L	L	cm3
Volume	1.49998	0.999982	499.999

Variable	Value	Brine	Apparatus
Multiplier		1.00180	1072.96

Stream Parameters

- ✓ Add the N2 stream to the mixer and calculate
- ✓ Review the Total volume in the report. Adjust the multiplier until the total volume is 3.6 L.

Variable	Value	Brine	Apparatus	N2 (100% hu
Multiplier		1.00180	1072.96	0.0876000

Stream Parameters

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
Mole (True)	1128.54	55.4943	0.0869863	1072.96
Mole (App)	1128.46	55.4085	0.0869863	1072.96
	g	g	g	g
Mass	2077.19	1001.82	2.41621	1072.96
	L	L	L	cm3
Volume	3.59987	1.00043	2.09944	499.999

Create the remaining autoclaves

- ✓ Add a new mixer – label it Autoclave Step 2
- ✓ Change the T to 21 C and add the streams Autoclave Step 1 and H2S

Autoclave Step 2 (Charge with H2S)

Description Definition Plot Report File Viewer

Available Streams: Brine - [MSE], N2 (100% humidity @23C) - [MSE], Apparatus - [MSE], CO2 - [MSE], SinglePoint - [MSE], Autoclave Step 3 (Charge with CO2), Autoclave Step 4 (Heat to test T) - [MSE], SinglePoint-1 - [MSE]

Selected: Autoclave Step 1 (Water + Apparatus), H2S

Variable	Value	Autoclave Step 1 (H2S
Multiplier		1.00000	1.00000

Stream Parameters

Total Inflow		1128.46 mol	0.100000 mol
Temperature (°C)	21.0000	21.0000	21.0000
Pressure (atm)	1.00000	1.00000	1.00000

- ✓ Add a new mixer – label it Autoclave Step 3
- ✓ Change the T to 21 C and add the streams Autoclave Step 2 and CO2

Autoclave Step 3 (Charge with CO2)

Description Definition Plot Report File Viewer

Available Streams Selected

Brine - [MSE]
N2 (100% humidity @23C) - [MSE]
Apparatus - [MSE]
H2S - [MSE]
SinglePoint - [MSE]
Autoclave Step 1 (Water + Apparatus)
Autoclave Step 4 (Heat to test T) - [MSE]
SinglePoint-1 - [MSE]

>>
<<

Autoclave Step 2 (Charge with H2S)
CO2

Variable	Value	Autoclave Step 2 (CO2
Multiplier		1.00000	1.00000
Stream Parameters			
Total Inflow		1128.38 mol	0.100000 mol
Temperature (°C)	21.0000	21.0000	21.0000
Pressure (atm)	1.00000	1.00000	1.00000

- ✓ Add a new mixer – label it Autoclave Step 3
- ✓ Change the T to 130 C and add the streams Autoclave Step 3

Autoclave Step 4 (Heat to test T)

Description Definition Plot Report File Viewer

Available Streams Selected

Brine - [MSE]
N2 (100% humidity @23C) - [MSE]
Apparatus - [MSE]
H2S - [MSE]
CO2 - [MSE]
SinglePoint - [MSE]
Autoclave Step 1 (Water + Apparatus)
Autoclave Step 2 (Charge with H2S)
SinglePoint-1 - [MSE]

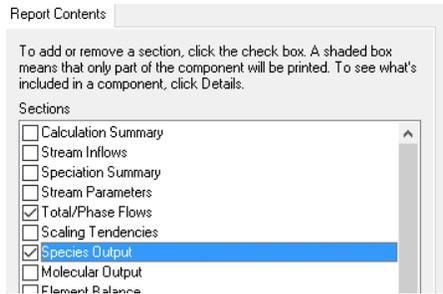
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Autoclave Step 3 (Charge with CO2)

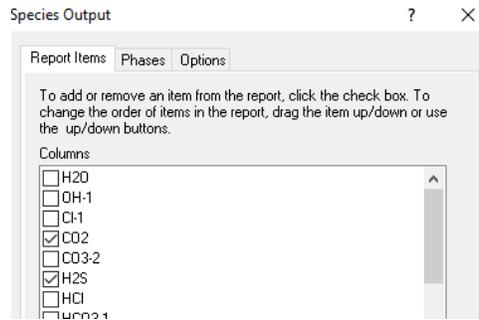
Variable	Value	Autoclave Step 3 (Charge with CO2)
Multiplier		1.00000
Stream Parameters		
Total Inflow		1129.07 mol
Temperature (°C)	130.000	21.0000
Pressure (atm)	1.00000	1.00000

Modify the H₂S and CO₂ multipliers and the Test Pressures to match Test Concentrations

- ✓ Press the Calculate button in Autoclave Step 4 – this will create a cascading calculation for all mixers and streams.
- ✓ Click on the Report for Autoclave Step 4. Modify the report so that the Total Volume and Species Output (True Species) tables are at the top
- ✓ Click on the Customize button. Clear All tables except for Total/Phase Flow and Species Output. Close the window.



- ✓ Click on the Species Output True Species title to open the Table editor. Deselect all Report items except for CO2 and H2S



The Report should now look like this. This will speed up the manual adjustments required in this case

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Vapor	Solid
	mol	mol	mol
Mole (True)	1128.65	55.6068	1073.05
Mole (App)	1128.65	55.6068	1073.05
	g	g	g
Mass	2085.00	1006.87	1078.13
	L	L	cm3
Volume	1823.55	1823.05	502.377

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Vapor	Solid
	mol	mole %	mol
CO2	0.101491	0.182515	0.0
H2S	0.1	0.179834	0.0

- ✓ Adjust the total pressure until the total Volume reads 3.6 liters.

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
Mole (True)	1128.74	55.3717	0.411693	1072.96
Mole (App)	1128.66	55.2838	0.411693	1072.96
	g	g	g	g
Mass	2085.00	1000.38	11.6625	1072.96
	L	L	L	cm3
Volume	3.59908	1.06955	2.02954	499.999

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mg/L	mole %	mol
CO2	0.102184	535.326	21.6603	0.0
H2S	0.0978086	974.902	16.3264	0.0

- ✓ Review the CO2 and H2S concentrations.

The target CO2 is 3500 mg/l and the target H2S is 500 mg/l. you will change the multiplier in the Apparatus Step 2, Apparatus Step 3, and total pressure in Apparatus Step 4 to meet these targets.

- ✓ Reduce the H2S multiplier in Autoclave Step 2 from 1 to 0.5

Variable	Value	Autoclave Step 1 (H2S
Multiplier		1.00000	0.500000
Stream Parameters			
Total Inflow		1128.46 mol	0.0500000 mol

- ✓ Increase the CO2 multiplier in Autoclave Step 3 from 1 to 6

Variable	Value	Autoclave Step 2 (CO2
Multiplier		1.00000	6.00000
Stream Parameters			
Total Inflow		1128.56 mol	0.600000 mol

- ✓ Calculate Autoclave Step 4

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
Mole (True)	1129.19	55.0367	1.19508	1072.96
Mole (App)	1129.11	54.9504	1.19508	1072.96
	g	g	g	g
Mass	2105.30	994.399	37.9424	1072.96
	L	L	L	cm3
Volume	7.44430	1.06210	5.88221	499.999

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mg/L	mole %	mol
CO2	0.600632	1177.67	47.8804	0.0
H2S	0.0493622	213.66	3.57329	0.0

- ✓ Change the Total Pressure in Autoclave Step 4 until the Volume is 3.6 L

Variable	Value	Autoclave Step 3 (Charge with CO2)	^
Multiplier		1.00000	
Stream Parameters			
Total Inflow		1129.11 mol	
Temperature (°C)	130.000	21.0000	
Pressure (atm)	13.0400	1.00000	

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
Mole (True)	1129.19	55.4105	0.821231	1072.96
Mole (App)	1129.11	55.3243	0.821231	1072.96
	g	g	g	g
Mass	2105.30	1002.48	29.8577	1072.96
	L	L	L	cm3
Volume	3.59919	1.07491	2.02428	499.999

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mg/L	mole %	mol
CO2	0.600555	3061.1	64.0247	0.0
H2S	0.0494298	486.194	4.15179	0.0

✓ Repeat these steps until the target specifications are met.

Variable	Value	Autoclave Step 1 (H2S	^
Multiplier		1.00000	0.515000	
Stream Parameters				
Total Inflow		1128.46 mol	0.0515000 mol	

Variable	Value	Autoclave Step 2 (CO2
Multiplier		1.00000	6.89000
Stream Parameters			
Total Inflow		1128.51 mol	0.689000 mol

Variable	Value	Autoclave Step 3 (Charge with CO2)	^
Multiplier		1.00000	
Stream Parameters			
Total Inflow		1129.20 mol	
Temperature (°C)	130.000	21.0000	
Pressure (atm)	14.3000	1.00000	

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
Mole (True)	1129.28	55.4205	0.901707	1072.96
Mole (App)	1129.20	55.3343	0.901707	1072.96
	g	g	g	g
Mass	2109.27	1002.95	33.3569	1072.96
	L	L	L	cm3
Volume	3.59889	1.07614	2.02275	499.999

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mg/L	mole %	mol
CO2	0.689505	3498.54	66.9794	0.0
H2S	0.0509779	500.087	3.90233	0.0

Final Step – calculate the pressures in the Step 2 and Step 3 autoclaves

- ✓ Adjust the pressure in Autoclave Step 2 until the total volume is 3.6 L

Variable	Value	Autoclave Step 1 (H2S
Multiplier		1.00000	0.515000
Stream Parameters			
Total Inflow		1128.46 mol	0.0515000 mol
Temperature (°C)	21.0000	21.0000	21.0000
Pressure (atm)	1.27600	1.00000	1.00000

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
Mole (True)	1128.60	55.5242	0.111080	1072.96
Mole (App)	1128.51	55.4359	0.111080	1072.96
	g	g	g	g
Mass	2078.95	1002.73	3.25507	1072.96
	L	L	L	cm3
Volume	3.60030	1.00140	2.09889	499.999

- ✓ Adjust the pressure in Autoclave Step 3 until the total volume is 3.6 L

Variable	Value	Autoclave Step 2 (CO2
Multiplier		1.00000	6.89000
Stream Parameters			
Total Inflow		1128.51 mol	0.689000 mol
Temperature (°C)	21.0000	21.0000	21.0000
Pressure (atm)	6.75000	1.27600	1.00000

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
Mole (True)	1129.28	55.7171	0.604605	1072.96
Mole (App)	1129.20	55.6314	0.604605	1072.96
	g	g	g	g
Mass	2109.27	1011.35	24.9572	1072.96
	L	L	L	cm3
Volume	3.60025	1.00734	2.09291	499.999

Summary

The manual procedure presented is an example of how an autoclave can be modeled when there is no automatic procedure, or if a flowsheet modeling tool is not available.

Chapter 10 Advanced Calculations: REDOX, Adsorption & Kinetics

Introduction

In this section we will work on advanced reduction/oxidation, adsorption, and kinetics calculation.

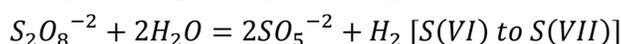
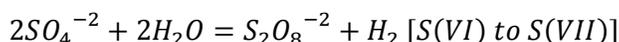
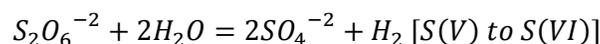
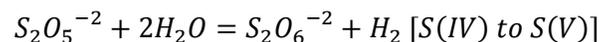
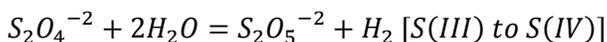
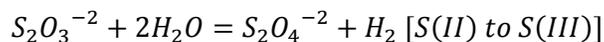
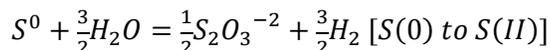
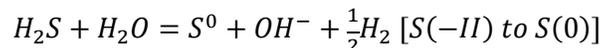
Section List

- 10.1 **REDOX Advanced Calculation:** calculating equilibrium of H₂S subsystems (page 10-2)
- 10.2 **Adsorption – Basic Surface Complexation:** modeling the adhesion of ions to a surface (page 10-4)
- 10.3 **Adsorption – Basic Ion Exchange:** adsorption with Exchange database (page 10-8)
- 10.4 **Kinetics – Basic Gas-Phase Reaction:** using kinetics in the OLI Studio (page 10-12)

10.1 REDOX Advanced Calculation

Overview

Oxidation reduction reactions can be kinetically limited, and as a result, having REDOX enabled can result in incorrect output. The sulfur system below is an example:



The thermodynamic result of oxidizing H₂S with O₂ is the formation of sulfate, S(VI). However, the reaction generally ends at elemental sulfur, S(0) because oxidizing elemental sulfur to sulfate is a slow process. For example, sulfuric acid production involves burning sulfur to form SO₂, followed by an oxidation step to sulfate. Since most calculations in OLI Studio are flash calculations of electrolyte solutions, oxidizing H₂S will generally stop at sulfur. However, without fine-tuning the calculation options, sulfate will form instead.

In this example, we will prepare a solution of H₂S and oxygen in water. We will calculate to equilibrium in two ways. In the first calculation, we will include all sulfur subsystems. In the second calculation, we will include only the S(-II) and S(0) subsystems.

Modifying the REDOX subsystems

- ✓ Create a new stream  **Add Stream** and rename it 'Advanced REDOX'  **Advanced REDOX**
- ✓ Enter the inflows from the table above

10.1 - Advanced REDOX Calculation					
Stream Name	Advanced Redox	Stream Amount	(calculated)	Inflows (mol)	
Name Style	Formula	Temperature	25 °C	H2O	55.508
Framework	Aqueous	Pressure	1 atm	H2S	0.001
Units Set	Default (moles)			O2	0.01
Settings	REDOX ON				

- ✓ Ensure that REDOX calculations are turned on 



- ✓ Ensure that Sulfur REDOX reactions is turned on
- ✓ Add a Single Point calculation > Isothermal calculation
- ✓ Calculate and review the Element Balance table at the bottom of the report

Element Balance

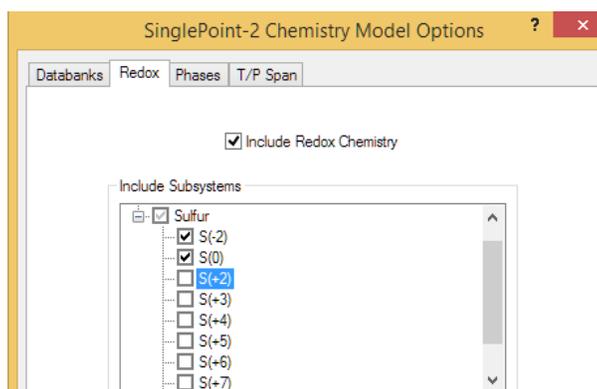
Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mol	mol	mol
H(+1)	111.018	111.018	4.40846e-4
O(-2)	55.512	55.5118	2.20423e-4
S(+4)	1.5834e-44	1.58242e-44	9.81536e-48
S(+6)	1.0e-3	1.0e-3	1.50748e-25
H	4.43242e-44	4.47458e-45	3.98496e-44
O(0)	0.016	2.44274e-3	0.0135573
S(+8)	2.34248e-25	2.34248e-25	0.0
S(+3)	3.08788e-126	3.08788e-126	0.0
S(+5)	4.10714e-62	4.10714e-62	0.0
S(+7)	4.1829e-36	4.1829e-36	0.0

All the H₂S was oxidized to S(VI), which is known to be the most thermodynamically stable oxidation state of sulfur in the presence of excess oxygen. However, this result is impractical because process applications would not produce sulfate. Rather, the product would be elemental sulfur. To accommodate for such limitations, the OLI Studio allows us to select or allow specific oxidation states

- ✓ Click on Chemistry>Model Options from the Menu bar
- ✓ Click on the Redox tab
- ✓ Expand the Sulfur Subsystem section and deselect all the oxidation states higher than S(0)



- ✓ Close the window, Calculate, and review the Element balance table

Element Balance

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor	Solid
	mol	mol	mol	mol
H(+1)	111.018	111.017	5.38426e-4	0.0
O(-2)	55.509	55.5087	2.69213e-4	0.0
S(-2)	4.68805e-37	4.50243e-37	1.85615e-38	0.0
H	5.3145e-44	4.47482e-45	4.86702e-44	0.0
O(0)	0.019	2.44275e-3	0.0165573	0.0
S(0)	1.0e-3	4.25942e-39	0.0	1.0e-3

The results now show that two oxidation states are possible. Furthermore, the total sulfur is 100% elemental sulfur.

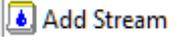
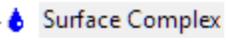
10.2 Adsorption – Basic Surface Complexation

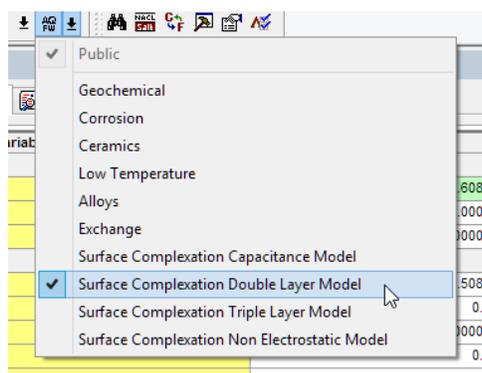
Overview

Adsorption onto reactive surfaces is a common natural and industrial phenomenon. The OLI Studio has a special database and mechanisms that allow us to model these reactions. The database is called the Surface Complexation Double Layer Model. Surface Complexation refers to the chemical reaction, and Double Layer Model refers to the electrostatic double layer theory used to compute the attraction of ions to and from the surface.

Adsorption reactions are available in the Aqueous Framework. They have not been transferred to the MSE framework (as of V9.1.5). This database contains a single-surface active functional group, $\equiv\text{Fe-OH}$, which is based on the hydrous ferric oxide surface data developed by Dzombak and Morel (1990)¹.

Setting up the Case

- ✓ Create a new stream  and rename it 'Surface Complex' 
- ✓ Select the Surface Complexation Double Layer Model from the AQ database dropdown list



- ✓ Enter the inflows from the table below

10.2 - Surface Complexation Calculation					
Stream Name	Surface Complexation	Stream Amt	(calculated)	Inflows (mol)	
Name Style	Formula	Temperature	25 °C	H2O	55.508
Framework	Aqueous	Pressure	1 atm	HOHFO1CPM	0.1
Units Set	Default (moles)			Na2HPO4	0.1
Database	Surface Complexation Double layer model			Na2HAsO4	
				PbCl2	

- ✓ Add a Single Point calculation and confirm the type of Calculation is Isothermal
- ✓ Confirm the initial concentrations of 0.1 mole for Na2HPO4 and HOHFO1CPM
- ✓ Calculate then click on the Report and review the Species Output table

¹ Dzombak, D.A and Morel, F.M.M. (1990), Surface Complexation Modeling: Hydrous Ferric Oxide, Wiley-Interscience, New York, 393 pp.

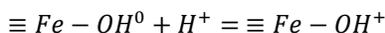
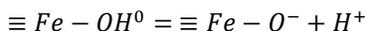
Species Output (True Species)

Row Filter Applied: Only Non Zero Values

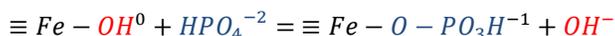
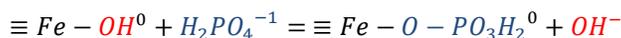
column Filter Applied: Only Non Zero Values

	Total	Aqueous	Solid
	mol	mol	mol
H2O	55.6039	55.6039	0.0
H+1	3.63531e-10	3.63531e-10	0.0
OH-1	4.53775e-5	4.53775e-5	0.0
H2P2O7-2	4.82446e-13	4.82446e-13	0.0
H2PO4-1	7.81093e-6	7.81093e-6	0.0
H3P2O7-1	1.24025e-20	1.24025e-20	0.0
H3PO4	2.40581e-13	2.40581e-13	0.0
H4P2O7	9.20193e-29	9.20193e-29	0.0
HP2O7-3	1.27286e-9	1.27286e-9	0.0
HPO4-2	4.27821e-3	4.27821e-3	0.0
Na+1	0.2	0.2	0.0
P2O7-4	1.64599e-8	1.64599e-8	0.0
PO4-3	2.70806e-5	2.70806e-5	0.0
H2OHFO1OH	1.92447e-5	0.0	1.92447e-5
HPO4HFO1H	2.81129e-3	0.0	2.81129e-3
OHFO1H	2.76878e-3	0.0	2.76878e-3
PO4HFO1H	0.0928741	0.0	0.0928741
HOHFO1CPM	1.52511e-3	0.0	1.52511e-3
H2PO4HFO1CPM	1.44517e-6	0.0	1.44517e-6
Total (by phase)	55.9082	55.8082	0.1

In some versions of the software, the bottom of the table will show six surface complexes. Three of the surfaces are the protonation-deprotonation reactions of the ferric oxide surface.



The remaining species are the adsorbed phosphate, and represent the following reactions



Furthermore, in some versions of the software certain species in the table will have two suffixes, -CPM, -OH and -H. The -CPM suffix indicates that the surface has a zero charge. The -OH and -H suffixes indicates that the surface is charged and that the counter-ions (to balance the charge) is either the OH⁻ or H⁺ ion.

Based on the calculation, the surface distribution is as follows

OLI Variable Name	Surface Species	Calculated amount (moles)
H2OHFO1OH	$\equiv Fe - OH^+$	1.924e-5
HPO4HFO1H	$\equiv Fe - O - PO_3H^{-1}$	2.811e-3
OHFO1H	$\equiv Fe - O^-$	2.769e-3
PO4HFO1H	$\equiv Fe - O - PO_3^{-2}$	0.0929
HOHFO1CPM	$\equiv Fe - OH^0$	1.525e-3
H2PO4HFO1CPM	$\equiv Fe - O - PO_3H_2^0$	1.445e-6

- ✓ Recalculate the stream using 0.1 mole of Na2HAsO4 instead of Na2HPO4 (set Na2HPO4 to 0.0)
- ✓ Click on the Report and view the Species Output table

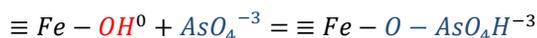
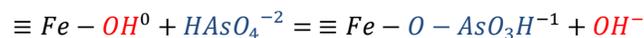
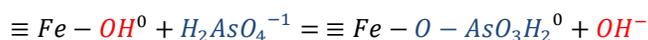
Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Solid
	mol	mol	mol
H2O	55.5093	55.5093	0.0
H+1	6.61868e-8	6.61868e-8	0.0
OH-1	2.93255e-7	2.93255e-7	0.0
Na+1	0.2	0.2	0.0
AsO4-3	1.34895e-9	1.34895e-9	0.0
H2AsO4-1	2.32729e-7	2.32729e-7	0.0
H3AsO4	1.89986e-12	1.89986e-12	0.0
HAsO4-2	0.0645294	0.0645294	0.0
H2OHFO1OH	0.0339747	0.0	0.0339747
HASO4HFO1H	9.95425e-4	0.0	9.95425e-4
HOASO4HFO1H	0.0344384	0.0	0.0344384
OHFO1H	6.04841e-4	0.0	6.04841e-4
HOHFO1CPM	0.0299501	0.0	0.0299501
H2ASO4HFO1CPM	3.65398e-5	0.0	3.65398e-5
Total (by phase)	55.8738	55.7738	0.1

The new species represent the following reactions



<i>OLI Variable Name</i>	<i>Surface Species</i>	<i>Calculated amount (moles)</i>
H ₂ OHFO ₁ OH	$\equiv Fe - OH^+$	0.0340
HASO ₄ HFO ₁ H	$\equiv Fe - O - AsO_3H^{-1}$	9.954e-4
HOASO ₄ HFO ₁ H	$\equiv Fe - O - AsO_4H^{-3}$	0.0344
OHFO ₁ H	$\equiv Fe - O^-$	6.048e-4
HOHFO ₁ CPM	$\equiv Fe - OH^0$	0.02995
H ₂ ASO ₄ HFO ₁ CPM	$\equiv Fe - O - AsO_3H_2^0$	3.654e-5

- ✓ Recalculate the stream by using 0.1 mole of PbCl2 instead of Na2HAsO4
- ✓ Click on the Report and view the Species Output table

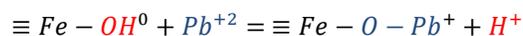
Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Solid
	mol	mol	mol
H2O	55.5082	55.5082	0.0
H+1	2.6272e-3	2.6272e-3	0.0
OH-1	5.99954e-12	5.99954e-12	0.0
Cl-1	0.119266	0.119266	0.0
HCl	1.20778e-10	1.20778e-10	0.0
HPbO2-1	3.27174e-23	3.27174e-23	0.0
PbCl2	0.0366446	1.93715e-3	0.0347074
PbCl3-1	1.13043e-4	1.13043e-4	0.0
PbCl4-2	1.70942e-5	1.70942e-5	0.0
PbCl+1	7.0377e-3	7.0377e-3	0.0
Pb+2	4.87434e-3	4.87434e-3	0.0
PbO	1.75839e-15	1.75839e-15	0.0
PbOH+1	1.26686e-6	1.26686e-6	0.0
H2OHFO1OH	0.048686	0.0	0.048686
OHFO1H	1.85827e-12	0.0	1.85827e-12
PbOHFO1OH	0.051312	0.0	0.051312
HOHFO1CPM	1.98727e-6	0.0	1.98727e-6
Total (by phase)	55.7788	55.6441	0.134707

The new species represent the following reactions



<i>OLI Variable Name</i>	<i>Surface Species</i>	<i>Calculated amount (moles)</i>
H2OHFO1OH	$\equiv Fe - OH^+$	0.0487
OHFO1H	$\equiv Fe - O^-$	1.86e-12
PbOHFO1OH	$\equiv Fe - O - Pb^+$	0.0513
HOHFO1CPM	$\equiv Fe - OH^0$	1.987e-6

This is a simple example of surface complexation.

- ✓ Enter the inflows from the table below

10.3 - Ion Exchange Calculation					
Stream Name	Ion Exchange	Stream Amt	(calculated)	Inflows (mol)	
Name Style	Formula	Temperature	25 °C	H2O	55.508
Framework	Aqueous	Pressure	1 atm	HKAOSOL	0.1
Units Set	Default (moles)			NiCl2	0.05
Database	Exchange			CuCl2	
				PbCl2	

- ✓ Add a Single Point calculation and confirm the type of Calculation is Isothermal
- ✓ Confirm the initial values of 0.05 mole for NiCl2 and 0.1 mole for HKAOSOL
- ✓ Calculate
- ✓ Click on the Report and review the Species Output table

There are two exchange surfaces at the bottom of the table, HKAOSOL and NiKAO₂SOL. The NiKAO₂SOL exchange species is comprised of one nickel and two KAOSOL functional groups. It is a bidentate structure. This is why the total solids is 0.076 moles instead of the 0.1 moles that we originally added. According to the calculation, 52% of the -KAOSOL surface is still protonated, which is an indication of the selectivity of this surface for Ni or H.

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Solid
	mol	mol	mol
H2O	55.5082	55.5082	0.0
H+1	0.0479949	0.0479949	0.0
OH-1	3.7298e-13	3.7298e-13	0.0
Cl-1	0.0999135	0.0999135	0.0
HCl	1.70938e-9	1.70938e-9	0.0
Ni2OH+3	1.95105e-12	1.95105e-12	0.0
Ni4(OH)4+4	4.60232e-29	4.60232e-29	0.0
NiCl+1	8.65304e-5	8.65304e-5	0.0
Ni+2	0.025916	0.025916	0.0
Ni(OH)2	1.11118e-25	1.11118e-25	0.0
Ni(OH)3-1	1.22514e-29	1.22514e-29	0.0
Ni(OH)4-2	8.49952e-43	8.49952e-43	0.0
NiOH+1	1.64006e-10	1.64006e-10	0.0
HKAOSOL	0.0520051	0.0	0.0520051
NIKASO2SOL	0.0239975	0.0	0.0239975
Total (by phase)	55.7582	55.6822	0.0760025

Note the H+ concentration, it is 0.048 moles, and represents the H⁺ exchanged off the 0.1 moles of HKAOSOL (0.1-0.052005=0.047995 moles). This system should therefore have a low pH.

- ✓ Scroll up to the Stream Parameters and record the pH

Aqueous Properties

pH	1.42766	
Ionic Strength (x-based)	2.25978e-3	mol/mol
Ionic Strength (m-based)	0.125829	mol/kg

The pH is computed to be low, 1.43. Thus, this exchange reaction results in a lower pH. Had Ni(OH)₂ been added instead of NiCl₂, then the H⁺ would have been neutralized.

- ✓ Recalculate the case using 0.05 mole of CuCl₂ instead of NiCl₂
- ✓ Review the results

The fraction of exchange sites populated by Cu⁺² is only slightly different from Ni⁺², indicating that the selectivity coefficient for Ni⁺² and Cu⁺² are similar (assuming ideal surface activity).

HKAOSOL	0.0528348	0.0	0.0528348
CUKAO2SOL	0.0235826	0.0	0.0235826
Total (by phase)	55.7543	55.6779	0.0764174

- ✓ Recalculate the case using 0.05 mole of PbCl₂ instead of CuCl₂
- ✓ Review the results

HKAOSOL	0.0678286	0.0	0.0678286
PBKAO2SOL	0.0160857	0.0	0.0160857
Total (by phase)	55.7312	55.6417	0.0895475

According to these results, there is less selectivity for Pb⁺² than for either Ni⁺² or Cu⁺². The selectivity is about 50% less. The cause of this difference appears to be in part due to the precipitation of PbCl₂ solid. As a result, only half the Pb⁺² exists as a soluble species, compared to the Ni⁺² and Cu⁺².

PbCl2	0.0575838	1.95049e-3	0.0556333
PbCl3-1	6.81523e-5	6.81523e-5	0.0
PbCl4-2	6.21075e-6	6.21075e-6	0.0
PbCl+1	0.011649	0.011649	0.0
Pb+2	0.0146069	0.0146069	0.0
PbO	3.32003e-17	3.32003e-17	0.0
PbOH+1	2.87075e-7	2.87075e-7	0.0
HKAOSOL	0.0678286	0.0	0.0678286
PBKAO2SOL	0.0160857	0.0	0.0160857
Total (by phase)	55.7812	55.6417	0.139548

- ✓ Change the inflows to the following

Inflows (mol)	
H2O	55.5082
HKAOSOL	0.100000
NiCl2	0.0250000
CuCl2	0.0250000
PbCl2	0.0250000

- ✓ Calculate and review the Species Output

This calculation represents competition among the three cations for the surface. Most of the surface is still protonated, and only a fraction of the Pb⁺² has adsorbed, again because of the PbCl₂ solid phase.

PbCl2	8.55244e-3	1.93652e-3	6.61591e-3
PbCl3-1	1.16136e-4	1.16136e-4	0.0
PbCl4-2	1.99129e-5	1.99129e-5	0.0
PbCl+1	7.6841e-3	7.6841e-3	0.0
Pb+2	6.84652e-3	6.84652e-3	0.0
PbO	6.24048e-18	6.24048e-18	0.0
PbOH+1	8.23489e-8	8.23489e-8	0.0
HKAOSOL	0.0518373	0.0	0.0518373
NIKASO2SOL	0.0116094	0.0	0.0116094
CUKAO2SOL	0.0106911	0.0	0.0106911
PBKAO2SOL	1.78081e-3	0.0	1.78081e-3
Total (by phase)	55.8055	55.723	0.0825346

We can better see the amount of Ni⁺², Cu⁺², and Pb⁺² removed from the water with another section of the table.

- ✓ Scroll down to the Element balance table

According to the table, of the 0.025 moles Ni⁺², Cu⁺², and Pb⁺² added to the water, about 50-60% of the metal still remains dissolved. Thus, adding more exchange material, or modeling this as a plug-flow column reactor, rather than a batch reactor, would improve the removal efficiency.

Element Balance

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

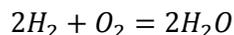
	Total	Aqueous	Solid
	mol	mol	mol
H(+1)	111.116	111.065	0.0518373
Cu(+2)	0.025	0.0143089	0.0106911
Pb(+2)	0.025	0.0166033	8.39672e-3
Ni(+2)	0.025	0.0133906	0.0116094
O(-2)	55.5082	55.5082	0.0
Cl(-1)	0.15	0.136768	0.0132318
KAOSOL	0.1	0.0	0.1

10.4 Kinetics – Basic Gas-Phase Reaction

Overview

In this section, we will look at the OLI Studio's approach to kinetics. The kinetics function is available within single point calculations. This function works by overriding the equilibrium equation for the reaction we select. It can also create a reaction mechanism that is not part of the standard OLI database.

In the case below, we will model the following gas-phase chemical reaction:

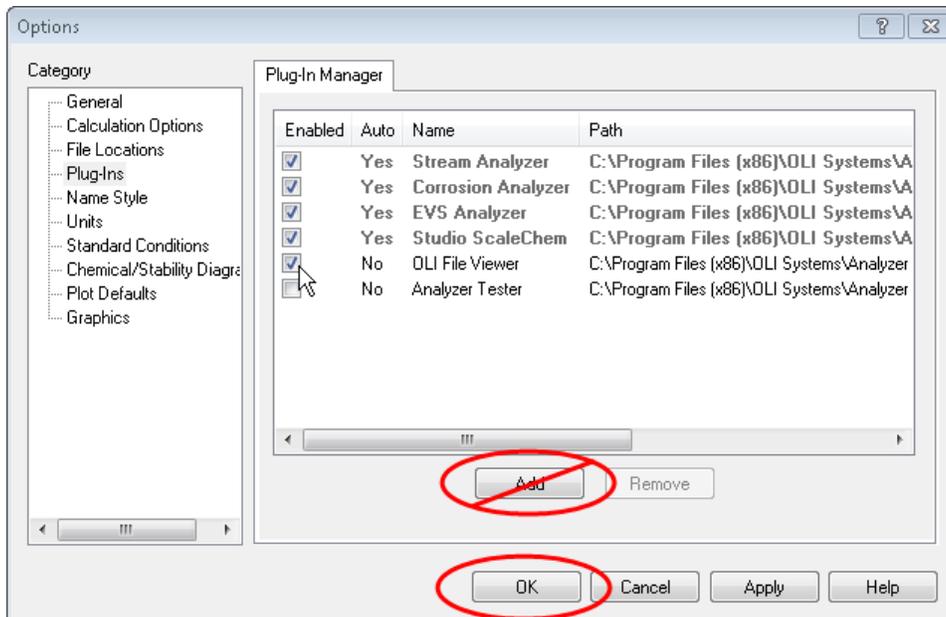


NOTIFICATION – The kinetics model is functional as of V9.1.5 (November 2014). However, calculations with the standard Arrhenius equation are not working properly for gas-phase reactions. Therefore, to develop your own kinetics reaction, we recommend contacting OLI Technical Support.

10.4a Adding the File Viewer plug-in

Before we get started, we will enable the File Viewer tab. This tab lets us view internal calculation results, which contain reaction rate details. In the future software versions, the reaction rate details will be available within the Report tab.

- ✓ Save all the files that need to be saved from the previous section because we will need to restart the software
- ✓ From the menu bar, select Tools> Options> Plug-ins
- ✓ Add a check to the OLI File Viewer box
- ✓ Press the OK button at the bottom of the screen (NOT THE ADD button)



- ✓ Restart the software
- ✓ Reopen the previous cases

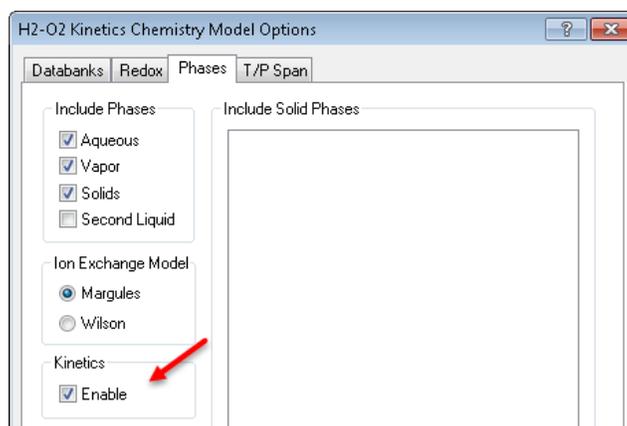
10.4b Setting up the Kinetics Case

- ✓ Create a new stream  Add Stream and rename it "H2-O2 Kinetics"  H2-O2 Kinetics

- ✓ Select the Names Manager, then select the Formula view and press OK
- ✓ Enter H2 and O2 into the input grid
- ✓ Enter 1 mole each of H2O, O2 and H2

Variable	Value
Stream Parameters	
Stream Amount (mol)	3.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	1.00000
H2	1.00000
O2	1.00000

- ✓ Select Chemistry>Model Options>Phases from the menu
- ✓ Click on the Kinetics box in the lower left and press OK to close the window



- ✓ Add a Single Point Calculation and name it "Isothermal Flash"  Isothermal Flash
- ✓ Calculate and record the Species Output concentrations

Notice that there is no reaction between H₂ and O₂.

Species Output (True Species)

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

	Total	Aqueous	Vapor
	mol	mol	mol
H2	1.0	6.40556e-6	0.999994
H2O	1.0	0.935007	0.0649932
H+1	1.69793e-9	1.69793e-9	0.0
OH-1	1.69793e-9	1.69793e-9	0.0
O2	1.0	1.02895e-5	0.99999
Total (by phase)	3.0	0.935023	2.06498

- ✓ Return to the 'H2-O2 Kinetics' stream and add a new Single-Point calculation
- ✓ Rename it "Isothermal REDOX"  Isothermal REDOX

- ✓ Click the Re (REDOX) button on the Ribbon bar -
- ✓ Calculate and view the results



In this case, 100% of the H₂ has reacted, which is expected, because the reaction is highly exothermic.

Species Output (True Species)

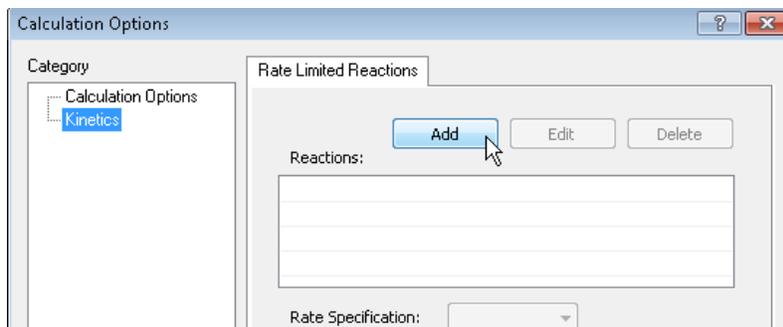
Row Filter Applied: Only Non Zero Values
column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mol	mol	mol
H2	1.4697e-42	7.99591e-47	1.46962e-42
H2O	2.0	1.98374	0.0162581
H+1	3.60239e-9	3.60239e-9	0.0
OH-1	3.60239e-9	3.60239e-9	0.0
O2	0.5	4.36488e-5	0.499956
Total (by phase)	2.5	1.98379	0.516214

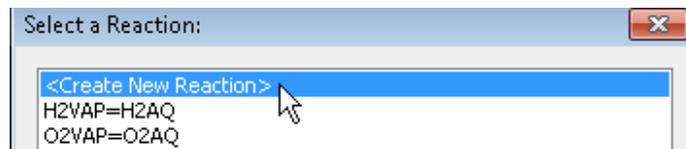
- ✓ Return to the 'H2-O2 Kinetics' stream and add a new Single-Point calculation
- ✓ Rename it "Isothermal Kinetics"
- ✓ Click the Specs button
- ✓ Select Kinetics from the Category section

The kinetics category is empty, but we will add a kinetic reaction here.

- ✓ Click the Add button at the top to create a new reaction and press OK



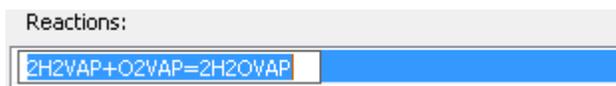
- ✓ Double-click on <Create New Reaction>



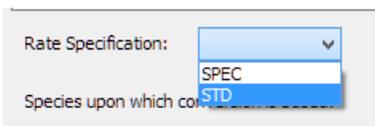
- ✓ Enter the following reaction exactly as shown (this part of the software requires specific typing) then press <ENTER>:



The reaction will appear in the field.



- ✓ Next select STD from the Rate Specification drop-down

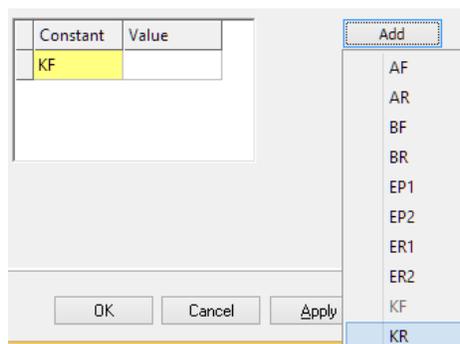


- ✓ Click on the Add button in the center right to add the rate constants



- ✓ Select KF and KR from the add list

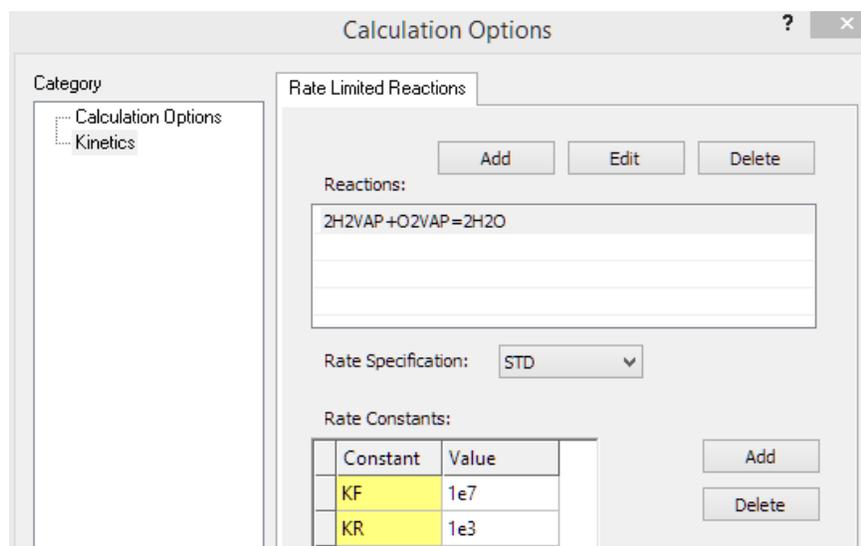
This is the Forward and Reverse rate constant- it is temperature independent



- ✓ Enter the following values for the constants

Constant	Value
KF	1e7
KR	1e3

These constants represent the forward and reverse rate of the reaction.



- ✓ Close the Calculation Options window
- ✓ Calculate
- ✓ Select the Report tab and view the Species Output table

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mol	mol	mol
H2	2.69096e-3	1.45021e-7	2.69081e-3
H2O	1.99731	1.98092	0.0163893
H+1	3.59726e-9	3.59726e-9	0.0
OH-1	3.59726e-9	3.59726e-9	0.0
O2	0.501345	4.33541e-5	0.501302
Total (by phase)	2.50135	1.98096	0.520382

The reactants and products have the following values:

Constant	Value
H2VAP	2.69e-3
O2VAP	0.5014
H2OVAP	0.0164

Adding this to the overall rate equation

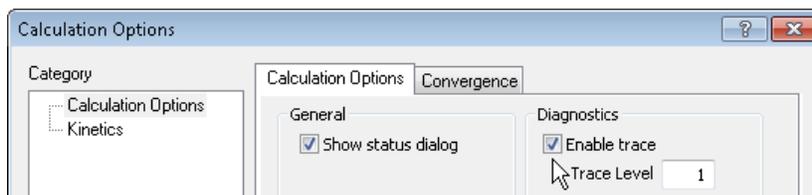
$$K_{rxn} = \frac{k_f}{k_r} = \frac{H2OVAP^2}{O2VAP * H2VAP^2} = \frac{0.0164^2}{0.5014 * 0.00269^2} = 74.13$$

- ✓ View the new results

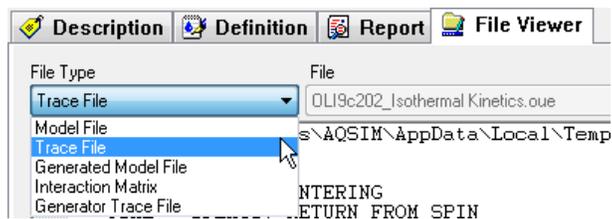
Viewing the Kinetics calculation details

Kinetics calculation results became part of the report in V9.3. For earlier versions, the information is in one of the Output files. You can view these results in the File Viewer tab. This output is not on by default, so our first step will be to turn it on. If you are using V9.3 or newer, then skip this next set of instructions

- ✓ Return to the Definition tab (if not already there)
- ✓ Click on the Specs... button
- ✓ Click the Enable trace button



- ✓ Close the window then recalculate
- ✓ Click on the File Viewer tab
- ✓ Select Trace File from the File Type dropdown menu on the left side of the screen



- ✓ Click anywhere within the trace screen (to make this the focus of the mouse)

- ✓ Scroll down to about row 54 and see the values and units associated with the components
- ✓ **V9.2.1 or Newer** - click on the Report Tab and the Customize Button.
- ✓ Select the Reaction kinetics box at the bottom of the Report Contents List

Gibbs Free Energy of Formation
 Entropy
 Entropy - Standard State
 Reaction Kinetics

- ✓ View the results using this output

Hour 1

```

054BLOCK:
055 STAGE: 1 TIME STEP: 1.00000 HR
056 REACTION: 1 2 H2VAP + O2VAP = 2 H2OVAP
057 AF 0.000000
058 BF 0.000000
059 AR 0.000000
060 BR 0.000000
061 ER1 2.00000
062 ER2 1.00000
063 EP1 2.00000
064 K FORWARD 1.000000E+07 GMOL/HR/M^3
065 K REVERSE 1000.00 GMOL/HR/M^3
066 RATE FORWARD 0.489475 GMOL/HR/HR
067 RATE REVERSE 3.493724E-05 GMOL/HR/HR
068 RATE 0.489440 GMOL/HR/HR
069 EXTENT 0.489440 GMOL/HR
  
```

Hour 2

```

180BLOCK:
181 STAGE: 2 TIME STEP: 1.00000 HR
182 REACTION: 1 2 H2VAP + O2VAP = 2 H2OVAP
183 AF 0.000000
184 BF 0.000000
185 AR 0.000000
186 BR 0.000000
187 ER1 2.00000
188 ER2 1.00000
189 EP1 2.00000
190 K FORWARD 1.000000E+07 GMOL/HR/M^3
191 K REVERSE 1000.00 GMOL/HR/M^3
192 RATE FORWARD 9.249814E-03 GMOL/HR/HR
193 RATE REVERSE 3.528150E-05 GMOL/HR/HR
194 RATE 9.214533E-03 GMOL/HR/HR
195 EXTENT 9.214533E-03 GMOL/HR
196
  
```

Note the EXTENT value; this represents the progress of the reaction at each time step

$$Extent = rate = \frac{\text{moles}}{\text{time step}} = -2 * \frac{dH_2}{dt} = -\frac{dO_2}{dt} = 2 * \frac{dH_2O}{dt}$$

The overall rate is the sum of the extent after each time step

$$Overall\ rate = Extent_{t=1} + Extent_{t=2} + \dots + Extent_{t=n}$$

The Extent of reaction after hour 1 and 2 (Stage 1 and Stage 2) is:

$$0.4894 + 0.0092 = 0.4897\ gmol$$

For O₂, starting with 1 mole, the remaining O₂ amount is:

$$1\ gmol - 0.4897\ gmol = 0.5013\ gmol$$

For H₂, starting with 2 moles, the remaining H₂ amount is:

$$2\ gmol - 2 * 0.4897\ gmol = 0.002691\ gmol$$

Both values can be observed for O₂ (vapor) and H₂ (vapor).

It is noted above that 99.94% of the reaction is completed after the first hour.

Using the Hold-up time and reaction steps

There is an option on the grid that allows the user to fix the overall reaction time and the individual time steps. In the previous case, the calculation time (Holdup time) was set to two hours, and this was divided into two steps. These values are needed to compute the RATE FORWARD, RATE REVERSE, and EXTENT variables.

Calculation Parameters	
Kinetics Holdup Time (hr)	2.00000
Kinetics Steps	2

- ✓ Recalculate using the following holdup time and steps (1 hr and 1 step)

Calculation Parameters	
Kinetics Holdup Time (hr)	1.00000
Kinetics Steps	1

- ✓ Select the File Viewer tab and view the Trace File
- ✓ Scroll down to about line 190 to find the rate values

```

189BLOCK:
190 STAGE: 1 TIME STEP: 1.00000 HR
191 REACTION: 1 2 H2VAP + O2VAP = 2 H2OVAP
192 AF 0.000000
193 BF 0.000000
194 AR 0.000000
195 BR 0.000000
196 ER1 2.00000
197 ER2 1.00000
198 EP1 2.00000
199 K FORWARD 1.000000E+07 GMOL/HR/M^3
200 K REVERSE 1000.00 GMOL/HR/M^3
201 RATE FORWARD 0.489475 GMOL/HR/HR
202 RATE REVERSE 3.493724E-05 GMOL/HR/HR
203 RATE 0.489440 GMOL/HR/HR
204 EXTENT 0.489440 GMOL/HR

```

According to these results, the overall extent is 0.489 gmol/hr, the same as in the 2-hr case, but this is largely because the reaction has already come to equilibrium. Note the rate derivative values *Rate Forward* and *Rate Reverse* values. These values are computed based on the initial concentrations and the rate coefficients. The overall rate derivative is Rate Forward-Rate Reverse = 0.489 gmol/hr². The time is one hour, and there is only one time step. Therefore the overall rate extent is 0.489 gmol/hr²*1 hr*1 step=0.489 gmol/hr.

- ✓ Return to the Report tab and view the Species Output table

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mol	mol	mol
H2	0.02112	1.06841e-6	0.021119
H2O	1.97888	1.96159	0.0172877
H+1	3.56216e-9	3.56216e-9	0.0
OH-1	3.56216e-9	3.56216e-9	0.0
O2	0.51056	4.14471e-5	0.510519
Total (by phase)	2.51056	1.96163	0.548925

The O₂ value is 0.5109 moles 0.489 moles less than the starting value. The H₂O is 0.0219 moles, or 2*0.489 moles less than the starting value.

Using the Arrhenius Equation

There is a second way to create the rate constant for this reaction. The KF above is a temperature-independent rate constant. Many reactions are temperature dependent, based on kinetic theory (the higher temperature the faster they move). The Standard Arrhenius equation is part of the software construct and has the following form:

$$rate = Ae^{-\frac{E_a}{RT}}$$

The OLI Version is:

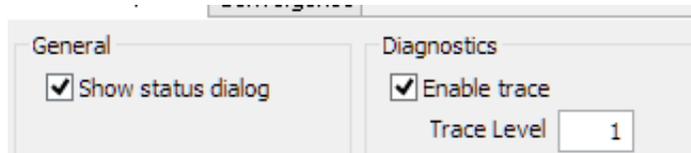
$$rate = Ae^{-\frac{B}{RT}}$$

Since the reaction has a forward and reverse form, the OLI version becomes

$$Forward\ rate = A_F e^{-\frac{B_F}{RT}}$$

$$Reverse\ rate = A_R e^{-\frac{B_R}{RT}}$$

- ✓ Add a new single point calculation; rename it "Isothermal Arrhenius"  Isothermal Arrhenius
- ✓ Open the Specs window and select Enable Trace



- ✓ Click on the Kinetics category
- ✓ Select the Add button then enter the H₂ combustion reaction: **2H2VAP+O2VAP=2H2OVAP**
- ✓ Select STD in the Rate Specification dropdown menu
- ✓ Click on the Add button and select the following variables, AF, BF, AR, BR

These are the forward and reverse constants of the Arrhenius equation.

- ✓ Enter the following values for the constants

Constant	Value
AF	1e5
BF	300
AR	10
BR	600

The screen should look like the following

Reactions:

2H2VAP+O2VAP=2H2OVAP

Rate Specification: STD

Rate Constants:

Constant	Value
AF	1e5
BF	300
AR	10
BR	600

Add

Delete

- ✓ Set the Hold-up time and steps to 1

Calculation Parameters	
Kinetics Holdup Time (hr)	1.00000
Kinetics Steps	1

- ✓ Calculate, and view the Species Output in the Report

The extent of reaction is $1 - 0.92112 = 0.0788$ moles, and since the holdup time is 1 hr, $r=0.0788$ mol/hr.

Species Output (True Species)

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

	Total	Aqueous	Vapor
	mol	mol	mol
H2	0.842277	7.20179e-6	0.842269
H2O	1.15772	1.10042	0.0573071
H+1	1.9983e-9	1.9983e-9	0.0
OH-1	1.9983e-9	1.9983e-9	0.0
O2	0.921138	1.2651e-5	0.921126
Total (by phase)	2.92114	1.10044	1.8207

- ✓ Click on the File Viewer, select Trace and view the Kinetics values

The values for EXTENT confirm these results.

```

050BLOCK:
051 STAGE: 1 TIME STEP: 1.00000 HR
052 REACTION: 1 2 H2VAP + O2VAP = 2 H2OVAP
053 AF 100000.
054 BF 300.000
055 AR 10.0000
056 BR 600.000
057 ER1 2.00000
058 ER2 1.00000
059 EP1 2.00000
060 K FORWARD 36560.4 GMOL/HR/M^3
061 K REVERSE 1.33666 GMOL/HR/M^3
062 RATE FORWARD 7.886180E-02 GMOL/HR/HR
063 RATE REVERSE 2.619730E-08 GMOL/HR/HR
064 RATE 7.886177E-02 GMOL/HR/HR
065 EXTENT 7.886177E-02 GMOL/HR
066

```

Appendix

Introduction

This section describes features of the OLI Studio. The chapter starts with an overview of the OLI Studio Interface, including some calculation objects discussed previously.

A.1 Creating Custom Units

Overview

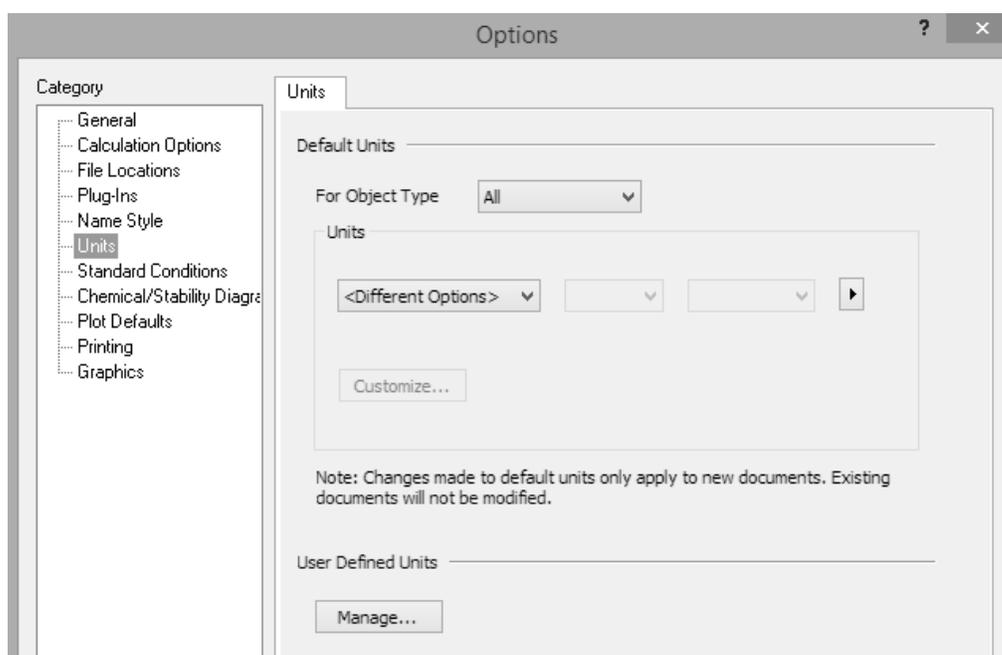
The OLI Studio has many actions that take time to setup but may be useful later. These include developing custom units or names, using private databases, selecting a thermodynamic framework, and modifying calculation options. The purpose of this section is to explain some of these features so that the reader can best use their capabilities

Creating Custom Units

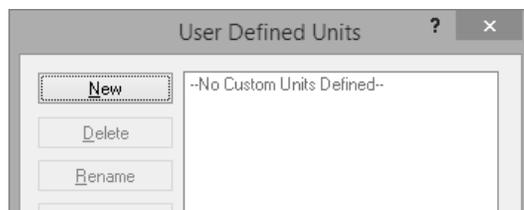
Custom units are created through the Tools-Options menu. It is at this location where the user manages the internal files that save these units. You will create a sample custom unit set.

- ✓ Add a new Stream. Label it Training Units -  Training Units .
- ✓ Select Tools>Options>Units from the menu

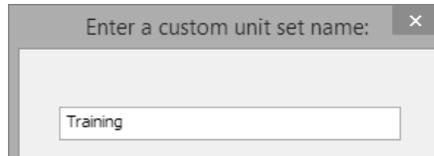
The Units tab contains two sections, Default units and User Defined units. You will work in the User Defined units.



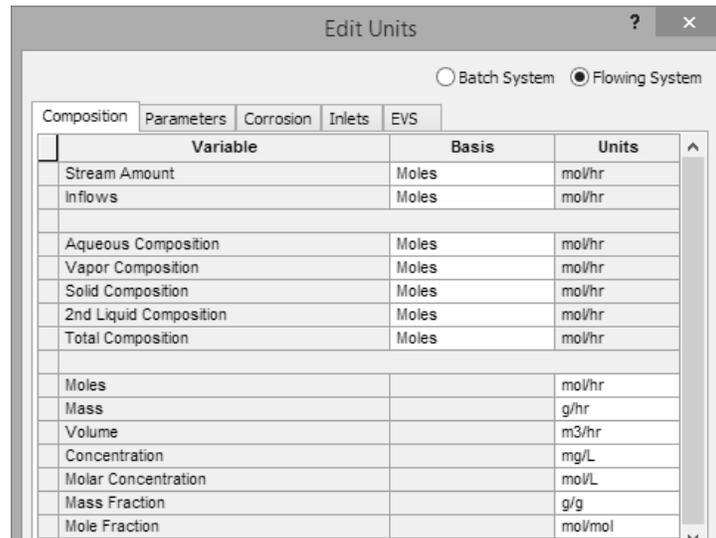
- ✓ Click on the Manage button at the bottom of the window. This will open a User Defined Units dialog window



- ✓ Select the New button. This opens another dialog window: Enter a custom unit set name:
- ✓ Enter the name Training and press OK



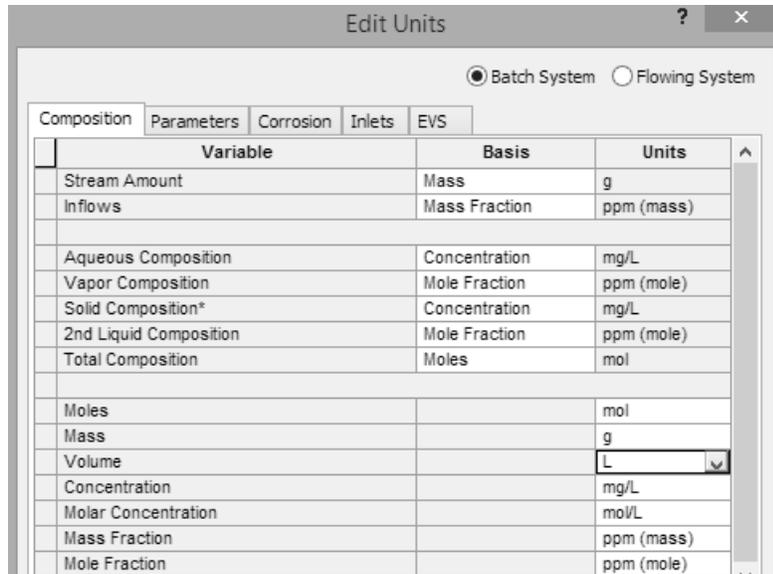
This opens a new window, called Edit Units. This window should look familiar, as it is the main edit window for all unit modifications. The basis units set is moles-grams-m3-hr. Each of these are editable.



- ✓ Change the Composition tab to the following. Note, that the gray areas are not editable (they are set by other cells, or there is no information to enter)
- ✓ Change the system to Batch from Flowing

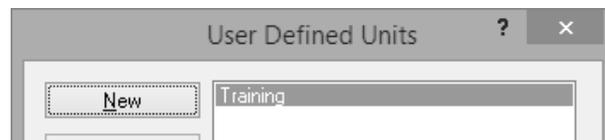
Variable	Basis	Units
Stream Amount	Mass	
Inflows	Mass Fraction	
Aqueous Composition	Concentration	
Vapor Composition	Mole Fraction	
Solid Composition	Concentration	
2 nd Liquid Composition	Mole Fraction	
Total Composition	Moles	
Moles		mol
Mass		g
Volume		L
Concentration		mg/l
Molar Concentration		mol/l
Mass Fraction		ppm (mass)
Mole Fraction		ppm (mole)

The window should look like the screenshot below.



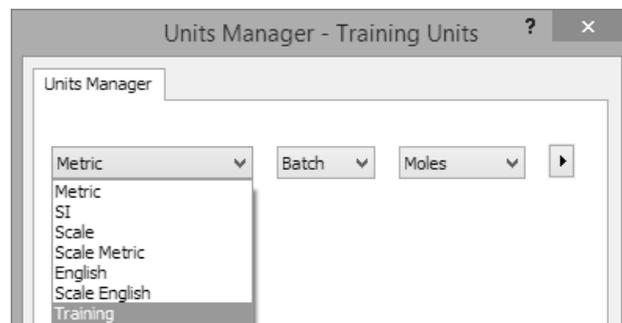
- ✓ Press Save to close the window

The User Defined Units window now contains the Training units.



- ✓ Close the Options
- ✓ Click on the Units Manager radio button in the Ribbon
- ✓ Click on the first-down-arrow button in the Units Manager

The new units we created will be available when we start the software. It is important that we exit the software normally for this to be saved. So, if we are at a point where we can stop, close the software and restart it.

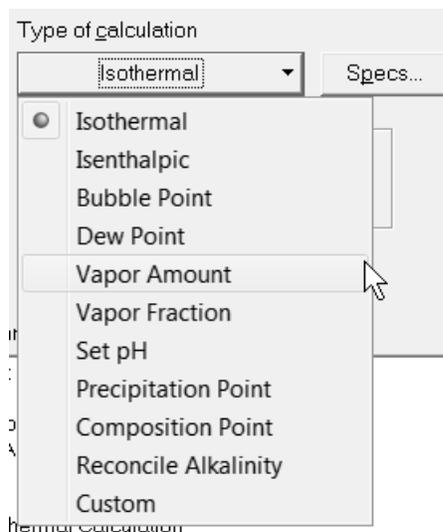


It is also possible to set these units to be the default units set. This can be done in a few ways, instructions for which will be provided by the instructor.

A.2 Single Point Calculations

The OLI Studio has 11 types of single point calculations. This includes 10 standard calculations and 1 customizable option. These calculations are only available when a Stream is active or highlighted in the Navigator. Calculations are “added” to the Navigator as branches to the active stream.

When added, the screen will show the Description grid of the default single point calculation type, *Isothermal*. To the right of the Description grid, After selecting the single point option from the Actions Pane, the client will see the *Type of Calculation* dropdown menu to the right of the Description grid. When selected, the calculation



A stream's single point calculation selection menu

Isothermal: This is a constant temperature and pressure calculation.

Isenthalpic: In this calculation, a client enters a constant heat loss or heat gain to determine how the pressure or temperature changes meet the new heat content.

Bubble Point is when the temperature or pressure is adjusted to reach a condition where a small amount of vapor begins to appear.

Dew Point is when the temperature or pressure is adjusted to reach a condition where a small amount of aqueous liquid appears.

Vapor Amount is when the temperature or pressure is adjusted to produce a specified amount of vapor.

Vapor Fraction is when the temperature or pressure is adjusted to produce a specified amount of vapor as a fraction of the total quantity.

Set pH is when the pH of the solution can be specified by adjusting the flow rate of a species.

Precipitation Point is the amount of a solid (solubility point) may be specified by adjusting the flow rate of a species.

Composition Point is the aqueous concentration of a species may specified by adjusting the flow rate of a species

Reconcile Alkalinity is Compute the total alkalinity of a fluid at the standard 4.5 pH end point or at a value specific to your system.

Custom Combinations of the above calculations can be created.

A.3 Species Names Icons and Selecting Display Names

What are the small symbols adjacent to the species in the input grid?

The species in the OLI databases are sorted by several different names. The sort order can be modified by the user and this will be discussed later in this document. The symbols appear next to the species names:

Variable	Unit	Value
Stream Parameters		
Stream Amt - Total Inflow	mol	55.5087
Temperature	°C	25.0000
Pressure	atm	1.00000
Inflows		
H2O	mol	55.5087

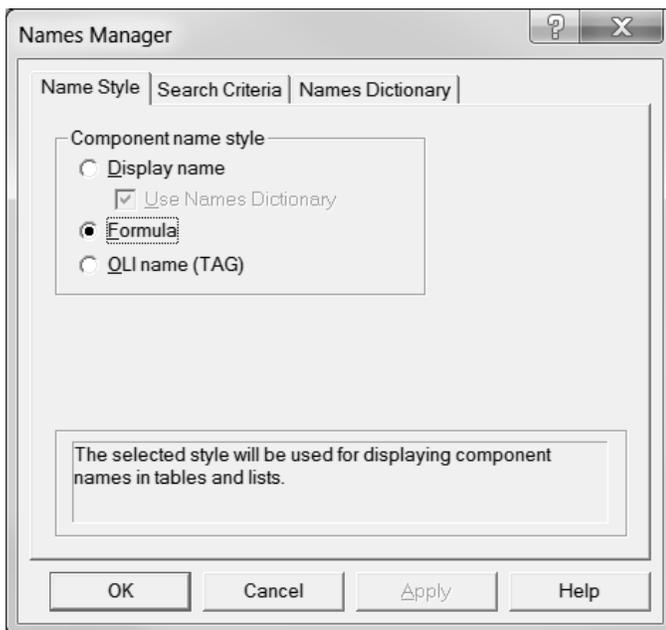
Display Name	OLI Name
SYN (-)-(S)-Proline	HLPROLINE
SYN (-)-2-Pyrrolidinecarboxylic acid	HLPROLINE
SYN (-)-alpha-Amino-p-hydroxyhydrocinnamic acid	LTYROSINE
SYN (-)-Asparagine	LASPARAGN
SYN (-)-beta-Phenylalanine	LPHENLALAN
SYN (-)-Cholesterol	CHOLESTROL
SYN (-)-Menthol	MENTHOL1
SYN (-)-Proline	HLPROLINE
SYN (-)-Tartaric acid	H2TARTR
SYN (-)-Tryptophan	HLTRYPTOPH
SYN (+)-Pyrethronyl (+)-pyrethrate	PYRETHRIN2
SYN (+)-Pyrethronyl (+)-trans-chrysanthemate	PYRETHRIN1
SYN (+/-)-2-Aminopropanoic acid	DLALANINE
SYN (+/-)-Alanine	DLALANINE
SYN (+/-)-alpha-Aminobutyric acid	DLAM2BUTCD
SYN (+/-)-alpha-Aminobutyric acid	DLAM2BUTCD
SYN (+/-)-beta-Phenyl-alpha-alanine	DLPHENLALN
SYN (+/-)-Isoleucine	DLILEUCINE
SYN (+/-)-Methionine	HDLMETHN
SYN (+/-)-Norvaline	NORVALINE

Each symbol has a different meaning.

SYN Carbonochloridic acid, propyl ester	PROPCLFRMT	SYN is a component synonym.
* Propyl chloroformate	PROPCLFRMT	STAR is the species Display Name – it is one of the display options in the Names Manager toolbar.
C4H7ClO2	PROPCLFRMT	Test Tube is the component's chemical formula. A green drop is the common formula name is displayed. A yellow drop is the alphabetical formula name.
LOL Propyl chloroformate	PROPCLFRMT	LOL is the EPA list of list name.
CAS 109-61-5	PROPCLFRMT	CAS is the Chemical Abstracts Service registry number for the species.
OLI PROPCLFRMT	PROPCLFRMT	OLI is the OLI program variable name, which is used internally by the OLI Engine.

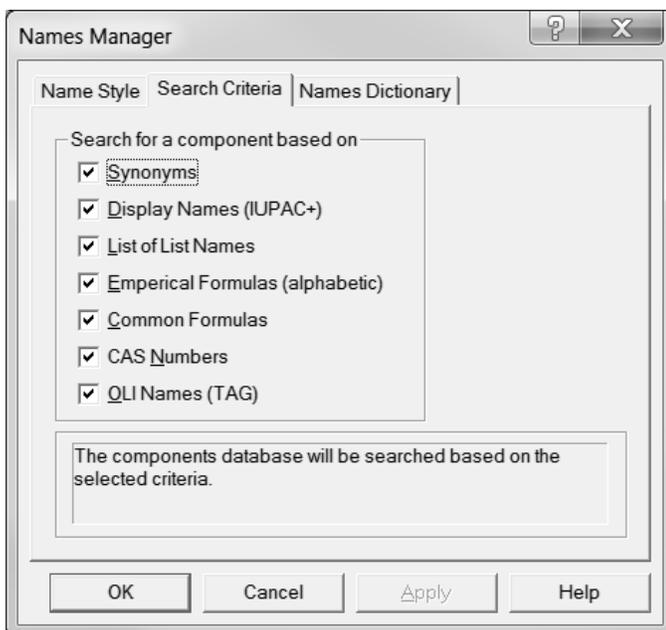
How to speed up the search for components?

Select Tools > Names Manager



You can speed up the selection of names by limiting the search order for the various symbols. This is not recommended for stand-alone systems but network systems may experience increased search speed by limiting the species types.

Select Search Criteria from the tabs.



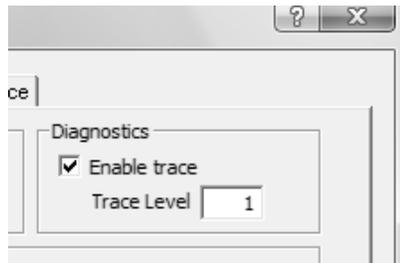
Uncheck any item you do not wish to have searched.

A.4 Viewing Critical Pseudocomponent & Assay Data

These steps will walk you through viewing the critical properties of pseudocomponents that you generated. The procedure for determining the critical parameters for assay pseudocomponents is almost the same as for a single pseudocomponent. The only difference is that the resultant file has more components.

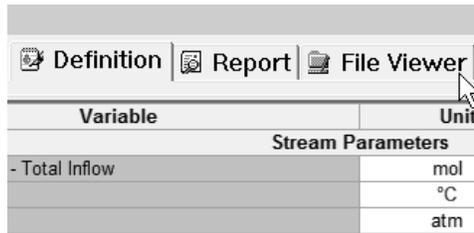
Click on Specs and Enable Trace on the Calculation Option tab Calculate

After you have completed entering the data for pseudocomponents or assays, you will normally go to the Enable trace option in the Specs menu to turn on the debugging information. Then you will calculate as normal.



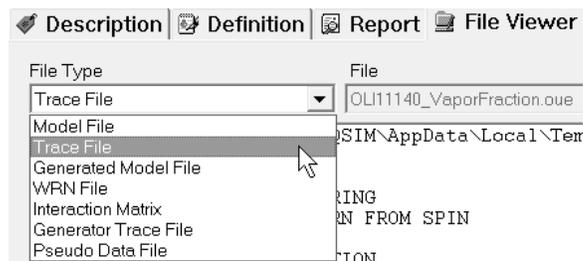
Select the File Viewer tab

If the File Viewer tab is not visible, then you may need to enable the File Viewer Plug-in (previous section of Appendix).



Select the list of file types and select Trace File

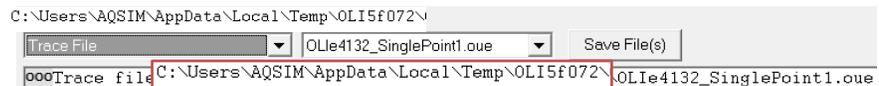
The Trace File is stored in a temporary file area within Windows. As the program runs, these files are created then automatically deleted. In order to view the file, you will have to do so while the software is running.



Copy the first line of the Trace File which is the location of the temporary file

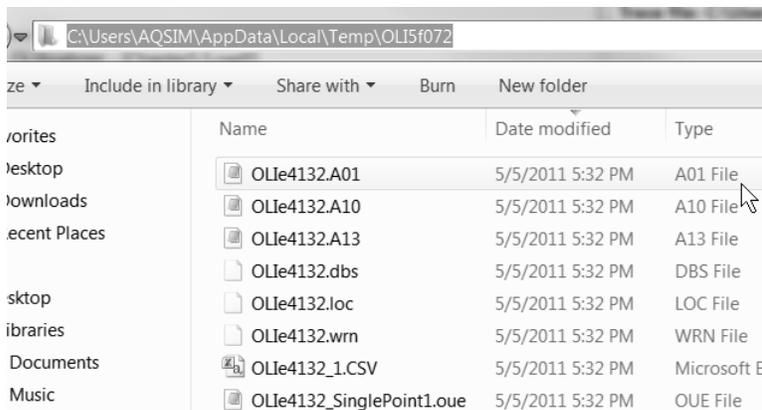
The first line in the Trace File view shows the temporary file location. In this case, the file location is

C:\Users\AQSIM\AppData\Local\Temp\OL15f072.



Notice that the trace file name here is *OL1e4132_SinglePoint1.oue*. You can also search for this file name using Windows explore

Paste file address in an explorer window



Find the file with the *.A01 extension

This is a partial list of the generated thermodynamic values in Notepad.

Open the file with Notepad

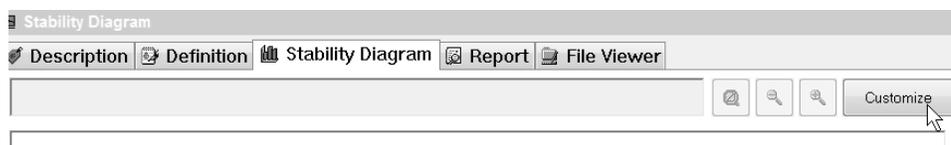


This table explains some of the units used in this report.

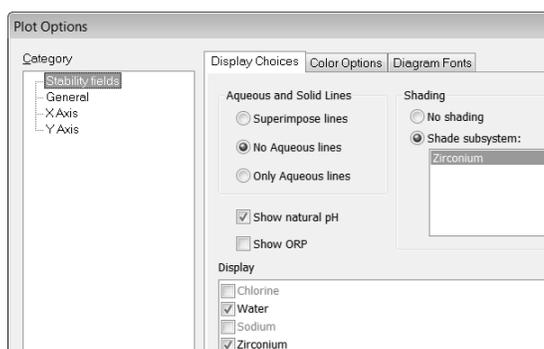
KEYWORD	Definition	Units
MOLW	Molecular Weight	g/mole
ACEN	Acentric Factor	
TCRI	Critical Temperature	K
PCRI	Critical Pressure	Pa
VCRIT	Critical Volume	m ³ /mol
BOIL	Normal Boiling Point	K
CP	Heat Capacity	J/mol/K
HREF	Reference State Enthalpy	J/mol

A.5 Stability Diagram Plot Options

Within the Stability Diagrams tab, several options are available to customize your view. We will focus on the Display Choices tab within the Plot Options window, which we open by selecting the Customize button.



Display Choices is one of three tabs in the Plot Options window. The other two tabs are self-explanatory: Color Options and Diagram Fonts.

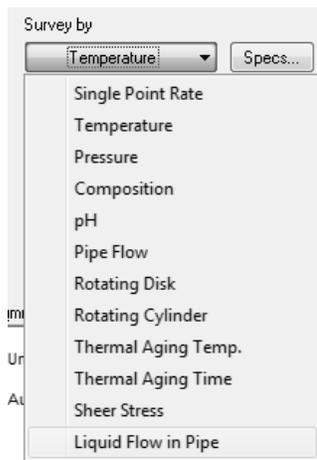


Display Choices contains the following options:

- Aqueous and Solid Lines – Choose one of the three display options.
- Natural pH – Toggle the pH line
- Show ORP – Toggle the Oxidation Reduction Potential circle
- Shading – Add or remove plot coloring or change the metal/subsystem that is colored. Only one metal/subsystem can be selected for coloring.
- Display Subsystems – Choose which subsystem will be displayed on the plot. Only subsystems where REDOX is on will be active. The others will be grayed out. You can turn on the REDOX subsystem by selecting Chemistry>Model Options> Redox from the menu bar

A.6 Corrosion Rate Survey by Options

There are 12 calculations available. They fall into three general categories, the first six (Single Point through pH) are thermochemical variations. Four of the remaining six (Pipe Flow to Rotating Cylinder, and Shear Stress) are hydrodynamic variations, and two deal with the thermal aging of a weld. The last, Liquid Flow in pipe, is an estimate of multi-phase flow (oil-water) mixing on corrosion.



Grid Section

Description		Definition		General Corr. Rate	
Variable		Value			
Stream Parameters					
Stream Amount (mol)		55.5082			
Temperature (°C)					
Pressure (atm)		1.00000			
Calculation Parameters					
Flow Type		Static			
Ignore Influence of Scales		<input type="checkbox"/>			
Inflows (mol)					
H2O		55.5082			
Fe		0.0			
Contact Surface					
Carbon steel G10100 (generic)					

The Grid section looks similar to the other objects. The Calculation Parameters section is used in Single Point and Survey calculations, and the Contact Surface is used in the Pourbaix Diagrams.

Calculation Parameters

Depending on the survey selected, the Calculation Parameters grid changes its appearance. When the calculation type is Single Point, Temperature, Pressure, or Composition, the following grid is used. The only option is to set the flow type and effect of corrosion related scales.

Calculation Parameters	
Flow Type	Static
Ignore Influence of Scales	<input type="checkbox"/>

Survey by Single Point Rate, Temperature, Pressure, or Composition

When the survey type is pH, the grid includes the description of the pH variables.

Calculation Parameters	
<input checked="" type="radio"/> pH - Aqueous	
<input type="radio"/> pH Acid Titrant: Not specified	
<input type="radio"/> pH Base Titrant: Not specified	
Flow Type	Static
Ignore Influence of Scales	<input type="checkbox"/>
Inflows (mol)	

Survey by pH

The calculation grids for other survey options are shown below.

Calculation Parameters	
Flow Type	Pipe Flow
Pipe Diameter (m)	0.100000
Pipe Flow Velocity (m/s)	
Ignore Influence of Scales	<input type="checkbox"/>

Survey by Pipe Flow

Calculation Parameters	
Flow Type	Defined Sheer Stress
Sheer Stress (Pa)	
Ignore Influence of Scales	<input type="checkbox"/>

Survey by Sheer Stress

Calculation Parameters	
Flow Type	Rotating Disk
Disk Diameter (m)	0.0100000
Disk Rotation Speed (cycle/min)	
Ignore Influence of Scales	<input type="checkbox"/>

Survey by Rotating Disk

Calculation Parameters	
Flow Type	Static
Ignore Influence of Scales	<input type="checkbox"/>

Thermal Aging Temperature and Thermal Aging Time

Calculation Parameters	
Flow Type	Rotating Cylinder
Rotor Diameter (m)	0.0100000
Rotor Rotation (cycle/min)	
Ignore Influence of Scales	<input type="checkbox"/>

Survey by Rotating Cylinder

Calculation Parameters	
Flow Type	Approximate Multiphase
Pipe Diameter (m)	0.100000
Liquid Flow in Pipe (m ³ /s)	
Gas Flow in Pipe (m ³ /s)	0.0100000
Pipe Roughness (m)	4.00000e-4
Visc, Abs 2ndLiq (cP)	10.0000
Water Cut at Point of Dispersion Inversion	0.500000
Max Rel Viscosity of Dispersion at Inversi	7.06000
Ignore Influence of Scales	<input type="checkbox"/>

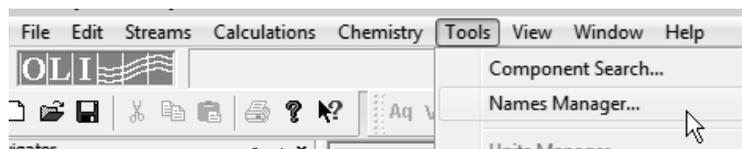
Survey by Liquid Flow in Pipe

A.7 Adding a Names Dictionary and Private Database

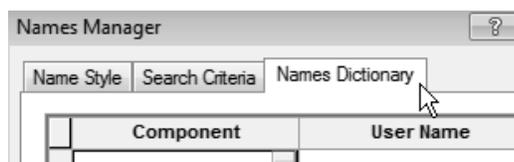
Creating the Names Dictionary

The Names Dictionary creates a list of client-generated “user names” for species within the OLI database. The feature may help a client who wants to call up a species with something other than its formula, display name, or OLI Tag. For instance, we can give the hydrocarbon $C_{21}H_{44}$ a simpler name like *C21* and enter this as an inflow instead of the formula or display name (n-Heneicosane). The Names Dictionary may be especially helpful for anyone who works extensively with hydrocarbons.

- ✓ Select Tools> Names Manager

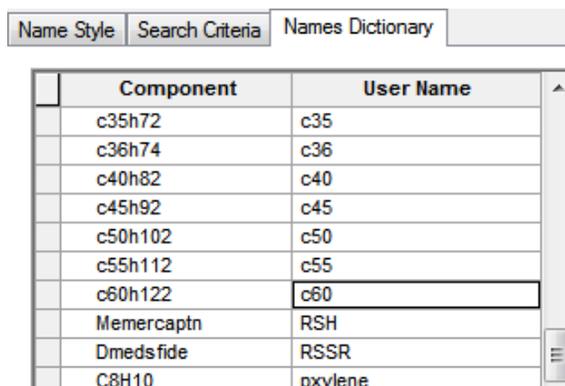


- ✓ Select the Names Dictionary tab



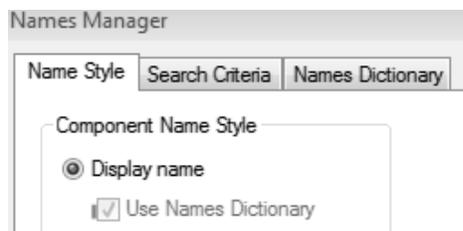
- ✓ Enter a component (e.g. C₂₁H₄₄) and give it unique name (e.g. C₂₁)
- ✓ Press <Enter> to advance to the next cell

We can also use the right-mouse button menu to copy/paste a two-column component/username list into the Names Dictionary.

A screenshot of the 'Names Manager' dialog box, 'Names Dictionary' tab. A table is populated with the following data:

Component	User Name
c35h72	c35
c36h74	c36
c40h82	c40
c45h92	c45
c50h102	c50
c55h112	c55
c60h122	c60
Memercaptn	RSH
Dmedsfide	RSSR
C8H10	pxylene

- ✓ Select the Names Style tab
- ✓ Select the Display Name button and check the Use Names Dictionary box

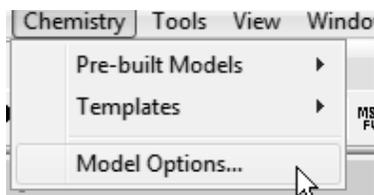


- ✓ Press OK to exit the Names Manager when finished

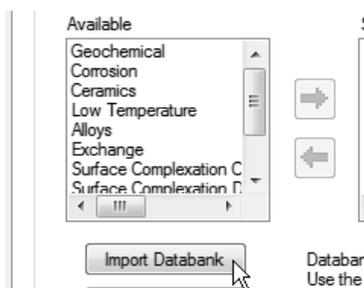
Inserting a private database

This section describes how to import a database.

- ✓ Select Chemistry > Model Options from the Menu bar



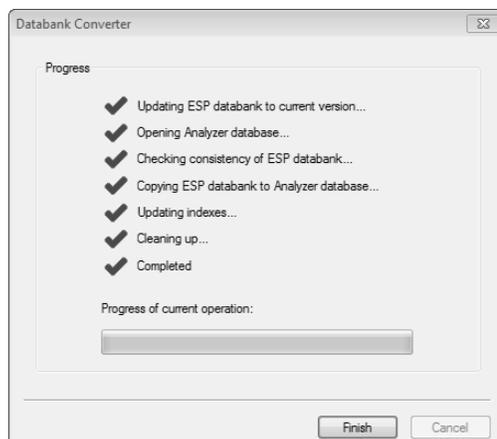
- ✓ Click on the Import Databank button



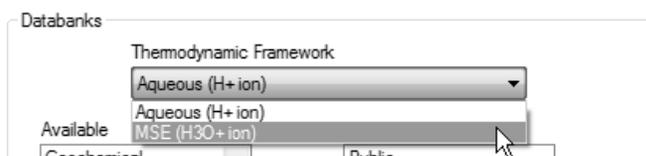
- ✓ Click on the Browse button
- ✓ Find the database, for example, AminesHCL.DIC

As of OLI Studio Version 9.1, all databanks end with the *.dic extension.

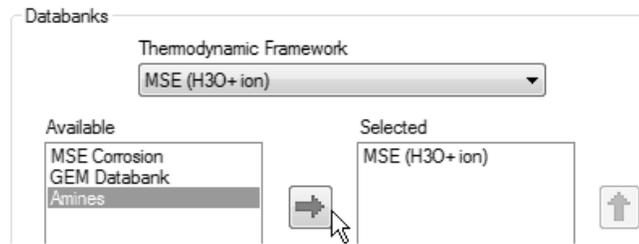
- ✓ Click Next



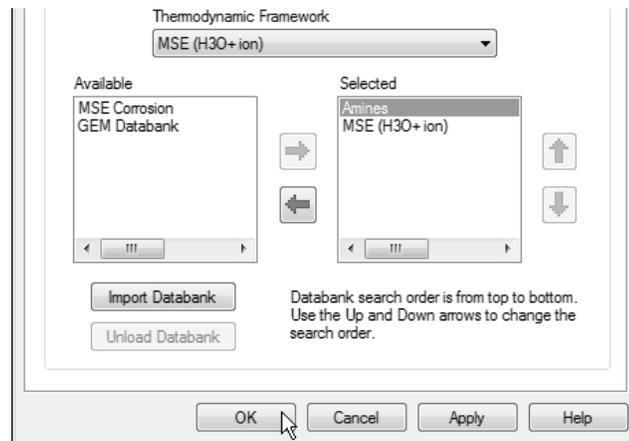
- ✓ When you see the green check mark next to Completed, select the Finish button
- ✓ Click on the down arrow in the Thermodynamic Framework field and change the selection to MSE (H3O+ ion)



- ✓ Highlight the database and send to right hand side then press the OK button



✓ Press OK



✓ Save the file