A Guide to Using

OLI Studio

Version 9.5

Including
Stream Analyzer
ScaleChem
Corrosion Analyzer
EVS

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Disclaimer:

This manual was produced using the OLI Studio / OLI Analyzer version 9.5 build 3 (9.5.3). 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.

1. Welcome to OLI

Who is OLI Systems?

OLI Systems was founded in 1971 by Dr. Marshall Rafal. During the past four decades OLI, has developed, at a cost of almost $40,000,000, commercial computer software which has established the company as the world leader in simulating aqueous-based chemical systems

OLI's unique capability is providing the world with the only **predictive thermodynamic framework** for calculating the physical and chemical properties of multi-phase, aqueous-based systems. This framework is applicable to most multi-component mixtures of chemicals in water, and is predictive over almost any conceivable temperature, pressure and concentration of interest.

Employing this unique and powerful framework, the OLI Engine, supported by a very large, in-place databank, allows users to predict the chemical and phase behavior (including aqueous, vapor, non-aqueous liquid and multiple solids), of most mixtures of inorganic or organic chemicals in water. The resulting phase separation into aqueous, vapor, organic liquid and multiple solids is performed automatically. In the laboratory, in steady-state or dynamic process conditions or in the natural environment, the OLI Engine is broad-based and accurate.

OLI's world leadership is reflected in many ways, including authorship of AIChE's Handbook of Aqueous Electrolyte Thermodynamics. OLI software is used by nearly all of the largest companies in the Chemicals and Oil & Gas sectors of the Chemical Process Industries (CPI) as well as companies in other sectors such as Metals and Mining, Forest Products and Pharmaceuticals. In addition, OLI software is used extensively in Environmental, E & C and Basic Research.
OLI has created several widely-used products:

OLI Engine

OLI's aqueous thermodynamics are at the heart of the OLI software. OLI Engine refers to the thermodynamic database, thermodynamic framework, and supporting numerical computation to simulate the chemical and phase behavior of aqueous-based systems.

OLI Studio

Never has aqueous chemistry problem solving been easier. The OLI Studio combines ease of learning, ease of use with the power of the OLI Engine. It supports single and multiple point calculations, utilizing OLI's extensive PUBLIC databanks. **Ionic input is possible.** The OLI Studio allows customers to input, store, manipulate, adjust and reconcile laboratory data, with facilities to adjust laboratory errors in pH and charge balance.

Environmental Simulation Program (ESP)

ESP is OLI’s **steady-state flowsheet simulation** package capable of simulating rigorous environmental unit operations including stripping/scrubbing, pH control, ion exchange, biotreatment, clarification, UF/RO, electrodialysis, and many others. Feedback control and recycle convergence are included.

Corrosion Analyzer

CSP provides a framework to **analyze metal and alloy redox solution chemistry** for any mixture of chemicals at almost any condition of interest. The package provides for real-solution stability diagrams (e.g., Pourbaix and Yield) and accurate prediction of electrical conductivity and ORP. CSP supports calculation of predictive rates of corrosion for a limited set of chemistry.

DynaChem

Dynamic is a **flowsheet simulation** package for time-dependent and transient processes. DynaChem includes support for scheduled entry feeds, PID control, open and closed loop, feedback and feed-forward, multi-cascade, adaptive gain, pH, compositional control and many others. Operator intervention to introduce upsets, manually adjust valves and control settings is also possible.

OLI ScaleChem

OLI ScaleChem is OLI’s solution for **oil-field applications** including surface and subsurface mineral scale prediction, saturation profiles, and produced/formation water mixing. OLI ScaleChem is based upon accurate fitting of binary, ternary and quaternary data up for several common scales, and many more "not-so-common" scales!

OLI is comprised of an extraordinary staff of advanced degree scientists and engineers who enable OLI to maintain a high-level of Research & Development while offering a full range of Support Services and Professional Services.

What does OLI Systems do?

As the recognized experts in modeling aqueous electrolyte thermodynamics, backed by a large in-place databank, we provide computer software tools to solve your problems quickly and accurately for:

Aqueous Simulation

It is essential for scientists and engineers to understand the effects of aqueous chemistry of their processes. This includes the effects of trace components, pH, temperature, and other factors on their process systems. Over the past 30 years, OLI has refined software which accurately models multiphase, multi-component aqueous solutions for virtually any mixture of chemicals. The basis for OLI's Software is the "OLI Engine." The OLI Engine is made up of the Solvers and the Databanks.

The OLI Databank contains proprietary coefficients for the prediction of thermodynamic, transport, and physical properties for **80 inorganic elements** of the periodic table, and their associated aqueous species, as well as **over 8000 organic species.** Thus, most mixtures of chemicals in water can be modeled, provided the solvent of the solution is water.

Upon the user's request, the aqueous model can incorporate redox chemistry, co-precipitation and reaction kinetics. Also available are surface phenomena such as ion exchange, surface complexation and molecular adsorption. Transport properties such as electrical conductivity, viscosity and diffusivity are also available.

Oil-Field Chemistry

ScaleChem is software which assesses potential scaling problems for oil-field applications. The ability to calculate the high temperature and pressure effects typically found in oil-field production is solved using the OLI Engine. OLI Systems is a recognized leader in the world of aqueous chemistry, and has a generalized modeling capability, the OLI Aqueous Thermodynamic Model which is being applied here specifically to the problems of the oil-field industry.

Corrosion Chemistry

Most corrosion problems are addressed by treating the symptoms. A treatment plan would constitute:

- ***measuring corrosion rates,***
- ***determining life expectancy,***
- ***Regularly replacement of corroded material and equipment.***

Corrosion Analyzer and CSP are unique software used to investigate **the Rate of Corrosion** and determine the **causes of corrosion before they happen**, allowing preventive actions to be evaluated and implemented. This includes choosing correct operating conditions and corrosion resistant materials.

Elemental and alloy metal oxidation and reduction reactions for 79 inorganic elements and thousands of species are available in the OLI Databank. The software automatically generates the redox reactions and the resulting species and solves for the equilibrium conditions using its predictive thermodynamic model.

Because of OLI's unique, predictive aqueous model featuring accurate activity coefficients, the corrosion software offers a few types of real-solution diagrams for your analysis. Our competitors only offer idealized solution diagrams and none of a general prediction of rates of uniform corrosion.

Real Solution Pourbaix Diagrams

Graphical depiction of EH vs. pH for any mixture of chemicals in water is available to evaluate stable and meta-stable corrosion and redox products. This allows assessment of the effect of passivating species in real solutions without any simplifying assumptions.

Real Solution Stability Diagrams

Flexible selection of independent variables and graphical depiction of local and global equilibria in various projections is available in CSP. Depictions include EH vs. composition and composition vs. pH for any chemical mixture, including trace components, to assess stable and meta-stable species in real solutions.

Uniform corrosion rates and predicted polarization curves are featured in OLI's unique Rates of Corrosion calculations. Single-Point and Multiple-Point calculation points are available.

Process Modeling

The Environmental Simulation Program (ESP) is a steady-state process simulator with a proven record in enhancing the productivity of engineers and scientists. With applications industry-wide, the software is not only applied to environmental applications but to any aqueous chemical processes.

A wide range of conventional and environmental unit operations are available:

Mix
Split
Separate
Neutralizer
Absorber
Stripper
Reactor
Exchanger
Precipitator
Extractor
Component Split
Incinerator
Compressor
Bioreactor
Manipulate
Controller
Feedforward
Crystallizer
Clarifier
Sensitivity
Membrane (UF, RO)
Electrodialysis
Saturator
Dehydrator

ESP provides the engineer or scientist accurate answers to questions involving complex aqueous systems. Design, debottlenecking, retrofitting, troubleshooting and optimizing of existing or new processes is easy with ESP. Upstream waste minimization, as well as the waste treatment itself, is possible with ESP. The dynamic response of a process can be studied using the dynamic simulation program, DynaChem, to examine control strategy, potential upsets, scheduled waste streams, controller tuning, and startup/shutdown studies.

Process Flow-sheeting and Control

Process flow-sheeting with multiple recycles and control loops are allowed. Feed-forward and feedback Controllers and Manipulate blocks help to achieve process specifications.

2. Introduction to Aqueous Speciation

Overview

It is our belief that the predictive modeling of aqueous systems requires that the system be fully speciated. This allows for smoother extrapolation of experimental data with less “Faith” placed on corrections.

The user, after completing this section, should have a better understanding of why full speciation is required and how the OLI Studio performs calculations.

What is the pH of the Following Stream?

Temperature	=	**25 Centigrade**
Pressure	=	**1 Atmosphere**
H_2O	=	**55.508[1] moles**
$FeCl_3$	=	**1.0 moles**

We will now take our first look at the OLI Studio software to answer this question.

We start by first clicking on the OLI Studio icon or by selecting the OLI Studio from the Start button. The OLI Studio momentarily displays a Splash Screen.

After a few moments, the main OLI Studio window will display. A tips box may also appear; you can close it.

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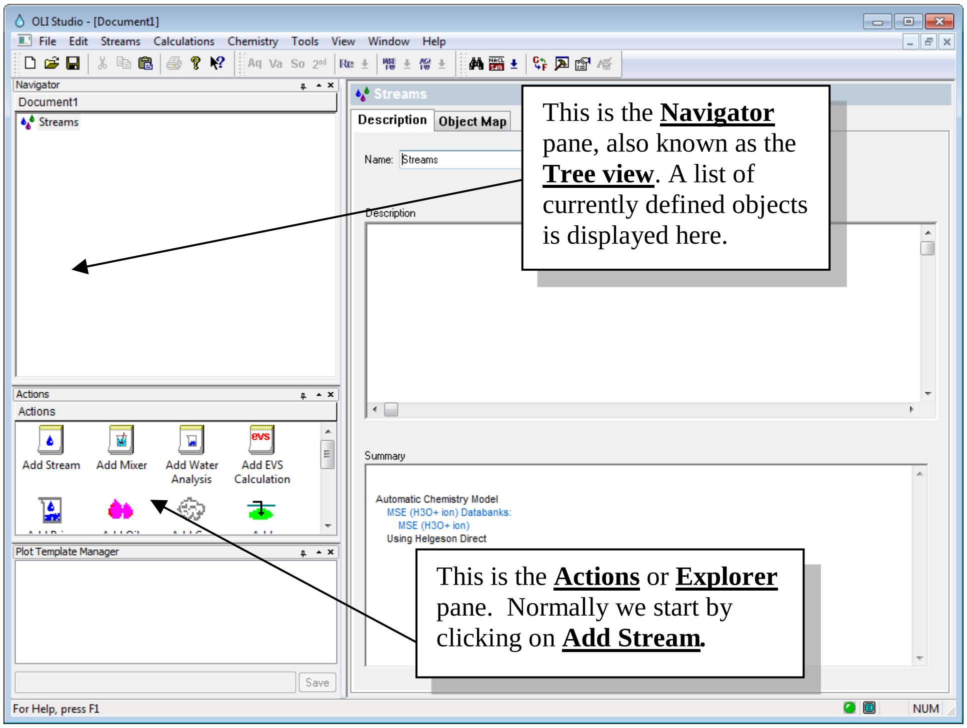
[1] This is 1 kilogram of water. All of OLI’s internal aqueous concentrations are based on the molal concentration scale. You will see this value frequently in the course.



Name: Streams

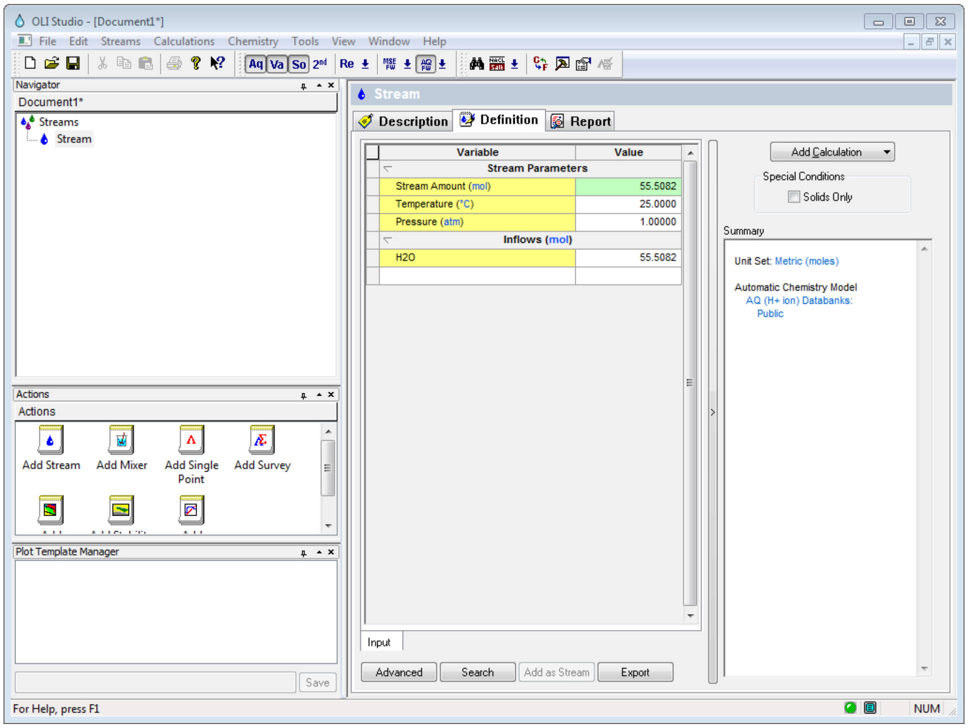
Automatic Chemistry Model
MSE (H3O+ ion) Databanks:
MSE (H3O+ ion)
Using Helgeson Direct

This is the **Navigator** pane, also known as the **Tree view**. A list of currently defined objects is displayed here.

This is the **Actions** or **Explorer** pane. Normally we start by clicking on **Add Stream.**

Figure 2-1 The main OLI Studio window

Click on the **Add Stream** icon.



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

☐ Solids Only

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

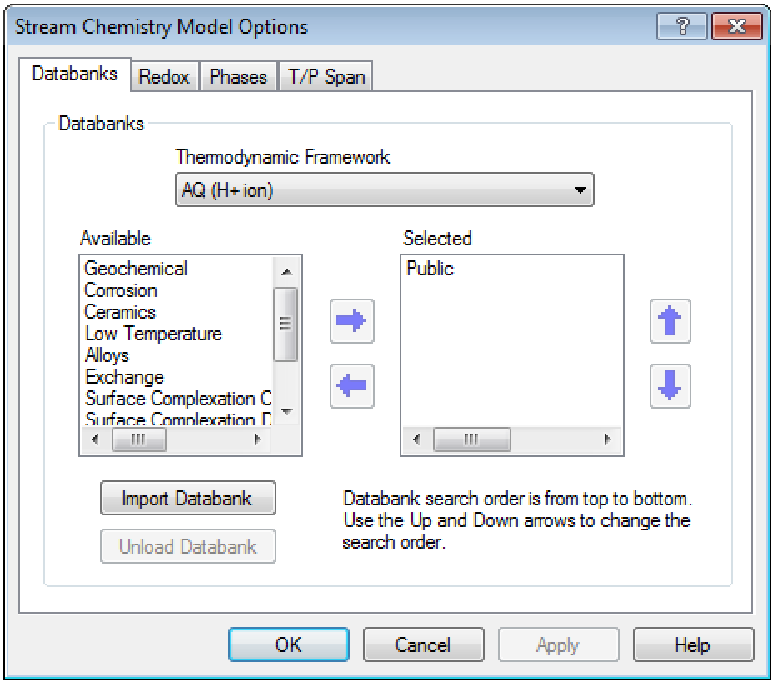
Figure 2-2 Adding a new stream

Note: The OLI Studio now allows users to choose the type of thermodynamic framework used to perform simulations. Two thermodynamic frameworks/models are available:

Aqueous (H^+ ions): This is the traditional framework applicable to most multi-component mixtures of chemicals in water and is predictive over almost any conceivable temperature, pressure and concentration of interest.

Mixed Solvent Electrolyte / MSE (H_30^+ ion): The MSE framework is OLI's newly developed model capable of reproducing speciation, chemical, and phase equilibria applicable to water-organic-salt systems in the full range of concentrations as well as aqueous electrolytes from dilute solutions to the fused salt limit.

Unless otherwise noted, all examples discussed in this guide use the Aqueous model. Make sure that the Aqueous Model is being used by selecting **Model Options…** from the **Chemistry** menu.



Thermodynamic Framework: AQ (H+ ion)

Selected: Public

Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

Figure 2-3: Selecting the thermodynamic framework used for simulation.

Or by clicking the AQ/FW button from the toolbar:

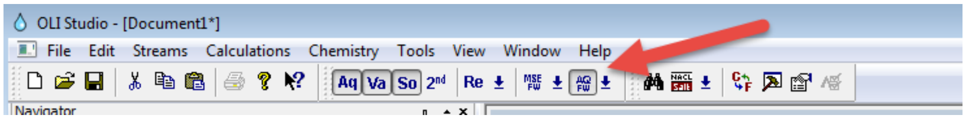
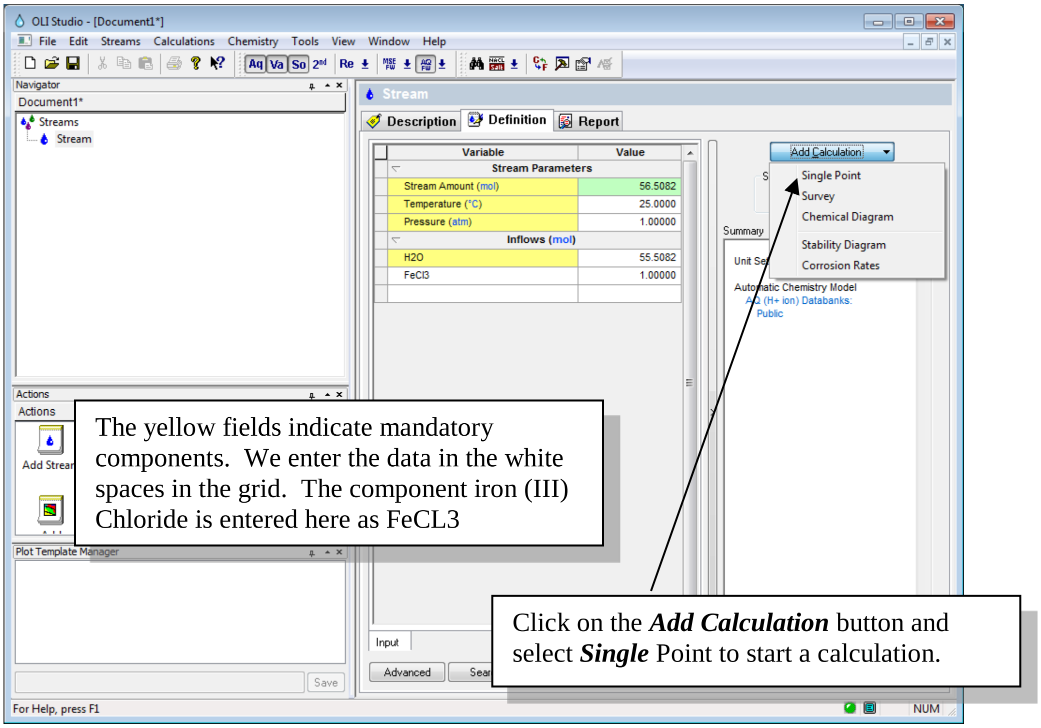


Figure 2-4 Toolbar - AQ framework Selected



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

The yellow fields indicate mandatory components. We enter the data in the white spaces in the grid. The component iron (III) Chloride is entered here as FeCL3

Click on the ***Add Calculation*** button and select ***Single*** Point to start a calculation.

Figure 2-5 Entering Stream Information

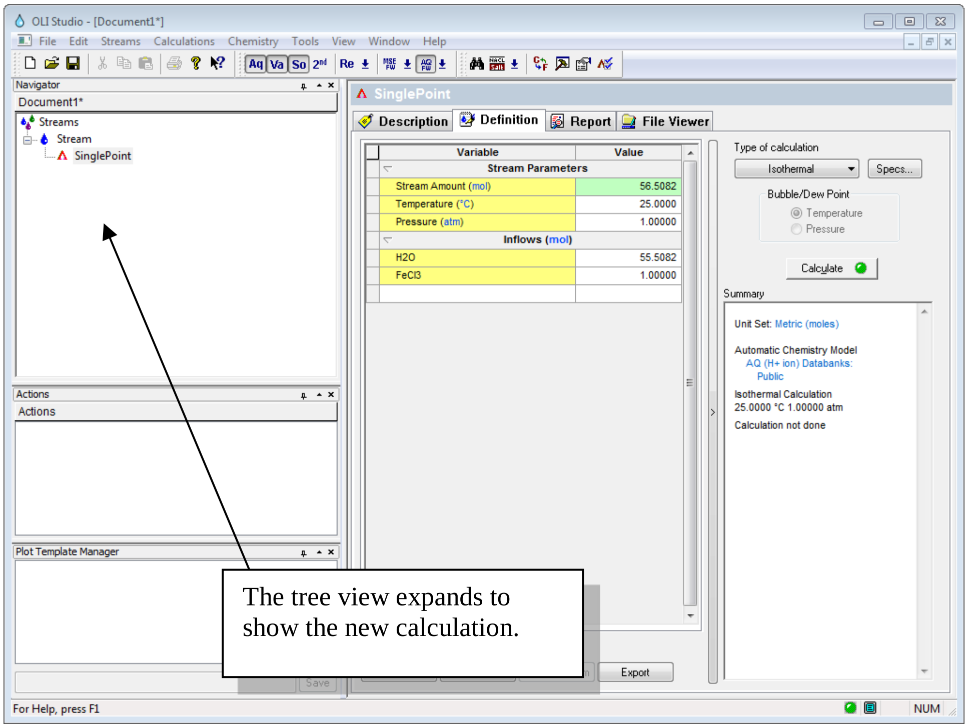
The shaded areas of the stream definition are required by the program. By default, we will start at 25 degrees centigrade, 1 atmosphere and 55.5082 moles of water. This amount of water is 1 kilogram of water. This effectively makes any component concentration a molal concentration.

If a red X appears next to the name you entered, then the program does not recognize the name. Please check to see if the spelling is correct. There will be more about entering user data later in this course.

We enter the chemical formula of $FeCl_3$ in the inflow grid and then enter a value of 1.0. You may use the mouse or tabs keys to move around the grid.

The concept employed here is that the user will define a stream (or import it from another program or process) whose values will propagate throughout all subsequent calculations.

Enter the chemical formula ***FeCl3*** and then enter a value of ***1.0*** in mole units. ***Click*** on the **Add Calculation** button and select **Single Point** when finished.



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

Unit Set: Metric (moles)

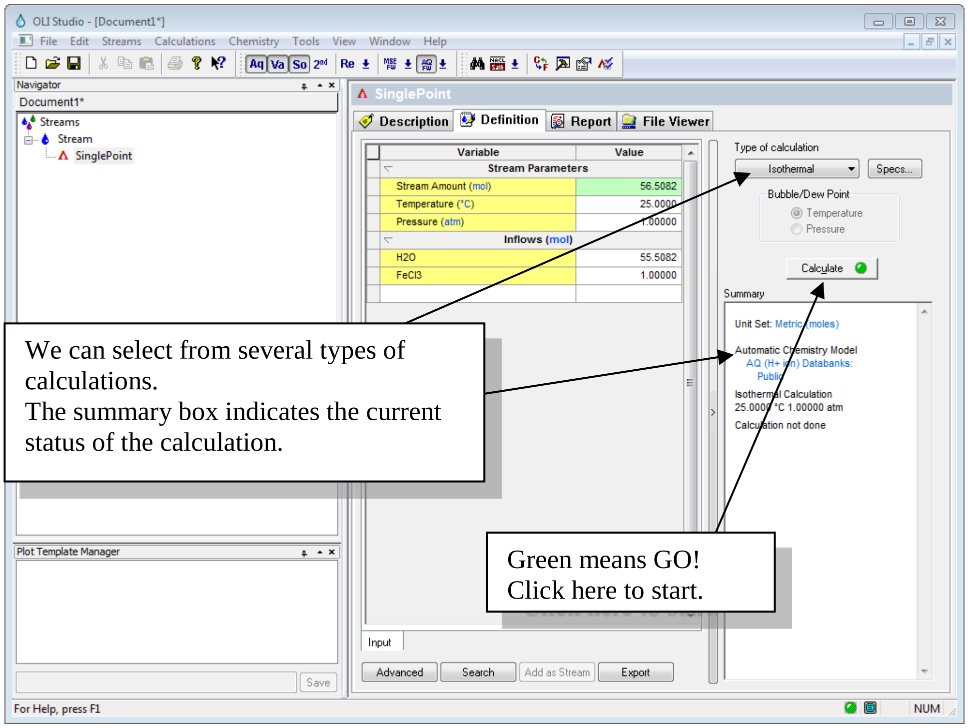
Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
25.0000 °C 1.00000 atm
Calculation not done

The tree view expands to show the new calculation.

Figure 2-6 Starting the calculation

We are now ready to start the calculations but let us review some options on this screen.



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

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
25.0000 °C 1.00000 atm
Calculation not done

We can select from several types of calculations.
The summary box indicates the current status of the calculation.

Green means GO!
Click here to start.

Figure 2-7 Entering the calculation conditions.

The data in the **Definition** grid has been propagated from the stream that we just entered. You may change the values or add to the list of species. This does not affect the original stream definition.

Please note: The names that you enter in the grid may be different from what is displayed depending on settings in the Tools menu. This will be discussed later.

We will leave the values as is, ***click*** the **Type of Calculation** button.

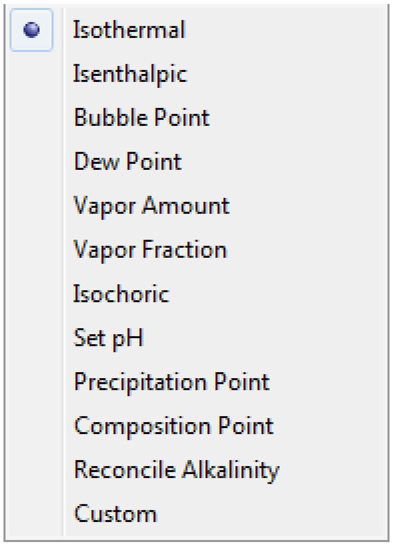


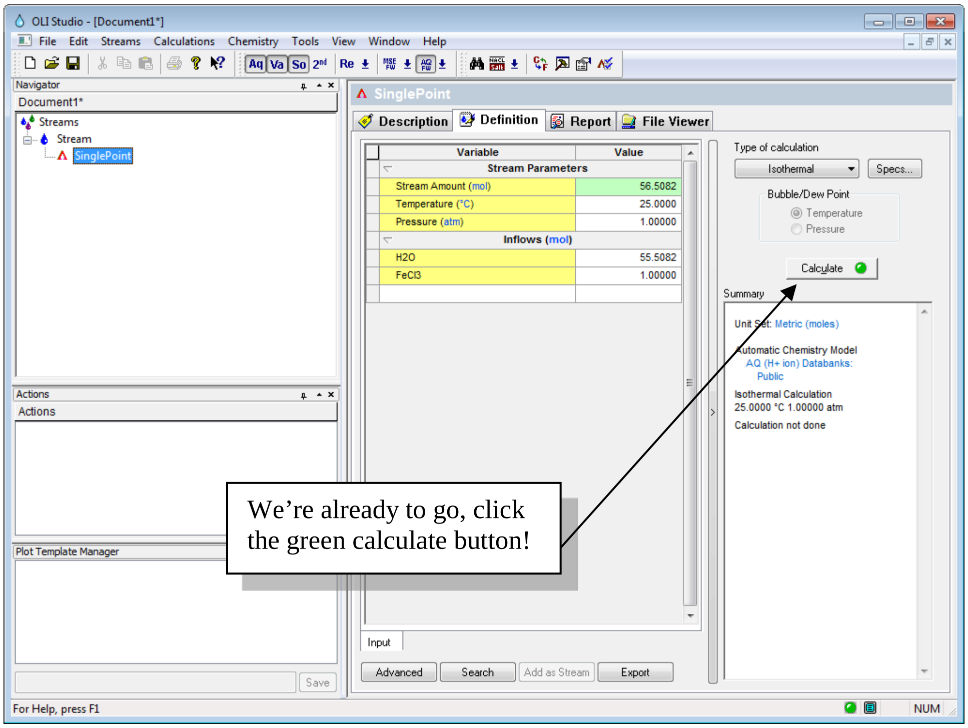
Figure 2-8 Single Point Calculation Types

There are several types of calculations that can be performed. We will use the default calculation type of **Isothermal** for this demonstration. The following types of calculations are defined:

Isothermal	A constant temperature and pressure calculation.
Isenthalpic	A constant heat loss/gain is applied to the calculation and a temperature or pressure can be adjusted to meet this new heat content.
Bubble Point	The temperature or pressure is adjusted to reach a condition where a small amount of vapor begins to appear.
Dew Point	The temperature or pressure is adjusted to reach a condition where a small amount of aqueous liquid appears.
Vapor Amount	The temperature or pressure is adjusted to produce a specified amount of vapor.
Vapor Fraction	The temperature or pressure is adjusted to produce a specified amount of vapor as a fraction of the total quantity.
Isochoric	The temperature or pressure is adjusted to produce a total volume.
Set pH	The pH of the solution can be specified by adjusting the flowrate of species.
Precipitation Point	The amount of a solid (solubility point) may be specified by adjusting the flowrate of a species.

Composition Point	The aqueous concentration of a species may specified by adjusting the flowrate of a species.
Reconcile Alkalinity	The alkalinity of a solution can be specified by adjusting the flowrate of species.
AutoClave	This simulates a closed pressure vessel.[2]
Custom	Combinations of the above calculations can be created.

Select **Isothermal** calculations.



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

Type of calculation: Isothermal

Bubble/Dew Point
○ Temperature
○ Pressure

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
25.0000 °C 1.00000 atm
Calculation not done

We're already to go, click the green calculate button!

Figure 2-9 Let's GO! Click the Calculate button!

Click the green **Calculate** button.

The program will now start the calculation. After a moment, an "Orbit" will appear illustrating that the calculation is proceeding. For long-time users of the OLI Software, the graphic might seem familiar.

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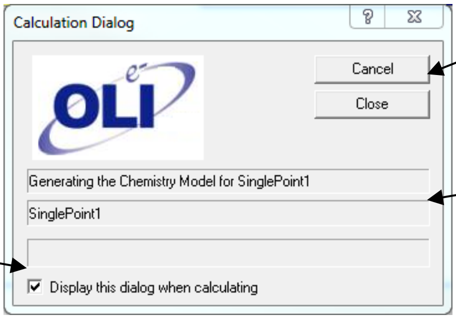
[2] You may have to enable this calculation from Tools | Options | Enable Features Under Development



Generating the Chemistry Model for SinglePoint1

SinglePoint1

☑ Display this dialog when calculating

Cancel will end the calculation. Close hides this dialog and the calculation keeps going.

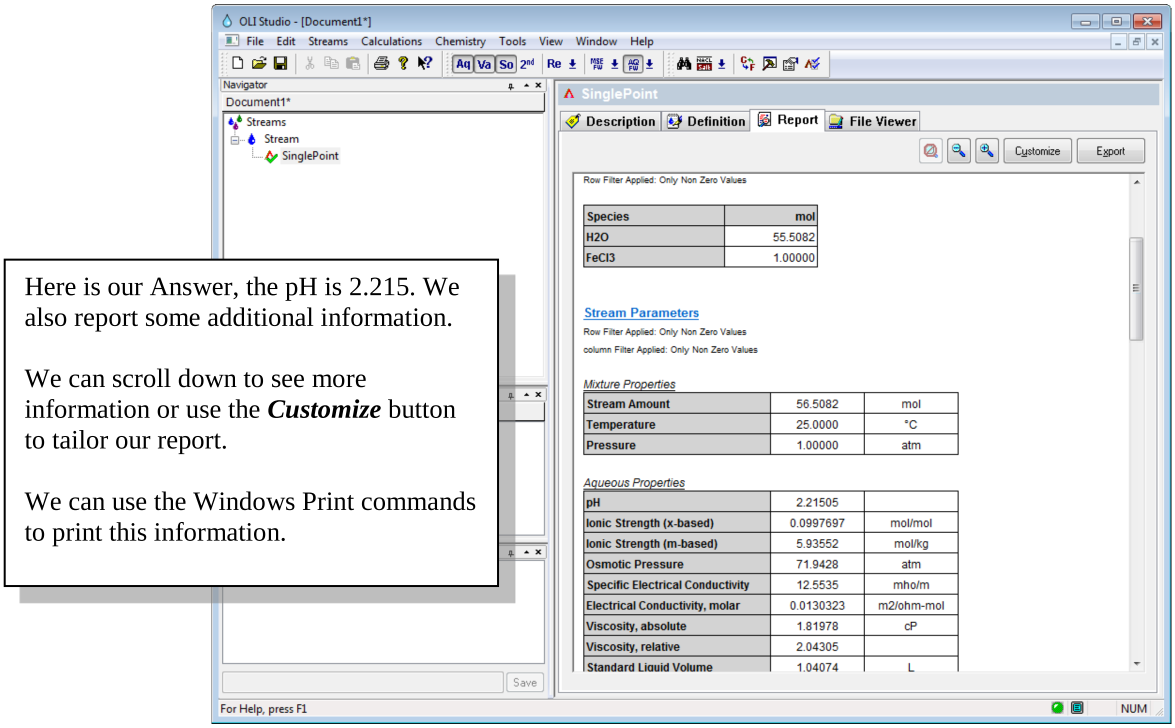
The current operation is displayed as well as the current calculation point.

For surveys a progress indicator will show here.

Figure 2-10 The OLI Calculation Status Dialog

The calculation may continue for several moments. When it is done, you will be returned to the same **Definition** screen.

Click on the **Report** tab.



Row Filter Applied: Only Non Zero Values

Species	mol
H2O	55.5082
FeCl3	1.00000

Stream Parameters

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

Mixture Properties

Stream Amount	56.5082	mol
Temperature	25.0000	°C
Pressure	1.00000	atm

Aqueous Properties

pH	2.21505	
Ionic Strength (x-based)	0.0997697	mol/mol
Ionic Strength (m-based)	5.93552	mol/kg
Osmotic Pressure	71.9428	atm
Specific Electrical Conductivity	12.5535	mho/m
Electrical Conductivity, molar	0.0130323	m2/ohm-mol
Viscosity, absolute	1.81978	cP
Viscosity, relative	2.04305	
Standard Liquid Volume	1.04074	L

Here is our Answer, the pH is 2.215. We also report some additional information.

We can scroll down to see more information or use the ***Customize*** button to tailor our report.

We can use the Windows Print commands to print this information.

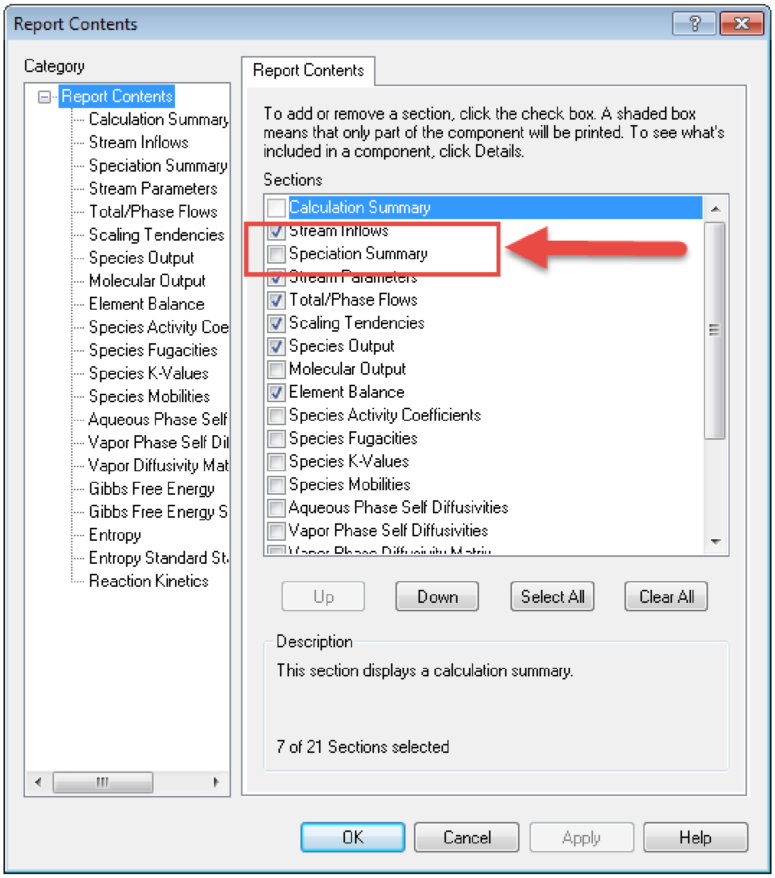
Figure 2-11 The Answer to our question

The answer to our question is that the pH of the solution is approximately 2.215. This is fairly acidic and a good question to ask is why it is so acidic. To see the full list of species we need to modify the report.

The linked image cannot be displayed. The file may have been moved, renamed, or deleted. Verify that the link points to the correct file and location.

Figure 2-12 Click on the customize button

Click on the **Customize** button.



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

Sections

- ☐ Calculation Summary
- ☑ Stream Inflows
- ☐ Speciation Summary
- ☑ Stream Parameters
- ☑ Total/Phase Flows
- ☑ Scaling Tendencies
- ☑ Species Output
- ☐ Molecular Output
- ☑ Element Balance
- ☐ Species Activity Coefficients
- ☐ Species Fugacities
- ☐ Species K-Values
- ☐ Species Mobilities
- ☐ Aqueous Phase Self Diffusivities
- ☐ Vapor Phase Self Diffusivities
- ☐ Vapor Phase Diffusivity Matrix

Description

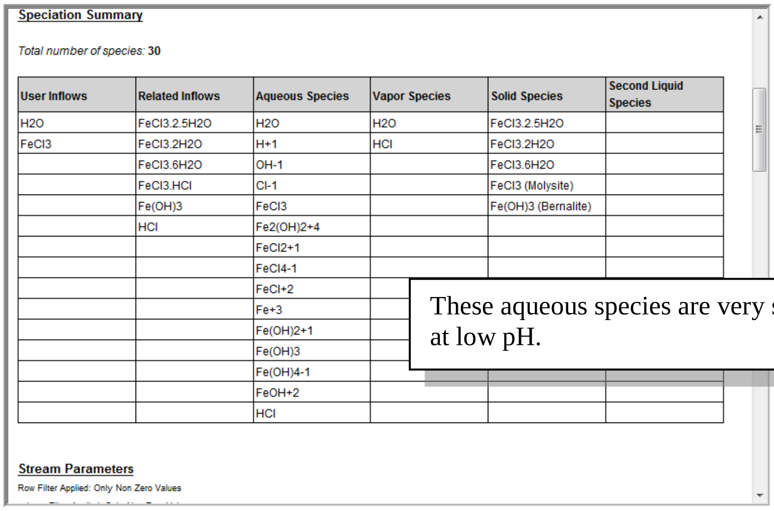
This section displays a calculation summary.

7 of 21 Sections selected

Figure 2-13 Report content options

Locate the **Speciation Summary** check box and select it.

Click the **OK** button. Click on definition tab to refresh the report tab.



Speciation Summary

Total number of species: **30**

User Inflows	Related Inflows	Aqueous Species	Vapor Species	Solid Species	Second Liquid Species
H2O	FeCl3.2.5H2O	H2O	H2O	FeCl3.2.5H2O	
FeCl3	FeCl3.2H2O	H+1	HCl	FeCl3.2H2O	
	FeCl3.6H2O	OH-1		FeCl3.6H2O	
	FeCl3.HCl	Cl-1		FeCl3 (Molysite)	
	Fe(OH)3	FeCl3		Fe(OH)3 (Bernalite)	
	HCl	Fe2(OH)2+4			
		FeCl2+1			
		FeCl4-1			
		FeCl+2			
		Fe+3			
		Fe(OH)2+1			
		Fe(OH)3			
		Fe(OH)4-1			
		FeOH+2			
		HCl			

Stream Parameters

Row Filter Applied: Only Non Zero Values

These aqueous species are very stable, even at low pH.

Figure 2-14 Modifying the report

Answer:

pH = 2.215

Why is the pH so low? The aqueous iron species form complexes with the hydroxide ion which shifts the water dissociation in the direction to replenish the hydroxide ions[3]. This also produces hydrogen ions which do not have a corresponding place to go and therefore remain free, lowering the pH.

This equilibrium is always present:

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

Speciation:

Fe^{+3}
Cl^{-1}
H^{+1}
OH^{-1}
H_2O^0

$FeCl^{+2}$
$FeCl_2^{+1}$
$FeCl_3^0$
$FeCl_4^{-1}$
HCl^0

$FeOH^{+2}$
$Fe(OH)_2^{+1}$
$Fe(OH)_3^0$
$Fe(OH)_4^{-1}$
$Fe_2(OH)_2^{+4}$

This is a weak species at 25ºC.

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

Speciation in Sour Water

Now we will look at a different system; the sour water system ($NH_3/H_2S/CO_2/H_2O$).

Sour Water Species

Vapor Species:

H_2O, CO_2, H_2S and NH_3

Aqueous Neutral Species:

H_2O, CO_2, H_2S and NH_3

Aqueous Ionic Species:

H^+, OH^-, NH_4^+, HS^-, S^{2-}, HCO_3^-, CO_3^{2-}, and $NH_2CO_2^-$

Chemistry Summary (Molecular Equilibrium)

Vapor - Liquid equilibrium reactions considered:

$H_2O_{(vap)} = H_2O$

$NH_{3(vap)} = NH_{3(aq)}$

$CO_{2(vap)} = CO_{2(aq)}$

$H_2S_{(vap)} = H_2S_{(aq)}$

Chemistry Summary (Electrolyte Equilibrium)

Additional electrolyte reactions needed

$H_2O = H^+ + OH^-$

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

$CO_{2(aq)} + H_2O = H^+ + HCO_3^-$

$HCO_3^- = H^+ + CO_3^{2-}$

Notice that this is the hydrolysis of an ion.

$NH_2CO_2^- + H_2O = NH_{3(aq)} + HCO_3^-$

$H_2S_{(aq)} = H^+ + HS^-$

$HS^- = H^+ + S^{2-}$

Calculating Partial Pressures

In oil and gas refining, it is frequently important to remove impurities from the gas and oil. This may be done via a scrubbing mechanism in which a gas is scrubbed with a liquid. Alternatively, a polluted waste stream may be stripped of the pollutant using air. In either case, the calculating the partial pressures of the components is very important.

We now want to calculate the partial pressures of CO2, H2S, and NH3 with and without the aqueous phase equilibrium considered.

Data Summary[4,5]

Temperature 20ºC & 60ºC

Solution Composition

NH_3: 1.126 - 2.160 molal (1.8 - 3.3 wt %)

CO_2: 0.424 - 1.601 molal (1.8 - 6.4 wt %)

H_2S: 0.040 - 0.407 molal (0.1- 1.3 wt %)

H_2O: Balance

***Table 2-1** Experimental and Calculated Partial Pressures of NH3, H2O and CO2*

	Liquid Concentration (molality)			Partial Pressure (mmHg)								
				NH3			CO2			H2S		
Temp (C)	NH3	CO2	H2S	Experimental	OLI	VLE	Experimental	OLI	VLE	Experimental	OLI	VLE
60	2.076	1.516	0.064	14.744	12.388	121.6	751.488	592.192	79594.8	31.616	36.936	1033.6
	2.098	1.601	0.052	13.604	10.792	129.2	738.112	744.572	84762.8	23.256	35.112	843.6
	1.954	1.471	0.04	11.476	11.172	114	691.904	638.4	76820.8	22.8	25.004	638.4
	2.16	1.581	0.05	13.68	12.92	129.2	705.28	590.52	83524	22.42	28.12	813.2
20	1.231	0.424	0.196	4.104	3.648	12.16	1.444	1.672	8580.4	3.192	3.04	1292
	1.236	0.507	0.201	2.888	2.66	12.16	3.496	3.42	10290.4	5.092	4.484	1325.44
	1.45	0.517	0.407	2.432	2.736	14.44	3.724	4.028	10526	12.54	10.944	2690.4
	1.439	0.665	0.396	1.52	1.444	14.44	13.072	13.148	13611.6	26.98	20.672	2634.16
	1.132	0.681	0.1	1.368	1.216	11.4	12.16	13.984	13892.8	5.32	4.94	663.48
	1.234	0.694	0.199	1.292	1.216	12.16	13.072	16.036	14181.6	11.172	11.096	1322.4
	1.238	0.712	0.203	1.292	1.064	12.16	19	18.62	14561.6	15.276	12.464	1345.2
	1.234	0.725	0.199	0.912	0.988	12.16	20.444	20.672	14835.2	15.96	13.072	1079.2
	1.235	0.771	0.2	0.912	0.836	12.16	29.184	30.324	15808	27.36	17.024	1333.04
	1.126	0.794	0.095	0.684	0.684	11.4	35.188	36.252	16271.6	12.236	8.892	633.08

Table 2-1 Comparing Experimental Partial Pressures to Calculated values.

---

[4] IGT Process Research Division, "HYGAS, 1972 to 1974 Pipeline Gas from Coal - Hydrogenation (IGT Hydrogasification Process)" R & D Report No. 110; Interim Report No. 1. ERDA July 1975.

[5] D.W.VanKrevelen, P.J.Hoftijzer, and F.J Juntjens. "Composition and Vapour Pressures of Aqueous Solutions of Ammonia, Carbon Dioxide and Hydrogen Sulphide" Rec.Trav.Chem., Pay-Bas **68**, 191-216 (1949)

The data contained in **Table 2-1**compares the experimental partial pressures of carbon dioxide, ammonia and hydrogen sulfide against a VLE only model and the full OLI speciated model.

Considering only the Vapor-Liquid equilibria

Only the following equilibria are considered in these calculations:

$H_2O_{(vap)}$ = H_2O

$NH_{3(vap)}$ = $NH_{3(aq)}$

$CO_{2(vap)}$ = $CO_{2(aq)}$

$H_2S_{(vap)}$ = $H_2S_{(aq)}$

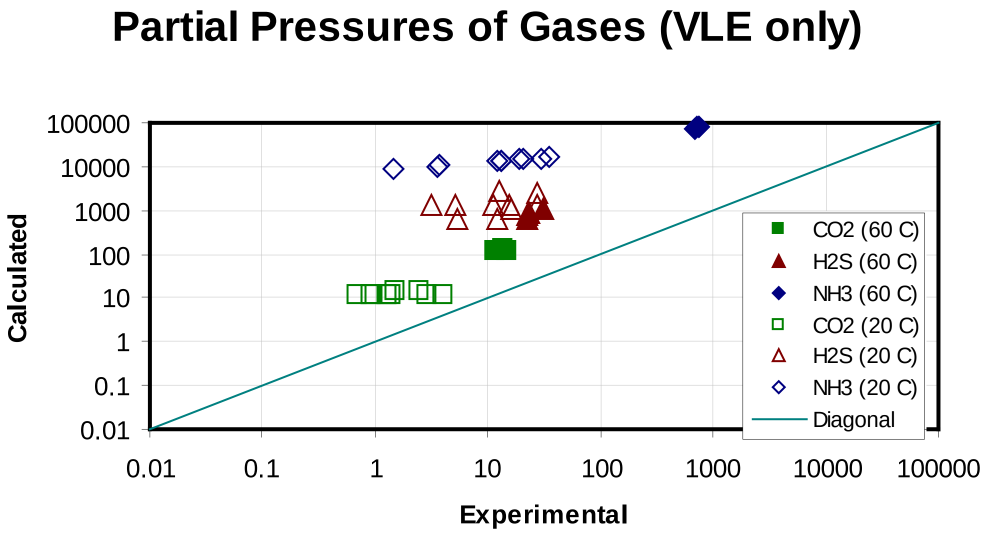


Figure 2-15 Parity plot of the partial pressures of gases without aqueous reactions

In Figure 2-15, the calculated partial pressures of the gases are over predicted. In the case of ammonia (filled and open diamonds), the over prediction may be as much a five orders of magnitude. This data can be improved with statistical corrections or by applying a strong activity model. These corrections, however, are in effect performing most of the "Work" in the calculation. If we desired conditions other than the conditions in these series of calculations, then perhaps the corrections will over-correct.

Considering the full OLI Speciation Model

All of these equilibria are no considered in these new series of calculations:

$H_2O_{(vap)}$ = H_2O

$NH_{3(vap)}$ = $NH_{3(aq)}$

$CO_{2(vap)}$ = $CO_{2(aq)}$

$H_2S_{(vap)}$ = $H_2S_{(aq)}$

H_2O = $H^+ + OH^-$

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

$CO_{2(aq)} + H_2O$ = $H^+ + HCO_3^-$

HCO_3^- = $H^+ + CO_3^{2-}$

$H_2S_{(aq)}$ = $H^+ + HS^-$

$HS^- \quad = \quad H^+ + S^{2-}$

$NH_2CO_2^- + H_2O \quad = \quad NH_4^+ + HCO_3^-$

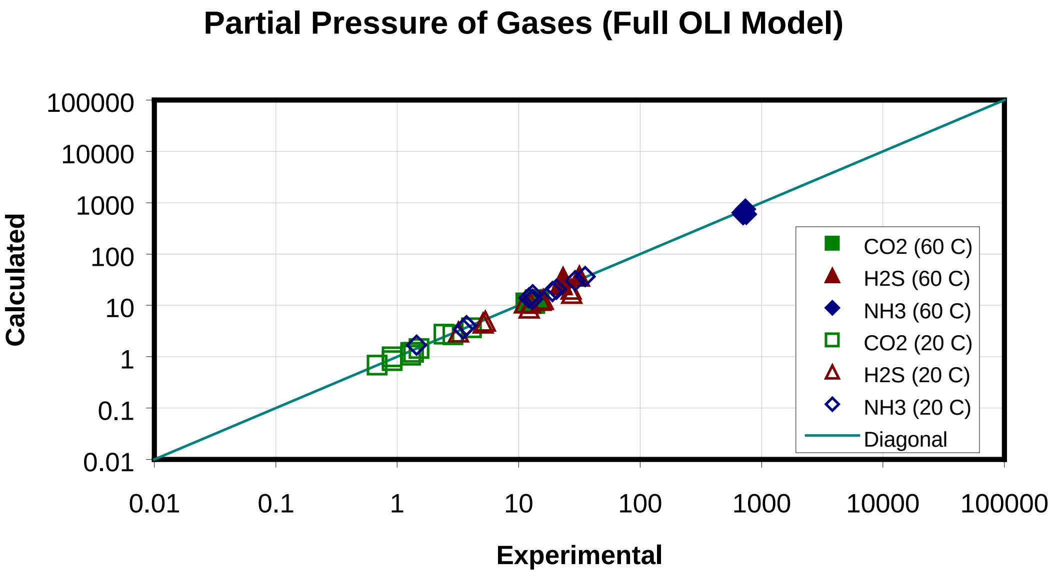


Figure 2-16 Parity plot of the partial pressures of gases with aqueous reactions

When all the equilibria are included in the calculations, the calculated partial pressure of the gases agrees with the experimental values. This was done without specialized data regression to the general range of this data. We may now have confidence that our predictions will hold at other conditions.

An Example of Speciation

A 0.1 molal (moles/ Kg H_2O) hydrofluoric acid sample is to be titrated with calcium chloride ($CaCl_2$). What will the titration curve look like?

a)

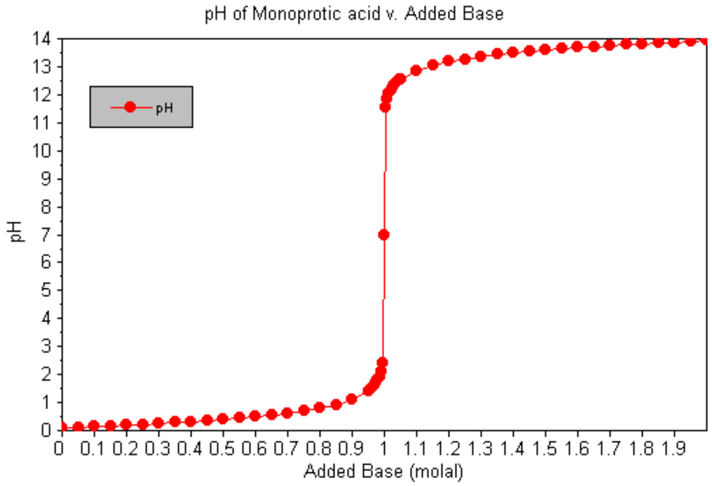


Figure 2-17 a mono protic acid titration curve

b)

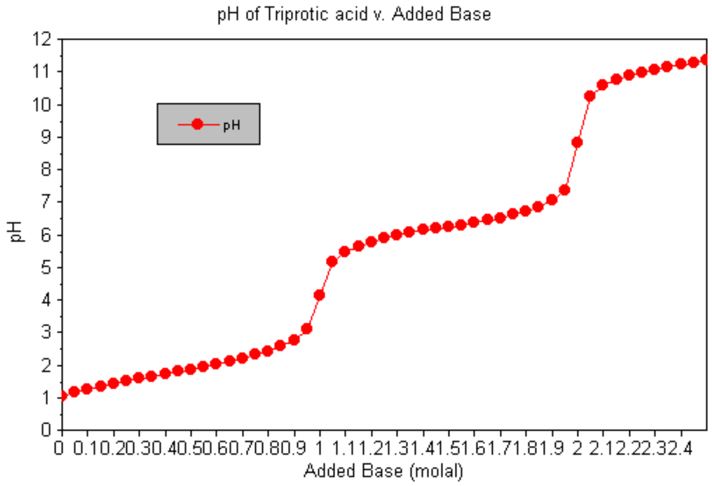


Figure 2-18 a triprotic acid titration curve

c)

Something Else??

The Answer is “C”, Something Else

Before we investigate this problem, let’s look at some of the underlying parts to this problem. First, what is the pH of the hydrofluoric acid stream at 30 ºC? Let’s use the OLI Studio to find out.

The Stream definition would be:

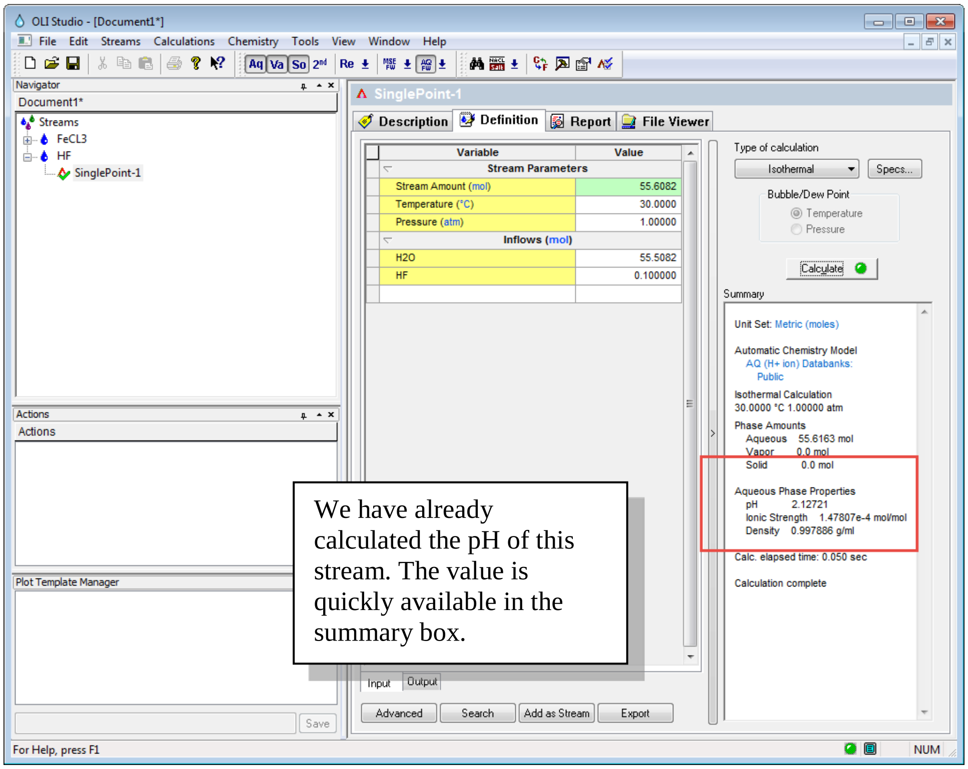
Temperature = 30 ºC

Pressure = 1 Atmosphere

H2O = 55.5082 moles

HF = 0.1

The input should look like this:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Temperature (°C)	30.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
HF	0.100000

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
30.0000 °C 1.00000 atm

Phase Amounts
Aqueous 55.6163 mol
Vapor 0.0 mol
Solid 0.0 mol

Aqueous Phase Properties
pH 2.12721
Ionic Strength 1.47807e-4 mol/mol
Density 0.997886 g/ml

Calc. elapsed time: 0.050 sec

Calculation complete

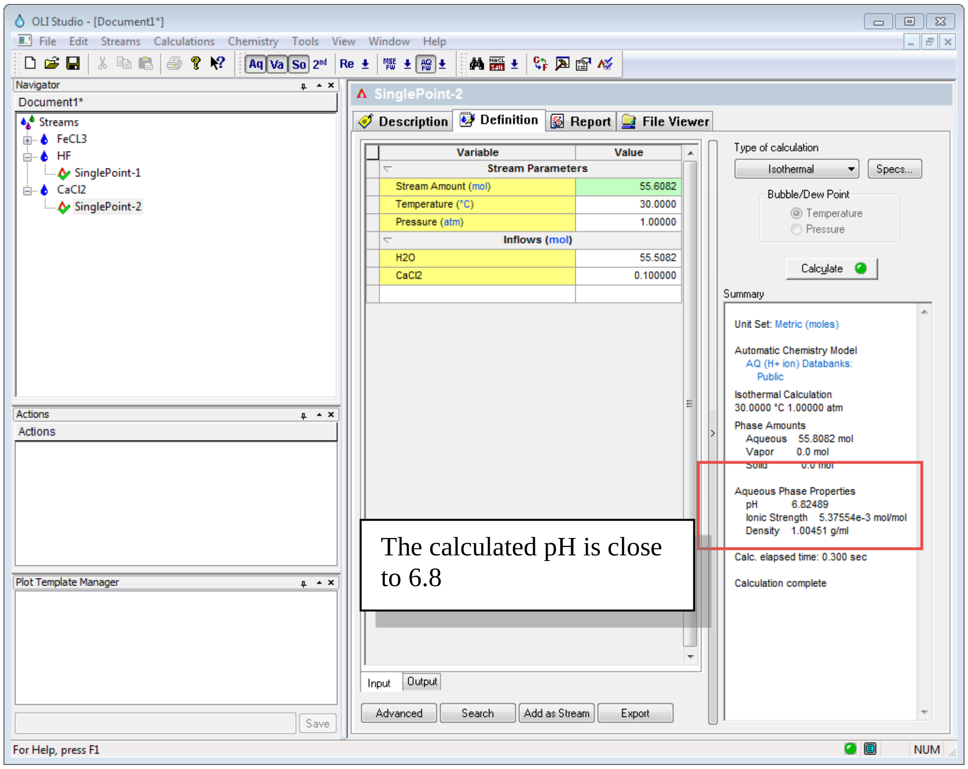
We have already calculated the pH of this stream. The value is quickly available in the summary box.

Figure 2-19 the pH of the HF stream

The calculated pH of this stream is approximately **2.13**.

Now let’s find the pH of the calcium chloride stream. The conditions are:

Temperature = 30 °C
Pressure = 1 Atmosphere
H_2O = 55.5082 moles
$CaCl_2$ = 0.1



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Temperature (°C)	30.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
CaCl2	0.100000

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
30.0000 °C 1.00000 atm

Phase Amounts
Aqueous 55.8082 mol
Vapor 0.0 mol
Solid 0.0 mol

Aqueous Phase Properties
pH 6.82489
Ionic Strength 5.37554e-3 mol/mol
Density 1.00451 g/ml

Calc. elapsed time: 0.300 sec

Calculation complete

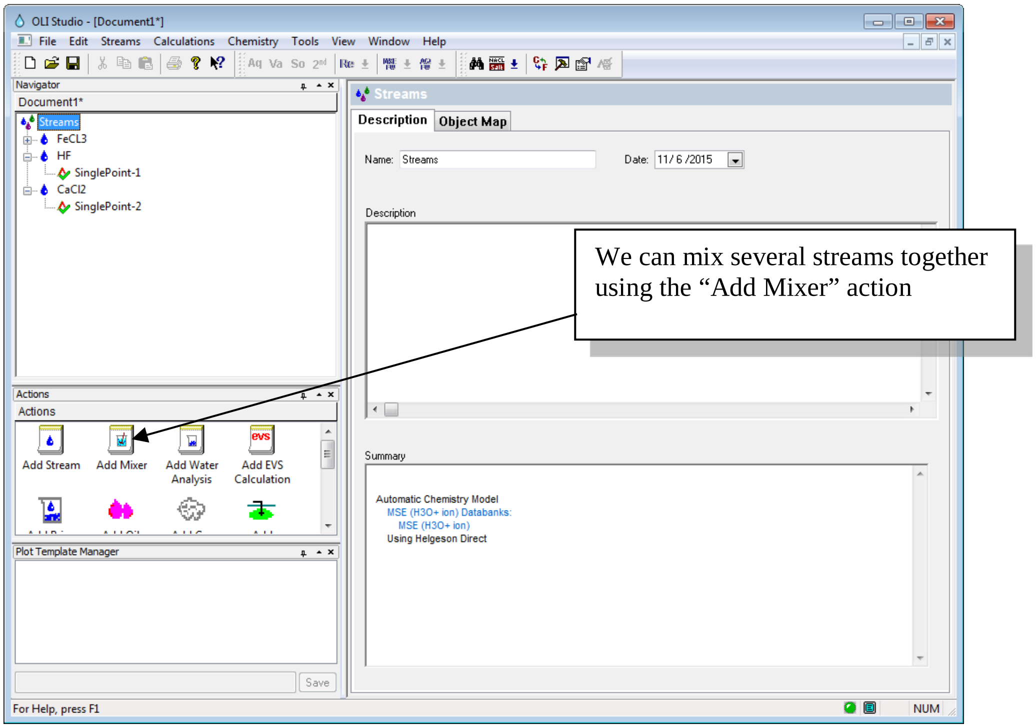
The calculated pH is close to 6.8

Figure 2-20 The pH of the Calcium chloride stream.

The pH is approximately **6.8**.

What happens if we mix equal volumes of the two streams? We have the Mix calculation to help us determine the resultant pH.

We click on the “**Add Mixer”** icon to start adding streams together.



Name: Streams

Date: 11/ 6 /2015

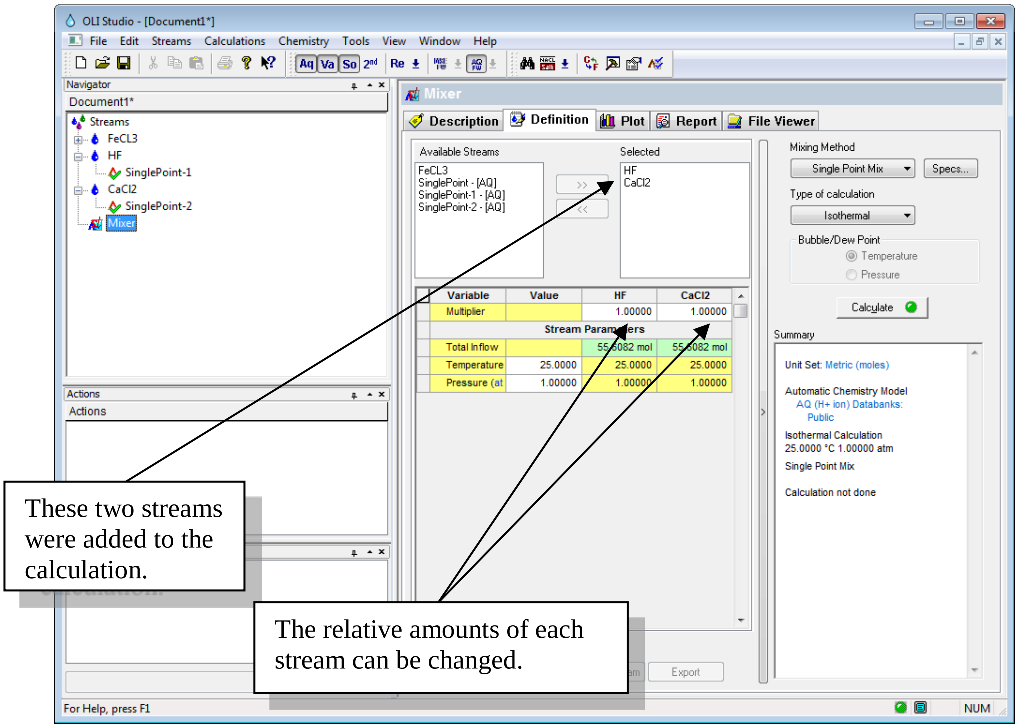
Description

Summary

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

We can mix several streams together using the “Add Mixer” action

Figure 2-21 The main explorer window. Locating the Mix calculation.



Available Streams

FeCL3
SinglePoint - [AQ]
SinglePoint-1 - [AQ]
SinglePoint-2 - [AQ]

Selected

HF
CaCl2

Variable	Value	HF	CaCl2
Multiplier		1.00000	1.00000
Stream Parameters			
Total Inflow		55.5082 mol	55.5082 mol
Temperature	25.0000	25.0000	25.0000
Pressure (at	1.00000	1.00000	1.00000

Mixing Method: Single Point Mix

Type of calculation: Isothermal

Bubble/Dew Point
◉ Temperature
○ Pressure

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
25.0000 °C 1.00000 atm

Single Point Mix

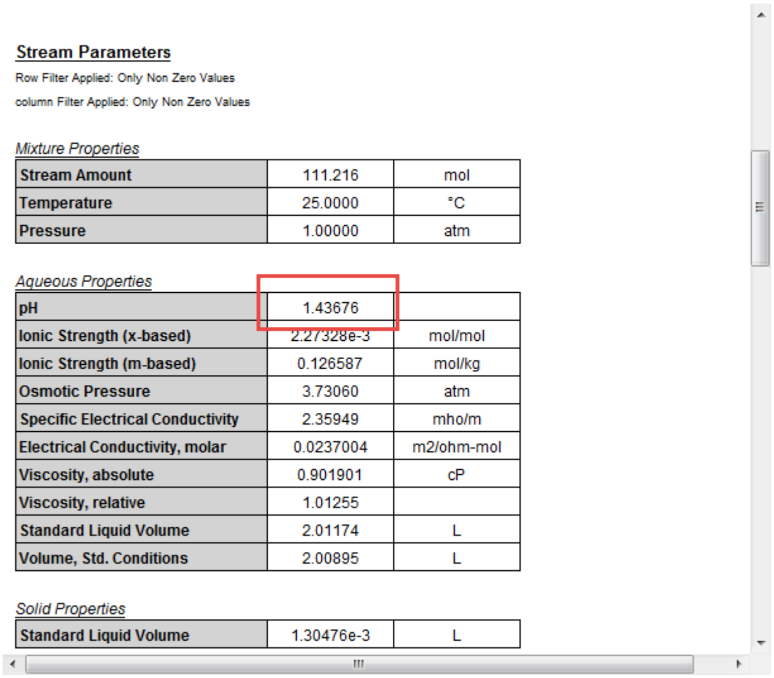
Calculation not done

These two streams were added to the calculation.

The relative amounts of each stream can be changed.

Figure 2-22 The completed mix calculation.

We now need to click on the report tab to see the resultant pH.



Stream Parameters

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

Mixture Properties

Stream Amount	111.216	mol
Temperature	25.0000	°C
Pressure	1.00000	atm

Aqueous Properties

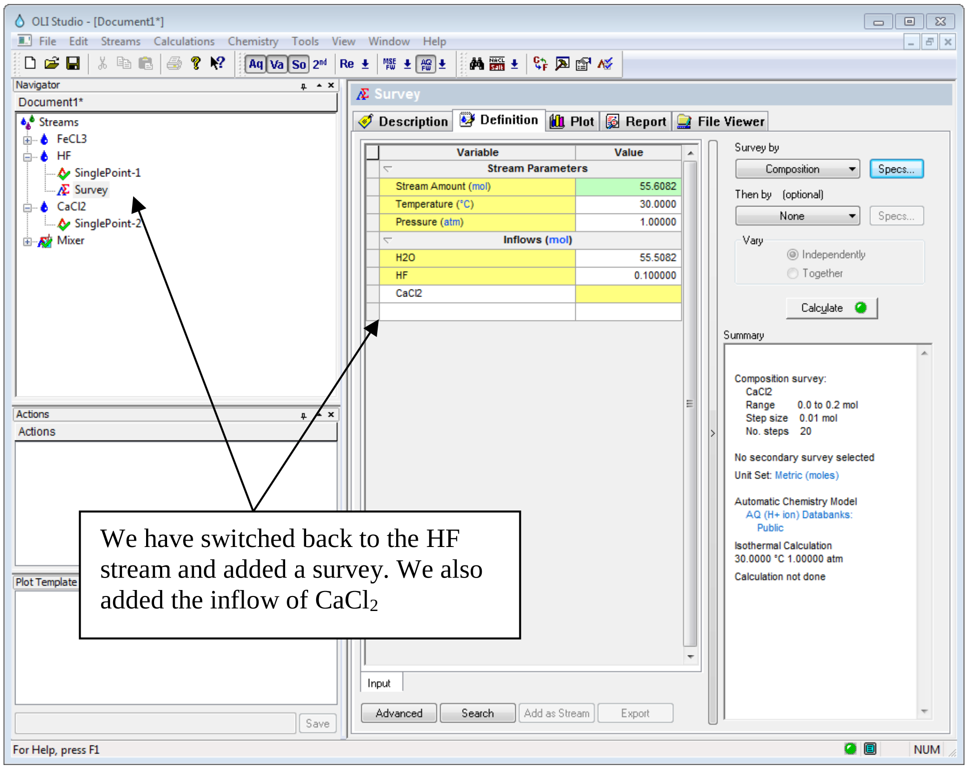
pH	1.43676	
Ionic Strength (x-based)	2.27328e-3	mol/mol
Ionic Strength (m-based)	0.126587	mol/kg
Osmotic Pressure	3.73060	atm
Specific Electrical Conductivity	2.35949	mho/m
Electrical Conductivity, molar	0.0237004	m2/ohm-mol
Viscosity, absolute	0.901901	cP
Viscosity, relative	1.01255	
Standard Liquid Volume	2.01174	L
Volume, Std. Conditions	2.00895	L

Solid Properties

Standard Liquid Volume	1.30476e-3	L

The resultant pH is 1.44. How can this be? An acid stream (the HF stream had a pH of approximately 2.13) and a nominally basic stream (the $CaCl_2$ stream had a pH of 6.8) are mixed and the pH is outside the value of either stream.

Let's use the OLI Studio to examine the chemistry in more detail. First, we will perform a composition survey on the HF stream. To do this we will now titrate the stream with $CaCl_2$.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Temperature (°C)	30.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
HF	0.100000
CaCl2	

Composition survey:
CaCl2
Range 0.0 to 0.2 mol
Step size 0.01 mol
No. steps 20

No secondary survey selected

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
30.0000 °C 1.00000 atm

Calculation not done

We have switched back to the HF stream and added a survey. We also added the inflow of $CaCl_2$

Figure 2-23 The composition survey prior to calculation.

We set the survey to automatically add $CaCl_2$ in the range of 0.0 moles to 0.2 moles in 0.01 mole increments. When the calculation was complete, we displayed the plot.

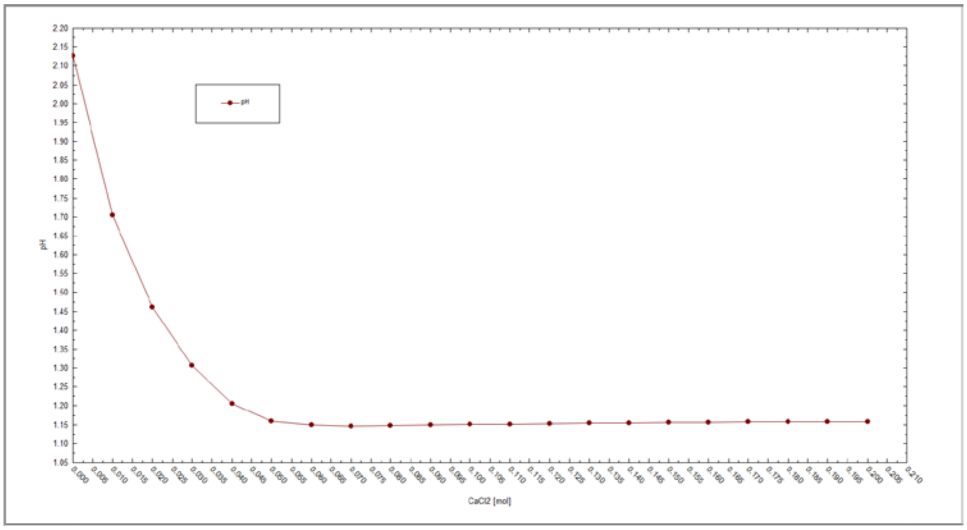


Figure 2-24 pH response to CaCl2 titration

As you can see, adding CaCl2 to this solution lowers the pH initially. The pH does begin to slowly increase after 0.06 moles of CaCl2 have been added.

Why the unusual pH behavior? At low values of $CaCl_2$ the hydrogen fluoride dissociates because of the formation of a solid phase, $CaF_{2(cr)}$. This effectively removes fluoride ion from solution according to the following equation:

$$Ca^{2+} + 2F^{-1} \rightarrow CaF_{2(cr)}$$

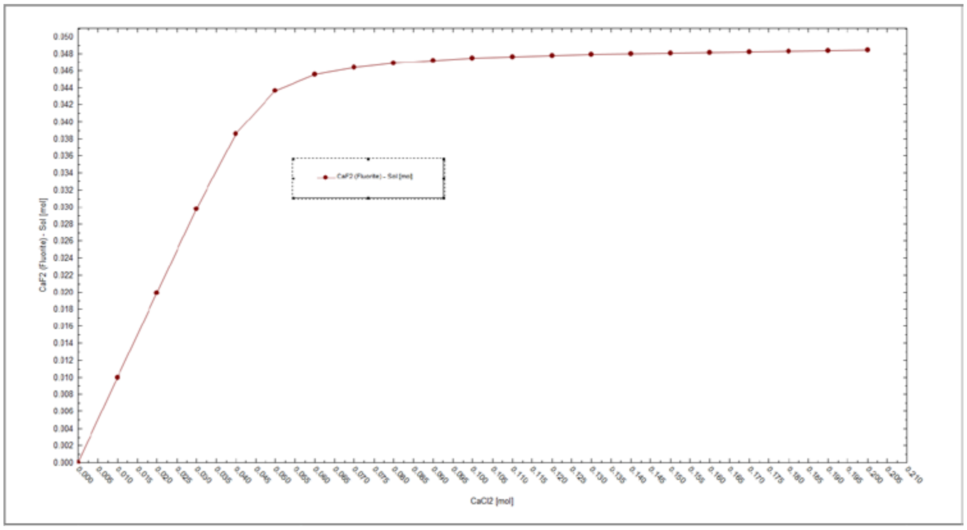


Figure 2-25 the formation of CaF_2

This shifts the following equilibrium to the right.

Is Hydrofluoric Acid a strong Acid?

No, HF is a weak acid with a pKa = 3.45. Compare this to other weak acids:

Acetic Acid: pKa=4.75

Citric Acid: pKa1=3.14
HF is between these values.

$$HF^{o} \rightarrow H^{+} + F^{-}$$

As CaF_2 is formed, the amount of fluoride ion in solution is decreased. *Le Chatlier's* principle states that any equilibrium under stream which shift to relieve the stress. Thus, more hydrogen ion is produced, lowering pH.

What are the fluoride species doing in solution? The next figure illustrates this:

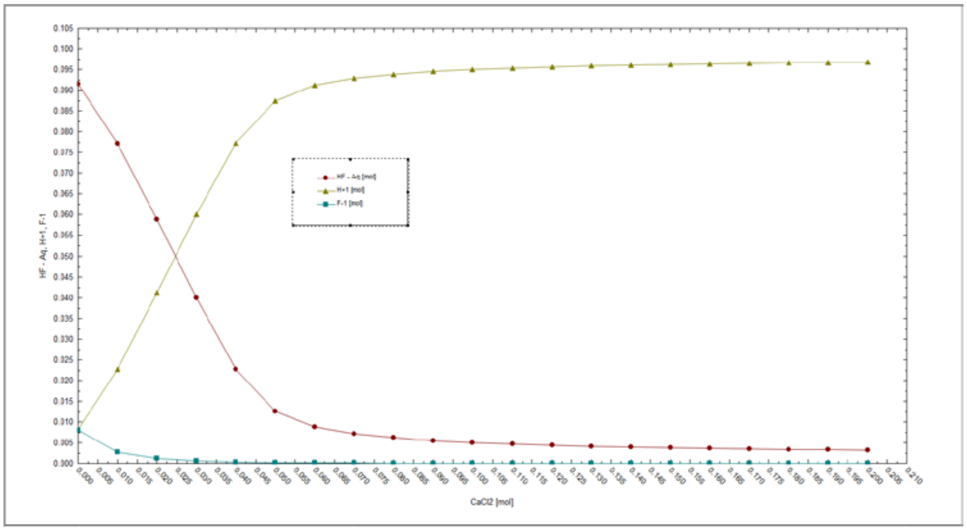


Figure 2-26 The dominant fluoride species in solution.

The neutral HF species continues to dissociate until almost 0.05 moles of calcium chloride. At the same time hydrogen ion is produced. The fluoride ion in solution also decreased as the formation of CaF_2 continues.

Summary:

1. Full aqueous Speciation is required to fully simulate the chemistry
2. Frequently there is more chemistry involved than simple acid/base chemistry.
3. Species concentrations can vary dramatically over relatively small range of conditions.

Click here for a finished Stream Analyzer file for this section: Chapter 02 Tour

3. Removing Nickel from Wastewater

The Removal of Nickel using the OLI Studio

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

In this application, a user is discharging a wastewater that contains nickel ion at a concentration of 0.002 moles/Kg H_2O. The existing treatment strategy is to precipitate the nickel ion as Nickel Hydroxide ($Ni(OH)_2$). The soluble nickel remaining after precipitation is less than 1 ppm, which is a design specification.

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

The power of OLI Studio becomes apparent when we are seeking to study the chemistry of individual streams.

We will illustrate the steps necessary to solve these problems in detail. This section is designed to be used as a guide for future reference.

How to run the tour?

In this tour, and all subsequent tours, when action is required by the user, the instruction will be in ***Bold and Italic*** type. When you are referred to a feature on a screen, the information will be **<u>Bold and underlined</u>**. Any mouse clicks are left-mouse button clicks unless otherwise noted. This is summarized below:

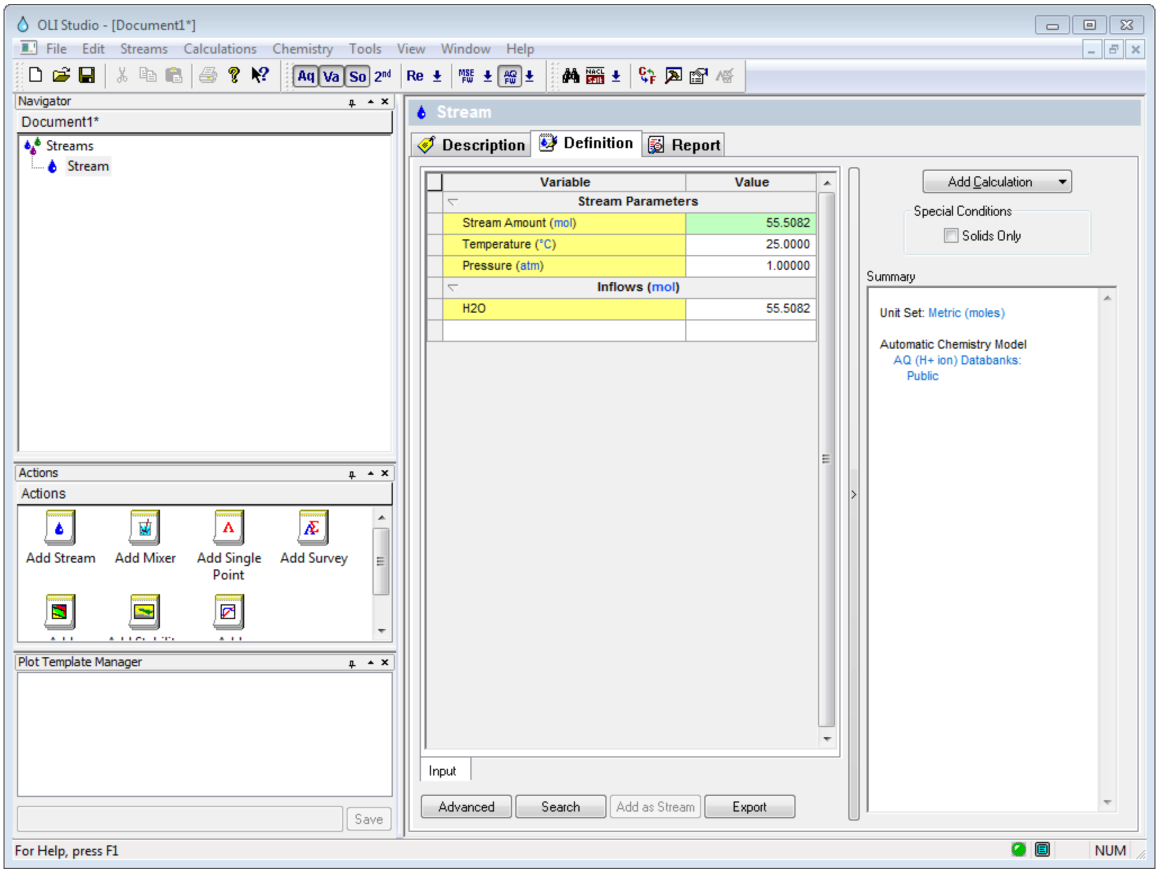
Type Face	User Action
Bold and Italic	The user is required to enter this information
<u>Bold and Underlined</u>	The user is directed to look for this feature in the program windows
Click	Left-mouse button
Right-Click	Right-mouse button

The Tour Starts Here...

We begin by starting the OLI Studio Program. This may be accomplished by ***clicking*** on the OLI Studio icon or by using the Start button and finding OLI Studio under *Programs*.

Once started, the OLI Splash screen will appear momentarily.

After a few moments, the main OLI Studio window will appear.



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

☐ Solids Only

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

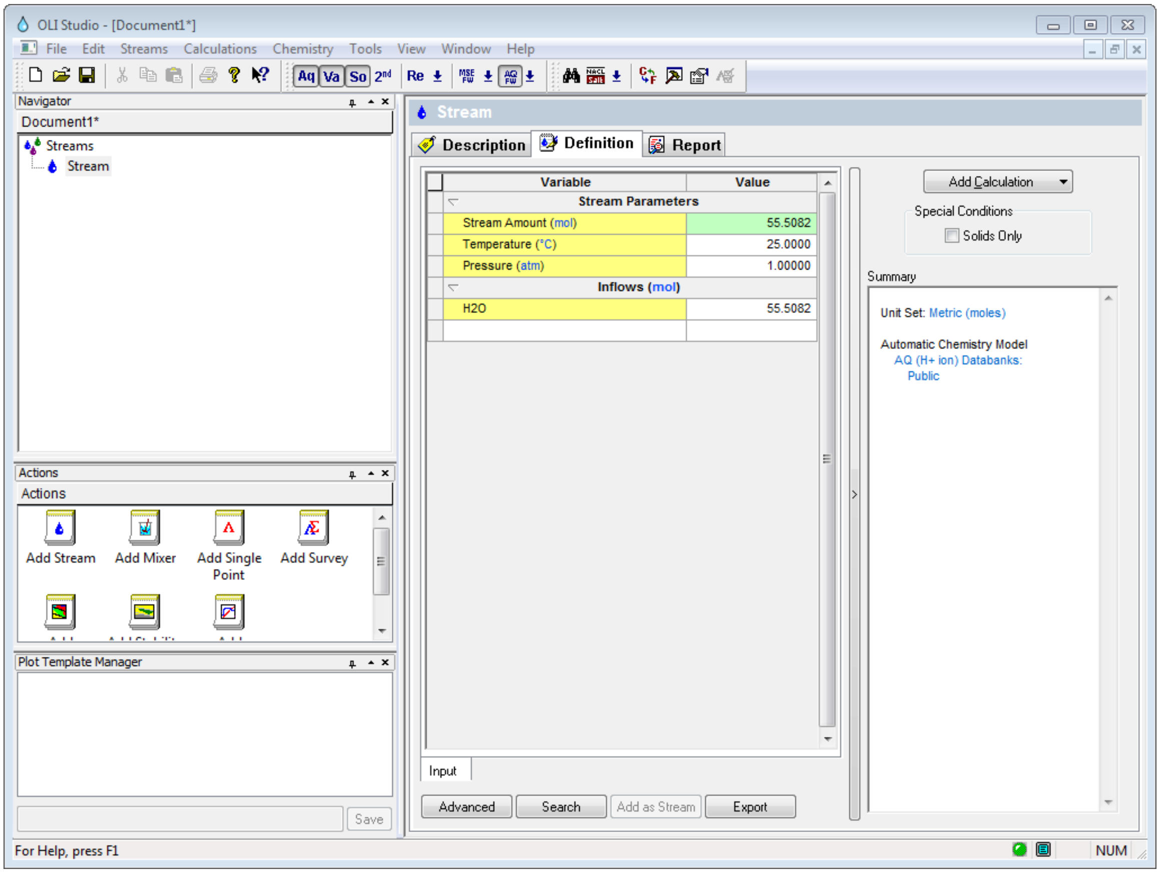
Figure 3-1 The OLI Studio main window

We now need to define the wastewater stream.

Scenario 1: Wastewater without additives

Step 1: Add the Stream

Click on the **Add Stream** icon**.** This will display the **Definition** window.



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

☐ Solids Only

Unit Set: Metric (moles)

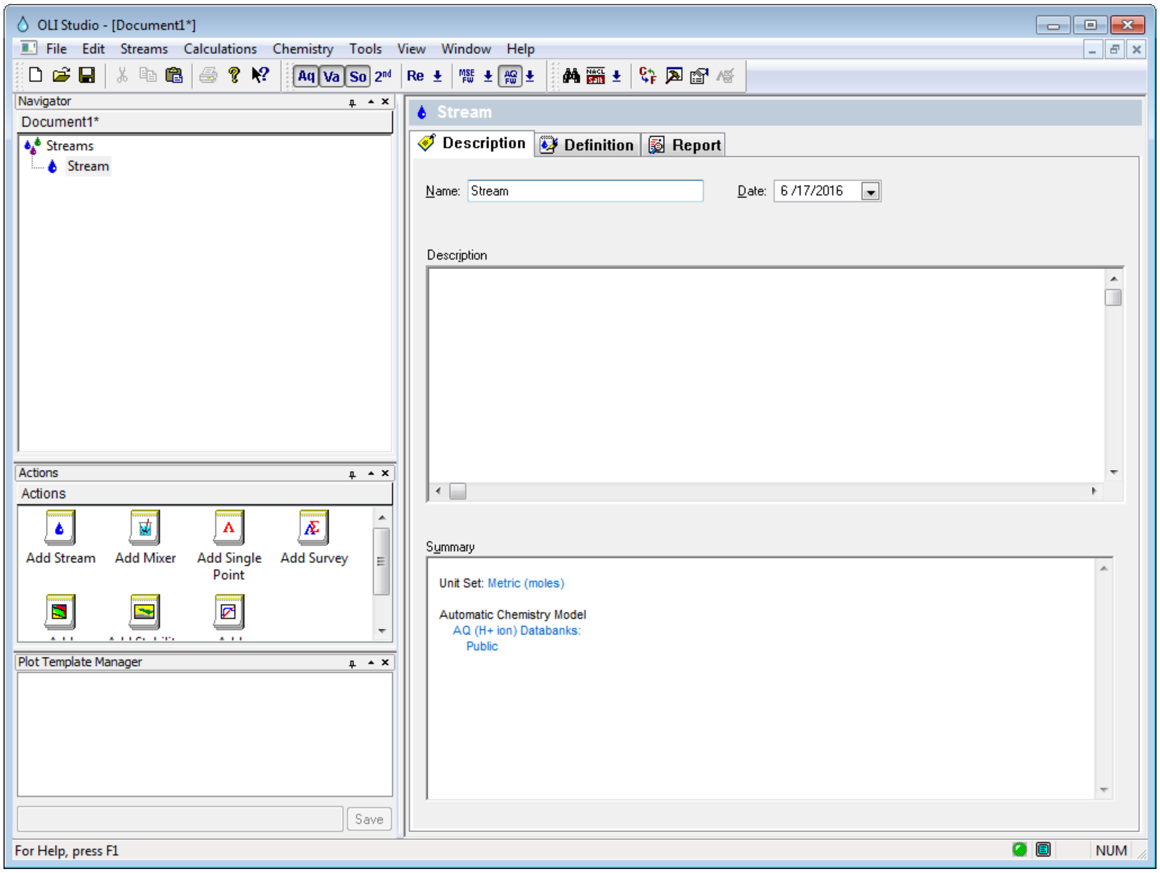
Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 3-2 The streams definition view.

We should add some descriptive information about this stream so we can later identify the stream.

Step 2: Adding definitions

Click on the **<u>Description</u>** tab**.** This will display the description information



Name: Stream

Date: 6 /17/2016

Description

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 3-3 The Stream Description tab.

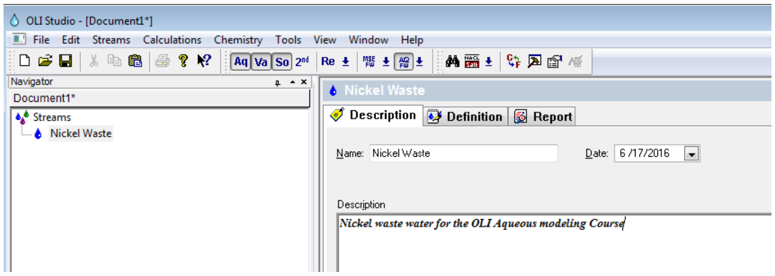
It is advisable to change the name of the stream from the default name. You may be entering many streams and will need to sort them out at a later time.

Step 3: Enter Stream Names and Definition

Replace the name ***Stream*** with the name ***Nickel Waste.***

Add the following text to the description box: "***Nickel waste water for the OLI Aqueous Modeling Course."***

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



Name: Nickel Waste

Date: 6 /17/2016

Description

Nickel waste water for the OLI Aqueous modeling Course

Figure 3-4 The filled-out description window

Click on the **Definition** tab.

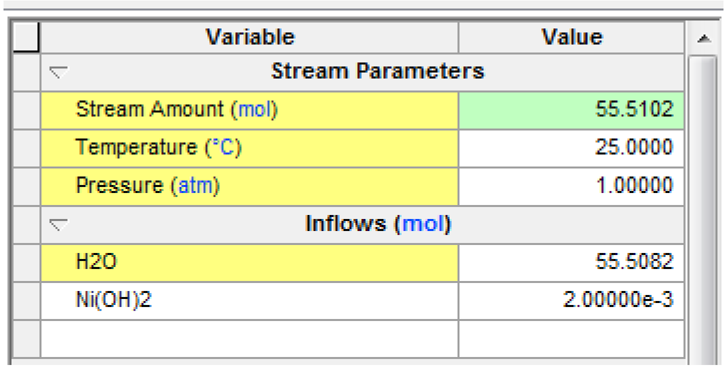
Step 4: Enter component inflows

Click in the white box in the grid below the **Inflows** line.

Add the formula ***Ni(OH)$_2$*.**

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

After entering the values, the grid should look like the following:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3

Figure 3-5 The filled-out grid, notice the name Ni(OH)2 changed.

OLI Studio will automatically change the name of the species to the selected display name. In this instance, the name you entered was ***Ni(OH)$_2$*** but it may have changed to a different form. If it changed you can specify which display system to use in the following optional steps.

Optional

The default display name can be changed using a Menu Item called

Tool | Names Manager.

Step 4a: Select Tools from the Menu

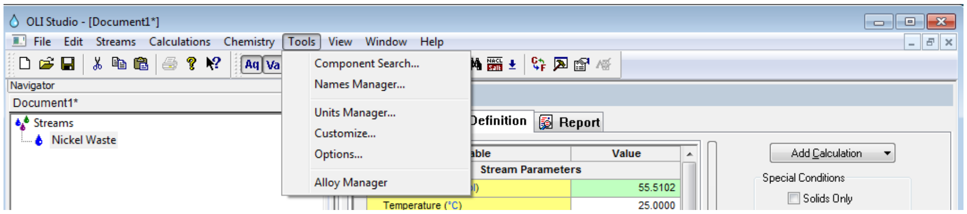


Figure 3-6 the Tools Menu

Select **Names Manager** from the Tools list.

The linked image cannot be displayed. The file may have been moved, renamed, or deleted. Verify that the link points to the correct file and location.

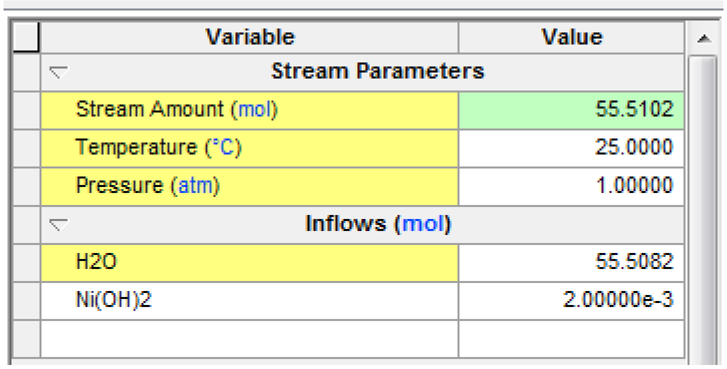
Figure 3-7 The Names Manager

The components can be displayed using the **Display Name** (default) or by the **Formula Name**. Alternatively, the traditional OLI Tag name[6] can be used.

Select the **Formula** radio button.

Click on the **Apply** button.

Click on the **OK** button.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3

Figure 3-8 The filled-out grid in with formula names.

The remainder of this tour will use this name display system.

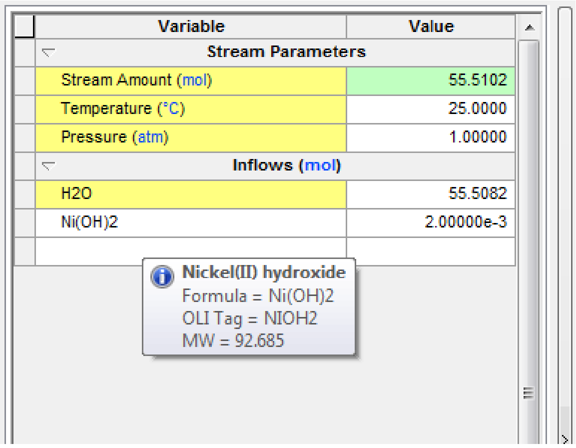
Now enter the 0.002 moles of $Ni(OH)_2$.

---

[6] This is also known as the ESP name.

We are now ready to begin the calculations. Our first task is to determine the pH of this solution.

OLI has added a new feature to the inflow grid. If you hover the cursor over the inflow components, you will see information about that particular chemical.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3

Nickel(II) hydroxide
Formula = Ni(OH)2
OLI Tag = NIOH2
MW = 92.685

Step 5: Add a Single Point calculation to the Stream

Figure 3-9 Selecting Single Point

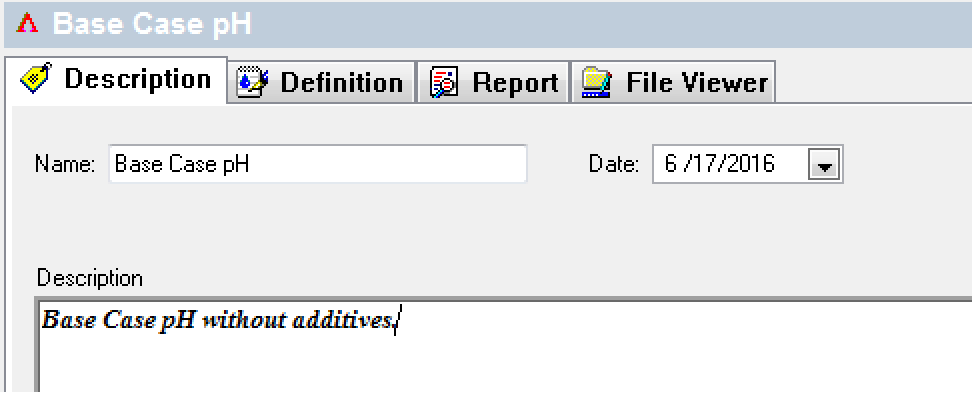
Click on the ***Add Calculation*** Button and then select **Single Point.**

As with the stream definition, each calculation can have its own name and definition. We will add our definition for this calculation to remind us of what we did here. Click on the ***Description*** Tab.

Replace the Calculation name with ***Base Case pH.***

Add a description: ***Base Case pH without additives.***

The summary box will update with the status of the calculation. The following window shows this information.



Name: Base Case pH

Date: 6 /17/2016

Description

Base Case pH without additives.

Figure 3-10 The filled out description

We can now start the calculation.

Click on the **Definition** tab.

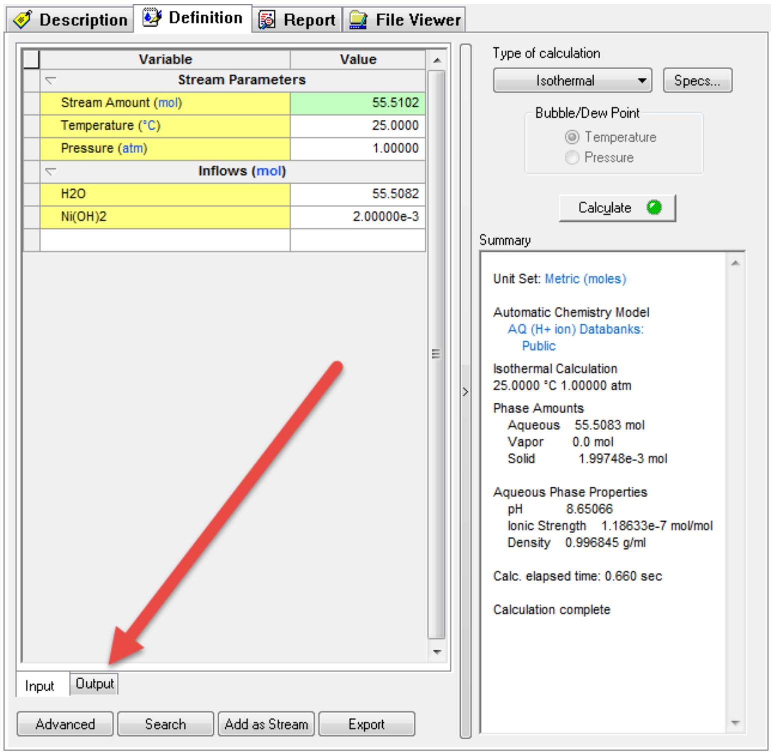
The information on this page does not need to be changed Please

Click on the **Calculate** button.

When the program is completed (the orbiting ***e*** stops) we are ready to review the results. This may be done in several ways. This tour will examine several of the methods.

Step 6: Obtaining results

Click on the **Output** tab.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
25.0000 °C 1.00000 atm

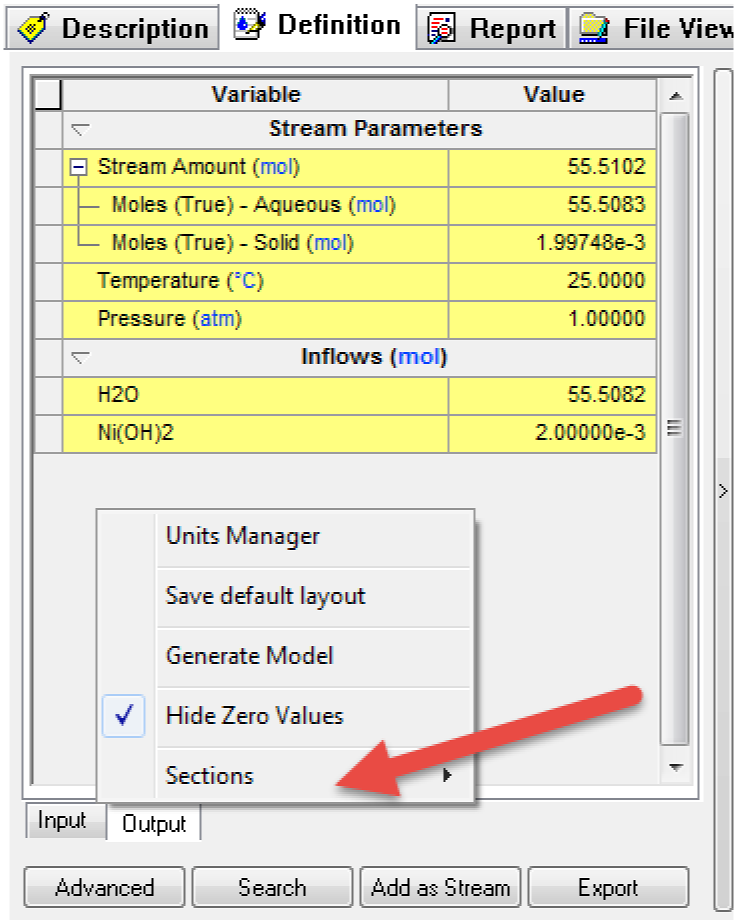
Phase Amounts
Aqueous 55.5083 mol
Vapor 0.0 mol
Solid 1.99748e-3 mol

Aqueous Phase Properties
pH 8.65066
Ionic Strength 1.18633e-7 mol/mol
Density 0.996845 g/ml

Calc. elapsed time: 0.660 sec

Calculation complete

Next right-click anywhere in the gray field to display a pop-up menu.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
Moles (True) - Aqueous (mol)	55.5083
Moles (True) - Solid (mol)	1.99748e-3
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3

Figure 3-11 Displaying additional sections

Select **Sections.**

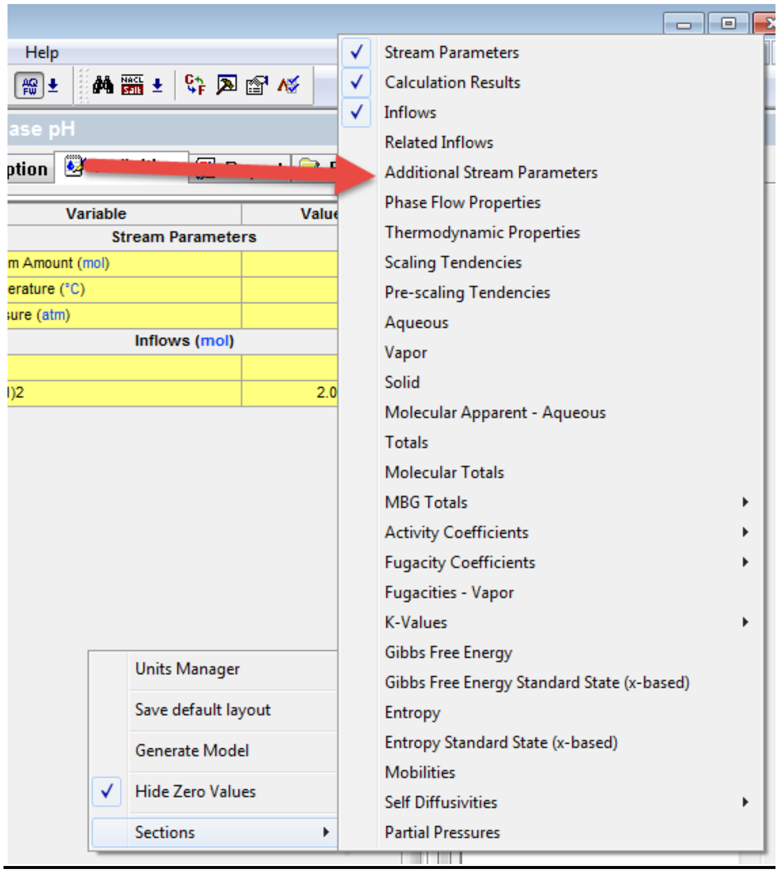
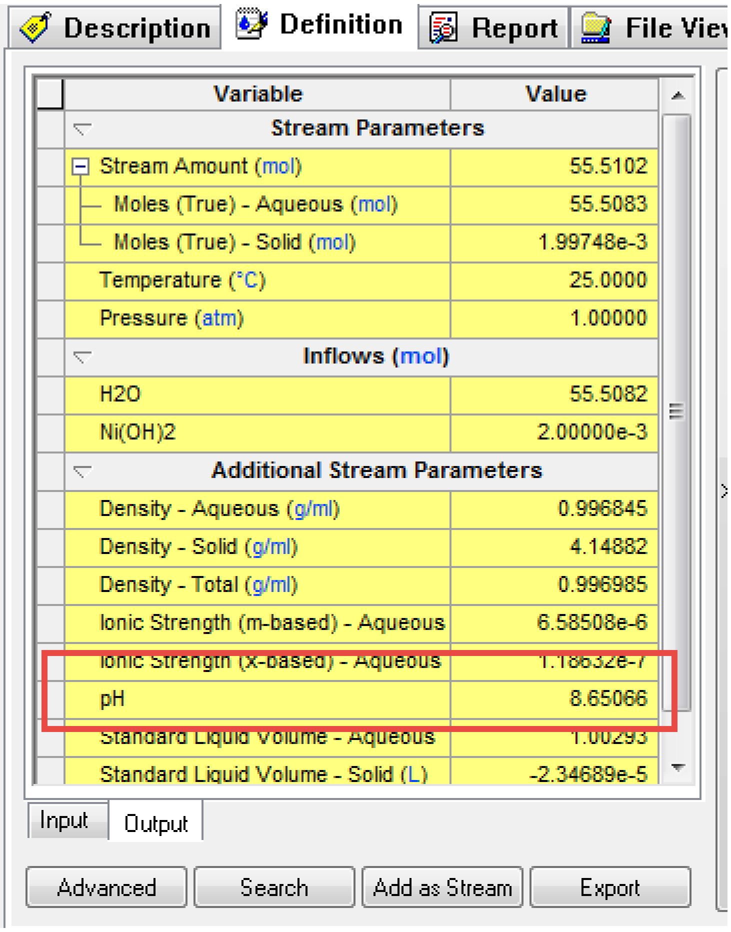


Figure 3-12 Displaying all the sections available

Select **Additional Stream Parameters**

The grid will now change to yellow cells to indicate that these are calculated values. The pH can be found in the grid.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
Moles (True) - Aqueous (mol)	55.5083
Moles (True) - Solid (mol)	1.99748e-3
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3
Additional Stream Parameters	
Density - Aqueous (g/ml)	0.996845
Density - Solid (g/ml)	4.14882
Density - Total (g/ml)	0.996985
Ionic Strength (m-based) - Aqueous	6.58508e-6
Ionic Strength (x-based) - Aqueous	1.18632e-7
pH	8.65066
Standard Liquid Volume - Aqueous	1.00293
Standard Liquid Volume - Solid (L)	-2.34689e-5

3-13 Scroll down to see more data if necessary

The pH is approximately 8.65. Your value may be different if the version you are using is more recent than the version used to create this manual.

Our primary interest in this application is finding the optimum pH for nickel removal. To create a plot of the data, we will need to make a survey.

Step 7: Adding a pH Survey

There are many ways to move around in the OLI Studio. We will constantly highlight them as we move around in the tours. Remember that there is frequently more than one method to achieve a desired result.

Click on the **Nickel Waste** stream icon in the tree view on the left-hand side of the window.

This will bring you back to the top of the series of calculations by displaying just the stream information.

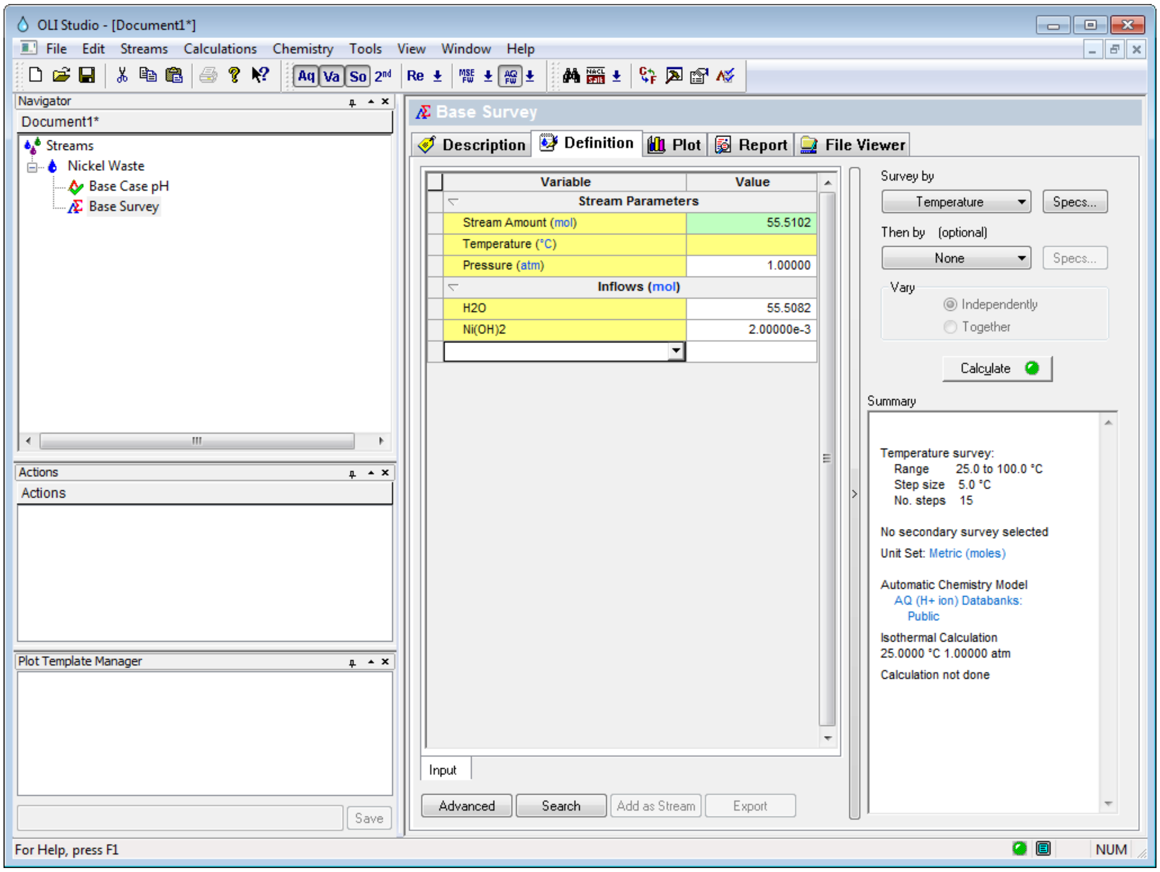
Click on the **Add Calculation** button and select **Survey.**

You can now add descriptive information about this calculation. We recommend the following (please note: We will only display windows that require new explanations)

Enter a new Survey name of **Base Survey**.

Enter a Description: ***Base pH survey without additives.***

Click on the **Definition** tab.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
Temperature (°C)	
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3

Survey by: Temperature
Then by (optional): None
Vary: ● Independently ○ Together

Summary

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

No secondary survey selected
Unit Set: Metric (moles)

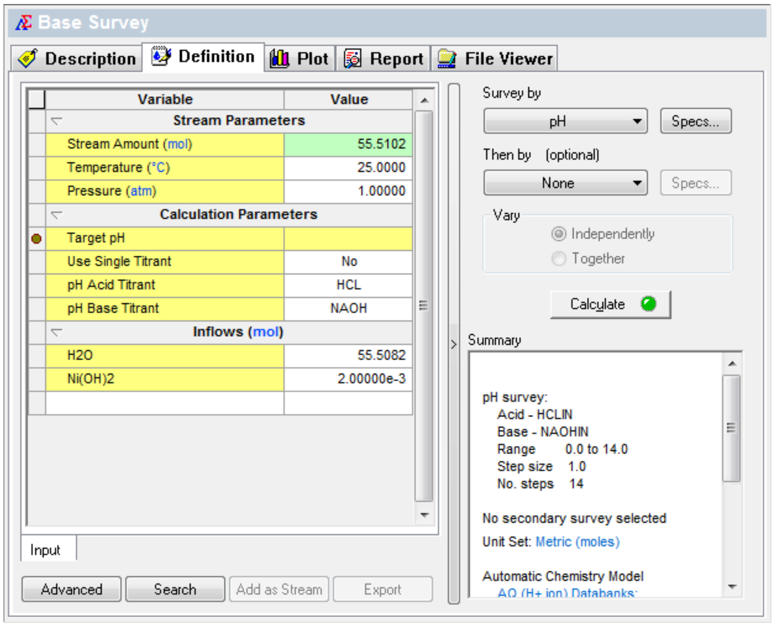
Automatic Chemistry Model
AQ (H+ ion) Databanks: Public

Isothermal Calculation
25.0000 °C 1.00000 atm
Calculation not done

Figure 3-14 The Default Survey Definition Tab.

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

Click on the **Survey by** button and then select **pH.**



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
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	2.00000e-3

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

Summary

pH survey:
Acid - HCLIN
Base - NAOHIN
Range 0.0 to 14.0
Step size 1.0
No. steps 14

No secondary survey selected
Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:

Figure 3-15 Survey Summary (Default Values)

The default acid titrant and the base titrant are already defined (HCl and NaOH.)

We are now ready to begin the calculations.

Step 8: Save, save, save!!!

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

We will recommend that you save the name of the file as **Chapter 03**. Of course, you may use any name you want. We also recommend that you create a working folder and save the file there. We will create a folder named **OLI Calcs.**

Select **File** and then **Save As** from the menu.

Step 9: Ok then, we're ready to continue

Click on the **Calculate** button.

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

A small calculation result window may appear. If it does, simply close it.

Step 10: Obtaining results

We can now obtain some graphical results.

Click on the **Plot** tab.

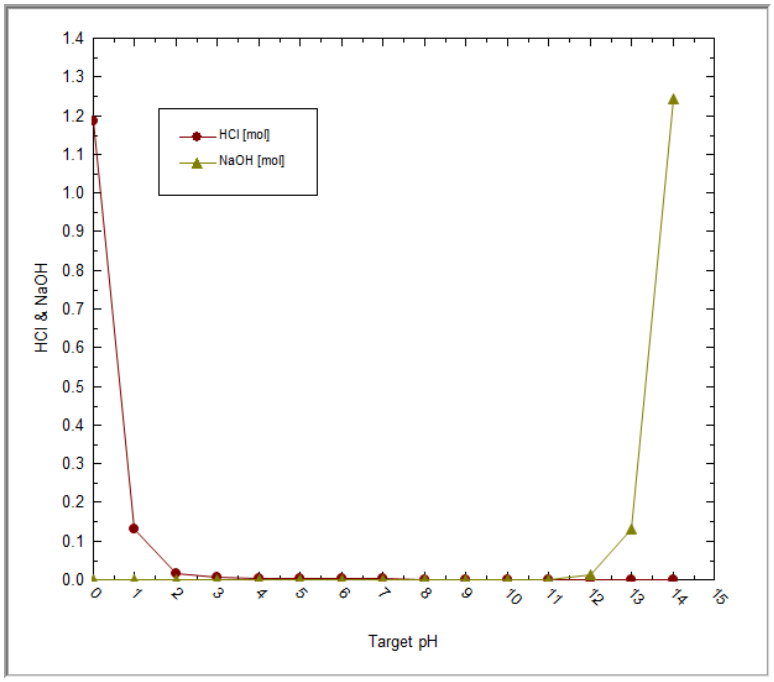


Figure 3-16 the default plot

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

Above the plot window locate and select the **Options** button

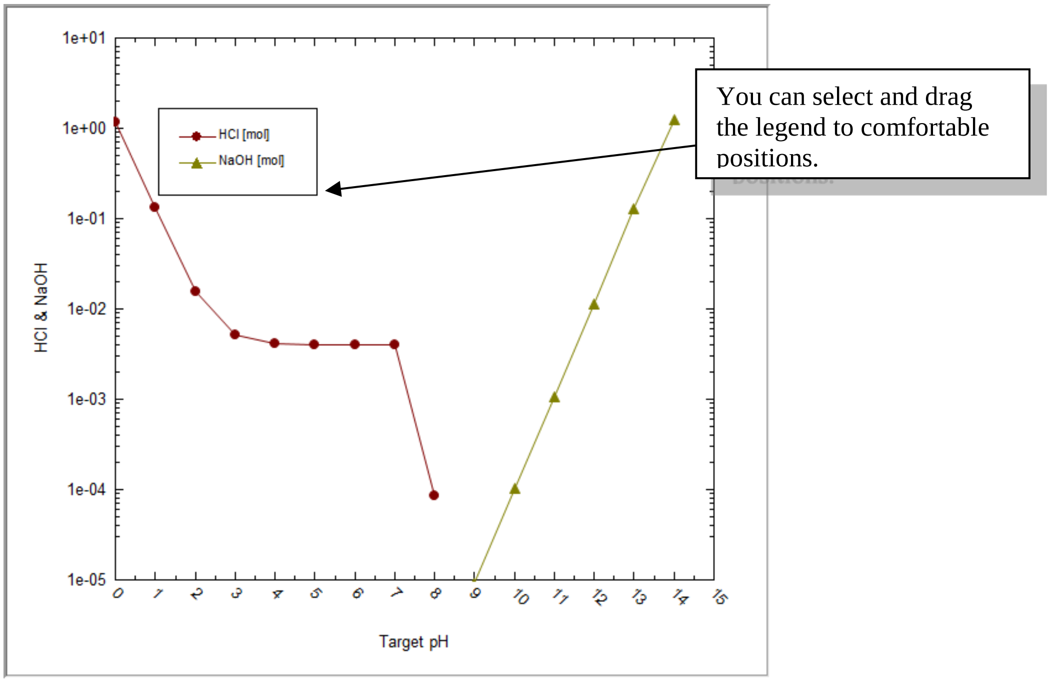
Figure 3-17 Plot Options

Select Y-Axis from the Category List.

Figure 3-18 Setting log for Y-Axis

Check the **Logarithmic Scale** Box and then **Click** on the **OK** box**.**

The display will now change.

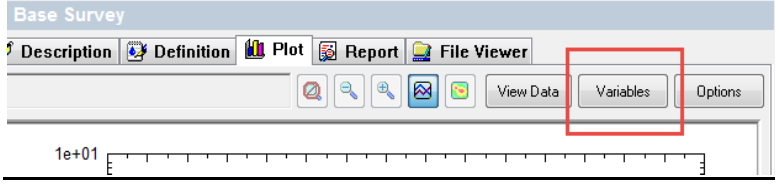


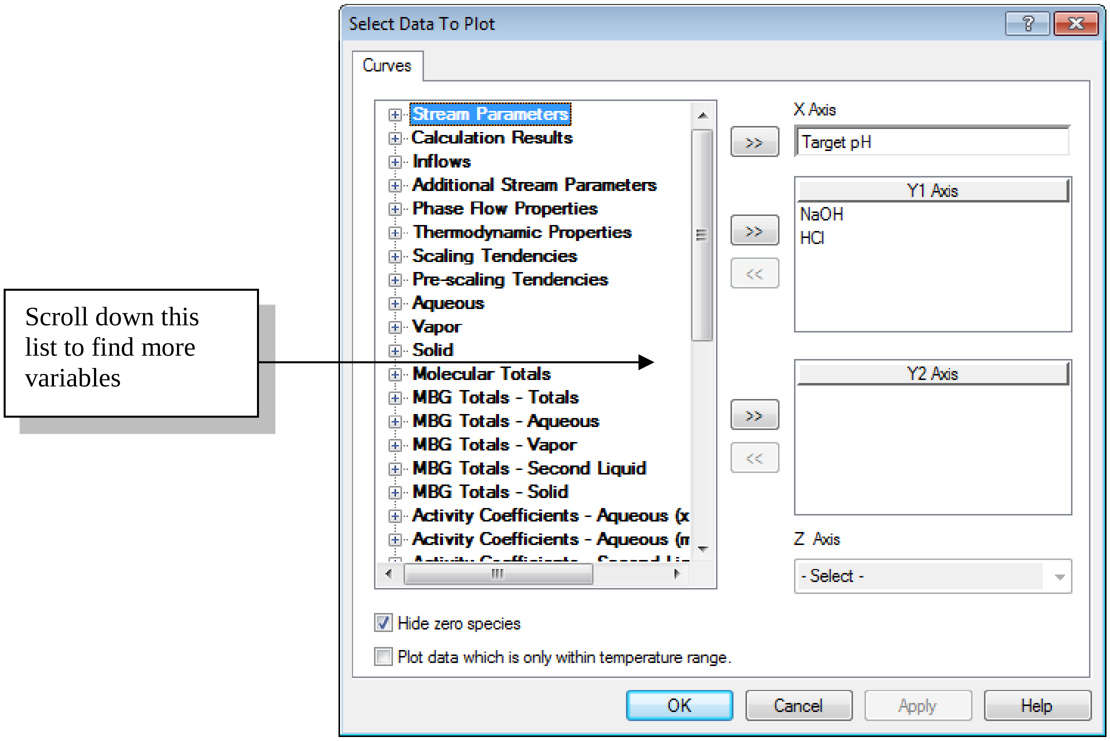
You can select and drag the legend to comfortable positions.

Figure 3-19 log axis plot

Although this plot tells us a great deal, we require more specific information about nickel species. Remember, there is a limit to the amount of soluble nickel that can be discharged. We need to clean this diagram up.

Click on the **Variables** button.





Scroll down this list to find more variables

X Axis: Target pH

Y1 Axis: NaOH, HCl

Y2 Axis:

Z Axis: - Select -

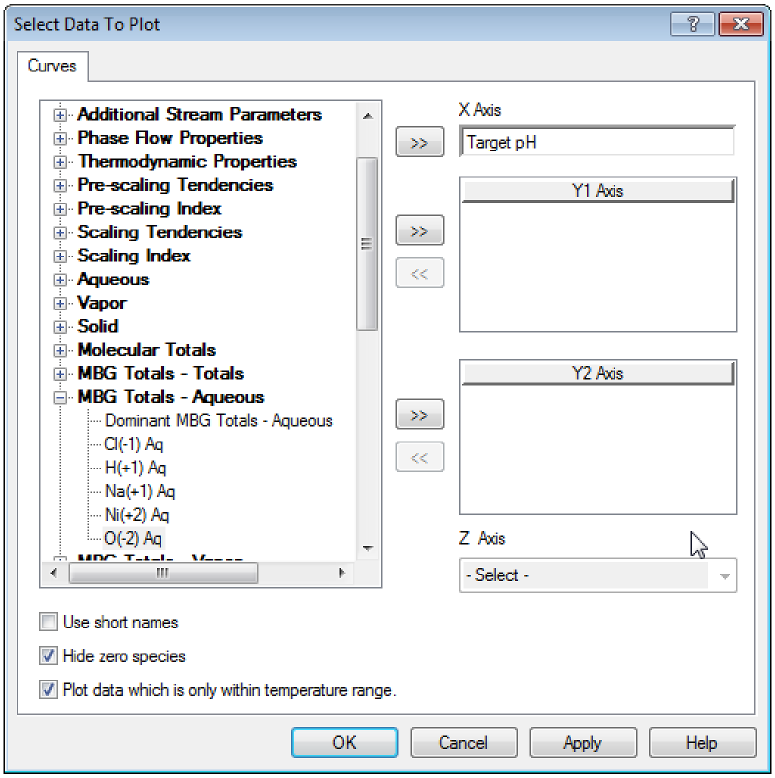
☑ Hide zero species

☐ Plot data which is only within temperature range.

Figure 3-20 The curves plot dialog

The **NaOH and HCl** variables in the **Y-Axis** box should be displayed. Select them and then ***Click*** on the left **double-arrow (<<)** button which will remove it from the plot.

Scroll down the left-hand window to find **MBG Totals - Aqueous** and expand the list by clicking the small “+” icon.



X Axis: Target pH

Y1 Axis:

Y2 Axis:

Z Axis: - Select -

☐ Use short names

☑ Hide zero species

☑ Plot data which is only within temperature range.

Figure 3-21 Selecting more variables

MGB is an abbreviation for Material Balance Groups

The grid updates to show the material balance totals available to display. In this case we desire the Nickel (+2) species. The variable displayed will be the sum of all nickel containing species in the aqueous phase.

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

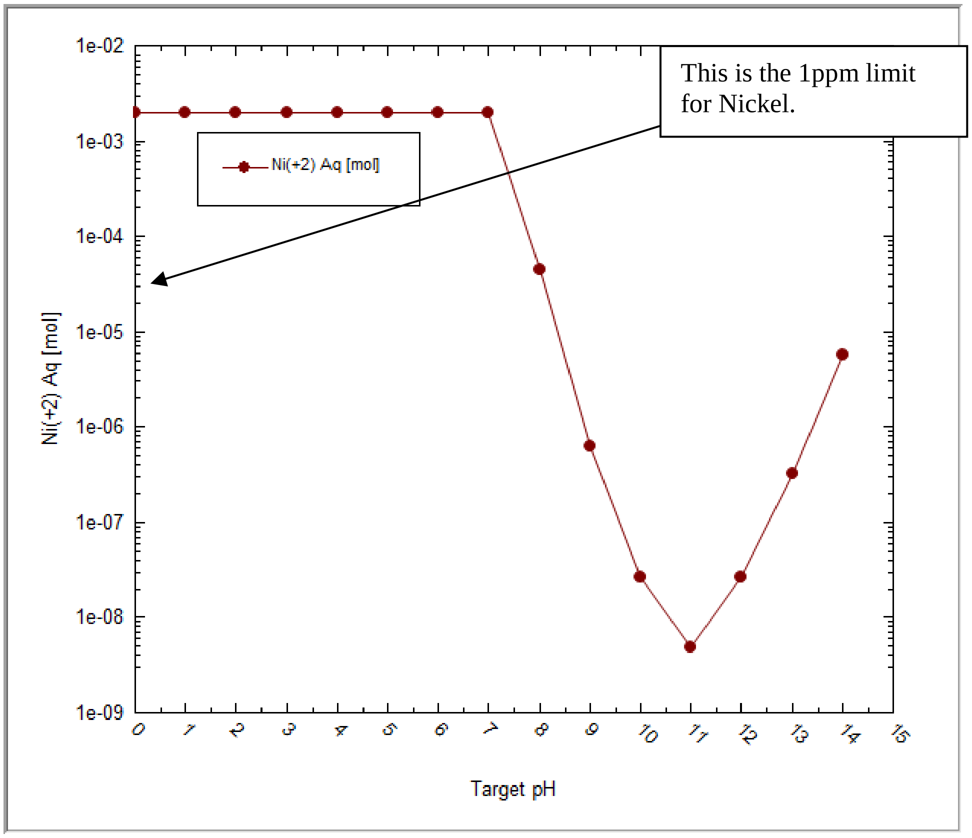


Figure 3-22 The results of the pH survey.

The material balance group variable is a sum of all the species for that material in the phase requested. For example, in this case all the NI(+2) –Aq variable is a sum of all nickel containing ions in solution. Any solids are excluded.

You can see that a minimum in aqueous solubility seems to occur in the pH=11 range. This is the result of nickel solids forming and leaving the aqueous phase.

The limit of 1 ppm for Ni^{+2} is approximately 2 x 10^{-5} moles. At a pH=10, we are several orders of magnitude below this limit.

What else is important in this solution?

Click on the Variables button and add the following species to the plot (you may need to scroll up or down to find all the species).

Aqueous:

Ni(OH)2

NiOH+1

Ni+2

Ni(OH)3-1

Solids:

Ni(OH)2

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

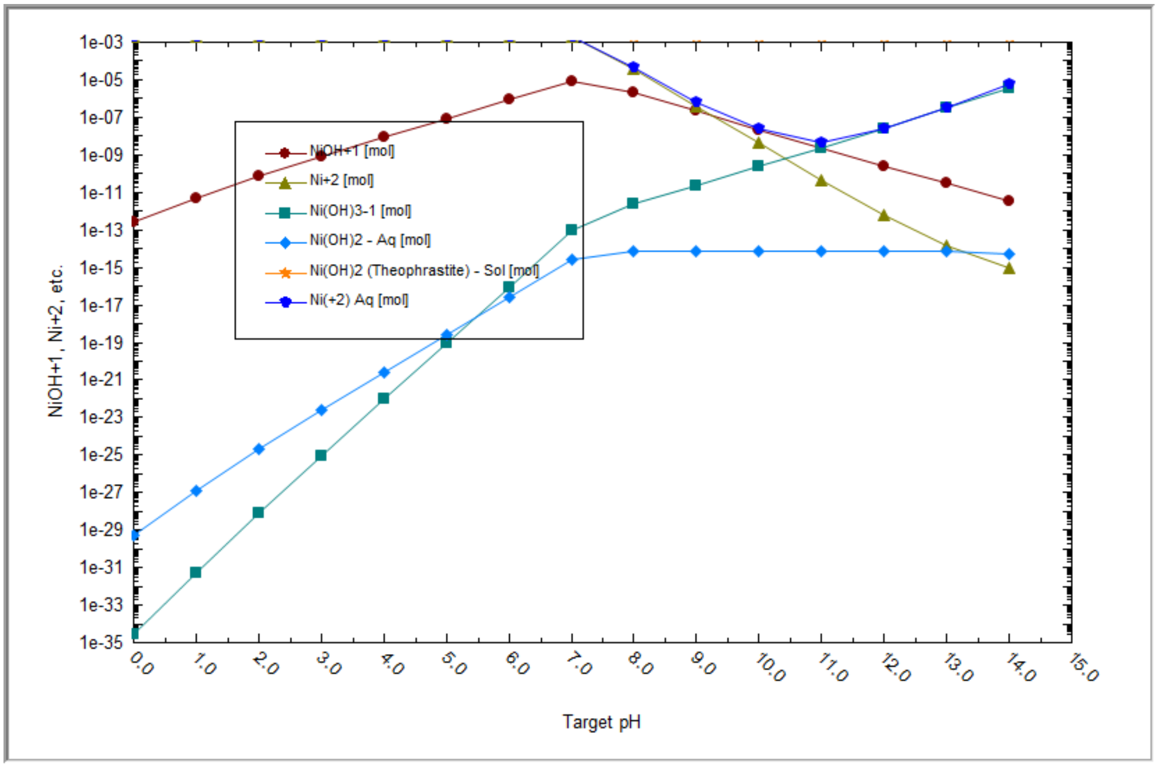
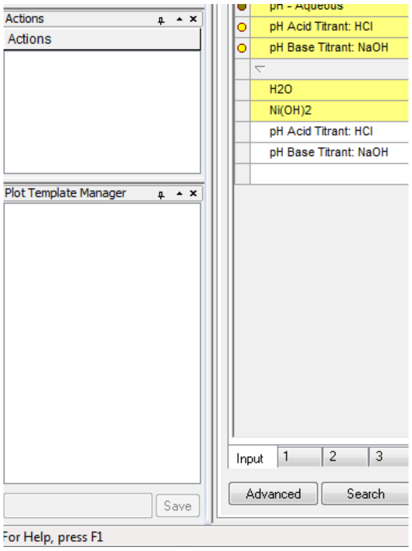


Figure 3-23 Important nickel species

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

Plot Template Manager:



This newly added tool in OLI software is designed to help users save their most frequent plots. For example, you may not want to always look at the dominant Aqueous plot vs. pH in all cases.

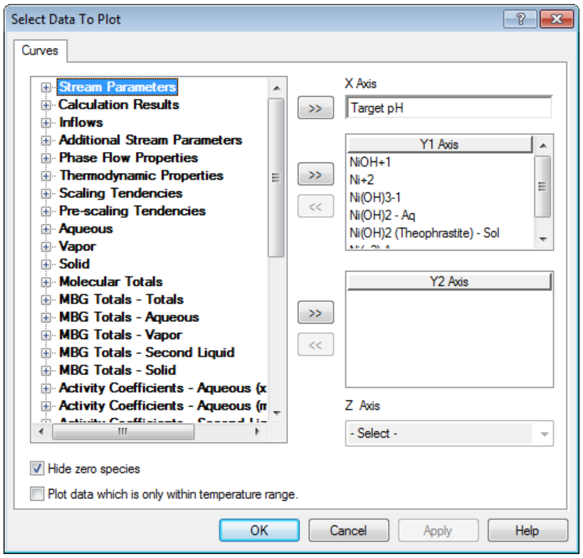
For example, if you are always using nickel chemistry you can have a custom plot available. We will create a plot where the MBG Aqueous Totals for Ni(+2) are always displayed. To create this template, please follow the steps:

1. Create the case with desired chemistry and inflows

2. Add a survey depending on type of calculation

3. Customize the survey to your everyday parameters you are interested in, like mass/solids/MBG totals etc

Basically, it could be any combination form the list below:



X Axis: Target pH

Y1 Axis: NiOH+1, Ni+2, Ni(OH)3-1, Ni(OH)2 - Aq, Ni(OH)2 (Theophrastite) - Sol

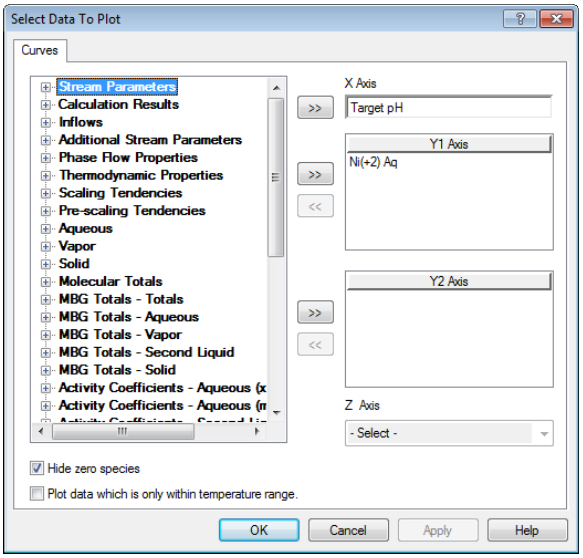
Z Axis: - Select -

☑ Hide zero species

☐ Plot data which is only within temperature range.

Figure 3-24 Plot data from the previous example.

Remove all the variables from the Y1 Axis box except for **Ni(+2) Aq**



X Axis: Target pH

Y1 Axis: Ni(+2) Aq

Z Axis: - Select -

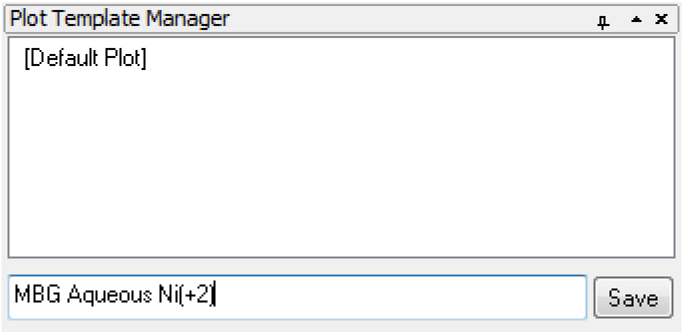
☑ Hide zero species

☐ Plot data which is only within temperature range.

Figure 3-25 Selected variables

Click OK.

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



MBG Aqueous Ni(+2)

Figure 3-26 Saving a new template for plotting

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

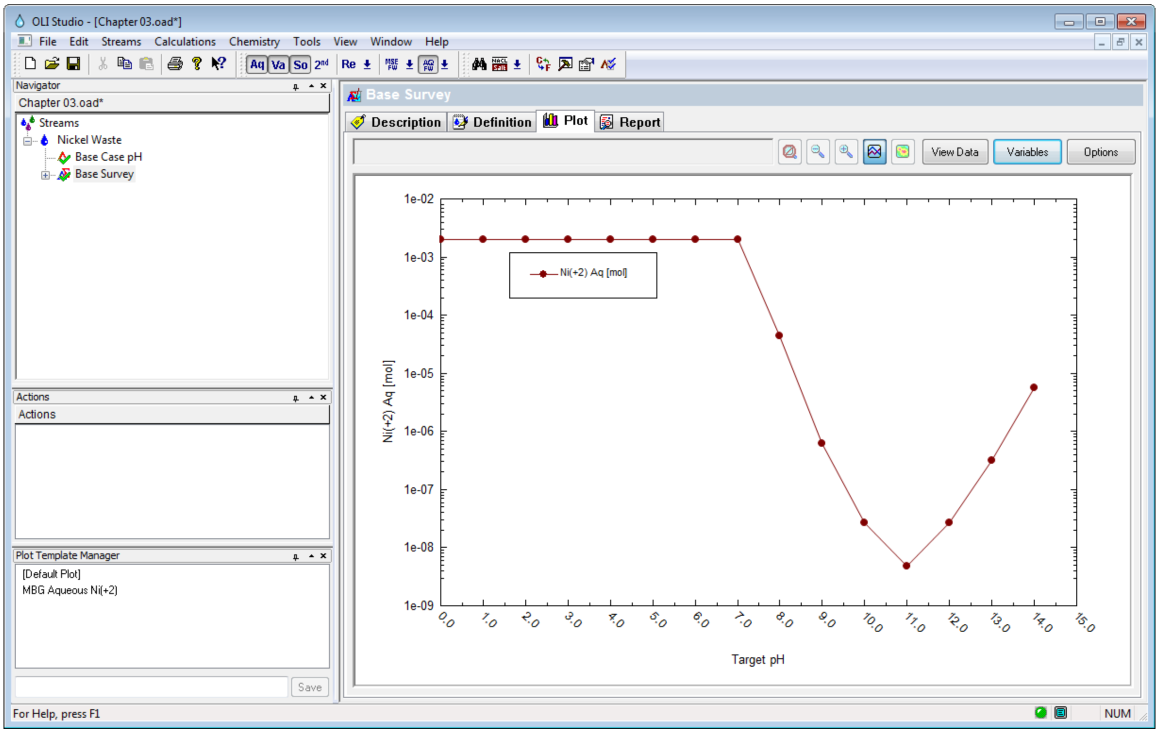


Figure 3-27 Newly added plot template in lower left hand corner

As you can see, if the **MBG Aqueous Ni(+2** lot is selected (there is a cursor hovering above it) and the graph looks like above. If you click on the option instead of hovering over, this look of the plot gets saved for those conditions, and you will see this template every time you open the case.

Scenario 2: Now, What about the Real Waste?

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

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

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

Step 1: Add a new Single Point calculation

***Click on the* Nickel Waste *stream in the* Tree view.**

This will display the **Actions** pane in the bottom left corner of the OLI Studio window.

Click on the **Add Single Point** icon in the **Actions** pane.

Change the ***Name*** and ***description:***

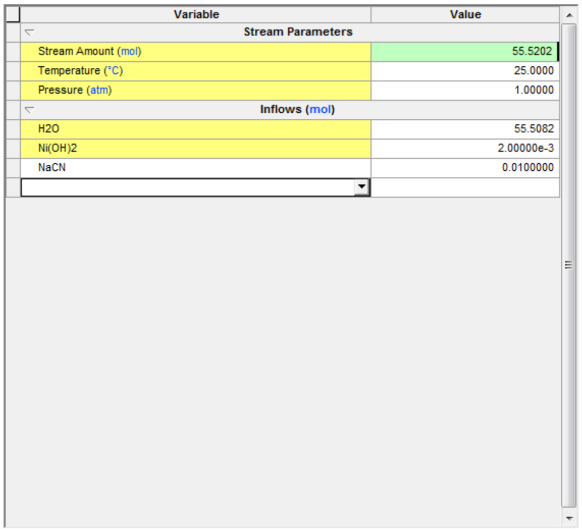
Name: ***Waste with CN.***

Description: ***Nickel waste with cyanide added.***

Click on the **Definition** tab.

Add **NaCN** to the grid and a value of 0.01 moles.

The grid should now look like this:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5202
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3
NaCN	0.0100000

Figure 3-28 Adding NaCN

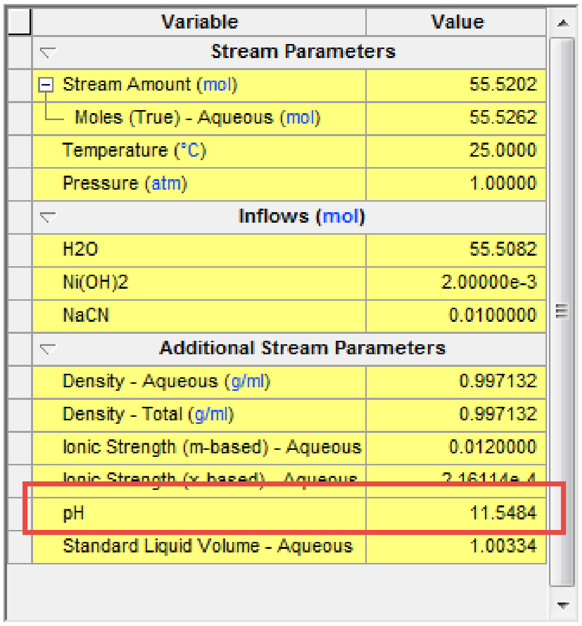
When the* Calculate Button *light turns green, Click on the button.

Step 2: Getting results of the Single Point Calculation.

Next locate the **"Output"**mini-tab at the bottom of the definition:

As before, ***Right-Click*** anywhere on the grid and select **Sections** and then **Additional Stream Parameters** from the fly out (see Figure 3-12 on page 44).

The resultant pH should be approximately 11.6.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5202
Moles (True) - Aqueous (mol)	55.5262
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3
NaCN	0.0100000
Additional Stream Parameters	
Density - Aqueous (g/ml)	0.997132
Density - Total (g/ml)	0.997132
Ionic Strength (m-based) - Aqueous	0.0120000
Ionic Strength (x-based) - Aqueous	2.16114e-4
pH	11.5484
Standard Liquid Volume - Aqueous	1.00334

Figure 3-29The pH = 11.5484 which is close to 11.6

Step 3: Setup and run the pH survey.

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

This will display the **Actions** pane in the bottom left corner of the OLI Studio window.

Click on the **Add Survey** icon in the **Actions** pane.

Click on the **Description Tab.**

Enter a New name: ***Waste Survey with CN.***

Enter a Description: ***pH survey with both Nickel and CN.***

Click on the **Definition Tab**

Add ***NaCN*** to the grid with a value of ***0.01*** moles

Click on the **Survey By** button and select pH.

(HCl and NaOH are the default titrants and are automatically added)

Click on the **Calculate** button.

Step 4: Reviewing results.

Let's start by using the **Plot Template Manager.** Select **MBG Aqueous Ni(+2** that you created previously.

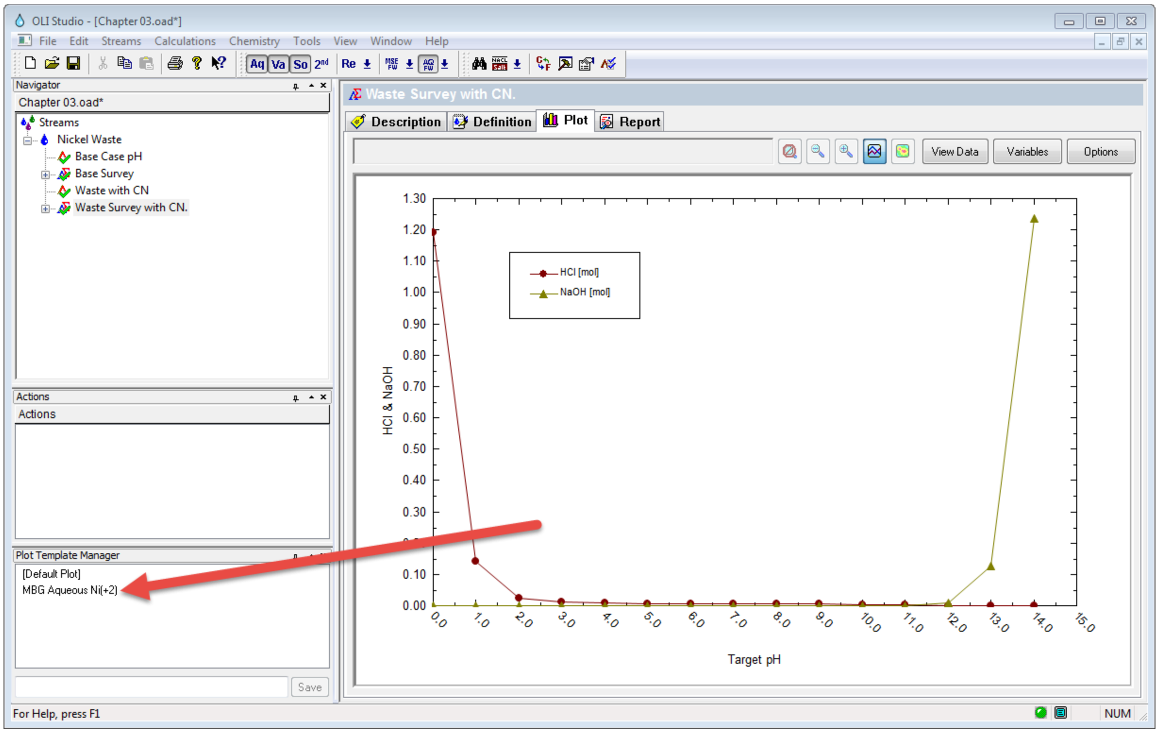


Figure 3-30Select Plot Template

This will display the MBG Totals – Aqueous plot:

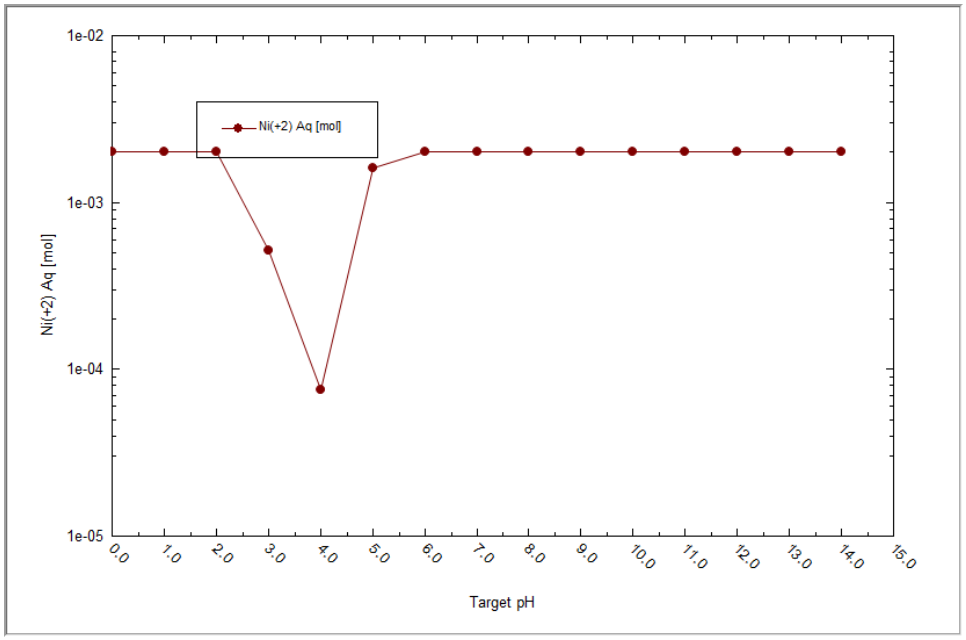


Figure 3-31 The result of the plot template

We can now modify this to display more variables.

Review the steps in **Scenario 1: Step 10** on page 3-47. We wish to plot the following variables in addition to the value already selected from the plot template:

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

2. Aqueous Species: Ni+2
3. Aqueous Species: NiOH+1
4. Aqueous Species: Ni(OH)3-1
5. Aqueous Species Ni(OH)2
6. Solid Species: NiNi(CN)4-Solid

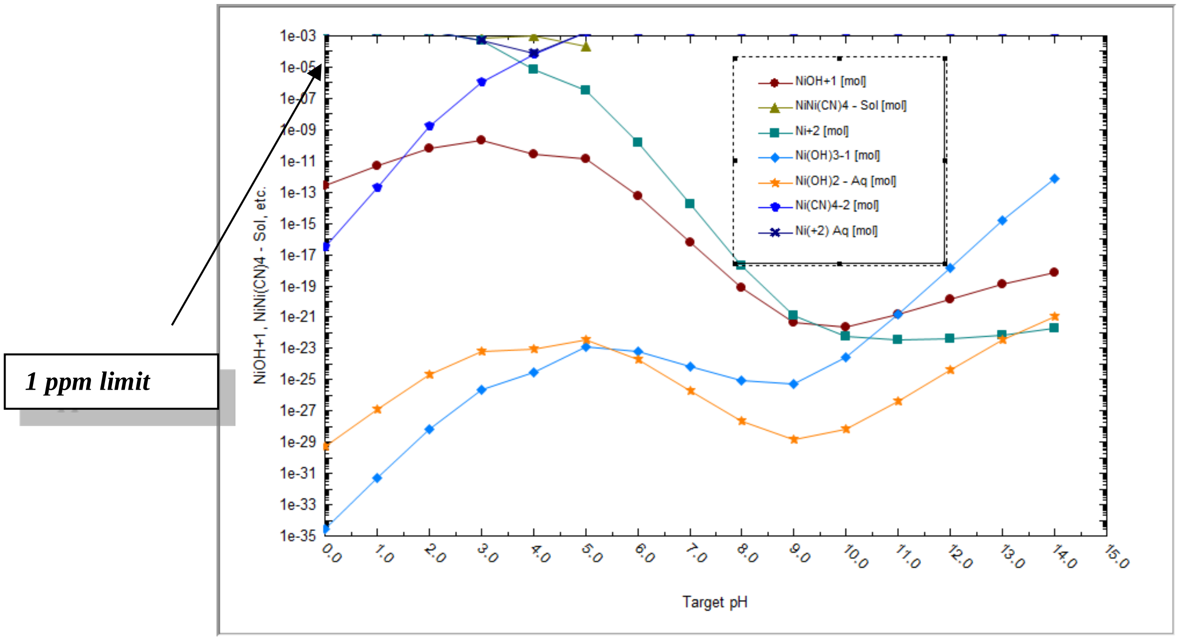


Figure 3-32 Nickel Waste Stream with NaCN added

The results have changed very dramatically. The new optimum pH for Ni removal is around 4.0, rather than 10.0. The lowest total Ni remaining in solution is now on the order of 10^{-4} which is actually well over 1 ppm.

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

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

Scenario 3: Is All Really Lost?

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

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

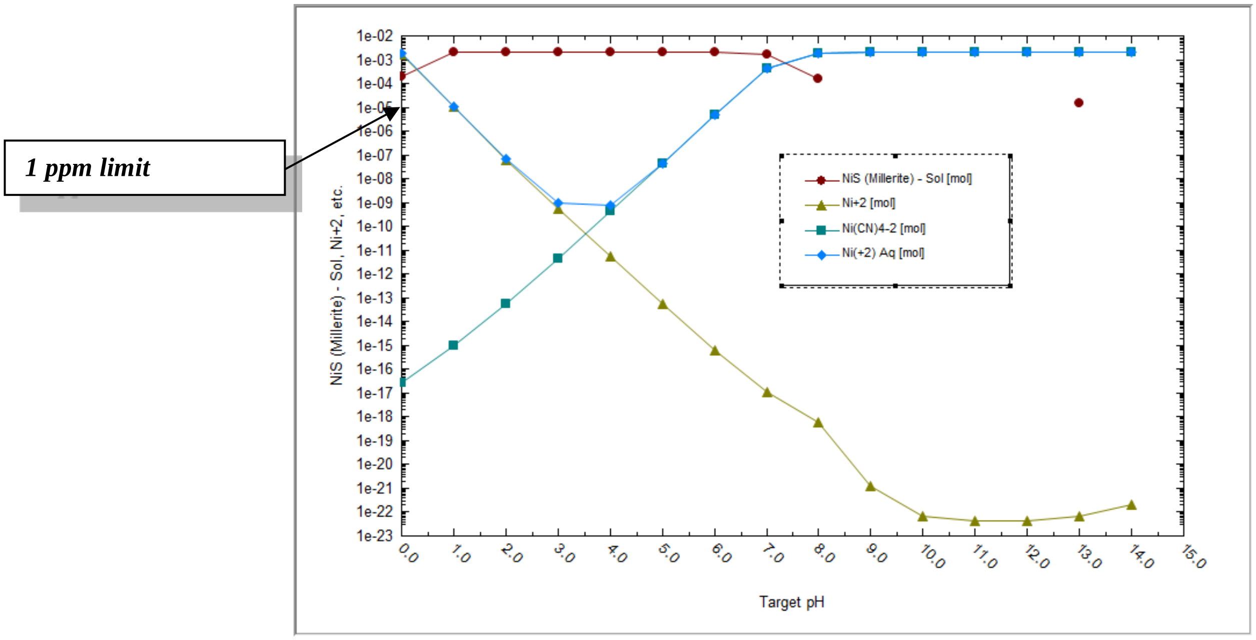
Add ***0.01*** moles of ***NaCN***

Add ***0.01*** moles of ***H2S***

As we did in the previous scenario, use the plot template manager to start off with the MBG Totals – Aqueous (Ni+2) and then the following variables when the calculations are complete**:**

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

2. Aqueous Species: Ni+2
3. Solid Species: NiS-Solid



1 ppm limit

Figure 3-33 Waste Stream pH with both NaCN and H2S added

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

Final Thoughts...

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

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

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

Save, Save and then Save again

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

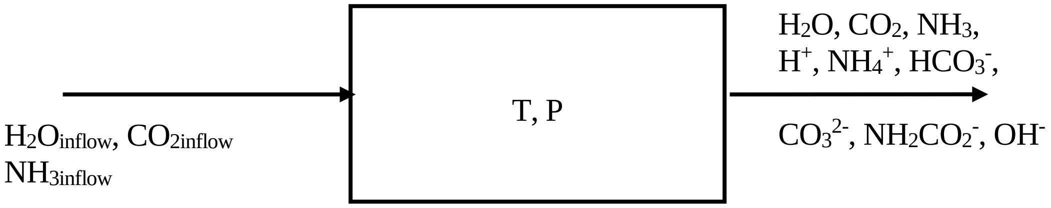
Click here for a completed OLI Analyzer file for this tour: Chapter 03 Tour

4. The Mathematical Model

Overview

The user should become familiar with the components of the simulator. In addition, the user should have a basic understanding of how the mathematical model is constructed.

Specific Problem



For the practical purposes of this section, we will take an actual problem and work it through. The problem is described as:

Given:

Temperature and pressure, represented by T and P respectively, water, carbon dioxide and ammonia, the relative amounts of which are represented by H2OIN, CO2IN, and NH3IN respectively.

Calculate:

The nine unknowns:

The amount of water (*H2O*)
The concentration of hydrogen ion (mH^+)[7]
The concentration of hydroxyl ion (mOH^-)
The concentration of molecular carbon dioxide (*mCO2*)
The concentration of molecular ammonia (*mNH3*)
The concentration of bicarbonate ion ($mHCO3^-$)
The concentration of carbonate ion ($mCO2^{-2}$)
The concentration of ammonium ion ($mNH4^+$)
The concentration of carbamate ion ($mNH2CO2^-$)

Recipe for Writing the Model

Step 1a: Write an equilibrium mass action for all of the independent aqueous intraphase equilibrium reactions.

---

[7] The symbol ***m*** is used to denote Molality (moles of solute / Kg H_2O)

$$\begin{array}{lcl} H_2O_{(aq)} & = & H^+ + OH^- \\ CO_{2(aq)} + H_2O_{(aq)} & = & H^+ + HCO_3^- \\ HCO_3^- & = & H^+ + CO_3^{-2} \\ NH_{3(aq)} + H_2O_{(aq)} & = & NH_4^+ + OH^- \\ NH_2CO_2^- + H_2O_{(aq)} & = & NH_{3(aq)} + HCO_3^- \end{array}$$

Step 1b: Write an equilibrium K-equation for all of the independent aqueous intraphase equilibrium reactions.

For the example posed, these equations are:

$$K_{H2O} = (\gamma_{H+} m_{H+})(\gamma_{OH-} m_{OH-})/a^*_{H2O}$$

$$K_{CO2(AQ)} = (\gamma_{H+} m_{H+})(\gamma_{HCO3-} m_{HCO3-})/((\gamma_{CO2} m_{co2}) a_{H2O})$$

$$K_{HCO3-} = (\gamma_{H+} m_{H+})(\gamma_{CO3-2} m_{CO3-2})/ (\gamma_{HCO3-} m_{HCO3-})$$

$$K_{NH3aq} = (\gamma_{NH4+} m_{NH4+})(\gamma_{OH-} m_{OH-})/((\gamma_{NH3aq} m_{NH3}) a_{H2O})$$

$$K_{NH2CO2-} = (\gamma_{NH3aq} m_{NH3})(\gamma_{HCO3-} m_{HCO3-})/((\gamma_{NH2CO2-} m_{NH2CO2-}) a_{H2O})$$

Note: This gives us the first 5 equations of the required set of 9 equations.

Step 2: Write an electroneutrality equation.

$$mH^+ + mNH_4^+ = mHCO_3^- + mNH_2CO_2^- + 2mCO_3^{-2} + mOH^-$$

We multiply by a factor of 2 because of the divalent charge on the carbonate ion

This gives us the sixth equation.

---

[*] In aqueous systems, it is more convenient to use the activity of water rather than the concentration. The concentration of water on the molal concentration scale is always 55.508 moles/Kg H2O.

Step 3: Write a sufficient number of material balances to complete the model.

Writing material balances in aqueous systems can be a bit tricky. Remembering the following rules can be quite helpful:

You can only write one of the following three balances:

Hydrogen

Oxygen

Overall.

For simplicity we will choose the hydrogen balance.

A separate material balance should be written for each remaining element. In this example, we will write material balances for carbon and nitrogen. Some elements may be present in the chemistry model in several oxidation states.

Such an element is sulfur. In our sour water system presented in an earlier chapter, the sulfur was present in the S(-2) oxidation state, also known as sulfide. Sulfur may also be present as the elemental sulfur – S(0), Sulfite – S(+4), and Sulfate S(+6).

By default, the program will not consider changes in oxidation state thus in the case of sulfur, a separate material balance will be written for each oxidation state. The only time that separate balances would not be written would be in a case where there was REDOX. Such cases are beyond the scope of this present treatment.

$H^{(+1)}$ Balance:

$$2H_2O_{IN} + 3NH_{3IN} = 2H_2O + W(mH^+ + mOH^- + 3mNH_3 + 4mNH_4^+ + mHCO_3^- + 2mNH_2CO_2^-)$$

For each balance, the amount of each species is multiplied by the number of atoms. In this case, for Hydrogen, we multiply by 4 for NH_4^+

$N^{(-3)}$ Balance:

$$NH_{3IN} = W(mNH_3 + mNH_4^+ + mNH_2CO_2^-)$$

$C^{(+4)}$ Balance:

$$CO_{2IN} = W(mCO_2 + mHCO_3^- + mNH_2CO_3^- + mCO_3^{2-})$$

W is a constant, approximately equal to $H_2O/55.508$.

We now have nine equations and nine unknowns.

The Components of the Simulator

For each OLI program, there are several components which we need to discuss.

The Database

The following databases are supplied with the software.[8]

These databases are:

Table 2 OLI Supplied Databanks

AQ Databank Name	MSE Databank Name	Description
Alloys	<none>	This contains special solids that are like alloys. Such an example is CuNi alloys. This is an AQ thermodynamic framework only databank. There is no corresponding MSE databank
Ceramics	<none>	This contains special solids that are like ceramics. This was to support work done for the ceramics lab at the Rutgers University. This is an AQ thermodynamic framework only databank. There is no corresponding MSE databank
Corrosion	MSE Corrosion	This contains special elements to generate Pourbaix diagrams. Some of the species have had their Gibb's Free Energy of Formation values adjusted to match traditional Pourbaix Diagrams. It is not recommended for use with OLI Flowsheet
Exchange	<none>	This contains ion-exchanging resins. This is an AQ thermodynamic framework only databank. There is no corresponding MSE databank
Geochemical	MSE Geochemical	This contains minerals that are primarily found in geothermal applications. These minerals typically do not reform under traditional chemical process conditions.
Low Temperature	<none>	This databank contains minerals that form below 0 °C (273.15 K). This is an AQ thermodynamic framework only databank. There is no corresponding MSE databank
Surface Complexation Capacitance Model	<none>	This databank contains surface species following Dzombak's model for capacitance. This is an AQ thermodynamic framework only databank. There is no corresponding MSE databank
Surface Complexation Double Layer Model	XSC Databank	This databank contains surface species following Dzombak's model for Double-layers capacitance.
Surface Complexation Non Electrostatic Model	<none>	This databank contains surface species following Dzombak's model for non-electrostatic interactions. This is an AQ thermodynamic framework only databank. There is no corresponding MSE databank
Surface Complexation Triple Layer Model	<none>	This databank contains surface species following Dzombak's model for Triple-layers. This is an AQ thermodynamic framework only databank. There is no corresponding MSE databank
<none>	MSE Urea	This databank contains surface species that support high temperature formation of urea. It is not recommended unless urea is known to form from NH_3 and CO_2. Generally such formations are kinetically limited. This is an MSE thermodynamic framework only databank. There is no corresponding AQ databank

The database(s) contain the thermochemical data required to calculate a fully speciated model. The databases are user-selectable which means chemical models can be tailored to specific situations.

---

[8] This is only a partial list of databanks, less commonly used databanks are available but will not be discussed here.

The Chemistry Model

The Chemistry Model contains the equilibria corresponding to the user specified chemistry. This model is automatically created for you by OLI Studio. Normally you will not be required to alter the chemistry.

The thermodynamic data stored in the database is retrieved via the ***Generator*** for all the specified chemistry and stored in the chemistry model.

The chemistry model does not contain composition data, temperature, pressure or flowrates. It is a general model which can be used in many calculations over a broad range of temperature, pressure and composition.

The Generator

The Generator is a combination of programs which sort and retrieve data from the database based on the user-specified chemistry and place that data into a format which allows subsequent simulation.

The generator creates the framework which the ***Analyzers*** use to simulate the conditions specified by the user.

The generator is used every time new chemistry is specified or when the chemistry is modified. Under normal operating conditions, the user will not directly interact with the generator.

The OLI Engine

This is the heart of the program. All the user-specified chemistries and the resultant equilibrium stream simulations are provided for by the OLI Engine.

All the OLI programs use the OLI/Engine in evaluating the specified conditions.

Phase Selection

The basic chemical model generally considers three types of phases:

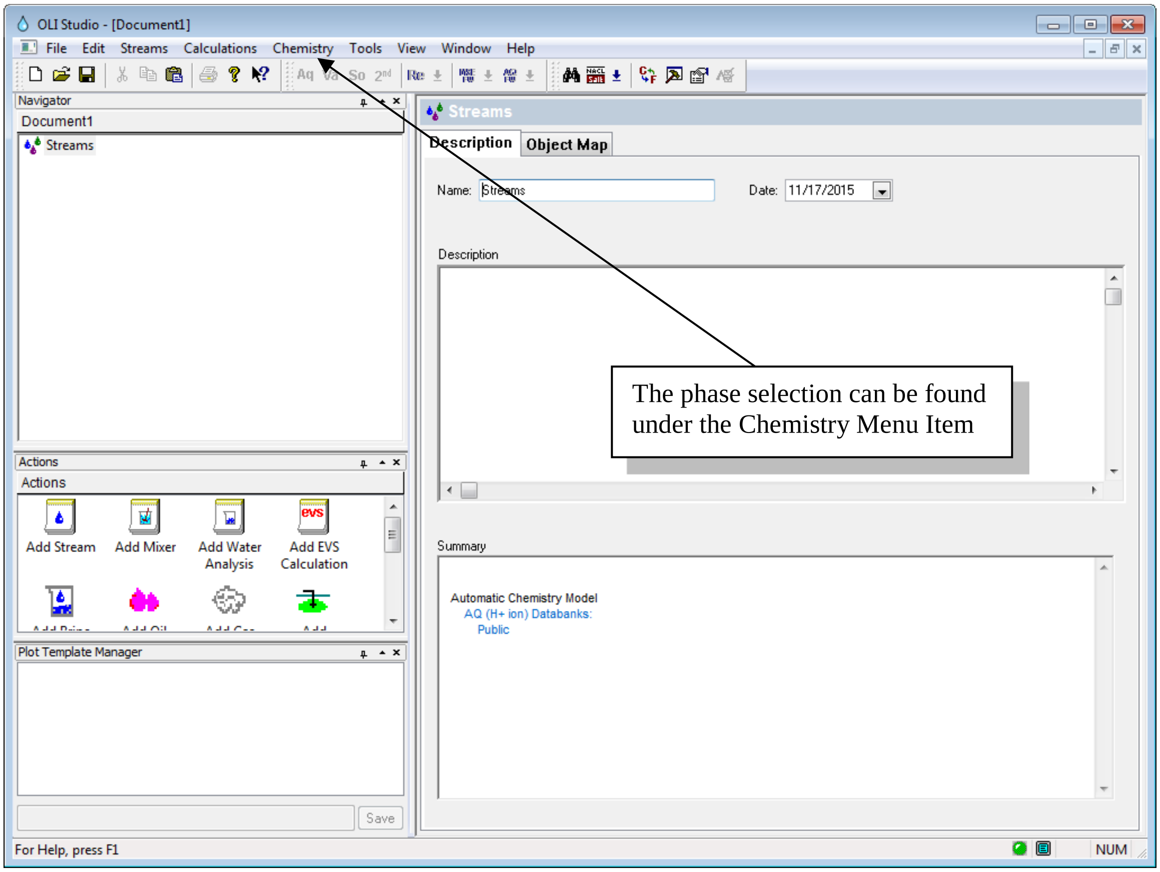
i. *Vapor*
ii. *Aqueous*
iii. *Solid*

The user may specify to exclude one of these default[9] phases during the creation of the chemistry model. In addition, a second liquid phase, normally an organic phase, may also be selected.

The phase selection can be found in the Chemistry menu item of OLI Studio.

---

[9] Default is defined as the set of choices made by the program in the absence of any user input.



Name: Streams

Date: 11/17/2015

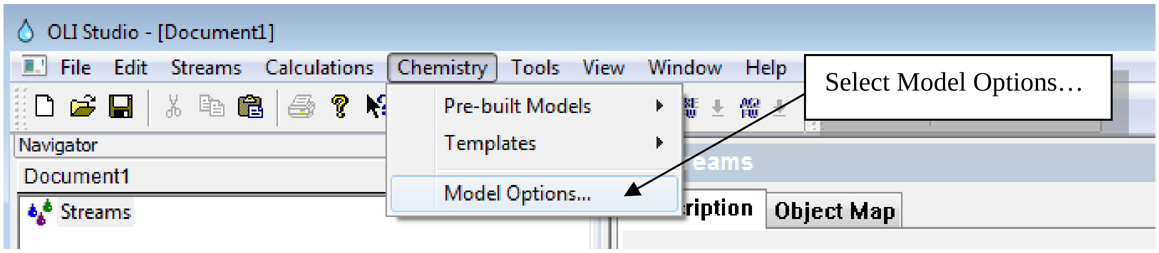
Description

Summary

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

The phase selection can be found under the Chemistry Menu Item

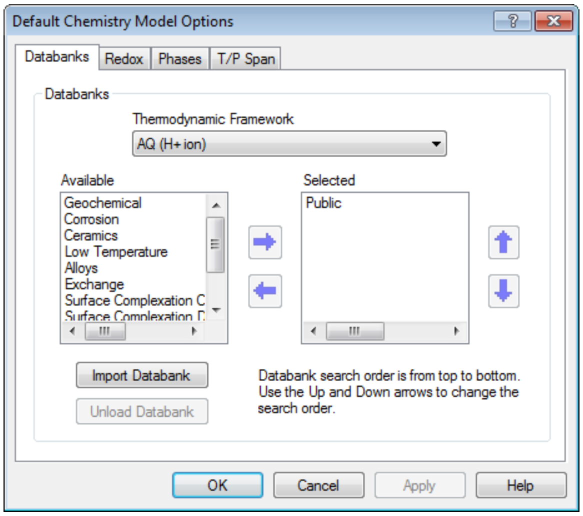
Figure 4-1 The Welcome window for OLI Studio



Select Model Options…

Figure 4-2 Chemistry Menu Items

.


Default Chemistry Model Options

Databanks

Thermodynamic Framework: AQ (H+ ion)

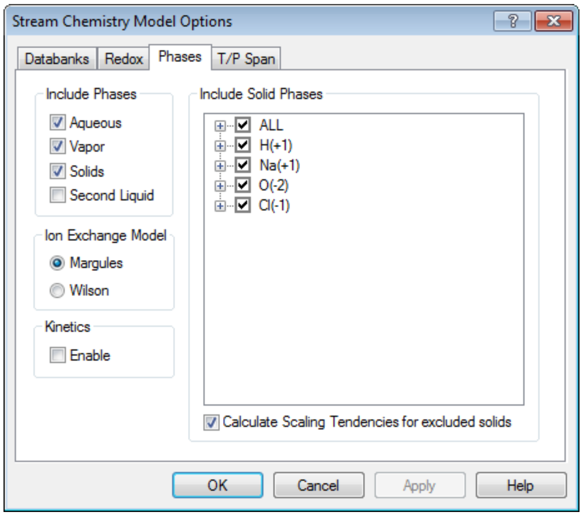
Available:
- Geochemical
- Corrosion
- Ceramics
- Low Temperature
- Alloys
- Exchange
- Surface Complexation C
- Surface Complexation D

Selected:
- Public

Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

Figure 4-3 Model Options

Click on the ***Phases*** tab


Stream Chemistry Model Options

Include Phases
- ☑ Aqueous
- ☑ Vapor
- ☑ Solids
- ☐ Second Liquid

Ion Exchange Model
- ● Margules
- ○ Wilson

Kinetics
- ☐ Enable

Include Solid Phases
- ☑ ALL
- ☑ H(+1)
- ☑ Na(+1)
- ☑ O(-2)
- ☑ Cl(-1)

☑ Calculate Scaling Tendencies for excluded solids

This is the phase selection dialog. In addition, an organic (non-aqueous liquid) phase can be selected.

Figure 4-4 Selecting phases

In this figure, the Aqueous, vapor and the solid phases are selected. For the electrolyte model, the aqueous phase is always assumed to exist if the chosen thermodynamic framework is Aqueous. OLI currently offers two frameworks; the Aqueous thermodynamic framework and the Mixed-Solvent-Electrolyte (MSE) thermodynamic framework. The check box is used to indicate if a phase is included or not.

The organic liquid phase is a second phase in which water is not the dominant species. Some water must be present in any organic phase.

When the organic liquid phase is selected it may be possible to “Dry Up” the aqueous phase.

It is also possible to select individual solid phases. Your simulation may depend on a solid being excluded since it will not form in the time frame of your calculation. For example, the mineral Dolomite ($CaMg(CO_3)_2$) thermodynamically stable if calcium, magnesium and carbonates are present in solution yet the solid does not form except under severe conditions of temperature and pressure and with long (geologic) time frames.

5. Solids Precipitation

Overview

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

It is sometimes desirable to determine the solubility of the less stable solid independently of the more stable solid. In this tour, we will examine the solubility calcium carbonate as calcite in a solution containing magnesium and calcium chloride and carbon dioxide.

In certain instances, the formation of calcite is prohibited kinetically and the less stable form of aragonite will form. Such cases include coral reefs where aragonite is preferred to form via biological action.

In this tour, we will take a solution of 0.1 molal $CaCl_2$, 0.1 molal $MgCl_2$ and 0.01 molal CO_2 at 25 degrees centigrade and 1 atmosphere and determine the solubility of $CaCO_3$ solids.

The Tour

Objectives

In this tour, we wish to accomplish several objectives:

1. Learn how to perform a precipitation point calculation.
2. View and select an additional databank.
3. Modify the chemistry to include and exclude individual solid phases.
4. Units manager new look

Let’s begin

If you have not done so, please start OLI Studio. After a few moments, the main window will appear. If the Tip-of-the-Day box appears, please close it.

Double-click on the **Add Stream** icon.

At this point we are assuming that you are familiar with navigating through the software. We will only provide guidance for new items of interest.

Click on the **Description** Tab.

You may enter a new name for the stream and a description. We recommend ***CaCO3 Solubility*** as a name for the stream.

Select the **Definition** Tab.

The input conditions are:

Temperature	25	*°C*
Pressure	1	*Atmosphere*
Water	55.5082	*mol* (this is the default value)
$CaCl_2$	0.1	*mol*
$MgCl_2$	0.1	*mol*
CO_2	0.01	*mol*
$CaCO_3$	0.0	*mol*

The entry should look the same as in Figure 5-1

The linked image cannot be displayed. The file may have been moved, renamed, or deleted. Verify that the link points to the correct file and location.

Figure 5-1 Component Inflows

It is frequently difficult to use the display name for the components. For this tour we will change the way the names are displayed.

Select **Tools** from the Menu Bar.

Select **Names Manager** from the list.

The list of Tools is displayed in Figure 5-2

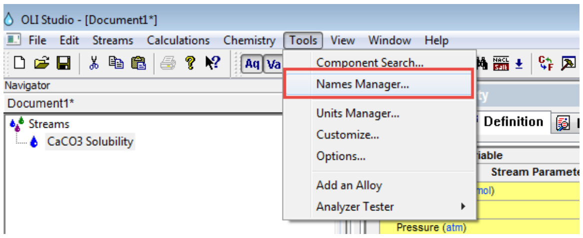
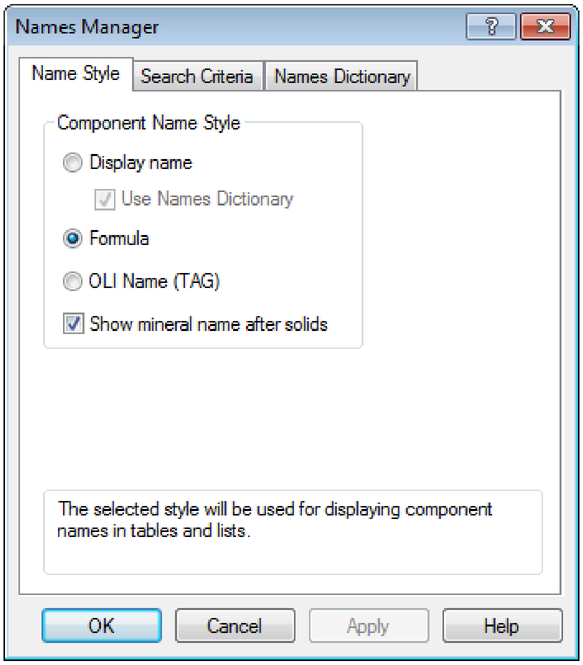


Figure 5-2 The Tools Menu

Selecting the **Names Manager** from the tools menu will display several options.



Component Name Style

○ Display name

☑ Use Names Dictionary

● Formula

○ OLI Name (TAG)

☑ Show mineral name after solids

The selected style will be used for displaying component names in tables and lists.

Figure 5-3 The Names Manager.

There are several items that can be changed. We will discuss each of them in turn.

Name Style Tab

The name of the component can be displayed in several ways.

Display name This is the name is that is commonly displayed when a species is entered. This is the default display. So the species CO2 is displayed as carbon dioxide.

Formula This is the chemical formula name. Species such as aluminum nitrate is displayed as Al(NO3)3.

OLI name (TAG) This is the traditional name for the species stored internally in the OLI software. Users who have used the older ESP software may be more comfortable with this display.

Show mineral names after solids (Check Box)

This check box will allow the stored mineral name (if available) to be displayed next to the formula name or OLI Tag name.

Search Criteria Tab

When a species is entered, the program may search in several ways to find the corresponding data. Such areas that may be searched are Display Name, Formula, OLI name, synonyms, IUPAC names, etc. It is recommended that the default options be left as is.

Names Dictionary

The user may wish to define a species with a name that does not exist in the software. For example, NaOH is frequently referred to as caustic. This can be selected if required.

For this tour, we will use the OLI name.

Click the **OLI name (TAG)** radio button. Select **OK** when done.

Your display should have changed to that of Figure 5-4

Figure 5-4 The Input in the Traditional OLI names

There is only a small difference in this view. The OLI tag name is in all capital letters.

Selecting the precipitation point calculation

We are now ready to begin the precipitation point calculation.

Click on the **Add Calculation** button and select **Single Point.**

If you so desire, you may enter descriptive information about this calculation. It is recommended that you do so since the default naming system will create a large number of calculations with very similar names (for example, single1, single2, single3, etc.)

Click on the **Description Tab** and enter a name. We recommend ***Calcite Solubility***.

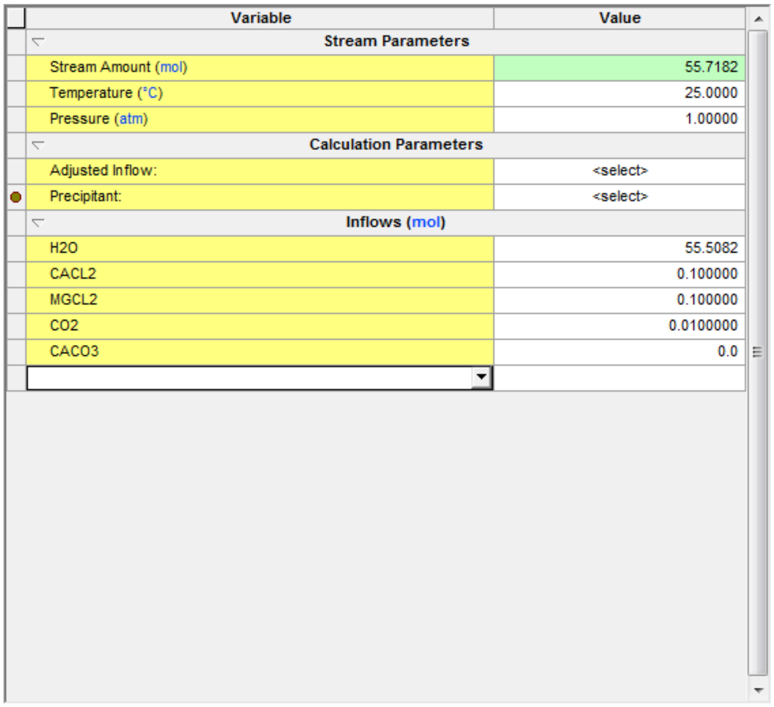
Click on the **Definition Tab**.

The default calculation is the **Isothermal** calculation. We need to change this option.

Click on the **Type of calculation b**utton.

Select **Precipitation Point**

The input grid now has two new items. We need to have these filled out properly prior to the start of the calculation.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.7182
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Adjusted Inflow:	<select>
Precipitant:	<select>
Inflows (mol)	
H2O	55.5082
CACL2	0.100000
MGCL2	0.100000
CO2	0.0100000
CACO3	0.0

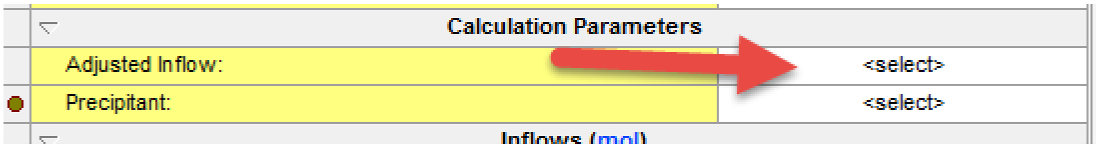
Figure 5-5 The input grid before specifications added.

The **Calc Parameters** section on the grid in Figure 5-5 shows that the solid that is to be precipitated (**Precipitant**) is unspecified and that the adjusted variable (**Adjusted Variable**) is also unspecified.

The precipitation point calculation uses the user selected solid as a target. The user either enters an amount of solid that they desire or uses the default value (indicated by a blank box). This value is $1.0\text{x}10^{-10}$ times the stream amount - a really small number.

The inflow amount of the yet unspecified species is then adjusted to match that target value. The adjusted amount is then the solubility of the species. Care should be taken in trying infeasible cases.

Click in the ***Adjusted Inflow:*** box.



Calculation Parameters

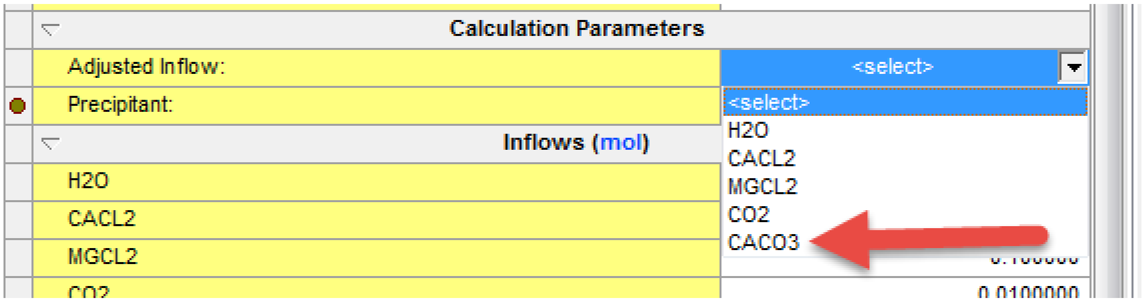
Adjusted Inflow: <select>

Precipitant: <select>

Inflows (mol)

Figure 5-6

select **CACO3**



Calculation Parameters

Adjusted Inflow: <select>

Precipitant:

Inflows (mol)

H2O

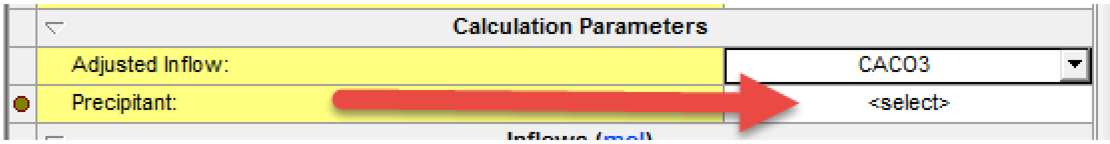
CACL2

MGCL2

CO2 0.0100000

Figure 5-7

Next ***Click*** in the ***Precipitant:*** box.



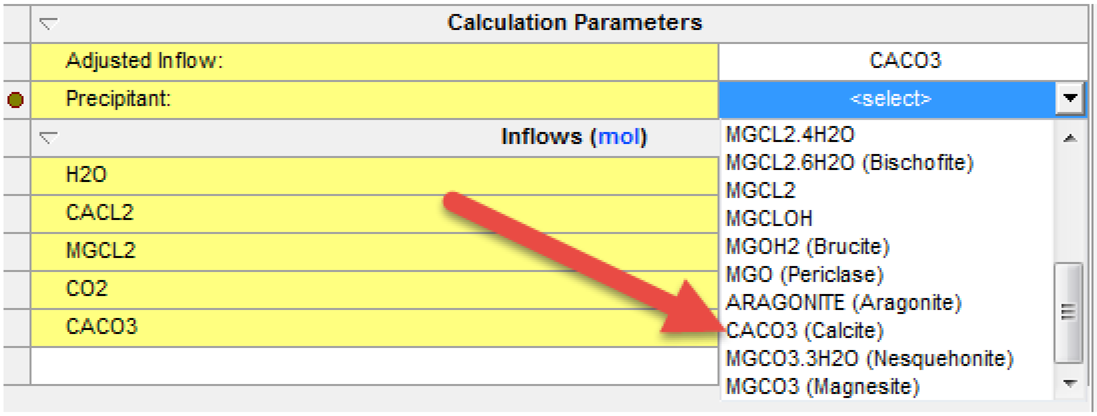
Calculation Parameters

Adjusted Inflow: CACO3

Precipitant: <select>

Figure 5-8

And then select **CACO3 (Calcite)** you may need to scroll down to find it!



Calculation Parameters

Adjusted Inflow: CACO3

Precipitant: <select>

Inflows (mol)

H2O

CACL2

MGCL2

CO2

CACO3

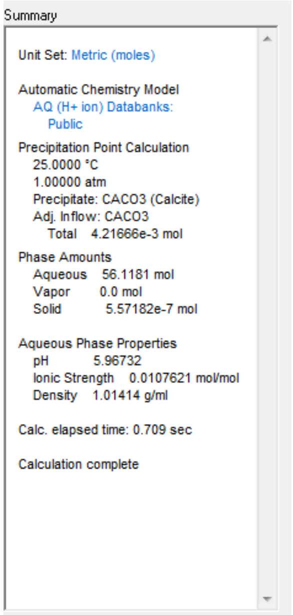
Figure 5-9

We are now ready to start the calculation.

Click on the **Calculate** button.

When the calculation is completed, the program will return to the same window.

In the **Summary Box** you will see a quick report.



```
Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
   AQ (H+ ion) Databanks:
      Public

Precipitation Point Calculation
   25.0000 °C
   1.00000 atm
   Precipitate: CACO3 (Calcite)
   Adj. Inflow: CACO3
      Total    4.21666e-3 mol

Phase Amounts
   Aqueous    56.1181 mol
   Vapor       0.0 mol
   Solid        5.57182e-7 mol

Aqueous Phase Properties
   pH          5.96732
   Ionic Strength    0.0107621 mol/mol
   Density    1.01414 g/ml

Calc. elapsed time: 0.709 sec

Calculation complete
```

Figure 5-10 Summary of Calcite Solubility

In this case, approximately 0.0042 moles of $CaCO_3$ was added to this solution (in 55.5082 mol of H_2O, which makes this a molal concentration) to precipitate out a very small amount of solid.

Save early and save often…

Now would be a good time to save our work. Any name will suffice. We recommend ***Chapter 5 Tour.***

Expanding the Chemistry

Frequently there is more to the chemistry than what is covered in the PUBLIC database.[10] The following is a partial list of additional databases available from OLI:

Geochemical	This database contains thermodynamic data for species that appear in geological time frames or are available for chemical weathering. We do not normally expect to see these species under industrial conditions.
Corrosion	This database is provided for use with the Corrosion Analyzer component of OLI Studio. It is user selectable if the user is a lessee of the Corrosion Analyzer.

Back to the tour…

Select **<u>Chemistry</u>** from the menu.

Select **<u>Model Options…</u>** from the menu list.

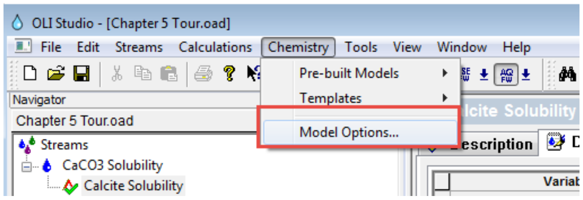


Figure 5-11 The Chemistry Menu

We will now be given a selection of database to choose from. The Public Databank is always selected and must be used.

Select **<u>Geochemical</u>** Databank and ***click*** the right arrow. ***Click* <u>OK</u>** to continue.

---

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

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

Figure 5-12 Selecting the Geochemical databank

Figure 5-13 Geochemical databank selected

Removing Solids

After we have selected the Geochemical databank, we now need to change the chemistry. The inclusion of the following species: Ca^{+2}, Mg^{+2}, and CO_2 in the chemical model will allow for many new solids to potentially form. Carbon dioxide, of course, creates the carbonate and bicarbonate ions.

These new solids are:

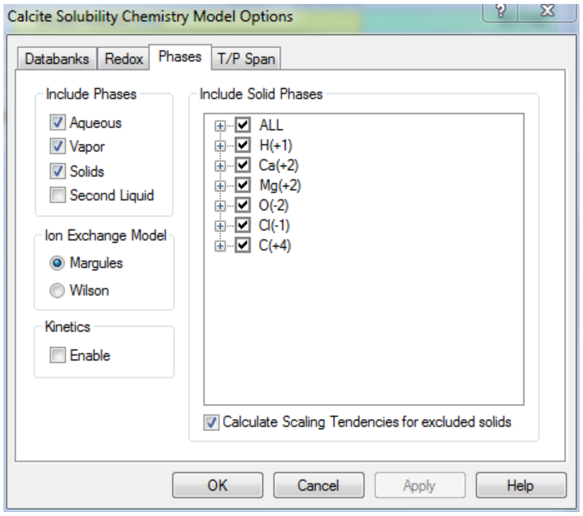
Calcite	$CaCO_3$
Aragonite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$

Calcite is the most thermodynamically stable solid among the two calcium carbonates. In this scenario, we wish to determine the solubility of the less thermodynamically stable solid, aragonite.

A problem with equilibrium based models is that we will always get the most thermodynamically stable solid unless we modify the model.

For this we will go back to the **Chemistry Menu** and **Model Options…** (See Figure 5-11 and Figure 5-12). This will bring up a Select Phases dialog.

Select the **Phases** tab.



Include Phases
☑ Aqueous
☑ Vapor
☑ Solids
☐ Second Liquid

Ion Exchange Model
● Margules
○ Wilson

Kinetics
☐ Enable

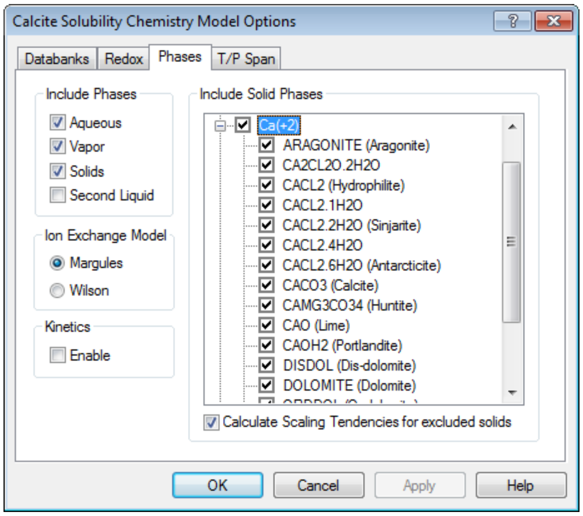
Include Solid Phases
☑ ALL
☑ H(+1)
☑ Ca(+2)
☑ Mg(+2)
☑ O(-2)
☑ Cl(-1)
☑ C(+4)

☑ Calculate Scaling Tendencies for excluded solids

Figure 5-14 Removing Calcite (CaCO3) from the chemistry model

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

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



Include Phases
☑ Aqueous
☑ Vapor
☑ Solids
☐ Second Liquid

Ion Exchange Model
● Margules
○ Wilson

Kinetics
☐ Enable

Include Solid Phases
☑ Ca(+2)
☑ ARAGONITE (Aragonite)
☑ CA2CL2O.2H2O
☑ CACL2 (Hydrophilite)
☑ CACL2.1H2O
☑ CACL2.2H2O (Sinjarite)
☑ CACL2.4H2O
☑ CACL2.6H2O (Antarcticite)
☑ CACO3 (Calcite)
☑ CAMG3CO34 (Huntite)
☑ CAO (Lime)
☑ CAOH2 (Portlandite)
☑ DISDOL (Dis-dolomite)
☑ DOLOMITE (Dolomite)

☑ Calculate Scaling Tendencies for excluded solids

Figure 5-15 Expanding Calcium Solids

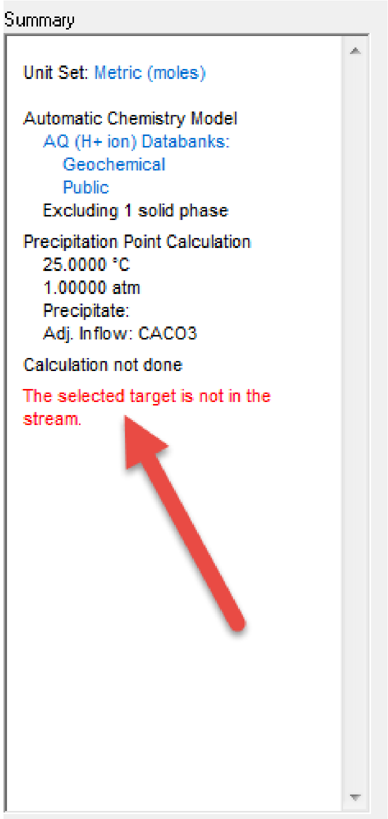
Scroll down to find **CACO3(Calcite)** and uncheck this solid. ***Click*** **OK** continue.

Repeating the precipitation point calculation

We have now modified the chemistry model to excluded calcite ($CaCO_3$). We now want to determine the solubility of aragonite (also a $CaCO_3$ solid).

Repeat the steps to begin a precipitation point calculation.

We will receive an error message in the summary box:



Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Geochemical
Public
Excluding 1 solid phase

Precipitation Point Calculation
25.0000 °C
1.00000 atm
Precipitate:
Adj. Inflow: CACO3

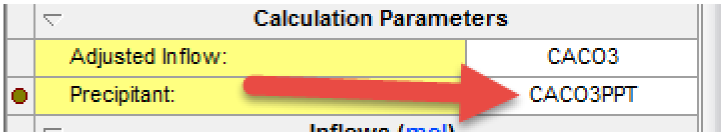
Calculation not done

The selected target is not in the stream.

Figure 5-16

Our original target of CACO3(Calcite) is not available (we just removed it) so we need to change to our new desired target ARAGONITE(Aragonite)/

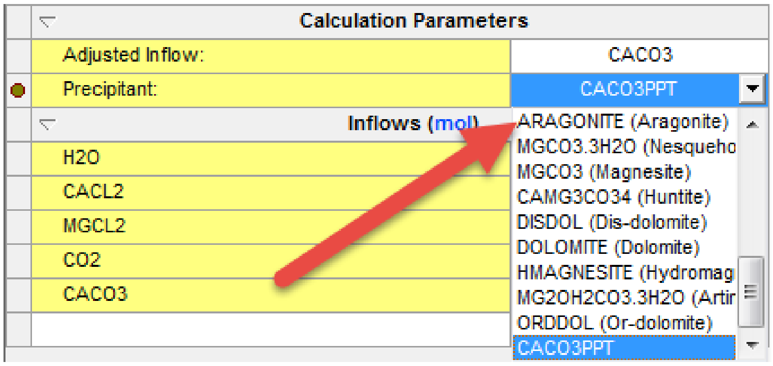
Click in the ***Precipitant:*** box.



Calculation Parameters
Adjusted Inflow: CACO3
Precipitant: CACO3PPT

Figure 5-17

Change selection from CACO3PPT to **<u>ARAGONITE (Aragonite)</u>** from the solids list.



Calculation Parameters
Adjusted Inflow: CACO3
Precipitant: CACO3PPT
Inflows (mol)
H2O
CACL2
MGCL2
CO2
CACO3

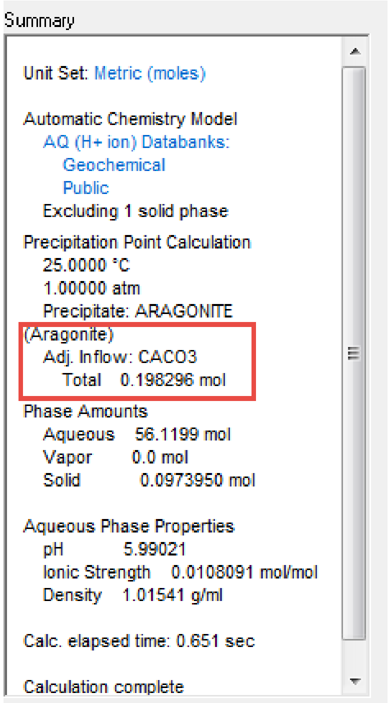
Figure 5-18

<u>CACO3</u> remains as the **<u>Adjusted Inflow.</u>**

When ready, click **Calculate**.

When the calculation finishes, we need to review how much aragonite is soluble in water. It would appear from the summary box that approximately 0.2 moles of Aragonite are soluble in 1 kilogram of water (55.508 moles of water). This is considerably larger than the 0.0044 moles of CaCO3 (calcite) case.

Almost 0.2 moles of Aragonite ($CaCO_3$) is soluble in 1 Kg of water



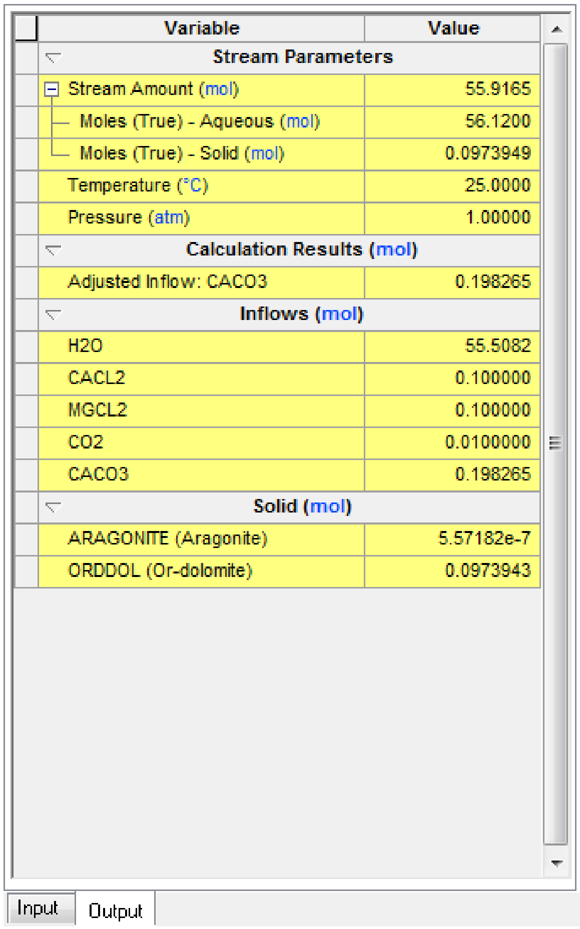
```
Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
   AQ (H+ ion) Databanks:
      Geochemical
      Public
   Excluding 1 solid phase

Precipitation Point Calculation
   25.0000 °C
   1.00000 atm
   Precipitate: ARAGONITE
(Aragonite)
   Adj. Inflow: CACO3
      Total    0.198296 mol
Phase Amounts
   Aqueous    56.1199 mol
   Vapor      0.0 mol
   Solid        0.0973950 mol

Aqueous Phase Properties
   pH          5.99021
   Ionic Strength    0.0108091 mol/mol
   Density    1.01541 g/ml

Calc. elapsed time: 0.651 sec

Calculation complete
```

Figure 5-19 Summary of aragonite solubility

In general, when a large change in solubility is observed, we should check to see if other species have precipitated.

Click on the ***Output*** tab located below the grid.

Using methods described previously add the **Solid** section:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.9165
Moles (True) - Aqueous (mol)	56.1200
Moles (True) - Solid (mol)	0.0973949
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Results (mol)	
Adjusted Inflow: CACO3	0.198265
Inflows (mol)	
H2O	55.5082
CACL2	0.100000
MGCL2	0.100000
CO2	0.0100000
CACO3	0.198265
Solid (mol)	
ARAGONITE (Aragonite)	5.57182e-7
ORDDOL (Or-dolomite)	0.0973943

Figure 5-20 The Calculated results, showing that ORDDOL (Ordered Dolomite or $CaMg(CO_3)_2$) is present

This report shows that approximately 0.097 moles of ordered dolomite ($CaMg(CO_3)_2$) has also precipitated with the aragonite. The solution must first become saturated with dolomite before aragonite will precipitate. This means that dolomite is more thermodynamically stable, at these conditions, than aragonite.

Removing Dolomite

We will repeat the steps to select phases using the **Chemistry Menu** and Select Phases.

Select the **Chemistry Menu Item.**

Select **Model Options…** from the menu list. Then select the **Phases** tab. You can expand either the CA(+2) solids or MG(+2) solids since dolomite contains both species.

Scroll down the list to find these three solids (CACO3 should remain excluded) and uncheck them:

DOLOMITE

DISDOL

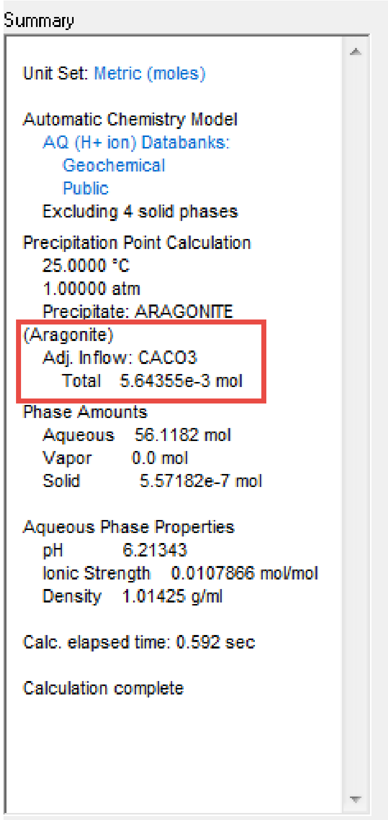
ORDDOL

The latter two solids are alternative forms of dolomite.

Click OK to continue.

Repeat the precipitation point calculation with only aragonite and record the solubility point.

Click Calculate when ready.



Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Geochemical
Public
Excluding 4 solid phases

Precipitation Point Calculation
25.0000 °C
1.00000 atm
Precipitate: ARAGONITE
(Aragonite)
Adj. Inflow: CACO3
Total 5.64355e-3 mol

Phase Amounts

Aqueous	56.1182 mol
Vapor	0.0 mol
Solid	5.57182e-7 mol

Aqueous Phase Properties

pH	6.21343
Ionic Strength	0.0107866 mol/mol
Density	1.01425 g/ml

Calc. elapsed time: 0.592 sec

Calculation complete

Figure 5-21 Solubility with Dolomite Turned off

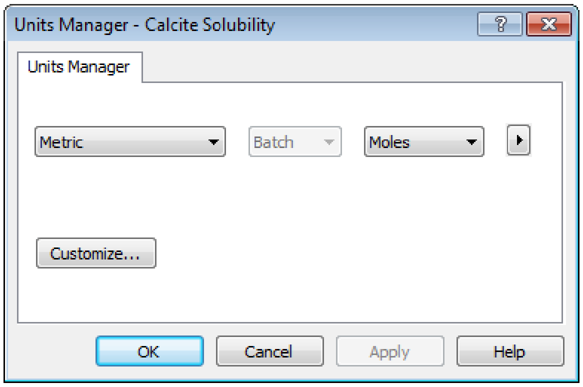
The solubility is now 0.0056 moles per kilogram of water. This is more in line with the calcite solubility.

The user should always remember that although a species is more thermodynamically stable, it may not form due to kinetic limitations.

Units manager (alternative Entry)

There are two ways to get to the Units Mmanager. One is through tools-> Units manager. Second is clicking on

C F this icon at the top toolbar. Both options should lead to the pop up window below.



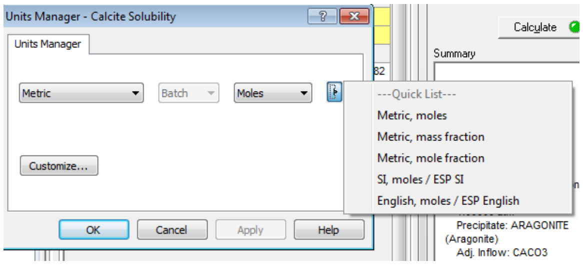
Units Manager - Calcite Solubility

Units Manager

Metric | Batch | Moles

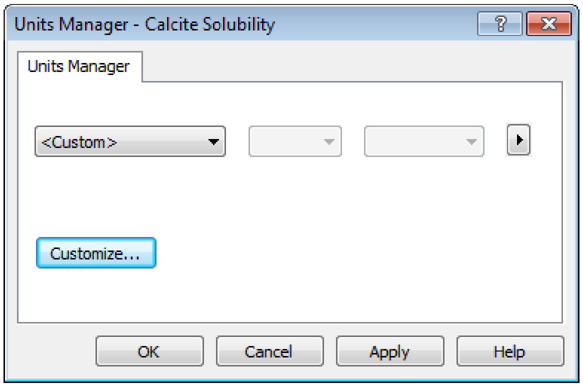
This Units manager gives more control at a higher level.

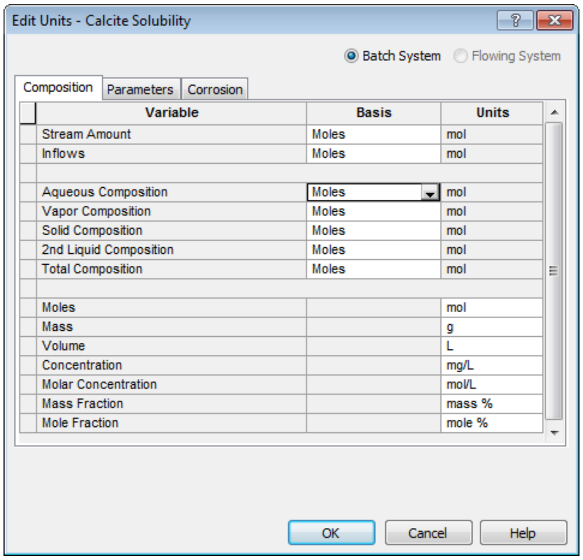
You can set your desired set of units from quick list option below.



Each combination has its own set of units for phases, inflows and stream parameters. If you want to alter the specific units or create your own set of units, click on customize.

That takes you back to the old inter phase where you could use the dropdowns to set each variable. Once you set that, you first layer of UI looks like the image below; it says custom because now you have altered one of the default variables unit.





Variable	Basis	Units
Stream Amount	Moles	mol
Inflows	Moles	mol
Aqueous Composition	Moles	mol
Vapor Composition	Moles	mol
Solid Composition	Moles	mol
2nd Liquid Composition	Moles	mol
Total Composition	Moles	mol
Moles		mol
Mass		g
Volume		L
Concentration		mg/L
Molar Concentration		mol/L
Mass Fraction		mass %
Mole Fraction		mole %

Now would be a good time to save your files.

Save, save, save…

Click here for a completed example file: Chapter 05 Tour

6. Aqueous Thermodynamics

Overview

Understanding aqueous thermodynamics can be a daunting task. In this chapter we will describe some of the essential topics in aqueous thermodynamics and present them in a logical, relatively easy to understand manner. We will be using the AQ thermodynamic framework for these examples.

The Equilibrium Constant

The evaluation of the following equation is central to the OLI Software:

$$\Delta_R \overline{G}^o = -RT \ln K$$

Where $\Delta_R \overline{G}^o$ is the partial molal, standard-state Gibbs Free Energy of Reaction, R is the Gas Constant (8.314 J/mole/K), T is the temperature (Kelvin) and K is the equilibrium constant. The subscript **R** refers not to the gas constant but to an equilibrium reaction.

We define $\Delta_R \overline{G}$ as:

$$\Delta_R \overline{G} = \sum_i v_i \Delta_f \overline{G}_i (PRODUCTS) - \sum_i v_i \Delta_f \overline{G}_i (REACTANTS)$$

Where ν_i is the Stoichiometric coefficient and $\Delta_f \overline{G}_i$ is the Gibbs Free Energy of Formation for a species.

Question:

Consider the equilibrium:

$$Na_2SO_4 = 2Na^+ + SO_4^{2-}$$

What is the Gibbs Free Energy of Reaction? What is the equilibrium constant at 25 ºC (298.15K)[11]?

The reference state thermodynamic values are readily available:[12]

---

[11] 25ºC (298.15K) is also known as the reference temperature.

[12] NBS Tables of Chemical Thermodynamic Properties - Selected Values for Inorganic and C1-C2 Organic Substances in SI Units, Wagman, D.D., et al, 1982

$$\Delta_f \overline{G}^R(Na_2SO_4) = -1270100 J/mole$$ [13]

$$\Delta_f \overline{G}^R(Na^+) = -261800 J/mole$$

$$\Delta_f \overline{G}^R(SO_4^{2-}) = -744460 J/mole$$

For the Gibbs Free Energy of reaction:

$$\Delta_R \overline{G}^R = \left(2\Delta_f \overline{G}^R(Na^+) + \Delta_f \overline{G}^R(SO_4^{2-})\right) - \Delta_f \overline{G}^R(Na_2SO_4)$$

$$\Delta_R \overline{G}^R = \left(2(-261800) + (-744460)\right) - (-1270100) = 2640 J/mole$$

By rearranging our equilibrium equation we get:

$$\ln K^R = -\frac{\Delta_R \overline{G}^R}{RT}$$

By now substituting the appropriate numbers we get:

$$\ln K^R = -(2640 \text{ J/mole}) /((8.314 \text{ J/mole/K})(298.15\text{K})) = -1.07$$

$$K^R=0.34$$

Principal Thermodynamic Properties

Each thermodynamic property is composed of two parts. The first is the standard state part which is only a function of temperature and pressure (denoted by the superscript ^{o}).

The second is the excess part which is a function of temperature and pressure as well as concentration (denoted by the superscript ^{E}).

Partial Molal Gibbs Free Energy

$$\overline{G}_i = \overline{G}_i^o + \overline{G}_i^E$$

Partial Molal Enthalpy

$$\overline{H}_i = \overline{H}_i^o + \overline{H}_i^E$$

Partial Molal Entropy

---

[13] The subscript **f** refers the energy of formation from the elements. The superscript **R** refers to the reference state. This is a special case of the standard state normally denoted with a superscript **o**.

$$\overline{S_i} = \overline{S_i^o} + \overline{S_i^E}$$

Partial Molal Heat Capacity

$$\overline{Cp_i} = \overline{Cp_i^o} + \overline{Cp_i^E}$$

Partial Molal Volume

$$\overline{V_i} = \overline{V_i^o} + \overline{V_i^E}$$

Note: Superscript ^{0} = Standard State Property
Superscript ^{E} = Excess Property

HKF (Helgeson-Kirkham-Flowers)Equation of State[14,15]

Working since 1968, Helgeson, et. al., have found that the standard-state thermodynamic property of any species in water can be represented by a function with seven terms which have specific values for each species.

These seven terms (a_{1-4}, c_{1-2}, and ω) are integration constants for volume (a), heat capacity (c) and temperature and pressure properties of water (ω). They are independent of the data system used to obtain them.

$$\overline{H_i^o} = \overline{H_i^R} + f_{Hi}(a_1,....,a_4,c_1,c_2,\omega)$$

$$\overline{G_i^o} = \overline{G_i^R} - \overline{S_i^R}(T - T^R) + f_{Gi}(a_1,....,a_4,c_1,c_2,\omega)$$

$$\overline{S_i^o} = \overline{S_i^R} + f_{Si}(a_1,....,a_4,c_1,c_2,\omega)$$

$$\overline{Cp_i^o} = \overline{Cp_i^R} + f_{Cpi}(a_1,....,a_4,c_1,c_2,\omega)$$

$$\overline{V_i^o} = \overline{V_i^R} + f_{Vi}(a_1,....,a_4,c_1,c_2,\omega)$$

Superscript ^{R}	– Reference State Property (25°C, 1 bar)
Superscript ^{o}	– Standard State Property
$a_1...a_4$	– Pressure Effects
c_1, c_2	– Temperature Effects
ω	– Pressure, Temperature Effects

The Helgeson Equation of State Parameters are used to predict equilibrium constants.

---

[14] H.C.Helgeson, D.H.Kirkham, G.C.Flowers. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures - Parts I through IV. American Journal of Science 1974, 1976, 1981.

[15] J.C.Tanger, IV Doctorial Thesis. “Calculation of the Standard Partial Molal Thermodynamic Properties of Aqueous Ions and Electrolytes at High Pressures and Temperatures” University of California at Berkley, 1986 H.C.Helgeson Advisor.

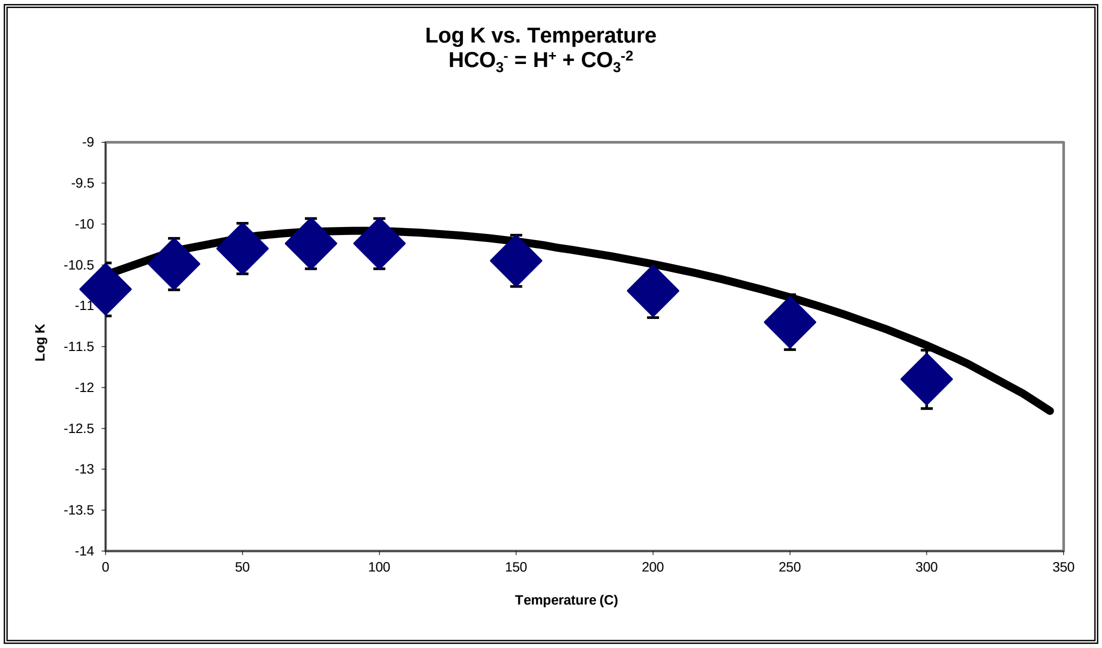


Figure 6-1 The logarithm of the equilibrium constant (LOG K) for the dissociation of the bicarbonate ion as a function of temperature at saturation pressure. The symbols represent the data taken from the references listed in the footnotes [16,17,18,19,20] but the line was generated from the equation of state.

The Helgeson Equation of State

Enthalpy

$$\Delta\overline{H^o_{P,T}} = \Delta\overline{H^o_f} + c_1(T-T_r) - c_2\left[\left(\frac{1}{T-\Theta}\right)-\left(\frac{1}{T_r-\Theta}\right)\right] + a_1(P-P_r) + a_2\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)$$

$$+\left(a_3(P-P_r)+a_4\ln\left[\frac{\Psi+P}{\Psi+P_r}\right]\right)\left[\frac{2T-\Theta}{(T-\Theta)^2}\right]+\omega\left(\frac{1}{\varepsilon}-1\right)+\omega TY - T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_P$$

---

[16] H.S.Harned and S.R.Scholes. The Ionization Constant of HCO_3 – from 0 to 50°. *J.Am.Chem.Soc.* ***63,****1706 (1941)*

[17] R.Nasanen. Zur Einwirkung der Saure und Basenzusatze auf die Fallungskurvevon Bariumcarbonate. *Soumen Kemistilehti* ***90****,24 (1946)*

[18] F. Cuta and F.Strafelda. The second dissociation constant of carbonic acid between 60 and 90°C. *Chem. Listy* ***48****,1308 (1954)*

[19] B.N.Ryzhenko. *Geochemistry International* ***1****,8 (1963)*

[20] C.S.Patterson, G.H.Slocum, R.H.Busey and R.E.Mesmer. Carbonate equilibrium in hydrothermal systems: First ionization of carbonic acid in NaCl media to 300°C. *Geoch.Cosmoh.Acta* ***46****,1653 (1982)*

$$-\omega_{\mathrm{Pr},Tr}\left(\frac{1}{\varepsilon_{\mathrm{Pr},Tr}}-1\right)-\omega_{\mathrm{Pr},Tr}T_rY_r$$

Gibbs Free Energy

$$\Delta\overline{G^{o}_{P,T}}=\Delta\overline{G^{o}_{f}}-\overline{S^{o}_{\mathrm{Pr},Tr}}\left(T-T_r\right)-c_1\left[T\ln\left(\frac{T}{T_r}\right)-T+T_r\right]+a_1\left(P-P_r\right)+a_2\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\left(\frac{\Psi+P}{\Psi+P_r}\right)$$
$$+\left[a_3\left(P-P_r\right)+a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right]\left(\frac{1}{T-\Theta}\right)-c_2\left[\left(\left(\frac{1}{T-\Theta}\right)-\left(\frac{1}{T_r-\Theta}\right)\right)\left(\frac{\Theta-T}{\Theta}\right)-\frac{T}{\Theta^2}\ln\left(\frac{T_r\left(T-\Theta\right)}{T\left(T_r-\Theta\right)}\right)\right]$$
$$+\omega\left(\frac{1}{\varepsilon}-1\right)-\omega_{\mathrm{Pr},Tr}\left(\frac{1}{\varepsilon_{\mathrm{Pr},Tr}}-1\right)+\omega_{\mathrm{Pr},Tr}Y_{\mathrm{Pr},Tr}\left(T-T_r\right)$$

Volume

$$\overline{V^o}=a_1+a_2\left(\frac{1}{\Psi+P}\right)+\left[a_3+a_4\left(\frac{1}{\Psi+P}\right)\right]\left(\frac{1}{T-\Theta}\right)-\omega Q+\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial P}\right)_T$$

Heat Capacity at Constant Pressure

$$\overline{Cp^o}=c_1+c_2\left(\frac{1}{T-\Theta}\right)^2-\left(\frac{2T}{\left(T-\Theta\right)^3}\right)\left[a_3\left(P-P_r\right)+a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right]+\omega TX+2TY\left(\frac{\partial\omega}{\partial T}\right)_P-T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_p$$

Entropy

$$\overline{S^o}=\overline{S^o_{\mathrm{Pr},Tr}}+c_1\ln\frac{T}{T_t}-\frac{c_2}{\Theta}\left\{\left(\frac{1}{T-\Theta}\right)-\left(\frac{1}{T_r-\Theta}\right)+\frac{1}{\Theta}\ln\left(\frac{T_r\left(T-\Theta\right)}{T\left(T_r-\Theta\right)}\right)\right\}+\left(\frac{1}{T-\Theta}\right)^2\left[a_3\left(P-P_r\right)+a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right]$$
$$+\omega Y-\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_P-\omega_{\mathrm{Pr},Tr}Y_{\mathrm{Pr},Tr}$$

Where,
H = Enthalpy
G = Gibbs Free Energy
V = Volume
Cp = Heat Capacity at constant Pressure
S = Entropy
T = Temperature
P = Pressure
Θ = 228 K
Ψ = 2600 Bar
ω = Temperature and Pressure dependent term for electrostatic nature of the electrolytes
Q = Pressure functions of the dielectric constant

ε = Dielectric constant of water

$a1 \ldots a4$ = Pressure dependent terms

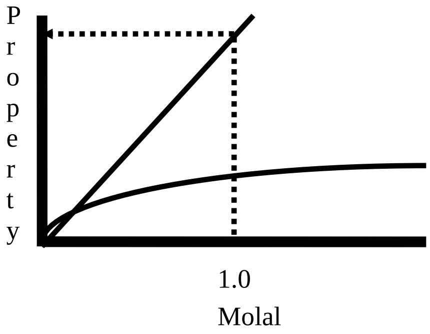
$c1, c2$ = Temperature dependent terms

What is the standard State?

The standard state refers to a thermodynamic value at a defined state (temperature, pressure and concentration)[21].

Aqueous:

The hypothetical 1.0 molal solution extrapolated from infinite dilution.



Vapor:

The Ideal Gas Pure Component (mole fraction = 1.0)

Organic Liquid:

The Ideal Gas Pure Component (mole fraction = 1.0)

Solid:

The pure component solid.

Excess Properties

Excess properties are a function of temperature, pressure and composition. It is with the excess properties that we begin to introduce the concept of activities and activity coefficients.

The excess property that we are most concerned with is the excess Gibbs Free Energy.

The activity of a species in solution can be defined as:

$$a_i = \gamma_i m_i$$

$$\overline{G_i} = \overline{G^o} + RT \ln a_i$$

---

[21] M. Rafal, J.W. Berthold, N.C. Scrivner and S.L. Grise."Chapter 7:Models for Electrolyte Solutions", Models for Thermodynamic and Phase Equilibria Calculations. Stanley I Sandler, ed. Marcel-Dekker, Inc. New York: 1994. pp. 686.

$$\overline{G_i} = \overline{G^o} + RT \ln m_i + RT \ln \gamma_i$$

$$\overline{G_i^E} = RT \ln \gamma_i$$

Note: Other excess properties involve various partial derivatives of γ_i with respect to temperature and/or pressure.

$$\overline{H}_i^E = RT^2 \left.\frac{\delta \ln \gamma_i}{\delta T}\right]_P$$

Ionic Strength

Ionic Strength is defined by the following equation:

$$I = 1/2 \sum_{i=1}^{nI} (z_i^2 \, m_i)$$

where,

nI = number of charged species

For Example, a 1.0 molal solution of NaCl has 1.0 moles of Na^{+1} ion and 1.0 moles of Cl^{-1} ion per Kg H_2O.

$$I = \frac{1}{2}\left(\left(Z_{Na^{+1}}\right)^2\left(m_{Na^{+1}}\right) + \left(Z_{Cl^{-1}}\right)^2\left(m_{Cl^{+1}}\right)\right) = \frac{1}{2}\left((1)^2(1) + (-1)^2(1)\right) = 1$$

Therefore the ionic strength is 1.0 molal.

For Example, a 1.0 molal solution of $CaCl_2$ has 1.0 moles of Ca^{+2} ion and 2.0 moles of Cl^{-1} ion per Kg of H_2O.

$$I = \frac{1}{2}\left(\left(Z_{Ca^{+2}}\right)^2\left(m_{Ca^{+2}}\right) + \left(Z_{Cl^{-1}}\right)^2\left(m_{Cl^{+1}}\right)\right) = \frac{1}{2}\left((2)^2(1) + (-1)^2(2)\right) = 3$$

There for the ionic strength is 3.0 molal, or we can say that a 1.0 Molal solution of $CaCl_2$ behaves similar to a 3.0 molal Solution of NaCl

Definition of Aqueous Activity Coefficients

$$\log \gamma_i = \text{long range} + \text{short range}$$

Long Range:	Highly dilute solutions (e.g., 0.01 m NaCl). The ions are separated sufficiently such that the only interactions are between the ions and the solvent.
Short Range:	Increased concentrations. The ions are now beginning to interact with themselves (oppositely charged species attract, like charged species repel) in addition to the interactions with the solvent.

Long Range Terms

$$\ln\gamma_i = \frac{-z^2 A(T)\sqrt{I}}{1+\mathring{A}\,B(T)\sqrt{I}}$$

Where,

Å	ion size parameter
A(T), B(T)	Debye-Huckel parameters related to dielectric constant of water.

At 25 ºC and 1 Atmosphere[22]:

A(T) = 0.5092 $kg^{1/2}/mole^{1/2}$

B(T) = 0.3283 kg1/2/mole1/2-cm x10-8

---

[22] H.C.Helgeson and D.H.Kirkham. American Journal of Science Vol. 274, 1199 (1974)

Short Range Terms

$$\sum_{j=1}^{n^o} (b_{ij}(T,I)m_j)$$

Where,

n^o = Number of oppositely charged species.

For example, consider $H_2O/CO_2/NH_3$

Cations: H^+, NH_4^+

Anions: OH^-, HCO_3^{-1}, CO_3^{-2}, $NH_2CO_2^-$

Short Range Term for $NH4^+$:

$$b_{11}(T,I) * m_{HCO3} + b_{12}(T,I) * m_{CO3} + b_{13}(T,I) * m_{OH} + b_{14}(T,I) * m_{NH2CO2}$$

11 = NH4:HCO3

12 = NH4:CO3

13 = NH4:OH

14 = NH4:NH2CO2

Modern Formulations

1. Bromley - Meissner : Semi-Correlative[23,24]

Can predict and extrapolate excess properties when data is limited or unavailable.

2. Pitzer: Highly Interpolative[25]

Somewhat model dependent. Considerable caution is required when using the large amount of published data to verify the standard state model employed.

3. Helgeson: Limited in Scope[26]

4. Mixed Solvent Electrolyte: OLI's New Framework

---

[23] L.A.Bromley. J.Chem.Thermo.,**4**,669 (1972)

[24] H.P.Meissner. AIChE Symp.Ser.No. 173,74,124 (1978)

[25] K.S.Pitzer,et.al. J.Soln.Chem,**4**,249(1975); J.Phys.Chem.,**81**,1872(1977); J.Soln.Chem. **7**,327(1978); J.Am.Chem.Soc.**96**,5701(1974)

[26] H.C.Helgeson, D.H.Kirkham and G.C.Flowers. Am.J.Sci. **281**,1249(1981)

Bromley

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

Where,

A = Debye-Huckel Constant
I = Ionic Strength
B = Bromley parameter
γ = Mean activity coefficient
Z+ = Charge of the cation
Z- = Charge of the anion

Meissner

$$\Gamma = \gamma_{\pm}^{1/Z_{+}Z_{-}}$$

$$\Gamma^{o} = \left(1.0 + B(1.0+0.1I)^{q} - B\right)\Gamma^{*}$$

$$B = 0.75 - 0.065q$$

$$Log\Gamma^{*} = \frac{-0.5107\sqrt{I}}{1+C\sqrt{I}}$$

$$C = 1.0 + 0.055q\exp(-0.02312I^{3})$$

Where Γ is the reduced activity coefficient, q is the Meissner q value, I is the ionic strength.

The family of q values are:

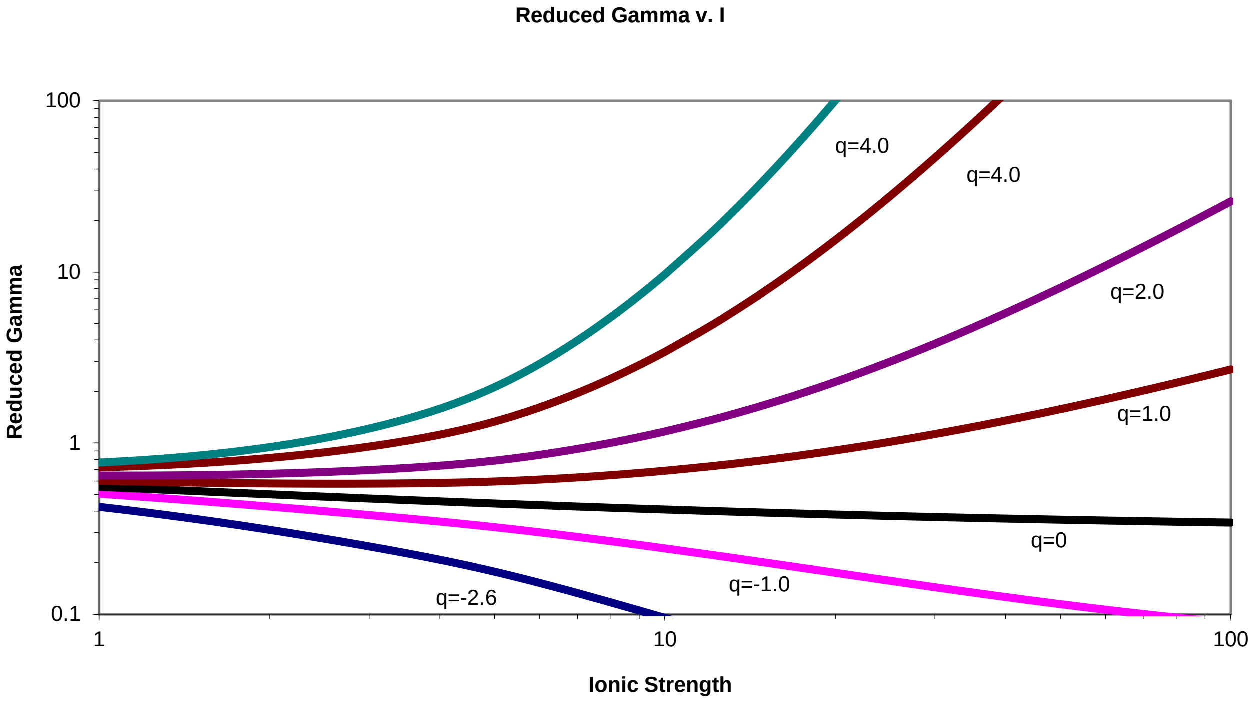


Figure 6-2 The Meissner q lines

Bromley-Zematis

Joseph Zematis, of OLI Systems, Inc., now deceased, extended the work of Bromley in that he added two new terms[27]. The Bromley-Zematis activity model is:

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

Where C and D are new terms. Each of the B, C, and D terms have the following temperature functionality.

$$B \quad = \quad B_1 + B_2T + B_3T^2$$ (Where T is temperature in centigrade)

The other coefficients have the same form:

$$C \quad = \quad C_1 + C_2T + C_3T^2$$

$$D \quad = \quad D_1 + D_2T + D_3T^2$$

---

[27] Zemaitis, J.F., Jr, Clark, D.M., Rafal, M. and Scrivner, N.C., *Handbook of Aqueous Electrolyte Thermodynamics,* American Institute of Chemical Engineers, New York, 1986.

Pitzer

$$\ln \gamma_{\pm} = | Z_{+} Z_{-} | \; f^{\gamma} + m \left(\frac{2(\nu_{+}\nu_{-})}{\nu} \right) B_{\pm}^{\gamma} + m^{2} \left(\frac{2(\nu_{+}\nu_{-})^{1.5}}{\nu} \right) C_{\pm}^{\gamma}$$

Where,

f^{γ} = The “Debye-Huckel” term.[28]

ν_{+} = Stoichiometric coefficient for the cation

ν_{-} = Stoichiometric coefficient for the anion

ν = $\nu_{+} + \nu_{-}$

m = Concentration in molal

$B_{\pm}^{\gamma}$ = Pitzer B term, containing the adjustable parameters

$C_{\pm}^{\gamma}$ = Pitzer C term, containing adjustable parameters

Helgeson

$$Log \; \overline{\gamma}_{\pm} = \frac{-A_{\gamma} \, | Z_i Z_l | \sqrt{\bar{I}}}{1 + a_0 B\gamma \sqrt{\bar{I}}} + \Gamma_{\gamma} + \left(\frac{\omega_k}{\nu_k} \sum_k b_k Y_k \bar{I} + \frac{\nu_{i,k}}{\nu_k} \sum_l \frac{b_{il} \overline{Y}_l \sqrt{\bar{I}}}{\Psi_l} + \frac{\nu_{l,k}}{\nu_k} \sum_i \frac{b_{il} \overline{Y}_i \sqrt{\bar{I}}}{\Psi_i} \right)$$

Where,

A_{γ} = Debye-Huckel constant according to Helgeson

Z_i = Charge on the cation

Z_l = Charge on the anion

a_0 = ion size parameter

B_{γ} = Extended Debye-Huckel term according to Helgeson

$\bar{I}$ = True ionic strength which includes the effects of complexation

Γ_{γ} = Conversion of molal activity to mole fraction activity

ω_k = Electrostatic effects on the solvent due to the species k

ν_k = moles of electrolyte (summation)

$\nu_{i,k}$ = moles of cation per mole of electrolyte

$\nu_{l,k}$ = moles of anion per mole of electrolyte

$b_{i,l}$ = adjustable parameter for the ion-ion interaction.

$\overline{Y}_i$ = fraction of ionic strength on a true basis attributed to the cation

$\overline{Y}_l$ = fraction of ionic strength on a true basis attributed to the anion

Ψ_i = ½ the cation charge

Ψ_l = ½ the anion charge

Z_i = the cation charge

Z_l = the anion charge

---

[28] IBID, Page 74

Neutral Species

Neutral molecules in water are affected by other species in solution. The salting in and out of a gas is a typical example. When Oxygen is dissolved into pure water, it has a typical solubility. When salt is added, the solubility decreases. This is most-likely due to an interaction between the sodium ions and the neutral oxygen molecule and the interaction between the chloride ions and the neutral oxygen molecule.

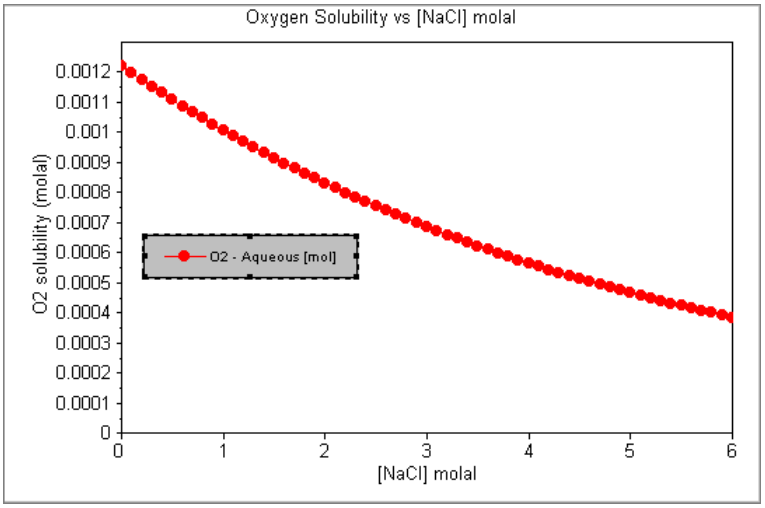


Figure 6-3 The solubility of oxygen in NaCl solutions at 25 C, 1 Atmosphere

1. Setschenow[29]

This characterizes a phenomena known as salting in/out. The formulation is in terms of the ratio of solubilities in pure water to an aqueous salt solution at a constant temperature.

$$Ln\gamma_{aq} = \frac{S_0}{S_S} = km_S$$

Where,

S_0 = Solubility of the gas in pure water

S_S = Solubility of the gas in a salt solution

K = Setschenow coefficient

m_S = Concentration of the salt.

In this case, the K is approximately equal to -0.0002.

Unfortunately, this approach is limited to a single temperature.

---

[29] J.Setchenow., Z.Physik.Chem., **4**,117 (1889)

2. Pitzer[30]

A more rigorous approach than Setschenow. Effects of temperature and composition can be modeled.

$$Ln\,\gamma_{aq} = 2\beta_{0(m-m)} m_m + 2\beta_{0(m-s)} m_s$$

Where,

$\beta_{0(m-m)}$ = The adjustable parameter for molecule – molecule interactions.

(a function of temperature)

$\beta_{0(m-s)}$ = The adjustable parameter for molecule – ion interactions.

(A function of temperature)

m_S = The concentration of the neutral species.

Multiphase Model

Solid-Aqueous Equilibrium

General Equilibrium Form:

$$S_i = p_1 P_1 + p_2 P_2 + \ldots p_p P_p$$

Examples:

$$NaCl(cr) = Na^{+}\,(aq) + Cl^{-}(aq)$$

$$CaSO4.2H2O(cr) = Ca^{+2}(aq) + SO4^{-2}(aq) + 2H2O$$

---

[30] K.S.Pitzer,et.al. J.Soln.Chem,**4**,249(1975); J.Phys.Chem.,**81**,1872(1977); J.Soln.Chem. **7**,327(1978); J.Am.Chem.Soc.**96**,5701(1974)

Solid Phase Thermodynamic Properties

$$\overline{G}_{Si} = \overline{G}_{Si}^{R} + \overline{S}_{Si}^{R}(T - T^{R}) + \int_{T^R}^{T} CpdT + \int_{P^R}^{P} VdP$$

Under the typical simulation conditions, the compressibility of the solid remains constant.

$$Cp = a_1 + a_2T + a_3T^{-2}$$

$$V = b_1$$

$$Log_{10}K_{sp}(T,P) = A + B/T_K + CT_K + DT^2{}_K + E + FP + GP^2$$

Mixed EOS Model

General Thermodynamic Equation:

Vapor-Aqueous

$$\overline{G_{V_i}} = \overline{G_{Aqi}}$$

$$\overline{G^o_{Vi}} + RTln(\phi_{Vi}\, y_i\, P) = \overline{G^o_{Aqi}} + RTln(\gamma_i\, m_i)$$

$$a_{Aqi} = \gamma_i\, m_i$$

$$f_{Vi} = \phi_{Vi}\, y_i\, P$$

The reference state for the vapor is the ideal gas.

$$\overline{G^o_{Vi}} + RTln(f_{Vi}) = \overline{G^o_{Aqi}} + RTln(a_{Aqi})$$

$$K = \text{EXP}\left[\frac{(\overline{G^o_{Aqi}} - \overline{G^o_{Vi}})}{RT}\right] = \frac{a_{Aqi}}{f_{Vi}}$$

Non-Aqueous Liquid-Aqueous

$$\overline{G_{Li}} = \overline{G_{Aqi}}$$

Notice that the reference state for the non-aqueous liquid is the ideal gas vapor.

$$\overline{G^o_{Vi}} + RTln(\phi_{Li} x_i P) = \overline{G^o_{Aqi}} + RTln(\gamma_i m_i)$$

$$f_{Li} = \phi_{Li} X_i P$$

$$\overline{G^o_{Vi}} + RTln(f_{Li}) = \overline{G^o_{Aqi}} + RTln(a_{Aqi})$$

$$K = \text{EXP}[\frac{(\overline{G^o_{Aqi}} - \overline{G^o_{Li}})}{RT}] = \frac{a_{Aqi}}{f_{Li}}$$

Limitations of the Current OLI Thermodynamic Model[31]

Aqueous Phase

$X_{H2O} > 0.65$

-50°C < T < 300°C

0 Atm < P < 1500 Atm

0 < I < 30

Non-aqueous Liquid

Currently no separate activity coefficient Model (i.e., no NRTL, Unifaq/Uniqac)

Non-aqueous and vapor fugacity coefficients are determined from the Enhanced SRK[32] Equation of State.

Vapor critical parameters (T_c, P_c, V_c, and ω[33]) are correlated to find a Fugacity coefficient.

---

[31] This refers only to the traditional OLI Aqueous Model and not the MSE model.

[32] G.Soave.Chem.Eng.Sci.**27**,1197(1972)

[33] This is the acentric factor which is not the same as Helgeson's ω term)

Scaling Tendencies

What is a scaling tendency?

It is the ratio of the real-solution solubility product to the thermodynamic limit based on the thermodynamic equilibrium constant.

For Example, Consider this dissolution:

$$NaHCO_{3(s)} = Na^{+} + HCO_3^{-}$$

The Ion Activity Product (IAP) is defined as the product of specific ions (in this case the ions resulting from the dissociation of a particular solid).

Let's consider a 1.0 molal $NaHCO_3$ solution:

$$IAP = \gamma_{Na} m_{Na} \gamma_{HCO3} m_{HCO3}$$

Assuming Ideal Solution Activities:

γ_{Na} = 1.0 γ_{HCO3} = 1.0

m_{na} = 1.0 m_{HCO3} = 1.0

$IAP = (1.0)(1.0)(1.0)(1.0)$

$IAP = 1.0$

The Solubility Product (K_{SP}) is the thermodynamic limit of ion availability:

$$K_{SP} = 0.265038$$[34]

The Scaling Tendency is then the ratio of available ions to the thermodynamic limit.

$$ST = IAP/K_{SP}$$

$$ST = 1.0/0.265038$$

$$ST = 3.77$$

Was assuming ideal conditions valid??

The actual species concentration and activity coefficients are:

γ_{Na} = 0.566 γ_{HCO3} = 0.566

---

[34] Based on the OLI PUBLIC databank version 9.2.6

m_{Na} = 0.764 m_{HCO3} = 0.739

This results in a different IAP:

$$IAP= (0.566)(0.764)(0.566)(0.739)$$

$$IAP=0.181$$

The new Scaling Tendency is therefore:

$$ST = IAP/Ksp$$

$$ST = 0.181/0.265038$$

$$ST = 0.682$$

Why the concentrations were not equal to 1.0? Speciation and chemical equilibria tend to form complexes which provide a “Sink” for carbonate species. In this example:

CO_2^o = 0.014 molal

$NaHCO_3^o$ = 0.233 molal

CO_3^{2-} = 0.011 molal

$NaCO_3^-$ = 0.003 molal

What does the Scaling Tendency Mean?

If ST < 1, then the solid is under-saturated
If ST > 1, then the solid is super-saturated
If ST = 1, then the solid is at saturation

$$\text{Scaling Index} = \text{Log (ST)}$$

What is the TRANGE?

TRANGE is a nomenclature for solids that have been fit to a polynomial form rather than pure thermodynamics.

The polynomial has this functional form:

$$\text{Log } K = A + B/T + CT + DT^2$$

It is known that polynomials may not extrapolate well. Incorrect predictions of Scaling Tendency may result. Therefore the applicable range is generally limited to data set.

Consider Na2CO3/H2O

There are 4 solids of interest in this system. They are:

Table 6-1 Sodium Carbonate hydrate transition ranges

Solid	**Temperature Range (C)**
$Na_2CO_3 \bullet 10H_2O$	0-35
$Na_2CO_3 \bullet 7H_2O$	35-37
$Na_2CO_3 \bullet 1H_2O$	37-109
$Na2CO_3$	109-350

This table implies that these solids change their form as the temperature increases. Each solid was fit to the above polynomial. There may be problems if the extrapolated values from higher number hydrates extend to the regions where the lower number hydrates are stable.

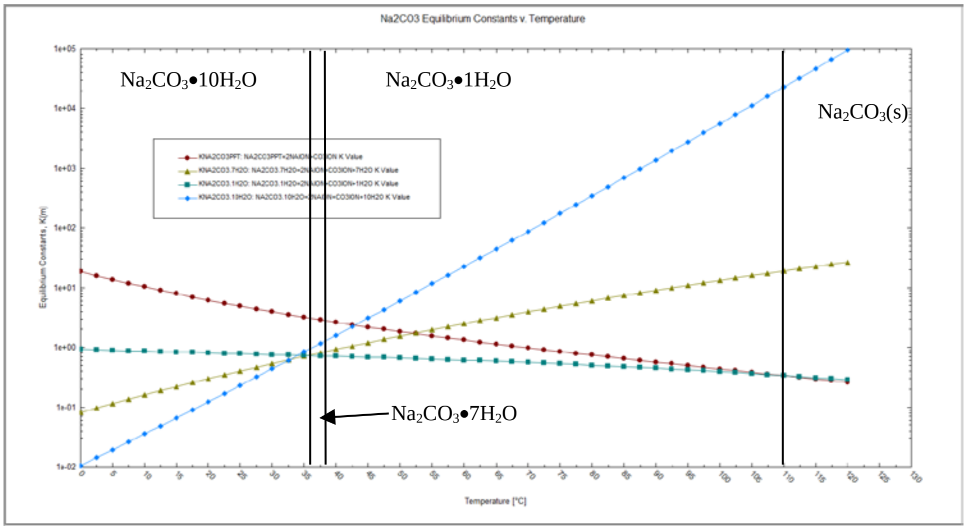


Figure 6-4 Plot of K vs. Temperature. The K's have been extrapolated.

In this plot, the concentration of Na^{+1} ion and CO_3^{2-} ion is held constant. This means that the more stable solid (higher scaling tendency) will be the solid with the smaller K value.

It can be seen that the mono-hydrate species does not extrapolate well to lower temperatures. In the range 35 to 37 ^{o}C, that the mono-hydrate equilibrium constant is smaller than the hepta-hydrate. If we concern ourselves with 36^{o}C, we can see that if the mono-hydrate solid was allowed to be in the model, the equilibrium based solver will attempt include it over the actual solid which is the hepta-hydrate.

Since the mono-hydrate species is outside its temperature range in this region, it will be mathematically eliminated from the equations.

Pre-scaling Tendencies

What is a Pre-scaling tendency?

OLI Defines a Pre-Scaling tendency is the scaling tendency before any solids have been formed. Many industries, notably the up-stream oil & gas industry, use the pre-scaling tendency to make design decisions about adding anti-scaling and anti-fouling agents or if the asset is as risk.

The normal convergence path for any OLI equilibrium calculation is the following:

1. Perform an initial estimate of all variables in the calculation. Our equation set is a series of non-linear equations. These typically need an initial estimate to get things started.
2. Take the ion activities at this point and then save them for pre-scale calculations
3. Converge the equation set and test to see if there are indications of a phase change (vapor/solid/organic). This could be the addition or removal of a phase
4. Adjust the mass of components to account for the change in phase
5. Re-converge the equation set and test for phase changes again. If there is a change, repeat the above steps
6. If no change in phases, conclude the calculation and make final calculations
    a. Transport properties (viscosity, electrical conductivity, etc.)
    b. Final values for post-scaling tendencies
    c. Additional thermodynamic calculations for heat capacity
7. Generate the report.

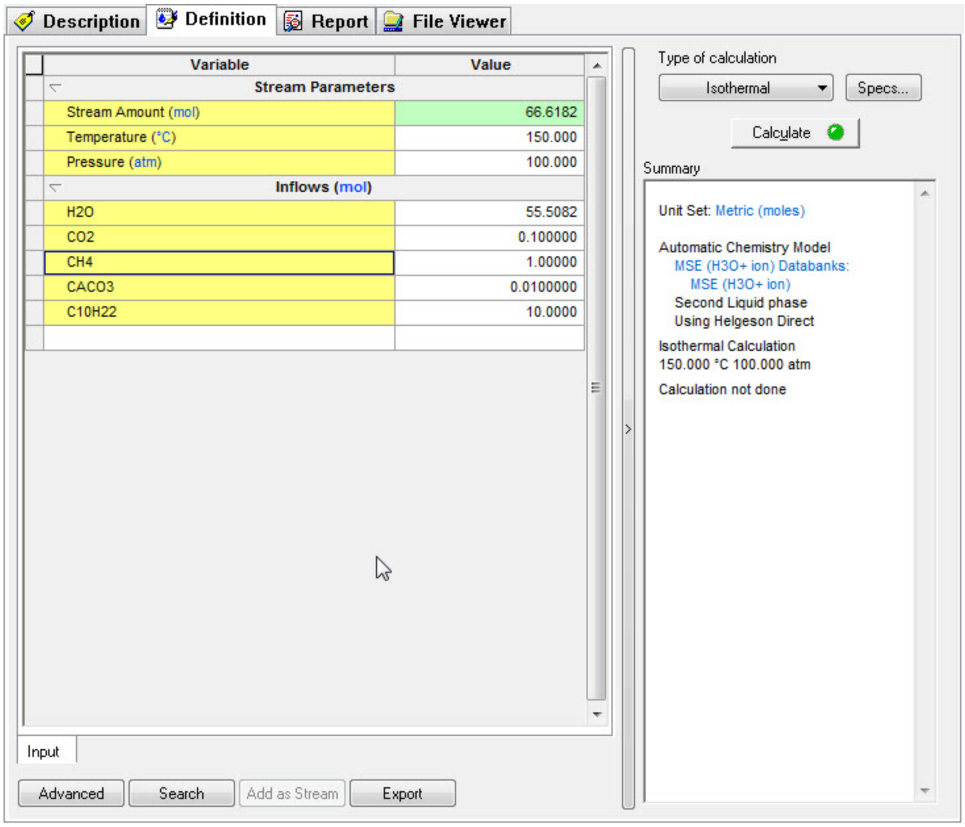
Estimated Pre-Scales

The procedure described above is for Estimated Pre-scaling tendencies. The reason we consider this estimated is that we have not obtained a final convergence when the values are taken. This is usually ok since the rigorous values are usually very close in value and this method is much faster.

We have an example created in version 9.5.4 which can be found here Pre-scaling example (OAD, v9.5.4)

Let's look at an example.

We have created a simple case in MSE.



Variable	Value
Stream Parameters	
Stream Amount (mol)	66.6182
Temperature (°C)	150.000
Pressure (atm)	100.000
Inflows (mol)	
H2O	55.5082
CO2	0.100000
CH4	1.00000
CACO3	0.0100000
C10H22	10.0000

Type of calculation: Isothermal

Summary

Unit Set: Metric (moles)

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

Isothermal Calculation
150.000 °C 100.000 atm

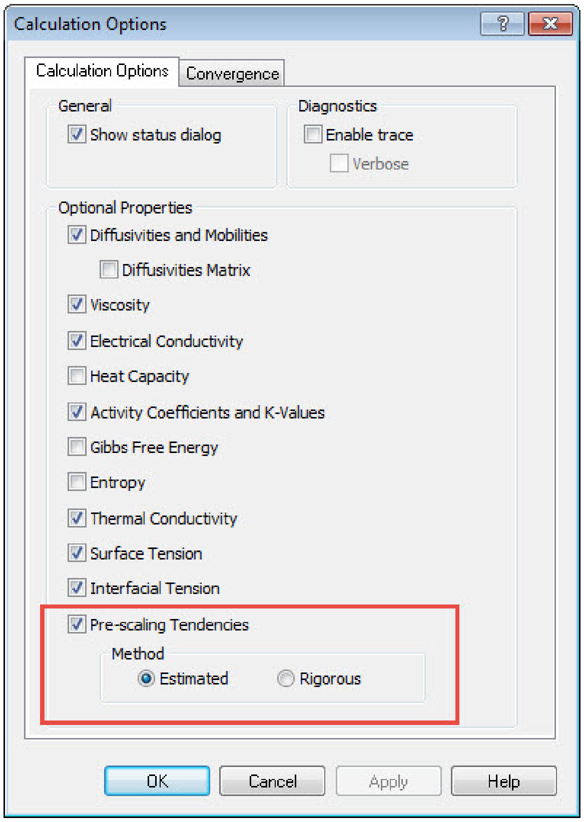
Calculation not done

Figure 6-5 An MSE case, example of pre-scaling

While this not representative of a true case in the upstream oil % gas industry, it does show some of the common components.

We now need to activate the Pre-scaling calculation (different OLI programs do this step in different ways, we are using OLI Studio as an example)

Use the **Specs** button to find the calculation option



Calculation Options

Calculation Options | Convergence

General
☑ Show status dialog

Diagnostics
☐ Enable trace
☐ Verbose

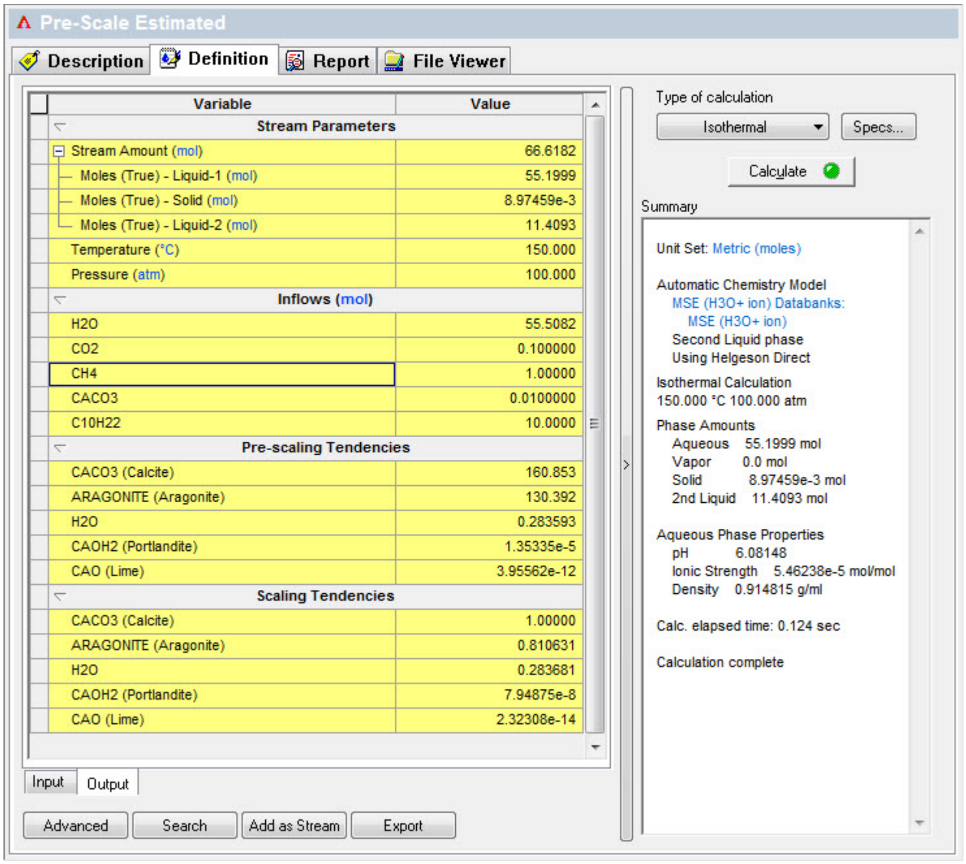
Optional Properties
☑ Diffusivities and Mobilities
☐ Diffusivities Matrix
☑ Viscosity
☑ Electrical Conductivity
☐ Heat Capacity
☑ Activity Coefficients and K-Values
☐ Gibbs Free Energy
☐ Entropy
☑ Thermal Conductivity
☑ Surface Tension
☑ Interfacial Tension
☑ Pre-scaling Tendencies

Method
● Estimated ○ Rigorous

Figure 6-6 Calculation Options for a single point case

Check the Pre-Scaling Tendencies box and then the Estimated radio button.

We will run this case and look at the output.



Variable	Value
Stream Parameters	
Stream Amount (mol)	66.6182
Moles (True) - Liquid-1 (mol)	55.1999
Moles (True) - Solid (mol)	8.97459e-3
Moles (True) - Liquid-2 (mol)	11.4093
Temperature (°C)	150.000
Pressure (atm)	100.000
Inflows (mol)	
H2O	55.5082
CO2	0.100000
CH4	1.00000
CACO3	0.0100000
C10H22	10.0000
Pre-scaling Tendencies	
CACO3 (Calcite)	160.853
ARAGONITE (Aragonite)	130.392
H2O	0.283593
CAOH2 (Portlandite)	1.35335e-5
CAO (Lime)	3.95562e-12
Scaling Tendencies	
CACO3 (Calcite)	1.00000
ARAGONITE (Aragonite)	0.810631
H2O	0.283681
CAOH2 (Portlandite)	7.94875e-8
CAO (Lime)	2.32308e-14

Unit Set: Metric (moles)

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

Isothermal Calculation
150.000 °C 100.000 atm

Phase Amounts

Aqueous	55.1999 mol
Vapor	0.0 mol
Solid	8.97459e-3 mol
2nd Liquid	11.4093 mol

Aqueous Phase Properties

pH	6.08148
Ionic Strength	5.46238e-5 mol/mol
Density	0.914815 g/ml

Calc. elapsed time: 0.124 sec

Calculation complete

Figure 6-7 Results with estimated pre-scaling tendencies

Look the pre-scaling tendencies for $CaCO_3$(Calcite). This value is 160.853 If you look at the Scaling Tendencies (this is also known as the post-scaling tendencies) the value for the same species is 1.0 which means the solid has formed. The calculation time is 0.124 seconds.

Rigorous Pre-Scales

For version 9.5.4 of the OLI Engine (which affects all the OLI software) we have added rigorous pre-scales. We added this feature because in some cases the estimated value was too far off from reality. This is especially true when you have scaling solids which have common ions such as $CaCO_3$and $MgCO_3$ in the same model or with very soluble species such as Na_2CO_3

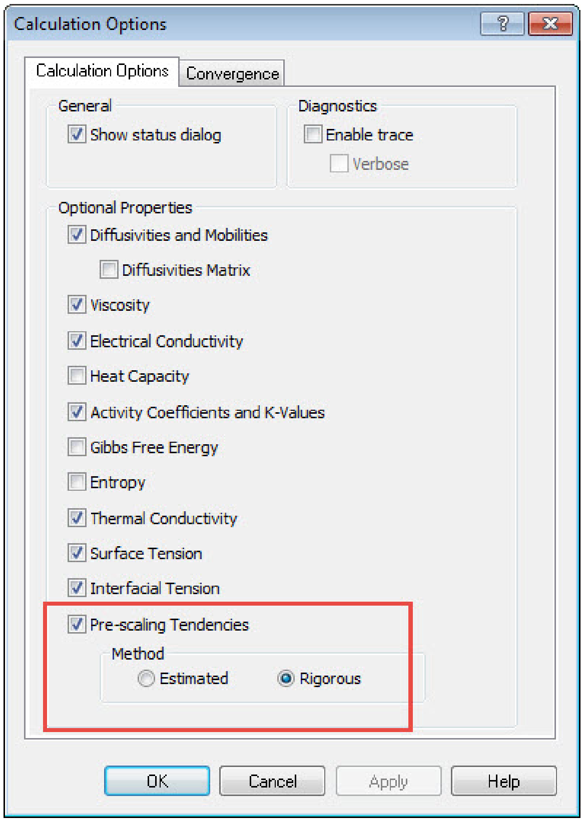
The overall calculation path is like the previously described path, but it has one major change:

1. Perform an initial estimate of all variables in the calculation. Our equation set is a series of non-linear equations. These typically need an initial estimate to get things started.
2. Converge the equation set and test to see if there are indications of a phase change (vapor/solid/organic). This could be the addition or removal of a phase
3. Adjust the mass of components to account for the change in phase
4. Re-converge the equation set and test for phase changes again. If there is a change, repeat the above steps
5. If no change in phases, conclude the calculation and make final calculations
    a. Transport properties (viscosity, electrical conductivity, etc.)
    b. Final values for post-scaling tendencies
    c. Additional thermodynamic calculations for heat capacity
6. Mathematically eliminate all solids from the calculation and repeat the convergence steps above
7. When converged, store the scaling tendencies as pre-scaling tendencies.

8. Generate the report.

In the past, if you wanted to have rigorous pre-scaling tendencies you had to recreate the chemistry model without any solids and then re-calculate the equation set. This manual step is now automatically done for you internally.

Here is an example, we are using the same input stream, but we are activating the rigorous pre-scaling option. Use the Specs button to select Rigorous



General
☑ Show status dialog

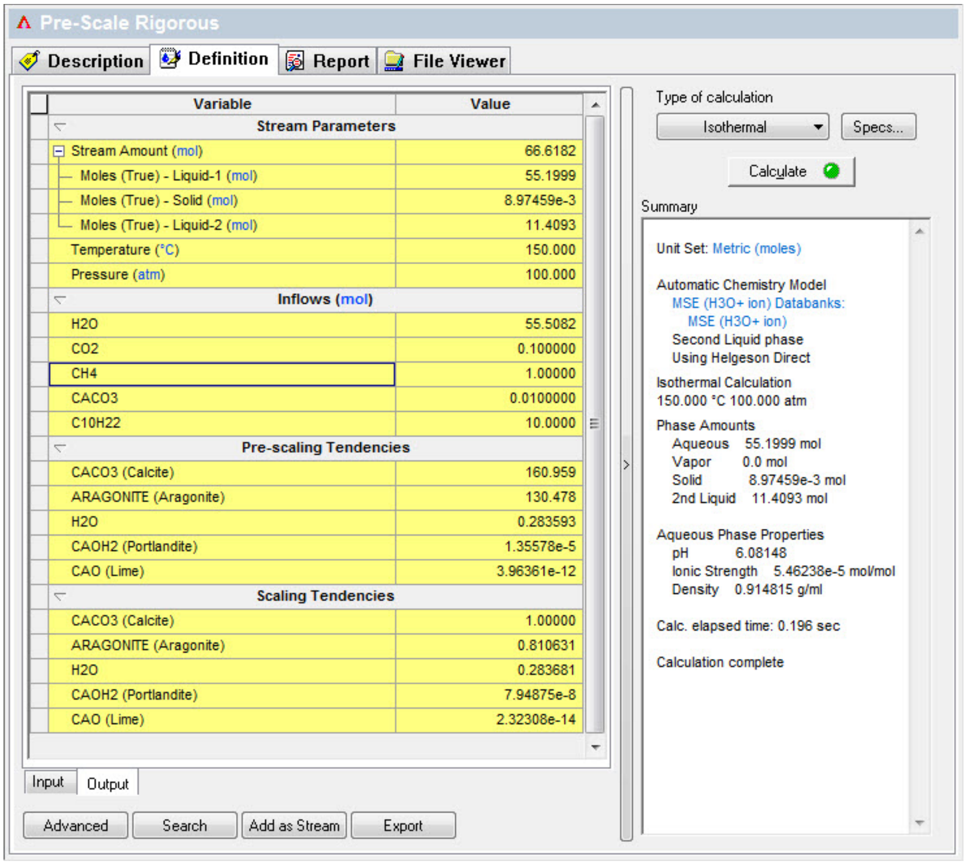
Diagnostics
☐ Enable trace
☐ Verbose

Optional Properties
☑ Diffusivities and Mobilities
☐ Diffusivities Matrix
☑ Viscosity
☑ Electrical Conductivity
☐ Heat Capacity
☑ Activity Coefficients and K-Values
☐ Gibbs Free Energy
☐ Entropy
☑ Thermal Conductivity
☑ Surface Tension
☑ Interfacial Tension
☑ Pre-scaling Tendencies

Method
○ Estimated ● Rigorous

Figure 6-8 Calculation options for rigorous pre-scaling tendencies

Run the calculation



Variable	Value
Stream Parameters	
Stream Amount (mol)	66.6182
Moles (True) - Liquid-1 (mol)	55.1999
Moles (True) - Solid (mol)	8.97459e-3
Moles (True) - Liquid-2 (mol)	11.4093
Temperature (°C)	150.000
Pressure (atm)	100.000
Inflows (mol)	
H2O	55.5082
CO2	0.100000
CH4	1.00000
CACO3	0.0100000
C10H22	10.0000
Pre-scaling Tendencies	
CACO3 (Calcite)	160.959
ARAGONITE (Aragonite)	130.478
H2O	0.283593
CAOH2 (Portlandite)	1.35578e-5
CAO (Lime)	3.96361e-12
Scaling Tendencies	
CACO3 (Calcite)	1.00000
ARAGONITE (Aragonite)	0.810631
H2O	0.283681
CAOH2 (Portlandite)	7.94875e-8
CAO (Lime)	2.32308e-14

Type of calculation: Isothermal

Summary

Unit Set: Metric (moles)

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

Isothermal Calculation
150.000 °C 100.000 atm

Phase Amounts
Aqueous 55.1999 mol
Vapor 0.0 mol
Solid 8.97459e-3 mol
2nd Liquid 11.4093 mol

Aqueous Phase Properties
pH 6.08148
Ionic Strength 5.46238e-5 mol/mol
Density 0.914815 g/ml

Calc. elapsed time: 0.196 sec

Calculation complete

Figure 6-9 Results for rigorous pre-scaling tendencies

Look the pre-scaling tendencies for $CaCO_3$(Calcite). This value is 160.959 If you look at the Scaling Tendencies (this is also known as the post-scaling tendencies) the value for the same species is 1.0 which means the solid has formed. The calculation time is 0.196 seconds.

Differences

The values for the rigorous pre-scaling tendencies are different. The differences are small in this case but in larger models the differences can be significant.

In this case The Estimated v. Rigorous pre-scaling tendency for $CaCO_3$ is 160.853 v 160.959 which is small difference. The Estimated v. Rigorous calculation time is 0.124 seconds v. 0.196 seconds. While that doesn't seem like much, in a large calculation or flowsheet simulation, that extra 0.07 seconds can add up significantly.

Calculating Osmotic Pressures

OLI is asked frequently how the osmotic pressure calculated in the software. We use a very traditional method of calculating the osmotic pressure.

$$\pi = -RT \, Ln \, a_{H2O} V_{H2O}$$

Where

π is the osmotic pressure

R is the gas constant

T is the temperature

a_{H2O} is the activity of water at temperature T

V_{H2O} is the partial molal volume of water at temperature T

Summary

We have seen that the evaluation of the equilibrium constant is an important factor in simulating aqueous systems. A rigorous thermodynamic framework has been developed to support the simulation.

7. Single Point Calculations

Objectives

By this point we have learned a great deal about the thermodynamics of the OLI Software and the internal workings of the simulation engine. We have also learned how to enter data and perform useful calculations.

We now wish to explore some of the other calculations in the OLI Studio. In the process of exploring these calculations, we will introduce some additional features.

In this chapter, we will learn about:

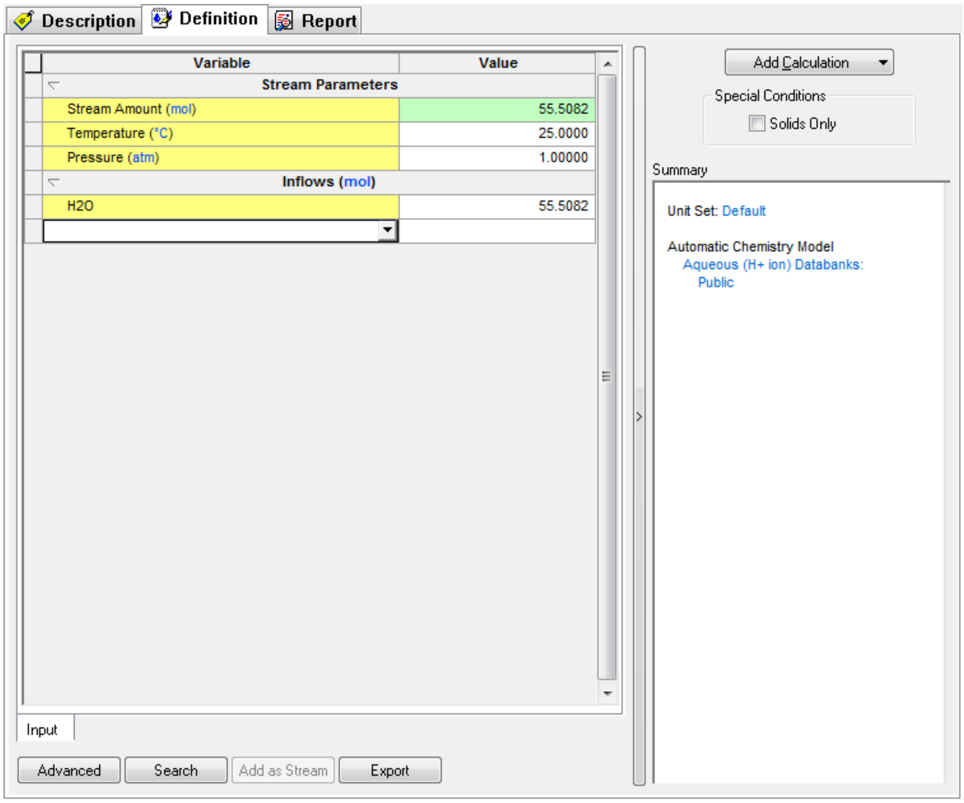
1. Isothermal Calculations
    - Using Custom Units
2. Adiabatic Calculation
    - Using the Names Manager
3. Bubble Point Calculations
    - Using new custom units
    - Modifying the report
4. Dew Point Calculations
    - Modifying model options
5. Vapor Amount/Fraction Calculations
    - Using custom report units

Isothermal

In this example, we will explore an isothermal calculation. We wish to determine the pH of a 10-weight percent acetic acid solution. The temperature and pressure will be 75 ºC and 1 atmosphere.

We have already entered stream and calculation data in previous examples so we will not dwell on them here. If you have not done so, please start the OLI Studio.

1. Select the **Add Stream** icon.
2. Select the **Description** tab.
3. Replace ***Stream1*** with ***Acetic Acid Solutions.***
4. Select **Definition**. The following grid list should be displayed.



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

Unit Set: Default

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

Figure 7-1 Stream Definition Input Grid

Since we wish to determine the pH of a 10-weight percent solution (a fraction type of unit) we should change our input units.

5. From the **Tools** menu item, select **Units Manager.**

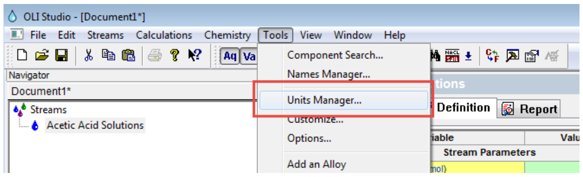


Figure 7-2 Menu Item/Tools/Units Manager

We can now modify the default set of units. The window, displayed in the following figure, shows that the **Standard** set of units are selected. We need to change these units.

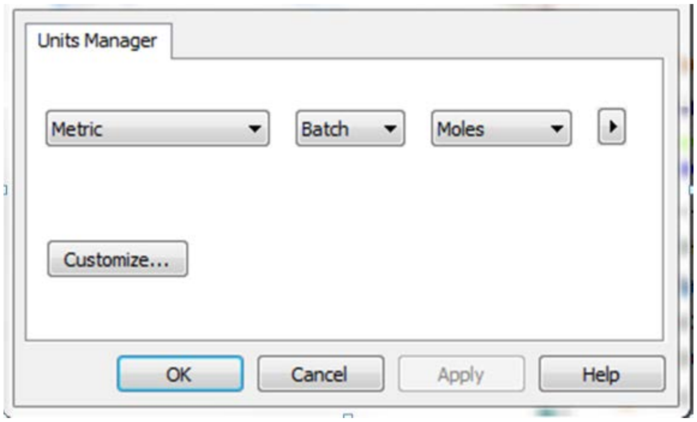
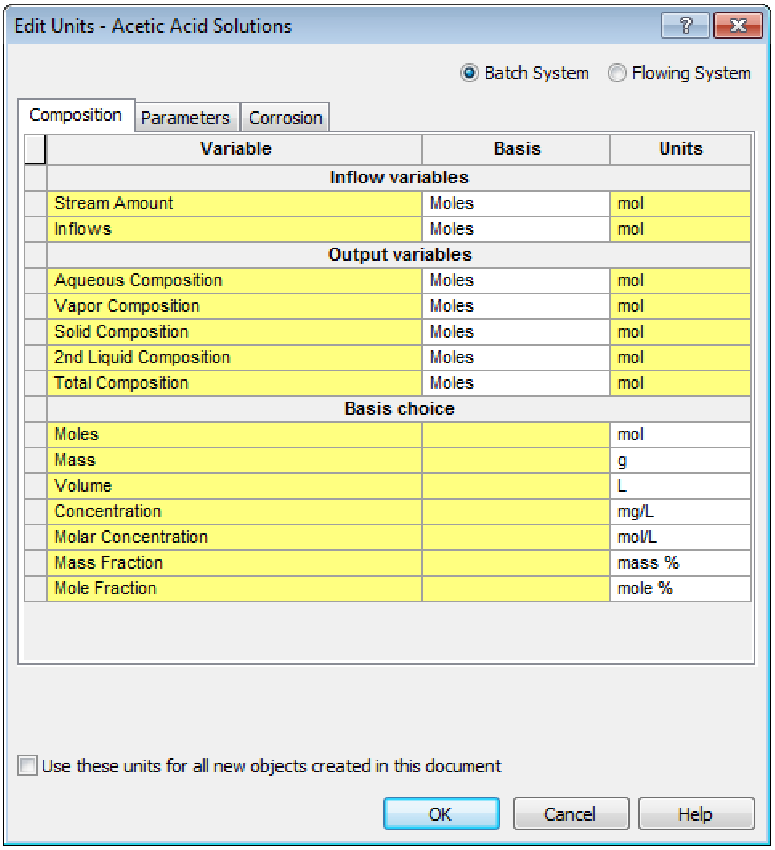


Figure 7-3 Units Manager Dialog

6. ***Click*** on the **Customize** radio button.



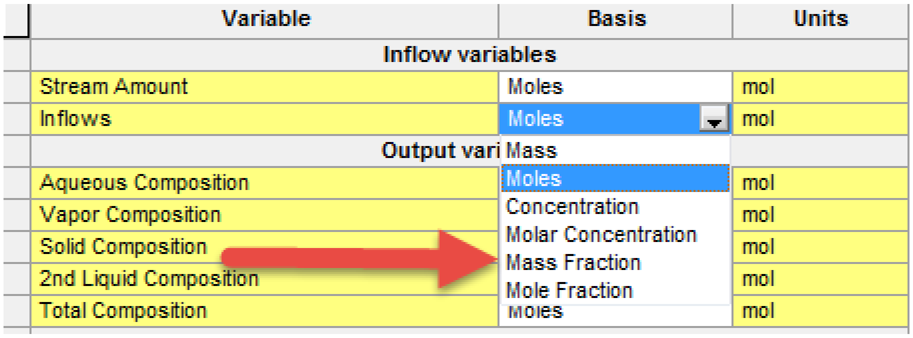
● Batch System ○ Flowing System

Variable	Basis	Units
Inflow variables		
Stream Amount	Moles	mol
Inflows	Moles	mol
Output variables		
Aqueous Composition	Moles	mol
Vapor Composition	Moles	mol
Solid Composition	Moles	mol
2nd Liquid Composition	Moles	mol
Total Composition	Moles	mol
Basis choice		
Moles		mol
Mass		g
Volume		L
Concentration		mg/L
Molar Concentration		mol/L
Mass Fraction		mass %
Mole Fraction		mole %

☐ Use these units for all new objects created in this document

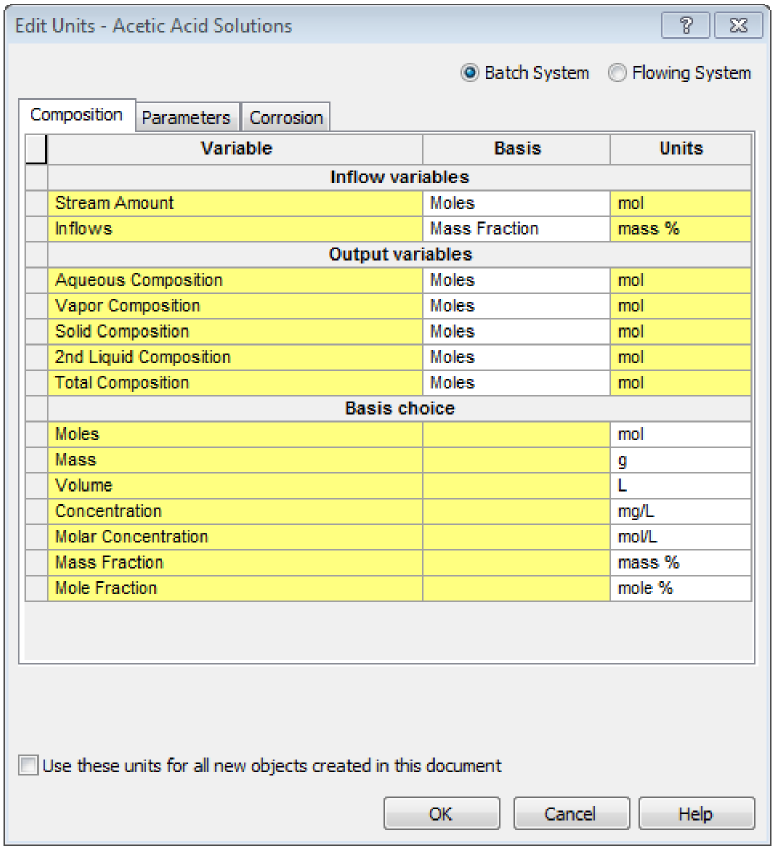
Figure 7-4

7. Locate the **Inflows** line currently displaying ***Moles.*** Click in the cell and change it to **Mass Fraction.**



Variable	Basis	Units
Inflow variables		
Stream Amount	Moles	mol
Inflows	Moles	mol
Output vari		
Aqueous Composition		mol
Vapor Composition		mol
Solid Composition		mol
2nd Liquid Composition		mol
Total Composition	Moles	mol

Figure 7-5 Selecting Mass Fraction



Edit Units - Acetic Acid Solutions

● Batch System ○ Flowing System

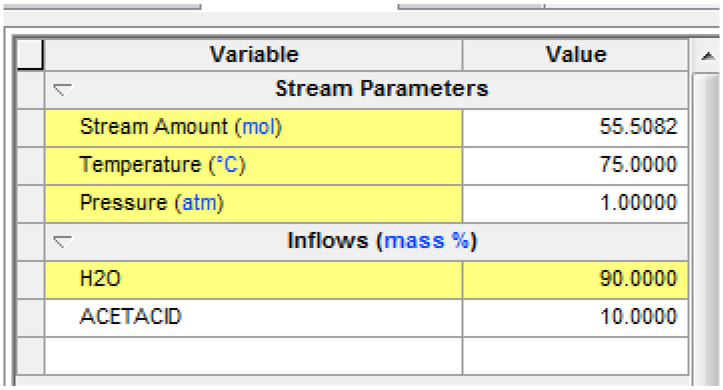
Variable	Basis	Units
Inflow variables		
Stream Amount	Moles	mol
Inflows	Mass Fraction	mass %
Output variables		
Aqueous Composition	Moles	mol
Vapor Composition	Moles	mol
Solid Composition	Moles	mol
2nd Liquid Composition	Moles	mol
Total Composition	Moles	mol
Basis choice		
Moles		mol
Mass		g
Volume		L
Concentration		mg/L
Molar Concentration		mol/L
Mass Fraction		mass %
Mole Fraction		mole %

☐ Use these units for all new objects created in this document

Figure 7-6

8. ***Click* <u>**OK**</u>** to close the **<u>Units Manager</u>** until you are back at the **<u>Definition</u>** tab.
9. We are now ready to enter the conditions. When using mass-fraction units, it is assumed that the amount of water will be the difference of the components entered. In this case, the value field is highlighted in yellow to inform you that the value will be determined from the values of the other components.

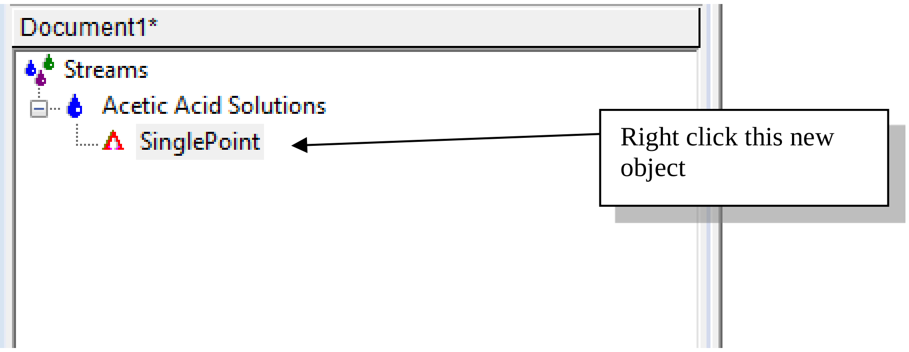
Enter a value of 10 % for acetic acid, 75 °C, 1 atmosphere pressure.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	75.0000
Pressure (atm)	1.00000
Inflows (mass %)	
H2O	90.0000
ACETACID	10.0000

Figure 7-7 the filled out grid for 10 % Acetic Acid

10. ***Click*** on the **Add Calculation** ***button and select*** **Single Point**.
11. Select the default calculation type – **Isothermal**.
12. ***Right-click*** the new object in the tree-view (usually with a name similar to SinglePoint1).



Right click this new object

Figure 7-8 Right-click the new object

This will display a menu.

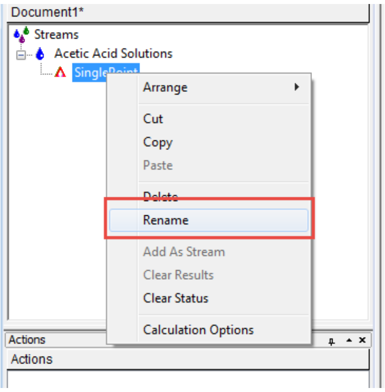


Figure 7-9 Right-click menu choices for the tree-view

Select **Rename** from the list. (Double click on the object name works too)

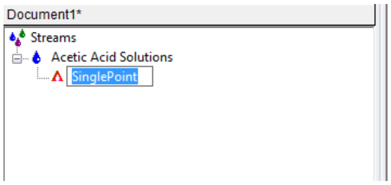


Figure 7-10 Renaming the object

The original text is now high-lighted so you can edit this field. Rename the value to ***pH.***

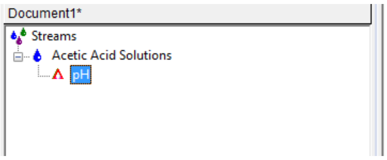
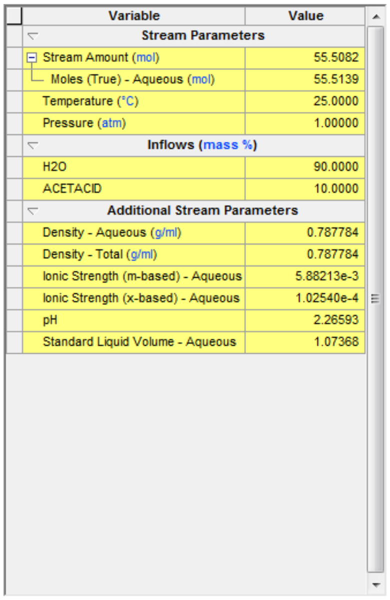


Figure 7-11 The renamed object

13. ***Click*** on the **Calculate** button to start the calculation.
14. After the calculation is complete you may:
    a. ***Click*** on the ***Output*** mini-tab display **Calculated** values.
    b. ***Right-click*** on the grid to display **Sections>** **Additional Stream Parameters**



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Moles (True) - Aqueous (mol)	55.5139
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mass %)	
H2O	90.0000
ACETACID	10.0000
Additional Stream Parameters	
Density - Aqueous (g/ml)	0.787784
Density - Total (g/ml)	0.787784
Ionic Strength (m-based) - Aqueous	5.88213e-3
Ionic Strength (x-based) - Aqueous	1.02540e-4
pH	2.26593
Standard Liquid Volume - Aqueous	1.07368

Figure 7-12 Results, the pH is approximately 2.3

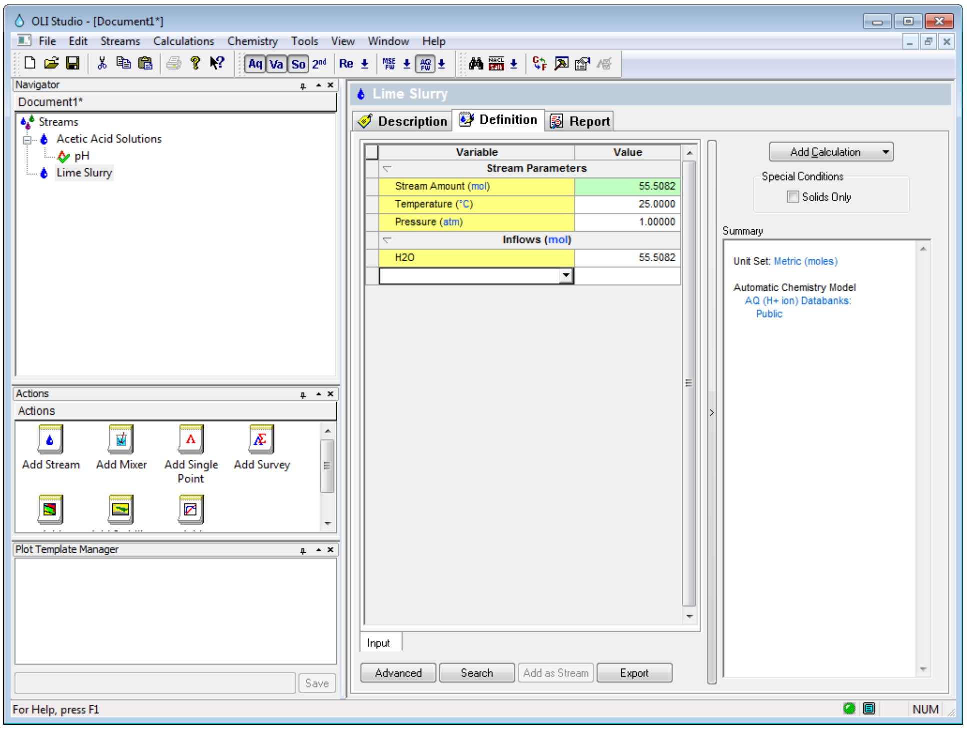
The resultant pH is approximately 2.3.

Mix Calculations

In this example, we are going to mix two streams of different compositions. In doing so we will determine the temperature rise of a 10-weight percent solution of calcium hydroxide mixed with pure 10 weight percent HCl. To do this, we will need to create both streams separately. Along the way, we will rename a species to a more useful name.

If you have not already done so, please start the OLI Studio. We will be adding a 10 weight-percent calcium hydroxide slurry. By now you should be familiar with adding these components.

1. Create a stream named ***Lime Slurry.***
2. ***Click*** on the **Definition** Tab.



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

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 7-13 Standard Stream Definition

3. ***Click*** on the **Tools/Names Manager** menu item (see next figure).

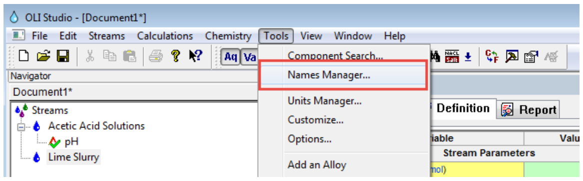
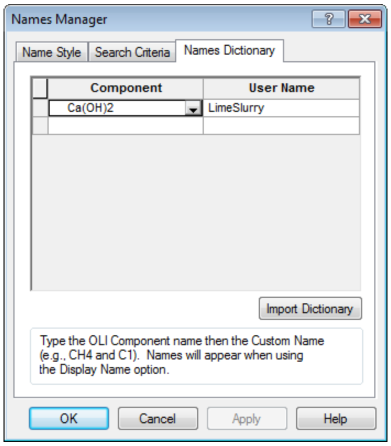


Figure 7-14 Menu Item/Tools/Names Manager

4. ***Click*** on the **Names Dictionary** tab.

We can now enter a name of a species already defined in the software. This will be entered in the **Component** column. We can then rename the species in the **User Name** column.

5. *Scroll down to find an empty cell.*
6. Enter ***$Ca(OH)_2$*** in the **Component** column. ***Left-click*** on the **User Name** column and enter ***LimeSlurry.*** (Note: Do not use spaces or special characters)



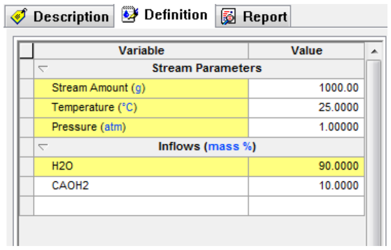
Component	User Name
Ca(OH)2	LimeSlurry

Type the OLI Component name then the Custom Name (e.g., CH4 and C1). Names will appear when using the Display Name option.

Figure 7-15 Defining Calcium Hydroxide as "Lime Slurry"

7. ***Click*** on **<u>Apply</u>** and then **<u>OK</u>.**
8. As you did in the previous example for the **"**Isothermal**"** calculation. Select ***Mass-Fraction*** units from the Units Manager for **<u>inflows</u>** and ***Mass*** for **<u>Stream Amount</u>**.
9. ***Enter the following conditions***:

   - Temperature = 25 °C
   - Pressure = 1 atmosphere
   - Stream Amount = 1000 g
   - LimeSlurry = 10 mass %



Variable	Value
Stream Parameters	
Stream Amount (g)	1000.00
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mass %)	
H2O	90.0000
CAOH2	10.0000

Figure 7-16 Lime Slurry Stream Definition (using display name from Names Manager Tool)

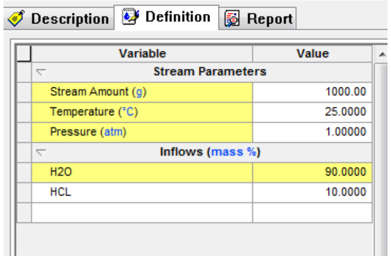
The entered name will revert to the standard name.

We will now repeat these steps but using a 10-weight percent Hydrochloric acid solution. The input for this step is shown in the following figure.

10. Create a new Stream named ***Acid.***

11. Enter the following conditions:

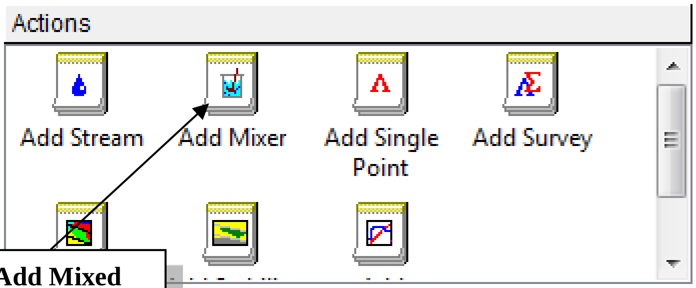
   - Temperature = 25 °C
   - Pressure = 1 atmosphere
   - Stream Amount = 1000 g
   - HCl = 10 mass %



Variable	Value
Stream Parameters	
Stream Amount (g)	1000.00
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mass %)	
H2O	90.0000
HCL	10.0000

Figure 7-17 Standard stream definition for 10 wt % HCl

We will now have to add a mix calculation to determine the temperature raise.

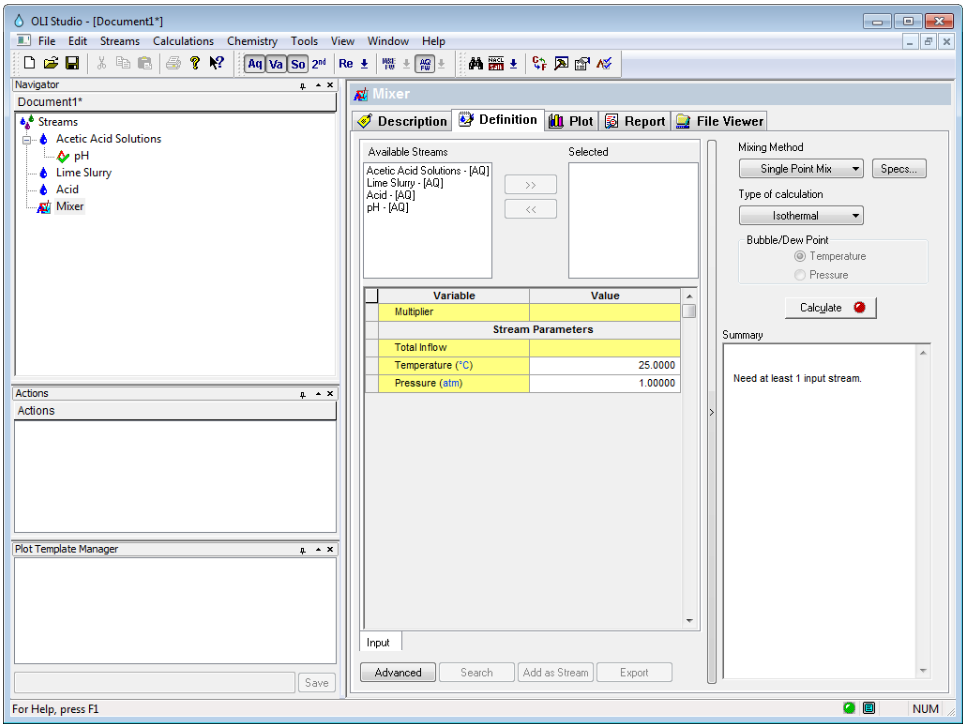


Click on the **Add Mixed Stream** icon.

igure 7-18 Adding a mixer calculation.

12. ***Click*** on the **<u>Add Mixer</u>** icon in the **<u>Actions</u>** panel.

This will display all possible streams for the mix calculation. There is no limit to the number of streams to be mixed. We will only select two streams.



Available Streams:
Acetic Acid Solutions - [AQ]
Lime Slurry - [AQ]
Acid - [AQ]
pH - [AQ]

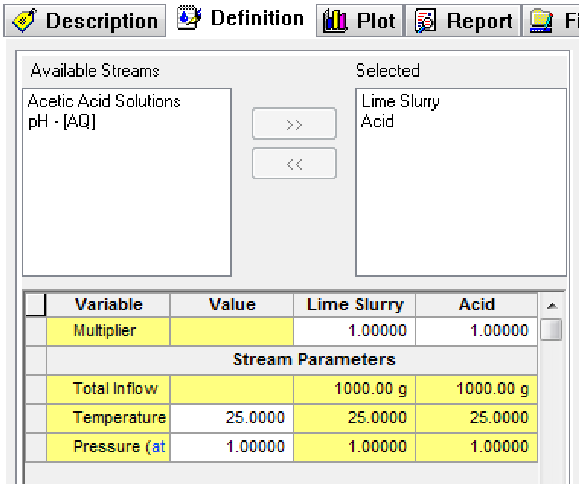
Variable	Value
Multiplier	
Stream Parameters	
Total Inflow	
Temperature (°C)	25.0000
Pressure (atm)	1.00000

Need at least 1 input stream.

Figure 7-19 The input for the mix calculations.

13. Select the **<u>Lime Slurry</u>** stream from the available list and ***click*** on the <u>>></u> button.

14. Select the **<u>Acid</u>** ***stream*** and ***click*** on the <u>>></u> button. The display should look like this:



Available Streams
Acetic Acid Solutions
pH - [AQ]

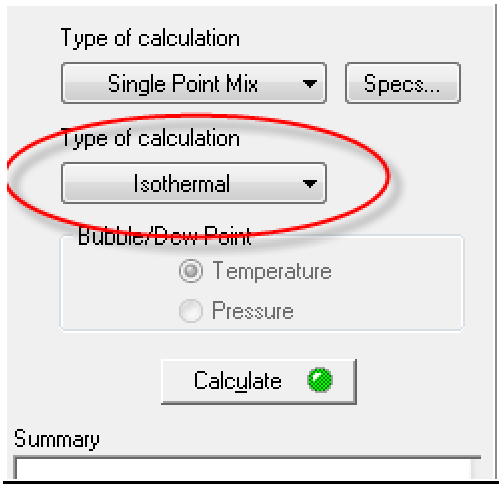
Selected
Lime Slurry
Acid

Variable	Value	Lime Slurry	Acid
Multiplier		1.00000	1.00000
Stream Parameters			
Total Inflow		1000.00 g	1000.00 g
Temperature	25.0000	25.0000	25.0000
Pressure (at	1.00000	1.00000	1.00000

Figure 7-20 Selecting streams. You may have a different list.

The default calculation is to hold a single point calculation at isothermal conditions. We want to see if a temperature rise will occur. An adiabatic calculation is required to see this effect.

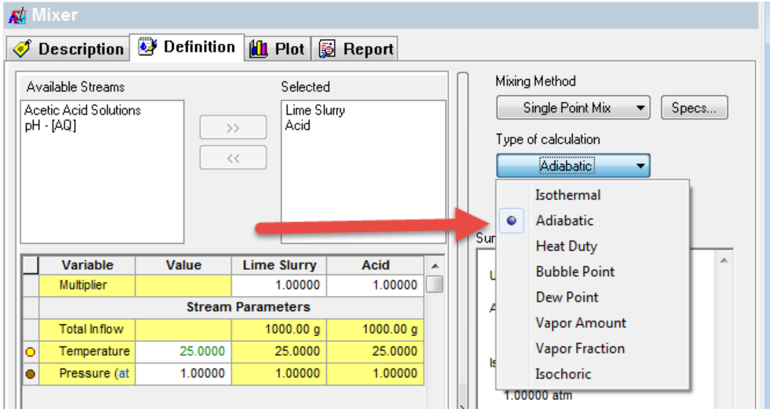
15. ***Click*** on the second **<u>Type of Calculation</u>** button.



Type of calculation
Single Point Mix

Type of calculation
Isothermal

Figure 7-21 Changing the type of calculation



Available Streams: Acetic Acid Solutions, pH - [AQ]

Selected: Lime Slurry, Acid

Mixing Method: Single Point Mix

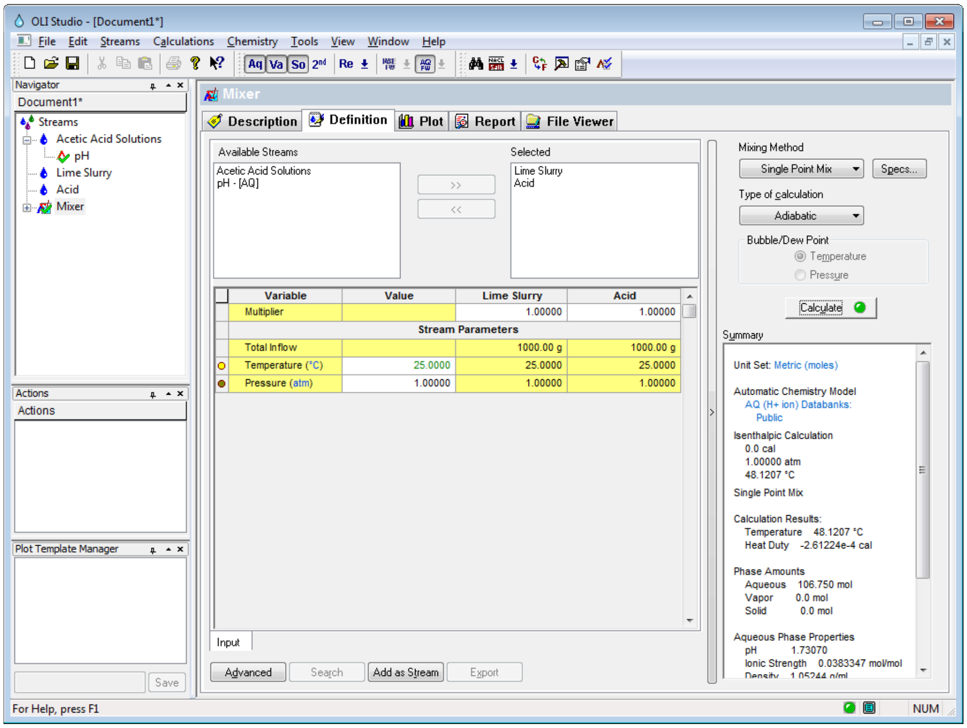
Type of calculation: Adiabatic

Variable	Value	Lime Slurry	Acid
Multiplier		1.00000	1.00000
Stream Parameters			
Total Inflow		1000.00 g	1000.00 g
Temperature	25.0000	25.0000	25.0000
Pressure (at	1.00000	1.00000	1.00000

Figure 7-22 Selecting the mix calculation type.

***Select* <u>Adiabatic</u>.**

16. Click on the **<u>Calculate</u>** button.



Available Streams: Acetic Acid Solutions, pH - [AQ]

Selected: Lime Slurry, Acid

Mixing Method: Single Point Mix

Type of calculation: Adiabatic

Variable	Value	Lime Slurry	Acid
Multiplier		1.00000	1.00000
Stream Parameters			
Total Inflow		1000.00 g	1000.00 g
Temperature (°C)	25.0000	25.0000	25.0000
Pressure (atm)	1.00000	1.00000	1.00000

Summary

```
Unit Set: Metric (moles)

Automatic Chemistry Model
   AQ (H+ ion) Databanks:
      Public
Isenthalpic Calculation
   0.0 cal
   1.00000 atm
   48.1207 °C
Single Point Mix

Calculation Results:
   Temperature   48.1207 °C
   Heat Duty   -2.61224e-4 cal

Phase Amounts
   Aqueous   106.750 mol
   Vapor      0.0 mol
   Solid       0.0 mol

Aqueous Phase Properties
   pH         1.73070
   Ionic Strength   0.0383347 mol/mol
   Density   1.05244 g/ml
```

Figure 7-23 The results of the mix.

The **<u>Summary Box</u>** shows the results of the calculation. You can see that the temperature increased from 25 degrees centigrade to approximately 48.1 degrees centigrade. There was a considerable heat of reaction.

Bubble Point

Bubble points calculations are a calculation where the temperature or pressure of the system is adjusted such that a very small amount of vapor will form. This is another way of saying that the bubble point calculation is a determination of the boiling point.

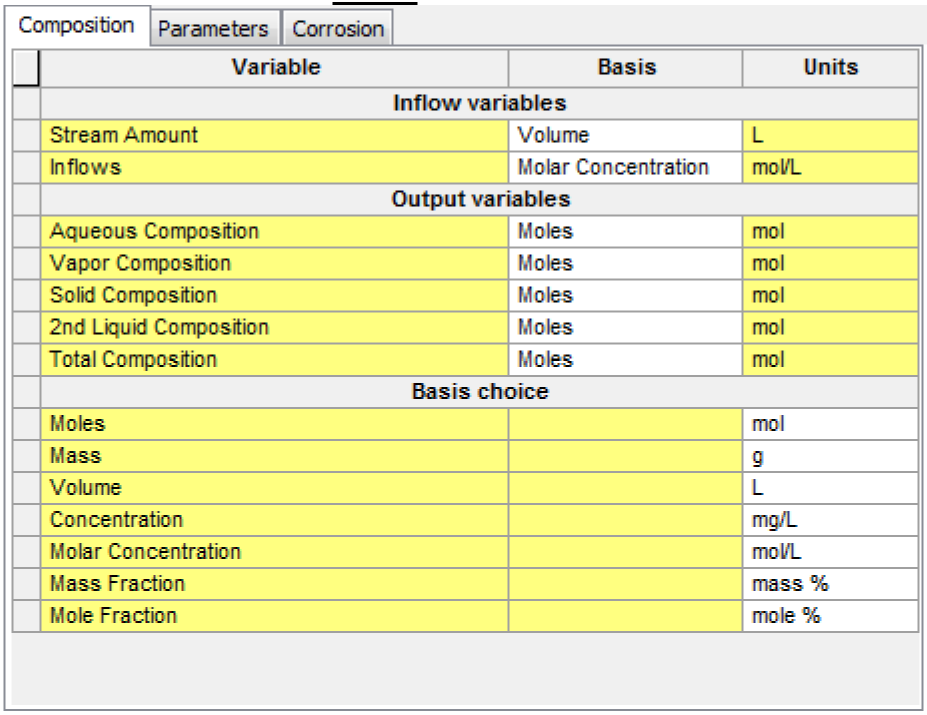
Normally we determine the temperature at which a solution will boil. If the pressure is set to 1 atmosphere, then we are calculating the **Normal Boiling Point**. If we hold the temperature constant then we can determine the bubble point pressure.

Bubble point calculations are useful for determining the saturation pressure or temperature of a system. Many systems will have a vapor phase when we least expect it. Calculating the saturation pressure or temperature will allow us to set our conditions appropriately.

In this example, we are using a 1 molar Acetone solution in water. Remember the molal concentration scale has moles of solute per kilogram of water. So, we have 1.0 moles of Acetone and 1 liter of solution.

We are going to let you set up this calculation primarily on your own. The following is a set of steps to help you along.

1. Define a new stream and call it ***Bubble.***
2. ***Click*** on the **Definition** tab.
3. Create a new set of units (see the Isothermal example for more details).
4. Select **Tools/Units Manager** from the **Tools** menu item.
5. Select the **Customize** button.
6. Set the **Inflows** to *Molar Concentration*



Variable	Basis	Units
Inflow variables		
Stream Amount	Volume	L
Inflows	Molar Concentration	mol/L
Output variables		
Aqueous Composition	Moles	mol
Vapor Composition	Moles	mol
Solid Composition	Moles	mol
2nd Liquid Composition	Moles	mol
Total Composition	Moles	mol
Basis choice		
Moles		mol
Mass		g
Volume		L
Concentration		mg/L
Molar Concentration		mol/L
Mass Fraction		mass %
Mole Fraction		mole %

Figure 7-24

7. ***Click*** on **Apply**, **OK** or **Close** as appropriate.
8. Enter the following conditions:
   - Stream Amount = 1 L
   - Temperature = 25 C
   - Pressure = 1 Atmosphere
   - Water = (adjusted)
   - Acetone = 1.0 molarity

9. Add a **Single Point** calculation.

10. From the **<u>Type of Calculation</u>** button, select **<u>Bubble Point</u>**.

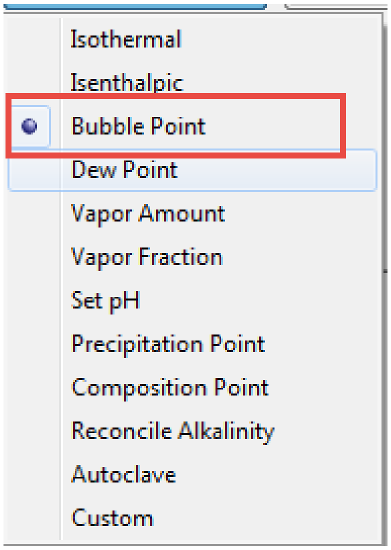
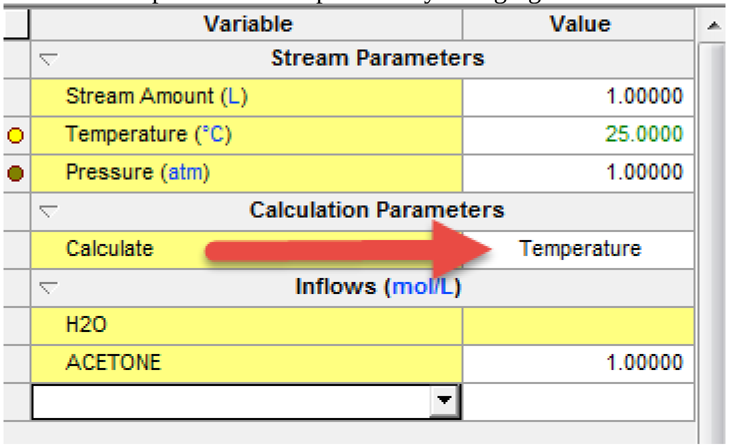


Figure 7-25 Selecting Bubble point calculations

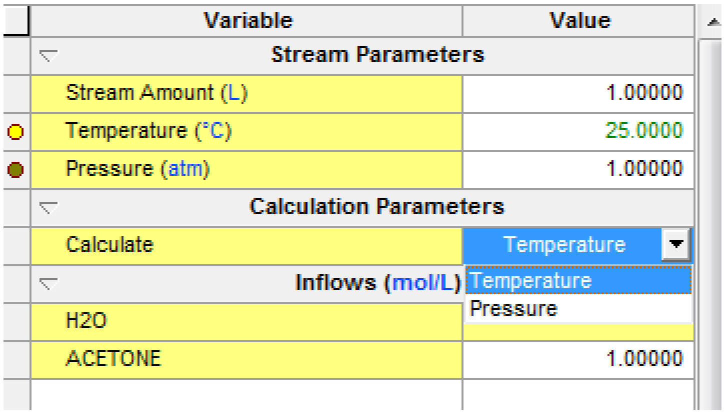
11. A new section appears in the grid. You can now select either a bubble point pressure or temperature by changing the value in the box:



	Variable	Value
	Stream Parameters	
	Stream Amount (L)	1.00000
○	Temperature (°C)	25.0000
●	Pressure (atm)	1.00000
	Calculation Parameters	
	Calculate	Temperature
	Inflows (mol/L)	
	H2O	
	ACETONE	1.00000

Figure 7-26

If you click in the box you can change the calculation from temperature to pressure:

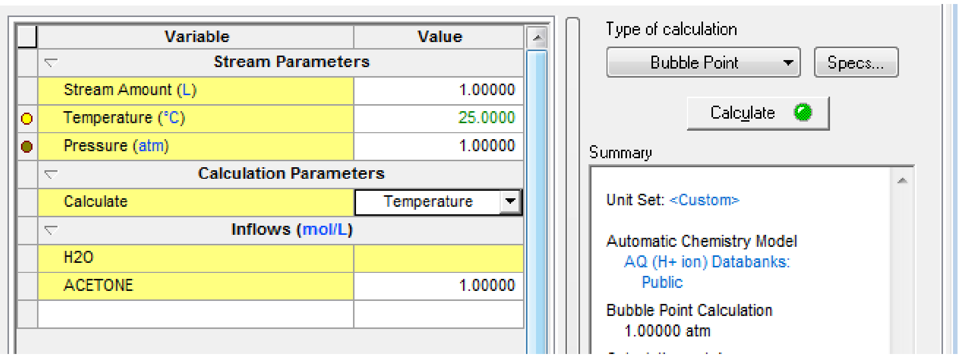


	Variable	Value
	Stream Parameters	
	Stream Amount (L)	1.00000
○	Temperature (°C)	25.0000
●	Pressure (atm)	1.00000
	Calculation Parameters	
	Calculate	Temperature
	Inflows (mol/L)	Temperature Pressure
	H2O	
	ACETONE	1.00000

Figure 7-27

For this calculation select ***Temperature***.

Notice the presence of a “Free Dot” next to **Temperature** to indicate that value will be adjusted.



	Variable	Value
	Stream Parameters	
	Stream Amount (L)	1.00000
○	Temperature (°C)	25.0000
●	Pressure (atm)	1.00000
	Calculation Parameters	
	Calculate	Temperature
	Inflows (mol/L)	
	H2O	
	ACETONE	1.00000

Type of calculation: Bubble Point

Summary

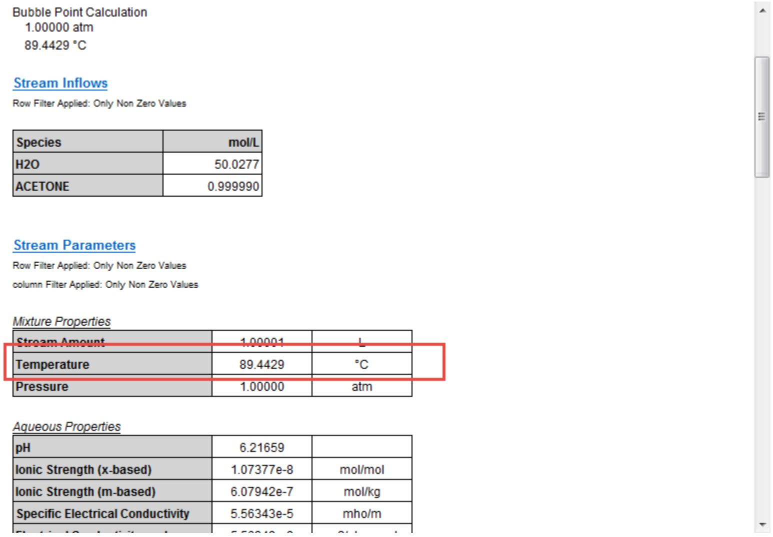
Unit Set: <Custom>

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Bubble Point Calculation
1.00000 atm

Figure 7-28 Bubble point temperatures are selected

12. ***Click*** on the **Calculate** button.
13. ***Click*** on the **Report** tab to see the results. The temperature is 89.4 C.
14. Scroll down to see more information.



Bubble Point Calculation
1.00000 atm
89.4429 °C

Stream Inflows

Row Filter Applied: Only Non Zero Values

Species	mol/L
H2O	50.0277
ACETONE	0.999990

Stream Parameters

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

Mixture Properties

Stream Amount	1.00001	L
Temperature	89.4429	°C
Pressure	1.00000	atm

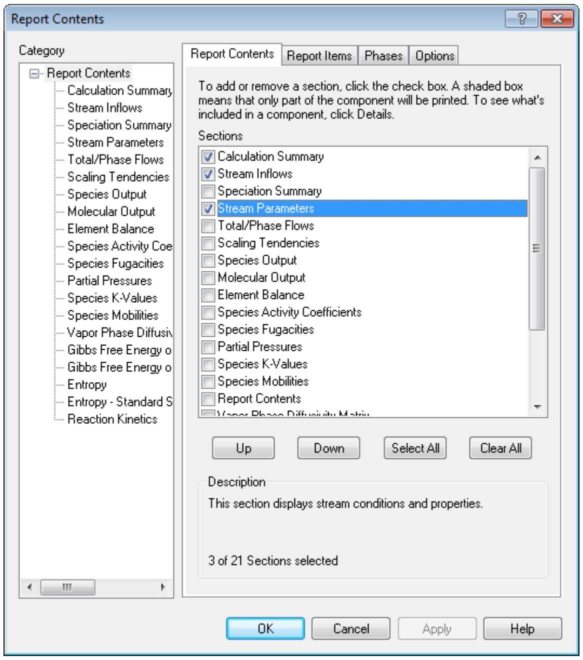
Aqueous Properties

pH	6.21659	
Ionic Strength (x-based)	1.07377e-8	mol/mol
Ionic Strength (m-based)	6.07942e-7	mol/kg
Specific Electrical Conductivity	5.56343e-5	mho/m

Figure 7-29 The bubble point is 89.4 C

There is a lot of information that is displayed just for this relatively simple case. The user does have the option to limit the display of data. Remember that the data is not lost, merely not displayed.

15. ***Click*** on the **Customize** button.
16. By default, all the options are selected. Clear all the **Check Boxes** leaving only **Calculation Summary**, **Stream Inflows** and **Stream Parameters** selected.



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

Sections

- ☑ Calculation Summary
- ☑ Stream Inflows
- ☐ Speciation Summary
- ☑ Stream Parameters
- ☐ Total/Phase Flows
- ☐ Scaling Tendencies
- ☐ Species Output
- ☐ Molecular Output
- ☐ Element Balance
- ☐ Species Activity Coefficients
- ☐ Species Fugacities
- ☐ Partial Pressures
- ☐ Species K-Values
- ☐ Species Mobilities
- ☐ Report Contents

Description

This section displays stream conditions and properties.

3 of 21 Sections selected

Figure 7-30 Customizing information displayed in a Report

17. ***Click** the **OK** button.* Scroll down to see that some of the information has been suppressed.

Dew Point

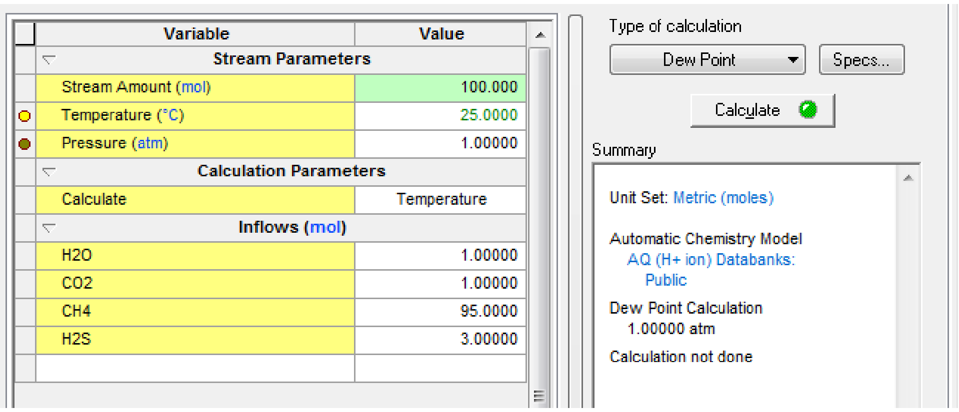
It is frequently useful to determine the temperature or pressure at which a gas will condense. In this example, we have a simple hydrocarbon laden gas. We wish to determine the condensation temperature otherwise known as the dew point temperature.

In this example, we have the following conditions:

Initial Temperature	=	25	°C	(This is an initial guess)
Pressure	=	1	atmosphere	
H_2O	=	1	mole	
CO_2	=	1	mole	
CH_4	=	95	moles	
H_2S	=	3	moles	

In previous examples you have entered data for the stream. We will not repeat them here. The following figure is the set up for the Dew Point calculation. Please enter the data.

Click on the Calculate button when ready.



Variable	Value
Stream Parameters	
Stream Amount (mol)	100.000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Calculate	Temperature
Inflows (mol)	
H2O	1.00000
CO2	1.00000
CH4	95.0000
H2S	3.00000

Type of calculation: Dew Point

Summary

Unit Set: Metric (moles)

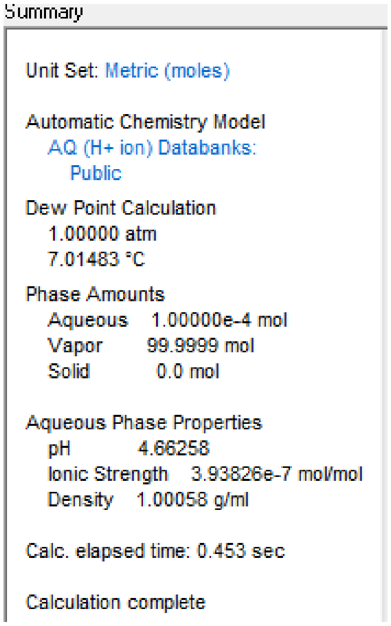
Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Dew Point Calculation
1.00000 atm

Calculation not done

Figure 7-31 Bubble Point Temperature Stream Definition

After the calculation is complete, the resultant temperature is approximately 7.01483 C.



Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Dew Point Calculation
1.00000 atm
7.01483 °C

Phase Amounts
Aqueous 1.00000e-4 mol
Vapor 99.9999 mol
Solid 0.0 mol

Aqueous Phase Properties
pH 4.66258
Ionic Strength 3.93826e-7 mol/mol
Density 1.00058 g/ml

Calc. elapsed time: 0.453 sec

Calculation complete

Figure 7-32 Results with standard model options

Vapor Amounts/Fractions

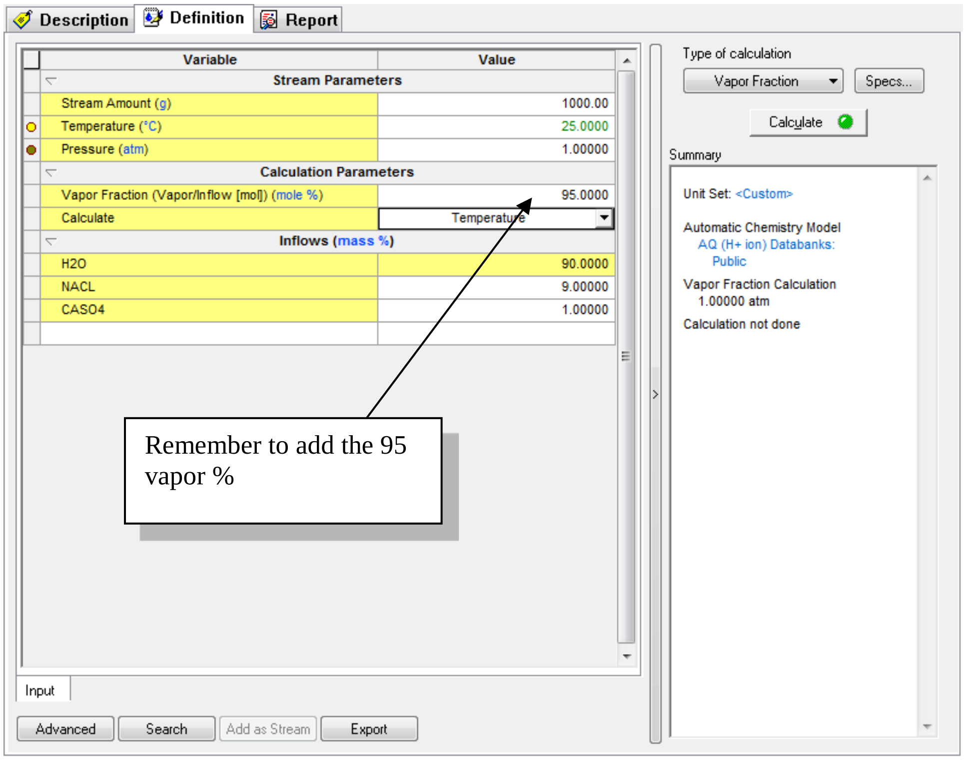
In this example, we have a brine in which we want to evaporate to concentrate the brine. To do this we will adjust the temperature (or pressure) to create a specified amount of vapor (or vapor fraction).

In this case we want to adjust the temperature such that our system is 95 percent vapor (on a mole basis). Please enter the following conditions into a stream definition:

Temperature	=	25	ºC
Pressure	=	1	Atmosphere
NaCl	=	9.0	mass %
$CaSO_4$	=	1.0	mass %
Vapor Fraction	=	95.0	mole %

The component compositions are grams of species per 100 grams of solution (a weight fraction). The vapor fraction is in moles of vapor per mole of solution and is a mole fraction.

You must change the units for this example. You already have done this previously.



Variable	Value
Stream Parameters	
Stream Amount (g)	1000.00
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Vapor Fraction (Vapor/Inflow [mol]) (mole %)	95.0000
Calculate	Temperature
Inflows (mass %)	
H2O	90.0000
NACL	9.00000
CASO4	1.00000

Unit Set: <Custom>

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Vapor Fraction Calculation
1.00000 atm

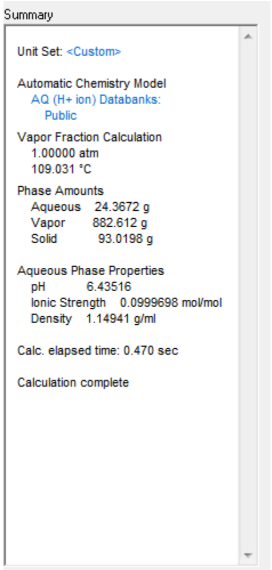
Calculation not done

Remember to add the 95 vapor %

Figure 7-33 Vapor Fraction Stream Definition

Click on **Calculate** to start.

After the program finishes the calculation, the temperature is approximately 109 °C. At this temperature, 95 percent of the system will be vapor.



Unit Set: <Custom>

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Vapor Fraction Calculation
1.00000 atm
109.031 °C

Phase Amounts
Aqueous 24.3672 g
Vapor 882.612 g
Solid 93.0198 g

Aqueous Phase Properties
pH 6.43516
Ionic Strength 0.0999698 mol/mol
Density 1.14941 g/ml

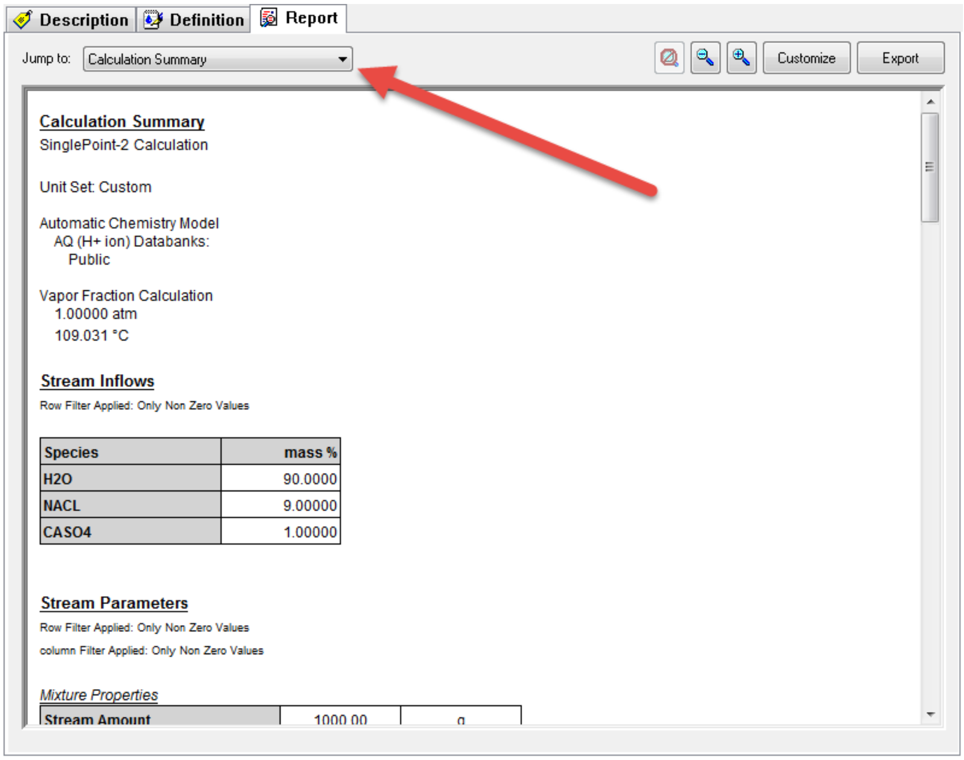
Calc. elapsed time: 0.470 sec

Calculation complete

Figure 7-34 Summary of Vapor Fraction

Desalinating brines often create solids known as scales. These scales are often detrimental to the operation of the desalination unit. We should review the reports to see how much solid has been produced.

Click on the **Report** tab.



Calculation Summary
SinglePoint-2 Calculation

Unit Set: Custom

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Vapor Fraction Calculation
1.00000 atm
109.031 °C

Stream Inflows
Row Filter Applied: Only Non Zero Values

Species	mass %
H2O	90.0000
NACL	9.00000
CASO4	1.00000

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

Mixture Properties

Stream Amount	1000.00	g

Figure 7-35

Use the drop-down box indicated in Figure 7-35 to find the **Species Output** section.

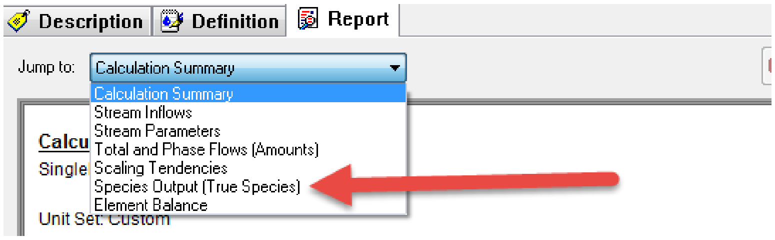
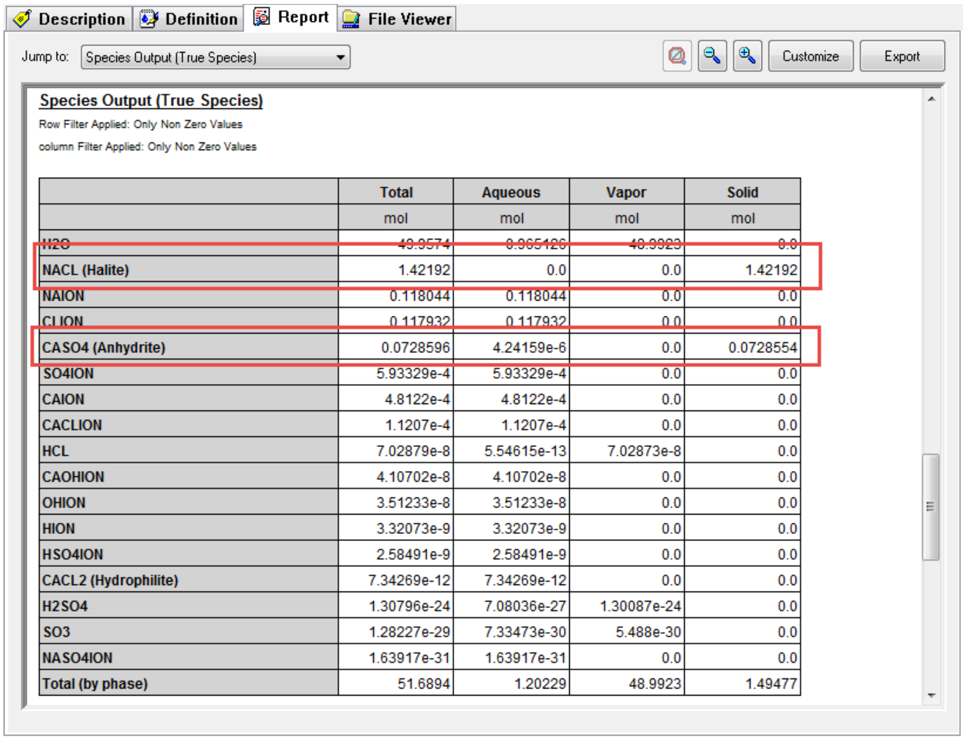


Figure 7-36

The following figure shows that both solid sodium chloride (halite) and calcium sulfate (anhydrite) have scaled out. The operator may wish to divide the desalination unit into smaller units to prevent scaling.



Jump to: Species Output (True Species)

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
H2O	49.9574	0.965126	48.9923	0.0
NACL (Halite)	1.42192	0.0	0.0	1.42192
NAION	0.118044	0.118044	0.0	0.0
CLION	0.117932	0.117932	0.0	0.0
CASO4 (Anhydrite)	0.0728596	4.24159e-6	0.0	0.0728554
SO4ION	5.93329e-4	5.93329e-4	0.0	0.0
CAION	4.8122e-4	4.8122e-4	0.0	0.0
CACLION	1.1207e-4	1.1207e-4	0.0	0.0
HCL	7.02879e-8	5.54615e-13	7.02873e-8	0.0
CAOHION	4.10702e-8	4.10702e-8	0.0	0.0
OHION	3.51233e-8	3.51233e-8	0.0	0.0
HION	3.32073e-9	3.32073e-9	0.0	0.0
HSO4ION	2.58491e-9	2.58491e-9	0.0	0.0
CACL2 (Hydrophilite)	7.34269e-12	7.34269e-12	0.0	0.0
H2SO4	1.30796e-24	7.08036e-27	1.30087e-24	0.0
SO3	1.28227e-29	7.33473e-30	5.488e-30	0.0
NASO4ION	1.63917e-31	1.63917e-31	0.0	0.0
Total (by phase)	51.6894	1.20229	48.9923	1.49477

Figure 7-37 Vapor Fraction results

Click here for a completed working file for this chapter: Chapter 07 Tour

8. Multiple Point Calculations

Objectives

We now continue to explore some of the other calculations in the OLI Studio. In this chapter, we'll explore multiple point calculations. As in chapter 7, we will introduce some additional features.

1. Temperature
    - Additional Specifications
2. Pressure
3. Composition
4. pH
5. Secondary Surveys
6. Mixer Surveys
7. Cascading Mixers

Temperature

Many thermodynamic properties are strong functions of temperature. It is useful to plot our systems as a function of temperature. In this example, we will determine the solubility of benzoic acid in the temperature range of 0 to 100 degrees centigrade.

As we do this, the aqueous composition of the solution will change as some of the benzoic acid in the solid phase will dissolve into the aqueous phase.

By now you should be very familiar with entering data into the grids. For this example, enter the following:

Stream Amount = **55.5082 mol (Default)**

Temperature = **25.0 C**

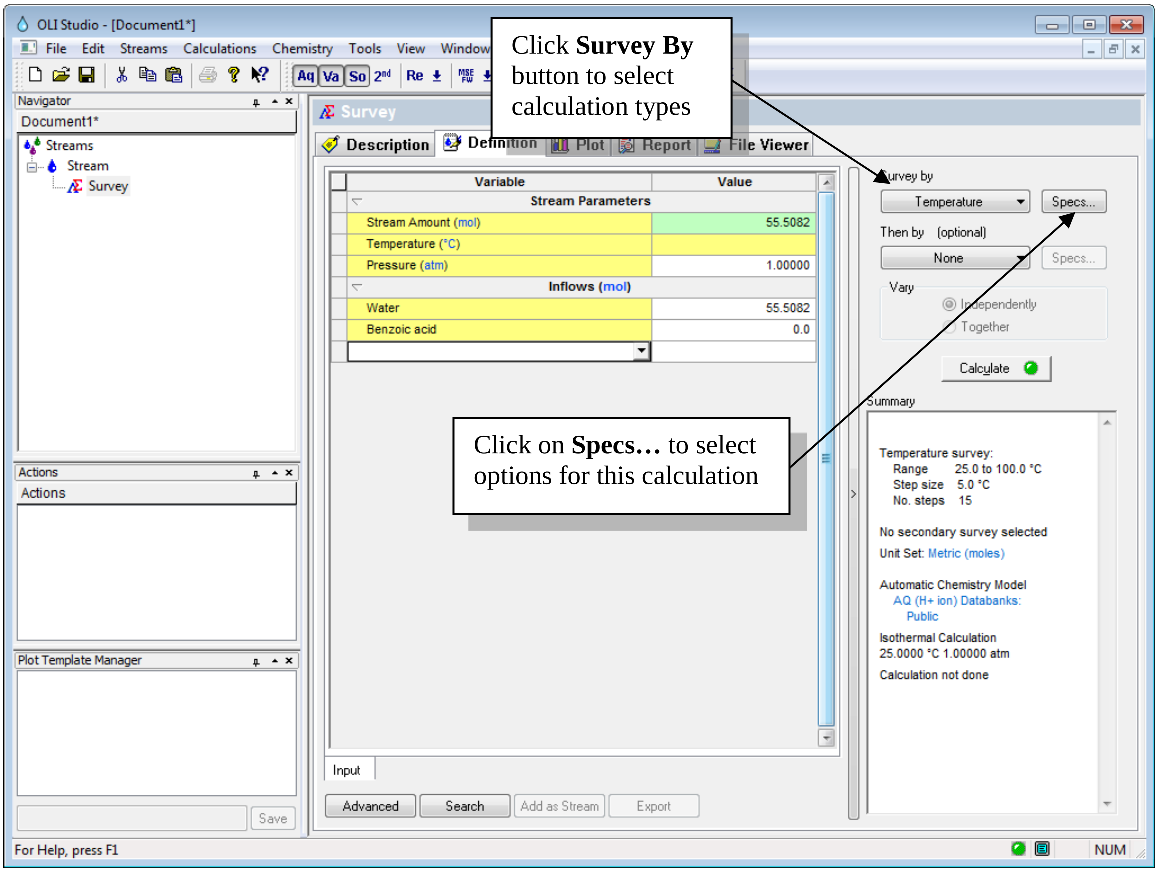
Pressure = **1.0 Atm**

Water = **55.5082 mol**

Benzoic Acid = **0.0 mol**

Select **<u>Survey</u>** for the calculation type.

The **<u>Definition</u>** should look like the figure below.



Click **Survey By** button to select calculation types

Click on **Specs…** to select options for this calculation

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	
Pressure (atm)	1.00000
Inflows (mol)	
Water	55.5082
Benzoic acid	0.0

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

No secondary survey selected

Unit Set: Metric (moles)

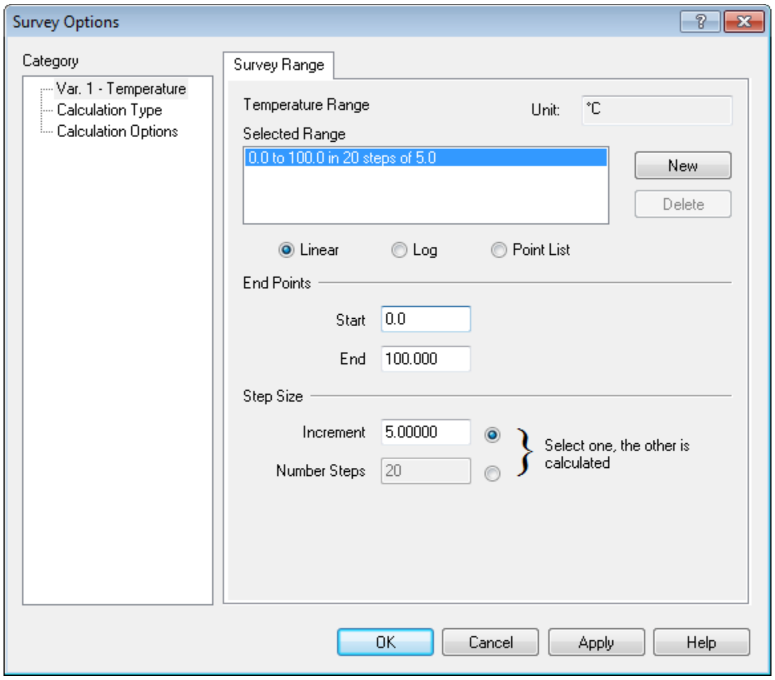
Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
25.0000 °C 1.00000 atm

Calculation not done

Figure 8-1 Stream Definition for Temperature survey

The temperature survey is the default. Now click on the **<u>Specs</u>** button to display this figure. We will be using a temperature range of 0 to 100 C.



Temperature Range

Unit: °C

Selected Range: 0.0 to 100.0 in 20 steps of 5.0

● Linear ○ Log ○ Point List

Start 0.0

End 100.000

Increment 5.00000 ●

Number Steps 20 ○

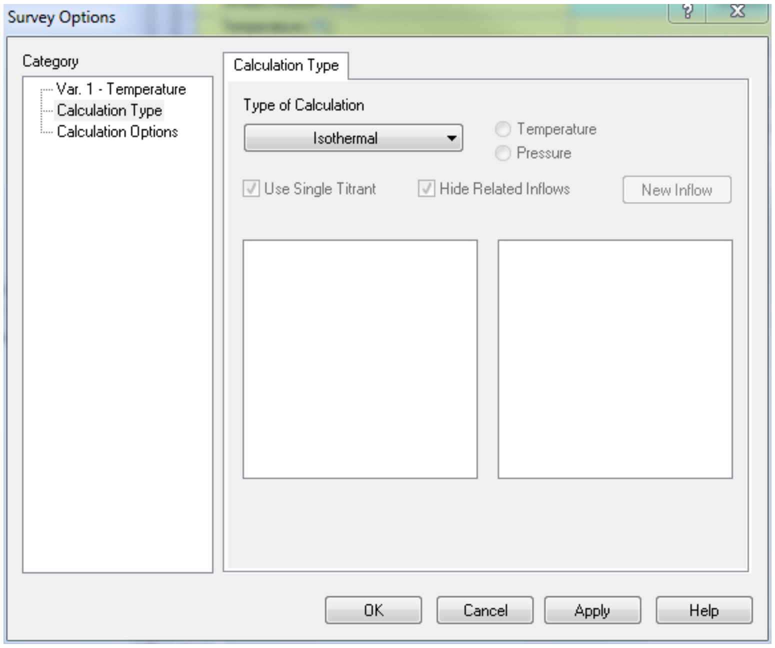
Select one, the other is calculated

Figure 8-2 Spec Options - Range

Make sure the **<u>Increment</u>** is set to 5 degrees C.

Now ***Click*** on **<u>Calculation Type</u>**

We will now set up a secondary calculation to determine the amount of benzoic acid necessary to saturate the solution (See Chapter 7 – Precipitation Point calculation)



Type of Calculation: Isothermal

○ Temperature

○ Pressure

☑ Use Single Titrant ☑ Hide Related Inflows

Figure 8-3 the default calculation type dialog.

Click on the **<u>Type of Calculation</u>** button.

The list of calculations is like ones found in the single point calculations chapter (see chapter 7).

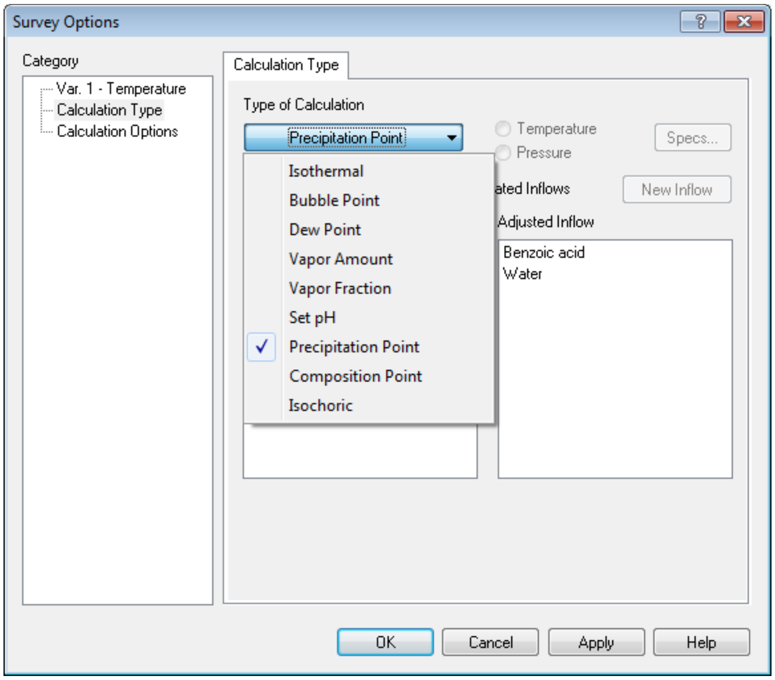


Figure 8-4 Specifying calculation type.

Select **Precipitation Point**.

You will now be given a choice of which solid to "FIX". In this case, there is only one possible choice, ***Benzoic Acid – Sol***. You will also be given a choice of an inflow to adjust. The inflow species is adjusted such that the scaling tendency of the selected solid is exactly 1.0. It is generally a good idea to pick an inflow with the same materials as the selected solid.

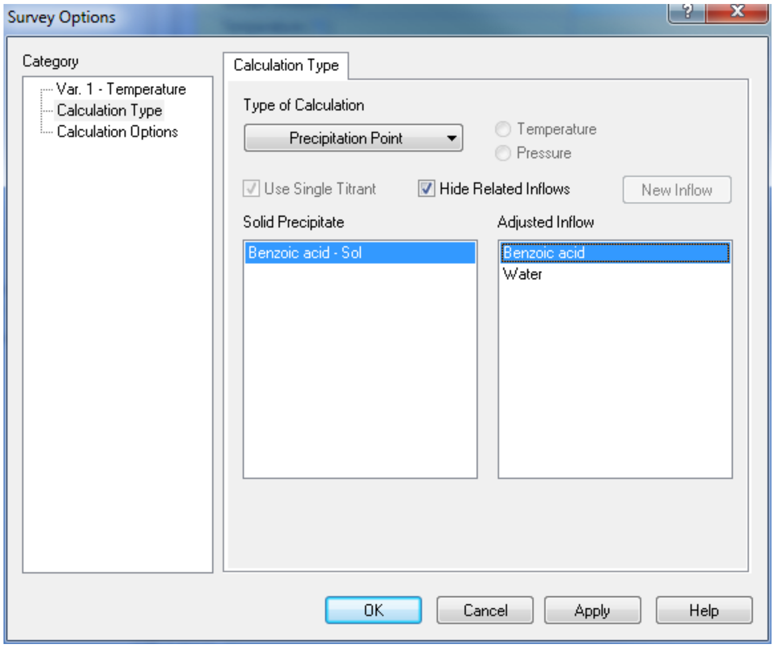


Figure 8-5 Selecting benzoic acid solid

Select ***Benzoic acid – Sol*** and ***Benzoic acid*** as the components.

Click on the **OK** button when you are ready.

The calculation is now set up correctly. Click on the **Calculate** button to start the calculation. This will now take more time than in the single point calculations since we are calculating many points.

When the program is finished, click on the **Plot** Tab.

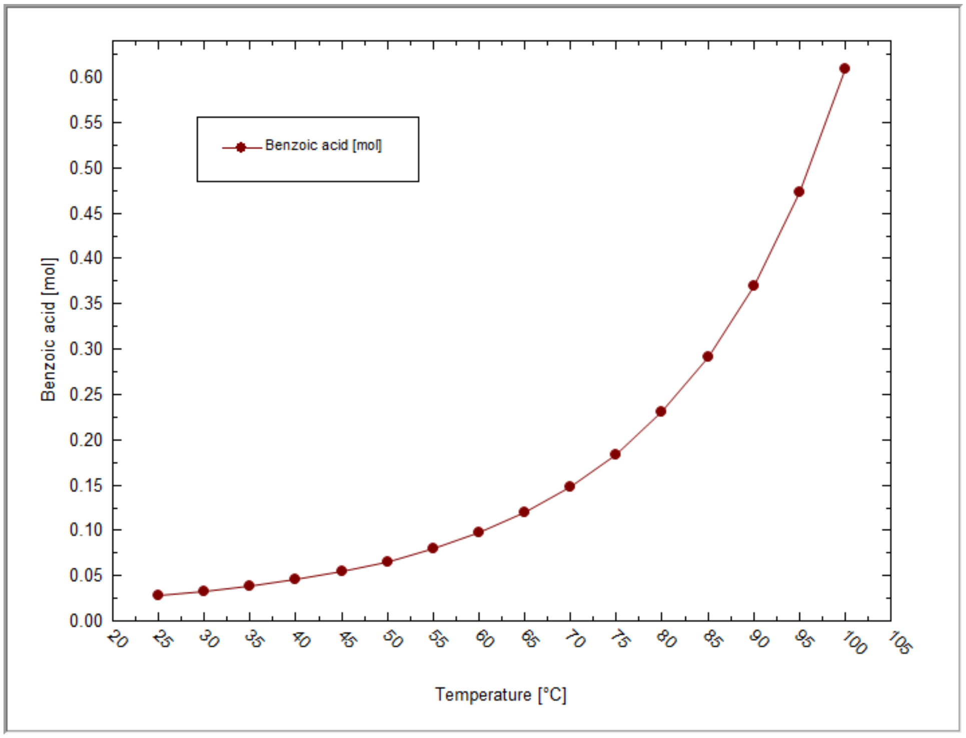
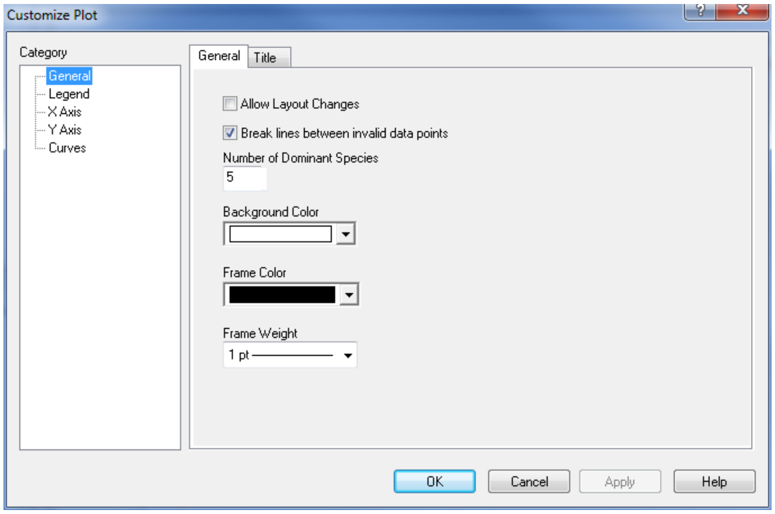


Figure 8-6 The Default Plot

This is the default plot. The program tries to intelligently plot what you calculated.

This plot shows the amount of benzoic acid required to saturate the solution as a function of temperature. The plot has many defaults which you may want to change.

Click the **Options** button.



☐ Allow Layout Changes

☑ Break lines between invalid data points

Number of Dominant Species

5

Background Color

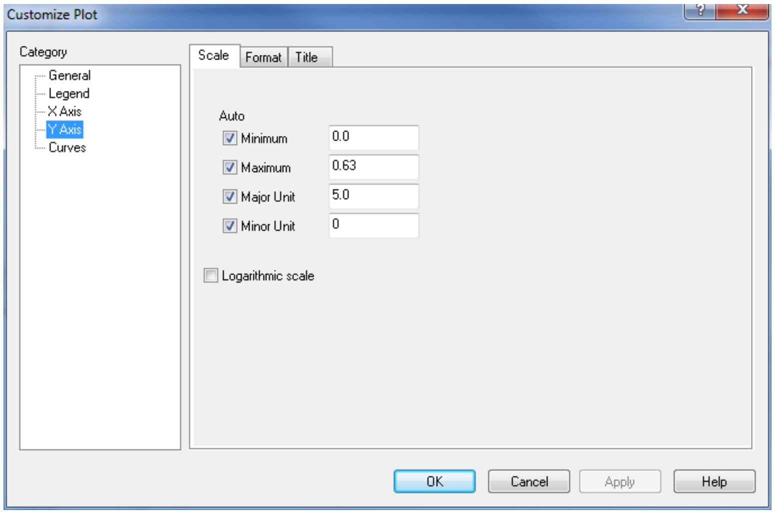
Frame Color

Frame Weight

1 pt

Figure 8-7 Plot Options

For example, you can ***Click*** on the **Y-Axis** category.



Auto

☑ Minimum 0.0

☑ Maximum 0.63

☑ Major Unit 5.0

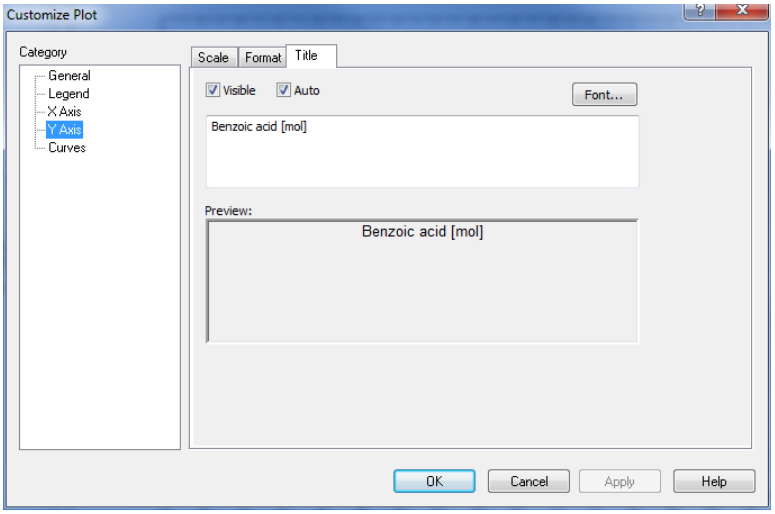
☑ Minor Unit 0

☐ Logarithmic scale

Figure 8-8 Y-axis options

To change the scale on the Y-axis.

Click on the **Title** tab.



☑ Visible ☑ Auto

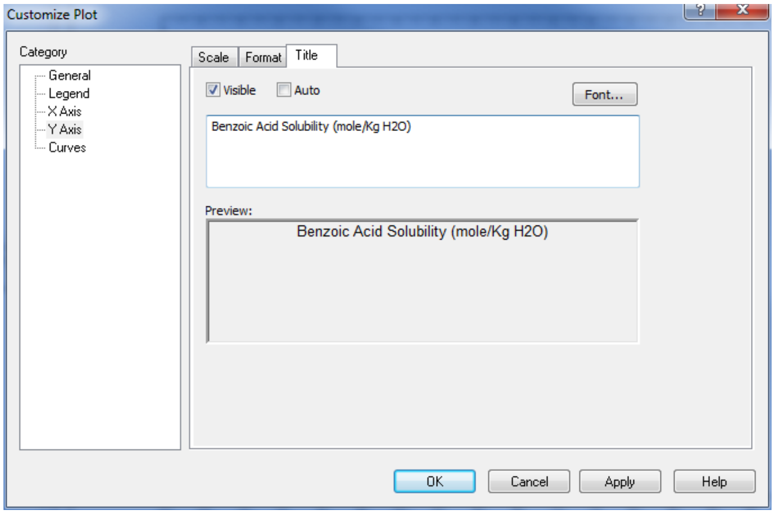
Benzoic acid [mol]

Preview:

Benzoic acid [mol]

Figure 8-9 Y-Axis title

Enter the text in the below box. Click on **OK** when ready.



☑ Visible ☐ Auto

Benzoic Acid Solubility (mole/Kg H2O)

Preview:

Benzoic Acid Solubility (mole/Kg H2O)

Figure 8-10 Entering a new Y-axis title.

You can see that the Preview box automatically updates with the new text and the **Auto** check box is automatically turned off.

The Y Axis title has changed. You can also change the font, scaling and grid lines as you require.

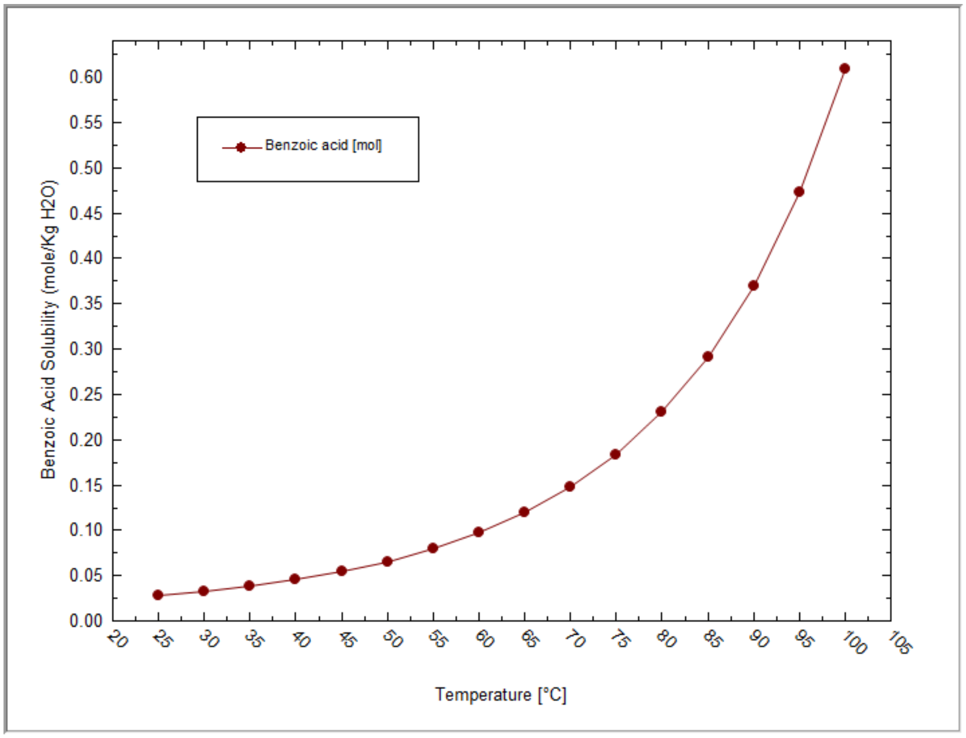


Figure 8-11 Revised Plot

You can directly change the axis properties by right-clicking the axis. For example, if you wanted to change the Y-axis to logarithmic right-click anywhere on the Y-axis:

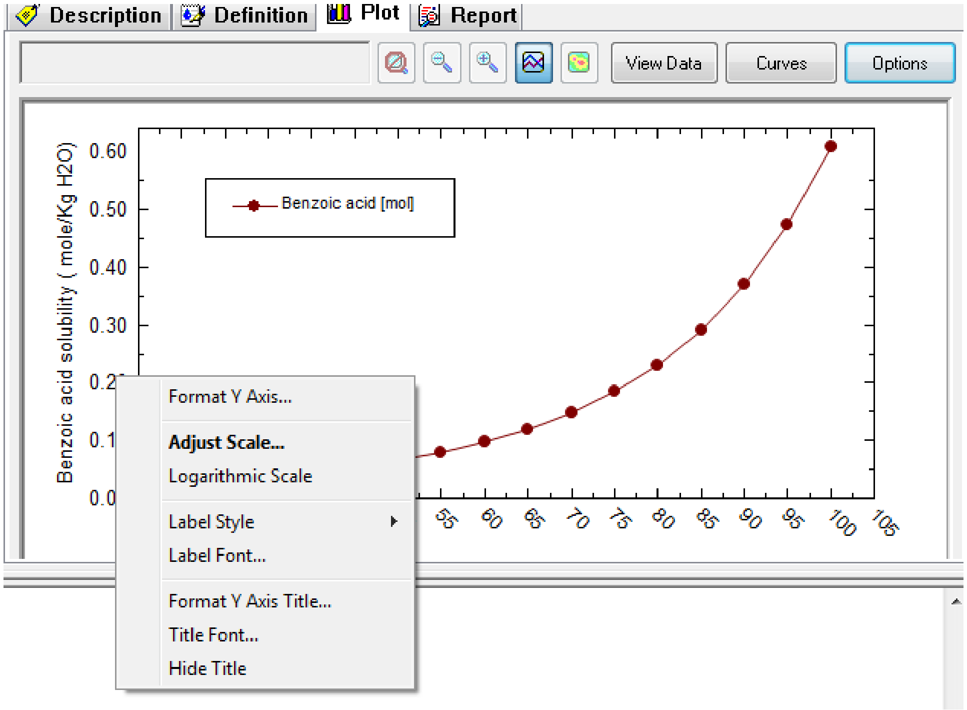


Figure 8-12Right-Click on axis and select Logarithmic

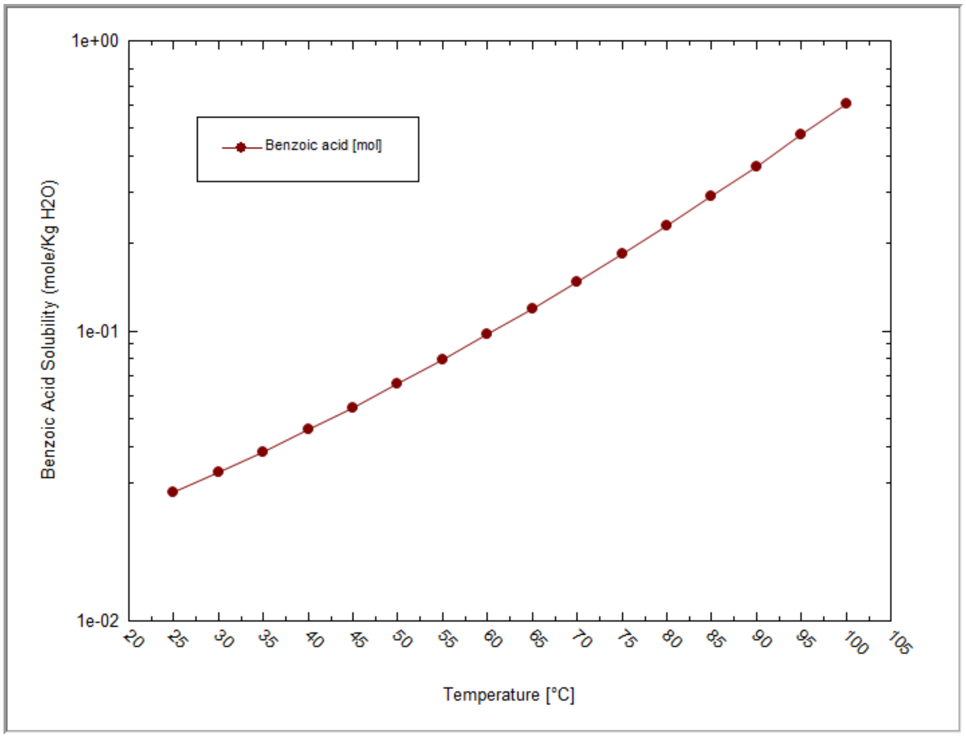


Figure 8-13 Now on a logarithmic scale

You can also display the data in table form. Click the **View Data** button:

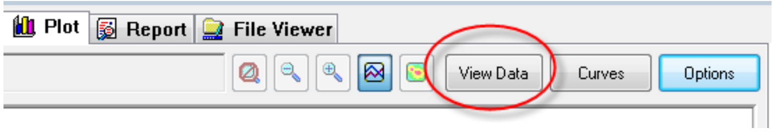
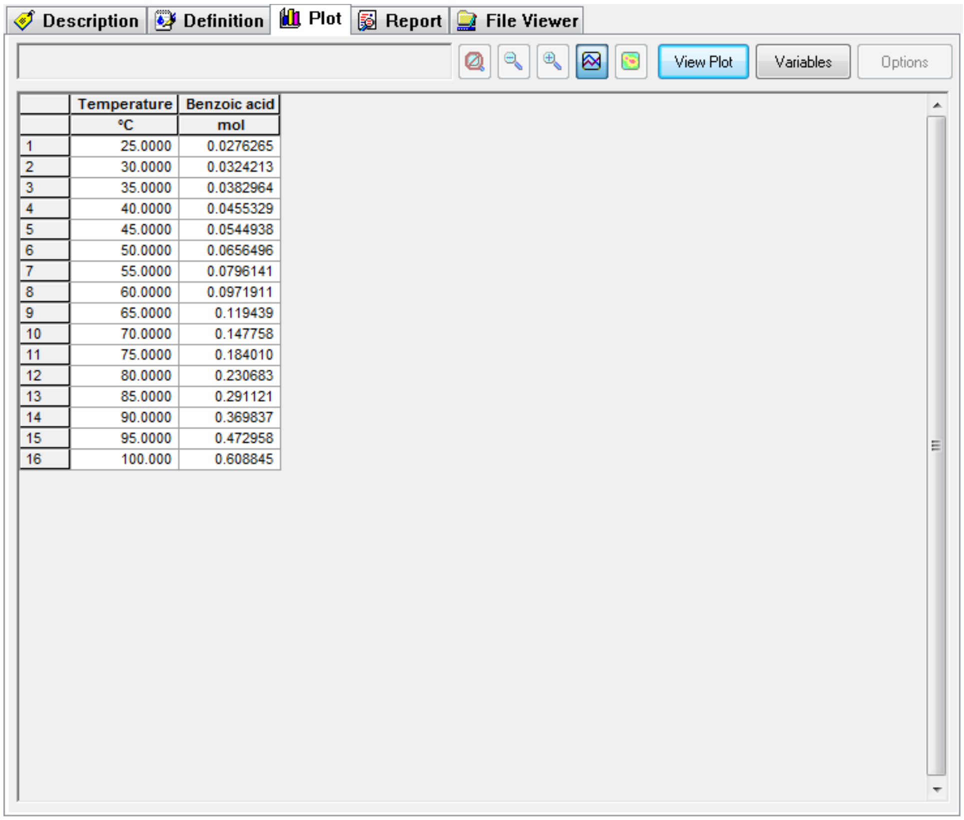


Figure 8-14 Select View Data

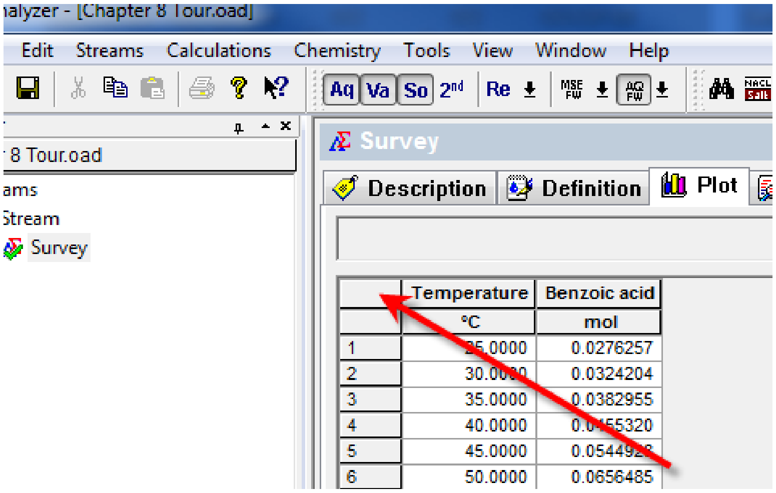


	Temperature	Benzoic acid
	°C	mol
1	25.0000	0.0276265
2	30.0000	0.0324213
3	35.0000	0.0382964
4	40.0000	0.0455329
5	45.0000	0.0544938
6	50.0000	0.0656496
7	55.0000	0.0796141
8	60.0000	0.0971911
9	65.0000	0.119439
10	70.0000	0.147758
11	75.0000	0.184010
12	80.0000	0.230683
13	85.0000	0.291121
14	90.0000	0.369837
15	95.0000	0.472958
16	100.000	0.608845

Figure 8-15 Table format

This table view has the same units as displayed in the plot. The data can be copied to the clipboard and pasted into other programs such as Microsoft's Excel.

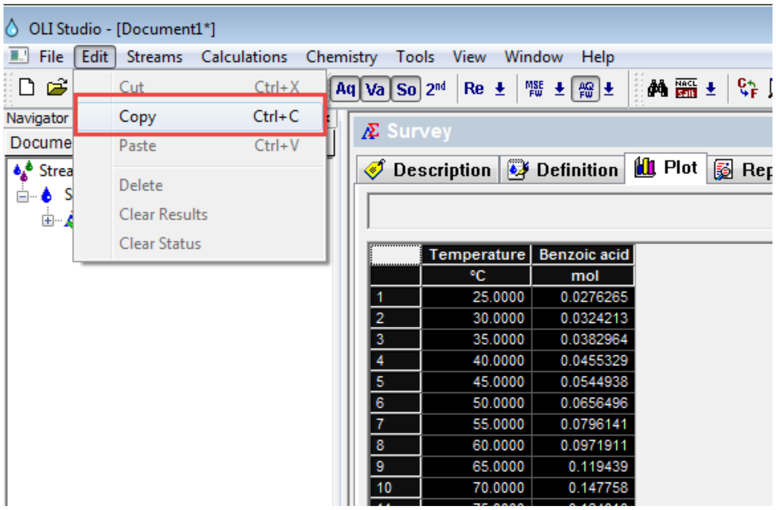
To copy all the data, click the empty box in the upper left-hand corner:



	Temperature	Benzoic acid
	°C	mol
1	25.0000	0.0276257
2	30.0000	0.0324204
3	35.0000	0.0382955
4	40.0000	0.0455320
5	45.0000	[illegible]
6	50.0000	0.0656485

Figure 8-16

Next use the Menu and select **Edit** > **Copy** to copy the data:



	Temperature °C	Benzoic acid mol
1	25.0000	0.0276265
2	30.0000	0.0324213
3	35.0000	0.0382964
4	40.0000	0.0455329
5	45.0000	0.0544938
6	50.0000	0.0656496
7	55.0000	0.0796141
8	60.0000	0.0971911
9	65.0000	0.119439
10	70.0000	0.147758

Figure 8-17

Now paste this data into the program of your choice.

Please save your file now!

Pressure

Many thermodynamic properties are less dependent on pressure than they are temperature. In this case, vapor-liquid equilibrium is more affected by pressure. In this example, a large amount of carbon dioxide will be placed under pressure. This simulates the charging of a pressure vessel.

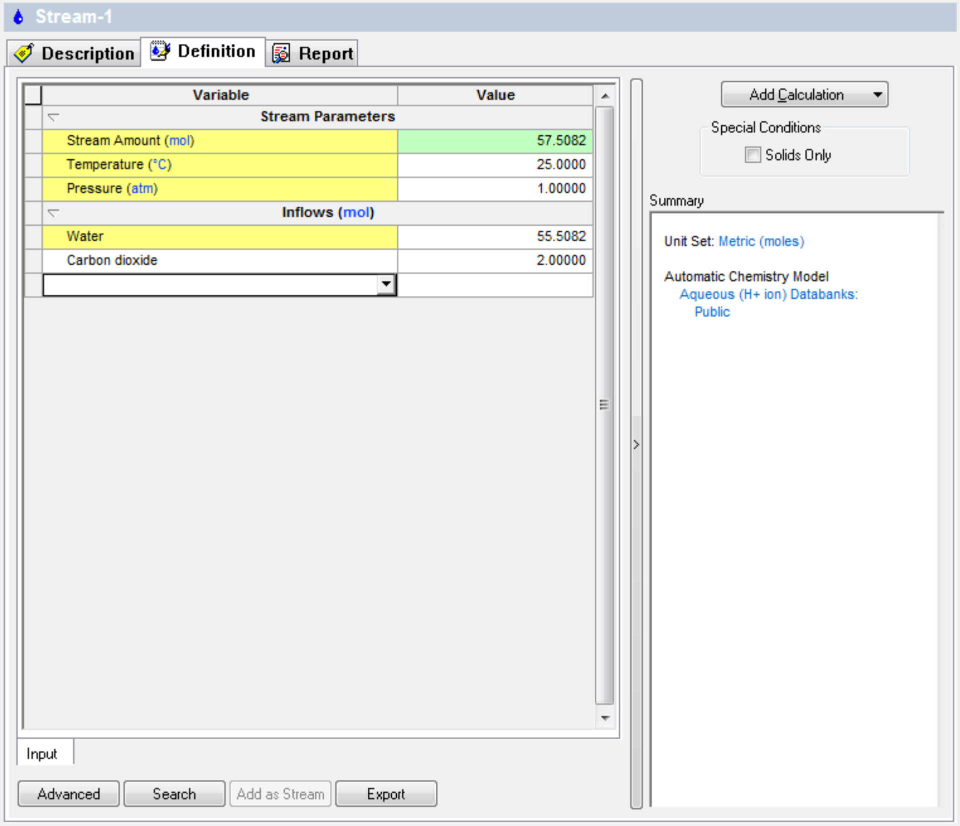
***Enter this Definition*:**

Temperature = 25 °C

Pressure = 1 Atm.

H2O = 55.508 mole

CO2 = 2.0 mole



Variable	Value
Stream Parameters	
Stream Amount (mol)	57.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
Water	55.5082
Carbon dioxide	2.00000

☐ Solids Only

Summary

Unit Set: Metric (moles)

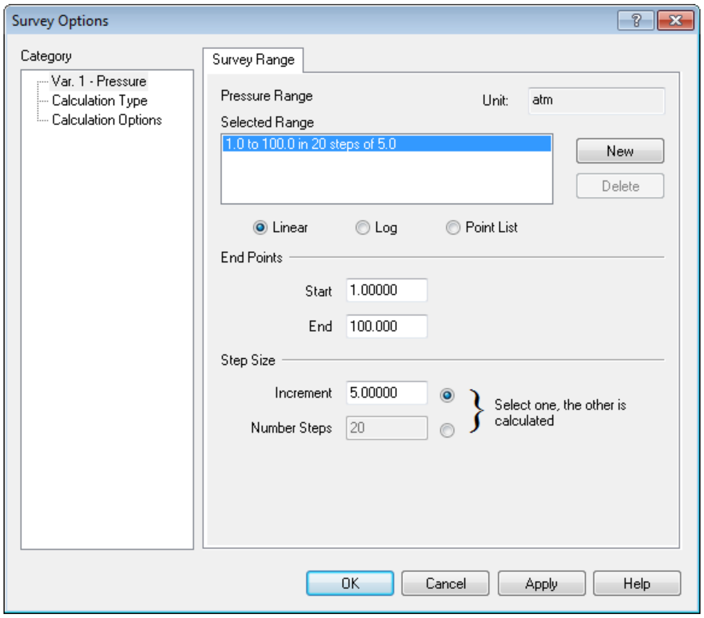
Automatic Chemistry Model
Aqueous (H+ ion) Databanks:
Public

Figure 8-18 Stream Definition for Pressure Survey

Click the* Add Calculation** button. Then ***Click on the **Survey by** button and then select **Pressure**.

The **Summary** box will display the current calculation options and status. The default range is from 1 to 10 atmospheres with increment of 1 atmosphere. We need to change the range to 100 atmospheres with an increment of 5 atmospheres.

Click on the **Specs** button.



Pressure Range
Unit: atm
Selected Range
1.0 to 100.0 in 20 steps of 5.0

● Linear ○ Log ○ Point List

End Points
Start 1.00000
End 100.000

Step Size
Increment 5.00000 ●
Number Steps 20 ○
Select one, the other is calculated

Figure 8-19 Changing the range

Change the increment from 1 to 5 as shown in the above figure. Change the end value to 100.

Click the **OK** button if you are ready. The calculation is now ready. Click the **Calculate** button to start the calculations.

When the program stops, click on the **Plot** tab to display the default plot.

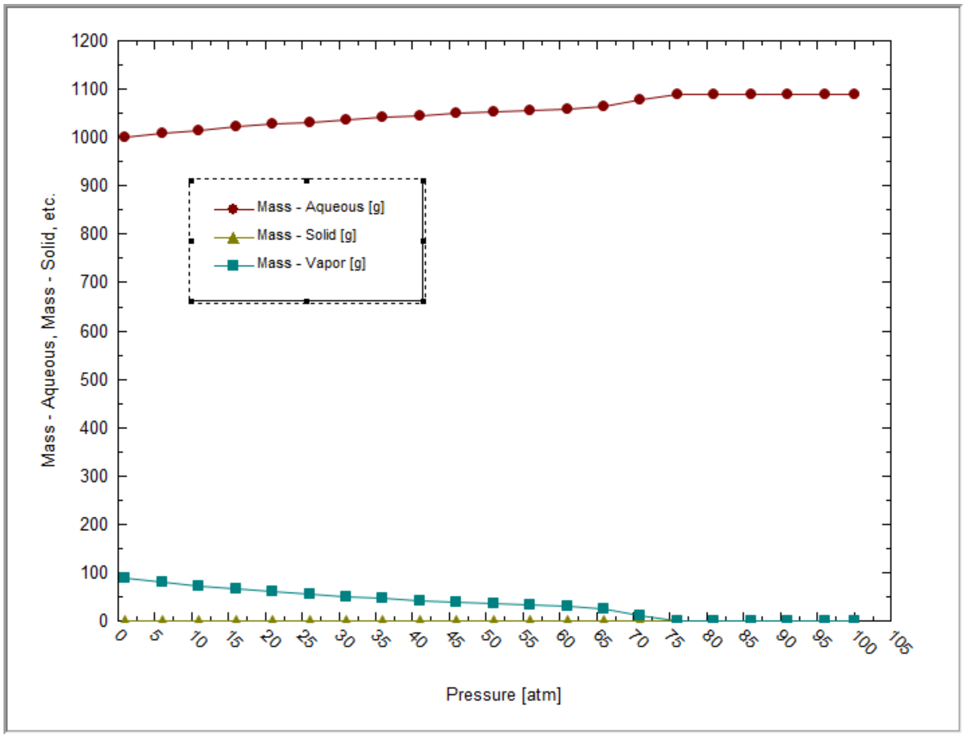


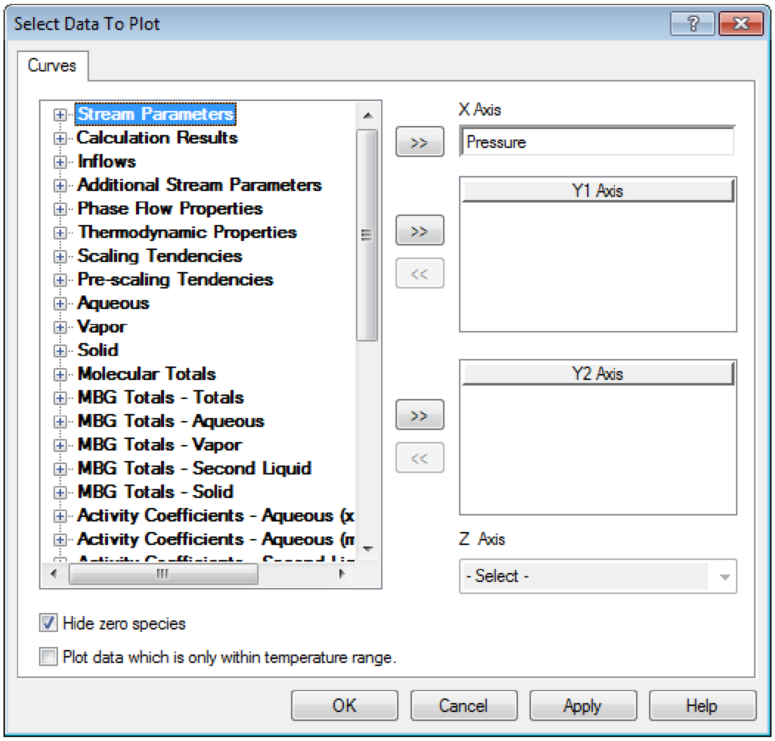
Figure 8-20 Default Dominant Aqueous species

The default plot of this type of calculation is a mass phase flow display. We can see that the mass of the aqueous phase is increasing until approximately 70 atmospheres where it becomes constant. At this point we will also notice that the mass of the vapor phase has become zero. This is the pressure where the vapor phase has collapsed and is no longer present.

There are other properties to view besides the mass phase flow. ***Click*** on the ***Variables*** button.

We no longer need to view the **Mass Flow Variables.** Select all of them and then ***click*** the left double arrow.

Scroll up/down to find **Additional Stream Parameters.**



X Axis: Pressure

☑ Hide zero species

☐ Plot data which is only within temperature range.

Figure 8-21 Classes of variables, select Additional Stream Parameters

From the new list, select **pH**

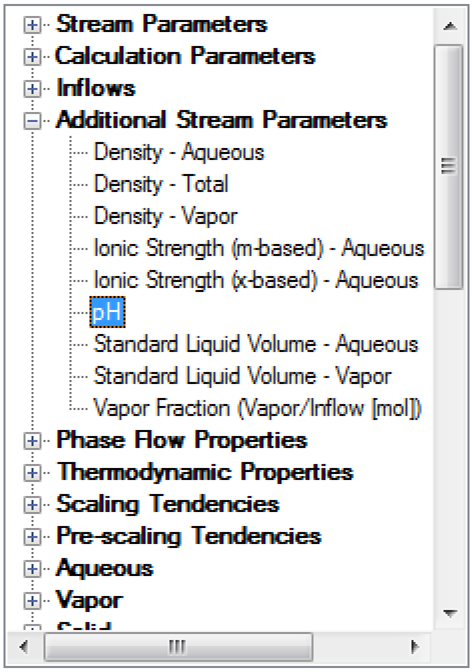
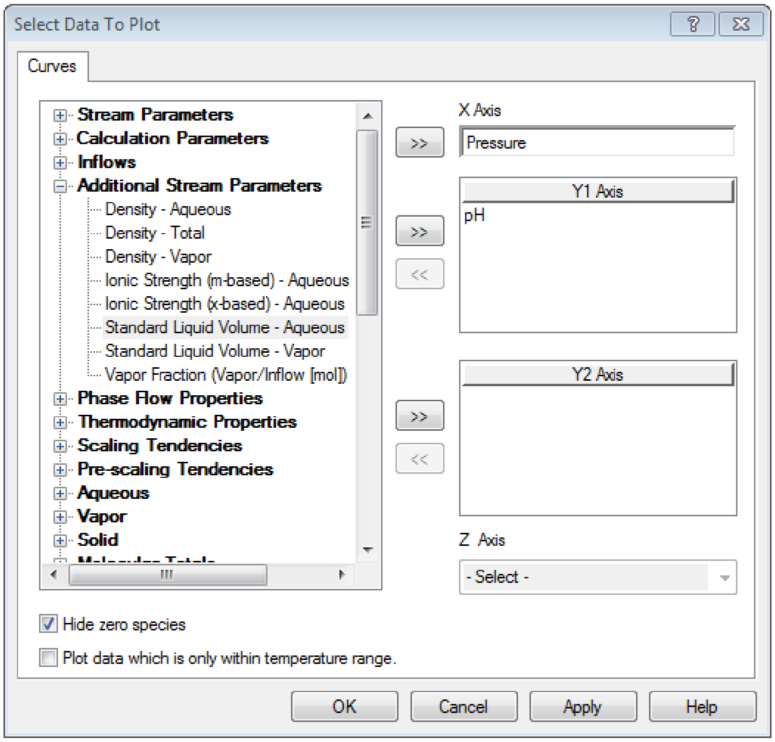


Figure 8-22 Locate and select pH

Then click on the **Right double-arrow** or ***double click*** the entry.



X Axis: Pressure

Y1 Axis: pH

Z Axis: - Select -

☑ Hide zero species

☐ Plot data which is only within temperature range.

Figure 8-23 Final Variables selection

Click on the **OK** button to display pH as a function of pressure.

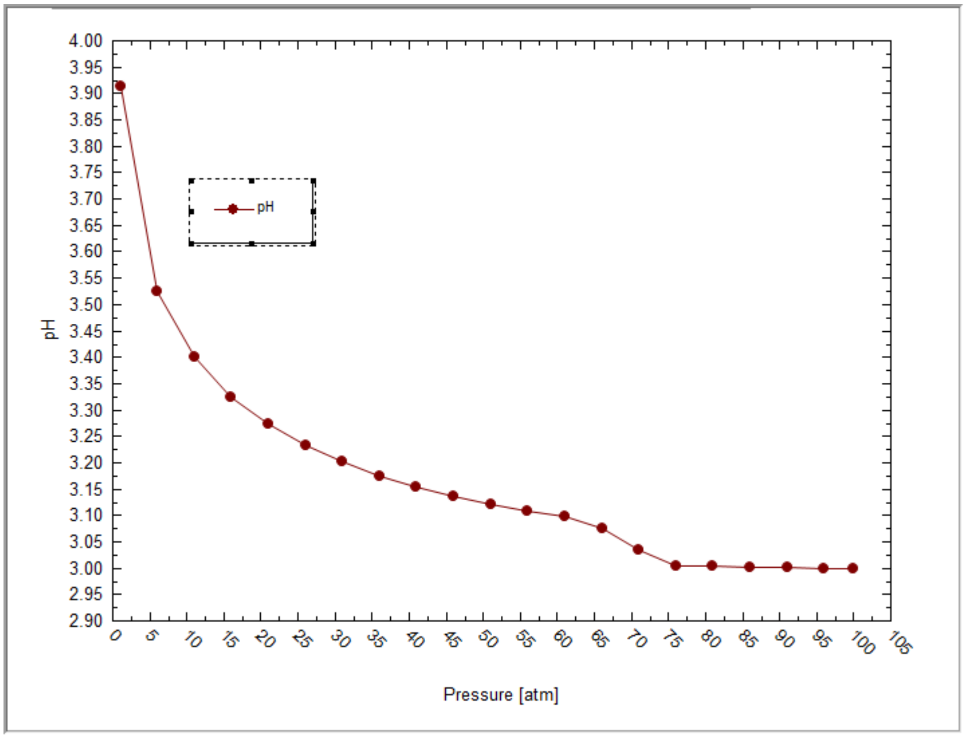


Figure 8-24 Final Plot

The pH decreases with pressure because of the increased solubility of carbon dioxide. Carbon dioxide is an acid gas. The pertinent equilibria are:

$$CO_{2(vap)} = CO_{2(aq)}$$

$$\mathbf{CO_{2(aq)} + H_2O = H^+ + HCO_3^-}$$

$$\mathbf{HCO_3^- = H^+ + CO_3^{2-}}$$

Thus, as the amount of carbon dioxide in the aqueous phase increases, more of it can dissociate producing hydrogen ions.

Please save your work now!

Composition

Often is in necessary to determine the effect of adding a species to a solution. One such case is the solubility of calcite ($CaCO_3$) as carbon dioxide is added to solution. Calcite is a scale that forms very easily in the production of oil. Carbon Dioxide is also produced in the production of oil. The addition of carbon dioxide frequently makes the formation of calcite scale unlikely.

In this example, we will add carbon dioxide at high pressure to a saturated calcium carbonate solution. Please enter the following:

Stream Amount[35] **= 55.558 moles**

Temperature = 25 C

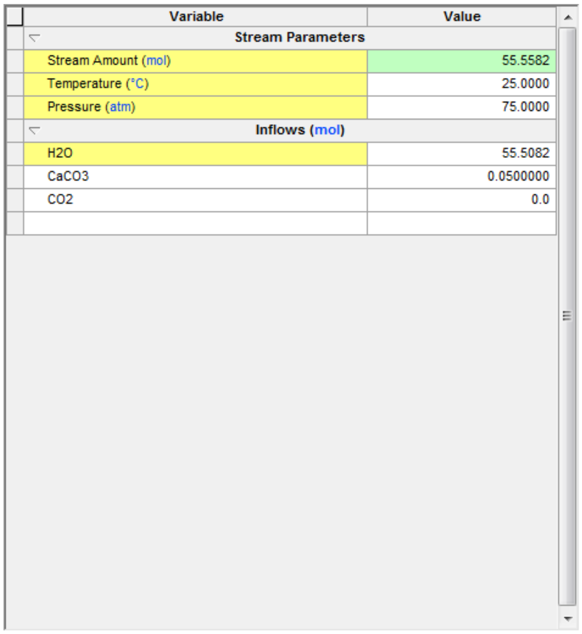
Pressure = 75.0 Atm

H2O = 55.508 mole

CaCO3 (Calcite) = 0.05 mole

CO2 = 0 mole

The following figure is filled out for this example.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5582
Temperature (°C)	25.0000
Pressure (atm)	75.0000
Inflows (mol)	
H2O	55.5082
CaCO3	0.0500000
CO2	0.0

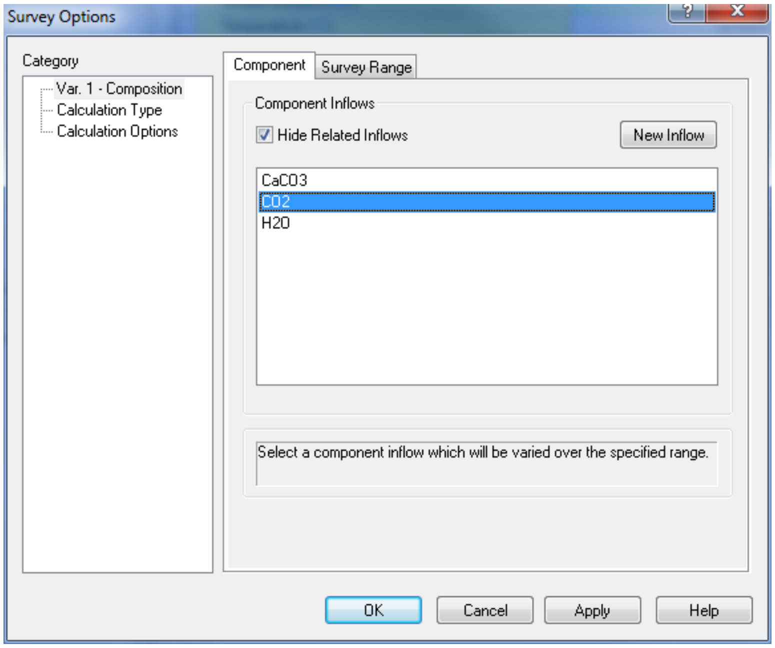
Figure 8-25 Composition Survey Definition

Add a Survey and then ***Click*** on the **Survey by** button and select **Composition**.

Next ***click*** on the **Specs** button and select the **Component tab**.

---

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



☑ Hide Related Inflows

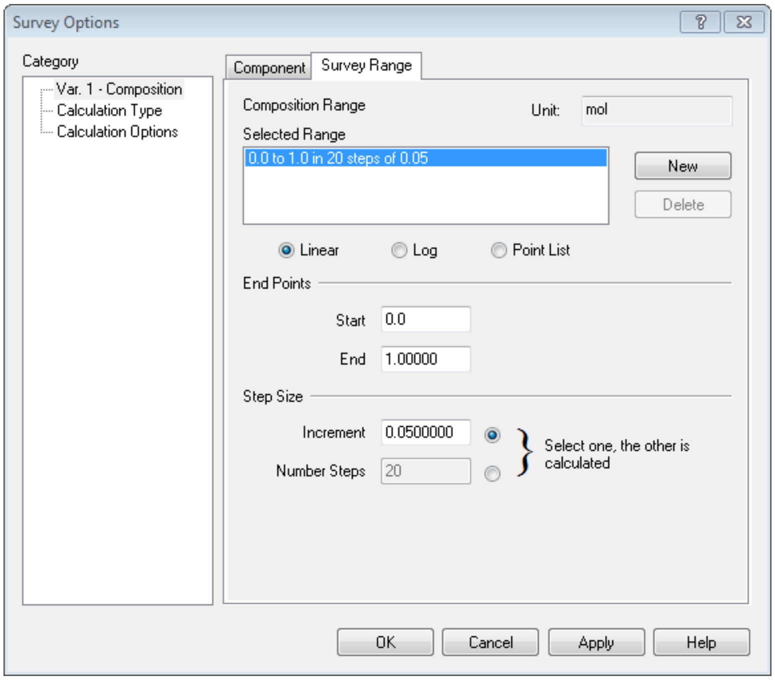
CaCO3
CO2
H2O

Select a component inflow which will be varied over the specified range.

Figure 8-26 Selecting the component CO2

Select ***Carbon dioxide, CO_2*** from this list. Next, ***click*** on the **Survey Range** tab.

We only want to see a narrow range of compositions for ***carbon dioxide***. Enter an increment of ***0.05***, and an ending value of ***1.0***.



Unit: mol

0.0 to 1.0 in 20 steps of 0.05

● Linear ○ Log ○ Point List

Start 0.0

End 1.00000

Increment 0.0500000 ●

Number Steps 20 ○

Select one, the other is calculated

Figure 8-27 Narrowing the range of the calculation

***Click* OK** when ready.

Click the **Calculate** button when ready.

Click on the Plot tab. The default plot is not what we need to see. Click on the Variables button.

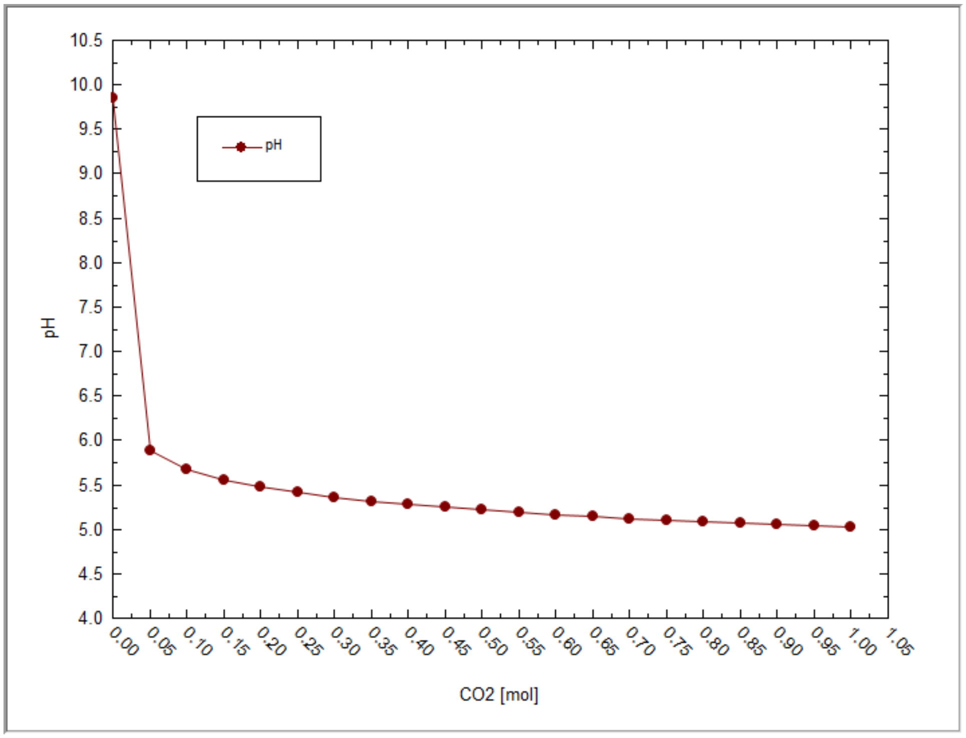
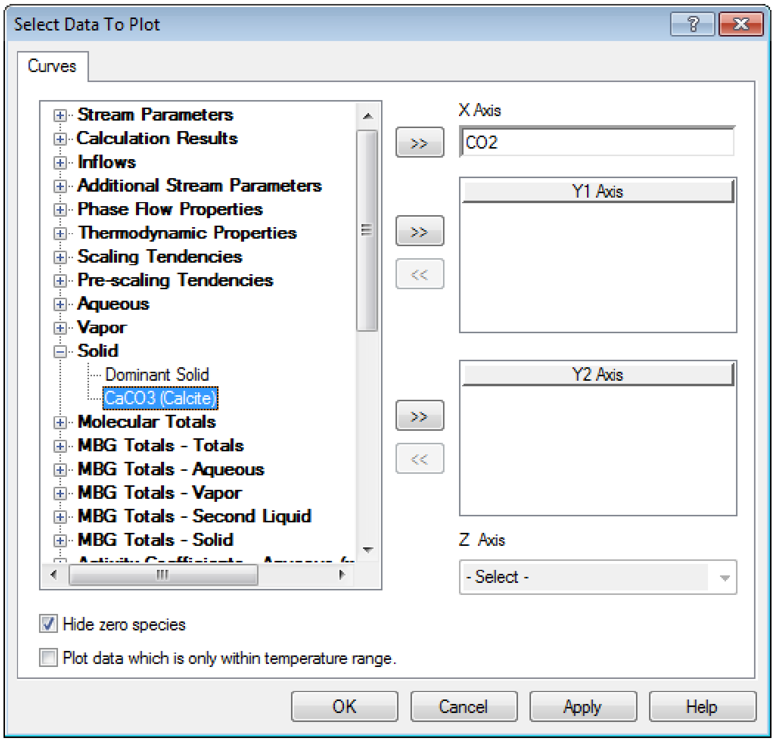


Figure 8-28 The default composition survey plot

Remove the existing entry. Scroll up or down to find and select **Solid**. Select **CaCO3 (Calcite)** from the list. Click on **OK** when ready.



X Axis: CO2

☑ Hide zero species

☐ Plot data which is only within temperature range.

Figure 8-29 Removing default variable and replacing it with the solid CaCO3

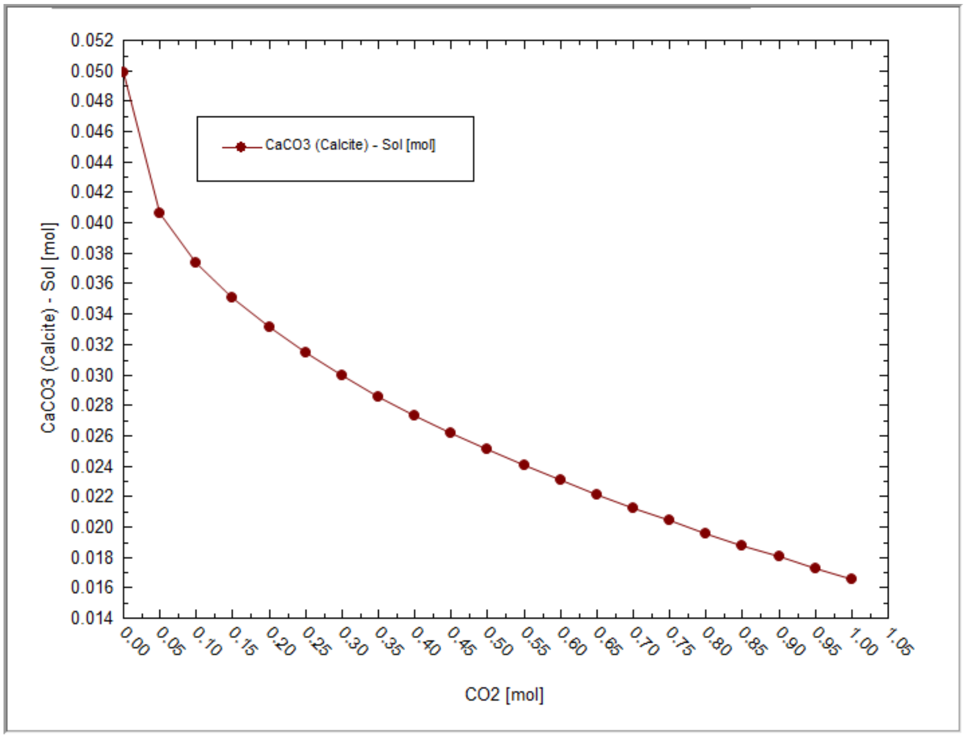


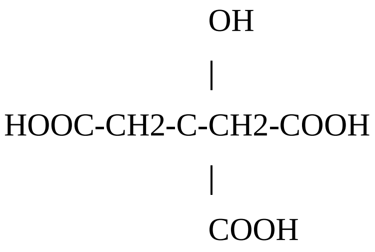
Figure 8-30 Our desired plot.

The amount of calcium carbonate decreases with increasing carbon dioxide. In an oil production setting, when there is a pressure drop (see previous tour) carbon dioxide will be lost. This will decrease the solubility of calcium carbonate and increase the likelihood of scale formation.

Please save this file now. We will be using the file in a later tour.

pH (Mixer)

We have already covered the pH survey in earlier chapter. In this example, we wish to discuss the dissociation of a tri-protic acid, citric acid. Citric Acid has the structure:



$$\begin{array}{c} OH \\ | \\ HOOC\text{-}CH2\text{-}C\text{-}CH2\text{-}COOH \\ | \\ COOH \end{array}$$

There are three acid hydrogen atoms and hence three pKa's.

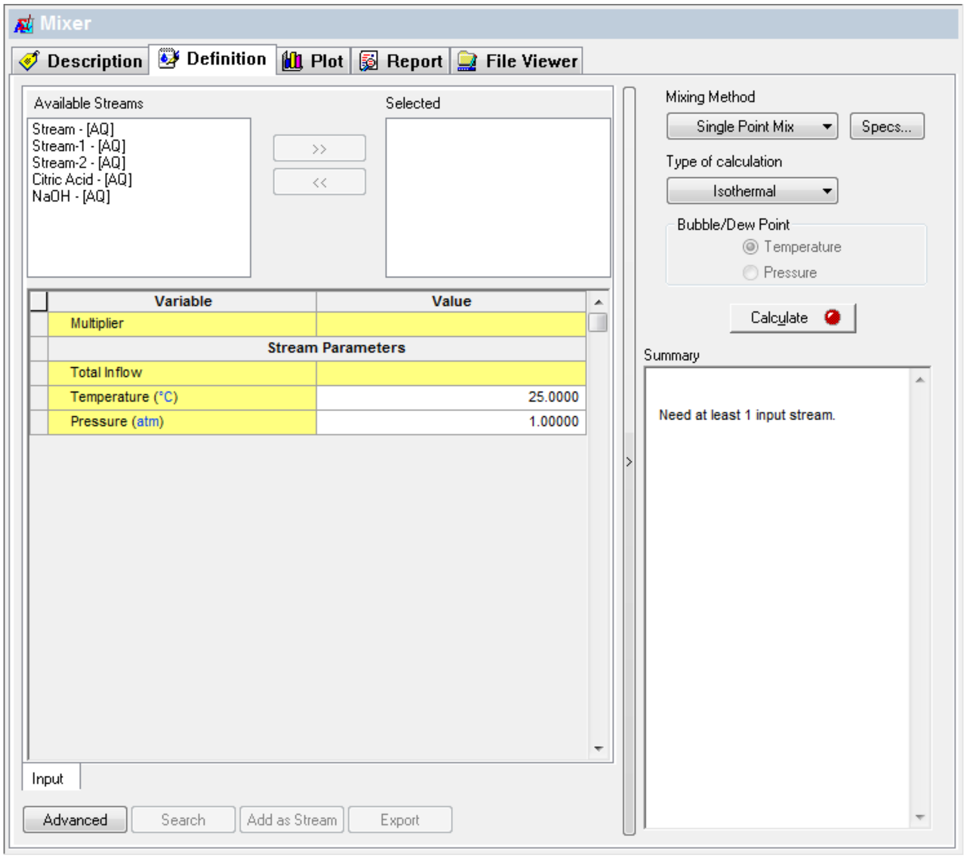
We will use the **MIX** calculation to perform an actual titration curve.

We need to create two new streams. You have already done this many times. Create the following two streams.

Stream Name = Citric Acid
Temperature = 25 ºC
Pressure = 1 Atmosphere
H2O = 55.5082 moles (default)
Citric Acid = 0.1 moles

Stream Name = NaOH
Temperature = 25 ºC
Pressure = 1 Atmosphere
H2O = 55.5082 moles (default)
NaOH = 0.1 moles.

Choose **Add Mixer** from the Action area.



Available Streams
Stream - [AQ]
Stream-1 - [AQ]
Stream-2 - [AQ]
Citric Acid - [AQ]
NaOH - [AQ]

Variable	Value
Multiplier	
Stream Parameters	
Total Inflow	
Temperature (°C)	25.0000
Pressure (atm)	1.00000

Mixing Method: Single Point Mix

Type of calculation: Isothermal

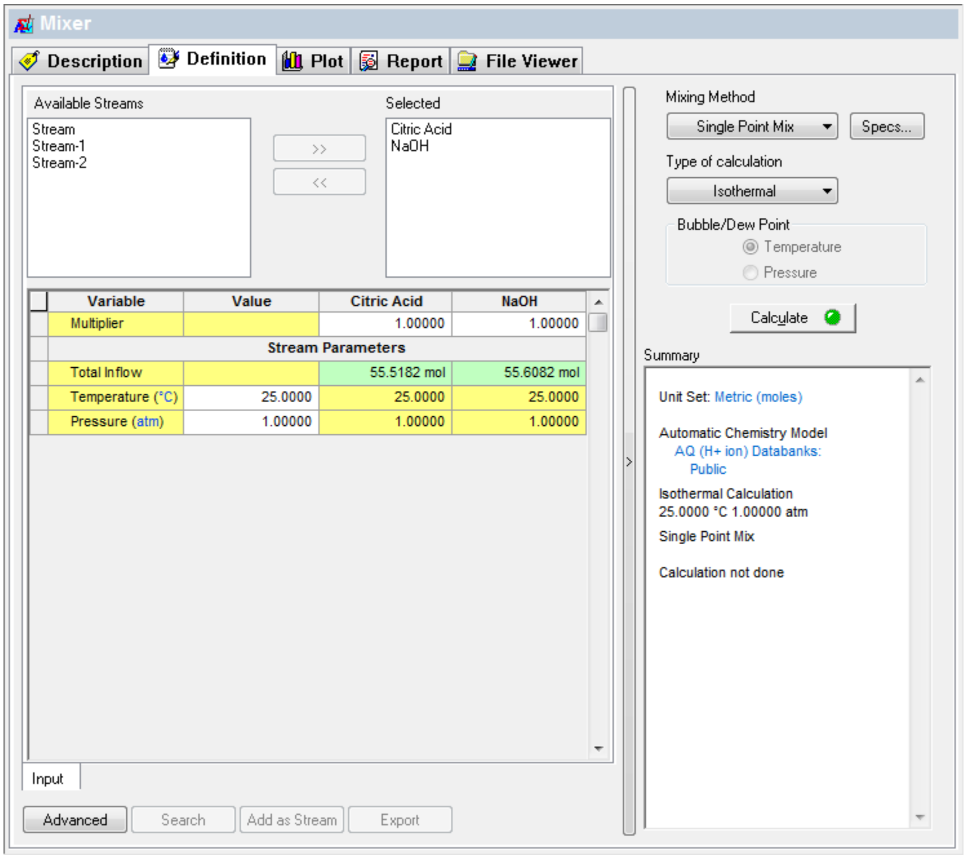
Summary: Need at least 1 input stream.

Figure 8-31 The Mixed Stream Input

We now have many streams from which to select[36]. Select the newly created ***Citric Acid*** and ***NaOH*** streams. Highlight the stream and use the double-arrow **(>>)** to select them.

---

[36] You can only add streams or calculation that share the same thermodynamic framework. Thus only AQ framework species are viewable since that is the framework selected. MSE framework objects are not displayed.



Variable	Value	Citric Acid	NaOH
Multiplier		1.00000	1.00000
Stream Parameters			
Total Inflow		55.5182 mol	55.6082 mol
Temperature (°C)	25.0000	25.0000	25.0000
Pressure (atm)	1.00000	1.00000	1.00000

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
25.0000 °C 1.00000 atm

Single Point Mix

Calculation not done

Figure 8-32 Selected Streams

The two streams (and more than two may be selected) are summarized in the grid below the selector box. We now want to vary the amount of the *NaOH* stream to simulate adding a base titrant to our acid system. Each solution is approximately 1 liter. We will add up to 2 liters of the *NaOH* stream.

Click the **Mixing Method** Button

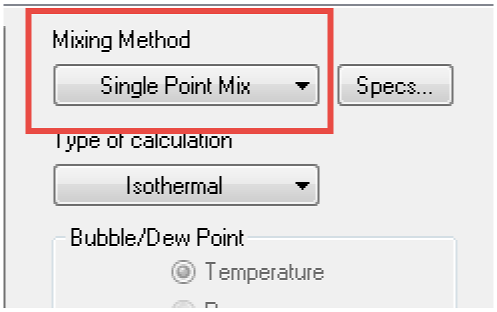
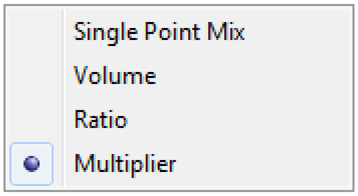
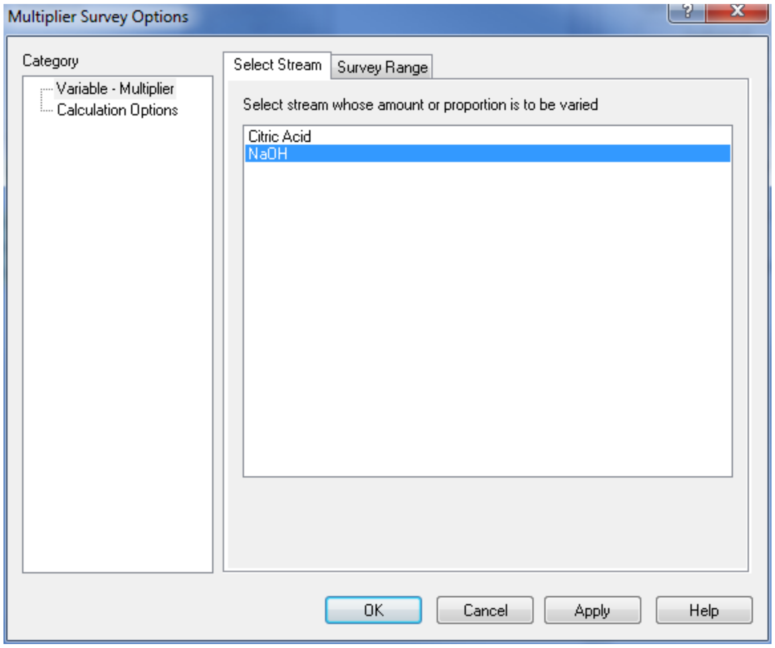


Figure 8-33

Then select **Multiplier**.



This will add the varied stream in a specific amount. Now select the **Specs…** button.



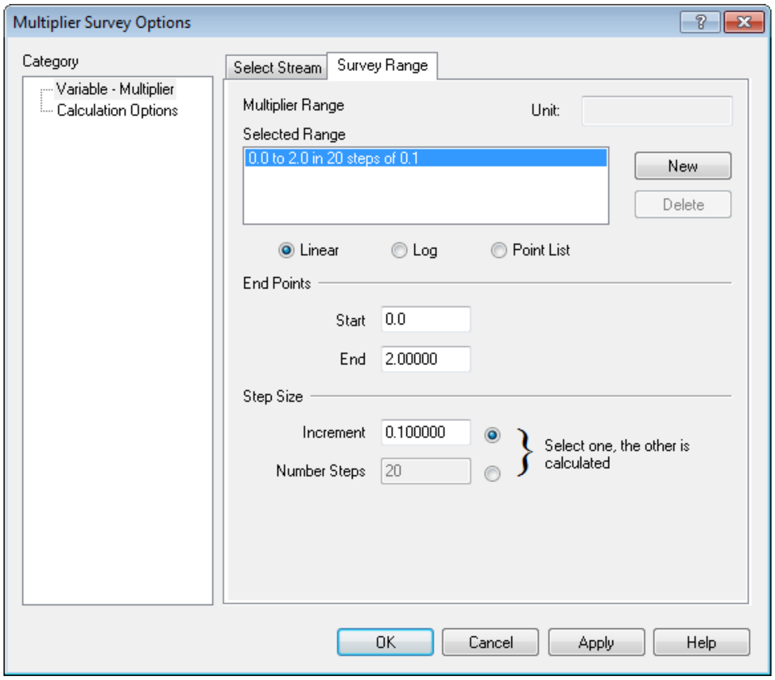
Select stream whose amount or proportion is to be varied

Citric Acid
NaOH

Figure 8-34 Selecting the NaOH stream.

Select the ***NaOH*** stream. This will tell the program we will adjust the multiplier of the two streams by adjusting the ***NaOH*** stream.

Now ***click*** on the **Survey Range** Tab.



Unit:

Selected Range: 0.0 to 2.0 in 20 steps of 0.1

● Linear ○ Log ○ Point List

Start: 0.0

End: 2.00000

Increment: 0.100000 ●

Number Steps: 20 ○

Select one, the other is calculated

Figure 8-35 Setting the range of the ratio variable.

We will set the ratio range from ***0*** to ***2*** in ***0.1*** increments.

What this means is that we will start off with the 1 liter of the ***citric acid solution*** and 0 liters of the ***NaOH*** stream. We will continue to increase the amount of ***NaOH*** stream until we have 2 volumes of the ***NaOH*** stream to 1 volume of the citric acid stream.

Click the **OK** button.

Click the **Calculate** button. When the calculation has completed, ***click*** on the **Plot** tab.

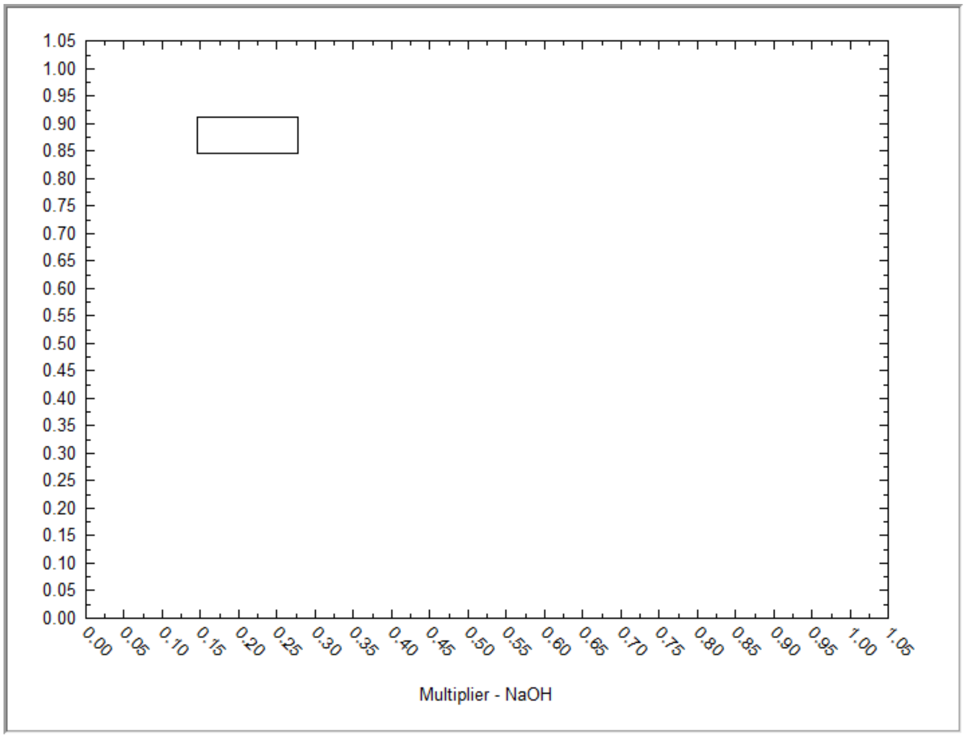


Figure 8-36 The default plot.

Occasionally our intelligent plot display cannot determine what to plot. We will have to make the selection ourselves.

Click the **Variables** button and select **pH** as the variable to display.

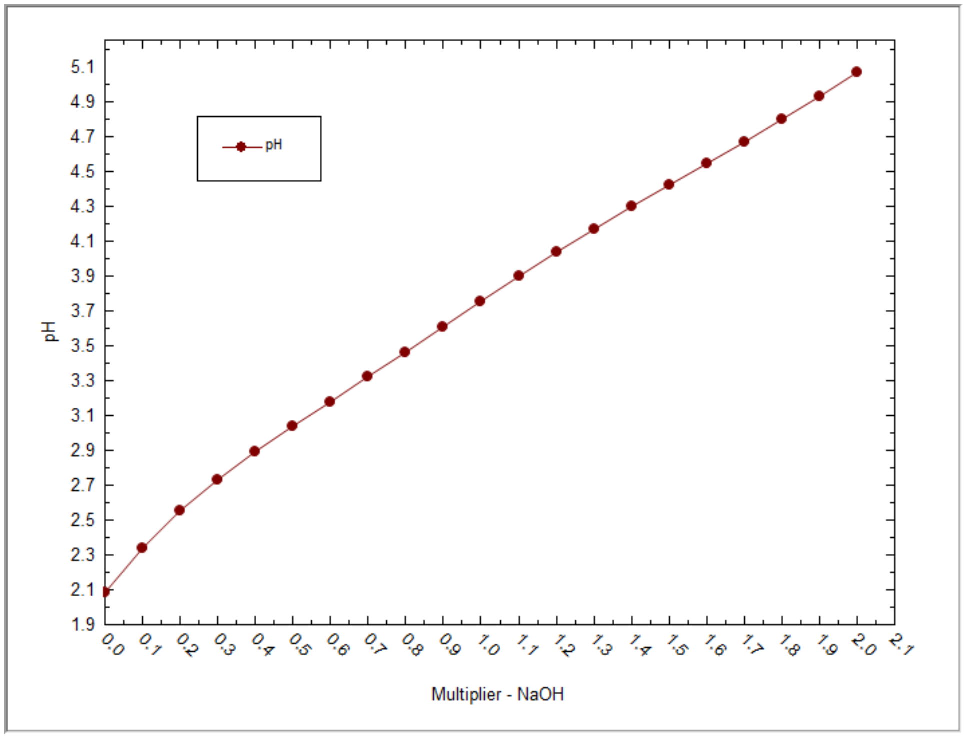
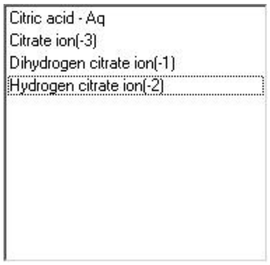


Figure 8-37 pH v. NaOH

The pH increases with adding NaOH. Now we want to select the following ions to see the changes in the citrate ion.[37] Use the **Variables** button and select the following ***Aqueous Species***. Remove pH.



Citric acid - Aq
Citrate ion(-3)
Dihydrogen citrate ion(-1)
Hydrogen citrate ion(-2)

Figure 8-38 species to select

---

[37] You may find it easier to locate the ion names if you switch the Names Manager to Display Name.

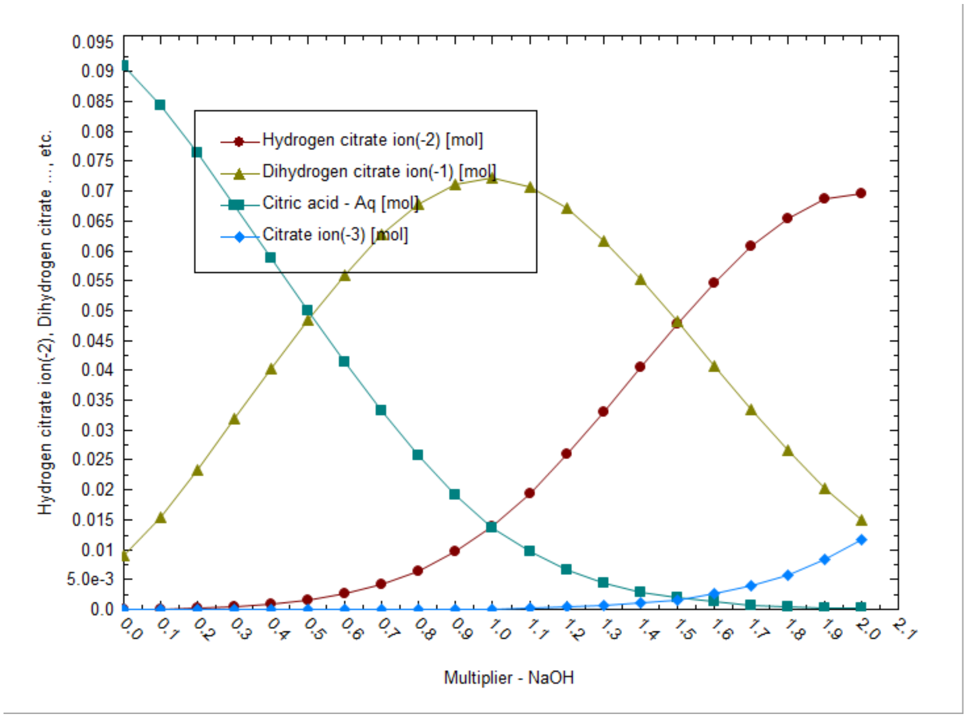


Figure 8-39 Citric Acid species v. NaOH

This plot shows that as the amount of NaOH is titrated the dominant citric acid species changes.

The resulting plot shows the various ions of citric acid changing form. The pH where each ion changes dominance is the pKa of that acid dissociation. For example, the change from H_2 Citrate^{-1} to H citrate^{-2-} occurs slightly above a ratio of 0.5. Another interpretation is that this is the amount of the NaOH stream necessary to make this change ~ 500 mL or 0.5 L.

Cascading Mixers

In this example, we will mix two streams, one basic and one acidic, and mix them together under adiabatic conditions. The output of this mixer will then be used as the input to a second mixer where a new caustic stream is added. The schematic in Figure 8-40 below illustrates the layout.

The linked image cannot be displayed. The file may have been moved, renamed, or deleted. Verify that the link points to the correct file and location.

Figure 8-40 Schematic of cascading mixers

For this example, we need to create three streams. You have already done this in other examples so we will only give you the input data (for all streams, we will use the AQ – default – thermodynamic framework)

Stream: Base Waste

Temperature	25.0	ºC
Pressure	1.0	Atmospheres
H2O	55.5082	moles (default value)
CO2	0.1	moles
NH3	0.01	moles
SO2	0.01	moles

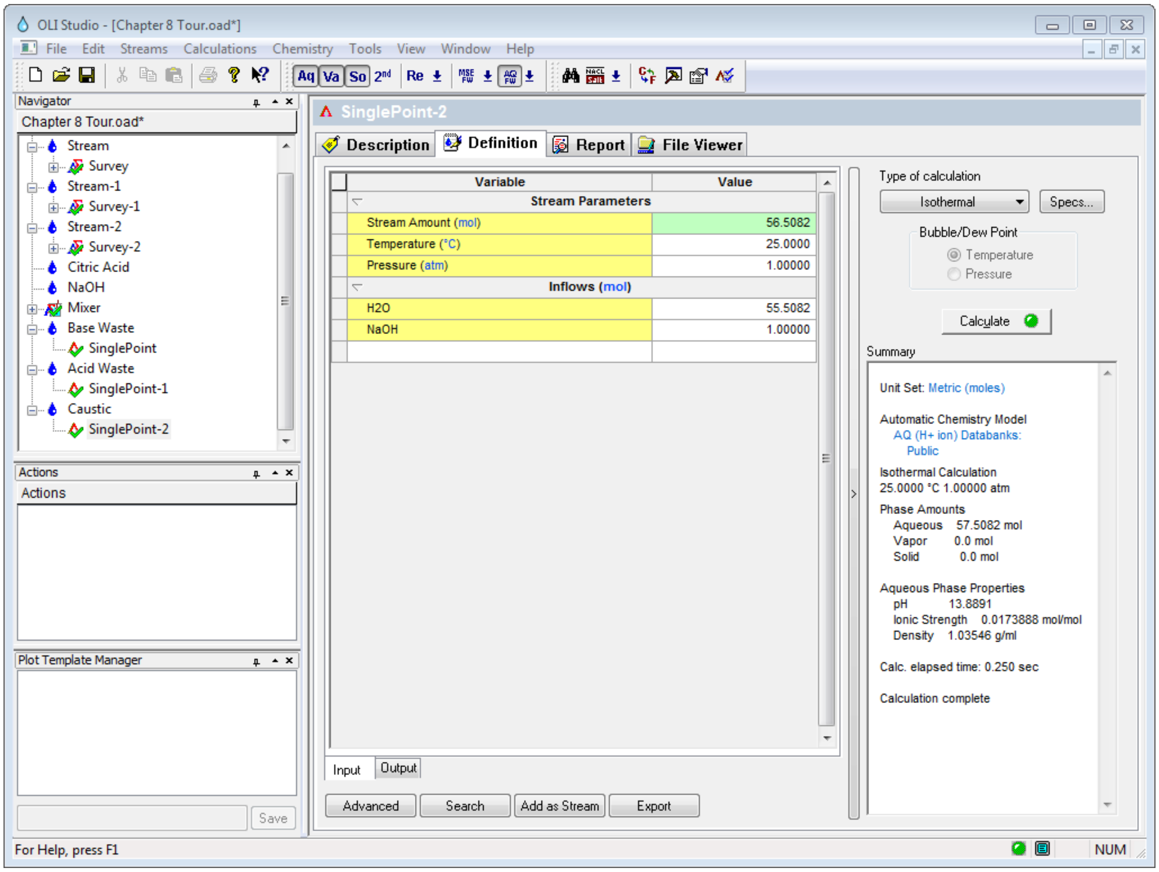
Stream: Acid Waste

Temperature	25.0	ºC
Pressure	1.0	Atmospheres
H2O	55.5082	moles (default value)
HCL	0.1	moles
H2SO4	1.0	moles

Stream: Caustic

Temperature	25.0	ºC
Pressure	1.0	Atmospheres
H2O	55.5082	moles (default value)
NaOH	1.0	moles

To test that our streams are representing their respective names, perform a single point isothermal flash on each stream. When you are done you should have a window that looks like Figure 8-41 below:



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

Type of calculation: Isothermal

Bubble/Dew Point
● Temperature
○ Pressure

Summary

```
Unit Set: Metric (moles)

Automatic Chemistry Model
   AQ (H+ ion) Databanks:
      Public
Isothermal Calculation
25.0000 °C 1.00000 atm
Phase Amounts
   Aqueous    57.5082 mol
   Vapor      0.0 mol
   Solid       0.0 mol

Aqueous Phase Properties
   pH          13.8891
   Ionic Strength    0.0173888 mol/mol
   Density    1.03546 g/ml

Calc. elapsed time: 0.250 sec

Calculation complete
```

Figure 8-41 completed inputs for cascading mixer

Now we are ready to begin. Click on the “Streams” at the top of the tree-view in the left-hand window and then select Add Mixer from the actions panel.

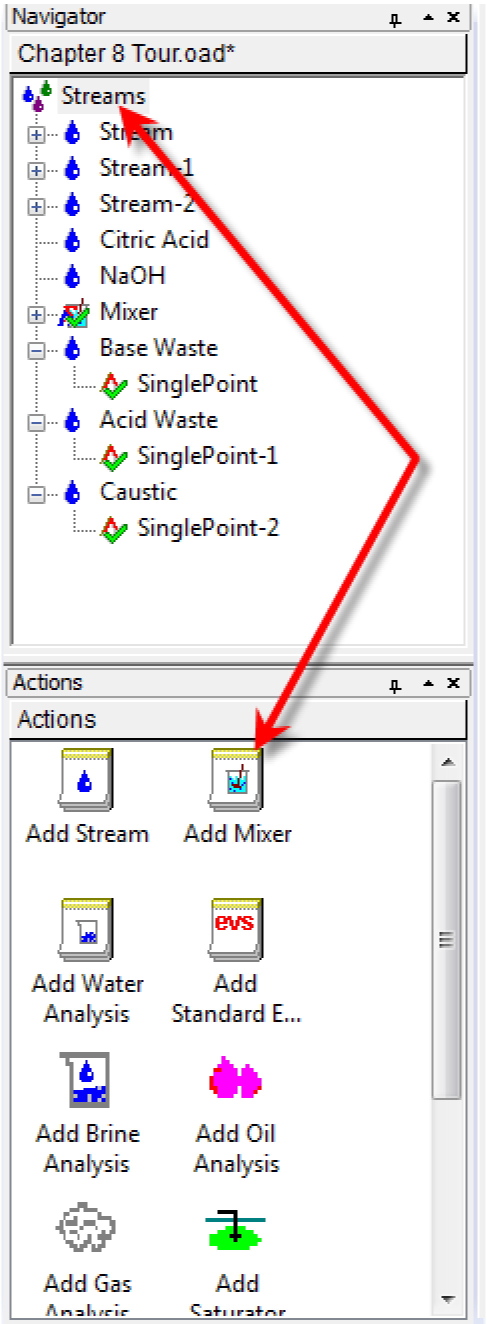
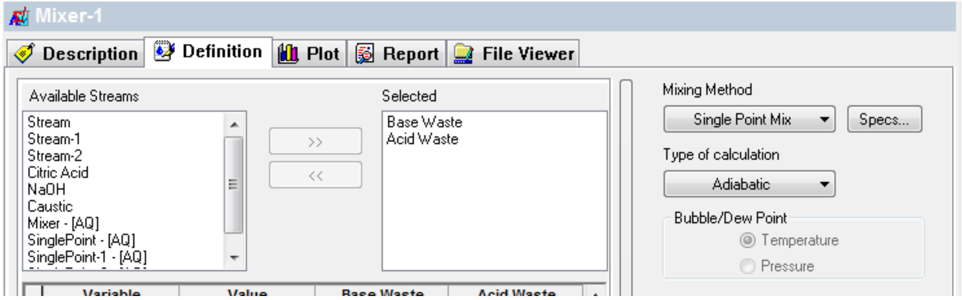


Figure 8-42 Adding a mixer

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



Available Streams
Stream
Stream-1
Stream-2
Citric Acid
NaOH
Caustic
Mixer - [AQ]
SinglePoint - [AQ]
SinglePoint-1 - [AQ]

Selected
Base Waste
Acid Waste

Mixing Method: Single Point Mix
Type of calculation: Adiabatic
Bubble/Dew Point
○ Temperature
○ Pressure

Figure 8-43 Selecting the Base and Acid waste stream

Let's calculate this mixer. Click the Calculate button. If everything is set up correctly the resultant mixed pH should be approximately 0.3[38]

In the stream tree-view panel, locate your mixer and click the "+" sign.

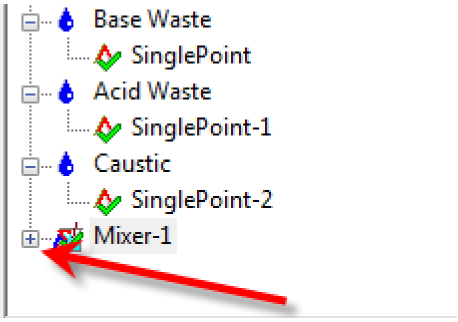


Figure 8-44 Click the "+" sign to expand the tree

Click the "+" sign to expand the tree.

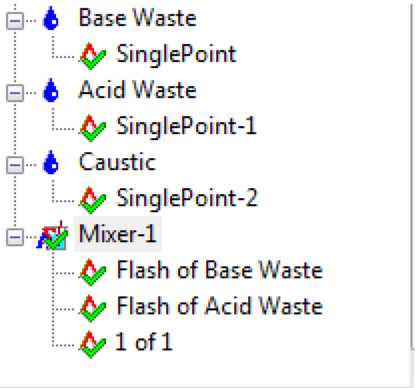


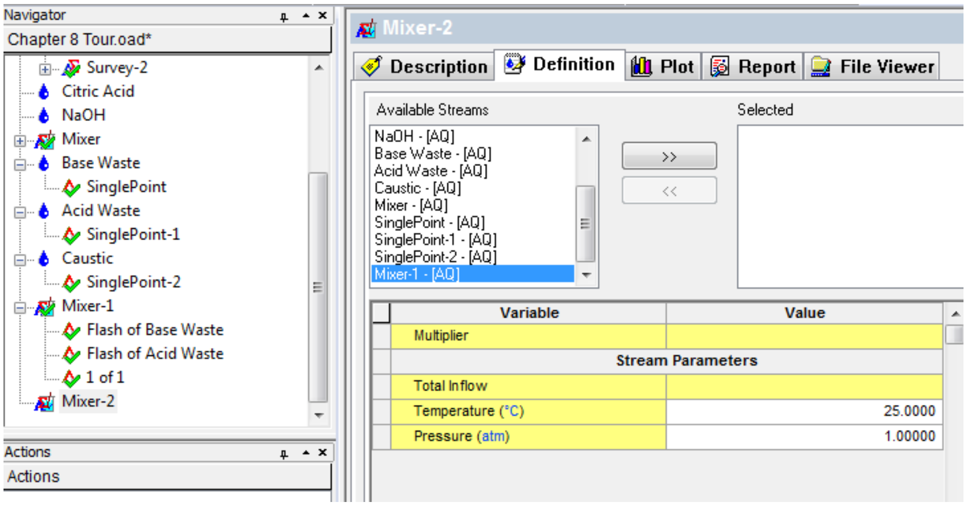
Figure 8-45 Expanded tree view

You can see that the program has performed an equilibrium calculation on each of our input streams as well as calculated the mixer. The results of the mixer are stored in the object "1 of 1".

We will now add a second mixer from the actions panel.

---

[38] You can use the Report Tab to find the pH value.

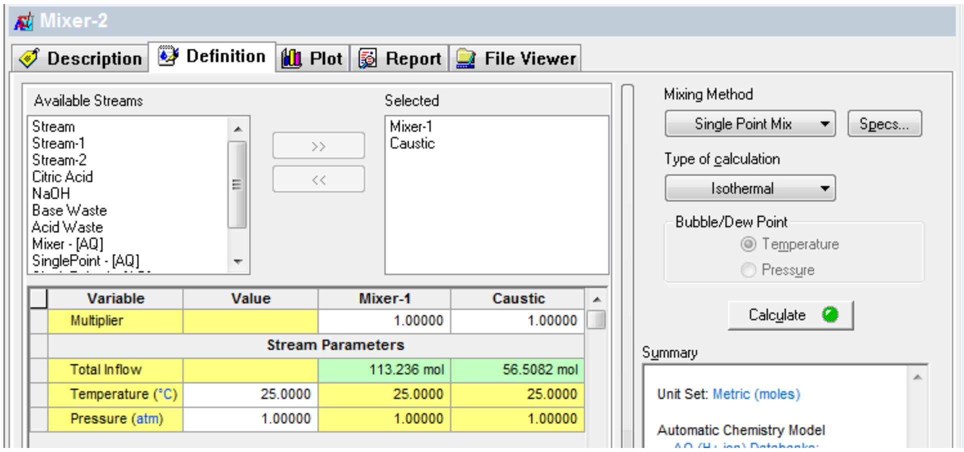


Variable	Value
Multiplier	
Stream Parameters	
Total Inflow	
Temperature (°C)	25.0000
Pressure (atm)	1.00000

Figure 8-46 Adding the second mixer

When we add a subsequent mixer we will see all of our previous objects still displayed. It is possible to reuse a stream that we already used (this is not possible in OLI's other simulators such as ESP or OLI Flowsheet.) We want to connect the output from our first mixer (Mixer1) to the inlet of the Caustic Reagent stream. Click the object **Mixer-1-(AQ)** as highlighted in Figure 8-46 above.

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



Mixing Method: Single Point Mix

Type of calculation: Isothermal

Unit Set: Metric (moles)

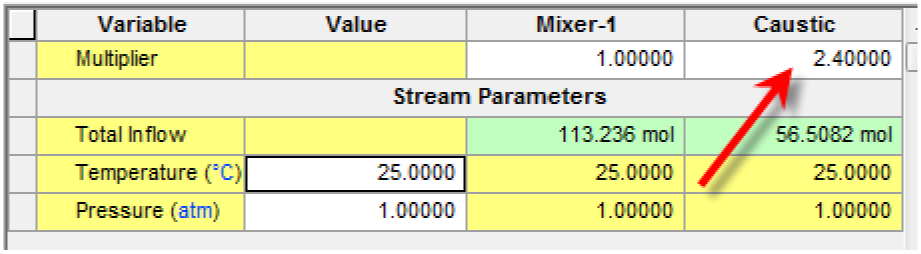
Automatic Chemistry Model

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

Figure 8-47 connecting the output of mixer 1 to the new mixer

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

The resultant pH should be approximately 0.95. We want to increase this value. Change the **Multiplier** value for Caustic Stream from 1.0 to 2.4

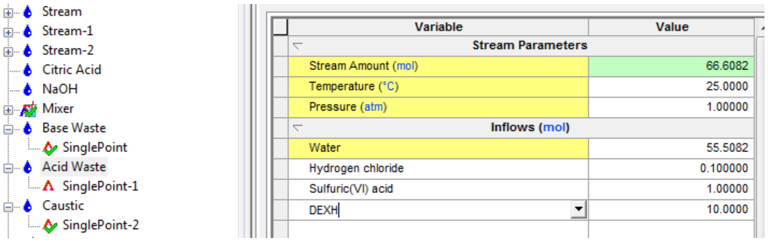


Variable	Value	Mixer-1	Caustic
Multiplier		1.00000	2.40000
Stream Parameters			
Total Inflow		113.236 mol	56.5082 mol
Temperature (°C)	25.0000	25.0000	25.0000
Pressure (atm)	1.00000	1.00000	1.00000

Figure 8-48 Changing the multiplier value

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

The real value of the cascading mixer is the quick ability to re-calculate the objects if we want to change something. Let's add some diethanolamine to the series of calculations. Click the **Acid Waste** stream (not the single point calculation below it) and add the component DEXH[39] to the grid with a value of 10.0 moles.

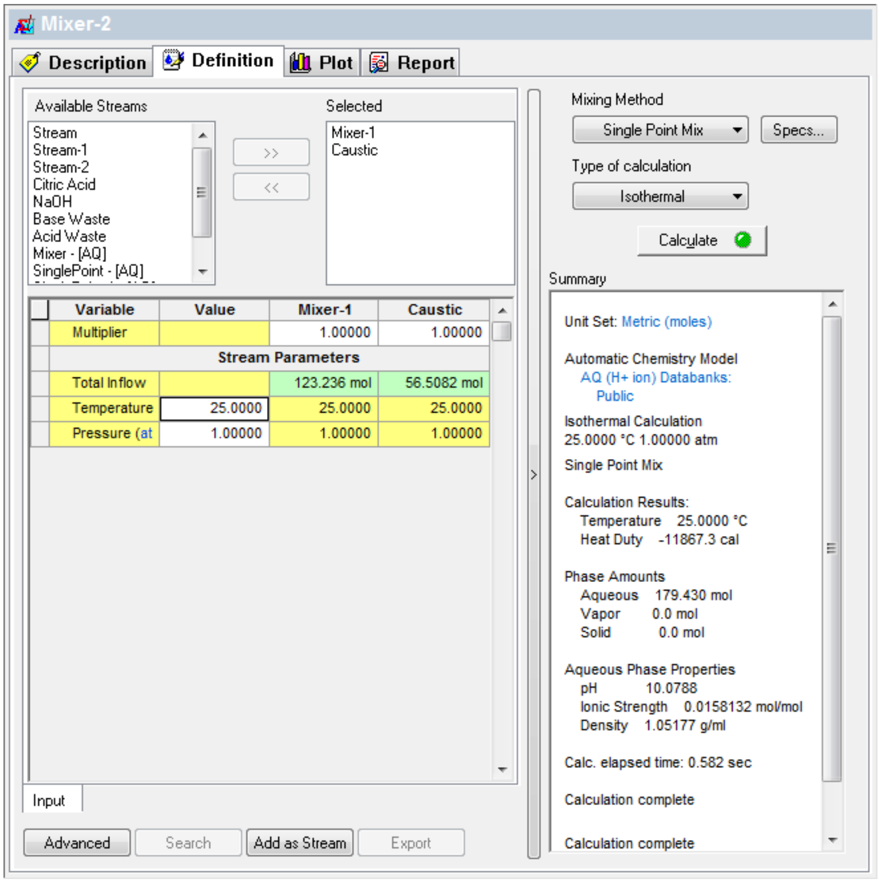


Variable	Value
Stream Parameters	
Stream Amount (mol)	66.6082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
Water	55.5082
Hydrogen chloride	0.100000
Sulfuric(VI) acid	1.00000
DEXH	10.0000

Figure 8-49 Adding diethanolamine, note that the Acid Waste Stream is highlighted.

Return to the last mixer you created (Mixer-2 in our example) and then reduce the ***Caustic Multiplier back to 1.0***

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



Mixing Method: Single Point Mix

Type of calculation: Isothermal

Variable	Value	Mixer-1	Caustic
Multiplier		1.00000	1.00000
Stream Parameters			
Total Inflow		123.236 mol	56.5082 mol
Temperature	25.0000	25.0000	25.0000
Pressure (at	1.00000	1.00000	1.00000

Summary

```
Unit Set: Metric (moles)

Automatic Chemistry Model
    AQ (H+ ion) Databanks:
      Public

Isothermal Calculation
25.0000 °C 1.00000 atm

Single Point Mix

Calculation Results:
    Temperature   25.0000 °C
    Heat Duty   -11867.3 cal

Phase Amounts
    Aqueous   179.430 mol
    Vapor      0.0 mol
    Solid       0.0 mol

Aqueous Phase Properties
    pH         10.0788
    Ionic Strength    0.0158132 mol/mol
    Density    1.05177 g/ml

Calc. elapsed time: 0.582 sec

Calculation complete

Calculation complete
```

Figure 8-50

---

[39] This is the OLI Tag name for diethanolamine, which is easier to type if you know the name.

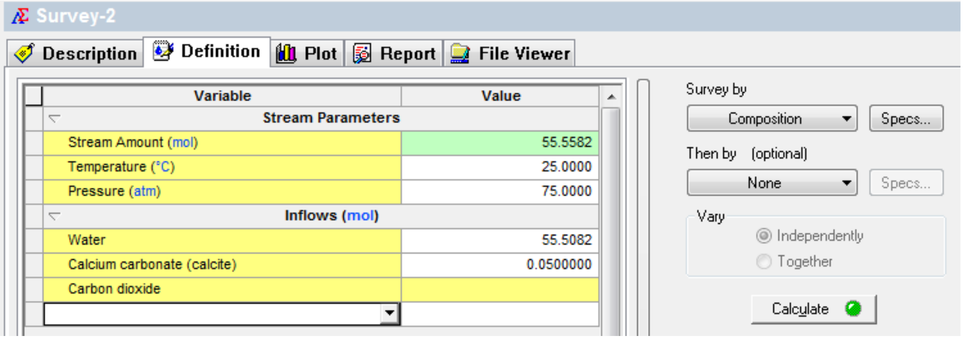
Secondary Surveys

On many occasions, we wish to study a system that varies two independent variables at the same time. This can be accomplished via the secondary survey. In this example, we will re-use the **composition** survey entered earlier.

We are not only interested in the solubility of calcium carbonate as a function of carbon dioxide; we also are interested in the temperature effects.

If you re-open this file, you can skip down to the section "***Starting from a saved case"*** *below.*

As a review, enter the **Definition** below.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5582
Temperature (°C)	25.0000
Pressure (atm)	75.0000
Inflows (mol)	
Water	55.5082
Calcium carbonate (calcite)	0.0500000
Carbon dioxide	

Survey by: Composition

Then by (optional): None

Vary: ● Independently ○ Together

Figure 8-51 Composition survey definition

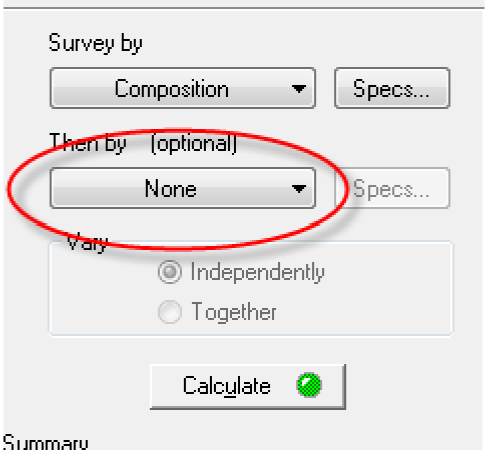
Select **Composition** from the **Survey by** button. Select the **Specs** button and then select ***CO2***.

Select the **Range** tab and adjust the increment to ***0.05***, the ending value is ***1.0.***

Starting from a saved case

Click on the **Definition** tab for the survey.

Now select the **Then by** button.



Survey by: Composition

Then by (optional): None

Vary: ● Independently ○ Together

Figure 8-52

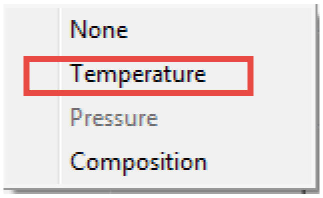


Figure 8-53 Selecting the Secondary Survey

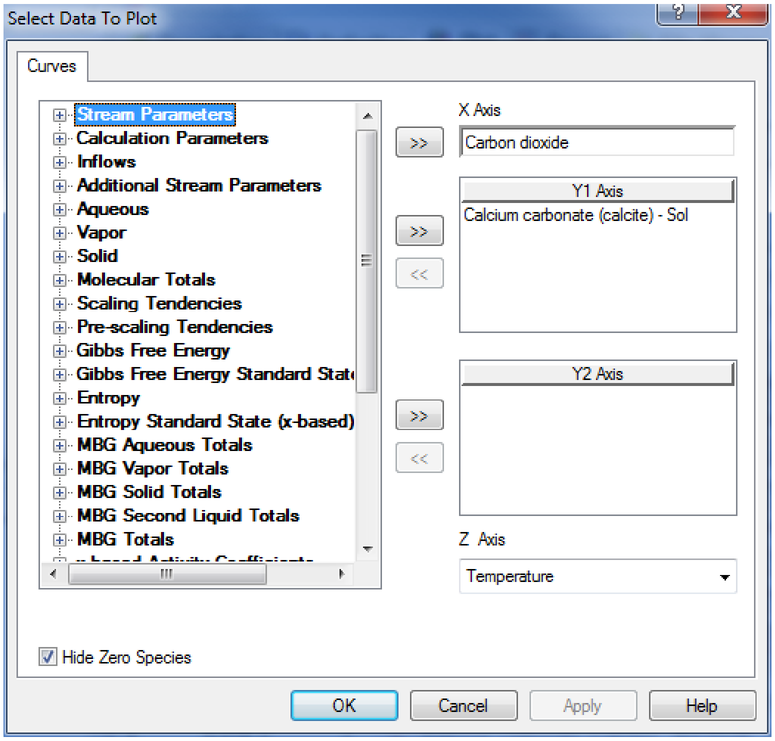
Select **Temperature**.

We are making no changes to the default range.

Click the Calculate button when ready.

This will now launch a very large series of calculations. Essentially, we multiple the range of the composition survey by the range of the temperature survey to get the number of calculations. The following figure shows the large number of points being calculated

When the calculation completes, click on the **Plot** tab. The plot options should be the same if you opened the file that was previously saved. If not click the **Variables** button and select the plot variables as shown below.



Select Data To Plot

X Axis: Carbon dioxide

Y1 Axis: Calcium carbonate (calcite) - Sol

Y2 Axis:

Z Axis: Temperature

☑ Hide Zero Species

Figure 8-54 Setting the plot variables

Click on **OK** to return to the plot. The plot now has points from 0 to 100 °C. Unfortunately, the legend is covering a large part of the graph.

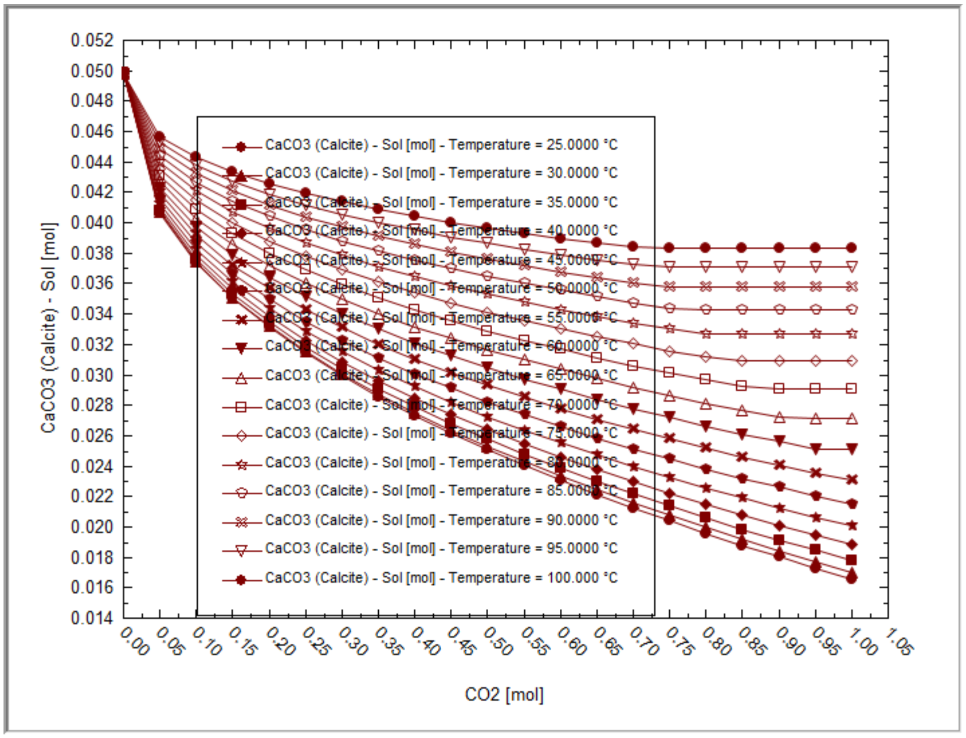


Figure 8-55 A family of Curves, the legend is in the way.

Right-clicking anywhere on the plot brings up the following menu:

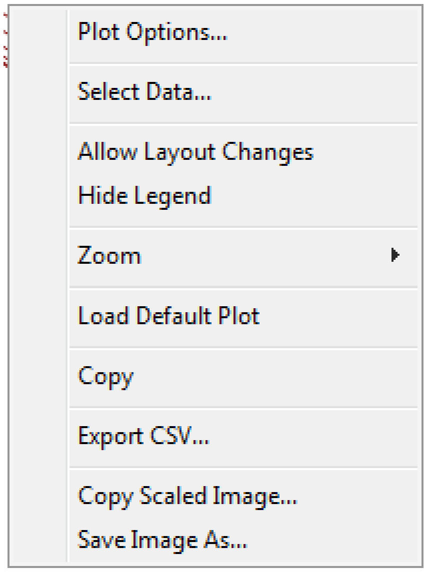


Figure 8-56 Right-Click on the plot to pop this up.

You may toggle the axes between linear and logarithmic, suppress the legend, allow changes to placement of titles (**Allow Layout Changes**) and save the design.

For now, ***click*** on **Hide Legend** to turn off the legend.

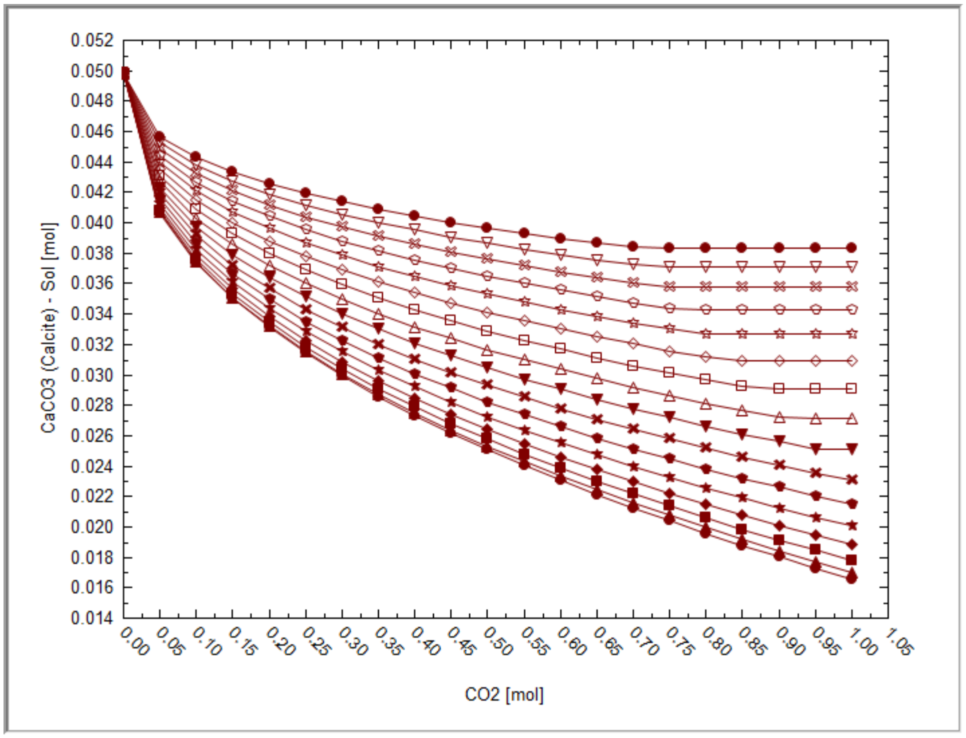


Figure 8-57 The uncluttered view.

The solubility of calcium carbonate increases with temperature. The lower temperatures are the bottom curves.

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

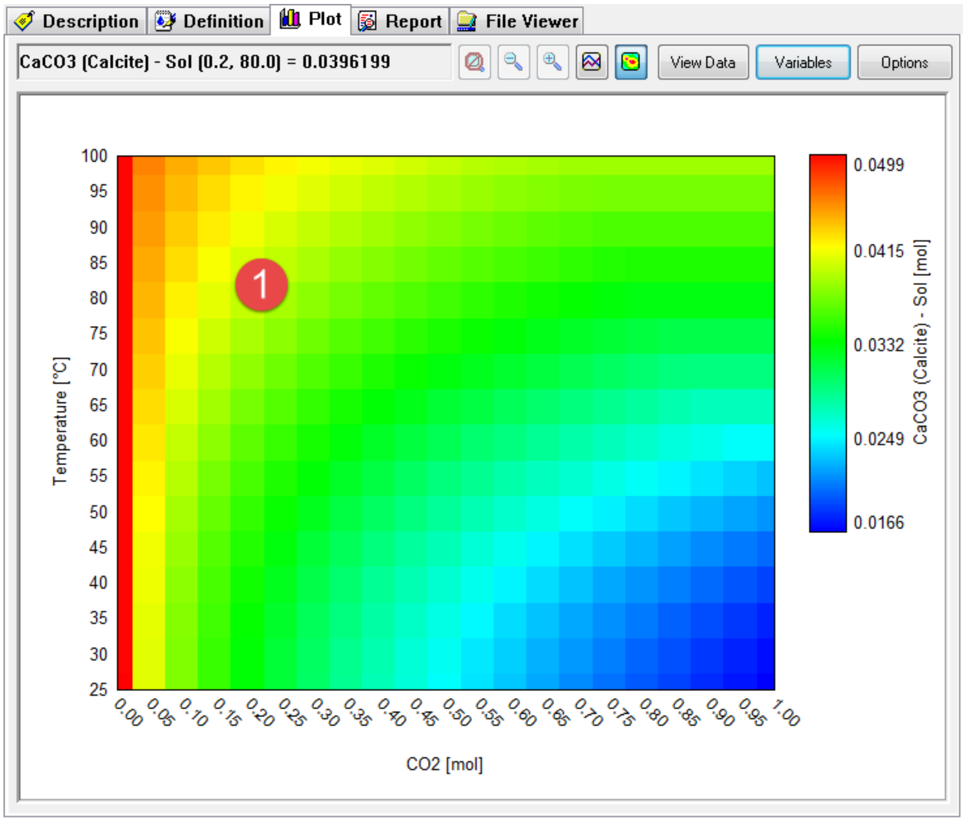
Please save the file now (you may want to use a different name since this is different from the previous composition survey).

Contour Plots

If you have created a dual survey, you can then create a contour plot. To do this you simply should click the contour plot button:

Figure 8-58 the contour plot button

This dramatically changes the display.



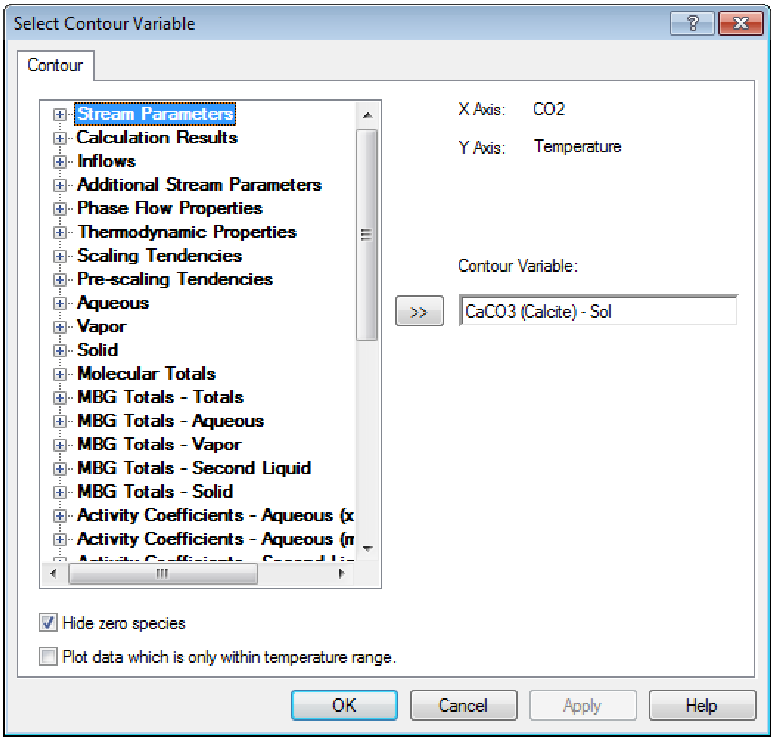
CaCO3 (Calcite) - Sol (0.2, 80.0) = 0.0396199

Figure 8-59 the contour plot

The plot shows a lot of information at once. The position of the mouse pointer is shown in the information bar at the top. (This is represented by the Number 1 in the figure) In this case the x,y coordinate of 0.2 moles of CO_2 and a temperature of 80 °C reports 0.0396 moles of $CaCO_3$ solid forming. The colors are indication of minimum (blue) and maximum (red) values on the plot.

Unlike the standard plot, we have limited some of the variables that can be plotted at once. For example, you can only plot a single variable and the axis variables cannot be changed. If you click the **Variables** button

You will see the following dialog:



X Axis: CO2

Y Axis: Temperature

Contour Variable: CaCO3 (Calcite) - Sol

☑ Hide zero species

☐ Plot data which is only within temperature range.

Figure 8-60 Contour variables

Only a single variable can be selected. If you expand some categories such as “Aqueous” you will find that the “Dominant” species is not present since that will attempt to plot more than a single variable.

To change back to the standard plot you need click the plot button:

Figure 8-61 The standard plot button

Please save your file.

Click here for a worked copy of this chapter’s tour: Chapter 08 Tour

9. Water Analysis in OLI Studio: An Overview

Overview:

Due to the nature of water analysis, most, if not all, samples entered in the OLI Studio are incomplete and/or are inaccurate in some manner. Thus, most samples will not be electrically neutral. This requires the OLI Studio to reconcile the sample for electroneutrality.

Many samples also have a measured pH. The sample that has been reconciled for electroneutrality will probably not have the same calculated pH as the measured pH. Normally this is a result of the incomplete or inaccurate description of the sample. The Water Analysis Tool will adjust the pH of the calculated sample to match the measured pH.

An Example:

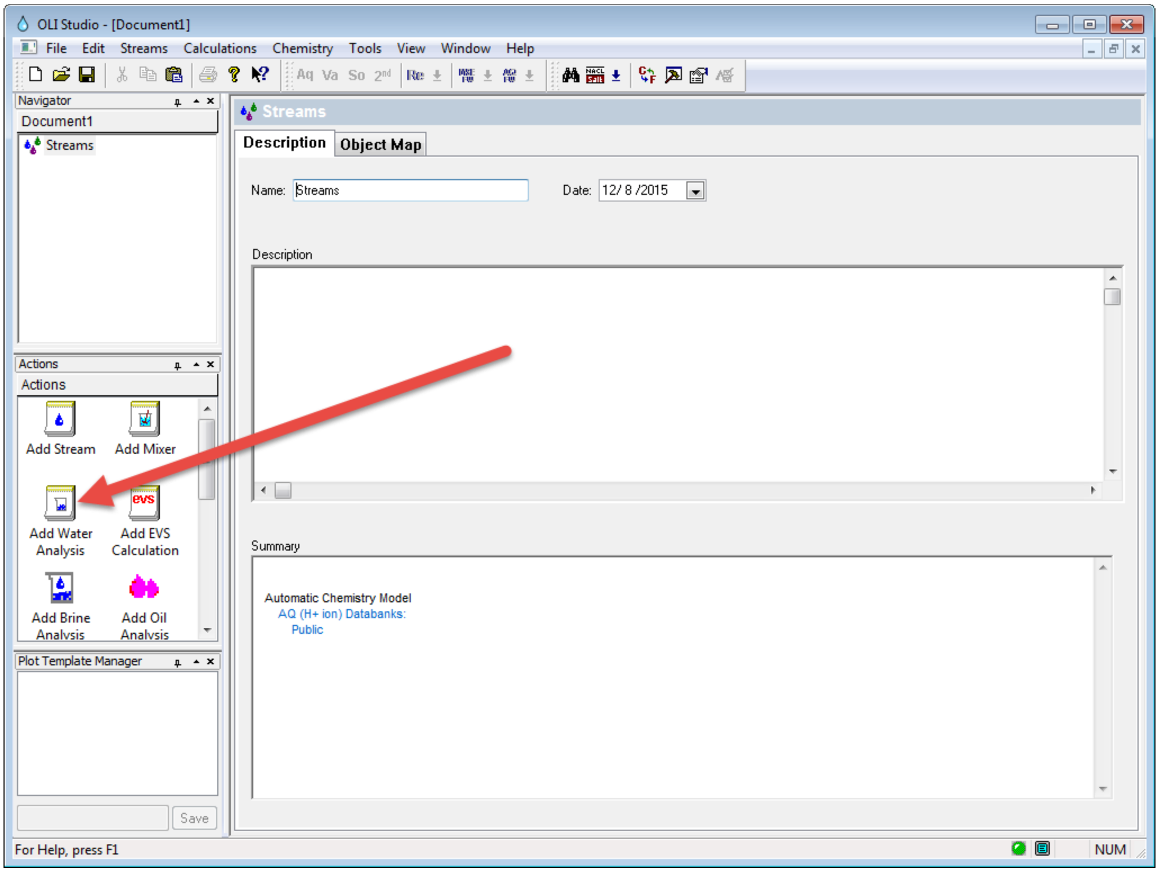
We have been given a sample of ground water with the following composition:

Table 9-1Ground Water Concentrations

Temperature	25.00	C
Pressure	1.00	Atm.
pH (measured)	6.70	

Cation	**mg/L**	**Anion**	**Mg/L**	**Dissolved Gas**	**mg/L**
Ba+2	0.46	Cl-	3896.00		
Ca+2	773.00	B(OH)4-	2.60	CH4	15.50
Fe+2	62.10	SO3-2	6.30	CO2	150.00
K+	50.00	SO4-2	54.00	Benzene	1.40
Mg+2	177.00			NH3	4.60
Mn+2	2.80				
Na+1	1060.00				
Al+3	0.74				
Sr+2	0.18				

Let's use OLI Studio to examine this sample. First, we double-click the icon on the desktop or use the Start menu to start the program.



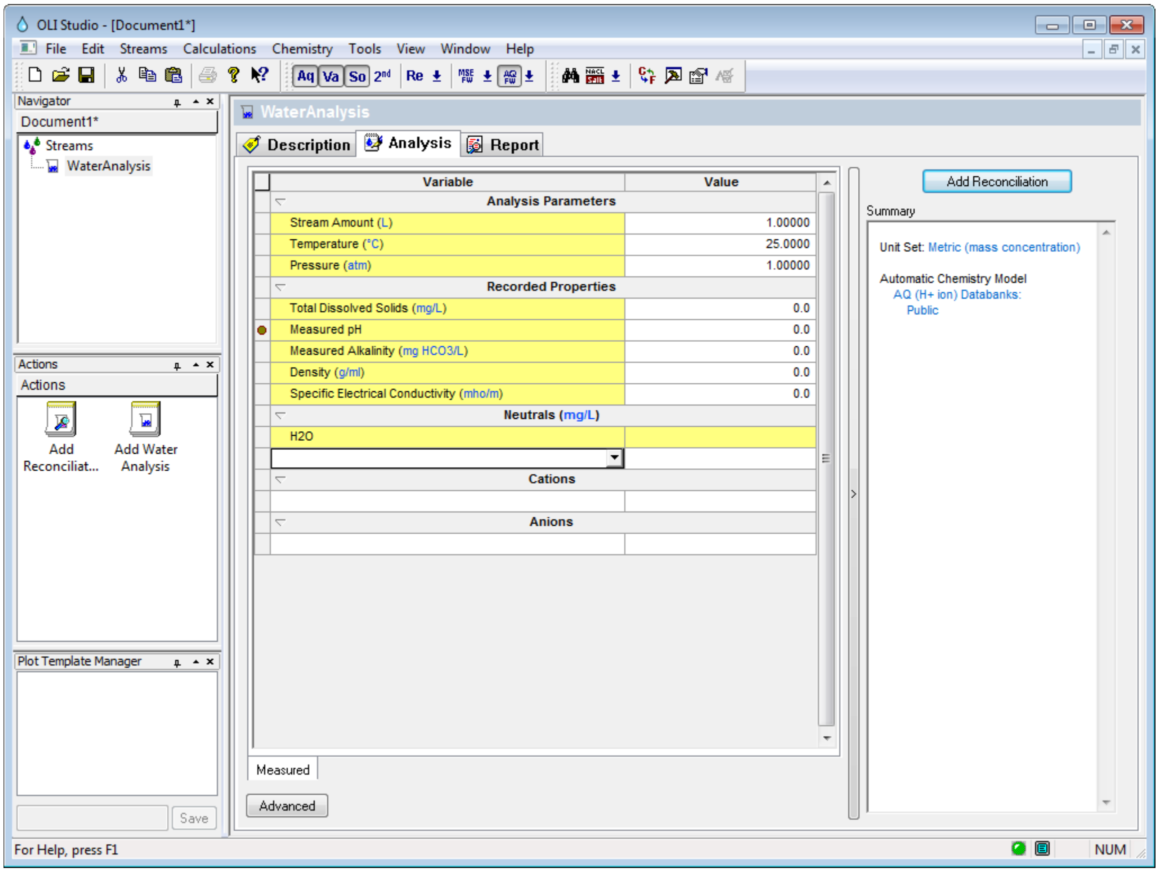
Name: Streams

Date: 12/ 8 /2015

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 9-1 The main window.

As with the other Analyzer calculations, we start by define the conditions.



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
● Measured pH	0.0
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (mho/m)	0.0
Neutrals (mg/L)	
H2O	
Cations	
Anions	

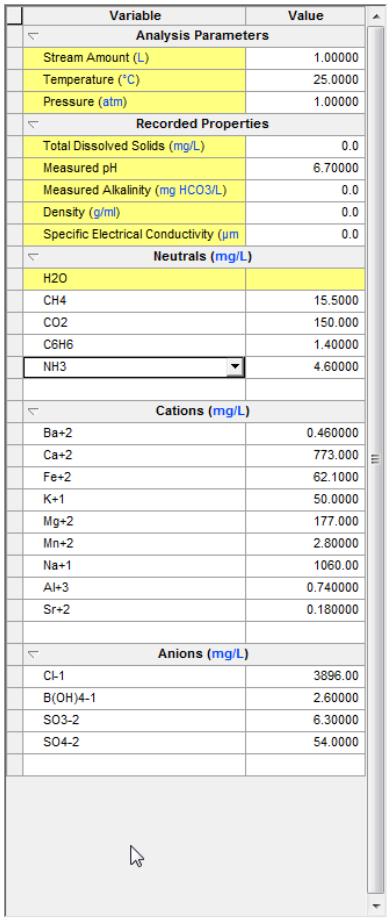
Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 9-2 The icons available for the analysis

We will enter the concentrations listed on the previous page.



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.70000
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (μm	0.0
Neutrals (mg/L)	
H2O	
CH4	15.5000
CO2	150.000
C6H6	1.40000
NH3	4.60000
Cations (mg/L)	
Ba+2	0.460000
Ca+2	773.000
Fe+2	62.1000
K+1	50.0000
Mg+2	177.000
Mn+2	2.80000
Na+1	1060.00
Al+3	0.740000
Sr+2	0.180000
Anions (mg/L)	
Cl-1	3896.00
B(OH)4-1	2.60000
SO3-2	6.30000
SO4-2	54.0000

Figure 9-3 A list of the conditions, cations, anions and neutrals

Enter the concentrations from the table above. Enter the cations in the **Cations** section; the anions in the **Anions** section. Enter the dissolved gases in the inflow section. You will have to use the scroll bar to move the grid.

Click on the **Add Reconciliation** button.

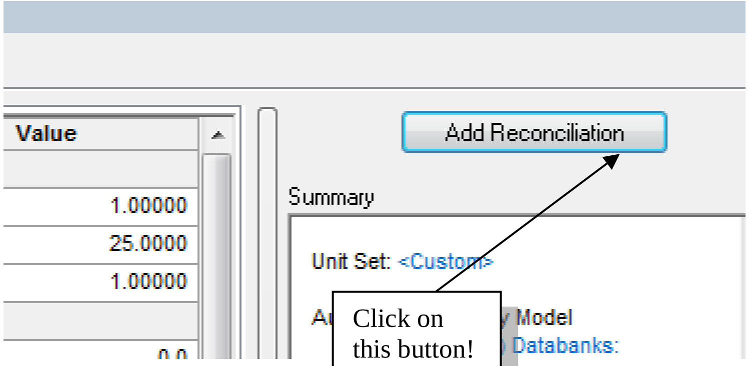
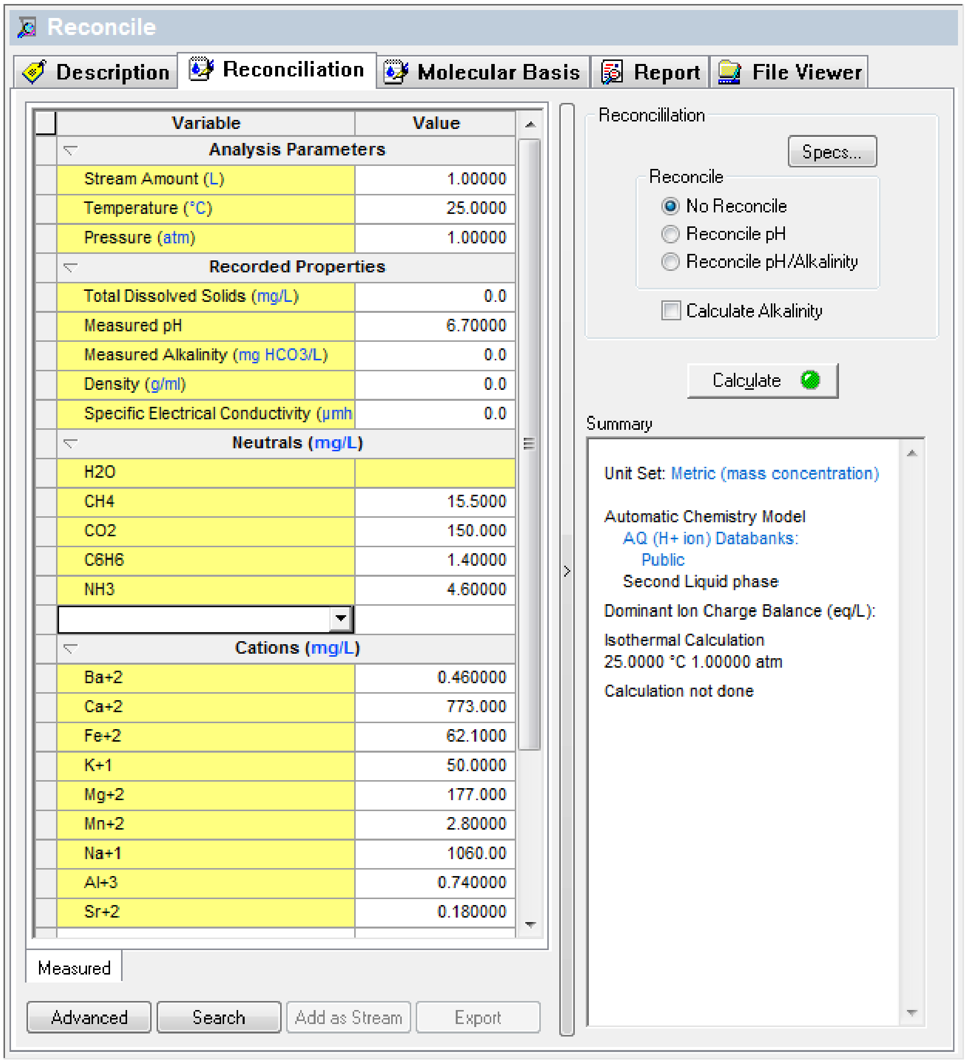


Figure 9-4 click on t tion button

This will automatically update the tree view on the left and place you in the description tab for the reconciliation.



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.70000
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (μmh	0.0
Neutrals (mg/L)	
H2O	
CH4	15.5000
CO2	150.000
C6H6	1.40000
NH3	4.60000
Cations (mg/L)	
Ba+2	0.460000
Ca+2	773.000
Fe+2	62.1000
K+1	50.0000
Mg+2	177.000
Mn+2	2.80000
Na+1	1060.00
Al+3	0.740000
Sr+2	0.180000

Reconcile
● No Reconcile
○ Reconcile pH
○ Reconcile pH/Alkalinity

☐ Calculate Alkalinity

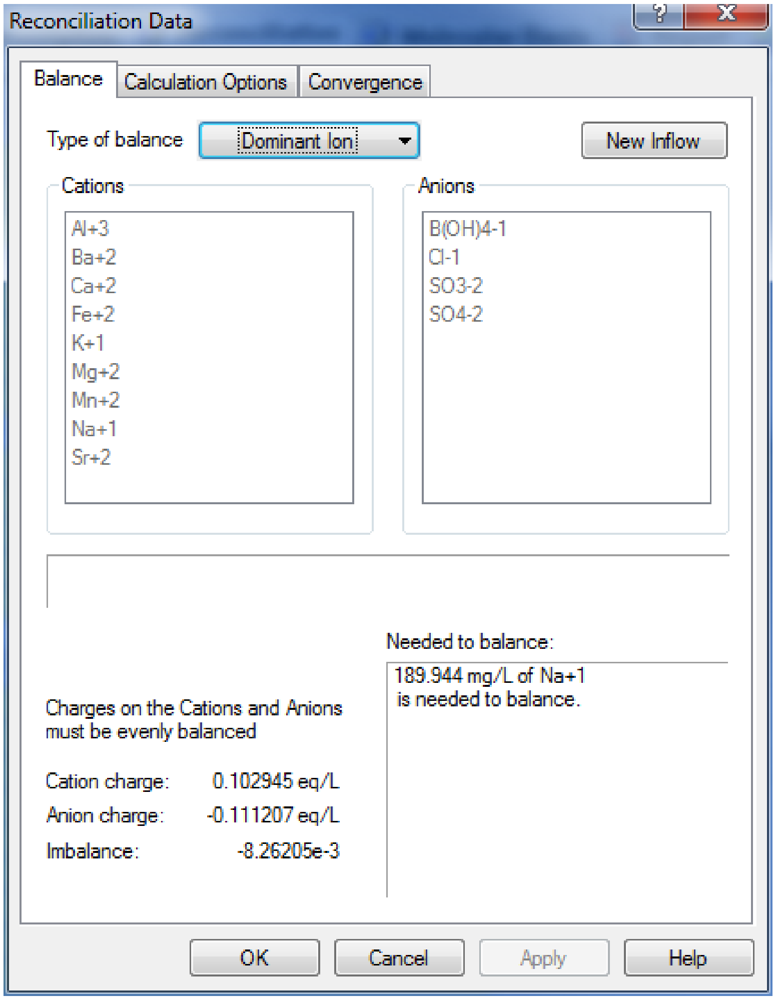
Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public
Second Liquid phase
Dominant Ion Charge Balance (eq/L):
Isothermal Calculation
25.0000 °C 1.00000 atm
Calculation not done

Figure 9-5 The reconciliation panel.

It is highly unlikely that this sample is electrically neutral. We need to make sure that there is no net charge to this sample. The Program will automatically balance the Electroneutrality. To view how this is done, click the ***Specs…*** button.



Type of balance: Dominant Ion

Cations: Al+3, Ba+2, Ca+2, Fe+2, K+1, Mg+2, Mn+2, Na+1, Sr+2

Anions: B(OH)4-1, Cl-1, SO3-2, SO4-2

Needed to balance:
189.944 mg/L of Na+1
is needed to balance.

Charges on the Cations and Anions
must be evenly balanced

Cation charge: 0.102945 eq/L
Anion charge: -0.111207 eq/L
Imbalance: -8.26205e-3

Figure 9-6 The Reconciliation Data dialog.

This window dialog has a great deal of information. The available cations are listed in the **Cations** list box and the anions are listed in the **Anions** list box. The current Cation charge is 0.102945 equivalents/L (or eq/L). The current Anion charge is –0.111207 eq/L. There is too much anion charge by –0.008262 eq/L.

There are several methods of reconciling the Electroneutrality. The default method is the **Dominant Ion** method. In this method, the imbalance in charge is determined. In this example there is an excess of negative charge.

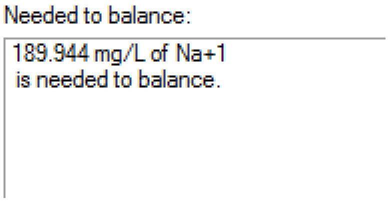

Needed to balance:
189.944 mg/L of Na+1
is needed to balance.

Figure 9-7 The largest concentration of cation to be entered.

We will now change the type of balance to ***Na/Cl***.

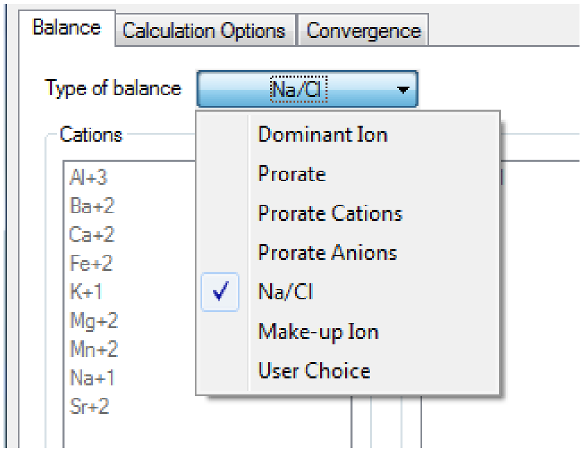


Figure 9-8 Na/Cl reconciliation method

This reconciliation is the same as the dominant ion method since sodium is the largest concentration of cation (the counter charge). The conversion of equivalents to milligrams occurred as follows:

$$\left(0.007138\frac{eq}{L}\right)\left(\frac{1 mole Na^{+}}{1 eq}\right)\left(\frac{22.99 grams Na^{+}}{mole Na^{+}}\right)\left(\frac{10^{3} mg Na^{+}}{grams Na^{+}}\right) = 189.944\frac{mg Na^{+}}{L}$$

There are other options for reconciliation. Click on the **Type of Balance** button to see the list.

Electroneutrality

Dominant Ion

The largest species concentration of the deficient charge is added.

In this case Na^{+} ion was added since there is an excess of negative charge.

Proration

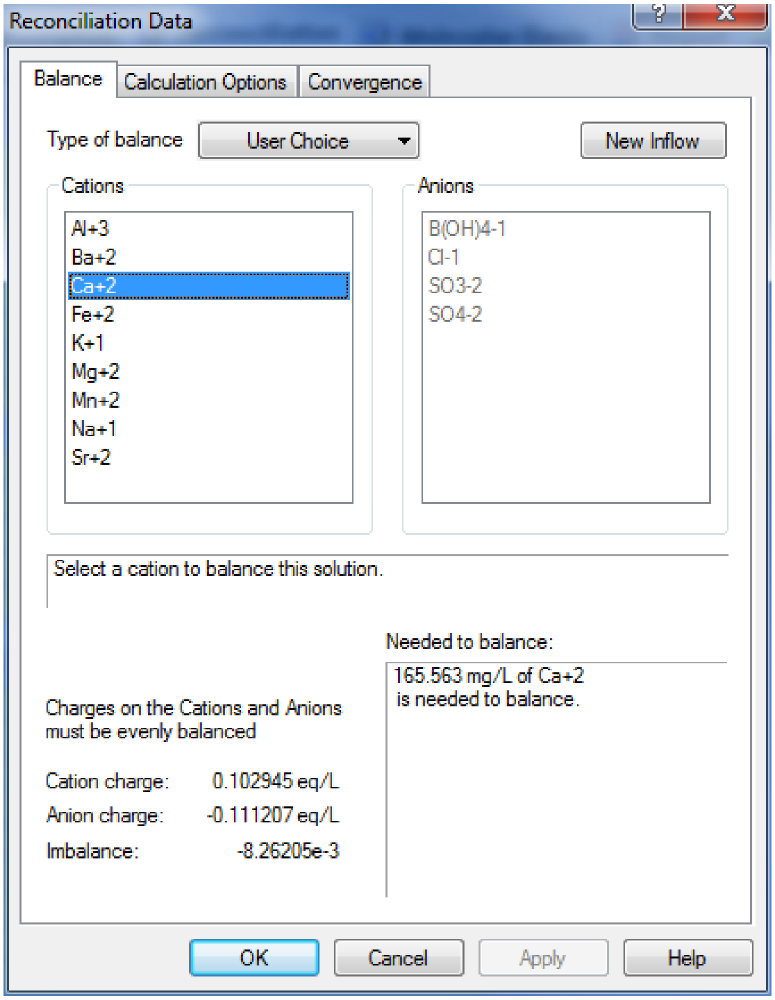
An equal percentage of all deficient species is added.

Na/Cl

Sodium is added when there is an excess of negative charge, chloride is added when there is an excess of positive charge.

User Specification

The user specifies the cation or anion required to balance the sample.



Type of balance: User Choice

Cations
Al+3
Ba+2
Ca+2
Fe+2
K+1
Mg+2
Mn+2
Na+1
Sr+2

Anions
B(OH)4-1
Cl-1
SO3-2
SO4-2

Select a cation to balance this solution.

Needed to balance:
165.563 mg/L of Ca+2
is needed to balance.

Charges on the Cations and Anions must be evenly balanced

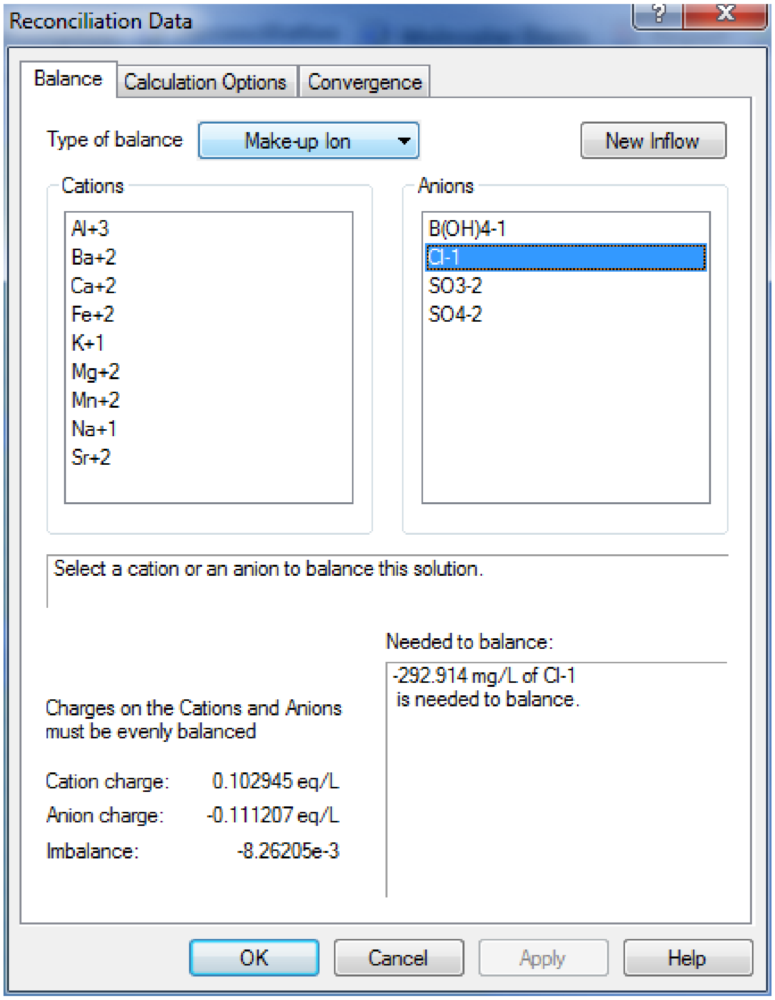
Cation charge: 0.102945 eq/L
Anion charge: -0.111207 eq/L
Imbalance: -8.26205e-3

Figure 9-9 User choice option

Since there is an excess of negative charge, only the cations are available for selection with this option. 165.563 mg/L of Ca^{+2} is needed to balance the sample.

Make Up Ion

The specified ion is either added or subtracted to balance the charge.



Type of balance: Make-up Ion

Cations: Al+3, Ba+2, Ca+2, Fe+2, K+1, Mg+2, Mn+2, Na+1, Sr+2

Anions: B(OH)4-1, Cl-1, SO3-2, SO4-2

Select a cation or an anion to balance this solution.

Needed to balance:

-292.914 mg/L of Cl-1
is needed to balance.

Charges on the Cations and Anions must be evenly balanced

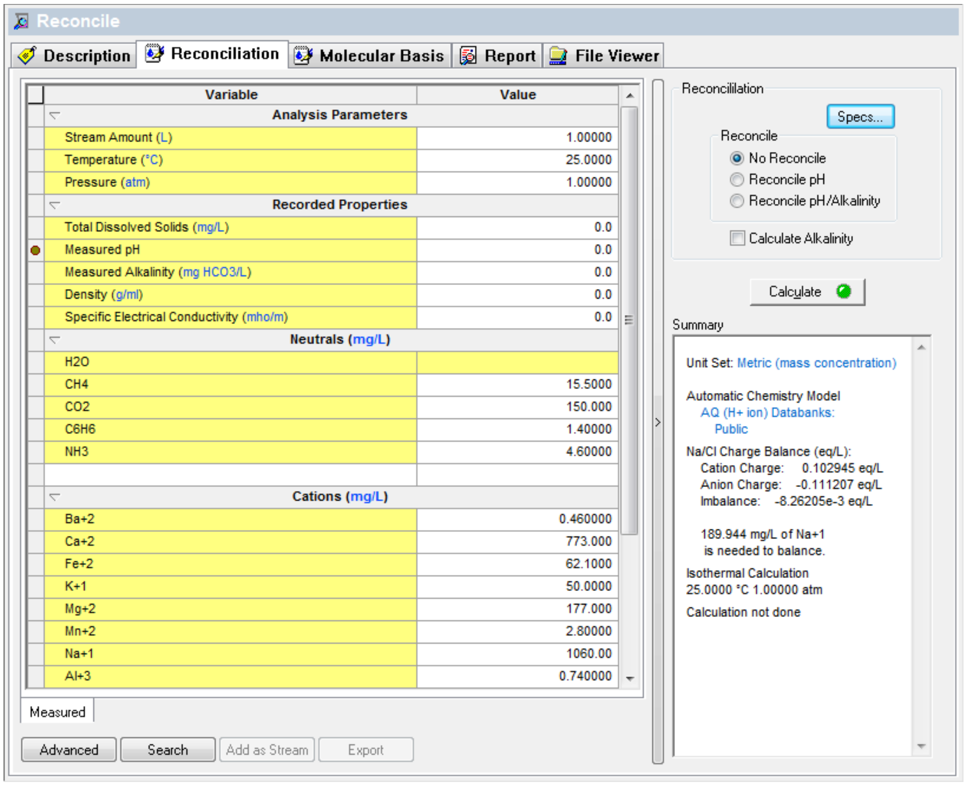
Cation charge:	0.102945 eq/L
Anion charge:	-0.111207 eq/L
Imbalance:	-8.26205e-3

Figure 9-10 Make Up Ion Option

With the make-up ion option, either a cation or anion can be used to adjust the Electroneutrality. Since in this example, there is an excess of negative charge, selecting a cation has the same result as the ***User Choice*** option. In the figure above, chloride ion has been selected. Since there is an excess of negative charge, 292.914 mg of Cl^- must be removed.

Make sure the **Type of Balance** button is set to **Na/Cl** and then ***click*** on the **OK** button.

The **Summary** box is now updated with the current Electroneutrality.



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
● Measured pH	0.0
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (mho/m)	0.0
Neutrals (mg/L)	
H2O	
CH4	15.5000
CO2	150.000
C6H6	1.40000
NH3	4.60000
Cations (mg/L)	
Ba+2	0.460000
Ca+2	773.000
Fe+2	62.1000
K+1	50.0000
Mg+2	177.000
Mn+2	2.80000
Na+1	1060.00
Al+3	0.740000

Reconcililation

Reconcile
● No Reconcile
○ Reconcile pH
○ Reconcile pH/Alkalinity

☐ Calculate Alkalinity

Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Na/Cl Charge Balance (eq/L):
Cation Charge: 0.102945 eq/L
Anion Charge: -0.111207 eq/L
Imbalance: -8.26205e-3 eq/L

189.944 mg/L of Na+1
is needed to balance.

Isothermal Calculation
25.0000 °C 1.00000 atm

Calculation not done

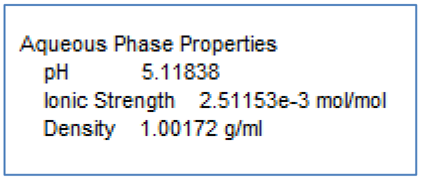
Figure 9-11 The updated summary box.

We can now either automatically reconcile the pH of the sample or first calculate the natural pH.

Click the **No pH Reconcile** radio button in the **Reconcile pH** options box.

Now ***click*** the **Calculate** button.

When the calculation has finished, scroll down the text in the **Summary** box to find pH.

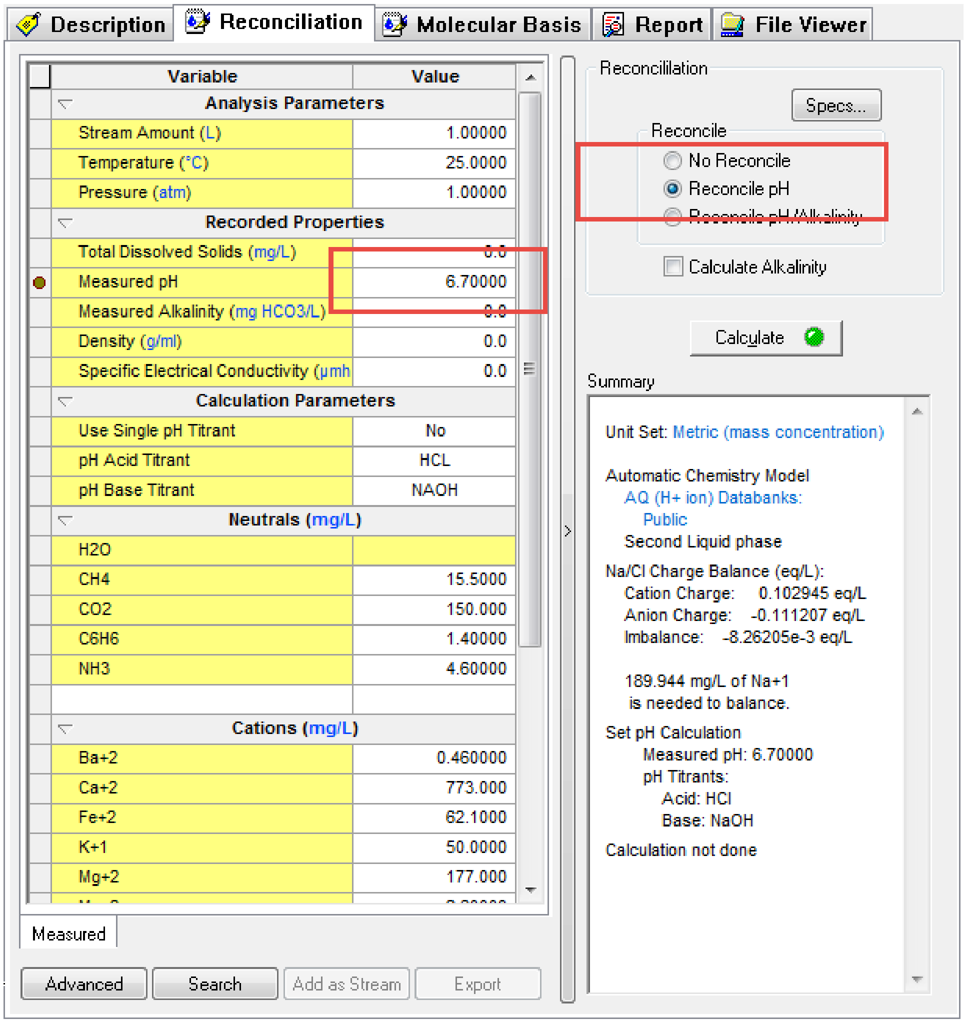


Aqueous Phase Properties
pH 5.11838
Ionic Strength 2.51153e-3 mol/mol
Density 1.00172 g/ml

Figure 9-12 The pH is approximately 5.1

This pH is much less than the reported pH of 6.7. What is the reason for this value? That will be explained in a moment. Right now, we wish to adjust the pH back to the reported value of 6.7.

Click on the **Reconcile pH** radio button.



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.70000
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (μmh	0.0
Calculation Parameters	
Use Single pH Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Neutrals (mg/L)	
H2O	
CH4	15.5000
CO2	150.000
C6H6	1.40000
NH3	4.60000
Cations (mg/L)	
Ba+2	0.460000
Ca+2	773.000
Fe+2	62.1000
K+1	50.0000
Mg+2	177.000

Reconcile
○ No Reconcile
● Reconcile pH
○ Reconcile pH/Alkalinity

☐ Calculate Alkalinity

```
Unit Set: Metric (mass concentration)

Automatic Chemistry Model
   AQ (H+ ion) Databanks:
      Public
   Second Liquid phase

Na/Cl Charge Balance (eq/L):
   Cation Charge:    0.102945 eq/L
   Anion Charge:    -0.111207 eq/L
   Imbalance:    -8.26205e-3 eq/L

   189.944 mg/L of Na+1
    is needed to balance.

Set pH Calculation
      Measured pH: 6.70000
      pH Titrants:
         Acid: HCl
         Base: NaOH

Calculation not done
```

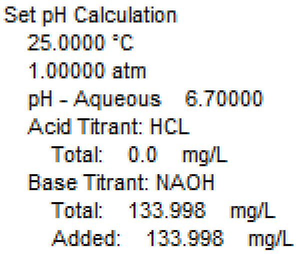
Figure 9-13 Choosing the Reconcile pH option.

The default acid/base titrants are HCl and NaOH (see the red box in the above figure). We will be using these titrants but they can be changed if you manually enter different acid and bases.

You should double-check that the **Measured pH** value is the value you want. On occasion, you may want to reconcile the pH to a value other than the recorded pH.

For this example, the initial pH is 5.1 and will be increased to 6.7 using NaOH. Click the ***Calculate*** button.

When the calculation is complete, scroll the **Summary** box down to find the amount of titrant required.



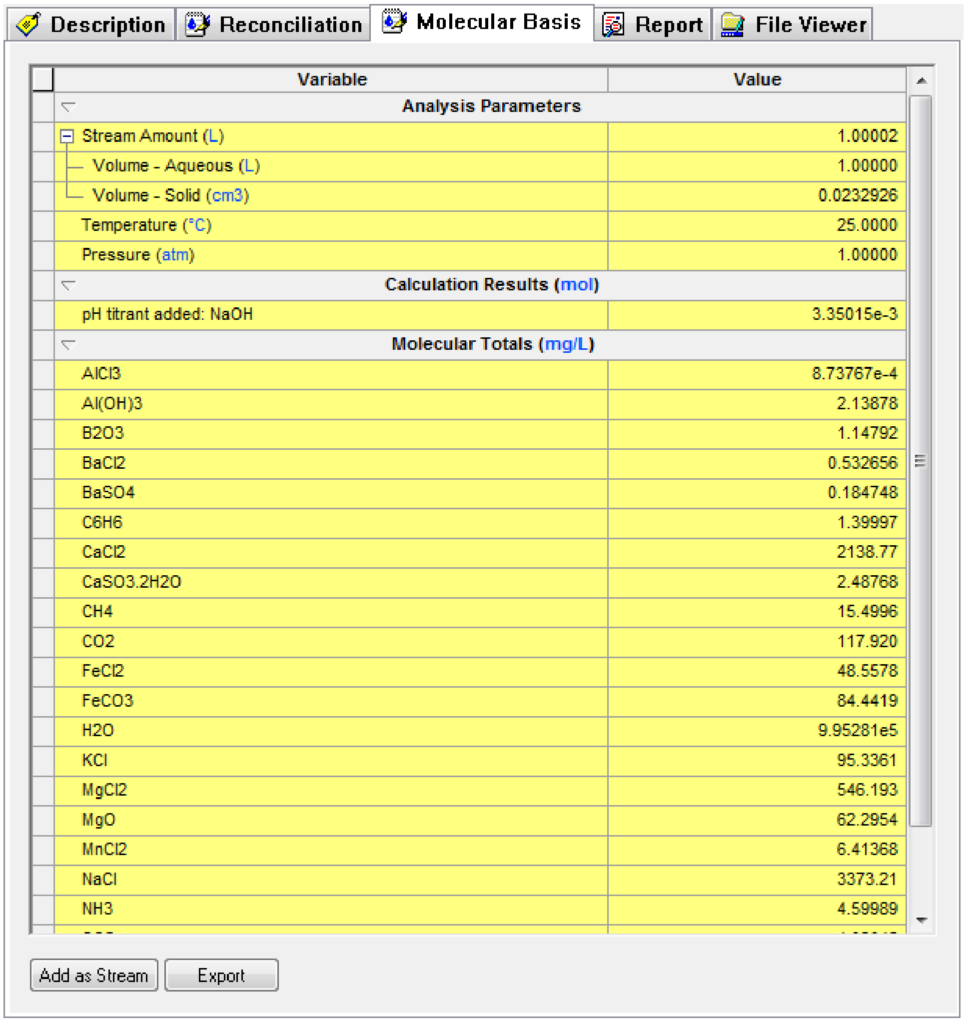
```
Set pH Calculation
   25.0000 °C
   1.00000 atm
   pH - Aqueous    6.70000
   Acid Titrant: HCL
      Total:    0.0    mg/L
   Base Titrant: NAOH
      Total:    133.998    mg/L
      Added:    133.998    mg/L
```

Figure 9-14 The amount of NaOH added.

Most OLI programs cannot use ionic inflows. This sample must be converted into a “Neutral” stream. In other words, a neutral molecular representation is required.

Fortunately, OLI Studio does the conversion automatically. The molecular stream displayed below was converted from the preceding sample after electroneutrality and pH have been reconciled. To find these values, click on the **Molecular Basis** tab.

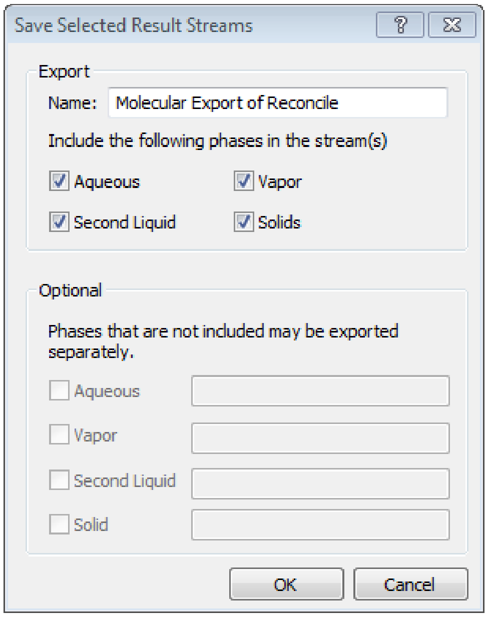
Click the **Add as Stream** button to save as a molecular (neutral) stream.



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00002
Volume - Aqueous (L)	1.00000
Volume - Solid (cm3)	0.0232926
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Results (mol)	
pH titrant added: NaOH	3.35015e-3
Molecular Totals (mg/L)	
AlCl3	8.73767e-4
Al(OH)3	2.13878
B2O3	1.14792
BaCl2	0.532656
BaSO4	0.184748
C6H6	1.39997
CaCl2	2138.77
CaSO3.2H2O	2.48768
CH4	15.4996
CO2	117.920
FeCl2	48.5578
FeCO3	84.4419
H2O	9.95281e5
KCl	95.3361
MgCl2	546.193
MgO	62.2954
MnCl2	6.41368
NaCl	3373.21
NH3	4.59989

Figure 9-15 Molecular basis. The grid has been scrolled down to see some values

The molecular view can be saved as a new stream for use in another OLI program. Click the **Add as Stream** button.



Save Selected Result Streams

Export

Name: Molecular Export of Reconcile

Include the following phases in the stream(s)

☑ Aqueous ☑ Vapor

☑ Second Liquid ☑ Solids

Optional

Phases that are not included may be exported separately.

☐ Aqueous

☐ Vapor

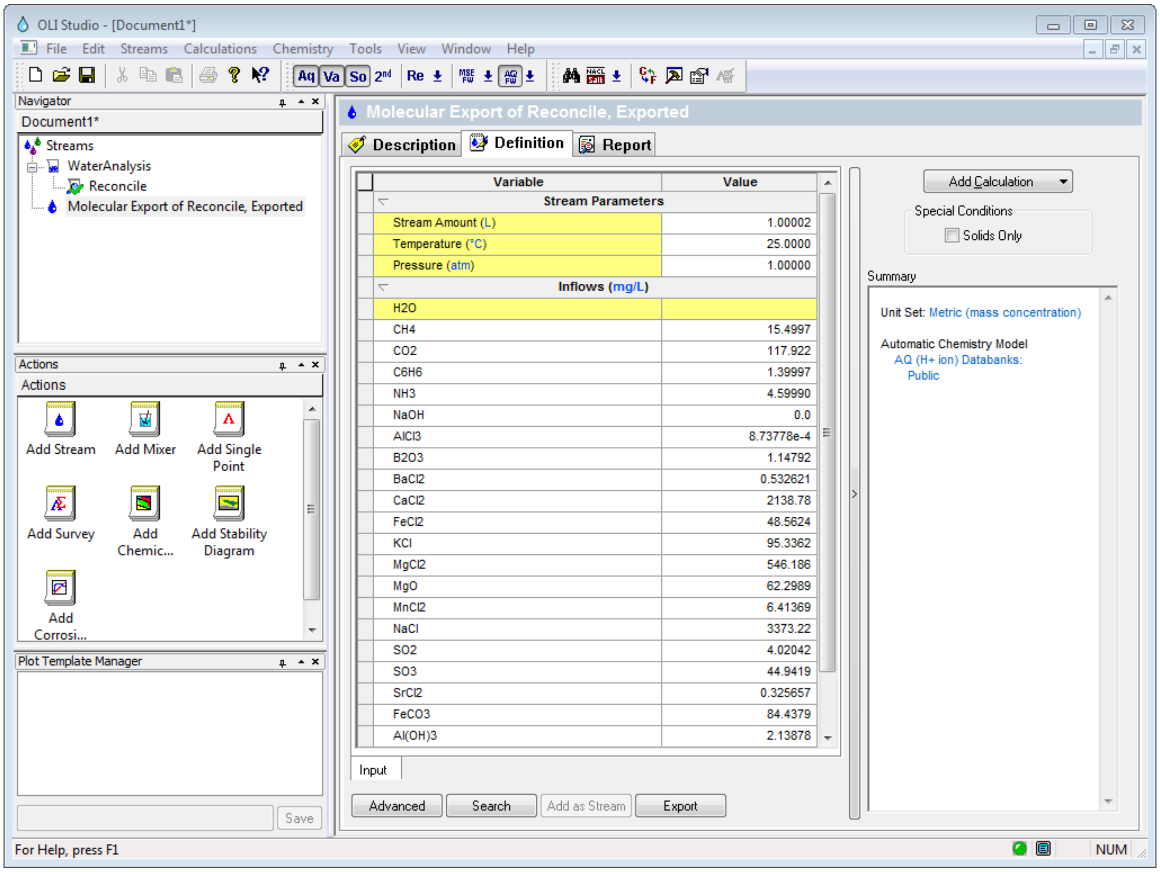
☐ Second Liquid

☐ Solid

Figure 9-16 Save As Stream dialog

Click the **OK** button to save all the phases in this stream.

The program automatically adds a new stream. Click on the new stream and then select the **<u>Definition</u>** tab.



Molecular Export of Reconcile, Exported

Variable	Value
Stream Parameters	
Stream Amount (L)	1.00002
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mg/L)	
H2O	
CH4	15.4997
CO2	117.922
C6H6	1.39997
NH3	4.59990
NaOH	0.0
AlCl3	8.73778e-4
B2O3	1.14792
BaCl2	0.532621
CaCl2	2138.78
FeCl2	48.5624
KCl	95.3362
MgCl2	546.186
MgO	62.2989
MnCl2	6.41369
NaCl	3373.22
SO2	4.02042
SO3	44.9419
SrCl2	0.325657
FeCO3	84.4379
Al(OH)3	2.13878

Special Conditions

☐ Solids Only

Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 9-17 The molecular stream

Summary

OLI Studio provides for alternative feed stream definition based upon a "Raw" Laboratory Analysis:

Flagging of Inconsistencies

- Determines the amount of imbalance with respect to electroneutrality
- Calculates pH based upon sample information

Reconciliation of Inconsistencies

- Adds or subtracts mass to balance electroneutrality
- Adds and acid or base to adjust pH

Simulation Options

- Surveys
- Single Point Calculations
- Conversion to Molecular streams

OLI Studio's Water Analysis module is an invaluable tool to correct deficiencies in laboratory analyses. Water Analysis is also essential for converting ionic flows to neutral.

Click here for a worked example of this chapter: Chapter 09 Introduction to Water Analysis

10. Water Analysis in OLI Studio: A Tour

Reconciling a Brine from an Oil Field

The Application

This application involves reconciliation of a water sample from an oil well. Reconciliation is done for both electroneutrality and pH.

In this application, we will take brine from an oil well that is producing water along with the oil. We will not consider the oil phase in this example.

It is quite common when reviewing laboratory analysis of water samples for the positive ions in solution (cations) and the negatively charged ions (anions) not to balance each other. This may be due to the precision limits of the various experimental procedures used to measure the ions and/or since some ions may not have been analyzed. These solutions must have a neutral charge. **OLI Studio will reconcile the charges to make a solution that is neutral.**

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

Finally, the reconciled sample can be converted into a molecular representation which can be used in other simulators. We will use OLI Studio to perform a simple calculation on our reconciled sample.

The power of the OLI Studio becomes apparent as we consider different reconciling options and pH considerations.

Tour Conventions

In this tour, we will use the following conventions:

Type Face	User Action
Bold and Italic	The user is required to enter this information
<u>Bold and Underlined</u>	The user is directed to look for this feature in the program windows
Click	Left-mouse button
Right-Click	Right-mouse button

The tour Starts here!

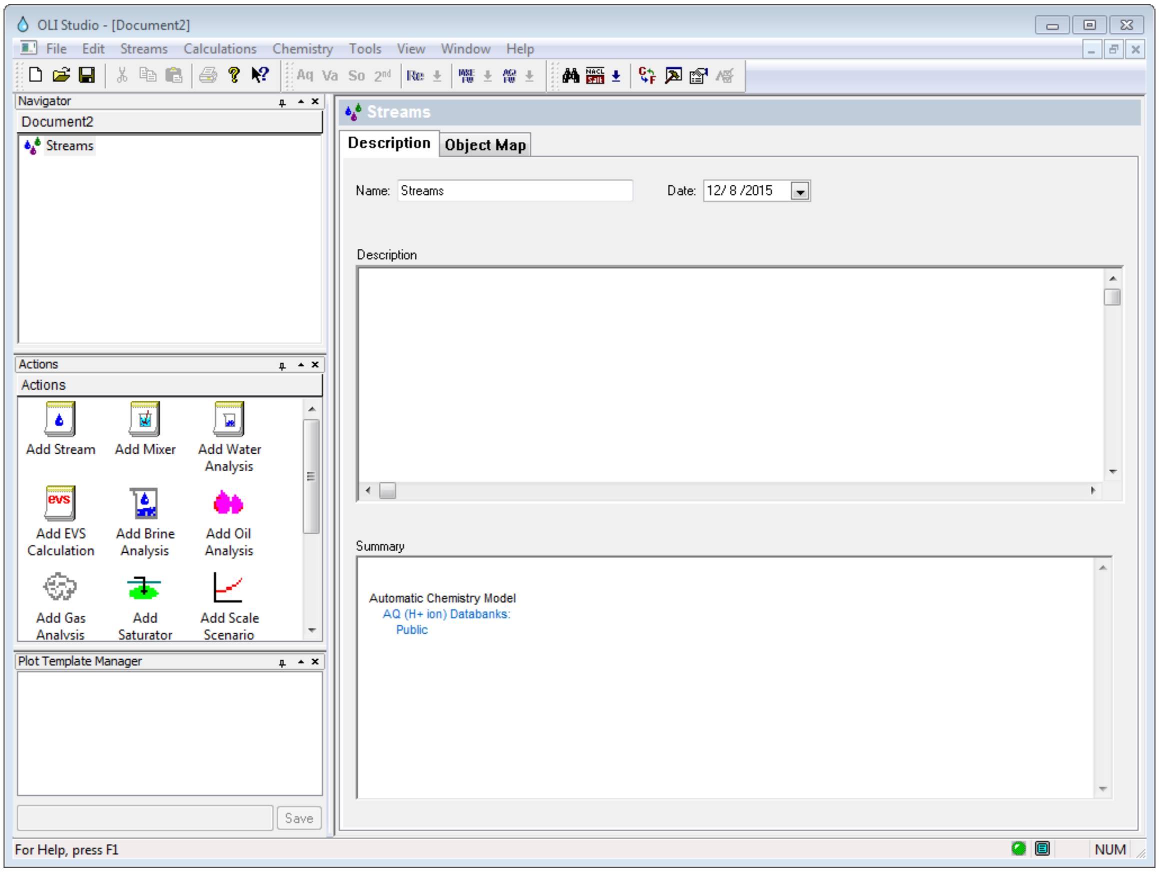
We have been given the produced water sample from an oil well in Thailand. The sample is listed below:

Table 10-1 Thailand Brine Sample data

Cations	***Concentration (mg/L)***	***Anions***	***Concentration (mg/L)***
Ba^{+2}	0.07	Cl^{-1}	39137
Ca^{+2}	3700	HCO_3^{-1}	561
Fe^{+2}	2.89	HS^{-1}	0.09
K^{+1}	402	SO_4^{-2}	2200
Mg^{+2}	262.8		
NH_4^{+1}	104	pH	6.1
Na^{+1}	20400		

Start the OLI Studio program by ***double-clicking*** the OLI Studio icon on the desktop or by using the Start menu.

The main window for the OLI Studio will display after the splash screen. The main window is similar to other OLI Studio products. There is a **<u>Tree-view</u>** or **<u>Navigator</u>** displayed on the left-hand side of the window. This shows all the objects currently in the document. Currently the display shows no objects. The bottom-left panel is the **<u>Actions</u>** or the **<u>Explorer</u>** view and shows the icons of the objects.



Name: Streams

Date: 12/ 8 /2015

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 10-1 the OLI/LabAnalyzer main window.

To set up this tour, we need to change some settings. Please locate and ***click*** on the ***Tools*** menu in the menu bar.

This will display a drop-down menu. We will not dwell on each of the items in this tour. Please select **Names Manager** by ***Clicking*** on the item.

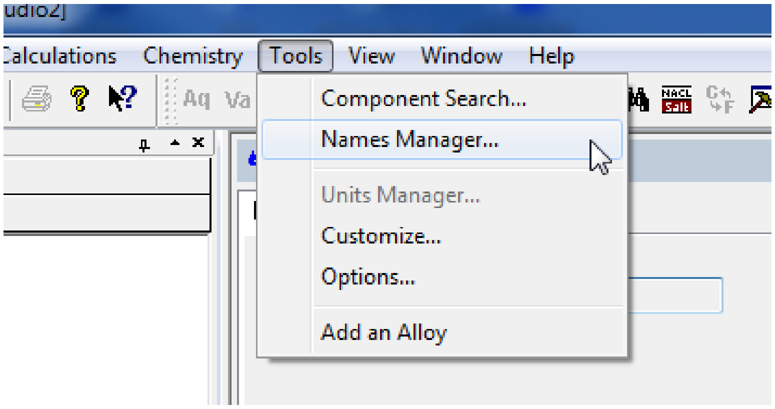
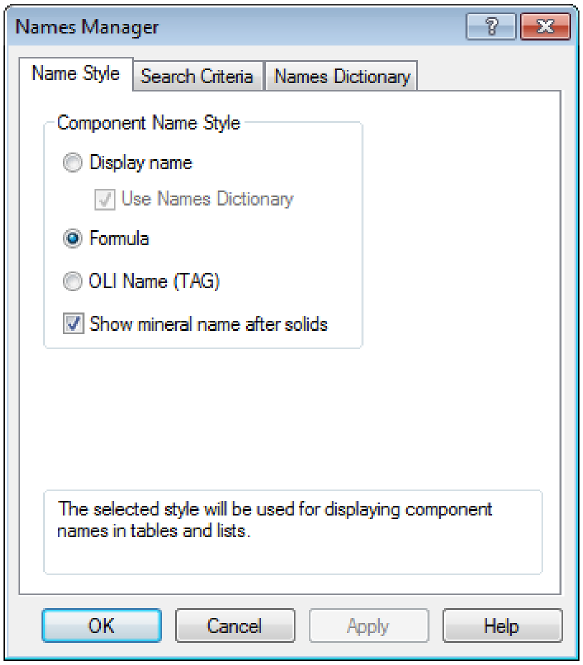


Figure 10-2 The Tools menu items.

There are several methods of displaying component names. For the moment we wish to use the formula names for our ions. ***Click*** the **Formula** radio button. ***Click*** the **OK** button when done.



Component Name Style

○ Display name

☑ Use Names Dictionary

● Formula

○ OLI Name (TAG)

☑ Show mineral name after solids

The selected style will be used for displaying component names in tables and lists.

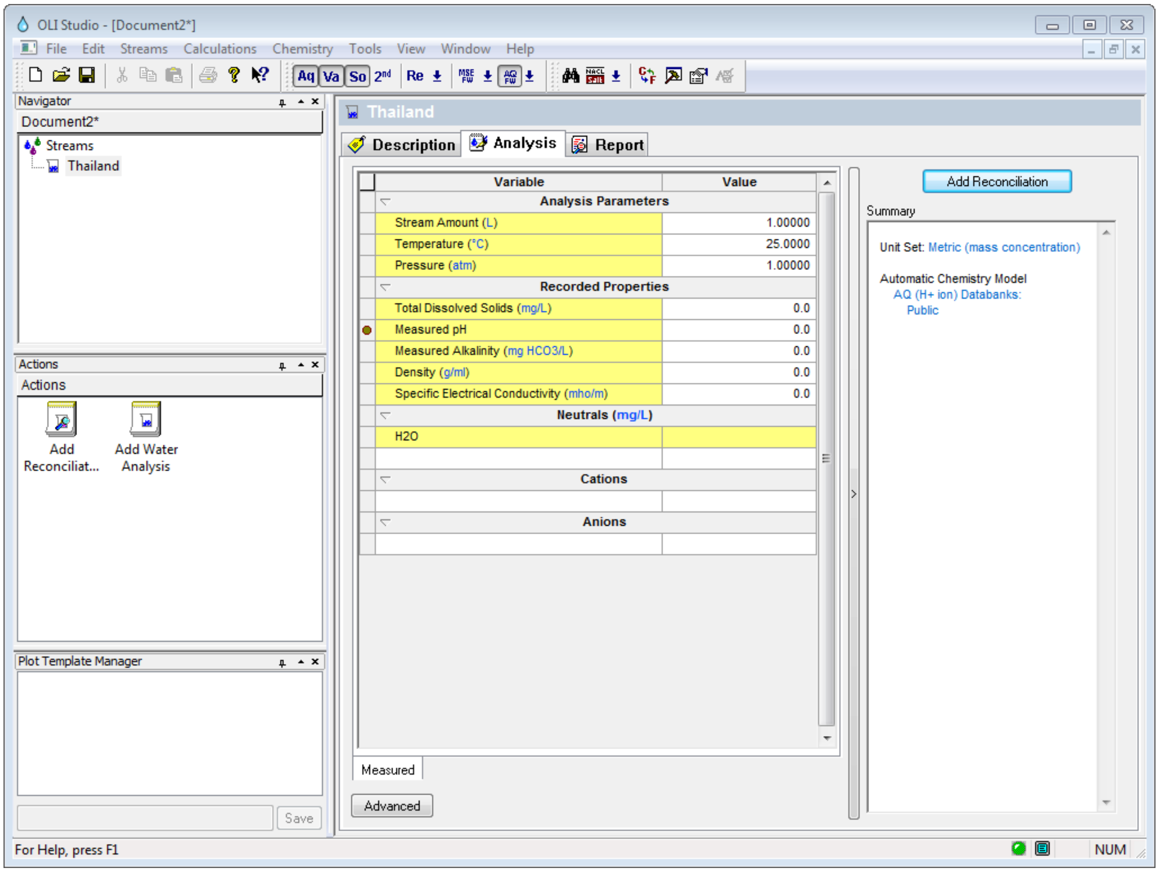
Figure 10-3 The Names Manager

When you return to the main window, locate the **Add Water Analysis** icon in the explorer view and ***double-click*** on the icon.

A "Water Analysis" object will be added to the Tree View. The **Explorer** view will now shows three new icons. You should now be on the **Analysis** tab, if not, please click it.

For this tour, we want you to rename the default analysis to the name ***Thailand.***

Right-click the new object in the tree-view and select **Rename.** Enter the name ***Thailand.***



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	0.0
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (mho/m)	0.0
Neutrals (mg/L)	
H2O	
Cations	
Anions	

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 10-4 The Water Analysis Definition.

This window has several parts. The main part is the input grid in the center of the window. Here the user will enter the species concentrations as well as reportable items such as density. The field is scrollable and is divided into several sections:

Analysis Parameters

This section has the total stream amount, the temperature and pressure of the sample. The default values are 1 liter, 25 ºC and 1 Atmosphere.

Recorded Properties

These are values reported from the lab. The pH of the solution, density, total dissolved solids and electrical conductivity may be entered.

Inflows

These are the molecular (neutral) species in solution. Water is entered by default but the user may not alter this value. Other neutrals such as dissolved gases (e.g., methane) may be entered in this section.

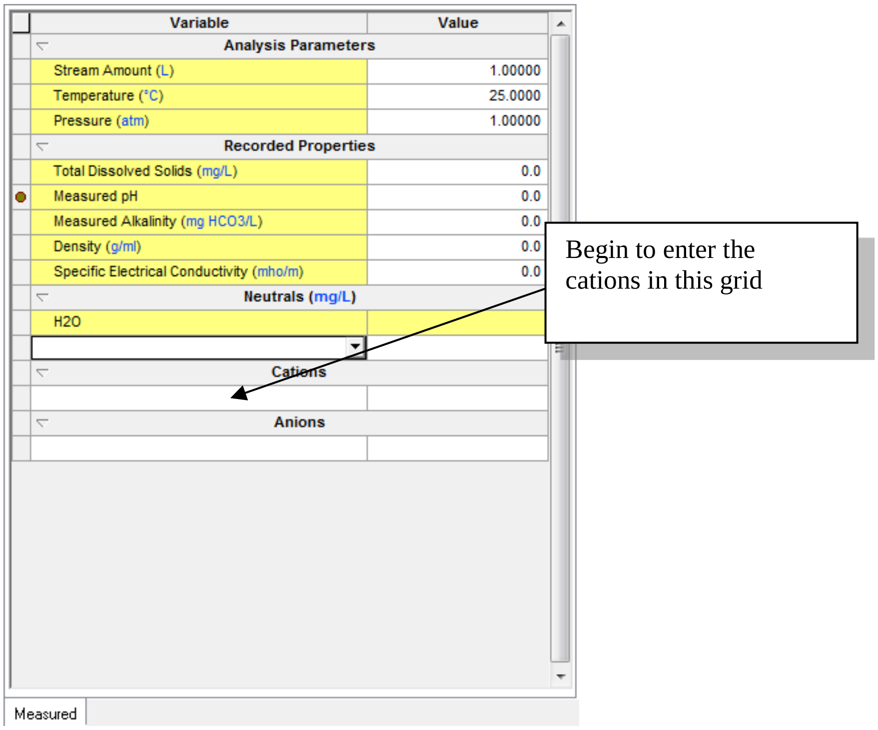
Cations

These are the positively charged species in solution.

Anions

These are the negatively charged species in solution.

Enter the cations listed in the table. The grid will scroll down to accept more entries.

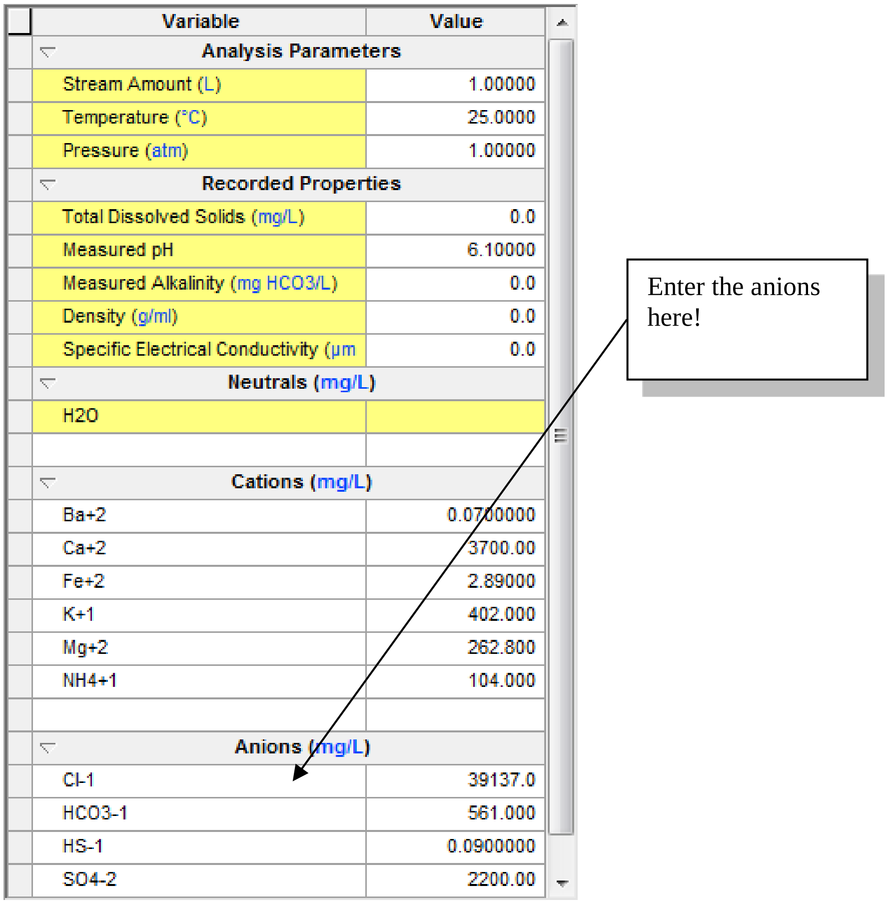


Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
● Measured pH	0.0
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (mho/m)	0.0
Neutrals (mg/L)	
H2O	
Cations	
Anions	

Begin to enter the cations in this grid

Figure 10-5 Entering the cations

Scroll down the grid and enter the anions:

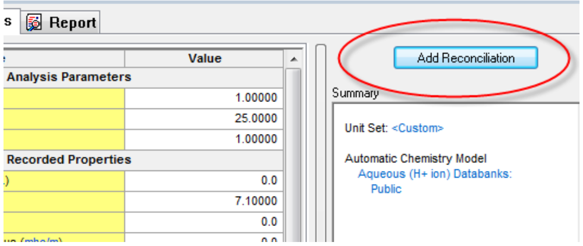


Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.10000
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (μm	0.0
Neutrals (mg/L)	
H2O	
Cations (mg/L)	
Ba+2	0.0700000
Ca+2	3700.00
Fe+2	2.89000
K+1	402.000
Mg+2	262.800
NH4+1	104.000
Anions (mg/L)	
Cl-1	39137.0
HCO3-1	561.000
HS-1	0.0900000
SO4-2	2200.00

Enter the anions here!

Figure 10-6 Entering the anions

We are now ready to perform some reconciliation calculations for this sample.



	Value
Analysis Parameters	
	1.00000
	25.0000
	1.00000
Recorded Properties	
)	0.0
	7.10000
	0.0

Summary

Unit Set: <Custom>

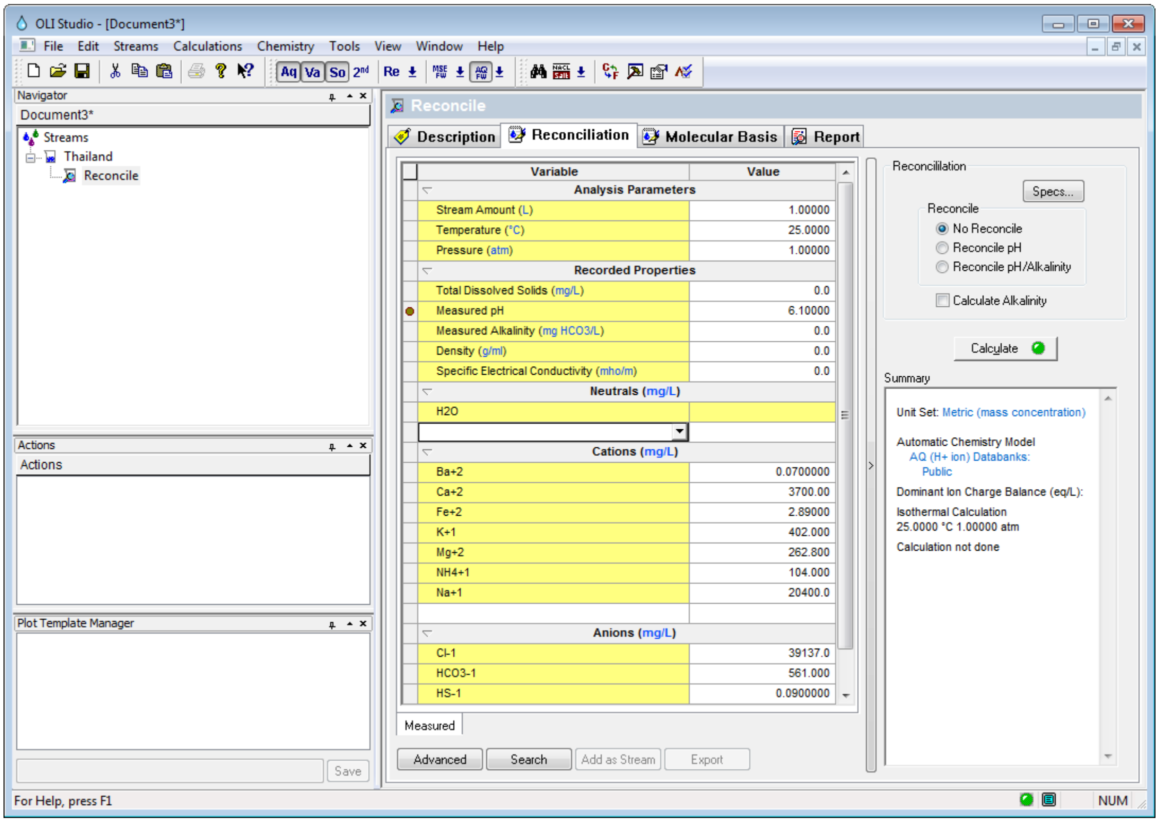
Automatic Chemistry Model
Aqueous (H+ ion) Databanks:
Public

Figure 10-7 Finished data entry

Click on the **<u>Add Reconciliation</u>** Button.

This will display more tabs for entering data about the reconciliation. A new object will appear under the **<u>Thailand</u>** object in the tree view. This is an indication that the new object, in this case a reconciliation, is related to the parent object.

There are several items on this display. The entered analysis is displayed in the input grid. It is important to note that this is a copy of what you originally input. The values may be changed without altering the values in the parent analysis.



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.10000
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (mho/m)	0.0
Neutrals (mg/L)	
H2O	
Cations (mg/L)	
Ba+2	0.0700000
Ca+2	3700.00
Fe+2	2.89000
K+1	402.000
Mg+2	262.800
NH4+1	104.000
Na+1	20400.0
Anions (mg/L)	
Cl-1	39137.0
HCO3-1	561.000
HS-1	0.0900000

Reconcile
● No Reconcile
○ Reconcile pH
○ Reconcile pH/Alkalinity
☐ Calculate Alkalinity

Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Dominant Ion Charge Balance (eq/L):

Isothermal Calculation
25.0000 °C 1.00000 atm

Calculation not done

Figure 10-8 Starting the reconciliation.

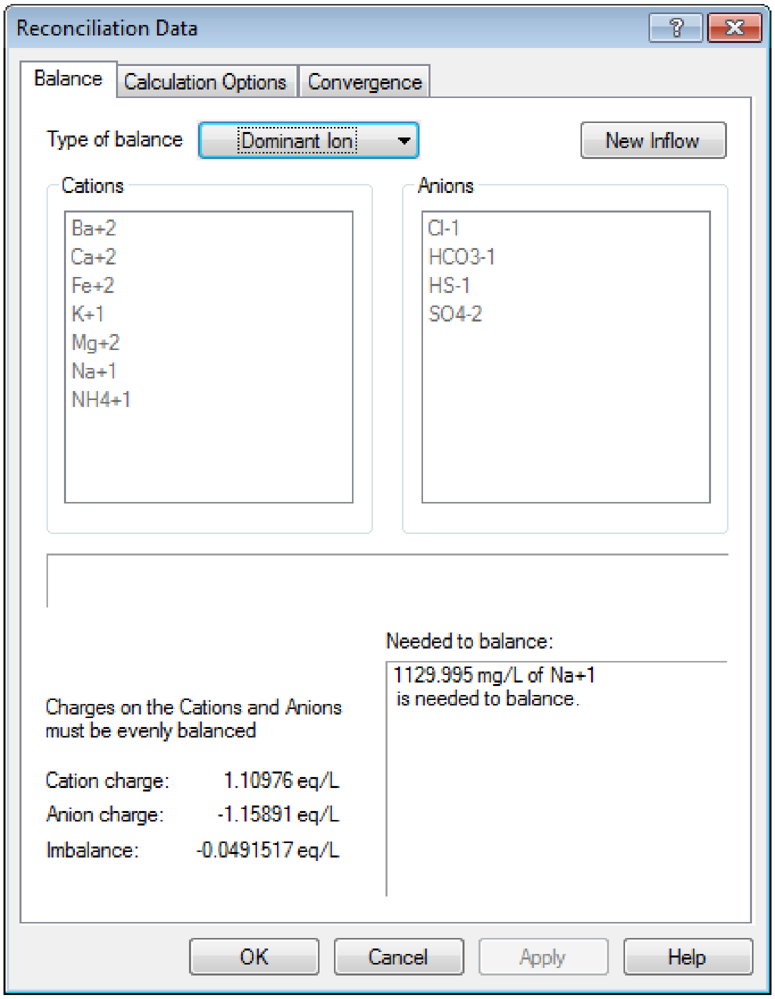
In addition to the input grid, there is a **Reconciliation** box and a **Summary** box.

Reconciliation
This box sets up both the electroneutrality reconciliation and the pH reconciliation. The user may allow the program to pick the species to adjust for reconciliation or they may manually choose the adjustment.

The pH of the solution may be adjusted (automatically by adding either hydrochloric acid or sodium hydroxide) or the user may adjust these acids and bases.

The pH and alkalinity can also be calculated from this box or if the ***Calculate Alkalinity*** check box is selected then just the alkalinity is reported.

Summary
This box will display a quick list of what was performed in this section.
Please *click* on the **Specs…** button. We will now review the options for electroneutrality.



Type of balance: Dominant Ion

Cations: Ba+2, Ca+2, Fe+2, K+1, Mg+2, Na+1, NH4+1

Anions: Cl-1, HCO3-1, HS-1, SO4-2

Needed to balance:
1129.995 mg/L of Na+1 is needed to balance.

Charges on the Cations and Anions must be evenly balanced

Cation charge: 1.10976 eq/L
Anion charge: -1.15891 eq/L
Imbalance: -0.0491517 eq/L

Figure 10-9 choosing electroneutrality

The default option for reconciling electroneutrality is the **Dominant Ion** method. This method determines the amount of imbalance in charge then uses the counter ion with the largest concentration on an equivalent basis. This sample currently has too much negative charge (approximately 0.049 equivalents). The largest counter charge will be added. In this case the value is 1129.995 mg/L of Na^{+1}.

There are other options that may be used:

To see all options for balancing charge ***Click*** the **Type of balance** button. The options are:

Dominant Ion

This is the default method. The largest counter ion is used to adjust the electroneutrality, as was noted.

Prorate Ion

In our example, there is too much positive charge. The Prorate Ion method, if employed, would keep the relative amounts of all the negatively charged species the same and add a percentage multiplier to all such species until the electroneutrality was achieved.

Na/Cl

This method chooses either sodium ion or chloride ion as the adjusting species (depending on imbalance) regardless of the largest species concentration.

Make-up Ion

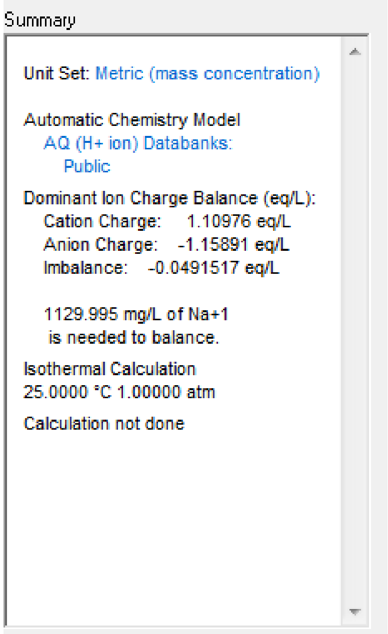
This option allows for a single ion species to be adjusted. In this example, there is too much positive charge. If the Magnesium ion was chosen, then it would be reduced in concentration to make the sample electrically neutral.

User Choice

The user may pick the cation/anion pair to use for adjusting. Unlike the Make-up ion method, this method always adds material since both a cation and an anion are provided.

For this tour, we will use the default method of **Dominant Ion**.

Click the **OK** button to continue.



Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Dominant Ion Charge Balance (eq/L):
Cation Charge: 1.10976 eq/L
Anion Charge: -1.15891 eq/L
Imbalance: -0.0491517 eq/L

1129.995 mg/L of Na+1
is needed to balance.

Isothermal Calculation
25.0000 °C 1.00000 atm

Calculation not done

Figure 10-10 the summary box

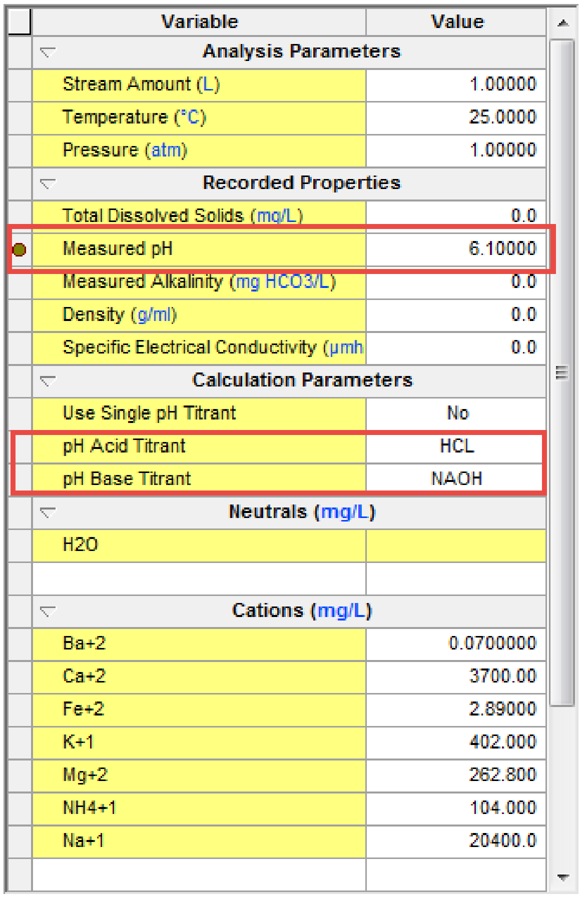
The summary box will update to show our selection.

We now want to reconcile for pH. We know that the measured pH is 6.1. We want to ensure that the solution pH is 6.1 when we are done. This will involve adding either an acid or a base to adjust the pH.

We need to add the pH value to two locations in the grid. The first is the target pH and this is required for the calculation. The second location is the reported pH. The reported pH may differ from the target pH. The user may want to see the effects on the solution at some other condition than the reported pH, hence the need for two locations.

In the **Reconcile pH** box *Click* on the **Reconcile pH** radio button**.** The titrants HCl and NaOH are the default titrants and we will use them in this tour.

Enter a pH value of ***6.1*** in the **Recorded Properties** **pH - Aqueous** section.



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.10000
Measured Alkalinity (mg HCO3/L)	0.0
Density (g/ml)	0.0
Specific Electrical Conductivity (μmh	0.0
Calculation Parameters	
Use Single pH Titrant	No
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Neutrals (mg/L)	
H2O	
Cations (mg/L)	
Ba+2	0.0700000
Ca+2	3700.00
Fe+2	2.89000
K+1	402.000
Mg+2	262.800
NH4+1	104.000
Na+1	20400.0

Figure 10-11 Entering pH information

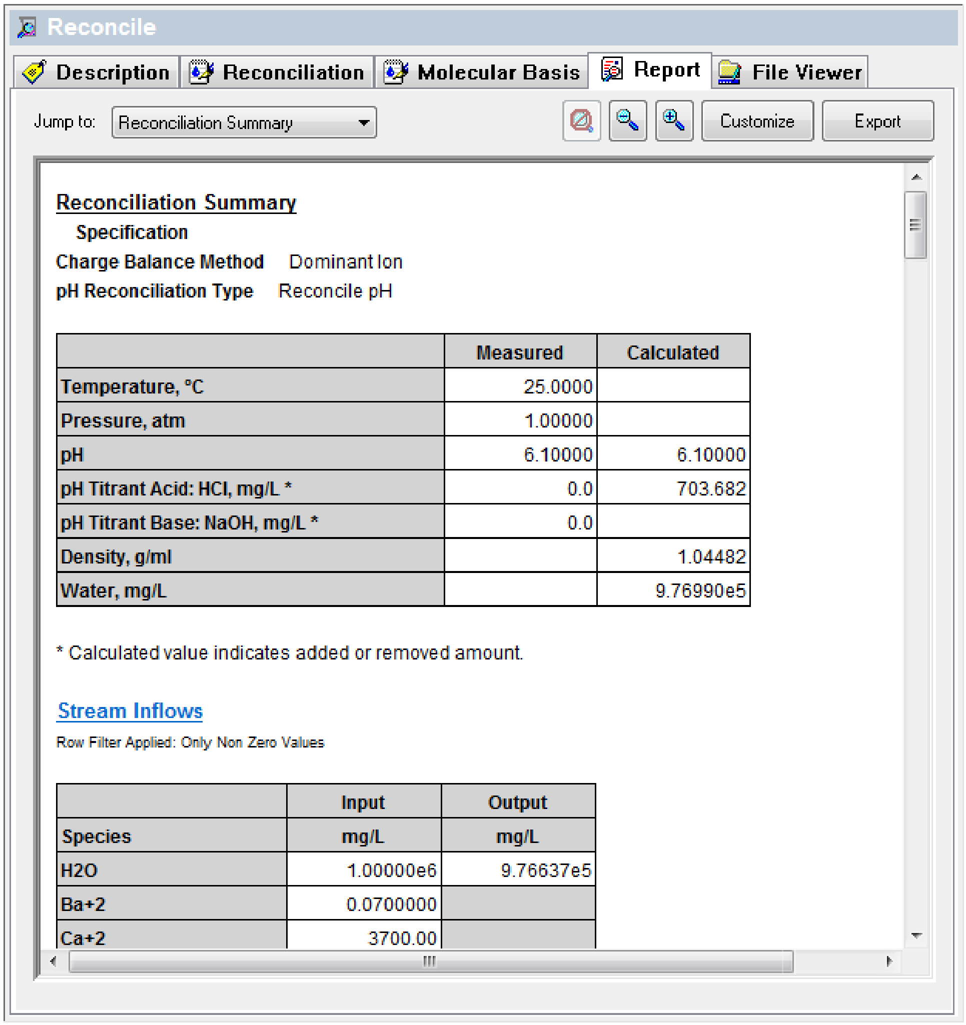
Click on the **Calculate** button to start the calculation.

When the calculation has finished, scroll down the **Summary** box to see that NaOH was added. Also, click on the **Calculated** tab to see the results of the calculation.

Click on the **Report** tab.

Notice that the Calculated pH is now 6.1. You can scroll down to see additional information for the sample

You may want to highlight the report area with your mouse in order to refresh the page. Even though the report is calculated, sometimes it is not visible immediately.



Jump to: Reconciliation Summary

Reconciliation Summary

Specification

Charge Balance Method Dominant Ion

pH Reconciliation Type Reconcile pH

	Measured	Calculated
Temperature, °C	25.0000	
Pressure, atm	1.00000	
pH	6.10000	6.10000
pH Titrant Acid: HCl, mg/L *	0.0	703.682
pH Titrant Base: NaOH, mg/L *	0.0	
Density, g/ml		1.04482
Water, mg/L		9.76990e5

* Calculated value indicates added or removed amount.

Stream Inflows

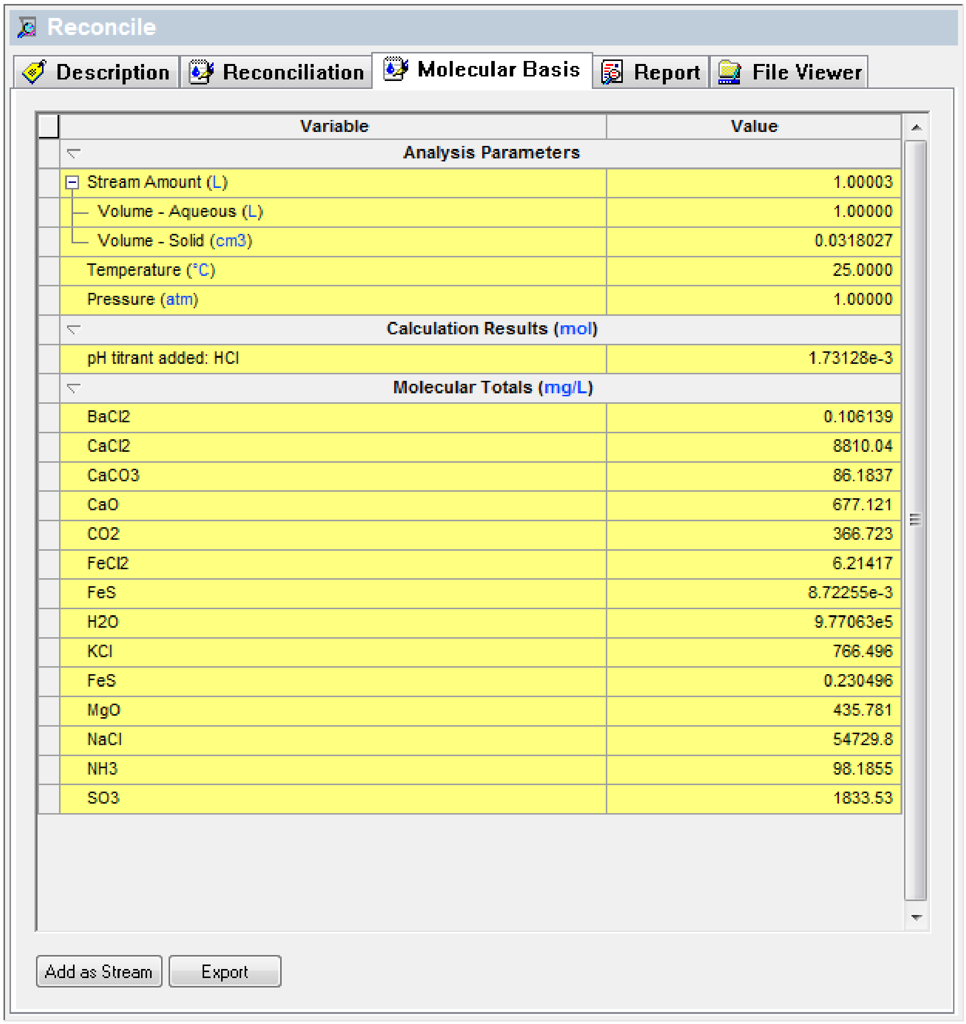
Row Filter Applied: Only Non Zero Values

	Input	Output
Species	mg/L	mg/L
H2O	1.00000e6	9.76637e5
Ba+2	0.0700000	
Ca+2	3700.00	

Figure 10-12 The Report tab

Click on the **Molecular Basis** tab.

This will display the sample in terms of molecular (neutral species). You can scroll down to see additional information.

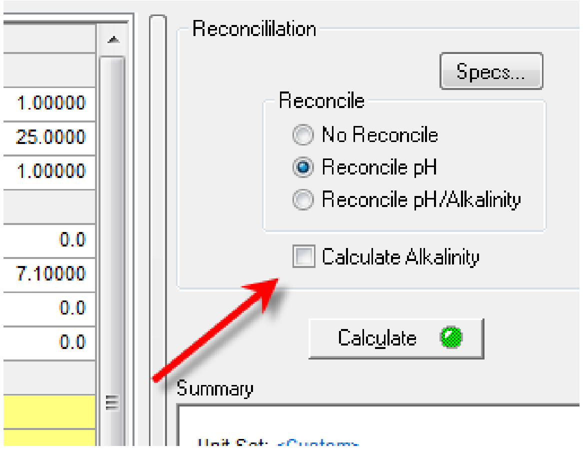


Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00003
Volume - Aqueous (L)	1.00000
Volume - Solid (cm3)	0.0318027
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Results (mol)	
pH titrant added: HCl	1.73128e-3
Molecular Totals (mg/L)	
BaCl2	0.106139
CaCl2	8810.04
CaCO3	86.1837
CaO	677.121
CO2	366.723
FeCl2	6.21417
FeS	8.72255e-3
H2O	9.77063e5
KCl	766.496
FeS	0.230496
MgO	435.781
NaCl	54729.8
NH3	98.1855
SO3	1833.53

Figure 10-13 The molecular view.

Calculating Alkalinity

Let us now determine the alkalinity of this pH reconciled sample. On the **Reconciliation Tab** locate the ***Calculate Alkalinity*** check box.



Reconcile

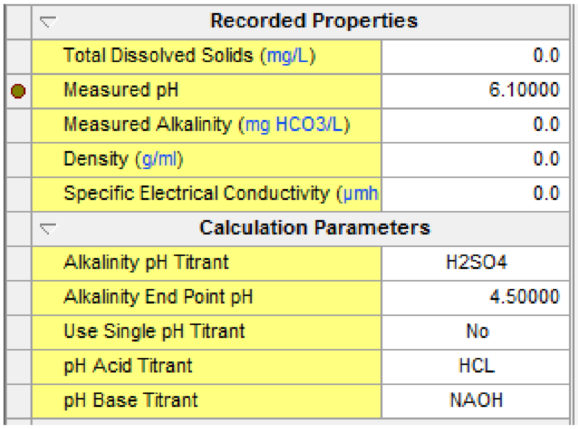
○ No Reconcile
● Reconcile pH
○ Reconcile pH/Alkalinity

☐ Calculate Alkalinity

Figure 10-14 Calculate Alkalinity

Check the box

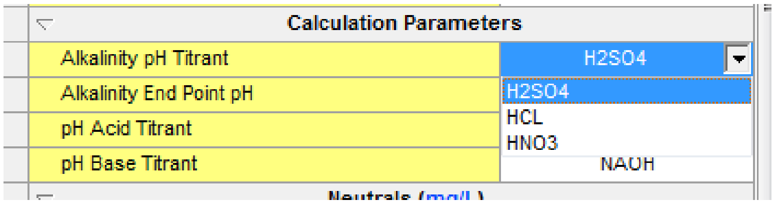
The input grid updates with a new set of parameters in the **Calc Parameters** section.



	Recorded Properties	
	Total Dissolved Solids (mg/L)	0.0
●	Measured pH	6.10000
	Measured Alkalinity (mg HCO3/L)	0.0
	Density (g/ml)	0.0
	Specific Electrical Conductivity (µmh	0.0
	Calculation Parameters	
	Alkalinity pH Titrant	H2SO4
	Alkalinity End Point pH	4.50000
	Use Single pH Titrant	No
	pH Acid Titrant	HCL
	pH Base Titrant	NAOH

Figure 10-15 Added the Alkalinity titrant H2SO4

The OLI Analyzer will perform a pH titration for total Alkalinity. This means the sample will be titrated down to a pH of 4.5 and the amount of acid used is converted into Alkalinity. The box is a drop-down box and several other titrants are available:



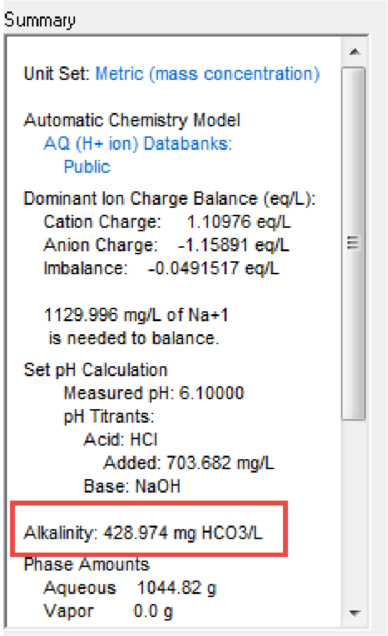
Calculation Parameters	
Alkalinity pH Titrant	H2SO4
Alkalinity End Point pH	H2SO4 HCL HNO3
pH Acid Titrant	
pH Base Titrant	NAOH

Figure 10-16 Additional Alkalinity Titrants

The Alkalinity Titrant is defaulted to H2SO4 and it is recommended that you use this value.

It is important to note that although a real equilibrium calculation is being performed, no species (such as the added H2SO4) is being added to the stream.

Click the Calculate button.



Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Dominant Ion Charge Balance (eq/L):
Cation Charge: 1.10976 eq/L
Anion Charge: -1.15891 eq/L
Imbalance: -0.0491517 eq/L

1129.996 mg/L of Na+1
is needed to balance.

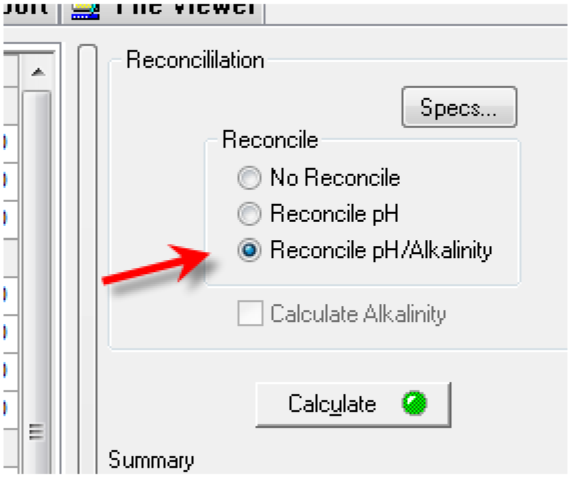
Set pH Calculation
Measured pH: 6.10000
pH Titrants:
Acid: HCl
Added: 703.682 mg/L
Base: NaOH

Alkalinity: 428.974 mg HCO3/L

Phase Amounts
Aqueous 1044.82 g
Vapor 0.0 g

Figure 10-17 Calculated Alkalinity

From the summary box we can see that the solution's calculated alkalinity is approximately 429 mg/L as HCO3.

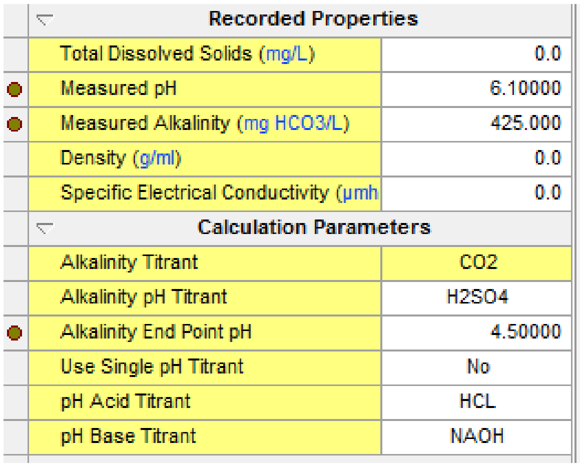


Reconcilillation

Reconcile
○ No Reconcile
○ Reconcile pH
● Reconcile pH/Alkalinity

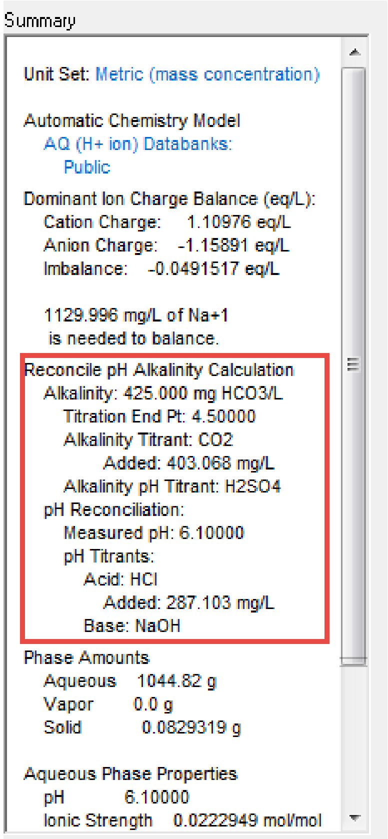
☐ Calculate Alkalinity

Figure 10-18 reconciling both pH and alkalinity



	Recorded Properties	
	Total Dissolved Solids (mg/L)	0.0
●	Measured pH	6.10000
●	Measured Alkalinity (mg HCO3/L)	425.000
	Density (g/ml)	0.0
	Specific Electrical Conductivity (µmh	0.0
	Calculation Parameters	
	Alkalinity Titrant	CO2
	Alkalinity pH Titrant	H2SO4
●	Alkalinity End Point pH	4.50000
	Use Single pH Titrant	No
	pH Acid Titrant	HCL
	pH Base Titrant	NAOH

Figure 10-19 User entered values note that the original pH of 6.1 is still used



```
Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
   AQ (H+ ion) Databanks:
      Public

Dominant Ion Charge Balance (eq/L):
   Cation Charge:     1.10976 eq/L
   Anion Charge:    -1.15891 eq/L
   Imbalance:    -0.0491517 eq/L

   1129.996 mg/L of Na+1
    is needed to balance.

Reconcile pH Alkalinity Calculation
   Alkalinity: 425.000 mg HCO3/L
      Titration End Pt: 4.50000
      Alkalinity Titrant: CO2
            Added: 403.068 mg/L
      Alkalinity pH Titrant: H2SO4
   pH Reconciliation:
      Measured pH: 6.10000
      pH Titrants:
         Acid: HCl
            Added: 287.103 mg/L
         Base: NaOH
Phase Amounts
   Aqueous    1044.82 g
   Vapor       0.0 g
   Solid          0.0829319 g

Aqueous Phase Properties
   pH          6.10000
   Ionic Strength    0.0222949 mol/mol
```

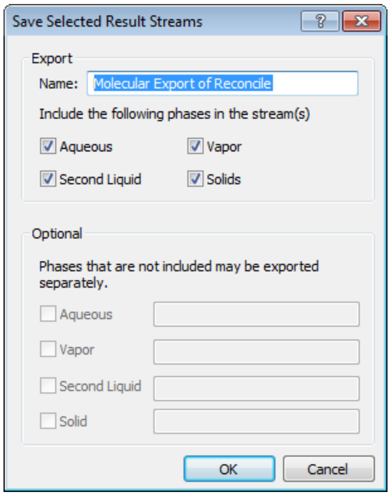
Figure 10-20 The red box shows the alkalinity values

Creating a stream from the sample

We now need to convert this sample to a molecular stream. ***Click*** the **Add as Stream** button.

The program will allocate the ion concentrations into molecules. The combination of these species is usually not unique, but however allocated; the elemental material balances will be preserved.

You have the option of separating phases during this step. Each phase can be removed from the created stream as well as saved as a new stream. This step, in effect, becomes a phase splitter.



Name: Molecular Export of Reconcile

Include the following phases in the stream(s)

☑ Aqueous ☑ Vapor

☑ Second Liquid ☑ Solids

Phases that are not included may be exported separately.

☐ Aqueous

☐ Vapor

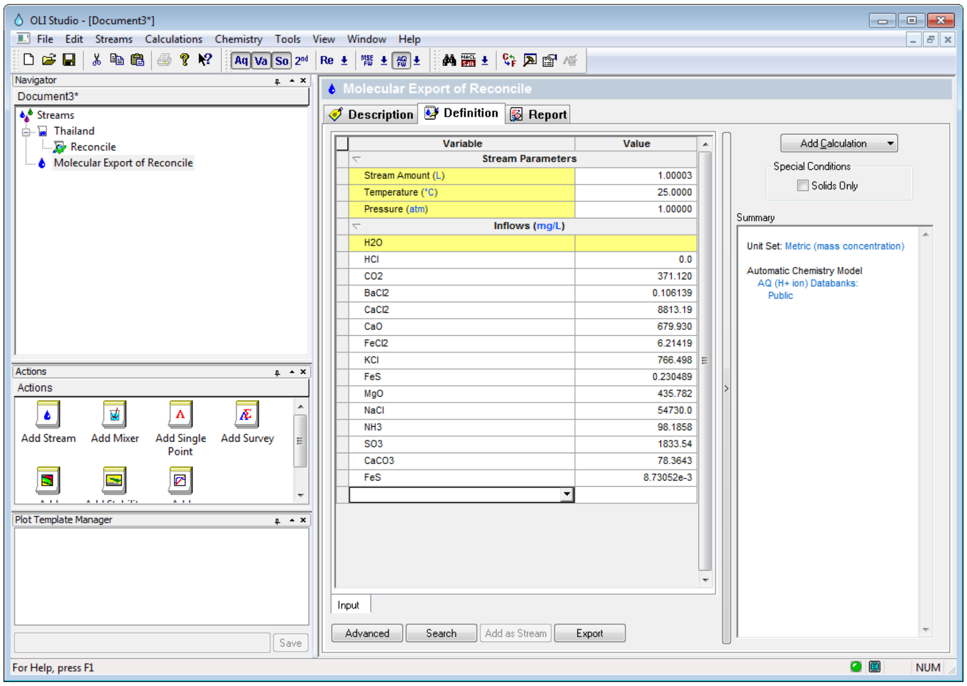
☐ Second Liquid

☐ Solid

Figure 10-21 Save As Stream dialog, default options selected

Click the ***OK*** button to save all the phases as a new stream.

The tree-view will be updated to display a new stream.



Molecular Export of Reconcile

Variable	Value
Stream Parameters	
Stream Amount (L)	1.00003
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mg/L)	
H2O	
HCl	0.0
CO2	371.120
BaCl2	0.106139
CaCl2	8813.19
CaO	679.930
FeCl2	6.21419
KCl	766.498
FeS	0.230489
MgO	435.782
NaCl	54730.0
NH3	98.1858
SO3	1833.54
CaCO3	78.3643
FeS	8.73052e-3

Special Conditions

☐ Solids Only

Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 10-22 A new stream object is displayed.

Click here for a worked example for this chapter: [Chapter 10 – Water Analysis Tour]()

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11. Autoclaves[40]

Overview

An autoclave is a high pressure, high temperature hydrometallurgy unit with carefully controlled conditions. In this chapter, we will simulate an autoclave using two different approaches. Some use a manual approach where the *Mixer* pressure or gas inflows is adjusted manually to match final volume. Others use the Custom calculation where pressure and total volume are linked, and lastly, some applications use the automatic *Autoclave* Calculation in which the partial pressures are fixed and the inflow composition is computed.

Basic Autoclave #1 – Ideal Gas Law, Inert Gas

In this section, we will add 1 kg water to a 2L autoclave then fill the void with N_2. The conditions are ambient, 25C and 1 atm. The amount of N_2 added is a combination of the dissolved N_2 (N_2 aqueous) and N_2 vapor filling the 1L void. N_2 has a low solubility in water, so nearly all the N_2 will remain in the vapor phase. H_2O will also evaporate to its vapor pressure, so the entire void will not contain N_2 alone. Since we know all the input parameters, we can use the Ideal Gas Law to estimate the amount of N_2 needed:

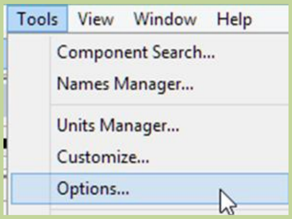
$$P * V = n * R * T$$

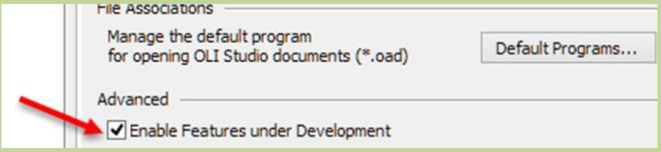
$$1\ atm * 1\ L = n * 0.082057\ \frac{L-atm}{K-mol} * 298.15\ K$$

$$n = 0.04087\ moles$$

Getting Started

Before adding a stream, some clients may have to enable the Autoclave feature. The steps below also require us to restart the software, so please save any open work.





Manage the default program for opening OLI Studio documents (*.oad)

☑ Enable Features under Development

- ✓ Press OK then Restart the software

---

[40] This chapter is authored by Anthony Gerbino of AQSim. Used with permission

✓ Start a new file and give it a name such as ***Chapter 9 Autoclaves***

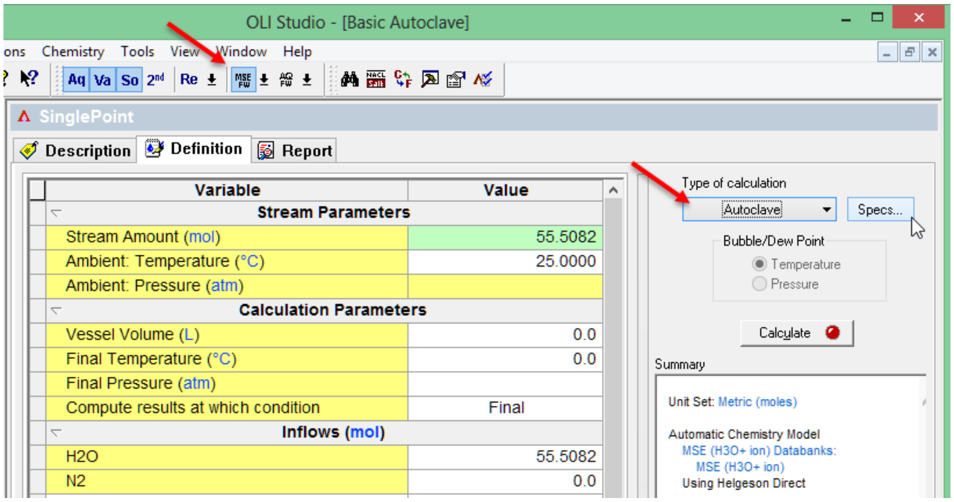
✓ Create a new stream and rename it ***Basic Autoclave – Inert Gas***

✓ 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. Click the Specs button



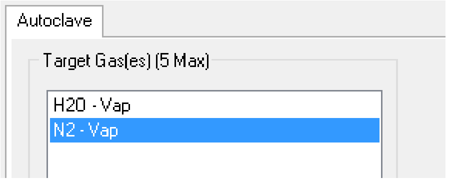
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation Parameters	
Vessel Volume (L)	0.0
Final Temperature (°C)	0.0
Final Pressure (atm)	
Compute results at which condition	Final
Inflows (mol)	
H2O	55.5082
N2	0.0

Unit Set: Metric (moles)

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

✓ Click the Specs button

✓ Highlight N2 in the gas field then press OK



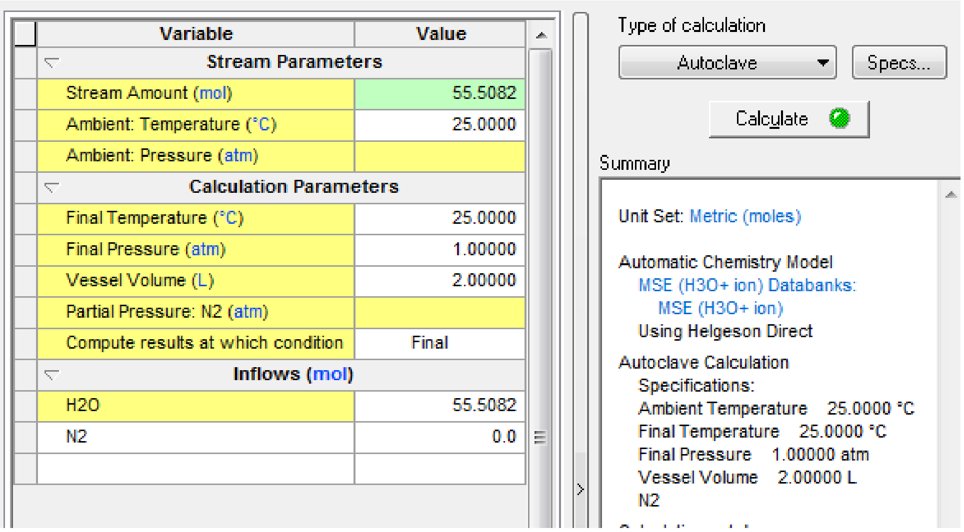
✓ Change the Vessel volume to 2L

✓ Change the final temperature to 25C and Final Pressure to 1 atm

✓ Confirm that the values in the grid match the information in the table below

✓

Basic Autoclave - Inert Gas Setup							
Setup		Stream Parameters		Calculation Parameters		Inflows (mol)	
Stream Name	Basic Autoclave – Inert Gas	Stream Amt	Calculated	Vessel Vol	2 L	H2O	55.508
Unit Set	Metric-Batch-Moles	Ambient T	25 C	Final T	25 C	N2	0
Unit Customize	none	Ambient P	calculated	Final P	1 atm		
Names Style	Formula			Gas : N2			
Framework	MSE (H3O+)						



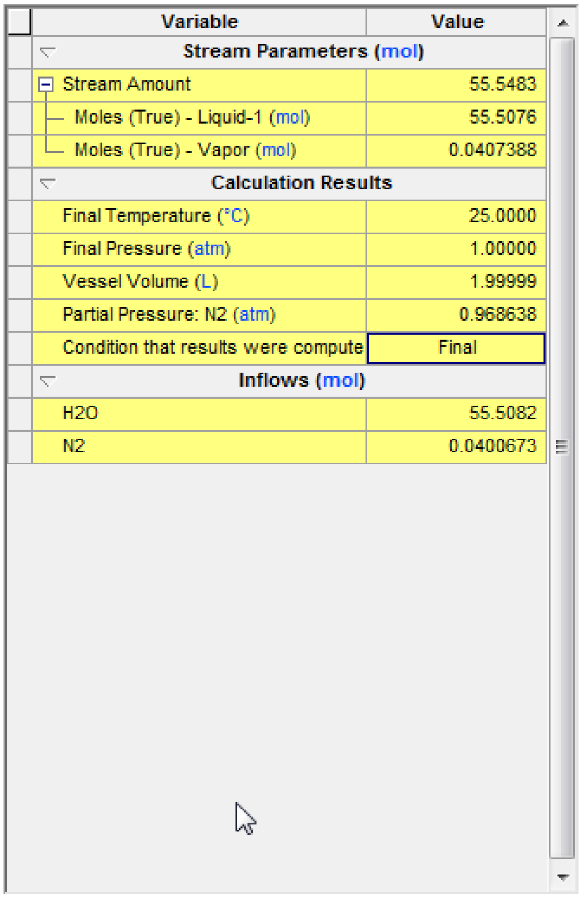
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Ambient: Temperature (°C)	25.0000
Ambient: Pressure (atm)	
Calculation Parameters	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	2.00000
Partial Pressure: N2 (atm)	
Compute results at which condition	Final
Inflows (mol)	
H2O	55.5082
N2	0.0

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
Final Temperature 25.0000 °C
Final Pressure 1.00000 atm
Vessel Volume 2.00000 L
N2

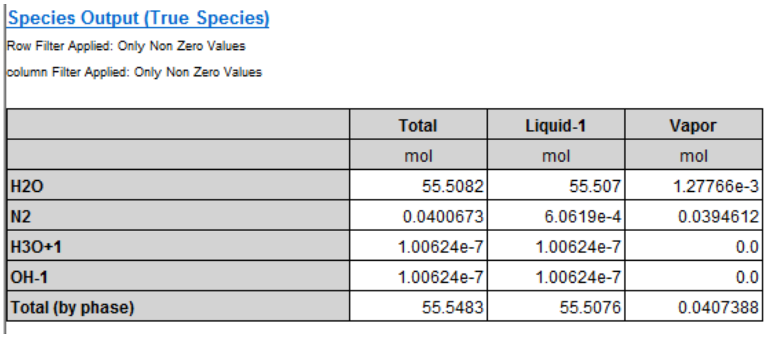
- ✓ Change the Compute results at which condition to Final
- ✓ Calculate



Variable	Value
Stream Parameters (mol)	
Stream Amount	55.5483
Moles (True) - Liquid-1 (mol)	55.5076
Moles (True) - Vapor (mol)	0.0407388
Calculation Results	
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 compute	Final
Inflows (mol)	
H2O	55.5082
N2	0.0400673

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

The computed N_2 inflow is 0.04007 moles. This compares to the Ideal Gas value of 0.0409 moles, a 2% deviation.



Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor
	mol	mol	mol
H2O	55.5082	55.507	1.27766e-3
N2	0.0400673	6.0619e-4	0.0394612
H3O+1	1.00624e-7	1.00624e-7	0.0
OH-1	1.00624e-7	1.00624e-7	0.0
Total (by phase)	55.5483	55.5076	0.0407388

✓

✓ Click on the Report tab and scroll down to the Species Output True Species table

✓

The software computes 0.03946 moles of N_2 in vapor. This is now 3.4% lower than the ideal gas value. When we include H_2O, the total gas amount ($N_2 + H_2O$) is 0.04074 moles, a 0.3% difference. Thus, a rigorous calculation (including fugacity) is consistent with a simple ideal gas calculation when computing total gas amount of an unreactive, low soluble gas.

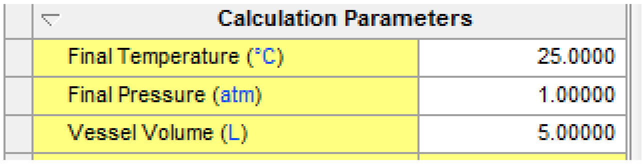
Setting the Vessel volume to 5L and 20L

The OLI Software computes gas properties and composition using an Enhanced Suave-Redlich-Kwong (SRK) cubic equation of state. The SRK equation for one mole gas looks like the following:

$$P = \frac{RT}{V - b} - \frac{a}{V(V +)}$$

When ‘a’ and ‘b’ are set to zero, SRK equation collapses to the Ideal Gas equation.

We will run the same calculation, except now the vessel volume will be five liters, that is, four liters of vapor. The ideal gas equation will predict: $4\ L * 0.04087\ {}^{moles}/_{L} = 0.1634\ moles$ of gas.



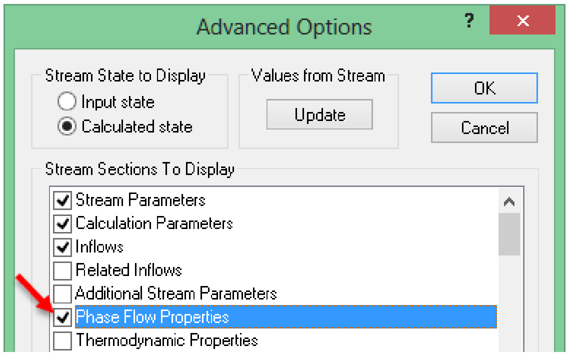
Calculation Parameters	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	5.00000

✓

✓ Select the Definition tab then change the Vessel volume to 5 L then Calculate

✓ Click on the Output tab at the bottom of the grid

✓ Click on the Advanced button below the grid and check the Phase Flow Properties box



Advanced Options

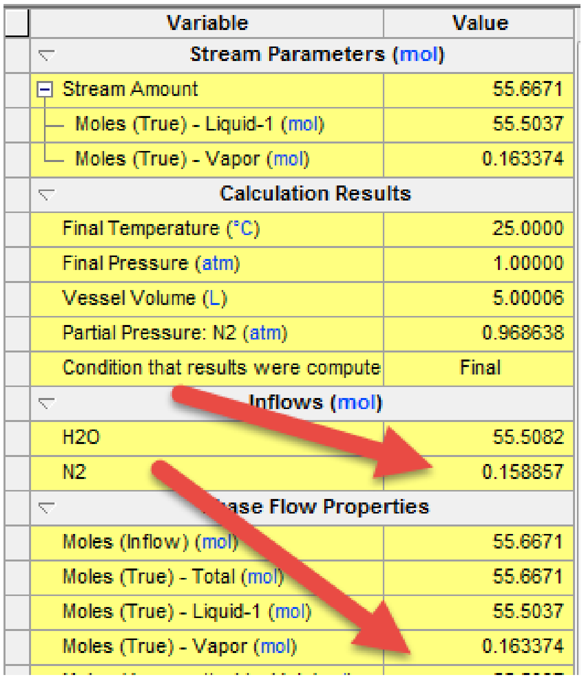
Stream State to Display
○ Input state
● Calculated state

Values from Stream
Update

OK
Cancel

Stream Sections To Display
☑ Stream Parameters
☑ Calculation Parameters
☑ Inflows
☐ Related Inflows
☐ Additional Stream Parameters
☑ Phase Flow Properties
☐ Thermodynamic Properties

✓ Press OK



Variable	Value
Stream Parameters (mol)	
⊟ Stream Amount	55.6671
Moles (True) - Liquid-1 (mol)	55.5037
Moles (True) - Vapor (mol)	0.163374
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	5.00006
Partial Pressure: N2 (atm)	0.968638
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	0.158857
Phase Flow Properties	
Moles (Inflow) (mol)	55.6671
Moles (True) - Total (mol)	55.6671
Moles (True) - Liquid-1 (mol)	55.5037
Moles (True) - Vapor (mol)	0.163374

✓

✓ Review the N2 input and total Gas moles values

The calculated value is 0.1589 moles about 2.9% lower than predicted using Ideal Gas Law. The total gas amount is 0.1633 moles, nearly identical to the gas amount computed using Ideal Gas Law.

✓ Click the Input tab at the bottom of grid

✓ Change the Vessel Volume to 20L

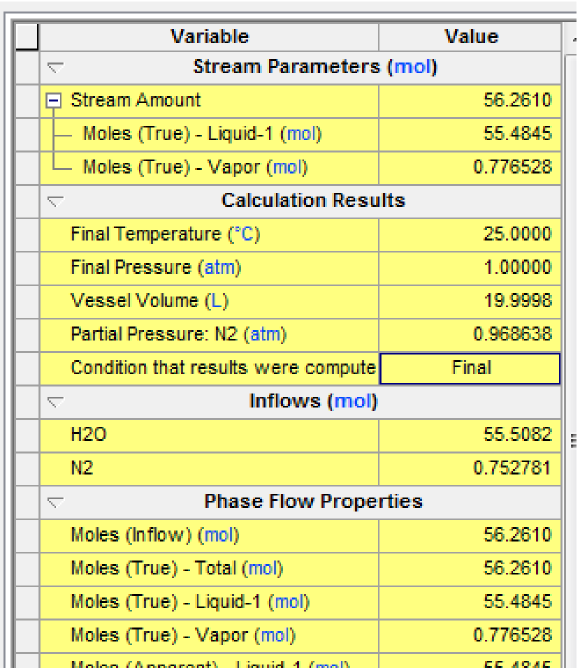
✓ Calculate

✓ Click the Output tab and view N2 inflow and Moles Vapor

The N_2 inflow is 0.7527 moles and total vapor is 0.7766 moles. The Ideal Gas Law predicts:

$$n = \frac{1\ atm * 19L}{0.082057\,\frac{L\ atm}{Kmol^{-1}}} = 0.776\ moles$$

The result from the equation matches the calculated result. Therefore, it appears that the Ideal Gas Law, will work at ambient conditions as well as when the vapor phase volume is much larger than the liquid phase volume

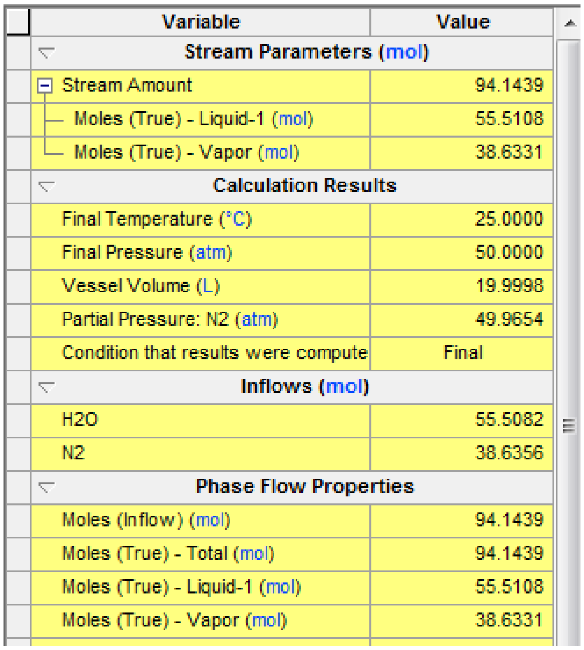


Variable	Value
Stream Parameters (mol)	
Stream Amount	56.2610
Moles (True) - Liquid-1 (mol)	55.4845
Moles (True) - Vapor (mol)	0.776528
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	19.9998
Partial Pressure: N2 (atm)	0.968638
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	0.752781
Phase Flow Properties	
Moles (Inflow) (mol)	56.2610
Moles (True) - Total (mol)	56.2610
Moles (True) - Liquid-1 (mol)	55.4845
Moles (True) - Vapor (mol)	0.776528

Testing a higher pressure

The software computes that the Ideal Gas Law works well at ambient conditions. It also works when the gas phase is larger than the water phase. The next test is to see how it works at elevated conditions.

- ✓ Click the Input tab at the bottom of the grid
- ✓ Change the Final Pressure to 50 atm then Calculate



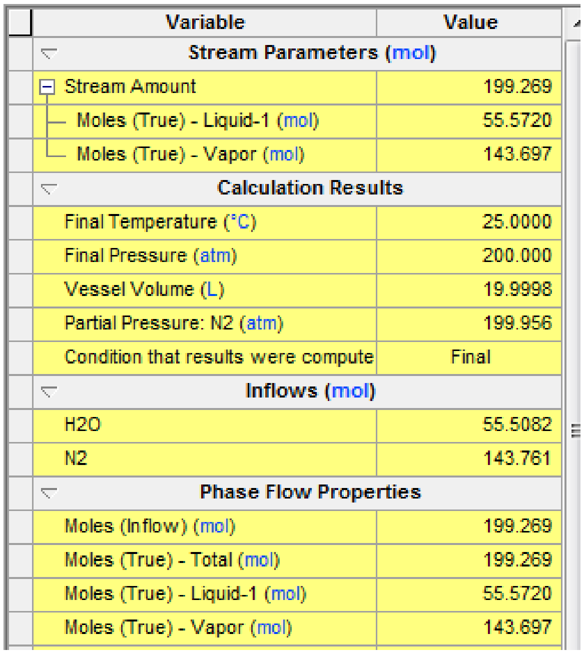
Variable	Value
Stream Parameters (mol)	
Stream Amount	94.1439
Moles (True) - Liquid-1 (mol)	55.5108
Moles (True) - Vapor (mol)	38.6331
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	50.0000
Vessel Volume (L)	19.9998
Partial Pressure: N2 (atm)	49.9654
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	38.6356
Phase Flow Properties	
Moles (Inflow) (mol)	94.1439
Moles (True) - Total (mol)	94.1439
Moles (True) - Liquid-1 (mol)	55.5108
Moles (True) - Vapor (mol)	38.6331

- ✓
- ✓ Click on the Output tab and view the results
- ✓ Calculate the gas amount using the Ideal Gas Law

$$n = \frac{50\ atm * 19\ L}{0.082057\ \frac{L-atm}{K-mol} * 298.15\ K} = 38.83\ moles$$

The ideal gas value is 38.83 moles compared to 38.66 moles computed by the software. The deviation is small, 0.4%.

- ✓ Select the Input tab, change the Final Pressure to 200 atm, recalculate, then select Output



Variable	Value
Stream Parameters (mol)	
⊟ Stream Amount	199.269
Moles (True) - Liquid-1 (mol)	55.5720
Moles (True) - Vapor (mol)	143.697
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	200.000
Vessel Volume (L)	19.9998
Partial Pressure: N2 (atm)	199.956
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	143.761
Phase Flow Properties	
Moles (Inflow) (mol)	199.269
Moles (True) - Total (mol)	199.269
Moles (True) - Liquid-1 (mol)	55.5720
Moles (True) - Vapor (mol)	143.697

The computed gas amount is 143.76 moles and is less than the 155.32 moles as per the Ideal Gas Law:

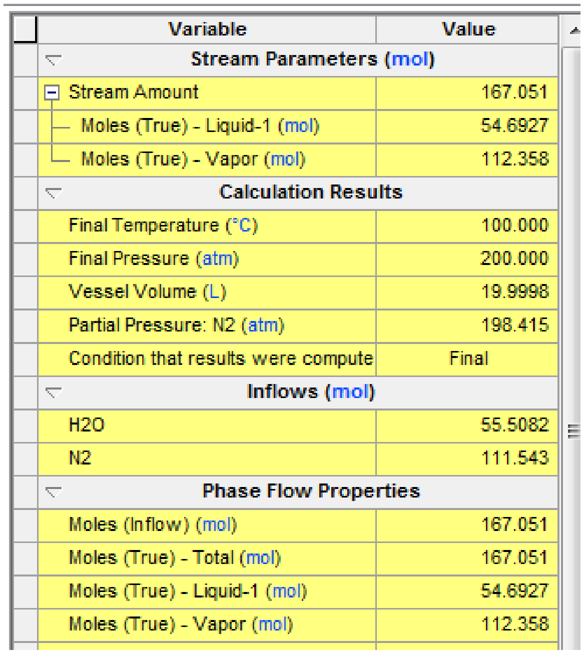
$$n = \frac{200\ atm * 19\ L}{0.082057\ \frac{L-atm}{K-mol} * 298.15\ K} = 155.32\ moles$$

Testing at High Temperature

Next, we will test the Ideal Gas Law against the Enhanced-SRK at higher temperatures.

- ✓ Select the Input tab then set the Final Temperature to 100C and calculate
- ✓ View the results in the lower Output tab
- ✓ Compare the results to what the Ideal Gas equation would produce

$$n = \frac{200\ atm * 19\ L}{0.082057\ \frac{L-atm}{K-mol} * 373.15\ K} = 124.104\ moles$$



Variable	Value
Stream Parameters (mol)	
⊟ Stream Amount	167.051
Moles (True) - Liquid-1 (mol)	54.6927
Moles (True) - Vapor (mol)	112.358
Calculation Results	
Final Temperature (°C)	100.000
Final Pressure (atm)	200.000
Vessel Volume (L)	19.9998
Partial Pressure: N2 (atm)	198.415
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	111.543
Phase Flow Properties	
Moles (Inflow) (mol)	167.051
Moles (True) - Total (mol)	167.051
Moles (True) - Liquid-1 (mol)	54.6927
Moles (True) - Vapor (mol)	112.358

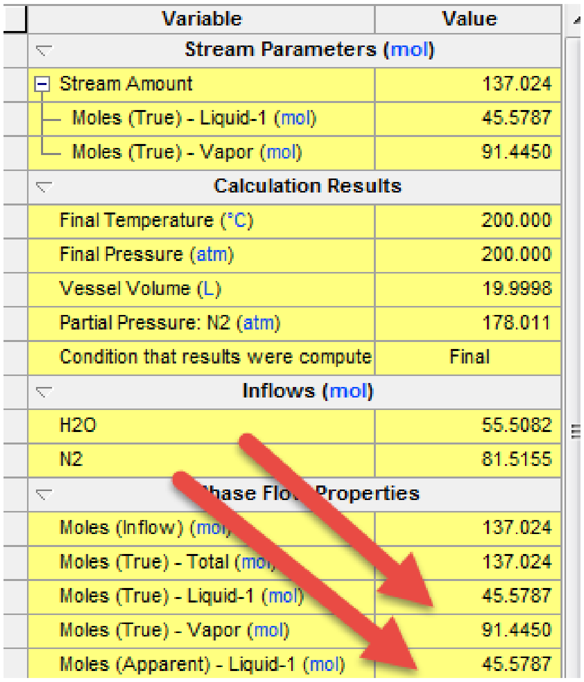
The difference is between 124.1 moles and 112.2 moles, or about 11% higher.

- ✓ Recalculate at 200C and compare the two equation of states

The Ideal Gas Law computes 97.87 moles of gas in the 19 liters.

$$n = \frac{200\ atm * 19\ L}{0.082057\,\frac{L-atm}{K-mol} * 473.15\ K} = 97.87\ moles$$

With enhanced SRK, the software computes 91.64 moles. Note also, that the Software computes a 19.02 L vapor volume.



Variable	Value
Stream Parameters (mol)	
Stream Amount	137.024
Moles (True) - Liquid-1 (mol)	45.5787
Moles (True) - Vapor (mol)	91.4450
Calculation Results	
Final Temperature (°C)	200.000
Final Pressure (atm)	200.000
Vessel Volume (L)	19.9998
Partial Pressure: N2 (atm)	178.011
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	81.5155
Phase Flow Properties	
Moles (Inflow) (mol)	137.024
Moles (True) - Total (mol)	137.024
Moles (True) - Liquid-1 (mol)	45.5787
Moles (True) - Vapor (mol)	91.4450
Moles (Apparent) - Liquid-1 (mol)	45.5787

Normalizing the moles to 19 L results in a value of 91.45 moles. This is 8% lower than the Ideal Gas predictions.

Basic Autoclave #2 – Ideal Gas Law, Reactive Gas

We will modify the approach taken in previous example by using a reactive gas, CO2, to fill the headspace. In addition, you will modify the chemistry by adding NaOH to the water so that CO2 reacts to form bicarbonate, changing the amount of CO2 that is needed to fill the headspace. We will use the same Ideal Gas Law calculations amount of CO2 needed, if the assumption was that no CO2 dissolved or reacted.

T	P	Vol	Ideal Gas Law	Calculated (total)	Calculated (vapor)	%Diff (vapor)
C	atm	L	Moles of inert gas mixed with 1L H2O			
25	1	1	0.041	0.040	0.039	3.4%
25	1	5	0.163	0.159	0.158	3.1%
25	1	20	0.78	0.75	0.75	3.1%
25	50	20	38.83	38.64	38.61	0.6%
25	200	20	255.32	143.76	143.67	43.7%

Getting Started

✓ Create a new stream and rename it ***Basic Autoclave – Reactive Gas***

✓ Change the framework to MSE

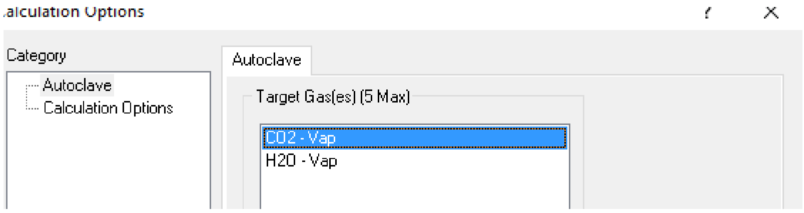
✓ Make sure the units are set to Metric-Batch-Moles

✓ Add CO2 and NaOH to the inflow list

✓ 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



✓ Change the Vessel volume to 2L

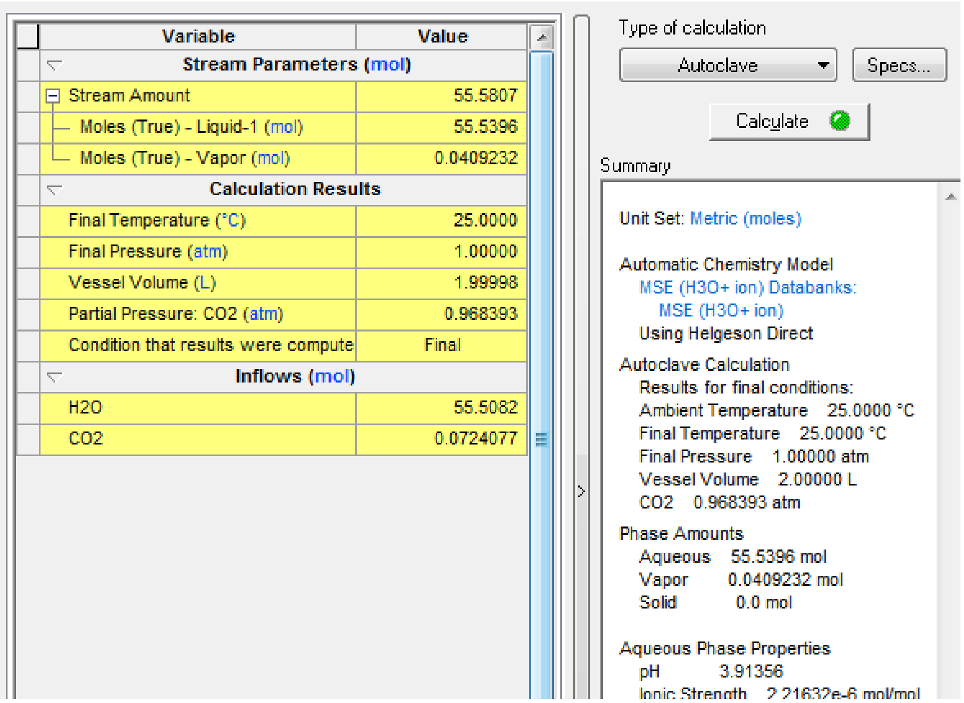
✓ Change the final temperature to 25C and Final Pressure to 1 atm

✓ Confirm that the values in the grid match the information in the table below

Basic Autoclave Setup							
Setup		Stream Parameters		Calculation Parameters		Inflows (mol)	
Stream Name	Basic Autoclave – Reactive Gas	Stream Amt	Calculated	Vessel Vol	2 L	H2O	55.508
Unit Set	Metric-Batch-Moles	Ambient T	25 C	Final T	25 C	N2	0
Unit Customize	none	Ambient P	calculated	Final P	1 atm	NaOH	
Names Style	Formula			Gas : CO2			
Framework	MSE (H3O+)						

✓

✓ Calculate



Variable	Value
Stream Parameters (mol)	
Stream Amount	55.5807
Moles (True) - Liquid-1 (mol)	55.5396
Moles (True) - Vapor (mol)	0.0409232
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	1.99998
Partial Pressure: CO2 (atm)	0.968393
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
CO2	0.0724077

Unit Set: Metric (moles)

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

Autoclave Calculation
Results for final conditions:
Ambient Temperature 25.0000 °C
Final Temperature 25.0000 °C
Final Pressure 1.00000 atm
Vessel Volume 2.00000 L
CO2 0.968393 atm

Phase Amounts
Aqueous 55.5396 mol
Vapor 0.0409232 mol
Solid 0.0 mol

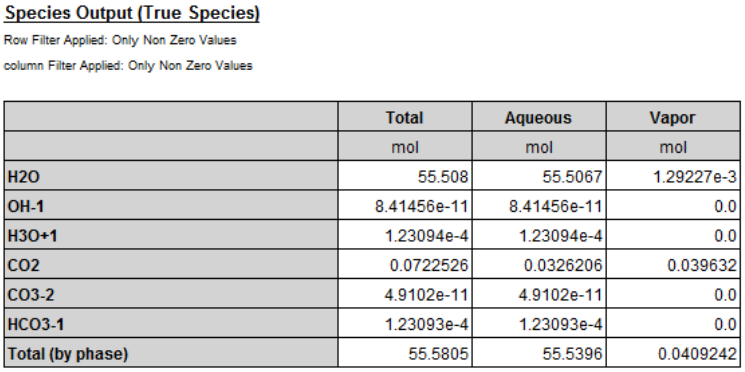
Aqueous Phase Properties
pH 3.91356
Ionic Strength 2.21632e-6 mol/mol

✓

✓ Click on the Output tab at the bottom of the grid

The computed CO_2 inflow is 0.0724 moles. This compares to the Ideal Gas value of 0.0409 moles, a 2% deviation.

Click on 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	Vapor
	mol	mol	mol
H2O	55.508	55.5067	1.29227e-3
OH-1	8.41456e-11	8.41456e-11	0.0
H3O+1	1.23094e-4	1.23094e-4	0.0
CO2	0.0722526	0.0326206	0.039632
CO3-2	4.9102e-11	4.9102e-11	0.0
HCO3-1	1.23093e-4	1.23093e-4	0.0
Total (by phase)	55.5805	55.5396	0.0409242

The software computes 0.0396 moles of CO_2 in vapor, consistent with the ideal gas value. The difference is that about 45% of the CO_2 added dissolved in water.

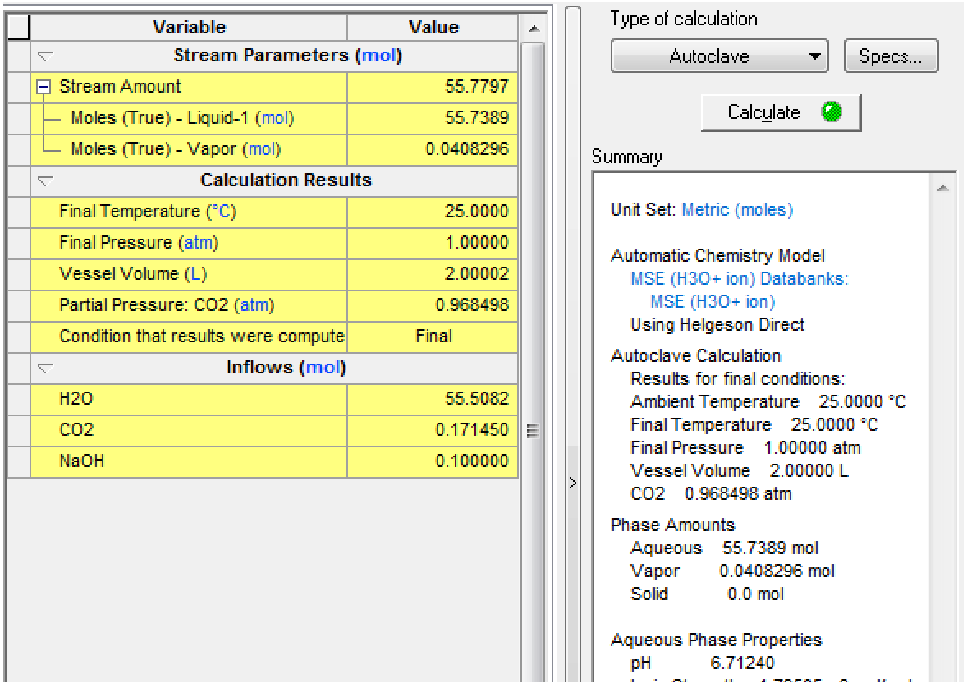
T	P	Vol	Ideal Gas Law	Calculated (total)	Calculated (vapor)	Calculated (total)	Calculated (vapor)
C	atm	L	Moles of N2 mixed with 1L H2O			Moles of CO2 mixed with 1L H2O	
25	1	1	0.041	0.040	0.039	0.073	0.040

Testing with 0.1m NaOH

You will repeat the study with NaOH added to the water. NaOH reacts with CO_2 to form HCO_3^{-1} and CO $^{-}$ 3

^{2}, increasing overall CO_2 solubility.

- ✓ Click on the Input tab
- ✓ Add 0.1 moles NaOH to the input grid



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 compute	Final
Inflows (mol)	
H2O	55.5082
CO2	0.171450
NaOH	0.100000

Unit Set: Metric (moles)

Automatic Chemistry Model
MSE (H3O+ ion) Databanks:
MSE (H3O+ ion)
Using Helgeson Direct
Autoclave Calculation
Results for final conditions:
Ambient Temperature 25.0000 °C
Final Temperature 25.0000 °C
Final Pressure 1.00000 atm
Vessel Volume 2.00000 L
CO2 0.968498 atm
Phase Amounts
Aqueous 55.7389 mol
Vapor 0.0408296 mol
Solid 0.0 mol

Aqueous Phase Properties
pH 6.71240

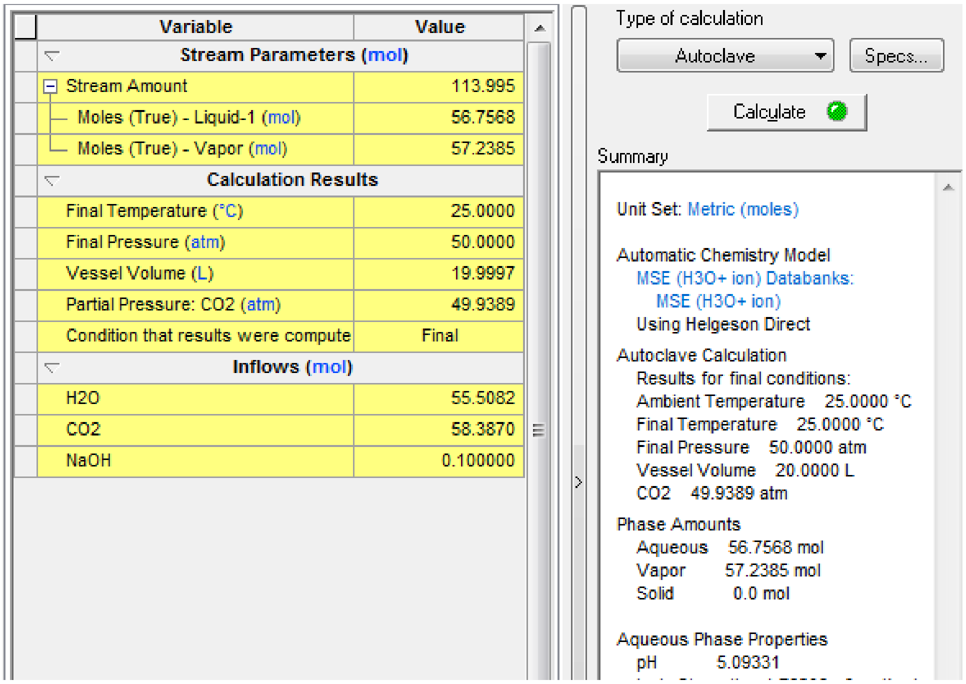
- ✓
- ✓ Calculate

The CO_2 inflow is approximately 0.1 moles greater than calculation without the NaOH, which is consistent with the CO_2 absorption and reaction by a base.

Testing a higher pressure

You will repeat the solubility calculations at 50atm.

- ✓ Click the Input tab at the bottom of the grid
- ✓ Change the Vessel volume to 20 L
- ✓ Change the Final Pressure to 50 atm
- ✓ Calculate



Variable	Value
Stream Parameters (mol)	
Stream Amount	113.995
Moles (True) - Liquid-1 (mol)	56.7568
Moles (True) - Vapor (mol)	57.2385
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	50.0000
Vessel Volume (L)	19.9997
Partial Pressure: CO2 (atm)	49.9389
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
CO2	58.3870
NaOH	0.100000

Type of calculation: Autoclave

Summary

Unit Set: Metric (moles)

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

Autoclave Calculation
Results for final conditions:
Ambient Temperature 25.0000 °C
Final Temperature 25.0000 °C
Final Pressure 50.0000 atm
Vessel Volume 20.0000 L
CO2 49.9389 atm

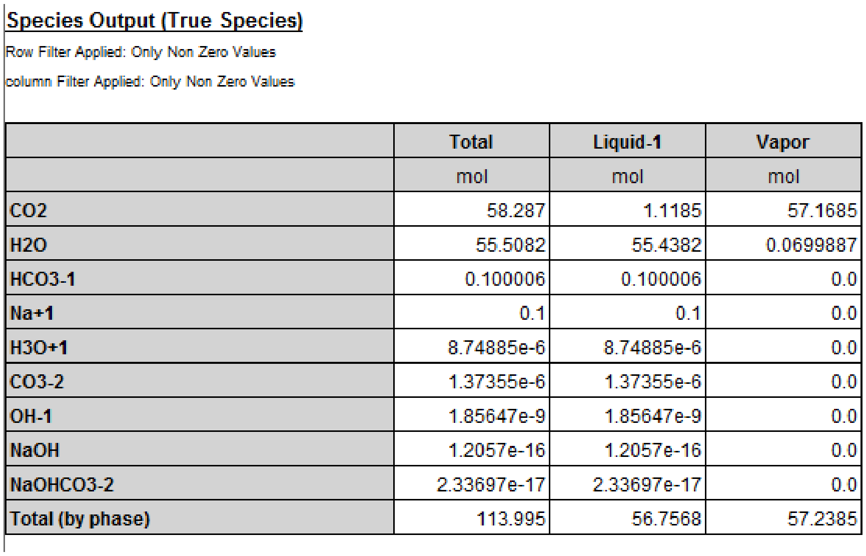
Phase Amounts
Aqueous 56.7568 mol
Vapor 57.2385 mol
Solid 0.0 mol

Aqueous Phase Properties
pH 5.09331

- ✓
- ✓ Click on the Output tab and view the results

The ideal gas value is 38.83 moles compared to 58.3 moles computed by the software.

- ✓ Click on the Report and view the Species Output



Species Output (True Species)

Row Filter Applied: Only Non Zero Values

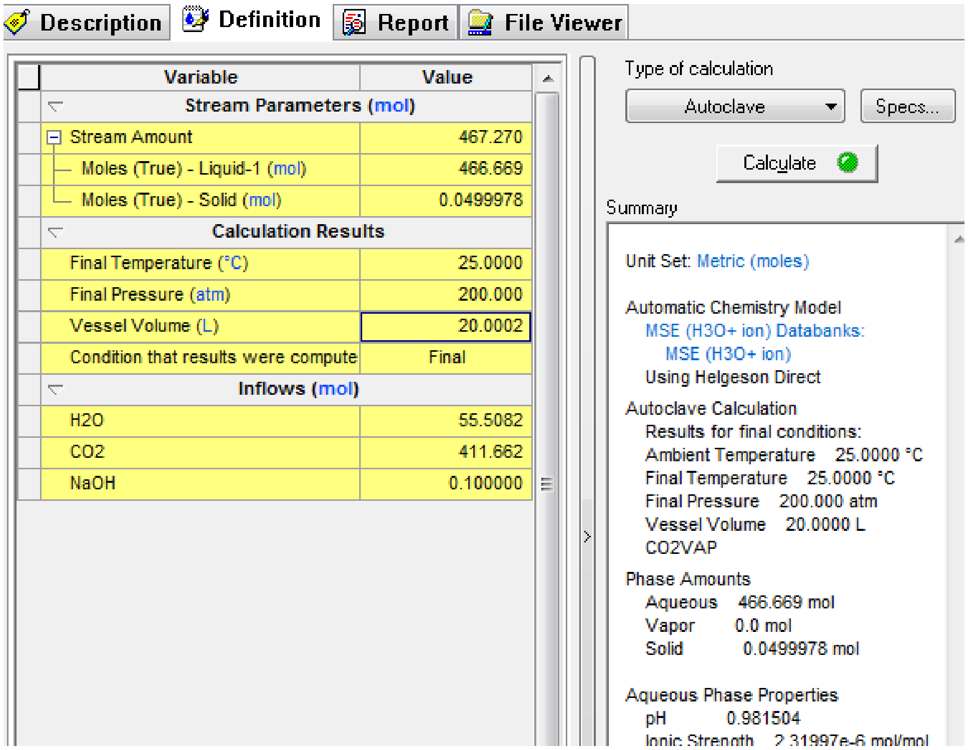
column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor
	mol	mol	mol
CO2	58.287	1.1185	57.1685
H2O	55.5082	55.4382	0.0699887
HCO3-1	0.100006	0.100006	0.0
Na+1	0.1	0.1	0.0
H3O+1	8.74885e-6	8.74885e-6	0.0
CO3-2	1.37355e-6	1.37355e-6	0.0
OH-1	1.85647e-9	1.85647e-9	0.0
NaOH	1.2057e-16	1.2057e-16	0.0
NaOHCO3-2	2.33697e-17	2.33697e-17	0.0
Total (by phase)	113.995	56.7568	57.2385

The vapor amount is 57.2 moles, compared to ~39 for ideal gas and with N_2. The primary difference is the CO2 fugacity.

T	P	Vol	Ideal Gas Law	Calculated (total)	Calculated (vapor)	Calculated (total)	Calculated (vapor)
C	atm	L	Moles of N2 mixed with 1L H2O			Moles of CO2 mixed with 1L H2O	
25	50	20	38.83	38.64	38.61	58.3	57.2

- ✓ Change the Final Pressure to 200 atm.
- ✓ Recalculate



Variable	Value
Stream Parameters (mol)	
Stream Amount	467.270
Moles (True) - Liquid-1 (mol)	466.669
Moles (True) - Solid (mol)	0.0499978
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	200.000
Vessel Volume (L)	20.0002
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
CO2	411.662
NaOH	0.100000

Unit Set: Metric (moles)

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

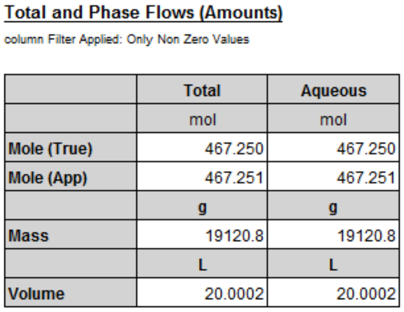
Autoclave Calculation
Results for final conditions:
Ambient Temperature 25.0000 °C
Final Temperature 25.0000 °C
Final Pressure 200.000 atm
Vessel Volume 20.0000 L
CO2VAP

Phase Amounts
Aqueous 466.669 mol
Vapor 0.0 mol
Solid 0.0499978 mol

Aqueous Phase Properties
pH 0.981504
Ionic Strength 2.31997e-6 mol/mol

Notice that the output differs significantly, and there is no vapor phase reported in the Summary section. The computed gas amount is 412 moles, which is far from the Ideal gas value of ~155 moles.

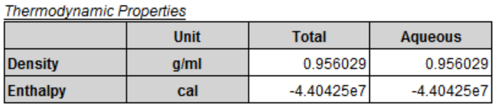
- ✓ Click on the Report tab and view the Total and Phase Flows table



Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous
	mol	mol
Mole (True)	467.250	467.250
Mole (App)	467.251	467.251
	g	g
Mass	19120.8	19120.8
	L	L
Volume	20.0002	20.0002



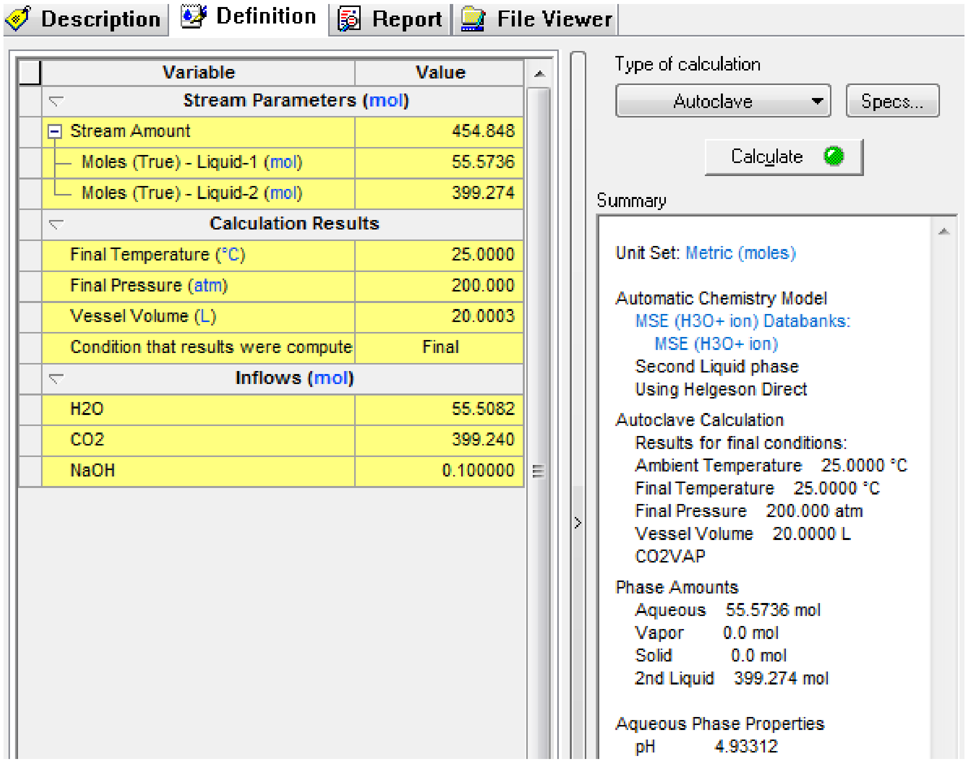
Thermodynamic Properties

	Unit	Total	Aqueous
Density	g/ml	0.956029	0.956029
Enthalpy	cal	-4.40425e7	-4.40425e7

According to the calculation, the stream is monophasic and the liquid density is 0.95. The software either computed the wrong results, or the system is monophasic under these conditions.

There is a setting that is off by default, the 2nd liquid phase. Normally a 2nd liquid is organic, but in this case it will be a supercritical CO2 phase. The software computed the wrong results, because this button is not on by default. OLI does not provide an automatic adjustment for this.

- ✓ Click on the 2nd button in the ribbon ad then calculate.



Variable	Value
Stream Parameters (mol)	
Stream Amount	454.848
Moles (True) - Liquid-1 (mol)	55.5736
Moles (True) - Liquid-2 (mol)	399.274
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	200.000
Vessel Volume (L)	20.0003
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
CO2	399.240
NaOH	0.100000

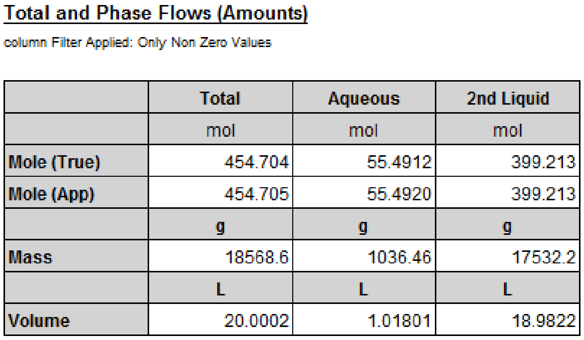
Unit Set: Metric (moles)

Automatic Chemistry Model
MSE (H3O+ ion) Databanks:
MSE (H3O+ ion)
Second Liquid phase
Using Helgeson Direct
Autoclave Calculation
Results for final conditions:
Ambient Temperature 25.0000 °C
Final Temperature 25.0000 °C
Final Pressure 200.000 atm
Vessel Volume 20.0000 L
CO2VAP
Phase Amounts
Aqueous 55.5736 mol
Vapor 0.0 mol
Solid 0.0 mol
2nd Liquid 399.274 mol

Aqueous Phase Properties
pH 4.93312

When the 2nd liquid phase is selected, the software compute a large 2nd liquid phase, and the CO2 amount is slightly lower, 399 moles.

- ✓ Click on the Report tab and review the Total and Phase Flows table.



Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	2nd Liquid
	mol	mol	mol
Mole (True)	454.704	55.4912	399.213
Mole (App)	454.705	55.4920	399.213
	g	g	g
Mass	18568.6	1036.46	17532.2
	L	L	L
Volume	20.0002	1.01801	18.9822

The calculated phases are 1.01 liters of water and 19 liters of critical CO2. The Autoclave filled the void space (~19 liters) with sufficient critical CO2 to match the specified vessel volume.

Click here for the final worked examples from this chapter: Chapter 11 - Autoclaves

12. Reaction Kinetics

Overview

In this chapter we discuss reaction kinetics. Most of the chemistry in OLI Studio/Analyzer assumes equilibrium. This means the forward and reverse reactions are considered to be very fast. OLI considers two types of reaction kinetics; 1-Arrhenius and 2-User defined. This chapter will consider both type.

Arrhenius type reaction kinetics

Arrhenius type reactions use a traditional form of a reaction rate constant. For the theoretical reaction of:

$$aA + bB \overset{k_f}{\rightarrow} cC + dD$$

Where:

$$k_f = A_f e^{\frac{-E_a}{RT}}$$

k_f	=	Forward rate constant
A_f	=	Pre-exponential factor
E_a	=	Energy of Activation
R	=	Gas constant
T	=	Temperature

The user is required to supply these values. OLI does not maintain a database of these parameters.

Reaction of Ammonia and Carbon Dioxide

For our example, we are going to consider the reaction of ammonia and carbon dioxide to form urea and water. We will also be using the AQ thermodynamic framework. Here is our reaction:

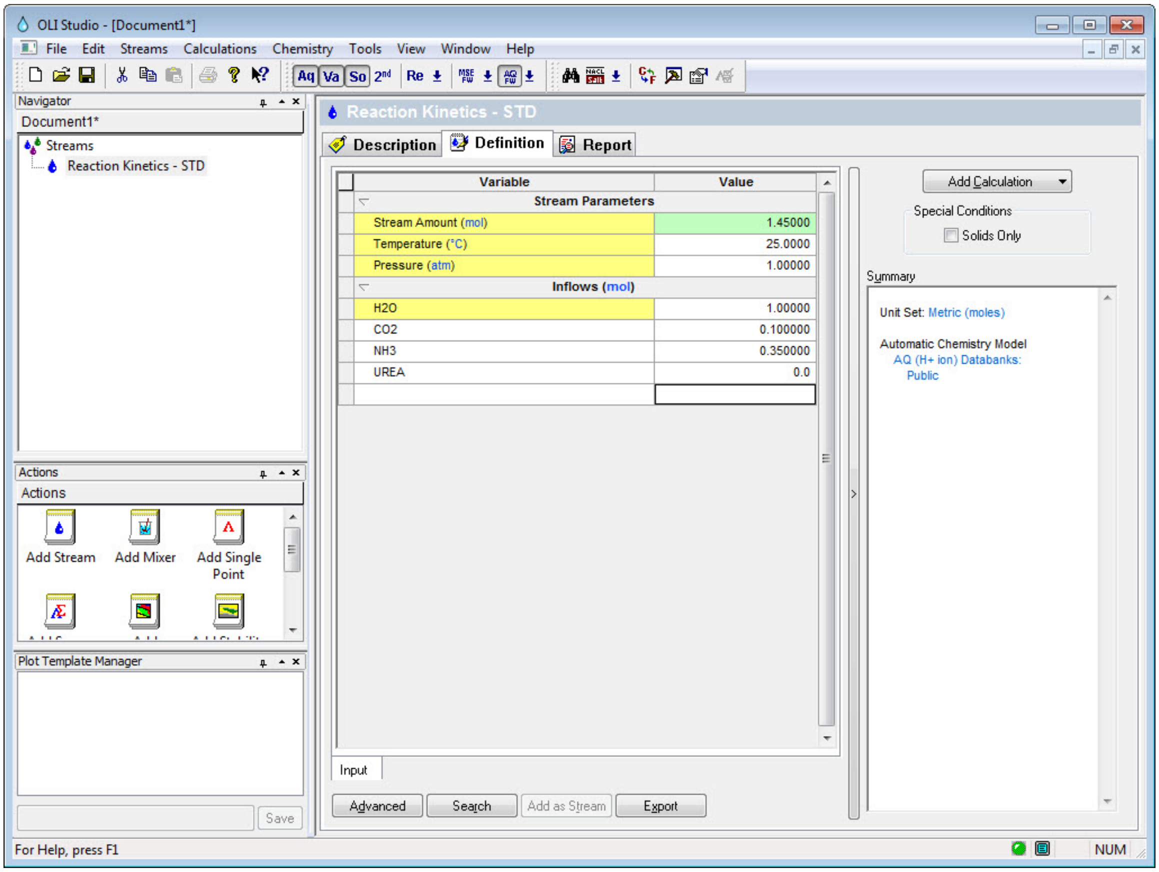
$$NH_{3(aq)} + CO_{2(aq)} \rightarrow NH_2CONH_{2(aq)} + H_2O$$

There is a forward and reverse reaction (a k_f and k_r) which we will have to define. We start by using OLI Studio and then entering the following components:

Table 2 Urea reaction kinetics inflow species

Standard Reaction Kinetics		
Thermodynamic Framework	Aqueous (H+ Ion)	A
Additional Databanks	None	
Phases	Default	
Inflows	Formula	OLI Tag Name
Water	H_2O	H2O
Carbon Dioxide	CO_2	CO2
Ammonia	NH_3	NH3
Urea	NH_2CONH_2	UREA

Here is the OLI Studio/Analyzer input screen.



Variable	Value
Stream Parameters	
Stream Amount (mol)	1.45000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	1.00000
CO2	0.100000
NH3	0.350000
UREA	0.0

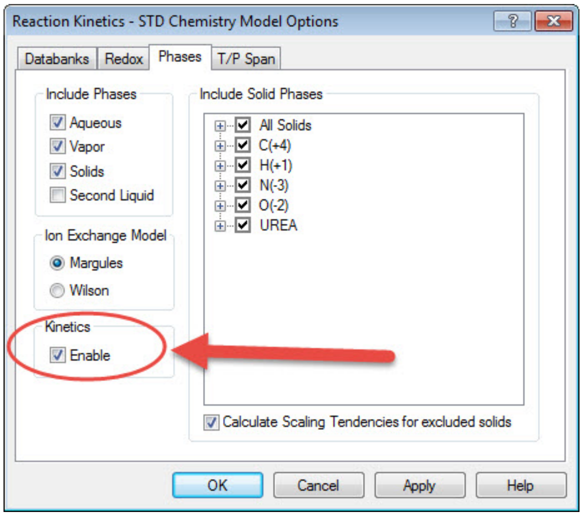
☐ Solids Only

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 12-1 Input conditions

We now need to enable reaction kinetics. **Click** the **Chemistry** menu item, then **Model Options** and finally select the **Phases** tab.



Include Phases
☑ Aqueous
☑ Vapor
☑ Solids
☐ Second Liquid

Ion Exchange Model
● Margules
○ Wilson

Kinetics
☑ Enable

Include Solid Phases
☑ All Solids
☑ C(+4)
☑ H(+1)
☑ N(-3)
☑ O(-2)
☑ UREA

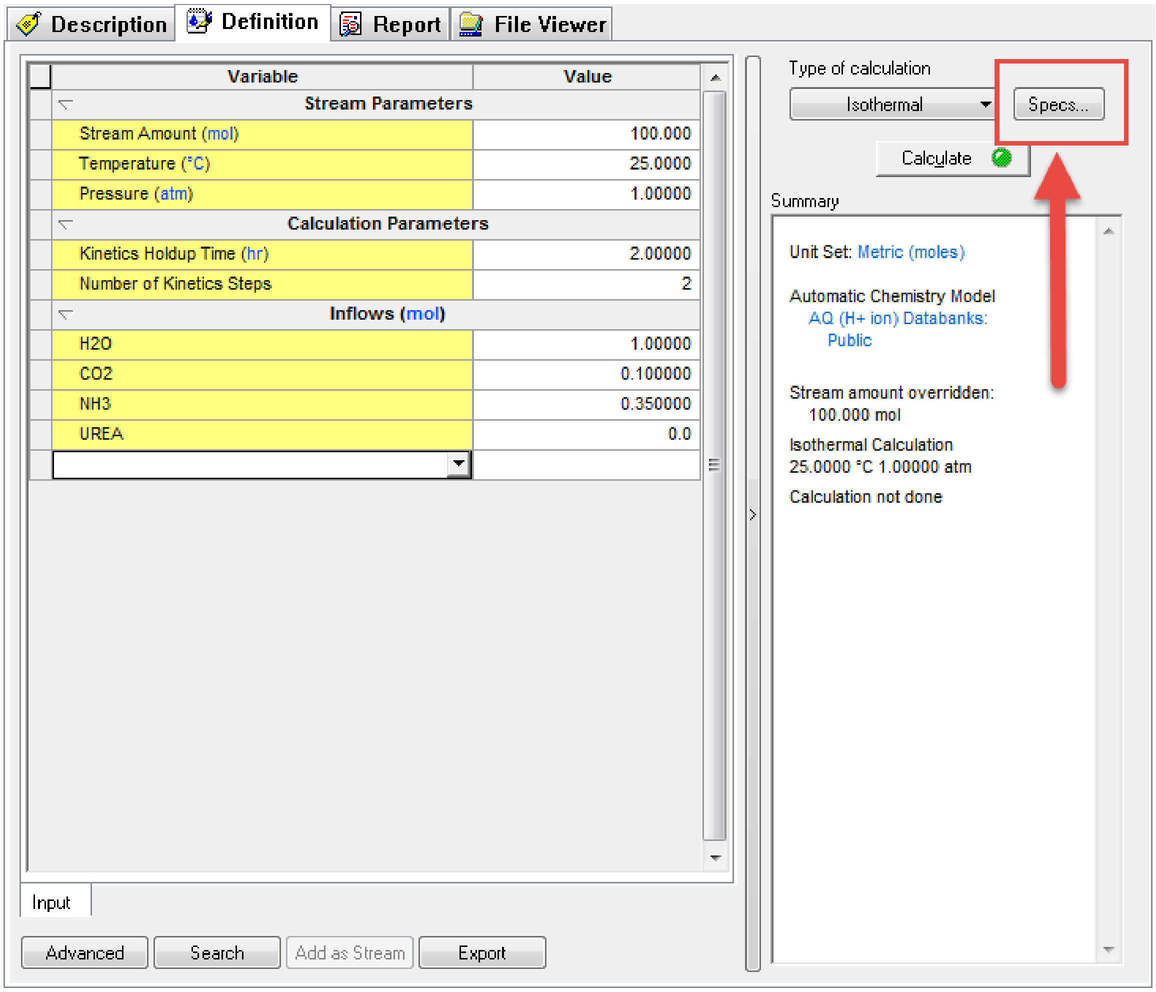
☑ Calculate Scaling Tendencies for excluded solids

Figure 12-2 Check the indicated box

Check the *Kinetics/Enable* box to turn on reaction kinetics.

We add the actual reaction kinetics in the calculation. For our example, add an isothermal single point calculation.

We will the reaction kinetics via the **Specs…** button.



Variable	Value
Stream Parameters	
Stream Amount (mol)	100.000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Kinetics Holdup Time (hr)	2.00000
Number of Kinetics Steps	2
Inflows (mol)	
H2O	1.00000
CO2	0.100000
NH3	0.350000
UREA	0.0

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Stream amount overridden:
100.000 mol

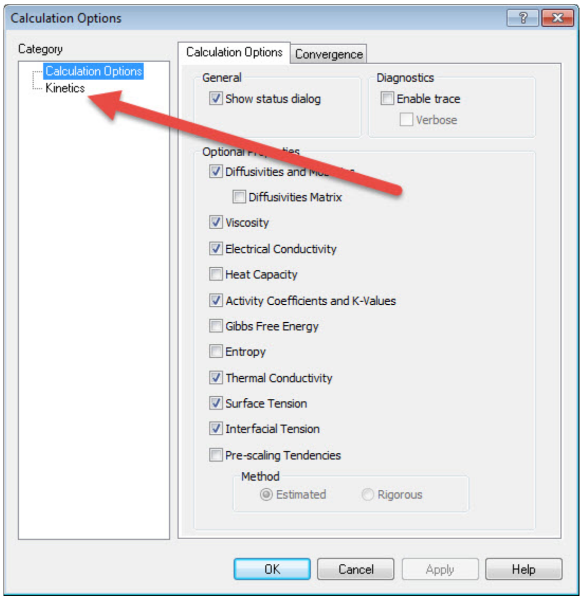
Isothermal Calculation
25.0000 °C 1.00000 atm

Calculation not done

Figure 12-3 Click the specs... button

Click the **Specs…** button.

This will display options for this calculation.



- ☑ Show status dialog
- ☐ Enable trace
  - ☐ Verbose
- ☑ Diffusivities and Mo
  - ☐ Diffusivities Matrix
- ☑ Viscosity
- ☑ Electrical Conductivity
- ☐ Heat Capacity
- ☑ Activity Coefficients and K-Values
- ☐ Gibbs Free Energy
- ☐ Entropy
- ☑ Thermal Conductivity
- ☑ Surface Tension
- ☑ Interfacial Tension
- ☐ Pre-scaling Tendencies
  - Method: ● Estimated ○ Rigorous

Figure 12-4 Calculation options

Click the category that says *Kinetics*.

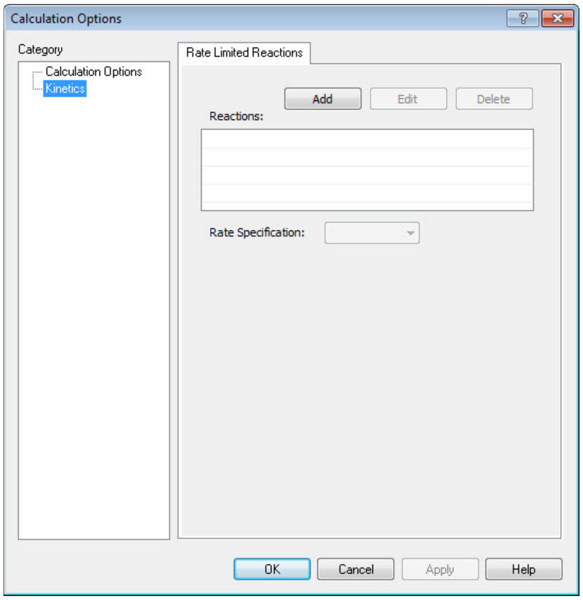
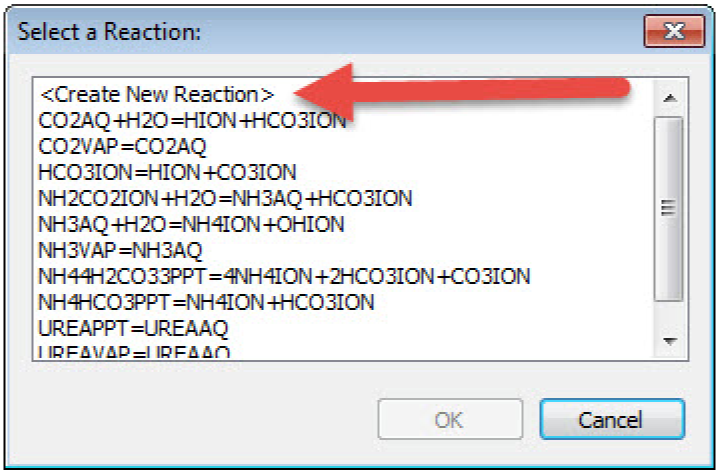


Figure 12-5 Kinetics Dialog

Click the **Add** button to start adding our reaction kinetics.

You will be given a list of reactions which are already in the chemistry model. These can be replaced if you require it. For our example, the reaction we need is not in the list:



<Create New Reaction>
CO2AQ+H2O=HION+HCO3ION
CO2VAP=CO2AQ
HCO3ION=HION+CO3ION
NH2CO2ION+H2O=NH3AQ+HCO3ION
NH3AQ+H2O=NH4ION+OHION
NH3VAP=NH3AQ
NH44H2CO33PPT=4NH4ION+2HCO3ION+CO3ION
NH4HCO3PPT=NH4ION+HCO3ION
UREAPPT=UREAAQ
UREAVAP=UREAAQ

Figure 12-6 List of reactions

We will create a new reaction. Click the **<Create New Reaction>** line and then click **OK**.

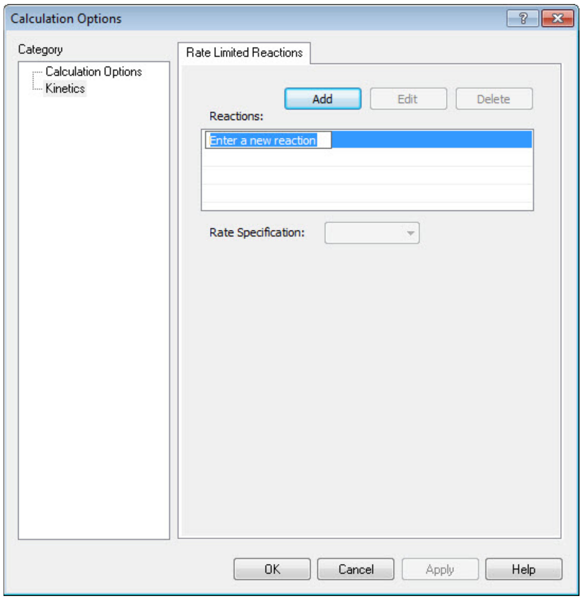
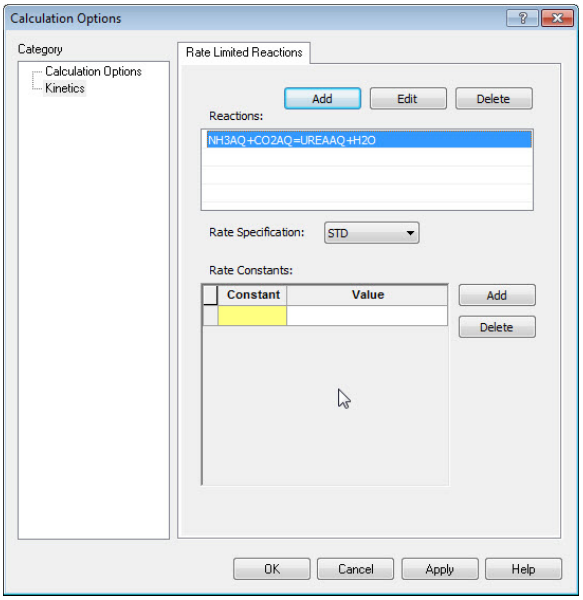


Figure 12-7 Adding a new reaction

You can now enter your reaction. You must use the OLI Tag Name for this step. Enter the following reaction:

NH3AQ+CO2AQ=UREAAQ+H2O

When you press the enter key the dialog will update:



Reactions: NH3AQ+CO2AQ=UREAAQ+H2O

Rate Specification: STD

Figure 12-8 Added ammonia reaction

There are two types of Rate Specification. For this example, we are using the standard or **STD** type. Leave the button **Rate Specification** as *STD*.

WE can now add our rate constant parameters.

The first comment we need to make is that we have combined some of the terms in the standard Arrhenius equation. The gas constant and the energy of activation are constant, so OLI had decided to make them another constant.[41]

$$B = \frac{E_a}{R}$$

The forward and reverse reactions have the same format. The mechanism of the rate is the following:

$$Rate = k_f[NH_3]^2[CO_2] - k_r[NH_2CONH_2]$$

The forward rate constant is fixed in value, but the reverse is:

$$k_r = A_r e^{\frac{-B_r}{T}} = 1.2x10^{-06} e^{\frac{3480.78}{T}}$$

Here are the parameters[42]

---

[41] The reason for this is lost to antiquity. Rather than upset the developers we have kept the format the same as when Marshall Rafal wrote the original program.

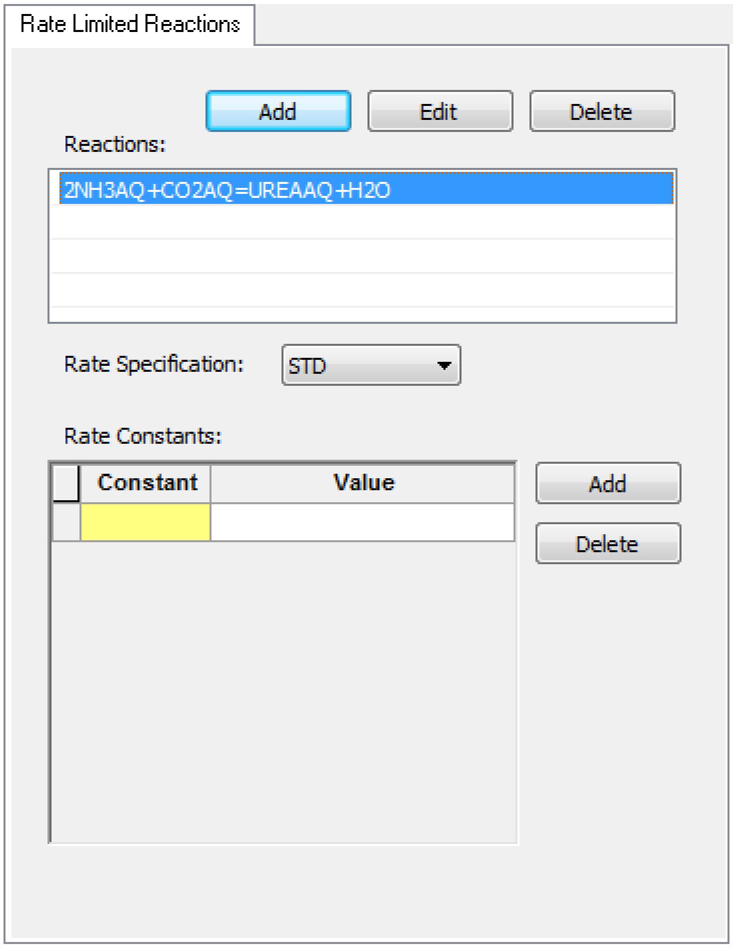
[42] It is unknown from whence these parameters were obtained. Do not use them for any real design work.

Table 3 Reaction Rate Parameters

Parameters	Value	Comment
k_f	20	forward rate constant
k_r	calculated	See above
A_r	1.2×10^{-6}	
B_r	3480.78	Determined from $B_r = -(-28939.9/8.3142)$
EP1	1	This is the exponent of product 1 in the mechanism. In this case $[NH_2CONH_2]$
EP2	0	H2O does not partake in the reaction
ER1	2	This is the exponent of reactant 1 $[NH_3]^2$
ER2	1	This is the exponent of reactant 2 $[CO_2]$

The values of EP and ER are based on the added reaction in Figure 12-8 on page 223 above.

Now that we have the parameters we can add them. Click the **Add** button in Figure 12-8



Reactions:

2NH3AQ+CO2AQ=UREAAQ+H2O

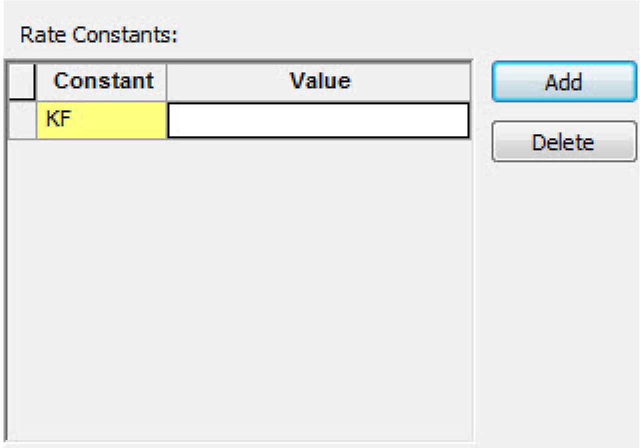
Rate Specification: STD

Rate Constants:

Constant	Value

Figure 12-9 Select a parameter

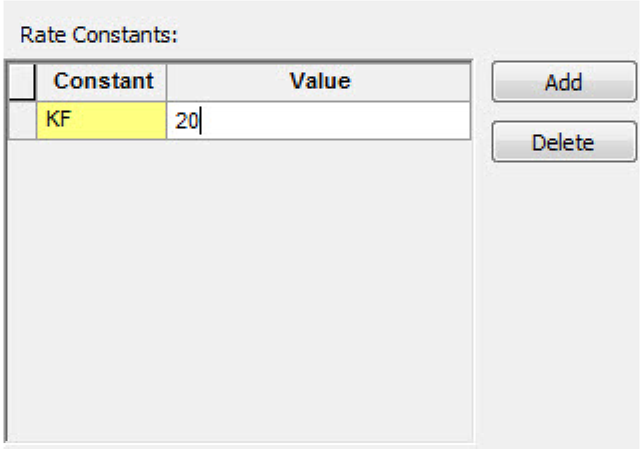
Select **KF**



Constant	Value
KF	

Figure 12-10 Selecting kf

Enter the value from the Table 3 Reaction Rate Parameters above:



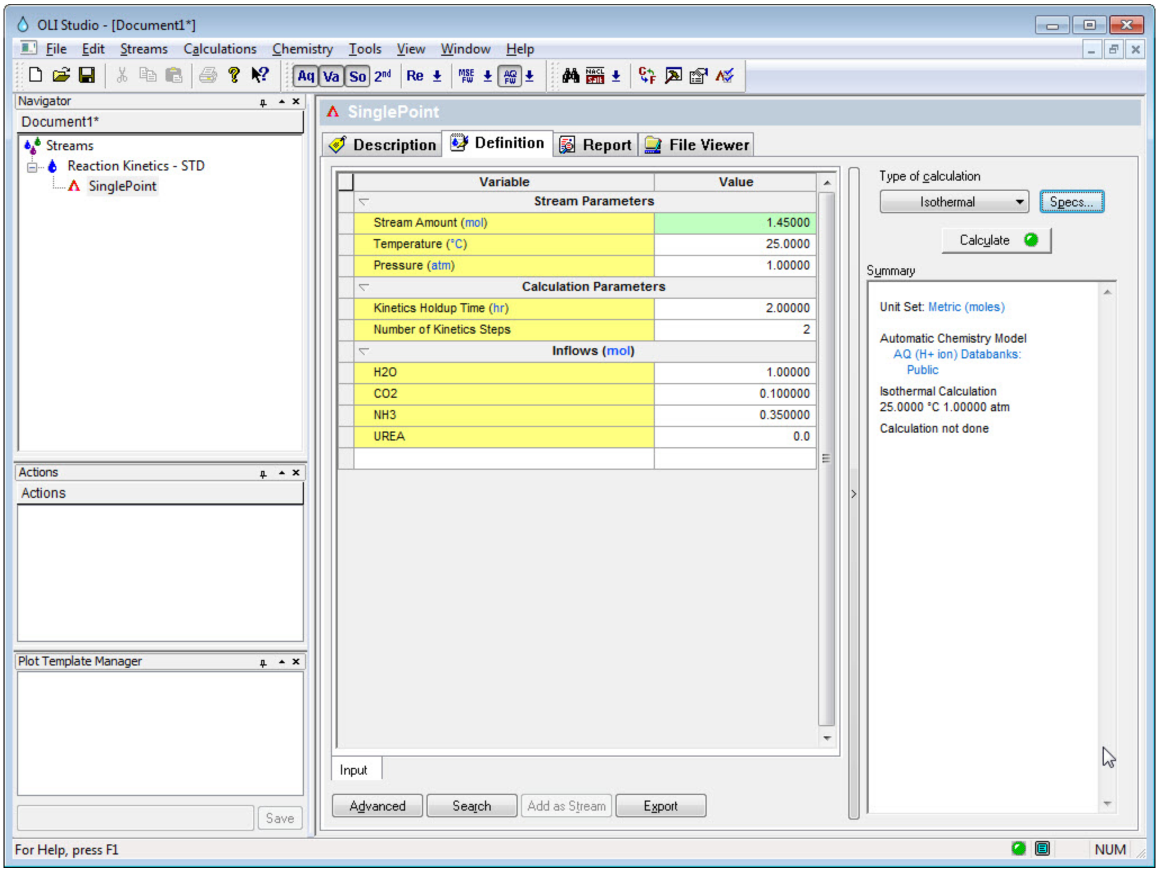
Constant	Value
KF	20

Figure 12-11 Entered kf

Repeat these steps for the remaining parameters (not k_r does not need to be entered)

Click **OK** when done.

You will see that the input grid has changed accommodate time parameters:



Variable	Value
Stream Parameters	
Stream Amount (mol)	1.45000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Kinetics Holdup Time (hr)	2.00000
Number of Kinetics Steps	2
Inflows (mol)	
H2O	1.00000
CO2	0.100000
NH3	0.350000
UREA	0.0

Type of calculation: Isothermal

Summary

Unit Set: Metric (moles)

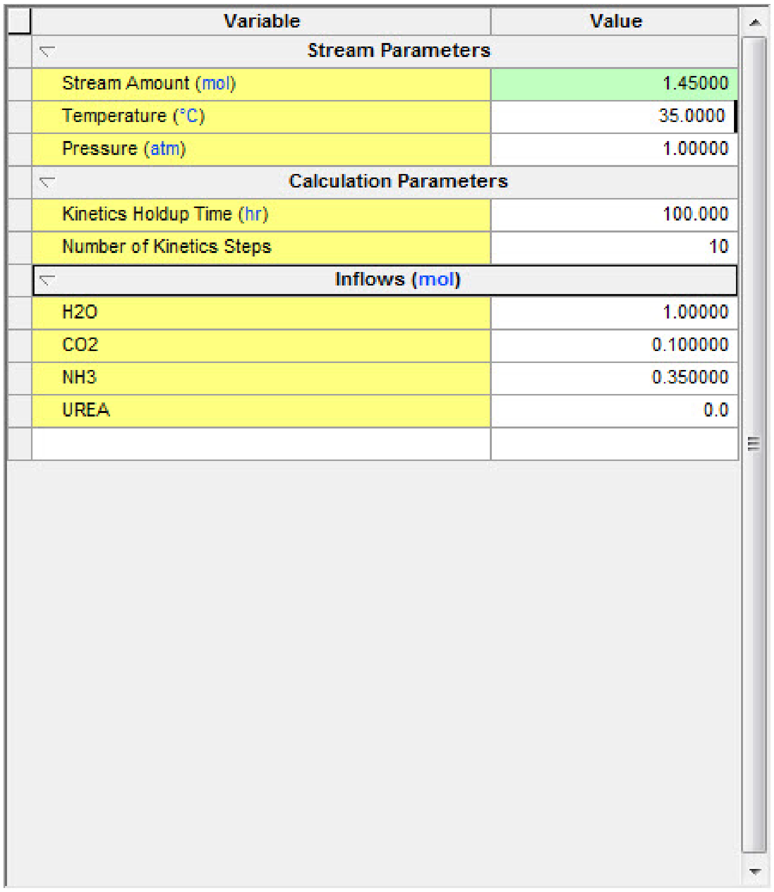
Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
25.0000 °C 1.00000 atm

Calculation not done

Figure 12-12 Updated time parameters

This example is simulating a chemical reactor with a residence time of 100 hours. We call this in OLI Studio/Analyzer *Kinetics Holdup Time*. We are also going to simulate this as a plug-flow reactor and divide the simulation into 10 stages (or plugs). Finally, we will increase the temperature to 35 °C.



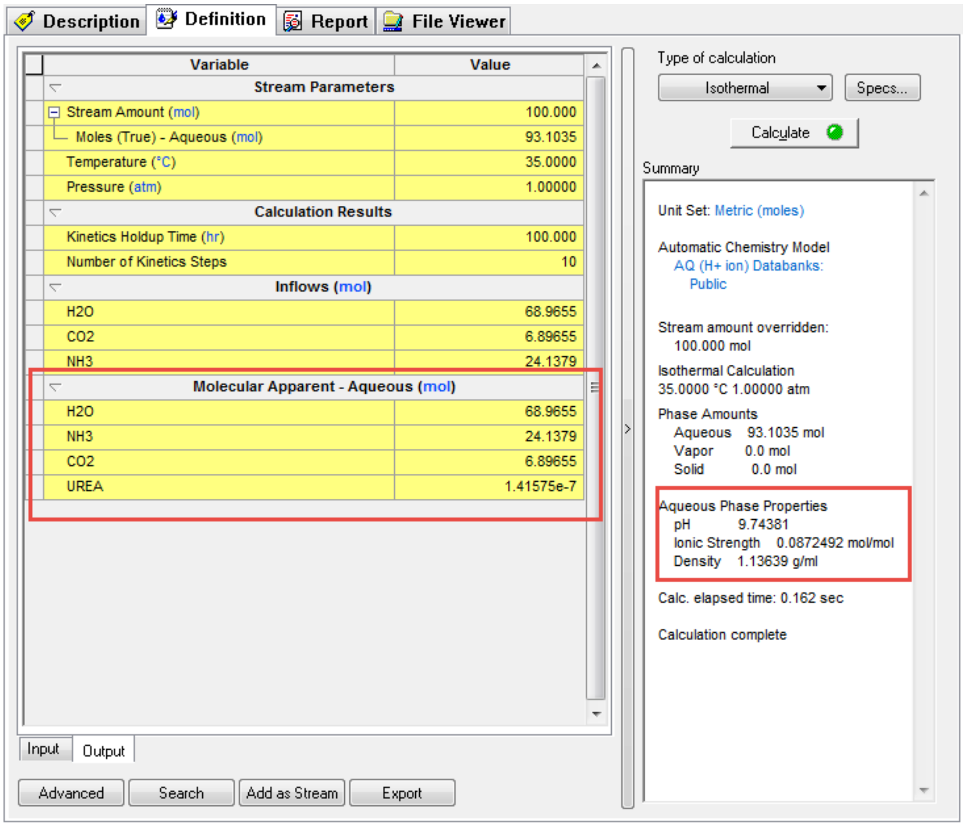
Variable	Value
Stream Parameters	
Stream Amount (mol)	1.45000
Temperature (°C)	35.0000
Pressure (atm)	1.00000
Calculation Parameters	
Kinetics Holdup Time (hr)	100.000
Number of Kinetics Steps	10
Inflows (mol)	
H2O	1.00000
CO2	0.100000
NH3	0.350000
UREA	0.0

Figure 12-13 Input conditions are filled out.

OLI recommends that you save the file at this time!

Click the **Calculate** button.

When the program calculation is complete click on the **Output** mini-tab and then add a section for *Molecular Apparent – Aqueous*.



Variable	Value
Stream Parameters	
Stream Amount (mol)	100.000
Moles (True) - Aqueous (mol)	93.1035
Temperature (°C)	35.0000
Pressure (atm)	1.00000
Calculation Results	
Kinetics Holdup Time (hr)	100.000
Number of Kinetics Steps	10
Inflows (mol)	
H2O	68.9655
CO2	6.89655
NH3	24.1379
Molecular Apparent - Aqueous (mol)	
H2O	68.9655
NH3	24.1379
CO2	6.89655
UREA	1.41575e-7

Type of calculation
Isothermal

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Stream amount overridden:
100.000 mol

Isothermal Calculation
35.0000 °C 1.00000 atm

Phase Amounts
Aqueous 93.1035 mol
Vapor 0.0 mol
Solid 0.0 mol

Aqueous Phase Properties
pH 9.74381
Ionic Strength 0.0872492 mol/mol
Density 1.13639 g/ml

Calc. elapsed time: 0.162 sec

Calculation complete

Figure 12-14 The results

So, it seems we have created some urea. Not much but some. The user is left to make changes to the holdup time and/or steps to see if the results change.

You can find this worked example file on our wiki page at:
http://wiki.olisystems.com/wiki/OLI_Studio_Stream_Analyzer_User_Guide_v9.5

Non-standard SPEC type reaction kinetics

These reactions do not necessarily follow Arrhenius kinetics or require a more complicated mechanism than can be represented by the standard OLI implementation of reaction kinetics.

Ammonia Hydrolysis

In this example we are using simpler chemistry. The hydrolysis reaction we are using is the following:

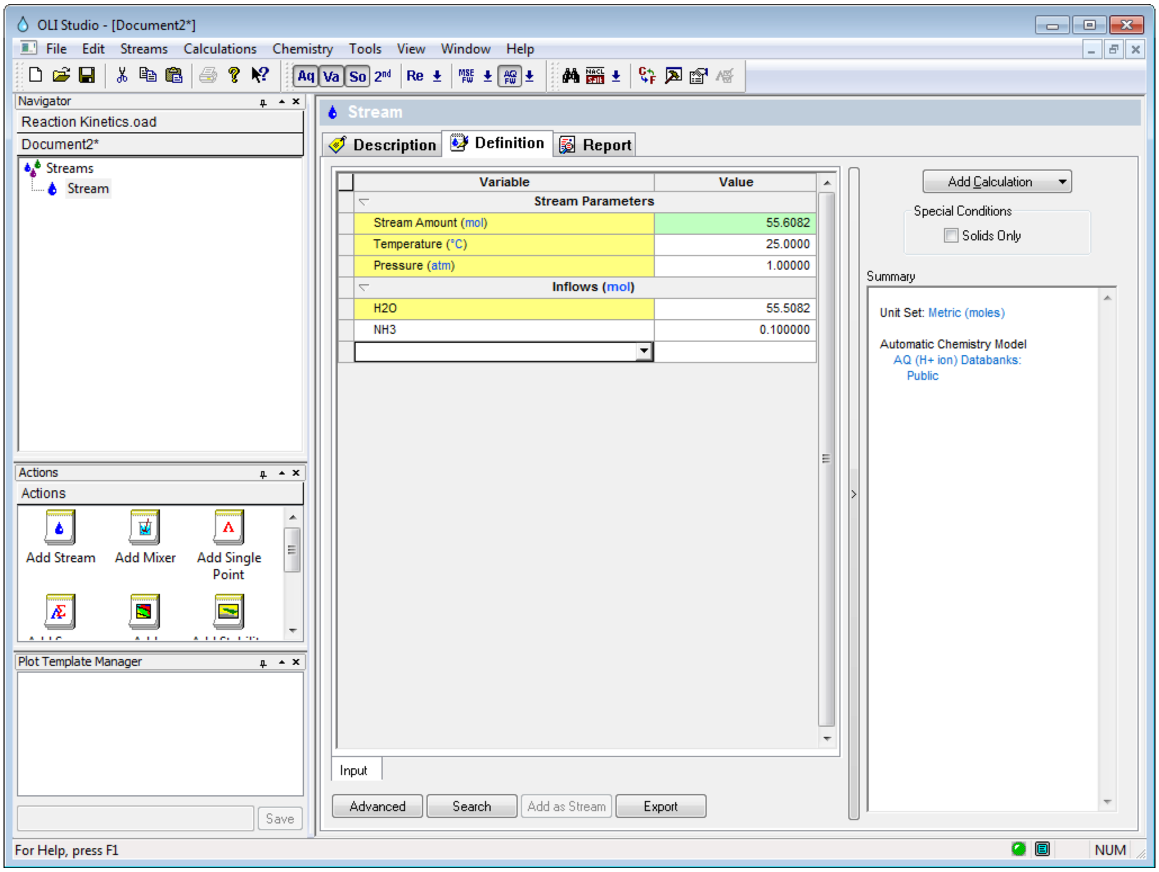
$$NH_{3(aq)} + H_2O \rightleftharpoons NH_4^+ + OH^-$$

For this example, we know the forward rate constant but need to constrain the reverse reaction to the thermodynamic equilibrium constant. This implies that we are going to replace an existing equation.

We are going to start off by creating a stream with the following parameters:

Non-standard Reaction Kinetics			
Thermodynamic Framework	Aqueous (H+ ion)		
Additional databanks	None		
Temperature	25 °C		
Pressure	1.0 atm		
Stream Value	automatic		
Inflows	Formula	OLI Tag Name	Value
Water	H_2O	H2O	55.5087 mol
Ammonia	NH_3	NH3	0.1 mol

The stream should look like this:



Stream

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
NH3	0.100000

☐ Solids Only

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 12-15 Non-standard kinetics stream

As with the previous example, we need to first enable kinetics via the **Chemistry | Model Options | Phases** menu items.

Review the steps illustrated in Figure 12-1 and Figure 12-2 on page 219.

Now we need to add a calculation, for the example we are adding a single point isothermal calculation.

As before we start with the **<u>Specs…</u>** button and then the **<u>Kinetics</u>** category.

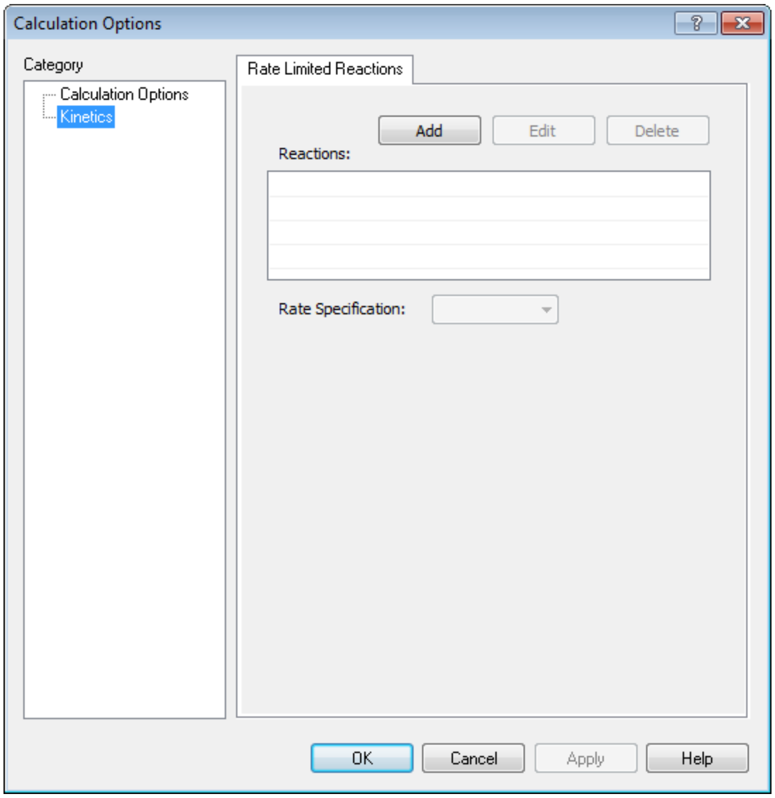
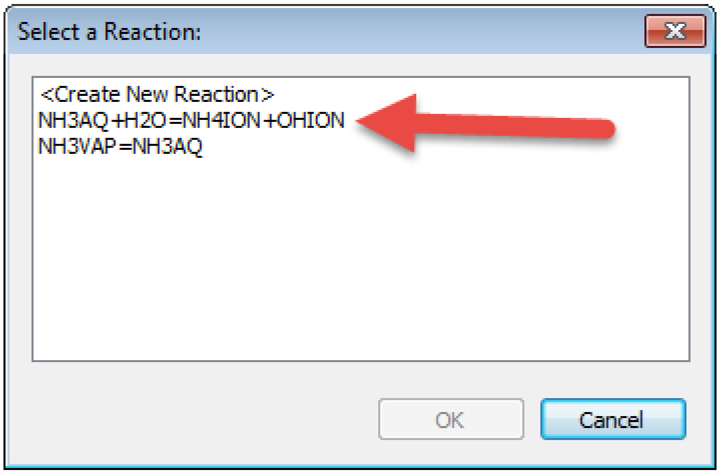


Figure 12-16 Adding a new reaction kinetics equation

Click the **<u>Add</u>** button

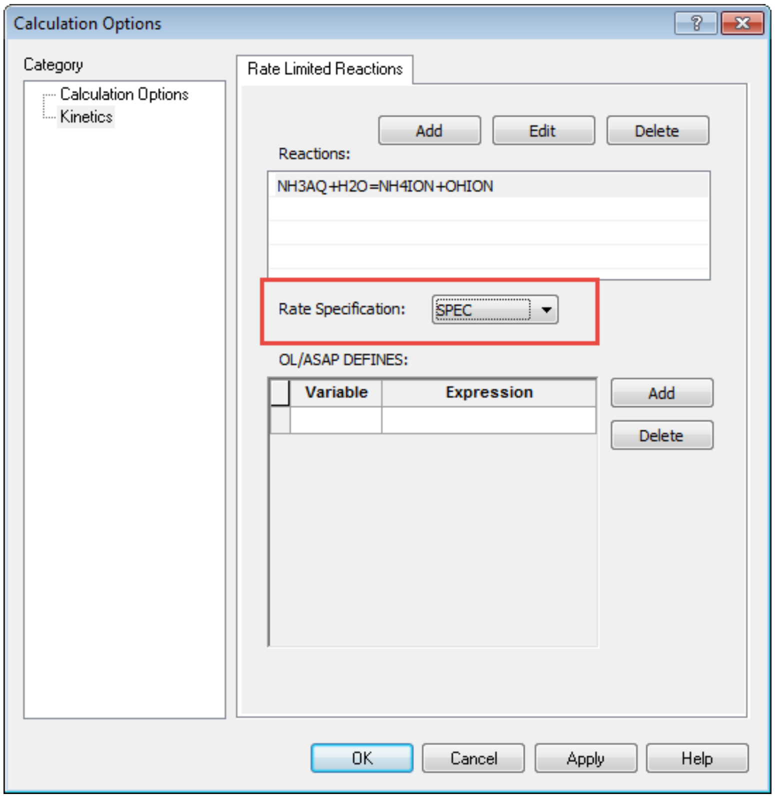
Once again we will see a list of equation in the OLI Tag Name format;



<Create New Reaction>
NH3AQ+H2O=NH4ION+OHION
NH3VAP=NH3AQ

Figure 12-17 Possible reactions

In this case our desired reaction is the second one. Click it and then click the **<u>OK</u>** button.



Reactions: NH3AQ+H2O=NH4ION+OHION

Rate Specification: SPEC

Figure 12-18 Clicking the SPEC type reaction.

These is where things get difficult. You now need to speak “OLI”. We have some rules for SPEC type equations. First we will show you the rate equations were using:

$$Rate_{forward} = k_f \gamma_{NH_{3(aq)}} [NH_{3(aq)}] \gamma_{H_2O} [H_2O]$$

$$Rate_{reverse} = k_r \gamma_{NH_4^+} [NH_4^+] \gamma_{OH^-} [OH^-]$$

$$k_f = 3$$

$$k_r = \frac{k_f}{K_{eq}}$$

$$rate = \left(k_f e^{Rate_{forward}} - k_r e^{Rate_{reverse}}\right) \frac{Volume}{1000}$$

We now need to turn these values into “OLI” terms[43].

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

Similarly, activity coefficients (γ) are also taken as the natural log so γ_{OH-} is used as $Log_e\ \gamma_{OH-}$ = AOHION.

KEQ is the thermodynamic equilibrium constant for the equation. AH2O is special in the Aqueous thermodynamic framework in that it is the variable $Log_e(a_{H2O})$.

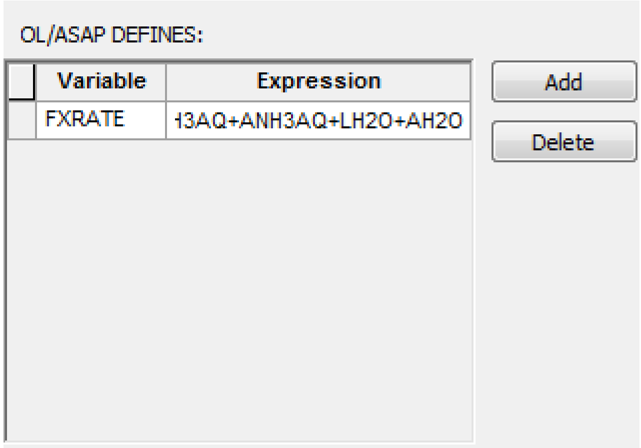
---

[43] Commonly referred to as ASAP variables.

We now need to add these variable to the kinetics window:

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

Start with the first line and keep going, in the variable field add FXRATE and in the expression, add the rest.

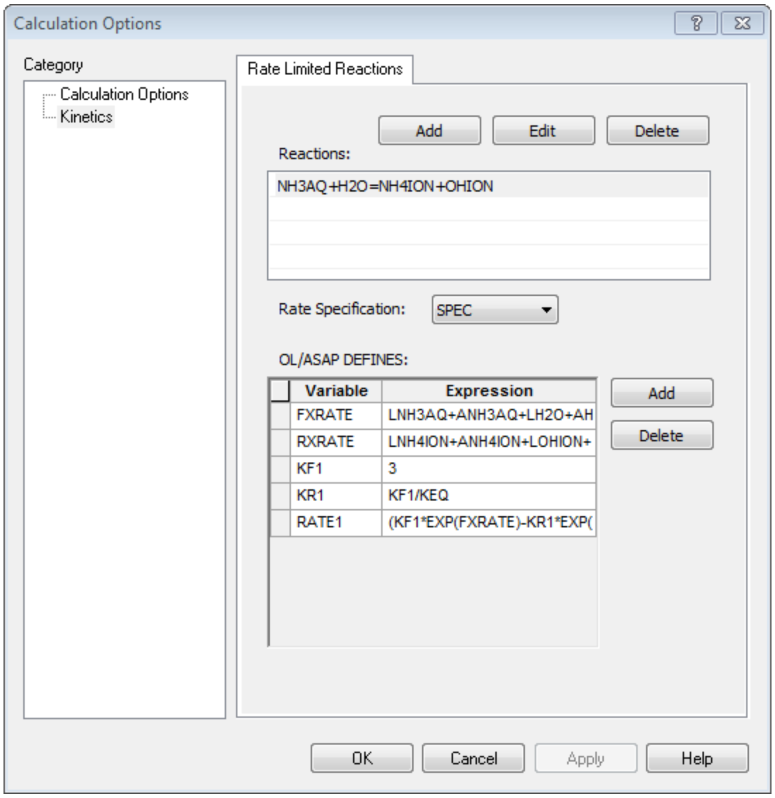


Variable	Expression
FXRATE	I3AQ+ANH3AQ+LH2O+AH2O

Figure 12-19 Adding variables

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

Complete the remainder of the variables.



Reactions:

NH3AQ+H2O=NH4ION+OHION

Rate Specification: SPEC

OL/ASAP DEFINES:

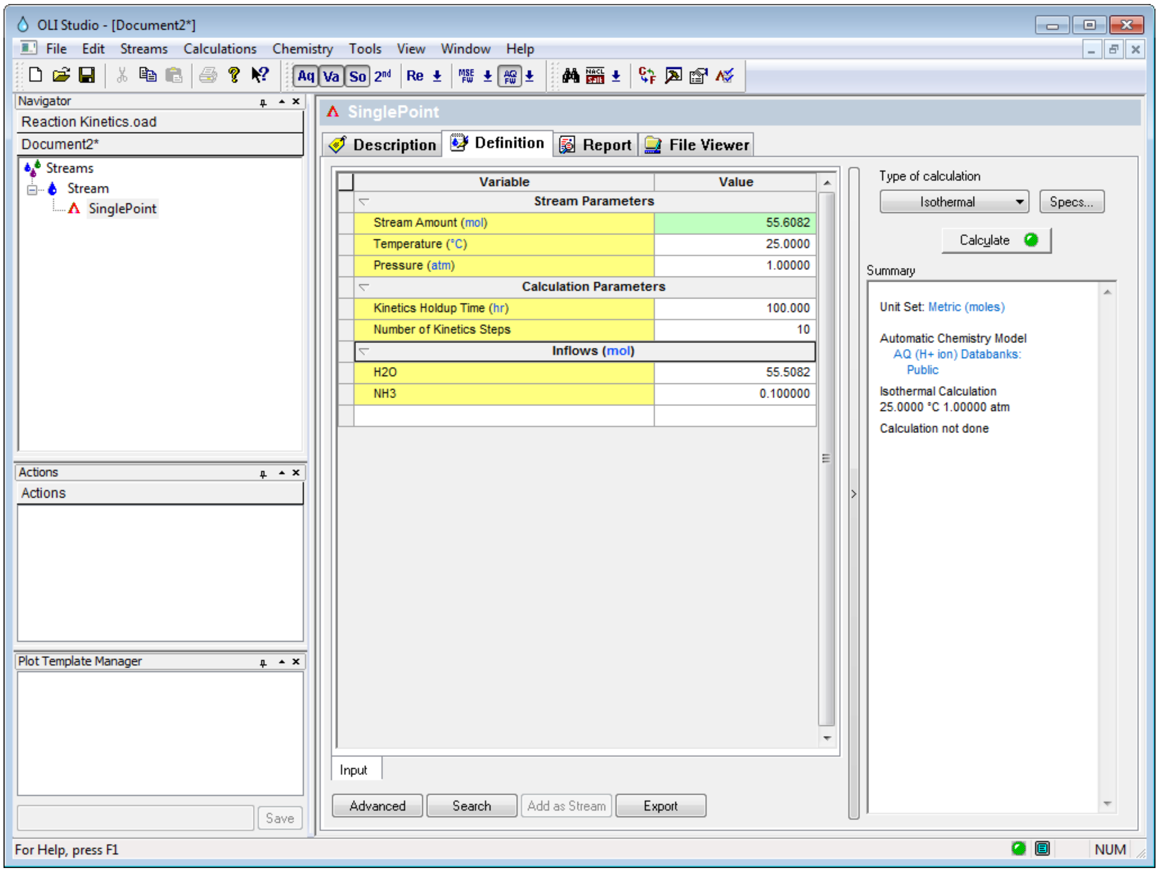
Variable	Expression
FXRATE	LNH3AQ+ANH3AQ+LH2O+AH
RXRATE	LNH4ION+ANH4ION+LOHION+
KF1	3
KR1	KF1/KEQ
RATE1	(KF1*EXP(FXRATE)-KR1*EXP(

Figure 12-20 The completed equations

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

Click the **OK** button.

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



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Kinetics Holdup Time (hr)	100.000
Number of Kinetics Steps	10
Inflows (mol)	
H2O	55.5082
NH3	0.100000

Type of calculation: Isothermal

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

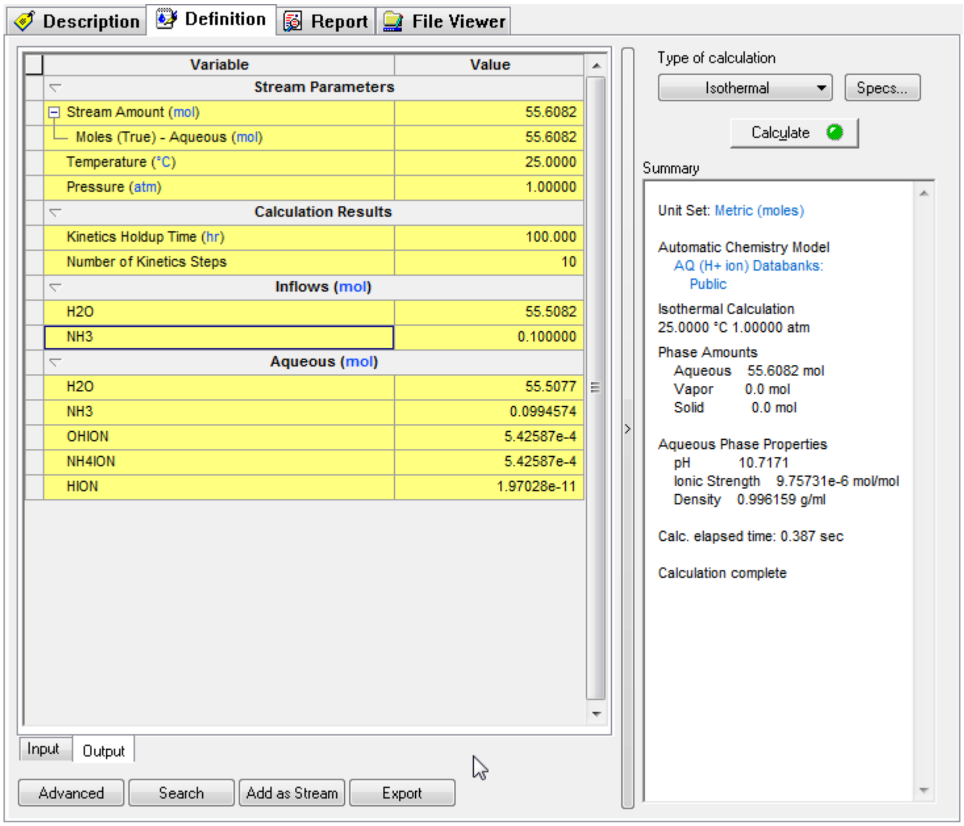
Isothermal Calculation
25.0000 °C 1.00000 atm

Calculation not done

Figure 12-21 Setting up the calculation

OLI recommends you save the file at this time:

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



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

Type of calculation: Isothermal

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Isothermal Calculation
25.0000 °C 1.00000 atm

Phase Amounts
Aqueous 55.6082 mol
Vapor 0.0 mol
Solid 0.0 mol

Aqueous Phase Properties
pH 10.7171
Ionic Strength 9.75731e-6 mol/mol
Density 0.996159 g/ml

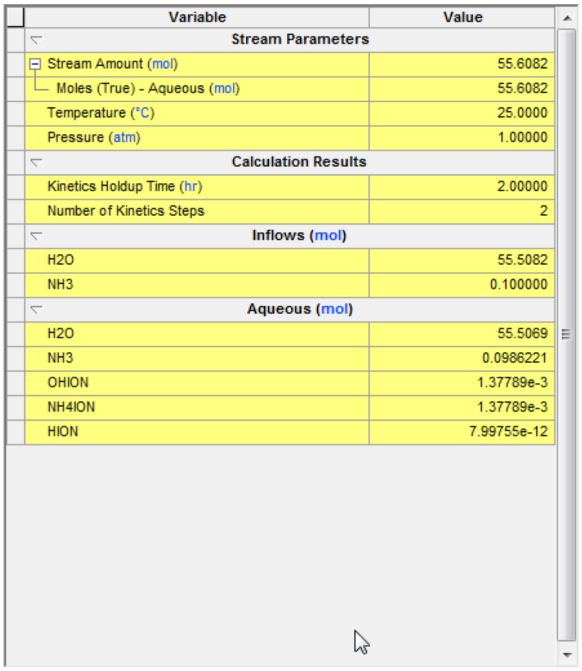
Calc. elapsed time: 0.387 sec

Calculation complete

Figure 12-22 The results

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

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



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Moles (True) - Aqueous (mol)	55.6082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Results	
Kinetics Holdup Time (hr)	2.00000
Number of Kinetics Steps	2
Inflows (mol)	
H2O	55.5082
NH3	0.100000
Aqueous (mol)	
H2O	55.5069
NH3	0.0986221
OHION	1.37789e-3
NH4ION	1.37789e-3
HION	7.99755e-12

Figure 12-23 No kinetics, only equilibrium results

The reaction kinetics have forced the back reaction to be dominant. In the equilibrium case, approximately $1.3x10^{-3}$ moles of NH_4^+ have been created. By limiting the forward reaction we allow the back reaction to take place and that only formed $5.4x10^{-4}$ moles of NH_4^+

13. Petroleum Calculations

Overview

Calculations with the OLI Software can be used to characterize crude oils. Here is a quote from the OLI Tricks of the Trade manual (AQSim)

> Crude oils are complex groups of organic molecules containing hundreds, perhaps thousands of pure components in a single oil. Modeling crude oils using pure components is impractical, because analyzing for each pure component is cost prohibitive and the number of species would make calculations overwhelming. A convenient solution to this problem and to modeling the properties of a crude oil is to create pseudo components. Crude Oil properties may be defined through a distillation curve, where each boiling point range is a progression of molecular weights, densities, solubilities, viscosities and other properties associated with that section. It is reasonable for low boiling point molecules to be low molecular weight, low density, low viscosity, and more soluble in water. We can dice boiling point curves using well accepted methods standard to create pseudocomponents that in combination reflect the property of the whole oil.
>
> There are two ways to create a crude oil stream on the Analyzers. The first is to start with a PVT curve and create pseudocomponents using one of the three thermodynamic methods coded into the software. The second is to enter the pseudocomponent data directly and using the same thermodynamic methods to predict the component properties.
>
> The three thermodynamic methods are API, Lee Kesler, and Cavett. At the time of writing, the software implementation specifications for these methods were not in hand.

This involves taking distillation data (such as ASTM D86) and converting that information into properties that the OLI software can use. This is generally referred to as “Creating Pseudo Components.”

There are two classes of this type of data. Actual assay (or distillation data) in which we cut the boiling point curves up into individual components or the actual entering of a pseudocomponent.

This section shows you how to enter each method.

Assays

For this example we will enter a distillation curve for a sample crude oil. This sample used ASTM method D86 to characterize the crude oil (see Chapter 14 on page 251 for a description of the distillation methods). The data for the distillation curve can be found in Table 13-1 on page 238.

Table 13-1 Sample Distillation data using ASTM method D86, API Gravity of 31

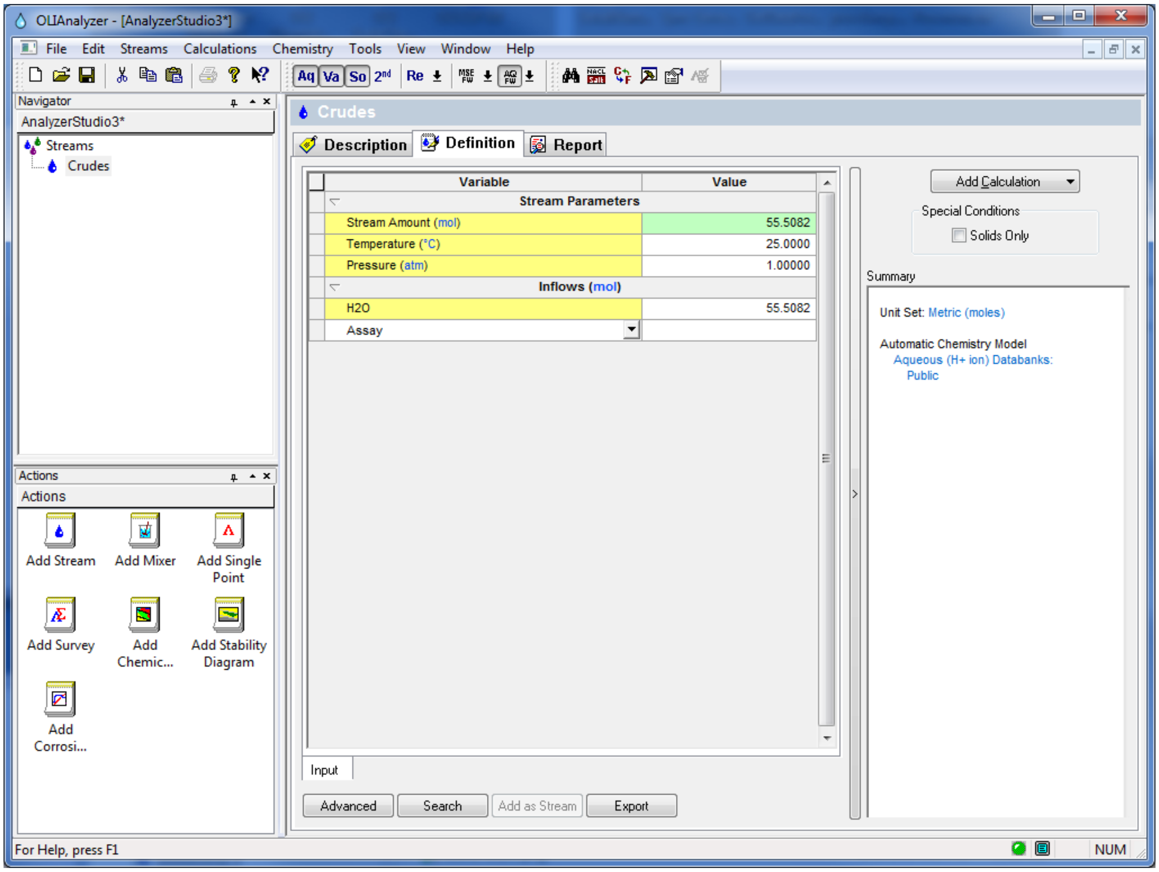
Distillation Data	
Volume Percent Distilled	Temperature, C
1	20
5	30
10	50
20	60
40	80
60	120
80	150
90	180
95	200
99	220
100	240

Create a standard OLI Studio stream at the following conditions

Stream Name	Crude	
Temperature	25	ºC
Pressure	1.0	atmospheres
H_2O	5	moles

You will need to enter the name of the assay. In our example we are using the name “Assay”. You are limited to only 5 characters for the name of the assay.

After entering the name Assay Do Not (repeat Do Not) press any other key! See Figure 13-1



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

☐ Solids Only

Unit Set: Metric (moles)

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

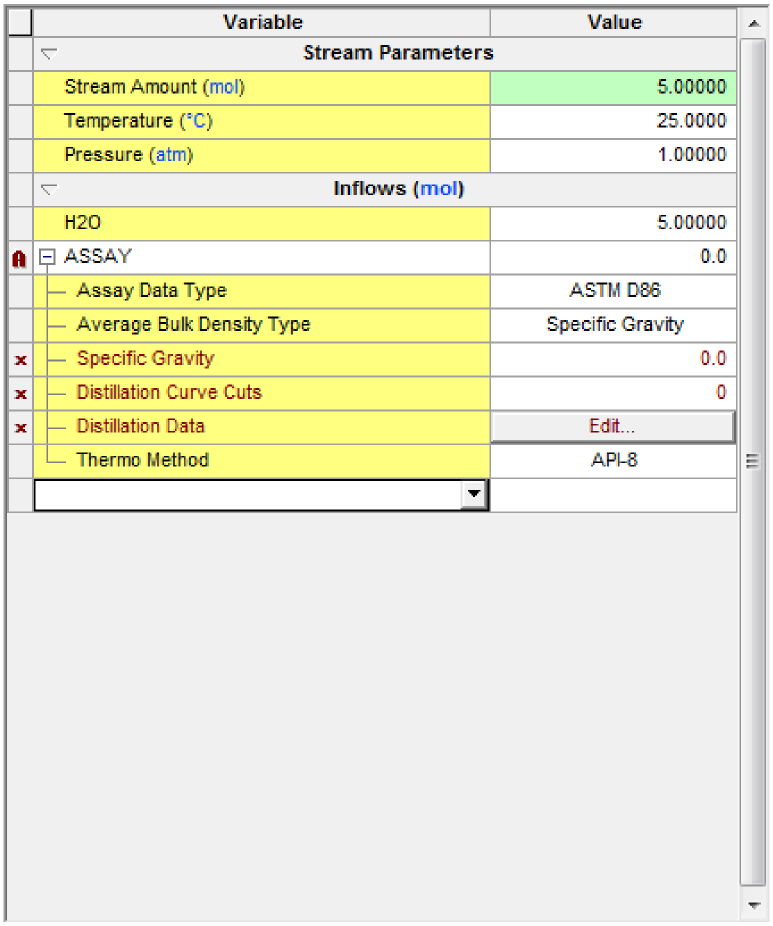
Figure 13-1 Entering a petroleum sample, Don't press ENTER yet!

The OLI Analyzer requires a different series of key strokes to enable the entering of the assay data.

After typing the name “Assay” you will need to use the following key combination

Shift – Enter

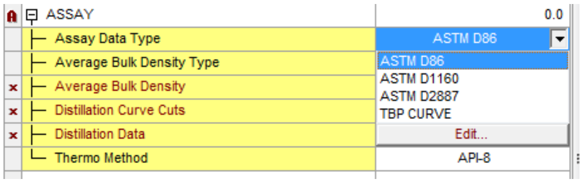
Press both of these keys together. You should be able to view the screen as shown in Figure 13-2 on page 240.



Variable	Value
Stream Parameters	
Stream Amount (mol)	5.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	5.00000
ASSAY	0.0
Assay Data Type	ASTM D86
Average Bulk Density Type	Specific Gravity
Specific Gravity	0.0
Distillation Curve Cuts	0
Distillation Data	Edit...
Thermo Method	API-8

Figure 13-2 Blank Assay input grids

We will begin by defining the type of assay data. Click in the cell next to the **Assay Data Type** to see a list of distillation types.



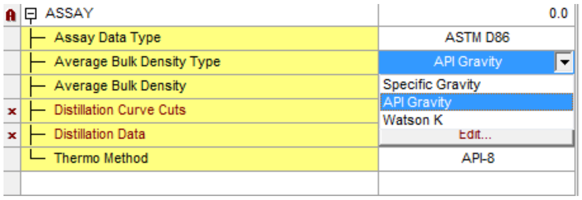
ASSAY	0.0
Assay Data Type	ASTM D86
Average Bulk Density Type	
Average Bulk Density	
Distillation Curve Cuts	
Distillation Data	Edit...
Thermo Method	API-8

Figure 13-3Assay Data Types

There are four types, select **ASTM D86**

Next click in the cell next to the

Average Bulk Density Type



ASSAY	0.0
Assay Data Type	ASTM D86
Average Bulk Density Type	API Gravity
Average Bulk Density	
Distillation Curve Cuts	
Distillation Data	Edit...
Thermo Method	API-8

Figure 13-4 Average Bulk Density options

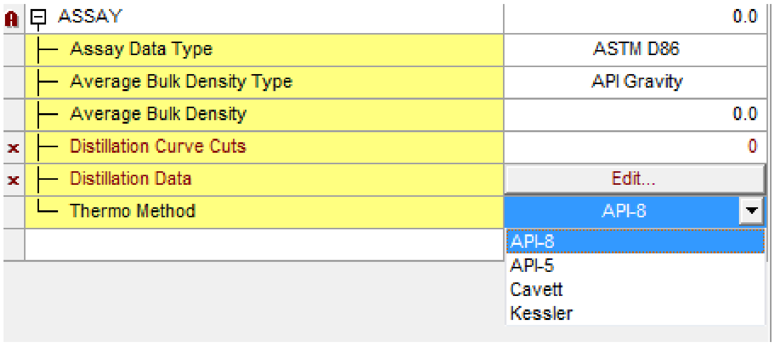
There are three types (see 14 on page 251)

Select **API Gravity**

Finally we need to select the thermodynamic method. Click in the cell next to

Thermo Method

There are four types (see 14 on page 251)



ASSAY	0.0
Assay Data Type	ASTM D86
Average Bulk Density Type	API Gravity
Average Bulk Density	0.0
Distillation Curve Cuts	0
Distillation Data	Edit...
Thermo Method	API-8

Figure 13-5 Thermodynamic methods

Select **API-8** (Default)

We are now ready to enter the distillation data. Click the **Edit** button next to the **Distillation Data** cell. You should see Figure 13-6 below

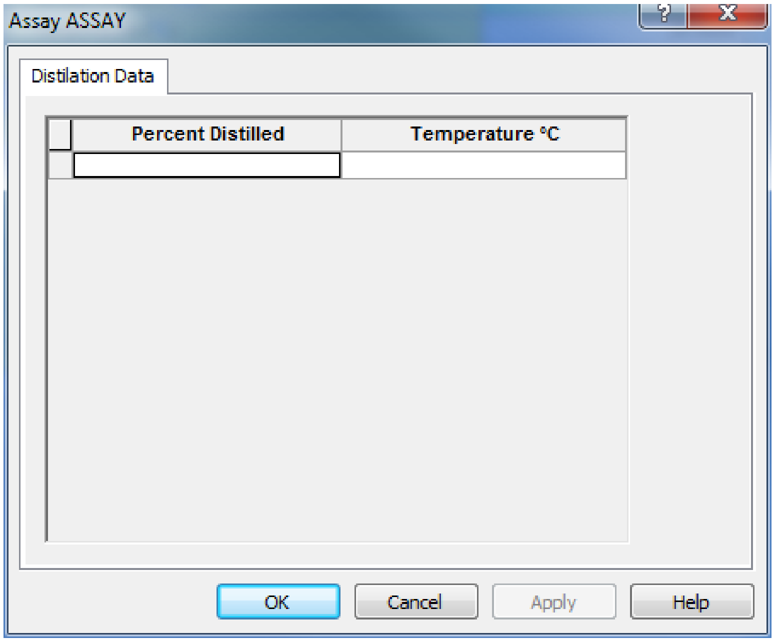
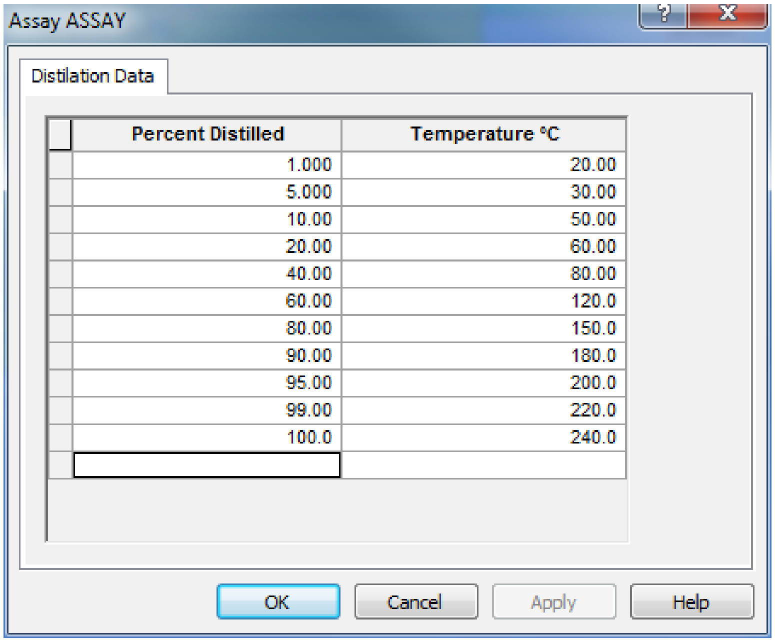


Figure 13-6 Blank Distillation Data, cut and paste works here!

Enter the data from Table 13-1on page 238



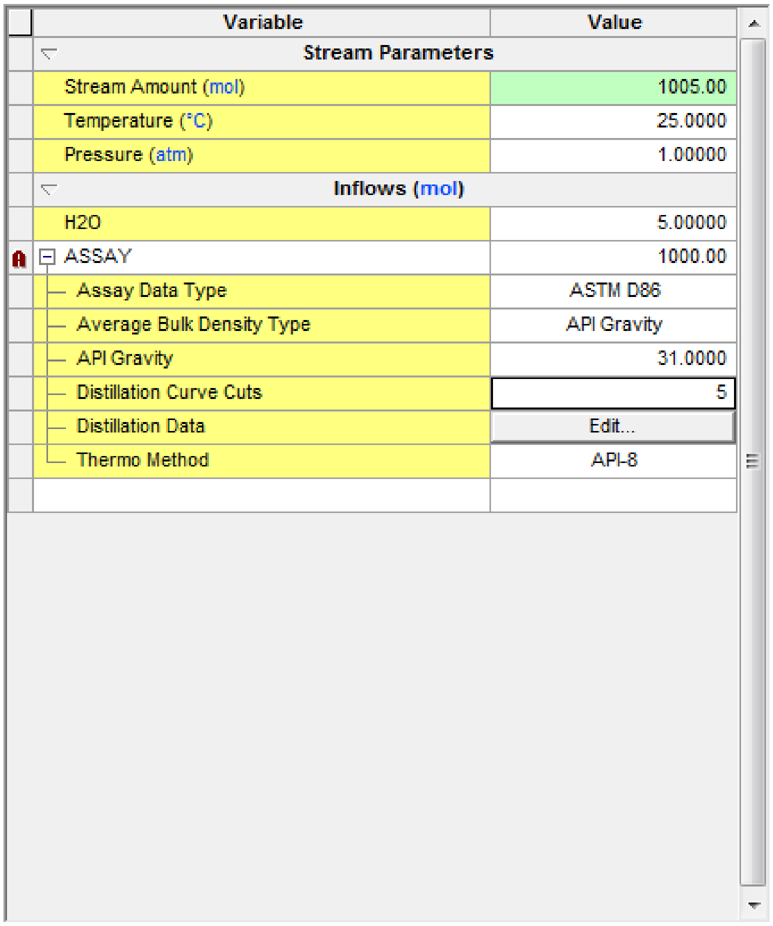
Percent Distilled	Temperature °C
1.000	20.00
5.000	30.00
10.00	50.00
20.00	60.00
40.00	80.00
60.00	120.0
80.00	150.0
90.00	180.0
95.00	200.0
99.00	220.0
100.0	240.0

Figure 13-7 Completed Data

When done click the **OK** button.

We can now finish the entering of the data.

Temperature	25.0	ºC
Pressure	1.0	Atm
H2O	5.0	mole
Assay	1000.0	mole
Density (API)	31	
Distillation Curve Cuts	5	



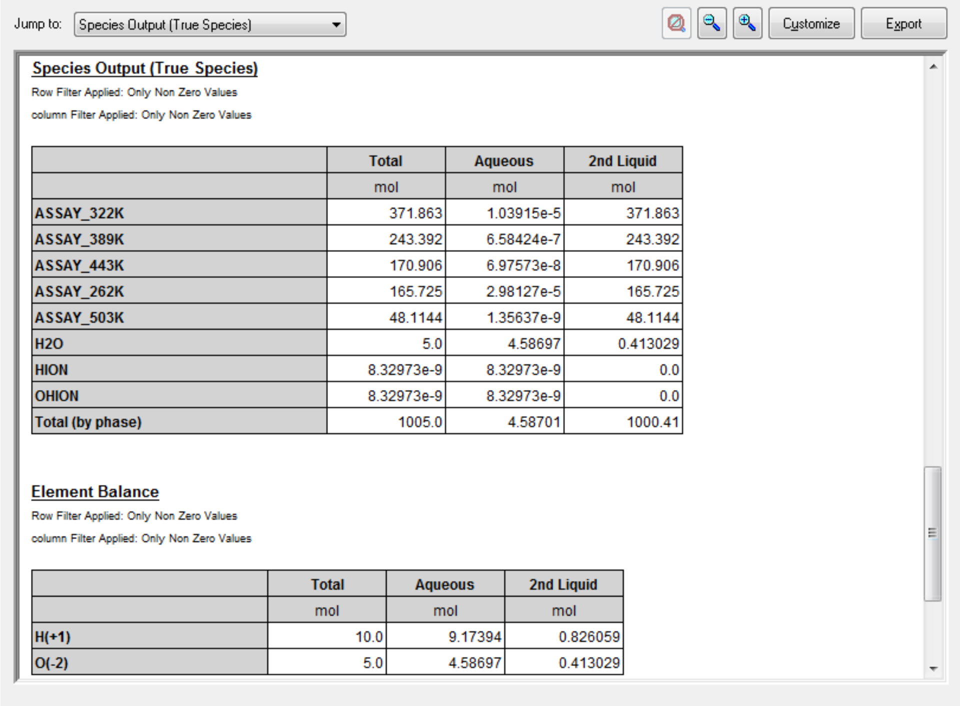
Variable	Value
Stream Parameters	
Stream Amount (mol)	1005.00
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	5.00000
ASSAY	1000.00
Assay Data Type	ASTM D86
Average Bulk Density Type	API Gravity
API Gravity	31.0000
Distillation Curve Cuts	5
Distillation Data	Edit...
Thermo Method	API-8

Figure 13-8 Completed Assay Data Entry

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

After entering the data, select an Isothermal calculation and click the **Calculate** button.

Figure 13-9 below shows the range of composition.



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_322K	371.863	1.03915e-5	371.863
ASSAY_389K	243.392	6.58424e-7	243.392
ASSAY_443K	170.906	6.97573e-8	170.906
ASSAY_262K	165.725	2.98127e-5	165.725
ASSAY_503K	48.1144	1.35637e-9	48.1144
H2O	5.0	4.58697	0.413029
HION	8.32973e-9	8.32973e-9	0.0
OHION	8.32973e-9	8.32973e-9	0.0
Total (by phase)	1005.0	4.58701	1000.41

Element Balance

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	2nd Liquid
	mol	mol	mol
H(+1)	10.0	9.17394	0.826059
O(-2)	5.0	4.58697	0.413029

Figure 13-9 Results of a single point Calculation

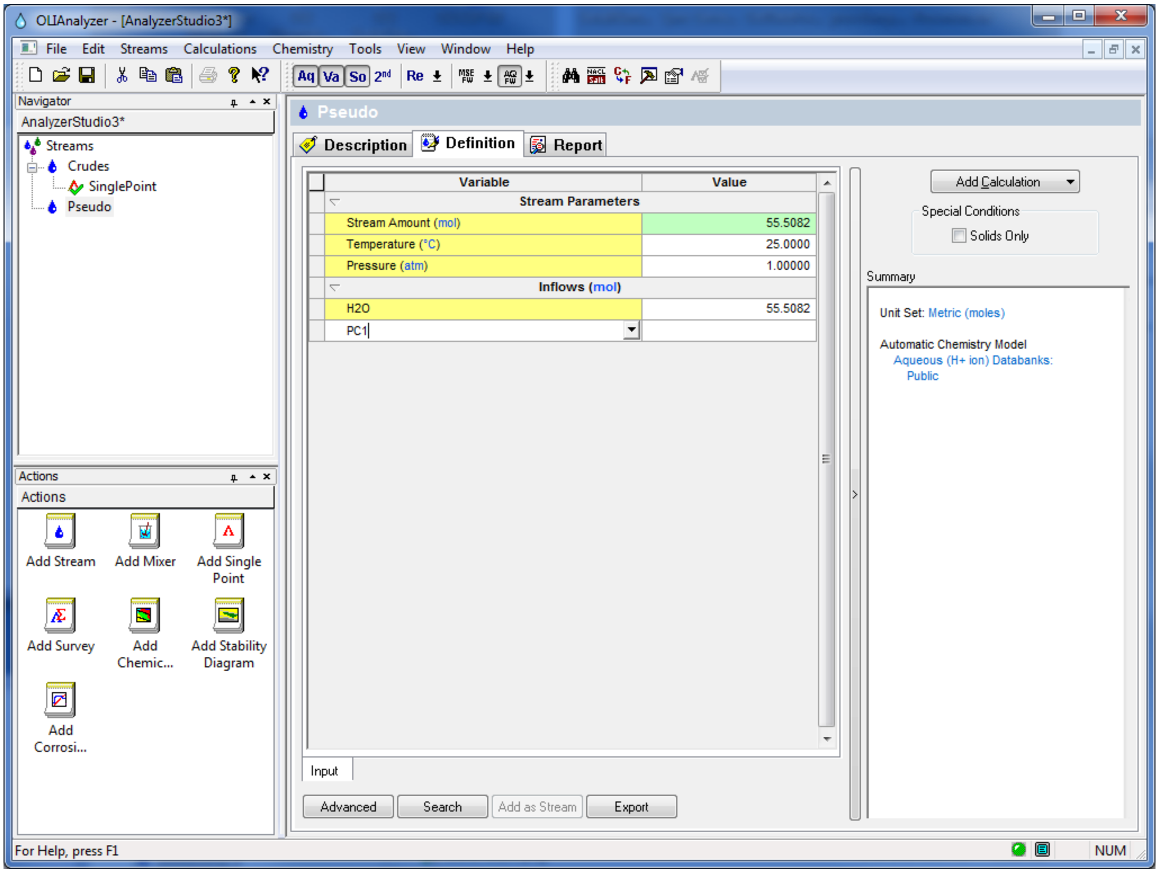
You can see that the program calculated a Liquid-Liquid case in which we have some organic liquid and some aqueous liquid. Our crude oil named “Assay” has been split apart into 5 individual components (remember the “Cuts” above?). Each component has the parent assay name and temperature of the cut in Kelvin.

Pseudocomponents

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

We will start by creating a standard stream. On the input grid we will enter our pseudocomponent name. In Figure 13-10 below we are entering the name PC1.

Press the Control-Enter keys to open the dialog.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
PC1	

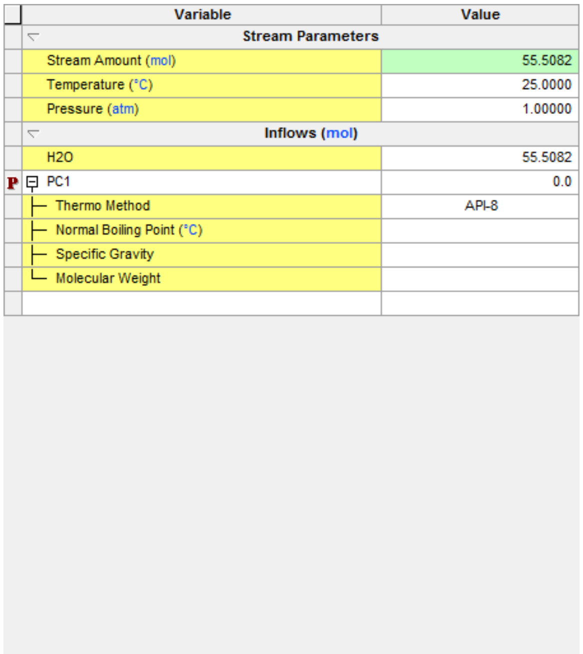
☐ Solids Only

Unit Set: Metric (moles)

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

Figure 13-10 Starting to enter a pseudocomponent

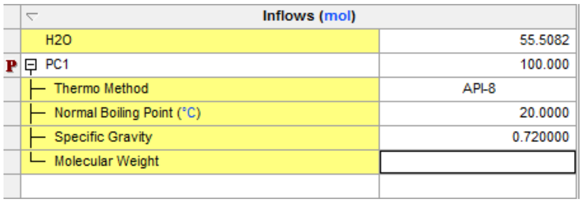
This will create an empty data grid for the pseudocomponent. As with the assays, we need to enter some data for the pseudocomponent.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
PC1	0.0
Thermo Method	API-8
Normal Boiling Point (°C)	
Specific Gravity	
Molecular Weight	

Figure 13-11 An empty Pseudocomponent grid

For this example we will have 100 moles of the component which has a normal boiling point of 20ºC and a specific gravity of 0.72. The third parameter, molecular weight, will be calculated in this example. In general, only two of the three parameters need be entered.



Inflows (mol)	
H2O	55.5082
PC1	100.000
Thermo Method	API-8
Normal Boiling Point (°C)	20.0000
Specific Gravity	0.720000
Molecular Weight	

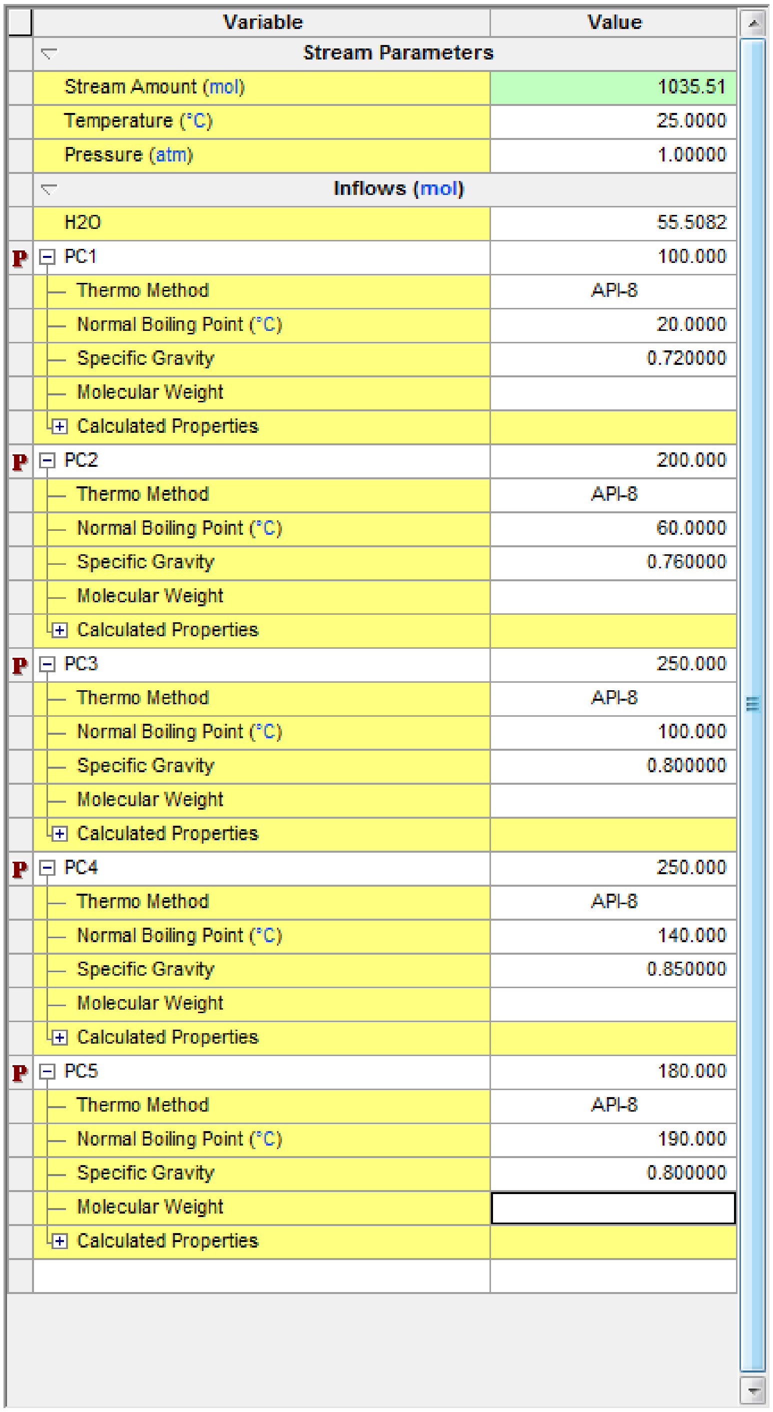
Figure 13-12 Entering data for PC1, note only 2 of 3 parameters entered

After entering the pseudocomponent, please enter the remaining pseudocomponents as found in Table 13-2 below.

Table 13-2 Sample pseudocomponent data

Pseudocomponent	Amount (moles)	Method	Normal Boiling Point, C	Specific Gravity
PC1	100	API	20	0.72
PC2	200	API	60	0.76
PC3	250	API	100	0.8
PC4	250	API	140	0.85
PC5	180	API	190	0.9

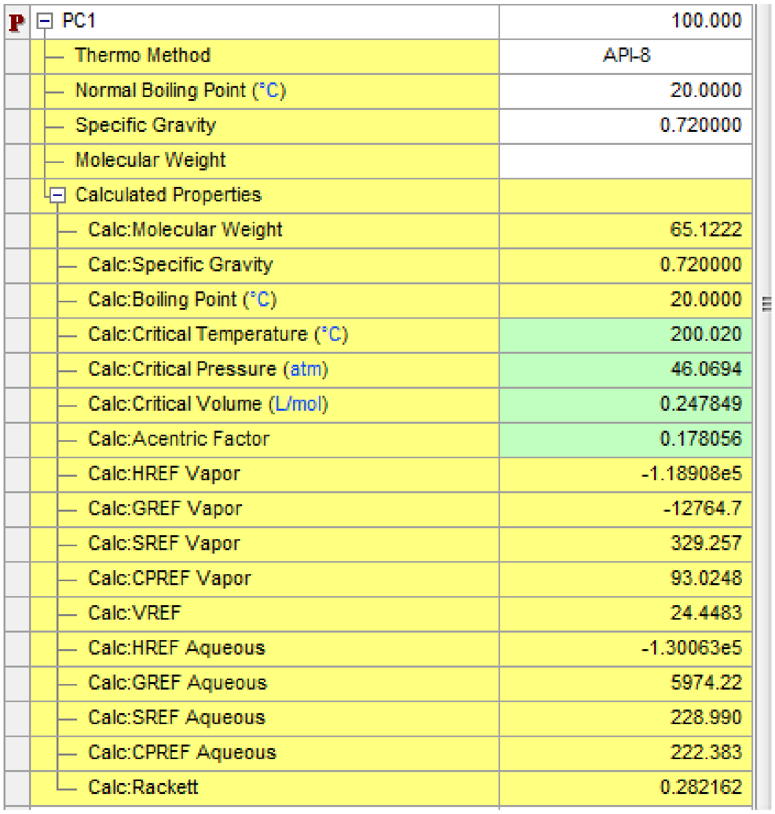
Figure 13-13 below shows the completed input grid.



Variable	Value
Stream Parameters	
Stream Amount (mol)	1035.51
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
P ⊟ PC1	100.000
Thermo Method	API-8
Normal Boiling Point (°C)	20.0000
Specific Gravity	0.720000
Molecular Weight	
⊞ Calculated Properties	
P ⊟ PC2	200.000
Thermo Method	API-8
Normal Boiling Point (°C)	60.0000
Specific Gravity	0.760000
Molecular Weight	
⊞ Calculated Properties	
P ⊟ PC3	250.000
Thermo Method	API-8
Normal Boiling Point (°C)	100.000
Specific Gravity	0.800000
Molecular Weight	
⊞ Calculated Properties	
P ⊟ PC4	250.000
Thermo Method	API-8
Normal Boiling Point (°C)	140.000
Specific Gravity	0.850000
Molecular Weight	
⊞ Calculated Properties	
P ⊟ PC5	180.000
Thermo Method	API-8
Normal Boiling Point (°C)	190.000
Specific Gravity	0.800000
Molecular Weight	
⊞ Calculated Properties	

Figure 13-13 Completed PC input grid

Notice that at the bottom of each pseudo component there is a “+” and a field called calculated properties. OLI Studio immediately predicts all the calculated properties for each pseudocomponent. Click the “+” sign next to PC1.

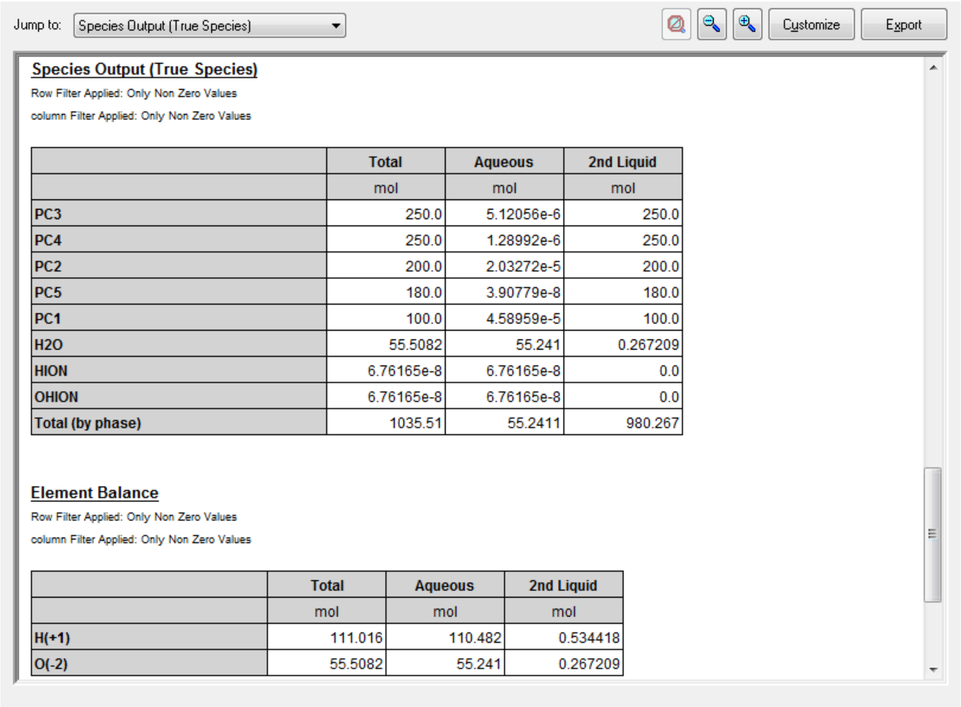


PC1	100.000
Thermo Method	API-8
Normal Boiling Point (°C)	20.0000
Specific Gravity	0.720000
Molecular Weight	
Calculated Properties	
Calc:Molecular Weight	65.1222
Calc:Specific Gravity	0.720000
Calc:Boiling Point (°C)	20.0000
Calc:Critical Temperature (°C)	200.020
Calc:Critical Pressure (atm)	46.0694
Calc:Critical Volume (L/mol)	0.247849
Calc:Acentric Factor	0.178056
Calc:HREF Vapor	-1.18908e5
Calc:GREF Vapor	-12764.7
Calc:SREF Vapor	329.257
Calc:CPREF Vapor	93.0248
Calc:VREF	24.4483
Calc:HREF Aqueous	-1.30063e5
Calc:GREF Aqueous	5974.22
Calc:SREF Aqueous	228.990
Calc:CPREF Aqueous	222.383
Calc:Rackett	0.282162

Figure 13-14

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

Create a single point calculation, set the conditions to 15ºC and 1.0 atmospheres and press the calculate button.



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
PC3	250.0	5.12056e-6	250.0
PC4	250.0	1.28992e-6	250.0
PC2	200.0	2.03272e-5	200.0
PC5	180.0	3.90779e-8	180.0
PC1	100.0	4.58959e-5	100.0
H2O	55.5082	55.241	0.267209
HION	6.76165e-8	6.76165e-8	0.0
OHION	6.76165e-8	6.76165e-8	0.0
Total (by phase)	1035.51	55.2411	980.267

Element Balance

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	2nd Liquid
	mol	mol	mol
H(+1)	111.016	110.482	0.534418
O(-2)	55.5082	55.241	0.267209

Figure 13-15 PC Output

14. ScaleChem Overview

Why Use ScaleChem?

Scale problems arise in high rate gas wells for the same basic reason that they occur in water flood operations: produced brines become supersaturated with mineral scales as a result of changing conditions between the reservoir and the point of deposition.

A complicating factor in the assessment of these scale problems is that significant changes in the brine composition may occur between the reservoir and the surface conditions, due to the exchange of water between the liquid and vapor phases.

Thus, scaling tendencies that are important at downhole conditions may not be evident based on the produced brine composition.

The ScaleChem program estimates scale formation under CO_2 and water flood conditions. ScaleChem can be used to evaluate stimulation compatibility amongst formation waters.

ScaleChem's Development

Shell Oil originally developed the technology for the high temperature and pressure effects used in ScaleChem's calculations and linked this technology to the OLI's unique, predictive aqueous model. A consortium of companies which co-funded and steered ScaleChem's development include

BP

Conoco-Phillips in its entirety

Shell.

Initial development phase for ScaleChem started in 2007. One of the reasons to formulate this product was to unify the code base. Prior to ScaleChem, there were two separate products viz. OLI Stream Analyzer and ScaleChem Standard. Each program with different source codes, two different numerical engines and two data banks. To eliminate that, OLI needed a new feature added to existing Stream Analyzer.

A second reason was that at that time new best practices were emerging for performing scaling calculations. ScaleChem Standard had multistep procedures for such calculations. OLI wanted to target the new approach for optimized calculations. To mention a few of the fixes offered by ScaleChem product:

Unit handling

Report writing

Graphical reports

Cumbersome calculations

ScaleChem has a completely new calculation type in addition to other improvements. It is called contour plot.

Flexibility of the analyzer code enabled OLI to add features and calculations which were impossible in ScaleChem Standard.

15. ScaleChem Chemistry

Aqueous Chemistry

The ScaleChem chemistry uses the OLI Aqueous Model as well as the MSE model to predict the distribution of species. The OLI Aqueous Model is unique because it can predicatively model the speciation of a wide range of chemicals in water. Like other process simulation software, the OLI Aqueous and MSE Model consider the vapor-liquid equilibrium (VLE) of a given chemistry for the molecular species.

ScaleChem Standard Chemistry

ScaleChem Standard was developed with a specifically defined chemistry set. It is known as the Standard Chemistry Model.

As ScaleChem Standard use grew, users requested additional chemistry. From this development work, an Expanded Chemistry Model was created.

The Standard Chemistry Model

As originally developed, the Standard Chemistry model contained a vapor phase, an aqueous phase and a limited number of solid phases.

Standard Chemistry: Aqueous phase

$Na^{+,}$ K^{+}, Ca^{+2}, Mg^{+2}, Fe^{+2}, Ba^{+2}, Sr^{+2}
Cl^{-}, SO_4^{-2}, HCO_3^{-}, HS^{-}, $B(OH)4^{-}$, $CH3COO^{-}$
H_2S^{o}, CO_2^{o}, SiO2, B(OH)3, CH_4^{o}

Standard Chemistry: Vapor phase

H_2O, H_2S, CO_2, CH_4

Standard Chemistry: Solid phases

anhydrite	$CaSO_4$	barite	$BaSO_4$
calcite	$CaCO_3$	gypsum	$CaSO_4$.2H2O
siderite	$FeCO_3$	pyrrhotite	FeS
halite	NaCl	celestite	$SrSO_4$

Disordered Dolomite ($CaMg(CO_3)_2$), or simply dolomite is not the Standard Chemistry but is represented as an inflow only species in the expanded chemistry.

Dolomite is not considered to be a possible scaling solid under most oil field operations.

The Expanded Chemistry Model

Expanded Chemistry: Aqueous phase

This includes the Standard model plus:

Cations: H^+, Cs^+, Zn^{+2} Pb^{+2}, Ni^{+2}, Cu^+, Cu^{+2}, NH_4^+, Fe^{+3}, Al^{+3},
Anions: OH^-, F^-, Br^-, $H_2SiO_4^-$, $H_3SiO_4^-$, SO_3^{-2}, S^{-2}, CO_3^{-2}, NO_3^-, NO_2^-, $COOH^-$, $C_3H_7COO^-$ $C_4H_9COO^-$ $C_5H_{11}COO^-$
Organic acids: formic, acetic, propanoic, butanoic, pentanoic
Alcohols: methanol, ethanol, ethylene glycol,
Mineral Acids: HF, HCl, H2SO4, HBr, HNO3, H2SO4,
Hydrocarbons: methane, ethane, and propane
Other: NH3, N2, CO2

Expanded Chemistry: Vapor phase

This includes the Standard Model plus:
Ethane, propane, butane, isobutane, pentane, isopentane, hexane, cyclohexane, heptanes, octane, isooctane, nonane, and decane

Expanded Chemistry: Solid phases

The Expanded Solids phases include fifty-nine solids that are practical to oilfield operations. This allows solids analysis from the new cations and anions which have been added.

Expanded solids is automatically accessed when using the expanded chemistry. It can also be accessed for the standard chemistry by using the radio buttons on the Precipitates Page, in any Scaling request.

Scaling tendencies for every solid with a scaling tendency > 1.0E-05 are reported for a calculation using expanded solids.

Hydrocarbon Petroleum Fractions

Frequently a hydrocarbon analysis is the only data available for entry into the software. This analysis is usually a distillation curve where the volume distilled as a function of temperature of a petroleum fraction has been analyzed. This information must be turned into a vapor, organic and aqueous component for use in the simulator.

ASTM D86

Used for light and medium crudes, and is carried out at atmospheric pressure. The results are converted internally in the OLI model generator to a TBP (True Boiling Point) Curve. This curve is fit to a spline to smooth the curve. The cuts are taken from the spline.

ASTM D1160

Used for heavier crudes, and is carried out under vacuums as low as 1 mm Hg. The results are converted internally in the OLI model generator to a TBP Curve. This curve is fit to a spline. The cuts are taken from the spline.

ASTM D2887

Uses gas chromatography to produce the distillation curve and is applicable to a wide range of petroleum products. The results are reported on a volume percent basis. The results are converted internally in the OLI model generator to a TBP Curve. This curve is fit to a spline. The cuts are taken from the spline

TBP

This is the true boiling point curve. These curves, in practice, are difficult to obtain. The other methods are usually used instead.

Density

The density units for the average bulk density are:

Specific Gravity

Unitless

Degrees API (°API)

This is calculated via the following equation:

$$°API(60F) = \left(\frac{141.5}{s.g.(60F)}\right) - 131.5$$

where, SG is the specific gravity at 60 °F.

Watson K

The Watson K has no units but is calculated via:

$$K = \left(\frac{NBP^{1/3}}{SG}\right)$$

where NBP is the normal Boiling point.

Thermodynamic Methods (pseudo-components and petroleum fractions)

API	Uses the specific gravity to estimate the critical parameters. The specific gravity, if not entered, can be estimated from the API gravity or the Watson K. The boiling points are taken from the assay data.
Cavett	This method uses the API gravity method to determine the critical properties. The API gravity, if not entered can be estimated from the actual specific gravity or the Watson K. The boiling points for the pseudo-components are taken from the assay.
Lee-Kesler	This method uses the Watson K and the specific gravity (which can be estimated via the Watson K) to determine the critical parameters.

Summary

The use of a full speciation model allows for more accurate calculations. Using just a simple vapor-liquid equilibrium approach is not valid for aqueous systems.

16. ScaleChem Getting Started

Terminology

Before we can discuss how to use ScaleChem we must first discuss some terms. This will help us define some of the concepts in ScaleChem that will be expanded in later sections.

Analysis

There are three analysis types, brines gases, and Oils. Each type must be reconciled.

Brines

ScaleChem refers to all waters and aqueous samples as brines. A brine can be a surface water, an injection water, a formation water, a production water or any other type of aqueous fluid you can create. Brine compositions are entered in terms of ionic concentrations. In addition, the brine pH, density and alkalinity are also specified.

A brine is entered by means of the **Add Water** function, located in the ***Analyses*** menu.

Gases

A gas is any hydrocarbon mixture which may or may not contain water, carbon dioxide or hydrogen sulfide. The default hydrocarbon is methane (CH_4) but the hydrocarbon list may be expanded to include higher carbon numbers.

A gas is entered by means of the **Add Gas** function, located in the ***Analyses*** menu.

Oils

An oil is a non-aqueous phase. The oil sample may consist of pure component hydrocarbons (e.g., alkanes), distillation data, pseudocomponent or all three.

A hydrocarbon is entered by means of the Hydrocarbon function, located in the Analyses menu.

Reconciliation

Corrections must be made for deficiencies in the sample measurements.

Electroneutrality

Due to the nature of experimentation, most, if not all water analyses are incomplete or inaccurate in some manner. Thus, no analysis is electrically neutral. Yet, a real water must be. To solve this problem ScaleChem reconciles each brine analysis for

Electroneutrality or charge balance. The reconciliation method will be discussed in a later section.

pH

Many brines have a measured pH. This pH may or may not match the ScaleChem-calculated pH. The cause may be an incomplete and/or inaccurate brine description. ScaleChem reconciles this difference by adding or removing HCl and CO2 to match the measured pH.

Alkalinity

Alkalinity is a brine's capacity to absorb acid to a given pH. In oilfield applications, this pH is 4.5, and the alkalinity is referred to as the Carbonate alkalinity.

The standard alkalinity measurement involves titrating the brine with a known acid to 4.5 pH. ScaleChem performs a mini-titration on the brine to 4.5 (or specified) pH. It then:

1. Calculates the alkalinity for the given water analysis
2. Adjusts HCl and CO2 inflow to match the calculated alkalinity with the reported alkalinity

CO_2 Fraction in Gas

Frequently it is simpler and more stable to measure the gas-phase CO_2 that is separated from the brine at the sampling point. When matched with another measured variable, usually alkalinity, the concentration of the carbonate species and the pH can be calculated. ScaleChem performs a CO2 gas fraction calculation by taking the PCO2 and the calculated alkalinity (based on the water analysis data) to reconcile the system for pH and carbonate properties.

Scaling Tendency

The scaling tendency is defined as the ratio of the activity product to the solubility product for a particular solid. This ratio is related to the saturation index.

When this ratio is greater than 1.0, then there is a thermodynamic tendency for this solid to form. When less than 1.0 then there is no thermodynamic tendency for the solid to form.

The Activity product is the product of all the species on the right hand side of the equation, also known as the Available ions.

The solubility product, usually represented as K_{sp} is the thermodynamic equilibrium constant and is a function of temperature and pressure.

Calculating a Scaling Tendency

The Scaling Tendency is defined as the ratio of the activity product of an equilibrium equation to the solubility product for the same equation. We define the activity product as Q, therefore the Scaling Tendency (ST) = Q/K_{sp}.

As an example, consider the equilibrium for gypsum solubility. The chemical formula for gypsum is $CaSO_4 \bullet 2H_2O$ and the equilibrium expression is:

$CaSO_4 \bullet 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$

The activity product, Q, is defined as:

$Q = a_{ca++} \, a_{so4-2} \, a^2_{H2O}$

Where a_i is the activity of the species.

$$a_i = \gamma_i \, m_i$$

Where γ_i is the activity coefficient for species i. and m_i is the molal concentration.

The solubility product, K_{sp} is a thermodynamic quantity and is a function of temperature and pressure (although in most cases, the pressure functionality for solids can be ignored). ScaleChem has stored the K_{sp} for all of the solids used in the chemistry model.

When the ratio Q/K_{sp} is greater than 1.0, then the solid has tendency to form. When the ratio is less than 1.0, then there is little tendency to form.

For example: consider a 0.01 molal solution of calcium sulfate at 25 C and 1 atmosphere.

The equilibrium concentrations are:

$[Ca^{+2}]$ = 0.008 molal
$[SO_4^{-2}]$ = 0.008 molal
γ_{Ca} = 0.5
γ_{SO4} = 0.5
a_{H2O} = 0.99977
K_{sp} = 2.68×10^{-5}

The Q value is:

$Q = (0.5)(0.008)(0.5)(0.008)(0.99977)^2$

The Scaling Tendency is Q/Ksp

ST = 0.000016/(2.68E-05) = 0.596

Thus the solution is under-saturated with respect to calcium sulfate.

Why are the concentrations of the ions not exactly equal to 0.01 molal (which is the feed concentration)? The neutral complex $CaSO_4^o$ exists and ties up 0.002 moles of each ion. The ions are not available for precipitation and thus do not appear in the scaling tendency calculation.

Calculating a Scale Index

The scale index is very much related to the Scaling Tendency. The relationship is:

Scale Index (SI) = Log_{10}(ST).

When the SI is less than zero (SI < 0), then the solid is said to be undersaturated. When the SI is greater than zero (SI > 0) then solid is said to be oversaturated.

Putting together a calculation

Now that we have defined some terms we are now ready to begin entering the information required to run a calculation. In this calculation we will be entering the concentrations of a single brine. This sample will be calculated at a range of temperatures and pressures. The amount of any solids produced will be displayed graphically.

Starting the ScaleChem Program

ScaleChem can be accessed via the OLI Studio. Objects for ScaleChem are Brine, Gas, Oil, Saturator and Contour plots.

To access these objects click on Streams in the Navigator and you will see these objects amongst others in the Actions Panel.

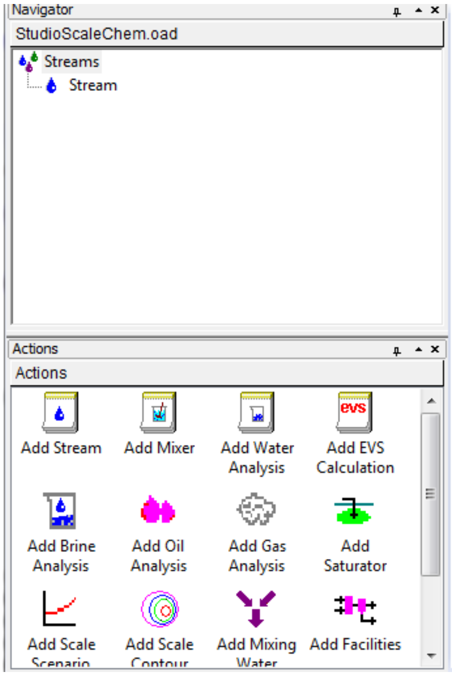
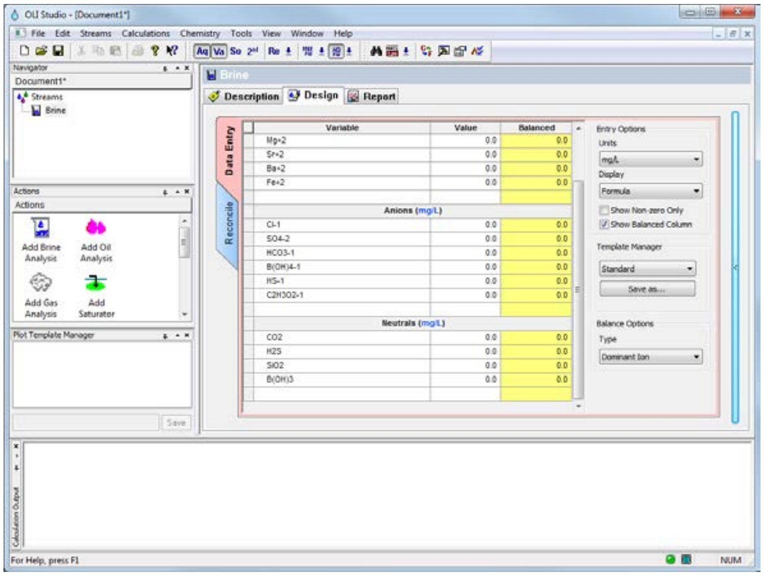


Figure 16-1 ScaleChem objects.

ScaleChem Tour

In this tour we will create a brine (water analysis) and calculate its scale tendency. Let’s begin.

Add Brine Analysis from Actions Panel.



Variable	Value	Balanced
Mg+2	0.0	0.0
Sr+2	0.0	0.0
Ba+2	0.0	0.0
Fe+2	0.0	0.0
Anions (mg/L)		
Cl-1	0.0	0.0
SO4-2	0.0	0.0
HCO3-1	0.0	0.0
B(OH)4-1	0.0	0.0
HS-1	0.0	0.0
C2H3O2-1	0.0	0.0
Neutrals (mg/L)		
CO2	0.0	0.0
H2S	0.0	0.0
SiO2	0.0	0.0
B(OH)3	0.0	0.0

Entry Options

Units: mg/L

Display: Formula

☐ Show Non-zero Only

☑ Show Balanced Column

Template Manager: Standard

Save as...

Balance Options

Type: Dominant Ion

Figure 16-2 Brine Analysis

Brine Analysis Data

The chemistry of the brine needs to be entered. This information includes concentrations, alkalinity, pH and density.

Entering a brine description

Click on the description Tab. If the <u>*Description*</u> tab is not currently displayed, click on the tab.

Name: SSC_Brine

Figure 16-3 Brine description tab

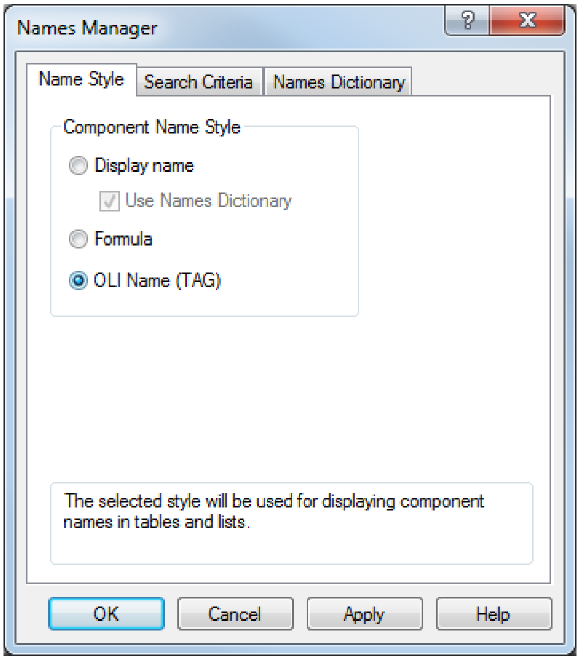
We can fill several items on this screen. All of the items (except the name) are optional.

Well	This name, if entered in a Well View calculation, is the name of the well. It is frequently blank.
Date	The date of the sample. Defaults to the current date.
Comments	Up to 256 characters may be entered as text to describe the well. Brief, direct comments are recommended.

Entering Brine Species

The Design Tab is where you enter the cations, anions and dissolved gases (or neutrals). The species formulas (default) or species names may be displayed. This display By Formula or By Name can be changed by clicking the names manager logo on the toolbar which looks like this:

A window will pop up where you can choose to select what display method you prefer. The pop up window will look like below:



Component Name Style

○ Display name

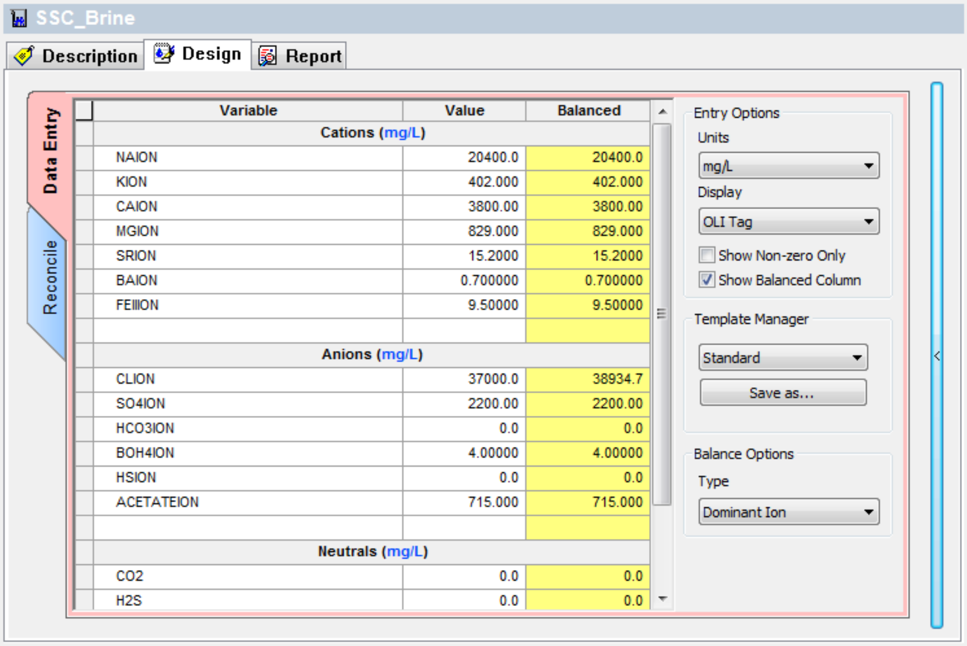
☑ Use Names Dictionary

○ Formula

● OLI Name (TAG)

The selected style will be used for displaying component names in tables and lists.

Data entry tab under Design tab is designed to provide means to input cation/anion and neutrals composition.



Variable	Value	Balanced
Cations (mg/L)		
NAION	20400.0	20400.0
KION	402.000	402.000
CAION	3800.00	3800.00
MGION	829.000	829.000
SRION	15.2000	15.2000
BAION	0.700000	0.700000
FEIIION	9.50000	9.50000
Anions (mg/L)		
CLION	37000.0	38934.7
SO4ION	2200.00	2200.00
HCO3ION	0.0	0.0
BOH4ION	4.00000	4.00000
HSION	0.0	0.0
ACETATEION	715.000	715.000
Neutrals (mg/L)		
CO2	0.0	0.0
H2S	0.0	0.0

Entry Options

Units: mg/L

Display: OLI Tag

☐ Show Non-zero Only

☑ Show Balanced Column

Template Manager: Standard

Balance Options

Type: Dominant Ion

Figure 16-4 Brine data entry

Fields

Cations: The positive ions are entered in grid. The units may be changed by clicking on the Units button under entry options. The default units are mg/l (milligrams per liter).

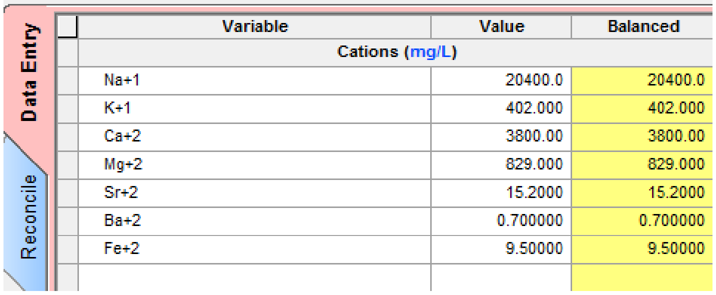
Anions:	This field is similar to the Cations field except that negative ions are added.
Neutrals:	Neutral gases such as dissolved CO_2, H_2S and methane (CH4) are added. These dissolved gases do not affect the Electroneutrality of the sample but can have an overall affect on pH and alkalinity.

Reconcile tab: This tab gives options from three calculation types:-
Equilibrium calculation
CO2 Fraction in Gas
pH Alkalinity Reconcile

Entering Brine Species - Balance Button

It is highly unusual for the data to be electrically neutral. Therefore. samples are reconciled for Electroneutrality. After entering each species concentrations, you will notice that Balanced values show up in the column next to values. The Column header says Balanced.

Ionic samples measured experimentally are almost always not electrically neutral. Before we can proceed we must reconcile this sample for Electroneutrality.



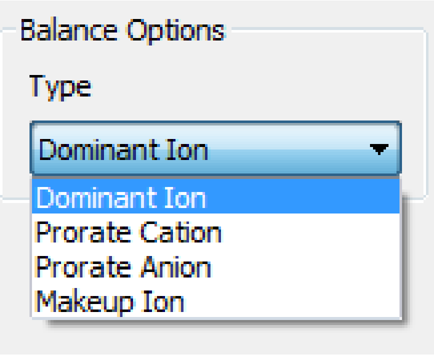
Variable	Value	Balanced
Cations (mg/L)		
Na+1	20400.0	20400.0
K+1	402.000	402.000
Ca+2	3800.00	3800.00
Mg+2	829.000	829.000
Sr+2	15.2000	15.2000
Ba+2	0.700000	0.700000
Fe+2	9.50000	9.50000

Figure 16-5 Electroneutrality balance column

When adding or removing ions to balance charge, the solute mass is altered. We must make a decision as to whether we keep the mass of the solution constant (thereby adjusting the amount of water) or keeping the amount of water constant and adjusting the solution mass.

The user can select from a variety of balancing methods

Dominant Ions	The deficient charged species with the largest concentration is added.
Proration	Equal ratios of the deficient charge is added.
Make Up Ion	The selected ion is either added or removed to balance the solution.



Balance Options

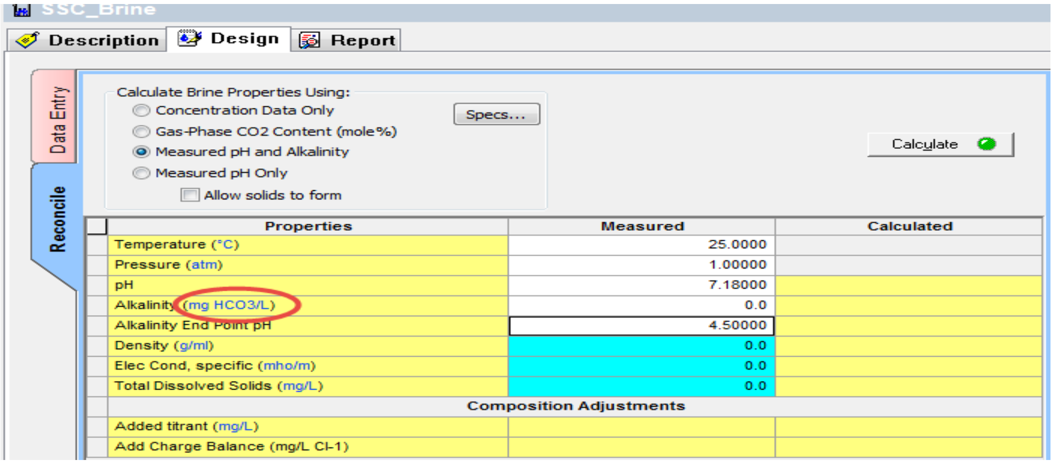
Type: Dominant Ion

Figure 16-6 Balance Options

Reconciling a brine

We are now ready to reconcile the sample for pH and alkalinity.

Click the *Reconciliations* tab. Make sure if you are choosing the pH and Alkalinity type of calculation, you need to specify the HCO3 concentration in the grid under reconciliation tab.



Calculate Brine Properties Using:

○ Concentration Data Only
○ Gas-Phase CO2 Content (mole%)
● Measured pH and Alkalinity
○ Measured pH Only
☐ Allow solids to form

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
pH	7.18000	
Alkalinity (mg HCO3/L)	0.0	
Alkalinity End Point pH	4.50000	
Density (g/ml)	0.0	
Elec Cond, specific (mho/m)	0.0	
Total Dissolved Solids (mg/L)	0.0	
Composition Adjustments		
Added titrant (mg/L)		
Add Charge Balance (mg/L Cl-1)		

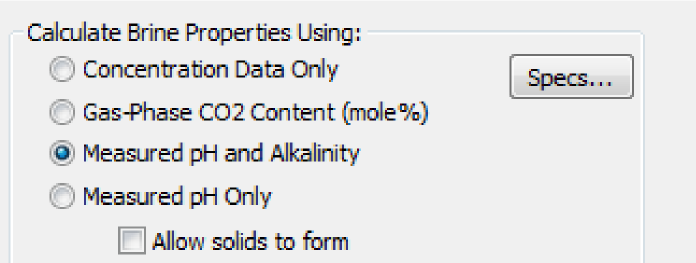
Figure 16-7 The reconciliations tab

Reconciliations (Select one).

Due to experimental uncertainty and error, the measured values for a water sample may not match the calculated values. Therefore, we need to reconcile the calculated values. There are four reconciliation types.

Concentration Data Only	Using the entered ionic and neutral compositions, the pH, density and alkalinity are calculated for this sample.
Gas-Phase CO2 Content	The CO2 is adjusted to match a saturated gas composition
Measured pH and Alkalinity	This adds or removes Hydrochloric Acid (HCl) to match the specified pH and alkalinity. This is default calculation.
Measured pH Only	The pH of the solution can be specified by adjusting the titrant/s.

Radio buttons for the above types can be found under reconciliation options



Calculate Brine Properties Using:

○ Concentration Data Only

○ Gas-Phase CO2 Content (mole%)

● Measured pH and Alkalinity

○ Measured pH Only

☐ Allow solids to form

Figure 16-8 Radio buttons

Variables

The following variables are part of the Reconciliation step. Several variables are user-entered and other are calculated.

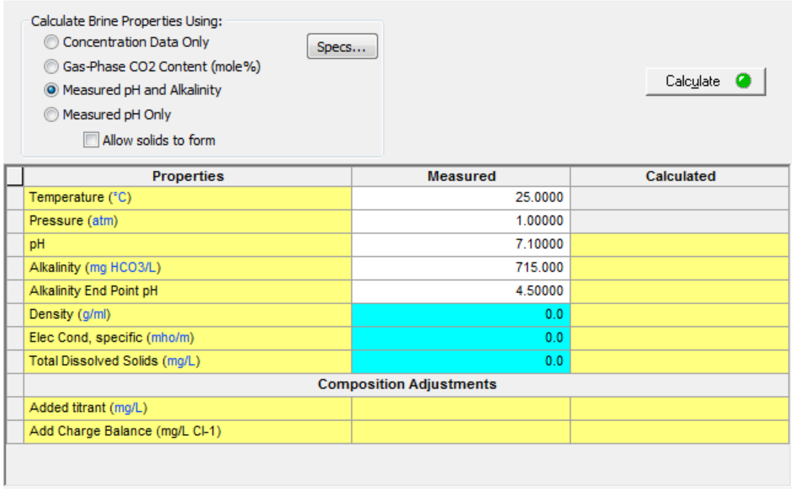
Temperature	The default temperature is at ambient conditions. The user may change these values as required.
Pressure	The default pressure is at ambient conditions. The user may change these values as required.
pH	A measured pH is considered to be an unreliable value.. Therefore, users enter the measured pH and compares it to the calculated pH. A user can also force ScaleChem to adjust the concentrations so that the calculated pH matches the measured pH.
Density	The water density is a very reliable number. The program can adjust the total volume or amount of water to match this value. If no density information has been entered, then a calculated density will be used.
Alkalinity	This is generally a reliable value, unless solids have precipitated in the sample. Alkalinity is often but not always the same value as the bicarbonate ion (HCO3$^-$). ScaleChem can reconcile on a measured alkalinity by adjusting the solution composition.
Titration pH	This is the end point for the experiment used by the lab to determine the Alkalinity. The default value is 4.5.
CO2 Fraction in Gas	This is the gas phase, partial pressure of CO2 on a mole-fraction basis. ScaleChem adjusts the dissolved CO2 concentration to match this measured CO2 mole fraction. The CO2 value is assumed to be on a dry basis (no water) and that the complimentary gas is methane (CH4).
HCl Added	This is the amount of HCl either added or removed to match the measured pH and Alkalinity. This value is calculated by ScaleChem.
CO2 Added	This is the amount of carbon dioxide either added or removed to match the measured pH and alkalinity. This value is calculated by ScaleChem.
Total Dissolved Solids	This is the calculated TDS as reported by ScaleChem. It is used as a check to see if all the solutes were properly accounted for in the analysis. This value is calculated by ScaleChem.
Electrical Conductivity	This is the solution electrical conductivity. This value is calculated by ScaleChem.

.

Once the reconciliation options have been selected, the Calculate button is clicked.

Buttons	Calculate Button This button begins the reconciliation calculation.
Allow Solids to form	This check box allows solids to form

Enter a value of pH = 7.1 and alkalinity = 715 as HCO3-, mg/L



Calculate Brine Properties Using:

○ Concentration Data Only

○ Gas-Phase CO2 Content (mole%)

● Measured pH and Alkalinity

○ Measured pH Only

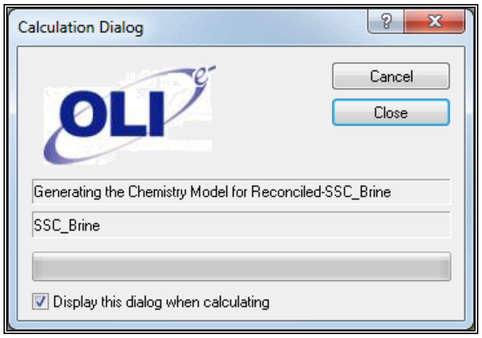
☐ Allow solids to form

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (atm)	1.00000	
pH	7.10000	
Alkalinity (mg HCO3/L)	715.000	
Alkalinity End Point pH	4.50000	
Density (g/ml)	0.0	
Elec Cond, specific (mho/m)	0.0	
Total Dissolved Solids (mg/L)	0.0	
Composition Adjustments		
Added titrant (mg/L)		
Add Charge Balance (mg/L Cl-1)		

Figure 16-9 Entering pH and alkalinity

Click the *Calculate* button.

The OLI calculation orbit will now display.



Calculation Dialog

Generating the Chemistry Model for Reconciled-SSC_Brine

SSC_Brine

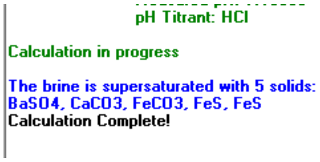
☑ Display this dialog when calculating

Figure 16-20 the revolving electron

This dialog will close automatically.

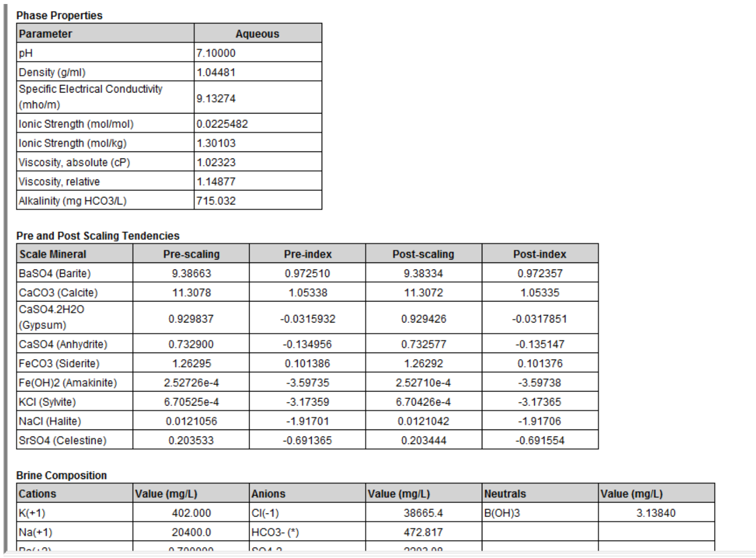
Super saturation Warning

Experimental inaccuracies in sample measurement may, on occasion, result in a calculation that indicates that solid is supersaturated. This can normally be ignored providing that the super saturation is not excessive.



```
pH Titrant: HCl

Calculation in progress

The brine is supersaturated with 5 solids:
BaSO4, CaCO3, FeCO3, FeS, FeS
Calculation Complete!
```

Figure 16-31 Super saturation warning.



Phase Properties

Parameter	Aqueous
pH	7.10000
Density (g/ml)	1.04481
Specific Electrical Conductivity (mho/m)	9.13274
Ionic Strength (mol/mol)	0.0225482
Ionic Strength (mol/kg)	1.30103
Viscosity, absolute (cP)	1.02323
Viscosity, relative	1.14877
Alkalinity (mg HCO3/L)	715.032

Pre and Post Scaling Tendencies

Scale Mineral	Pre-scaling	Pre-index	Post-scaling	Post-index
BaSO4 (Barite)	9.38663	0.972510	9.38334	0.972357
CaCO3 (Calcite)	11.3078	1.05338	11.3072	1.05335
CaSO4.2H2O (Gypsum)	0.929837	-0.0315932	0.929426	-0.0317851
CaSO4 (Anhydrite)	0.732900	-0.134956	0.732577	-0.135147
FeCO3 (Siderite)	1.26295	0.101386	1.26292	0.101376
Fe(OH)2 (Amakinite)	2.52726e-4	-3.59735	2.52710e-4	-3.59738
KCl (Sylvite)	6.70525e-4	-3.17359	6.70426e-4	-3.17365
NaCl (Halite)	0.0121056	-1.91701	0.0121042	-1.91706
SrSO4 (Celestine)	0.203533	-0.691365	0.203444	-0.691554

Brine Composition

Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)
K(+1)	402.000	Cl(-1)	38665.4	B(OH)3	3.13840
Na(+1)	20400.0	HCO3- (*)	472.817		

Figure 16-4 Reconciled Brine report

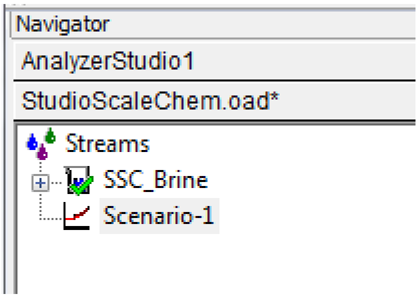
The results show that the pH has been reconciled to 7.18 and the alkalinity to 715 mg HCO3-/L. To do this approximately 20 mg/L of HCl was removed (i.e., H+ and Cl-) and approximately 24.66mg/L CO2 was added.

Report is one of the peculiar features of ScaleChem. Navigation and customization of the output data has been made much easier in this format.

Now that we have specified the flow rate of the brine, we need to specify the temperatures and pressures that we wish to simulate as shown in the following example.

Scaling Scenario

Once the Brine Analysis data is entered and the sample reconciled, we can begin the scaling calculation. We now begin to describe the conditions of the calculation.
Select Add Scale Scenario from Actions panel.



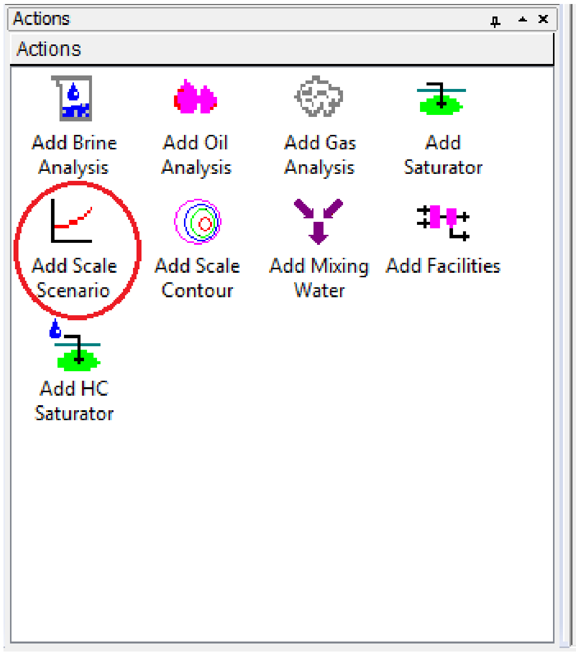
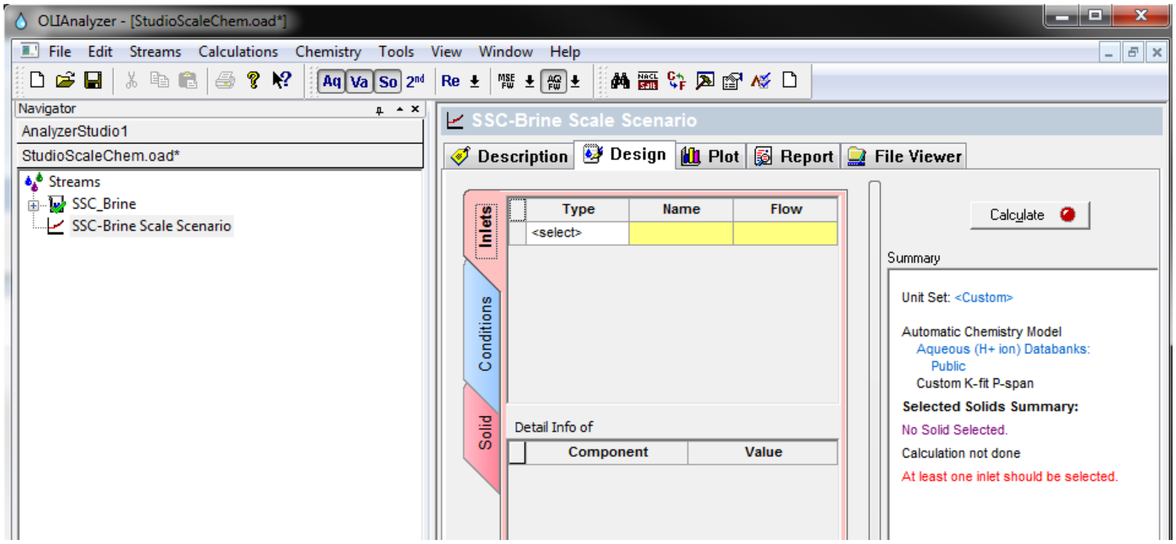


Figure 16-53 Scaling Scenario object

Click on the description tab and rename the Scale Scenario as " SSC-Brine Scale Scenario".

Your screen should now look like image 3-14



Unit Set: <Custom>

Automatic Chemistry Model
Aqueous (H+ ion) Databanks:
Public
Custom K-fit P-span

Selected Solids Summary:
No Solid Selected.
Calculation not done
At least one inlet should be selected.

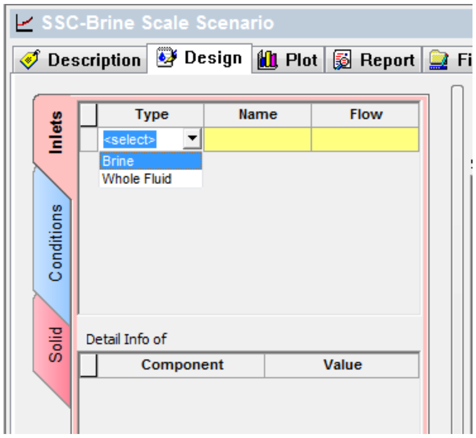
Figure 16-14 Scaling Scenario Design tab

Brine and Gases

The brines and gases that are to be considered for this calculation must now be selected.

Click the *Drop-Down* arrow in the box next to the word *"Select"* under the *"Type"* heading.

This will display all the available brines in this document.

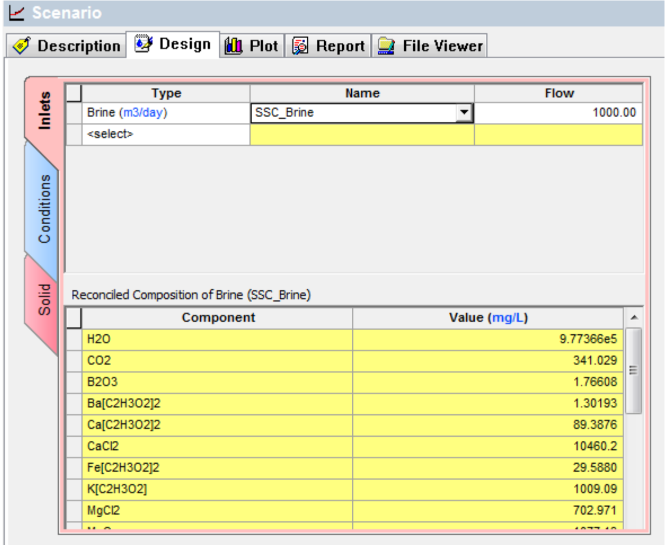


Type	Name	Flow
<select>		

Component	Value

Figure 16-15 Selecting a brine

In this example we are going to use only a single Brine SSC- Brine at 1000L/hr.



Type	Name	Flow
Brine (m3/day)	SSC_Brine	1000.00
<select>		

Reconciled Composition of Brine (SSC_Brine)

Component	Value (mg/L)
H2O	9.77366e5
CO2	341.029
B2O3	1.76608
Ba[C2H3O2]2	1.30193
Ca[C2H3O2]2	89.3876
CaCl2	10460.2
Fe[C2H3O2]2	29.5880
K[C2H3O2]	1009.09
MgCl2	702.971

Figure 16-16 The completed case

Input Box	
Type	You can select the brine, gas or hydrocarbon of interest
Name	Click in the Name field. As you position the cursor in the field, a Down Arrow will appear. You can then select from a list of brines, gases or oils already entered into this ScaleChem document.
Flow	Enter the flow rate for the gas, hydrocarbon or brine.

Conditions

Now that we have specified the flow rate of the brine, we need to specify the temperatures and pressures that we wish to simulate as shown in the following example.

Click on the *Conditions* tab.

For our example we are going to perform a temperature survey at constant pressure.

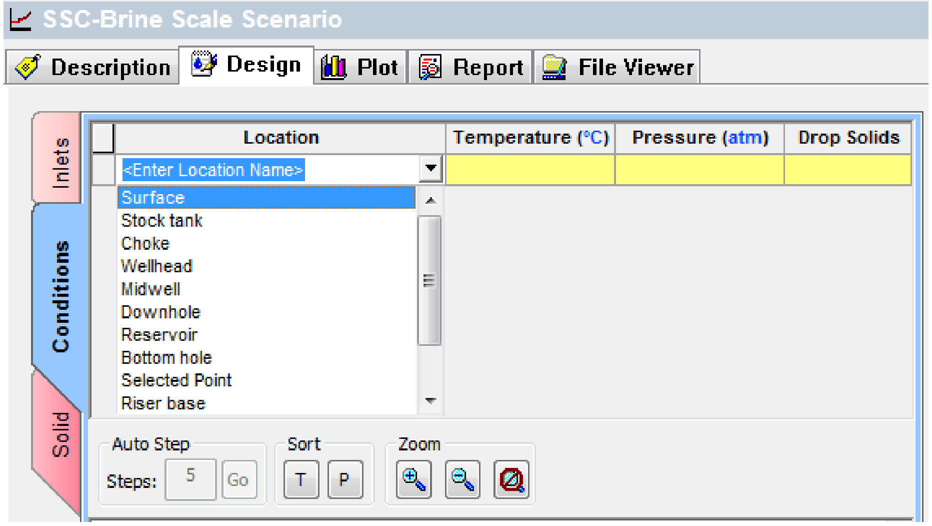
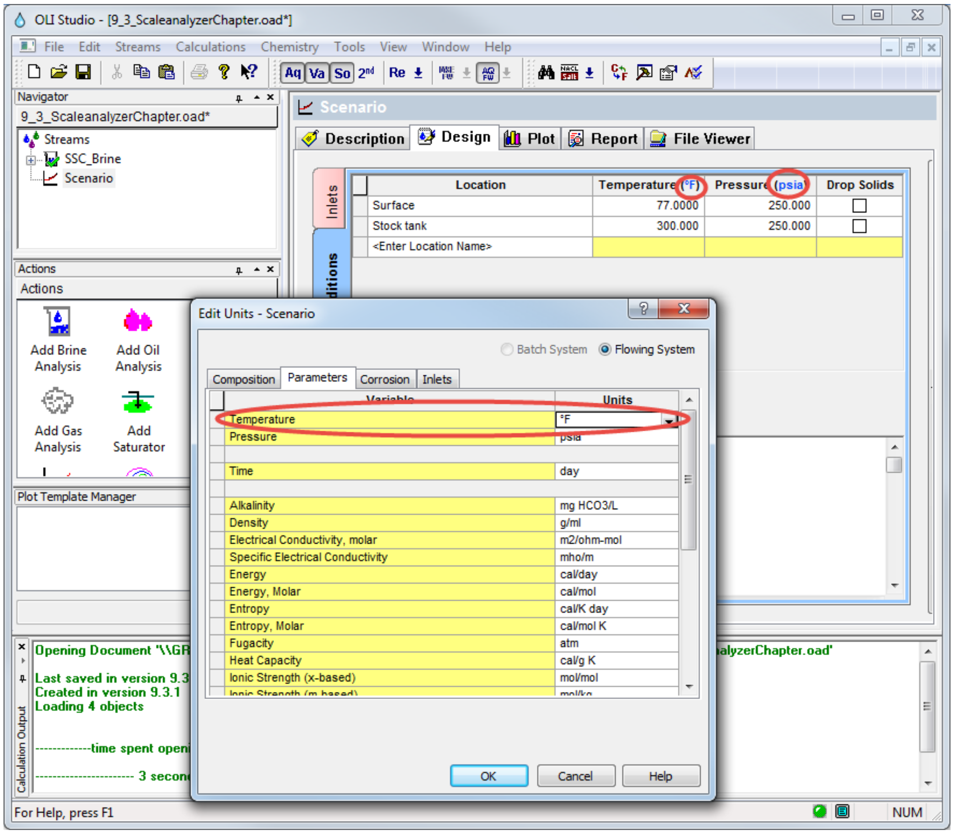


Figure 16-67 The empty conditions tab.

Click on surface and move on to the temperature tab. Change the units by clicking the hyperlinked (^{0}C) and (atm) via units manager second layer. Input the temperature as 77 ^{0}F. Change the Pressure field to 250 psia. Add second point at a temperature of 300 F.



Location	Temperature (°F)	Pressure (psia)	Drop Solids
Surface	77.0000	250.000	☐
Stock tank	300.000	250.000	☐
<Enter Location Name>			

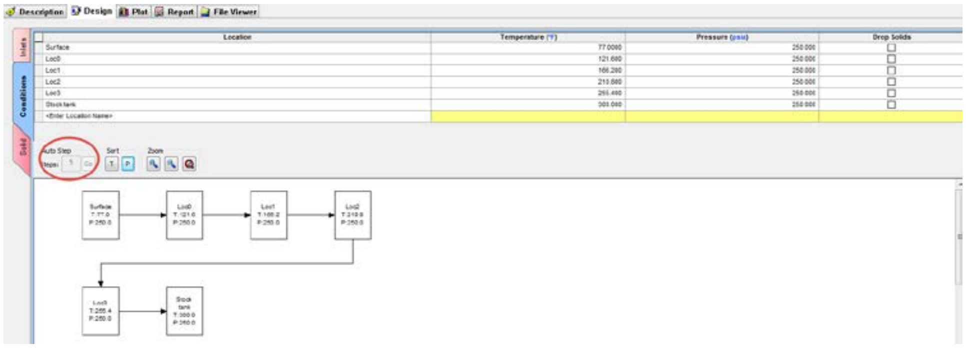
Variable	Units
Temperature	°F
Pressure	psia
Time	day
Alkalinity	mg HCO3/L
Density	g/ml
Electrical Conductivity, molar	m2/ohm-mol
Specific Electrical Conductivity	mho/m
Energy	cal/day
Energy, Molar	cal/mol
Entropy	cal/K day
Entropy, Molar	cal/mol K
Fugacity	atm
Heat Capacity	cal/g K
Ionic Strength (x-based)	mol/mol
Ionic Strength (m based)	mol/kg

```
Opening Document '\\GR                  alyzerChapter.oad'

Last saved in version 9.3
Created in version 9.3.1
Loading 4 objects

------------time spent open

-------------------- 3 secon
```

Figure 16-18 The first and second point added.

We now want to add additional points between the two we've just entered.

Click the *__Auto Step__* button.



Location	Temperature (°F)	Pressure (psia)	Drop Solids
Surface	77.0000	250.000	☐
Loc0	121.600	250.000	☐
Loc1	166.200	250.000	☐
Loc2	210.800	250.000	☐
Loc3	255.400	250.000	☐
Stock tank	300.000	250.000	☐
<Enter Location Name>			

Figure 16-19 The completed conditions tab.

__Sort options__

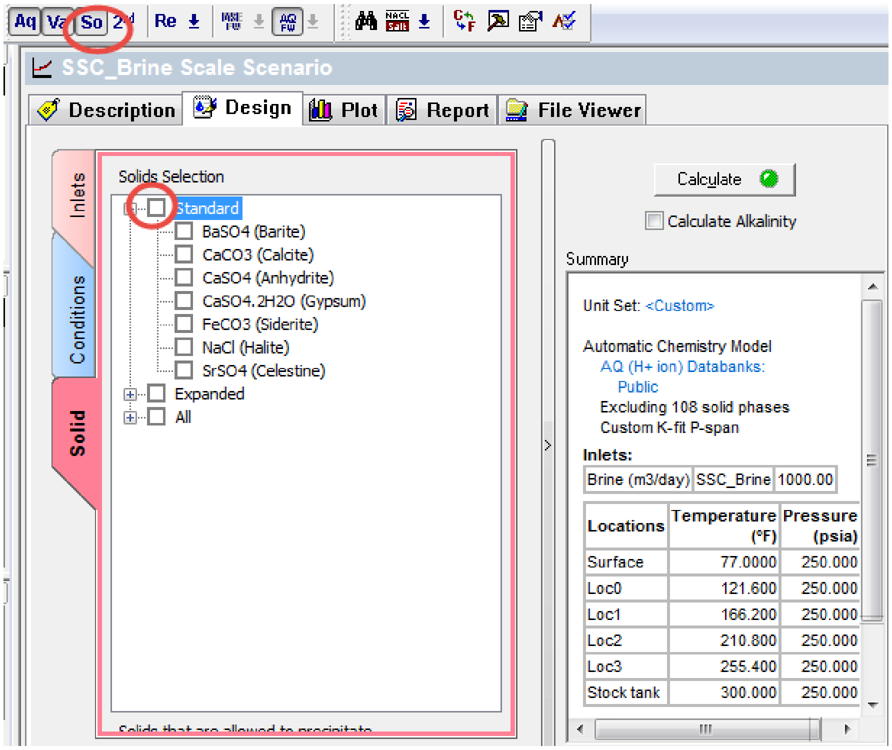
Temperature/Pressure	Sort the list according to the temperature or pressure fields.

The graphical view clearly shows the five locations and their Temperature and pressure conditions. The Drop Solids checkbox column at the very end of the grid is designed to help the users decide if they want to carry forward solids from certain locations or not.

Precipitates

ScaleChem allows for many solid phases to be considered in the actual calculation. For this example we want to consider all the available solids

In ScaleChem, you have to manually turn the solids on at the top of the toolbar in order to enable the solids tab.



Solids Selection

- ☐ Standard
  - ☐ BaSO4 (Barite)
  - ☐ CaCO3 (Calcite)
  - ☐ CaSO4 (Anhydrite)
  - ☐ CaSO4.2H2O (Gypsum)
  - ☐ FeCO3 (Siderite)
  - ☐ NaCl (Halite)
  - ☐ SrSO4 (Celestine)
- ☐ Expanded
- ☐ All

☐ Calculate Alkalinity

Summary

Unit Set: <Custom>

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public
Excluding 108 solid phases
Custom K-fit P-span

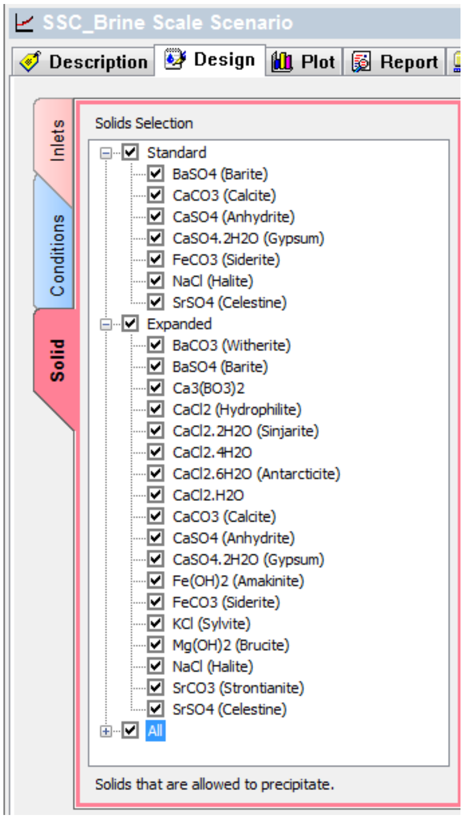
Inlets:

Brine (m3/day)	SSC_Brine	1000.00

Locations	Temperature (°F)	Pressure (psia)
Surface	77.0000	250.000
Loc0	121.600	250.000
Loc1	166.200	250.000
Loc2	210.800	250.000
Loc3	255.400	250.000
Stock tank	300.000	250.000

Figure 16-20 possible precipitates

All the possible precipitates could be seen if + sign before all is clicked.



Solids Selection

- ☑ Standard
  - ☑ BaSO4 (Barite)
  - ☑ CaCO3 (Calcite)
  - ☑ CaSO4 (Anhydrite)
  - ☑ CaSO4.2H2O (Gypsum)
  - ☑ FeCO3 (Siderite)
  - ☑ NaCl (Halite)
  - ☑ SrSO4 (Celestine)
- ☑ Expanded
  - ☑ BaCO3 (Witherite)
  - ☑ BaSO4 (Barite)
  - ☑ Ca3(BO3)2
  - ☑ CaCl2 (Hydrophilite)
  - ☑ CaCl2.2H2O (Sinjarite)
  - ☑ CaCl2.4H2O
  - ☑ CaCl2.6H2O (Antarcticite)
  - ☑ CaCl2.H2O
  - ☑ CaCO3 (Calcite)
  - ☑ CaSO4 (Anhydrite)
  - ☑ CaSO4.2H2O (Gypsum)
  - ☑ Fe(OH)2 (Amakinite)
  - ☑ FeCO3 (Siderite)
  - ☑ KCl (Sylvite)
  - ☑ Mg(OH)2 (Brucite)
  - ☑ NaCl (Halite)
  - ☑ SrCO3 (Strontianite)
  - ☑ SrSO4 (Celestine)
- ☑ All

Solids that are allowed to precipitate.

Figure 16-71 All solids selected.

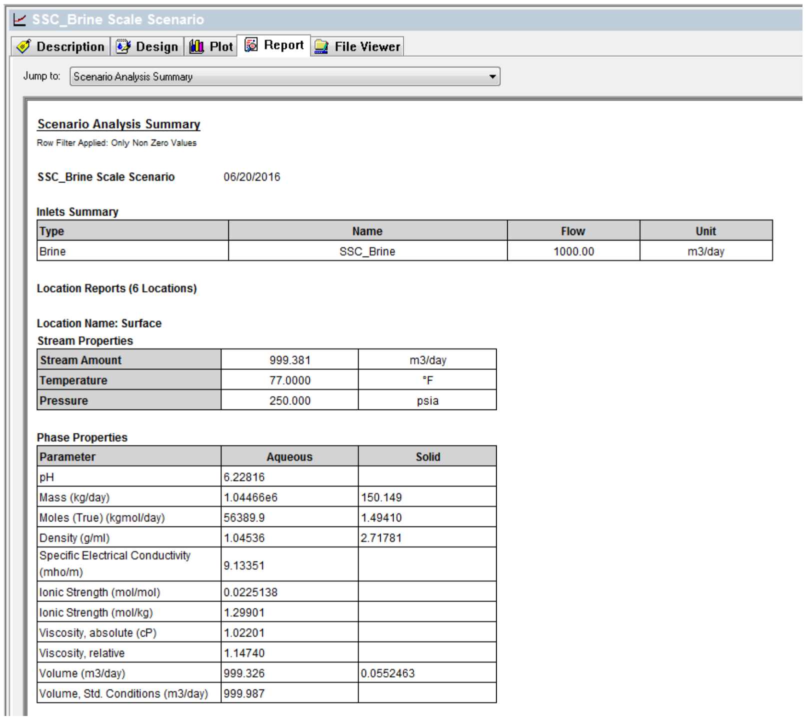
Calculate

We are now ready to calculate

Click on the *Calculate* tab.

Results

After ScaleChem has finished calculating, there will be information of the type shown below available for review. Click on any report tab to display more information.



Scenario Analysis Summary

Row Filter Applied: Only Non Zero Values

SSC_Brine Scale Scenario 06/20/2016

Inlets Summary

Type	Name	Flow	Unit
Brine	SSC_Brine	1000.00	m3/day

Location Reports (6 Locations)

Location Name: Surface

Stream Properties

Stream Amount	999.381	m3/day
Temperature	77.0000	°F
Pressure	250.000	psia

Phase Properties

Parameter	Aqueous	Solid
pH	6.22816	
Mass (kg/day)	1.04466e6	150.149
Moles (True) (kgmol/day)	56389.9	1.49410
Density (g/ml)	1.04536	2.71781
Specific Electrical Conductivity (mho/m)	9.13351	
Ionic Strength (mol/mol)	0.0225138	
Ionic Strength (mol/kg)	1.29901	
Viscosity, absolute (cP)	1.02201	
Viscosity, relative	1.14740	
Volume (m3/day)	999.326	0.0552463
Volume, Std. Conditions (m3/day)	999.987	

Figure 16-82 The report tab.

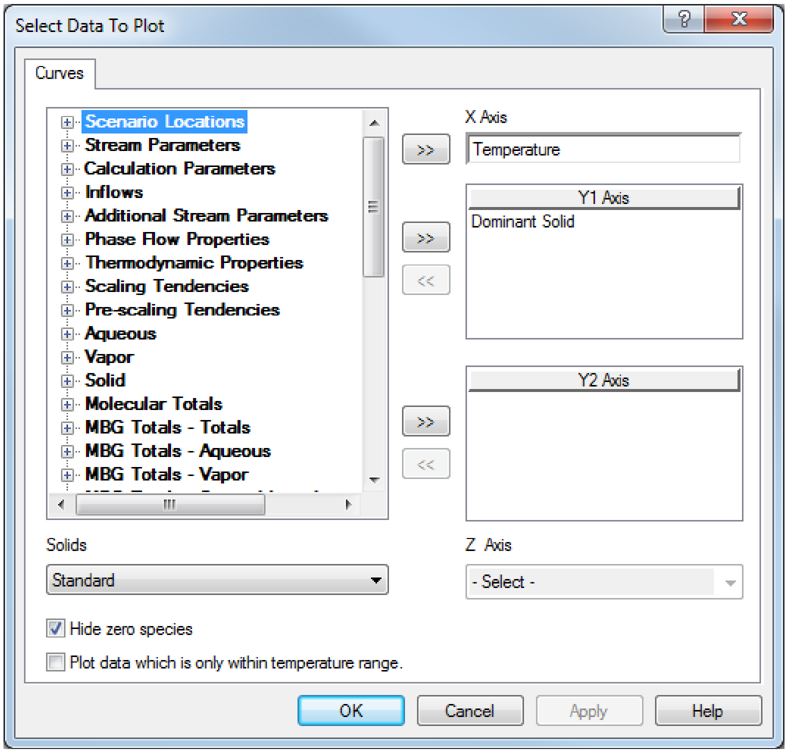
Information in reports

Reprint of individual brines	Each brine as it was entered and reconciled will appear in the report. All known information about the brine will be displayed. Input gases will also be displayed.
Input brine mixture	Prior to each calculation, brines may be mixed with other brines and gases. The sum of these mixtures is displayed in the report.
Output brine and gas mixture	After each calculation, the resultant brine and gas compositions are displayed.
Pre and Post Scaling tendencies and solids	The resultant formation of solids and their tendency to form is displayed.
Location reports	Parameters like Temperature, pressure, viscosity etc will be calculated for both aqueous and solid phase existing at each individual location is calculated and reported.

Plot This tab when selected, will display a plot of scaling scenario.

Go to plot and click on Variables.

A window will pop up named Select Data to plot. Get rid of the pre-scaling tendencies and plot Solids against Temperature on X-axis.



X Axis: Temperature

Y1 Axis: Dominant Solid

Solids: Standard

Z Axis: - Select -

☑ Hide zero species

☐ Plot data which is only within temperature range.

Figure 16-93 Editing the plot.

Plot looks as below:

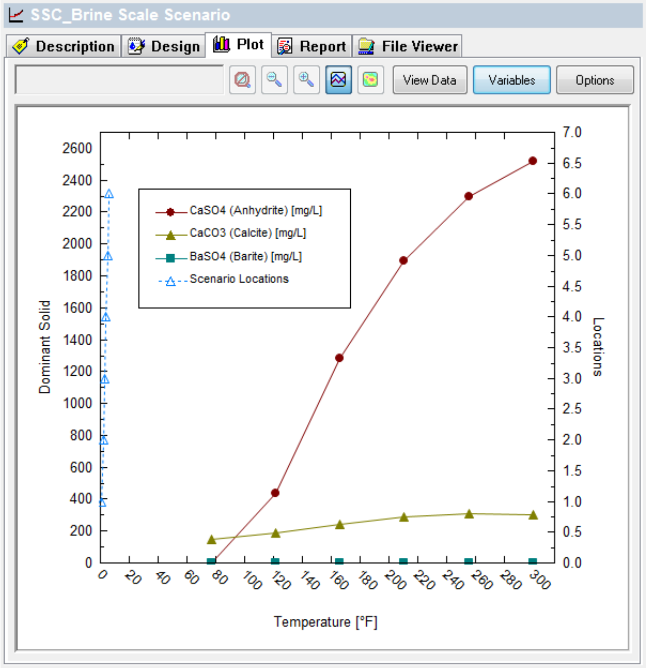


Figure 16-104 The resultant plot.

Most importantly name your file SSC_tutorial and save!save!save!

17. ScaleChem Calculations

Calculations Overview

ScaleChem can be used to calculate scaling at one or more user specified temperatures and pressures. Other calculation options include the ability to mix waters at user specified ratios to find compatible waters, and the ability to saturate a water with respect to one or more solids to simulate reservoir conditions.

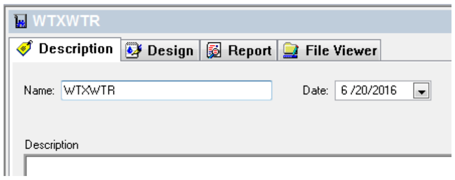
We have already entered a scaling calculation in the ScaleChem Tour, you are referred there to review that information

We will need to add some additional brines, gases and oils to continue.

Calculations: Adding a new brine sample

Add Brine Analysis

Position the mouse on the Actions Panel and select object name Add brine analysis which looks like a logo above and double click. Rename the brine in Descriptions tab



Name: WTXWTR

Date: 6 /20/2016

Description

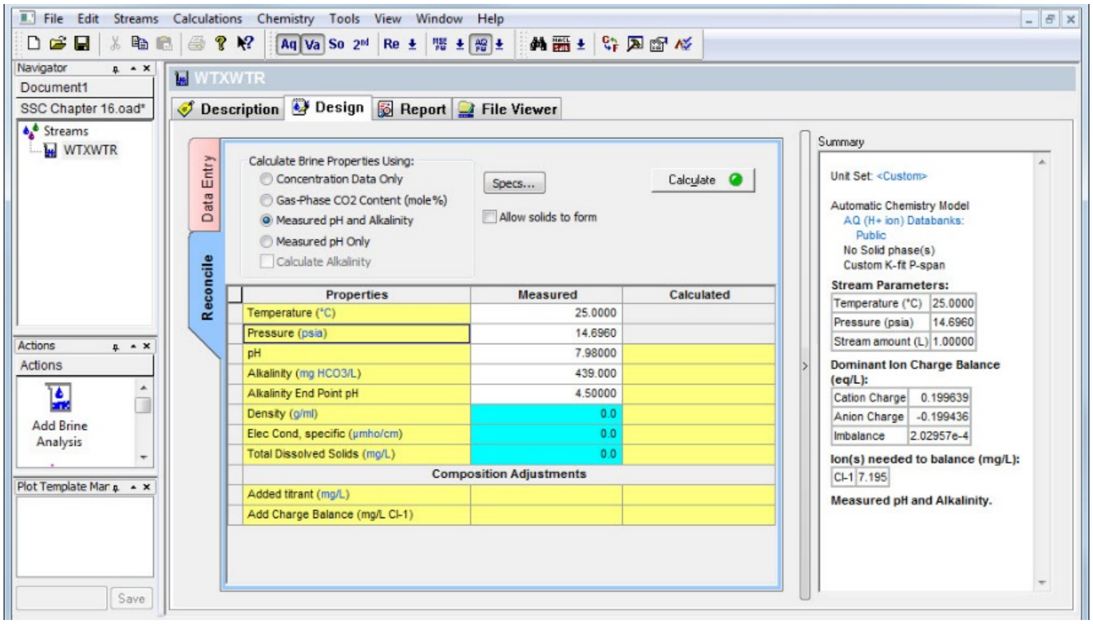
Figure 17-1 The default brine sample description

You must reconcile the sample for both electroneutrality, pH and alkalinity.

Name	WTXWTR	
Type of water	Aquifer Water	
Comment:	West Texas Water Supply	
Species:		
Na^+	3074	mg/L
Ca^{+2}	910	mg/L
Mg^{+2}	249	mg/L
Fe^{+2}	0.77	mg/L
Cl^{-1}	4474	mg/L
SO_4^{-2}	2960	mg/L
HS^{-1}	146.2	mg/L
HCO_3^-	439	mg/L

Conditions:	
pH	7.98
Alkalinity	439 mg/L as HCO_3^-
Titration pH	4.5

Temperature	77 F	
Pressure	14.7	PSI
Density 0	(will be estimated)	



WTXWTR

Calculate Brine Properties Using:
- ○ Concentration Data Only
- ○ Gas-Phase CO2 Content (mole%)
- ● Measured pH and Alkalinity
- ○ Measured pH Only
- ☐ Calculate Alkalinity

☐ Allow solids to form

Properties	Measured	Calculated
Temperature (°C)	25.0000	
Pressure (psia)	14.6960	
pH	7.98000	
Alkalinity (mg HCO3/L)	439.000	
Alkalinity End Point pH	4.50000	
Density (g/ml)	0.0	
Elec Cond, specific (µmho/cm)	0.0	
Total Dissolved Solids (mg/L)	0.0	
Composition Adjustments		
Added titrant (mg/L)		
Add Charge Balance (mg/L Cl-1)		

Unit Set: <Custom>

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public
No Solid phase(s)
Custom K-fit P-span

Stream Parameters:

Temperature (°C)	25.0000
Pressure (psia)	14.6960
Stream amount (L)	1.00000

Dominant Ion Charge Balance (eq/L):

Cation Charge	0.199639
Anion Charge	-0.199436
Imbalance	2.02957e-4

Ion(s) needed to balance (mg/L):

Cl-1	7.195

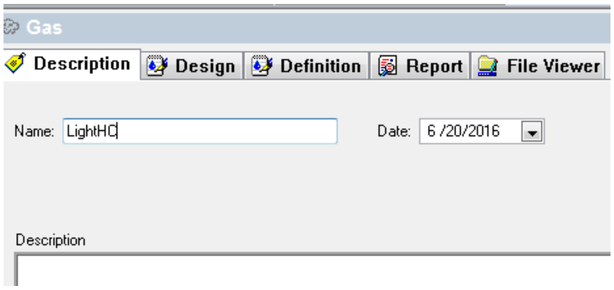
Measured pH and Alkalinity.

Figure 17-2 The calculated Brine WTXWTR

Calculations: Adding a Gas Sample

Add Gas Analysis

From the Actions Panel click on Add Gas Analysis. Input the name in the description tab. We recommend that you use a suitable name



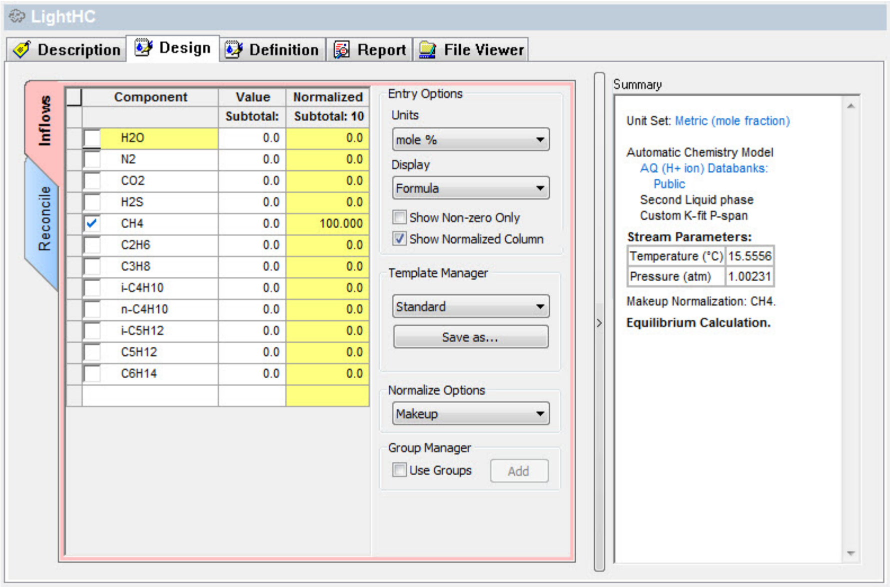
Name: LightHC

Date: 6 /20/2016

Description

Figure 17-3 Entering a gas sample

To add more descriptive information, click on the Design tab.



☐	Component	Value Subtotal:	Normalized Subtotal: 10
☐	H2O	0.0	0.0
☐	N2	0.0	0.0
☐	CO2	0.0	0.0
☐	H2S	0.0	0.0
✓	CH4	0.0	100.000
☐	C2H6	0.0	0.0
☐	C3H8	0.0	0.0
☐	i-C4H10	0.0	0.0
☐	n-C4H10	0.0	0.0
☐	i-C5H12	0.0	0.0
☐	C5H12	0.0	0.0
☐	C6H14	0.0	0.0

Units: mole %
Display: Formula
☐ Show Non-zero Only
☑ Show Normalized Column
Template Manager: Standard
Normalize Options: Makeup
☐ Use Groups

Unit Set: Metric (mole fraction)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public
Second Liquid phase
Custom K-fit P-span

Stream Parameters:

Temperature (°C)	15.5556
Pressure (atm)	1.00231

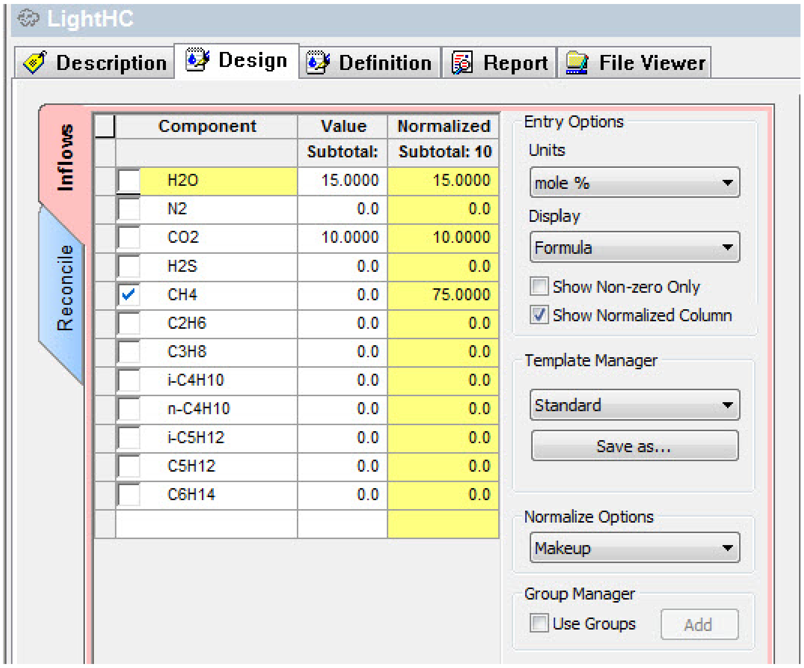
Makeup Normalization: CH4.

Equilibrium Calculation.

Figure 17-4 The blank gas entry. Initially 100 % methane (CH_4)

Please enter the following composition

Carbon dioxide (CO2)	10	mole %
Water (H2O)	15	mole %



☐	Component	Value Subtotal:	Normalized Subtotal: 10
☐	H2O	15.0000	15.0000
☐	N2	0.0	0.0
☐	CO2	10.0000	10.0000
☐	H2S	0.0	0.0
✓	CH4	0.0	75.0000
☐	C2H6	0.0	0.0
☐	C3H8	0.0	0.0
☐	i-C4H10	0.0	0.0
☐	n-C4H10	0.0	0.0
☐	i-C5H12	0.0	0.0
☐	C5H12	0.0	0.0
☐	C6H14	0.0	0.0

Units: mole %
Display: Formula
☐ Show Non-zero Only
☑ Show Normalized Column
Template Manager: Standard
Normalize Options: Makeup
☐ Use Groups

Figure 17-5 Entered gas.

Gas The gas composition is entered as mole% or volume% (these are equivalent for an ideal gas). The total must be 100% and can be adjusted by normalizing, or by letting the program determine the amount of hydrocarbon gases present. The gases that are displayed here will be either the standard gases or expanded gases . Toggling from the standard to expanded can be achieved by clicking the Gases button.

Normalizing

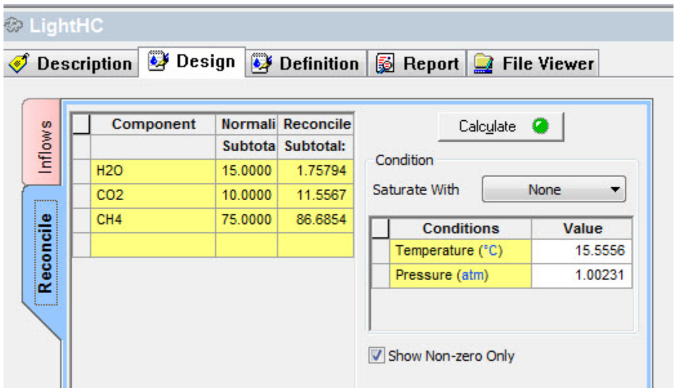
You can enter just the amounts of carbon dioxide, hydrogen sulfide and water and let the program Calculate Hydrocarbon Percent (default) or enter all values and then normalize to 100%.

Displaying Gases

You can display the name of the gases by Name (the default) or by Formula. ScaleChem will assume that all of the hydrocarbon gas is methane (CH4). If you want to use a more detailed list of hydrocarbon gases, click on Gases to expand the list.

Frequently the data received by the user refers to gas compositions that are reported on a "Dry" Basis. Any water that was present in the actual gas has been removed mathematically and reported as a dry sample.

The dew point corresponds to the temperature or pressure where a gas will begin to condense and form a liquid (aqueous) phase. The Dew Point calculation will allow you to determine the amount of water that could be contained in the gas at the stated temperature, pressure and composition.



Component	Normali Subtota	Reconcile Subtotal:
H2O	15.0000	1.75794
CO2	10.0000	11.5567
CH4	75.0000	86.6854

Condition

Saturate With: None

Conditions	Value
Temperature (°C)	15.5556
Pressure (atm)	1.00231

☑ Show Non-zero Only

Figure 17-6 Reconcile tab

Type of Calculation

Saturated water Content

At the entered conditions, the amount of water that the gas can contain before an aqueous liquid will form is determined. If the Water Vapor field is entered, then that value is used as an initial guess to the calculation.

The calculated value is NOT updated in the actual gas composition. The user must enter that value manually if desired.

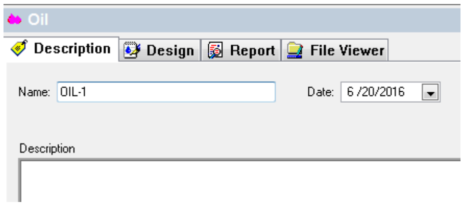
At Conditions

Enter the temperature, pressure and water content of the gas. Click the Calculate button to start the calculation.
You can change the units of the calculation by clicking the Units button. When the calculation is complete, you may view the internal files by clicking the View Files button (currently grayed-out in the above example).

Calculations: Adding an Oil sample

Add Oil Analysis

From the Actions Panel click Add Oil Analysis. Enter the name in the Description Tab.



Name: OIL-1

Date: 6 /20/2016

Description

Figure 17-7 Input name for the Oil Analysis

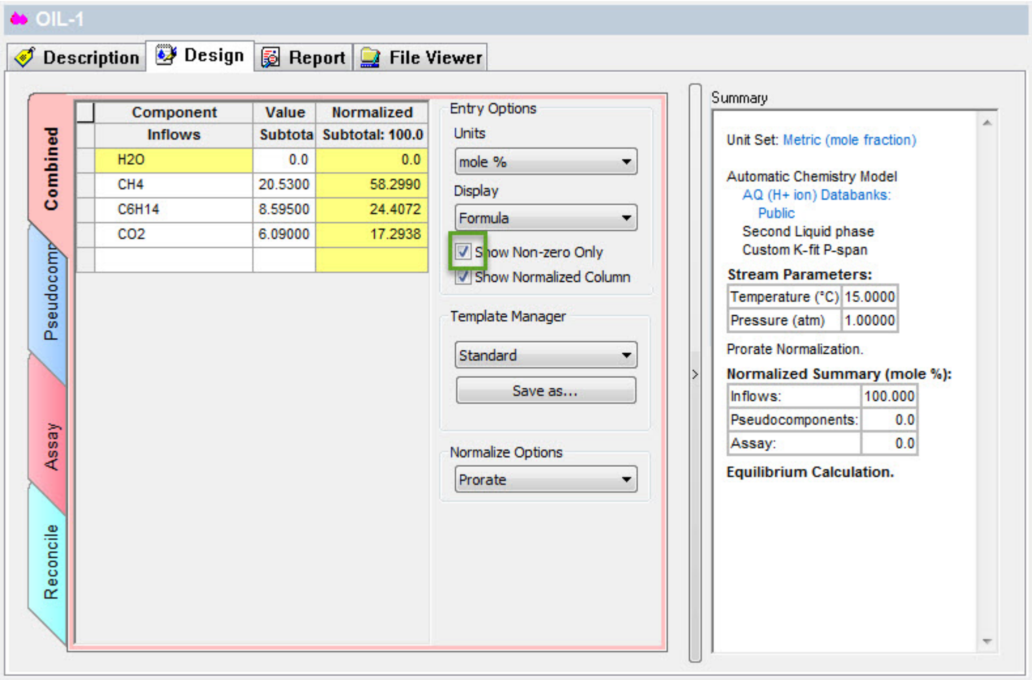
Input the composition information in the design tab.

Calculations: Hydrocarbon - Pseudocomponent approach

There are three entry types. The first is pure components (organic and inorganic), the second is pseudocomponents, and the third is a distillation curve (termed petroleum fraction. ScaleChem groups the pseudocomponent and assays together.

For this example we will enter pure component and pseudocomponent data.

Entering Pseudocomponent data



Component Inflows	Value Subtota	Normalized Subtotal: 100.0
H2O	0.0	0.0
CH4	20.5300	58.2990
C6H14	8.59500	24.4072
CO2	6.09000	17.2938

Entry Options

Units: mole %

Display: Formula

☑ Show Non-zero Only

☑ Show Normalized Column

Template Manager: Standard

Normalize Options: Prorate

Summary

Unit Set: Metric (mole fraction)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public
Second Liquid phase
Custom K-fit P-span

Stream Parameters:

Temperature (°C)	15.0000
Pressure (atm)	1.00000

Prorate Normalization.

Normalized Summary (mole %):

Inflows:	100.000
Pseudocomponents:	0.0
Assay:	0.0

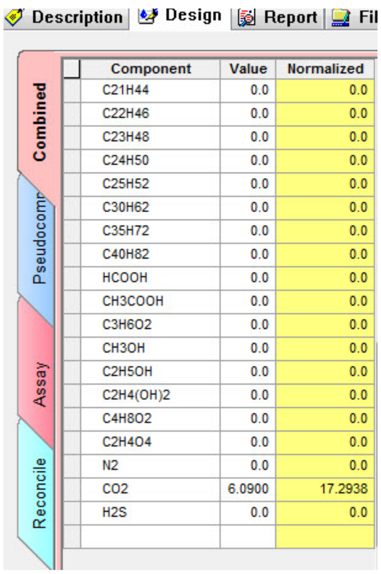
Equilibrium Calculation.

Figure 17-8 Starting to add compositions.

We will start by entering the following composition:

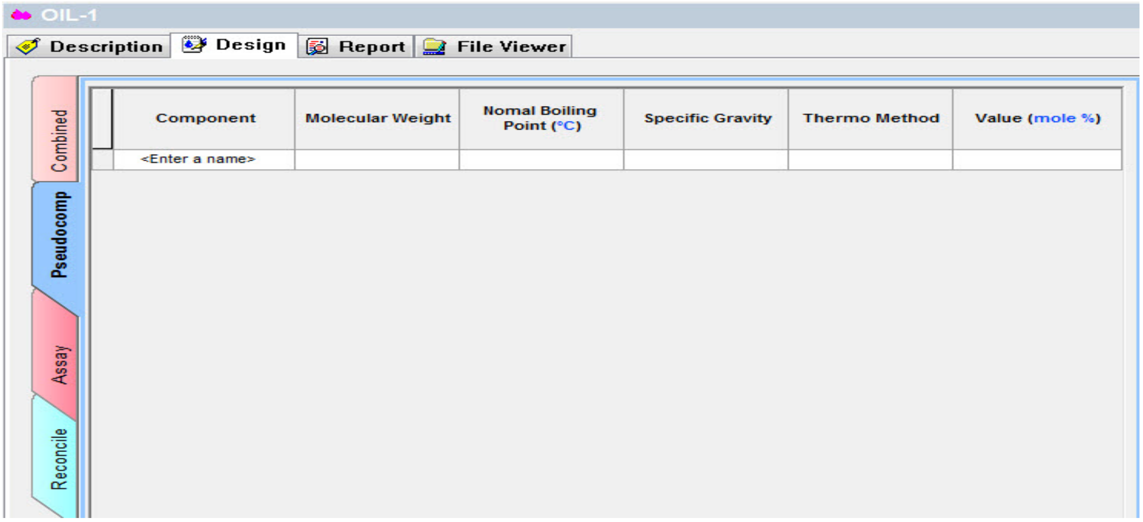
Methane (C1)	20.53mole %
Hexane (C6)	8.595mole %
CO2	6.09mole %

(you will have to scroll down to find the CO2 entry).



Component	Value	Normalized
C21H44	0.0	0.0
C22H46	0.0	0.0
C23H48	0.0	0.0
C24H50	0.0	0.0
C25H52	0.0	0.0
C30H62	0.0	0.0
C35H72	0.0	0.0
C40H82	0.0	0.0
HCOOH	0.0	0.0
CH3COOH	0.0	0.0
C3H6O2	0.0	0.0
CH3OH	0.0	0.0
C2H5OH	0.0	0.0
C2H4(OH)2	0.0	0.0
C4H8O2	0.0	0.0
C2H4O4	0.0	0.0
N2	0.0	0.0
CO2	6.0900	17.2938
H2S	0.0	0.0

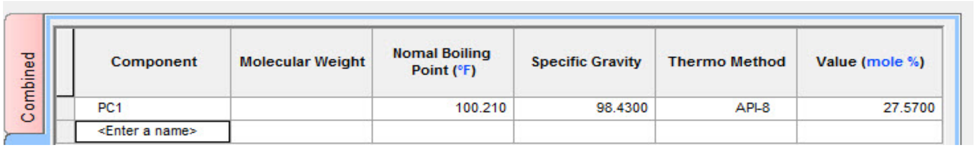
Figure 17-9 C1 to C20 entered. Scroll down to find CO2



Component	Molecular Weight	Nomal Boiling Point (°C)	Specific Gravity	Thermo Method	Value (mole %)
<Enter a name>					

Figure 17-10 Entering pseudocomponents.

Type the name PC1 in the section <Enter Name> below column heading Component. Please enter the following information. Add a mole percentage of 27.57 %



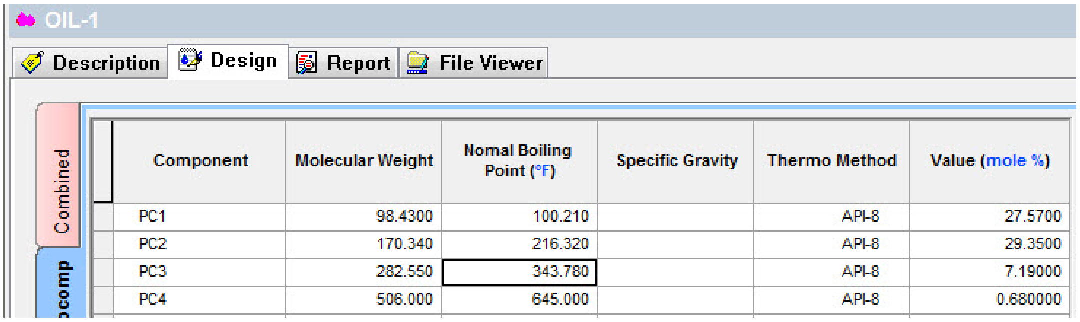
Component	Molecular Weight	Nomal Boiling Point (°F)	Specific Gravity	Thermo Method	Value (mole %)
PC1		100.210	98.4300	API-8	27.5700
<Enter a name>					

Figure 17-11 Adding the first pseudocomponent.

We have now entered the first pseudocomponent. Keep typing in the Enter Name section to add more pseudocomponents. We have 3 additional entries.

Name	MW (g/mol)	nBP (F)	Method	mole %
PC2	170.34	216.32	API	29.35
PC3	282.55	343.78	API	7.19
PC4	506.0	645.00	API	0.68

The completed input looks like this:

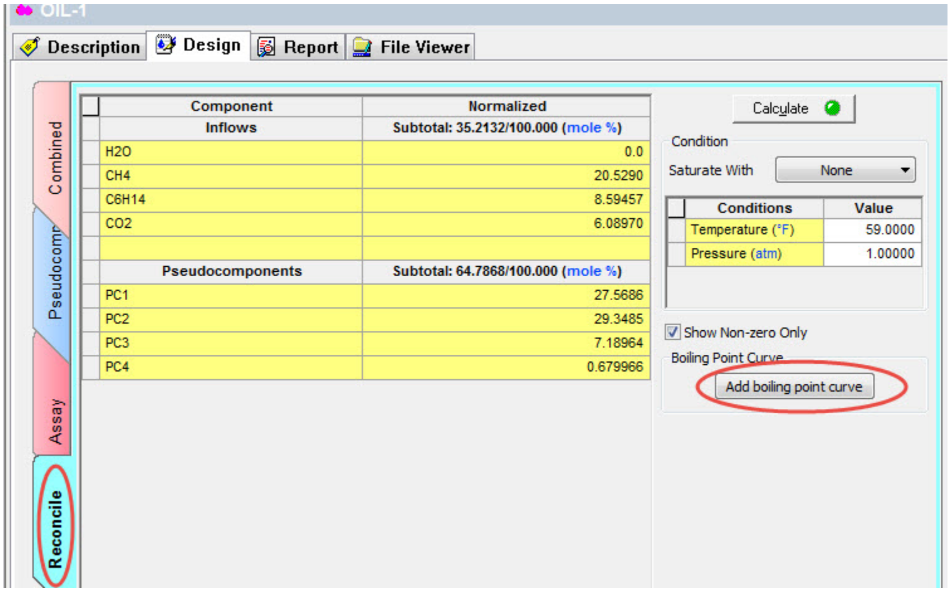


Component	Molecular Weight	Nomal Boiling Point (°F)	Specific Gravity	Thermo Method	Value (mole %)
PC1	98.4300	100.210		API-8	27.5700
PC2	170.340	216.320		API-8	29.3500
PC3	282.550	343.780		API-8	7.19000
PC4	506.000	645.000		API-8	0.680000

Figure 17-12 Completed input

Reconciling the Pseudocomponent

Click on the ***Reconciliation*** tab to see how well the pseudocomponent will predict the phase behavior of the hydrocarbon sample. You will be presented with the following display:



Component	Normalized
Inflows	Subtotal: 35.2132/100.000 (mole %)
H2O	0.0
CH4	20.5290
C6H14	8.59457
CO2	6.08970
Pseudocomponents	Subtotal: 64.7868/100.000 (mole %)
PC1	27.5686
PC2	29.3485
PC3	7.18964
PC4	0.679966

Condition

Saturate With: None

Conditions	Value
Temperature (°F)	59.0000
Pressure (atm)	1.00000

☑ Show Non-zero Only

Boiling Point Curve

Figure 17-13 Reconciliation Tab

We will hold the temperature constant at 204 F and vary the pressure from 200 to 2000 PSI in 100 PSI increments.

Click the *Boiling point* button. A new calculation appears in the navigation panel below OIL1 Object.

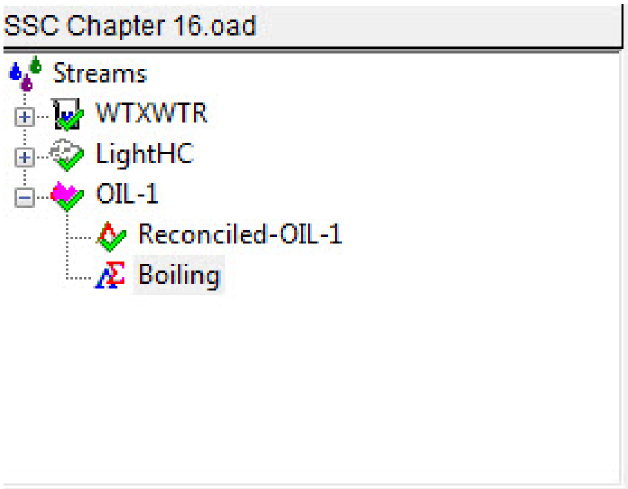


Figure 17-14 Boiling Point calculation

This is a survey by Pressure. Click on the specs button and specify the conditions below.

Enter a fixed value of *204 deg F*

Enter a pressure range:

Start	200 psia
End	2000 psia
Start	100 psia

Click the *Calculate* button.

Click on the plot tab, you will see the following graph: You could adjust the parameters by clicking on curves.

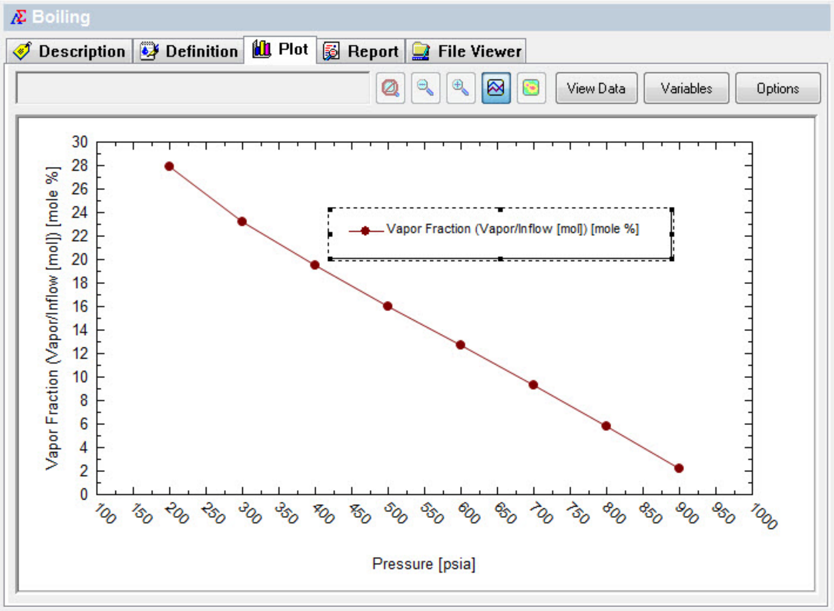


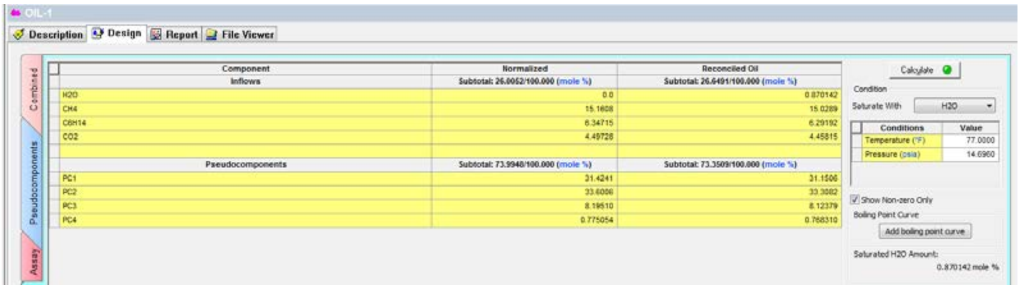
Figure 17-15 Boiling point curve

If the curve does not meet expectations, you will have to adjust the mole percentages or the pseudocomponent properties. This is a manual iterative approach. You can see the actual data by clicking the View data button.

Saturating the hydrocarbon with water

Frequently the hydrocarbon was saturated with water.

Click on the _Saturate with_ drop down. Select H20



Component	Normalized	Reconciled Oil
Inflows	Subtotal: 26.0052/100.000 (mole %)	Subtotal: 26.6491/100.000 (mole %)
H2O	0.0	0.870142
CH4	15.1608	15.0289
C6H14	6.34715	6.29192
CO2	4.49728	4.45815
Pseudocomponents	Subtotal: 73.9948/100.000 (mole %)	Subtotal: 73.3509/100.000 (mole %)
PC1	31.4241	31.1506
PC2	33.6006	33.3082
PC3	8.19510	8.12379
PC4	0.775054	0.768310

Condition

Saturate With: H2O

Conditions	Value
Temperature (°F)	77.0000
Pressure (psia)	14.6960

☑ Show Non-zero Only

Boiling Point Curve

Saturated H2O Amount:
0.870142 mole %

Figure 17-16 Saturate with H2O

In this example we are saturating the hydrocarbon sample at 77 F and 14.7 PSI. The program requires an initial "Guess" for the concentration of the water. When done, we will save the saturated hydrocarbon as the object **SatOIL1**.

Click on the _Calculate_ button.

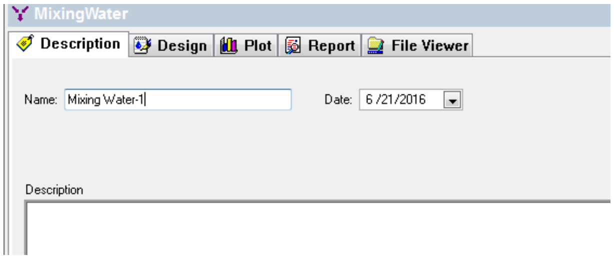
Mix Calculation: Overview

The Mixer calculation determines if two waters (brines) can be mixed. Frequently the mixing of two waters will cause precipitates to form which were not present in original brines. This can lead to the plugging of a formation when an injection water is mixed with the natural fluids in the formation.

Mix Calculation: Set Up

Add Mixing
Water

From the Actions Panel, click on the Add Mixing Water logo. After double clicking the logo, you will the object in the Navigation Panel.



Name: Mixing Water-1

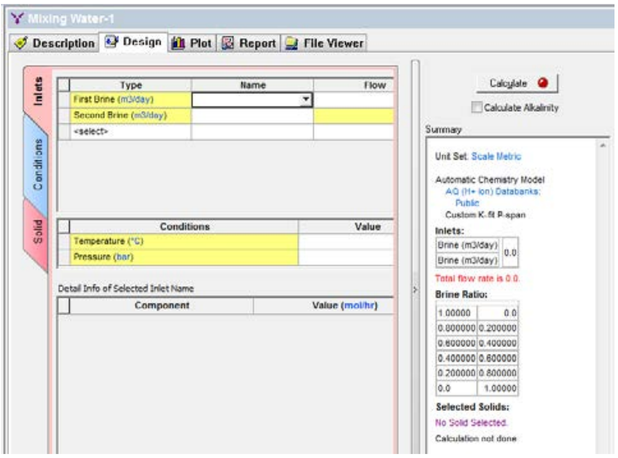
Date: 6 /21/2016

Description

Figure 17-17 Input name for Mixing Water object

Click on the design tab to enter more information.

Selecting objects for the calculation



Type	Name	Flow
First Brine (m3/day)		
Second Brine (m3/day)		
<select>		

Conditions	Value
Temperature (°C)	
Pressure (bar)	

Component	Value (mol/hr)

Unit Set: Scale Metric

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public
Custom K-fit P-span

Inlets:

Brine (m3/day)	0.0
Brine (m3/day)	

Total flow rate is 0.0.

Brine Ratio:

1.00000	0.0
0.800000	0.200000
0.600000	0.400000
0.400000	0.600000
0.200000	0.800000
0.0	1.00000

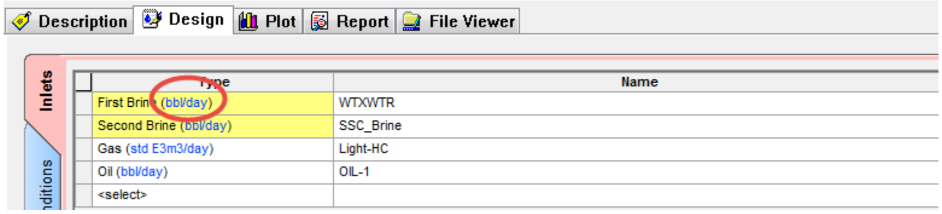
Selected Solids:
No Solid Selected.
Calculation not done

Figure 17-28 Setting up the mix calculation

Select your brines, gases and oils as shown in the next figure. Enter the indicated brine flow rate of 1000 bbl/day, gas flow of 230 stdMft3/day and oil flow of 7 bbl/day.

There are two ways to change the units.

Method 1: To change units on brine, oil and gas, click on the hyperlinked (blue) units inside of the bracket next to Inlets First Brine, Second Brine etc. This is under the column heading Type.

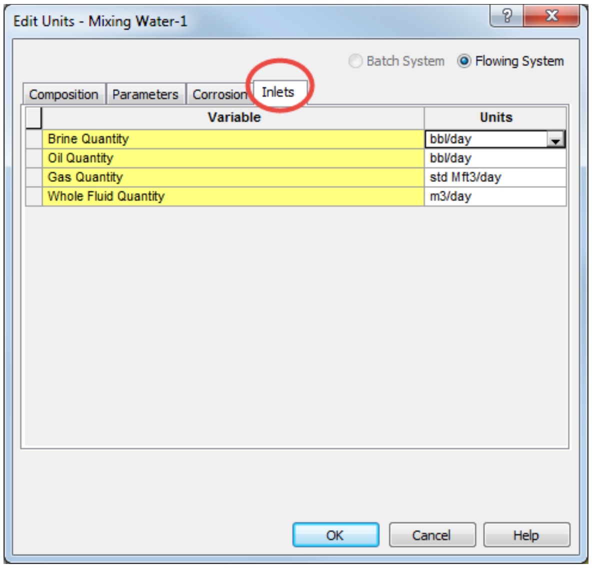


Type	Name
First Brine (bbl/day)	WTXWTR
Second Brine (bbl/day)	SSC_Brine
Gas (std E3m3/day)	Light-HC
Oil (bbl/day)	OIL-1
<select>	

Figure 17-19 Changing units

This should pop the following window up. Click on Inlets tab and change the units.

Inlets tab looks like below. Changing units on Brine:

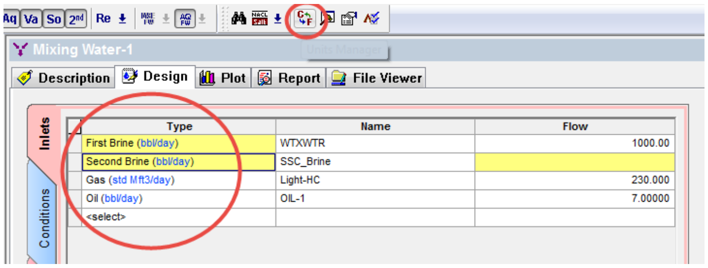

Edit Units - Mixing Water-1

○ Batch System ● Flowing System

Variable	Units
Brine Quantity	bbl/day
Oil Quantity	bbl/day
Gas Quantity	std Mft3/day
Whole Fluid Quantity	m3/day

Figure 17-20 Units manager layering

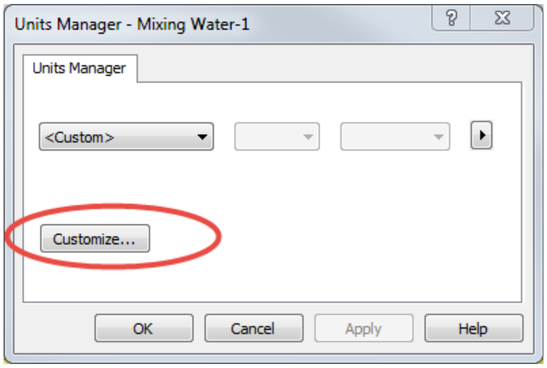
Method 2: This can also be done in one other way, that is through the units manager button on the toolbar. which looks like .



Type	Name	Flow
First Brine (bbl/day)	WTXWTR	1000.00
Second Brine (bbl/day)	SSC_Brine	
Gas (std Mft3/day)	Light-HC	230.000
Oil (bbl/day)	OIL-1	7.00000
<select>		

Figure 17-21 Units Manager accessibility

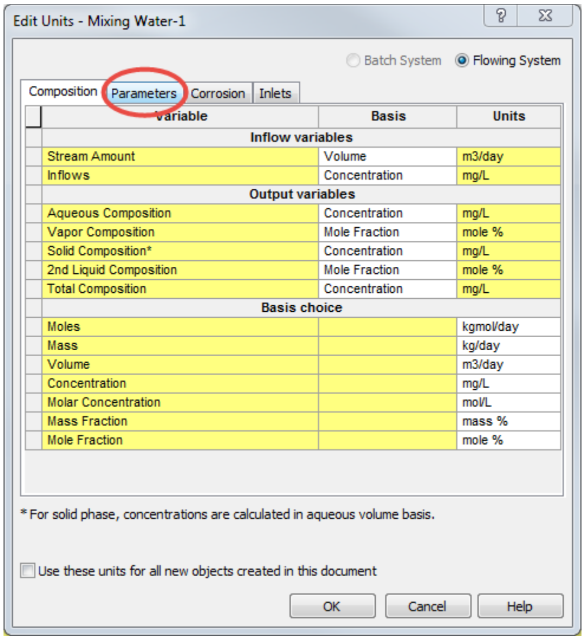
When you click on units manager, following windows pops up.


Units Manager - Mixing Water-1

<Custom>

Figure 17-22 Units Manager first layer

Click on Customize. Change the individual parameters as shown below.

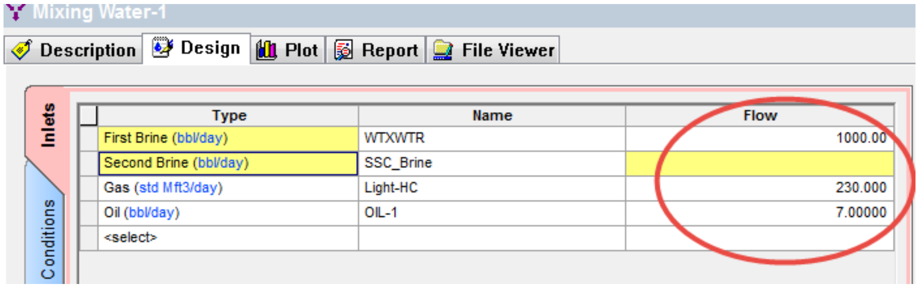


Variable	Basis	Units
Inflow variables		
Stream Amount	Volume	m3/day
Inflows	Concentration	mg/L
Output variables		
Aqueous Composition	Concentration	mg/L
Vapor Composition	Mole Fraction	mole %
Solid Composition*	Concentration	mg/L
2nd Liquid Composition	Mole Fraction	mole %
Total Composition	Concentration	mg/L
Basis choice		
Moles		kgmol/day
Mass		kg/day
Volume		m3/day
Concentration		mg/L
Molar Concentration		mol/L
Mass Fraction		mass %
Mole Fraction		mole %

* For solid phase, concentrations are calculated in aqueous volume basis.

☐ Use these units for all new objects created in this document

Figure 17-23 Changing units for parameters



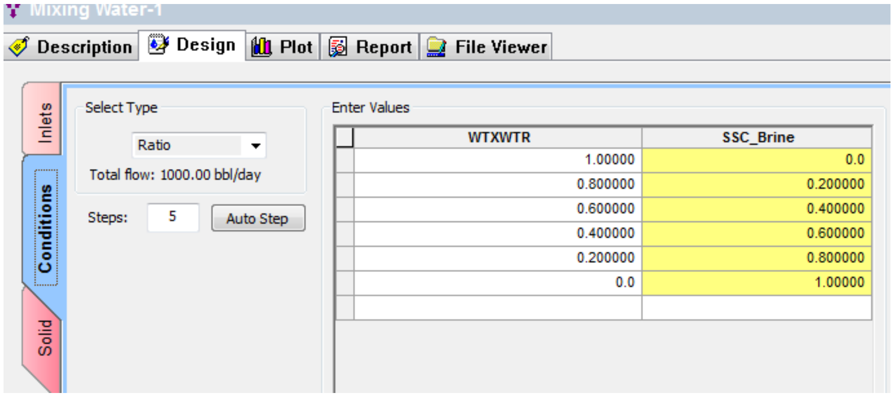
Type	Name	Flow
First Brine (bbl/day)	WTXWTR	1000.00
Second Brine (bbl/day)	SSC_Brine	
Gas (std Mft3/day)	Light-HC	230.000
Oil (bbl/day)	OIL-1	7.00000
<select>		

Figure 17-24 Mixer with inflows entered (Inlets Tab)

In this example we will mix two brines, created in other sections at a total brine flow rate of 1000 barrels per day. In addition, we will add a gas and a hydrocarbon to the calculation.

Entering Conditions

In this example, we are mixing the brines at 100 F and 200 PSIA. The first brine specified (brine1 in the example) is the one we compare to when evaluating the ratios. In this case we start out with all brine1 and none of the brine WTXWTR and end up with none of brine1 and all of WTXWTR.



Select Type: Ratio

Total flow: 1000.00 bbl/day

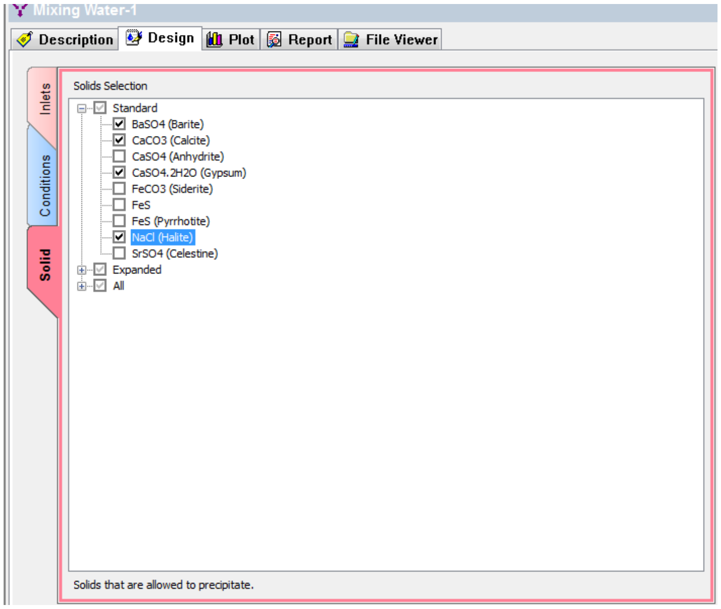
Steps: 5

Enter Values

WTXWTR	SSC_Brine
1.00000	0.0
0.800000	0.200000
0.600000	0.400000
0.400000	0.600000
0.200000	0.800000
0.0	1.00000

Figure 17-25 the mixing conditions (Conditions tab)

Selecting Precipitates



Solids Selection

- ☑ Standard
  - ☑ BaSO4 (Barite)
  - ☑ CaCO3 (Calcite)
  - ☐ CaSO4 (Anhydrite)
  - ☑ CaSO4.2H2O (Gypsum)
  - ☐ FeCO3 (Siderite)
  - ☐ FeS
  - ☐ FeS (Pyrrhotite)
  - ☑ NaCl (Halite)
  - ☐ SrSO4 (Celestine)
- ☑ Expanded
- ☑ All

Solids that are allowed to precipitate.

Figure 17-27 Selecting a few solids. (Solids tab)

For this calculation we are only selecting a few of the possible solids. Mark a check box next to desired solids ($BaSO_4$, $CaCO_3$, $CaSO_4.2H_2O$, NaCl).

Click on the Calculate button.

View the report. Click on the Plot tab and view Plot

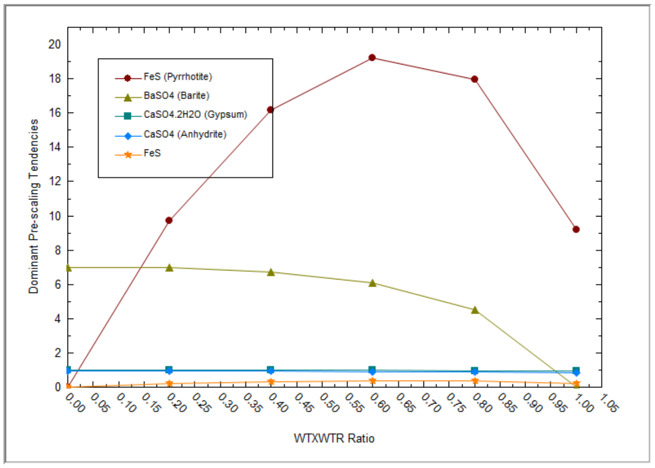


Figure 17-28 Default plot

To study the effects better go to the variables button and eliminate other solids precipitated by the << arrow. Keep only one solid (in this case BaSO4). The ratio is relative to the first brine specified. This means at a ratio of 0.0 (all the first brine and none of the second) we have no BaSO4 scaling. As we add the second brine, the amount of BaSO4 increases. These waters are perhaps incompatible.

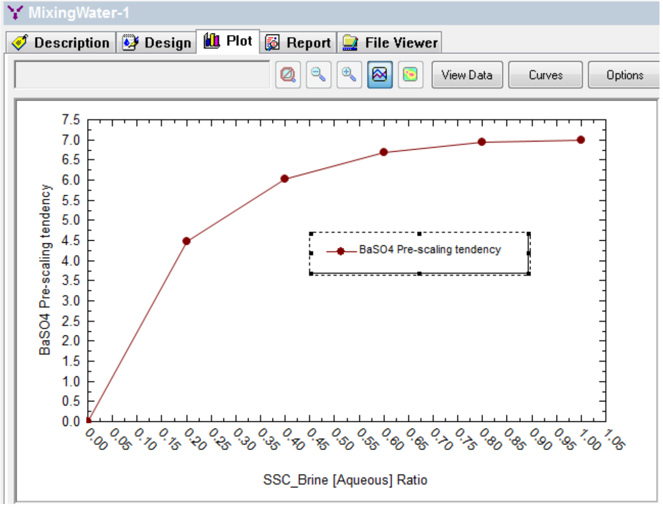
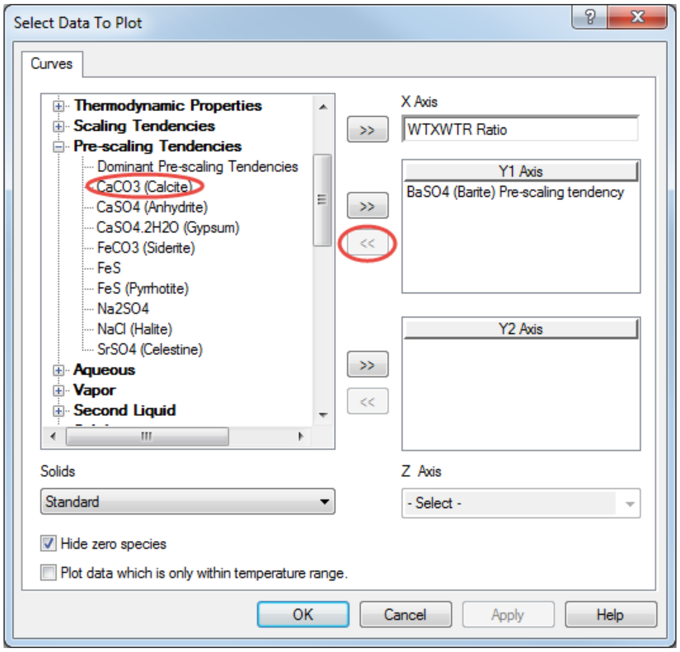


Figure 17-29 Mixing results



X Axis: WTXWTR Ratio

Y1 Axis: BaSO4 (Barite) Pre-scaling tendency

Solids: Standard

Z Axis: - Select -

☑ Hide zero species

☐ Plot data which is only within temperature range.

Figure 17-30 Editing the plot via variables button

You could choose to select any of the other solids that could be precipitated from the above pre-scaling tendencies. The red marked << arrow removes the existing component from Y1-axis and >> arrow adds components to axis. Simply double clicking the component/parameter name under axis works for removing it from the list to display on plot too.

Saturate Calculations: Overview

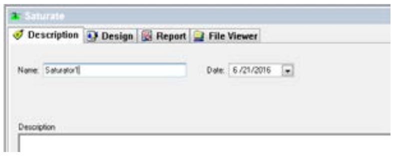
Water and gas samples at the surface are not necessarily representative of conditions in the reservoir. The processing of the samples may involve significant changes in the chemistry.

The Saturate option (often referred to as "Saturate at reservoir conditions") allows the user to "Back" calculate the conditions down hole.

Saturate Calculations: Set Up

Add Saturator

Select Add Saturator from the Actions Panel. Rename the object in the descriptions tab.



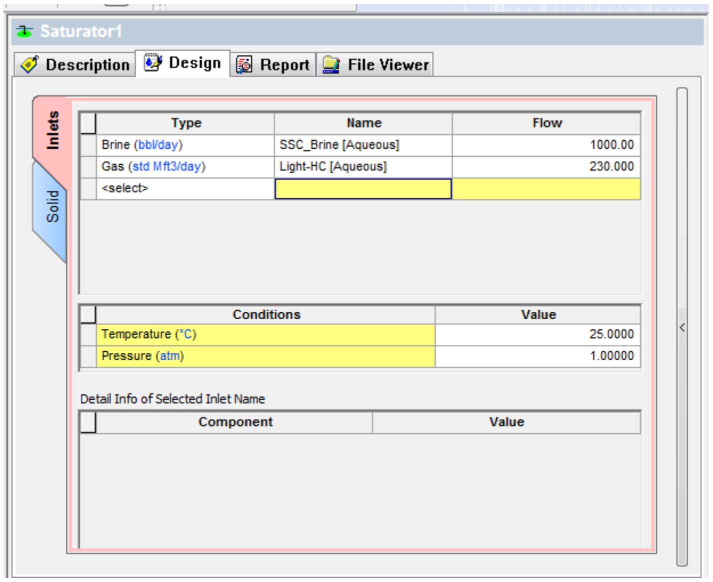
Name: Saturator1

Date: 6/21/2016

Figure 17-31 Description tab

The default location will be the ***Component*** tab.

We will select objects that we have already defined.



Type	Name	Flow
Brine (bbl/day)	SSC_Brine [Aqueous]	1000.00
Gas (std Mft3/day)	Light-HC [Aqueous]	230.000
<select>		

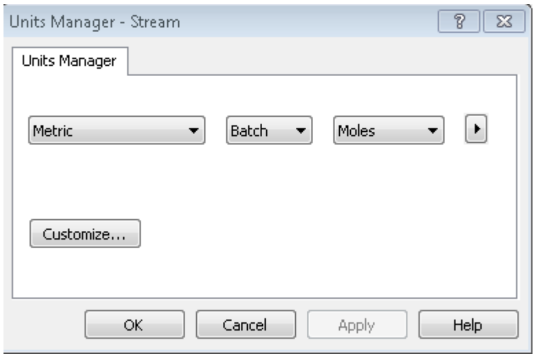
Conditions	Value
Temperature (°C)	25.0000
Pressure (atm)	1.00000

Detail Info of Selected Inlet Name

Component	Value

Figure 17-32 Selecting saturating components

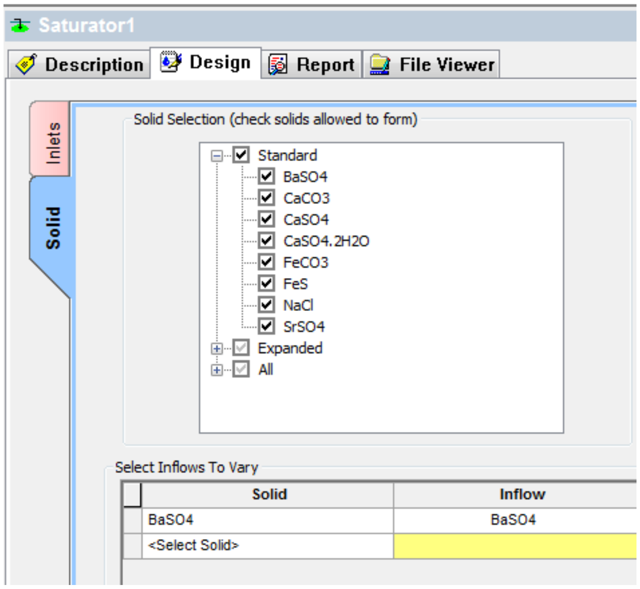
For the Gas and Brine flow and Conditions units for temperature and pressure, we have to make sure to have bbl/day, Mft3/day and F, PSIA respectively. Set these units as custom units for all new objects in Units manager.



Metric | Batch | Moles

Figure 17-33 Customize the unit sets

We have to select solids inflow to vary for Saturator1. Under the solids tab select the solids allowed to be formed. Under the table select inflows to vary, choose the solid to vary from the dropdown list.



Solid Selection (check solids allowed to form)

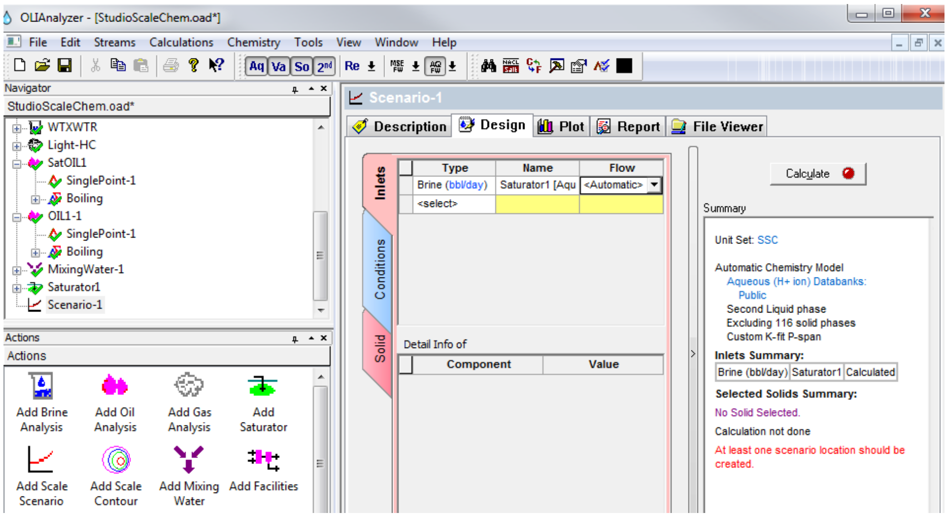
- ☑ Standard
  - ☑ BaSO4
  - ☑ CaCO3
  - ☑ CaSO4
  - ☑ CaSO4.2H2O
  - ☑ FeCO3
  - ☑ FeS
  - ☑ NaCl
  - ☑ SrSO4
- ☑ Expanded
- ☑ All

Select Inflows To Vary

Solid	Inflow
BaSO4	BaSO4
<Select Solid>	

Figure 17-34 Selecting solids to vary

To study the saturator brine at various locations we need to add a Scaling Scenario from the saturator.



Type	Name	Flow
Brine (bbl/day)	Saturator1 [Aqu	<Automatic>
<select>		

Detail Info of

Component	Value

Summary

Unit Set: SSC

Automatic Chemistry Model
Aqueous (H+ ion) Databanks:
Public
Second Liquid phase
Excluding 116 solid phases
Custom K-fit P-span

Inlets Summary:

Brine (bbl/day)	Saturator1	Calculated

Selected Solids Summary:

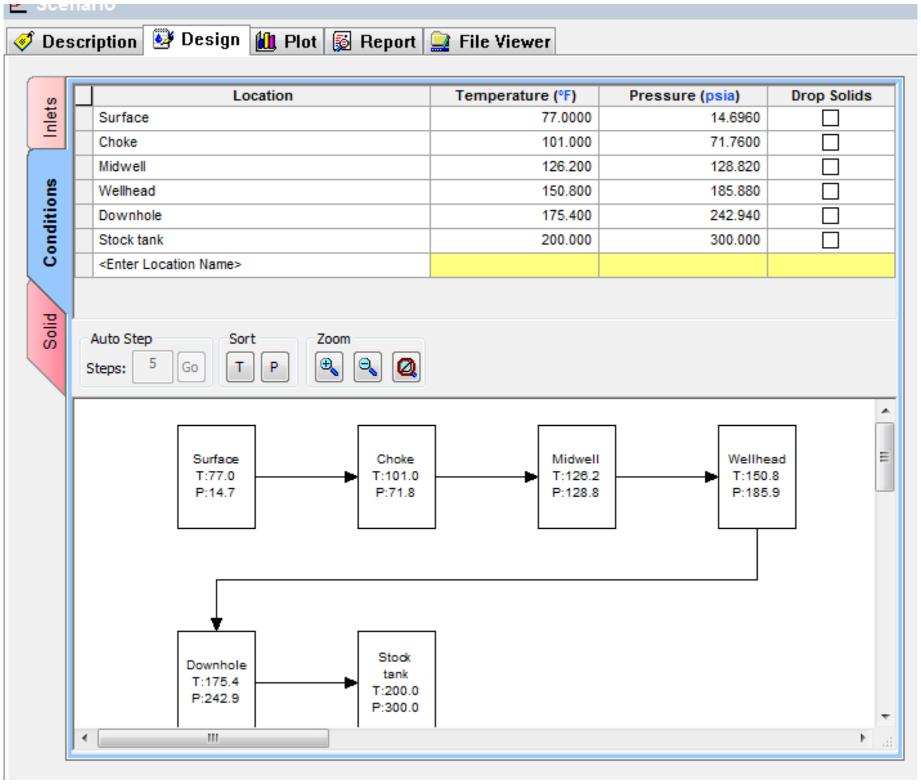
No Solid Selected.

Calculation not done

At least one scenario location should be created.

Figure 17-35 Adding a scaling Scenario

We have to make sure when we add brine under the inlets tab, under Type column, that we are selecting brine from Saturator1 and not SSC brine or WTXWTR brine. Flow will be automatically controlled. Locations can be input under the conditions tab.

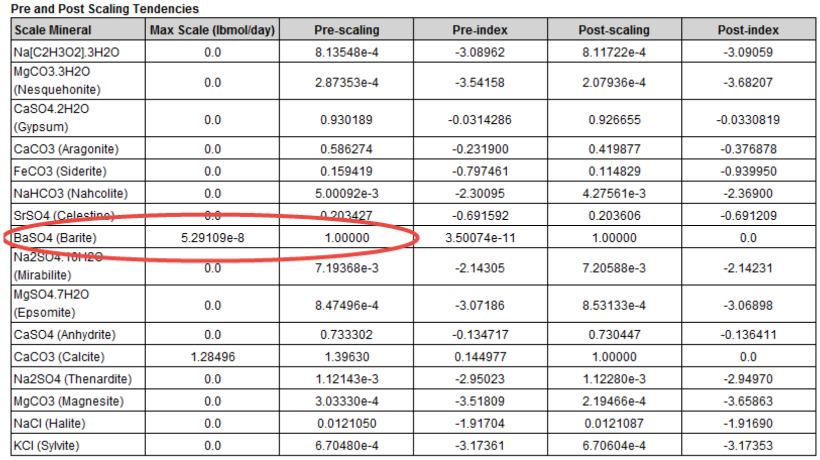


Location	Temperature (°F)	Pressure (psia)	Drop Solids
Surface	77.0000	14.6960	☐
Choke	101.000	71.7600	☐
Midwell	126.200	128.820	☐
Wellhead	150.800	185.880	☐
Downhole	175.400	242.940	☐
Stock tank	200.000	300.000	☐
<Enter Location Name>			

Figure 17-36 Conditions set up

We will start at 77 ºF and 14.696 PSIA and end at 200 ºF and 300 PSIA. We will use 5 steps.

This case differs from the other calculations in that we will force a scale to appear just at its solubility limit. The scaling tendency is forced to be equal to 1.0 exactly. See report tab on the Saturator 1where Pre and Post Scaling Tendency table shows more details.



Pre and Post Scaling Tendencies

Scale Mineral	Max Scale (lbmol/day)	Pre-scaling	Pre-index	Post-scaling	Post-index
Na[C2H3O2].3H2O	0.0	8.13548e-4	-3.08962	8.11722e-4	-3.09059
MgCO3.3H2O (Nesquehonite)	0.0	2.87353e-4	-3.54158	2.07936e-4	-3.68207
CaSO4.2H2O (Gypsum)	0.0	0.930189	-0.0314286	0.926655	-0.0330819
CaCO3 (Aragonite)	0.0	0.586274	-0.231900	0.419877	-0.376878
FeCO3 (Siderite)	0.0	0.159419	-0.797461	0.114829	-0.939950
NaHCO3 (Nahcolite)	0.0	5.00092e-3	-2.30095	4.27561e-3	-2.36900
SrSO4 (Celestine)	0.0	0.203427	-0.691592	0.203606	-0.691209
BaSO4 (Barite)	5.29109e-8	1.00000	3.50074e-11	1.00000	0.0
Na2SO4.10H2O (Mirabilite)	0.0	7.19368e-3	-2.14305	7.20588e-3	-2.14231
MgSO4.7H2O (Epsomite)	0.0	8.47496e-4	-3.07186	8.53133e-4	-3.06898
CaSO4 (Anhydrite)	0.0	0.733302	-0.134717	0.730447	-0.136411
CaCO3 (Calcite)	1.28496	1.39630	0.144977	1.00000	0.0
Na2SO4 (Thenardite)	0.0	1.12143e-3	-2.95023	1.12280e-3	-2.94970
MgCO3 (Magnesite)	0.0	3.03330e-4	-3.51809	2.19466e-4	-3.65863
NaCl (Halite)	0.0	0.0121050	-1.91704	0.0121087	-1.91690
KCl (Sylvite)	0.0	6.70480e-4	-3.17361	6.70604e-4	-3.17353

Figure 17-37 Pre and post Scaling tendencies at location one-surface

We want to force the BaSO4 (barite) solid to appear. It is generally a good idea to select a maximum of one or two solids. As we can see above, BaSO4 has a scaling tendency of exactly one.

After the calculation is complete, the plot for scale scenario shows that other solids are appearing. In this case both Anhydrite and calcite and disordered dolomite are appearing.

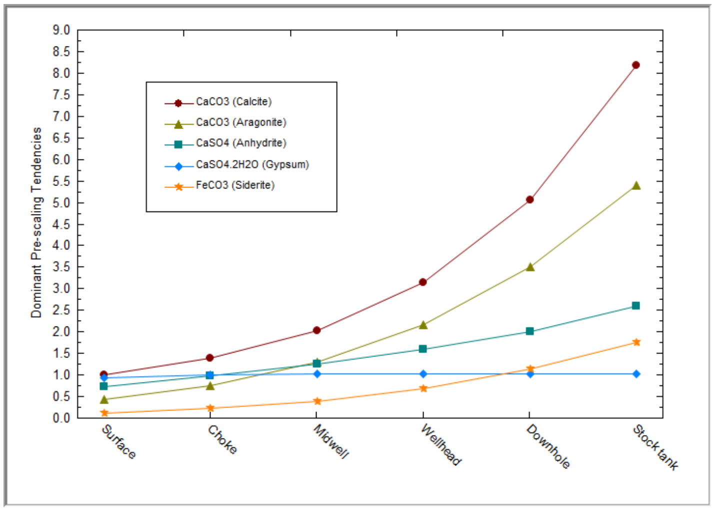
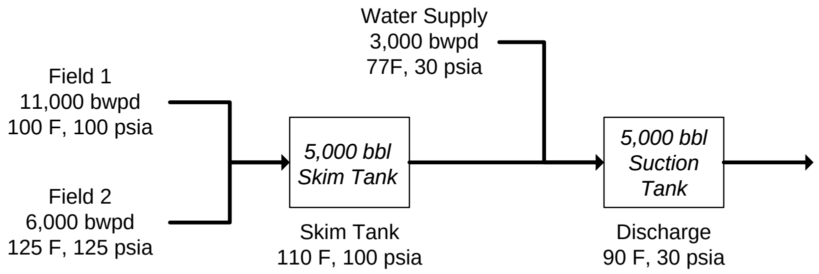


Figure 17-38 The plotted results

At this point it may be beneficial to saturate with other solids. We will leave that as an exercise for the user.

Facility Calculation: Overview

ScaleChem has the ability to link together several individual calculations to create a flow sheet facility. An example of a facility calculation is shown in the figure below.



It is a simple process in which two field brines mix in a skim tank.   The discharge from this tank then mixes with a water supply in a discharge tank.   Below are the compositions and conditions of the inlet fluids

Name	Field1 .	Field2 .	Water Supply
Na+	38209	27078	3074
Ca+2	6600	4480	910
Mg+2	1531	1191	249
Fe+2	120	6.6	0.77
Cl-1	73150	51134	4474
SO4-2	2453	1840	2960
HS-1	244	146.2	0
HCO3-	421	677	439
Conditions			
Temperature	100F	125 F	77 F
Pressure	100 PSI	125 PSI	30 PSI
Alkalinity (As HCO3 mg/L)	421	677	439
Titration pH	4.5	4.5	4.5
Sample pH	6.97	7.53	7.98

Create the above brines

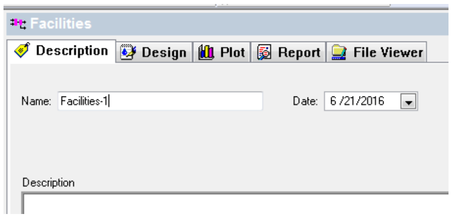
You start this example by first creating the above three brines:. Use the Add Brine Analysis object as you have done before to create them. *Reconcile these three brines for **measured pH and alkalinity**.* Make sure that the *Allow solids to form* box is uncheck at the bottom of the reconciliation options for all the brines.

Facility Calculation: Set Up

Add Facilities

The facilities calculation is based upon transferring information between calculations through nodes. These nodes can be thought of as pseudo brines and gases.. These pseudo brines are not stored as individual brine rather they are used internally in the calculation. The concentration and flow rates for these nodes can be viewed in the output.

Select ***Add Facilities*** from the Action Panel.



Name: Facilities-1

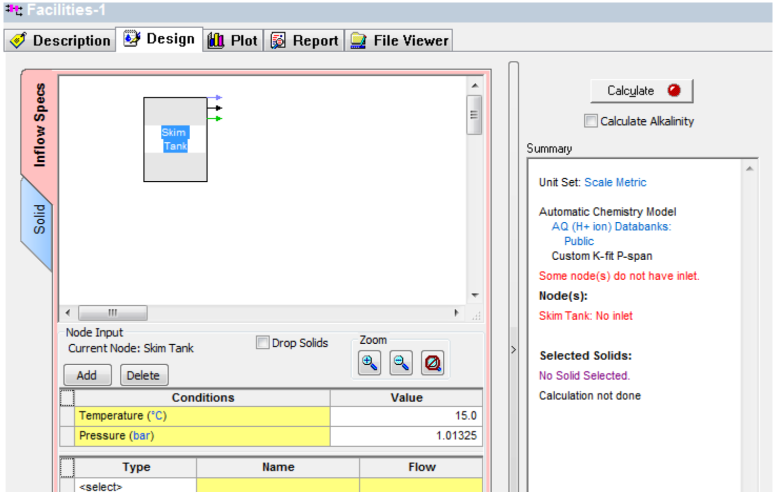
Date: 6 /21/2016

Description

Figure 17-39 The Description tab for the Facilities

Under design tab, within Inflow Specs, we can add Nodes via Node input options. There will be one default node added. Click on the node name and type "Skim Tank" That populates the name field below Node Input section.

At the start the panel contains Node #1. It has default conditions and no inlet streams. This node will be the Skim Tank.



Node Input

Current Node: Skim Tank

☐ Drop Solids

☐ Calculate Alkalinity

Conditions	Value
Temperature (°C)	15.0
Pressure (bar)	1.01325

Type	Name	Flow
<select>		

Summary

Unit Set: Scale Metric

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public
Custom K-fit P-span

Some node(s) do not have inlet.

Node(s):

Skim Tank: No inlet

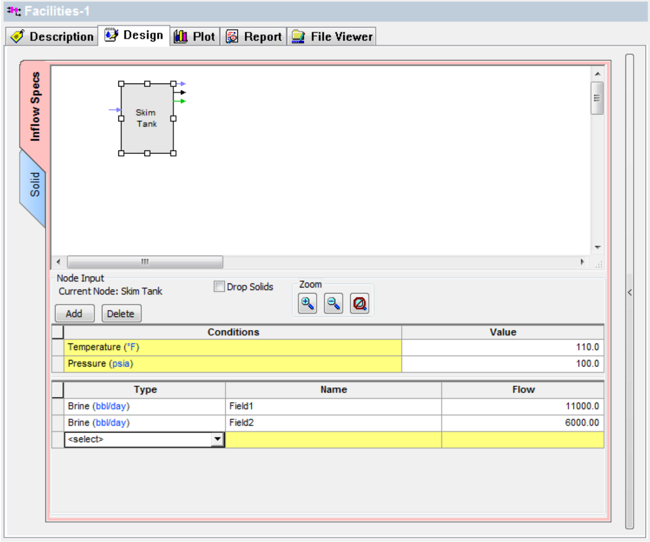
Selected Solids:

No Solid Selected.

Calculation not done

Figure 17-40 Node input Screen

Enter the name, description, conditions, and streams for the Skim Tank shown above. When complete, your screen should look like this.



Node Input
Current Node: Skim Tank

☐ Drop Solids

Conditions	Value
Temperature (°F)	110.0
Pressure (psia)	100.0

Type	Name	Flow
Brine (bbl/day)	Field1	11000.0
Brine (bbl/day)	Field2	6000.00
<select>		

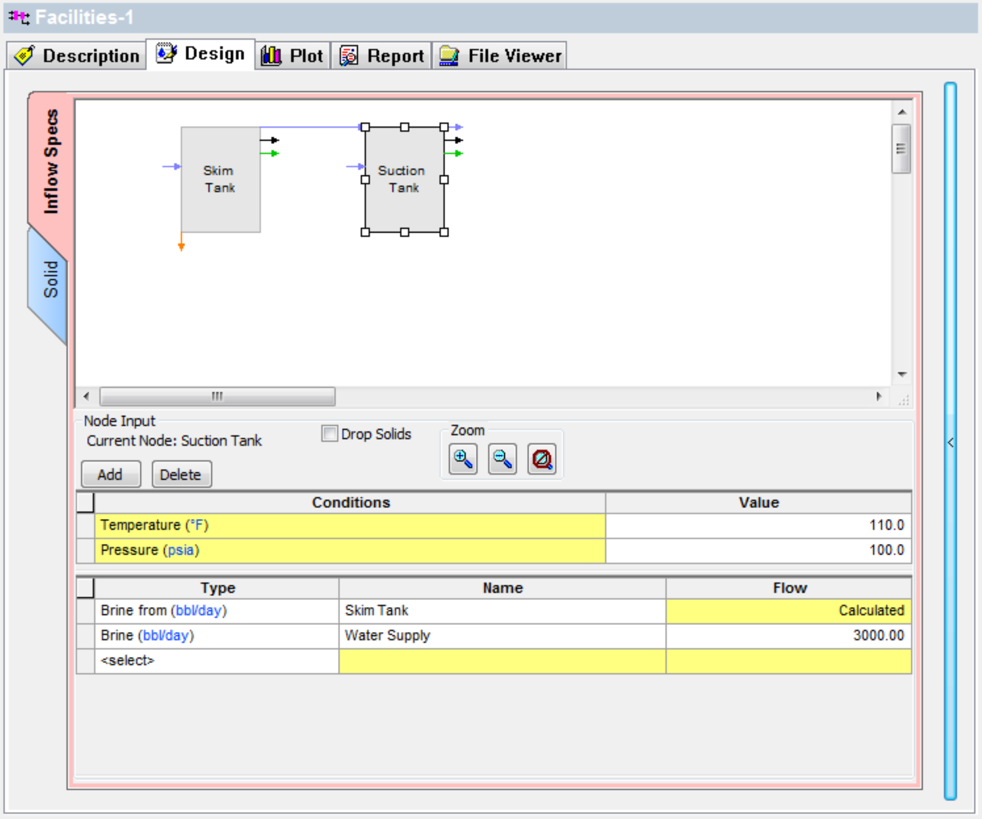
Figure 17-41 Node 1 is complete

The temperature and pressure of the calculation is 110 F and 100 PSI. A default node name is supplied and it is sufficient for our use. The output of this calculation will go to the next node. Make sure to select drop solids checkbox at the Skim Tank node.

Next, enter the information for the second node, Suction Tank. We will select the output brine of the Skim tank, which is a ***brine from node*** The temperature and pressure as well as the flow of the brine are calculated.

When a brine is calculated in a facilities calculation, we have the option of allowing any produced solids to be considered (that is they traveled along with the brine) or to ***eliminate*** them as they precipitate out. We will eliminate the solids in this case. The orange downward arrow from Skim Tank indicate dropped solids.

We are also adding the **Water Supply** to this tank.



Node Input

Current Node: Suction Tank

☐ Drop Solids

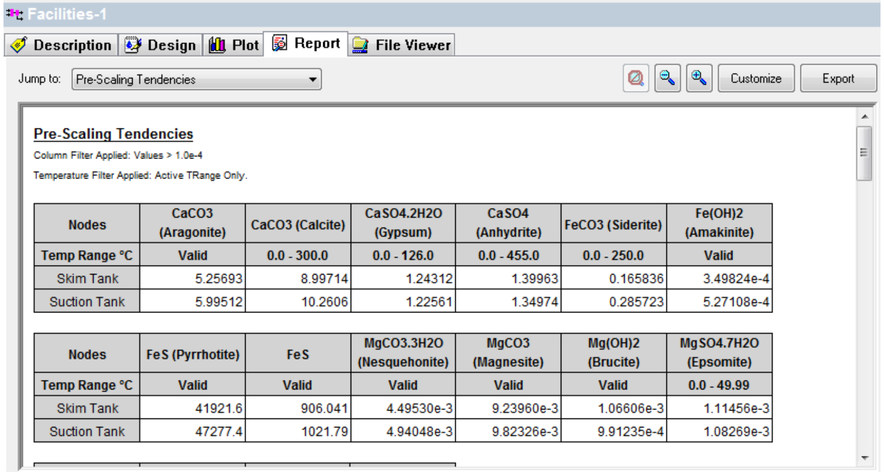
	Conditions	Value
	Temperature (°F)	110.0
	Pressure (psia)	100.0

	Type	Name	Flow
	Brine from (bbl/day)	Skim Tank	Calculated
	Brine (bbl/day)	Water Supply	3000.00
	<select>		

Figure 17-42 Node 2 is entered

The program assigns a default node name of **Node2** which is sufficient for our use. We have added the description **"Suction Tank"**.

Click on the Calculate button. Or press Ctrl+F9.



Jump to: Pre-Scaling Tendencies

Pre-Scaling Tendencies

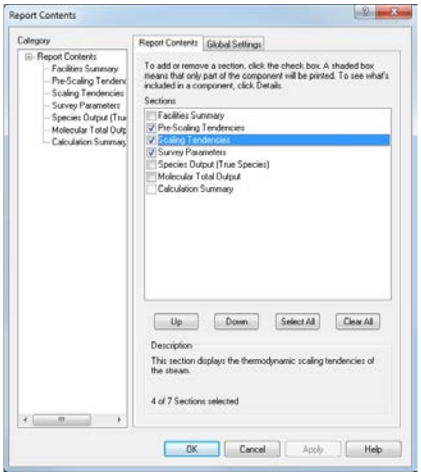
Column Filter Applied: Values > 1.0e-4

Temperature Filter Applied: Active TRange Only.

Nodes	CaCO3 (Aragonite)	CaCO3 (Calcite)	CaSO4.2H2O (Gypsum)	CaSO4 (Anhydrite)	FeCO3 (Siderite)	Fe(OH)2 (Amakinite)
Temp Range °C	Valid	0.0 - 300.0	0.0 - 126.0	0.0 - 455.0	0.0 - 250.0	Valid
Skim Tank	5.25693	8.99714	1.24312	1.39963	0.165836	3.49824e-4
Suction Tank	5.99512	10.2606	1.22561	1.34974	0.285723	5.27108e-4

Nodes	FeS (Pyrrhotite)	FeS	MgCO3.3H2O (Nesquehonite)	MgCO3 (Magnesite)	Mg(OH)2 (Brucite)	MgSO4.7H2O (Epsomite)
Temp Range °C	Valid	Valid	Valid	Valid	Valid	0.0 - 49.99
Skim Tank	41921.6	906.041	4.49530e-3	9.23960e-3	1.06606e-3	1.11456e-3
Suction Tank	47277.4	1021.79	4.94048e-3	9.82326e-3	9.91235e-4	1.08269e-3

Figure 17-43 the reports tab



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

Sections

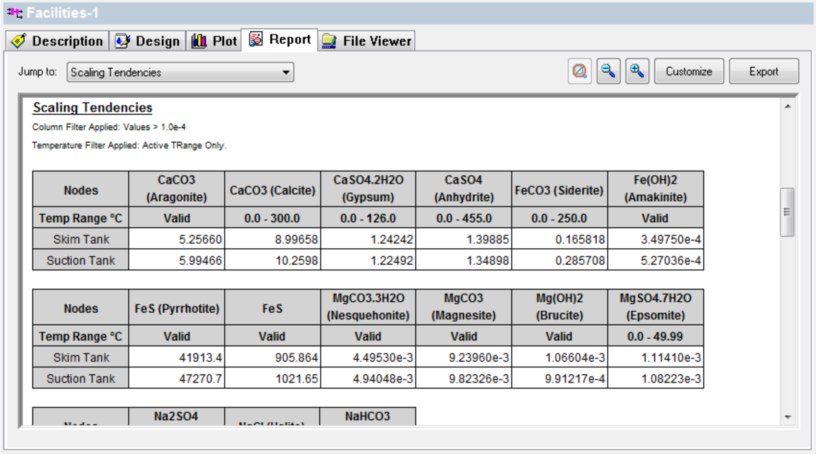
☐ Facilities Summary
☑ Pre-Scaling Tendencies
☑ Scaling Tendencies
☑ Survey Parameters
☐ Species Output (True Species)
☐ Molecular Total Output
☐ Calculation Summary

Description

This section displays the thermodynamic scaling tendencies of the stream.

4 of 7 Sections selected

Figure 17-4 Results for nodes



Jump to: Scaling Tendencies

Scaling Tendencies

Column Filter Applied: Values > 1.0e-4

Temperature Filter Applied: Active TRange Only.

Nodes	CaCO3 (Aragonite)	CaCO3 (Calcite)	CaSO4.2H2O (Gypsum)	CaSO4 (Anhydrite)	FeCO3 (Siderite)	Fe(OH)2 (Amakinite)
Temp Range °C	Valid	0.0 - 300.0	0.0 - 126.0	0.0 - 455.0	0.0 - 250.0	Valid
Skim Tank	5.25660	8.99658	1.24242	1.39885	0.165818	3.49750e-4
Suction Tank	5.99466	10.2598	1.22492	1.34898	0.285708	5.27036e-4

Nodes	FeS (Pyrrhotite)	FeS	MgCO3.3H2O (Nesquehonite)	MgCO3 (Magnesite)	Mg(OH)2 (Brucite)	MgSO4.7H2O (Epsomite)
Temp Range °C	Valid	Valid	Valid	Valid	Valid	0.0 - 49.99
Skim Tank	41913.4	905.864	4.49530e-3	9.23960e-3	1.06604e-3	1.11410e-3
Suction Tank	47270.7	1021.65	4.94048e-3	9.82326e-3	9.91217e-4	1.08223e-3

	Na2SO4		NaHCO3

Figure 17-45 Scaling tendencies

18. ScaleChem Interpreting Results

Overview

ScaleChem reports and displays data in a variety of forms. This information can be confusing to a new user. In this chapter we will examine the various types of output and interpret the meaning of that output.

Some of the data that is reported are reported in summaries and other data are reported in dialog boxes. We will look at several examples of each.

Valid Water Analysis Data

Using valid water (brine) analysis data is the key concept behind using ScaleChem. If the water analysis is not valid then the resulting calculations are not valid.

Assumptions

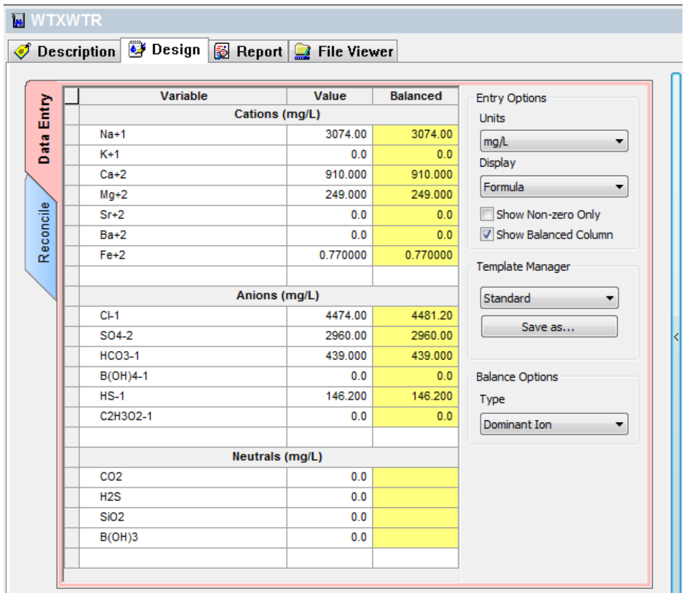
Reconciliations within the Water Analysis are assumed to be at ambient conditions, 77°F and 14.7 PSIA (25 °C and 1 atmosphere). The default temperature and pressure are set to ambient conditions.

Electroneutrality

Ionic concentrations, even when measured with the best available techniques, tend to have some degree of uncertainty associated with them. These uncertainties will results in an aqueous solution which, when the concentrations are summed together, appears to be not electrically neutral.

In addition to having uncertainties in the measured concentration, some ions may be misreported. For example, the pH of a solution may indicate that the dominant form of carbonate ion in solution should be bicarbonate ion but the reported value is carbonate ion. For the same mass, there is approximately twice as much negative charge in misreporting the carbonate ion.

Correcting for the Electroneutrality of a solution is essential for proper simulations. The following sample is not electrically neutral.

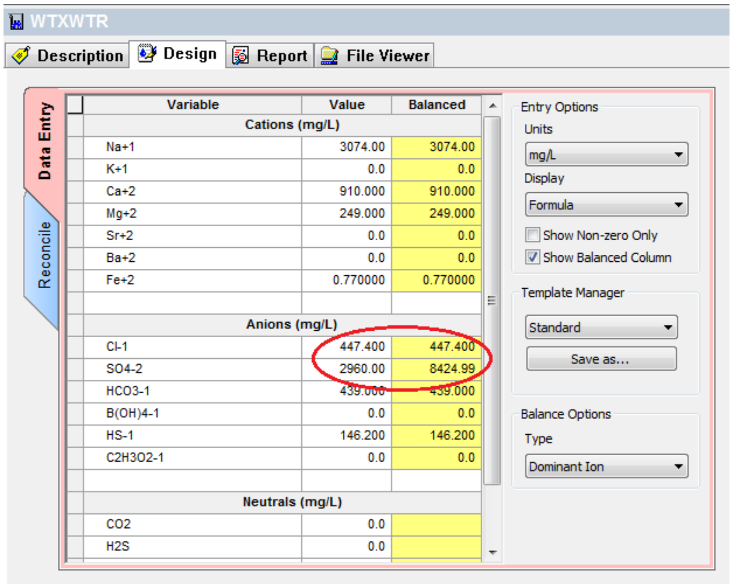


Variable	Value	Balanced
Cations (mg/L)		
Na+1	3074.00	3074.00
K+1	0.0	0.0
Ca+2	910.000	910.000
Mg+2	249.000	249.000
Sr+2	0.0	0.0
Ba+2	0.0	0.0
Fe+2	0.770000	0.770000
Anions (mg/L)		
Cl-1	4474.00	4481.20
SO4-2	2960.00	2960.00
HCO3-1	439.000	439.000
B(OH)4-1	0.0	0.0
HS-1	146.200	146.200
C2H3O2-1	0.0	0.0
Neutrals (mg/L)		
CO2	0.0	
H2S	0.0	
SiO2	0.0	
B(OH)3	0.0	

Entry Options
Units: mg/L
Display: Formula
☐ Show Non-zero Only
☑ Show Balanced Column
Template Manager: Standard
Save as...
Balance Options
Type: Dominant Ion

Figure 18-1 A non-electrically neutral sample

In ScaleChem we will receive a report of the required amount of material required to balance the sample in the yellow column headed as Balanced. Stream is balanced as soon as the components are entered.



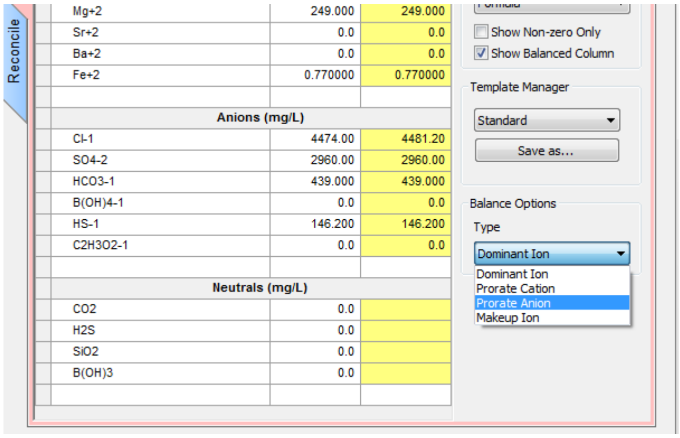
Variable	Value	Balanced
Cations (mg/L)		
Na+1	3074.00	3074.00
K+1	0.0	0.0
Ca+2	910.000	910.000
Mg+2	249.000	249.000
Sr+2	0.0	0.0
Ba+2	0.0	0.0
Fe+2	0.770000	0.770000
Anions (mg/L)		
Cl-1	447.400	447.400
SO4-2	2960.00	8424.99
HCO3-1	439.000	439.000
B(OH)4-1	0.0	0.0
HS-1	146.200	146.200
C2H3O2-1	0.0	0.0
Neutrals (mg/L)		
CO2	0.0	
H2S	0.0	

Entry Options
Units: mg/L
Display: Formula
☐ Show Non-zero Only
☑ Show Balanced Column
Template Manager: Standard
Save as...
Balance Options
Type: Dominant Ion

Figure 18-2 Switching of dominant ion

If Cl- quantity is change from 4474 to 447.4 then automatically SO4-2 ion becomes the dominant ion. And its balanced quantity increases by almost 5464

mg/L as opposed to 2960mg/L of SO4-2 ions.



Mg+2	249.000	249.000
Sr+2	0.0	0.0
Ba+2	0.0	0.0
Fe+2	0.770000	0.770000
Anions (mg/L)		
Cl-1	4474.00	4481.20
SO4-2	2960.00	2960.00
HCO3-1	439.000	439.000
B(OH)4-1	0.0	0.0
HS-1	146.200	146.200
C2H3O2-1	0.0	0.0
Neutrals (mg/L)		
CO2	0.0	
H2S	0.0	
SiO2	0.0	
B(OH)3	0.0	

☐ Show Non-zero Only
☑ Show Balanced Column

Type: Dominant Ion

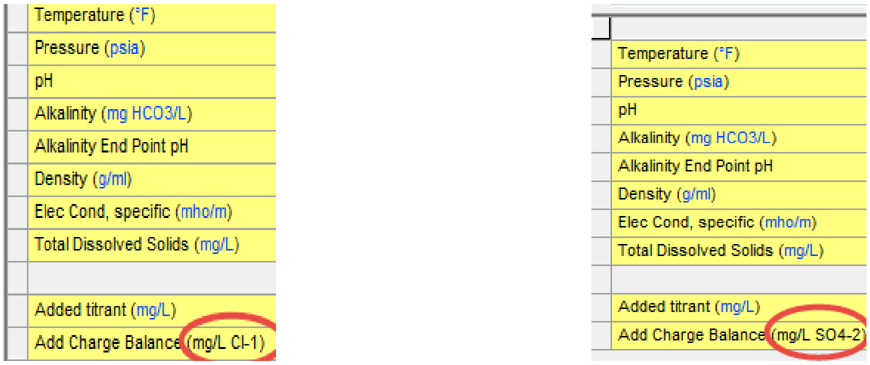
Figure 18-2a Balance options

This report shows us that 5464mg/l of SO4-2 ions must be added. Since the original sample only had 2960 mg/l of SO4-2 ion (see Figure 18-12a) there is probably an error.

In general, an added value of less than 10% of an ion concentration is acceptable. In this case we would have expected a value of less than 45 mg/l and that of chloride ion rather than Sulfate ion.

Another consideration is the type water that this analysis represents. This water is an aquifer water. The concentration of the sodium and chloride ions, on a mole basis, tends to be roughly equal. If we have 3074 mg/l of sodium (see Figure 18-1) or 134 mmoles (1000 mmoles =1 mole), then we would expect 4481 mg/l of chloride.

Therefore the concentration of the chloride seems to be in error. Perhaps a typographical error occurred either in the analysis or in the input. Change the value of the chloride concentration by increasing the number one order of magnitude from 447.4 mg/l chloride ion to 4474 mg/l chloride ion.



Temperature (°F)
Pressure (psia)
pH
Alkalinity (mg HCO3/L)
Alkalinity End Point pH
Density (g/ml)
Elec Cond, specific (mho/m)
Total Dissolved Solids (mg/L)

Added titrant (mg/L)
Add Charge Balance (mg/L Cl-1)

Temperature (°F)
Pressure (psia)
pH
Alkalinity (mg HCO3/L)
Alkalinity End Point pH
Density (g/ml)
Elec Cond, specific (mho/m)
Total Dissolved Solids (mg/L)

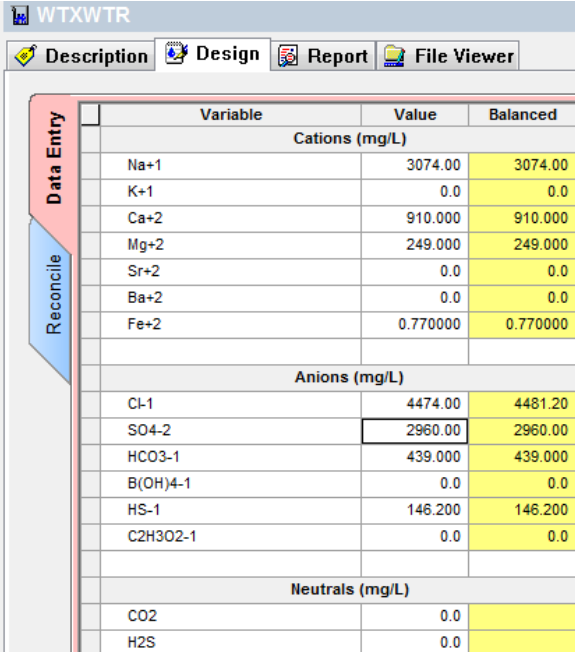
Added titrant (mg/L)
Add Charge Balance (mg/L SO4-2)

Figure 18-3 Reconcile tab when Chloride ion quantity is 4474 mg/L and Chloride ion is 447.4 mg/L(SO4-2 becomes adjustment parameter in the second image on the right).

Each species concentration has been altered.

!

Only the chloride concentration value changed



Variable	Value	Balanced
Cations (mg/L)		
Na+1	3074.00	3074.00
K+1	0.0	0.0
Ca+2	910.000	910.000
Mg+2	249.000	249.000
Sr+2	0.0	0.0
Ba+2	0.0	0.0
Fe+2	0.770000	0.770000
Anions (mg/L)		
Cl-1	4474.00	4481.20
SO4-2	2960.00	2960.00
HCO3-1	439.000	439.000
B(OH)4-1	0.0	0.0
HS-1	146.200	146.200
C2H3O2-1	0.0	0.0
Neutrals (mg/L)		
CO2	0.0	
H2S	0.0	

Figure 18-4 The chloride ion has been increased to 4474 mg/l

pH/Alkalinity

The pH of a solution is related to the alkalinity of the solution. In the simplest terms, the alkalinity is the acid neutralizing capacity of the solution. In practice we often refer to the alkalinity as the concentration of carbonate species in the sample.

The actual alkalinity experiment involves the titration of a known acid concentration against the sample. A predetermined Titration End Point (usually a pH of 4.5) is the end of the experiment. The Titration End Point is set sufficiently low to ensure that all of the neutralizing species in solution have been neutralized.

The pH/Alkalinity reconciliations have many options.

Reconciling pH/Alkalinity

The measured pH and alkalinity can be reconciled The user enters a measured pH and an alkalinity.

Alkalinity

The alkalinity can be entered as:
meq/l
mg/l as HCO3
mg/l as CaCO3

The units meq/l is the actual base capacity of the solution regardless of speciation. The units mg/l as HCO3 are the most common unit in the industry. It is important to note however, that the sample does not have to contain carbonates to have the alkalinity reported as HCO_3^-. The last unit, mg/l as CaCO3 is also used frequently.

Titration pH

The titration pH is the end point of the actual alkalinity experiment. Normally this value is a pH of 4.5. The only requirement here is that the alkalinity pH must be less than the measured pH. An error will occur if this is not true.

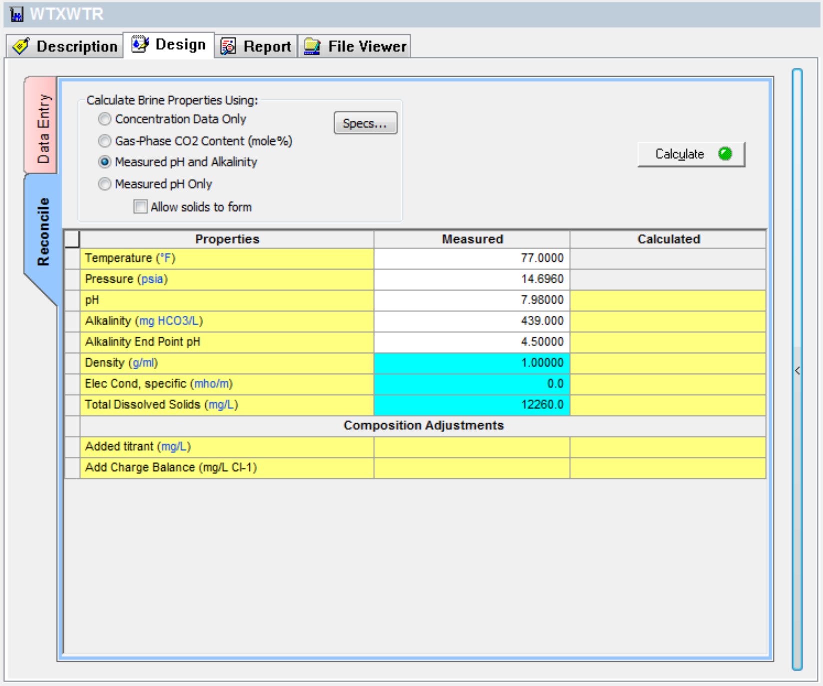
Clicking on ***Calculate*** will execute the procedure.

When the calculation is complete, ScaleChem will report the values required to reconcile the sample.

The calculated pH is somewhat higher than the measured pH. HCl will have to be added to adjust the pH.

The calculated alkalinity is approximately 700 mg/l as HCO_3^-

The reconciled values are approximately 159 mg/l HCl added and 183 mg/l of CO_2 removed



Calculate Brine Properties Using:

○ Concentration Data Only
○ Gas-Phase CO2 Content (mole%)
● Measured pH and Alkalinity
○ Measured pH Only
☐ Allow solids to form

Properties	Measured	Calculated
Temperature (°F)	77.0000	
Pressure (psia)	14.6960	
pH	7.98000	
Alkalinity (mg HCO3/L)	439.000	
Alkalinity End Point pH	4.50000	
Density (g/ml)	1.00000	
Elec Cond, specific (mho/m)	0.0	
Total Dissolved Solids (mg/L)	12260.0	
Composition Adjustments		
Added titrant (mg/L)		
Add Charge Balance (mg/L Cl-1)		

Figure 18-5 Reconciled pH and alkalinity

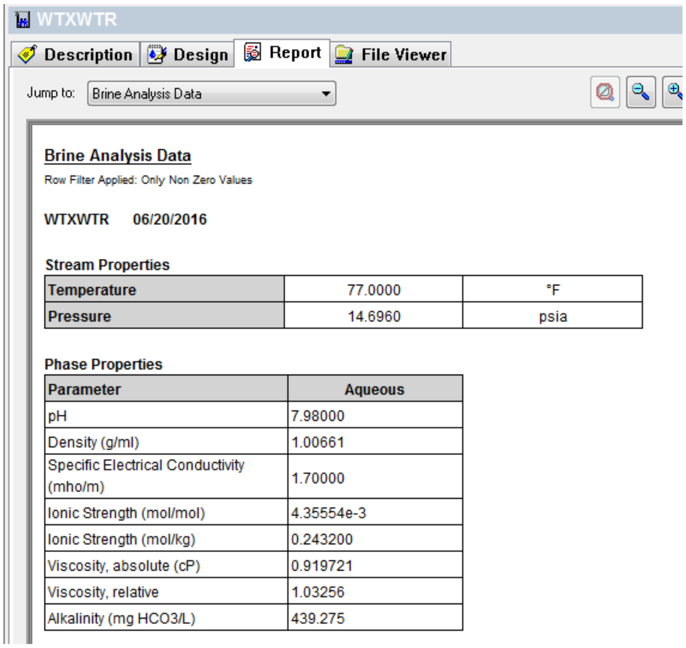
Calculating pH and Alkalinity

Sometimes it is desirable to determine the pH and alkalinity of the solution prior to reconciling.

Select the Equilibrium option

Click on ***Calculate*** to begin.

ScaleChem will then return the calculated pH and alkalinity.



Jump to: Brine Analysis Data

Brine Analysis Data

Row Filter Applied: Only Non Zero Values

WTXWTR 06/20/2016

Stream Properties

Temperature	77.0000	°F
Pressure	14.6960	psia

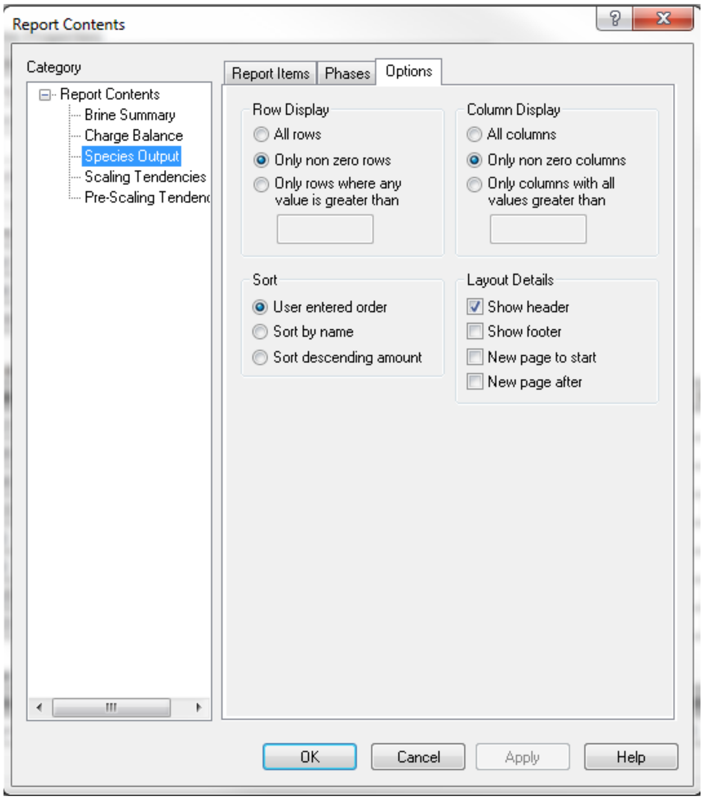
Phase Properties

Parameter	Aqueous
pH	7.98000
Density (g/ml)	1.00661
Specific Electrical Conductivity (mho/m)	1.70000
Ionic Strength (mol/mol)	4.35554e-3
Ionic Strength (mol/kg)	0.243200
Viscosity, absolute (cP)	0.919721
Viscosity, relative	1.03256
Alkalinity (mg HCO3/L)	439.275

Figure 18-6 Calculated pH and alkalinity.

Speciation

The display of the ionic species can be altered to meet user requirements. By default the display of the ionic species are the standard list and the reconciled values.



Row Display
○ All rows
● Only non zero rows
○ Only rows where any value is greater than

Column Display
○ All columns
● Only non zero columns
○ Only columns with all values greater than

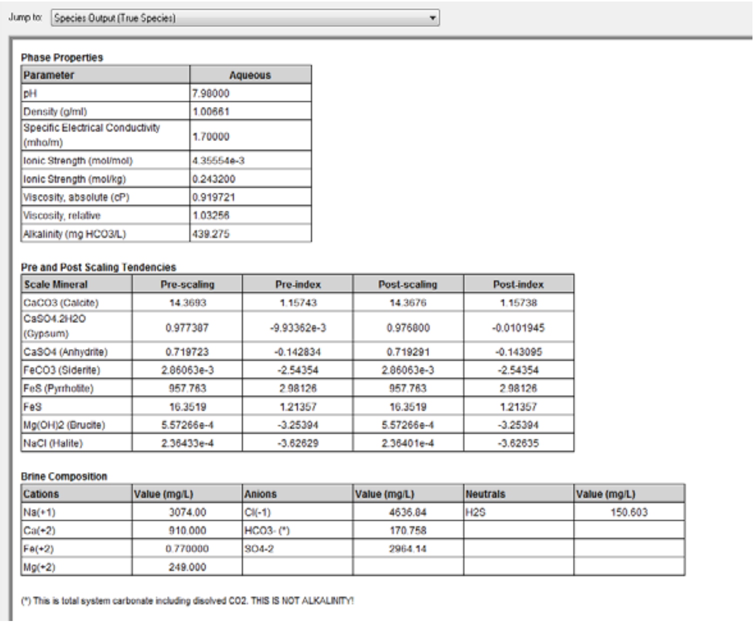
Sort
● User entered order
○ Sort by name
○ Sort descending amount

Layout Details
☑ Show header
☐ Show footer
☐ New page to start
☐ New page after

Figure 18-7 The default species display

Default Speciation Display

See **Chapter 2: Thermodynamics** for a more complete description of the standard chemistry.



Phase Properties

Parameter	Aqueous
pH	7.98000
Density (g/ml)	1.00661
Specific Electrical Conductivity (mho/m)	1.70000
Ionic Strength (mol/mol)	4.35554e-3
Ionic Strength (mol/kg)	0.243200
Viscosity, absolute (cP)	0.919721
Viscosity, relative	1.03256
Alkalinity (mg HCO3/L)	439.275

Pre and Post Scaling Tendencies

Scale Mineral	Pre-scaling	Pre-index	Post-scaling	Post-index
CaCO3 (Calcite)	14.3693	1.15743	14.3676	1.15738
CaSO4.2H2O (Gypsum)	0.977387	-9.93362e-3	0.976800	-0.0101945
CaSO4 (Anhydrite)	0.719723	-0.142834	0.719291	-0.143095
FeCO3 (Siderite)	2.86063e-3	-2.54354	2.86063e-3	-2.54354
FeS (Pyrrhotite)	957.763	2.98126	957.763	2.98126
FeS	16.3519	1.21357	16.3519	1.21357
Mg(OH)2 (Brucite)	5.57266e-4	-3.25394	5.57266e-4	-3.25394
NaCl (Halite)	2.36433e-4	-3.62629	2.36401e-4	-3.62635

Brine Composition

Cations	Value (mg/L)	Anions	Value (mg/L)	Neutrals	Value (mg/L)
Na(+1)	3074.00	Cl(-1)	4636.84	H2S	150.603
Ca(+2)	910.000	HCO3- (*)	170.758		
Fe(+2)	0.770000	SO4-2	2964.14		
Mg(+2)	249.000				

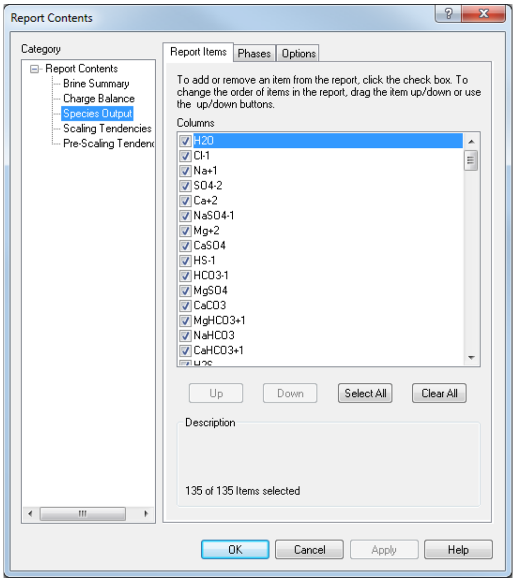
(*) This is total system carbonate including disolved CO2. THIS IS NOT ALKALINITY!

Figure 18-8 The standard display

Expanded Species Display

Click on Customize under the report tab. Click on ***Species output*** and then by checking boxes before the species name will display ***Species List***. Click on ***OK*** to redisplay the **Report** tab.

The expanded species lists are scrollable



To add or remove an item from the report, click the check box. To change the order of items in the report, drag the item up/down or use the up/down buttons.

☑ H2O
☑ Cl-1
☑ Na+1
☑ SO4-2
☑ Ca+2
☑ NaSO4-1
☑ Mg+2
☑ CaSO4
☑ HS-1
☑ HCO3-1
☑ MgSO4
☑ CaCO3
☑ MgHCO3+1
☑ NaHCO3
☑ CaHCO3+1

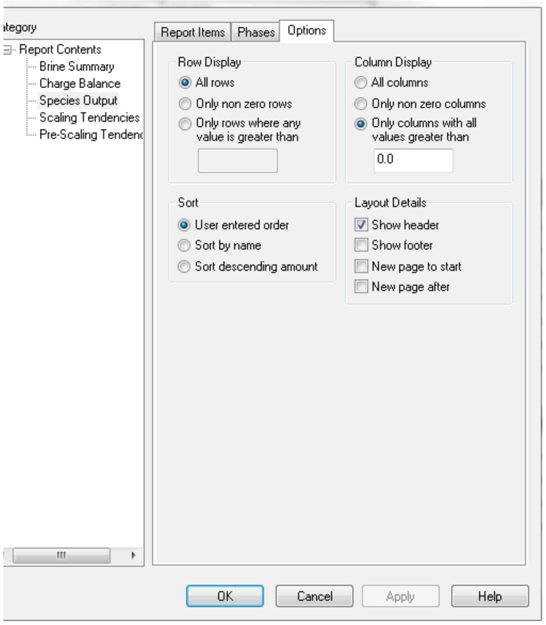
135 of 135 Items selected

Figure 18-9 Displaying the Expanded Species lists

The complete list of the expanded ions can be found in **Chapter 2: Thermodynamics.**

The Non-Zero species Display

Sometimes viewing species with zero concentrations can be difficult to read. The Species Display dialog allows the user to mask zero valued species. Customize report-> Species Output->Options leads to display options where we can select to view species only greater than value 0. Column and rows are adjustable according to the user's preference.



Row Display
● All rows
○ Only non zero rows
○ Only rows where any value is greater than

Column Display
○ All columns
○ Only non zero columns
● Only columns with all values greater than
0.0

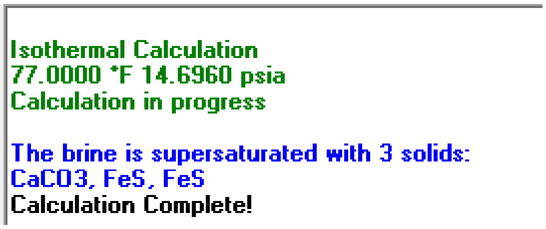
Sort
● User entered order
○ Sort by name
○ Sort descending amount

Layout Details
☑ Show header
☐ Show footer
☐ New page to start
☐ New page after

Figure 18-10 Water Analysis with zero values masked

Supersaturation of Solids

Frequently a measurement of a water sample (brine) may have a small uncertainty associated with the measurement. This uncertainty, especially when the sample was in contact with solid minerals, may lead to ScaleChem reporting that the sample is supersaturated.



```
Isothermal Calculation
77.0000 °F 14.6960 psia
Calculation in progress

The brine is supersaturated with 3 solids:
CaCO3, FeS, FeS
Calculation Complete!
```

Figure 18-11 A warning that the sample is supersaturated.

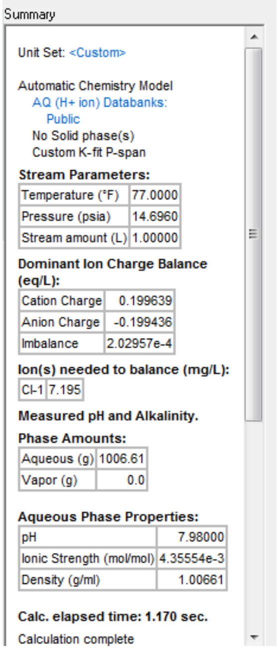
Summary Content

Reconciliation summary

Water Analysis

The results of a reconciliation for pH, alkalinity and neutrality are reported for each sample.

This field has been "Scrolled Down" to display the dew point temperature



Summary

Unit Set: <Custom>

Automatic Chemistry Model
  AQ (H+ ion) Databanks:
    Public
  No Solid phase(s)
  Custom K-fit P-span

Stream Parameters:

Temperature (°F)	77.0000
Pressure (psia)	14.6960
Stream amount (L)	1.00000

Dominant Ion Charge Balance (eq/L):

Cation Charge	0.199639
Anion Charge	-0.199436
Imbalance	2.02957e-4

Ion(s) needed to balance (mg/L):

Cl-1	7.195

Measured pH and Alkalinity.

Phase Amounts:

Aqueous (g)	1006.61
Vapor (g)	0.0

Aqueous Phase Properties:

pH	7.98000
Ionic Strength (mol/mol)	4.35554e-3
Density (g/ml)	1.00661

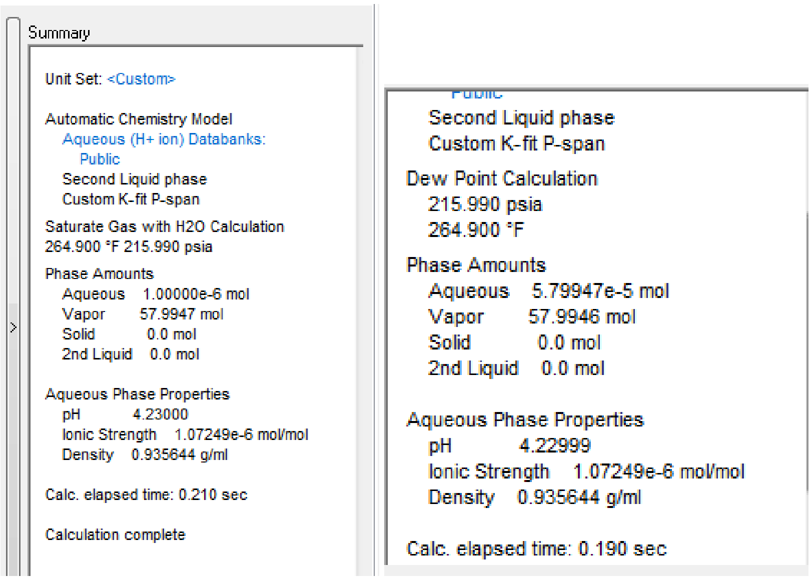
Calc. elapsed time: 1.170 sec.

Calculation complete

Figure 18-12 The summary for a water analysis

Gas Analysis

The information that can be displayed for a gas analysis is rather limited. Unless a **Dew Point** calculation had been performed, the output is an echo of the input.



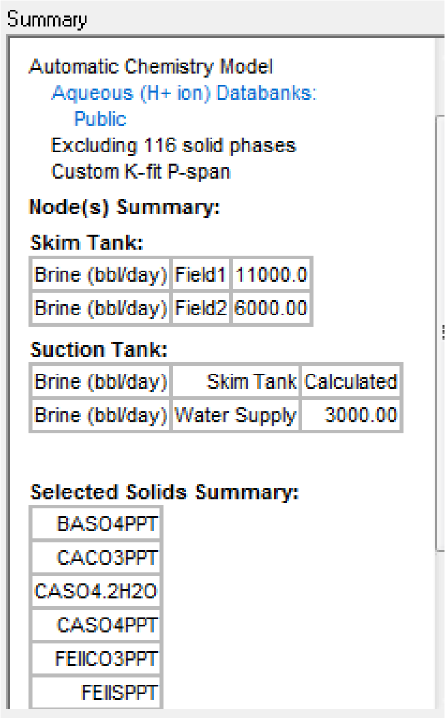
```
Summary

Unit Set: <Custom>

Automatic Chemistry Model
  Aqueous (H+ ion) Databanks:
    Public
  Second Liquid phase
  Custom K-fit P-span
Saturate Gas with H2O Calculation
264.900 °F 215.990 psia
Phase Amounts
  Aqueous   1.00000e-6 mol
  Vapor     57.9947 mol
  Solid     0.0 mol
  2nd Liquid  0.0 mol

Aqueous Phase Properties
  pH        4.23000
  Ionic Strength   1.07249e-6 mol/mol
  Density   0.935644 g/ml

Calc. elapsed time: 0.210 sec

Calculation complete
```

```
  Second Liquid phase
  Custom K-fit P-span
Dew Point Calculation
  215.990 psia
  264.900 °F
Phase Amounts
  Aqueous   5.79947e-5 mol
  Vapor     57.9946 mol
  Solid     0.0 mol
  2nd Liquid  0.0 mol

Aqueous Phase Properties
  pH        4.22999
  Ionic Strength   1.07249e-6 mol/mol
  Density   0.935644 g/ml

Calc. elapsed time: 0.190 sec
```

Figure 18-13 Gas Analysis Summary and the Dew Point summary

Node Summary

The brines and/or gases collected at the node are displayed along with the flow rate of each item. The temperature and pressure of the node is also displayed.


Summary

Automatic Chemistry Model

Aqueous (H+ ion) Databanks:

Public

Excluding 116 solid phases

Custom K-fit P-span

Node(s) Summary:

Skim Tank:

Brine (bbl/day)	Field1	11000.0
Brine (bbl/day)	Field2	6000.00

Suction Tank:

Brine (bbl/day)	Skim Tank	Calculated
Brine (bbl/day)	Water Supply	3000.00

Selected Solids Summary:

BASO4PPT
CACO3PPT
CASO4.2H2O
CASO4PPT
FEIICO3PPT
FEIISPPT

Figure 18-14 Node Summary Report

Overview of ScaleChem Output

There are three types of output which a user can request after a ScaleChem calculation: Plot, Reports, or File Viewer.

Summaries

Summaries is the default ScaleChem output. It is located on the right most corner of the software window under the calculate button.

After a successful calculation, internal files produced by the OLI Solver are scanned for available sections of data which can be viewed. A list of the available sections is displayed when customize section is clicked open under the reports tab. This includes check boxes which can include, or eliminate a section in the report.

Report Section Selection

Clicking on the individual check boxes toggles between including and eliminating that section from the report.

Facilities Summary

Report for each node and dropped phases are shown.

Pre-Scaling tendencies

Solids to be displayed can be chosen from an extensive list of possible precipitants.

Scaling Tendencies

Sorting options are more to choose from. TRANGES can be displayed. The solids analysis gives a report of the solids which precipitated (Scaled out), and of the pre-precipitation and post-precipitation scaling tendency.

If the solid was not selected as a possible precipitate, but if the scaling tendency is greater than 1.0E-04, the solid is included in the analysis list. The amount of solid precipitated is left as 0.0, and the scaling tendency is reported.

Survey Parameters

Stream Amount, Temperature, pressure etc is reported.

OLI Speciation Report

When this report is available, the full speciation which the OLI Solver uses to perform an equilibrium calculation is given. This report is activated by requesting detailed output, using the Tools… Options menu choice.

Convergence Pattern

When this report is available, the mathematical convergence pattern which was used in performing the equilibrium calculation is given. This report is not normally requested. It is included as a debugging aid when trying to identify convergence problems. This report is activated by requesting detailed output, using the Tools.. Option menu choice.

Plot

To view ScaleChem Plot Options click on Plot tab. This is located next to the design tab. This will show a default plot.

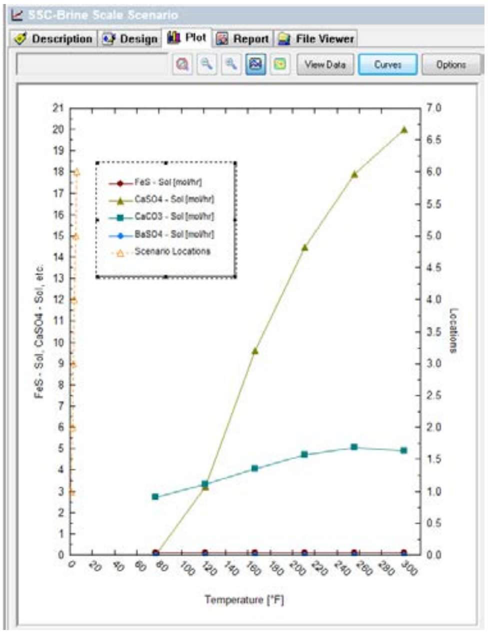


Figure 18-15 Displaying the Default plot

Determining the Default Plot

After returning from the OLI Solver, ScaleChem analyzes the output file to determine an acceptable default plot. The precedence followed is this:

X axis Variable
If the temperature varying, use Temperature
else if Pressure varying, use Pressure else use
Case number or Mix Ratio

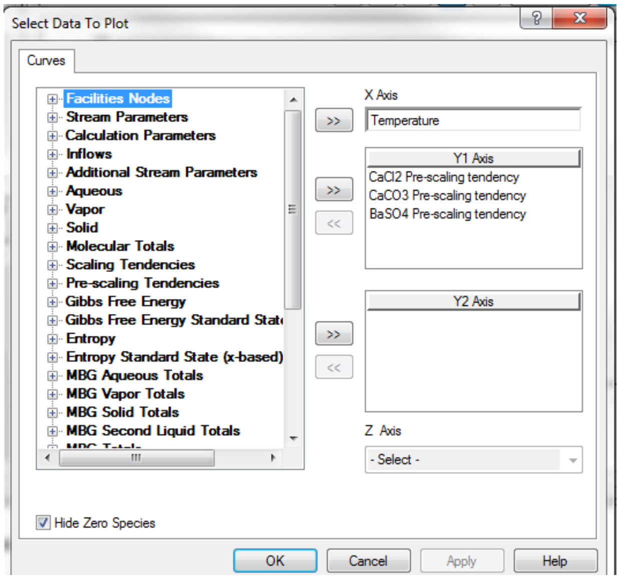
Y axis variable
If any precipitates, use the solids
else user any pre-scaling indices > 0
to a maximum of 8 variables

Viewing Data

The data which is used to create the plot can be viewed by using the View Data button. In general, the View Data button shows the report which has been created. Use the View Plot button to return to the plot.

Selecting Data

To add to the variables displayed or to change the variables which are displayed, use the Select Data button, which is to the right of the Plot. Right click on the X or Y axis will pop up a format plot window. It has options like Format X-axis, Adjust Scale, Label Axes etc. Curves Button will prompt a Select data window.



X Axis: Temperature

Y1 Axis:
CaCl2 Pre-scaling tendency
CaCO3 Pre-scaling tendency
BaSO4 Pre-scaling tendency

☑ Hide Zero Species

Figure 18-16 Selecting Data

Data Available

The list of variables which can be displayed are shown as Data Available. Stream parameters include Temperature and Pressure etc. Additional Stream parameters contain density, viscosity etc.

Selecting Data

To select different X and Y axis variables, highlight the variable in the Data Available box, and then click on >> button either before X or Y Axis. Of course, variables can also be removed from the axis variables by highlighting the selected variable, and clicking the << button.

Minimum Data Required

A minimum of one X variable and one Y variable must be selected from the Select Data facility, in order to leave Select Data. Of course, you always have the option of canceling, and returning to the original plot.

19. Scope of Corrosion Analyzer

Overview

Corrosion Analyzer™ is a component of OLI Studio, which is OLI’s Microsoft Windows™ based simulation software. Corrosion Analyzer has evolved from the Corrosion Simulation Program (CSP) developed in the latter half of the 1990’s.

The purpose of the CSP project was multifold:

- To create generalized “real solution” stability diagrams.
- Develop a comprehensive redox databank.
- To create a thermodynamic model for alloys.
- To develop a rates-of-corrosion model.
- Create a model for growth and breakdown of passive films.
- Create a model for localized corrosion.
- Create a model for predicting the time evolution of corrosion using extreme value statistics.

Much of the projected goals of the original CSP project have been completed but there is still much to do. Starting in year 1999, the CSP program was converted, with much effort, to Corrosion Analyzer.

This course assumes that the user is familiar with the basic functionality of OLI Studio. Many of the calculation techniques described in the OLI Studio User Guide are also used in Corrosion Analyzer.

Thermodynamics of Corrosion

The thermodynamics of corrosion is predicted using the traditional OLI thermodynamic model along with specific enhancements required for the Corrosion Analyzer. Specifically, the thermodynamics of corrosion answers the following questions:

1. When are metals immune to corrosion?
2. When can they passivate?

The tool that answers these questions is *Stability diagrams.*

Kinetics of general corrosion

Once the thermodynamics of corrosion have been determined, we would like to be able to predict rate of corrosion. Extensive research has been completed by OLI

Systems, Inc. in this area and will be discussed in later chapters. Specifically the question asked is:

What is the rate of corrosion?

A large database of corrosion data has been fit for this question. The program will determine amount of material that will corrode, in a generalized setting.

Other phenomena

Several other thermodynamic properties (not required to solve the equilibrium based model) were also developed for both the stability and rate of corrosion. Some of these phenomena are:

- Electrical conductivity
- Viscosity
- Diffusivity

Real-solution stability diagrams

The design goals of real-solution stability diagrams are:

- To predict the stability of metals, metal ions, oxides, etc. as a function of T, P and solution composition.
- Draw conclusions about the ranges of immunity to corrosion, possible passivation and dissolution of metals in the presence of species that promote or inhibit corrosion.

Some of the features of a real-solution stability diagram are:

- Potential versus pH with other variables fixed (a real-solution analog of the Pourbaix diagrams)
- Potential versus concentrations of active species (either inflows or species in equilibrium)
- Predominance areas as functions of concentrations of selected species without using E as an independent variable

Assumptions

We assume that you are already familiar with the OLI Studio software. We will not go into great discussions about how to use the software unless it is related to corrosion.

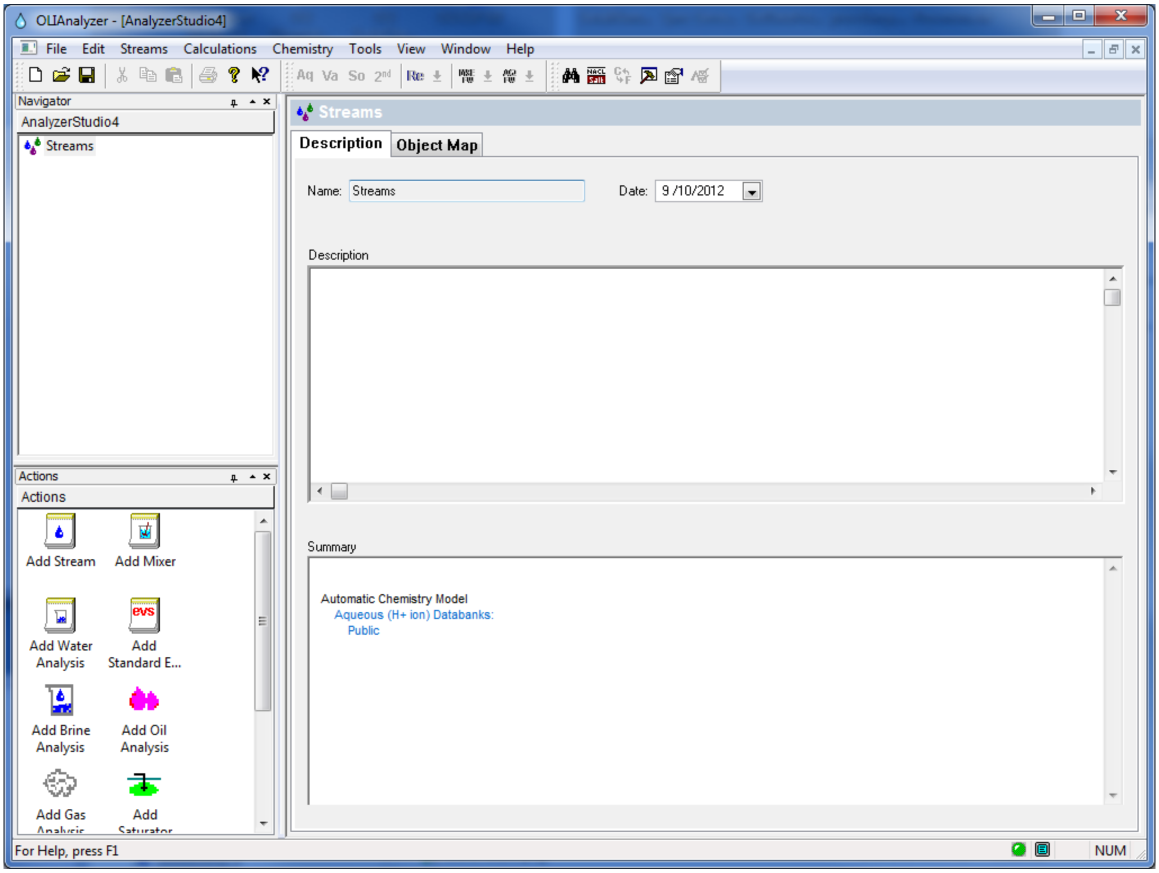
20. Generating Stability Diagrams in Corrosion Analyzer

An Example

Before we go into detail on how the diagram is created and how to interpret the results, we will walk through a sample stability diagram calculation for metallic iron in pure water at 25 °C and 1 atmosphere.

We begin by double-clicking the OLI Studio icon on the desktop or by using the Start menu.

- **Click** on the ***Add Stream*** icon.



Name: Streams

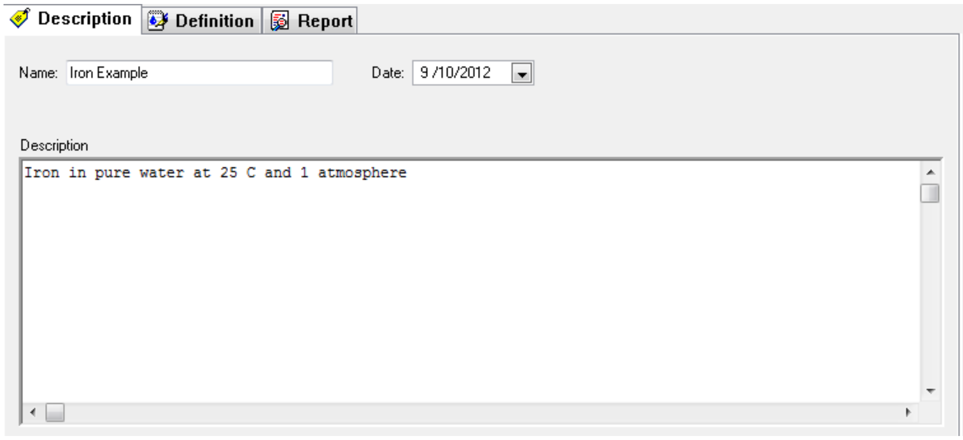
Date: 9 /10/2012

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

Figure 20-1 The OLI Studio main window.

- ***Click*** on the **Description** tab.

The **Description** tab is similar in functionality to other OLI software products. It is recommended that the user enter descriptive information to later identify the calculation and the streams.



Name: Iron Example

Date: 9 /10/2012

Description

```
Iron in pure water at 25 C and 1 atmosphere
```

Figure 20-2 The Description tab.

- Enter some descriptive information.
- Click on the **Definition** tab.

You may use the **Tools->Names Manager** menu option to change the display of the species.

If the units are not in moles, centigrade and atmospheres, select **Tools->Units Manager** and then select the **Standard** radio button. Select **Metric, moles** from the drop down box.

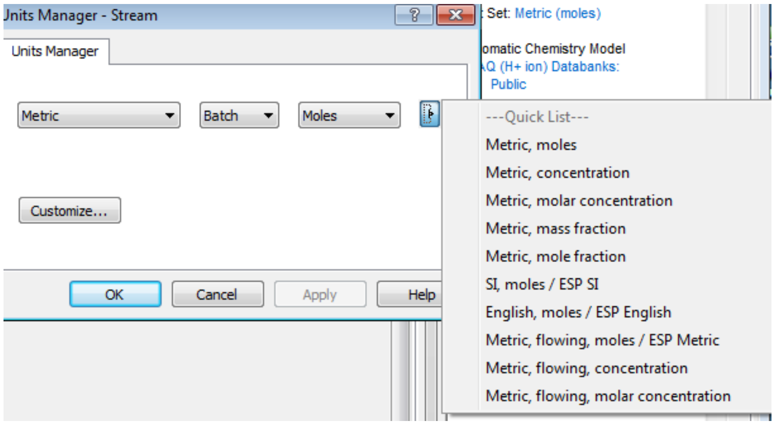
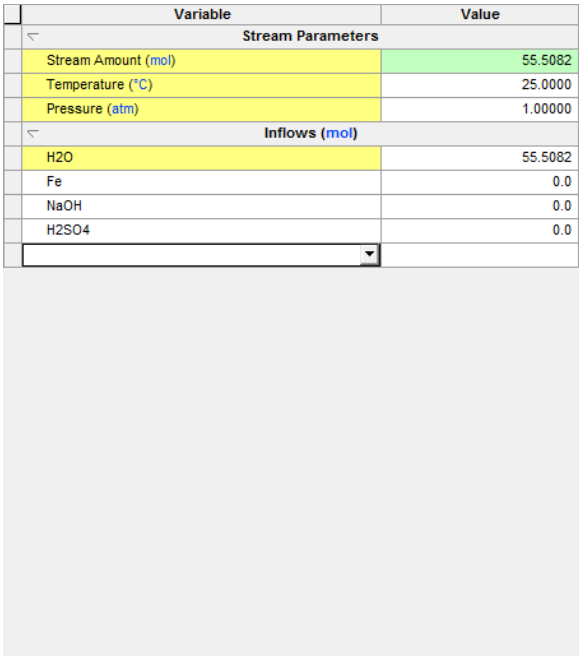


Figure 20-3 Units Manager

Enter ***Iron, Sodium Hydroxide*** and ***Sulfuric Acid*** to the grid as shown in Figure 20-4[44].

---

[44] Depending on the settings for names manager, the displayed names may be formulas or names.

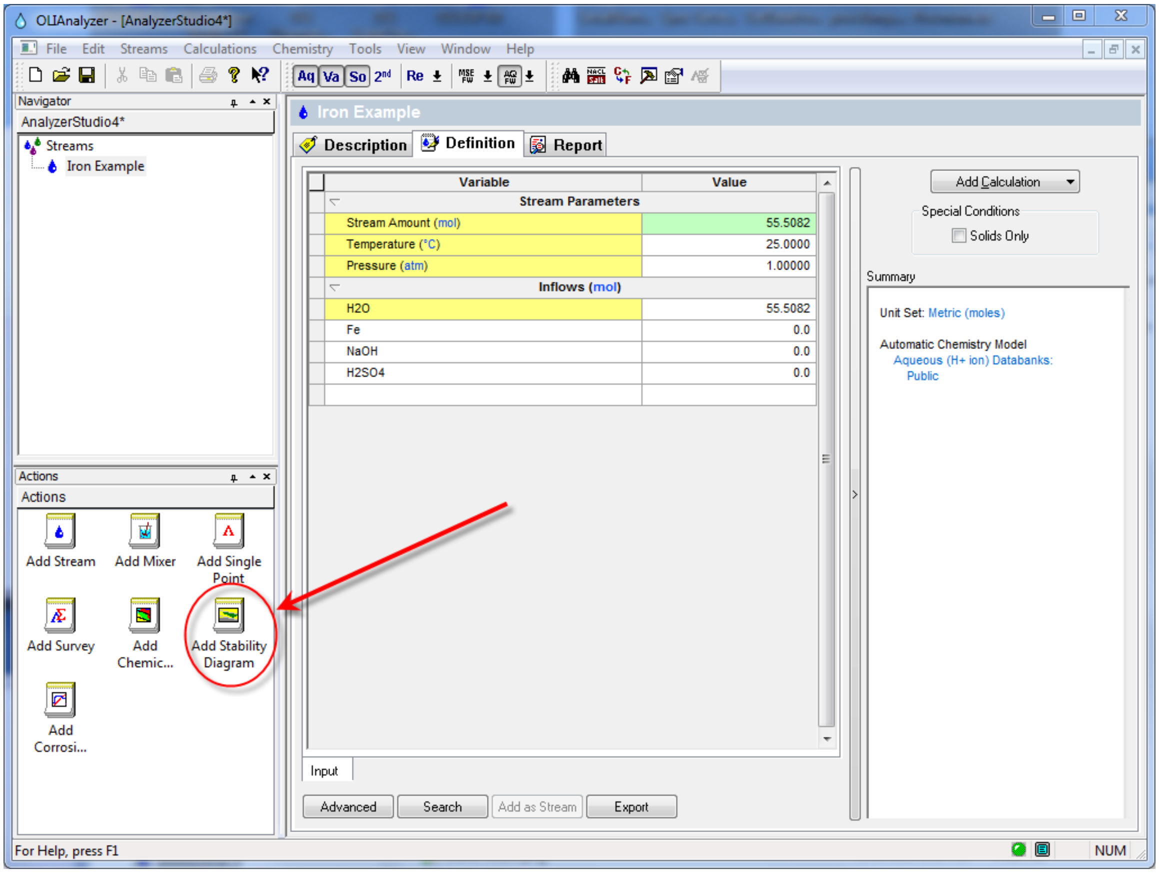


Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Fe	0.0
NaOH	0.0
H2SO4	0.0

Figure 20-4 The stream definition tab.

We are now ready to add a stability diagram to the calculation.

Click on the **Add Stability Diagram** icon in the Explorer/Actions panel.



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
NaOH	0.0
H2SO4	0.0

☐ Solids Only

Unit Set: Metric (moles)

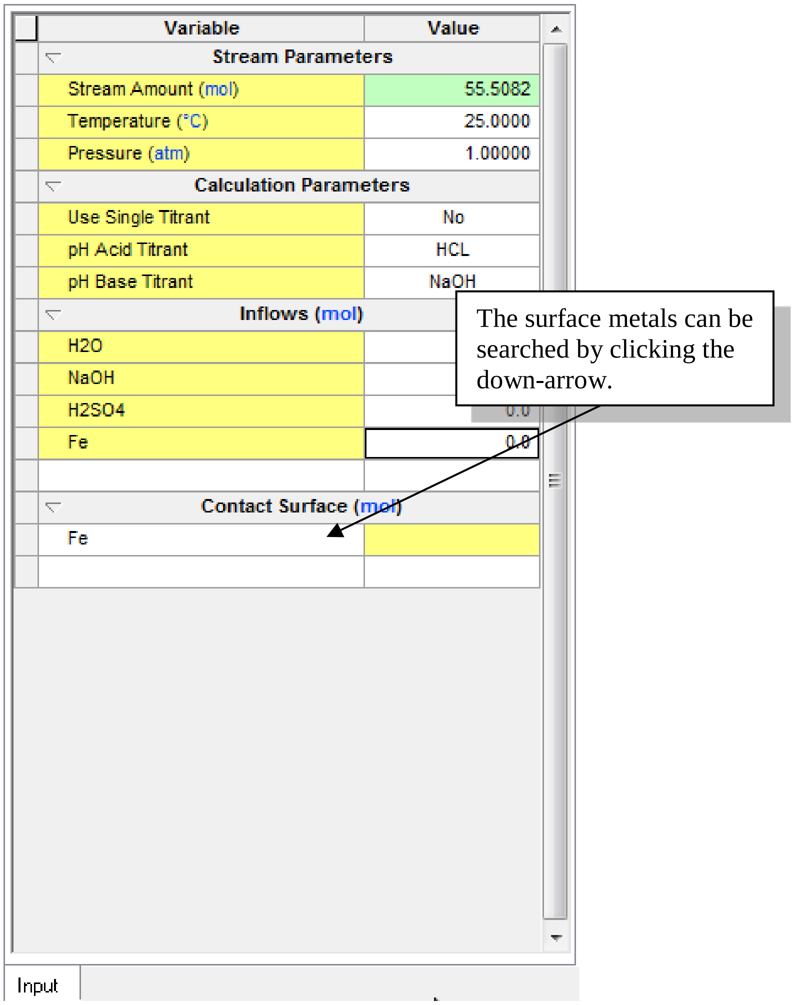
Automatic Chemistry Model
Aqueous (H+ ion) Databanks:
Public

Figure 20-5 Adding a stability diagram.

Add a description if necessary by clicking on the **Description** tab. Otherwise, click on the **Definition** tab.

The diagram definition is not complete when you first enter the grid. The metal of interest (in this case iron) must be defined to the calculation as the surface metal. The pH titrants must also be defined (The defaults are HCl and NaOH)

Enter ***Fe*** as 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	
NaOH	
H2SO4	0.0
Fe	0.0
Contact Surface (mol)	
Fe	

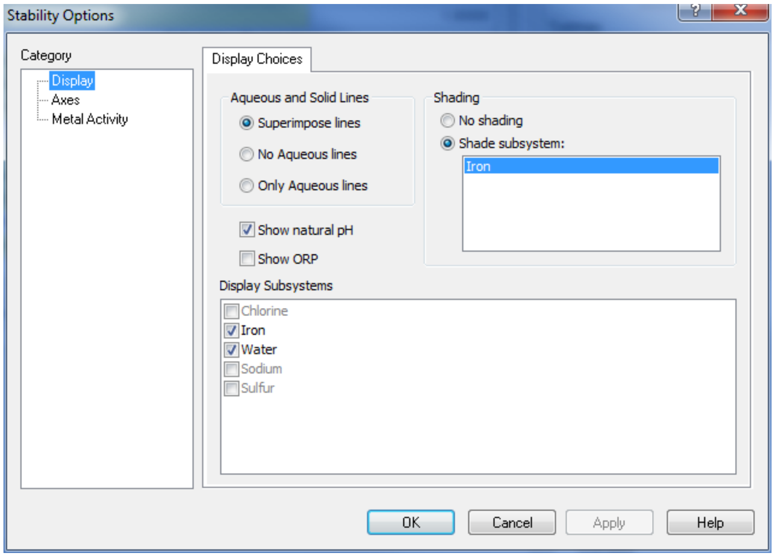
The surface metals can be searched by clicking the down-arrow.

Figure 20-6 The stability diagram Definition tab.

Now we need to set up the titrants and ranges of calculations. We do not want to use HCl (hydrochloric acid) since the chloride ion complexes with both ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions and will clutter our diagram.

Click on the **Specs…** button

The **Specs…** button has several tabs that should be reviewed.



Aqueous and Solid Lines
● Superimpose lines
○ No Aqueous lines
○ Only Aqueous lines

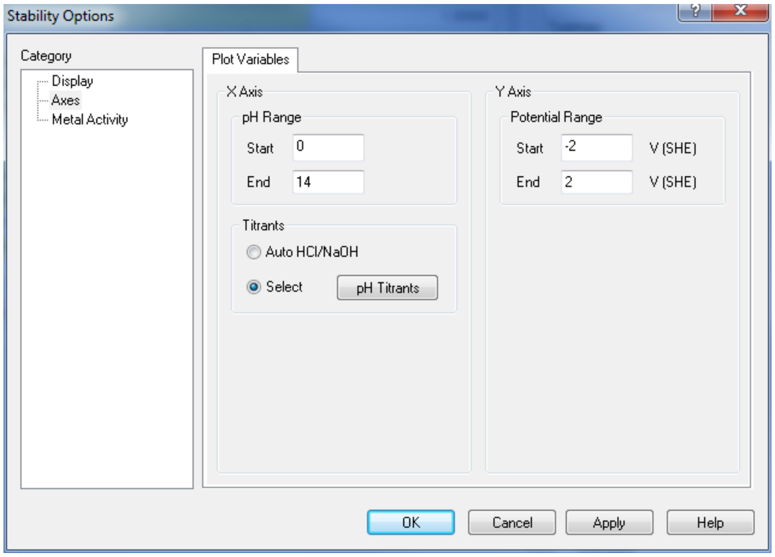
☑ Show natural pH
☐ Show ORP

Shading
○ No shading
● Shade subsystem:
Iron

Display Subsystems
☐ Chlorine
☑ Iron
☑ Water
☐ Sodium
☐ Sulfur

Figure 20-7 The X-variable Tab

Click on the **Axes** category. Choose the **Select** radio button in the **Titrants** section. This will enable the **pH Titrants** button.



X Axis
pH Range
Start 0
End 14

Titrants
○ Auto HCl/NaOH
● Select

Y Axis
Potential Range
Start -2 V (SHE)
End 2 V (SHE)

Figure 20-8 enabling the titrants button.

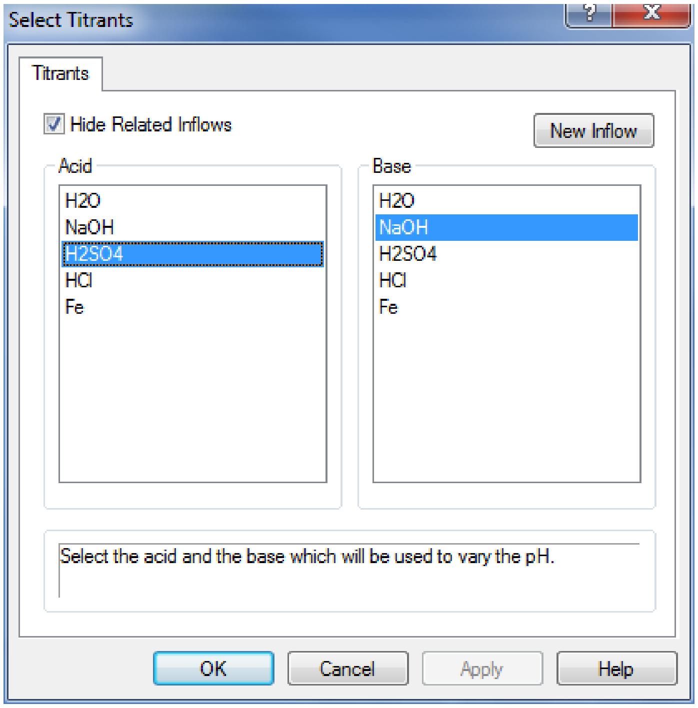
We wish to use sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) to adjust the pH.

Click on the **pH Titrants** button

As will other OLI applications, you can select an acid and a base.

Select **Sulfuric Acid (H_2SO_4)** as the acid titrant

Select **Sodium hydroxide (NaOH)** as the base titrant



☑ Hide Related Inflows

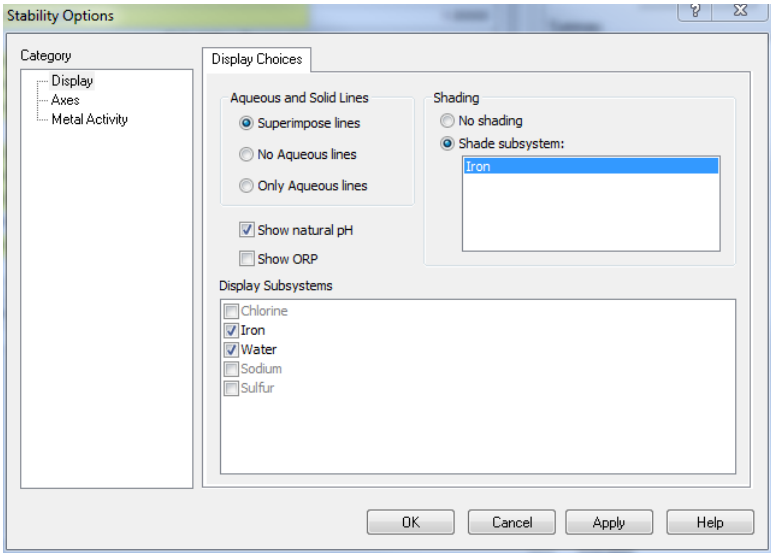
Acid	Base
H2O	H2O
NaOH	NaOH (selected)
H2SO4 (selected)	H2SO4
HCl	HCl
Fe	Fe

Select the acid and the base which will be used to vary the pH.

Figure 20-9 Selecting sulfuric Acid and sodium hydroxide as titrants

Click on the **OK** button

Click on the **Display** category. Look for the **Display Subsystems** section.



Aqueous and Solid Lines
● Superimpose lines
○ No Aqueous lines
○ Only Aqueous lines

☑ Show natural pH
☐ Show ORP

Shading
○ No shading
● Shade subsystem:
Iron

Display Subsystems
☐ Chlorine
☑ Iron
☑ Water
☐ Sodium
☐ Sulfur

Figure 20-10 Selecting displayed subsystems (using defaults)

The display of particular oxidation and reduction species and be turned on and off with the subsystems options. We want to see the various oxidation states of iron.

Check ***Iron*** and ***Water.***

Look for the **Shading** section. Ensure that **Shade subsystems:** is selected.

.

The user as some control over how the stability diagram will display. In this case we will accept the defaults.

Click **OK**

We are now returned to the **Definition**. The **Calculate** light should now be green.

Click **Calculate**

The program will run for several moments and finish.

Click on the **Stability Diagram** tab.

The following diagram is the stability diagram for Iron in pure water at 25 centigrade and 1 atmosphere. These diagrams are also referred to as Pourbaix diagrams.[45]

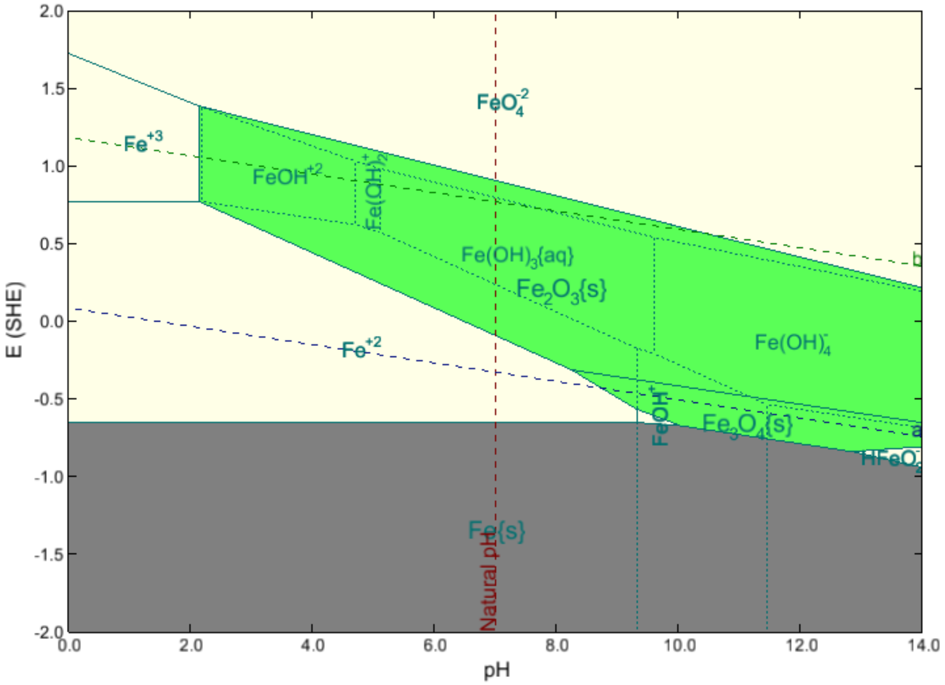


Figure 20-11 The finished stability diagram

How to Use Stability Diagrams

What is a redox subsystem?

- A set of species that contain a given element in all possible oxidation states.

Example: The iron subsystem consists of all species that contain Fe^{o}, Fe^{2+} and Fe^{3+}.

What are the solid lines?

- Boundaries between stability areas of a solid and an aqueous species or two aqueous species.
- Boundary between an aqueous and a solid species: A solid starts to precipitate or dissolve in an aqueous phase.
- Boundary between two aqueous species: The conditions for which the activities of the species are equal.

What are the dashed lines?

- Boundaries between stability areas of two aqueous species that coexist with at least one solid phase.

---

[45] Marcel Pourbaix, “Atlas of Electrochemical Equilibria in Aqueous Solutions”. Translated from the French by James. A. Franklin. Pergamon Press, Oxford (1965).

- They are found only within the stability ranges of solids.

What are the areas delimited by the solid lines?

- Stability fields of solid or aqueous species.
- If the conditions are within the stability field of a solid, the solid is stable and usually coexists with an aqueous phase

If the conditions are within the stability field of an aqueous species, no solid can be stable and this species is predominant in the solution.

What are the areas delimited by dashed lines?

- Stability fields of predominant aqueous species that coexist with one or more solid phases.
- Dashed lines can be found only within the stability fields of solid species.

Names of aqueous species that are predominant only in the presence of a solid phase but not in a homogeneous solution are printed with small characters. What is the line denoted by a?

- Equilibrium state between H^+ and H_2^0:
    - The oxidized form (i.e., H^+) is stable above this line;
    - The reduced form (i.e., H_2^0) is stable below it.

What is the line denoted by b?

- Equilibrium state between O_2^0 and O^{2-}:
    - The oxidized form (i.e., O_2^0) is stable above this line;
    - The reduced form (i.e., O^{2-}) is stable below it.

Water (which is a combination of H^+ and O^{2-}) is stable between ***a*** and ***b***.

Why is it useful to view a superposition of diagrams for selected subsystems?

- Corrosion is observed when oxidation of the metal of interest leads to the formation of soluble metal species and can occur simultaneously with some reduction reaction.
- Similarly, passivation is observed when the oxidation of the metal leads to the formation of a protective layer of a sparingly soluble compound.
- A line that represents a reduction reaction (e.g., reduction of atmospheric oxygen to water) must lie above the line that represents an oxidation reaction (e.g., oxidation of a metal to aqueous ions or a potentially passivating oxide).
- The corrosion potential will establish itself somewhere between the equilibrium potentials for the oxidation and reduction reactions.

- Thus, it is possible to find out whether a certain species from one subsystem can be oxidized and, simultaneously, a certain species from the other system can be reduced.

What is the range of immunity to corrosion?

Stability field of elemental metal.

What is the range of corrosion?

Stability fields of dissolved (ionic or neutral) metal species in which neither the metal nor passivating solids are stable.

What is the range of possible passivation?

Stability field of a sparingly soluble compound (usually an oxide or hydroxide or salt).

- This compound will form a layer on the surface of the metal, which may protect the metal from corrosion.
- Having determined that a layer is formed, it is necessary to verify whether it is protective or not because this depends on the crystalline structure of the sparingly soluble compound.

How to determine whether corrosion in the absence of oxygen is possible?

- In the absence of oxygen, the most common reduction reaction is the reduction of the proton to elemental hydrogen (as shown by line a)•For a corrosion process to proceed, the line a must lie above a line that corresponds to an equilibrium between the metal and metal-containing ions.
- In oxygen-containing solutions, O_2^0 can be reduced to H_2O (line ***b***)
- For a corrosion process to occur, the line b must lie above a line that corresponds to an equilibrium between the metal and metal-containing ions.
- Passivation is likely if ***b*** lies above a line that corresponds to an equilibrium between the metal and a sparingly soluble compound.

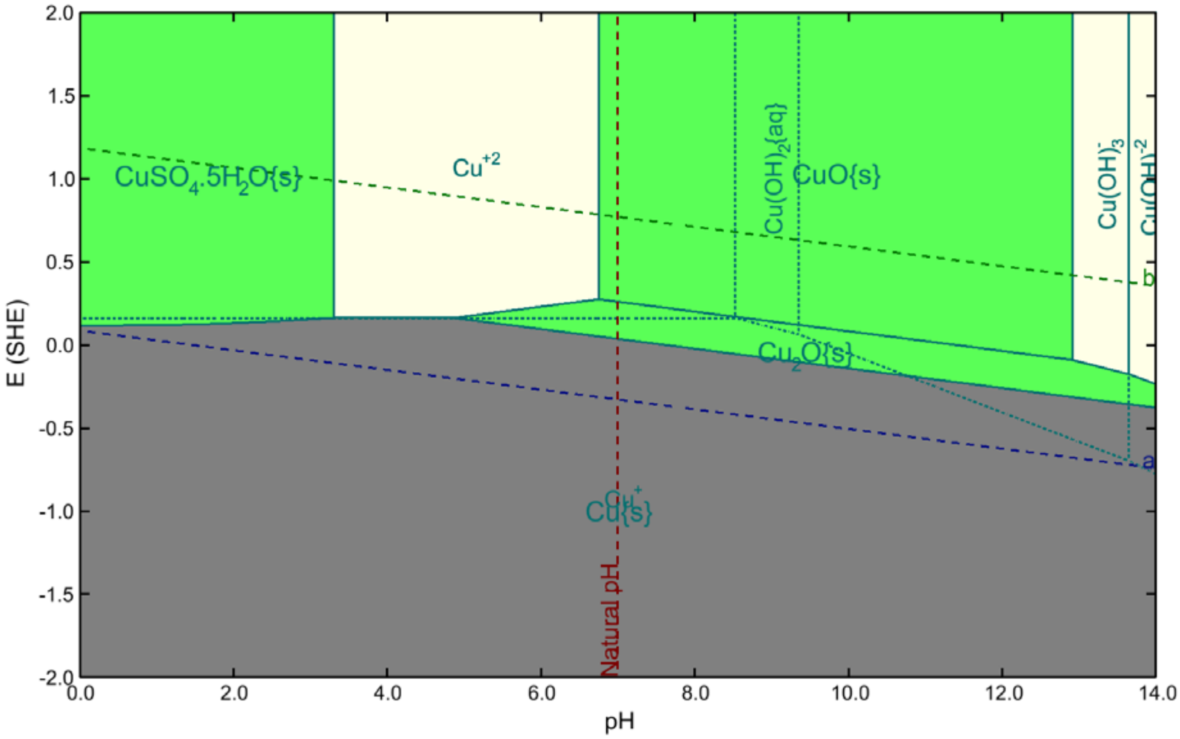


Figure 20-12 Stability diagram for Copper

Some conclusion about the copper diagram to be inserted

Features of real-solution stability diagrams

- Incorporation of solution non-ideality effects; there is no need to assume arbitrary values for the activities of species.
- Applicability to concentrated solutions.
- Applicability over wide temperature and pressure ranges.
- Usefulness for studying effects of various complexing, oxidizing and reducing agents because of OLI's comprehensive data bank.
- Facility to superimpose two or more stability diagrams to study interactions between different redox systems.
- Facility to screen various independent variables to find which one is really important.
- In contrast to the classical Pourbaix diagrams, pH variations result from adding realistic acids or bases.

You can download a worked copy of this chapter from the OLI Wiki Page

21. Generation of Stability Diagrams

Construction of real-solution stability diagrams

For each redox subsystem:

1. Construction of equilibrium equations.
2. Simulated titration to cover the whole range of independent variables.
3. Calculation of equilibrium lines for chemical reactions.
4. Calculation of equilibrium lines for electrochemical reactions.CA
5. Determination of predominance areas.

Construction of equilibrium equations

For each pair of species X and Y in a particular redox subsystem:

$$\nu_X X + \sum_{i=1}^{k} \nu_i A_i = Y + \nu_e e^-$$

where: A_i – basis species

General Formula:

$$X \equiv M_{X_1} H_{X_2} O_{X_3} C_{X_4} D_{X_5} E_{X_6} ....$$

$$Y \equiv M_{Y_1} H_{Y_2} O_{Y_3} C_{Y_4} D_{Y_5} E_{Y_6} ....$$

M-element associated with the redox system.

Basis species: Species that contain H, O, C, D, E, etc., but do not contain M:

(a) H^+ is the basis species that contains H,

(b) H_2O is the basis species that contains O,

(c) The basis species containing C, D, E, etc. are the ones with the minimum possible number of hydrogen and oxygen atoms in addition to C, D, E...

Examples

For a system composed of Cu, NH_3 and H_2O:

$$X \equiv Cu_{X_1} H_{X_2} O_{X_3} N^{-3}_{X_4}$$

Basis species: H^+, H_2O, $NH_{3(aq)}$

For a system composed of Fe, H_2O and sulfur-bearing species:

$$X \equiv Fe_{X_1} H_{X_2} O_{X_3} S^{-2}_{X_4} S^{0}_{X_5} S^{+6}_{X_6}$$

Basis species: H^+, H_2O, S^{2-}, $S^0_{(s)}$, SO_4^{2-}

Cases when both the metal and ligands are subject to redox equilibria

1. Determine which basis species are stable in which area of the stability diagram.
2. Retain only the stable species in the basis and delete the remaining ones. The deleted species are not used for constructing the equilibrium equations.

Simulated titrations

1. Titrate with a selected reactant (an acid, base, complexing agent) to vary the independent variable of interest.
2. Equilibrium calculations at each titration point involve the simultaneous solution of chemical (acid-base and redox) equilibria as well as phase equilibria.
3. Calculate the equilibrium compositions and activity coefficients for each titration point.
4. Use the compositions and and activity coefficients to calculate equilibrium lines.

Equilibrium lines for chemical reactions

Affinity of a reaction between X and Y:

$$\frac{A}{RT} = -\frac{1}{RT}\left(\overline{G}_Y - \nu_X \overline{G}_X - \sum_{i=1}^{k} \nu_i \overline{G}_{A_i}\right) =$$

$$= \ln K - \left(\ln a_Y - \nu_X \ln a_X - \sum_{i=1}^{k} \nu_i \ln a_{A_i}\right)$$

- Construct a discrete function of the independent variable:

$A_p = f(\mathrm{var}_p)$, $\quad p = 1 \ldots N$

- Find the root:

$f(\mathrm{var}_0) = 0$

Check which species are stable at var < var_0 and which at var > var_0.

Calculate equilibrium potentials for each pair of species X and Y:

$$E = E^0 + \frac{RT}{F\nu_e}\left(\ln a_Y - \nu_X \ln a_X - \sum_{i=1}^{k} \nu_i \ln a_{A_i}\right)$$

$$E^0 = \frac{\overline{G}_Y^0 - \nu_X \overline{G}_X^0 - \sum_{i=1}^{k} \nu_i \overline{G}_{A_i}^0}{F\nu_e}$$

Construct a discrete function of the independent variable:

$E_p = g(var_p)$ p=1,…N

Approximate the function using splines.

Determination of predominance areas

For each species:

1) Determine the boundaries:
    a) Upper boundaries: Equilibria with species in higher oxidation states
    b) Lower boundaries: Equilibria with species in lower oxidation states
    c) Right-hand side boundaries: Other species are more stable at higher independent variables
    d) Left-hand side boundaries: Other species are more stable at lower independent variables
2) Find intersections between boundaries
3) Determine which boundaries are active

22. A Tour of Corrosion Analyzer

Overview

We will now take a brief tour of the Corrosion Analyzer. We will first study the stability diagram for iron in pure water and then the stability diagram for iron in the presence of hydrogen sulfide.

Iron in Water

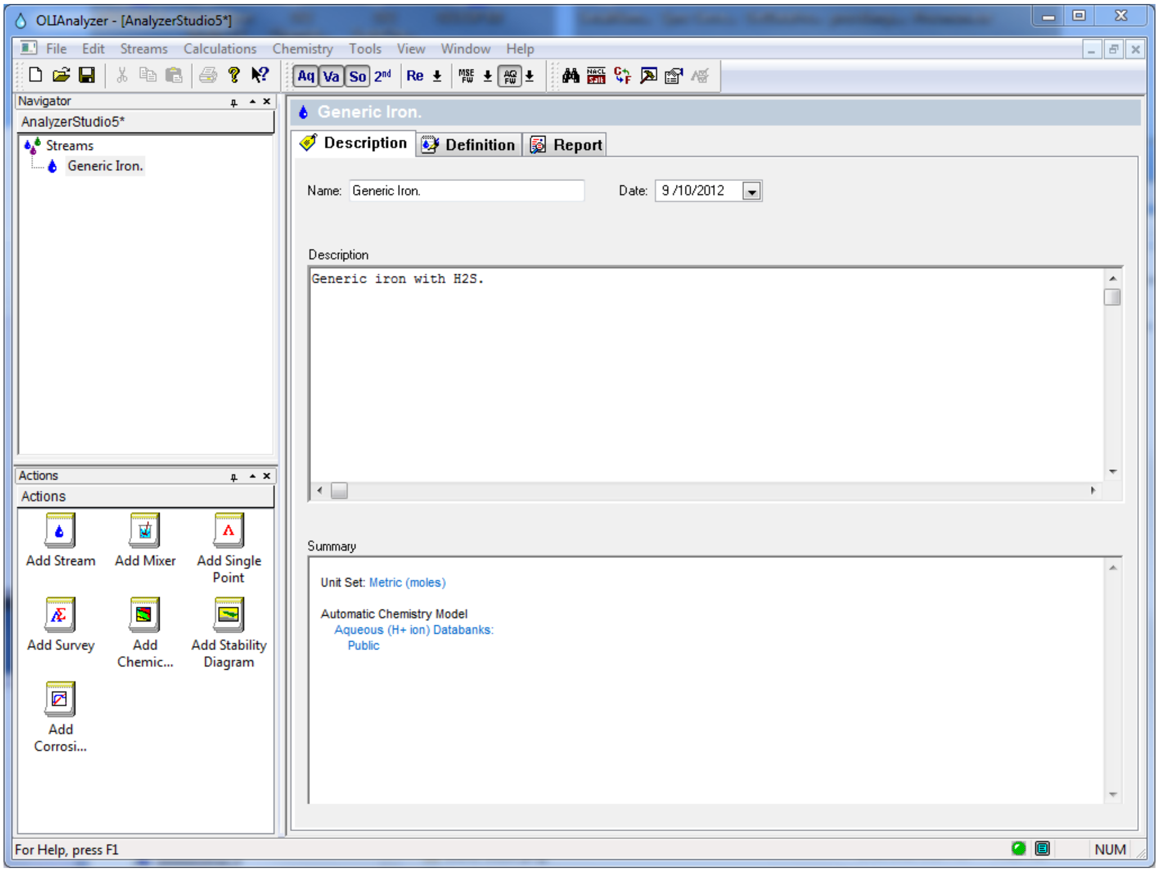
Double-Click on the OLI Studio icon on the desktop or select it from the Programs menu.

After the splash screen displays you will see main screen for analyzers.

Click the **Add Stream** icon to begin.

Select the **Definition** tab of the newly created stream. This is the default view for all new streams. You can use the default name or use the **Description** tab to rename the stream.

- ***Click*** on the **Description** tab.
- Enter the name ***Generic Iron***.
- Enter the description ***Generic iron with H2S.***



Name: Generic Iron.

Date: 9 /10/2012

Description

```
Generic iron with H2S.
```

Summary

Unit Set: Metric (moles)

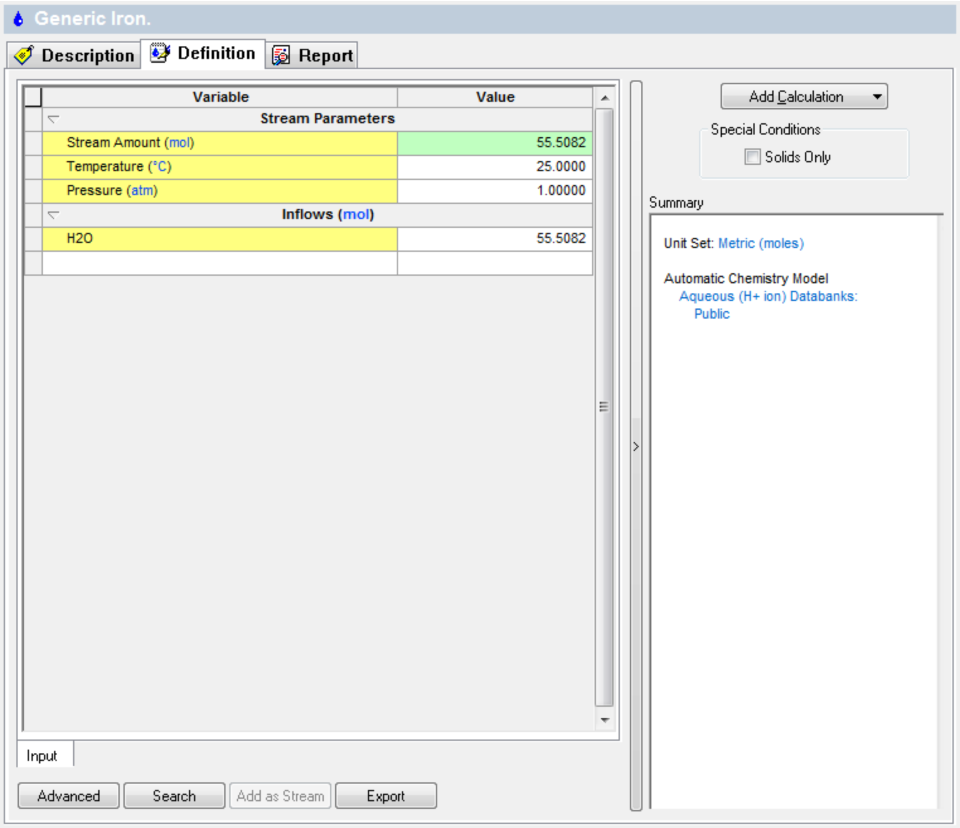
Automatic Chemistry Model
  Aqueous (H+ ion) Databanks:
    Public

Figure 22-1 The Description tab.

As in other OLI Studio modules, you may perform single point and multiple point (survey) calculations. You may also study stability diagrams and perform rate calculations.

For this tour, we will first define the stream.

- Click on the **Definition** tab.



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

Unit Set: Metric (moles)

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

Figure 22-2 Default stream definition grid.

The units for this stream may not be in the set required for the tour.

- Click on the **Tools** menu item.

The **Tools** menu will be displayed. Select **Units Manager** the list.

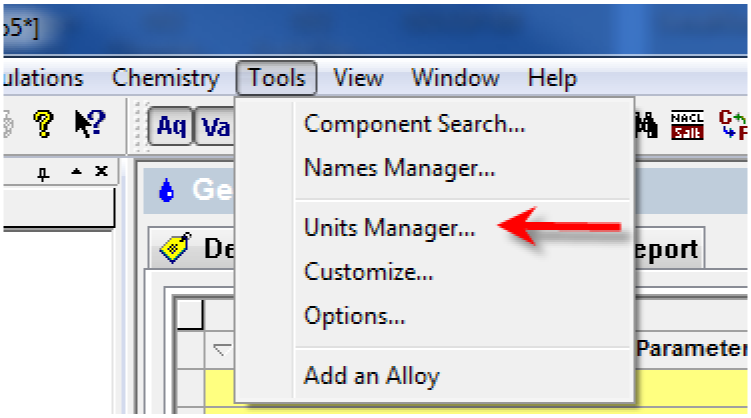


Figure 22-3 Tools Menu

We wish to use metric units. Click the down-arrow in the drop-down list box under the **Standard** radio button.

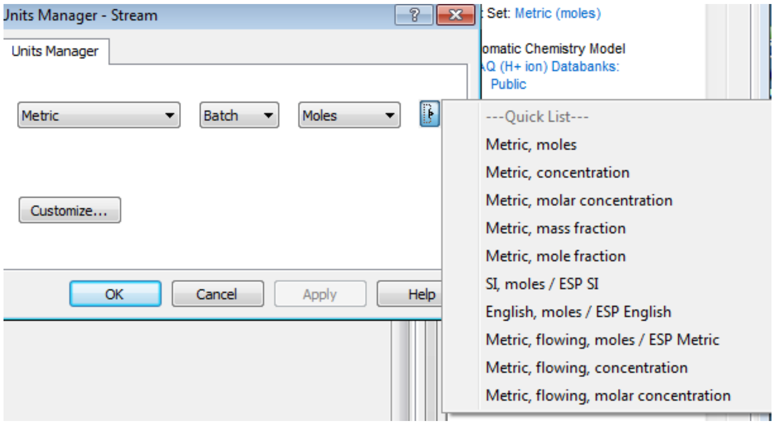


Figure 22-4 Default Units Manager

Scroll down and select **Metric, moles**.

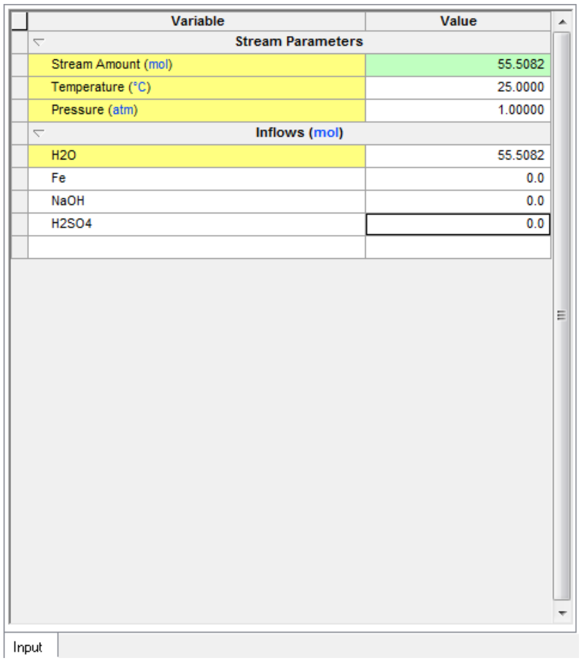
We now have the correct units for the tour. Enter the following species into the grid:

Fe

NaOH

H_2SO_4

Note: The display name may change these to a “Spelled out” display. You can use the **Names Manager** in the **Tools** menu to alter the display as you desire.



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
NaOH	0.0
H2SO4	0.0

Figure 22-5 Stream definition in correct units.

Water is the default species and defaults to a value of 55.5082 moles.

Leave the remaining fields blank. Thus, we will simulate the behavior of iron in water at ambient conditions. Note that it is not necessary to include any Fe (i.e., iron) in the stream composition. Although it is permissible to include a corroding metal in the stream, it would not correspond to reality (e.g., a steel pipe is not a component of a stream) and would markedly increase the computation time.

We now need to verify that oxidation and reduction have been turned on in the chemistry model.

- Click on the **Chemistry** menu item and then select **Model Options…**

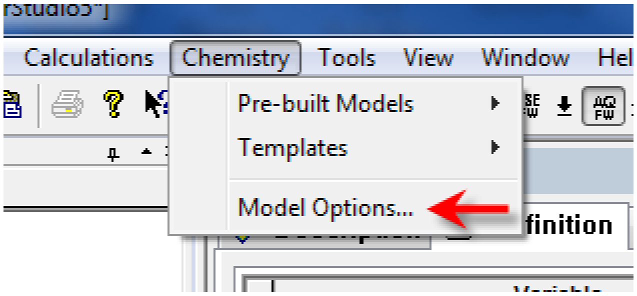


Figure 22-6 Chemistry Menu Items

This will display the model options.

- Click on the **Redox** tab.

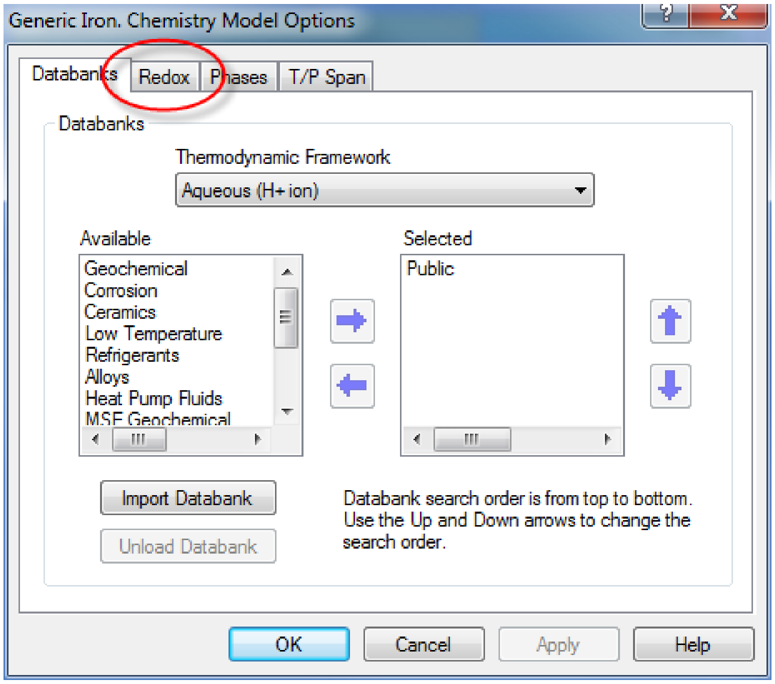
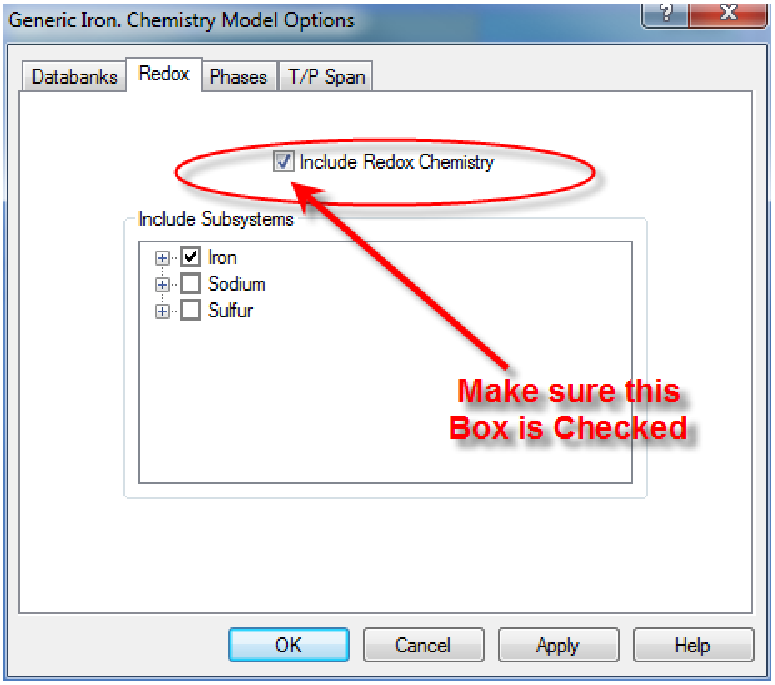


Figure 22-7 Model Options

We will now verify that the iron subsystems have been selected.



☑ Include Redox Chemistry

☑ Iron
☐ Sodium
☐ Sulfur

Make sure this Box is Checked

Figure 22-8 The selected redox subsystems.

Another way to make sure Redox is turned on is look at the top toolbar. Re button should be selected.

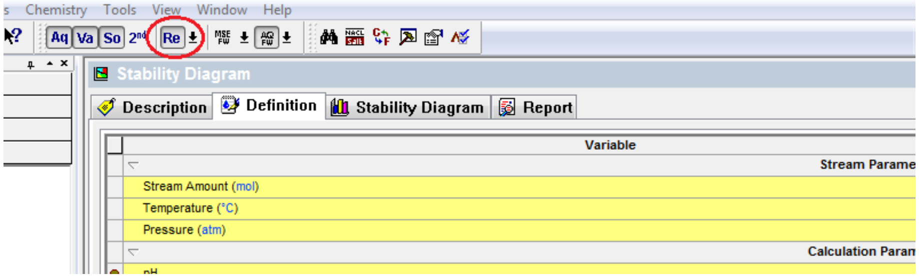


Figure 22-9 Shortcut to switch Redox On

You are free to choose all redox subsystems; this will usually result in longer computation times. It is advisable to choose the redox systems that are relevant to the studied corrosion processes.

In our example, we will choose the iron and sulfur systems. This means that the program will consider all redox states of iron (i.e., 0, +2 and +3) and those for sulfur (-2 to +6). You have the ability to turn individual redox elements on or off by expanding the element tag.

For the moment, leave the sulfur subsystem unchecked. We will eventually select sulfur when we add the hydrogen sulfide.

- Click on the **OK** button to return to the definition.

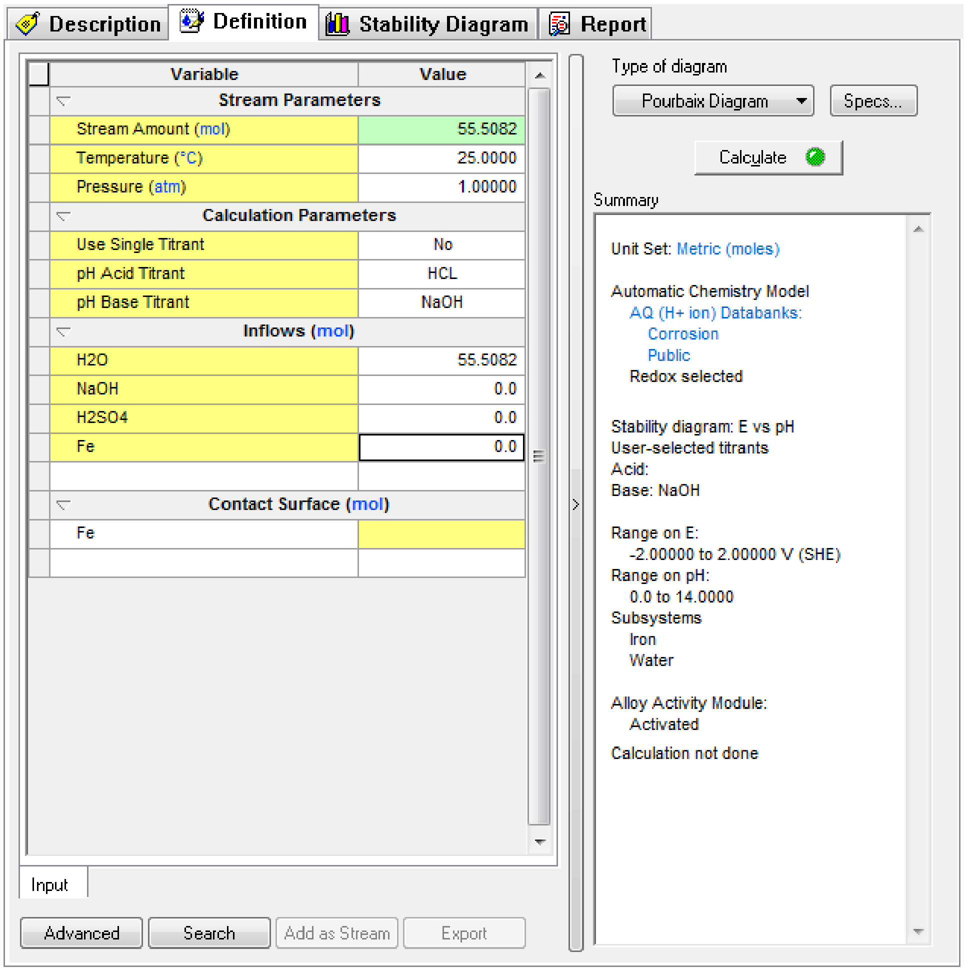
We have now defined the stream.

- Now click on the **Add Stability Diagram** Icon in the **Explorer**/**Actions** panel.

You can enter descriptive information if you want. Otherwise, click on the **Definition** tab.

Table 22-1Changing Conditions

Parameter	Value	Comment
Stream Amount (mol)	55.5082	Default value
Temperature (ºC)	25	
Pressure (atm)	1.0	
H2O (mol)	55.5082	Default Value
Contact Surface	Fe	



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
NaOH	0.0
H2SO4	0.0
Fe	0.0
Contact Surface (mol)	
Fe	

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: NaOH

Range on E:
-2.00000 to 2.00000 V (SHE)
Range on pH:
0.0 to 14.0000
Subsystems
Iron
Water

Alloy Activity Module:
Activated

Calculation not done

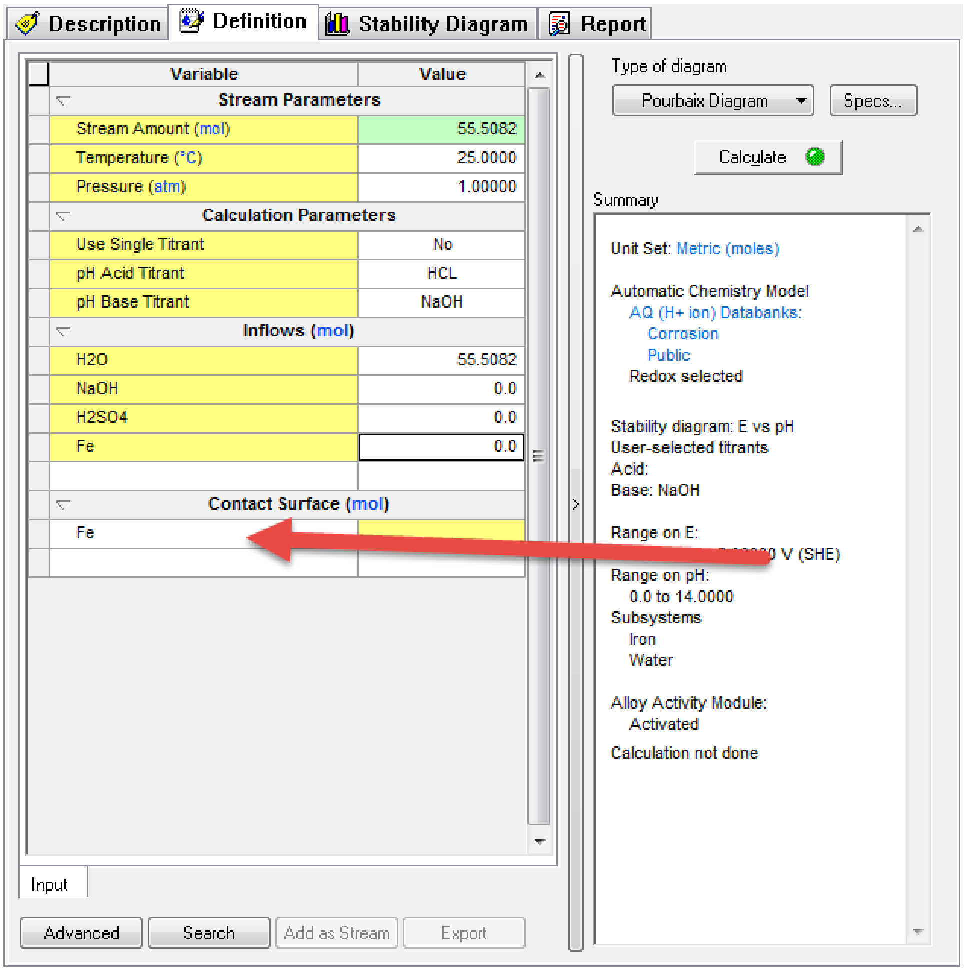
Figure 22-10 Diagram Definition

We now have some work to do to set up the calculation. Although the **Calculate** button is green we need additional information before we start calculating. We need to set some additional parameters for this tour.

We need to specify our surface metal. Frequently this will be Iron, as it is in this case, but we may use other metals. We also need to specify the titrants that will adjust the pH of the solution.

The summary box displays the current information about the calculation.

- Add the species **Fe** to the **Contact Surface** grid (if not already added)



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
NaOH	0.0
H2SO4	0.0
Fe	0.0
Contact Surface (mol)	
Fe	

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: NaOH

Range on E:
0 V (SHE)
Range on pH:
0.0 to 14.0000
Subsystems
Iron
Water

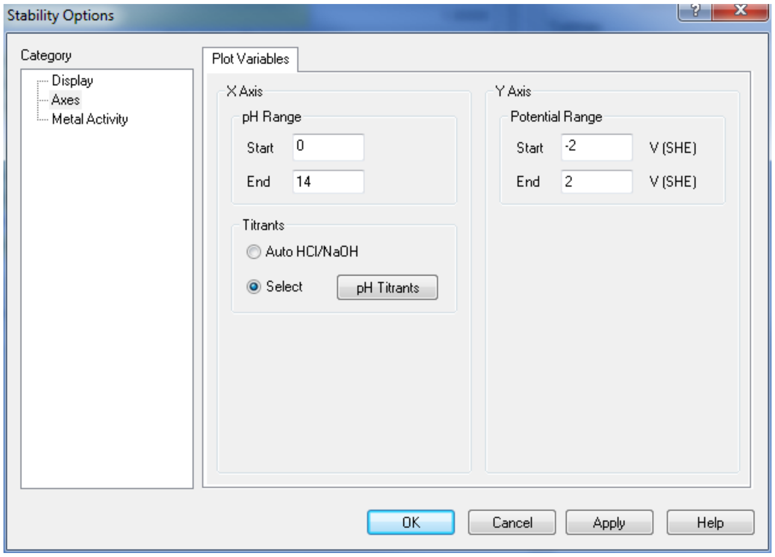
Alloy Activity Module:
Activated

Calculation not done

Figure 22-9 Adding Fe to the Contact Surface list.

Click on the **Specs…** button to fill out the remaining information.

- Click on the **Axes** category.



pH Range
Start 0
End 14

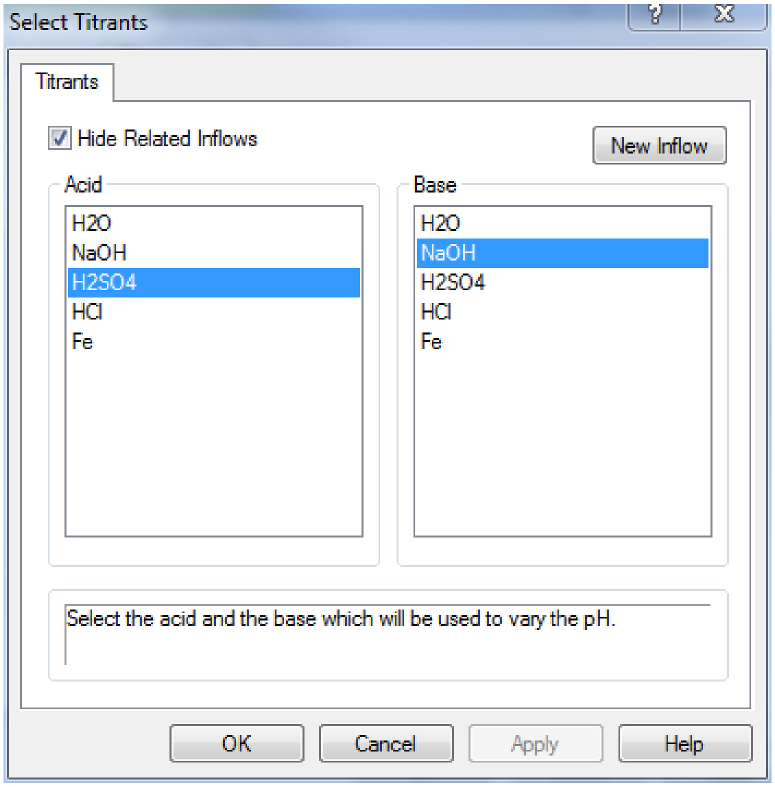
Potential Range
Start -2 V (SHE)
End 2 V (SHE)

Titrants
○ Auto HCl/NaOH
● Select

Figure 22-10 Select Titrants

Choose the **<u>Select</u>** radio button in the **<u>Titrants</u>** box. This will enable the **<u>pH Titrants</u>** button.

We now need to select an acid and a base. Select ***H_2SO_4*** as the acid (Sulfuric Acid) and ***NaOH*** as the base (sodium hydroxide).



☑ Hide Related Inflows

Acid: H2SO4

Base: NaOH

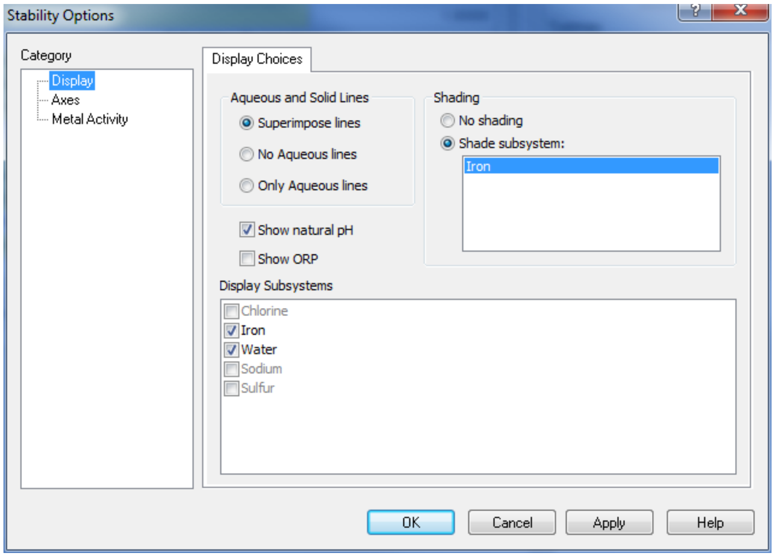
Select the acid and the base which will be used to vary the pH.

Figure 22-11 Choose an acid and base

- Click <u>OK</u>

The Y-Variable specifies voltage (E) as the variable; we wish to continue using it so will skip the category.

- Click on the **<u>Display</u>** category.



Aqueous and Solid Lines
- ● Superimpose lines
- ○ No Aqueous lines
- ○ Only Aqueous lines

☑ Show natural pH

☐ Show ORP

Shading
- ○ No shading
- ● Shade subsystem: Iron

Display Subsystems
- ☐ Chlorine
- ☑ Iron
- ☑ Water
- ☐ Sodium
- ☐ Sulfur

Figure 22-12 Make sure the Sulfur subsystem is unchecked.

Notice the **Display Subsystems** list. This tab will only display the selected subsystems. In this case only iron and water will be displayed. The subsystems are still calculated if they are not checked, merely not displayed.

Accept the default entries for the other options in this category.

- Click on the ***OK*** button.

We are now ready to calculate. Click the **Calculate** button and wait for the calculation to finish.

Once the calculation has finished, click on the **Stability Diagram** tab.

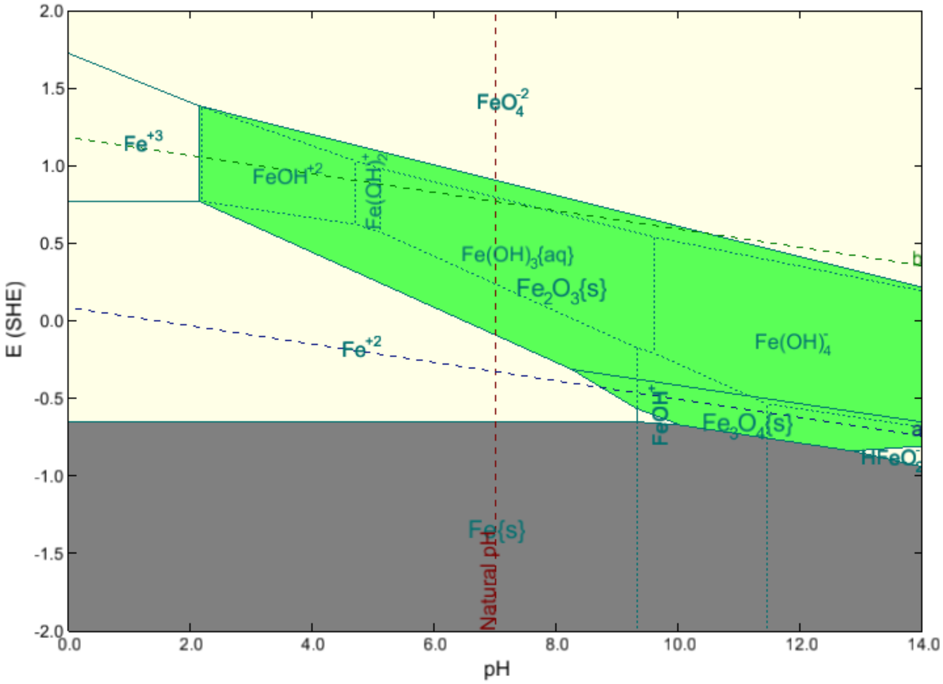


Figure 22-13 A Pourbaix diagram for iron

The obtained diagram is useful for assessing the corrosion behavior of iron. First, the equilibrium lines between elemental iron (i.e., Fe(s)) and other species can be found.

As shown in the diagram, elemental iron can be oxidized to the Fe^{2+} ions (i.e., FE+2) in acidic, neutral and weakly alkaline solutions (for pH below ca. 9.5) and to the $Fe(OH)_3^{-1}$ ions (i.e., FEIIOH3-1) in alkaline environments (for pH above ca. 11.5).

The oxidation of iron can be coupled with the reduction of the H^+ ions because the H^+/H_2^o equilibrium line (denoted by a) lies always above the lines that represent the oxidation of iron. Therefore, corrosion of iron can occur with the evolution of hydrogen and formation of soluble iron-containing ions (either Fe^{2+} or $Fe(OH)_3^-$).

Adding Hydrogen Sulfide

We will now **add 1.0 x 10^{-4} moles of H_2S** to the stream.

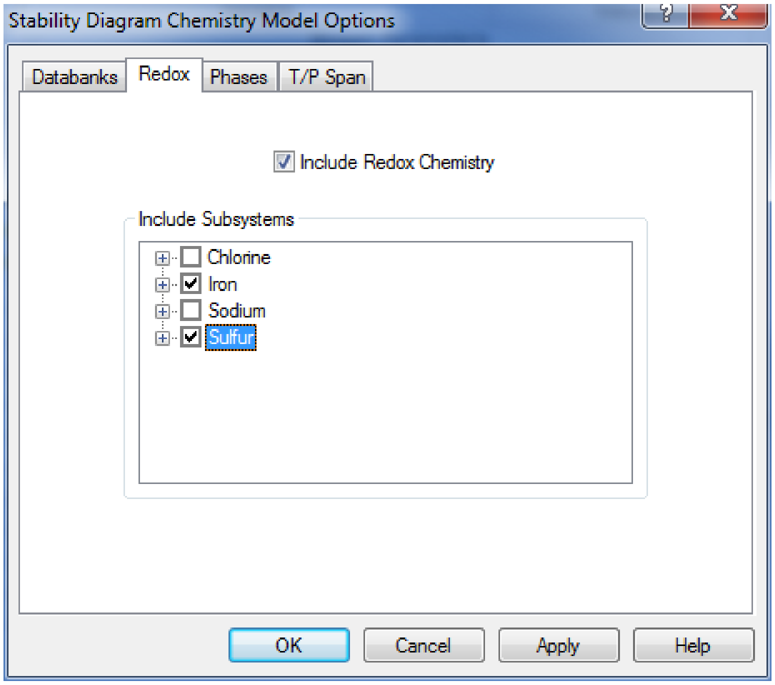
Click on the **Definition** tab.

In the grid, add hydrogen sulfide (H_2S) to the stream at a rate of 1.0000E-04 moles.

Click on the **Chemistry** menu item and select **Model Options…**

- Click on the **Redox** tab.

Select ***Sulfur*** from the list; ***Iron*** should also be checked.

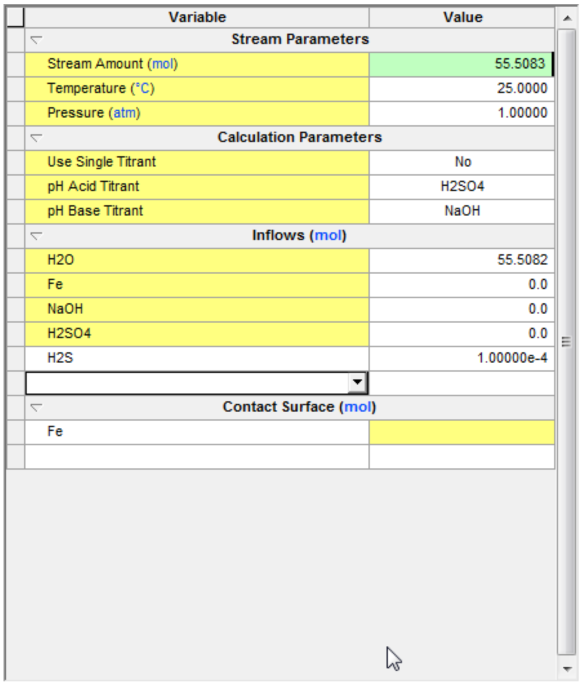


☑ Include Redox Chemistry

Include Subsystems

☐ Chlorine
☑ Iron
☐ Sodium
☑ Sulfur

Figure 22-14 Enabling the sulfur redox subsystem.

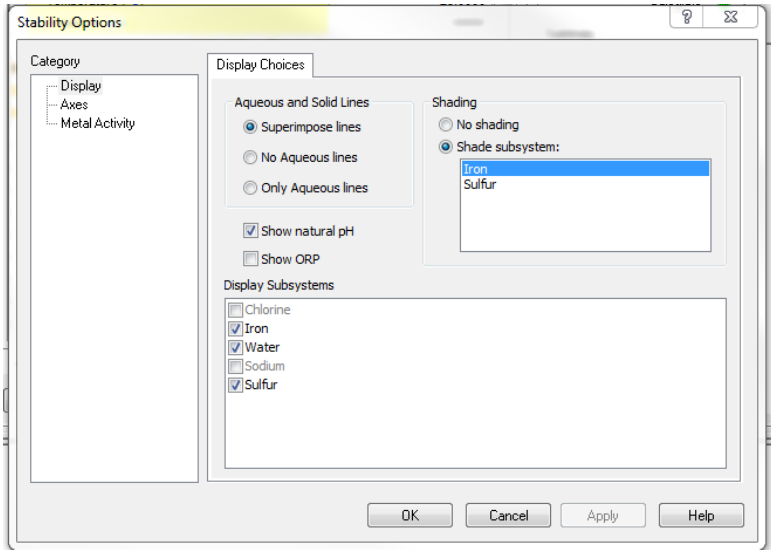


Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5083
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	H2SO4
pH Base Titrant	NaOH
Inflows (mol)	
H2O	55.5082
Fe	0.0
NaOH	0.0
H2SO4	0.0
H2S	1.00000e-4
Contact Surface (mol)	
Fe	

Figure 22-15 Add Hydrogen Sulfide

Though calculation is set up, use the **Specs…** button to review the settings. The only change will be in the subsystems. Since we are now calculating the sulfur redox subsystems, we want to make sure that we are displaying them correctly.

Check the sulfur subsystems.



Stability Options

Category
- Display
- Axes
- Metal Activity

Display Choices

Aqueous and Solid Lines
- ● Superimpose lines
- ○ No Aqueous lines
- ○ Only Aqueous lines

☑ Show natural pH

☐ Show ORP

Shading
- ○ No shading
- ● Shade subsystem:
  - Iron
  - Sulfur

Display Subsystems
- ☐ Chlorine
- ☑ Iron
- ☑ Water
- ☐ Sodium
- ☑ Sulfur

Figure 22-16 Turn on display on for Sulfur.

- Click the **OK** button

Click the Calculate button when you are ready. When the calculation finishes, click the ***Stability Diagram*** ***Tab***.

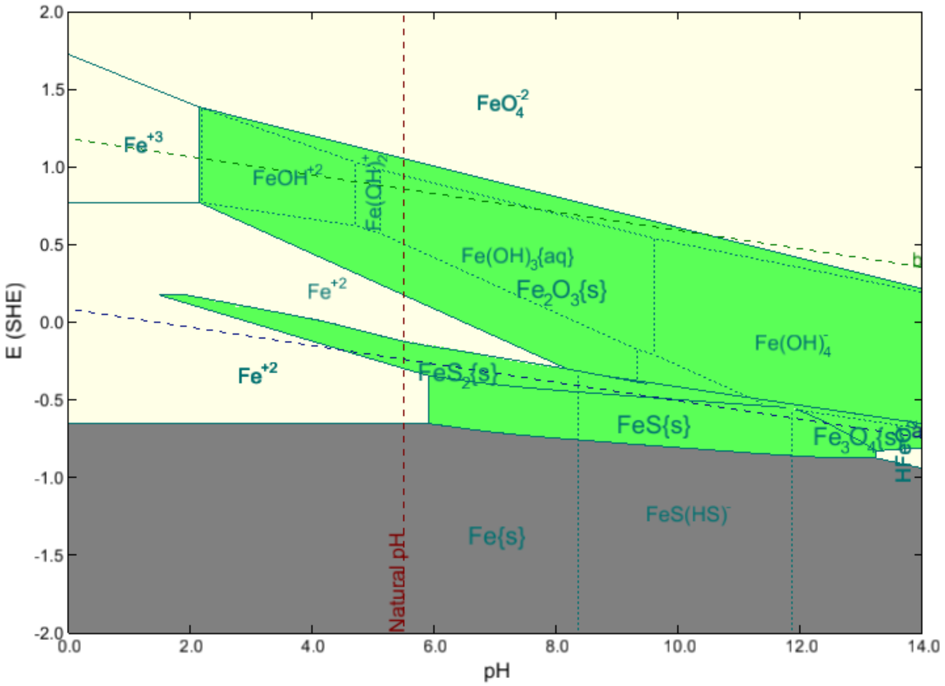


Figure 22-17 The stability diagram with Sulfur.

Inspection of the diagram reveals a profound effect of H_2S on the corrosion of iron. In addition to the species that were present in the first diagram, new stability fields of FeS and FeS_2 are observed. In particular, elemental Iron is found to be in equilibrium with FeS over for pH values ranging from ca. 6.0 to 12.5.

Since the Fe/FeS equilibrium line lies below the H^+ reduction line (**a**), a process consisting of the reduction of H^+ to H^0 and oxidation of Fe to FeS is likely in de-aerated environments. FeS forms a passive film and offers some protection against corrosion.

In fact, the protection due to the formation of FeS is possible over a much wider pH range than that due to the formation of Fe_3O_4 (magnetite) in the absence of H_2S. This has important implications for corrosion in refinery installations, where H_2S frequently occurs.

You can download a worked example for this chapter from the OLI Wiki Page

23. Modeling the Effects of Acidity & Alkalinity on Corrosion

Overview

In this section we take a brief look at the effects of acidity and alkalinity on corrosion. You should already be familiar with many of the features and controls of the Corrosion Analyzer; thus we will not dwell on the intricate details.

In this section we will generate a stability diagram for iron in water at high temperature, simulating a high temperature boiler. We then create a stability diagram for alkaline neutralization in an oil refinery.

High Temperature Iron in Water

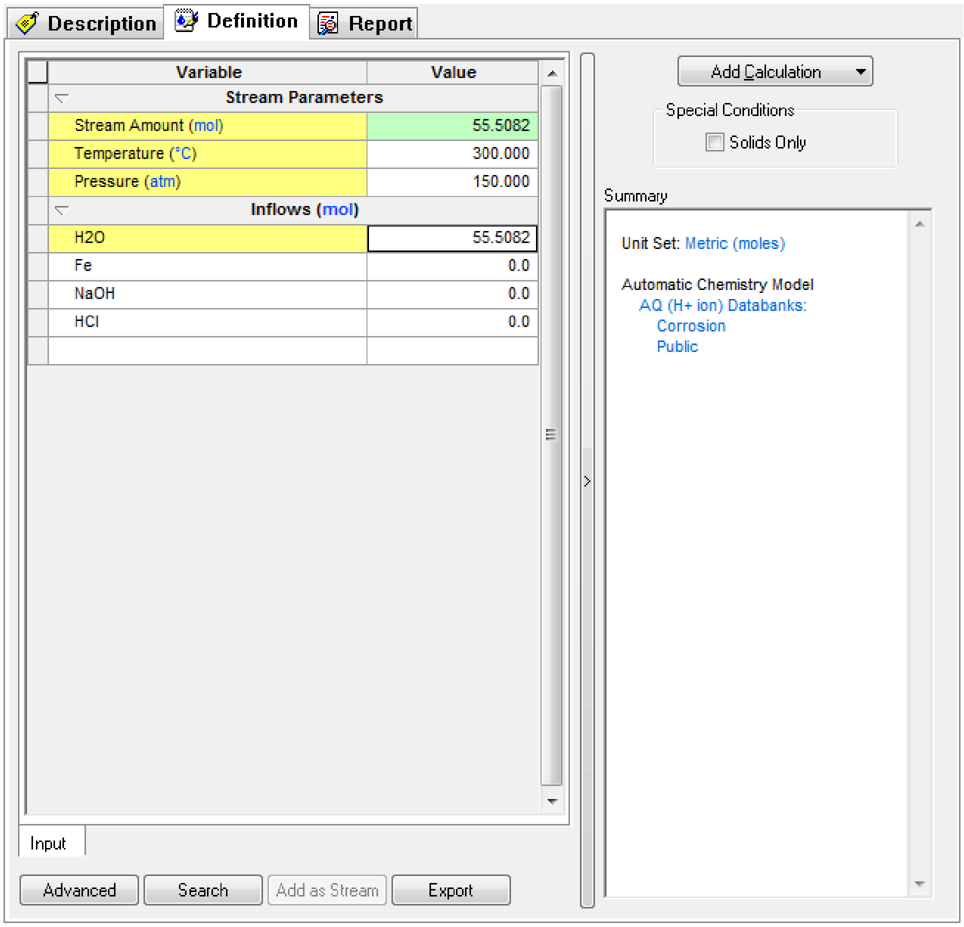
Using the skills you already know, create a stream and stability diagram definition for the following condition:

Table 23-1 High Temperature Iron Example Parameters

Parameter	Value	Comment
Stream Amount (mol)	55.5082	Default value
Temperature (ºC)	300	
Pressure (atm)	150	
H2O (mol)	55.5082	Default Value
Base Titrant	NaOH	No initial value
Acid Titrant	HCl	No Initial Value
Contact Surface	Fe	

As with the previous tour, the contact surface will be iron (Fe). The titrants will be hydrochloric acid (HCl) for the acid and sodium hydroxide (NaOH) for the base. Allow for only the iron subsystem to be displayed.

The input grid should look like the following figure:

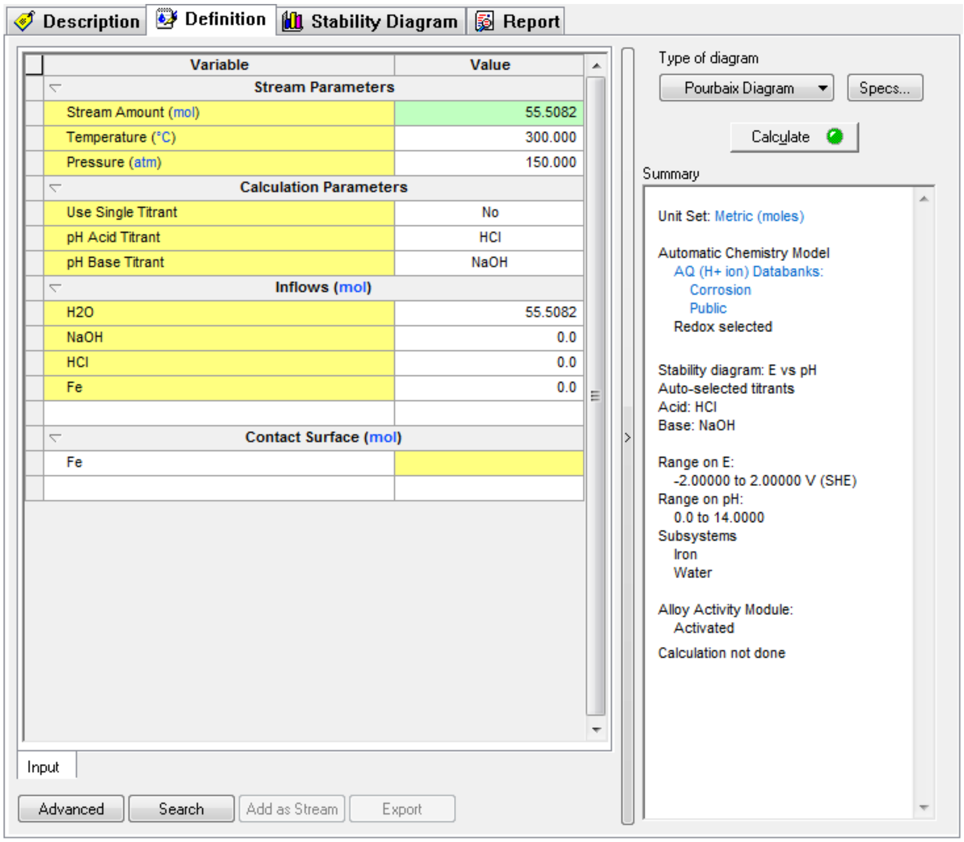


Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	300.000
Pressure (atm)	150.000
Inflows (mol)	
H2O	55.5082
Fe	0.0
NaOH	0.0
HCl	0.0

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Corrosion
Public

Figure 23-1 The stream definition.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	300.000
Pressure (atm)	150.000
Calculation Parameters	
Use Single Titrant	No
pH Acid Titrant	HCl
pH Base Titrant	NaOH
Inflows (mol)	
H2O	55.5082
NaOH	0.0
HCl	0.0
Fe	0.0
Contact Surface (mol)	
Fe	

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Corrosion
Public
Redox selected

Stability diagram: E vs pH
Auto-selected titrants
Acid: HCl
Base: NaOH

Range on E:
-2.00000 to 2.00000 V (SHE)
Range on pH:
0.0 to 14.0000
Subsystems
Iron
Water

Alloy Activity Module:
Activated

Calculation not done

Figure 23-2: The definition grid prior to calculation.

Click the **Calculate** button. When the calculation has finished, click the **Stability Diagram** tab.

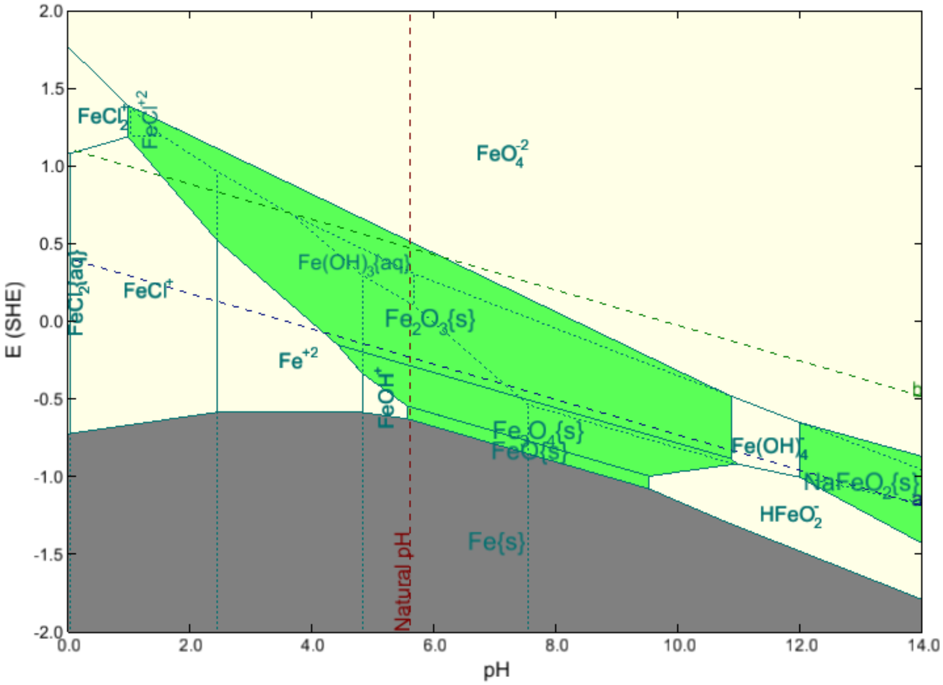


Figure 23-3 Iron in water at 300 °C and 150 atmospheres.

We can see from the diagram that passivation is only possible at moderate pH’s.

How does the prediction of passivation relate to corrosion rate data?[46]

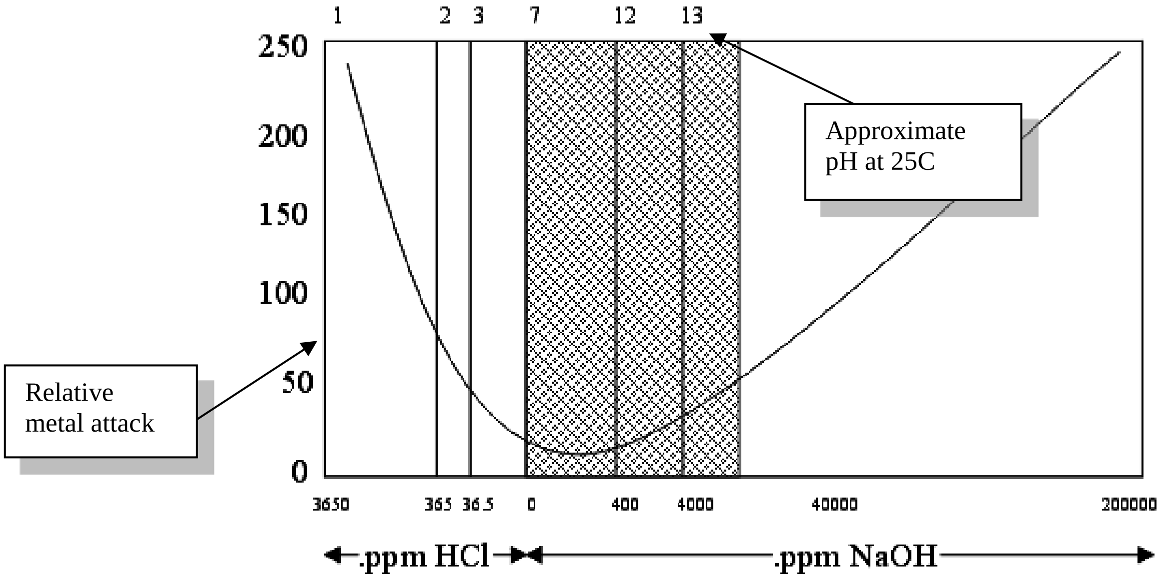


Figure 23-4 Relative metal attack v. pH and titrant concentration

The hatched area corresponds to the stability of a passivation layer. The corrosion rate is greatly reduced when a passivation layer is present.

Neutralization of Refinery Streams with Alkanolamines

Create a Stream Definition for the following conditions

Table 23-2 Alkanolamine Example

Parameter	Value	Comment
Stream Amount (mol)	55.5082	Default value
Temperature (°C)	50	
Pressure (atm)	1	
H2O (mol)	55.5082	Default Value
Acid Titrant	HCl	No initial value
Base Titrant	DEA[47]	No Initial Value
C8H18 (mol)	2E-07	

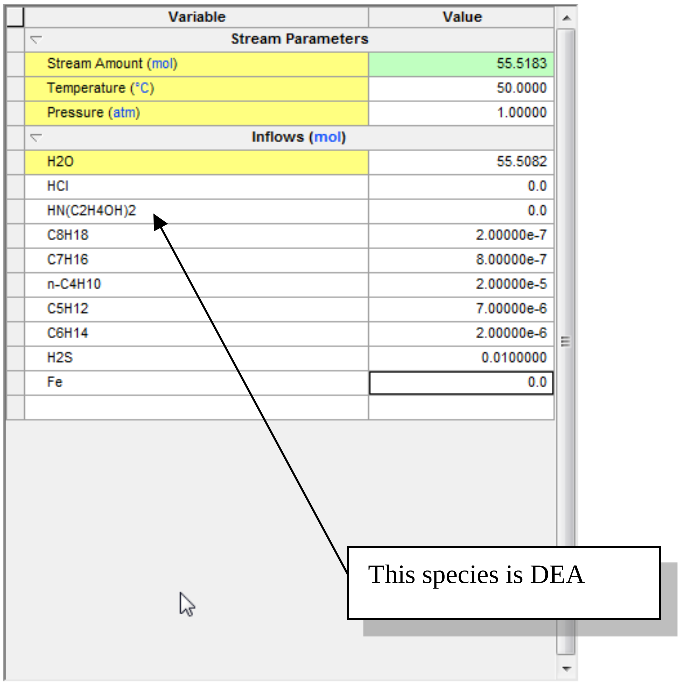
---

[46] Relative corrosion rate data as a function of HCl and NaOH added to Solution (Partridge and Hall, Trans. Am. Soc. Mech. Eng. 1939, 61, 597)

[47] The “ESP” name for this species is DEXH, which can be used as an input to make your life easier. The formula name is: HN(C2H4OH)2

C7H16 (mol)	8E-07	
C3H8 (mol)	1.2E-04	
C4H10 (mol)	2E-05	
C5H12 (mol)	7E-6	
C6H14 (mol)	2E-6	
H2S	0.01	
Contact Surface	Fe	

The input grid should look approximately like this:

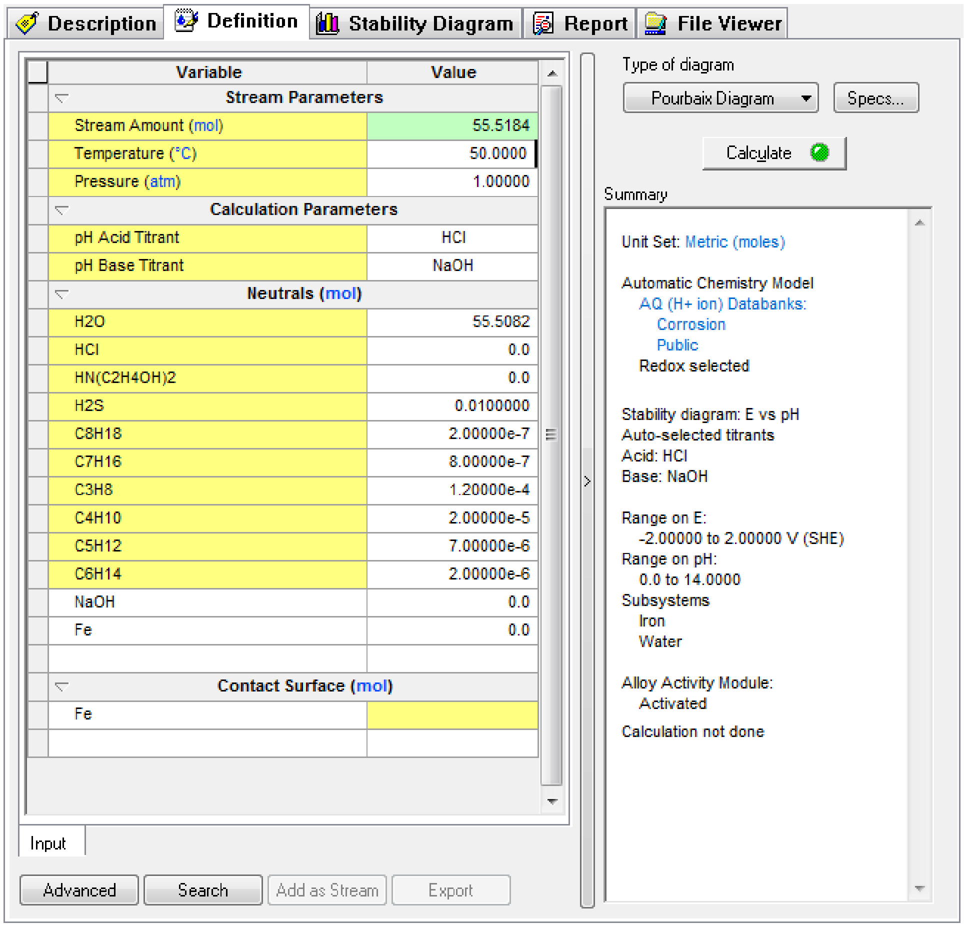


Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5183
Temperature (°C)	50.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
HCl	0.0
HN(C2H4OH)2	0.0
C8H18	2.00000e-7
C7H16	8.00000e-7
n-C4H10	2.00000e-5
C5H12	7.00000e-6
C6H14	2.00000e-6
H2S	0.0100000
Fe	0.0

This species is DEA

Figure 23-5 Stream input grid.

Create a stability diagram as in previous chapters



Type of diagram: Pourbaix Diagram

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5184
Temperature (°C)	50.0000
Pressure (atm)	1.00000
Calculation Parameters	
pH Acid Titrant	HCl
pH Base Titrant	NaOH
Neutrals (mol)	
H2O	55.5082
HCl	0.0
HN(C2H4OH)2	0.0
H2S	0.0100000
C8H18	2.00000e-7
C7H16	8.00000e-7
C3H8	1.20000e-4
C4H10	2.00000e-5
C5H12	7.00000e-6
C6H14	2.00000e-6
NaOH	0.0
Fe	0.0
Contact Surface (mol)	
Fe	

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
  AQ (H+ ion) Databanks:
    Corrosion
    Public
  Redox selected

Stability diagram: E vs pH
Auto-selected titrants
Acid: HCl
Base: NaOH

Range on E:
  -2.00000 to 2.00000 V (SHE)
Range on pH:
  0.0 to 14.0000
Subsystems
  Iron
  Water

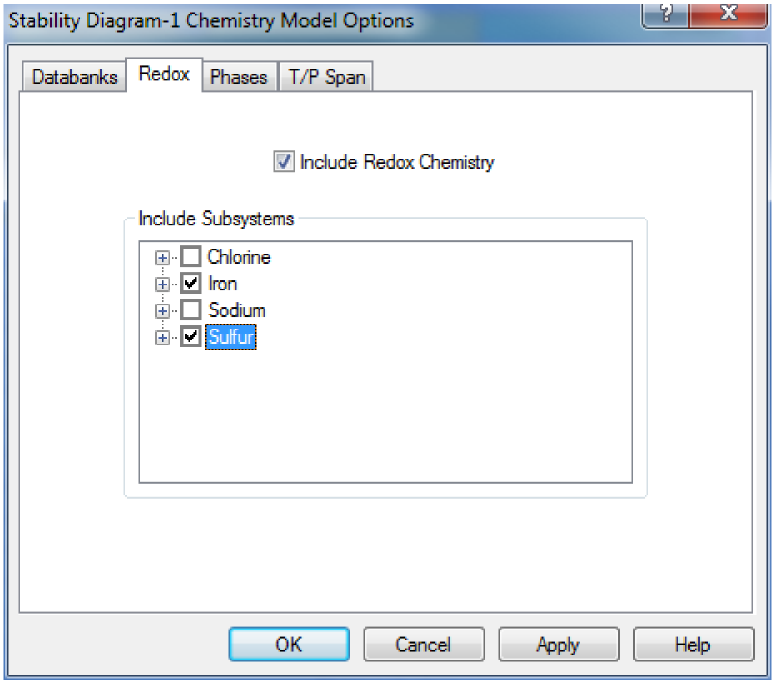
Alloy Activity Module:
  Activated
Calculation not done

Figure 23-6: The stability diagram definition.

Remember to use the **Specs…** button to select the pH titrants. You are using HCL and DEA as the titrants.

Let's review the redox subsystems via Chemistry | Model Options | Redox

Make sure ***Sodium*** is not checked in the list of included subsystems and that Sulfur is checked in the **Redox** section of the chemistry model options.



Stability Diagram-1 Chemistry Model Options

☑ Include Redox Chemistry

Include Subsystems

- ☐ Chlorine
- ☑ Iron
- ☐ Sodium
- ☑ Sulfur

23-7: Selecting the redox subsystems from the chemistry model options.

Click the **Calculate** button when you are ready. When the calculation finishes, click on the **Stability Diagram** tab.

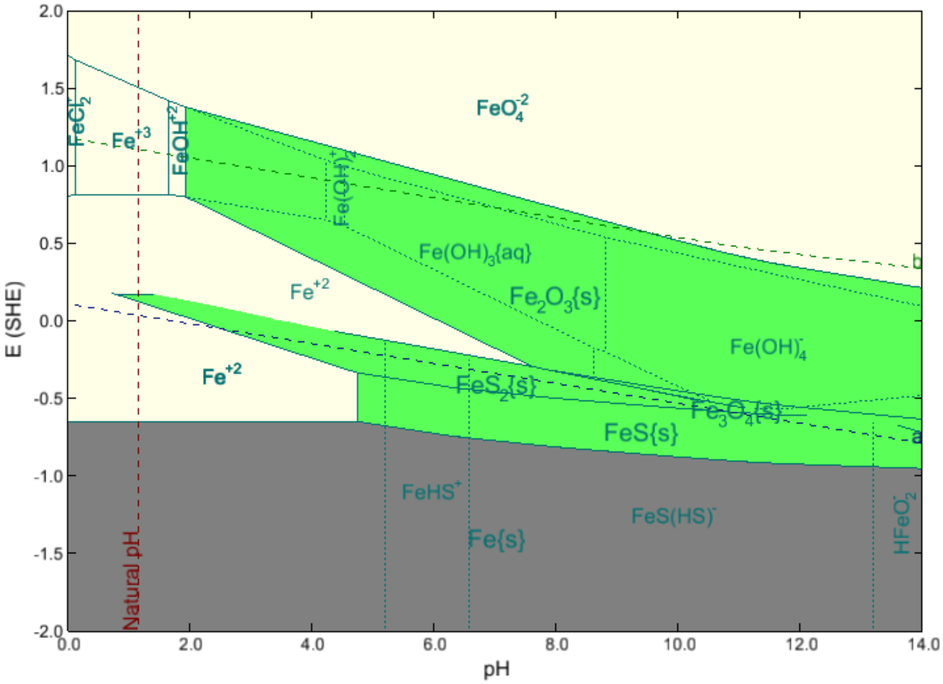


Figure 23-8 The stability of iron in DEA solutions.

You can download a worked example for this chapter from the OLI Wiki Page

24. Modeling the Effects of Complexation on Corrosion

Overview

We continue to review the Corrosion Analyzer and its capabilities in modeling corrosion. In this section we will simulate the reaction of Copper with Ammonia and Gold metal with Cyanide.

This section attempts to answer the question of how strong complexing agents affect the passivation of these metals.

Copper and Ammonia

Create a stream with the following conditions:

Table 24-1 Copper and Ammonia complexing example

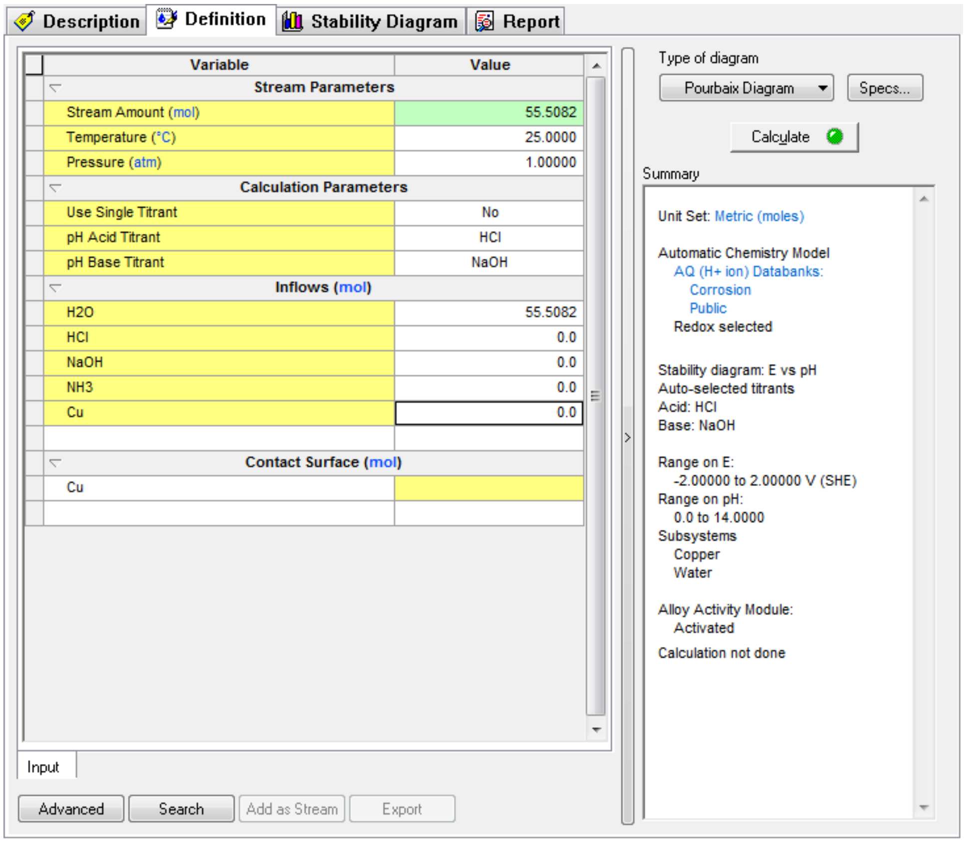
Parameter	Value	Comment
Stream Amount (mol)	55.5082	Default value
Temperature (ºC)	25	
Pressure (atm)	1	
H2O (mol)	55.5082	Default Value
Acid Titrant	HCl	No initial value
Base Titrant	NaOH	No Initial Value
NH3	0	No Initial Value used as a complexing agent
Contact Surface	Cu	

As with the other tours, please set the names manger to suit your personal preferences for names display.

Create a stability diagram using the above stream.

Verify that only Copper is the selected redox subsystem using the **Chemistry** menu item and **Model Options**.

The completed grid should look similar to the following figure:



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
HCl	0.0
NaOH	0.0
NH3	0.0
Cu	0.0
Contact Surface (mol)	
Cu	

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Corrosion
Public
Redox selected

Stability diagram: E vs pH
Auto-selected titrants
Acid: HCl
Base: NaOH

Range on E:
-2.00000 to 2.00000 V (SHE)
Range on pH:
0.0 to 14.0000
Subsystems
Copper
Water

Alloy Activity Module:
Activated
Calculation not done

Figure 24-1 The Cu-Ammonia stability diagram definition.

Click on the **Calculate** button when ready.

When the calculation has finished, click on the **Stability Diagram** tab.

The following diagram should be displayed.

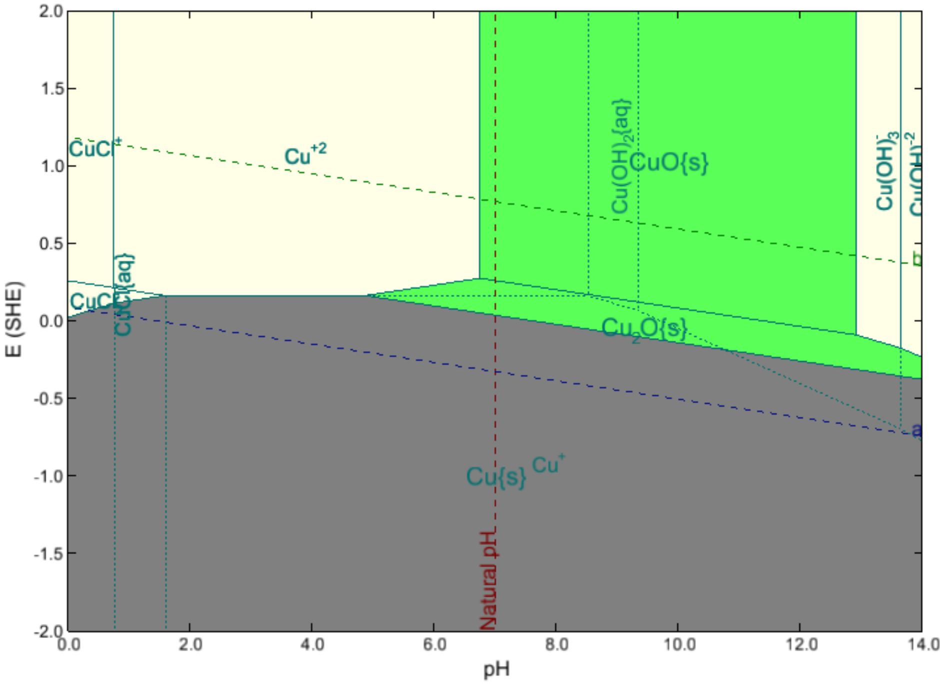


Figure 24-2 The stability diagram of Copper in the presence of Ammonia at 25° C and 1 atm.

In the absence of oxygen (looking at only the ***a*** line). We can see that the copper equilibrium line lays above the hydrogen ***a*** line. This means there is insufficient oxidizing power in the water to corrode copper metal in pure water.

We now wish to see the effects of ammonia on the stability of copper. Click on the **Definition** tab and enter ***0.1 moles of NH3.*** The diagram should still be set up, click on the **Calculate** button to start. When the calculation has finished, click on the **Stability Diagram** tab once again.

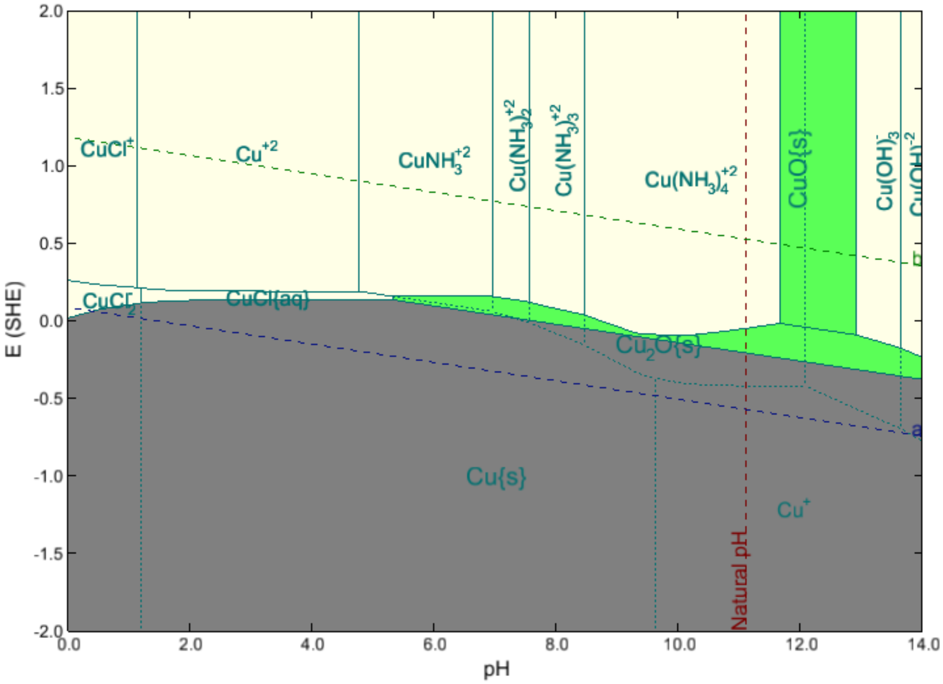


Figure 24-3 The effect of adding 0.1 moles of ammonia on the stability diagram.

A large area of corrosive liquid has appeared in the stability field for the copper oxides. This means that it is thermodynamically possible for the ammonia to break down the passivation layer of copper oxide in the presence of oxygen. Notice that in the absence of oxygen (the ***a*** line only), copper is still stable.

Now repeat the exercise with ***1.5 moles of NH3***.

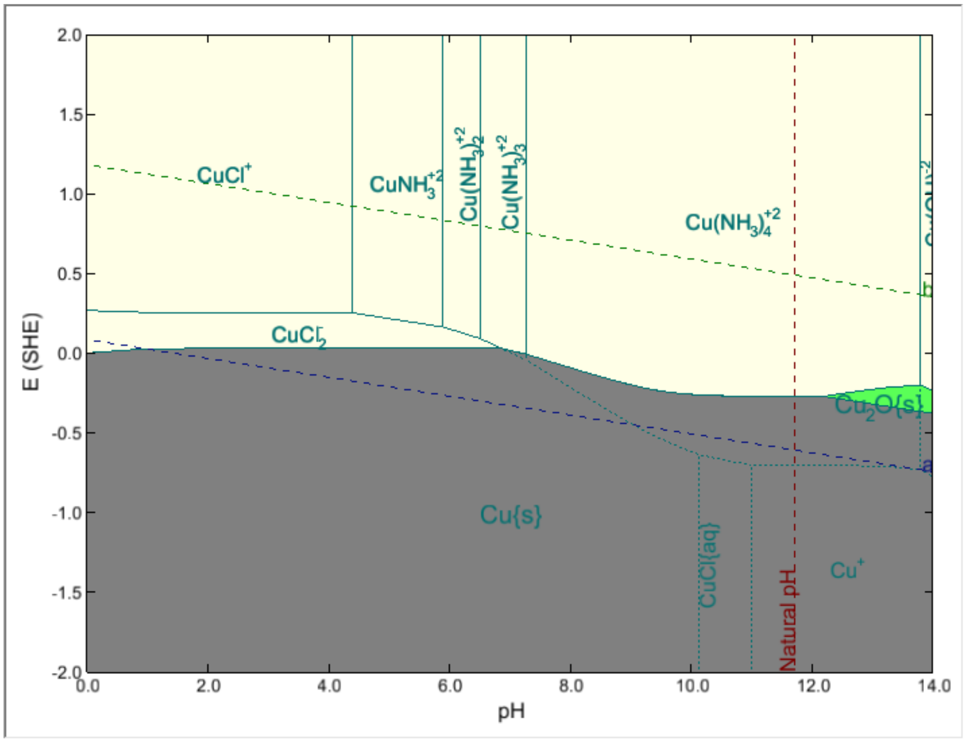


Figure 24-4 The effect of adding 1.5 moles of ammonia on the stability diagram.

At this concentration of ammonia, most, if not all the passivating copper oxide has been reacted away. Only at very high pH values are there any stable oxides.

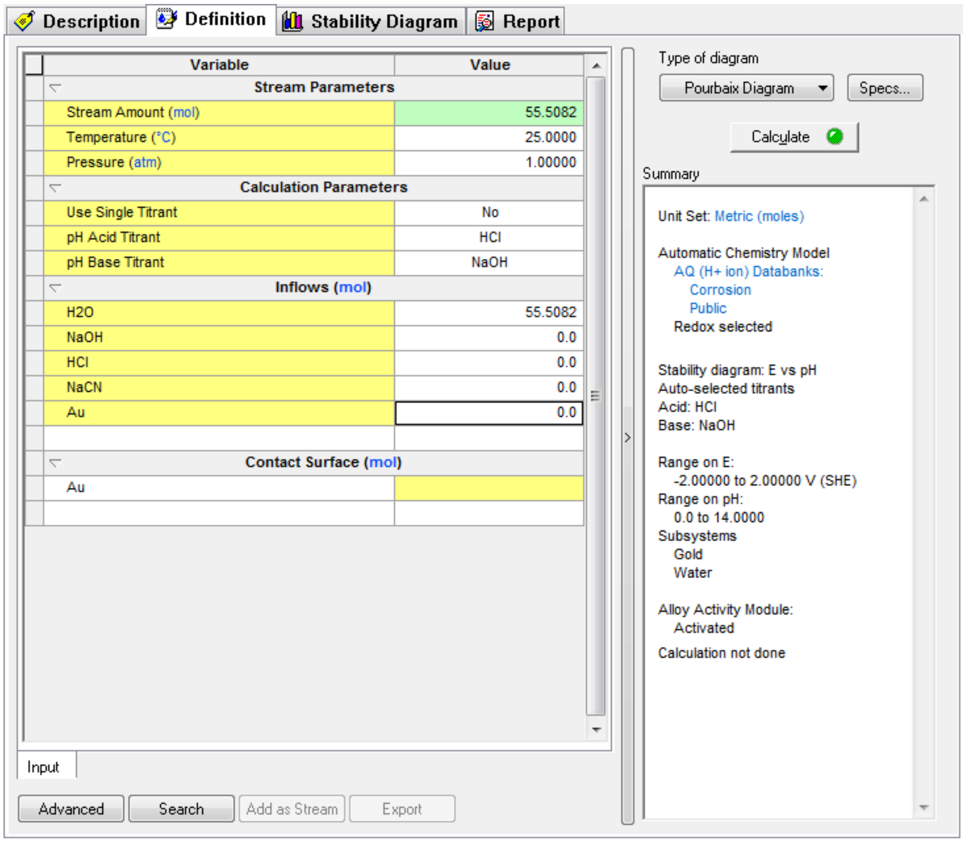
Gold in the presence of Cyanides

Create a new stream with the following composition:

Table 24-2 Gold in the presence of cyanide

Parameter	Value	Comment
Stream Amount (mol)	55.5082	Default value
Temperature (°C)	25	
Pressure (atm)	1	
H2O (mol)	55.5082	Default Value
Acid Titrant	HCl	No initial value
Base Titrant	NaOH	No Initial Value
NaCN	0	No Initial Value used as a complexing agent
Contact Surface	Au	

The input grid should be similar to this:



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
NaOH	0.0
HCl	0.0
NaCN	0.0
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
Auto-selected titrants
Acid: HCl
Base: NaOH

Range on E:
-2.00000 to 2.00000 V (SHE)
Range on pH:
0.0 to 14.0000
Subsystems
Gold
Water

Alloy Activity Module:
Activated

Calculation not done

Figure 24-5 The Gold-Cyanide stability diagram definition.

Click on the **Calculate** button when you are ready. When the calculation has finished, click on the **Diagram** tab.

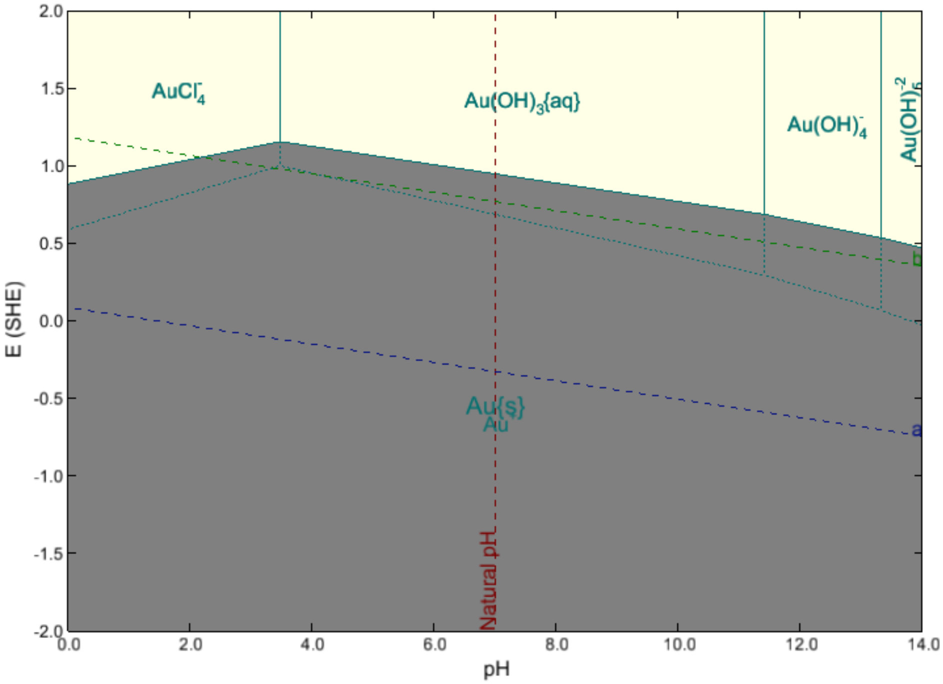


Figure 24-6 The stability diagram of Gold in the presence of Cyanide at 25° C and 1 atm.

You can see that without oxygen, gold metal is immune to corrosion. The hydrogen line ***a*** is below the gold equilibrium line. In the presence of oxygen, gold is still immune to corrosion except at very low pH.

Now repeat the exercise with ***1.0E-04 moles of NaCN.***

The figure should look like this:

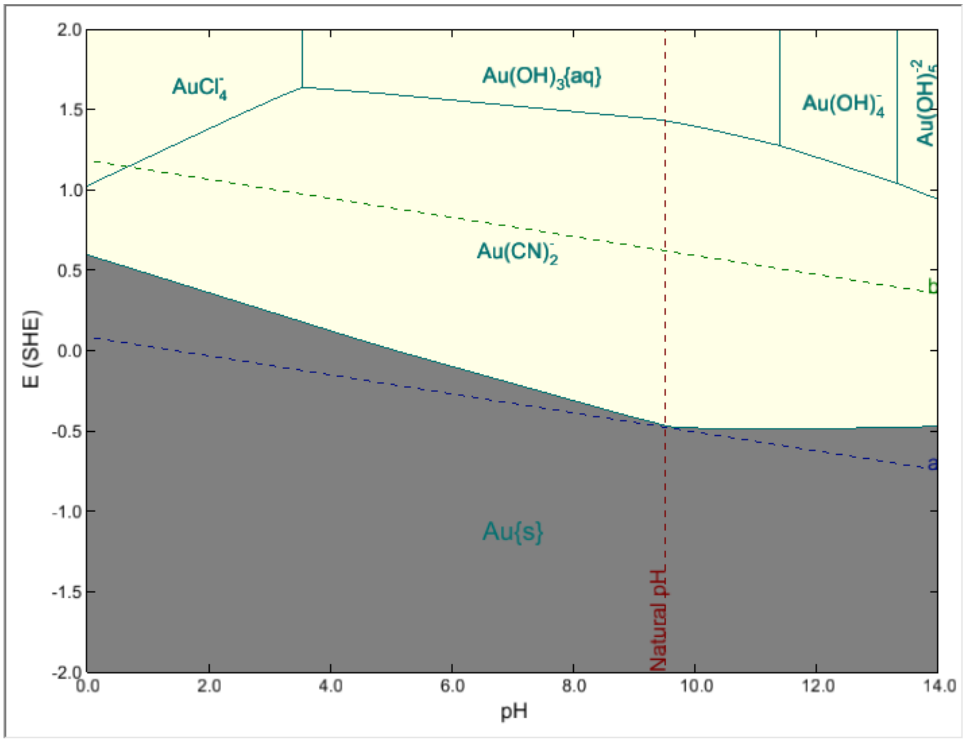


Figure 24-7 The effect of adding 1.0E-04 moles of NaCN on the stability diagram.

In the presence of oxygen, gold completely corrodes with cyanide. This is primarily due to the gold complex: $Au(CN)_2^{-1}$.

You can download a worked example of this chapter from the OLI Wiki Page

25. Modeling the Effect of Oxidizing Inhibitors on Corrosion

Overview

In this chapter we will look at the effect of modeling corrosion inhibitors. We will do this by superimposing two stability diagrams over one another. If one solid field overlaps the corrosion range of the other system, then passivation is likely.

Iron in the presence of chromates

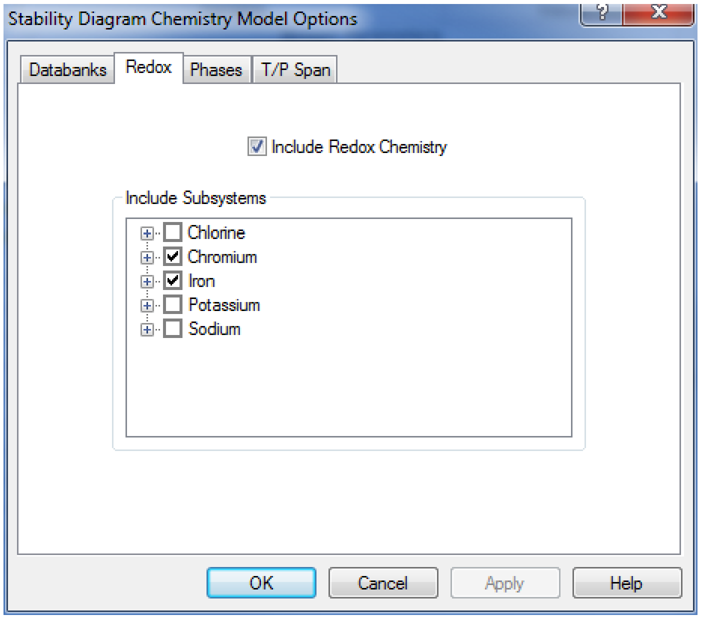
Create a stream with the following composition:

Table 25-1 Inhibition using chromates

Parameter	Value	Comment
Stream Amount (mol)	55.5082	Default value
Temperature (ºC)	25	
Pressure (atm)	1	
H2O (mol)	55.5082	Default Value
Acid Titrant	HCl	No initial value
Base Titrant	NaOH	No Initial Value
K2CrO4 (mol)	0.001	Used as an corrosion inhibitor
Contact Surface	Fe	
Contact Surface	Cr	

Create a stability diagram using the above stream. Select both ***Fe*** and ***Cr*** oxidation and reduction subsystems. In this case, the two metals will be used in addition to water in the redox subsystems.

Use the **Chemistry** model item and **Model Options > Redox** to ensure that Chromium and Iron are selected in the **Included Subsystems** list.



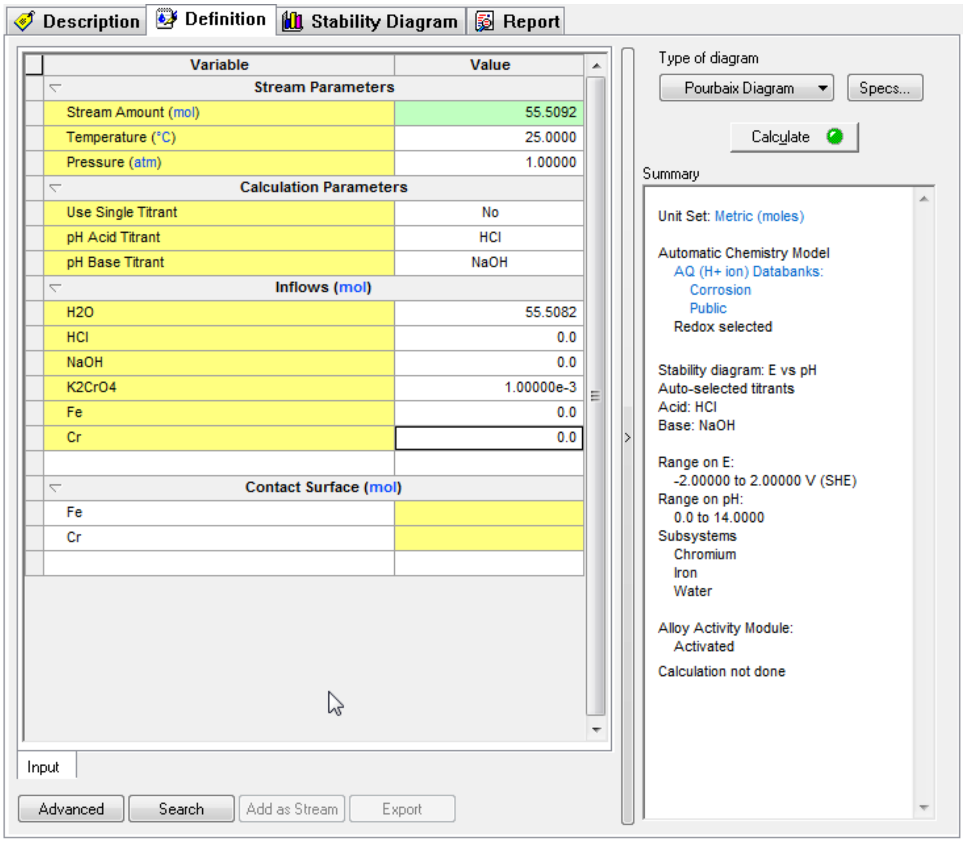
☑ Include Redox Chemistry

Include Subsystems

- ☐ Chlorine
- ☑ Chromium
- ☑ Iron
- ☐ Potassium
- ☐ Sodium

Figure 25-1 Selecting subsystems.

The filled out definition for the stability diagram should look like the following figure:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5092
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
HCl	0.0
NaOH	0.0
K2CrO4	1.00000e-3
Fe	0.0
Cr	0.0
Contact Surface (mol)	
Fe	
Cr	

Type of diagram: Pourbaix Diagram

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Corrosion
Public
Redox selected

Stability diagram: E vs pH
Auto-selected titrants
Acid: HCl
Base: NaOH

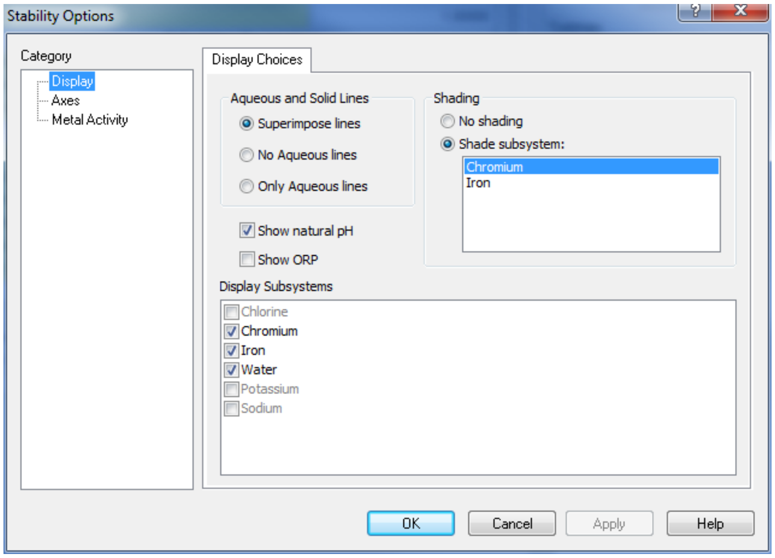
Range on E:
-2.00000 to 2.00000 V (SHE)
Range on pH:
0.0 to 14.0000
Subsystems
Chromium
Iron
Water

Alloy Activity Module:
Activated

Calculation not done

Figure 25-2 The filled out grid. Note that two metals are used.

We want to shade the chromium subsystem instead of the default iron subsystem. Click the **Specs…** button and then select the **Display** category**.**



Stability Options

Category
- Display
- Axes
- Metal Activity

Display Choices

Aqueous and Solid Lines
- ● Superimpose lines
- ○ No Aqueous lines
- ○ Only Aqueous lines

Shading
- ○ No shading
- ● Shade subsystem:
  - Chromium
  - Iron

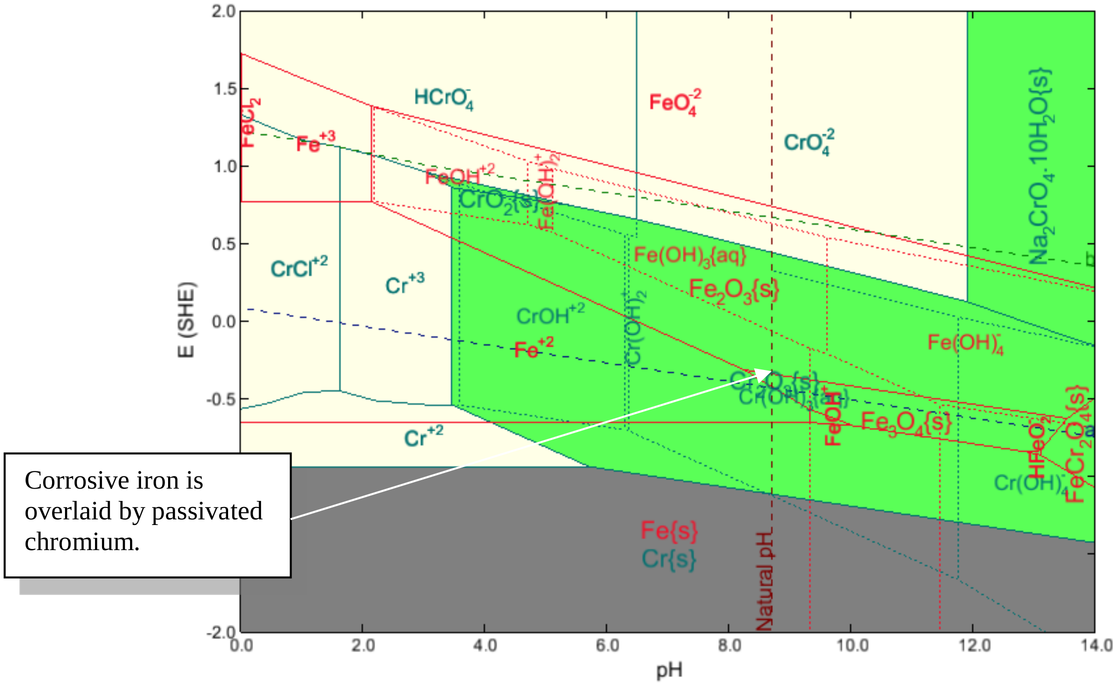
☑ Show natural pH

☐ Show ORP

Display Subsystems
- ☐ Chlorine
- ☑ Chromium
- ☑ Iron
- ☑ Water
- ☐ Potassium
- ☐ Sodium

Figure 25-3 Selecting chromium to be shaded.

Click on the **OK** button, and then click **Calculate**. When the calculation has finished, click the **Stability Diagram** tab.



Corrosive iron is overlaid by passivated chromium.

Figure 25-4 The stability diagram with both iron and chromium.

As you can see in the diagram, the shaded chrome passivating solid ($Cr(OH)_{3ppt}$) overlays the corrosive region of the iron system. This means that there is potential for passivating the metal in that region.

The $Cr(OH)_3$ field overlaps with the corrosion range of Fe in most of the pH range. This causes inhibition because of the coupling of:

> Oxidation of Fe to Fe^{+2}, reduction of chromates to $Cr(OH)_3$, deposition of a protective layer of $Cr(OH)_3$.

Iron in the presence of arsenates

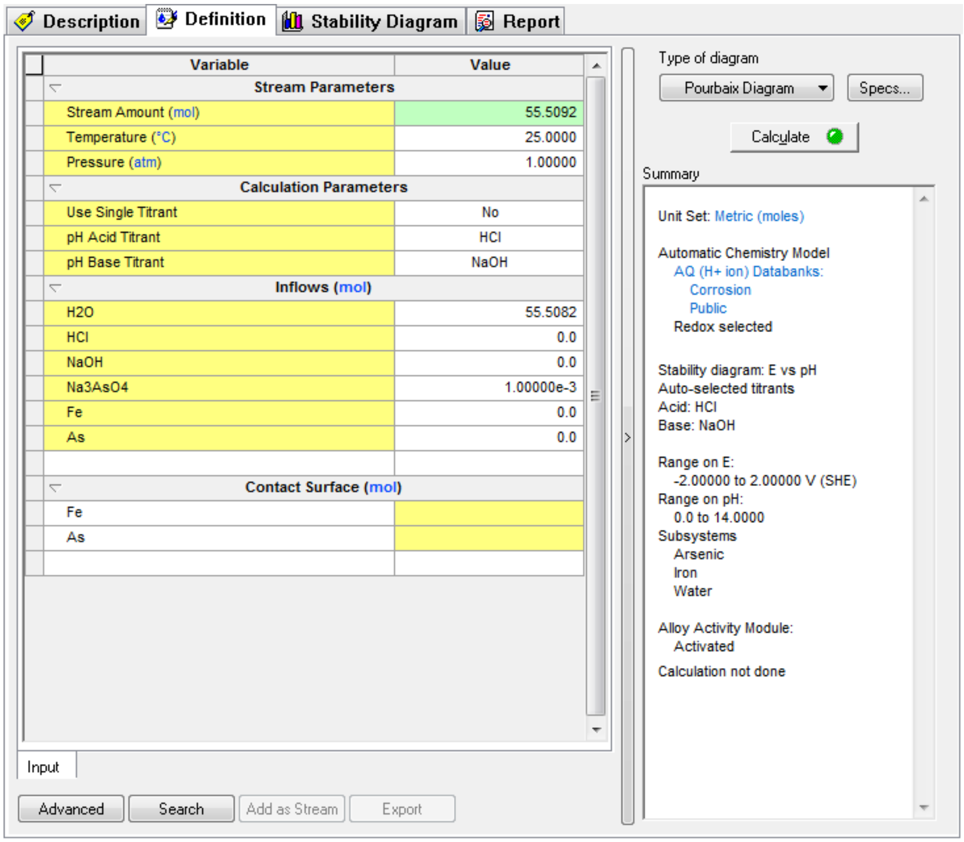
Create a stream with the following composition:

Table 25-2 Inhibition using arsenates

Parameter	Value	Comment
Stream Amount (mol)	55.5082	Default value
Temperature (ºC)	25	
Pressure (atm)	1	
H2O (mol)	55.5082	Default Value
Acid Titrant	HCl	No initial value
Base Titrant	NaOH	No Initial Value
Na3AsO4 (mol)	0.001	Used as an corrosion inhibitor
Contact Surface	Fe	
Contact Surface	As	

Create a stability diagram using the above stream. Select both ***Fe*** and ***As*** oxidation and reduction subsystems. In this case, the two metals will be used in addition to water in the subsystems.

The stability diagram definition should look similar to this:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5092
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
HCl	0.0
NaOH	0.0
Na3AsO4	1.00000e-3
Fe	0.0
As	0.0
Contact Surface (mol)	
Fe	
As	

Type of diagram
Pourbaix Diagram

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Corrosion
Public
Redox selected

Stability diagram: E vs pH
Auto-selected titrants
Acid: HCl
Base: NaOH

Range on E:
-2.00000 to 2.00000 V (SHE)
Range on pH:
0.0 to 14.0000
Subsystems
Arsenic
Iron
Water

Alloy Activity Module:
Activated

Calculation not done

Figure 25-5 Input for Iron/Arsenate diagram

Use the **Specs…** button and select the **Display** category to select ***Arsenic*** as the subsystem to shade.

Click the **Calculate** button when ready. Click on the **Stability Diagram** tab when finished.

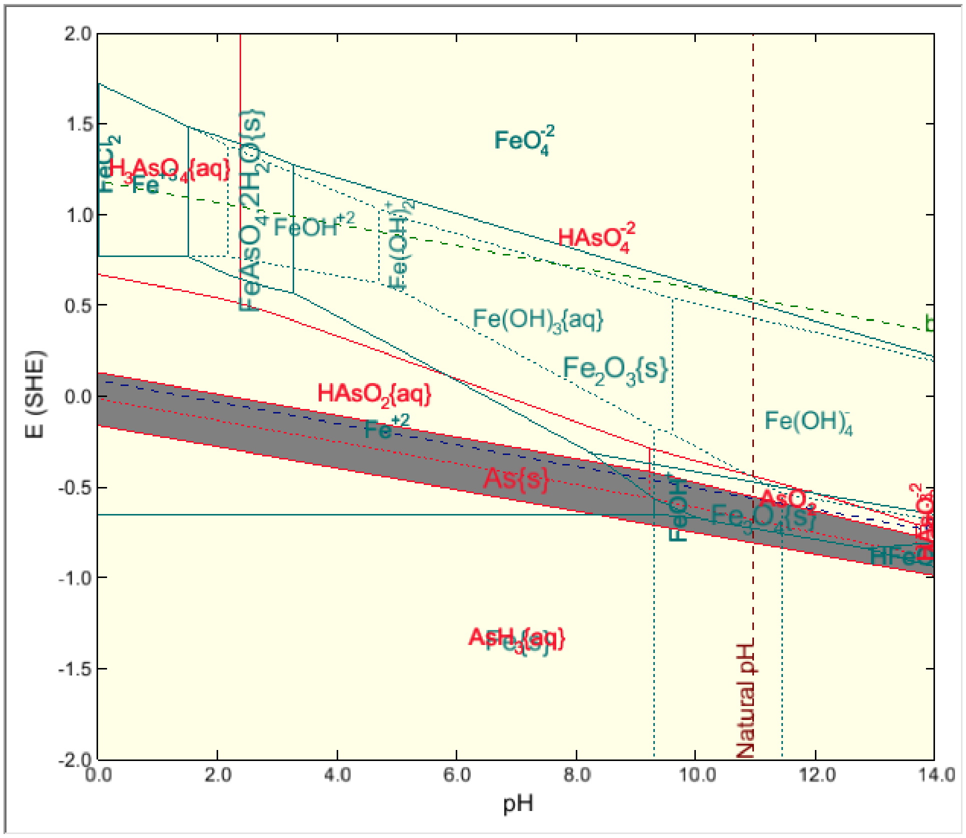


Figure 25-6 Iron with arsenates, arsenates are shaded

The elemental arsenic field overlaps with the corrosion range of ***Fe*** in most of the pH range provided that the conditions are reducing (absence of oxygen). This promotes inhibition because of the coupling of:

Oxidation of ***Fe*** to ***Fe***$^{+2}$, reduction of arsenates to elemental ***As***, deposition of a protective layer of ***As***. This can only work in reducing environments; otherwise the protective layer of ***As*** will oxidize and dissolve.

You can download a worked example of this chapter from the OLI Wiki Page

26. Implications of Stability Diagrams on Cathodic Protection

Overview

Cathodic protection works by shifting the potential of the metal into its immunity range. Stability diagrams can answer the questions:

- What is the potential range that ensures that the metal stays in the immunity range?

What is the effect of environmental variables on the immunity domain?

Example: Iron at 25 and 300 degree centigrade

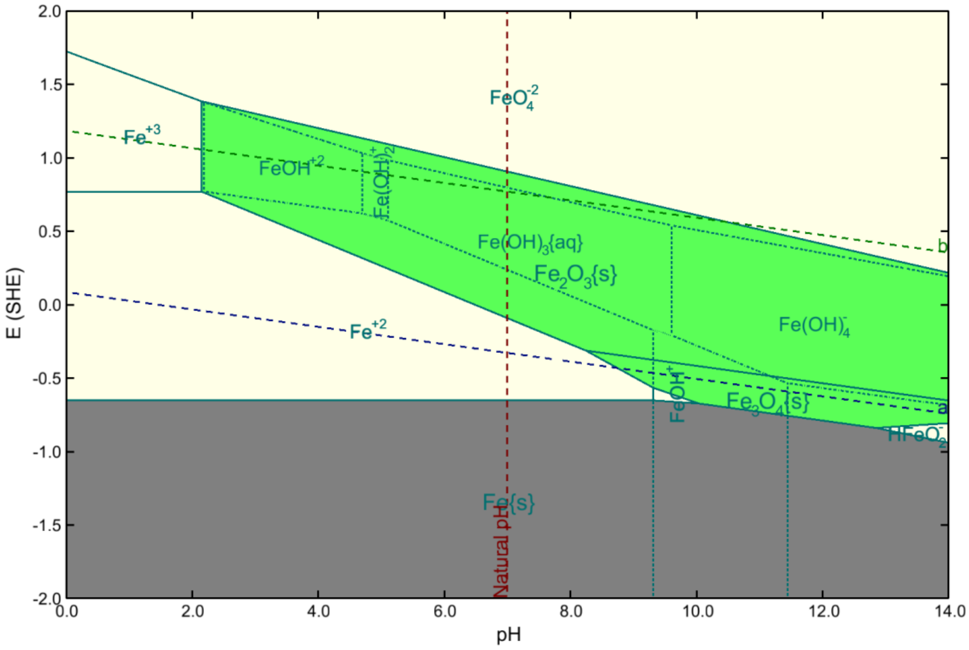


Figure 26-1 Iron in water at 25 °C and 1 Atm.

In the whole pH range, cathodic protection will require shifting the potential to moderately negative values.

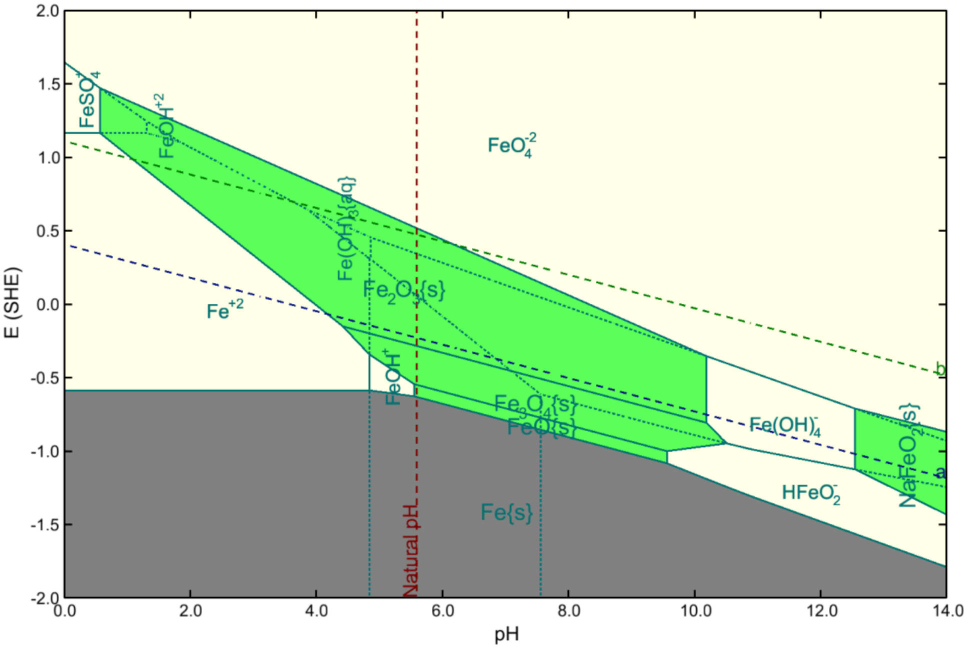


Figure 26-2 Iron in water at 300 °C and 100 Atm.

The immunity range in acidic and neutral solutions is weakly affected by temperature. However, the immunity range in alkaline solutions is shifted to much lower potentials which makes cathodic protection much more difficult.

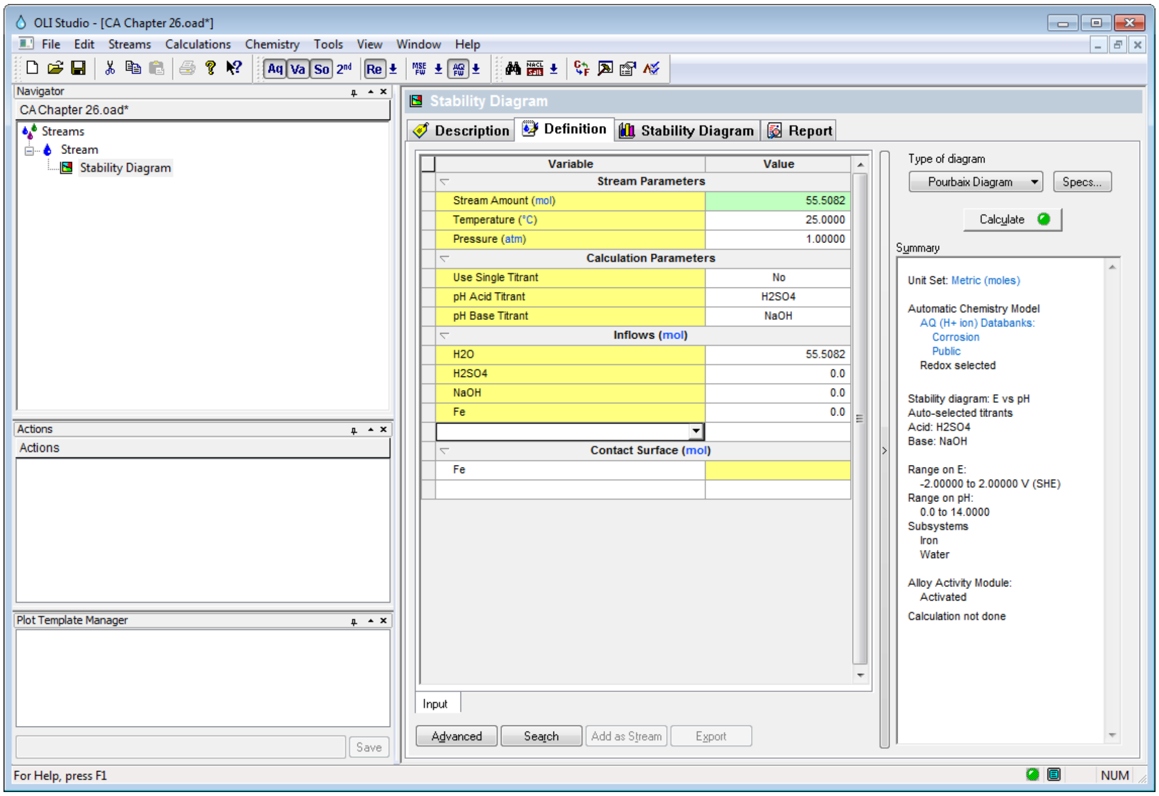
27. Selective Oxidation and Reduction Chemistry

Overview

Occasionally the user may want to remove a particular oxidation state for an element in the simulation. There are a variety of reasons to perform such an activity, one being that a particular oxidation state may be kinetically unavailable for the reaction. Another case is that perhaps a user needs to compare and contrast two systems. That is what we have here in this example.

Creating the default oxidation case

In this example we will create a Stability diagram for iron in water at ambient conditions. See 22 for details on how to create this stream. In Figure 27-1 we have created the input for our standard Iron stability diagram.



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	H2SO4
pH Base Titrant	NaOH
Inflows (mol)	
H2O	55.5082
H2SO4	0.0
NaOH	0.0
Fe	0.0
Contact Surface (mol)	
Fe	

Type of diagram: Pourbaix Diagram

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Corrosion
Public
Redox selected

Stability diagram: E vs pH
Auto-selected titrants
Acid: H2SO4
Base: NaOH

Range on E:
-2.00000 to 2.00000 V (SHE)
Range on pH:
0.0 to 14.0000
Subsystems
Iron
Water

Alloy Activity Module:
Activated

Calculation not done

Figure 27-1 Generating a standard Stability Diagram for Iron

Calculate this diagram as you have done in previous examples. Figure 27-2 is the result of the standard diagram. This diagram is frequently referred to as a Pourbaix diagram[48].

---

[48] Named after Marcel Pourbaix, who in the 1960's created a series of such diagrams. The latest reference is: Pourbaix, M., Atlas of electrochemical equilibria in aqueous solutions. 2d English ed. 1974, Houston, Tex.: National Association of Corrosion Engineers

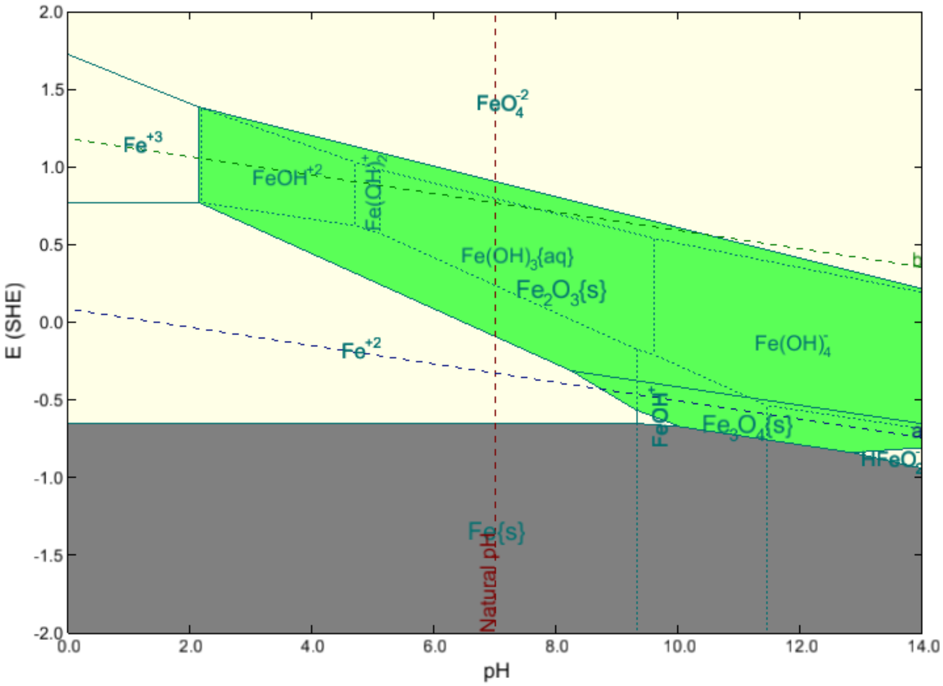


Figure 27-2 Standard OLI E-pH diagram for Iron

The issue here is that Pourbaix did not consider the FeO_4^{2-} ion in his work. This is iron in the +6 oxidation state for which there was little thermodynamic data available in the1960s. To reproduce his work we will need to remove the redox subsystem that pertains to Fe(+6).

Selective Redox, removing an undesired oxidation state.

To remove the undesired Fe(+6) oxidation state for this example we need to enter the model options for this diagram. To do that

Chemistry | Model Options…

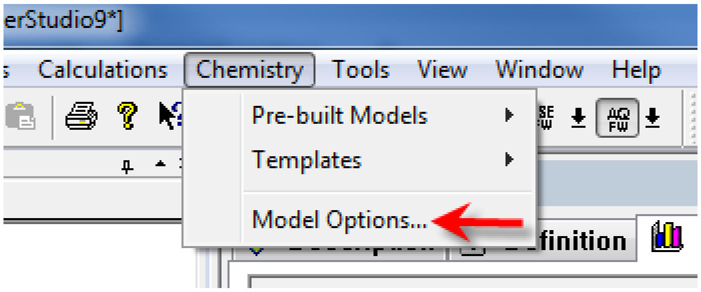
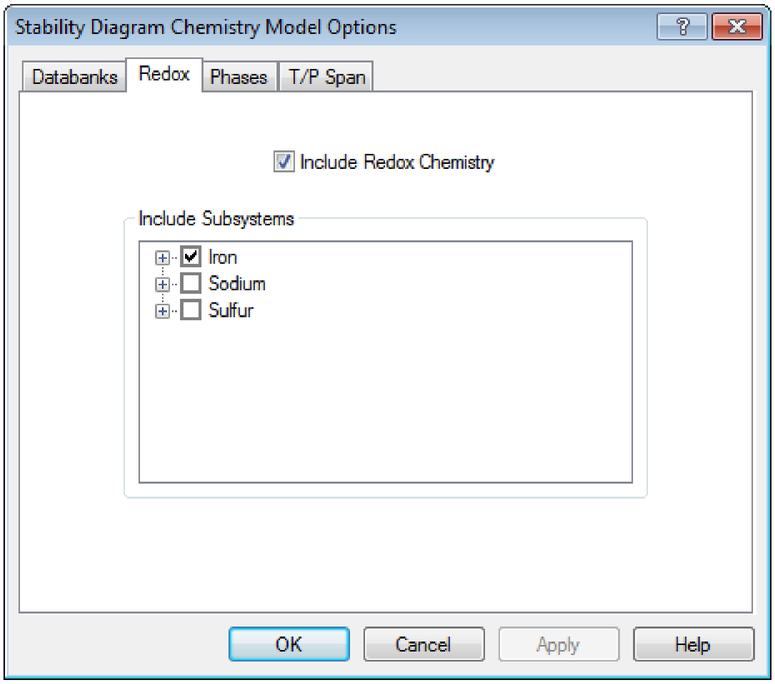


Figure 27-3 Selecting Chemistry | Model Options

Next select the **Redox** Tab.



☑ Include Redox Chemistry

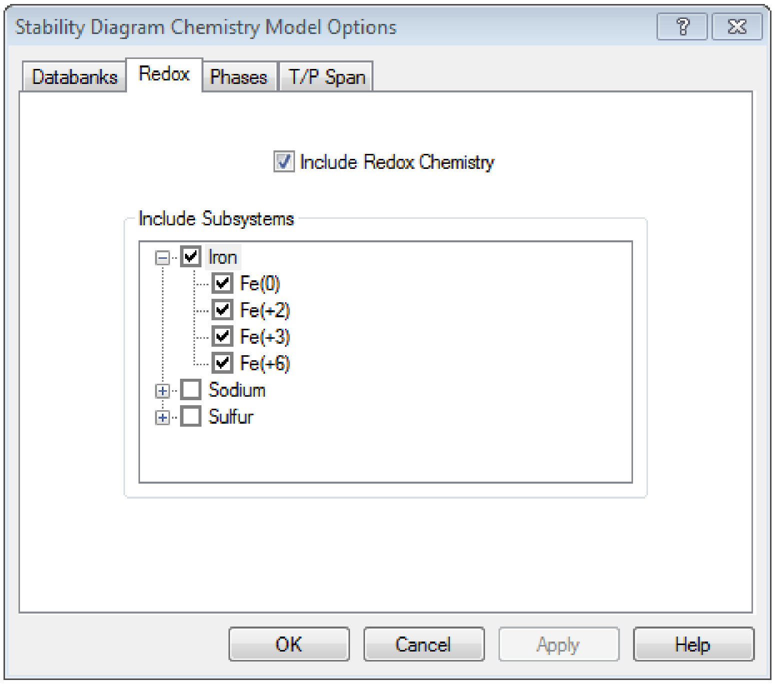
Include Subsystems

- ☑ Iron
- ☐ Sodium
- ☐ Sulfur

Figure 27-4 Selecting subsystems

Figure 27-4 shows the standard subsystems (collection of oxidation states) for each element. Please note that Hydrogen and Oxygen are automatically included and cannot be removed.

Expand the iron subsystem by clicking on the “+” next to the Iron subsystem.



☑ Include Redox Chemistry

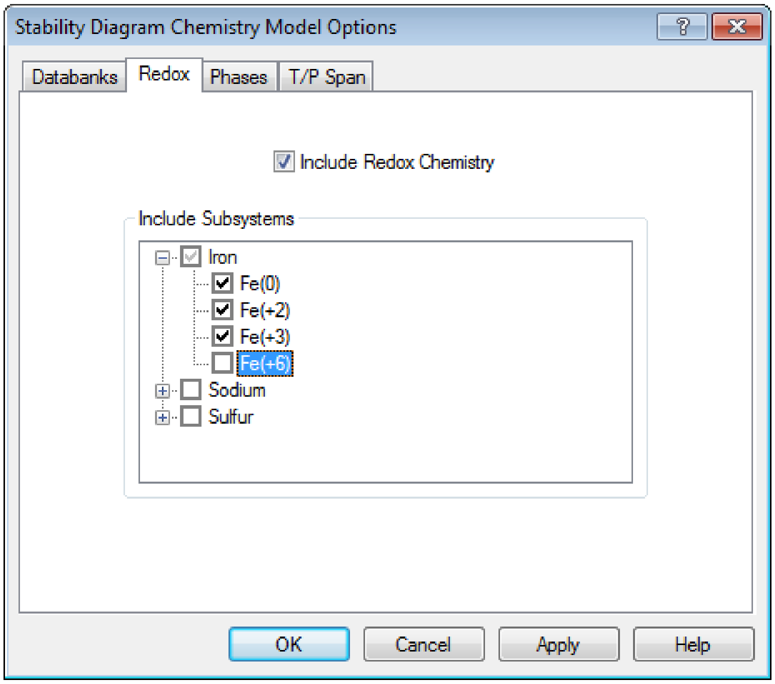
Include Subsystems

- ☑ Iron
  - ☑ Fe(0)
  - ☑ Fe(+2)
  - ☑ Fe(+3)
  - ☑ Fe(+6)
- ☐ Sodium
- ☐ Sulfur

Figure 27-5 Expanding the individual oxidation states

This has expanded the iron subsystem. You can see in our example that we have all the oxidation states from Fe(0) to Fe (+6).

Uncheck the Fe(+6) oxidation state to remove it from consideration. Note that if you have an inflow component with this oxidation state it will remain in the calculation.



☑ Include Redox Chemistry

☑ Iron
  ☑ Fe(0)
  ☑ Fe(+2)
  ☑ Fe(+3)
  ☐ Fe(+6)
☐ Sodium
☐ Sulfur

Figure 27-6 Unchecking the Fe(+6) oxidation state

Click the **OK** button to save your changes.

Rerun the calculation for the diagram. You can always press the **F9** key to calculate the object that you are currently viewing.

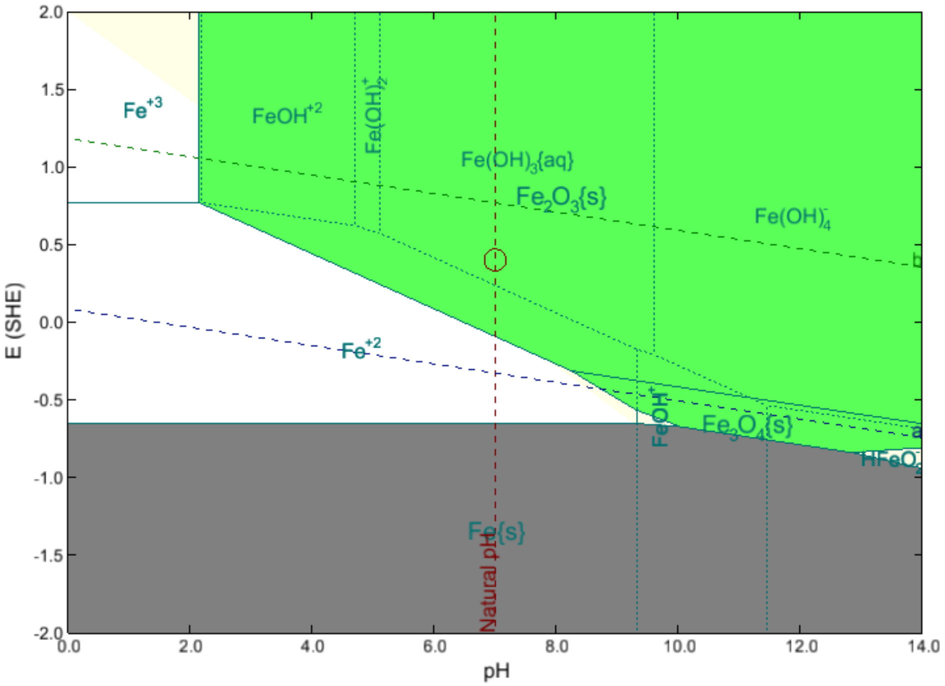


Figure 27-7 A more traditional Pourbaix diagram

Here you can see in Figure 27-7 that the region dominated by the FeO_4^{2-} ion is not present.

You can download a worked example of this chapter from the OLI Wiki Page

28. Introduction to Rates of Corrosion

Chemistry

The rates of corrosion use a subset of the OLI chemistry[49] and is currently only available with the AQ thermodynamic framework.

Neutral Species

H_2O, O_2, CO_2, H_2S, N_2, Cl_2 and all inert gases, SO_2 and NH_3, and organic molecules that do not undergo electrochemical reactions.

Anions

OH^-, Cl^-, Br^-, I^-, HCO_3^-, CO_3^{2-}, HS^-, S^{2-}, SO_4^{2-}, HSO_4^-, NO^{2-}, MoO_4^{2-}, ClO^-, ClO_4^-, Cr(VI) anions, As(III) anions, P(V) anions, W(VI) anions, and Si(IV) anions.

Cations

H^+, alkali metals, alkaline earth metals, Fe(II) cations, Fe(III) cations, Al(III) cations, Cd(II) cations, Sn(II) cations, Zn(II) cations, Pb(II) cations and $NH4^+$.

Calculation types

Single Point

The single point calculation will determine the rates of corrosion at only a single temperature and pressure.

The system may be flowing or static. If the system is flowing, only a single flowrate will be considered. Flowing systems also require the specification of diameter for the pipe or rotating cylinder.

pH Survey

This calculation is analogous to the pH Survey found in other OLI Studio components. The specification requires a titrant acid and base.

---

[49] These species are subject to change with time, most-likely to increase in number

Temperature Survey

A survey in temperature can be performed. The default range is from 25 to 100 degrees Centigrade. Any range may be used by changing the **Range** option.

The user should consider that some points in the survey may not converge due to phase changes (e.g., boiling off of aqueous liquids).

Composition Survey

A single titrant can be added to the solution and the effects of corrosion determined. The range of the component defaults to 0 to 1 mole with an increment of 0.1 moles. This range can be changed via the **Range** option.

Care should be taken when adding salts that can form hydrates (e.g., $CaCl_2.6H_2O$). When these hydrated salts begin to precipitate from solution, large amounts of water may be complexed with the crystal. The solution may desiccate and non-convergence may be the result.

Pressure Survey

The pressure of solution may be varied. The default range can be changed via the **Range** option.

Care should be taken when working at very low pressures since the solution may inadvertently boil off the liquid and non-convergence may results.

Flow Velocity Survey

In systems that are flowing, the flowrate of the stream can be varied.

Metal Chemistry

The default metal is the generic mild steel (G10100). The user can select from several classes of metals:

Iron/Mild Steels

- Fe (Zone Refined)
- Fe (Pure)
- Fe (ARMCO)
- Carbon Steel A212B
- Carbon Steel A216
- Carbon Steel 1018
- Carbon Steel G10100 (Generic)

300/400 Stainless

- Stainless Steel 304
- Stainless Steel 316
- Alloy 254SMO
- Duplex Stainless 2205

- 13% Cr

Aluminum

- Aluminum 1199 (Pure)
- Aluminum 1100

Nickel Based

- Ni
- Alloy 600
- Alloy 690
- Alloy 825
- Alloy 625
- Alloy C-276
- Alloy C-22

Copper

- Cu
- CuNi 9010
- CuNi 7030

Flow conditions

There are five flow conditions:

- Static Conditions
- Pipe Flow
- Rotating Disk
- Rotating Cylinder

Complete Agitation

Static Conditions

The solution is not flowing in this calculation.

Pipe Flow

The fluid is flowing through a pipe. The pipe diameter and flow velocity must be defined.

The default pipe diameter is **0.1 meters** and the default flow velocity is **2 meters/second**.

Rotating disk

This reproduces a type of experiment that is used quite frequently. A disk is rotated to bring fluid to the surface of the electrode in a predictable manner. The diameter of the disk is specified as well as the revolutions per minute (RPM).

The default diameter is **0.01 meters** and the default RPM is **5000 RPM**.

Rotating Cylinder

This reproduces a type of experiment that is used quite frequently. A cylindrical rotor is rotated to bring fluid to the surface of the electrode in a predictable manner. The diameter of the rotor is specified as well as the revolutions per minute (RPM).

The default diameter is **0.01 meters** and the default RPM is **5000 RPM**.

Complete Agitation

In this calculation, the liquid phase is completely agitated and no mass transfer limitations apply.

Kinetics of general corrosion

Elements of the approach:

- Electrode processes under activation control (Butler-Volmer kinetics)
- Reaction orders according to plausible reaction mechanisms
- Limiting current densities due to diffusion processes and homogeneous reactions in solution
- Effects of adsorption
- A model for the passive current density and the active-passive transition
- Effect of solution species on corrosion in the passive state

Synthesis of the partial processes to obtain a total polarization curve and, hence, corrosion rate

Butler-Volmer kinetics

$$i = i_o \exp [\alpha F (E - E_o) / RT]$$

Exchange current density depends on concentrations of active species:

$$i_o = i^* a_K^k \; a_L^l \; a_M^m \ldots$$

Reaction orders depend on various mechanisms

$$E_0 = E_0^0 + (RT/zF) \Pi a_i^{\nu i}$$

Activities of species that participate in the reaction:

$$a_i \ (i = 1, 2 \ldots)$$

Parameters that result from reaction mechanism:

Electrochemical transfer coefficients Reaction orders with respect to active species.

Parameters that depend only on the metal:

- Exchange current density after factoring out the chemical contribution (i.e., i^*).
- Temperature dependence of i^*, i.e., the activation energy.

Limiting current density due to the diffusion of species X to the interface:

$$i_{lim} = z\, k_m\, F \;\; a_{X,\, bulk}$$

- The mass transfer coefficient km depends on:
- Diffusivity of species X
- Viscosity
- Flow geometry (pipe, rotating cylinder, etc.)
- Flow velocity

29. Rates of General Corrosion – A Tour

Overview

In this tour we will simulate the corrosion rate of generic mild steel in a carbon dioxide containing brine. This is representative of a fluid recovered from oil production.

At this point you should be very familiar with entering data into OLI Studio. We will now focus on the rates of corrosion.

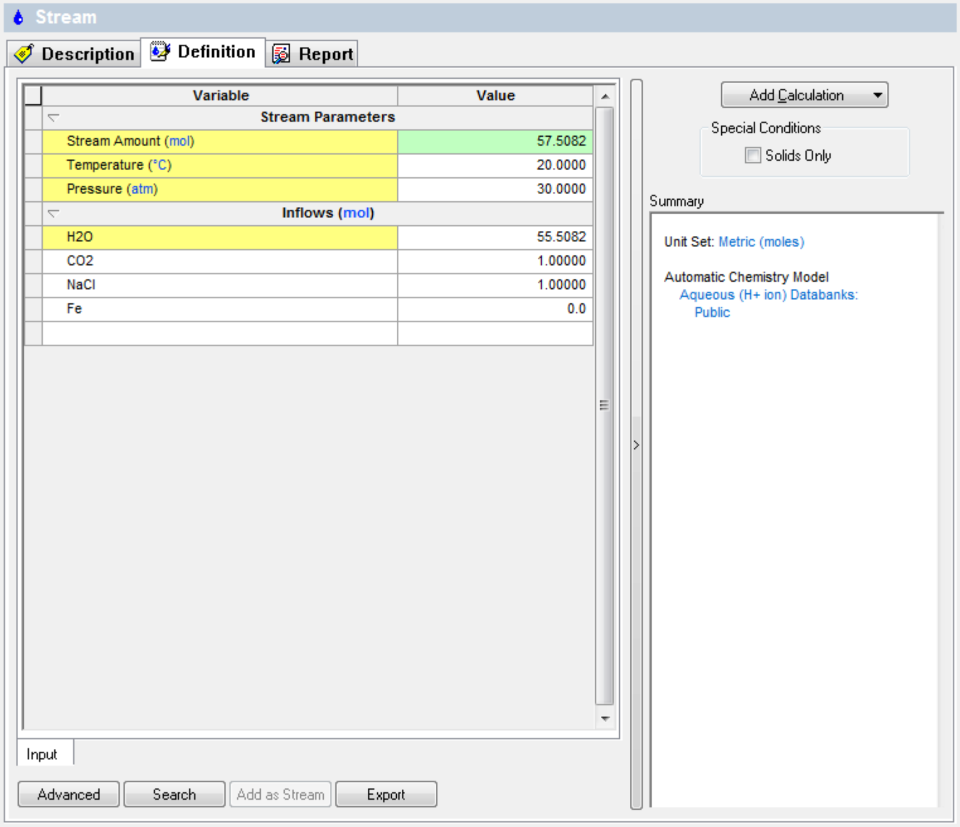
The Rates of Corrosion

Create a stream with the following composition.

Table 29-1 Introduction to rates of corrosion example

Parameter	Value	Comment
Stream Amount (mol)	55.5082	Default value
Temperature (°C)	20	
Pressure (atm)	30	
H2O (mol)	55.5082	Default Value
CO2 (mol)	1.0	
NaCl (mol)	1.0	No Initial Value
Contact Surface	Fe (Pure)	

Verify that only iron is selected in the redox subsystems list using the **Chemistry** menu item in the **Model Options/Redox** item. The definition grid of the stream should look similar to the following figure:



Variable	Value
Stream Parameters	
Stream Amount (mol)	57.5082
Temperature (°C)	20.0000
Pressure (atm)	30.0000
Inflows (mol)	
H2O	55.5082
CO2	1.00000
NaCl	1.00000
Fe	0.0

Unit Set: Metric (moles)

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

Figure 29-1 The stream definition.

Notice that there are no titrants for this type of diagram. We also have not specified any alloys. This will be done in the rates calculations. We did have to specify a base metal of iron.

With the above stream selected in the tree view, double-click on the **Add Corrosion Rates** icon in the **Actions/Explorer** pane.

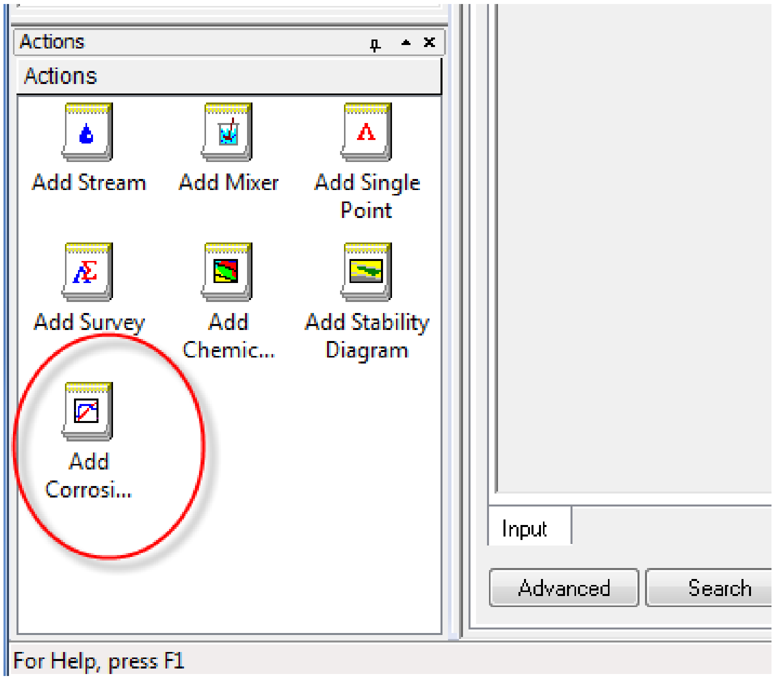


Figure 29-2 Click on the Add Corrosion Rates icon.

Click on the **Add Corrosion Rates** icon in the **Actions** pane.

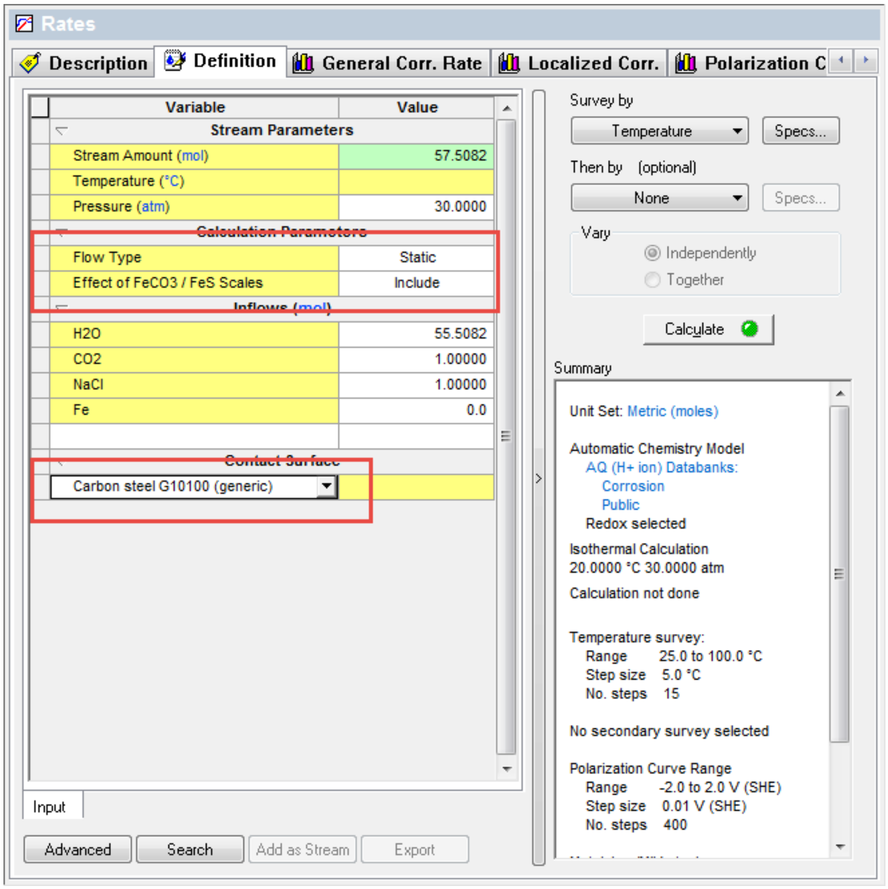
Click on the **Definition** tab.

Setting up the calculation

We will first perform a temperature survey. Change the ***Survey By*** button to **Temperature.** We will then change the default temperature range to 0 to 200 °C in 10 °C increments.

The contact surface is specified in the definition grid. For this tour we will consider the mild steel - ***Carbon Steel G10100 (generic).***

We will simulate in static conditions. The current default **Flow Condition** (which is “Static”) is acceptable.



Variable	Value
Stream Parameters	
Stream Amount (mol)	57.5082
Temperature (°C)	
Pressure (atm)	30.0000
Calculation Parameters	
Flow Type	Static
Effect of FeCO3 / FeS Scales	Include
Inflows (mol)	
H2O	55.5082
CO2	1.00000
NaCl	1.00000
Fe	0.0
Contact Surface	
Carbon steel G10100 (generic)	

Survey by: Temperature

Then by (optional): None

Vary: ● Independently ○ Together

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Corrosion
Public
Redox selected

Isothermal Calculation
20.0000 °C 30.0000 atm

Calculation not done

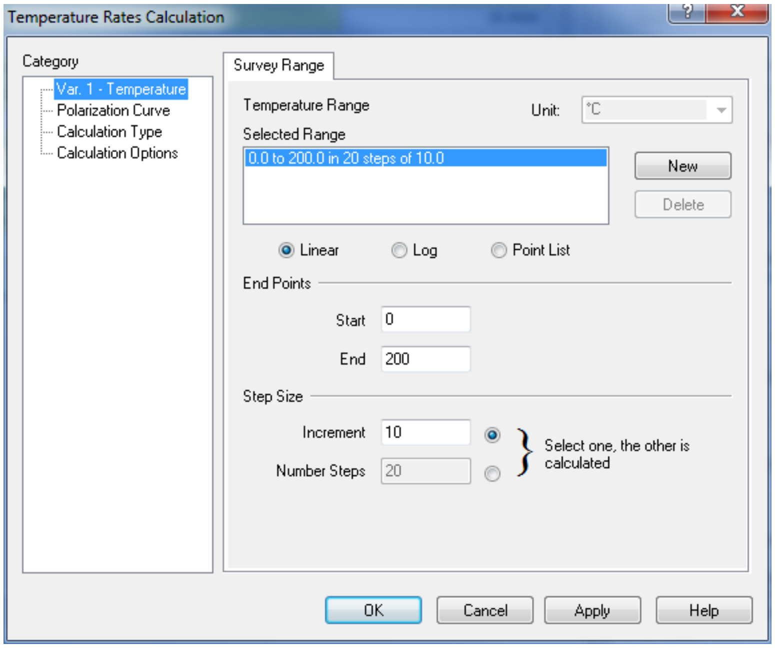
Temperature survey:
Range 25.0 to 100.0 °C
Step size 5.0 °C
No. steps 15

No secondary survey selected

Polarization Curve Range
Range -2.0 to 2.0 V (SHE)
Step size 0.01 V (SHE)
No. steps 400

Figure 29-3 Specifying contact surface and flow conditions.

Click on the **Specs…** button. Select the ***Var. 1 – Temperature*** category.



Temperature Range

Unit: °C

Selected Range: 0.0 to 200.0 in 20 steps of 10.0

● Linear ○ Log ○ Point List

End Points

Start 0

End 200

Step Size

Increment 10 ●

Number Steps 20 ○

Select one, the other is calculated

Figure 29-4 Specifying temperature range for the survey.

This dialog is analogous to the range display in the other OLI Studio modules. Set the **Start** temperature to 0°C, the **End** temperature to 200 °C and the increment to 10°C.

Click on **OK** then click the **Calculate** button.

When finished, click on the **General Corr. Rate** tab.

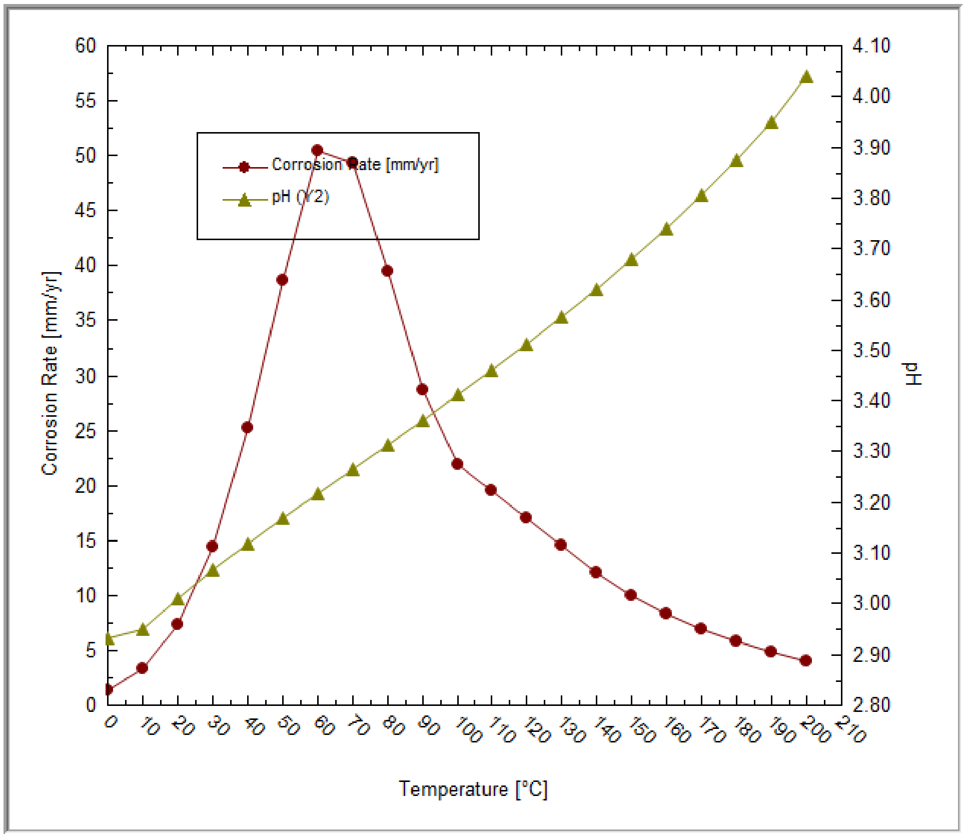
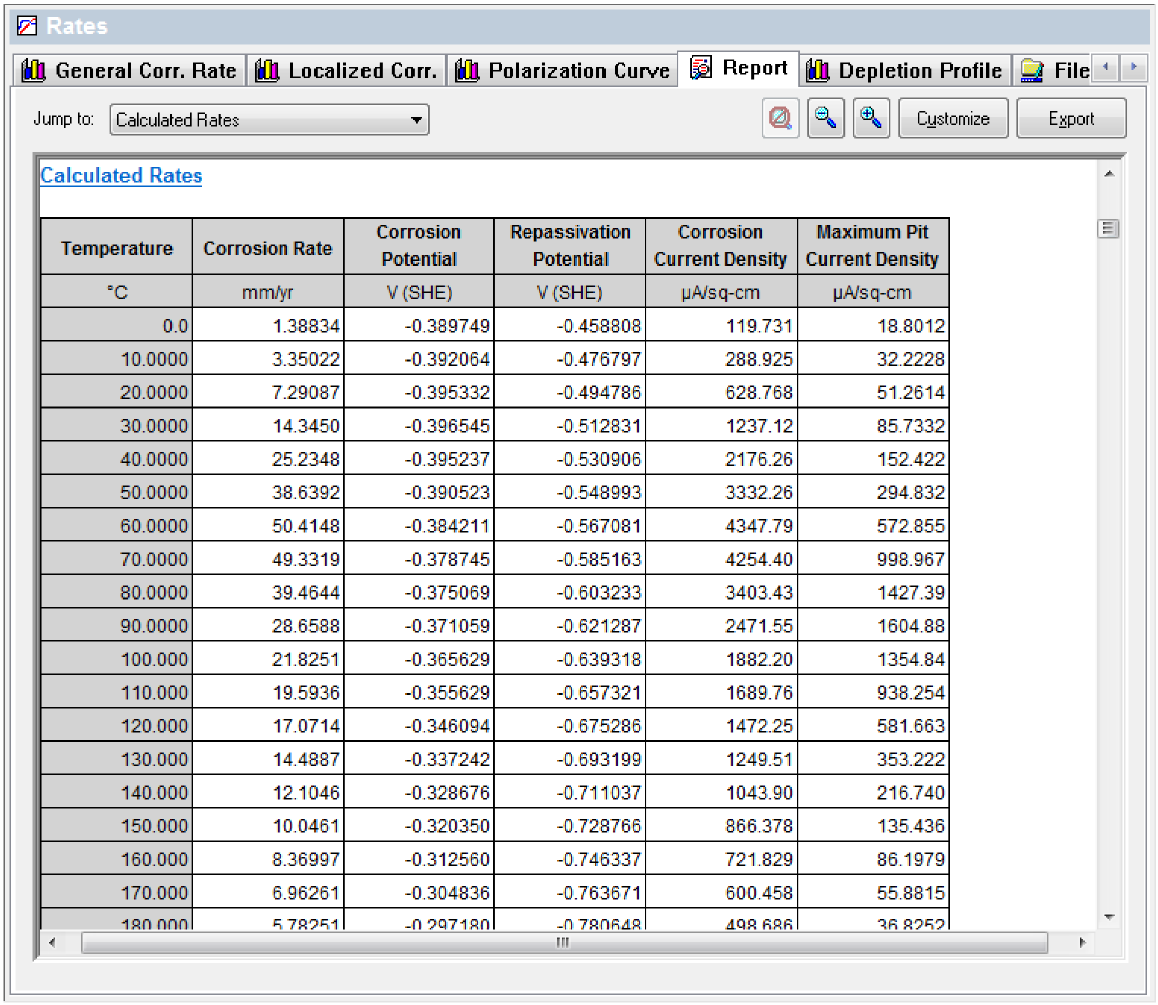


Figure 29-5 The rate of corrosion versus temperature plot.

This diagram shows that the rate of corrosion increases with increasing temperature till about 80 °C. Then the rate decreases. Further analysis would reveal that the solid $FeCO_3$ (Siderite) has precipitated and has formed a passivating layer.

Now click on the **Report** Tab. (You may have to use the scroll-arrow to see this tab)

Figure 29-6 Locating Scroll Arrows



Calculated Rates

Temperature	Corrosion Rate	Corrosion Potential	Repassivation Potential	Corrosion Current Density	Maximum Pit Current Density
°C	mm/yr	V (SHE)	V (SHE)	µA/sq-cm	µA/sq-cm
0.0	1.38834	-0.389749	-0.458808	119.731	18.8012
10.0000	3.35022	-0.392064	-0.476797	288.925	32.2228
20.0000	7.29087	-0.395332	-0.494786	628.768	51.2614
30.0000	14.3450	-0.396545	-0.512831	1237.12	85.7332
40.0000	25.2348	-0.395237	-0.530906	2176.26	152.422
50.0000	38.6392	-0.390523	-0.548993	3332.26	294.832
60.0000	50.4148	-0.384211	-0.567081	4347.79	572.855
70.0000	49.3319	-0.378745	-0.585163	4254.40	998.967
80.0000	39.4644	-0.375069	-0.603233	3403.43	1427.39
90.0000	28.6588	-0.371059	-0.621287	2471.55	1604.88
100.000	21.8251	-0.365629	-0.639318	1882.20	1354.84
110.000	19.5936	-0.355629	-0.657321	1689.76	938.254
120.000	17.0714	-0.346094	-0.675286	1472.25	581.663
130.000	14.4887	-0.337242	-0.693199	1249.51	353.222
140.000	12.1046	-0.328676	-0.711037	1043.90	216.740
150.000	10.0461	-0.320350	-0.728766	866.378	135.436
160.000	8.36997	-0.312560	-0.746337	721.829	86.1979
170.000	6.96261	-0.304836	-0.763671	600.458	55.8815
180.000	5.78251	-0.297180	-0.780648	498.686	36.8252

Figure 29-7 Tabulated results

The report displays the tabulated results. You may have to scroll down to see the same information as displayed above.

Now click on the **Polarization Curve**

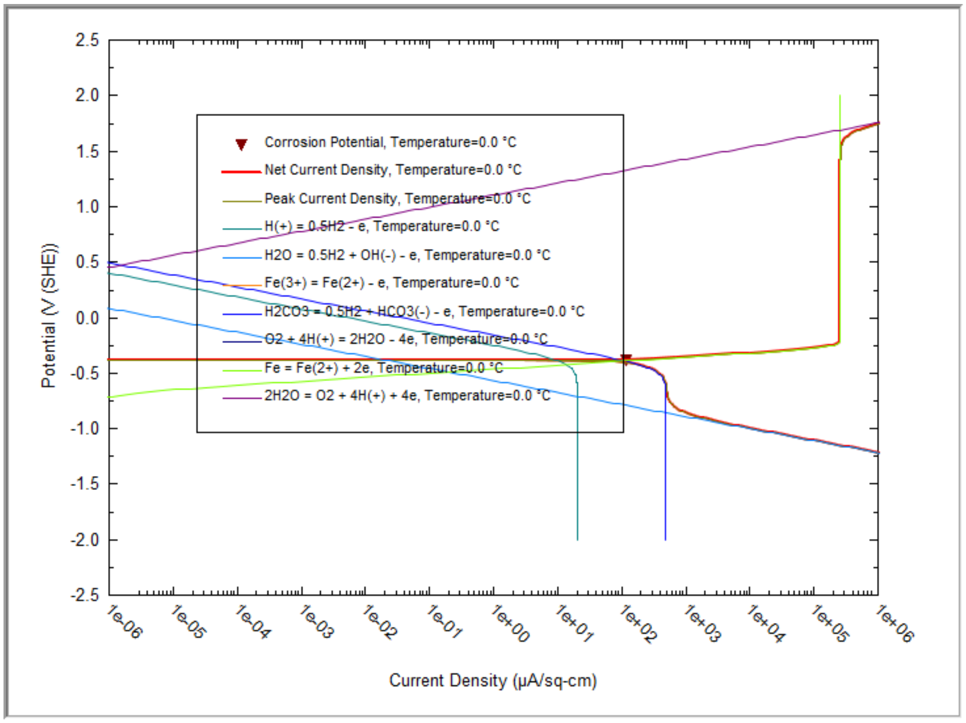


Figure 29-8 Polarization Curve at 0° C

The curve displayed corresponds to 0ºC. The customize button can be used to display the polarization curve at a different temperature.

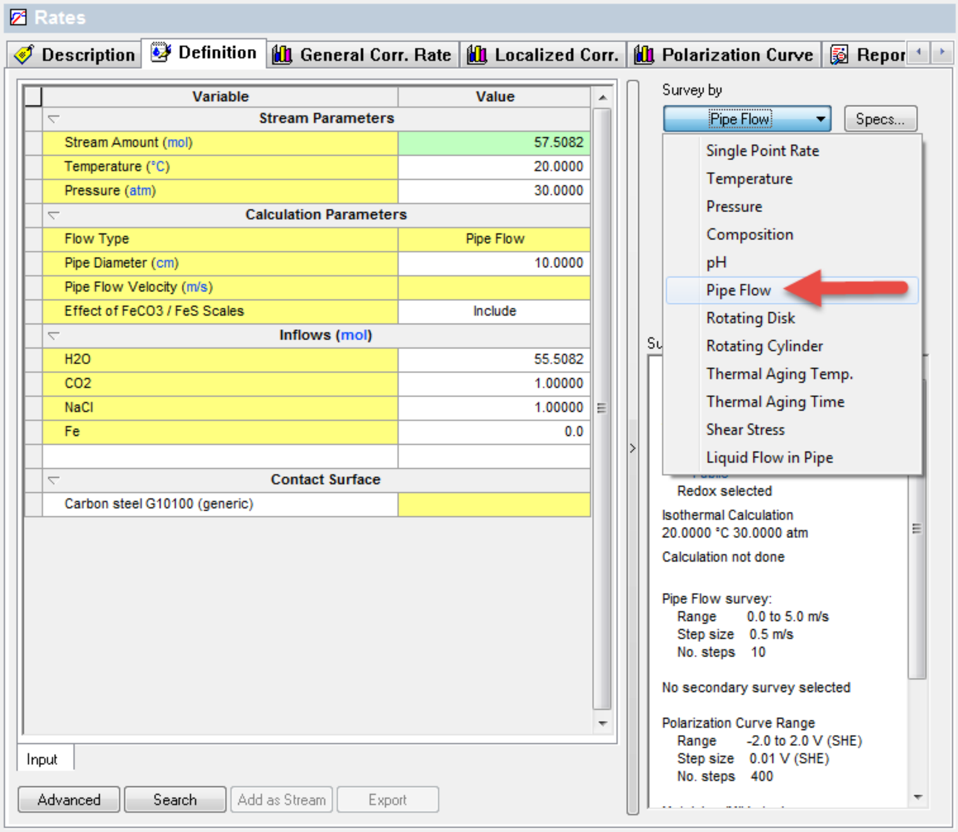
The ▼ symbol represents the mixed potential point. It is this point that determines the rates of corrosion calculation. The ▼ appears to be on the “3” and “2” lines. This means that carbon dioxide and water is controlling the rates of corrosion. If the ▼ appeared on a vertical line, then we could say that the current had reached a limiting or passivating amount.

Flow survey

We will now repeat our calculations but only at 20 °C. This time we will perform a flow survey. We will simulate the movement of a fluid through a pipe. We will need to specify the diameter of the pipe and the fluid flow.

Click on the **Definition** tab (you may need to use the scroll arrows)

Click on the **Types of rates calculation** and select ***Pipe Flow.***

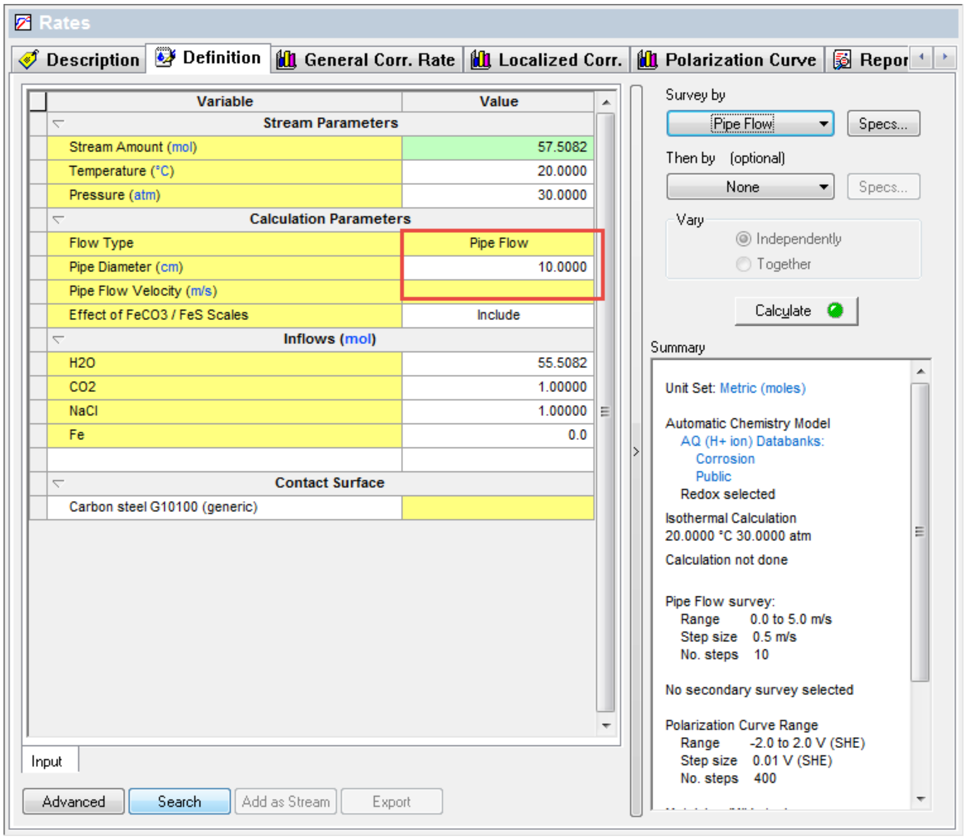


Variable	Value
Stream Parameters	
Stream Amount (mol)	57.5082
Temperature (°C)	20.0000
Pressure (atm)	30.0000
Calculation Parameters	
Flow Type	Pipe Flow
Pipe Diameter (cm)	10.0000
Pipe Flow Velocity (m/s)	
Effect of FeCO3 / FeS Scales	Include
Inflows (mol)	
H2O	55.5082
CO2	1.00000
NaCl	1.00000
Fe	0.0
Contact Surface	
Carbon steel G10100 (generic)	

```
   Redox selected
Isothermal Calculation
20.0000 °C 30.0000 atm
Calculation not done

Pipe Flow survey:
   Range      0.0 to 5.0 m/s
   Step size   0.5 m/s
   No. steps   10

No secondary survey selected

Polarization Curve Range
   Range      -2.0 to 2.0 V (SHE)
   Step size   0.01 V (SHE)
   No. steps   400
```

Figure 29-9 Selecting Pipe Flow

The flow specifications entered in the **Corrosion Values** section of the definition grid.



Variable	Value
Stream Parameters	
Stream Amount (mol)	57.5082
Temperature (°C)	20.0000
Pressure (atm)	30.0000
Calculation Parameters	
Flow Type	Pipe Flow
Pipe Diameter (cm)	10.0000
Pipe Flow Velocity (m/s)	
Effect of FeCO3 / FeS Scales	Include
Inflows (mol)	
H2O	55.5082
CO2	1.00000
NaCl	1.00000
Fe	0.0
Contact Surface	
Carbon steel G10100 (generic)	

Survey by: Pipe Flow

Then by (optional): None

Vary: ◉ Independently ○ Together

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Corrosion
Public
Redox selected

Isothermal Calculation
20.0000 °C 30.0000 atm

Calculation not done

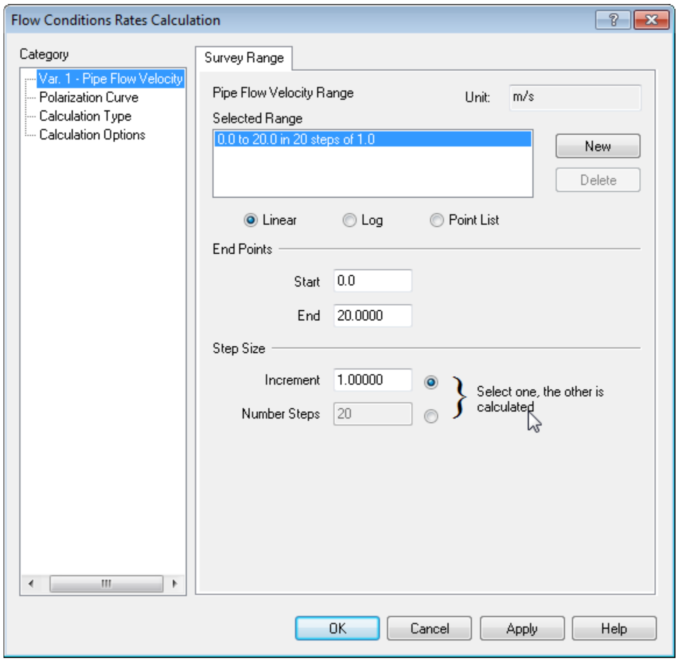
Pipe Flow survey:
Range 0.0 to 5.0 m/s
Step size 0.5 m/s
No. steps 10

No secondary survey selected

Polarization Curve Range
Range -2.0 to 2.0 V (SHE)
Step size 0.01 V (SHE)
No. steps 400

Figure 29-10 Specifying the Pipe Flow Diameter.

We will use the default ***Pipe Diameter*** of 10 cm (0.01 m). The Flow velocity will be adjusted by the **Specs** > **Survey Range** tab.



Pipe Flow Velocity Range Unit: m/s

Selected Range: 0.0 to 20.0 in 20 steps of 1.0

◉ Linear ○ Log ○ Point List

End Points
Start 0.0
End 20.0000

Step Size
Increment 1.00000 ◉
Number Steps 20 ○
Select one, the other is calculated

Figure 29-11 Range setting

The range of values indicates the lowest and highest velocity. The radio buttons in the **Step Size** section allow the user to perform quick conversion.

The **Increment** option allows for the starting and ending values to be entered along with the number of steps and then the increment between points will be automatically determined.

Optionally, the user may specify the **Number of Steps** by selecting the appropriate radio button, in which case the increment value will be calculated automatically.

We will enter a **Start** value of 0 and an **End** value of 20. The **Increment** will be 1.0.

Click on the **OK** button then click on the **Calculate** Button.

Click on the **General Corrosion Rate** tab when the calculation completes.

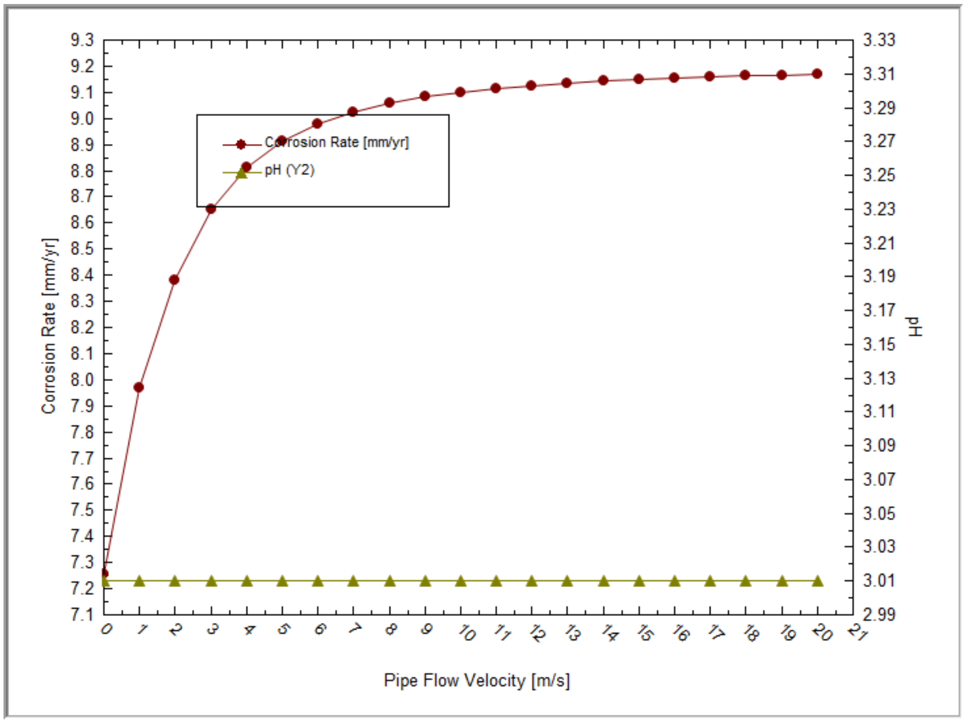


Figure 29-12 The flow survey

The asymptotic behavior of the rate is due to mass-transfer phenomena. At low flow rates, there is sufficient time for the corrosive agents to reach the pipe. At higher flows, a steady-state condition exists.

You can download a worked example of this chapter from the OLI Wiki Page

30. Thermal Aging and Variations in Alloy Composition Introduction

What can be simulated?

Localized corrosion of engineering alloys is a complex function of metallurgical factors and environmental conditions. Among metallurgical factors, effects of thermal instabilities are of interest for assessing the performance and expected service life of industrial components fabricated from nominally corrosion-resistant stainless steels and nickel-base alloys. Fabrication processes such as heat treatment and welding are known to introduce microstructural changes that may affect both the mechanical and corrosion performance of an alloy. In particular, thermal instability of stainless steels and nickel-base alloys may lead to the formation of complex metal carbides of the type M_3C_2, M_7C_3, M_6C, or $M_{23}C_6$ in which the metallic component M represents Cr, Mo, W, and Fe. The carbide is chromium- or molybdenum-rich depending on the carbide type, which in turn depends on the alloy composition and temperature. Also, various chromium-rich intermetallic phases can form in many alloys. Precipitation of such phases may occur at temperatures ranging from 500 to 900 °C depending on alloy composition. Formation of grain boundary carbides often results in the depletion of chromium and, possibly, molybdenum in the vicinity of the grain boundary because of the slow diffusion of substitutional elements such as chromium relative to the interstitial carbon. Similarly, the corrosion resistance of welded components may be affected by the segregation of alloying elements and precipitation of intermetallic phases, carbides or nitrides in the solidified weld and unmixed zones as well as the precipitation of carbides and other phases in the heat-affected zone adjacent to the weld.

Sensitization of Fe-Ni-Cr-Mo alloys and its effects on intergranular attack and intergranular stress corrosion cracking is the most directly observed effect of Cr depletion. It may result in intergranular attack and intergranular stress corrosion cracking. Localized corrosion can be also affected by Cr and Mo depletion.

Corrosion Analyzer contains the following technology that can help address these issues:

(1) A grain boundary microchemistry model for predicting the chromium and molybdenum depletion in the vicinity of grain boundaries as a result of carbide formation;
(2) An electrochemical model for calculating the repassivation potential of Fe-Ni-Cr-Mo-W alloys as a function of alloy composition and environmental

conditions including temperature and concentrations of aqueous solution species;

(3) A procedure for calculating the observable repassivation potential that corresponds to macroscopic localized corrosion by applying the electrochemical model to the depletion profiles and performing suitable integration.

More details about this technology are described by Anderko et al. (2008), Tormoen et al. (2009), Anderko et al. (2009), and Sridhar et al. (2009).

Alloy Chemistry

Simulations can be performed, in general, for alloys that belong to the Fe-Ni-Cr-Mo-W-N-C family (i.e., for stainless steels and nickel-base alloys).

Depletion profiles in the vicinity of grain boundaries and depletion parameters can be obtained for austenitic alloys (including stainless steels and Ni-base alloys). Also, the effect of Cr and Mo depletion on localized corrosion can be calculated. This effect can be examined using the repassivation potential, which provides a threshold potential for the stabilization of localized corrosion (Anderko et al., 2009).

For other alloys from the Fe-Ni-Cr-Mo-W-N-C family, the repassivation potential can be calculated if the alloy composition is known. This also includes experimental alloys and separate phases that may be formed as a result of various forms of heat treatment (Sridhar et al., 2009).

Calculation types

Thermal aging is an additional phenomenon that can be simulated within the framework of corrosion kinetics. All calculations types and, in particular, survey types, that are supported for corrosion kinetics are also supported in conjunction with the study of thermal aging.

If it is desired to make calculations on a thermally aged sample, the thermal aging temperature and time need to be specified in the **Calc Parameters** section in the **Definition** tab. The default values are 399 °C for the thermal aging temperature and 0.0 hours for the thermal aging time. If either of these default values is used, no thermal aging effects will be predicted. Thus, by default, Corrosion Analyzer performs calculations on samples that have not been thermally aged.

Thermal Aging Temperature Survey

This calculation makes it possible to vary the thermal aging temperature within a certain range. A fixed value of thermal aging time is assumed as specified by the user. Typically, the temperatures for which thermal aging effects can be observed range from ~500 °C to ~900 °C, with the effects being most pronounced in the middle of this range.

Thermal Aging Time Survey

This calculation can be used to examine the effect of aging time at a fixed thermal aging temperature.

Output specific to thermal aging

The following output can be generated:

(1) Chromium and molybdenum depletion profiles, i.e., the variation of Cr and Mo concentration within the grain as a function of grain boundary

(2) The depletion parameter, which provides compact information on the extent to which the depletion process reduces the grain boundary concentration below a certain critical value of, which can be defined by well-known criteria for maintaining passivity (e.g. x_{Cr}^{*} = 0.11 or 0.12). This parameter can be calculated as the area of the depletion profile below the threshold concentration x_{Cr}^{*}, divided by bulk Cr concentration, x_{Cr}^{0}:

$$\delta(x_{Cr}^{*}) = \frac{1}{x_{Cr}^{0}} \int_{0}^{z^{*}} \left(x_{Cr}^{*} - x_{Cr}(z) \right) dz$$

where z^{*} is the distance from the grain boundary that corresponds to the threshold concentration x_{Cr}^{*}.

(3) The repassivation potential, which is a key parameter for determining whether localized corrosion can occur, may be affected by thermal aging in a rather complex way.

31. Thermal Aging and Variations in Alloy Composition

Overview

In this tour we will show examples of simulating the effects of thermal aging on Fe-Ni-Cr-Mo-W-C-N alloys (i.e., stainless steels and nickel-base alloys). Specifically, we show how to predict:

- Chromium and molybdenum depletion profiles in the vicinity of grain boundaries, which result from heat treatment of austenitic alloys;
- Depletion parameters for sensitized austenitic alloys, which provide an indicator of whether the alloy is susceptible to intergranular corrosion
- Effect of thermal aging on the repassivation potential of austenitic alloys, which provides a threshold condition for localized corrosion (pitting or crevice corrosion)
- The repassivation potential of alloys with compositional variations that may or may not result from thermal aging. This facility can also be used for bulk alloys that are not in the database or to hypothetical or experimental alloys as long as they belong to the Fe-Ni-Cr-Mo-W-C-N family. An example will be given for a duplex ally, either annealed or thermally treated.

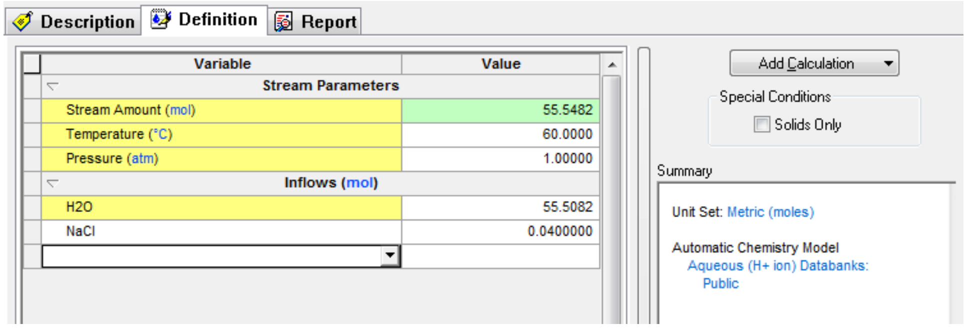
At this point you should be very familiar with entering data into OLI Studio. Also, you need to know the foundations of the use of the repassivation potential to predict the occurrence of localized corrosion (Anderko et al., 2004 and papers cited therein).

Example 1: Thermal aging of alloy 600

We will be studying the behavior of thermally aged alloy 600 in a dilute aqueous solution of sodium chloride. Therefore, click on **Add Stream** and start by creating a stream with the following conditions:

Temperature	**60**	**°C**
Pressure	**1**	**Atmospheres**
H2O	**55.5082**	**moles**
NaCl	**0.04**	**moles**

The definition grid of the stream should look similar to the following figure:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5482
Temperature (°C)	60.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
NaCl	0.0400000

Unit Set: Metric (moles)

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

Figure 31-1: The stream definition.

With the above stream selected in the tree view, double-click on the **Add Corrosion Rates** icon in the **Actions/Explorer** pane. Even though the thermal aging simulation facilities do not predict corrosion rates per se, they belong to the category of corrosion kinetics and, therefore, they are included in the Corrosion Rates section of the Corrosion Analyzer.

Then, click on the **Definition** tab.

Setting up the calculation

We will be simulating how the time of thermal aging affects a***lloy 600*** at a fixed thermal aging temperature of 700 °C. For this purpose:

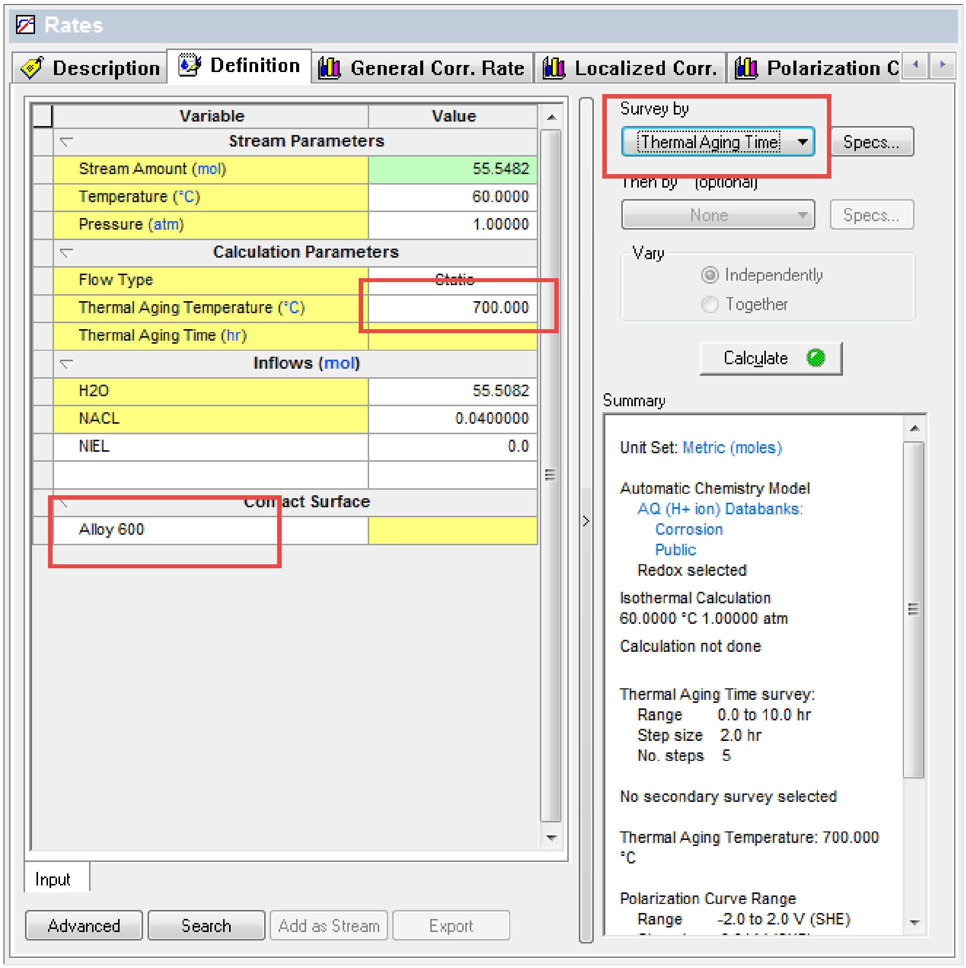
Select ***Alloy 600*** from the drop-down **Contact Surface** menu.

In the **Calc Parameters** section, replace the default value for the **Thermal Aging Temperature** with 700 °C.

Note that the default value for the **Thermal Aging Temperature** is 399 °C, which is a low value so that, in the default case, no effects of thermal aging will be calculated.

Then, from the **Survey By** button select Thermal Aging Time.

The definition grid for the Corrosion Rates should look similar to the following figure. The key specifications are highlighted using red squares:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5482
Temperature (°C)	60.0000
Pressure (atm)	1.00000
Calculation Parameters	
Flow Type	Static
Thermal Aging Temperature (°C)	700.000
Thermal Aging Time (hr)	
Inflows (mol)	
H2O	55.5082
NACL	0.0400000
NIEL	0.0
Contact Surface	
Alloy 600	

Survey by: Thermal Aging Time

Then by (optional): None

Vary
○ Independently
○ Together

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Corrosion
Public
Redox selected

Isothermal Calculation
60.0000 °C 1.00000 atm

Calculation not done

Thermal Aging Time survey:
Range 0.0 to 10.0 hr
Step size 2.0 hr
No. steps 5

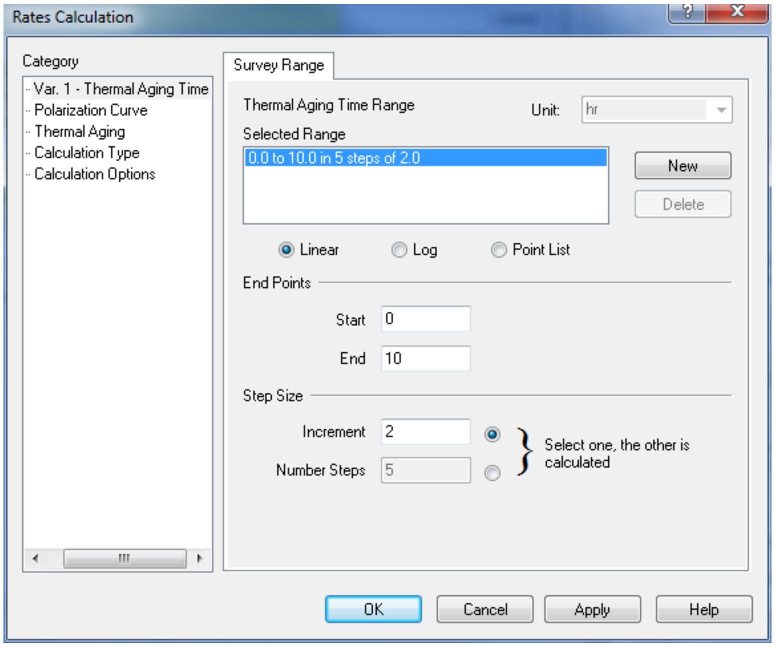
No secondary survey selected

Thermal Aging Temperature: 700.000 °C

Polarization Curve Range
Range -2.0 to 2.0 V (SHE)

Figure 31-2 Specifying contact surface, thermal aging temperature and type of calculations.

Now, click on the **Specs…** button. **The Survey Range** category allows you to specify the range for the thermal aging time survey. Change the range from 0 to 10 hours with a step of 2.0 hours.



Thermal Aging Time Range Unit: hr

Selected Range

0.0 to 10.0 in 5 steps of 2.0

● Linear ○ Log ○ Point List

End Points

Start 0

End 10

Step Size

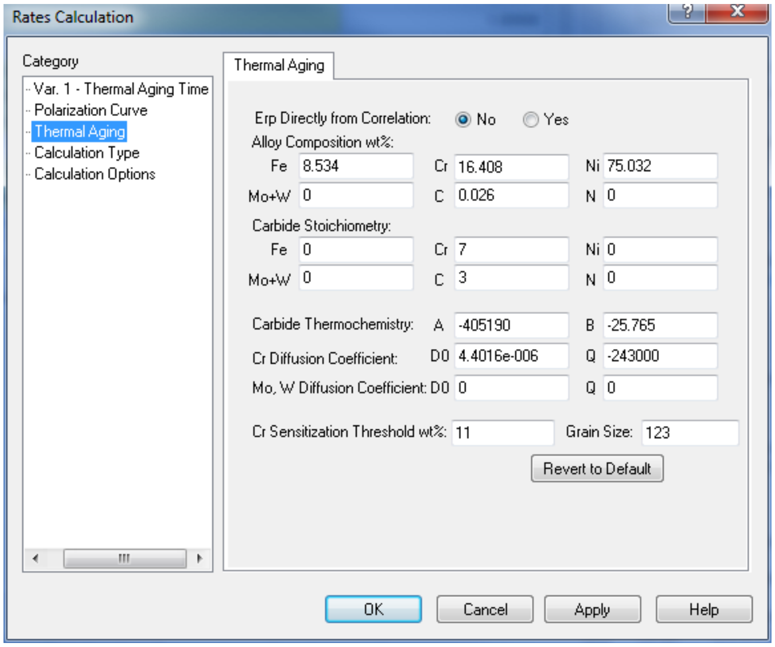
Increment 2 ●

Number Steps 5 ○

Select one, the other is calculated

Figure 31-3 Default Thermal Aging Survey Range

Then, click on the **Thermal Aging** category.



Erp Directly from Correlation: ● No ○ Yes

Alloy Composition wt%:

Fe 8.534 Cr 16.408 Ni 75.032

Mo+W 0 C 0.026 N 0

Carbide Stoichiometry:

Fe 0 Cr 7 Ni 0

Mo+W 0 C 3 N 0

Carbide Thermochemistry: A -405190 B -25.765

Cr Diffusion Coefficient: D0 4.4016e-006 Q -243000

Mo, W Diffusion Coefficient: D0 0 Q 0

Cr Sensitization Threshold wt%: 11 Grain Size: 123

Figure 31-4 Thermal Aging Parameters

In this category, you can change all parameters that are necessary for calculating chromium and (if applicable) molybdenum depletion profiles. You can change:

- The alloy composition (for example, to analyze the effect of a different carbon content);
- The stoichiometry of the carbide phase that may form at the grain boundary; the typical carbide stoichiometry is M_7C_3 or $M_{23}C_6$ (where M = Cr, Mo) but can be adjusted

- The parameters that define the equilibrium constant for the formation of the carbide
- The diffusion coefficient of Cr and, if applicable, Mo
- The threshold concentration of Cr for sensitization. This threshold concentration is used for calculating the depletion parameter.
- The average grain size, which affects the process of healing of chromium depletion as a function of time

Also, you can indicate whether the repassivation potential (E_{rp}) should be calculated directly from the correlation developed by Anderko et al. (2008), which expresses E_{rp} as a function of alloy composition or not. If it is not calculated directly, then the repassivation potential is calculated first using the alloy-specific parameters for the alloy of interest and only the decrement of E_{rp} (i.e., $E_{rp,\ \text{thermally aged}} - E_{rp,\ \text{bulk alloy}}$) is obtained from the correlation. This decrement is then added to the alloy-specific E_{rp} value. This option is set by default to "No" because this maximizes the accuracy of calculations for alloys that are already in the database.

For now, we will accept the default settings but we will return to them later in the tour. Therefore, click **OK** to close this window.

Then click the **Calculate** button.

Analyzing the results

When the calculations are finished, click on the **Depletion Profile** tab[50]. You will see a plot of concentrations of chromium and molybdenum within a grain as a function of the distance from the grain boundary (in μm). You will see that, for each condition, there are four lines:

Cr weight % : concentration of Cr in weight %

Mo+W weight % : sum of the concentrations of molybdenum and tungsten in weight %

Corrected Cr weight % - concentration of Cr corrected for beam scattering and related effects so that it can be directly compared with experimental results. The procedure for calculating the correction is described by Anderko et al. (2009).

Corrected Mo+W weight % sum of the concentrations of Mo and W corrected in the same way as those for Cr.

Since alloy 600 does not contain any molybdenum, the molybdenum curves will always be equal to zero. The plot will look similar to the following one:

---

[50] Remember to use the scroll-arrows if necessary

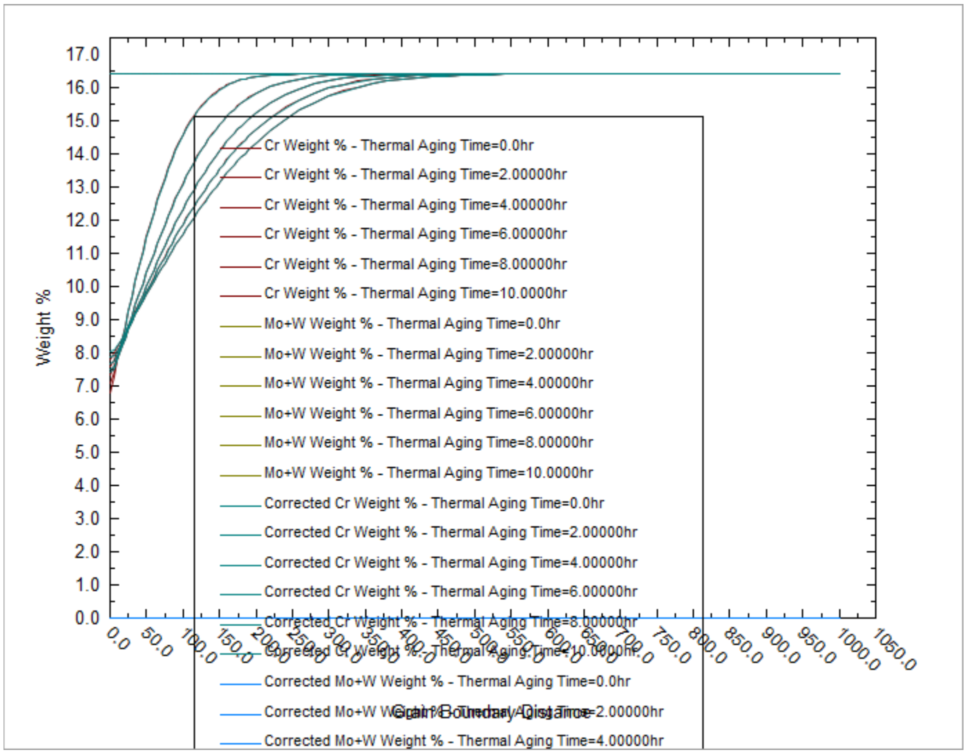
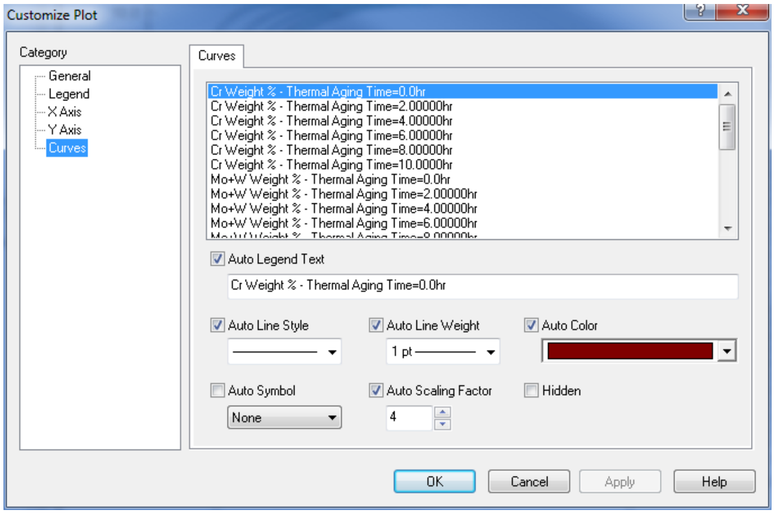


Figure 31-5 The plot of predicted depletion profiles for alloy 600 thermally aged at 700 °C as a function of time.

Let us customize the plot now by clicking on the **Options** button.

Since alloy 600 does not contain Mo or W, let us eliminate the Mo+W curves. To do this, select the **Curves** category from the left-hand side pane (**NOTE: this is not the same as the Curves Button!**)

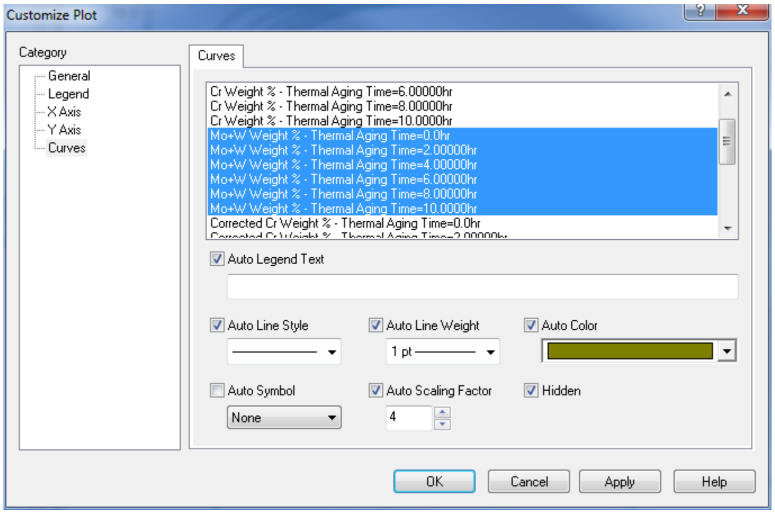


Cr Weight % - Thermal Aging Time=0.0hr
Cr Weight % - Thermal Aging Time=2.00000hr
Cr Weight % - Thermal Aging Time=4.00000hr
Cr Weight % - Thermal Aging Time=6.00000hr
Cr Weight % - Thermal Aging Time=8.00000hr
Cr Weight % - Thermal Aging Time=10.0000hr
Mo+W Weight % - Thermal Aging Time=0.0hr
Mo+W Weight % - Thermal Aging Time=2.00000hr
Mo+W Weight % - Thermal Aging Time=4.00000hr
Mo+W Weight % - Thermal Aging Time=6.00000hr

☑ Auto Legend Text
Cr Weight % - Thermal Aging Time=0.0hr
☑ Auto Line Style
☑ Auto Line Weight: 1 pt
☑ Auto Color
☐ Auto Symbol: None
☑ Auto Scaling Factor: 4
☐ Hidden

Figure 31-6 Plot Options | Curves Category

Then, highlight the Mo+W weight % curves by pressing the Shift key and moving the cursor. After highlighting these curves, check the **Hidden** button. The **Customize Plot** portion of the screen will look as follows:



Cr Weight % - Thermal Aging Time=6.00000hr
Cr Weight % - Thermal Aging Time=8.00000hr
Cr Weight % - Thermal Aging Time=10.0000hr
Mo+W Weight % - Thermal Aging Time=0.0hr
Mo+W Weight % - Thermal Aging Time=2.00000hr
Mo+W Weight % - Thermal Aging Time=4.00000hr
Mo+W Weight % - Thermal Aging Time=6.00000hr
Mo+W Weight % - Thermal Aging Time=8.00000hr
Mo+W Weight % - Thermal Aging Time=10.0000hr
Corrected Cr Weight % - Thermal Aging Time=0.0hr

☑ Auto Legend Text

☑ Auto Line Style

☑ Auto Line Weight: 1 pt

☑ Auto Color

☐ Auto Symbol: None

☑ Auto Scaling Factor: 4

☑ Hidden

Figure 31-7 The window for customizing the display of depletion profiles.

After *hiding* the Mo+W weight % curves, do the same for the Corrected Mo+W weight % curves. Then, press OK. The plot will look as follows:

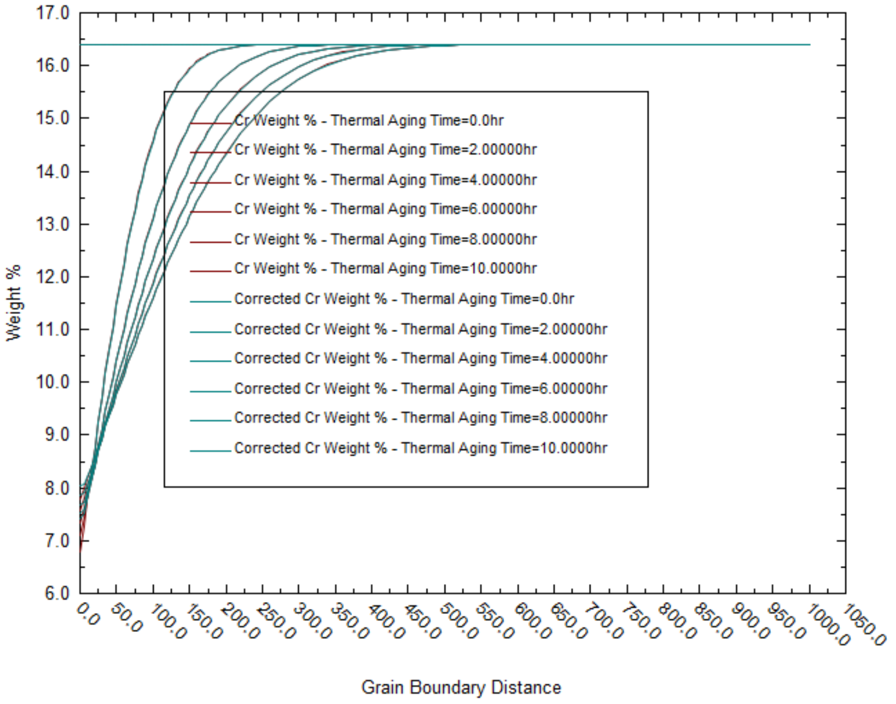


Figure 31-8 A customized depletion profile plot that shows only Cr depletion profiles

Now, let us focus on the differences between the uncorrected and corrected depletion profiles. To have a clear picture of the difference between them, let us focus on only one depletion profile – for 2 hours. For this purpose, click on **Options** again, then select the **Curves** category. Highlight all curves except the ones labeled

Cr Weight % - Thermal Aging Time = 2.00000 hr, and

Corrected Cr Weight % - Thermal Aging Time = 2.00000 hr

Check the Hidden box. Then, you will see a plot that looks like the following one:

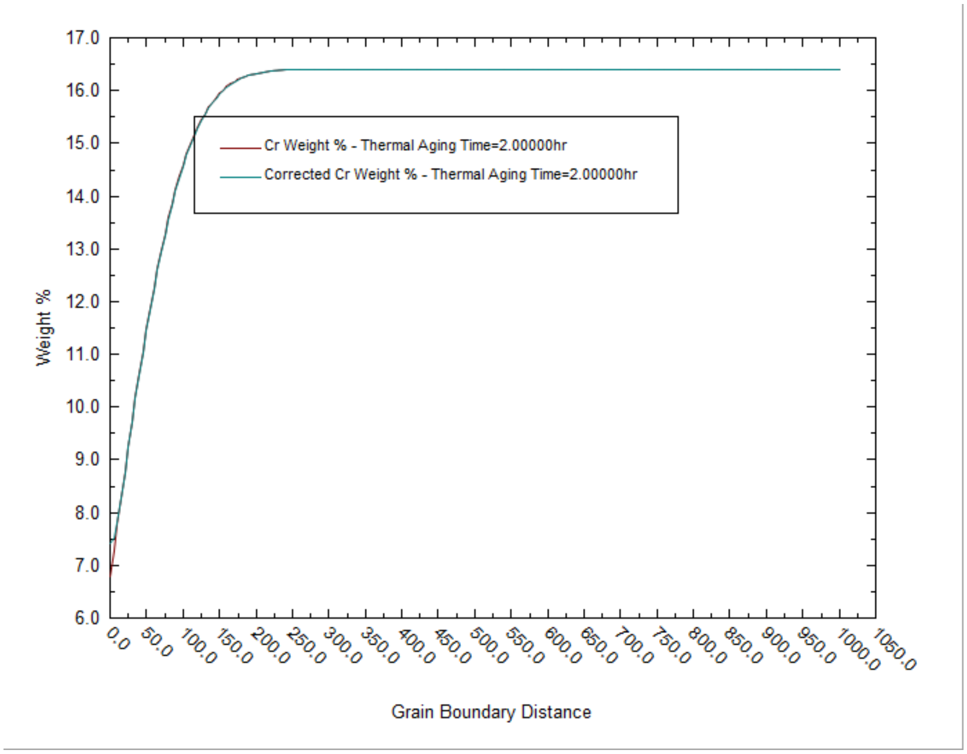
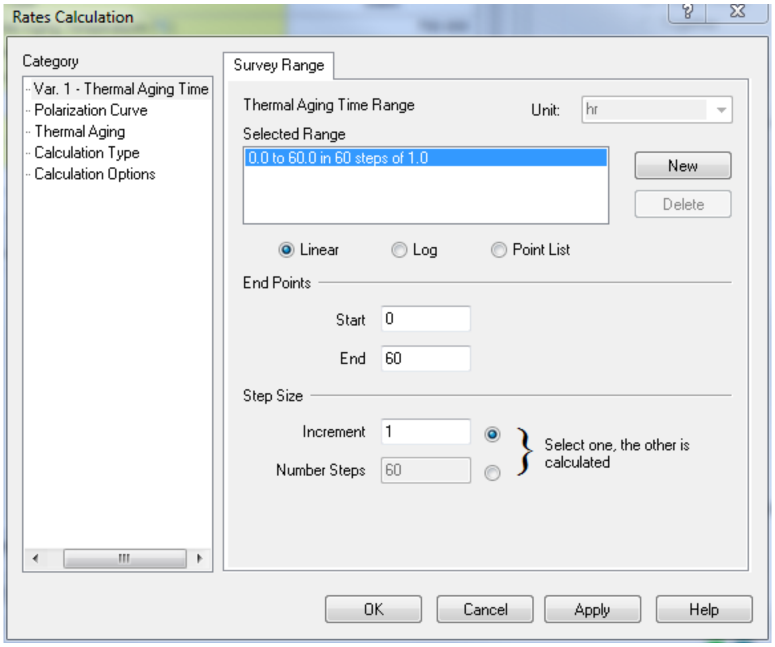


Figure 31-9 A customized depletion profile plot that shows uncorrected and corrected Cr depletion profiles only for 2 hours of thermal aging

In the obtained plot, you can see the difference between the two curves for small distances from the grain boundary (roughly below 30 μm). The corrected concentration is much more rounded in the vicinity of the minimum because instrumental measurement effects. At larger distances from the grain boundary, there is no difference between the two curves.

After analyzing the depletion profiles, let us focus on the effects of Cr depletion on corrosion. We will do it by analyzing two parameters – the depletion parameter and the repassivation potential.

To have more meaningful results, let us expand the range of thermal aging time and reduce the interval for calculations. To do it, go back to the **Definition** tab and click on **Specs**. In the **Thermal Aging Time** category, change the **End** to 60 hours and the **Increment** to 1 hour. The screen should look like the following one:



Thermal Aging Time Range

Unit: hr

Selected Range: 0.0 to 60.0 in 60 steps of 1.0

● Linear ○ Log ○ Point List

End Points

Start: 0

End: 60

Step Size

Increment: 1 ●

Number Steps: 60 ○

Select one, the other is calculated

Figure 31-10 Changing the survey range for thermal aging.

After making the change, click **OK**.

Then, click **Calculate**.

After the calculations are complete, click on the **Localized Corr.** tab. By default, this tab will show a plot of the corrosion potential and repassivation potential.

Let us add a new parameter – the depletion parameter to the plot. To do this, click on **Curves**. A new window titled "Select Data to Plot" will appear. Under **Corrosion Values** in the left-hand side pane, highlight **Depletion Parameter** and click on the >> button under **Y2 Axis**. The screen will look like:

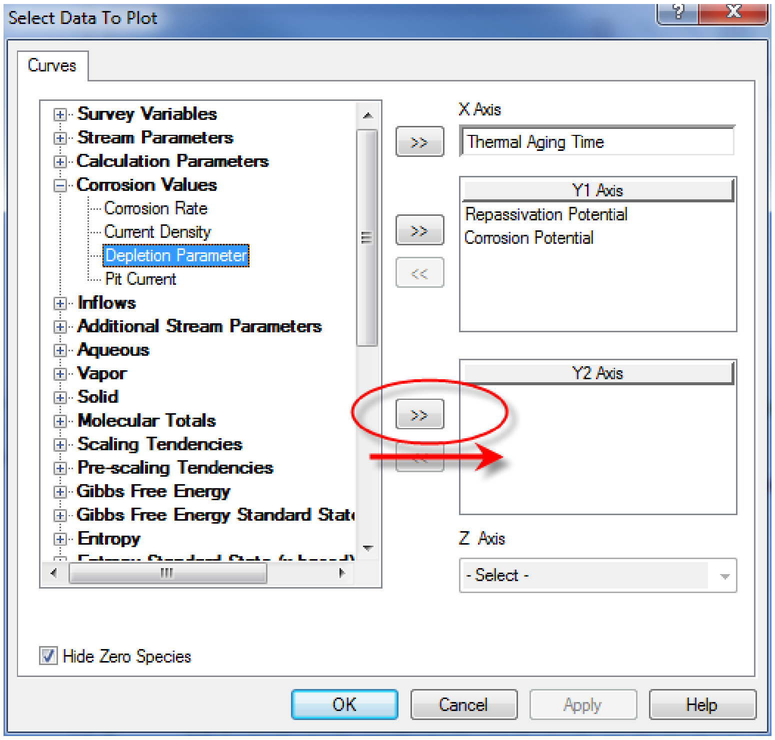


Figure 31-11 Including the depletion parameter in the plot on the Y2 axis.

Click **OK**. You will see a plot that should look like:

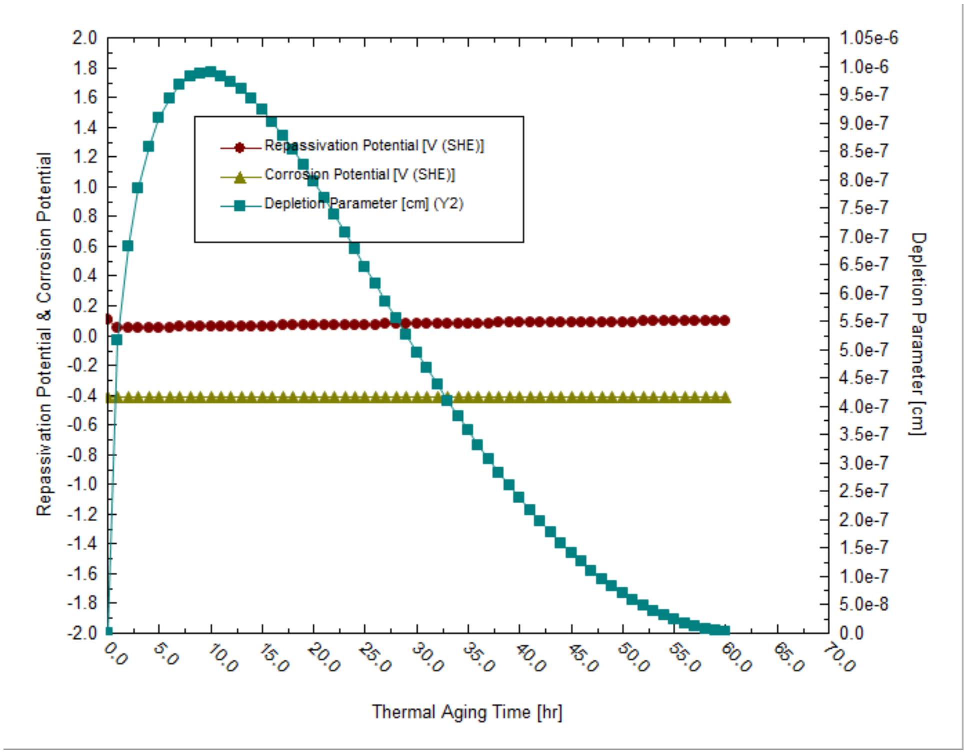


Figure 31-12 A plot of the repassivation potential and depletion parameter for thermally aged alloy 600 as a function of aging time.

It is clear that the depletion parameter reaches a maximum for aging time of about 10 hours. Since the depletion parameter is a measure of the susceptibility of an alloy to intergranular corrosion, we can expect that the alloy will be most susceptible to intergranular corrosion at intermediate aging times. When the depletion parameter is zero, intergranular corrosion or intergranular stress corrosion cracking are unlikely. The decrease of the depletion parameter as a function of time is a manifestation of the phenomenon of healing of Cr depletion.

The repassivation potential shows a minimum as a function of aging time. This indicates that the tendency of the alloy to undergo localized corrosion is enhanced as a result of thermal aging. However, the effect of thermal aging on the repassivation potential of alloy 600 is small (cf. Tormoen et al., 2009, Anderko et al., 2009). The repassivation potential shows a minimum at low aging times (ca. 1-2 hours). Therefore, the susceptibility to localized corrosion is enhanced the most for these aging times. It is noteworthy that the maximum in the depletion parameter does not coincide with the minimum in the repassivation potential. This is due to the fact that intergranular corrosion (which is related to the depletion parameter) and localized corrosion (which is controlled by the repassivation potential) are subject to different mechanisms. A general discussion of these differences is given by Tormoen et al. (2008).

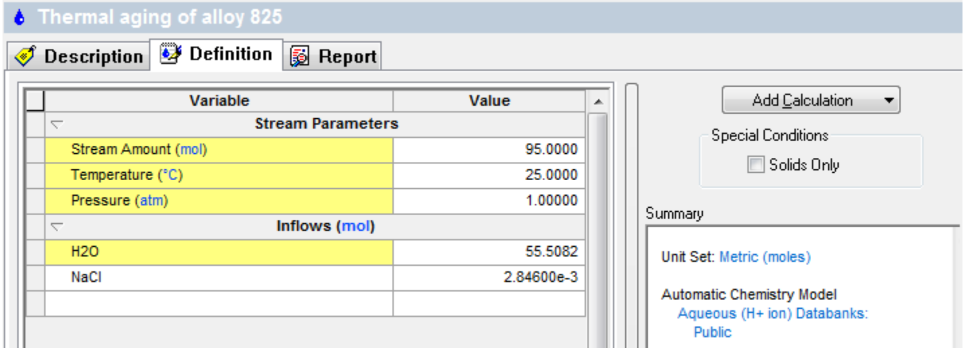
In general, the alloy will be susceptible to localized corrosion if the corrosion potential exceeds the repassivation potential. In the above example, the corrosion potential is low because we have no oxidizing agents in the system. Therefore, the alloy will not undergo localized corrosion at the conditions of this example. However, a rise in the corrosion potential due to the presence of oxidizing agents may cause localized corrosion. We will return to this topic later in this chapter.

Example 2: Thermal aging of alloy 825

In the second example, we will be studying the behavior of thermally aged alloy 825. Alloy 825 is appreciably different from alloy 600 because it contains molybdenum and, also, substantially more chromium in addition to other alloying elements. To make this simulation, click on **Add Stream** and create a stream with the following conditions:

Temperature	**95**	**°C**
Pressure	**1**	**Atmospheres**
H2O	**55.5082 moles**	
NaCl	**2.846e-3 moles**	

The definition grid of the stream should look similar to the following figure:



Variable	Value
Stream Parameters	
Stream Amount (mol)	95.0000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
NaCl	2.84600e-3

Unit Set: Metric (moles)

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

Figure 31-13 Stream definition for studying the effect of thermal aging on alloy 825.

Double-click on the **Add Corrosion Rates** icon in the **Actions/Explorer** pane.

Then, click on the **Definition** tab.

Setting up the calculation

In this example, we will simulate how the temperature of thermal aging affects alloy 825 at a fixed thermal aging time of 15 hours. For this purpose:

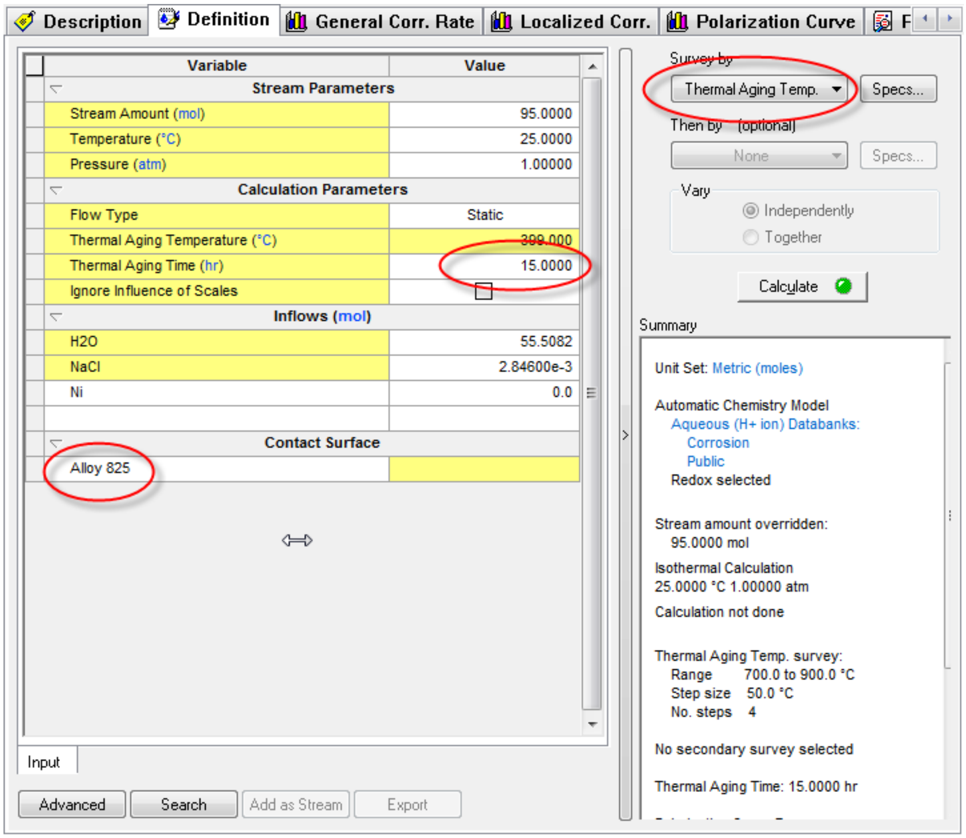
Select **alloy 825** from the drop-down **Contact Surface** menu.

In the **Calc Parameters** section, replace the default value for the **Thermal Aging Time** with 15 h.

Note that the default value for the **Thermal Aging Temperature** is 0, which means that no thermal aging is considered by default.

Then, from the Type of rates calculation drop-down menu, select **Thermal Aging Temperature.**

The definition grid for the Corrosion Rates should look similar to the following figure. The key specifications are highlighted using red ovals:



Variable	Value
Stream Parameters	
Stream Amount (mol)	95.0000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	
Flow Type	Static
Thermal Aging Temperature (°C)	300.000
Thermal Aging Time (hr)	15.0000
Ignore Influence of Scales	☐
Inflows (mol)	
H2O	55.5082
NaCl	2.84600e-3
Ni	0.0
Contact Surface	
Alloy 825	

Unit Set: Metric (moles)

Automatic Chemistry Model
Aqueous (H+ ion) Databanks:
Corrosion
Public
Redox selected

Stream amount overridden:
95.0000 mol

Isothermal Calculation
25.0000 °C 1.00000 atm

Calculation not done

Thermal Aging Temp. survey:
Range 700.0 to 900.0 °C
Step size 50.0 °C
No. steps 4

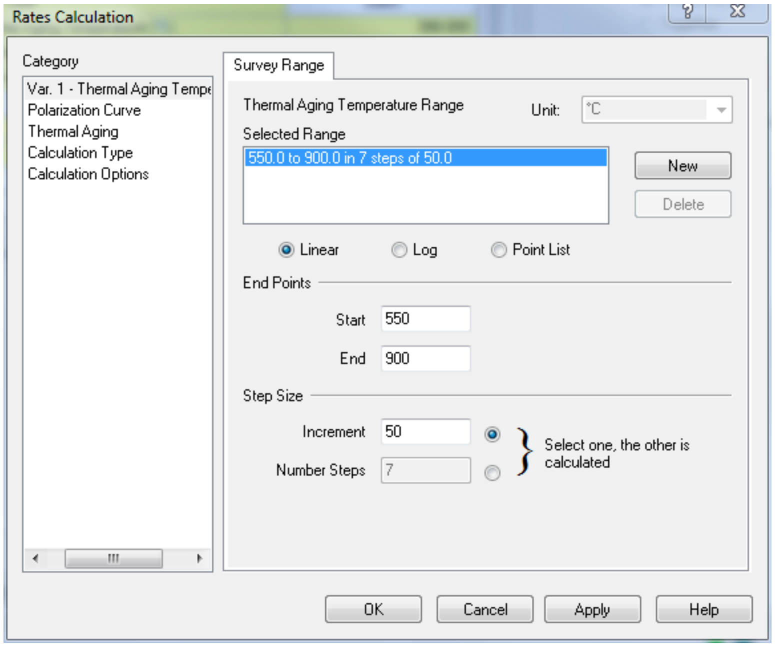
No secondary survey selected

Thermal Aging Time: 15.0000 hr

Figure 31-14 Specifying the type of calculation, thermal aging time, and contact surface.

Then, click on **Specs** to define the survey range.

In the **Thermal Aging Temp.** category, specify the start of the survey as **550** °C, the end of the survey as **900** °C, and the increment as 50 °C. The **Rates Definition** screen should look as follows:



Thermal Aging Temperature Range

Unit: °C

Selected Range: 550.0 to 900.0 in 7 steps of 50.0

● Linear ○ Log ○ Point List

End Points

Start: 550

End: 900

Step Size

Increment: 50 ●

Number Steps: 7 ○

Select one, the other is calculated

Figure 31-15 Defining the range for a thermal aging temperature survey.

Click **OK** to close this window. We will keep the other parameters at their default values. Then, click **Calculate**.

Analyzing the results

When the calculations are finished, click on the **Depletion Profile** tab.

Since alloy 825 contains Mo in addition to Cr, you will see the depletion profiles for both Cr and Mo. For clarity, customize the plot by removing the corrected depletion profiles and leaving only the uncorrected (or directly calculated) ones.

For this purpose, click on **Options,** select the **Curves** category, highlight the Corrected curves and check the hidden box as described in the previous example. The resulting plot should look similar to the following one:

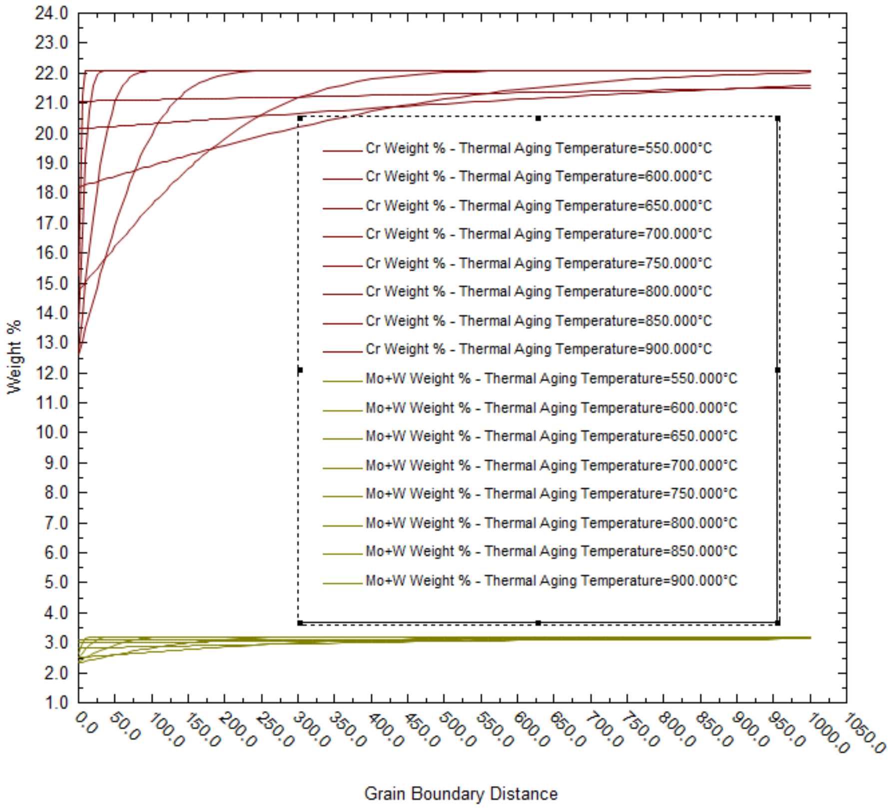


Figure 31-16 Predicted Cr and Mo depletion profiles for alloy 825 as a function of thermal aging temperature.

As shown in this plot, the depletion profile is very narrow at the lowest temperature, i.e., 550 °C. On the other hand, it becomes flat at high temperatures and it has a high minimum. The high minimum value is particularly important because it indicates that the local depletion of Cr and Mo is much less severe at high temperatures (due to much faster diffusion of substitutional elements and subsequent healing).

It should be noted that the Mo profile qualitatively parallels the Cr profile but has somewhat different slopes because of differences in diffusion coefficients of Cr and Mo.

To look at the effect of Cr and Mo depletion on corrosion, click on the **Localized Corrosion** tab and add the **Depletion Parameter** to the plot as described in the previous example. The plot should look similar to the following one:

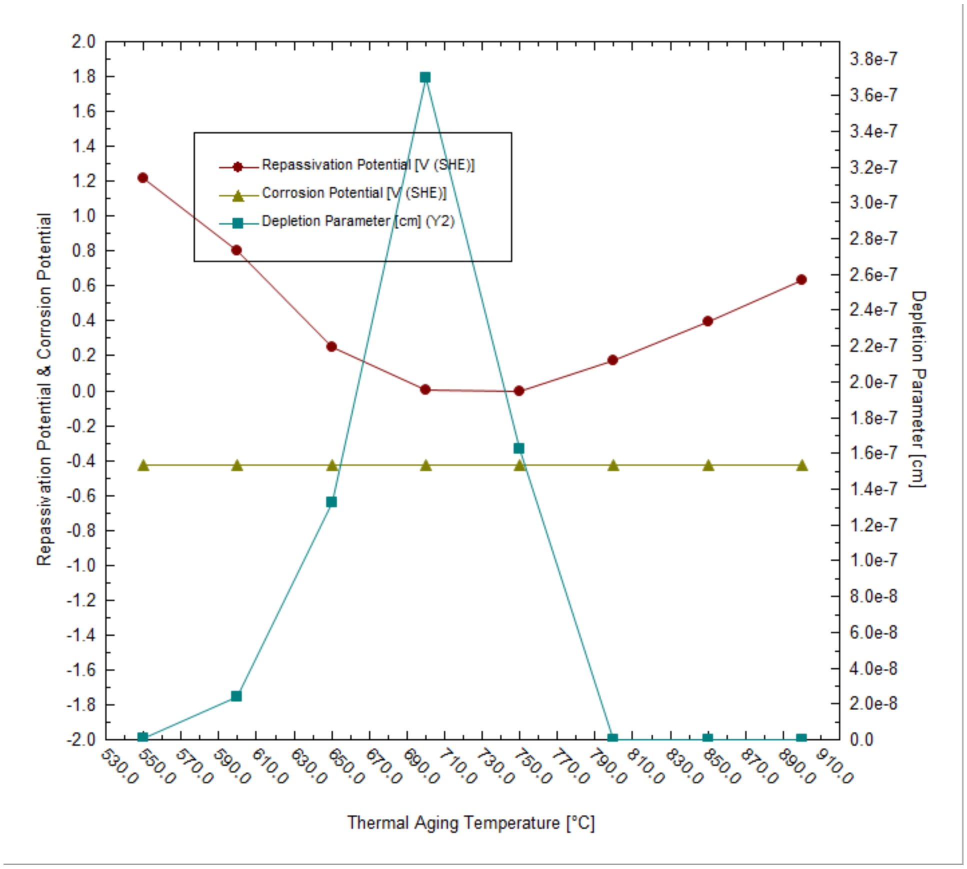


Figure 31-17 Calculated repassivation potential and depletion parameter for alloy 825 as a function of thermal aging temperature.

It is evident that both the depletion parameter and repassivation potential show their extreme values at intermediate temperatures of thermal aging. In the case of the depletion parameter, it is a maximum and, in the case of the repassivation potential, it is a minimum. This is in agreement with experimental data (Anderko et al., 2009). Non-zero values of the depletion parameter indicate the possibility of intergranular corrosion. A depression in the repassivation potential indicates an increased tendency for localized corrosion.

Example 3: Localized corrosion of annealed and thermally aged duplex alloy 2205

In the first and second tour, we used the Corrosion Analyzer's capabilities to predict the Cr and Mo depletion profiles for austenitic stainless steels and nickel-base alloys. However, we are not limited to such calculations. We can also use the Corrosion Analyzer to predict the localized corrosion behavior of other alloys and other phases, including those that are not stored in the database. This facility is based on a generalized correlation for predicting the repassivation potential of Fe-Ni-Cr-Mo-W-N alloys as a function of alloy composition (Anderko et al., 2008). This correlation can be applied to both bulk alloys that are not in the database and to phases that may result from thermal aging.

In this example, we will make two simulations:

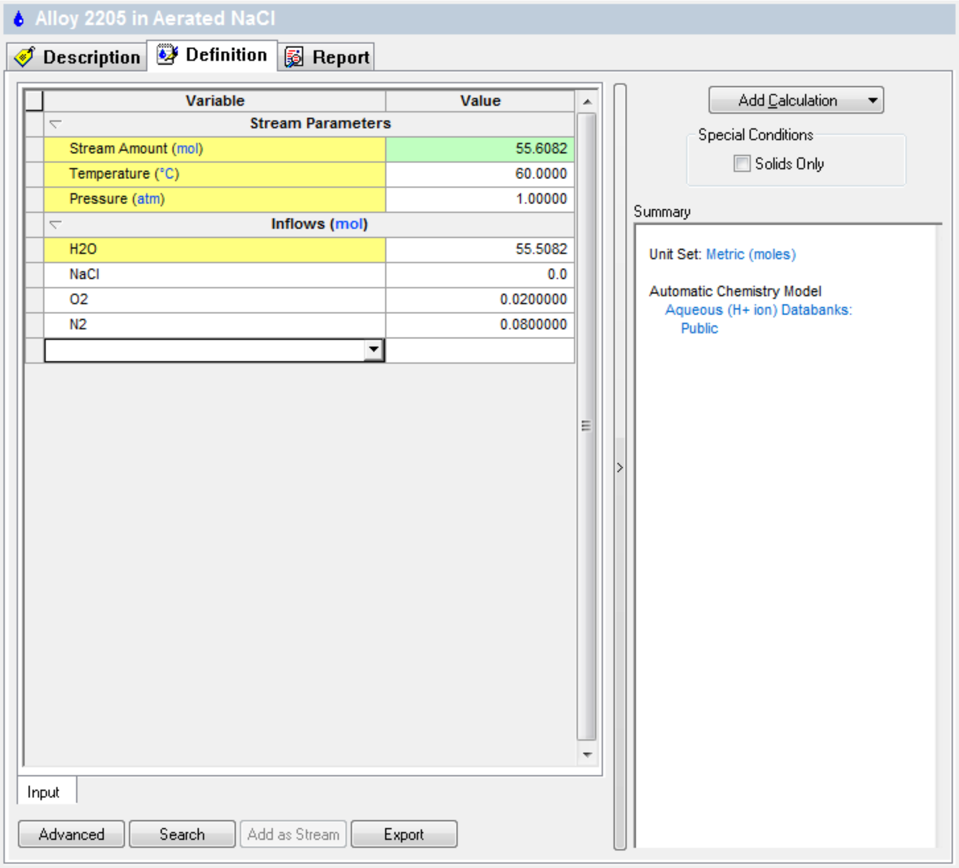
- First, we will predict the tendency for localized corrosion for the duplex alloy 2205 in an aerated chloride solution. Alloy 2205 is not in the database, so the repassivation potential will be calculated from the generalized correlation (Anderko et al., 2008). The corrosion potential will be calculated for a similar alloy because the corrosion potential does not differ much for many Fe-Cr-Ni-Mo alloys in the passive state in neutral solutions.
- Second, we will predict the localized corrosion tendency for alloy 2205 after thermal aging. Thermal aging of duplex steels in the temperature range of 900°C to 600°C leads to the formation of various phases - χ, σ, $M_{23}C_6$-type carbide, and secondary austenite (γ_2). The secondary austenite phase is primarily responsible for the increased tendency of the alloy for localized corrosion. This is due to a very significant depletion of chromium in the secondary austenite over relatively wide spatial areas (Sridhar et al., 2009). Since the composition of the secondary austenite cannot be predicted at present, we will use experimental microstructural data (Sridhar et al., 2009) in conjunction with the generalized correlation for the repassivation potential.

Click on **Add Stream** and create a stream with the following conditions:

Temperature	**60**	**°C**
Pressure	**1**	**Atmospheres**
H2O	**55.5082**	**moles**
NaCl	**0**	**moles**
Oxygen	**0.02**	**moles**
Nitrogen	**0.08**	**moles**

The oxygen and nitrogen have been added to simulate the presence of air.

The definition grid of the stream should look similar to the following figure:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Temperature (°C)	60.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
NaCl	0.0
O2	0.0200000
N2	0.0800000

Special Conditions
☐ Solids Only

Summary

Unit Set: Metric (moles)

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

Figure 31-18 Stream composition for simulating localized corrosion of alloy 2205.

Double-click on the **Add Corrosion Rates** icon in the **Actions/Explorer** pane.

Then, click on the **Definition** tab.

Setting up the calculation

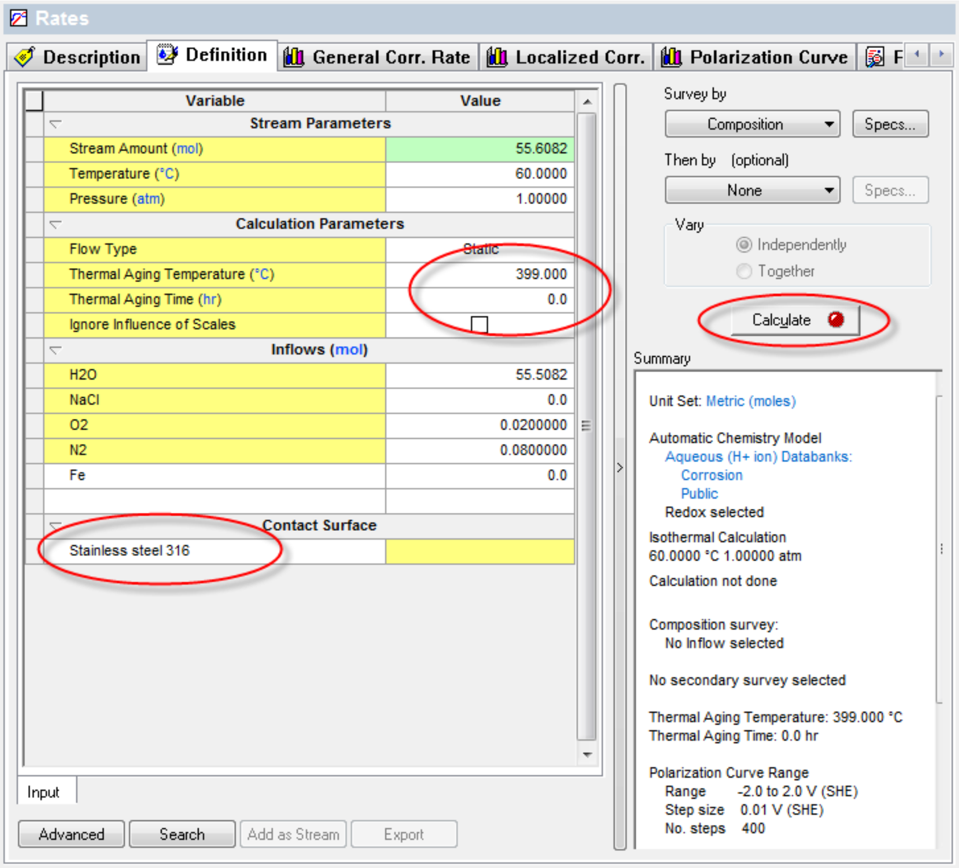
Since alloy 2205 is not available in the database, we will select stainless steel 316 as the contact surface. This will ensure that the predicted corrosion potential is very similar to that for alloy 2205.

Select **316 Stainless Steel** from the drop-down **Contact Surface** menu.

Unlike in the previous examples, do not make any changes in the **Calc Parameters** section. We will not make Cr depletion calculations; rather, we will be specifying the compositions of the phases.

From the Type of rates calculation drop-down menu, select **Composition**.

The definition grid for the Corrosion Rates should look similar to the following figure. The key specifications are highlighted using red ovals:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Temperature (°C)	60.0000
Pressure (atm)	1.00000
Calculation Parameters	
Flow Type	Static
Thermal Aging Temperature (°C)	399.000
Thermal Aging Time (hr)	0.0
Ignore Influence of Scales	☐
Inflows (mol)	
H2O	55.5082
NaCl	0.0
O2	0.0200000
N2	0.0800000
Fe	0.0
Contact Surface	
Stainless steel 316	

Survey by: Composition

Then by (optional): None

Unit Set: Metric (moles)

Automatic Chemistry Model
Aqueous (H+ ion) Databanks:
Corrosion
Public
Redox selected

Isothermal Calculation
60.0000 °C 1.00000 atm

Calculation not done

Composition survey:
No Inflow selected

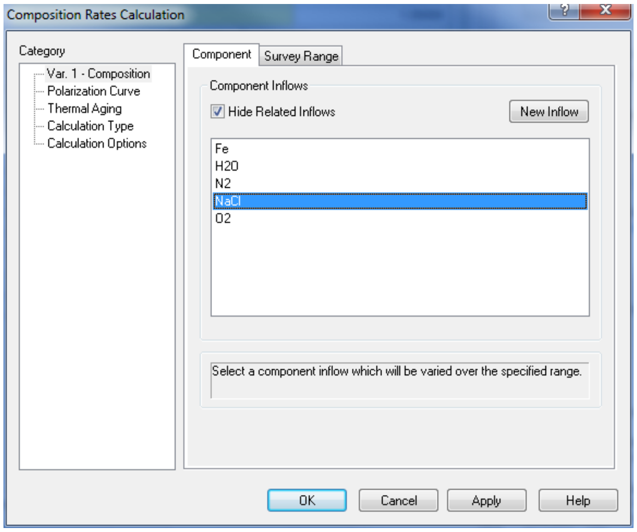
No secondary survey selected

Thermal Aging Temperature: 399.000 °C
Thermal Aging Time: 0.0 hr

Polarization Curve Range
Range -2.0 to 2.0 V (SHE)
Step size 0.01 V (SHE)
No. steps 400

Figure 31-19 Selection of contact surface and survey type.

We will be running a composition survey to see how the concentration of NaCl affects the propensity for localized corrosion. To define the survey type, click on **Specs**.



☑ Hide Related Inflows

Fe
H2O
N2
NaCl
O2

Select a component inflow which will be varied over the specified range.

Figure 31-20 Selecting the component for the survey (NACL)

In the **Var. 1 – Composition** category, select **Sodium Chloride** in the **Component** tab.

Then, click on the **Survey Range** tab and enter:

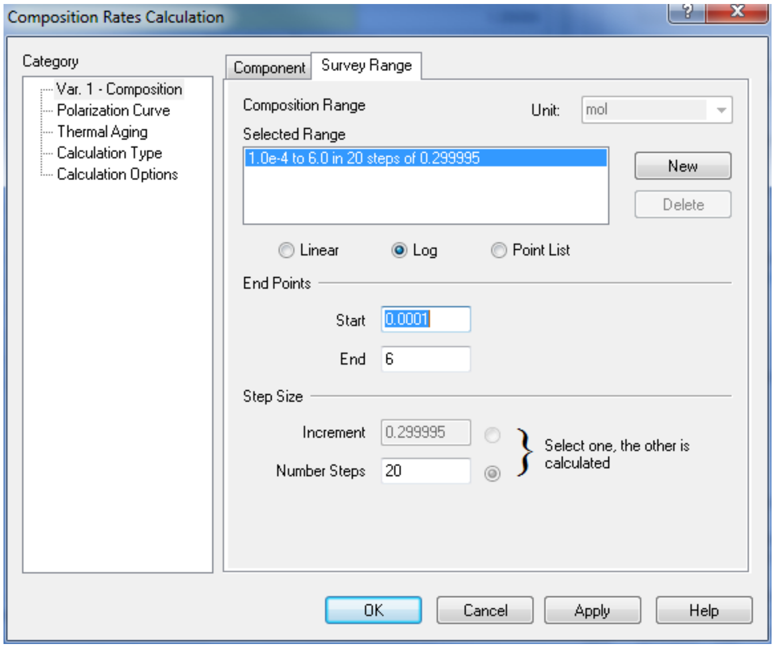
Start 0.0001

End 6

Number of steps 20

Click the “Log” radio button

The screen should look similar to:



Composition Range

Unit: mol

Selected Range

1.0e-4 to 6.0 in 20 steps of 0.299995

○ Linear ● Log ○ Point List

End Points

Start 0.0001

End 6

Step Size

Increment 0.299995 ○

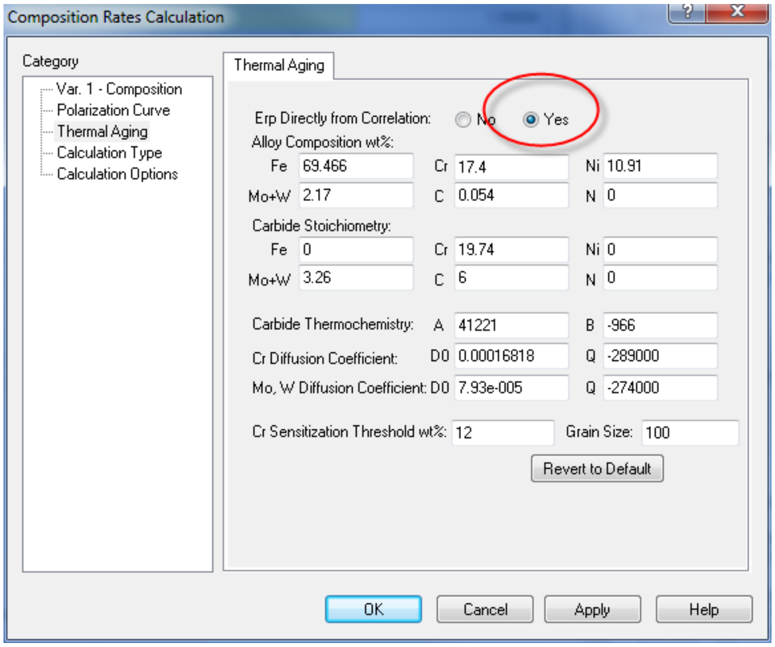
Number Steps 20 ●

Select one, the other is calculated

Figure 31-21 Defining the survey range for the NaCl concentration survey.

Then, click on the **Thermal Aging** category on the left-hand side pane. The screen will be populated with default parameters for type 316 stainless steel.

First, click on the **Yes** button next to **Erp directly from correlation**.



Erp Directly from Correlation: ○ No ● Yes

Alloy Composition wt%:

Fe 69.466 Cr 17.4 Ni 10.91

Mo+W 2.17 C 0.054 N 0

Carbide Stoichiometry:

Fe 0 Cr 19.74 Ni 0

Mo+W 3.26 C 6 N 0

Carbide Thermochemistry: A 41221 B -966

Cr Diffusion Coefficient: D0 0.00016818 Q -289000

Mo, W Diffusion Coefficient: D0 7.93e-005 Q -274000

Cr Sensitization Threshold wt%: 12 Grain Size: 100

Figure 31-22 Thermal Aging Parameters

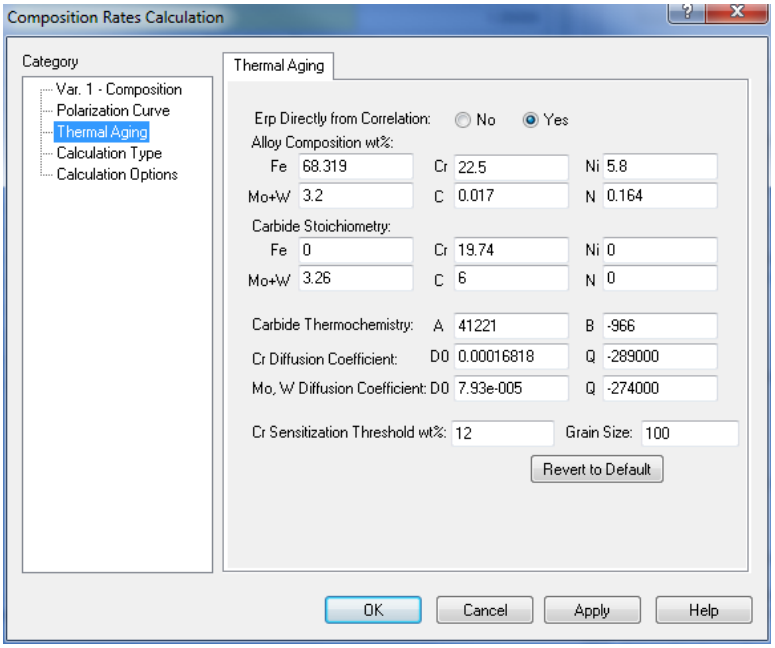
This is necessary because no parameters for alloy 2205 are stored in the databank and we have to rely exclusively on the correlation to predict the repassivation potential.

Then, enter the composition of alloy 2205 by replacing the default values for alloy 316.

Enter the following composition of alloy 2205:

Fe	68.319	wt. % (which is the balance that includes many minor elements)
Cr	22.5	wt. %
Ni	5.8	wt. %
Mo+W	3.2	wt. %
C	0.017	wt. %
N	0.164	wt. %

The remaining parameters in the Thermal Aging screen can remain the same because we will not be using them in this example (i.e., we will not be calculating any depletion profiles). After entering the values, the screen should look as follows:



Composition Rates Calculation

Category

- Var. 1 - Composition
- Polarization Curve
- Thermal Aging
- Calculation Type
- Calculation Options

Thermal Aging

Erp Directly from Correlation: ○ No ● Yes

Alloy Composition wt%:

Fe	68.319	Cr	22.5	Ni	5.8
Mo+W	3.2	C	0.017	N	0.164

Carbide Stoichiometry:

Fe	0	Cr	19.74	Ni	0
Mo+W	3.26	C	6	N	0

Carbide Thermochemistry:	A	41221	B	-966
Cr Diffusion Coefficient:	D0	0.00016818	Q	-289000
Mo, W Diffusion Coefficient:	D0	7.93e-005	Q	-274000

Cr Sensitization Threshold wt%: 12

Grain Size: 100

Figure 31-23 Defining the composition of alloy 2205 and specifying the direct use of the correlation for predicting the repassivation potential.

Click **OK** to accept the changes.

Then, click **Calculate**.

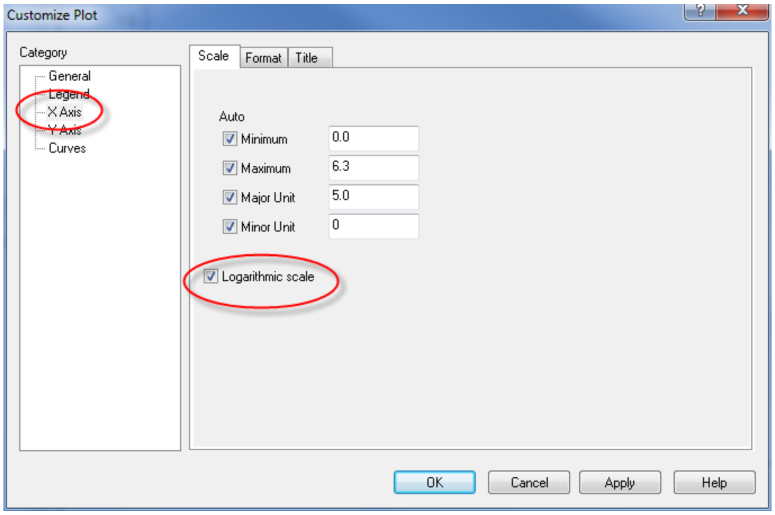
Analyzing the results

When the calculations are finished, click on the **Localized Corrosion** tab.

The same results can be also viewed in a numerical form by clicking on the **Report** tab. You will see a plot of the corrosion and repassivation potentials as a function of

NaCl concentration. To visualize the results better, change the horizontal axis to a logarithmic scale.

For this purpose, click on **Options**, select the **X Axis** category, check the **Logarithmic Scale** box and click **OK**. Then, the plot should look similar to the following one:



Customize Plot

Category: General, Legend, X Axis, Y Axis, Curves

Scale | Format | Title

Auto

☑ Minimum 0.0

☑ Maximum 6.3

☑ Major Unit 5.0

☑ Minor Unit 0

☑ Logarithmic scale

Figure 31-24 Changing the X-Axis to Log

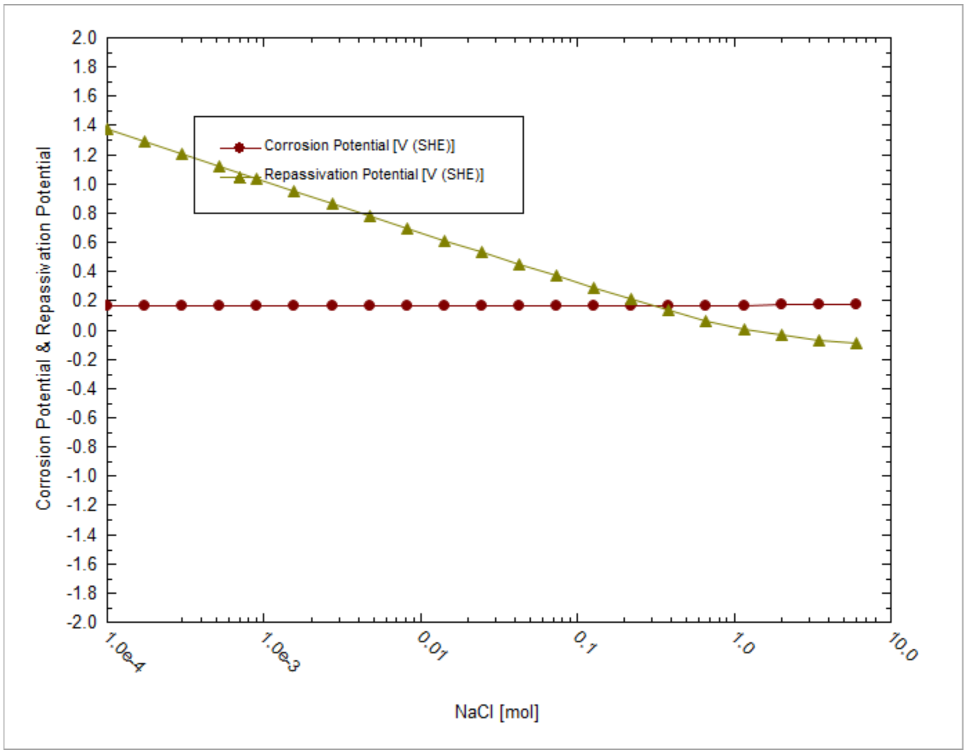


Figure 31-25 Predicted repassivation potential and corrosion potential for alloy 2205.

The plot indicates that alloy 2205 is susceptible to localized corrosion in aerated solutions when the chloride concentration exceeds ca. 0.3 molal. Above this concentration, the repassivation potential drops below the corrosion potential and, therefore, localized corrosion can be stabilized at these conditions.

Setting up the calculation

Now, we will perform the same calculations for thermally aged alloy 2205. We will use the experimental data of Sridhar et al. (2009), which show that the formation of a chromium-depleted secondary austenite phase is responsible for a much increased tendency for localized corrosion. This phase was identified after aging at 700 °C for 24 hours.

To make this simulation, click on the stream name that you used in the previous simulation. Then, double-click on the **Add Corrosion Rates** icon in the **Actions/Explorer** pane and click on the **Definition** tab.

As in the previous simulation, select **316 Stainless Steel** from the drop-down **Contact Surface** menu.

We will run the same concentration survey as in the previous case so that we can compare the results for bulk alloy 2205 with those for a heat-treated sample. To define the survey type, click on **Specs**. In the **Var. 1 – Composition** category, select **Sodium Chloride** in the **Component** tab. Then, click on the **Survey Range** tab and enter:

Start	0.0001
End	6
Number of steps	20

The screen should look similar to Figure 31-20 Selecting the component for the survey (NACL)

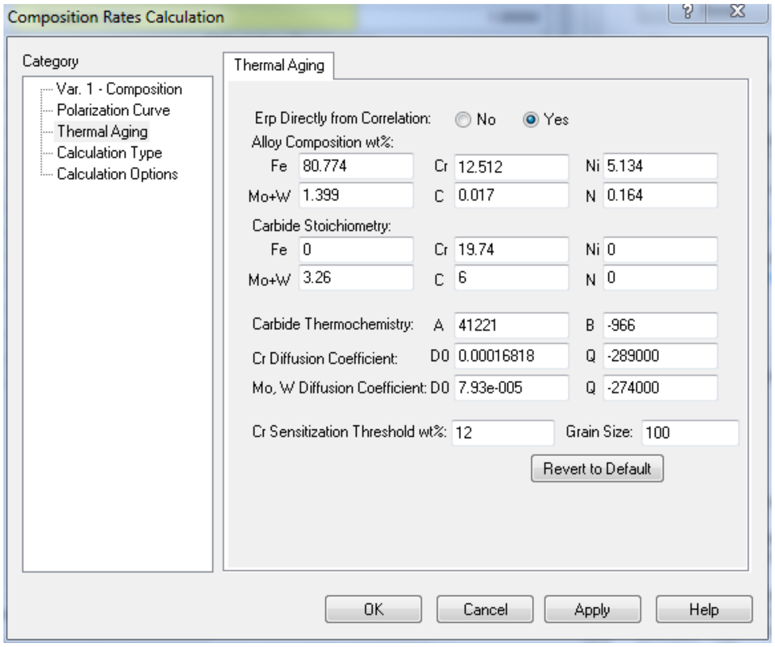
Then, click on the **Thermal Aging** category on the left-hand side pane. The screen will be populated with default parameters for type 316 stainless steel.

Click on the **Yes** button next to **Erp directly from correlation** because we will be running calculations for a completely new phase.

Then, enter the composition of the secondary austenite phase by replacing the default values for alloy 316. For more details how these compositions were determined, see the paper of Sridhar et al. (2009). Enter the following values:

Fe	80.774 wt.% (which is the balance that includes many minor elements)
Cr	12.512 wt.%
Ni	5.134 wt.%
Mo+W	1.399 wt.%
C	0.017 wt.%
N	0.164 wt.%

After entering the values, the screen should look as follows:



Erp Directly from Correlation: ○ No ● Yes

Alloy Composition wt%:

Fe	80.774	Cr	12.512	Ni	5.134
Mo+W	1.399	C	0.017	N	0.164

Carbide Stoichiometry:

Fe	0	Cr	19.74	Ni	0
Mo+W	3.26	C	6	N	0

Carbide Thermochemistry:	A	41221	B	-966
Cr Diffusion Coefficient:	D0	0.00016818	Q	-289000
Mo, W Diffusion Coefficient:	D0	7.93e-005	Q	-274000

Cr Sensitization Threshold wt%: 12 Grain Size: 100

Figure 31-26 Entering the composition of secondary austenite phase in a heat-treated sample of alloy 2205.

Click **OK** to save this information.

Then, click **Calculate**.

Analyzing the results

When the calculations are finished, click on the **Localized Corrosion** tab. You will see a plot of the corrosion and repassivation potentials as a function of NaCl concentration. As in the previous example, change the horizontal axis to a logarithmic scale. For this purpose, click on **Options**, select the **X Axis** category, check the **Logarithmic Scale** box and click **OK**. Then, the plot should look similar to the following one:

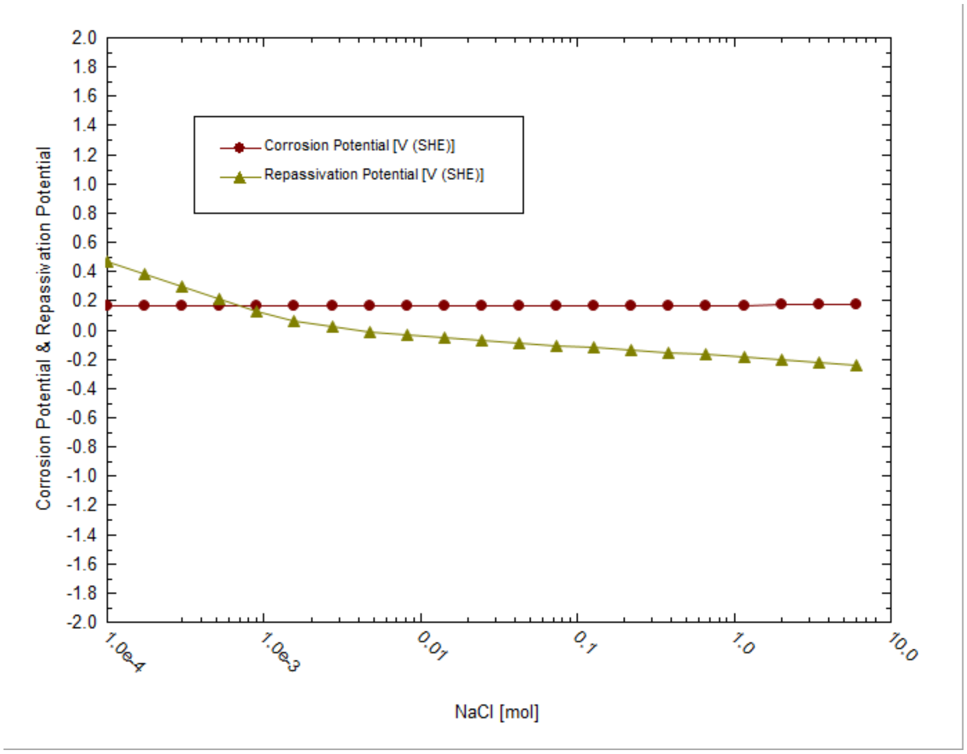


Figure 31-27 Predicted repassivation potential and corrosion potential for thermally aged alloy 2205. The calculations were made using the composition of the secondary austenite phase.

The obtained plot shows that the repassivation potential is much lower than that for bulk alloy 2205 (cf. Figure 31-25). Because of the strong depression of the repassivation potential, the corrosion potential exceeds the repassivation potential at chloride concentrations of ca. 0.0007 m. Thus, localized corrosion is predicted to be possible at concentrations above 0.0007 m. This indicates a very strong increase in the propensity for localized corrosion compared with bulk alloy 2205, for which the predicted threshold is ca. 0.3m.

In general, you can use this facility to predict the repassivation potential for any alloys, including unknown and experimental ones, as long as they belong to the Fe-Ni-Cr-Mo-W-N-C family.

You can download a worked example of this chapter from the OLI Wiki Page

32. Extreme Value Statistics for Predicting Pitting Damage – Intro

Extreme Value Statistics

Engineering systems may have a large number of pits and corroded areas of varying degree of severity. The first perforation, whose time and location will be a matter of probability, may cause the failure of the construction. Accordingly, the probability of such failure must be known as accurately as possible.

Extreme value statistics (EVS) is one of the most powerful statistical techniques that have been used extensively to extrapolate damage (maximum pit depth) from small samples in the laboratory to larger area samples in the field (see, for example, Eldridge G. 1957, Shibata T. et al. 1988, Kowaka et al. 1994). Thus, it was shown (Shibata T. et al. 1988) that probability of failure of a construction, P_f, i.e. the probability that at least one pit reaches the critical dimension, d, (for example wall thickness) in the system with area S is described by the equation:

$$P_f = 1 - \exp\{-\exp[-d - (u + \alpha \ln(S/s))]/\alpha\} \tag{1}$$

where location parameter, *u*, and scale parameter, α, are measured by using small samples with constant area, s. Equation (1) is to extrapolate corrosion damage from a small reference area, such as a coupon to a larger operation area, S. This is the classical use of Extreme Value Statistics. Experimental studies demonstrate that both the shape and location parameters are time-dependent. However, those dependencies must be established empirically and since no theory contained within classical EVS is available for the functional forms of u(t) and α(t), it is necessary to know answer (prediction) in advance for predicting the damage at long times. This has proven to be a severe constrains of the applicability of classical EVS.

This problem can be overcome by applying damage function analysis (DFA) method that considers propagation of corrosion damage by drawing an analogy between the growth of a pit and the movement of a particle (Engelhardt and Macdonald, 2004). In many cases DFA yields an analytical expression for u and α in terms of time of the hyperbolic form:

$$u = \frac{a_1 t}{1 + a_2 t} \quad \text{and} \quad \alpha = a_3 t \tag{2}$$

where a_1, a_2, and a_3 are readily determined by calibration from short term data in order to predict damage over the longer time. Namely, equations (2) are used now by OLI software for predicting damage in corroding systems. It must be noted that a different (power) form of such dependencies has been used by Laycock et al. 1990.

Input and Output

For applying this technique the user has to provide a set of experimental data (x_i, t_i, s_i), i = 1,2,…,N, where x_i is the depth of the deepest pit over area s_i, of a metal exposed to corrosion attack. The separate area, s_i, could be distinct coupons from a designed experiment or random samples at various times from different locations in the system. Experiments must be performed for at least two different times.

The output of the code yields the probability of failure as a function of time for a large system with area S. The code also allows the user to answers on several engineering questions, for example, what service life, t, will have the pipe with the width, d, and length L in order to ensure acceptable performance (probability of failure, P_f).

Advantages and Disadvantages of EVS

The advantage of this approach is self-evident. The prediction of corrosion damage for long times will be done by using experimental data for short times without requiring the explicit determination of any information about the kinetic parameters of the system. However, such approach has evident disadvantages, as follows:

a) The results of the analysis cannot be transferred for predicting corrosion damage to other systems (for example pipelines) due to the different technological and environmental conditions that generally exist. The results cannot be used for predicting damage in the same system if technological and environmental conditions change.

b) We can expect that when the depth of the pit increases some critical value, the nucleation of cracks can occur. It is clear that a purely statistical method cannot predict such a transition. This method also cannot predict any catastrophic event.

c) This method cannot be used for design of new constriction, because it relies upon calibration upon a pre-existing system.

33. Extreme Value Statistics for Predicting Pitting Damage – A Tour

Overview

In this tour, we will show examples of applications of Extreme Value Statistics for predicting pitting damage. Specifically, we will show how to predict

- The depth of the deepest pit in the engineering structure or laboratory systems as a function of time and the surface area of the system;
- Probability of failure for a given penetration depth and the area of the system as a function of observation time.
- Probability of failure for a given observation time and the area of the system as a function of penetration depth.
- Probability of failure for a given penetration depth and observation time as a function of the area of the system.

At this point you should be very familiar with entering data into OLI Studio. Also, you need to know the foundation of Extreme Value Statistics (Aziz, 1956, Kowaka et al. 1994, Laycock et al. 1990, Engelhardt and Macdonald, 2004).

Example 1: Corrosion of aluminum alloy in tap water

In this example, we will consider the classical data for pitting corrosion (Aziz, 1956). In this paper, we can find particularly the experimental data for the maximum pit depths developed on Alcan 2S-O coupons with area s ≈ 129 cm^2 immersed in Kingston tape water at 25 ^{0}C (see **Table 33-1**).

***Table 33-1** Maximum pit depth (in µm) developed on Alcan 2S-O coupons with immersed in Kingston tape water for different observation time*

Coupon #	One Week	One Month	Three Months	Six Month	One Year
1	180	460	480	620	640
2	266	500	578	620	680
3	290	510	610	620	700
4	306	580	610	680	760
5	334	580	610	680	800
6	340	640	660	720	810
7	340	654	690	740	820
8	410	680	718	740	840
9	410	692	760	760	840
10	545	692	798	760	900

Double-Click the Add Standard EVS Calculation icon

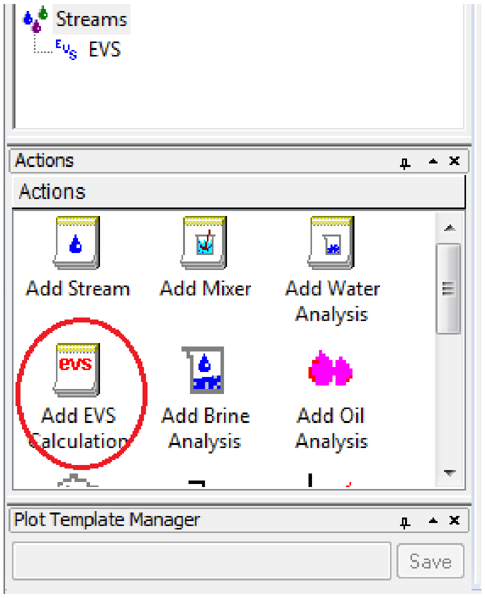


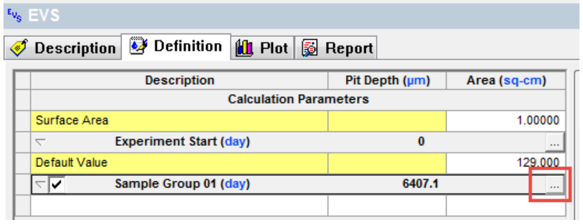
Figure 33-1 Starting EVS

Click on **Definition** tab and start by inputting experimental data.

Because all samples have the same area s = 129 cm^2 we input this value into **Default Value Area**. Other possible unit for area is m^2. The default value of pit depth is chosen to be in µm. Other possible units are Å, mm, ft, m, ft.

Because, in the first step, we will predict propagation of pitting damage in the same system (for the same coupons) we choose S = s = 0.0129 m^2.

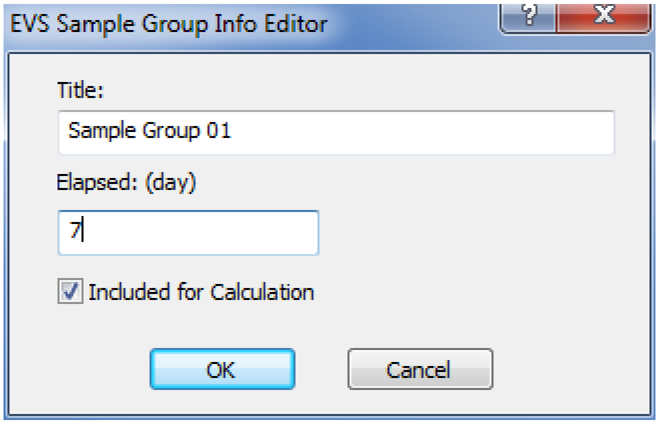
The definition grid of the system should look like Figure 33-2.



Description	Pit Depth (µm)	Area (sq-cm)
Calculation Parameters		
Surface Area		1.00000
Experiment Start (day)	0	...
Default Value		129.000
☑ Sample Group 01 (day)	6407.1	...

Figure 33-2: The system definition.

There are experimental data for 5 different times (5 groups). Click on the button inside the red oval (see Figure 33-2) and type time 7 days in empty space below Elapsed (Figure 33-3).



Title: Sample Group 01

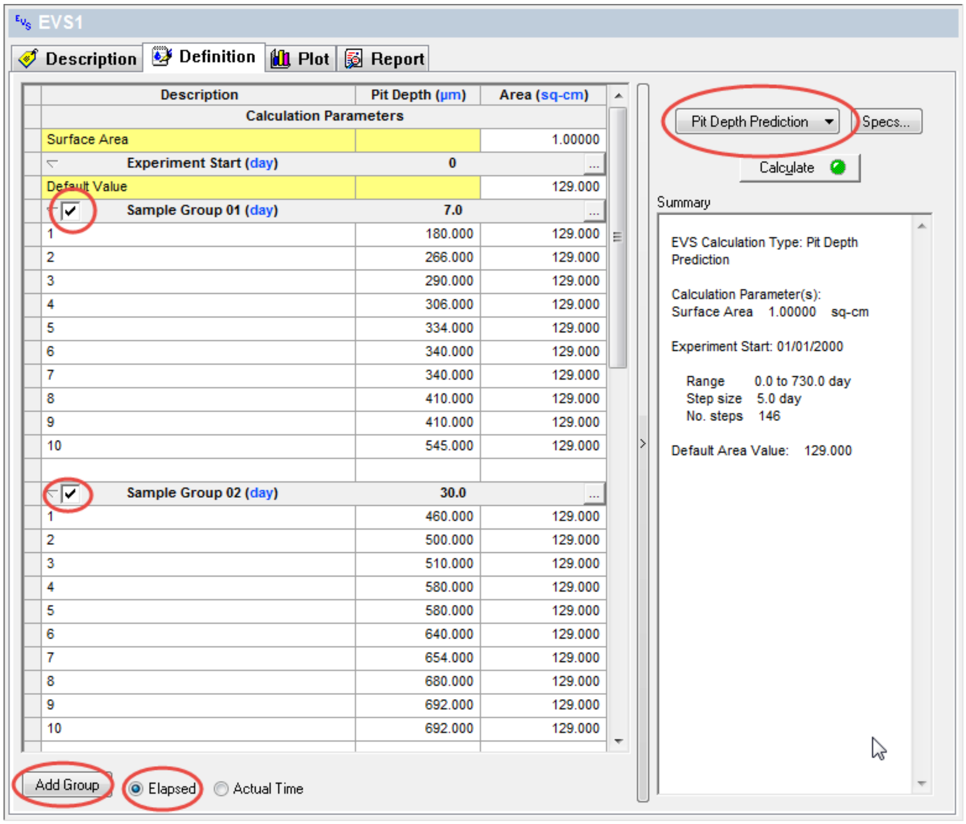
Elapsed: (day) 7

☑ Included for Calculation

Figure 33-3: Drop down-table for adding groups.

Insert data from the second column in **Table 33-1** into the Sample Group 01. Group 01 is representing 1 week.

After that, click on **Add Group** button (inside green oval), and in blank space type elapsed time = 30 days and insert all data from the third column for Sample Group 02. After inserting the data from Table 1 (from columns 1 and 3) the definition grid for EVS calculations should look like Figure 33-4.



Description	Pit Depth (μm)	Area (sq-cm)
Calculation Parameters		
Surface Area		1.00000
Experiment Start (day)	0	
Default Value		129.000
☑ Sample Group 01 (day)	7.0	
1	180.000	129.000
2	266.000	129.000
3	290.000	129.000
4	306.000	129.000
5	334.000	129.000
6	340.000	129.000
7	340.000	129.000
8	410.000	129.000
9	410.000	129.000
10	545.000	129.000
☑ Sample Group 02 (day)	30.0	
1	460.000	129.000
2	500.000	129.000
3	510.000	129.000
4	580.000	129.000
5	580.000	129.000
6	640.000	129.000
7	654.000	129.000
8	680.000	129.000
9	692.000	129.000
10	692.000	129.000

● Elapsed ○ Actual Time

EVS Calculation Type: Pit Depth Prediction

Calculation Parameter(s):
Surface Area 1.00000 sq-cm

Experiment Start: 01/01/2000

Range 0.0 to 730.0 day
Step size 5.0 day
No. steps 146

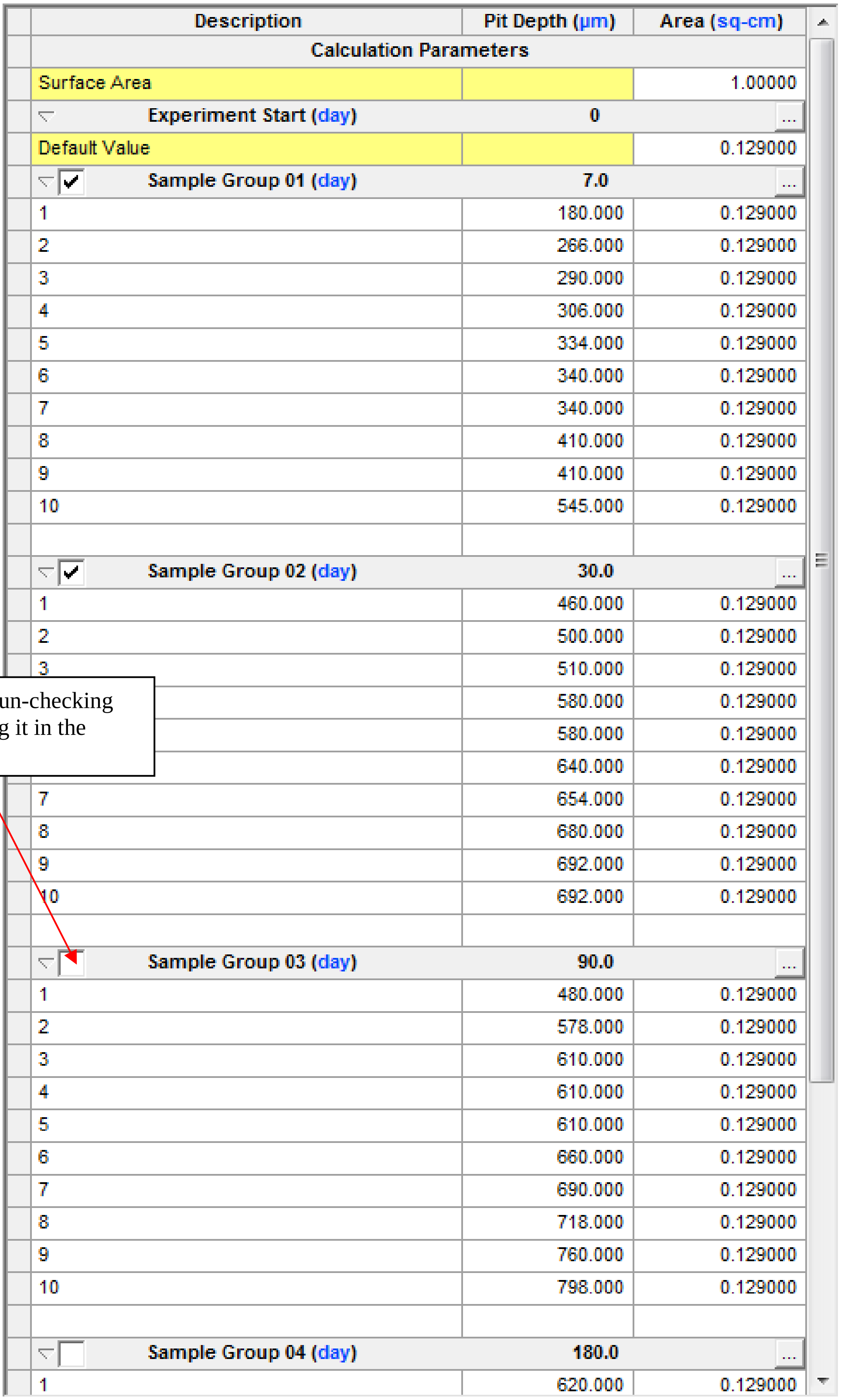
Default Area Value: 129.000

Figure 33-4: Specifying experimental data for depths of deepest pits (not completed)

Note the following:

- Here for the description of different experiments we simply used the number of the corresponding row in Table 1. However this description can be done in an arbitrary form.
- For each group, the order of samples relative depth can be arbitrary (not necessary in ascending order as in Table 1 or Figure 33-4).
- If coupons have different areas each area must be specified in the column **Area**.
- Radio button **Elapsed** (red ellipse in Figure 33-4) means the time after corrosion attack is used in calculations and namely this time is used usually in scientific publication. However it is possible to use also Actual Time of the experiments.

Enter the remaining data from Table 33-1 as new groups (columns 4 & 5), make sure the "Include boxes" are unchecked.



Description	Pit Depth (μm)	Area (sq-cm)
Calculation Parameters		
Surface Area		1.00000
Experiment Start (day)	**0**	...
Default Value		0.129000
☑ **Sample Group 01 (day)**	**7.0**	...
1	180.000	0.129000
2	266.000	0.129000
3	290.000	0.129000
4	306.000	0.129000
5	334.000	0.129000
6	340.000	0.129000
7	340.000	0.129000
8	410.000	0.129000
9	410.000	0.129000
10	545.000	0.129000
☑ **Sample Group 02 (day)**	**30.0**	...
1	460.000	0.129000
2	500.000	0.129000
3	510.000	0.129000
	580.000	0.129000
	580.000	0.129000
	640.000	0.129000
7	654.000	0.129000
8	680.000	0.129000
9	692.000	0.129000
10	692.000	0.129000
☐ **Sample Group 03 (day)**	**90.0**	...
1	480.000	0.129000
2	578.000	0.129000
3	610.000	0.129000
4	610.000	0.129000
5	610.000	0.129000
6	660.000	0.129000
7	690.000	0.129000
8	718.000	0.129000
9	760.000	0.129000
10	798.000	0.129000
☐ **Sample Group 04 (day)**	**180.0**	...
1	620.000	0.129000

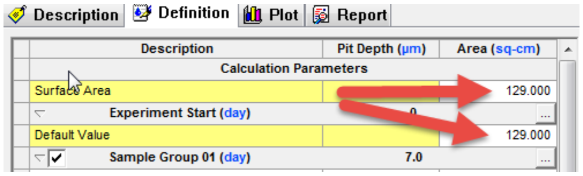
Group 03 was entered but by un-checking the box we are not considering it in the calculation.

Figure 33-5 Adding more data, un-checking groups not to be considered in the calculation

Setting up the calculation (Pit depth prediction)

We will simulate the results of Aziz's experiments assuming that only data for short-time experiments (for 1 week and 1 month) are available. To include these data into calculations we must mark the boxes (black ovals in Figure 33-4). It can be done also by using the drop-down menu for adding groups (see Figure 33-4). All others group (Groups 03 – 05) must not be marked.

Since we will predict corrosion on the samples with the same area, **the value of 129 cm^2** must be inserted into the property window Surface **Area**.



	Description	Pit Depth (µm)	Area (sq-cm)
	Calculation Parameters		
	Surface Area		129.000
	▽ Experiment Start (day)	0	...
	Default Value		129.000
	▽ ☑ Sample Group 01 (day)	7.0	...

Figure 33-6 Setting Surface Area

In the drop-down menu for the Type of calculations (inside the blue oval) we choose **Pit Depth Prediction**. Now, click on the **Specs…** button.

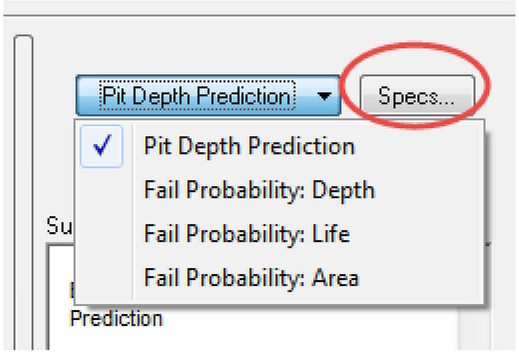


Figure 33-7 Selecting the type of calculation

The Survey Range category allows you to specify the range for the pit depth prediction survey. The default range is from 0 to 365 days that corresponds the available experimental data (Groups 01-05).

Then click **Calculate** button.

Analyzing the results

When the calculations are finished, click on the **Plot** tab.

You will see a plot of the predicted mean value of the depth of the deepest pit, x_m and the plots of values $x_m - \sigma$ and $x_m + \sigma$, where σ is the standard deviation of x_m.

It is important to note that only data for short term experiments (for 1 week and 1 month) denoted by black circles are included in calculations. Other data, denoted by red diamonds are shown only for demonstrating the accuracy of prediction. Of course, these additional data may be included in calculations by marking the corresponding boxes.

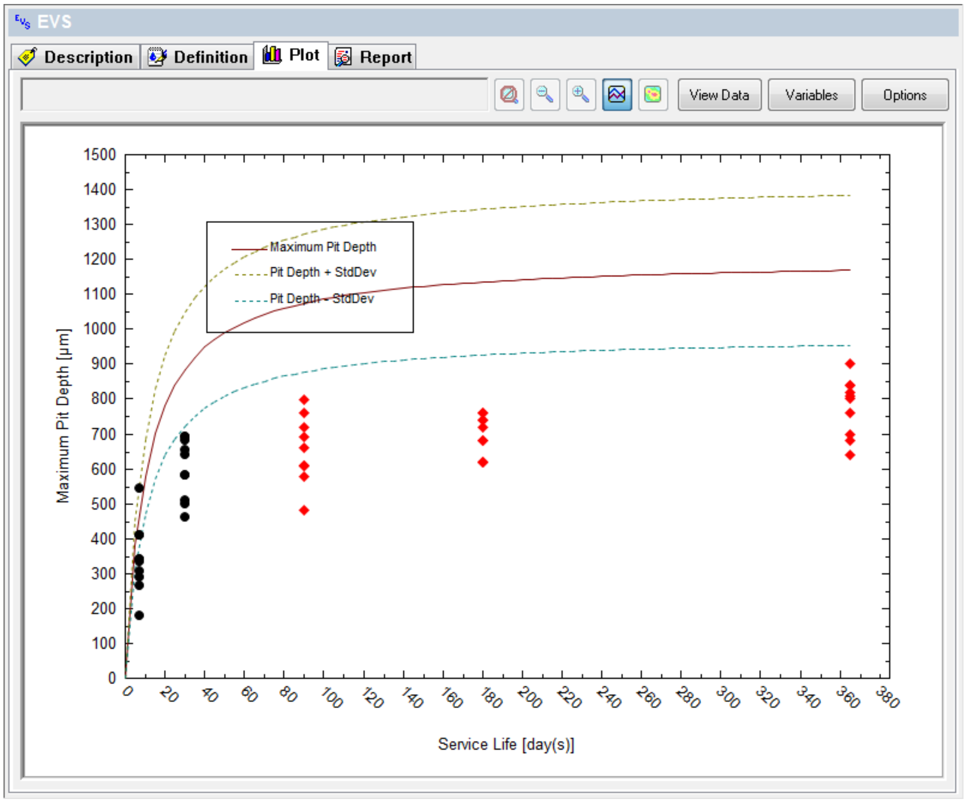


Figure 33-7: Predicted depth of the deepest pit. The experimental data for t = 1 week and 1 month are included into consideration. S = 129 cm^2.

Of course, the accuracy of prediction increases when additional group of experiments are included into consideration. Click back on the **Definition** tab.

Include (check) 90 days so that you now have 7 days (1 week), 30 days (1 month) and 90 days (3 months).

Click **Calculate**

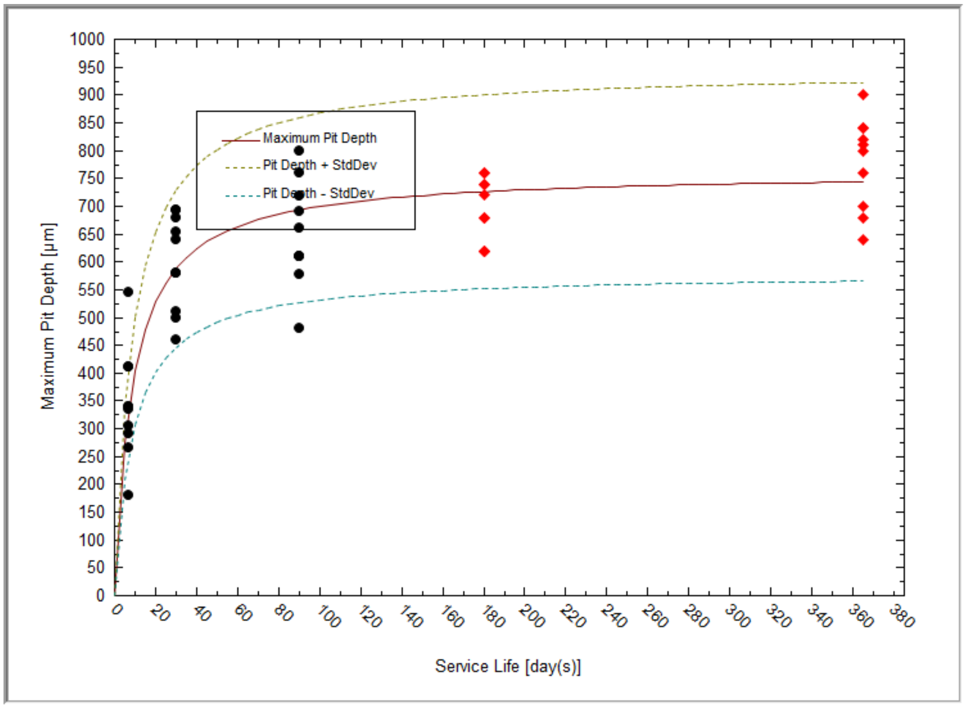
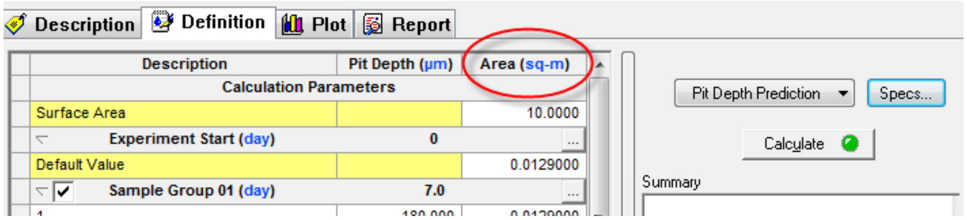


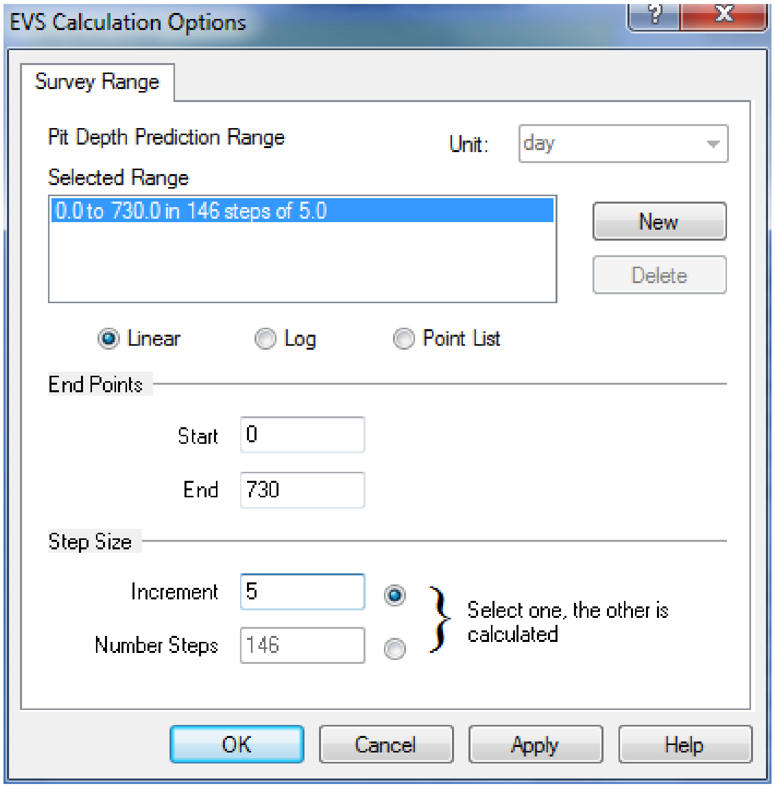
Figure 33-8:Predicted depth of the deepest pit. The experimental data for t = 1 week, 1 month, and 3 months are included into consideration.   S = 129 cm^2.

For predicting depth of the deepest pit in the system with a substantially larger area (say, 10 m^2) for the period of observation time of 2 years we have to input S = 10 (m^2) into **Surface Area** window and to specify the range [0, 2] (years) for observation time by clicking on **Specs…** button.



Description	Pit Depth (µm)	Area (sq-m)
Calculation Parameters		
Surface Area		10.0000
Experiment Start (day)	0	
Default Value		0.0129000
☑ Sample Group 01 (day)	7.0	

Figure 33-9 Changing the surface area, note the unit change from sq-cm to sq-m



Pit Depth Prediction Range

Unit: day

Selected Range

0.0 to 730.0 in 146 steps of 5.0

● Linear ○ Log ○ Point List

End Points

Start 0

End 730

Step Size

Increment 5 ●

Number Steps 146 ○

} Select one, the other is calculated

Figure 33-10 Changing the end time to 2 years (730 days)

The results of calculations are shown below.

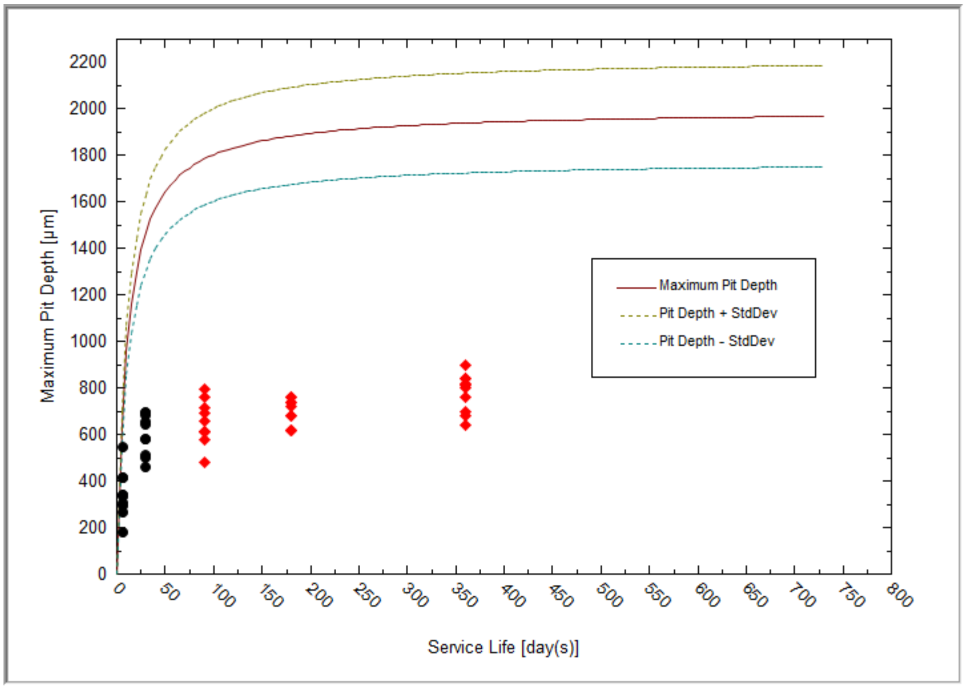


Figure 33-11: Predicted depth of the deepest pit. S = 10 m^2.

Setting up the calculations for engineering tasks

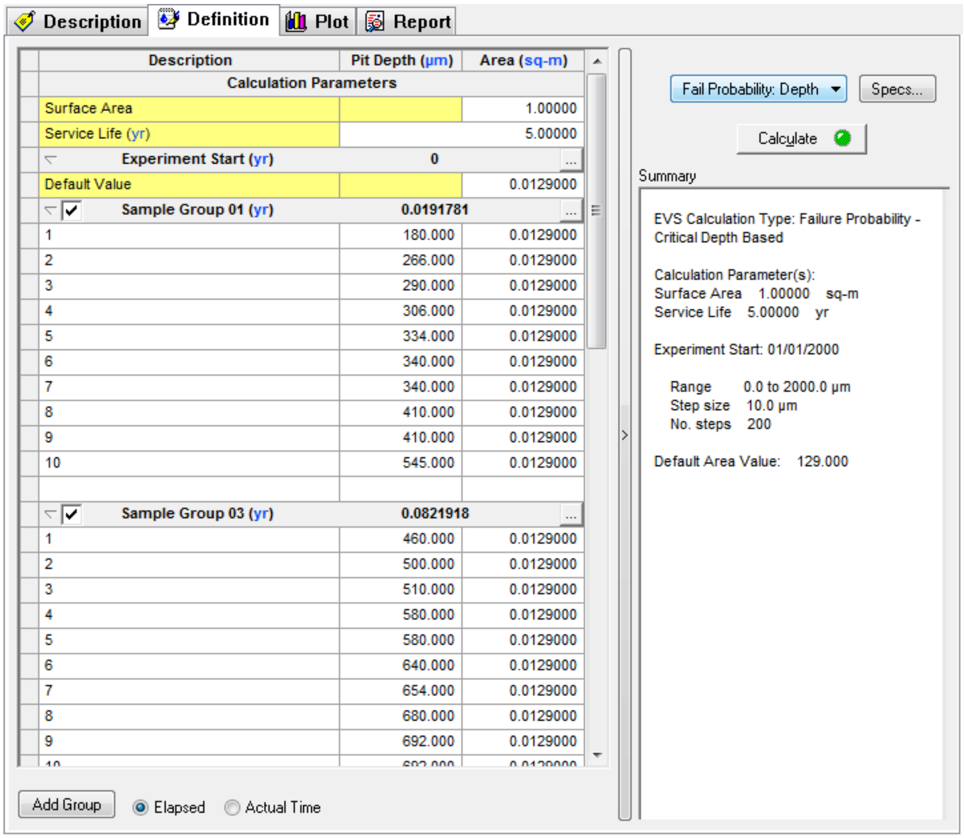
Here for the given system we consider some important engineering tasks.

First task:

Which thickness, d, does an the aluminum pipe with the area of S (say, 1 m^2) have to have in order to ensure acceptable performance (probability of failure, P_f , say, $P_f <$ 5%) at design service life, t_s , (say, 5 years)?

In order to do so we have to choose in drop-down menu **Fail Probability: Depth**, and insert into the window **Surface Area,** S = 1 (m^2) and insert into the window **Service Life**, t = 5 (years).

The definition grid for calculating the acceptable pipe wall width should look like Figure 33-18



Description	Pit Depth (µm)	Area (sq-m)
Calculation Parameters		
Surface Area		1.00000
Service Life (yr)		5.00000
Experiment Start (yr)	0	
Default Value		0.0129000
☑ **Sample Group 01 (yr)**	0.0191781	
1	180.000	0.0129000
2	266.000	0.0129000
3	290.000	0.0129000
4	306.000	0.0129000
5	334.000	0.0129000
6	340.000	0.0129000
7	340.000	0.0129000
8	410.000	0.0129000
9	410.000	0.0129000
10	545.000	0.0129000
☑ **Sample Group 03 (yr)**	0.0821918	
1	460.000	0.0129000
2	500.000	0.0129000
3	510.000	0.0129000
4	580.000	0.0129000
5	580.000	0.0129000
6	640.000	0.0129000
7	654.000	0.0129000
8	680.000	0.0129000
9	692.000	0.0129000

● Elapsed ○ Actual Time

Summary

EVS Calculation Type: Failure Probability - Critical Depth Based

Calculation Parameter(s):
Surface Area 1.00000 sq-m
Service Life 5.00000 yr

Experiment Start: 01/01/2000

Range 0.0 to 2000.0 µm
Step size 10.0 µm
No. steps 200

Default Area Value: 129.000

Figure 33-12: Specifying data for calculating probability of failure as a function of the width of the wall at given observation time and area of the pipe.

Then click **Calculate** button.

When the calculations are finished, click on the **Plot** tab. You will see a plot of predicted probability of failure

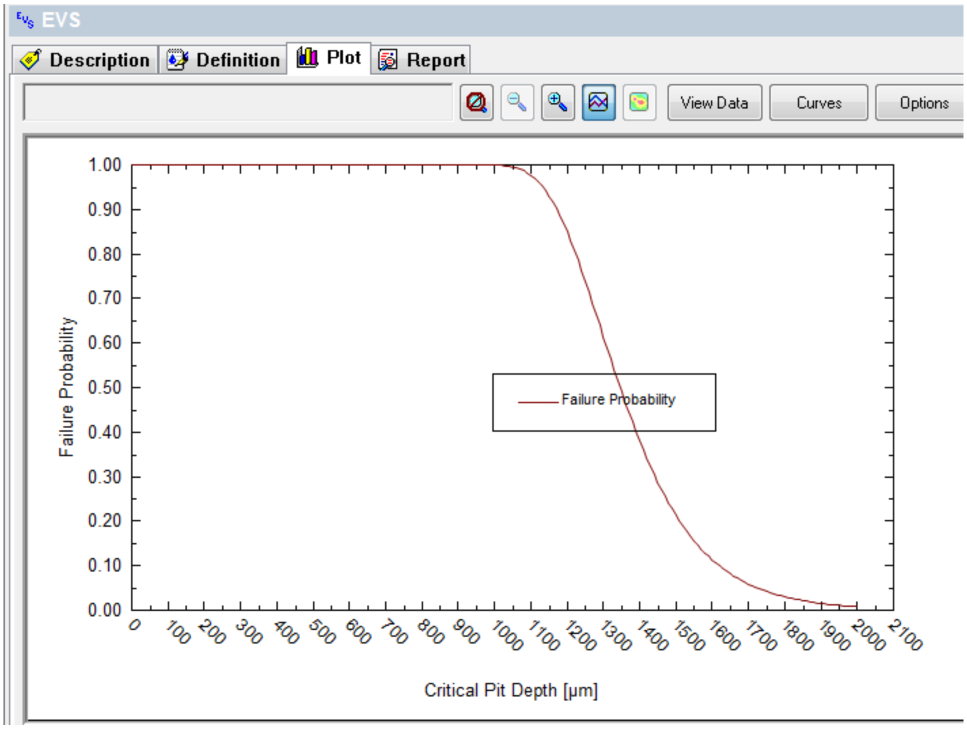


Figure 33-13: Probability of failure as a function of the width of the wall at given observation time and area of the pipe.

Click on the tab Report. From the Table: "**Calculation Results**" you can conclude that acceptable performance is reached at d > 1950 µm.

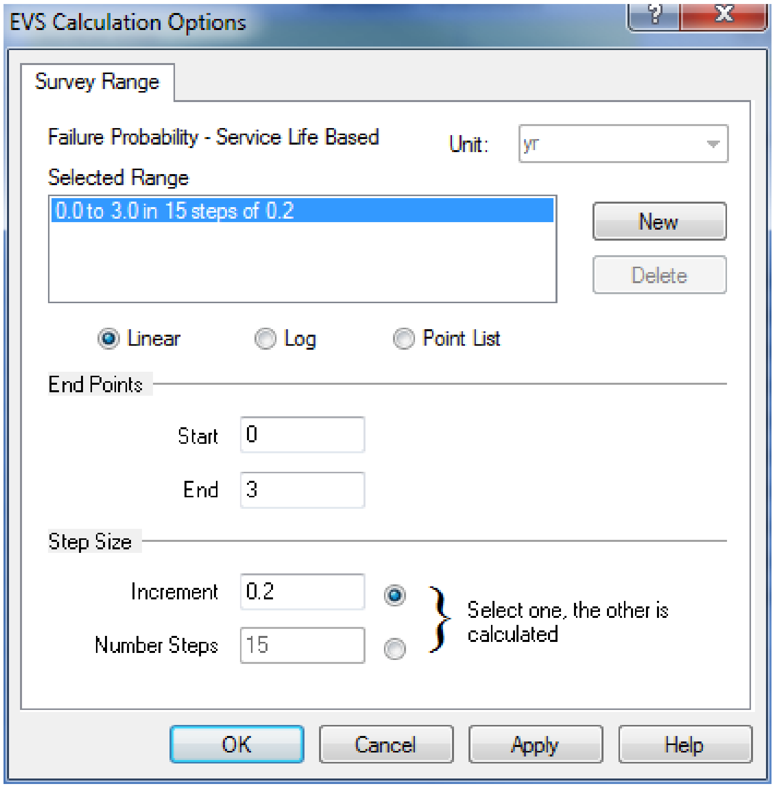
Second Task:

What service life, t, will have the aluminum pipe with the width, d, (say, 2300 µm), with area S (say, 10 m^2) in order to ensure acceptable performance (probability of failure, P_f , say P_f< 5 %).

In order to do so we have to choose in drop-down menu **Fail Probability: Life**, and insert into the window **Surface Area,** S = 10 (m^2) and insert into the window **Critical Pit Depth**, d = 2300 (µm).

We also wish to cover a sufficient period of time for the simulation. Click the **Specs…**button and change the range to 3 years in 0.2 year increments.

Also we need to deselect Groups 04 and 05 so un-check the appropriate group boxes.



Failure Probability - Service Life Based

Unit: yr

Selected Range

0.0 to 3.0 in 15 steps of 0.2

● Linear ○ Log ○ Point List

End Points

Start 0

End 3

Step Size

Increment 0.2 ●

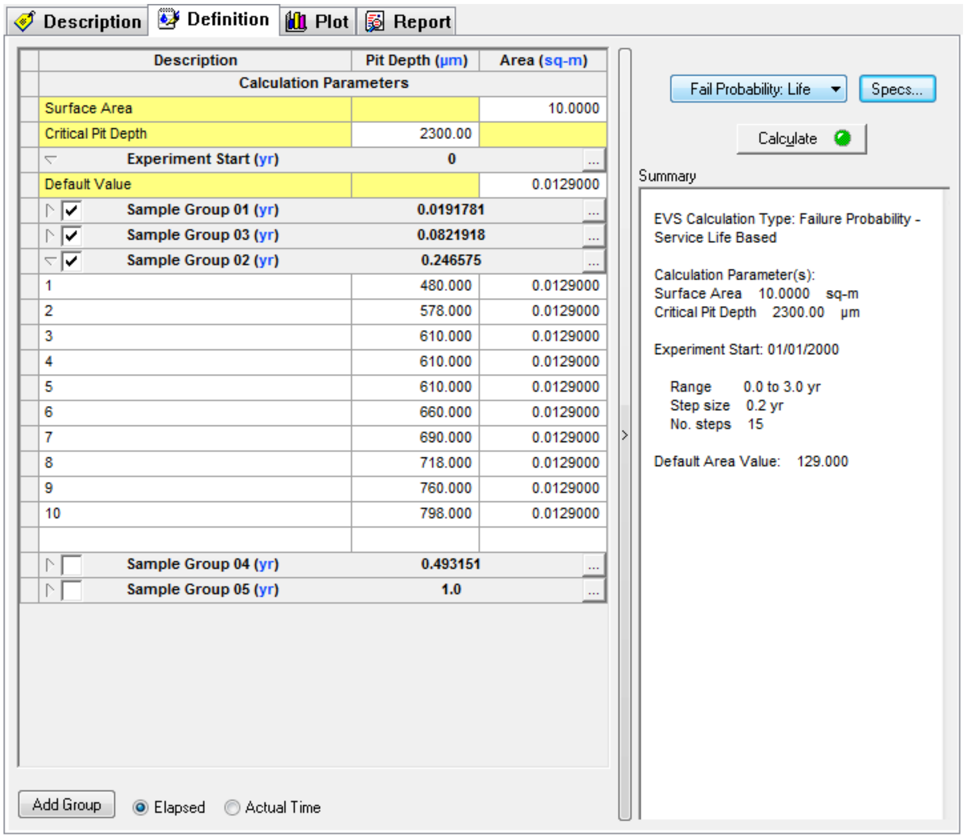
Number Steps 15 ○

Select one, the other is calculated

Figure 33-14 Changing the time to 3 years. Note the change in units from days to years

Click **OK**

The definition grid for calculating the acceptable pipe wall width should look similar to Figure 33-15



	Description	Pit Depth (µm)	Area (sq-m)
	Calculation Parameters		
	Surface Area		10.0000
	Critical Pit Depth	2300.00	
	Experiment Start (yr)	0	
	Default Value		0.0129000
☑	Sample Group 01 (yr)	0.0191781	
☑	Sample Group 03 (yr)	0.0821918	
☑	Sample Group 02 (yr)	0.246575	
	1	480.000	0.0129000
	2	578.000	0.0129000
	3	610.000	0.0129000
	4	610.000	0.0129000
	5	610.000	0.0129000
	6	660.000	0.0129000
	7	690.000	0.0129000
	8	718.000	0.0129000
	9	760.000	0.0129000
	10	798.000	0.0129000
☐	Sample Group 04 (yr)	0.493151	
☐	Sample Group 05 (yr)	1.0	

EVS Calculation Type: Failure Probability - Service Life Based

Calculation Parameter(s):
Surface Area 10.0000 sq-m
Critical Pit Depth 2300.00 µm

Experiment Start: 01/01/2000

Range 0.0 to 3.0 yr
Step size 0.2 yr
No. steps 15

Default Area Value: 129.000

Figure 33-15: Specifying data for calculating probability of failure as a function of the width of the wall at given observation time and area of the pipe.

Then click **Calculate** button.

When the calculation is finished, click on the **Plot** tab. You will see a plot of predicted probability of failure (Figure 33-16). (You may need to change the axis ranges via the **Options Button**)

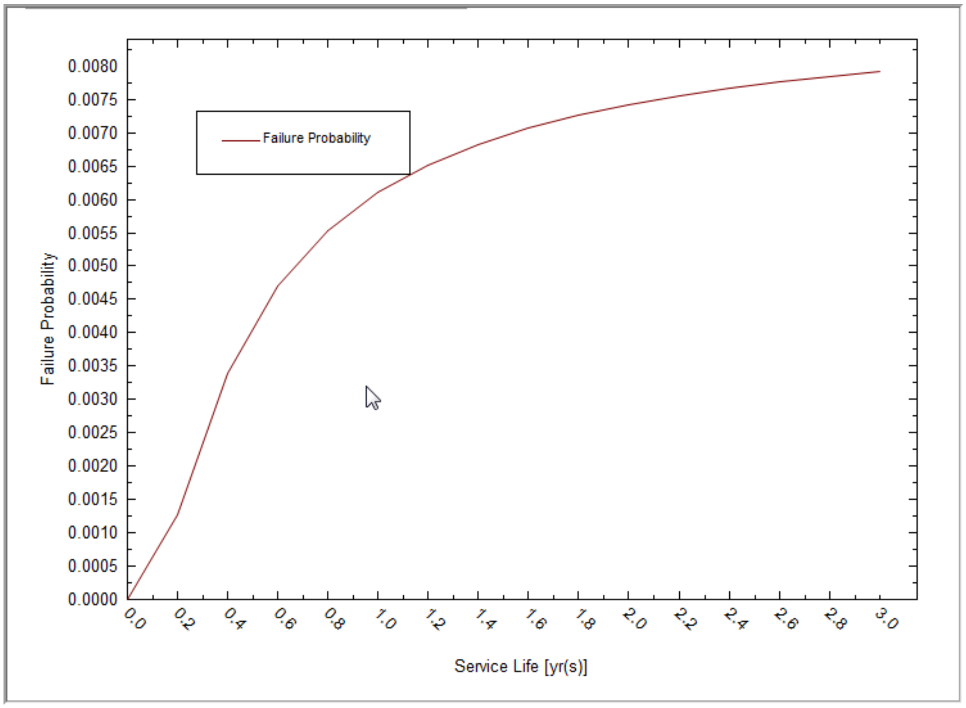


Figure 33-16: Probability of failure as a function of service life for a given width of the wall and given area of the pipe.

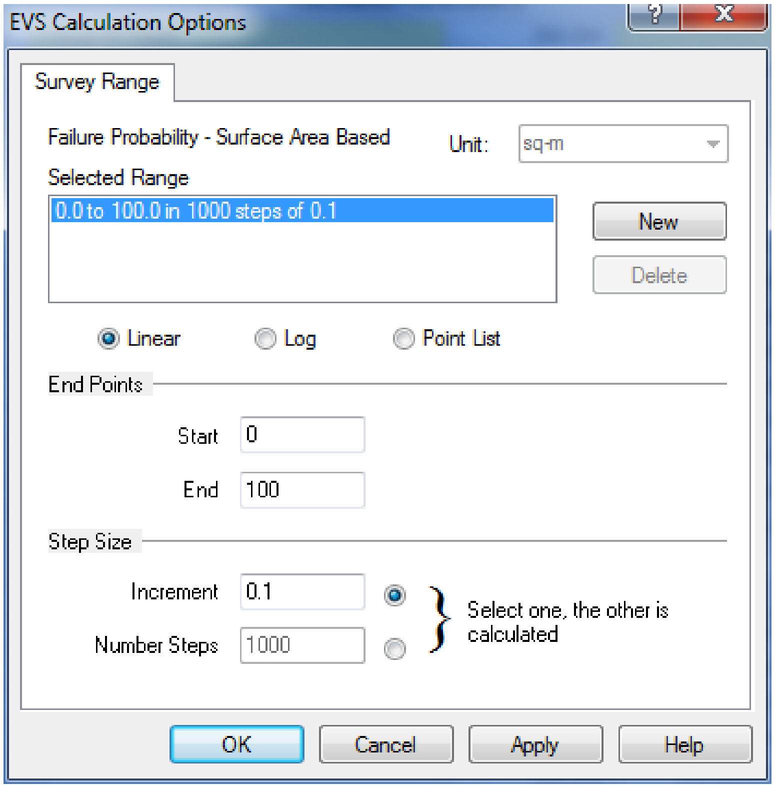
Click on the tab Report. From the Table: “**Calculation Results**” you can conclude that acceptable performance is reached at t < 657 days.

Third Task:

What area, S, can have the aluminum pipe with the width, d, (say, 2000 µm), and service life, t, (say, 5 years) in order to ensure acceptable performance (probability of failure, P_f , say, $P_f < 5$ %).

In order to do so we have to choose in the drop-down menu **Fail Probability: Area**, and insert into the cell ***Critical Pit Depth*** the value 2000 (µm) and into cell ***Service Life***, 5 (years).

We need to set the range for the area from 0 to 100 sq-m in 0.1 sq-m increments. Click the **Specs…** button.



Failure Probability - Surface Area Based

Unit: sq-m

Selected Range

0.0 to 100.0 in 1000 steps of 0.1

● Linear ○ Log ○ Point List

End Points

Start: 0

End: 100

Step Size

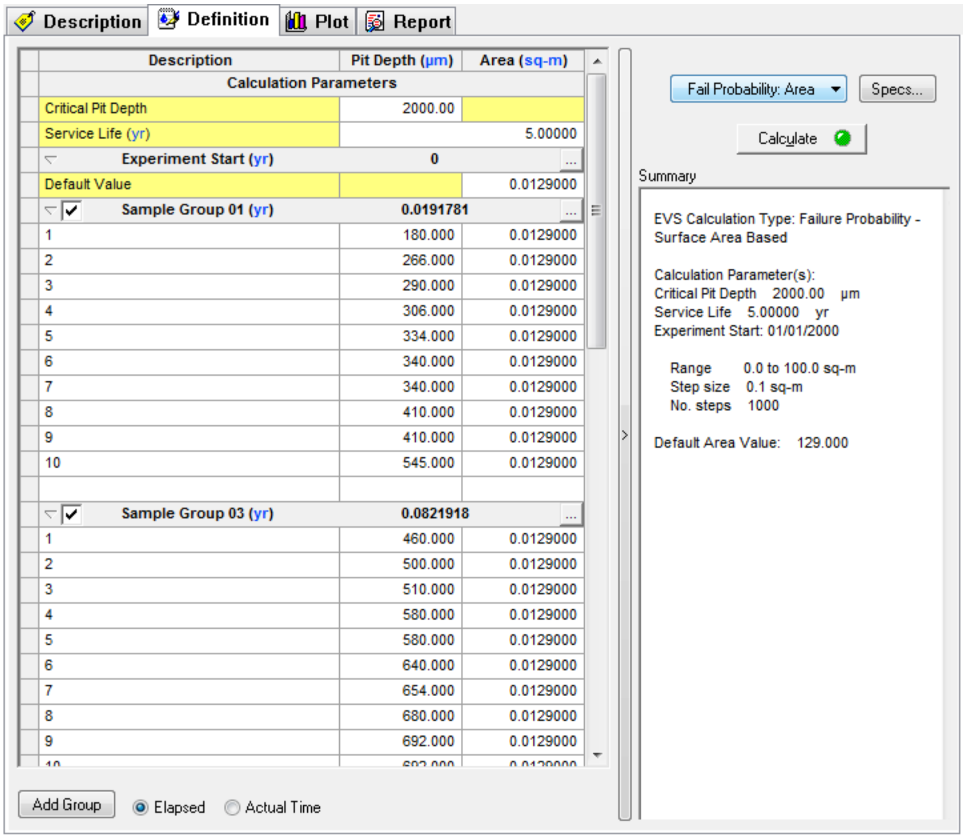
Increment: 0.1 ●

Number Steps: 1000 ○

Select one, the other is calculated

Figure 33-17 Setting the area range for Failure Probability

The definition grid for calculating the acceptable pipe wall width should look similar to Figure 33-18.



Description	Pit Depth (μm)	Area (sq-m)
Calculation Parameters		
Critical Pit Depth	2000.00	
Service Life (yr)		5.00000
Experiment Start (yr)	**0**	
Default Value		0.0129000
☑ **Sample Group 01 (yr)**	**0.0191781**	
1	180.000	0.0129000
2	266.000	0.0129000
3	290.000	0.0129000
4	306.000	0.0129000
5	334.000	0.0129000
6	340.000	0.0129000
7	340.000	0.0129000
8	410.000	0.0129000
9	410.000	0.0129000
10	545.000	0.0129000
☑ **Sample Group 03 (yr)**	**0.0821918**	
1	460.000	0.0129000
2	500.000	0.0129000
3	510.000	0.0129000
4	580.000	0.0129000
5	580.000	0.0129000
6	640.000	0.0129000
7	654.000	0.0129000
8	680.000	0.0129000
9	692.000	0.0129000

● Elapsed ○ Actual Time

Summary

EVS Calculation Type: Failure Probability - Surface Area Based

Calculation Parameter(s):
Critical Pit Depth 2000.00 μm
Service Life 5.00000 yr
Experiment Start: 01/01/2000

Range 0.0 to 100.0 sq-m
Step size 0.1 sq-m
No. steps 1000

Default Area Value: 129.000

Figure 33-18: Specifying data for calculating probability of failure as a function of area of the pipe at given width o f the wall and given service life.

For this simulation we will only be using Group 01 and Group 02. Un-check the remaining groups.

Then click **Calculate** button.

When the calculation is finished, click on the **Plot** tab. You will see a plot of predicted probability of failure (Figure 33-19).

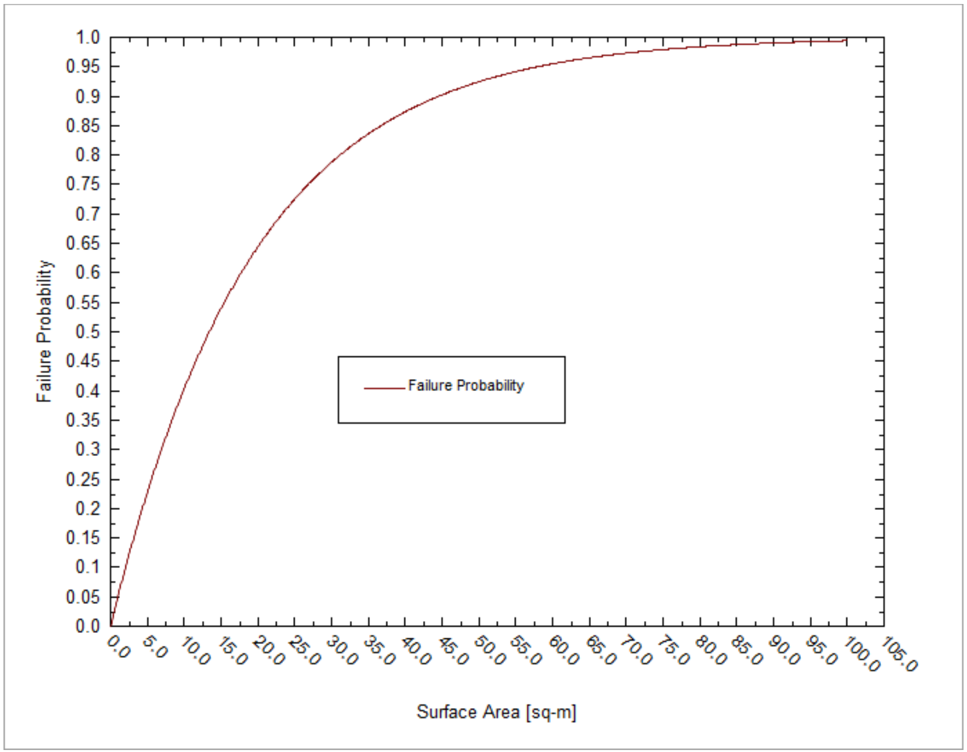


Figure 33-19: Probability of failure as a function of the area of the pipe at given width of the wall and given service life.

Click on the tab Report. From the Table: “**Calculation Results**” you can conclude that acceptable performance is reached at S < 14000 cm^2 = 1.4 m^2.

Example 2: Corrosion in Pipelines.

By using this example we would like to demonstrate that in some cases reliable prediction of corrosion damage can be done by using a very limited number of experimental points.

In Figure 33-21 you can see the results of direct measurements of the depth of the deepest pits in the pipeline between Samara and Moscow [Zikerman, 1972]. The data has been inserted, by the way, as was described in Example 1.

Table 33-2 *Pit depths(mm) for pipeline between Samara and Moscow*

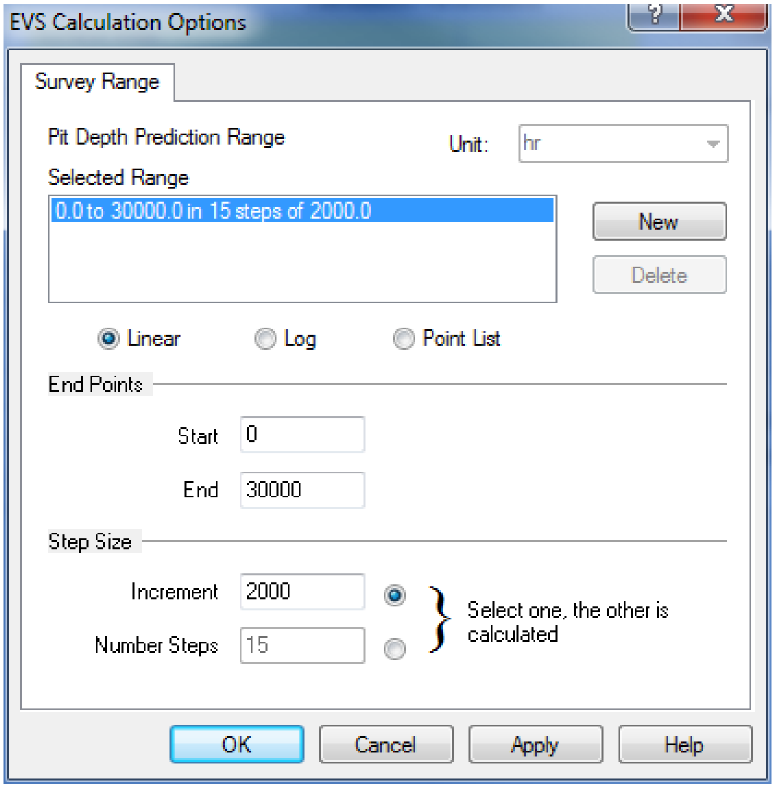
	Group 1	**Group 2**	**Group 3**	**Group 4**	**Group 5**	**Group 6**	**Group 7**	**Group 8**
Sample	**1440 hrs**	**5040 hrs**	**5760 hrs**	**8959 hrs**	**12624 hrs**	**17688 hrs**	**28032 hrs**	**28272 hrs**
1	0.1			1.4	1.7	1.9		2.1
2		0.49		1.95	2.1	2.08		2.25
3	0.3	1.6		1.8				
4	0.4			1.6	1.65	1.88		
5	0.9		1.57	2.1	2.21	2.4	2.4	
6	0.3		1.2	1.4	1.4	1.55	1.71	

We would like to simulate for 30,000 hours so we need to change the **Specs…**button.

Start 0.0 hrs

End 30000 hrs

Increment 2000 hrs



EVS Calculation Options

Survey Range

Pit Depth Prediction Range

Unit: hr

Selected Range

0.0 to 30000.0 in 15 steps of 2000.0

● Linear ○ Log ○ Point List

End Points

Start 0

End 30000

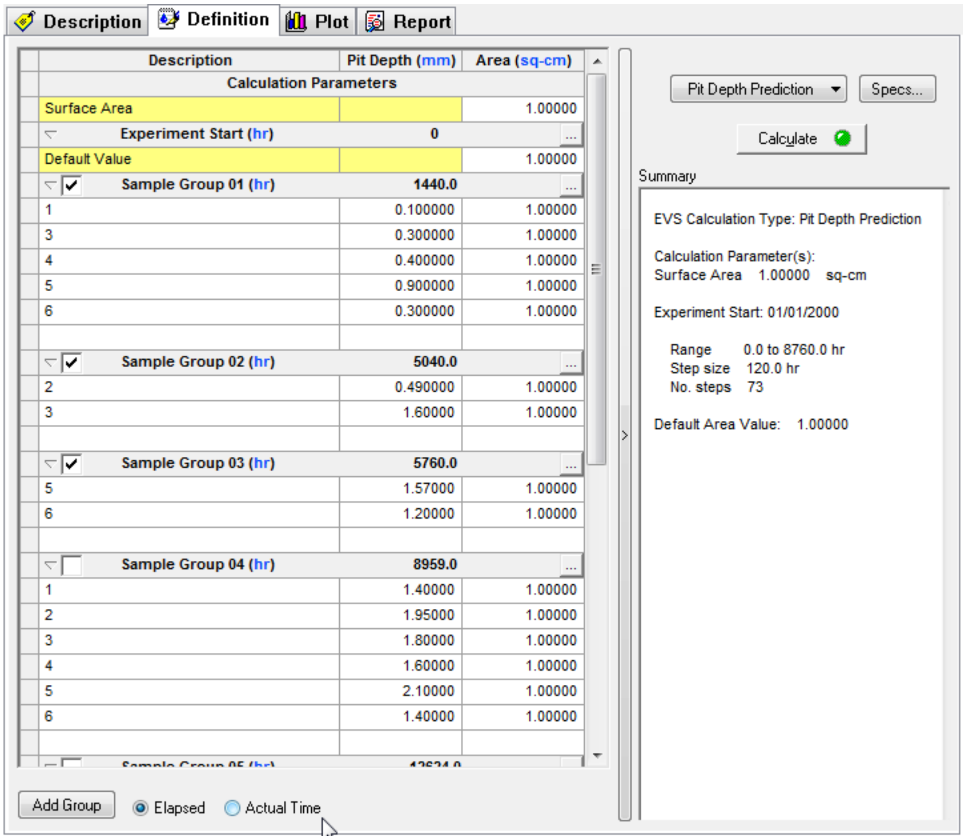
Step Size

Increment 2000 ●

Number Steps 15 ○

Select one, the other is calculated

Figure 33-20 Setting the range to 30,000 hours, Note the units for time



	Description	Pit Depth (mm)	Area (sq-cm)
	Calculation Parameters		
	Surface Area		1.00000
	Experiment Start (hr)	**0**	
	Default Value		1.00000
☑	**Sample Group 01 (hr)**	**1440.0**	
1		0.100000	1.00000
3		0.300000	1.00000
4		0.400000	1.00000
5		0.900000	1.00000
6		0.300000	1.00000
☑	**Sample Group 02 (hr)**	**5040.0**	
2		0.490000	1.00000
3		1.60000	1.00000
☑	**Sample Group 03 (hr)**	**5760.0**	
5		1.57000	1.00000
6		1.20000	1.00000
☐	**Sample Group 04 (hr)**	**8959.0**	
1		1.40000	1.00000
2		1.95000	1.00000
3		1.80000	1.00000
4		1.60000	1.00000
5		2.10000	1.00000
6		1.40000	1.00000

● Elapsed ○ Actual Time

Summary

EVS Calculation Type: Pit Depth Prediction

Calculation Parameter(s):
Surface Area 1.00000 sq-cm

Experiment Start: 01/01/2000

Range 0.0 to 8760.0 hr
Step size 120.0 hr
No. steps 73

Default Area Value: 1.00000

Figure 33-21: Specifying experimental data for depths of deepest pits for corrosion in pipelines. Only 3 observation times are used

Because the area of the pipelines metal was not changed with time the information about this area is not needed for extrapolation of corrosion damage in time. That is why all data for Area in Figure 33-21 are arbitrary.

Check only Groups 1 through 3 are used.

Click the **Calculate button.**

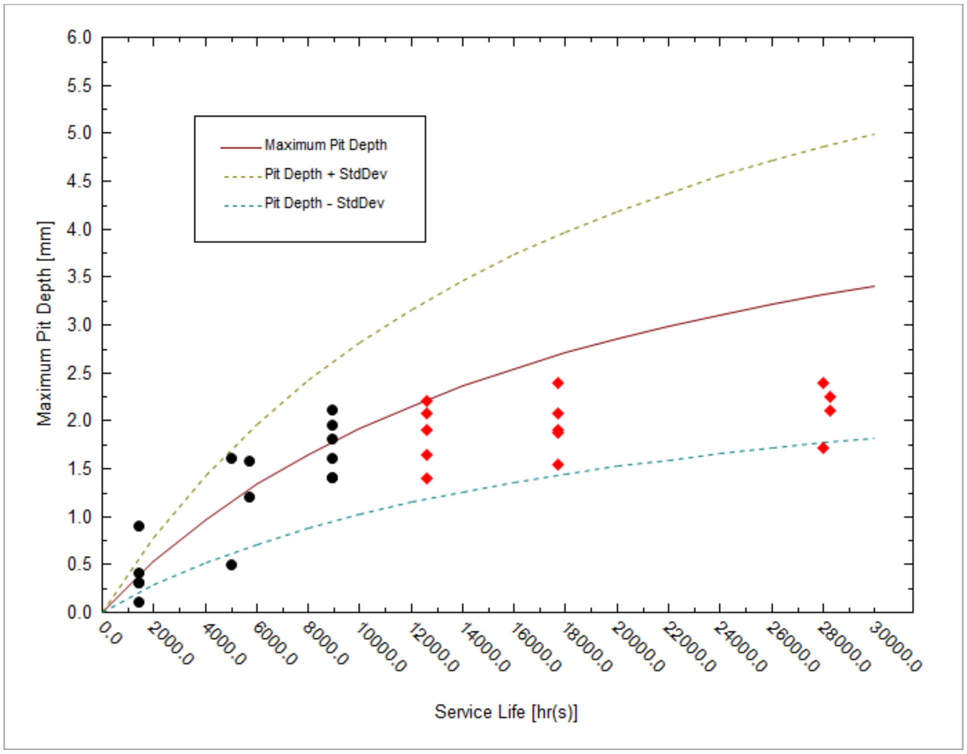


Figure 33-22: Predicted depth of the deepest pit with calibration on three observation times.

Click on the **Definition** tab and **Check** Groups 1 through 5.

Recalculate the diagram.

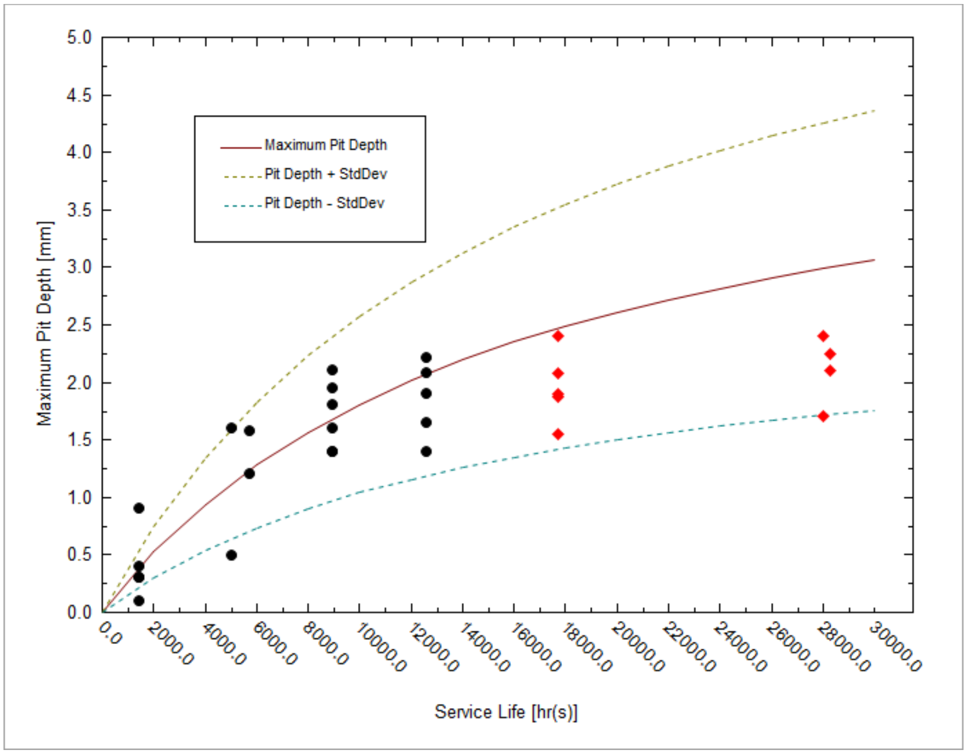


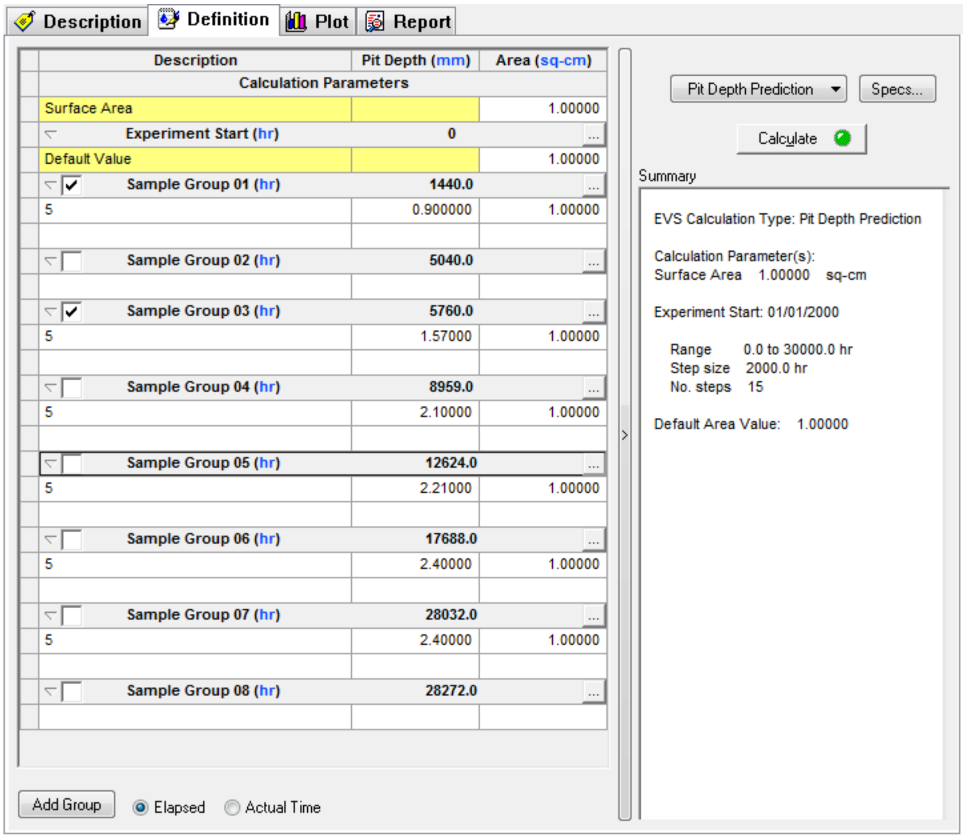
Figure 33-23: Predicted depth of the deepest pit with calibration on five observation times.

Figure 33-22 and Figure 33-23 show how the predicted results improved with increasing number of subsequent inspections. As previously, only points in black were used for predicting propagation of corrosion damage and other data, denoted by red diamonds, are shown only for demonstrating the accuracy of prediction

The predictions can be substantially improved if they were obtained on the same part of the pipe where conditions are approximately the same (see Figure 33-25and Figure 33-26).

Table 33-3Pit depth from measurements a single location.

Time (hours)	Pit depth (mm)
1440	0.9
5040	
5760	1.57
8959	2.1
12624	
17688	2.21
28032	2.4
28272	



Description	Pit Depth (mm)	Area (sq-cm)
Calculation Parameters		
Surface Area		1.00000
Experiment Start (hr)	**0**	...
Default Value		1.00000
☑ **Sample Group 01 (hr)**	**1440.0**	...
5	0.900000	1.00000
☐ **Sample Group 02 (hr)**	**5040.0**	...
☑ **Sample Group 03 (hr)**	**5760.0**	...
5	1.57000	1.00000
☐ **Sample Group 04 (hr)**	**8959.0**	...
5	2.10000	1.00000
☐ **Sample Group 05 (hr)**	**12624.0**	...
5	2.21000	1.00000
☐ **Sample Group 06 (hr)**	**17688.0**	...
5	2.40000	1.00000
☐ **Sample Group 07 (hr)**	**28032.0**	...
5	2.40000	1.00000
☐ **Sample Group 08 (hr)**	**28272.0**	...

● Elapsed ○ Actual Time

Summary

EVS Calculation Type: Pit Depth Prediction

Calculation Parameter(s):
Surface Area 1.00000 sq-cm

Experiment Start: 01/01/2000

Range 0.0 to 30000.0 hr
Step size 2000.0 hr
No. steps 15

Default Area Value: 1.00000

Figure 33-24: Specifying experimental data for depths of deepest pits for corrosion in pipeline. Experimental data are taken from one location on the pipe.

Only Groups 1 and 3 were used in the calculation.

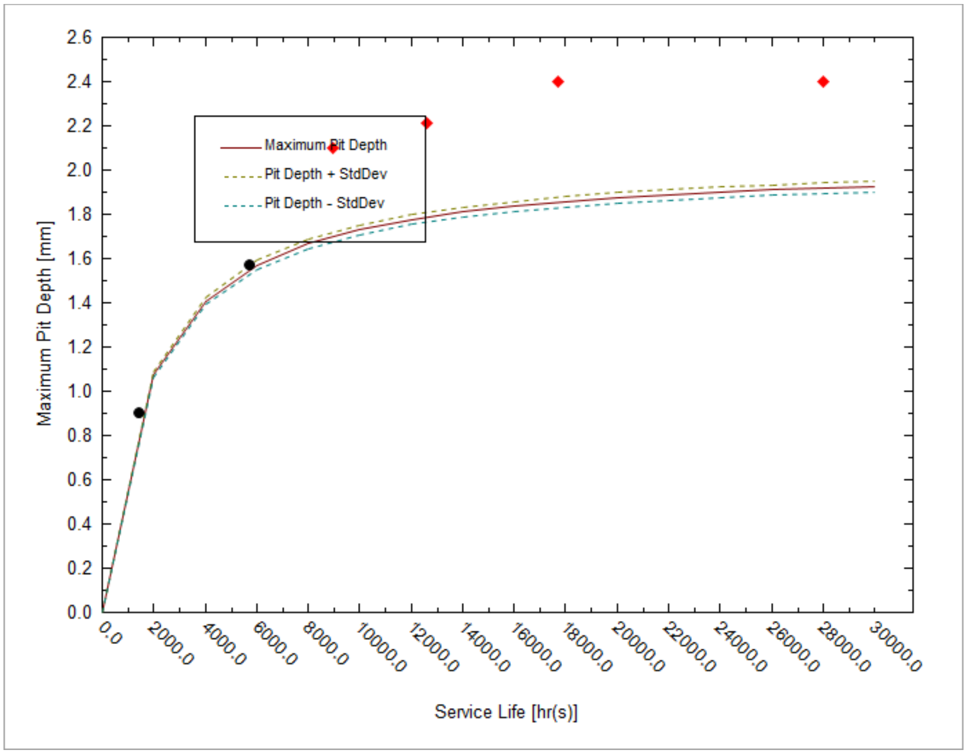


Figure 33-25: Predicted depth of the deepest pit with calibration on two observation times. Data are taken from one location on the pipe.

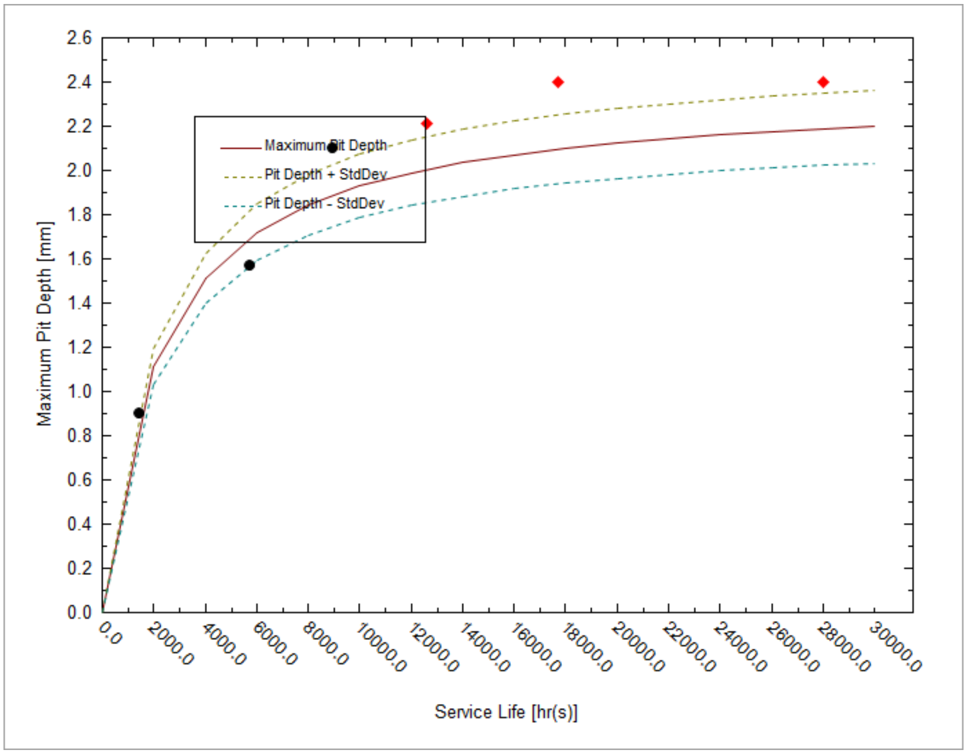


Figure 33-26: Predicted depth of the deepest pit with calibration on three observation times (groups 1,3 and 4). Data are taken from one location on the pipe.

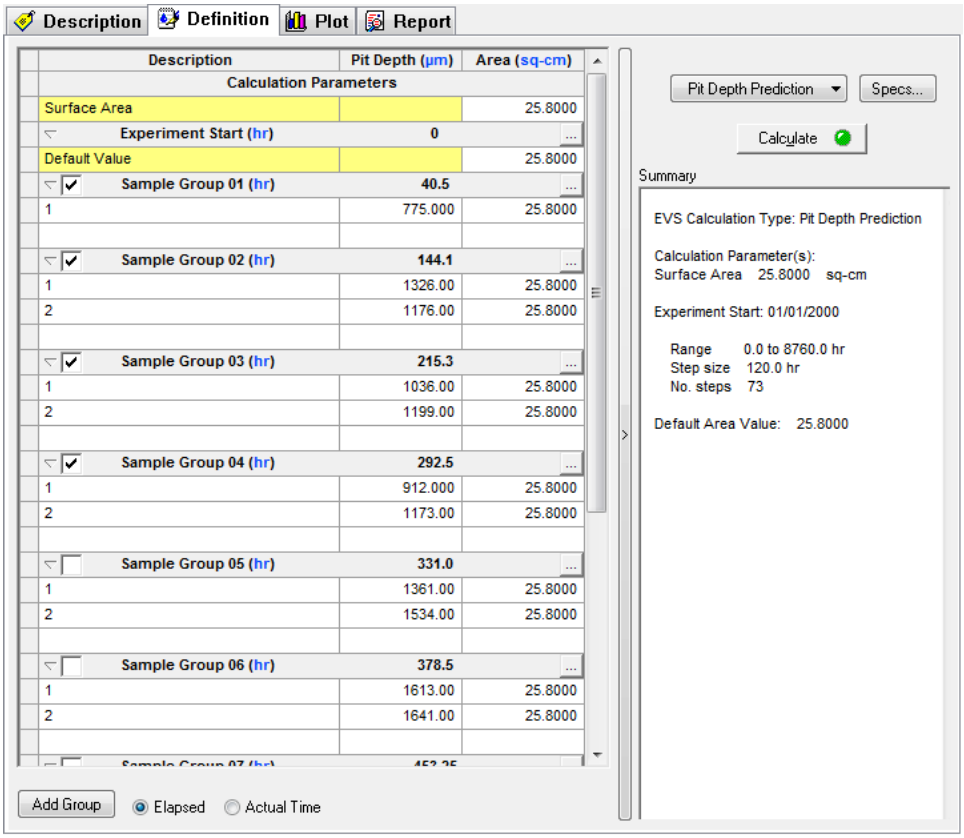
Figure 33-27: Predicted depth of the deepest pit with calibration on four observation times(groups 1, 3, 4, and 6). Data are taken from one location on the pipe.

Example 3: Possible Case of Insufficient Data

In some cases the data that provided by the user may be insufficient for reliable prediction of corrosion damage. Thus Figure 15-20 shows a part of experimental data that can be found in the paper (Laycock et al. 1990) for depths of the deepest pits that were measured on 316L coupons (2x2x1/2 in. thick) in a 10% ferric chloride solution at 50 ^{0}C. The full set of data from this paper is seen in Figure 33-28, which shows the predicted maximum pit depth for this system by using measurements at first three observation times.

Table 33-4 Pit depth data for 25.8 sq-cm, depth in micrometers

Sample	Grp 1	Grp 2	Grp3	Grp 4	Grp 5	Grp 6	Grp 7	Grp 8	Grp 9
	40.5 hrs	144.17 hrs	215.33 hrs	292.5 hrs	331.0 hrs	378.5 hrs	453.25 hrs	477.0 hrs	528.0 hrs
1	775	1326	1036	912	1361	1613	2101	1722	1714
2		1176	1199	1173	1534	1641	2024	1798	1767
3								1496	1775



Description	Pit Depth (µm)	Area (sq-cm)
Calculation Parameters		
Surface Area		25.8000
Experiment Start (hr)	0	...
Default Value		25.8000
☑ Sample Group 01 (hr)	40.5	...
1	775.000	25.8000
☑ Sample Group 02 (hr)	144.1	...
1	1326.00	25.8000
2	1176.00	25.8000
☑ Sample Group 03 (hr)	215.3	...
1	1036.00	25.8000
2	1199.00	25.8000
☑ Sample Group 04 (hr)	292.5	...
1	912.000	25.8000
2	1173.00	25.8000
☐ Sample Group 05 (hr)	331.0	...
1	1361.00	25.8000
2	1534.00	25.8000
☐ Sample Group 06 (hr)	378.5	...
1	1613.00	25.8000
2	1641.00	25.8000

Summary

EVS Calculation Type: Pit Depth Prediction

Calculation Parameter(s):
Surface Area 25.8000 sq-cm

Experiment Start: 01/01/2000

Range 0.0 to 8760.0 hr
Step size 120.0 hr
No. steps 73

Default Area Value: 25.8000

Figure 33-28: Specifying experimental data for depths of deepest pits for corrosion of 316L coupons in 10% ferric chloride solution.

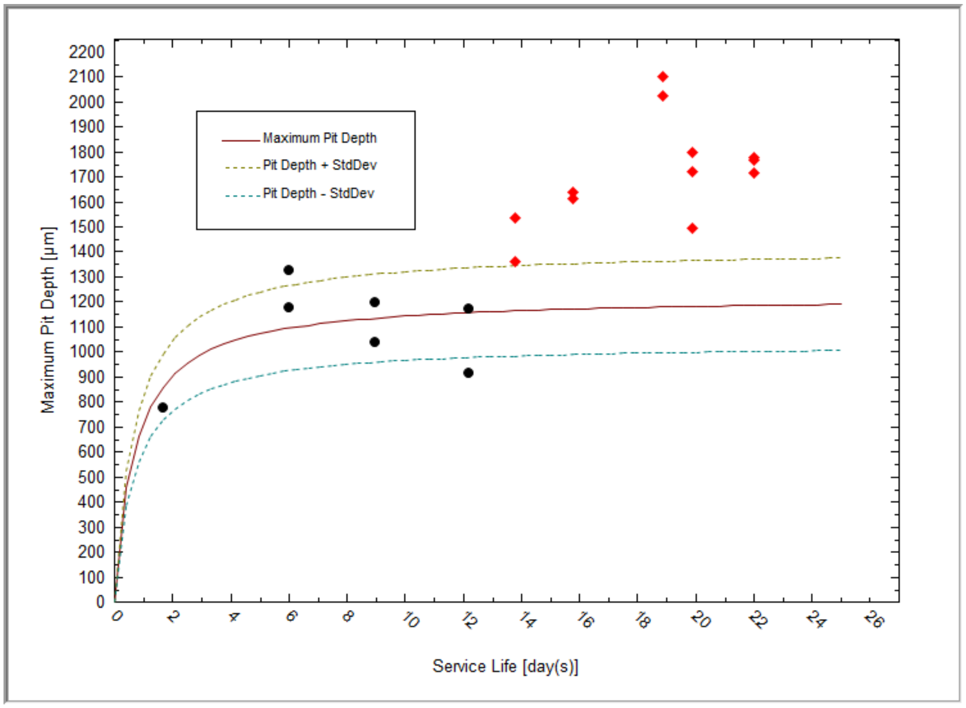


Figure 33-29: Predicted depth of the deepest pit on the stainless steel with calibration on the first four observation times (groups 1 through 4)

We see that in this case the prediction cannot be considered satisfactory. The reason is that for the second, third and fourth observation times the observed mean value of deepest pit decreases. Obviously such behavior of maximum pit depth has no physical foundation. Generally speaking such situation is the results of an insufficient numbers of experiments (used coupons) for given observation times. Accordingly, we can expect that after increasing the number of used coupons the situation can improve.

All of this does not mean that a full set of already available data cannot be used for predicting propagation of corrosion damage. Thus Figure 33-30 shows that the results of approximation of the full set of available experimental data from (Laycock et al. 1990) can be reasonably approximated by using EVS approach.

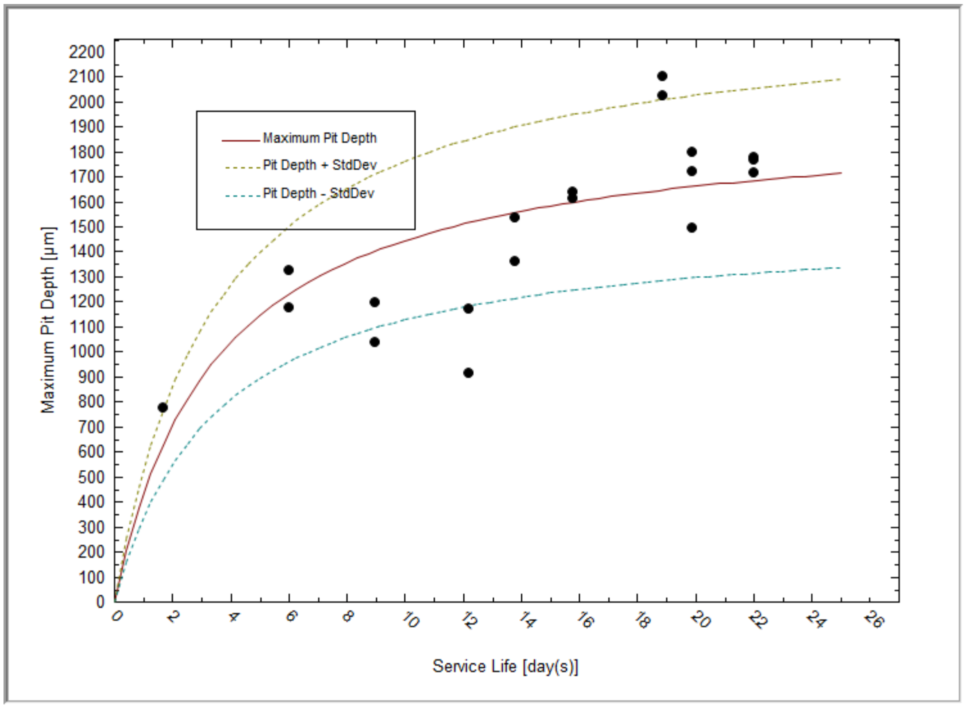


Figure 33-30: Predicted depth of the deepest pit on the stainless steel with calibration on full set of available data.

It means that sometimes the insufficient number of coupons (measurements at given observation times) can be compensated by increasing numbers of observation at different times.

You can download all the examples for this chapter from the OLI Wiki Page or from the support site

34. Petroleum Fraction Thermodynamic Methods

Distillation Methods of the ASTM

ASTM D86

Used for light and medium petroleum products and is carried out at atmospheric pressure. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline.

ASTM D1160

Used for heavier petroleum products and is often carried out under vacuum. Sometimes as low as 1 mm Hg. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline

ASTM D2887

Uses gas chromatography to produce the distillation curve and is applicable to a wide range of petroleum products. The results are always reported on a volume percent basis. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline

TBP

This is the true boiling point curve. These curves, in practice, are difficult to obtain. The other methods are usually used instead.

Average Bulk Density

Specific Gravity

Unitless, relative to pure water (H_2O) at 15 ^oC which has a density of 1.0 g/mL

API Gravity

Degrees API (^{o}API). This is calculated via the following equation:

$$ {}^{o}API(60F) = \left(\frac{141.5}{SG(60F)} \right) - 131.5 $$

Equation 34-1

SG is the specific gravity at 60 °F.

Watson K

The Watson K has no units but is calculated via:

$$ K = \left(\frac{NBP^{1/3}}{SG} \right) $$

Equation 34-2

Where NBP is the normal Boiling point and SG is the specific gravity.

Thermodynamic Methods

API

Uses the specific gravity to estimate the critical parameters. The specific gravity, if not entered, can be estimated from the API gravity or the Watson K. The boiling points are taken from the assay data. API version 5 (API-5) and API version 8 (API-8) are currently supported.

Cavett

This method uses the API gravity method to determine the critical properties. The API gravity, if not entered can be estimated from the actual specific gravity or the Watson K. The boiling points for the pseudo-components are taken from the assay.

Lee-Kesler

This method uses the Watson K and the specific gravity (which can be estimated via the Watson K) to determine the critical parameters.

35. How to create Chemical Diagrams

The OLI Analyzers have a feature that is seldom used which allows for a user to create a stability map for species based on concentration and other parameters such as pH. A contour map is created showing the user where some solids are stable and where others are not.

For this example we are reproducing work found in a paper that was published in ***Materials Research Innovations***, Volume 14, Number 1, February 1010 pp 9-15 by T. Andelman, M.C. Tan, and R.E. Riman.
Specifically we are going to investigate the stability fields where lanthanum acetate - $La(C_2H_3O_2)_3$ and potassium phosphate - K_3PO_4 are precursors to the plot.

To begin we start the OLI Analyzers and select a **New Stream**

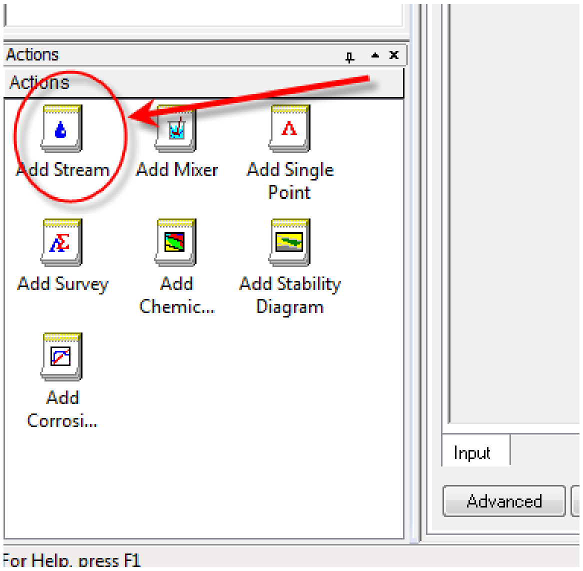
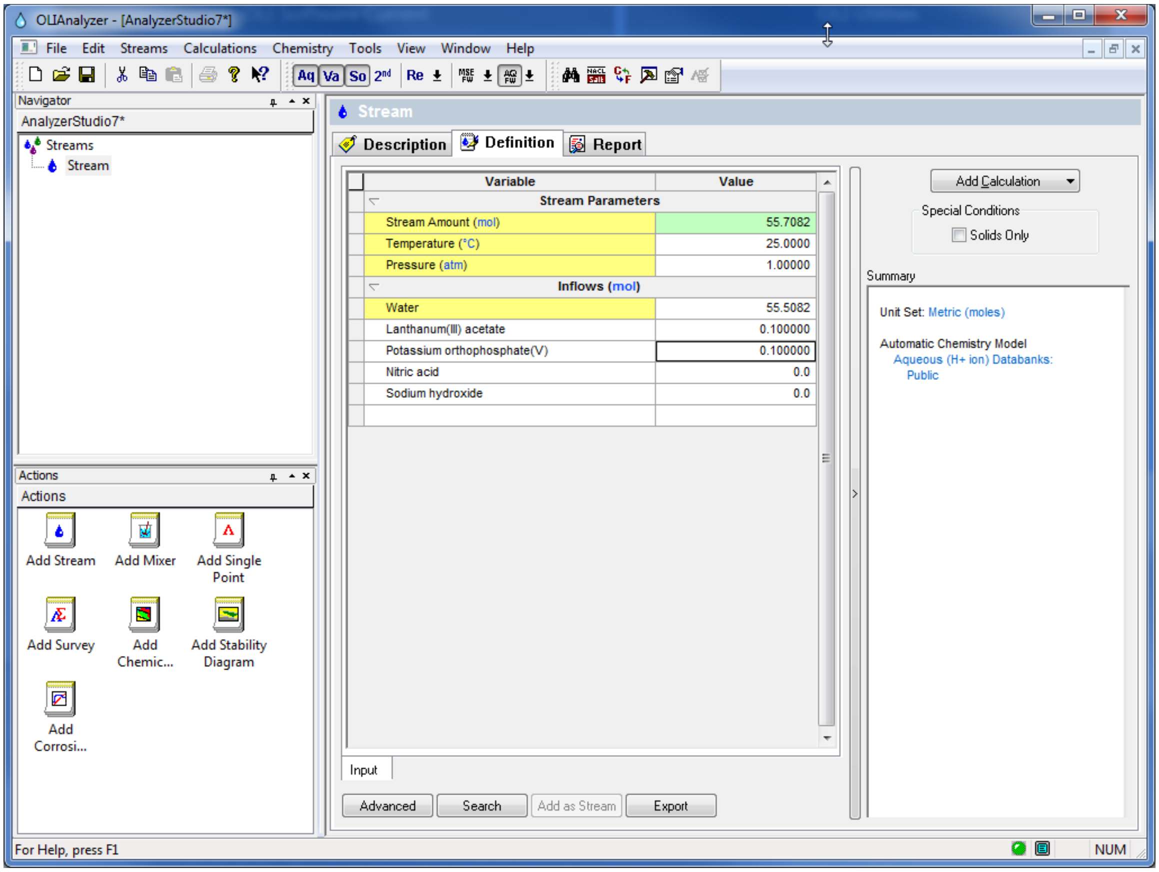


Figure 35-1 Selecting a new stream

We will not enter the conditions of the stream at this point. Don't worry, we can make modifications to the stream conditions later. For the moment we are using the display name for the species. Enter the names "**Lanthanum(III) acetate", "Potassium orthophosphate(V)", "Nitric Acid", and "Sodium Hydroxide"**.

The initial temperature and pressure will be the default values of 25 ^{o}C and 1 atmosphere. We will also use the default value for water of 55.5082 moles (which is 1 Kg)

The inflow amounts of the two precursor species will be set to 0.1 moles each. This keeps the molar ratio 1:1.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.7082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
Water	55.5082
Lanthanum(III) acetate	0.100000
Potassium orthophosphate(V)	0.100000
Nitric acid	0.0
Sodium hydroxide	0.0

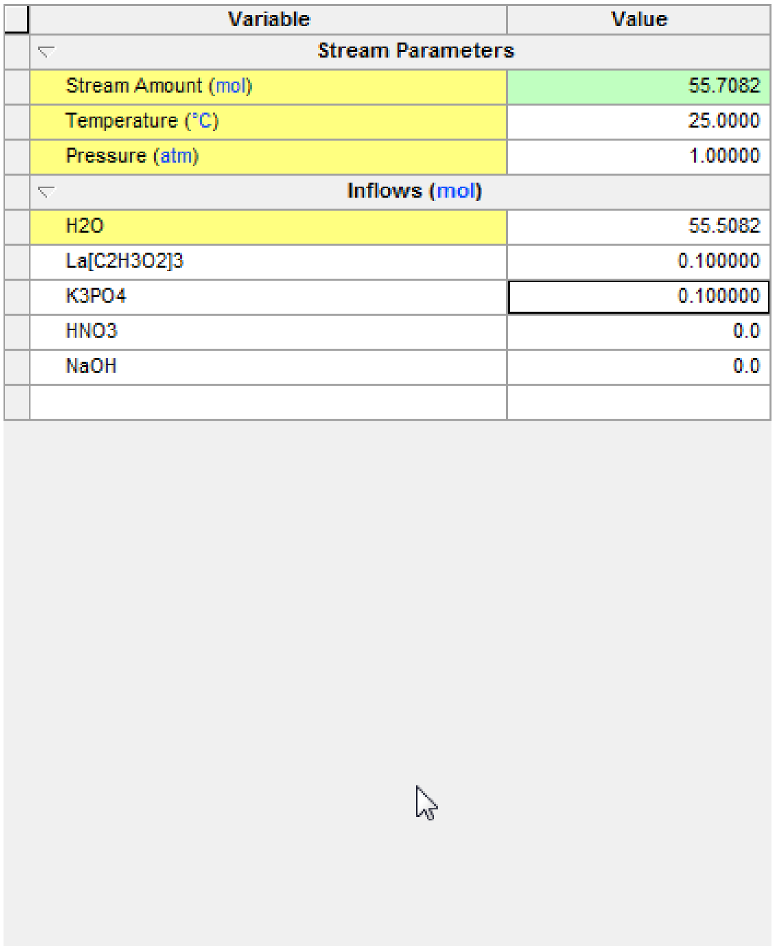
☐ Solids Only

Unit Set: Metric (moles)

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

Figure 35-2 Entering starting conditions

As a side note, you could have also entered the chemical formula names for the species. The formula names are:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.7082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
La[C2H3O2]3	0.100000
K3PO4	0.100000
HNO3	0.0
NaOH	0.0

Figure 35-3 Switching the names to Formula view

As you press the enter key or click a new cell, the name changes to the display name.

After entering the required values, click the **Add Calculation** button and select ***Chemical Diagram***

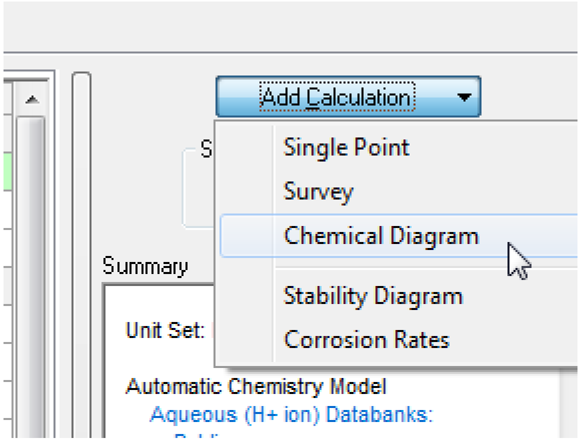
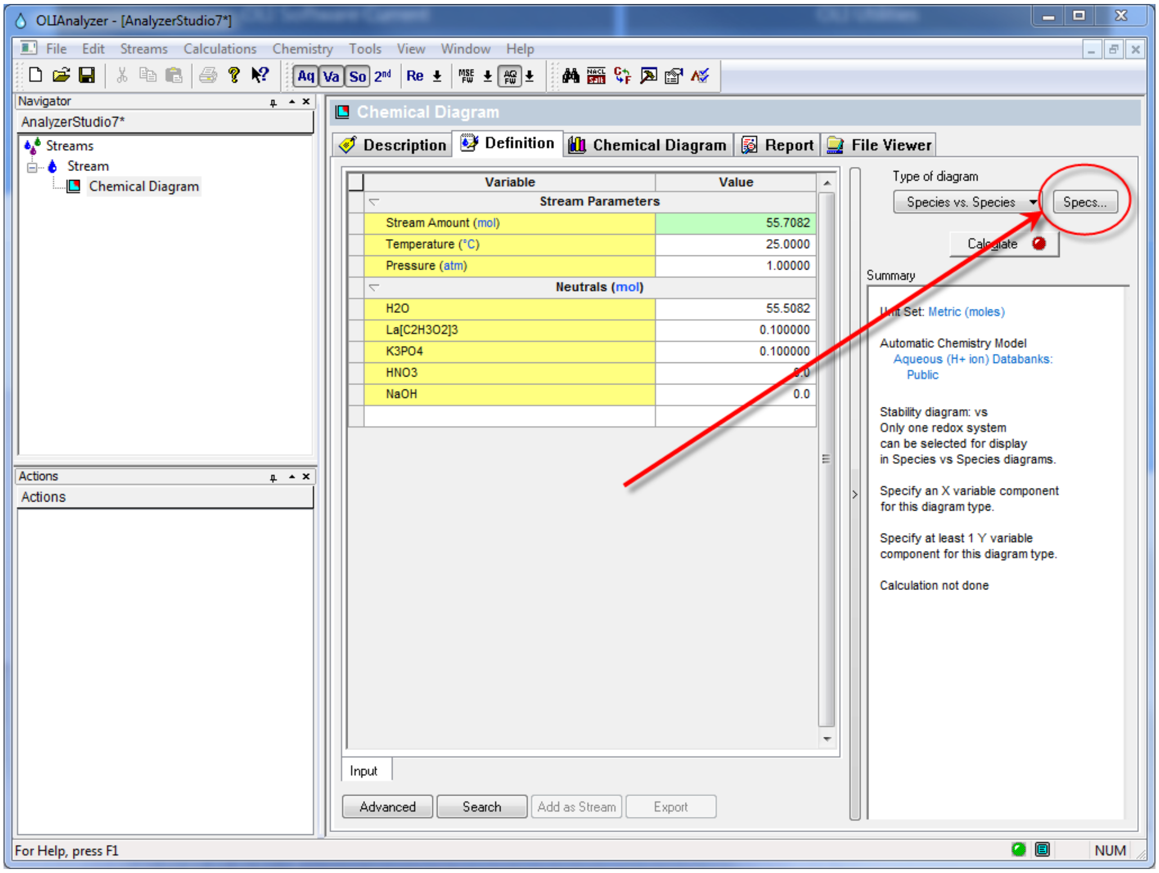


Figure 35-4 Selecting Chemical Diagrams

This will display a new object below the stream. Notice that all the stream values have been copied to this new object.

A chemical diagram requires the user to make some choices. Please click the **Specs...** button to start the selection process.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.7082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Neutrals (mol)	
H_2O	55.5082
La[C2H3O2]3	0.100000
K_3PO_4	0.100000
HNO_3	0.0
NaOH	0.0

Unit Set: Metric (moles)

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

Stability diagram: vs
Only one redox system
can be selected for display
in Species vs Species diagrams.

Specify an X variable component
for this diagram type.

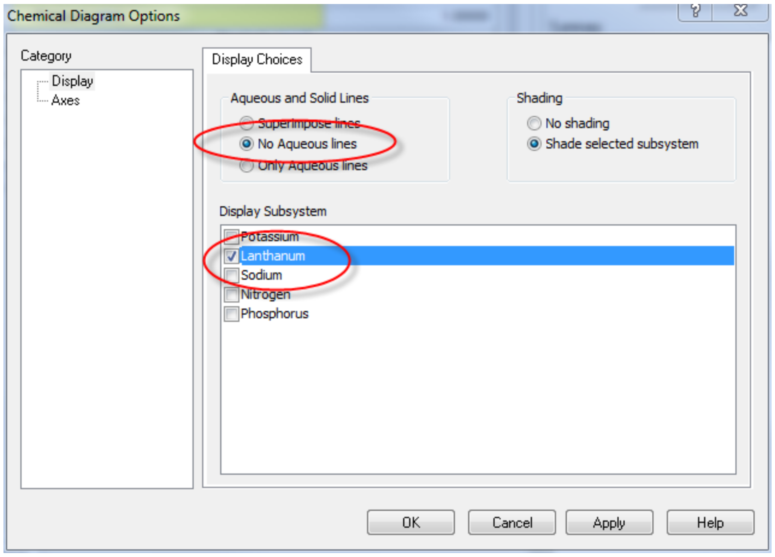
Specify at least 1 Y variable
component for this diagram type.

Calculation not done

Figure 35-5 Selecting the Specs... button

The initial specification option is the *Display Dialog*. For this demonstration we only want to display the boundaries between the solid phases and the liquid phases. We do not want to see both the solid phase boundaries and the boundaries between liquid species. Click here to see what the diagram looks like with aqueous lines enabled.

Click the **No Aqueous Lines** radio button. Also keep the **Shade selected subsystem** button selected. Finally we need to tell the program which chemical subsystem to plot. We can plot more than one but it gets very complicated. Since we are only interested in the lanthanum species, click the **Lanthanum Check Box.** Only one subsystem may be selected at a time.



Aqueous and Solid Lines
○ Superimpose lines
● No Aqueous lines
○ Only Aqueous lines

Shading
○ No shading
● Shade selected subsystem

Display Subsystem
☐ Potassium
☑ Lanthanum
☐ Sodium
☐ Nitrogen
☐ Phosphorus

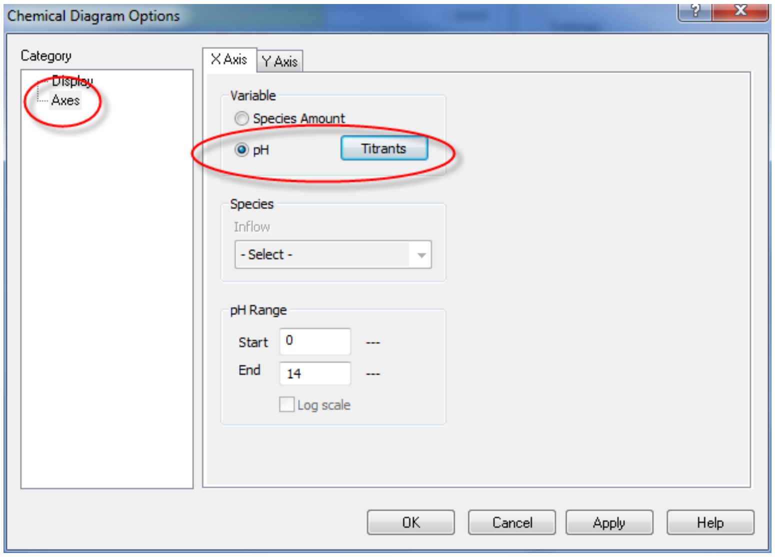
Figure 35-6

Now click on the **Axes** category. The dialog changes to display the **X Axis**.

To reproduce the diagram in the above paper, we need to change the X axis to be based on pH. Click the **pH** radio button.

When pH is selected, we need to choose our titrants. We previously entered nitric acid and sodium hydroxide. We now need to tell the program to use these species.

Click on the **Titrants** button.



Variable
○ Species Amount
● pH

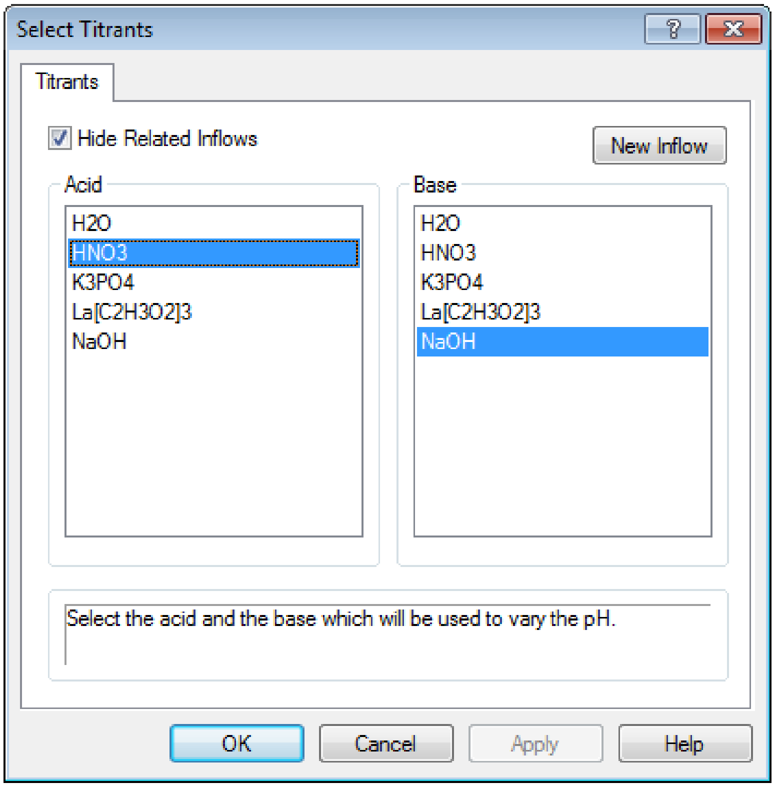
Species
Inflow: - Select -

pH Range
Start: 0 ---
End: 14 ---
☐ Log scale

Figure 35-7

The ***Select Titrants*** dialog is displayed. All of the inflows are displayed in both the ***Acid*** and ***Base*** selections. The reason that this occurs is that at this point in time the OLI Analyzer does not know if the species listed will act as an acid or a base. While it is true that nitric acid always acts as an acid, the same cannot be said of weak acids such as many organic acids.

Weak acids function like an acid when the concentration results in pH's less than the pKa of the acid. Conversely, weak acids function like a base when the pH is greater than the pKa. Thus, we display all the available species in both columns since we don't know the solution pH.
Select nitric acid (HNO_3) in the **Acid** column and sodium hydroxide (NaOH) in the **Base** column.

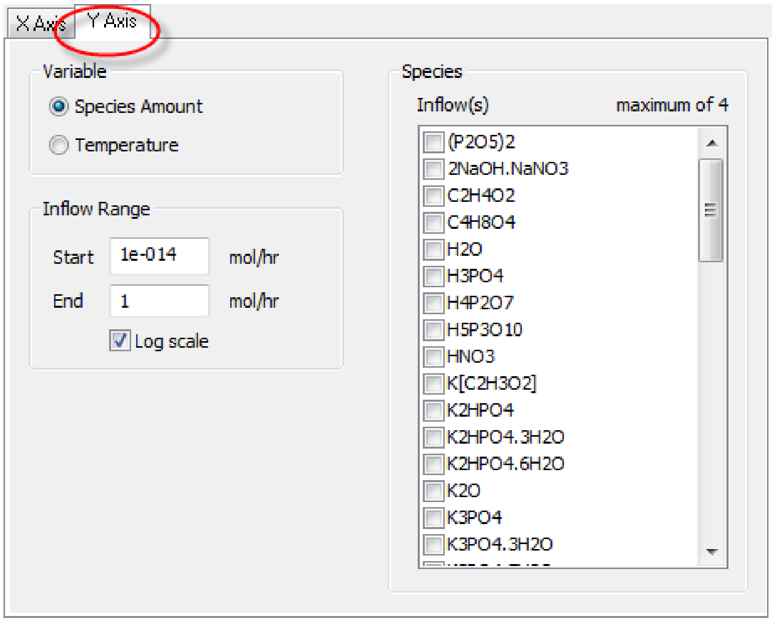


Select the acid and the base which will be used to vary the pH.

Figure 35-8

Click the **OK** button to close the dialog. We now have to decide on the pH range to cover. The default is 0 to 14. This is acceptable for this demonstration.

We are now ready to specify the Y axis. Click the **Y Axis** tab.



● Species Amount
○ Temperature

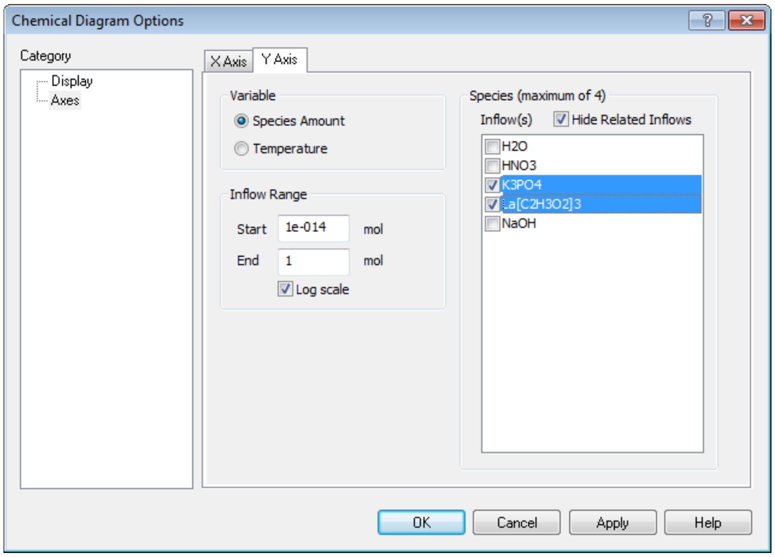
Start 1e-014 mol/hr
End 1 mol/hr
☑ Log scale

☐ (P2O5)2
☐ 2NaOH.NaNO3
☐ C2H4O2
☐ C4H8O4
☐ H2O
☐ H3PO4
☐ H4P2O7
☐ H5P3O10
☐ HNO3
☐ K[C2H3O2]
☐ K2HPO4
☐ K2HPO4.3H2O
☐ K2HPO4.6H2O
☐ K2O
☐ K3PO4
☐ K3PO4.3H2O

Figure 35-9

We will be adjusting the inflow species lanthanum acetate - $La(C_2H_3O_2)_3$ and potassium phosphate - K_3PO_4.

Since we specified the initial concentrations at 0.1 moles each, the ratio of the species will be 1:1. We must now select these species from the scroll box. We are keeping the default concentration range from 1E-14 to 1.0 moles on a log scale. This means we will have initially 1.0E-14 moles of $La(C_2H_3O_2)_3$ and 1.0E-14 moles of K_3PO_4 increasing equally until we have 1.0 moles of each.



● Species Amount
○ Temperature

Start 1e-014 mol
End 1 mol
☑ Log scale

☑ Hide Related Inflows

☐ H2O
☐ HNO3
☑ K3PO4
☑ La[C2H3O2]3
☐ NaOH

Figure 35-10

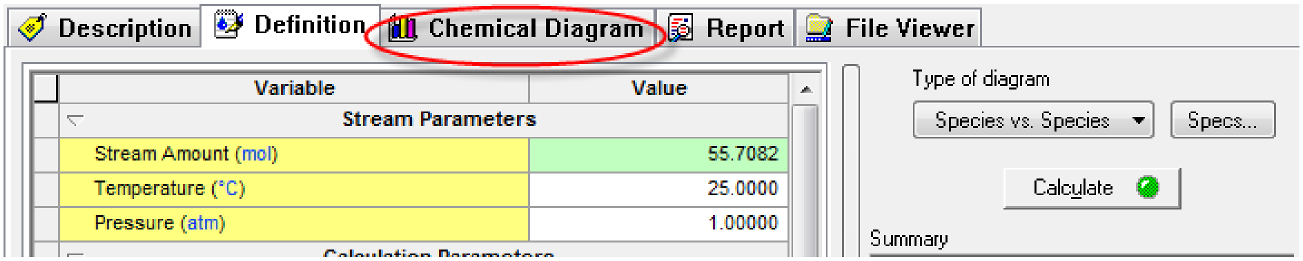
Scroll down and check the box next to lanthanum(III) acetate - or $La(C_2H_3O_2)_3$

Continue to scroll down to find potassium phosphate - K_3PO_4 and check that box.

We are now done, click the **OK** button to exit the Specifications for this calculation.

The calculation is now ready to start. Click the **Calculate** button.

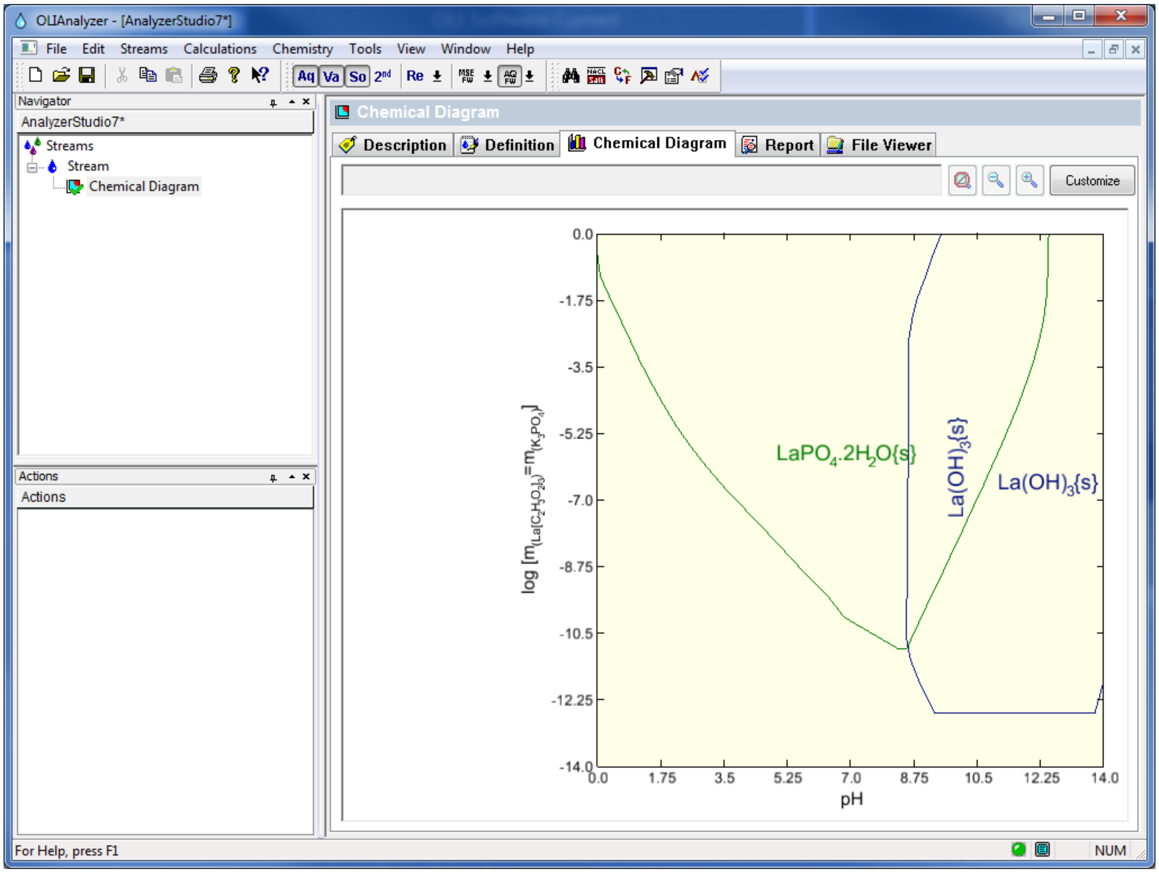
When the calculation is complete, click the **Chemical Diagram** tab.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.7082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters	

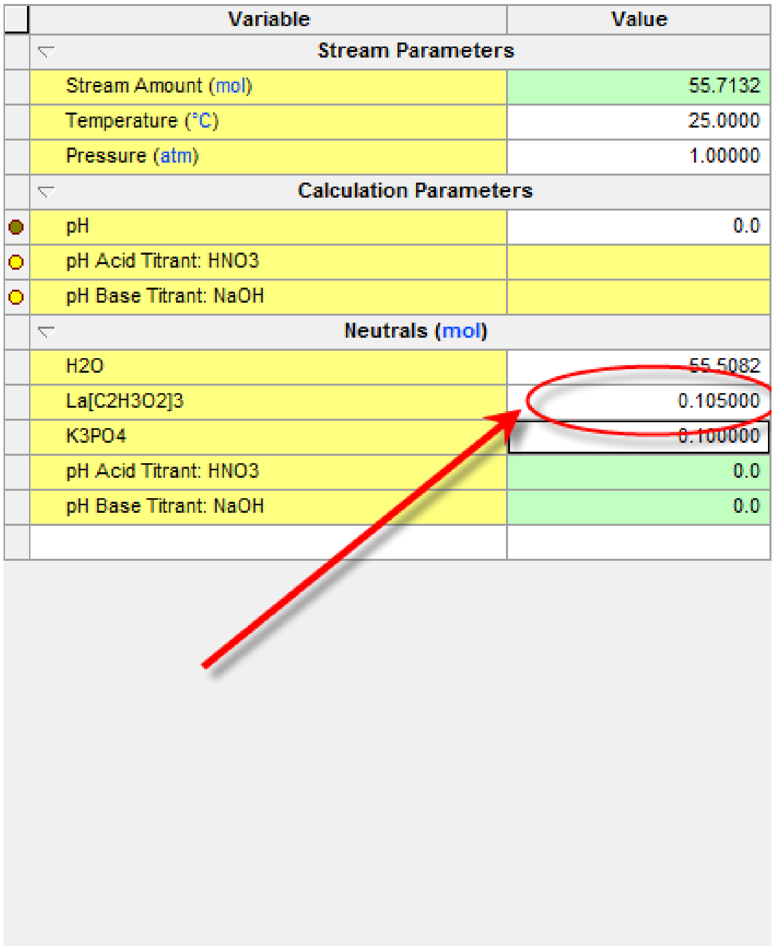
Type of diagram: Species vs. Species

This displays the Species - pH diagram for this calculation.



This diagram is very similar to the diagram in the above paper. It does different slightly since the author of the paper made some changes to the chemistry model that is not reflected here.

We can change the ratio of the precursor species very easily. For the second example we will use the same calculation except we will be adding 5 % more to the lanthanum acetate species. To do this click back on the **Definition** tab and change the inflow amount for lanthanum acetate from 0.1000 to 0.10500.



	Variable	Value
	Stream Parameters	
	Stream Amount (mol)	55.7132
	Temperature (°C)	25.0000
	Pressure (atm)	1.00000
	Calculation Parameters	
●	pH	0.0
○	pH Acid Titrant: HNO3	
○	pH Base Titrant: NaOH	
	Neutrals (mol)	
	H2O	55.5082
	La[C2H3O2]3	0.105000
	K3PO4	0.100000
	pH Acid Titrant: HNO3	0.0
	pH Base Titrant: NaOH	0.0

Figure 35-11

Re-Calculate and then click on the **Chemical Diagram** tab again.

Notice that the diagram is essentially the same. The Y axis label has changed to reflect the increased amount of the lanthanum acetate.

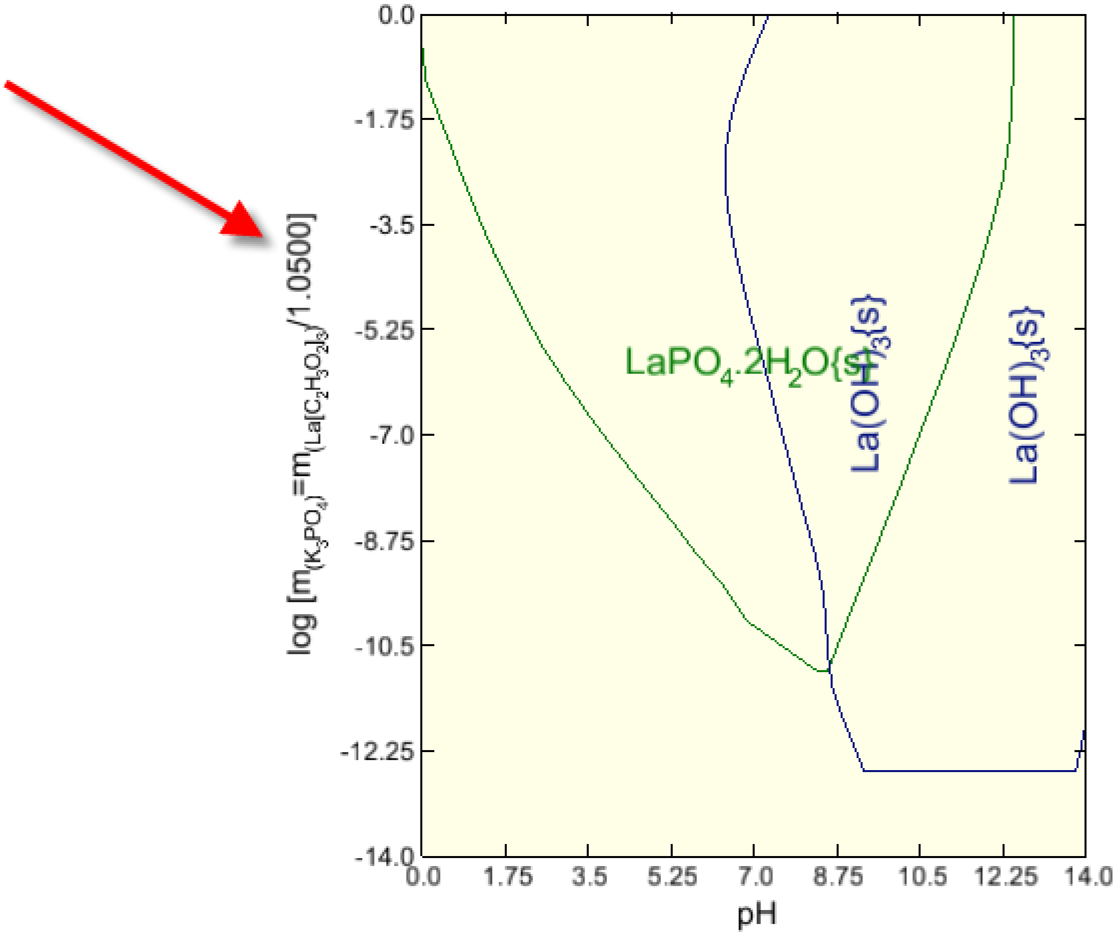
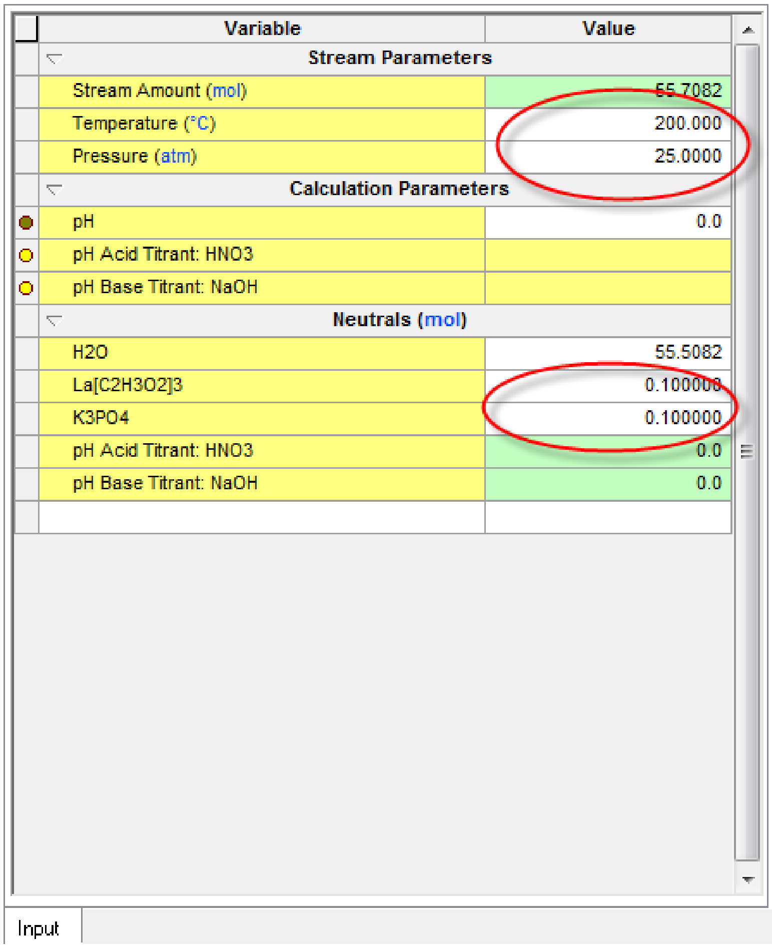


Figure 35-12

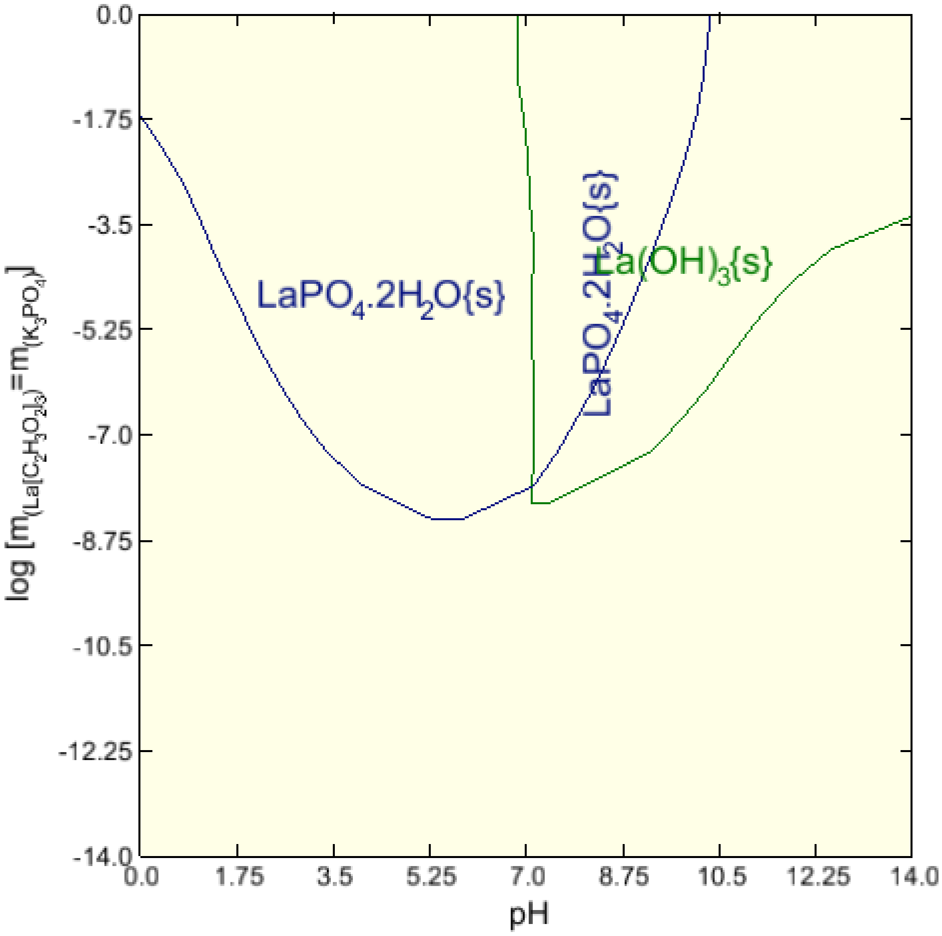
We can also run at different temperatures quite easily. Return to the **Definition** tab and change the temperature to 200 ºC and 25 atmospheres. We have also reset the Lanthanum Acetate value back to 0.1 moles.



	Variable	Value
	Stream Parameters	
	Stream Amount (mol)	55.7082
	Temperature (°C)	200.000
	Pressure (atm)	25.0000
	Calculation Parameters	
●	pH	0.0
○	pH Acid Titrant: HNO3	
○	pH Base Titrant: NaOH	
	Neutrals (mol)	
	H2O	55.5082
	La[C2H3O2]3	0.100000
	K3PO4	0.100000
	pH Acid Titrant: HNO3	0.0
	pH Base Titrant: NaOH	0.0

Figure 35-13

Re-calculate and then click on the **Chemical Diagrams** tab. You can see that the diagram is significantly different reflecting the change in solubility with respect to temperature.



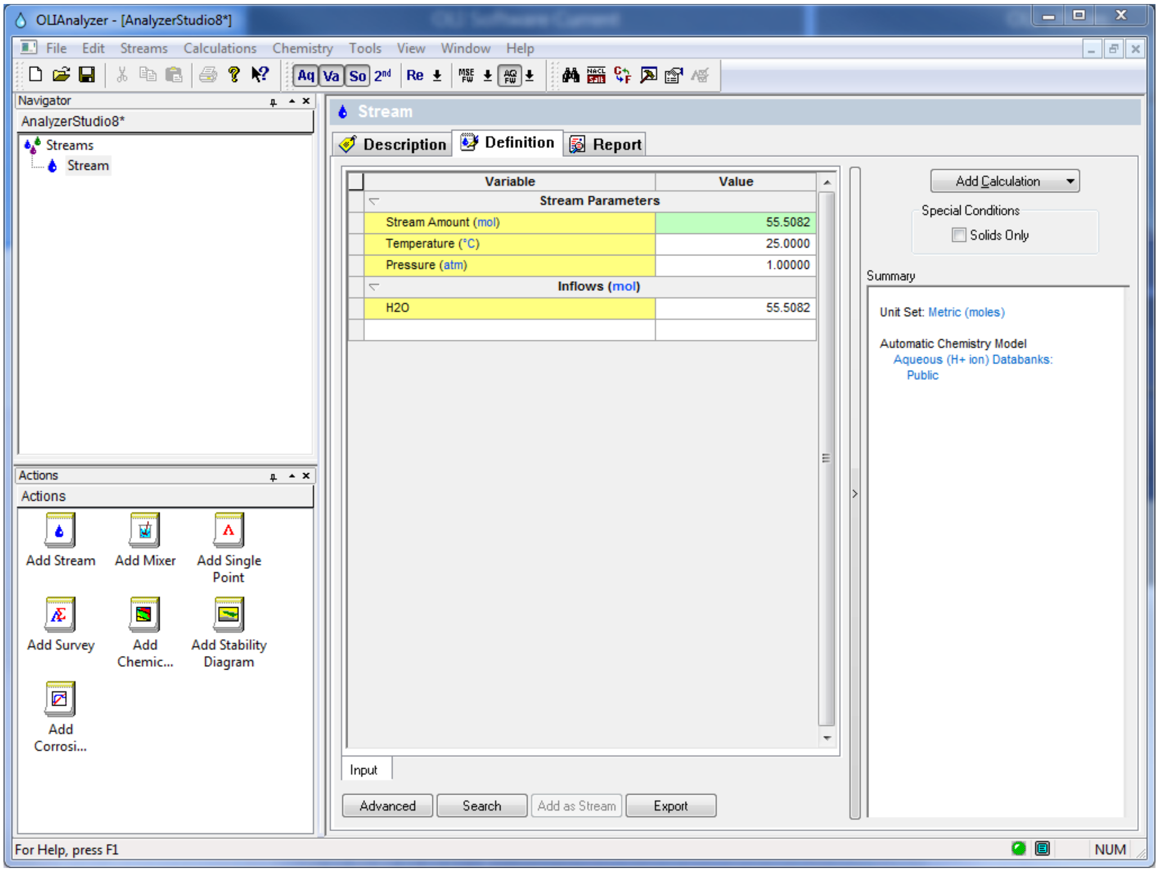
This concludes the demonstration.

36. Managing Private Databases in the OLI Analyzer

Selecting Databases

Data bases are OLI's store house of thermodynamic data. Not all the data is suitable for every calculation. Therefore the data is compartmentalized into many databases. In addition, data service work provided by OLI Systems, Inc. may also be a database.

There is architecture to using databases in the Analyzers. If you want a database to be used in all streams and calculations, you must specify the database at the topmost stream of the software. The top level dialog is displayed below. To use a database in only a stream or calculation, specify the database only in that object. The PUBLIC database is automatically specified and cannot be changed.



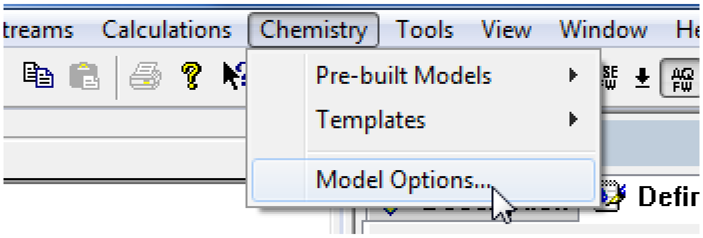
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082

Unit Set: Metric (moles)

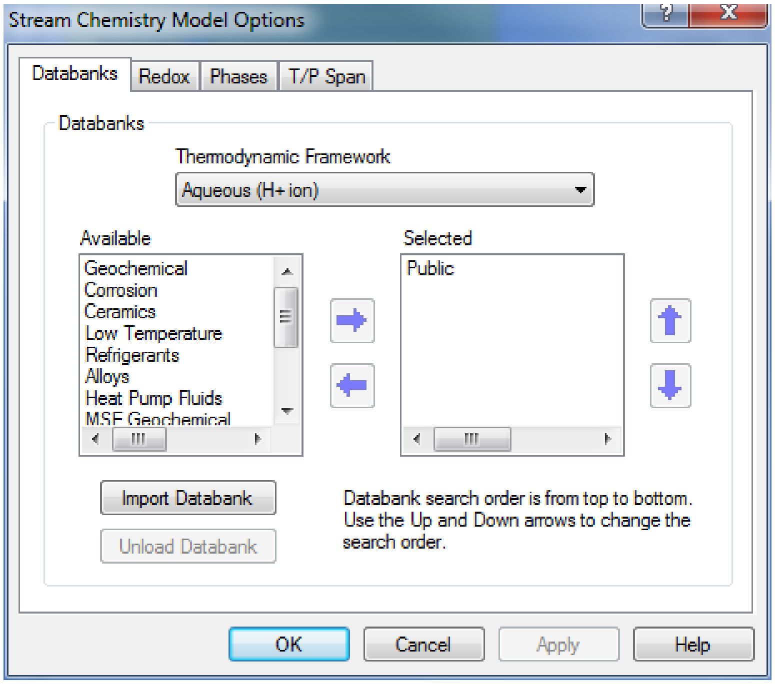
Automatic Chemistry Model
Aqueous (H+ ion) Databanks:
Public

Click on the **Chemistry** menu item.

This will display the chemistry options. **Select Model Options…**

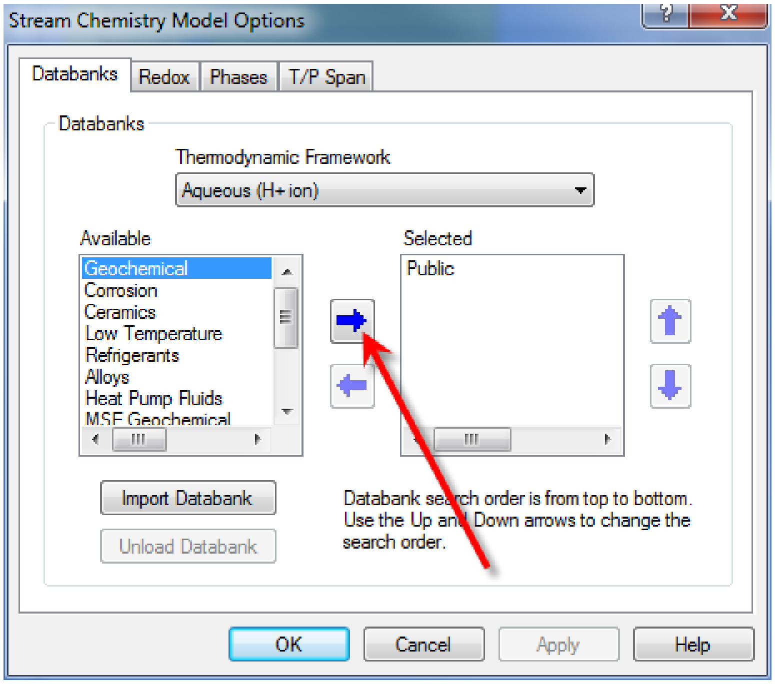


The currently loaded databases will be displayed as well as the current thermodynamic framework (AQ or MSE)



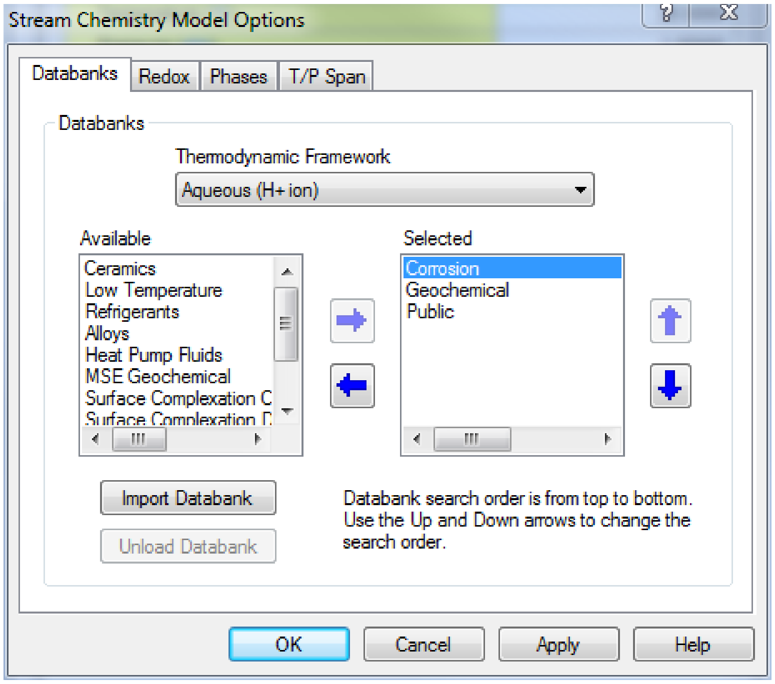
Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

Highlight **Geochemical**



Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

When the desired database is highlighted, click the right arrow to select it. We are also selecting the Corrosion Database for example purposes.



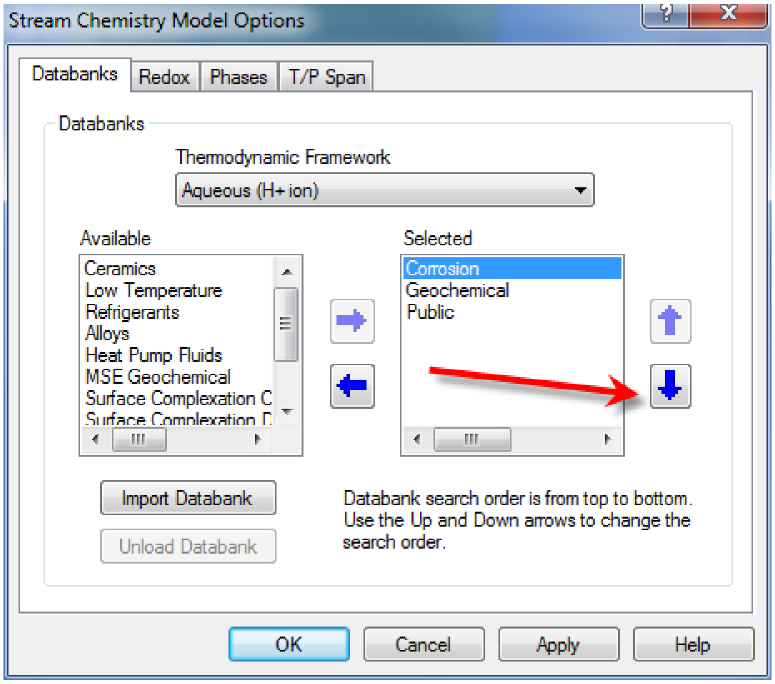
Thermodynamic Framework: Aqueous (H+ ion)

Available:
- Ceramics
- Low Temperature
- Refrigerants
- Alloys
- Heat Pump Fluids
- MSE Geochemical
- Surface Complexation C
- Surface Complexation D

Selected:
- Corrosion
- Geochemical
- Public

Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

Databases have priority. If a species exists in both of these selected database, then only the thermodynamic properties found in the first database will be used. You can change the priority of the database by highlighting it and clicking the up button.



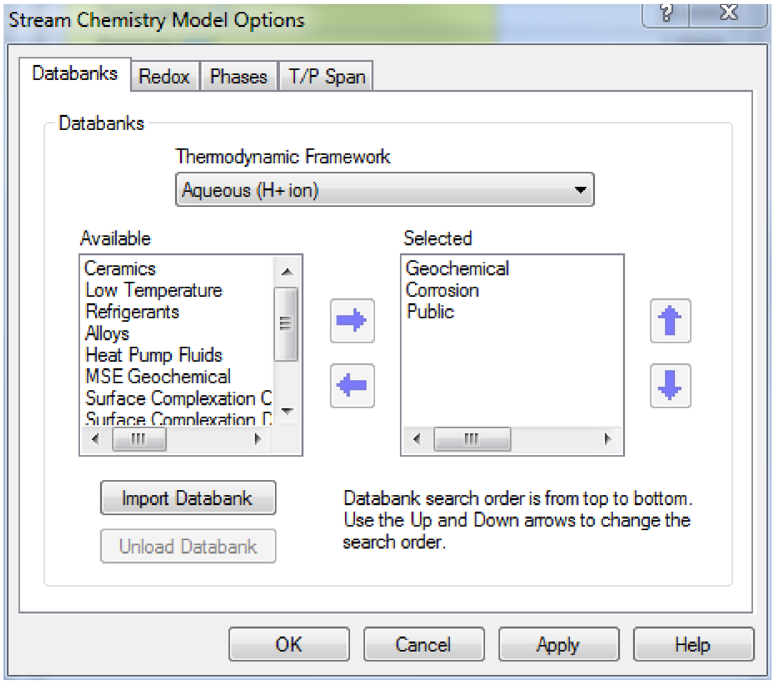
Thermodynamic Framework: Aqueous (H+ ion)

Available:
- Ceramics
- Low Temperature
- Refrigerants
- Alloys
- Heat Pump Fluids
- MSE Geochemical
- Surface Complexation C
- Surface Complexation D

Selected:
- Corrosion
- Geochemical
- Public

Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

Click the down-arrow to reorder the list:



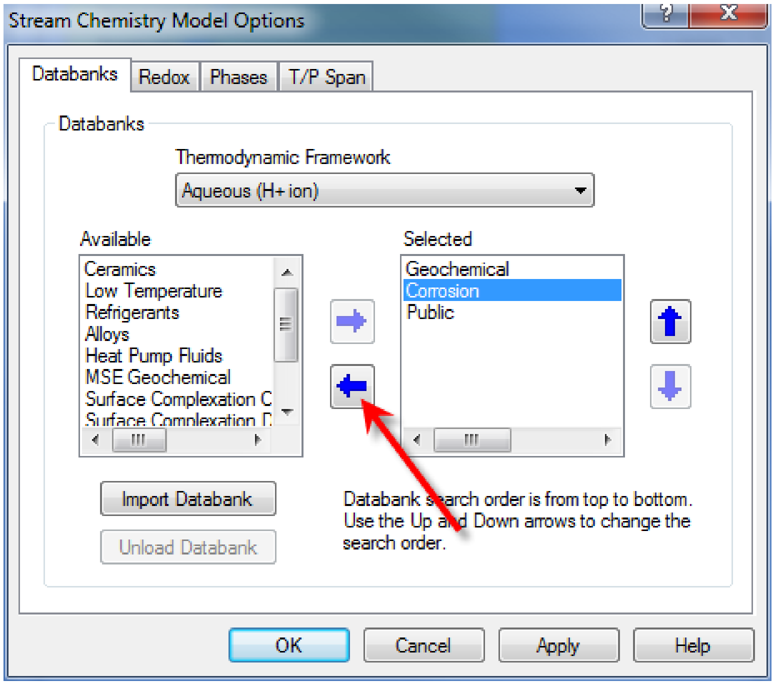
Thermodynamic Framework: Aqueous (H+ ion)

Available:
- Ceramics
- Low Temperature
- Refrigerants
- Alloys
- Heat Pump Fluids
- MSE Geochemical
- Surface Complexation C
- Surface Complexation D

Selected:
- Geochemical
- Corrosion
- Public

Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

You can remove a database if it is not required. This does not delete the data from the program but makes it unavailable. Select the database and click the left arrow.



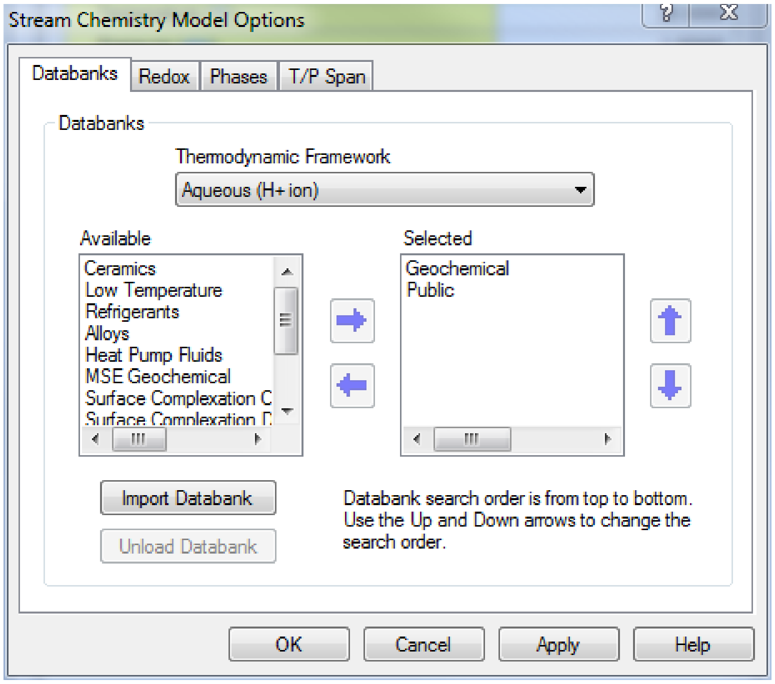
Thermodynamic Framework: Aqueous (H+ ion)

Available:
- Ceramics
- Low Temperature
- Refrigerants
- Alloys
- Heat Pump Fluids
- MSE Geochemical
- Surface Complexation C
- Surface Complexation D

Selected:
- Geochemical
- Corrosion
- Public

Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

Click the left-arrow and the Corrosion database will not be used in this calculation.



Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

The database has been removed. Click the Apply button and then OK to continue.

How to load a private database into the OLI Analyzers

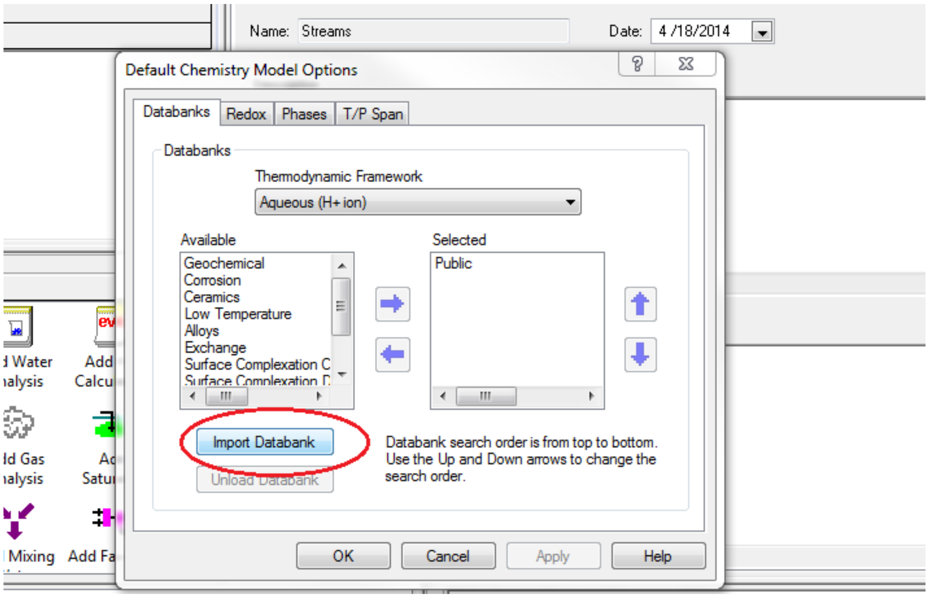
Currently OLI Systems, Inc. only supplies user databases (formerly known as private databases) in the OLI/ESP format. This is not directly usable by the OLI/Analyzers. These databases are normally compressed using a program such as WinZip. Please decompress (unzip) the file into a working folder.

You will then need to load and convert the supplied database. Fortunately there is a tool to do this for you. Please follow these steps:

Start the Analyzers

Select the **Chemistry** Menu Item

Select **Model Options**



Name: Streams

Date: 4 /18/2014

Thermodynamic Framework: Aqueous (H+ ion)

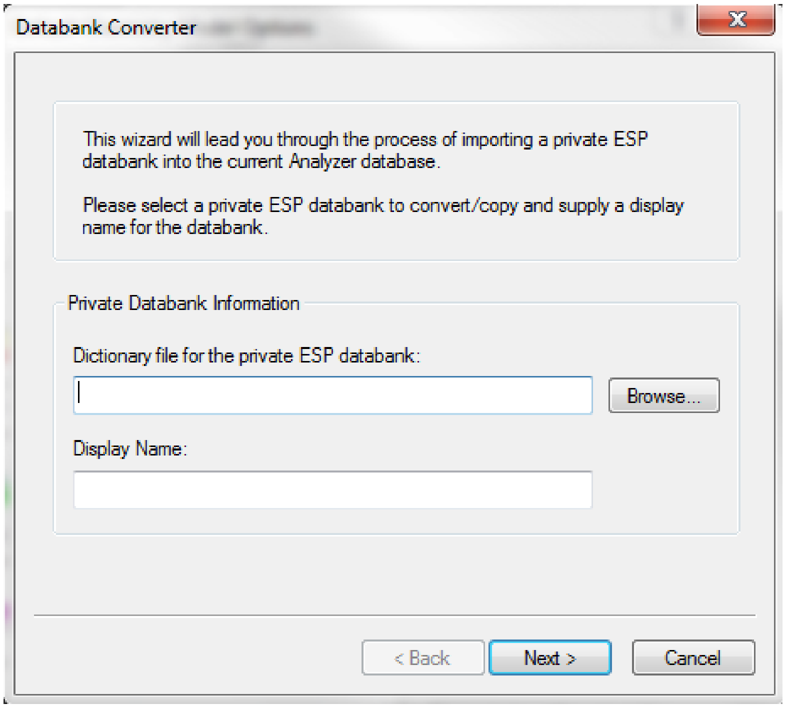
Available:
- Geochemical
- Corrosion
- Ceramics
- Low Temperature
- Alloys
- Exchange
- Surface Complexation C
- Surface Complexation D

Selected:
- Public

Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

You can load both Aqueous databases and MSE databases from the same screen.

Click the **Import Databank** button.



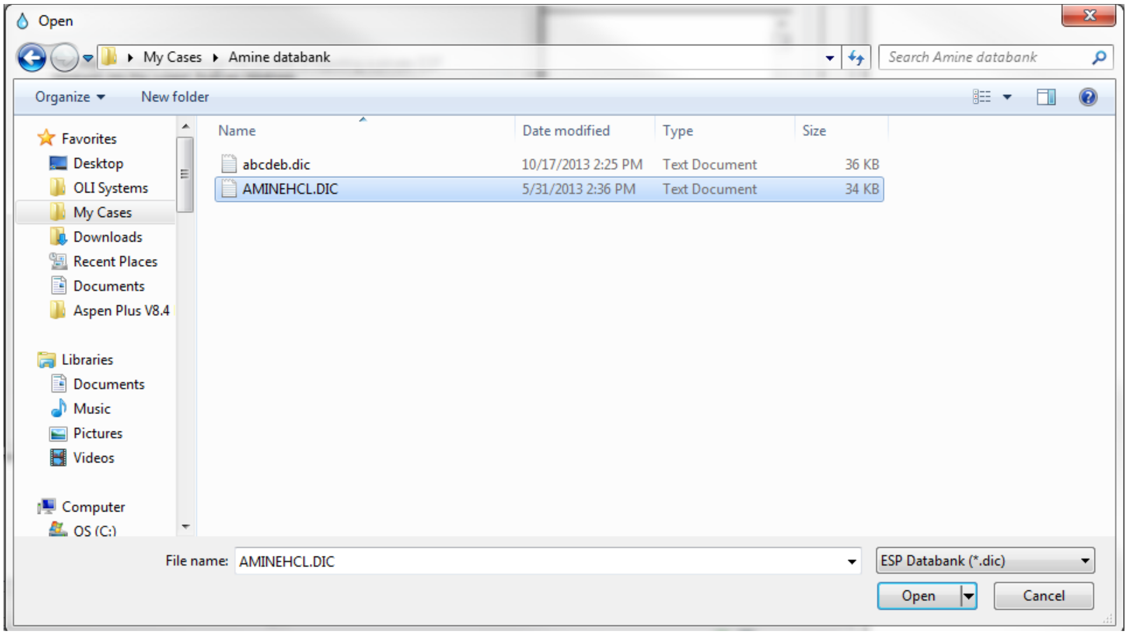
This wizard will lead you through the process of importing a private ESP databank into the current Analyzer database.

Please select a private ESP databank to convert/copy and supply a display name for the databank.

Dictionary file for the private ESP databank:

Display Name:

If you know the exact location of the ESP "dic" file, you can enter the location directly. It is usually easier to browse for this file. Click the **Browse** button



Name	Date modified	Type	Size
abcdeb.dic	10/17/2013 2:25 PM	Text Document	36 KB
AMINEHCL.DIC	5/31/2013 2:36 PM	Text Document	34 KB

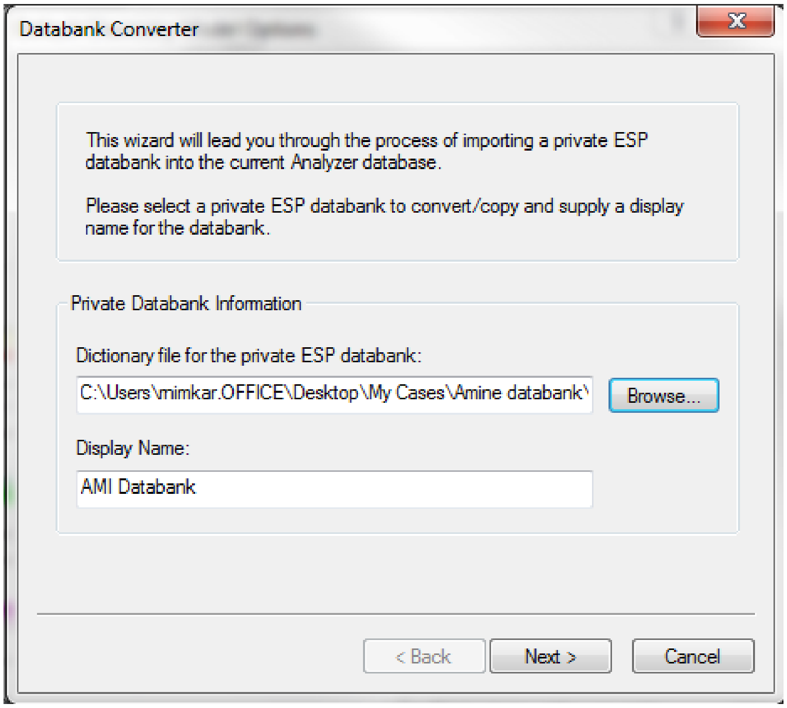
File name: AMINEHCL.DIC

ESP Databank (*.dic)

Locate the folder that has the decompressed ESP format file.

Click to select.

The available database will be displayed. The DIC file (short for dictionary) is the file required. Click the file in the open dialog and then click the Open button.



This wizard will lead you through the process of importing a private ESP databank into the current Analyzer database.

Please select a private ESP databank to convert/copy and supply a display name for the databank.

Dictionary file for the private ESP databank:

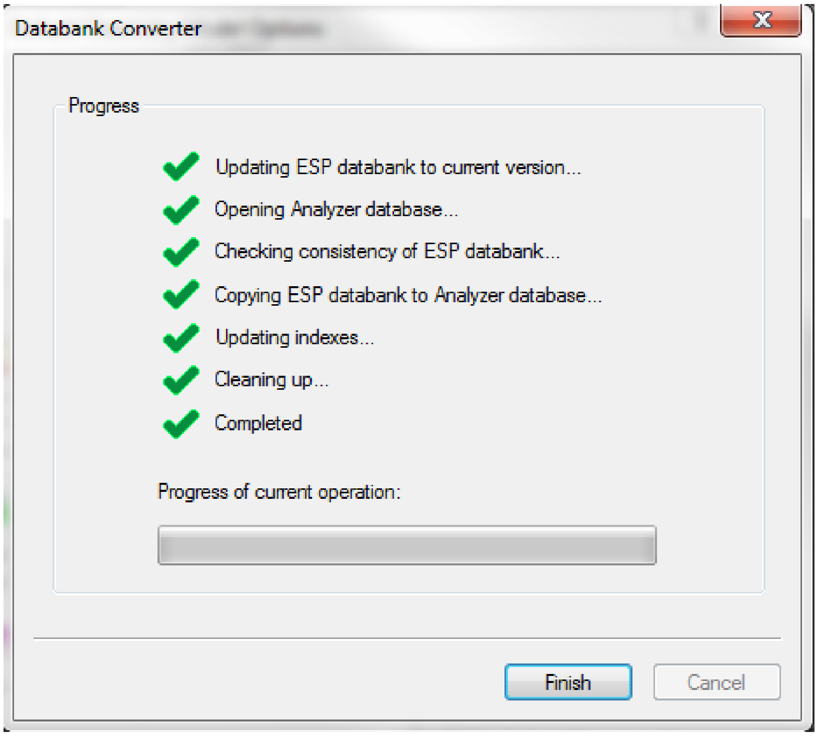
C:\Users\mimkar.OFFICE\Desktop\My Cases\Amine databank\

Display Name:

AMI Databank

The full path of the "Dic" file is displayed along with the display name of the database. You can rename this database if you desire. It is recommended that for most uses that the default name be used.

Click the **Next** button.

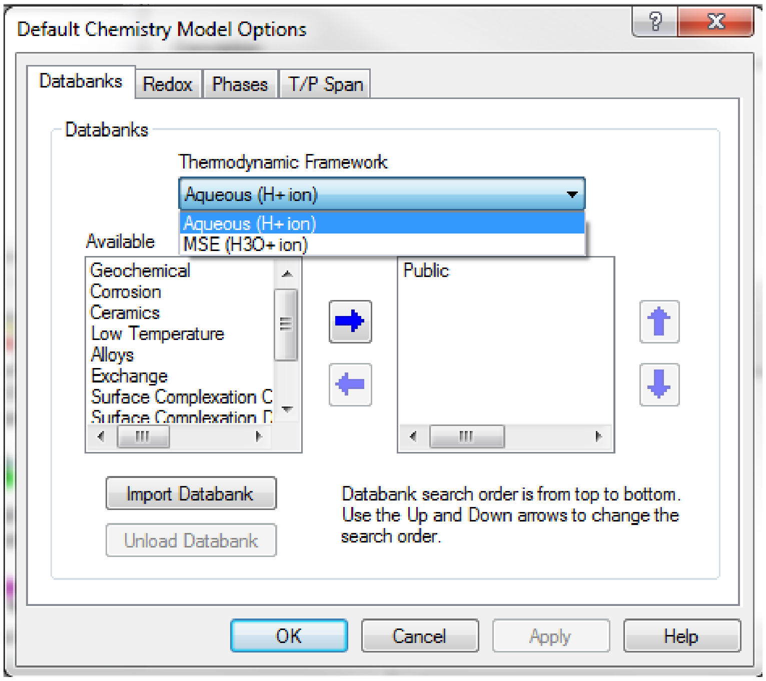


✓ Updating ESP databank to current version...
✓ Opening Analyzer database...
✓ Checking consistency of ESP databank...
✓ Copying ESP databank to Analyzer database...
✓ Updating indexes...
✓ Cleaning up...
✓ Completed

Progress of current operation:

The process of converting and uploading the file starts.

If all the lines are checked, then click the **Finish** button



Thermodynamic Framework: Aqueous (H+ ion)

Aqueous (H+ ion)
MSE (H3O+ ion)

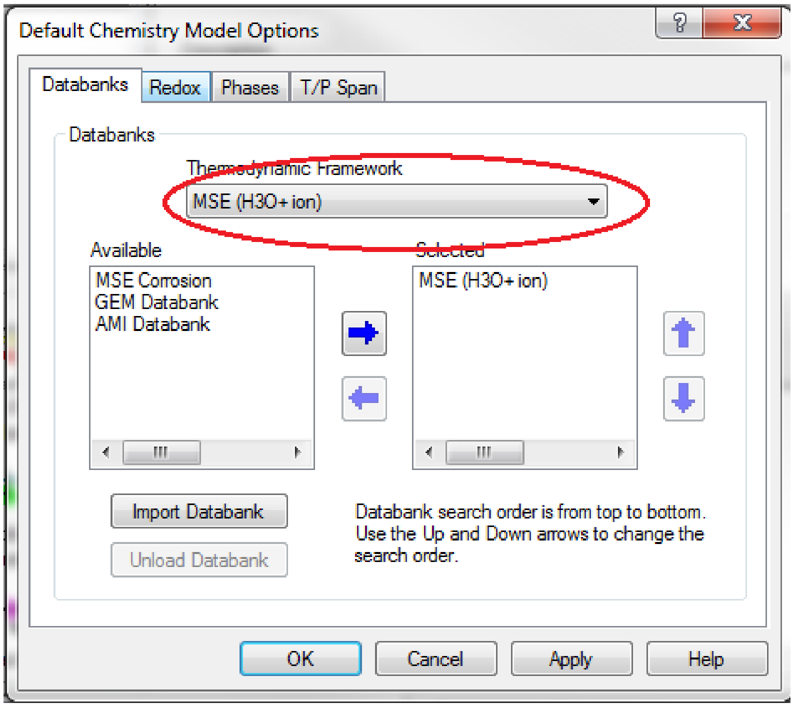
Public

Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

Your imported database is now ready for use. If your database was for the MSE framwork, as it is in this example, you will need to switch Thermodynamic Framework to use the database. Click the drop-down arrow.

If your database is in the MSE framework, select **MSE**

The newly imported MSE framework database is displayed.

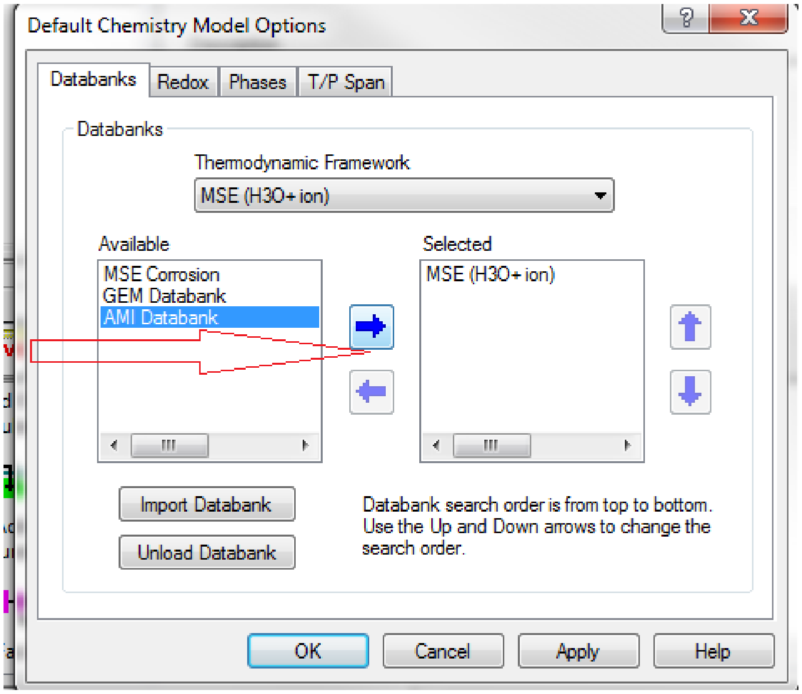


Thermodynamic Framework: MSE (H3O+ ion)

Available: MSE Corrosion, GEM Databank, AMI Databank

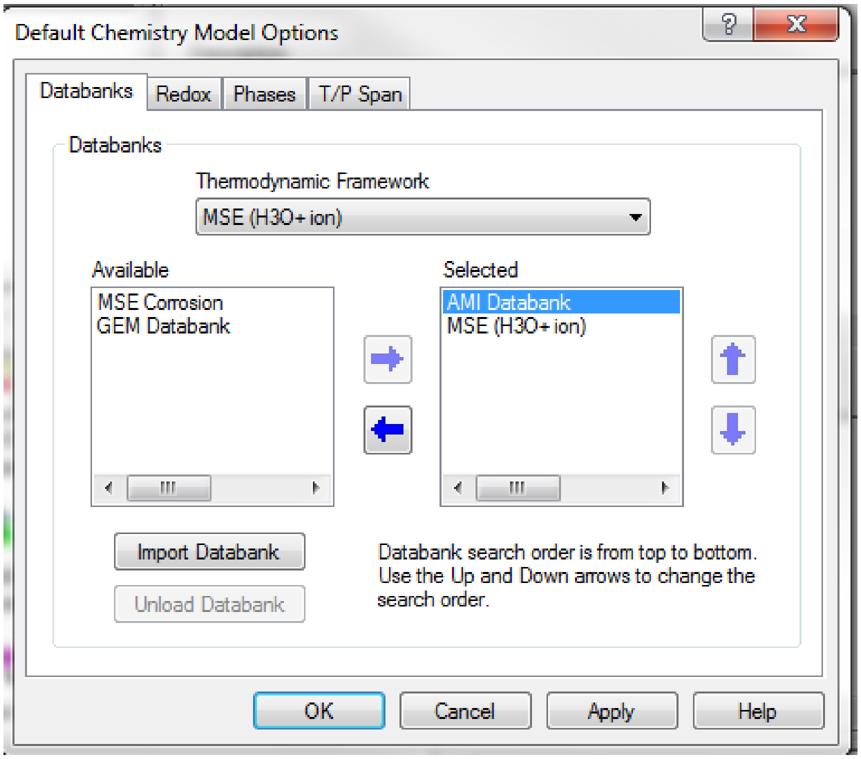
Selected: MSE (H3O+ ion)

Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.



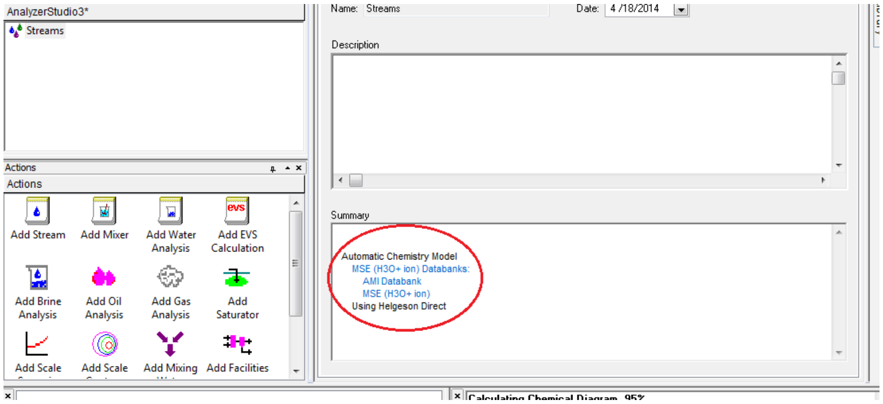
Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

Click it to select it. Then click the right-arrow.



Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

Click the OK button to continue.



Name: Streams

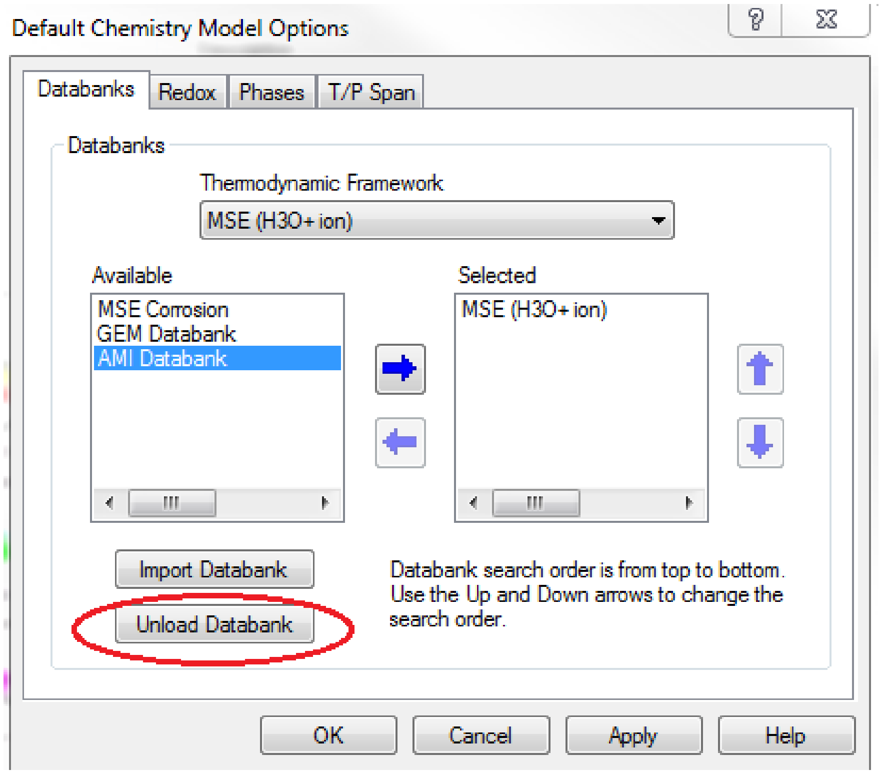
Date: 4 /18/2014

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

The newly imported database is now being used as indicated in the Summary window.

How to unload a database from the OLI Analyzers

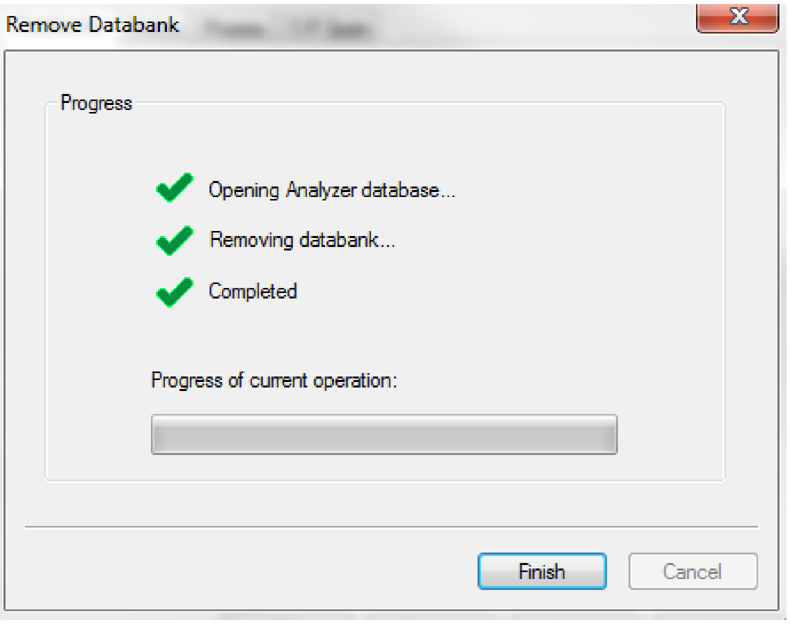
Sometimes a user will want to remove a database from consideration. To do this locate the Databanks Tab via the **Chemistry Menu Item** > **Model Options** path.



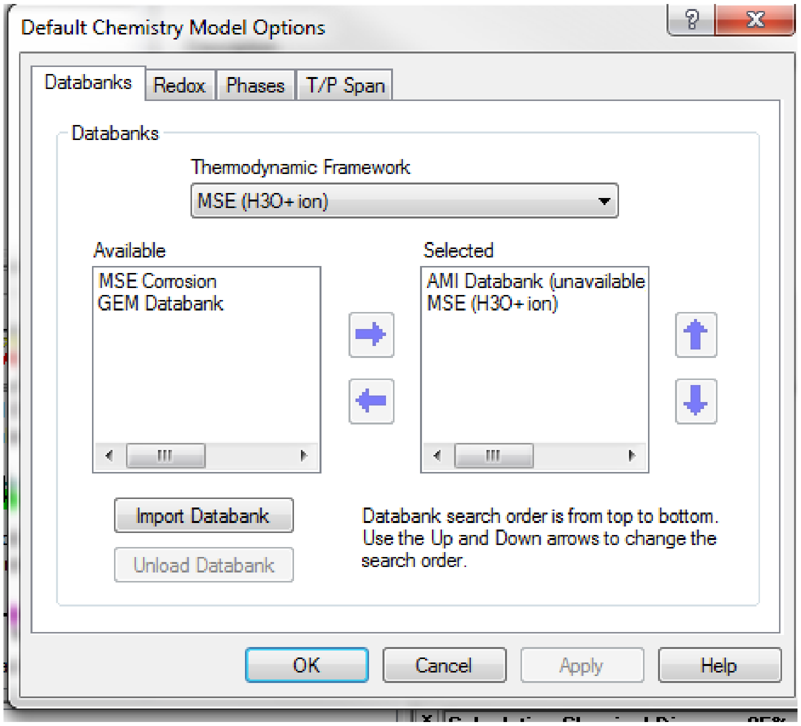
Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

There is no pop up warning to make sure you want to do this. Be careful

Click the **Unload Databank** button



This removes the selected databank.

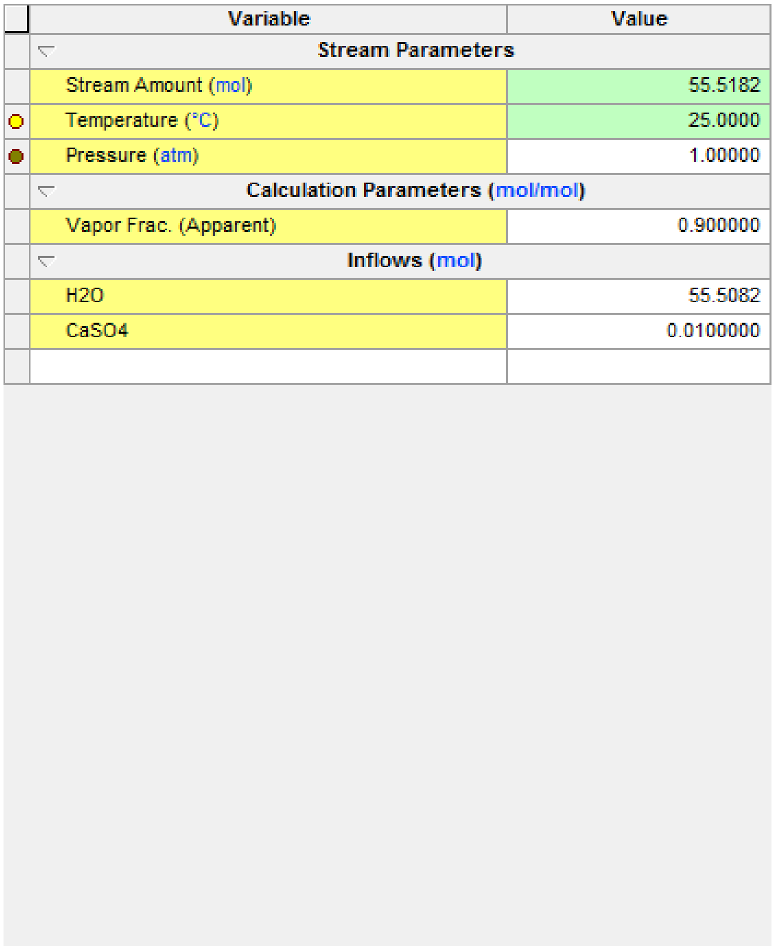


Databank search order is from top to bottom. Use the Up and Down arrows to change the search order.

The database has been removed. As you can see AMI databank is unavailable in the above screen capture.

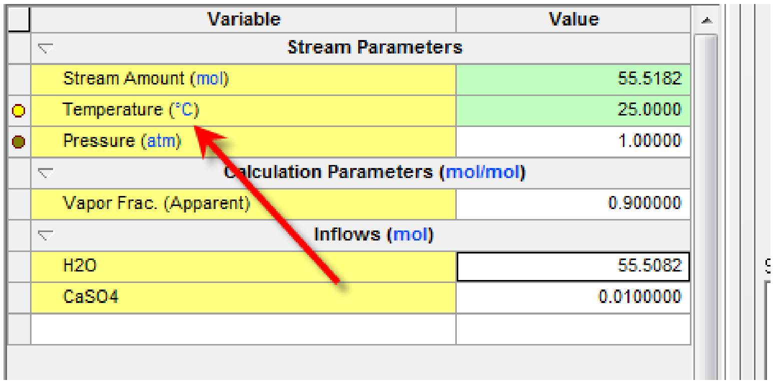
37. OLI Units Manager

The default units for the OLI Studio are moles, centigrade, atmospheres, calories and liters. In many (if not most) cases the user will need to change both the input and output units. In this example we have entered a simple case in the default units.



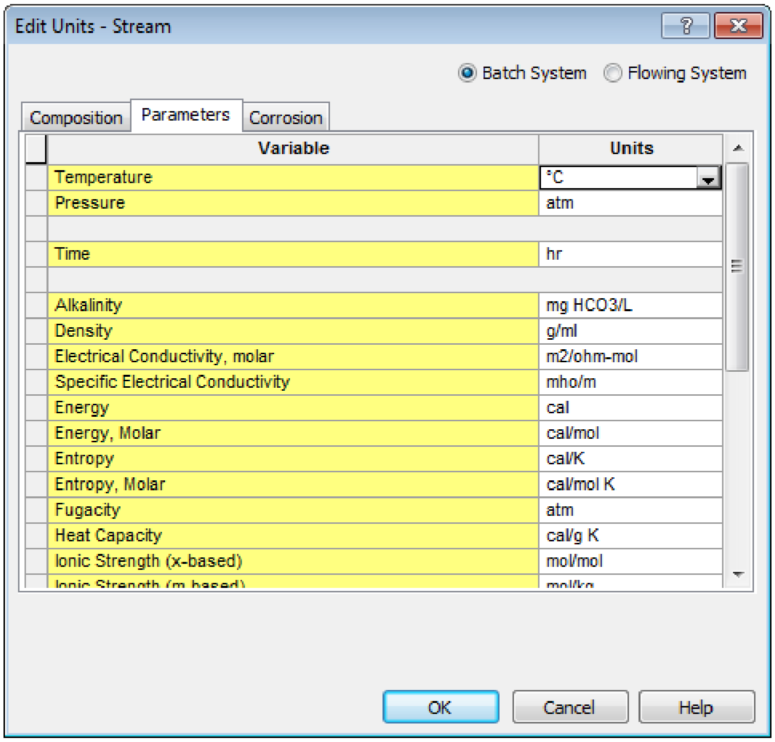
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5182
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters (mol/mol)	
Vapor Frac. (Apparent)	0.900000
Inflows (mol)	
H2O	55.5082
CaSO4	0.0100000

You can change the units of individual fields by clicking the blue unit. This is a hyperlink to the units manager dialog. Below we are going to change the unit field for temperature.



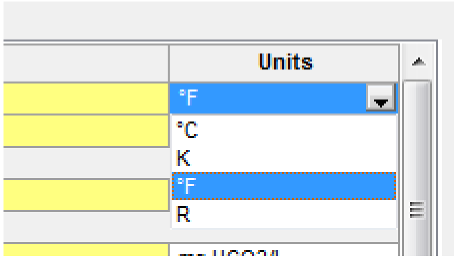
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5182
○ Temperature (°C)	25.0000
● Pressure (atm)	1.00000
Calculation Parameters (mol/mol)	
Vapor Frac. (Apparent)	0.900000
Inflows (mol)	
H2O	55.5082
CaSO4	0.0100000

Click on the blue **°C**



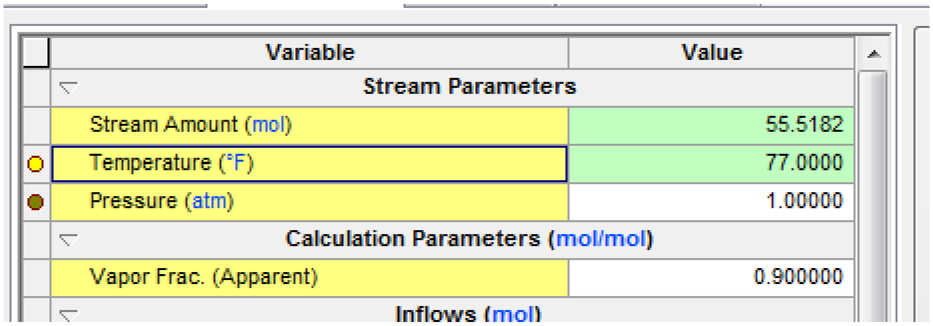
Variable	Units
Temperature	°C
Pressure	atm
Time	hr
Alkalinity	mg HCO3/L
Density	g/ml
Electrical Conductivity, molar	m2/ohm-mol
Specific Electrical Conductivity	mho/m
Energy	cal
Energy, Molar	cal/mol
Entropy	cal/K
Entropy, Molar	cal/mol K
Fugacity	atm
Heat Capacity	cal/g K
Ionic Strength (x-based)	mol/mol
Ionic Strength (m-based)	mol/kg

This displays the units manager with the selected unit already highlighted. To change the unit to Fahrenheit, click the drop down menu and make the appropriate selection.



You can select from a range of units For this example we are choosing Fahrenheit.

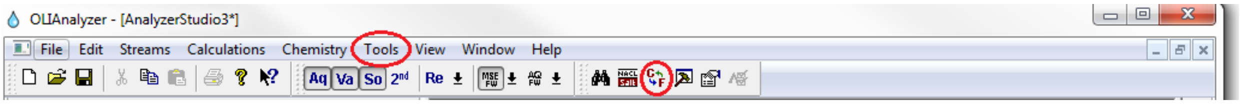
As you can see the 25 C value is now 77 F.



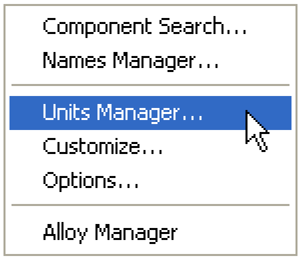
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5182
Temperature (°F)	77.0000
Pressure (atm)	1.00000
Calculation Parameters (mol/mol)	
Vapor Frac. (Apparent)	0.900000
Inflows (mol)	

It would be cumbersome to do this for each and every field. You can make systematic changes to the stream or to the calculation by using the Units Manager.

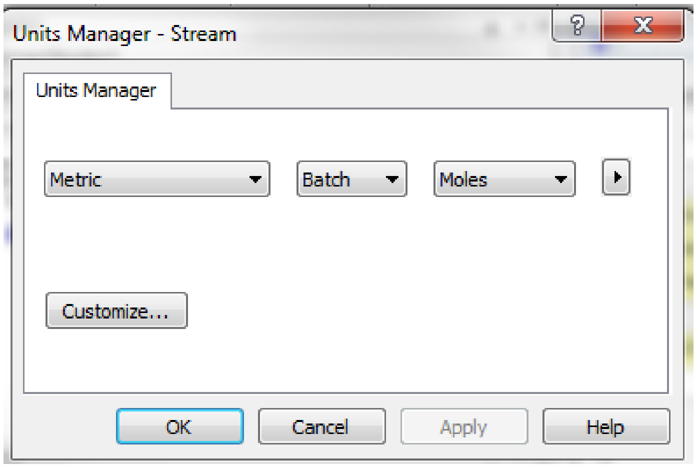
There are two ways to access the units manager in the Analyzers. The first is from the **Tools** menu and the second is from the tool bar. The figure below shows the location of each item.



For our example we are going to use the **tool bar**. Once selected, we will have a range of selections to make. Select **Units Manager...**



Below is the units manager dialog with the default standard units selected.

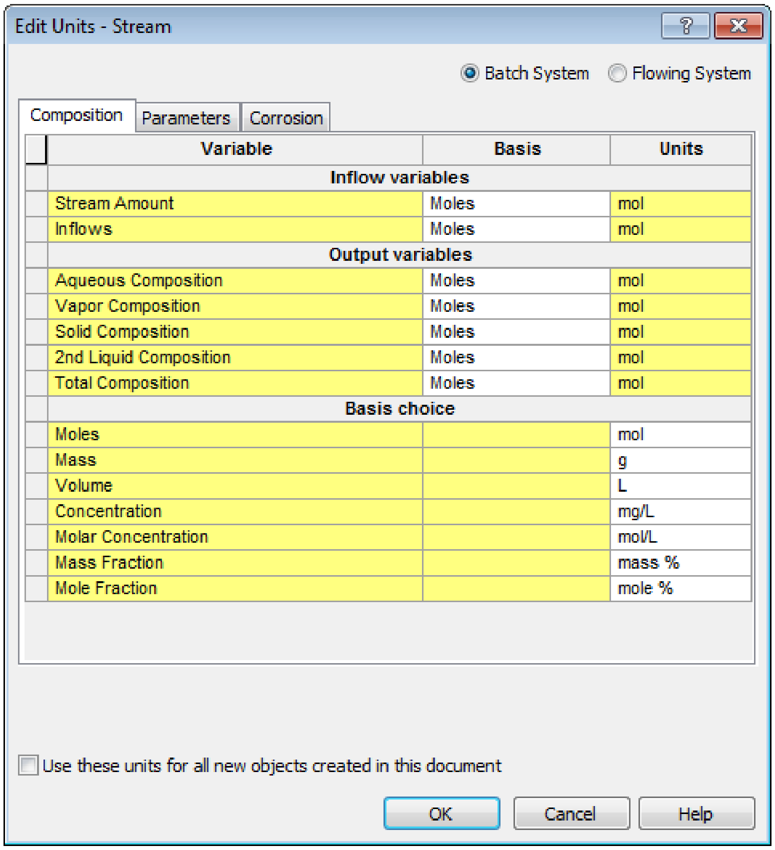


Units Manager - Stream

Units Manager

Metric ▾ Batch ▾ Moles ▾

For a quick units change we can click one of the radio buttons. Click the **Customize** button



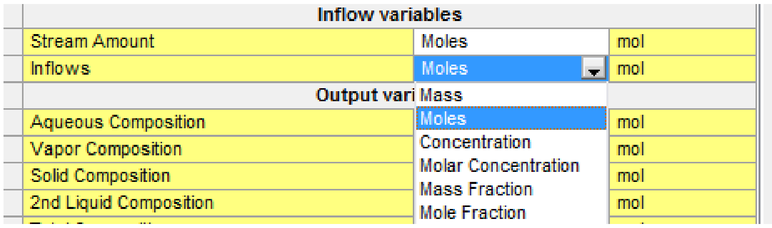
Edit Units - Stream

● Batch System ○ Flowing System

Variable	Basis	Units
Inflow variables		
Stream Amount	Moles	mol
Inflows	Moles	mol
Output variables		
Aqueous Composition	Moles	mol
Vapor Composition	Moles	mol
Solid Composition	Moles	mol
2nd Liquid Composition	Moles	mol
Total Composition	Moles	mol
Basis choice		
Moles		mol
Mass		g
Volume		L
Concentration		mg/L
Molar Concentration		mol/L
Mass Fraction		mass %
Mole Fraction		mole %

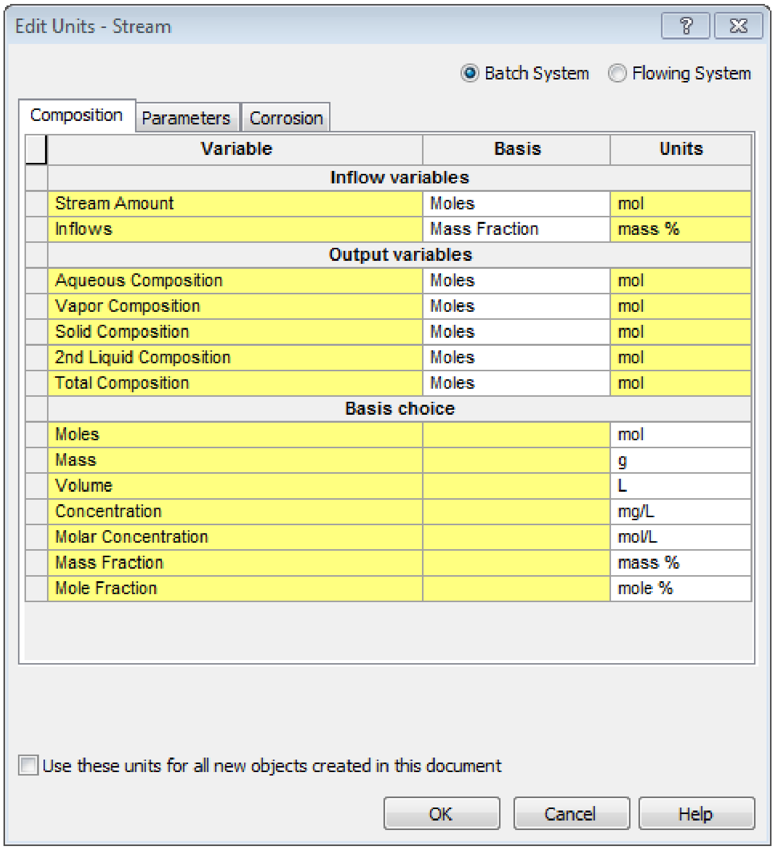
☐ Use these units for all new objects created in this document

Click the drop-down menu next to ***Inflows*** under the basis column:



Inflow variables		
Stream Amount	Moles	mol
Inflows	Moles	mol
Output vari		
Aqueous Composition		mol
Vapor Composition		mol
Solid Composition		mol
2nd Liquid Composition		mol

Next select ***Mass Fraction*** and the grid updates:



Edit Units - Stream

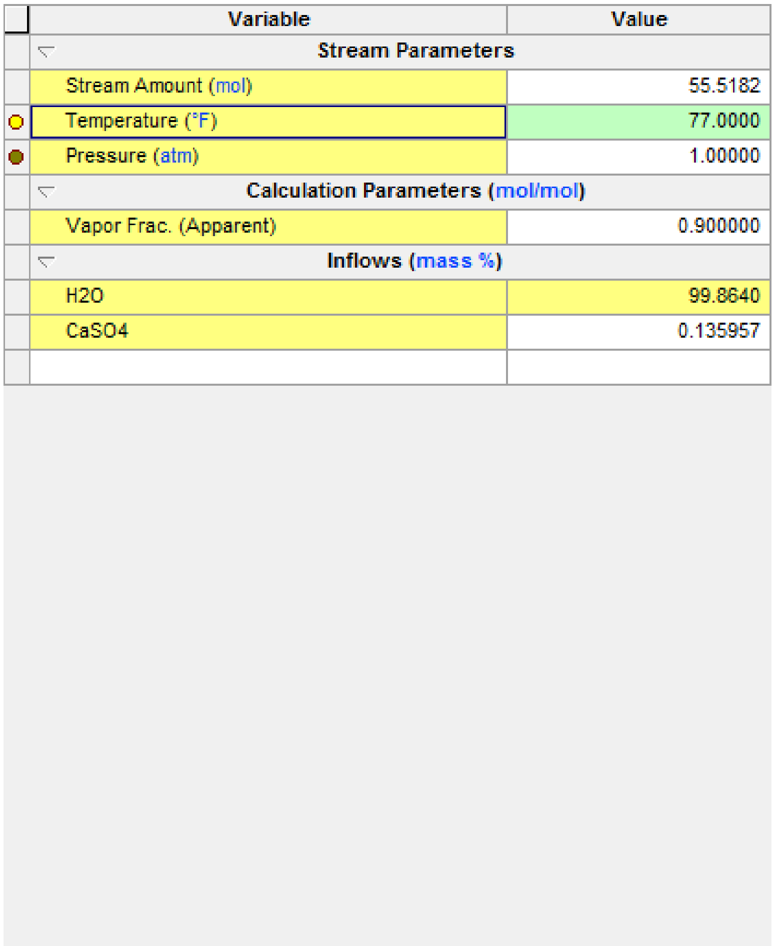
● Batch System ○ Flowing System

Variable	Basis	Units
Inflow variables		
Stream Amount	Moles	mol
Inflows	Mass Fraction	mass %
Output variables		
Aqueous Composition	Moles	mol
Vapor Composition	Moles	mol
Solid Composition	Moles	mol
2nd Liquid Composition	Moles	mol
Total Composition	Moles	mol
Basis choice		
Moles		mol
Mass		g
Volume		L
Concentration		mg/L
Molar Concentration		mol/L
Mass Fraction		mass %
Mole Fraction		mole %

☐ Use these units for all new objects created in this document

Notice that the units for Mass Fraction are set to **mass %** in this example. Lower in the grid displays the current setting for Mass Fraction. You can change this value by clicking its drop-down menu.

As you can see, the definition grid is updated with the new units set.



	Variable	Value
	Stream Parameters	
	Stream Amount (mol)	55.5182
○	Temperature (°F)	77.0000
●	Pressure (atm)	1.00000
	Calculation Parameters (mol/mol)	
	Vapor Frac. (Apparent)	0.900000
	Inflows (mass %)	
	H2O	99.8640
	CaSO4	0.135957

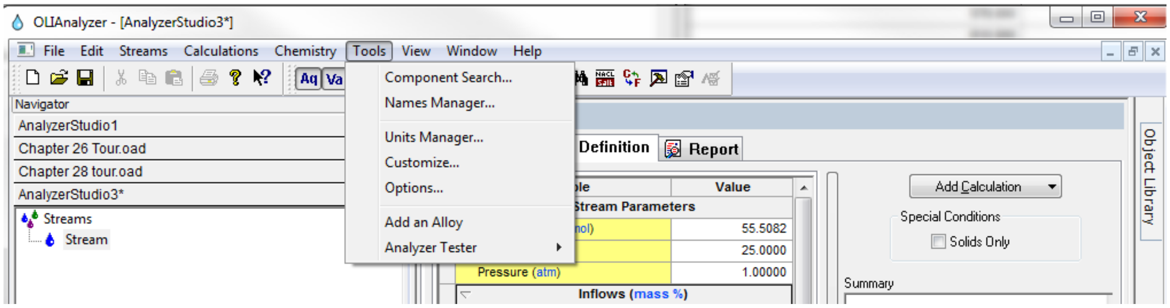
38. Tools | Options

Setting the Auto Save and Automatic Backup Features

Even though modern computers are very reliable, some software packages were written without full consideration of what else may be running. This may cause system crashes and you may lose your work.

OLI has provided a method to help recover lost data. By default OLI will backup any file you open with the OLI Analyzers so that you have the previous version saved. OLI will also automatically save your file every 5 minutes. You can change these settings.

To begin, select **Tools** from the menu line.

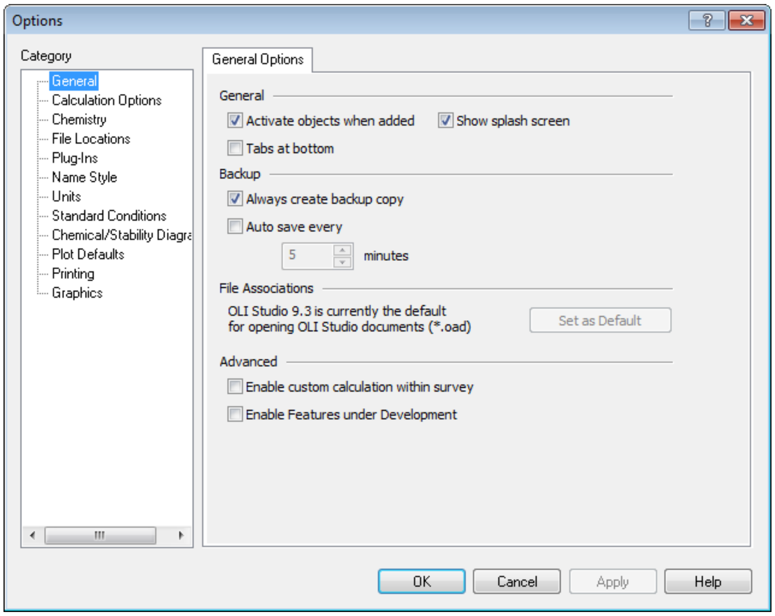


Next select **Options...**

Select the **General** category

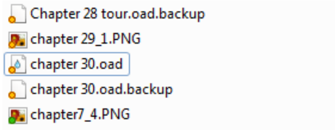
By default, the OLI Analyzers will create a back up copy of the file (if it was previously saved). If this was a large file you may want to disable this feature but unchecking the ***Always create backup copy*** check box.

Also by default, the OLI Analyzers will save your file every 5 minutes. You can decrease or increase this time as you require.



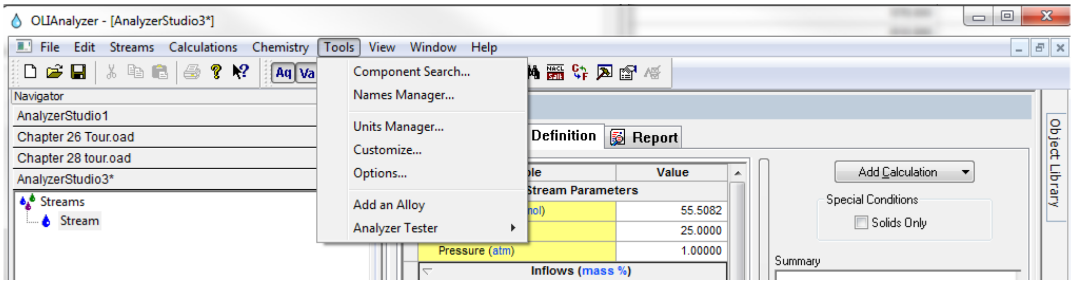
☑ Activate objects when added ☑ Show splash screen
☐ Tabs at bottom
☑ Always create backup copy
☐ Auto save every 5 minutes
OLI Studio 9.3 is currently the default for opening OLI Studio documents (*.oad)
☐ Enable custom calculation within survey
☐ Enable Features under Development

If you need to recover a file that you accidentally saved (or it got corrupted) OLI creates a file with essentially the same name except the extension "backup" is appended. You should copy or rename this file and then open it as you would any other OLI Analyzer file.


Chapter 28 tour.oad.backup
chapter 29_1.PNG
chapter 30.oad
chapter 30.oad.backup
chapter7_4.PNG

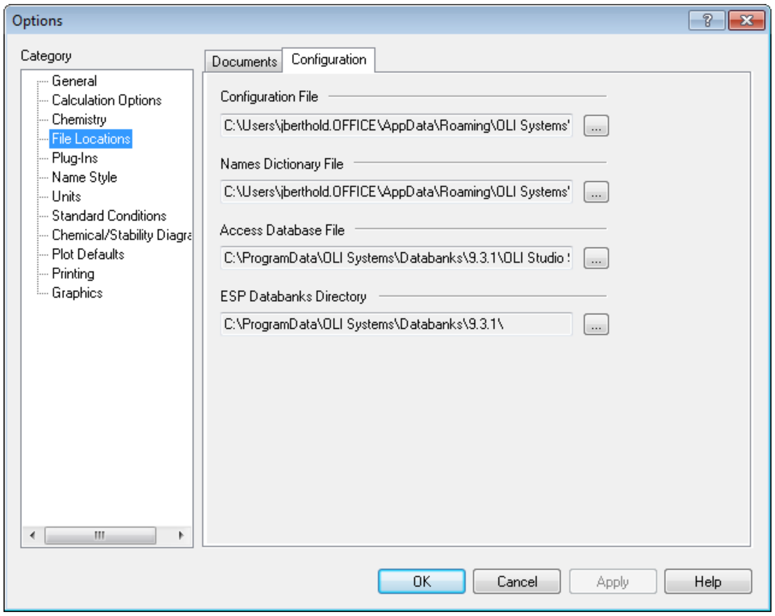
Changing the default file locations

Sometime a user will need to change the default file locations for the OLI Analyzers. There are many reasons to do this but frequently it is because the user is on a multi-user system with multiple user logins. To change or verify the file locations the user needs to select the ***Tools*** menu item:



Next select ***Options...***

Next select ***File Locations*** and then click on the ***Configuration*** tab.



Configuration File: C:\Users\jberthold.OFFICE\AppData\Roaming\OLI Systems'

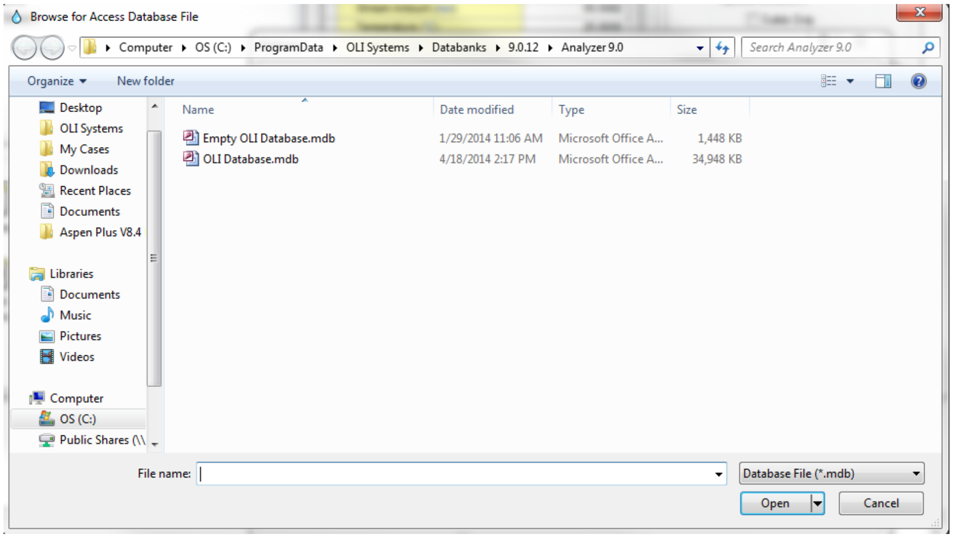
Names Dictionary File: C:\Users\jberthold.OFFICE\AppData\Roaming\OLI Systems'

Access Database File: C:\ProgramData\OLI Systems\Databanks\9.3.1\OLI Studio !

ESP Databanks Directory: C:\ProgramData\OLI Systems\Databanks\9.3.1\

This will display the current file locations. You may want to verify these locations (some OLI programs will inadvertently modify these locations).

If you need to change the file location, click on the "..." to open the dialog.



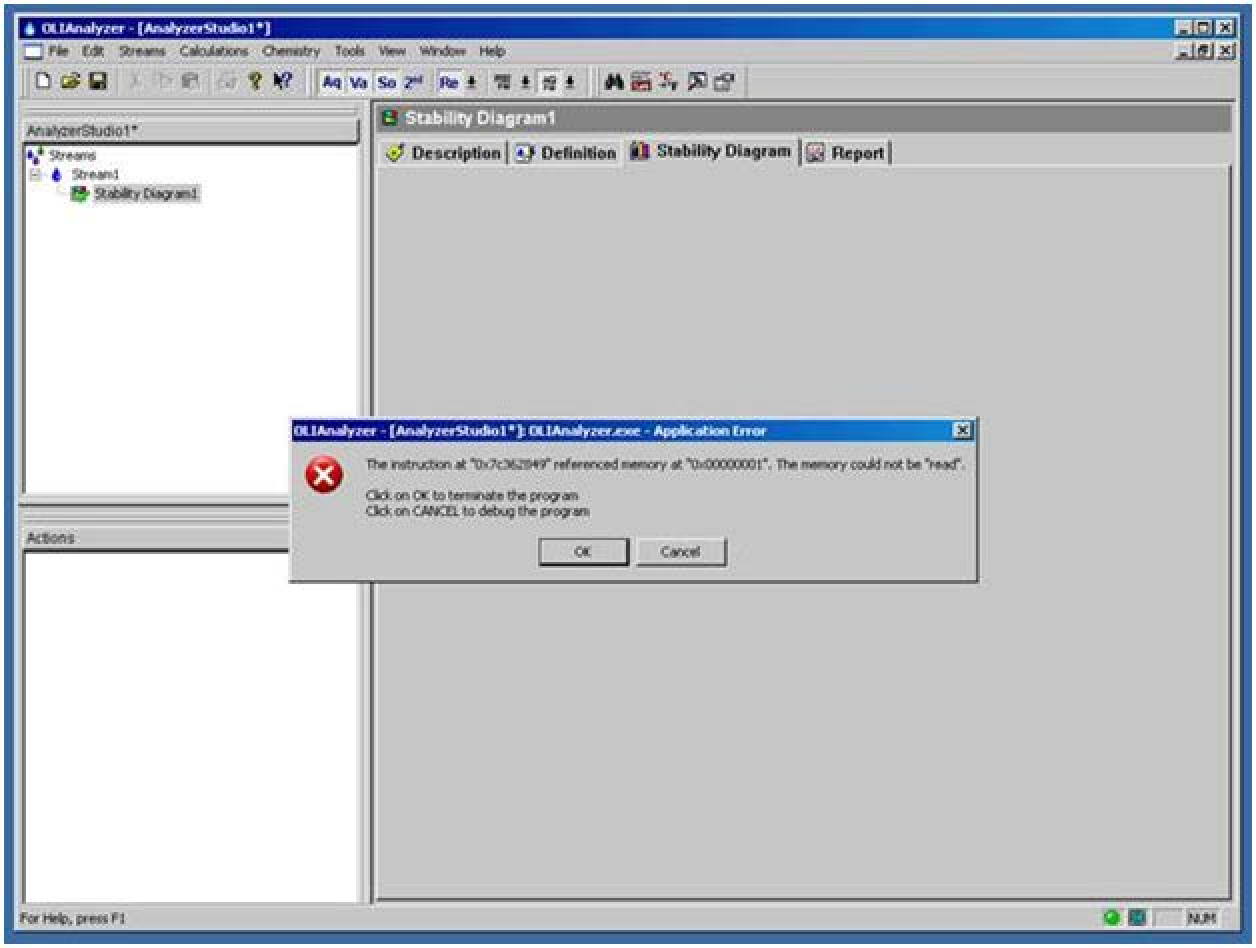
Name	Date modified	Type	Size
Empty OLI Database.mdb	1/29/2014 11:06 AM	Microsoft Office A...	1,448 KB
OLI Database.mdb	4/18/2014 2:17 PM	Microsoft Office A...	34,948 KB

File name:

Database File (*.mdb)

Turning off hardware acceleration

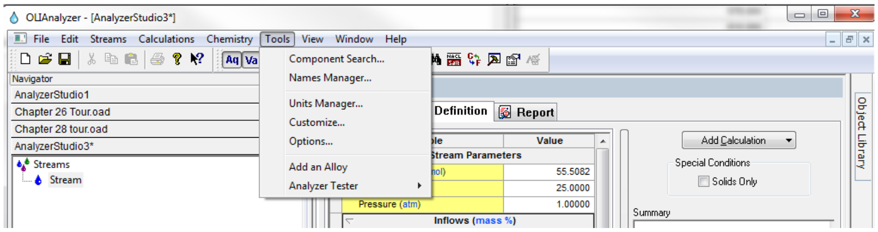
The OLI Analyzer program uses OpenGL to plot stability diagrams. To speed up the rendering of the plot, the OpenGL drivers will use some of your video cards hardware acceleration features. Some video drivers do not support this ability and will result in a crash when attempting to display a diagram such as the feature shown below.



```
The instruction at "0x7c362949" referenced memory at "0x00000001". The memory could not be "read".

Click on OK to terminate the program
Click on CANCEL to debug the program
```

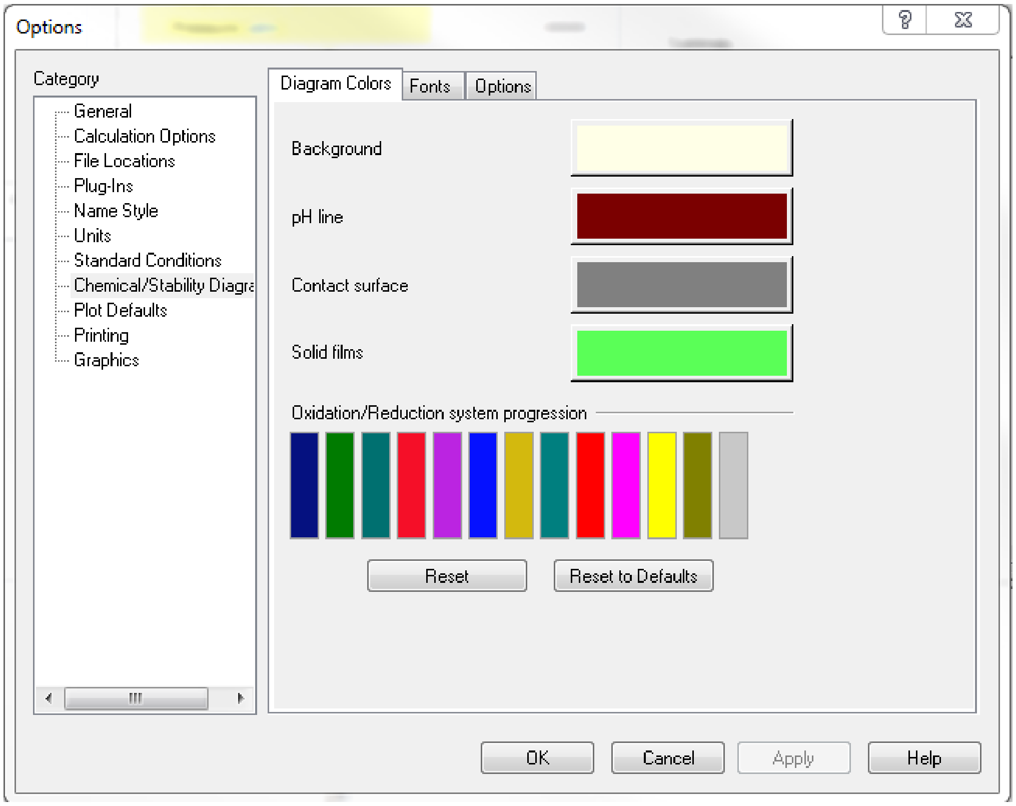
To remedy this error we need to turn off hardware acceleration for the OpenGL drivers. This affects the current document only.

Select Tools from the menu.

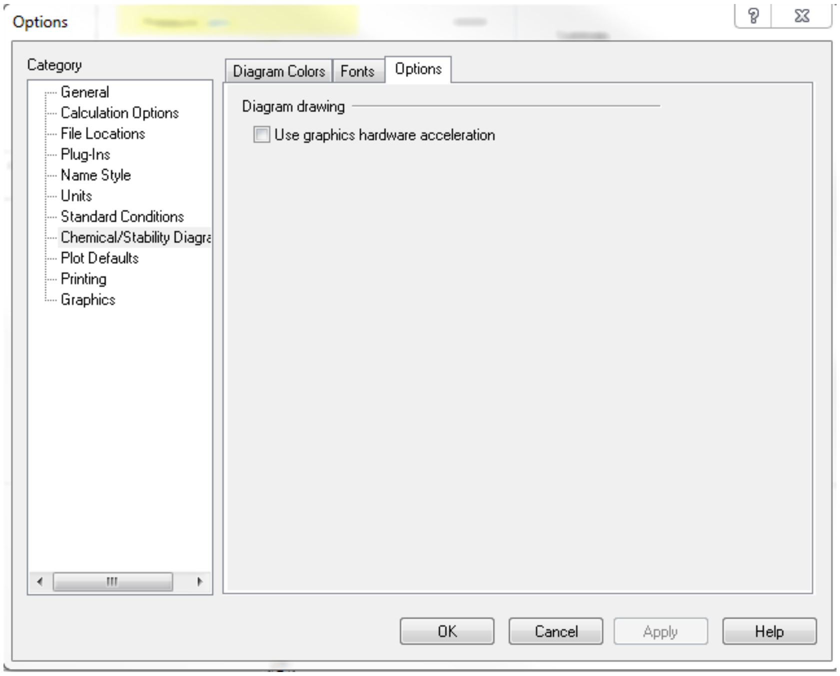


Then select Options from the drop down menu.

This will display the options available for the Analyzers. Select Chemical/Stability diagrams.



You can change the way your plots look. To turn off hardware acceleration click the Options tab.



☐ Use graphics hardware acceleration

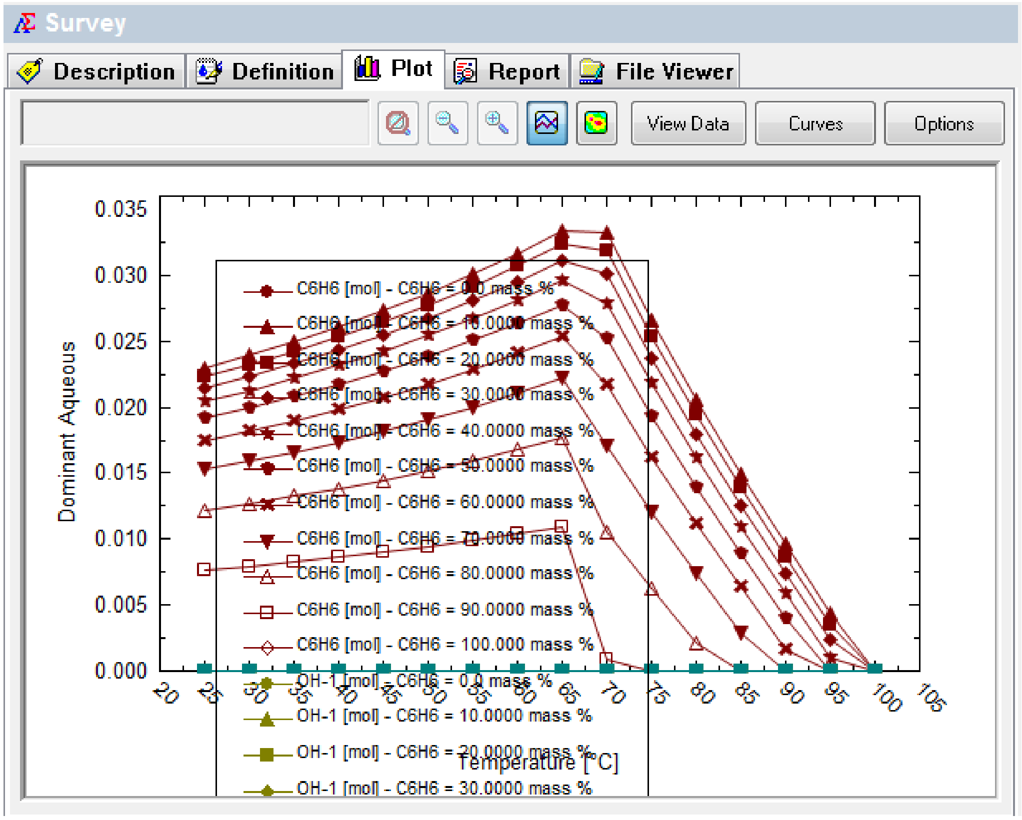
Uncheck the User graphics hardware acceleration box.

Click the OK button and then save the document. Reopen it and redisplay the diagram.

39. Modifying the plot

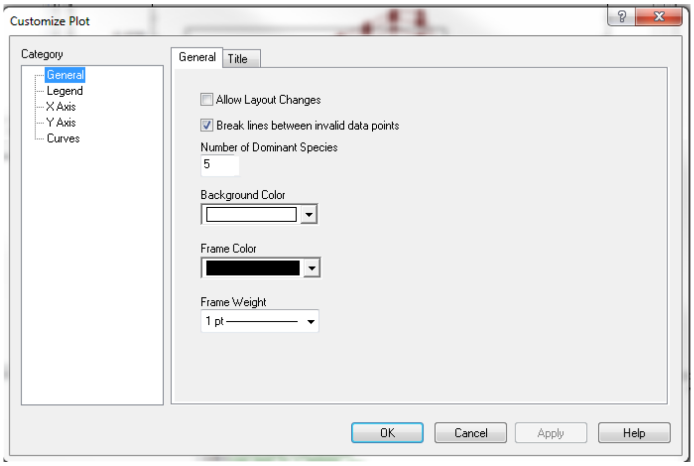
Hiding Curves

One nice feature of the OLI Analyzers is that you can generate a lot of points to plot many variables. You can also perform multiple series of plots such as plotting temperature curves as a function of pressure. This is what we are showing below. This is a pre-run temperature survey with pressure selected as the secondary (*then by...*) survey.



As you can see there is a lot of data, the plot is very hard to read. Fortunately we have created a tool to clean up the plot. Click the **Options** button in the upper right-hand corner.

This will display the **Customize Plot** dialog. Select the **Curves** category.



☐ Allow Layout Changes

☑ Break lines between invalid data points

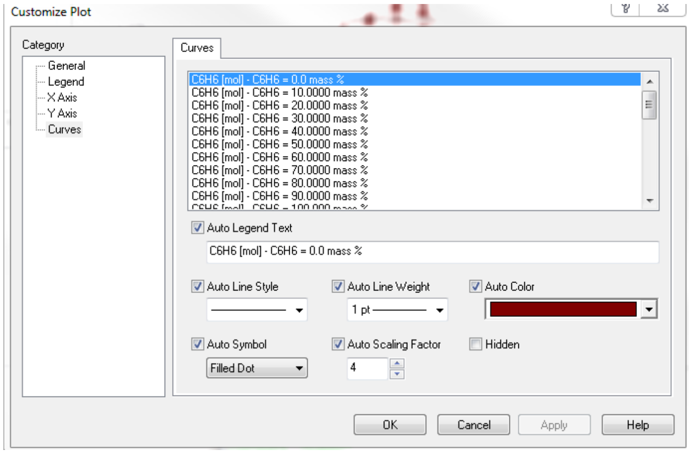
Number of Dominant Species: 5

Background Color

Frame Color

Frame Weight: 1 pt

Each data series in the current plot is displayed. As you can see in the dialog below there are many series currently displayed. You could hide each one individually or select groups to hide. We are first going to hide all the curves. Select the first item in the list and hold the **Shift Key.**



C6H6 [mol] - C6H6 = 0.0 mass %
C6H6 [mol] - C6H6 = 10.0000 mass %
C6H6 [mol] - C6H6 = 20.0000 mass %
C6H6 [mol] - C6H6 = 30.0000 mass %
C6H6 [mol] - C6H6 = 40.0000 mass %
C6H6 [mol] - C6H6 = 50.0000 mass %
C6H6 [mol] - C6H6 = 60.0000 mass %
C6H6 [mol] - C6H6 = 70.0000 mass %
C6H6 [mol] - C6H6 = 80.0000 mass %
C6H6 [mol] - C6H6 = 90.0000 mass %

☑ Auto Legend Text: C6H6 [mol] - C6H6 = 0.0 mass %

☑ Auto Line Style

☑ Auto Line Weight: 1 pt

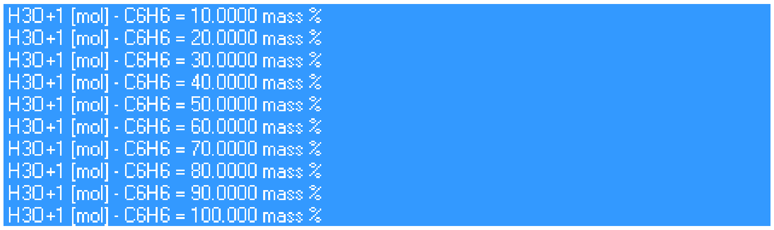
☑ Auto Color

☑ Auto Symbol: Filled Dot

☑ Auto Scaling Factor: 4

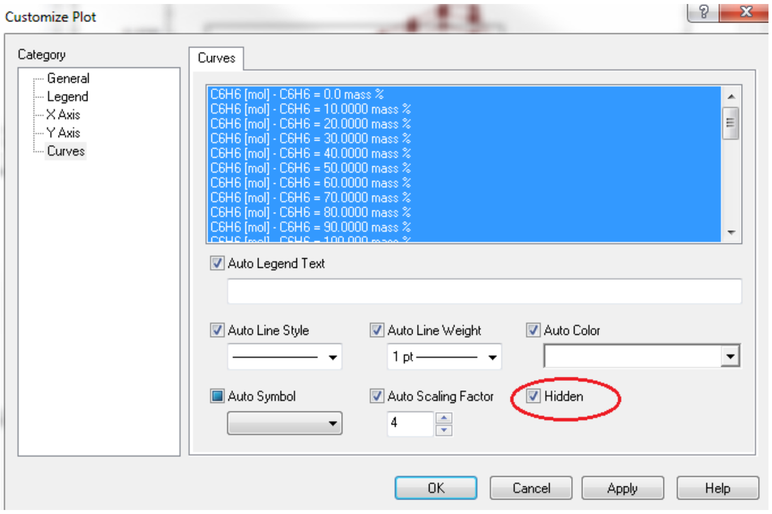
☐ Hidden

Scroll down to the last item in the list



H3O+1 [mol] - C6H6 = 10.0000 mass %
H3O+1 [mol] - C6H6 = 20.0000 mass %
H3O+1 [mol] - C6H6 = 30.0000 mass %
H3O+1 [mol] - C6H6 = 40.0000 mass %
H3O+1 [mol] - C6H6 = 50.0000 mass %
H3O+1 [mol] - C6H6 = 60.0000 mass %
H3O+1 [mol] - C6H6 = 70.0000 mass %
H3O+1 [mol] - C6H6 = 80.0000 mass %
H3O+1 [mol] - C6H6 = 90.0000 mass %
H3O+1 [mol] - C6H6 = 100.000 mass %

We have now selected all the items. Click the **Hidden** check box to hide these curves.

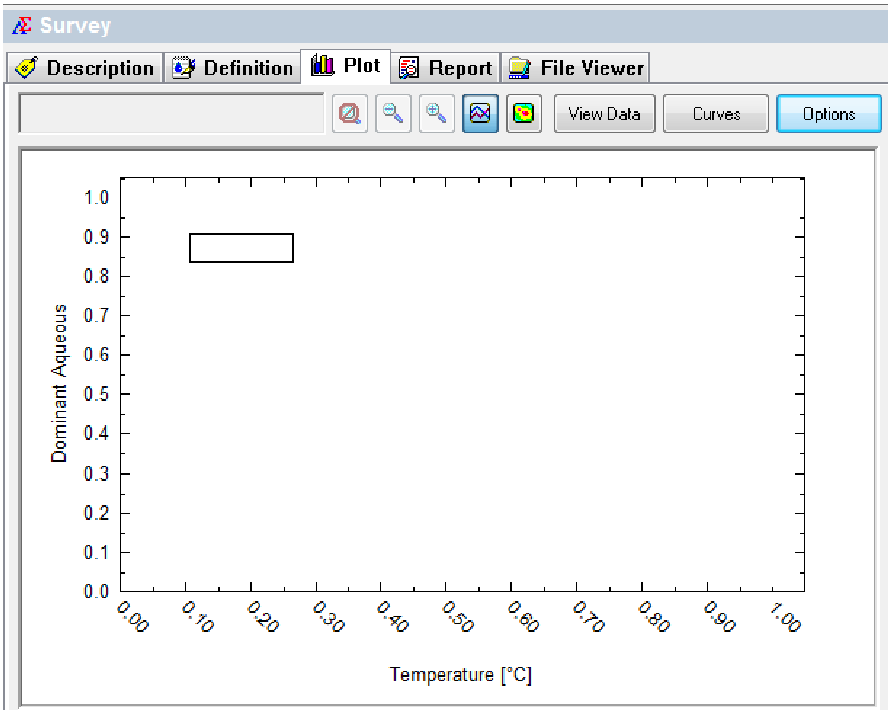


C6H6 [mol] - C6H6 = 0.0 mass %
C6H6 [mol] - C6H6 = 10.0000 mass %
C6H6 [mol] - C6H6 = 20.0000 mass %
C6H6 [mol] - C6H6 = 30.0000 mass %
C6H6 [mol] - C6H6 = 40.0000 mass %
C6H6 [mol] - C6H6 = 50.0000 mass %
C6H6 [mol] - C6H6 = 60.0000 mass %
C6H6 [mol] - C6H6 = 70.0000 mass %
C6H6 [mol] - C6H6 = 80.0000 mass %
C6H6 [mol] - C6H6 = 90.0000 mass %

☑ Auto Legend Text

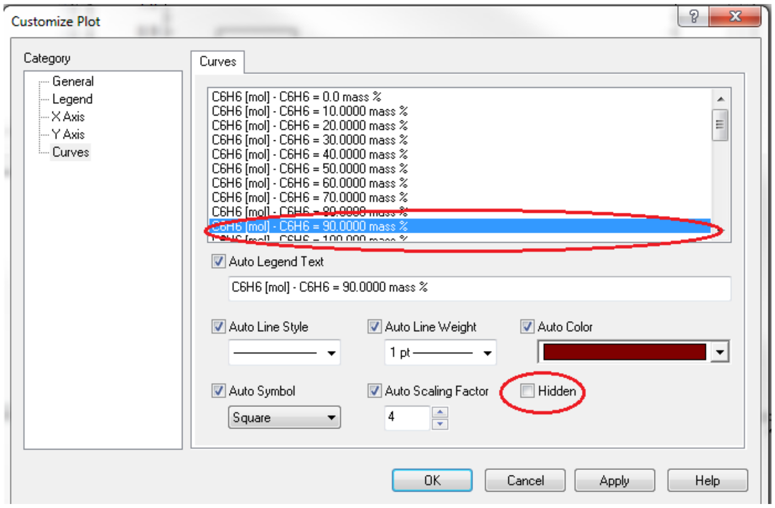
☑ Auto Line Style
☑ Auto Line Weight: 1 pt
☑ Auto Color
■ Auto Symbol
☑ Auto Scaling Factor: 4
☑ Hidden

Click the **Apply** and then **OK** buttons to see the plot.



This is not very helpful. We need to "Unhide" some curves. Once again, click the **Options** button and then reselect the **Curves** category.

For this example we want to see the highest pressure for this dual survey. Scroll to the bottom of the list and then uncheck the **Hidden** box.

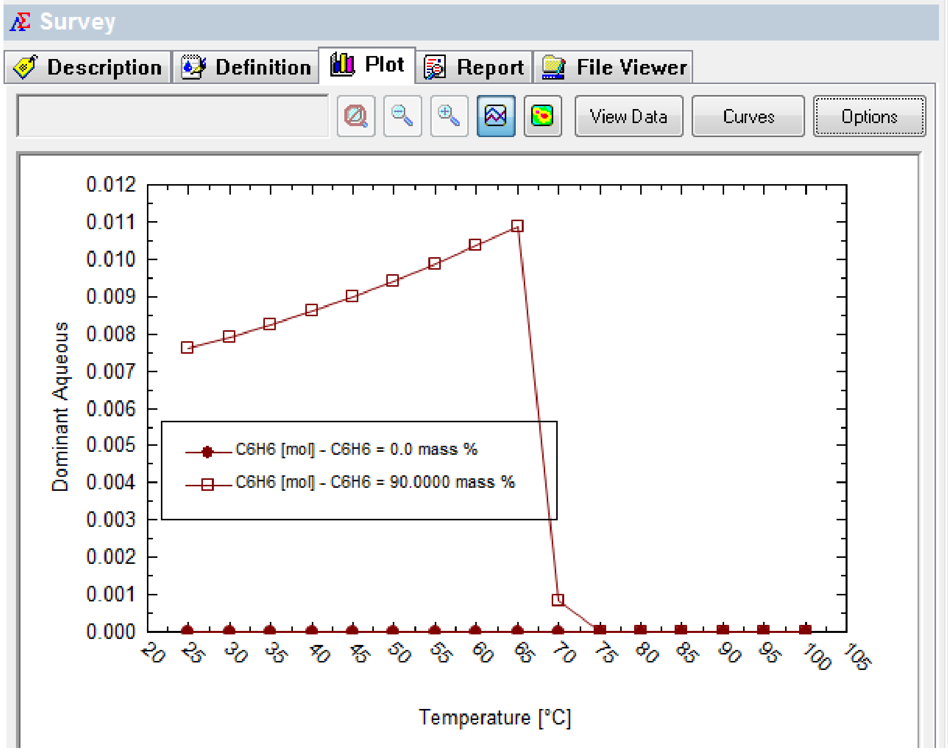


C6H6 [mol] - C6H6 = 0.0 mass %
C6H6 [mol] - C6H6 = 10.0000 mass %
C6H6 [mol] - C6H6 = 20.0000 mass %
C6H6 [mol] - C6H6 = 30.0000 mass %
C6H6 [mol] - C6H6 = 40.0000 mass %
C6H6 [mol] - C6H6 = 50.0000 mass %
C6H6 [mol] - C6H6 = 60.0000 mass %
C6H6 [mol] - C6H6 = 70.0000 mass %
C6H6 [mol] - C6H6 = 80.0000 mass %
C6H6 [mol] - C6H6 = 90.0000 mass %
C6H6 [mol] - C6H6 = 100.000 mass %

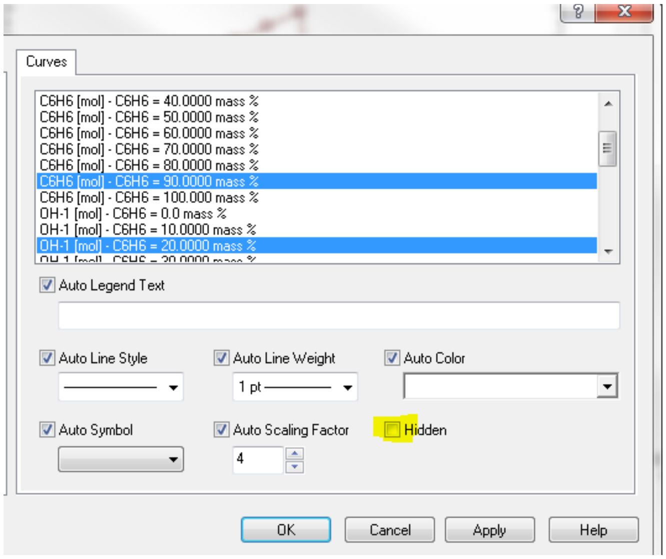
☑ Auto Legend Text
C6H6 [mol] - C6H6 = 90.0000 mass %

☑ Auto Line Style
☑ Auto Line Weight: 1 pt
☑ Auto Color
☑ Auto Symbol: Square
☑ Auto Scaling Factor: 4
☐ Hidden

Click the **Apply** and **OK** buttons to display the plot.



We now have our plot without all the clutter of extra points. We can now go back an add (or unhide) additional curves.Once again, click the **Options** button and then reselect the **Curves** category.



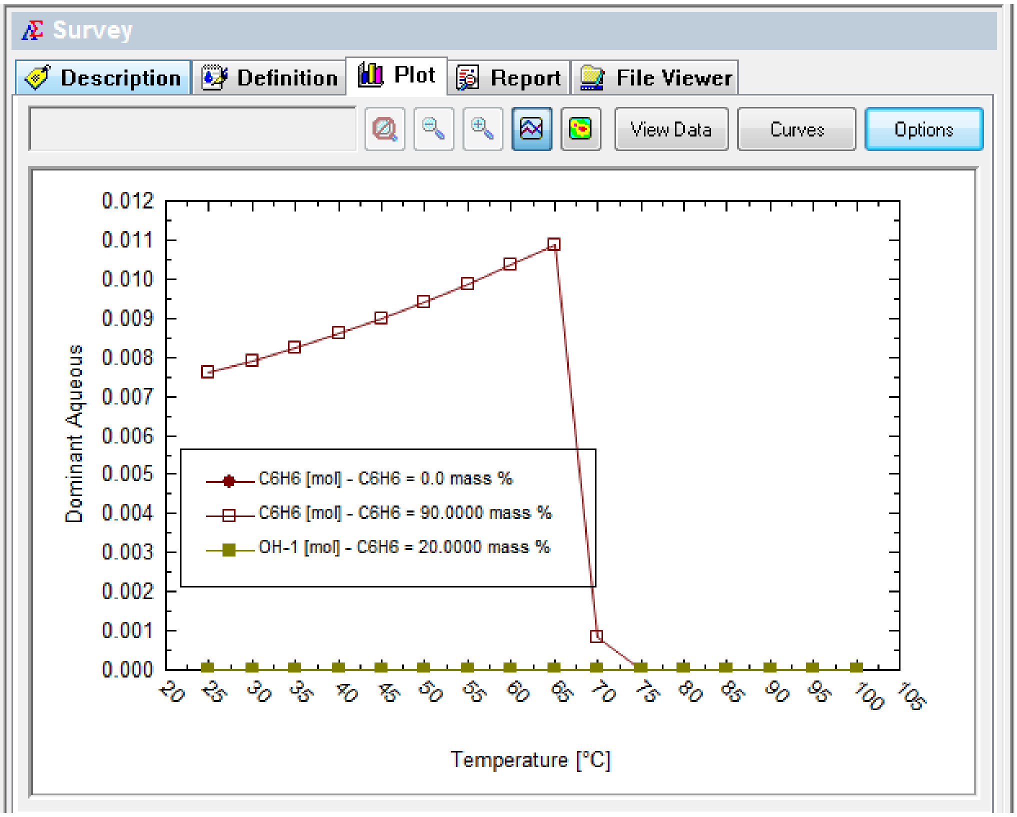
Curves

C6H6 [mol] - C6H6 = 40.0000 mass %
C6H6 [mol] - C6H6 = 50.0000 mass %
C6H6 [mol] - C6H6 = 60.0000 mass %
C6H6 [mol] - C6H6 = 70.0000 mass %
C6H6 [mol] - C6H6 = 80.0000 mass %
C6H6 [mol] - C6H6 = 90.0000 mass %
C6H6 [mol] - C6H6 = 100.000 mass %
OH-1 [mol] - C6H6 = 0.0 mass %
OH-1 [mol] - C6H6 = 10.0000 mass %
OH-1 [mol] - C6H6 = 20.0000 mass %

☑ Auto Legend Text

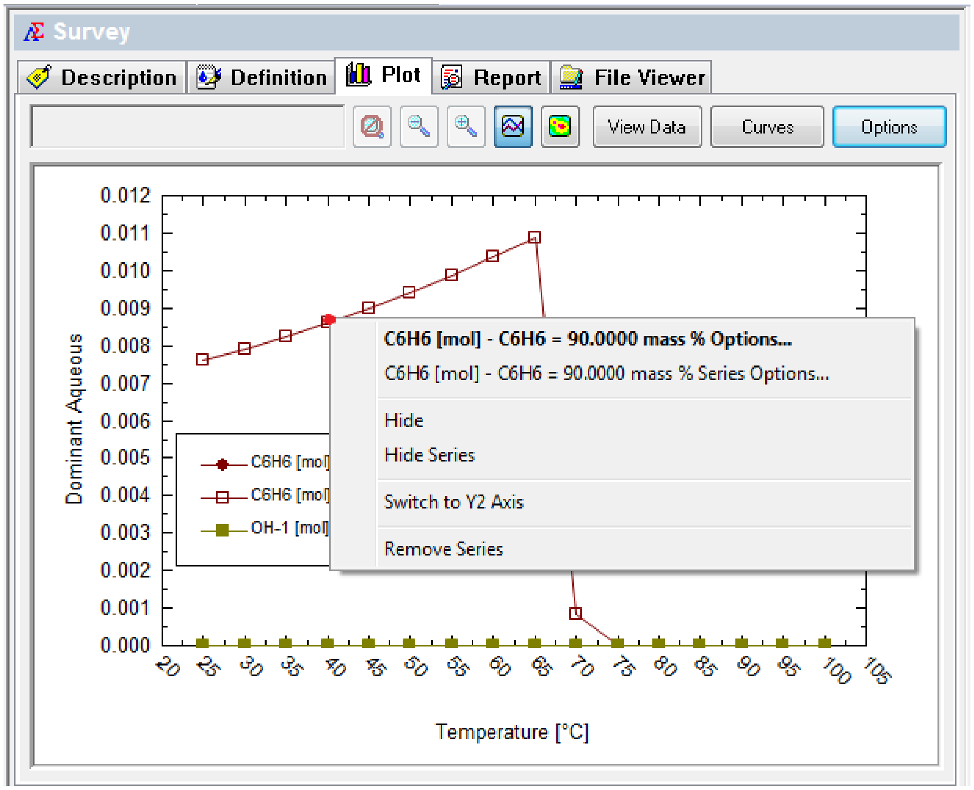
☑ Auto Line Style
☑ Auto Line Weight: 1 pt
☑ Auto Color
☑ Auto Symbol
☑ Auto Scaling Factor: 4
☐ Hidden

Locate a curve midway in the list (here we have chosen a different variable also at the highest pressure). Uncheck the **Hidden** check box. Click the **Apply** and **OK** buttons to display the plot.



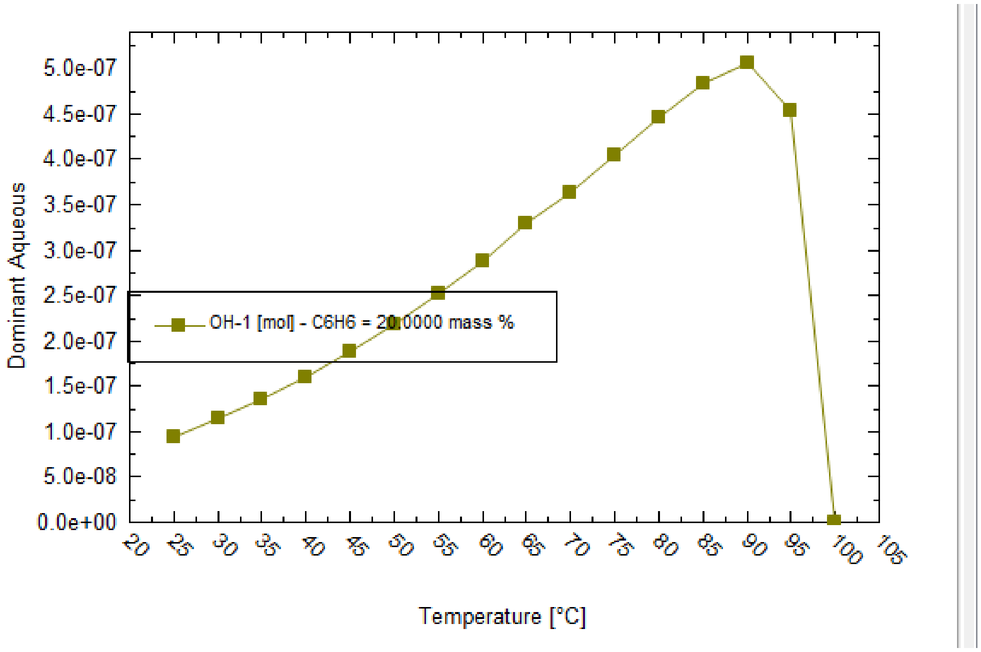
We now have to curves displayed. It is helpful to note that all the other curves are still present in the diagram. If you export this plot to a spreadsheet, all the data, not just the displayed values, will be used.

We can modify the plot directly without the use of the Options button. **Right-click** any displayed curve. We have chosen the upper curve.



This will display a pop-up menu. The name of the series is displayed. Select **Hide Series.**

This removed the series from display. Unfortunately the only method to "Unhide" the series is to use the Options button as we did above.


Dominant Aqueous
5.0e-07
4.5e-07
4.0e-07
3.5e-07
3.0e-07
2.5e-07
2.0e-07
1.5e-07
1.0e-07
5.0e-08
0.0e+00
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
Temperature [°C]
OH-1 [mol] - C6H6 = 20.0000 mass %

Switching Variables between plots

Occasionally it is necessary to quickly switch variables between the Y1 axis and the Y2 axis. This is frequently necessary because the range of the variables plotted is vastly different. In this example, we are using the files created in Chapter 8. See: http://wiki.olisystems.com/wiki/images/5/53/Chapter_08.zip for the latest version of the worked file or **pH (Mixer)**in Chapter 8 on page 150 above.

In this example, we are mixing an acidic stream containing citric acid with a basic stream containing NaOH. Here is the resultant plot. Here is the resultant plot:

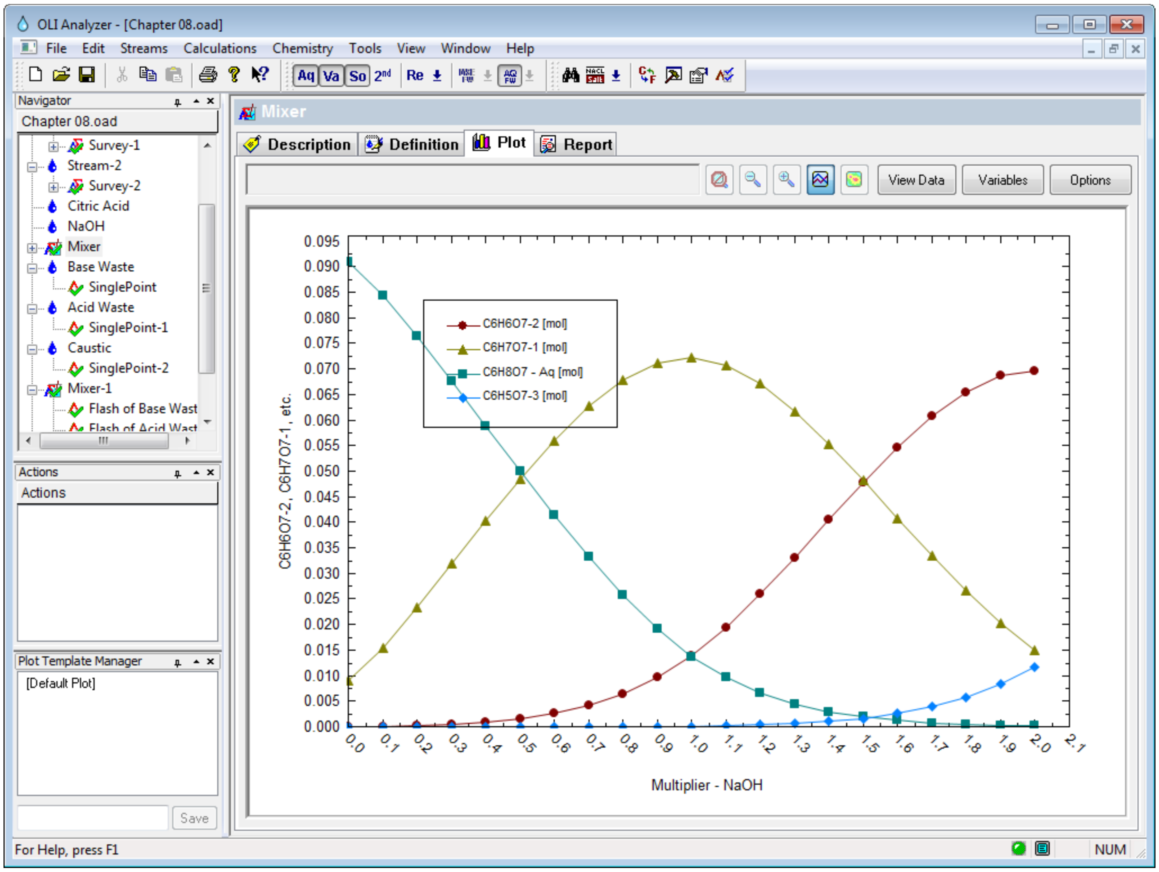


Figure 39-1 Chapter 8 citric acid survey

Perhaps we want to see an additional variable such as pH on this plot. Using the **Variables** button, select pH from the *Additional Stream Parameters* category.

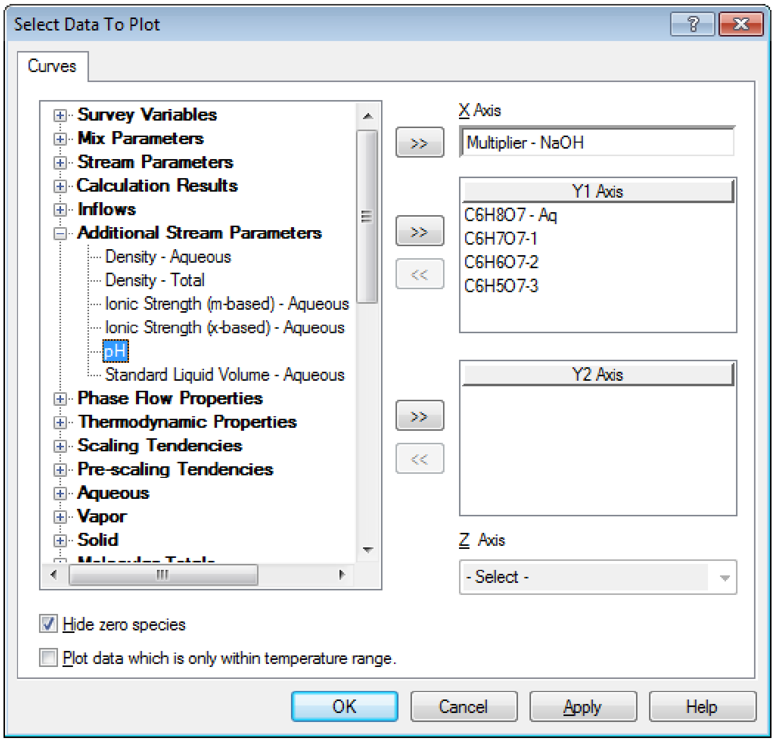


Figure 39-2 Selecting pH from the Additional Stream Parameters

This will put the pH on the Y1 axis by default. Here is the resultant plot:

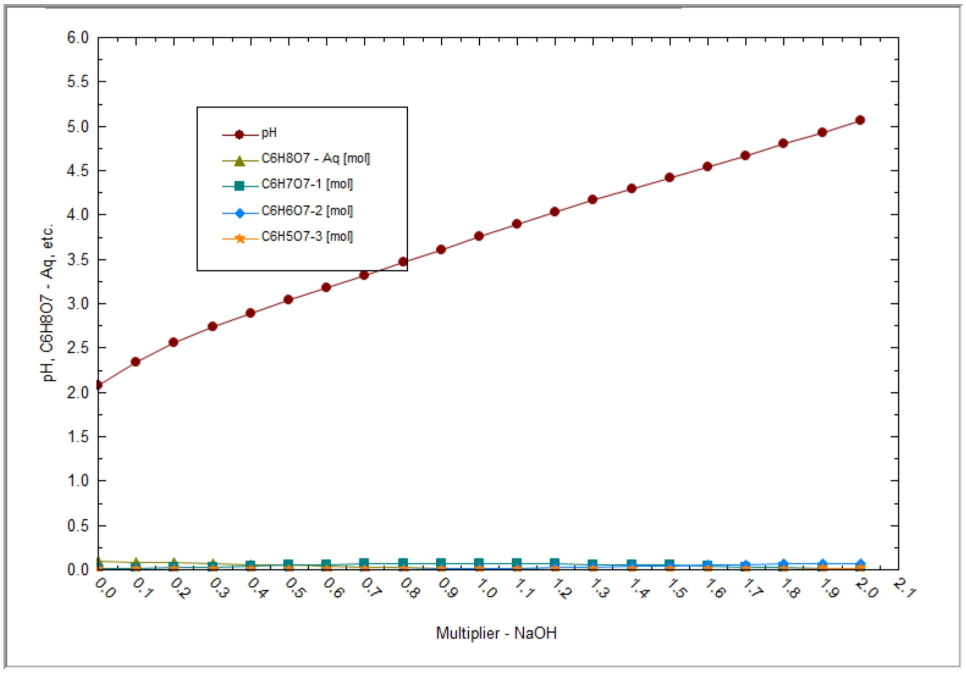


Figure 39-3 pH plotted, this skews the view

The variable "pH" has dominated the plot. Its values dwarf the vales of the ions. The pH variable should be plotted on the Y2 axis.

We can switch the variables easily. Using the **Variables** button. Highlight the pH variable in the Y1 axis box.

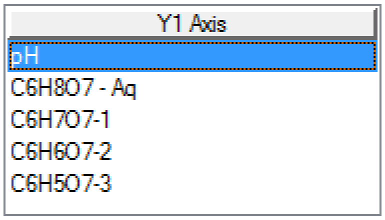


Figure 39-4

Now right-click the variable

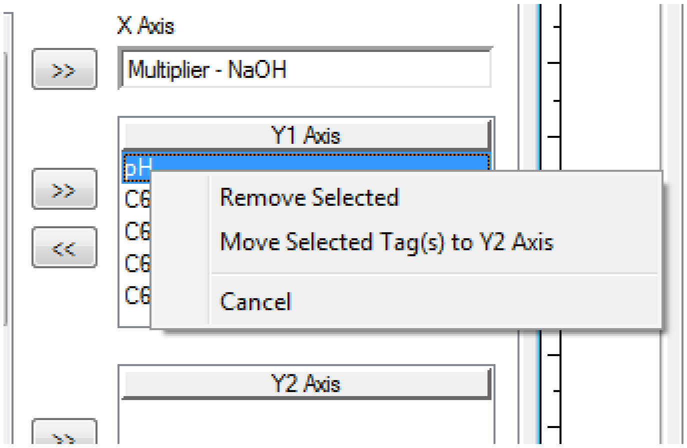


Figure 39-5 Right-clicking "pH"

Select **Move Selected Tag(s) to Y2 Axis**

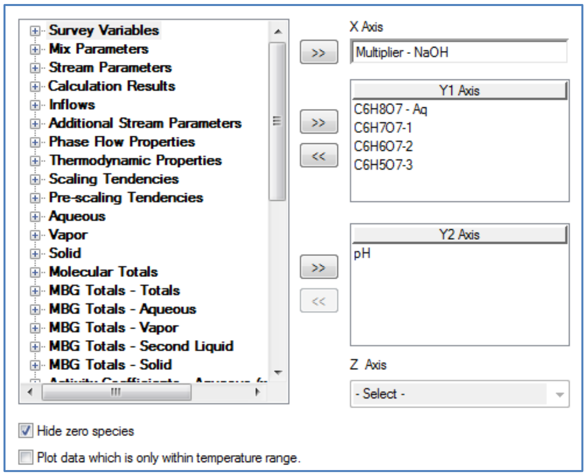


Figure 39-6 Variable moved

Here is the updated plot.

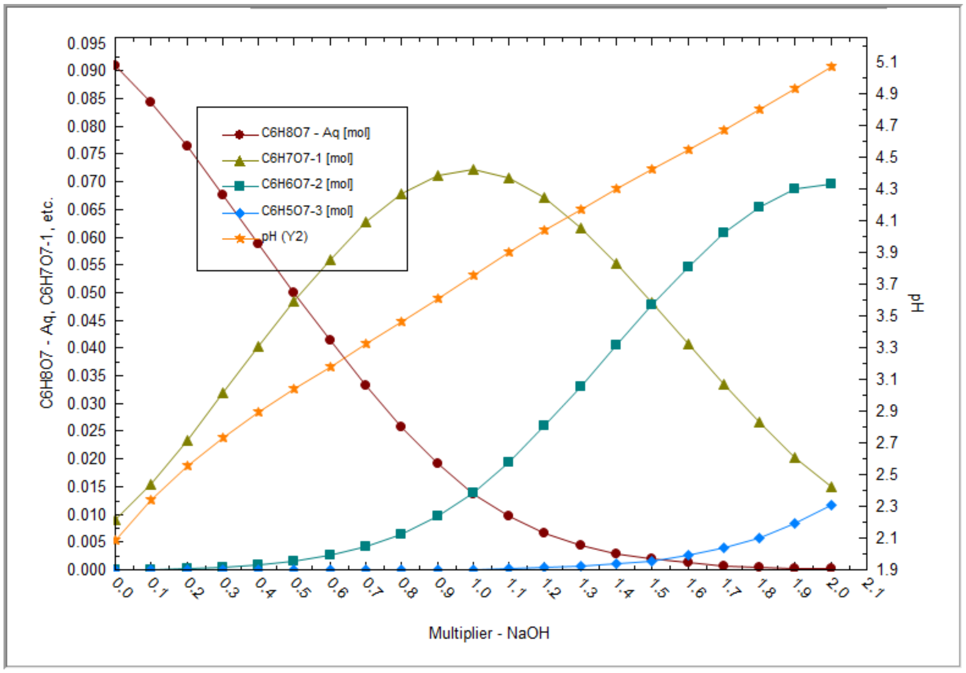


Figure 39-7 Updated plot with Y2 axis variable

Plotting two separate graphs at the same time

Frequently it is necessary to see two plots of two different systems at the same time. This is useful when comparing similar results between calculations. In this example, we have the results of a mixer calculation where we are absorbing chlorine into two different caustic (sodium hydroxide) solutions. Each caustic solution is at different concentrations.

You can download a copy of the example file from this location:
http://wiki.olisystems.com/wiki/images/5/5a/Chapter_38_-_2-Plots.zip

We will now open the file:

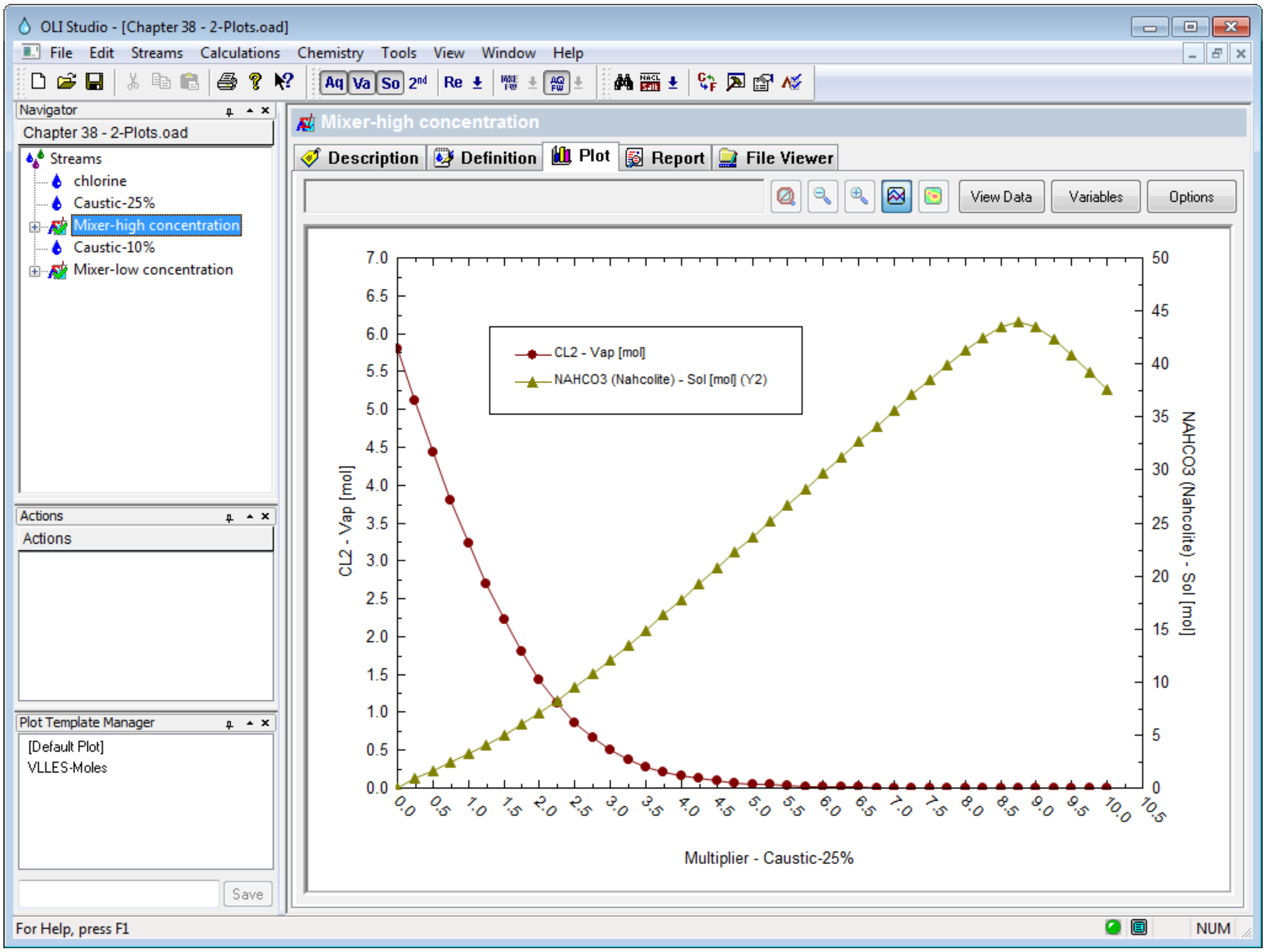


Figure 39-8 Our sample file

We have already set up our plot to display our variables. In this case, we have a 25 weight % caustic solution. It is beyond the scope of this tutorial to explain the chemistry and analysis of this case. We would like to simultaneously see the low concentration case.

To do this select **Window** from the menu line and then select **New Window**.

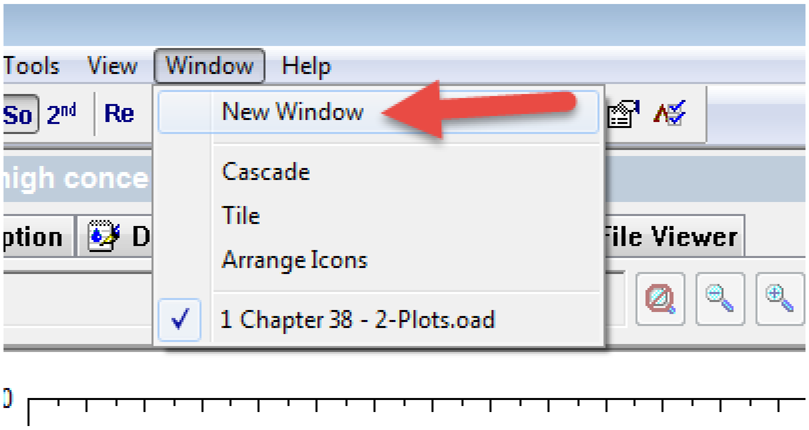
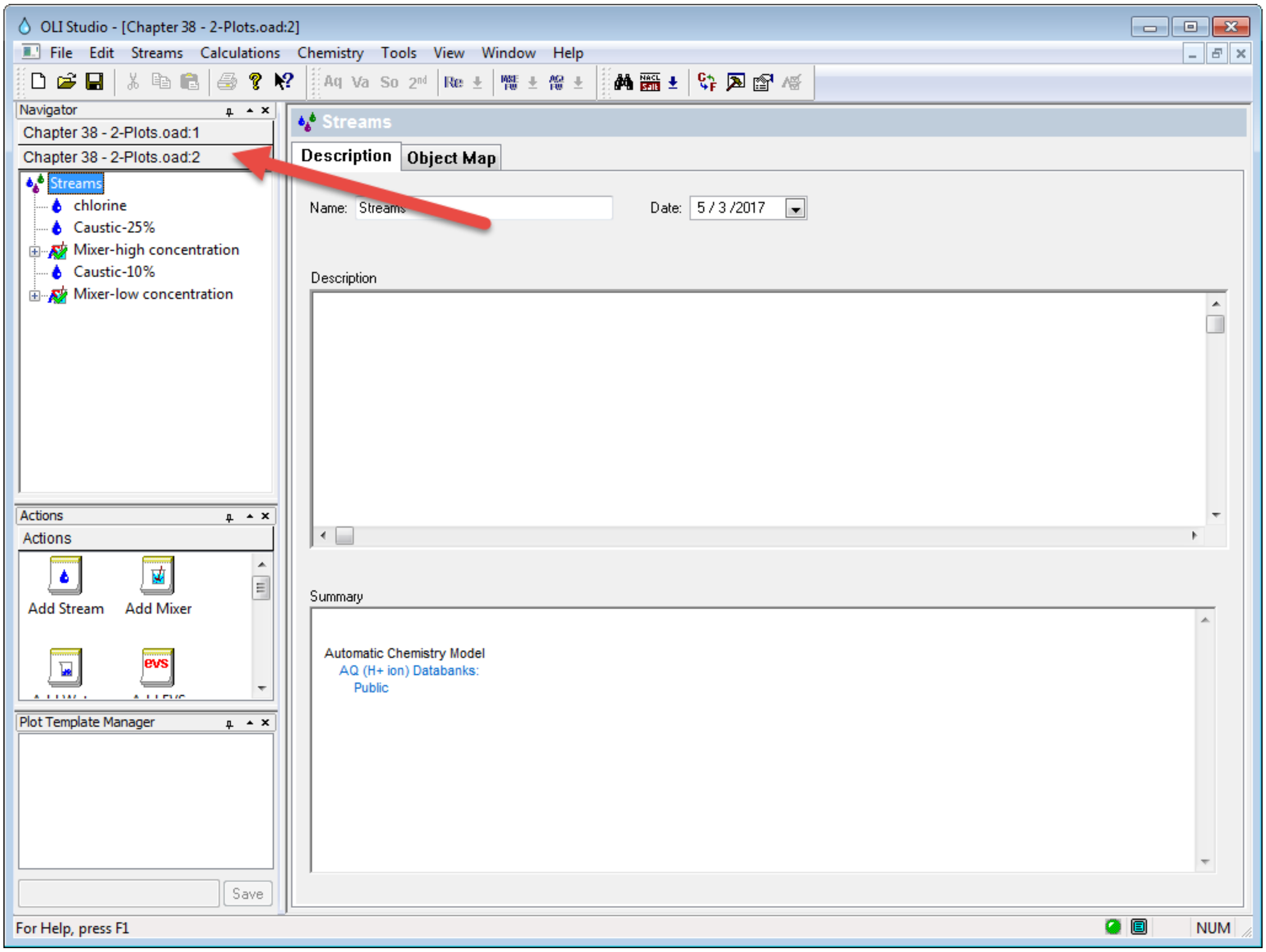


Figure 39-9 Creating a new window

This will create an exact reproduction of the same file. Notice that we have appended a window identifier for each file (the colon :1 or :2 in this case).



Name: Streams

Date: 5 / 3 /2017

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 39-10 The new window

Now we select the other mixer and set up the plot with the same variables as the first plot:

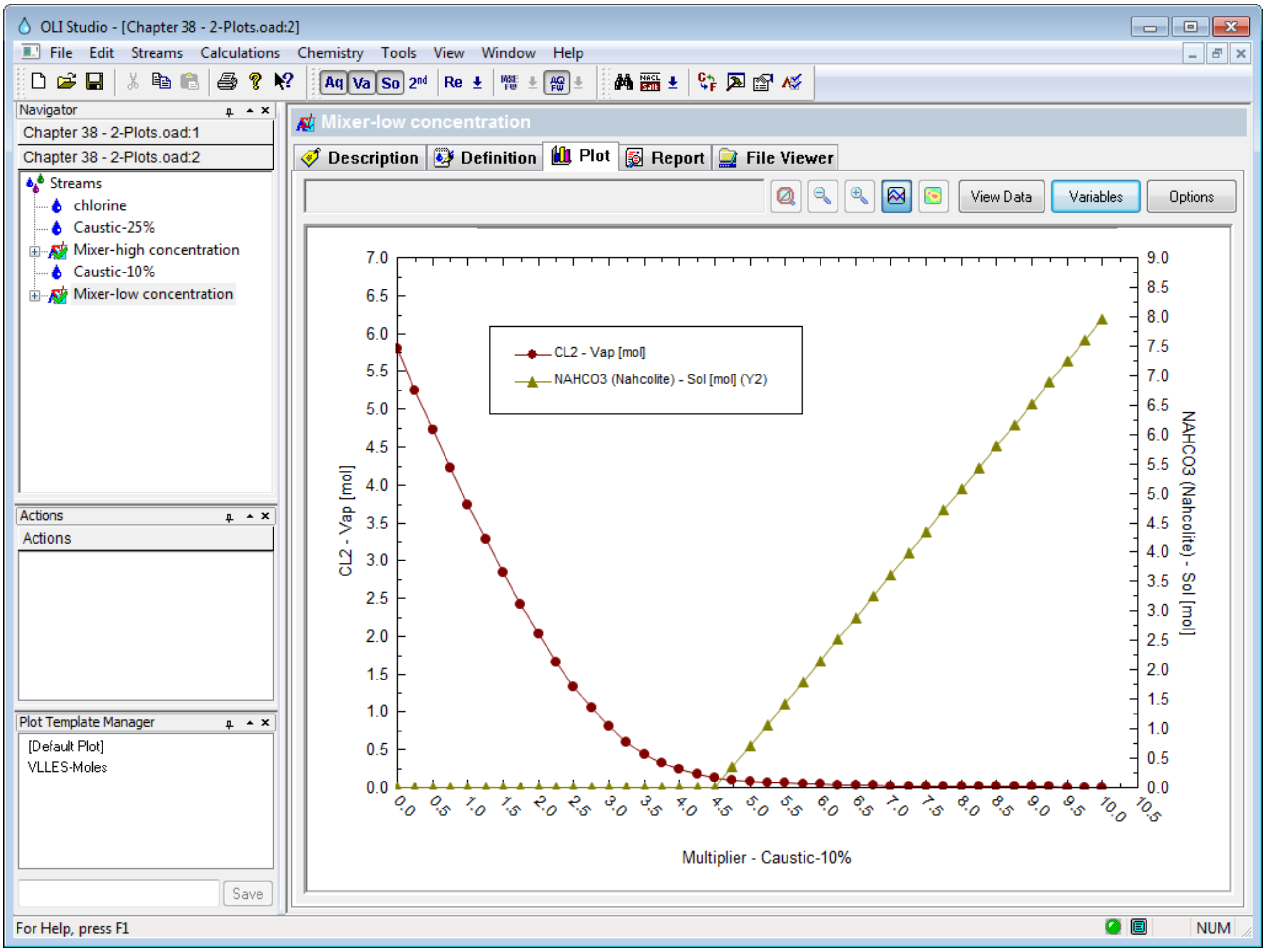


Figure 39-11 Plotting the low concentration case

Now we begin the process of putting both plots on the same display. Reselect **Window** and this time select **Tile**

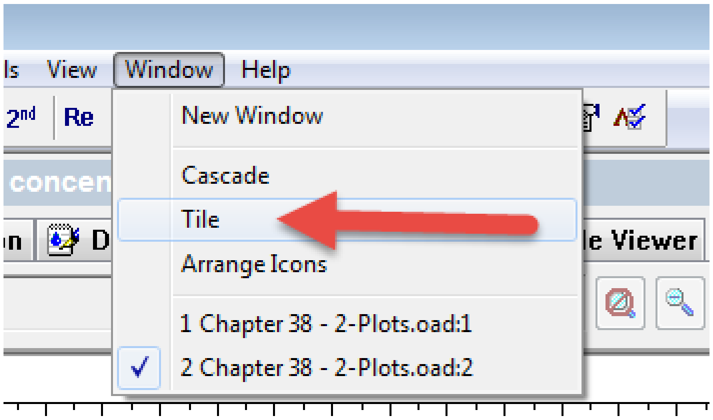


Figure 39-12 Tiling the images

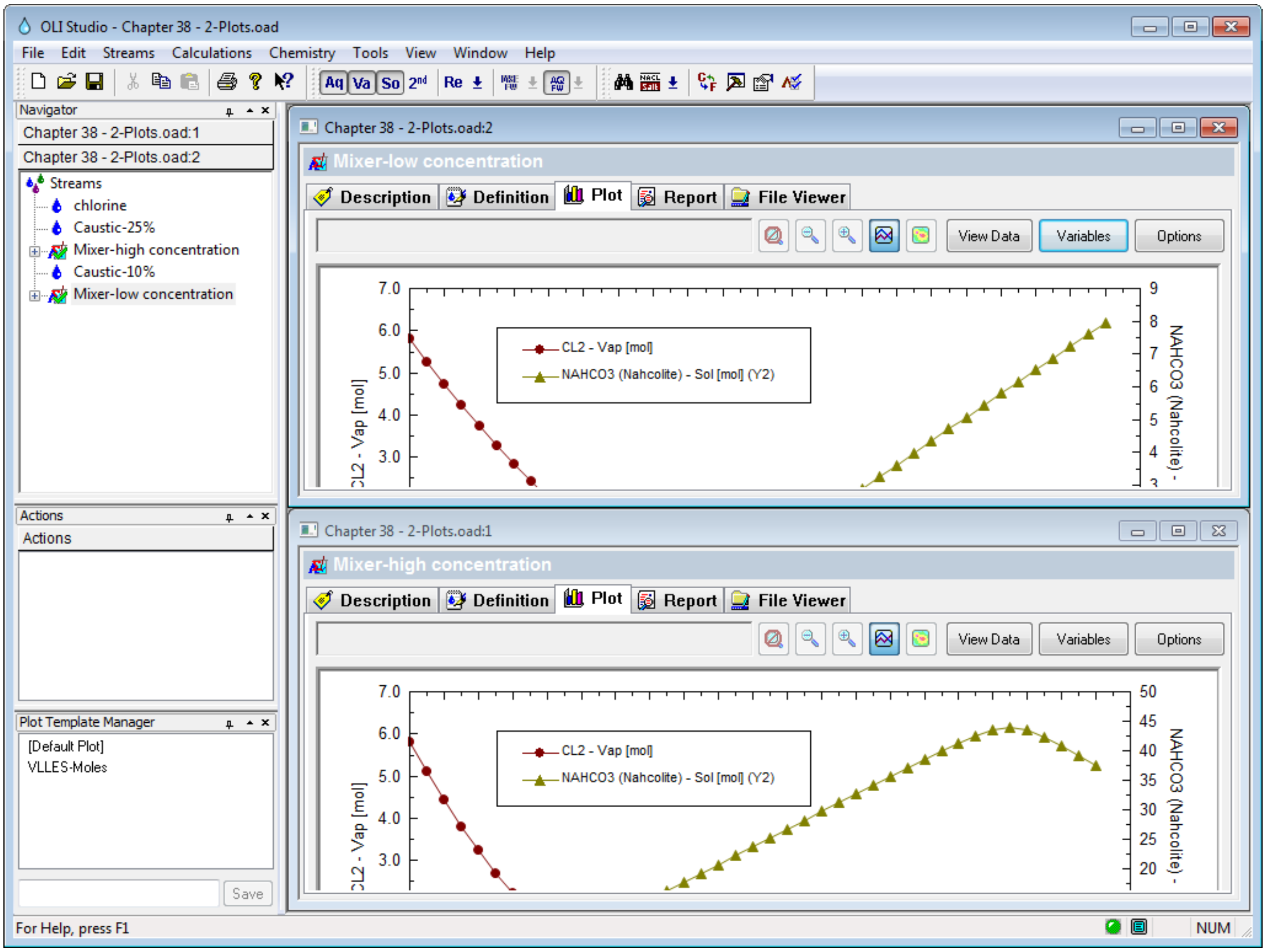


Figure 39-13 The tiled images

One of the limitations of a program such as Microsoft Word is that we are usually constrained by page width. To limit the amount of space we have artificially decreased the width of the OLI Studio window to make it fit on our page. What the user will have to do is resize the images so both fit at the same time.

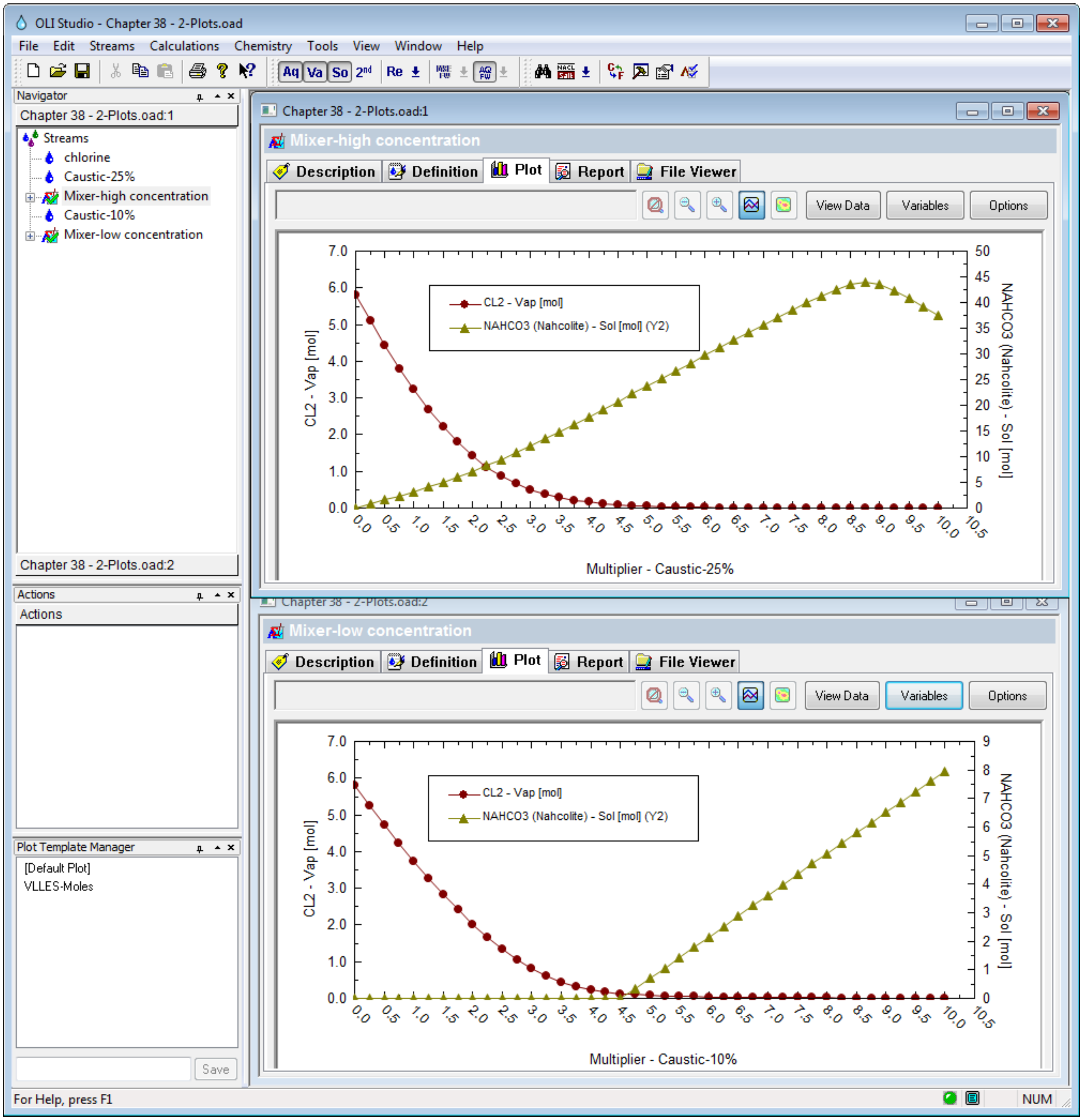


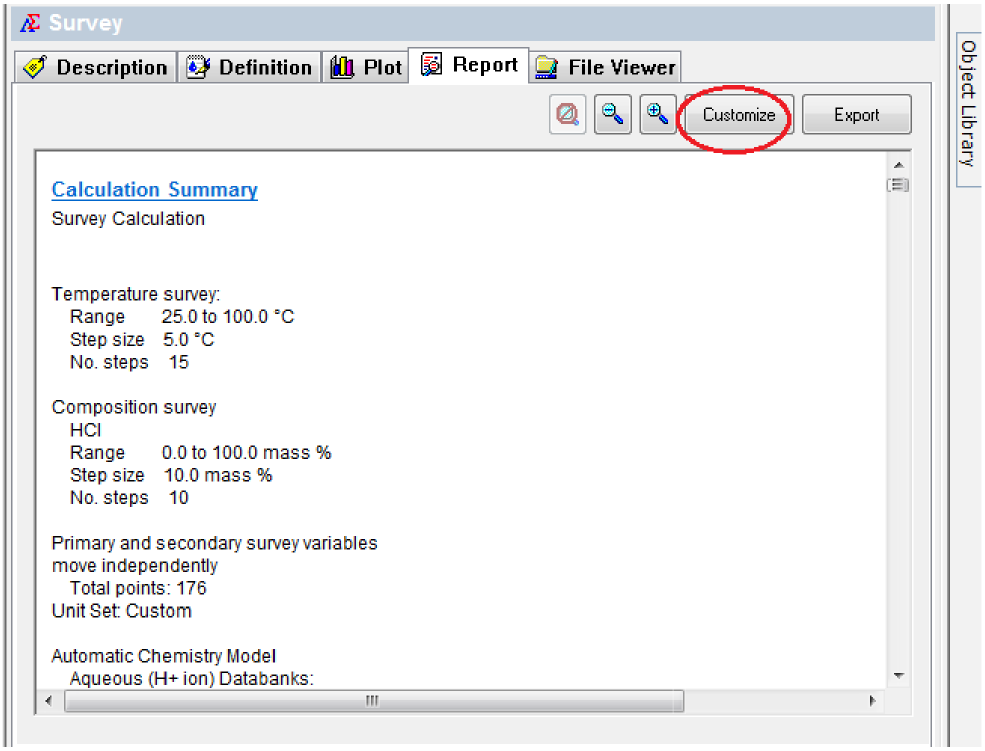
Figure 39-14 Resized Pictures

You will notice that the top window slightly overlaps the bottom window. This was done to make the image fit into Microsoft Word. You will get different results depending on the size of your monitor.

To complete the analysis here the top image is using a more concentrated solution of sodium hydroxide than the other and the formation of the solid sodium bicarbonate appears earlier than in the bottom (lower concentration) display. This may be important if you are designing multi-stage scrubbers.

40. Customizing the Report

The default report does not include some calculated values since they tend not to be used by most users. The extra thermodynamic values such as Gibb's Free Energy as well as diffusivity coefficients are not displayed. To display them click on the **Customize** button.



Calculation Summary
Survey Calculation

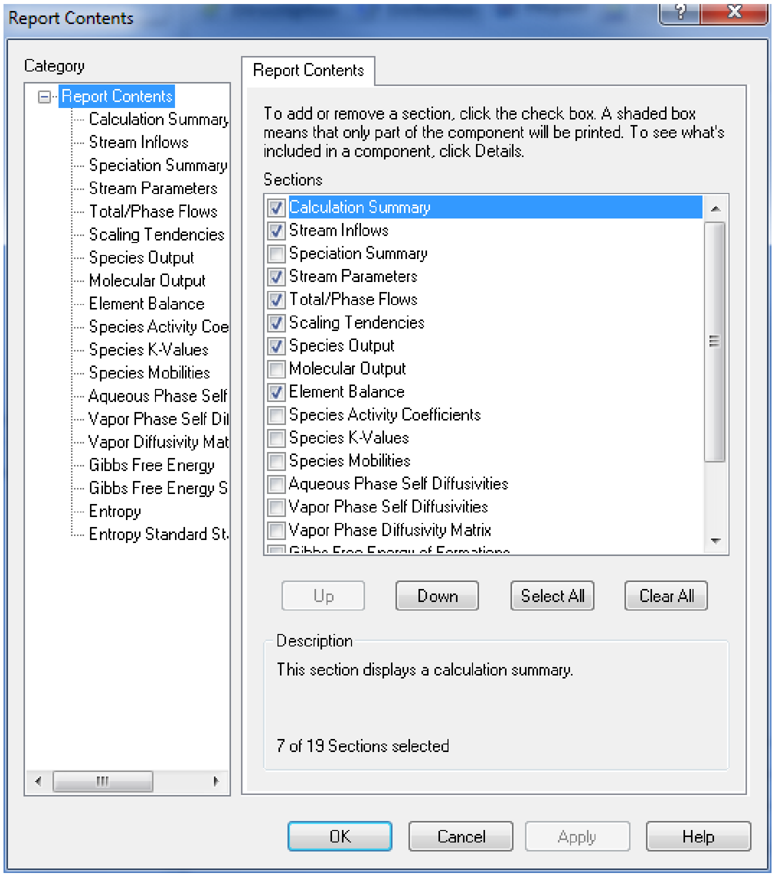
Temperature survey:
Range 25.0 to 100.0 °C
Step size 5.0 °C
No. steps 15

Composition survey
HCl
Range 0.0 to 100.0 mass %
Step size 10.0 mass %
No. steps 10

Primary and secondary survey variables move independently
Total points: 176
Unit Set: Custom

Automatic Chemistry Model
Aqueous (H+ ion) Databanks:

This will display the Report Contents dialog. The categories on the left will allow you to set options for each category. To display the hidden categories you will need to scroll down in the right-hand window.



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

Sections

☑ Calculation Summary
☑ Stream Inflows
☐ Speciation Summary
☑ Stream Parameters
☑ Total/Phase Flows
☑ Scaling Tendencies
☑ Species Output
☐ Molecular Output
☑ Element Balance
☐ Species Activity Coefficients
☐ Species K-Values
☐ Species Mobilities
☐ Aqueous Phase Self Diffusivities
☐ Vapor Phase Self Diffusivities
☐ Vapor Phase Diffusivity Matrix

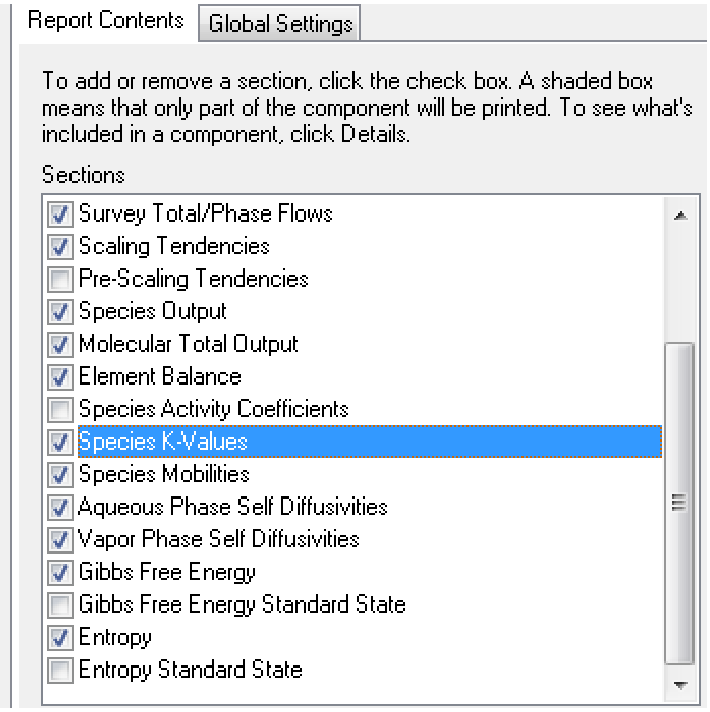
Description

This section displays a calculation summary.

7 of 19 Sections selected

Eventually you will find the unchecked categories.

Check the boxes you wish to display and then click the **OK** button.

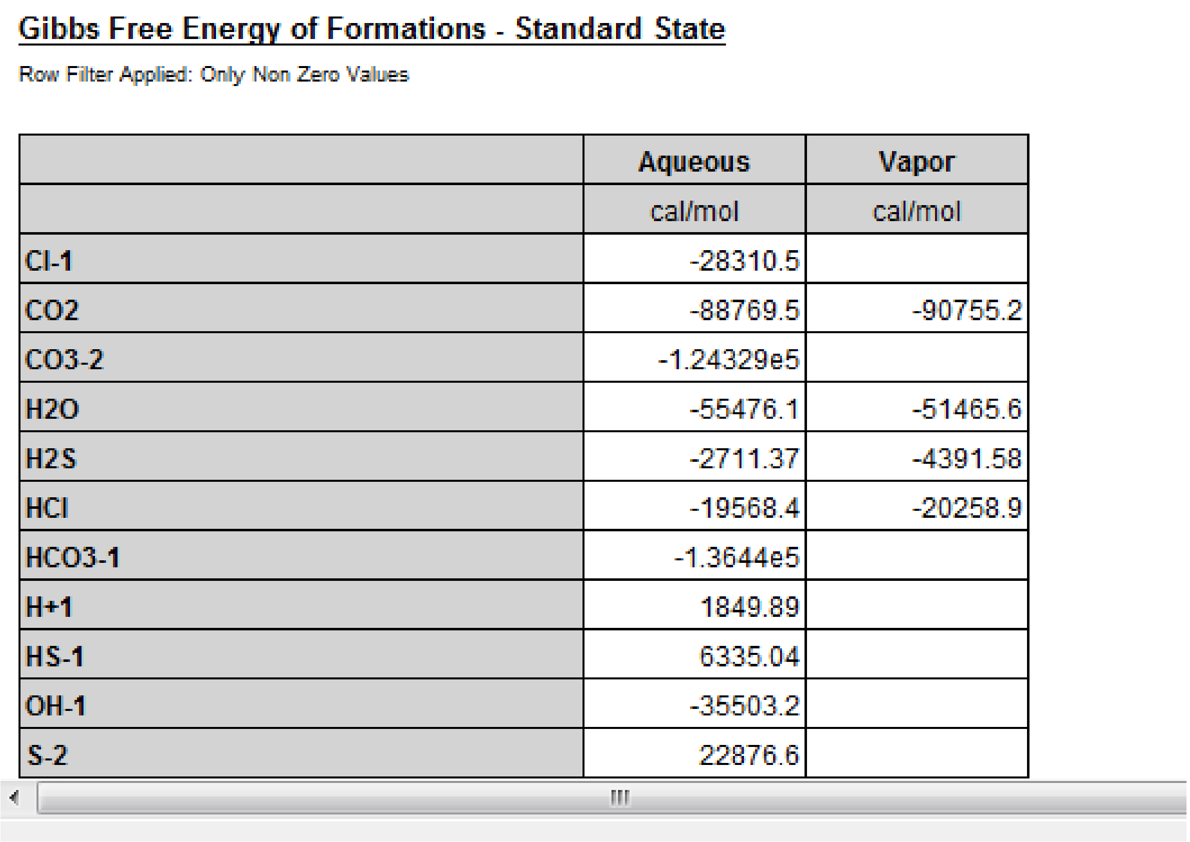


To add or remove a section, click the check box. A shaded box means that only part of the component will be printed. To see what's included in a component, click Details.

Sections

☑ Survey Total/Phase Flows
☑ Scaling Tendencies
☐ Pre-Scaling Tendencies
☑ Species Output
☑ Molecular Total Output
☑ Element Balance
☐ Species Activity Coefficients
☑ Species K-Values
☑ Species Mobilities
☑ Aqueous Phase Self Diffusivities
☑ Vapor Phase Self Diffusivities
☑ Gibbs Free Energy
☐ Gibbs Free Energy Standard State
☑ Entropy
☐ Entropy Standard State

By default, the newly displayed categories will appear at the end of the report. You can use the Customize Button to move these categories higher in the report if you desire.

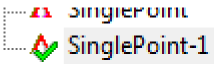


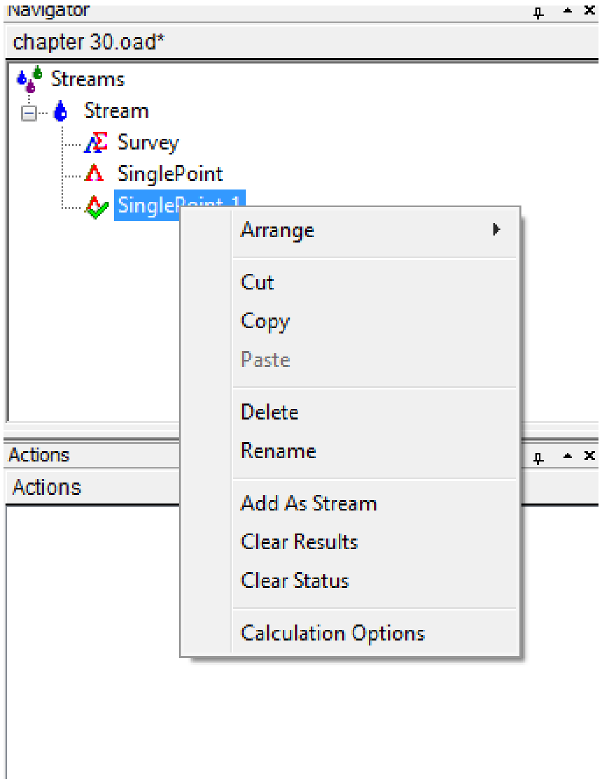
Gibbs Free Energy of Formations - Standard State

Row Filter Applied: Only Non Zero Values

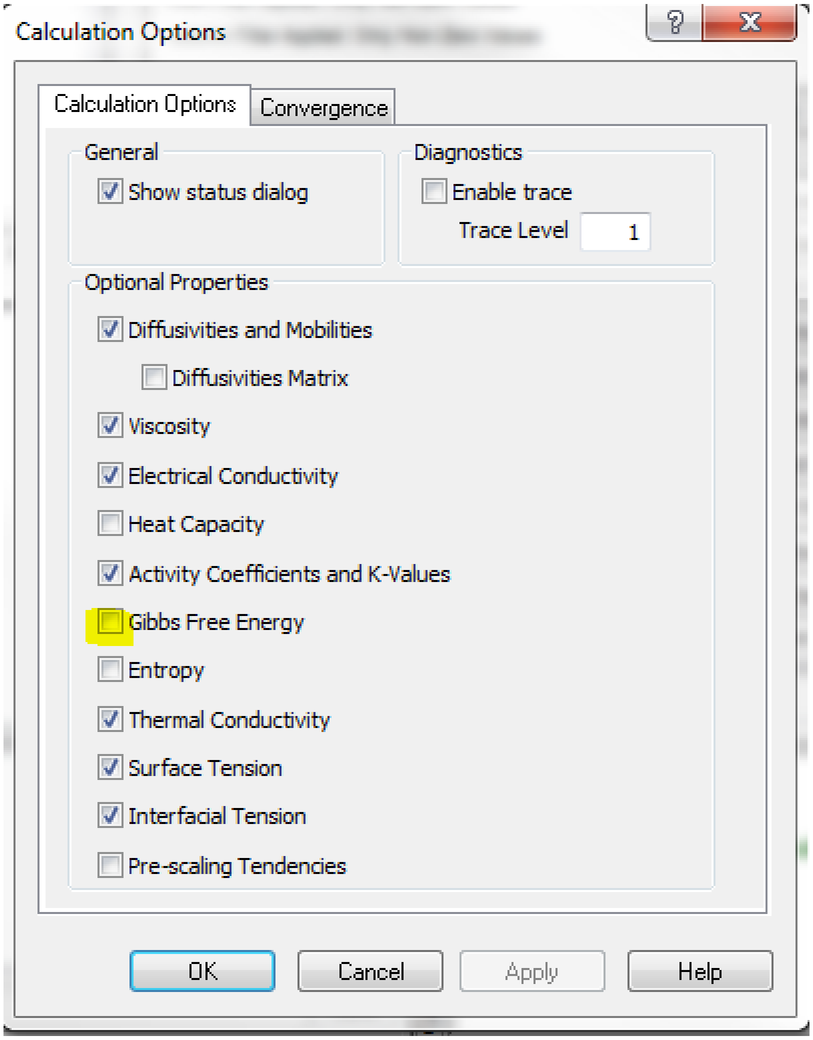
	Aqueous	Vapor
	cal/mol	cal/mol
Cl-1	-28310.5	
CO2	-88769.5	-90755.2
CO3-2	-1.24329e5	
H2O	-55476.1	-51465.6
H2S	-2711.37	-4391.58
HCl	-19568.4	-20258.9
HCO3-1	-1.3644e5	
H+1	1849.89	
HS-1	6335.04	
OH-1	-35503.2	
S-2	22876.6	

If you cannot see the above table, please right click on the single point calculation in the tree diagram under Navigator panel





Click on calculation options



General

☑ Show status dialog

Diagnostics

☐ Enable trace

Trace Level 1

Optional Properties

☑ Diffusivities and Mobilities

☐ Diffusivities Matrix

☑ Viscosity

☑ Electrical Conductivity

☐ Heat Capacity

☑ Activity Coefficients and K-Values

☐ Gibbs Free Energy

☐ Entropy

☑ Thermal Conductivity

☑ Surface Tension

☑ Interfacial Tension

☐ Pre-scaling Tendencies

Make sure you have Gibbs Free Energy selected.

Then you will be able to see Gibbs Free energy in the report tab. Please remember to recalculate.

41. Displaying Transport Properties and Extra Thermodynamic Parameters

Single Point Calculations

The OLI Analyzer program generates a lot of data. The program has attempted to sort out the most important data for you but some values are still hidden. You can expose those values by using the

Plotting two separate graphs at the same time

Frequently it is necessary to see two plots of two different systems at the same time. This is useful when comparing similar results between calculations. In this example, we have the results of a mixer calculation where we are absorbing chlorine into two different caustic (sodium hydroxide) solutions. Each caustic solution is at different concentrations.

You can download a copy of the example file from this location:
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We will now open the file:

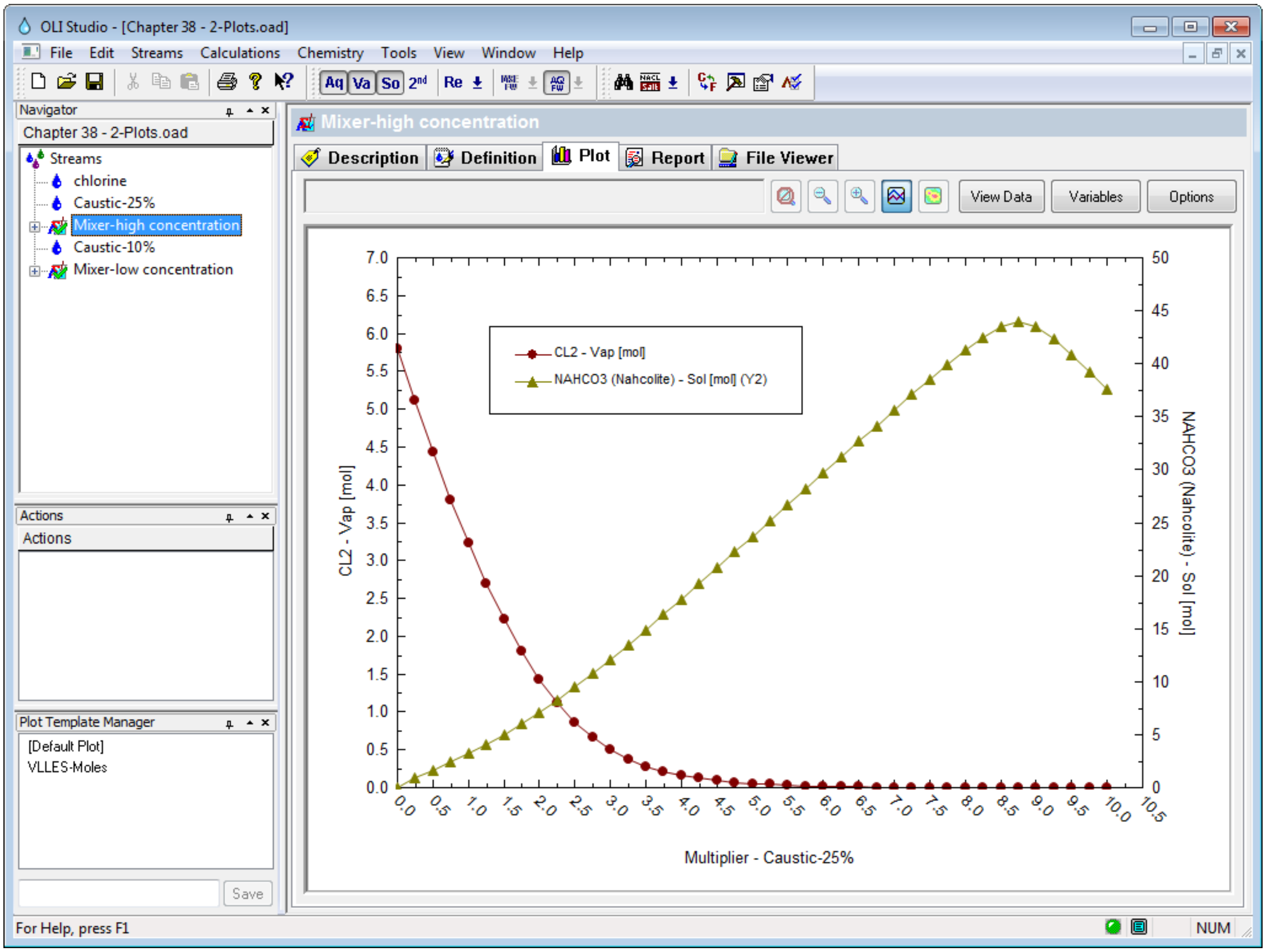


Figure 39-8 Our sample file

We have already set up our plot to display our variables. In this case, we have a 25 weight % caustic solution. It is beyond the scope of this tutorial to explain the chemistry and analysis of this case. We would like to simultaneously see the low concentration case.

To do this select **Window** from the menu line and then select **New Window**.

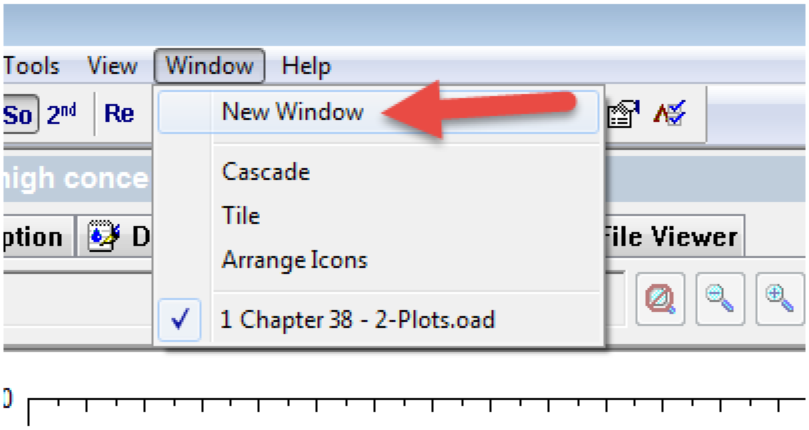
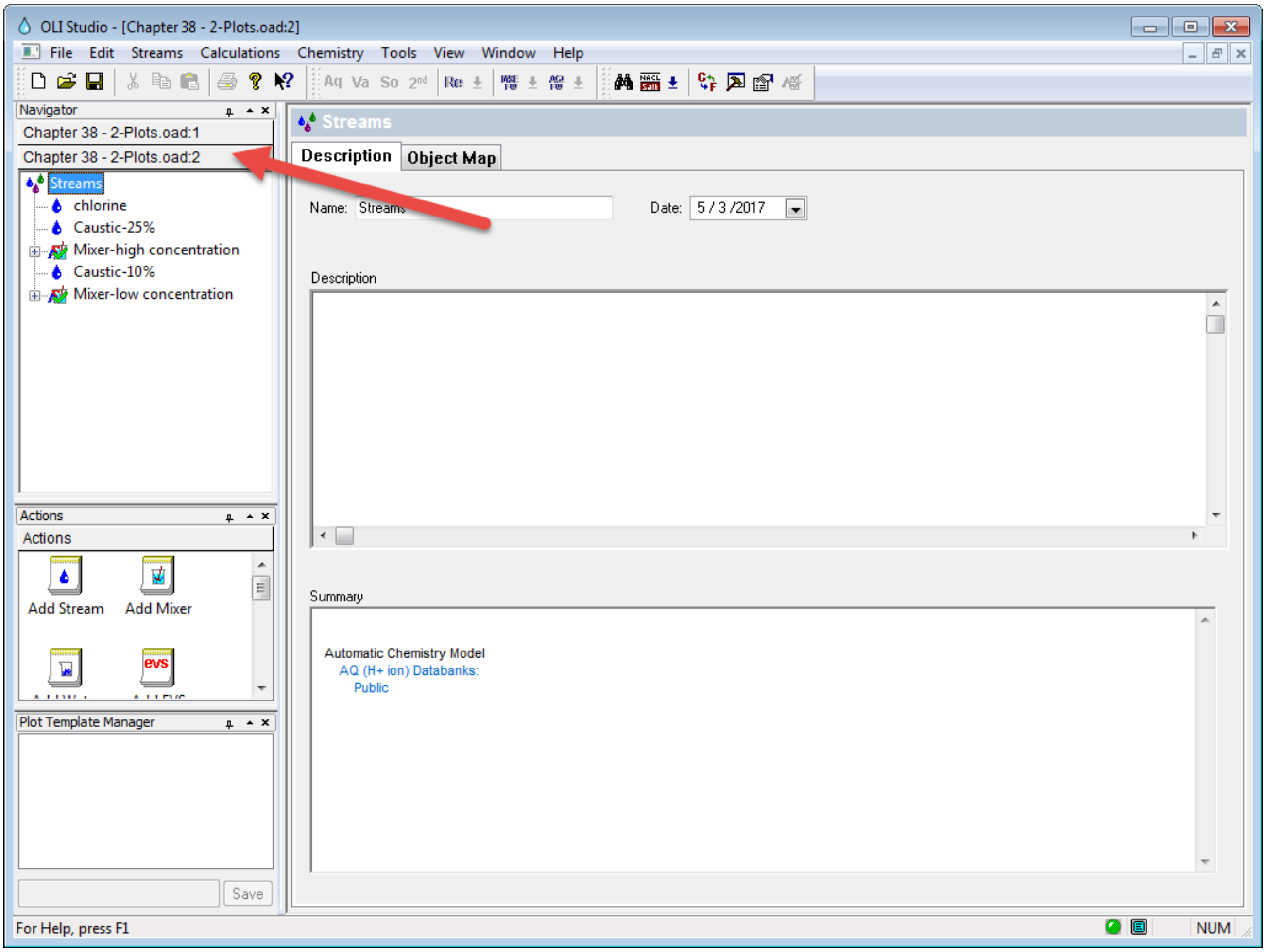


Figure 39-9 Creating a new window

This will create an exact reproduction of the same file. Notice that we have appended a window identifier for each file (the colon :1 or :2 in this case).



Name: Streams

Date: 5 / 3 /2017

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Figure 39-10 The new window

Now we select the other mixer and set up the plot with the same variables as the first plot:

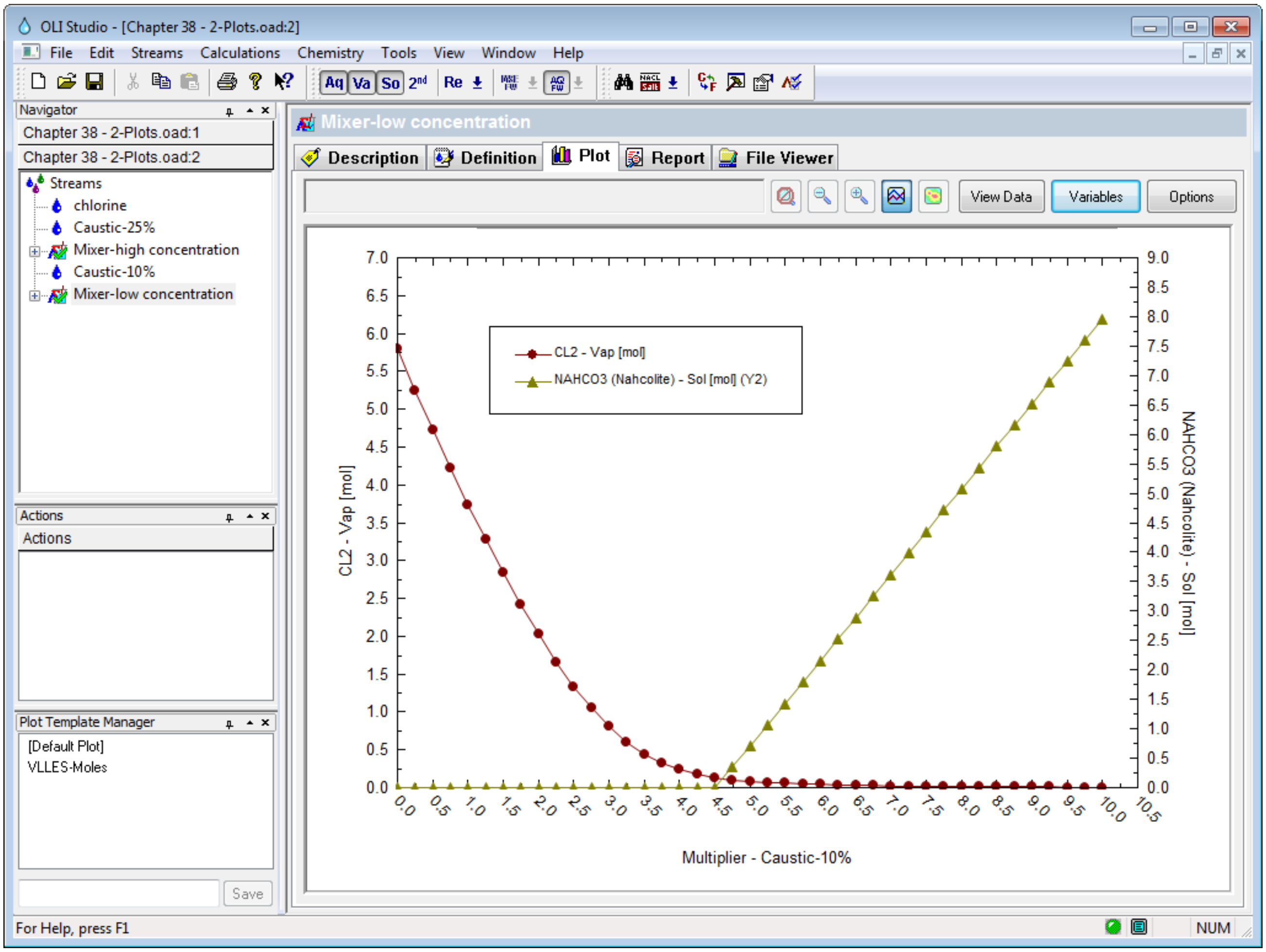


Figure 39-11 Plotting the low concentration case

Now we begin the process of putting both plots on the same display. Reselect **Window** and this time select **Tile**

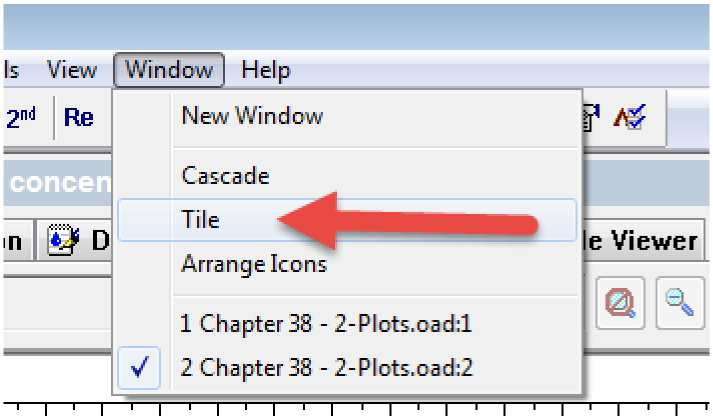


Figure 39-12 Tiling the images

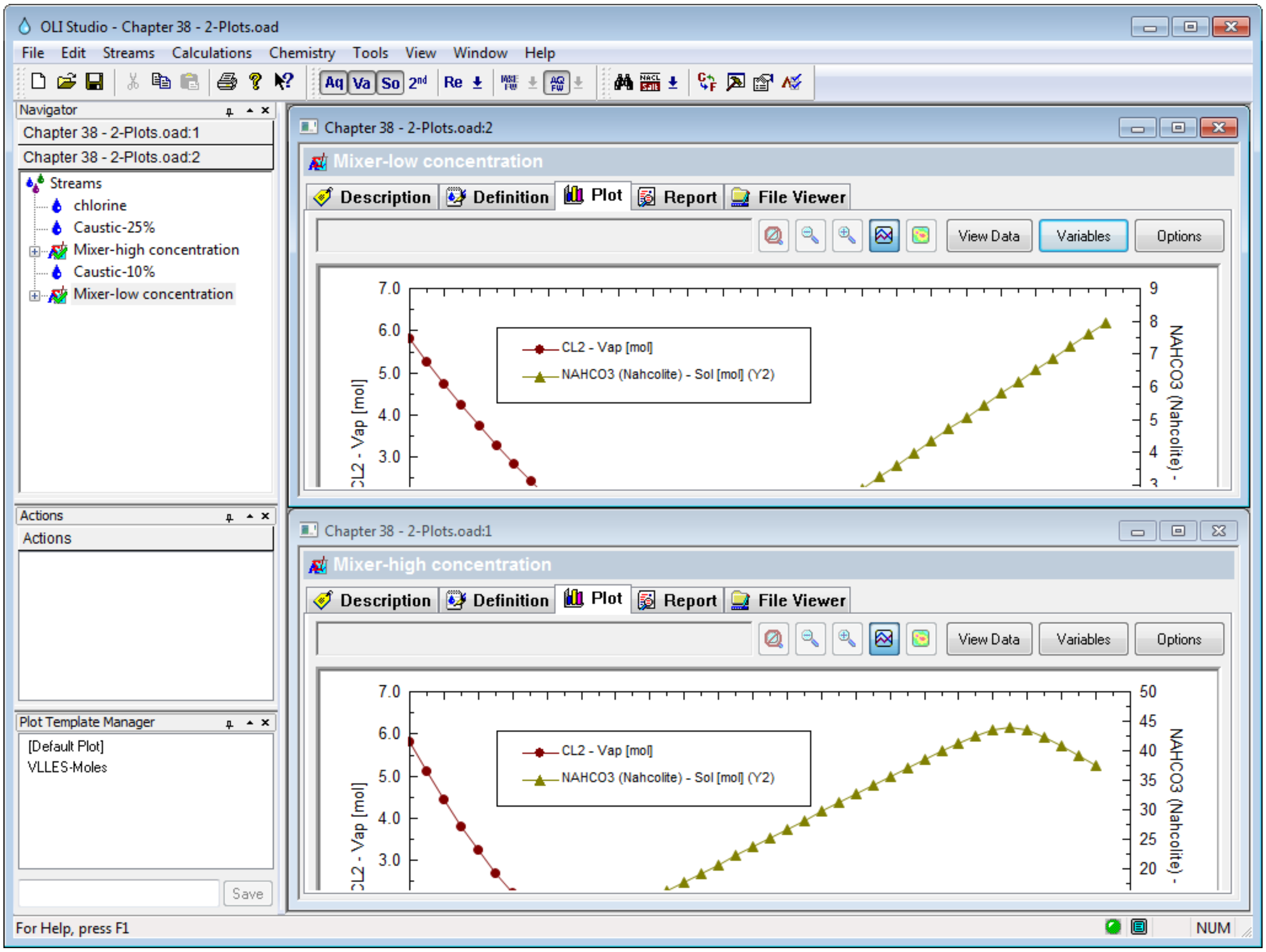


Figure 39-13 The tiled images

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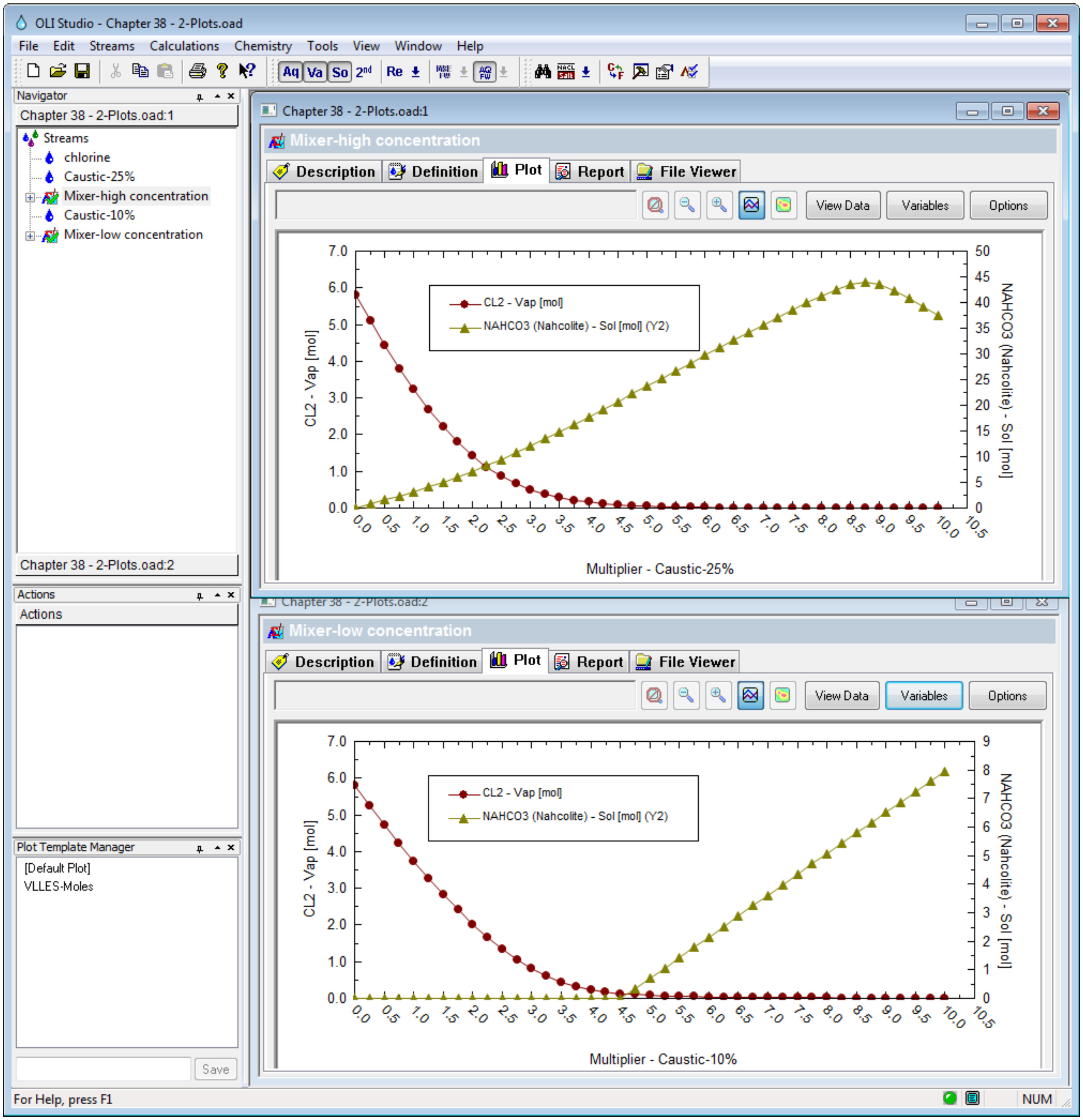


Figure 39-14 Resized Pictures

You will notice that the top window slightly overlaps the bottom window. This was done to make the image fit into Microsoft Word. You will get different results depending on the size of your monitor.

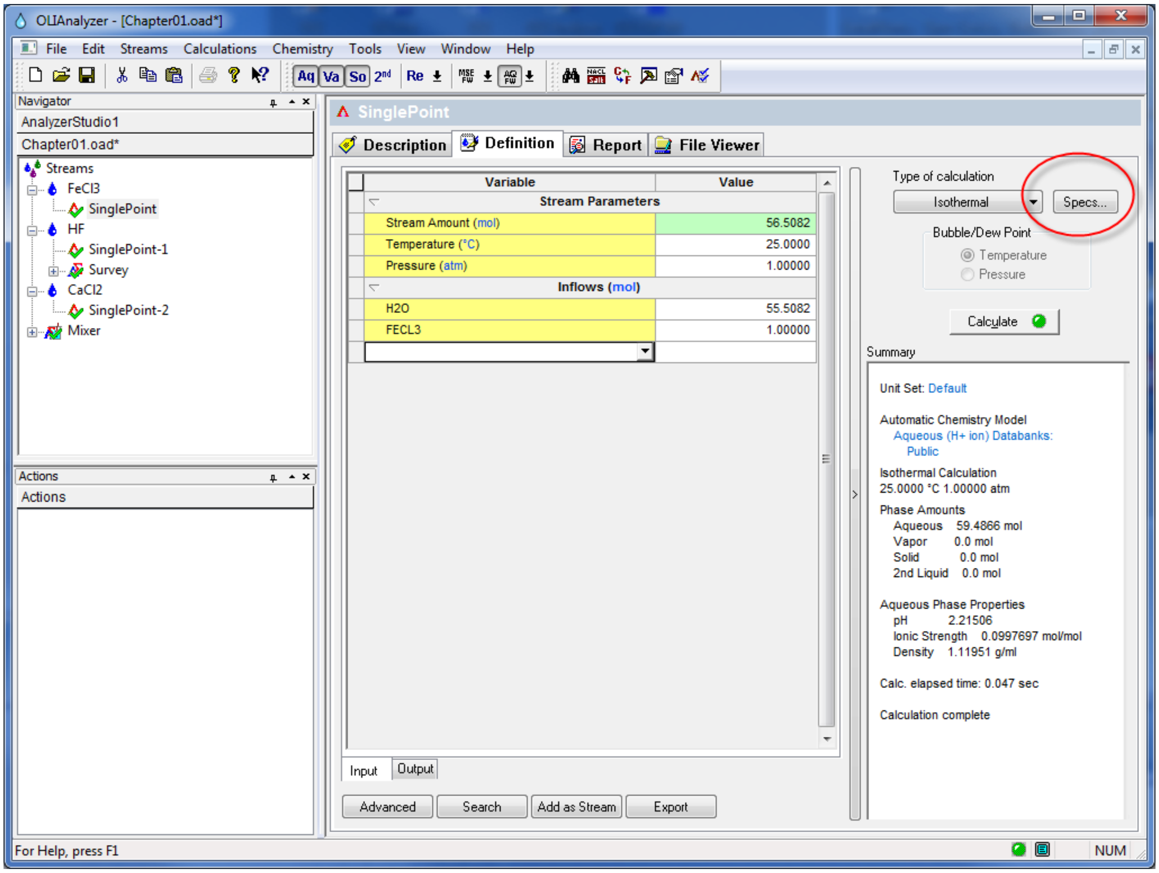
To complete the analysis here the top image is using a more concentrated solution of sodium hydroxide than the other and the formation of the solid sodium bicarbonate appears earlier than in the bottom (lower concentration) display. This may be important if you are designing multi-stage scrubbers.

Customizing the Report as discussed on page 507

Other values, such as the Gibb's Free Energy of a species are not automatically calculated since it can impart a large time burden on the calculation. To enable these types of calculations (Gibb's, Entropy and Heat Capacity) you need to enable them prior to starting the calculation.

For our example we have taken a simple chemistry and created a ***SinglePoint*** calculation.

Click the **Specs...** button to enable the extra thermodynamic calculations.



Variable	Value
Stream Parameters	
Stream Amount (mol)	56.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
FECL3	1.00000

Unit Set: Default

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

Isothermal Calculation
25.0000 °C 1.00000 atm

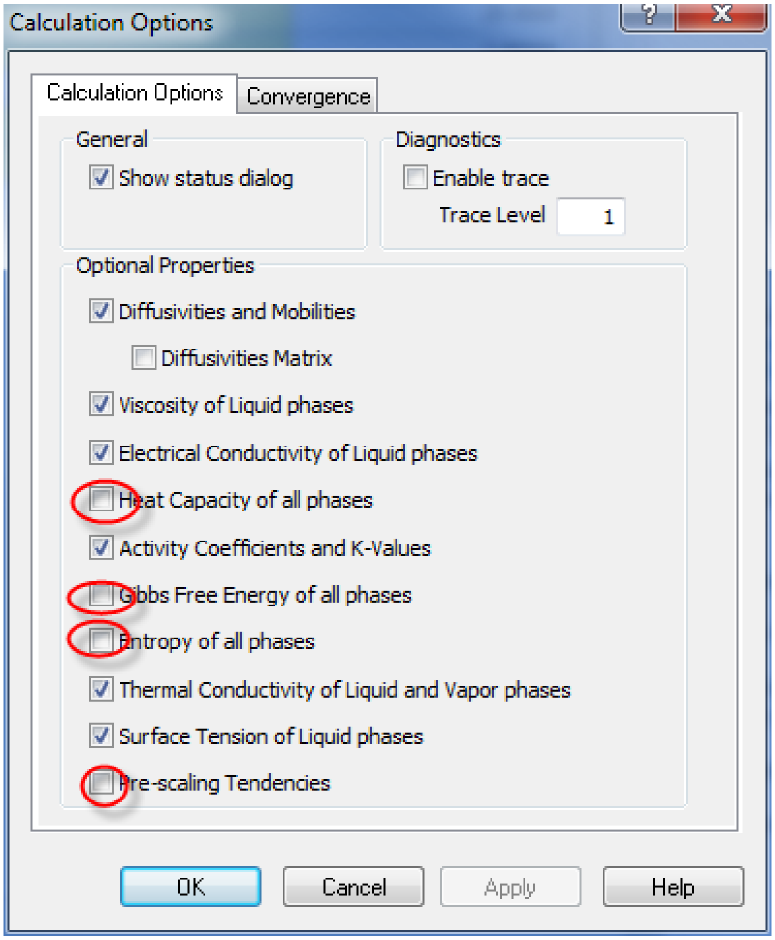
Phase Amounts
Aqueous 59.4866 mol
Vapor 0.0 mol
Solid 0.0 mol
2nd Liquid 0.0 mol

Aqueous Phase Properties
pH 2.21506
Ionic Strength 0.0997697 mol/mol
Density 1.11951 g/ml

Calc. elapsed time: 0.047 sec

Calculation complete

This will display the Calculation Options dialog. You will notice that we have left unchecked those calculations which take extra time to complete. You can enable any or all of them by checking the box.



General

☑ Show status dialog

Diagnostics

☐ Enable trace

Trace Level 1

Optional Properties

☑ Diffusivities and Mobilities

  ☐ Diffusivities Matrix

☑ Viscosity of Liquid phases

☑ Electrical Conductivity of Liquid phases

☐ Heat Capacity of all phases

☑ Activity Coefficients and K-Values

☐ Gibbs Free Energy of all phases

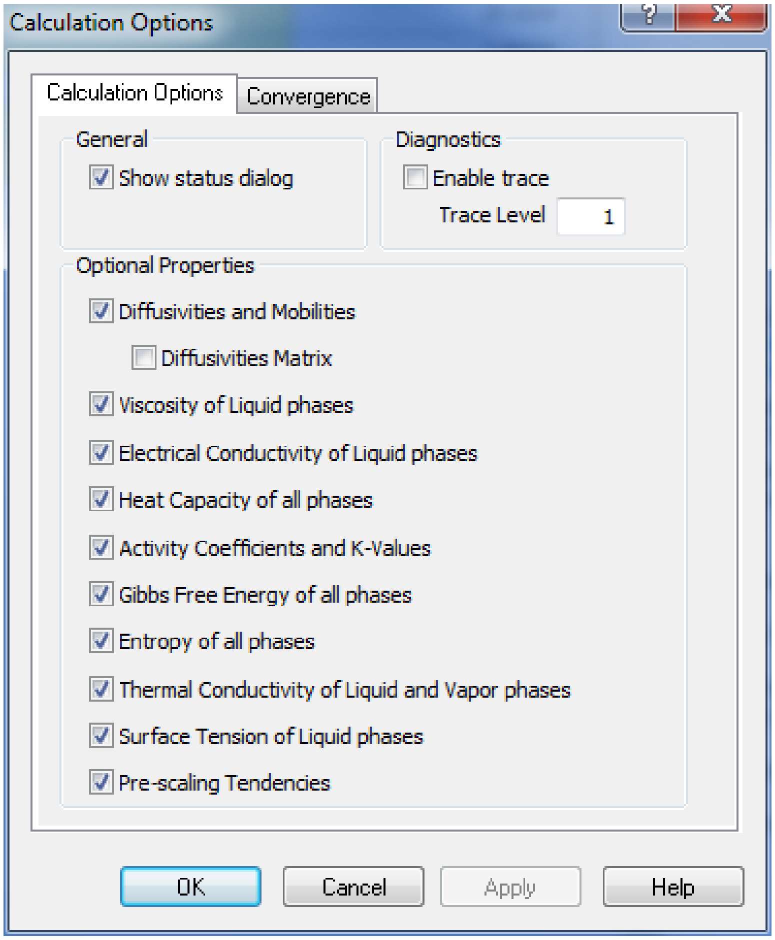
☐ Entropy of all phases

☑ Thermal Conductivity of Liquid and Vapor phases

☑ Surface Tension of Liquid phases

☐ Pre-scaling Tendencies

Here we have enabled all of the extra calculations.



General

☑ Show status dialog

Diagnostics

☐ Enable trace

Trace Level 1

Optional Properties

☑ Diffusivities and Mobilities

☐ Diffusivities Matrix

☑ Viscosity of Liquid phases

☑ Electrical Conductivity of Liquid phases

☑ Heat Capacity of all phases

☑ Activity Coefficients and K-Values

☑ Gibbs Free Energy of all phases

☑ Entropy of all phases

☑ Thermal Conductivity of Liquid and Vapor phases

☑ Surface Tension of Liquid phases

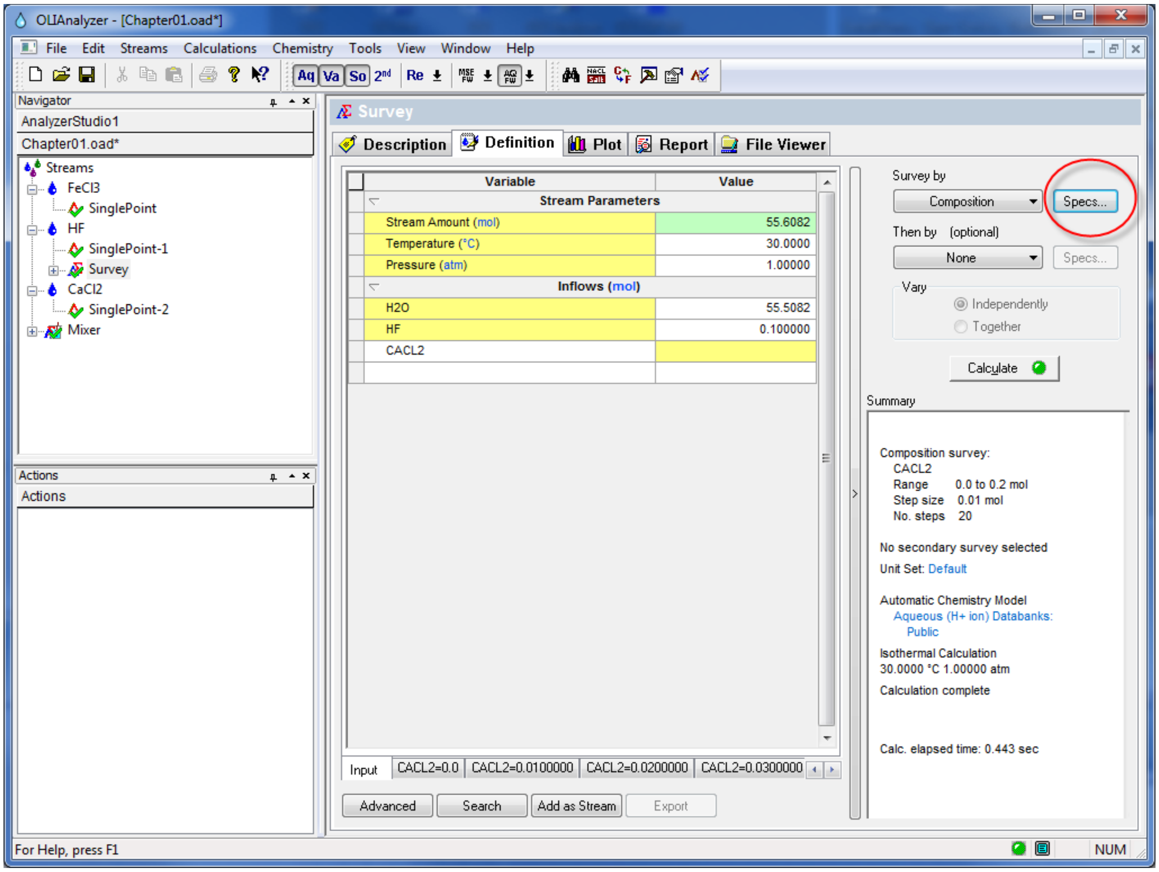
☑ Pre-scaling Tendencies

Click the **OK** button to continue

Click the **Calculate** button to continue. When the program finishes click on the **Report** tab and then the **Customize** button to enable the new values to be displayed.

Survey Calculations

To specify the extra thermodynamic values in a survey you need to follow similar steps as with the single point calculation. Here we have added a temperature survey. Click the **Specs...** button to add the additional calculations.



Survey by: Composition
Then by (optional): None

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6082
Temperature (°C)	30.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
HF	0.100000
CACL2	

Composition survey:
CACL2
Range 0.0 to 0.2 mol
Step size 0.01 mol
No. steps 20

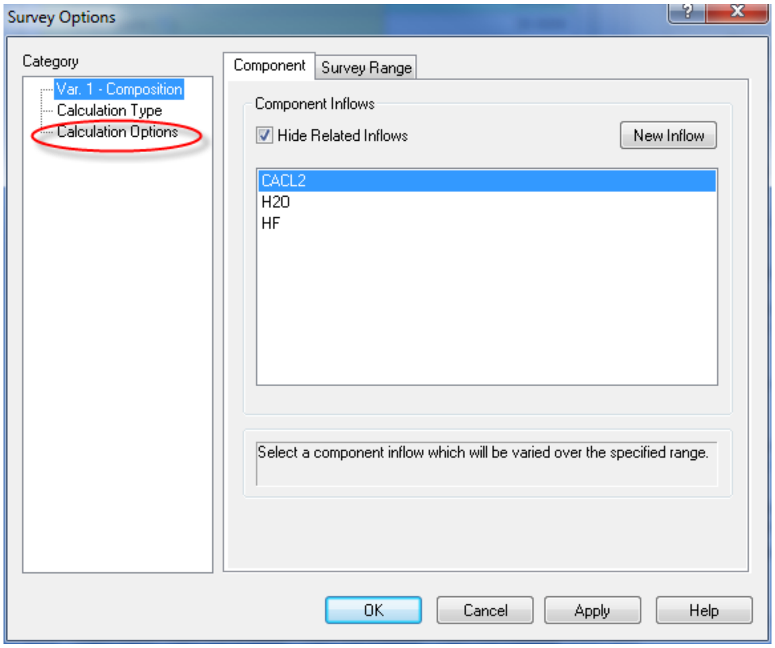
No secondary survey selected
Unit Set: Default

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

Isothermal Calculation
30.0000 °C 1.00000 atm
Calculation complete

Calc. elapsed time: 0.443 sec

The Survey Options dialog is different from the single point dialog. You now must select **Calculation Options** to select the new calculations.

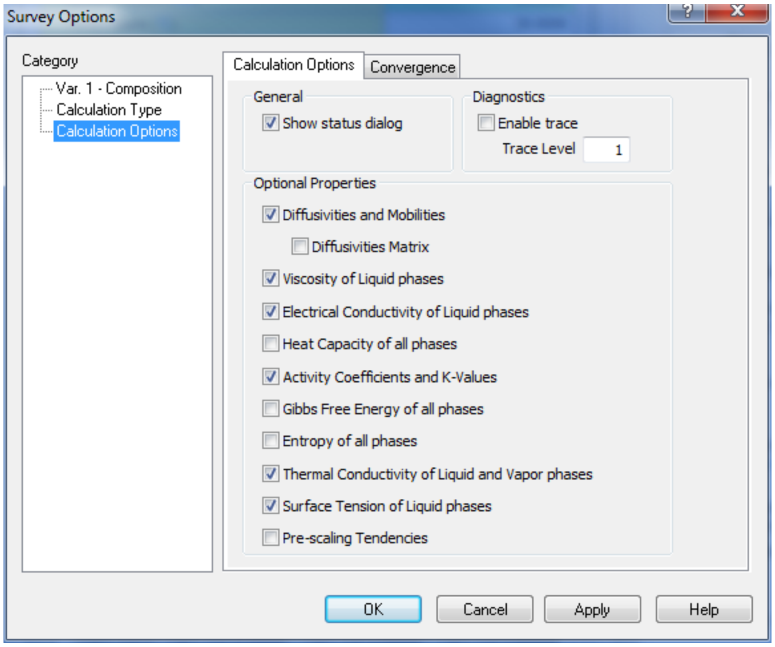


☑ Hide Related Inflows

CACL2
H2O
HF

Select a component inflow which will be varied over the specified range.

Once selected, the Calculation Options dialog is very similar to the single point dialog. Select the desired values. You will need to calculate (or recalculate) the survey when you are done.



Survey Options

Category

- Var. 1 - Composition
- Calculation Type
- Calculation Options

Calculation Options | Convergence

General

☑ Show status dialog

Diagnostics

☐ Enable trace

Trace Level 1

Optional Properties

☑ Diffusivities and Mobilities

☐ Diffusivities Matrix

☑ Viscosity of Liquid phases

☑ Electrical Conductivity of Liquid phases

☐ Heat Capacity of all phases

☑ Activity Coefficients and K-Values

☐ Gibbs Free Energy of all phases

☐ Entropy of all phases

☑ Thermal Conductivity of Liquid and Vapor phases

☑ Surface Tension of Liquid phases

☐ Pre-scaling Tendencies

42. Using the OLI Tester

Overview

The OLI Tester is an internal program used to compare results from the current version of the tester with previous versions. The results are stored in a database for easy comparisons. The OLI Tester is a separately licensed program and requires a new or updated serial number.

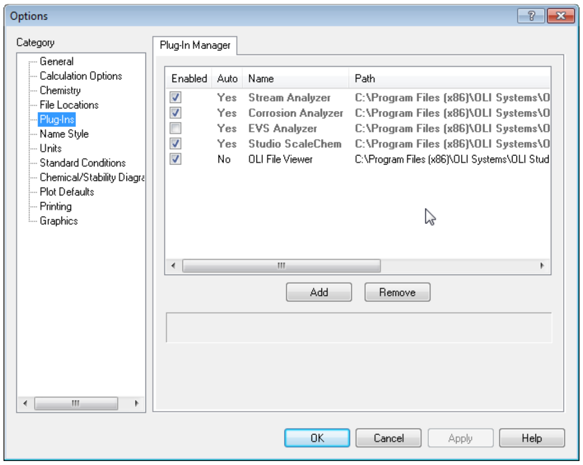
This section covers the installation and use of the OLI Tester in both single point and multiple point (surveys) calculations. The tester does not work with Stream Analyzer mixer calculations nor with ScaleChem objects.

Installation and Activation

The default installation does not include the OLI Tester. To check if OLI Tester is enabled you need to first go to the plug-ins menu.

Activating the Tester

The plug-ins menu is found from **Tools | Options | Category: Plug-ins**

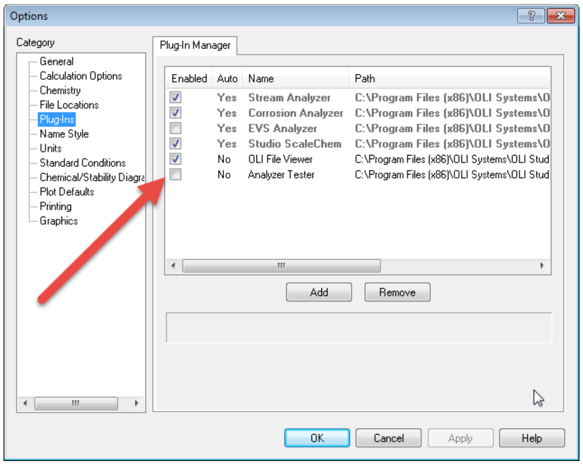


Enabled	Auto	Name	Path
☑	Yes	Stream Analyzer	C:\Program Files (x86)\OLI Systems\O
☑	Yes	Corrosion Analyzer	C:\Program Files (x86)\OLI Systems\O
☐	Yes	EVS Analyzer	C:\Program Files (x86)\OLI Systems\O
☑	Yes	Studio ScaleChem	C:\Program Files (x86)\OLI Systems\O
☑	No	OLI File Viewer	C:\Program Files (x86)\OLI Systems\OLI Stud

Figure 42-1 Default Plug-Ins menu

There is no mention of the **OLI Tester** in this list so you will need to contact OLI Systems for an updated serial number. A complete re-install of the software is required.

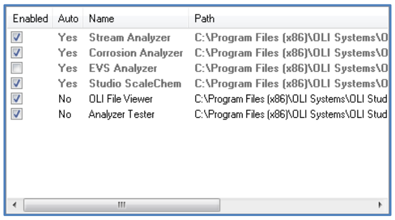
In the next image, OLI has installed the software with an updated serial number that enables the OLI Tester.



Enabled	Auto	Name	Path
☑	Yes	Stream Analyzer	C:\Program Files (x86)\OLI Systems\O
☑	Yes	Corrosion Analyzer	C:\Program Files (x86)\OLI Systems\O
☐	Yes	EVS Analyzer	C:\Program Files (x86)\OLI Systems\O
☑	Yes	Studio ScaleChem	C:\Program Files (x86)\OLI Systems\O
☑	No	OLI File Viewer	C:\Program Files (x86)\OLI Systems\OLI Stud
☐	No	Analyzer Tester	C:\Program Files (x86)\OLI Systems\OLI Stud

Figure 42-2 OLI Tester has been installed

Check the box to enable the OLI Tester.



Enabled	Auto	Name	Path
☑	Yes	Stream Analyzer	C:\Program Files (x86)\OLI Systems\O
☑	Yes	Corrosion Analyzer	C:\Program Files (x86)\OLI Systems\O
☐	Yes	EVS Analyzer	C:\Program Files (x86)\OLI Systems\O
☑	Yes	Studio ScaleChem	C:\Program Files (x86)\OLI Systems\O
☑	No	OLI File Viewer	C:\Program Files (x86)\OLI Systems\OLI Stud
☑	No	Analyzer Tester	C:\Program Files (x86)\OLI Systems\OLI Stud

Figure 42-3 OLI Tester enabled

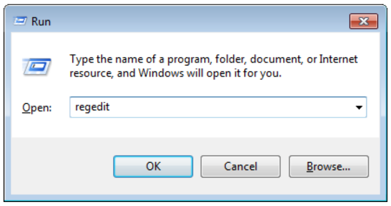
Please close the OLI Studio program.

Activating the Tester for multiple point surveys

The default activation for the OLI Tester does not enable multiple point surveys to be tested. This is an unfortunate condition but it can be remedied with a modification to the computer's registry.

Warning! Modifying your computer's registry settings can cause irreparable harm to your computer, proceed at your own risk.

Use the Windows Run command (Windows key + R) and enter the **Regedit** command.



Type the name of a program, folder, document, or Internet resource, and Windows will open it for you.

Open: regedit

Figure 42-4 entering the registry editor command

This will display the registry editor

Navigate to the key:

HKEY_CURRENT_USER\Software\OLI Systems\OLI Studio 9.5

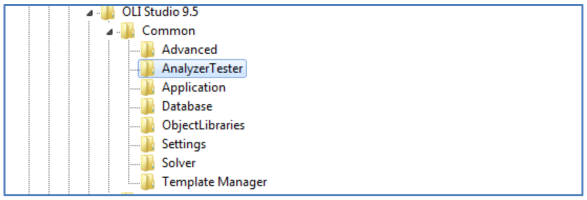
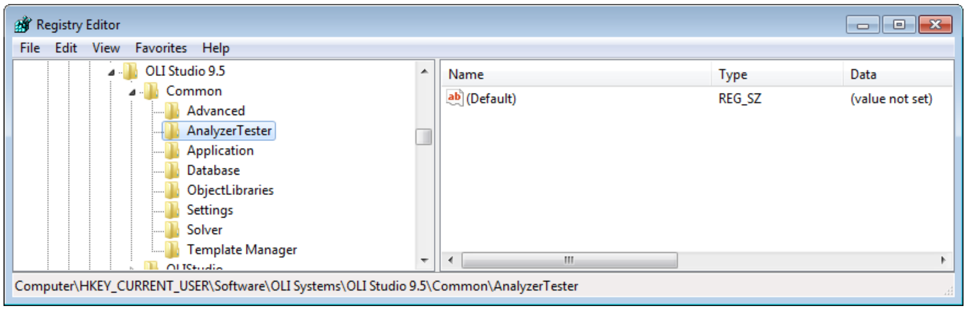


Figure 42-5 Navigating to the OLI Tester key

Click on the **AnalyerTester** key. In the right-hand window there should be only the default value:

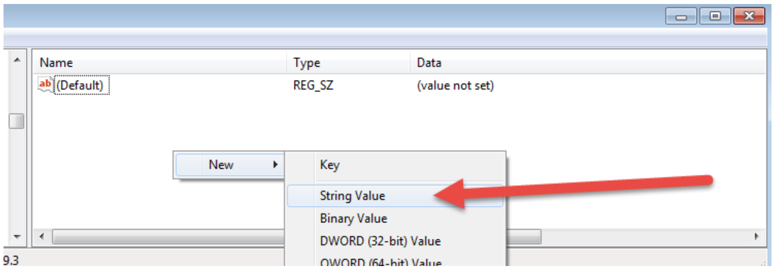


Name	Type	Data
(Default)	REG_SZ	(value not set)

Computer\HKEY_CURRENT_USER\Software\OLI Systems\OLI Studio 9.5\Common\AnalyzerTester

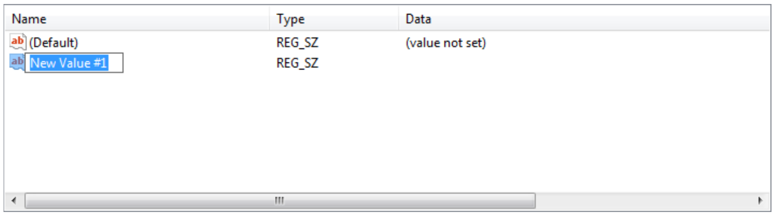
Figure 42-6 Default key value

Right-click in the right-hand windows and select **New | String Value**



Name	Type	Data
(Default)	REG_SZ	(value not set)

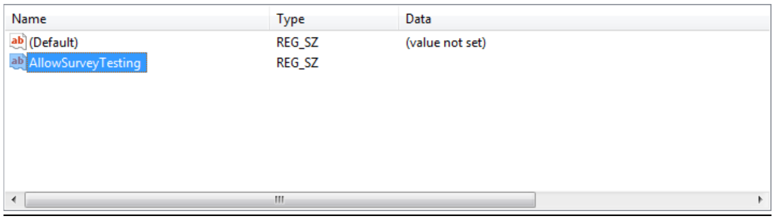
Figure 42-7 Selecting a new string value



Name	Type	Data
(Default)	REG_SZ	(value not set)
New Value #1	REG_SZ	

Figure 42-8 Creating a new variable

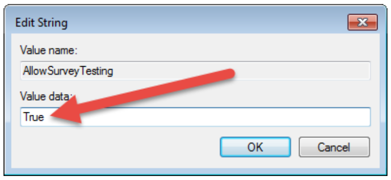
Rename the ***New Value #1*** variable to ***AllowSurveyTesting***



Name	Type	Data
(Default)	REG_SZ	(value not set)
AllowSurveyTesting	REG_SZ	

Figure 42-9 Renamed variable, spelling counts!

Double-click the new variable name ***AllowSurveyTesting*** and this will display a new dialog:



Value name:
AllowSurveyTesting

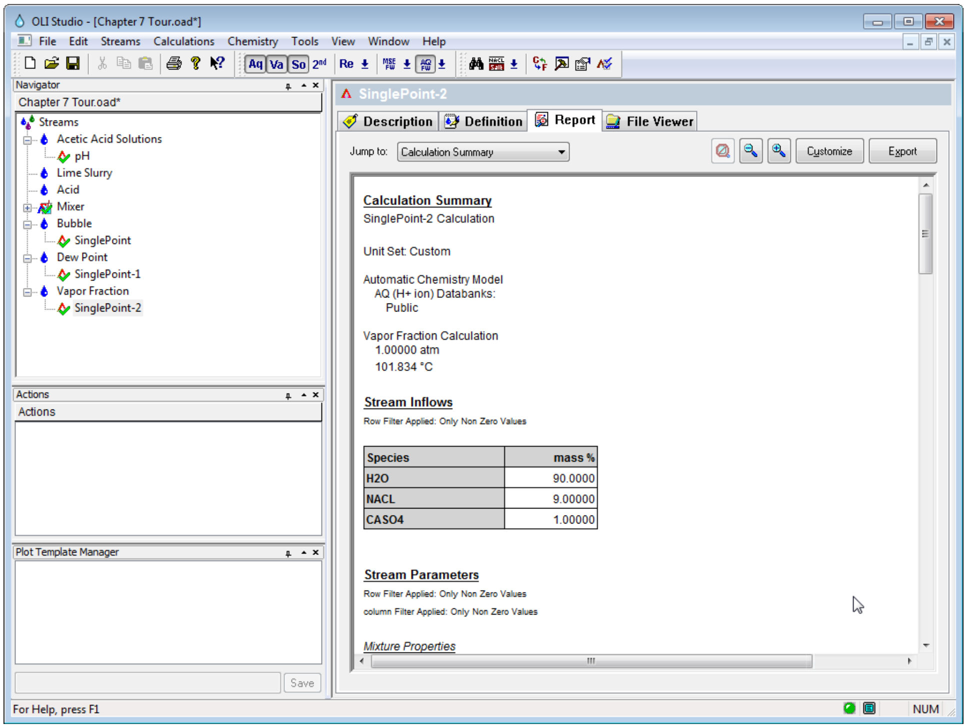
Value data:
True

Figure 42-10 Enter "True" in the blank box

Close the Registry Editor

Starting and Setting up the OLI Tester for the First Time

Now that the OLI Tester has been enabled we need to create the first database to store our data. Start the OLI Studio program as you would normally.



Calculation Summary
SinglePoint-2 Calculation

Unit Set: Custom

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Vapor Fraction Calculation
1.00000 atm
101.834 °C

Stream Inflows
Row Filter Applied: Only Non Zero Values

Species	mass %
H2O	90.0000
NACL	9.00000
CASO4	1.00000

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

Mixture Properties

Figure 42-11 Starting a case

For this example, we are using the Chapter 7 files created earlier in this manual. You can download the completed file from this link: http://wiki.olisystems.com/wiki/images/d/dc/Chapter_7_Tour.zip.

We need to create a database. Select **Tools | Analyzer Tester | Select Tester Database**

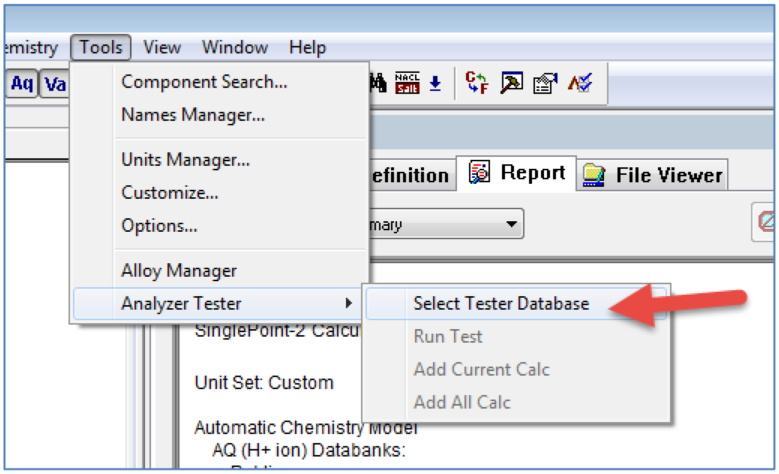
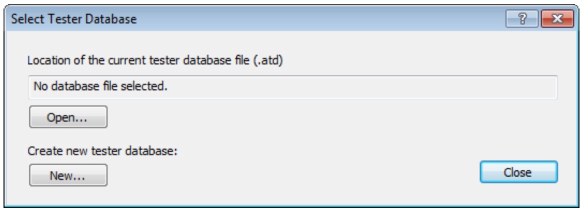


Figure 42-12 selecting the database

This will display a new dialog to either open a database or create a new database.



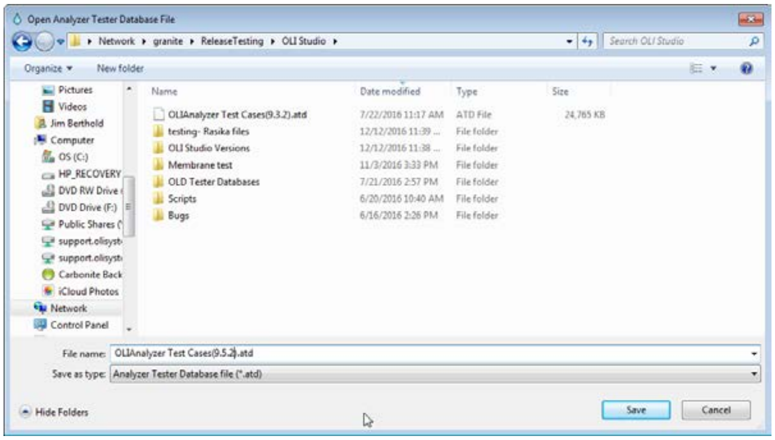
Location of the current tester database file (.atd)

No database file selected.

Create new tester database:

Figure 42-13 Database selection dialog

For this example, click the **New…** button.



Name	Date modified	Type	Size
OLIAnalyzer Test Cases(9.3.2).atd	7/22/2016 11:17 AM	ATD File	24,765 KB
testing- Rasika files	12/12/2016 11:39 ...	File folder	
OLI Studio Versions	12/12/2016 11:38 ...	File folder	
Membrane test	11/3/2016 3:33 PM	File folder	
OLD Tester Databases	7/21/2016 2:57 PM	File folder	
Scripts	6/20/2016 10:40 AM	File folder	
Bugs	6/16/2016 2:26 PM	File folder	

File name: OLIAnalyzer Test Cases(9.5.2).atd

Save as type: Analyzer Tester Database file (*.atd)

Figure 42-14 Determining a location for your database

You can place your database anywhere you have access and name it anything that makes sense to you. OLI uses many different people to test the software so a centralized location has been chosen. In this case a server location. We also name the database in some manner that indicates the source of the original data, in this case version 9.5.2 of the software. The name is arbitrary and should make sense to you. You may notice that we have a version 9.3.2 database located in this folder. This will be used in a subsequent portion of this chapter.

Click the **Save** button when ready.

Adding Single Point Calculations to the Database

In the example on page 534 you will notice that each object has already been calculated as noted by the green check mark. This means those results are now available to the database (remember mixers do not work in the tester so you cannot add them).

Click the ‘pH’ calculation

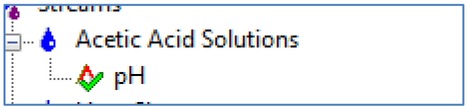


Figure 42-15 Clicking the object

Now select **Tools | Analyzer Tester | Add Current Calc**

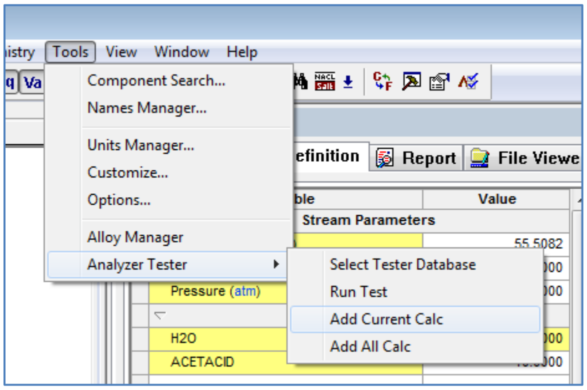


Figure 42-16 Adding the current calculation

This adds the currently selected calculation to the database. You can also add all the calculations to the database now but you may want to be selective in what is added.

For this example, we have added all the calculations to the database. You do not have to save the base file if you do not require it.

Adding Multiple Point Calculations (Surveys) to the Database

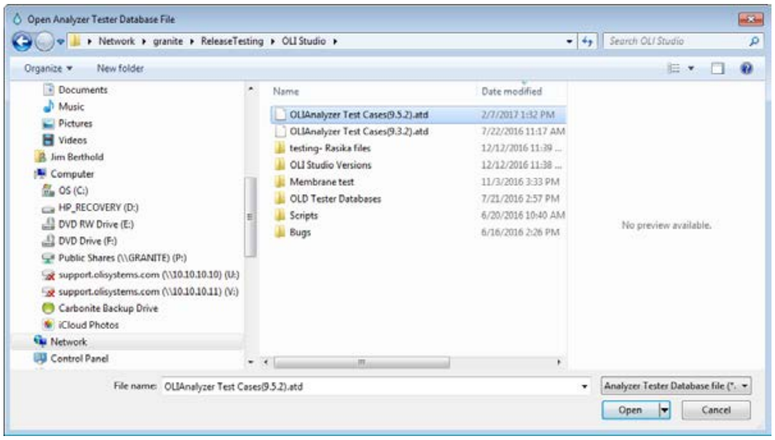
Adding surveys to the database is done in much the same way as single point calculations. In this example, we are using the file created from chapter 8 earlier in this guide. You can download the example file from: http://wiki.olisystems.com/wiki/images/0/0a/Chapter_8_Tour.zip

If you kept the file open from the previous section, then there is no need to reselect the database. Otherwise you will need to open the database you wish to add the cases.

Adding to an existing database

After opening your file, select **Tools | Analyzer Tester | Select Tester Database.** Select **Open…** (refer to Figure 42-12 through Figure 42-14).

Here we are opening the 9.5.2 file we created earlier:



Name	Date modified
OLIAnalyzer Test Cases(9.5.2).atd	2/7/2017 1:32 PM
OLIAnalyzer Test Cases(9.3.2).atd	7/22/2016 11:17 AM
testing- Rasika files	12/12/2016 11:39 ...
OLI Studio Versions	12/12/2016 11:38 ...
Membrane test	11/3/2016 3:33 PM
OLD Tester Databases	7/21/2016 2:57 PM
Scripts	6/20/2016 10:40 AM
Bugs	6/16/2016 2:26 PM

File name: OLIAnalyzer Test Cases(9.5.2).atd

Figure 42-17 Opening an existing database

Remember mixer objects and contour plots cannot be saved to the database. Select a survey and add it to the database. In this example, we are picking the first survey in the file:

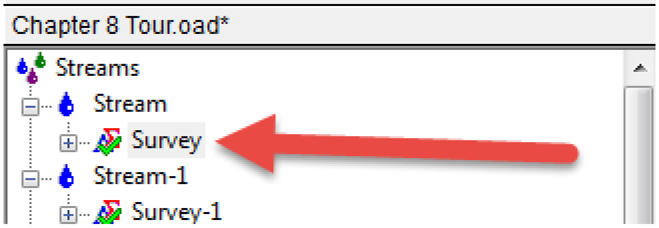


Figure 42-18 Selecting a survey

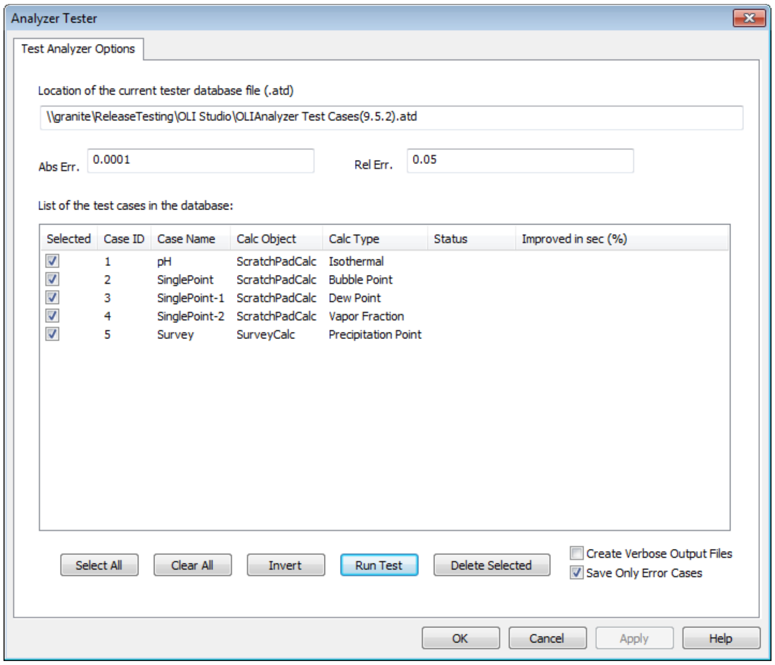
Now select **Tools | Analyzer Tester | Add Current Calc** (refer to Figure 42-16 on page 536).

The tester automatically updates and saves with the results.

Running the Tester

Running the tester is very straight forward. You first need to start with a blank OLI Studio file. Next you need to select the database to run the tests. Open the database you have been working with previously (see the previous section).

After opening the database, the program will still be in its natural state. Select **Tools | Analyzer Tester | Run Test**



Location of the current tester database file (.atd)

\\granite\ReleaseTesting\OLI Studio\OLIAnalyzer Test Cases(9.5.2).atd

Abs Err. 0.0001

Rel Err. 0.05

List of the test cases in the database:

Selected	Case ID	Case Name	Calc Object	Calc Type	Status	Improved in sec (%)
☑	1	pH	ScratchPadCalc	Isothermal		
☑	2	SinglePoint	ScratchPadCalc	Bubble Point		
☑	3	SinglePoint-1	ScratchPadCalc	Dew Point		
☑	4	SinglePoint-2	ScratchPadCalc	Vapor Fraction		
☑	5	Survey	SurveyCalc	Precipitation Point		

☐ Create Verbose Output Files

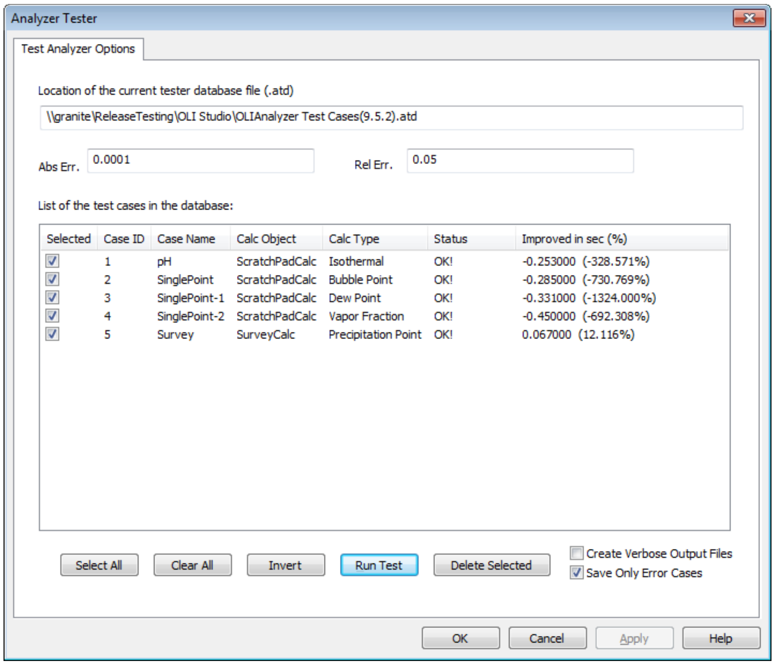
☑ Save Only Error Cases

Figure 42-19 The Tester roster of tests

This dialog has many features. At the moment, the test set has not been run so some information is missing.

Feature		Description
Abs Err		This is the absolute error in the calculation. If exceeded a message is created and a file saved
Rel Err.		This is the relative error in the calculation. If exceed a message is created and a file saved
Selected		This file is selected for the desired action (see buttons below)
Case ID		The case identifier in this database
Case Name		The name of the case in the original OLI Studio file
Calc Object		The class of calculation ScratchPadCalc (single point) or SurveyCalc (survey)
Calculation Type		The type of calculation
States		Passed, failed, error
Improved in sec (%)		How much faster is the current calculation than in the older version?
Buttons		
	Select All	Selects all tests
	Clear all	Deselects all tests
	Invert	Turns off all selected cases and turns on all unselected cases
	Run Test	Runs the calculation
	Delete Selected	Deletes the selected test, there is no restore facility
Create Verbose Output Files		All tests that are calculated will have an output file
Save only Error Cases		Only save cases that fail or exceed the error limits (see above)

We will now run this sample test. Since all cases are selected, click the **Run Test** button.



Location of the current tester database file (.atd)

\\granite\ReleaseTesting\OLI Studio\OLIAnalyzer Test Cases(9.5.2).atd

Abs Err. 0.0001

Rel Err. 0.05

List of the test cases in the database:

Selected	Case ID	Case Name	Calc Object	Calc Type	Status	Improved in sec (%)
☑	1	pH	ScratchPadCalc	Isothermal	OK!	-0.253000 (-328.571%)
☑	2	SinglePoint	ScratchPadCalc	Bubble Point	OK!	-0.285000 (-730.769%)
☑	3	SinglePoint-1	ScratchPadCalc	Dew Point	OK!	-0.331000 (-1324.000%)
☑	4	SinglePoint-2	ScratchPadCalc	Vapor Fraction	OK!	-0.450000 (-692.308%)
☑	5	Survey	SurveyCalc	Precipitation Point	OK!	0.067000 (12.116%)

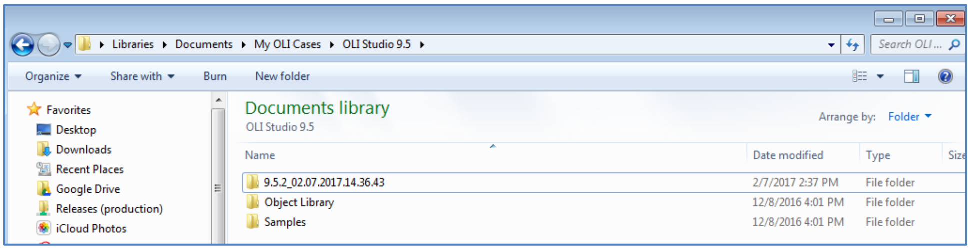
☐ Create Verbose Output Files

☑ Save Only Error Cases

Figure 42-20 The completed test

Of course, this is not a good test. We populated this database with the results from this version. The tests should all pass and have essentially the same results. This is really just a test that our database is connected properly. We now need to review the output files (if any).

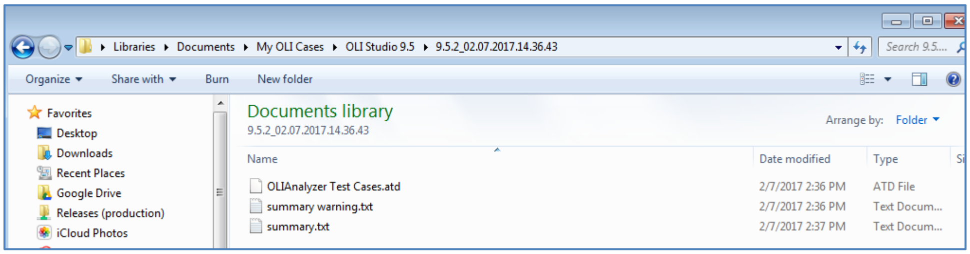
Be default, the results of the tests are stored in your documents folder under the My OLI Cases folder stored under the OLI Studio 9.5 folder since this is the version used to create the test. Please look for the folder for the version you used for the test.



Name	Date modified	Type
9.5.2_02.07.2017.14.36.43	2/7/2017 2:37 PM	File folder
Object Library	12/8/2016 4:01 PM	File folder
Samples	12/8/2016 4:01 PM	File folder

Figure 42-21 The results of the tests

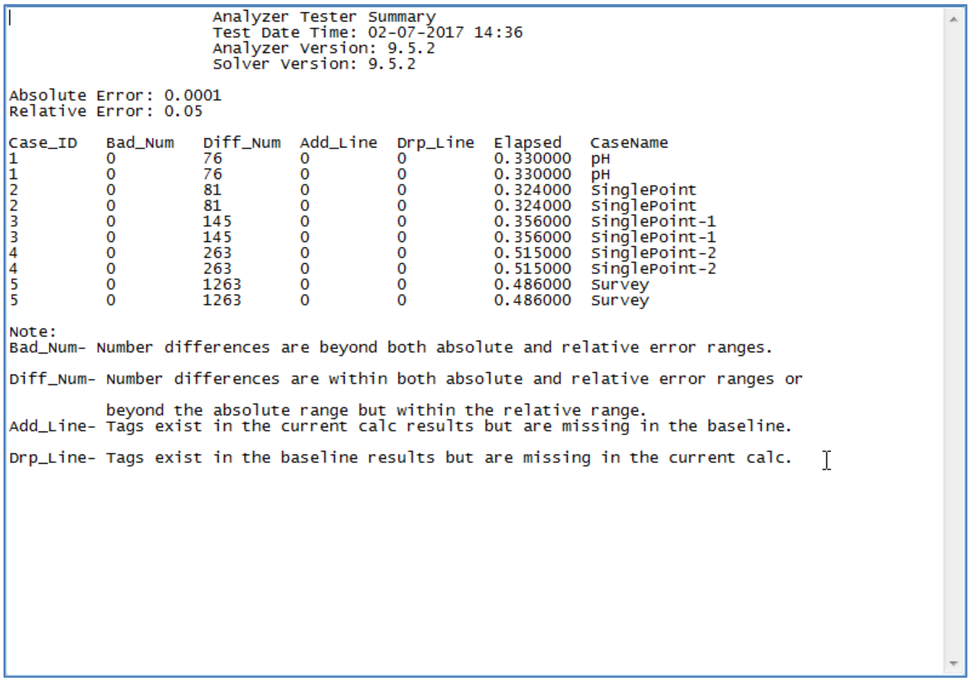
This is a very strange name for the folder. The name includes the version number and the time and date. Expand this folder.



Name	Date modified	Type
OLIAnalyzer Test Cases.atd	2/7/2017 2:36 PM	ATD File
summary warning.txt	2/7/2017 2:36 PM	Text Docum...
summary.txt	2/7/2017 2:37 PM	Text Docum...

Figure 42-22 the results details

As we said previously, this is not a real test. We have created a new database with the results of the test. This is the file named “OLIAnalyzer Test Cases.atd.” Since there are no errors only the summary files are created. Here are the rsults of the “Summary.txt” file:



```
                     Analyzer Tester Summary
                     Test Date Time: 02-07-2017 14:36
                     Analyzer Version: 9.5.2
                     Solver Version: 9.5.2

Absolute Error: 0.0001
Relative Error: 0.05

Case_ID   Bad_Num   Diff_Num  Add_Line  Drp_Line  Elapsed   CaseName
1         0         76        0         0         0.330000  pH
1         0         76        0         0         0.330000  pH
2         0         81        0         0         0.324000  SinglePoint
2         0         81        0         0         0.324000  SinglePoint
3         0         145       0         0         0.356000  SinglePoint-1
3         0         145       0         0         0.356000  SinglePoint-1
4         0         263       0         0         0.515000  SinglePoint-2
4         0         263       0         0         0.515000  SinglePoint-2
5         0         1263      0         0         0.486000  Survey
5         0         1263      0         0         0.486000  Survey

Note:
Bad_Num- Number differences are beyond both absolute and relative error ranges.

Diff_Num- Number differences are within both absolute and relative error ranges or

          beyond the absolute range but within the relative range.
Add_Line- Tags exist in the current calc results but are missing in the baseline.

Drp_Line- Tags exist in the baseline results but are missing in the current calc.
```

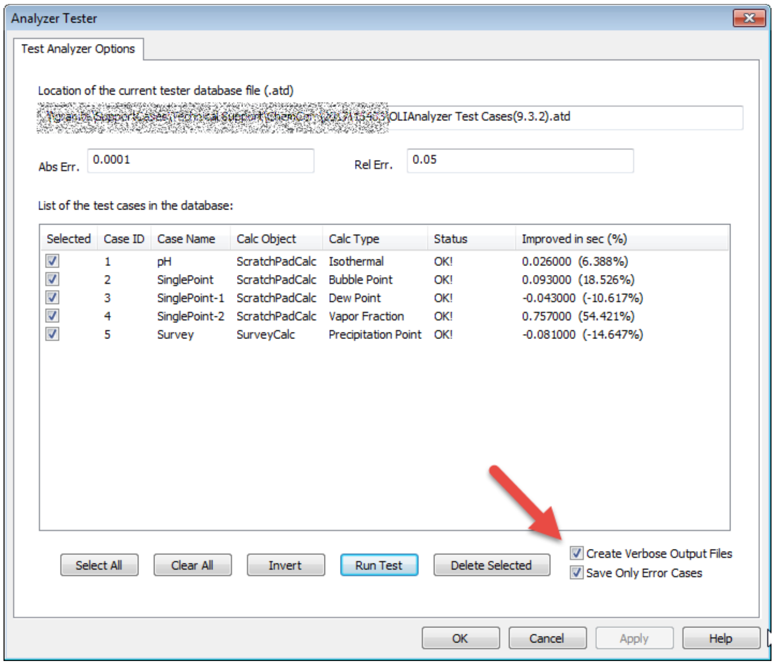
Figure 42-23 A very good test

Opening a database created in a previous version of OLI Studio

We have created the same database in version 9.3.2 of OLI Studio. This database can be found on the OLI Wiki page at: http://wiki.olisystems.com/wiki/images/d/de/OLIAnalyzer_Test_Cases%289.3.2%29.zip

Place this example file in a location to which you have access.

We now need to open this file as we have done previously in a later version of the program. You now need to run the test as we showed you in the previous section. For this test set, check the box **Create Verbose Output files**.



Location of the current tester database file (.atd)

[redacted]OLIAnalyzer Test Cases(9.3.2).atd

Abs Err. 0.0001

Rel Err. 0.05

List of the test cases in the database:

Selected	Case ID	Case Name	Calc Object	Calc Type	Status	Improved in sec (%)
☑	1	pH	ScratchPadCalc	Isothermal	OK!	0.026000 (6.388%)
☑	2	SinglePoint	ScratchPadCalc	Bubble Point	OK!	0.093000 (18.526%)
☑	3	SinglePoint-1	ScratchPadCalc	Dew Point	OK!	-0.043000 (-10.617%)
☑	4	SinglePoint-2	ScratchPadCalc	Vapor Fraction	OK!	0.757000 (54.421%)
☑	5	Survey	SurveyCalc	Precipitation Point	OK!	-0.081000 (-14.647%)

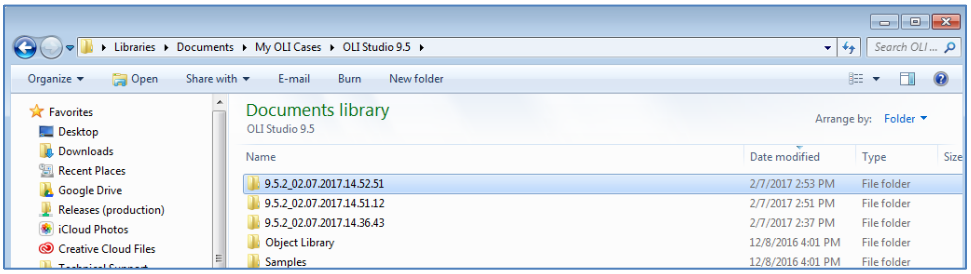
☑ Create Verbose Output Files

☑ Save Only Error Cases

Figure 42-24 Completed test set from an earlier version

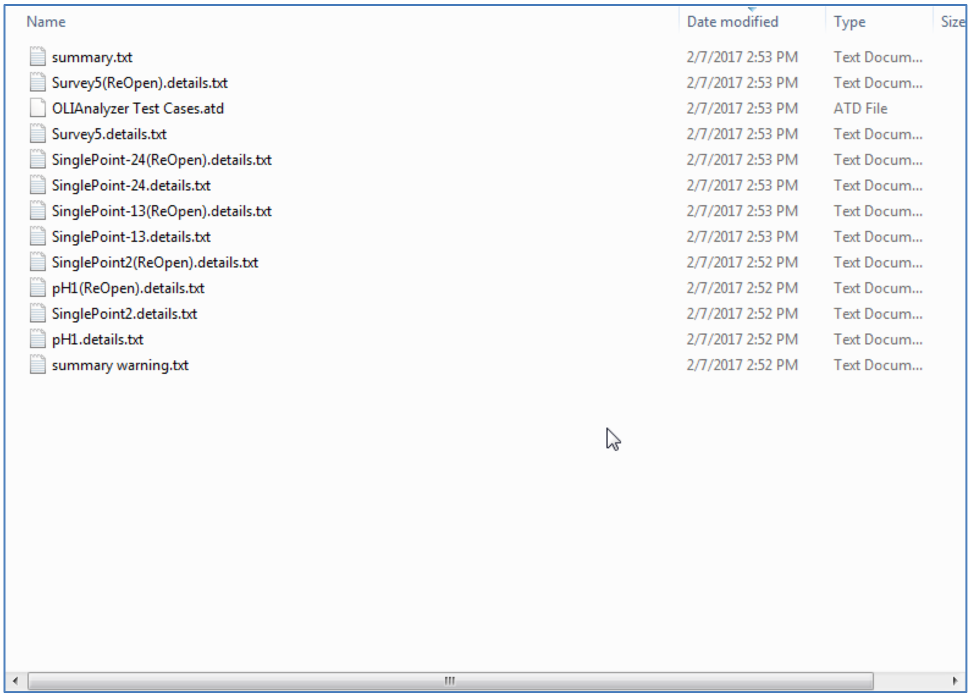
There is very little difference between 9.3.2 and 9.5.2 (the versions used for this example). This is true because the AQ thermodynamic framework was used in both cases and the database has not changed between these versions.

Let’s look at the results folder – remember that it will have a new file name under the documents folder.



Name	Date modified	Type	Size
9.5.2_02.07.2017.14.52.51	2/7/2017 2:53 PM	File folder	
9.5.2_02.07.2017.14.51.12	2/7/2017 2:51 PM	File folder	
9.5.2_02.07.2017.14.36.43	2/7/2017 2:37 PM	File folder	
Object Library	12/8/2016 4:01 PM	File folder	
Samples	12/8/2016 4:01 PM	File folder	

Figure 42-25 We want to look at the most recent set of results.

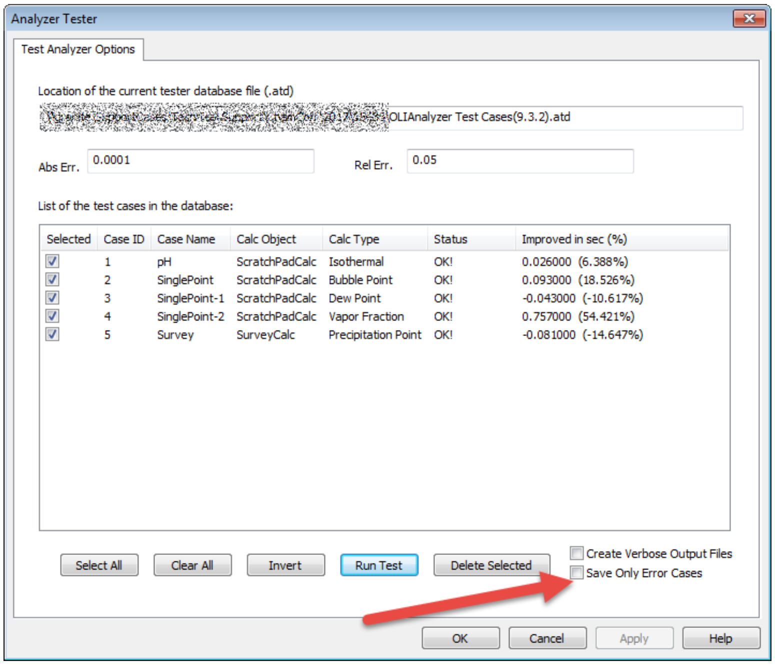


Name	Date modified	Type	Size
summary.txt	2/7/2017 2:53 PM	Text Docum...	
Survey5(ReOpen).details.txt	2/7/2017 2:53 PM	Text Docum...	
OLIAnalyzer Test Cases.atd	2/7/2017 2:53 PM	ATD File	
Survey5.details.txt	2/7/2017 2:53 PM	Text Docum...	
SinglePoint-24(ReOpen).details.txt	2/7/2017 2:53 PM	Text Docum...	
SinglePoint-24.details.txt	2/7/2017 2:53 PM	Text Docum...	
SinglePoint-13(ReOpen).details.txt	2/7/2017 2:53 PM	Text Docum...	
SinglePoint-13.details.txt	2/7/2017 2:53 PM	Text Docum...	
SinglePoint2(ReOpen).details.txt	2/7/2017 2:52 PM	Text Docum...	
pH1(ReOpen).details.txt	2/7/2017 2:52 PM	Text Docum...	
SinglePoint2.details.txt	2/7/2017 2:52 PM	Text Docum...	
pH1.details.txt	2/7/2017 2:52 PM	Text Docum...	
summary warning.txt	2/7/2017 2:52 PM	Text Docum...	

Figure 42-26 The details of the results

Opening any text file will give you details about what has changed in the file. In these tests, very little has changed.

The final option is to save each test as a separate OLI Studio file. Uncheck the "Save Only Error Cases" and run the tests again.



Location of the current tester database file (.atd)

[redacted]OLIAnalyzer Test Cases(9.3.2).atd

Abs Err. 0.0001

Rel Err. 0.05

List of the test cases in the database:

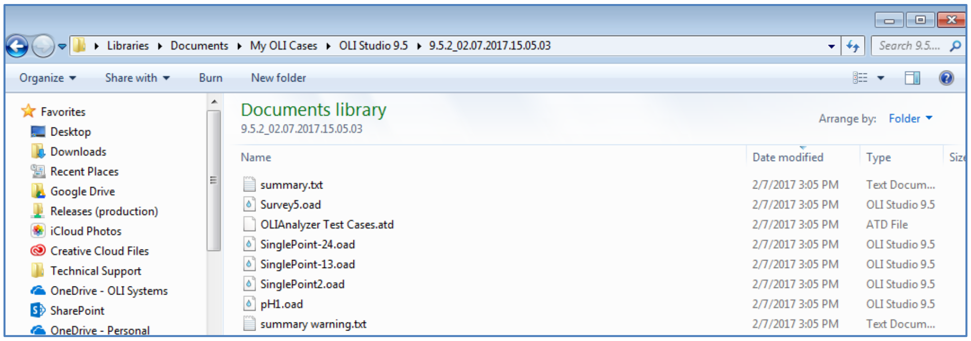
Selected	Case ID	Case Name	Calc Object	Calc Type	Status	Improved in sec (%)
☑	1	pH	ScratchPadCalc	Isothermal	OK!	0.026000 (6.388%)
☑	2	SinglePoint	ScratchPadCalc	Bubble Point	OK!	0.093000 (18.526%)
☑	3	SinglePoint-1	ScratchPadCalc	Dew Point	OK!	-0.043000 (-10.617%)
☑	4	SinglePoint-2	ScratchPadCalc	Vapor Fraction	OK!	0.757000 (54.421%)
☑	5	Survey	SurveyCalc	Precipitation Point	OK!	-0.081000 (-14.647%)

☐ Create Verbose Output Files

☐ Save Only Error Cases

Figure 42-27 Unchecking the save option

Now review the results in yet another new folder (most recent) in the same general location at the other results:



Name	Date modified	Type	Size
summary.txt	2/7/2017 3:05 PM	Text Docum...	
Survey5.oad	2/7/2017 3:05 PM	OLI Studio 9.5	
OLIAnalyzer Test Cases.atd	2/7/2017 3:05 PM	ATD File	
SinglePoint-24.oad	2/7/2017 3:05 PM	OLI Studio 9.5	
SinglePoint-13.oad	2/7/2017 3:05 PM	OLI Studio 9.5	
SinglePoint2.oad	2/7/2017 3:05 PM	OLI Studio 9.5	
pH1.oad	2/7/2017 3:05 PM	OLI Studio 9.5	
summary warning.txt	2/7/2017 3:05 PM	Text Docum...	

Figure 42-28 Individual tests are saved as files

Each of the test set cases are saved as individual files for further analysis if required.

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