A Guide to Using

OLI Studio

Version 9.6

Including
Stream Analyzer
ScaleChem
Corrosion Analyzer
EVS

OLI Systems, Inc.

240 Cedar Knolls Road
Suite 301
Cedar Knolls, NJ 07927
973-539-4996
(Fax) 973-539-5922
Oli.support@olisystems.com
www.olisystems.com

Disclaimer:

This manual was produced using the OLI Studio / OLI Analyzer version 9.6 build 1 (9.6.1). As time progresses, new data and refinements to existing data sets can result in values that you obtain being slightly different than what is presented in this manual. This is a natural progress and cannot be avoided. When large systematic changes to the software occur, this manual will be updated.

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** 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. The OLI Engine is made up of the Solvers and the Databanks. 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, real-solution diagrams for your analysis. Our competitors only offer idealized solution diagrams and none of a general prediction of rates of uniform corrosion. 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 OLI Flowsheet: ESP program 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	**Extractor**	**Feedforward**
Split	**Component Split**	**Sensitivity**
Separate	**Incinerator**	**Membrane (UF, RO)**
Neutralizer	**Compressor**	
Absorber	**Manipulate**	
Stripper	**Controller**	
Reactor	**Pump**	
Exchanger		

OLI Flowsheet: 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 OLI Flowsheet: 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.

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

This is the **Actions** or **Explorer** pane. Normally we start by clicking on **Add Stream**
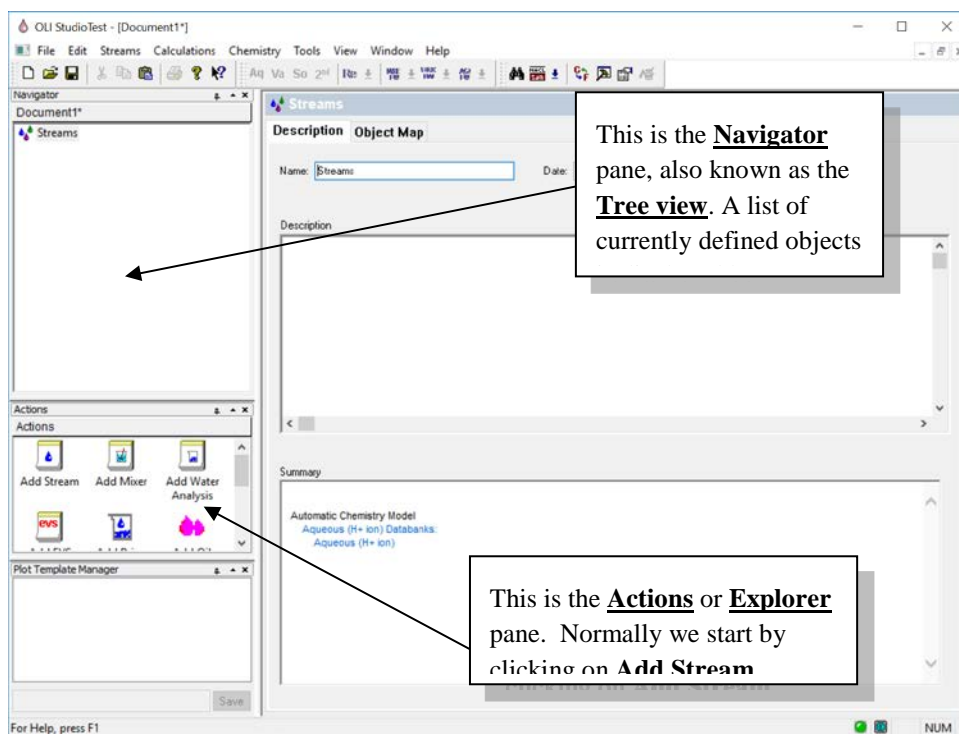
Figure 2-1 The main OLI Studio window

- *Click* on the **Add Stream** icon.
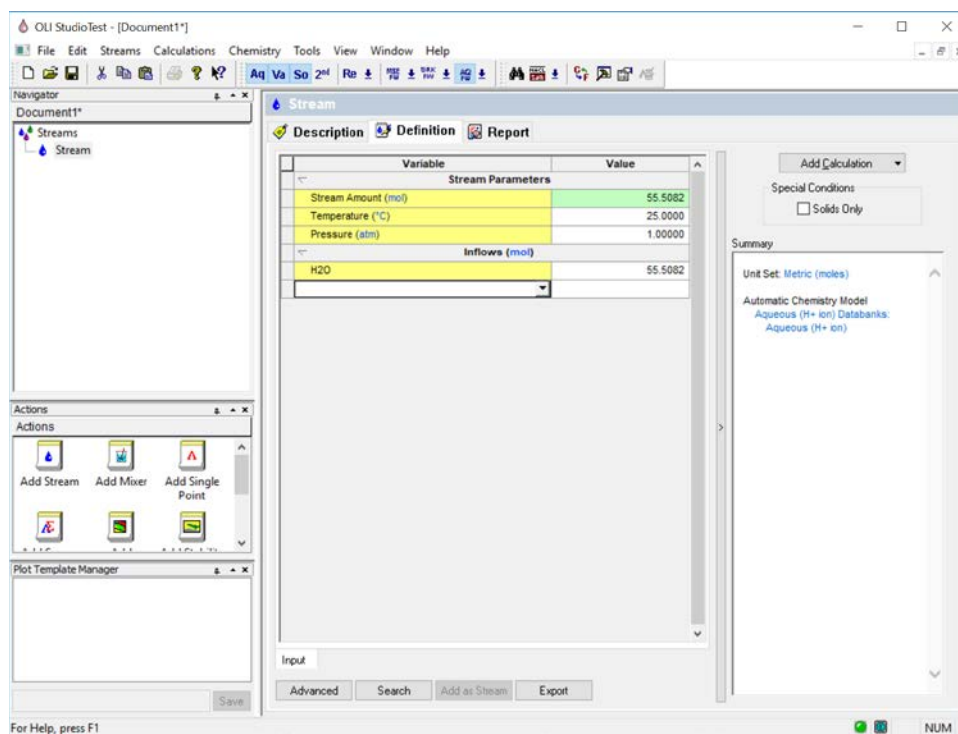
Figure 2-2 Adding a new stream

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 (H3O+ ion)

The MSE framework is OLI's 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.

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

The MSE-SRK thermodynamic framework solves a problem with high pressure hydrocarbons above the critical pressure of the liquid phase. This can cause some discontinuities in the VLLE phase envelope. MSE-SRK removes these discontinuities. See the wiki link for more information. http://wiki.olisystems.com/wiki/MSE-SRK

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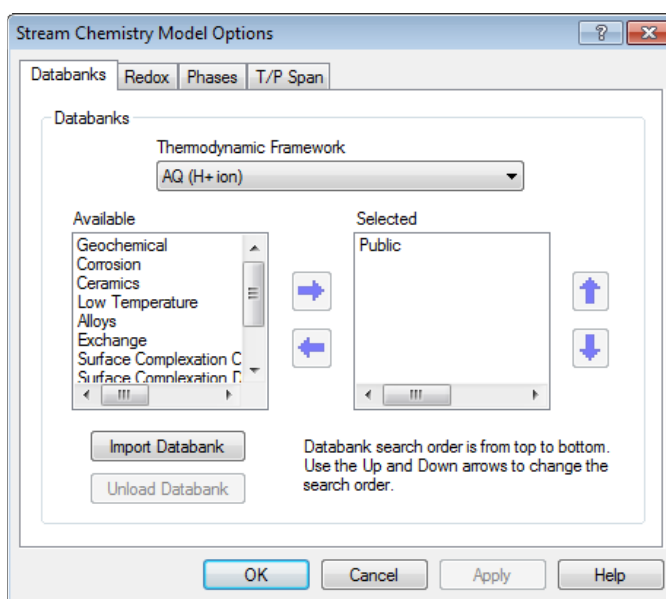
Figure 2-3: Selecting the thermodynamic framework used for simulation.

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

Figure 2-4 Toolbar - AQ framework Selected
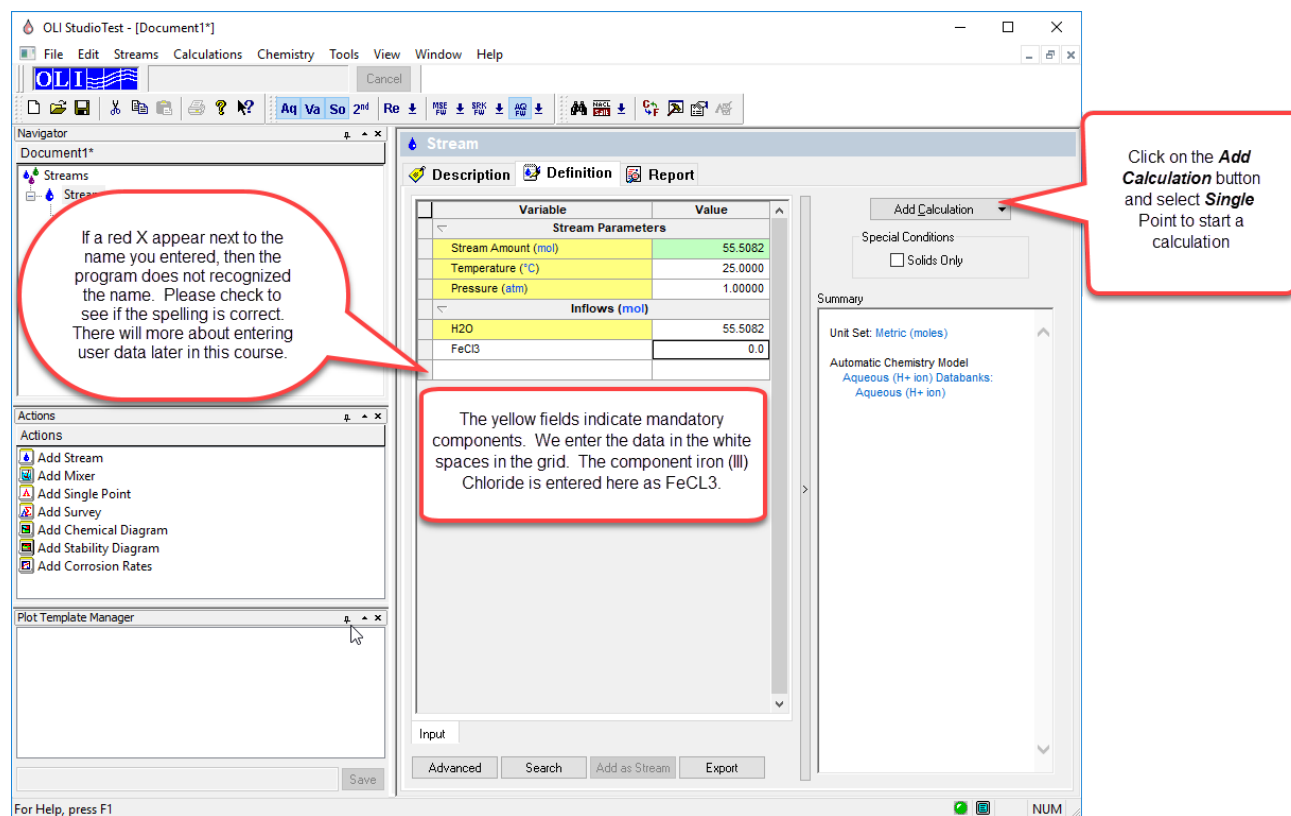
Figure 2-5 Entering Stream Information

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.

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.
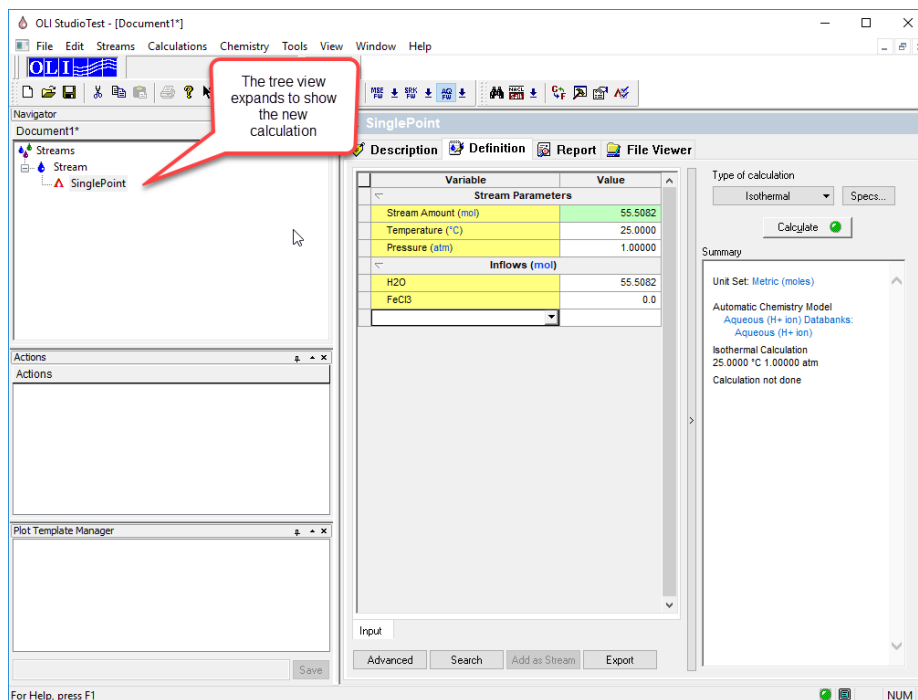
Figure 2-6 Starting the calculation

We are now ready to start the calculations but let us review some options on this screen.
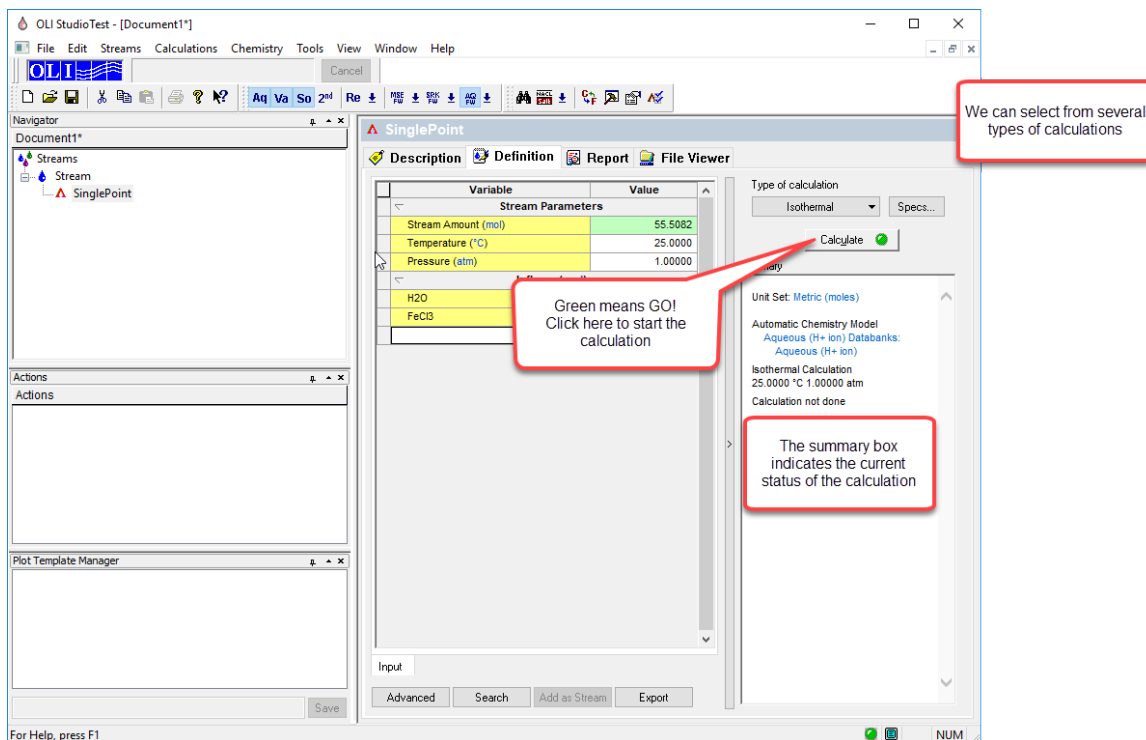
Figure 2-7 Entering the calculation conditions.

The data in the **<u>Definition</u>** 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 **<u>Type of Calculation</u>** button.
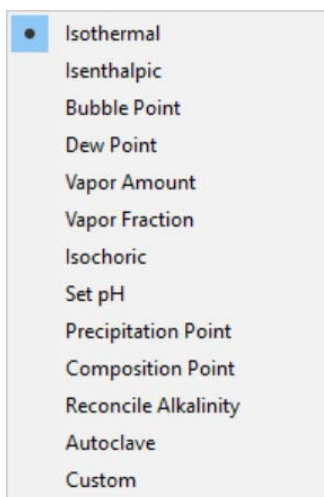
Figure 2-8 Single Point Calculation Types

There are several types of calculations that can be performed. We will use the default calculation type of **<u>Isothermal</u>** 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.
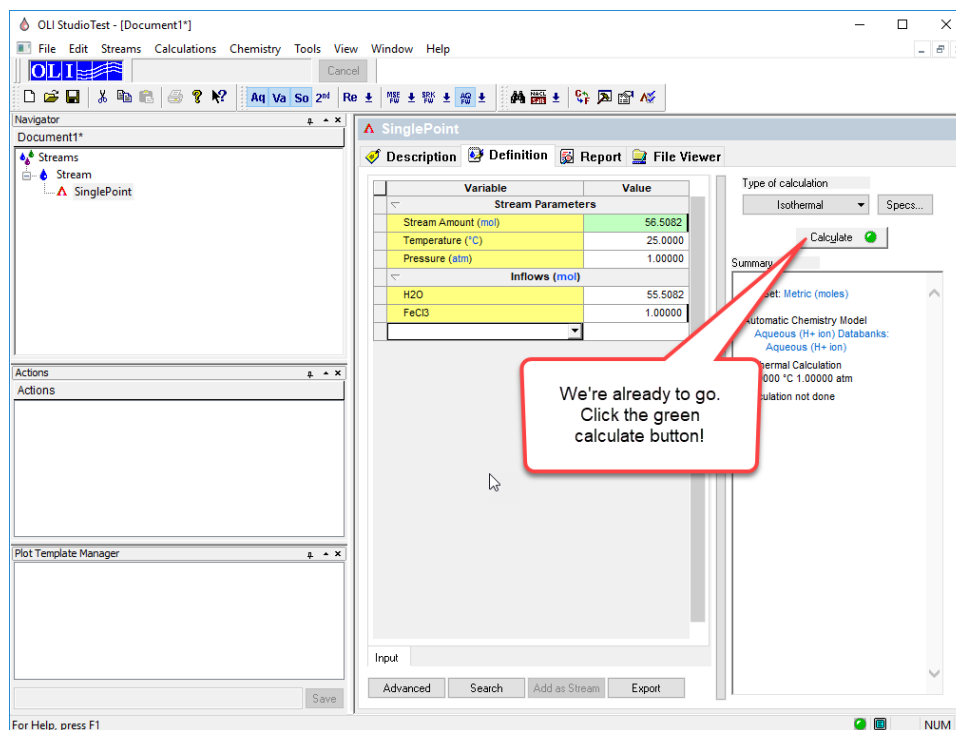
Figure 2-9 Let's GO! Click the Calculate button!

- *Click* the green **Calculate** button.

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

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.
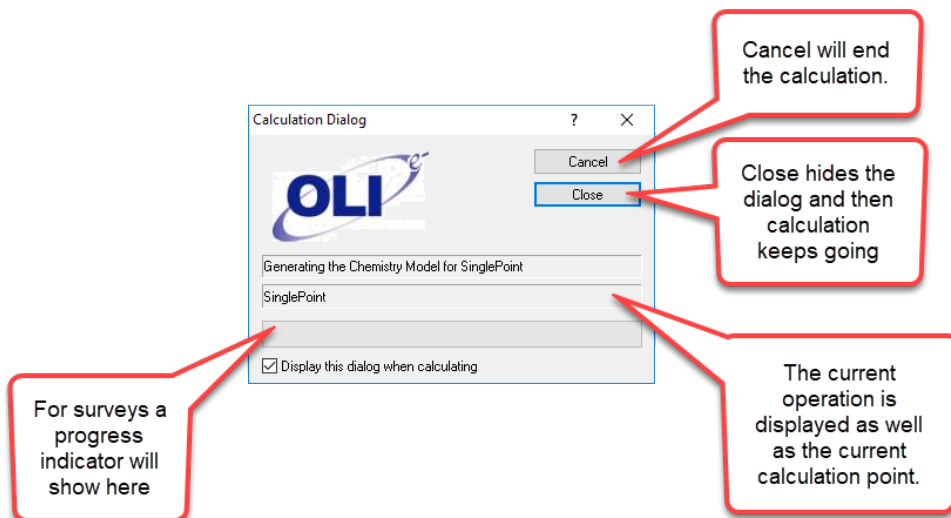
Figure 2-10 The OLI Calculation Status Dialog

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.

The answer to our question is that the pH of the solution is approximately 2.215. This is 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.
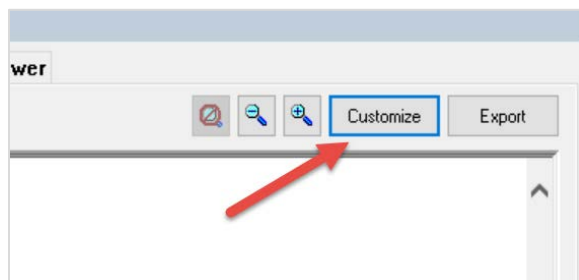
Figure 2-12 Click on the customize button

- *Click* on the **Customize** button.
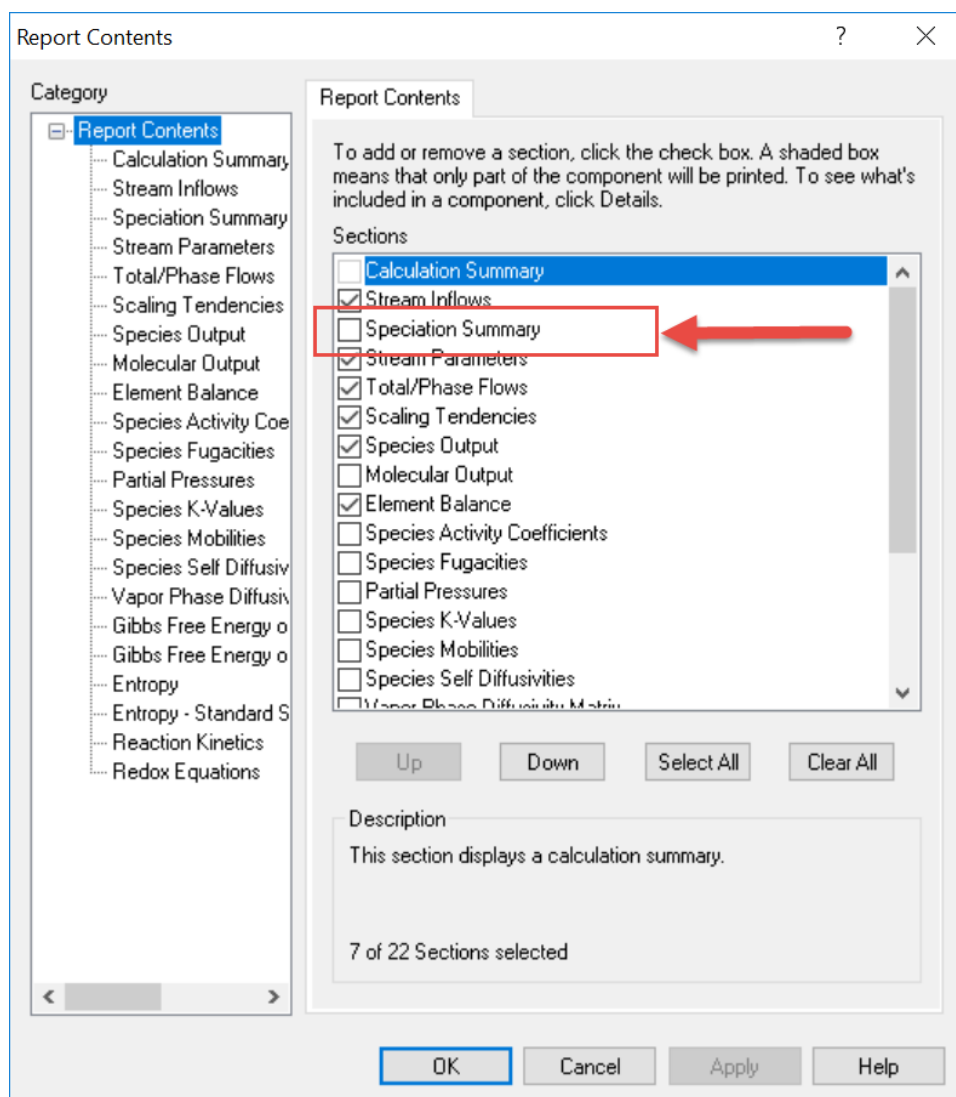
Figure 2-13 Report content options

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

Click the **OK** button. Click on definition tab to refresh the report tab.
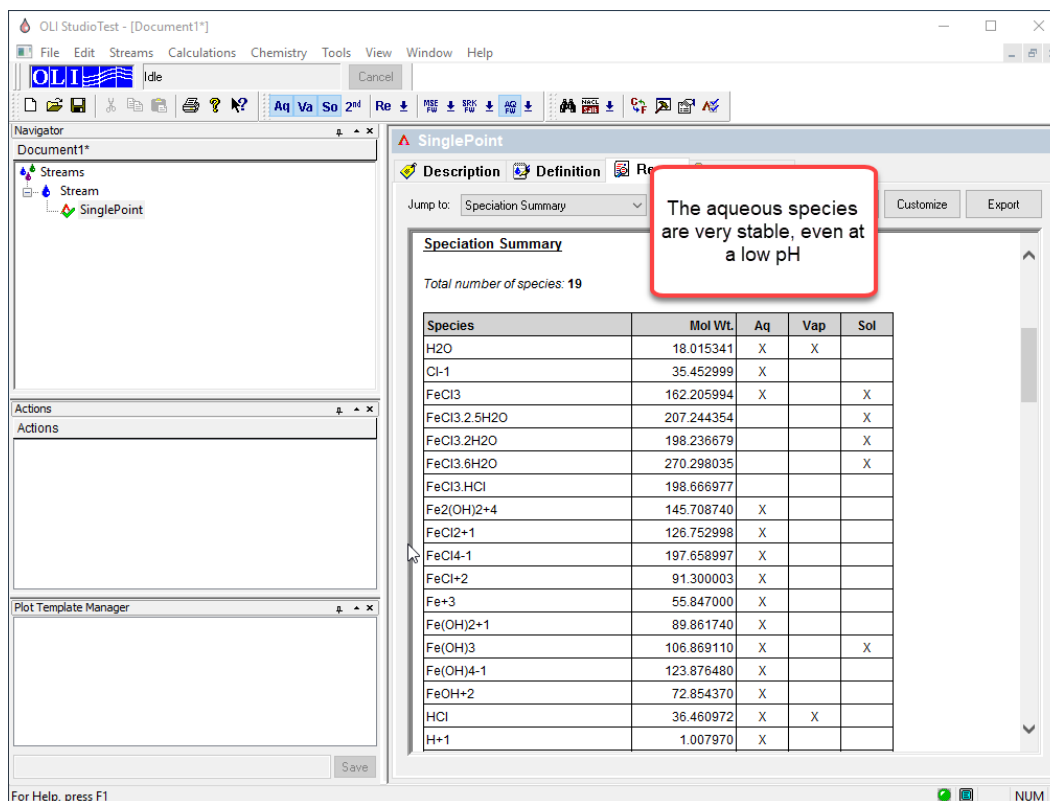
Figure 2-14 Modifying the report

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:

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

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

Speciation:

Fe^{+3}	$FeCl^{+2}$	$FeOH^{+2}$
Cl^{-1}	$FeCl_2^{+1}$	$Fe(OH)_2^{+1}$
H^{+1}	$FeCl_3^0$	$Fe(OH)_3^0$
OH^{-1}	$FeCl_4^{-1}$	$Fe(OH)_4^{-1}$
H_2O^0	HCl^0	$Fe_2(OH)_2^{+4}$
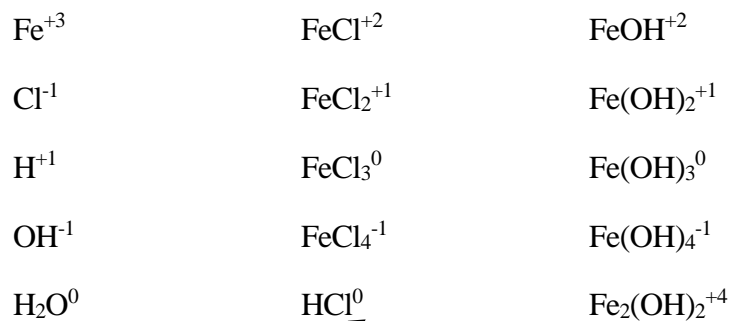
This is a weak species at 25°C.

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
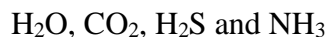
Aqueous Neutral Species:

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 $NH_2CO_2^-$
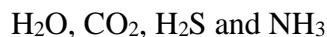
Chemistry Summary (Molecular Equilibrium)

Vapor - Liquid equilibrium reactions considered:

$H_2O_{(vap)}$	$=$	H_2O
$NH_{3(vap)}$	$=$	$NH_{3(aq)}$
$CO_{2(vap)}$	$=$	$CO_{2(aq)}$

$$H_2S_{(vap)} \quad = \quad H_2S_{(aq)}$$
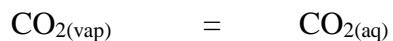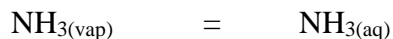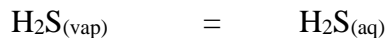
Chemistry Summary (Electrolyte Equilibrium)

Additional electrolyte reactions needed

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

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

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

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

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

Notice that this is the
~~hydrolysis of an ion~~

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

$$HS^- \qquad = \qquad H^+ + S^{2-}$$
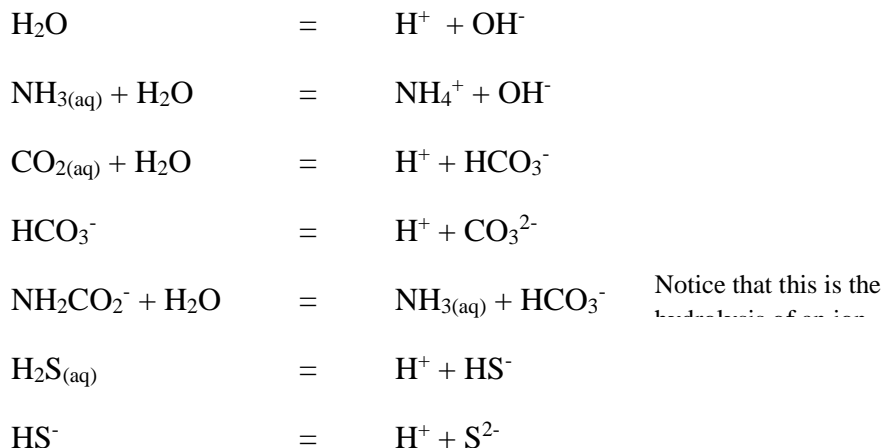
Calculating Partial Pressures

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, calculating the partial pressures of the components is very important.

We now want to calculate the partial pressures of CO_2, H_2S, and NH_3 with and without the aqueous phase equilibrium considered.

Data Summary[4,5]

Temperature 20°C & 60°C

Solution Composition

NH₃: 1.126 - 2.160 molal (1.8 - 3.3 wt %)

CO₂: 0.424 - 1.601 molal (1.8 - 6.4 wt %)

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[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)

H$_2$S: 0.040 - 0.407 molal (0.1- 1.3 wt %)

H$_2$O: 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	Exp.	OLI	VLE	Exp.	OLI	VLE	Exp.	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

The data contained in

Table 2-1compares 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

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

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

$H_2S_{(vap)} =$ $H_2S_{(aq)}$
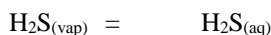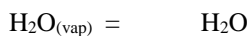
Partial Pressures of Gases (VLE only)
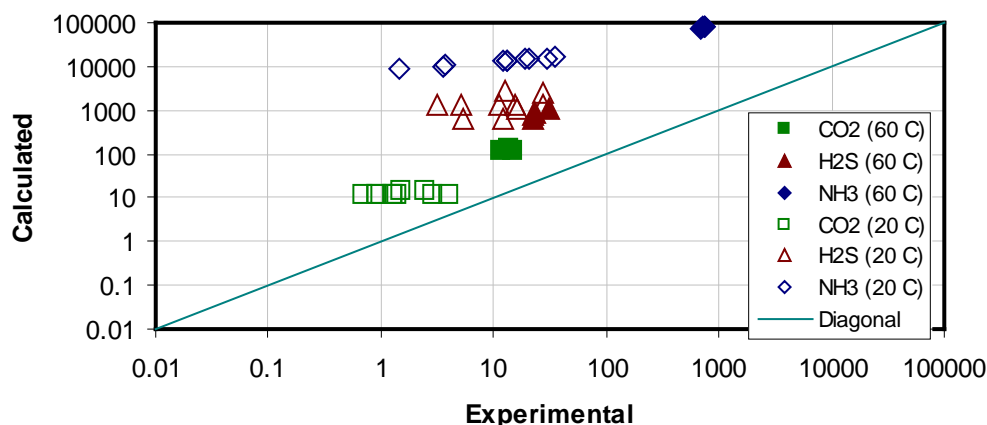
Figure 2-15 Parity plot of the partial pressures of gases without aqueous reactions

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 as 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 desire 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^-	=	$H^+ + S^{2-}$
$NH_2CO_2^- + H_2O$	=	$NH_4^+ + HCO_3^-$

Partial Pressure of Gases (Full OLI Model)
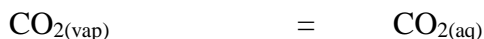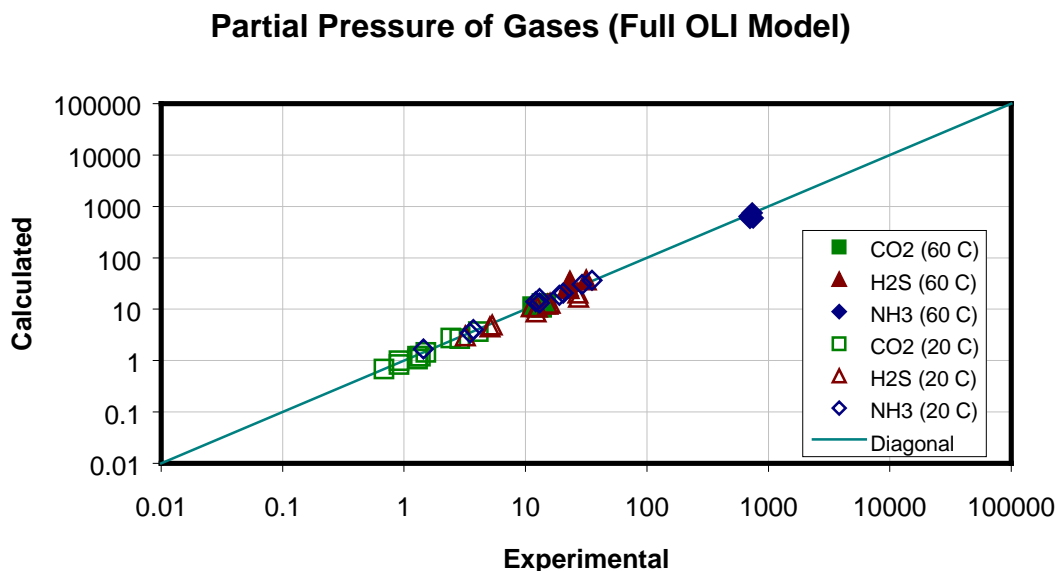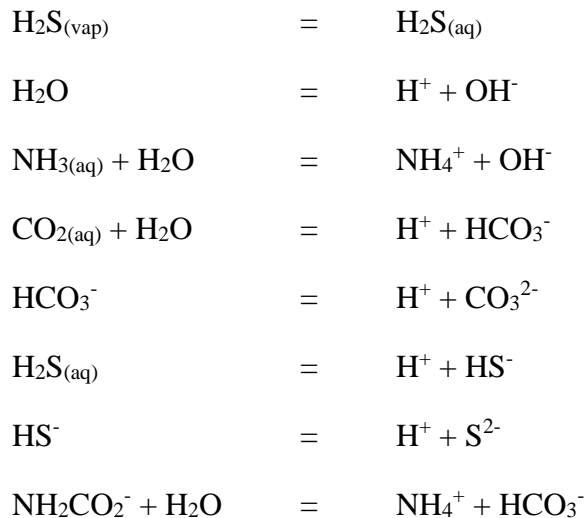
Figure 2-16 Parity plot of the partial pressures of gases with aqueous reactions

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)
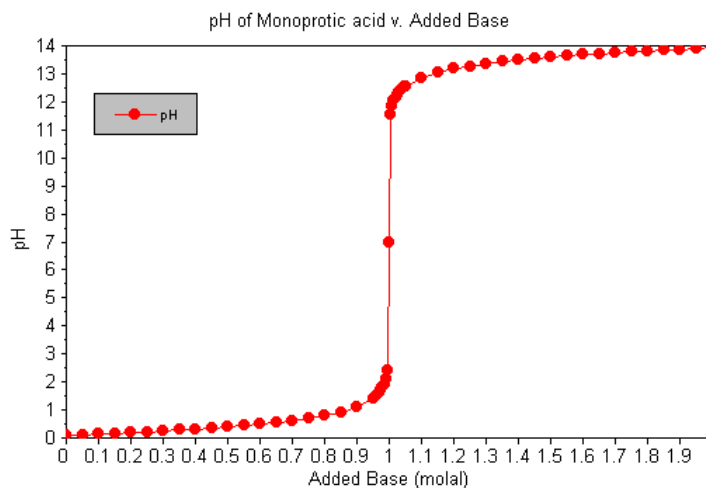
Figure 2-17 a mono protic acid titration curve

b)
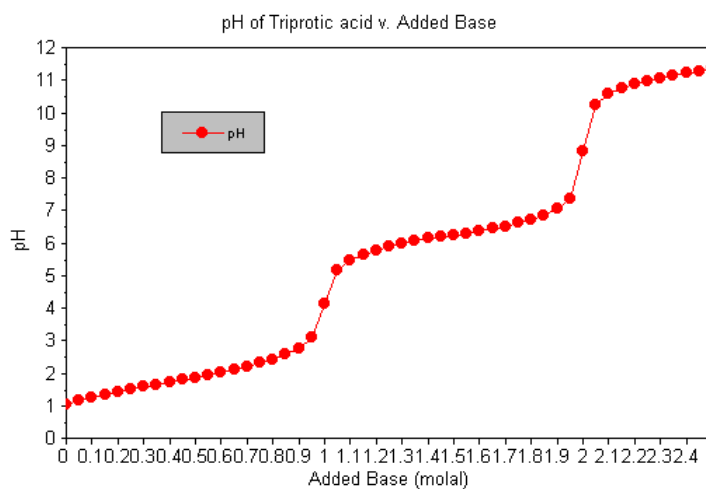
Figure 2-18 a triprotic acid titration curve

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:

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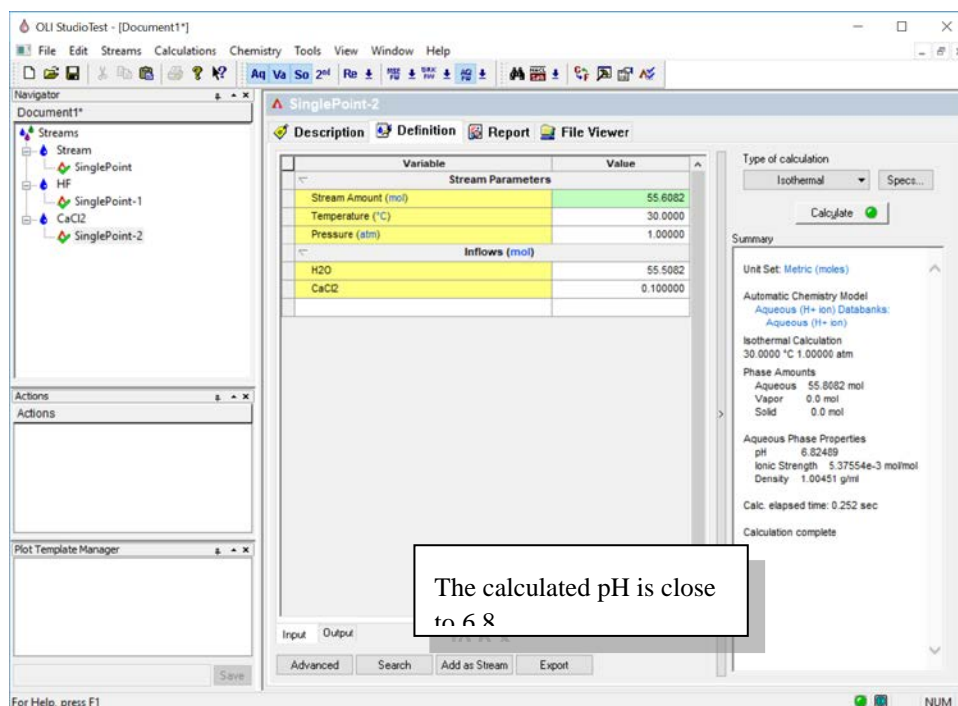
Figure 2-20 The pH of the Calcium chloride stream.

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.
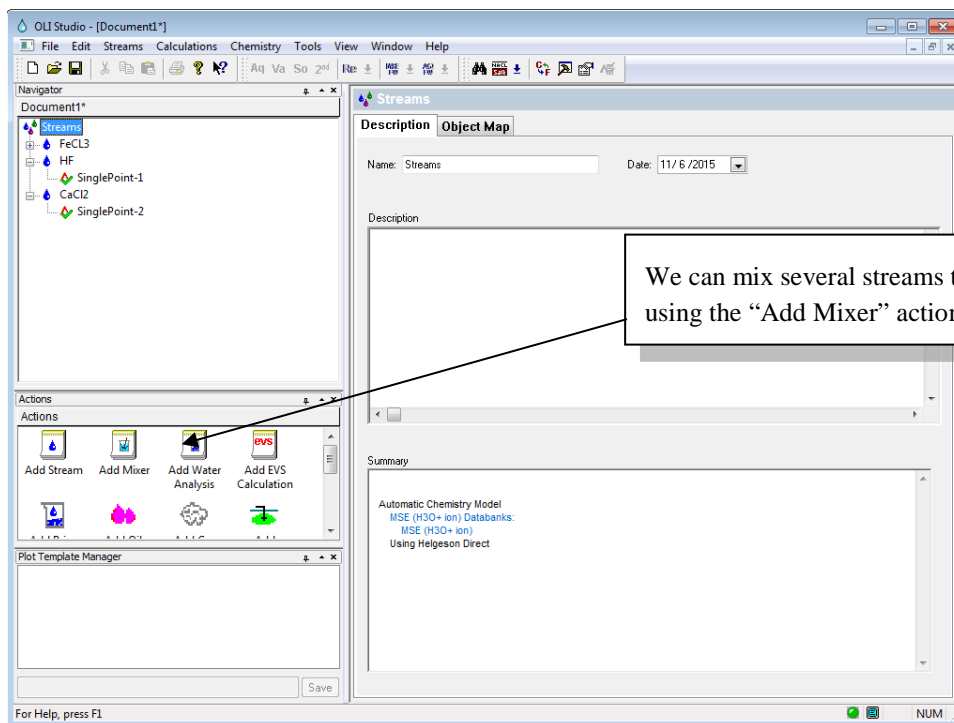
Figure 2-21 The main explorer window. Locating the Mix calculation.
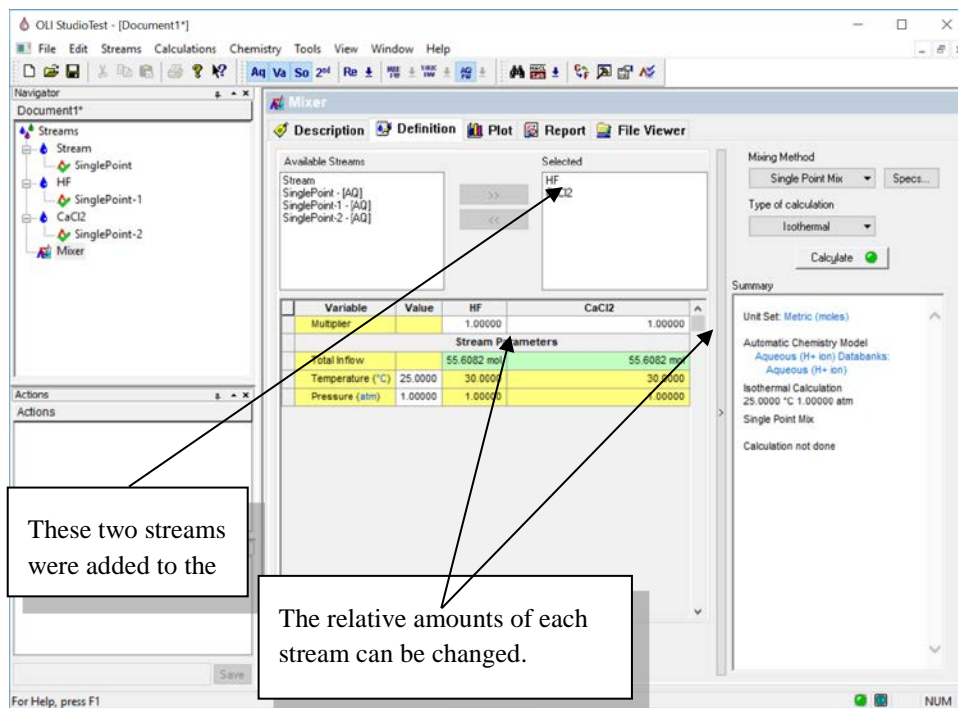
Figure 2-22 The completed mix calculation.

We now need to click Calculate button and then on the report tab to see the resultant pH.

Figure 2-23 Aqueous Properties

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 $CaCl_2$.

Figure 2-24 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.
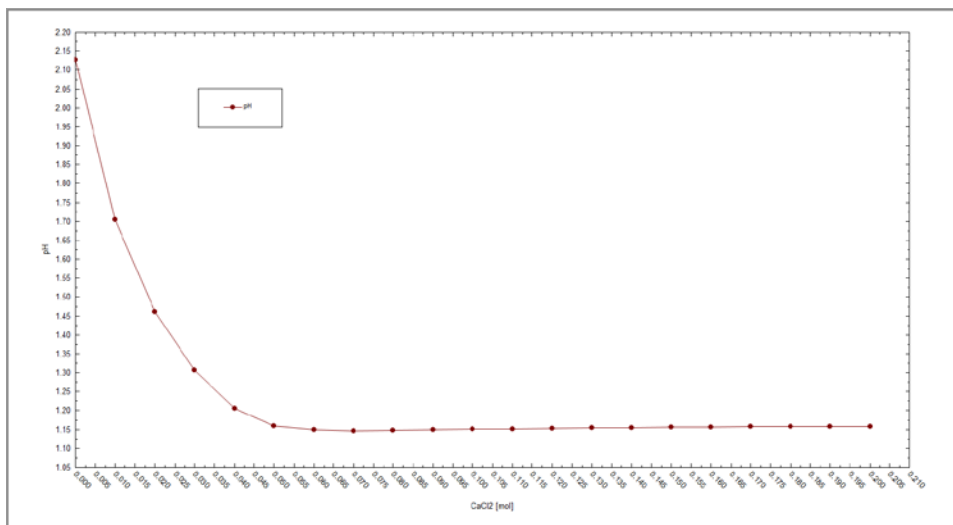
Figure 2-25 pH response to CaCl2 titration

As you can see, adding $CaCl_2$ to this solution lowers the pH initially. The pH does begin to slowly increase after 0.06 moles of $CaCl_2$ 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:

$$Ca^{2+} + 2F^{-1} \rightarrow CaF_{2(cr)}$$
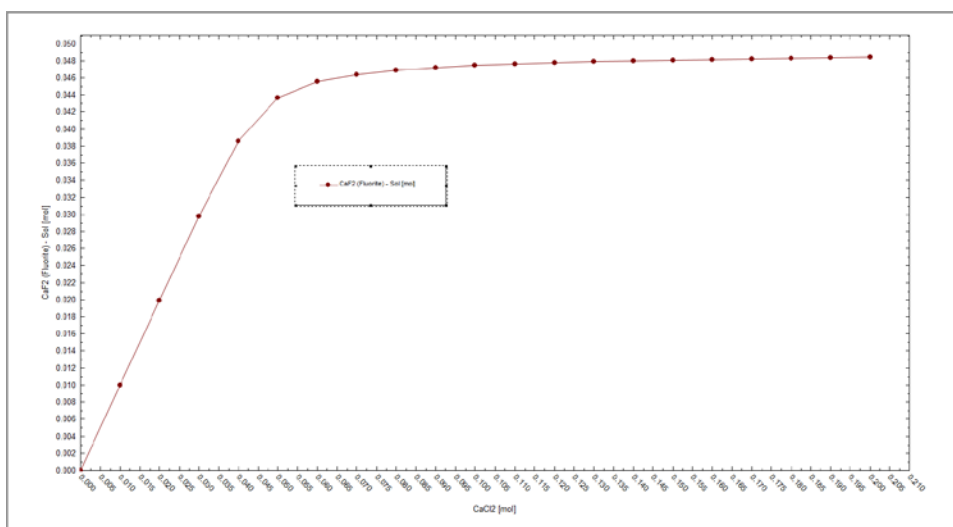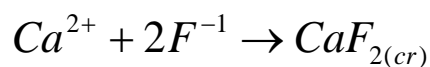
Figure 2-26 the formation of CaF_2

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

$$HF^o \rightarrow H^+ + F^-$$
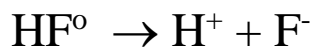
As CaF_2 is formed, the amount of fluoride ion in solution is decreased. *Le Chatlier's* principle states that any equilibrium under stream shifts to relieve the stress. Thus, more hydrogen ion is produced, lowering pH.

What are the fluoride species doing in solution? The next figure illustrates this:
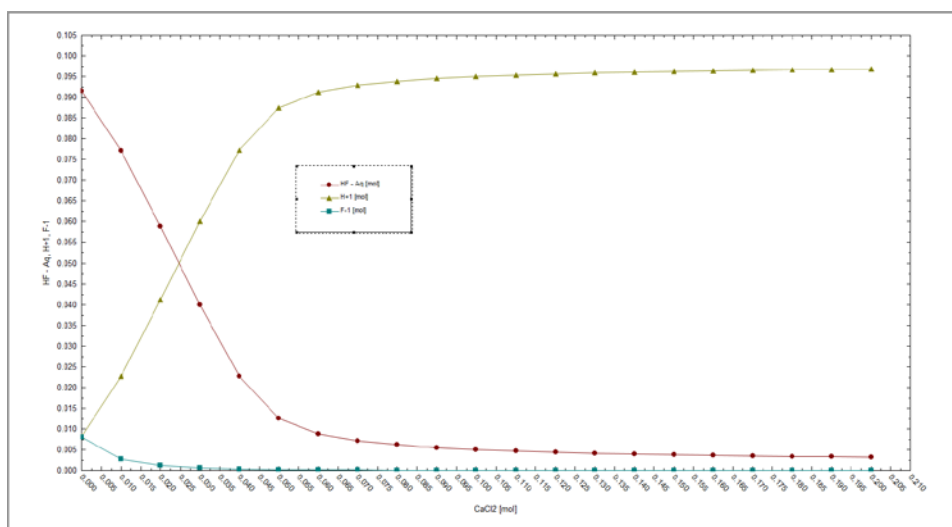
Figure 2-27 The dominant fluoride species in solution.

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
Bold and Underlined	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.
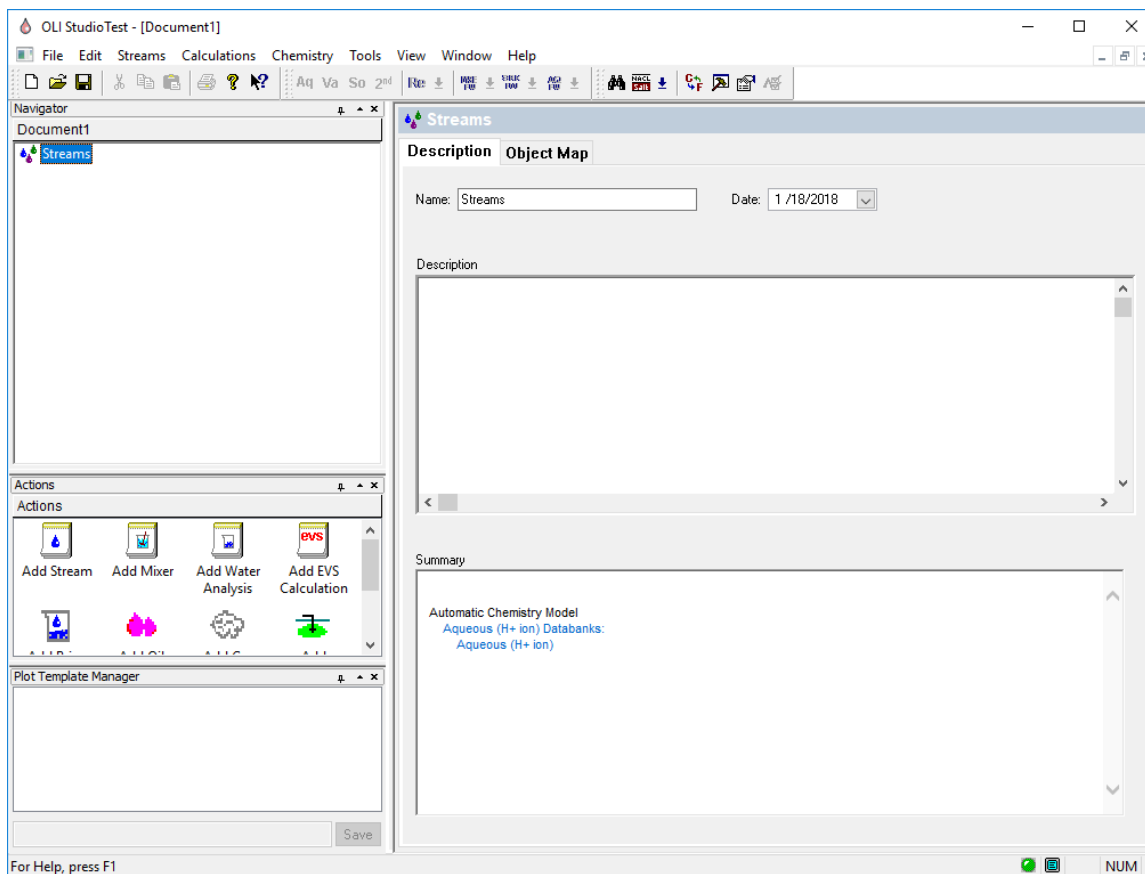
Figure 3-1 The OLI Studio main window

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.
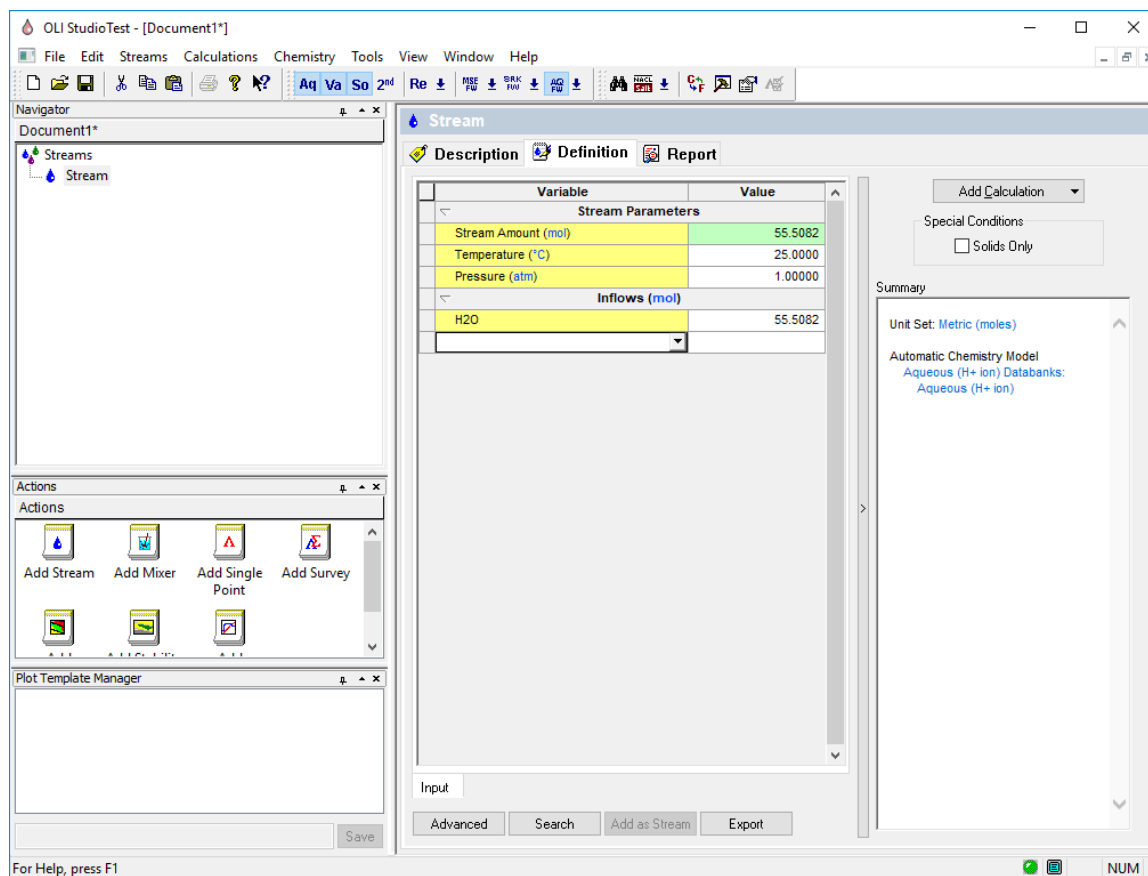
Figure 3-2 The streams definition view.

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

Step 2: Adding definitions

- *Click* on the **Description** tab. This will display the description information
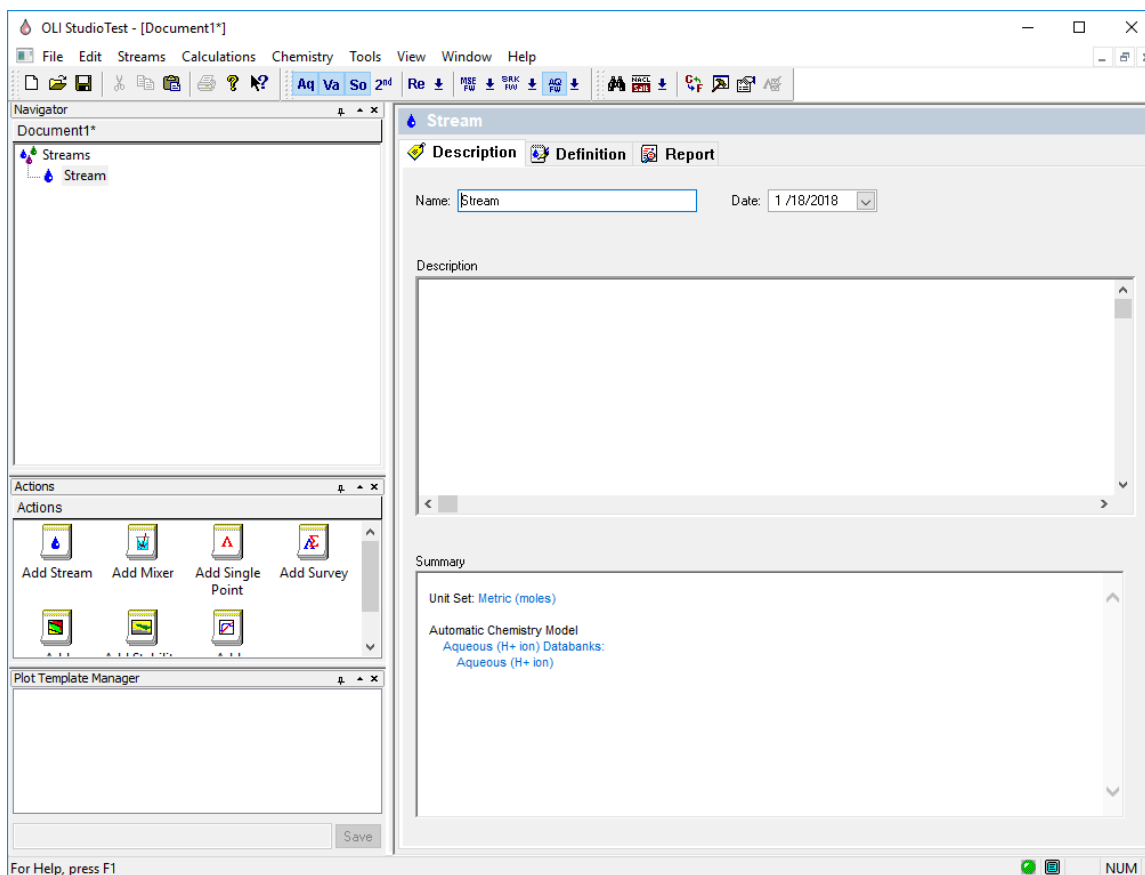
Figure 3-3 The Stream Description tab.

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 later.

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:
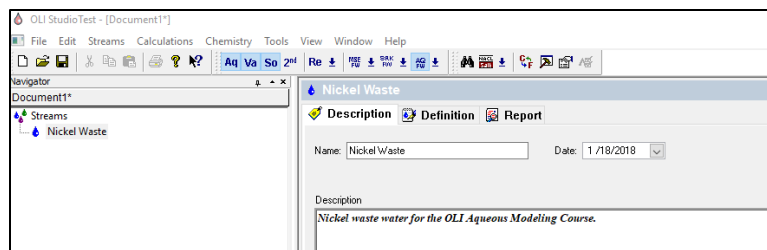
Figure 3-4 The filled-out description window

- *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
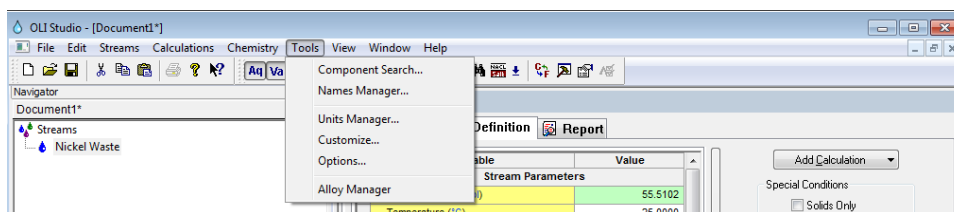
Figure 3-6 the Tools Menu

Select **Names Manager** from the Tools list.
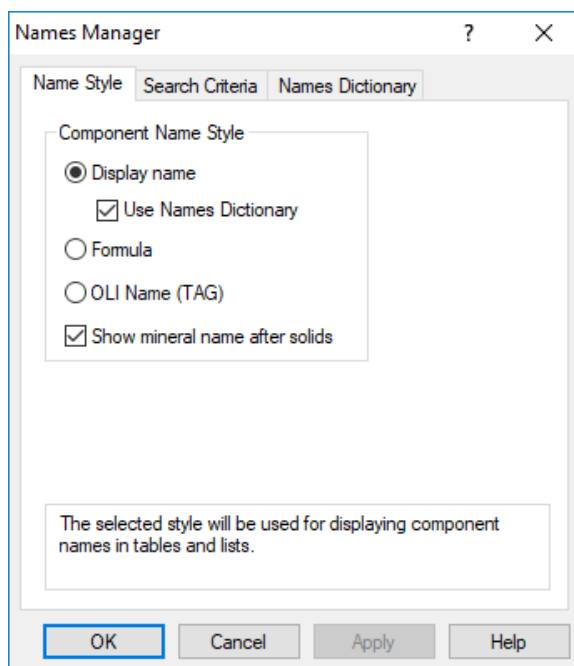
Figure 3-7 The Names Manager

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.

---

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

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 $Ni(OH)_2$.

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

If you hover the cursor over the inflow components, you will see information about that component.

Figure 3-9 Hover over component name to see additional details

Step 5: Add a Single Point calculation to the Stream

Figure 3-10 Selecting Single Point

- *Click* on the <u>*Add Calculation*</u> 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.
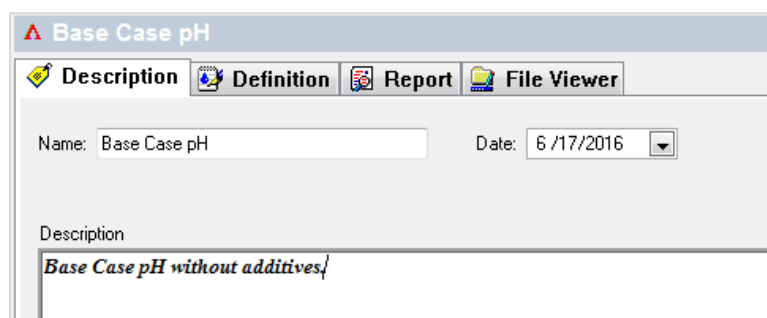
Figure 3-11 The filled-out description

We can now start the calculation.

- *Click* on the **Definition** tab.

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

- *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.
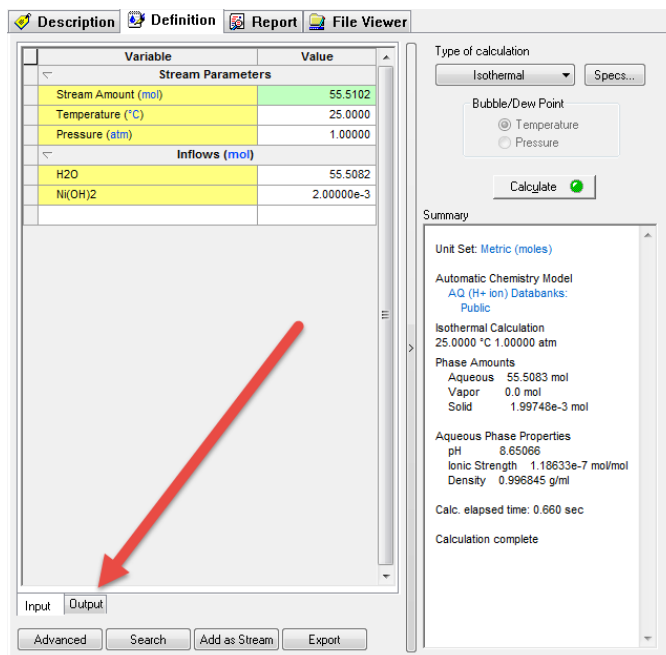
Next right-click anywhere in the gray field to display a pop-up menu.
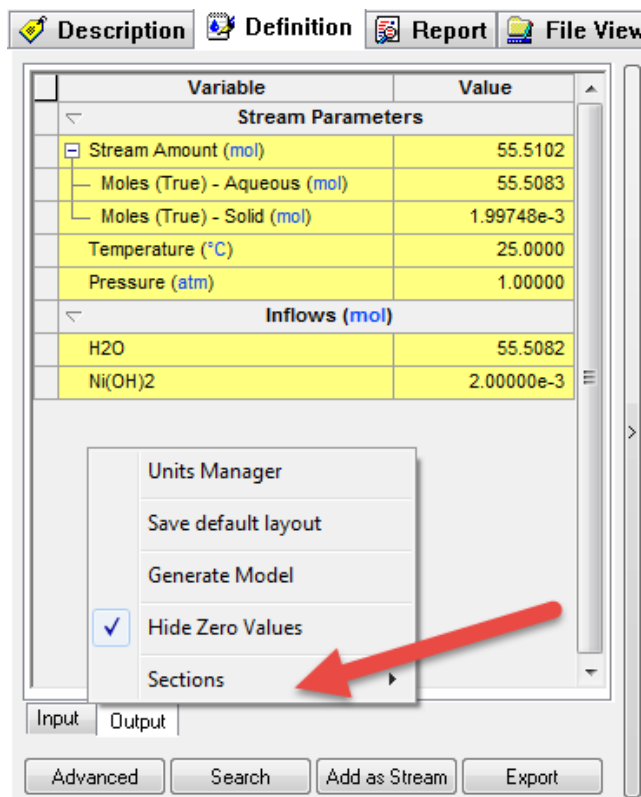
Figure 3-12 Displaying additional sections

- Select **Sections.**
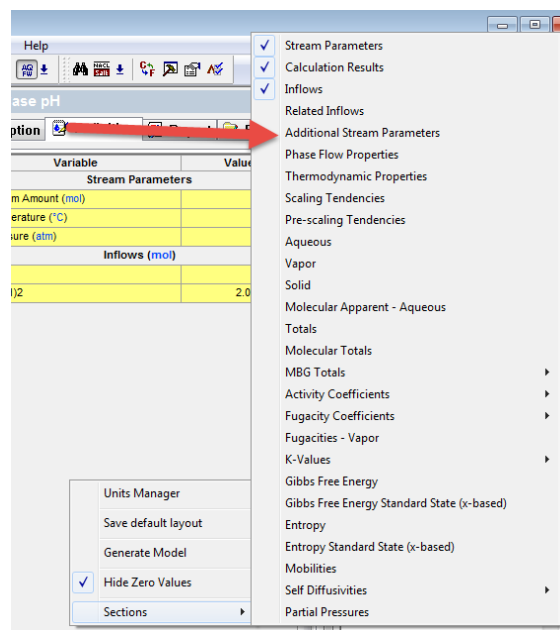
Figure 3-13 Displaying all the sections available

- 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.

3-14 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.

Figure 3-15 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.**
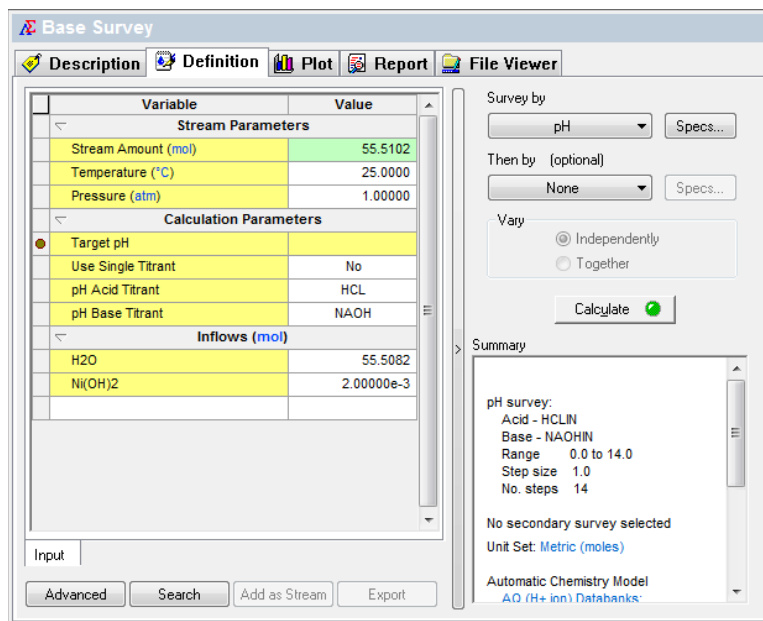
Figure 3-16 Survey Summary (Default Values)

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.
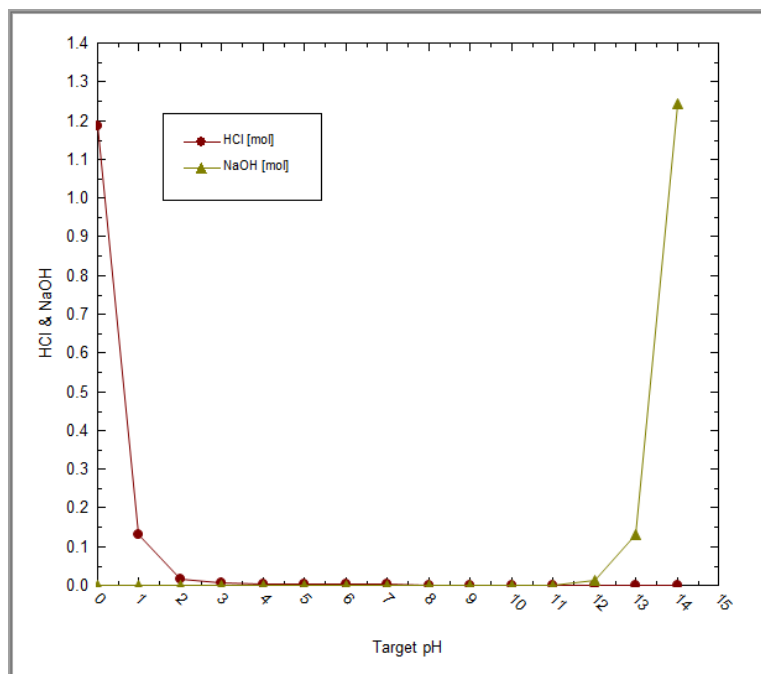
Figure 3-17 the default plot

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
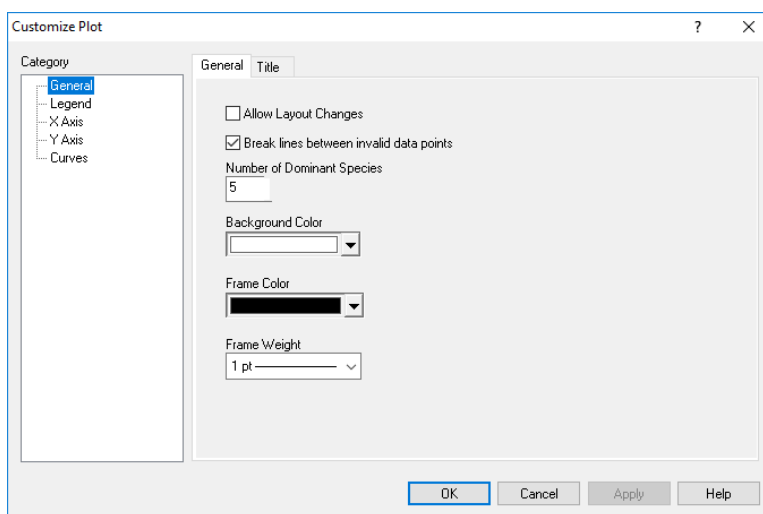
Figure 3-18 Plot Options

- Select **Y-Axis** from the Category List.
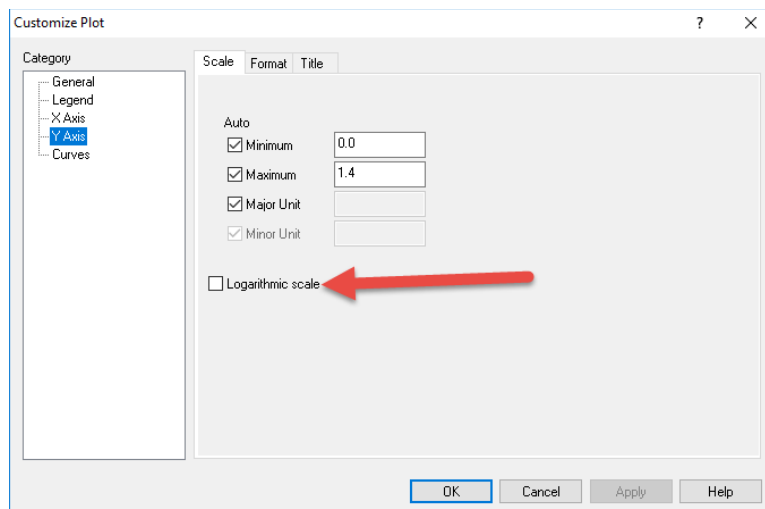
Figure 3-19 Setting log for Y-Axis

- Check the **<u>Logarithmic Scale</u>** Box and then **Click** on the **<u>OK</u>** box**.**

The display will now change.
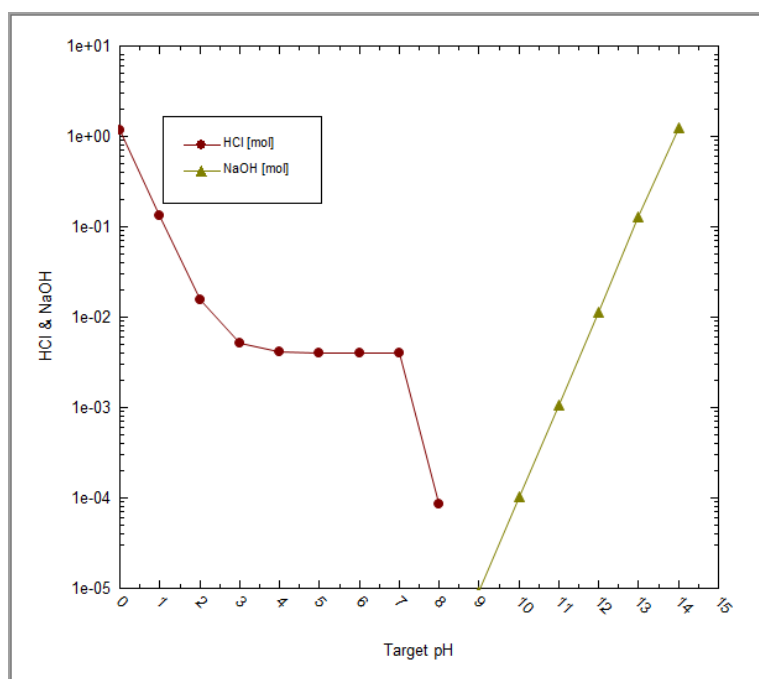
Figure 3-20 log axis plot

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 **<u>Variables</u>** button.
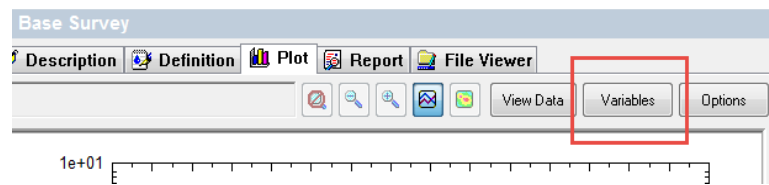
Figure 3-21 The Customize Button

Scroll down this list to find more variables
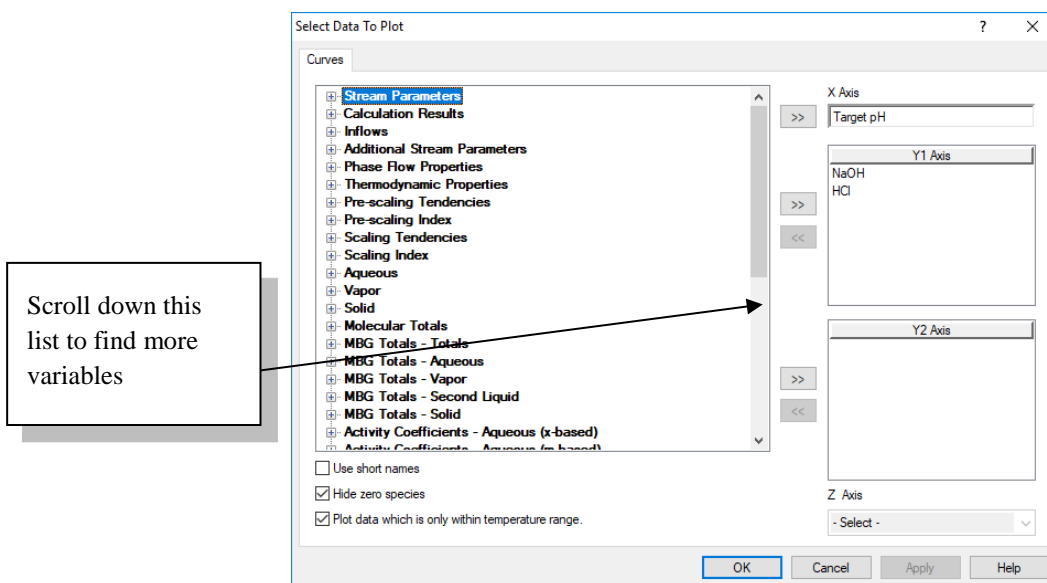
Figure 3-22 The curves plot dialog

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.
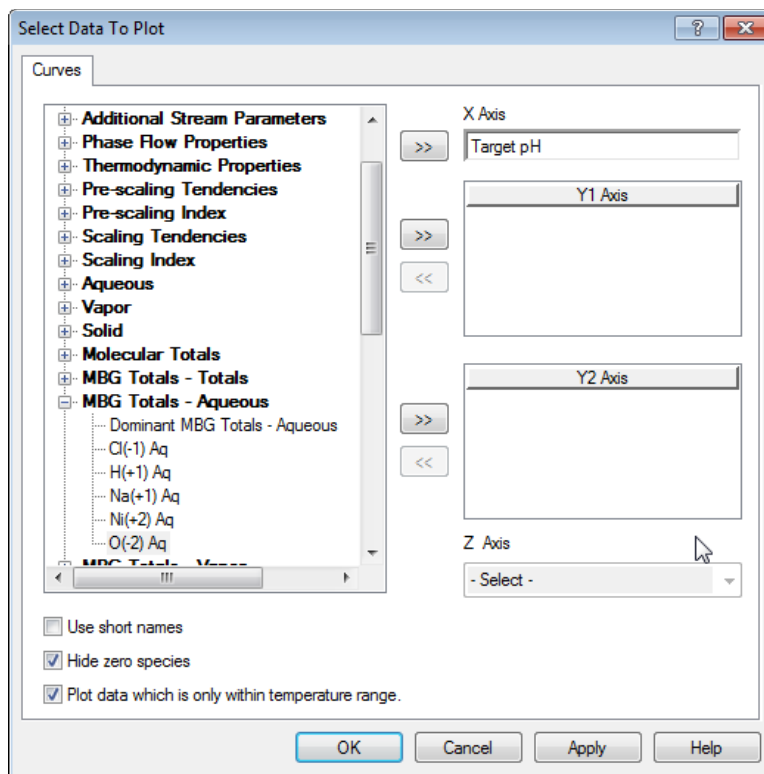
Figure 3-23 Selecting more variables

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.
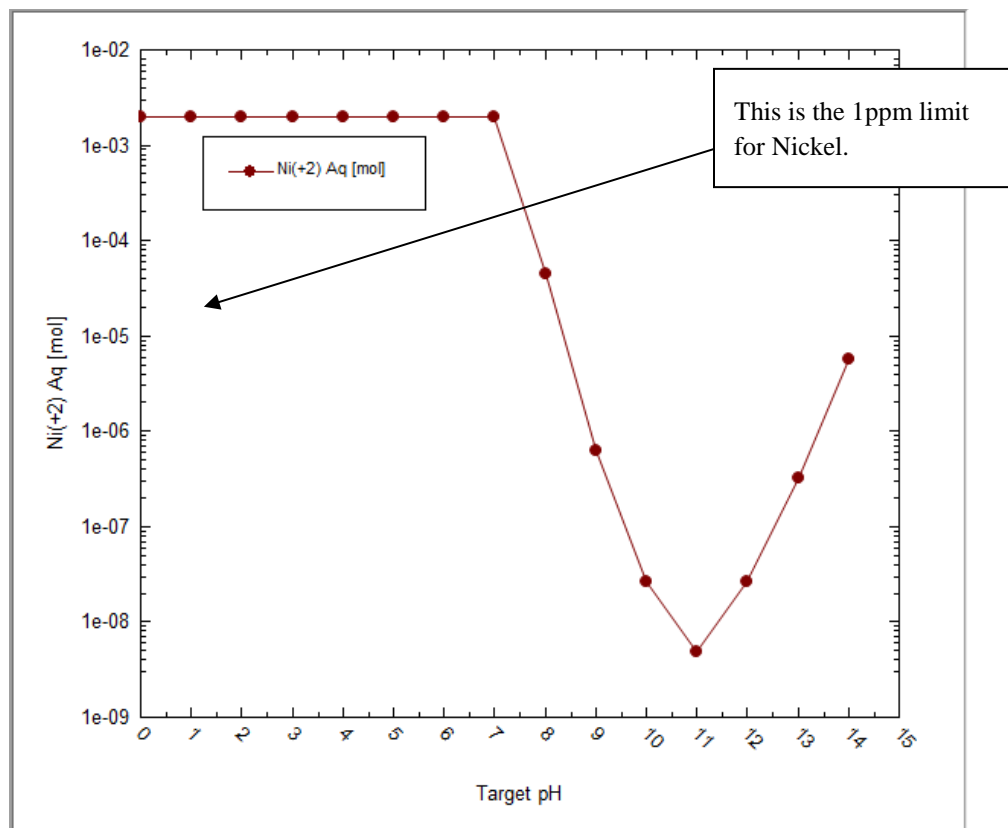
Figure 3-24 The results of the pH survey.

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 from the summation.

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.
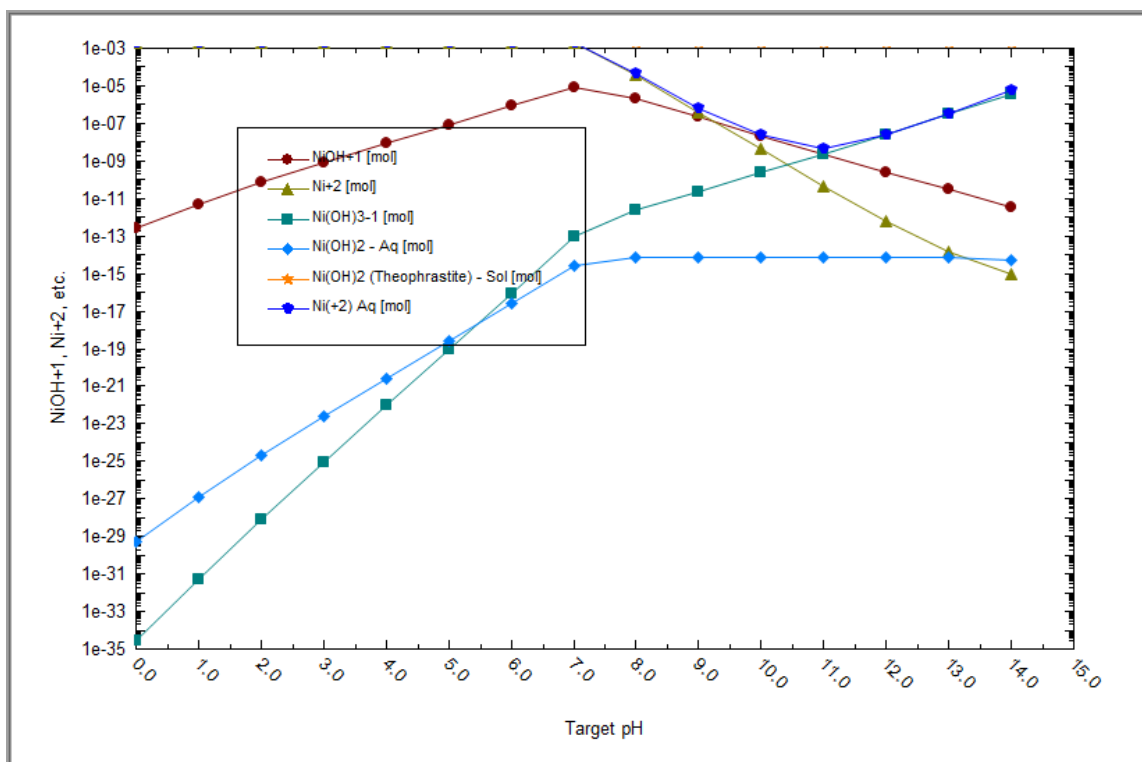
Figure 3-25 Important nickel species

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:
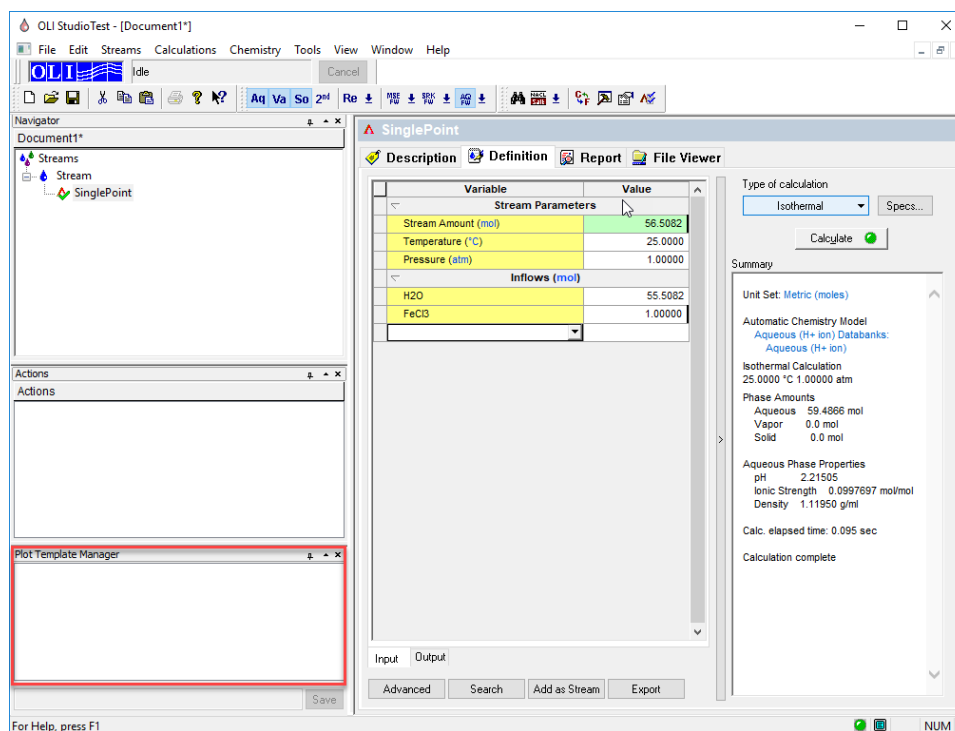
Figure 3-26. Plot Template Manager

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:
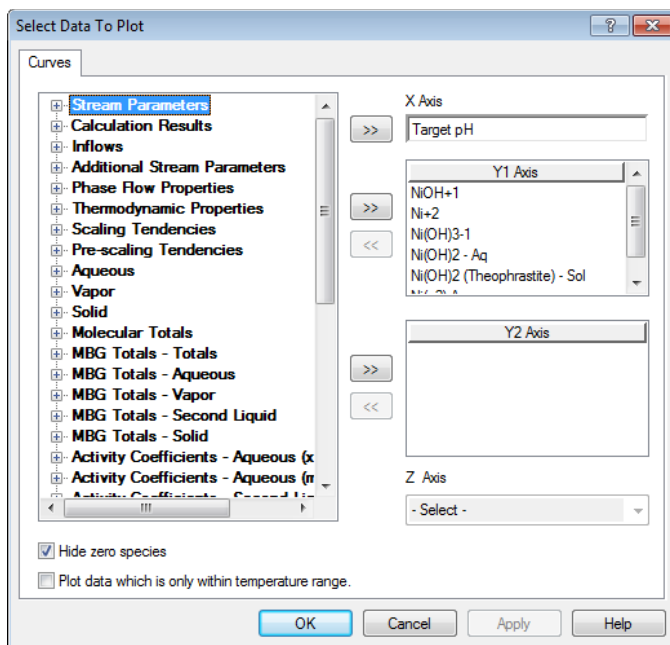
Figure 3-27 Plot data from the previous example.

Remove all the variables from the Y1 Axis box except for **Ni(+2) Aq**
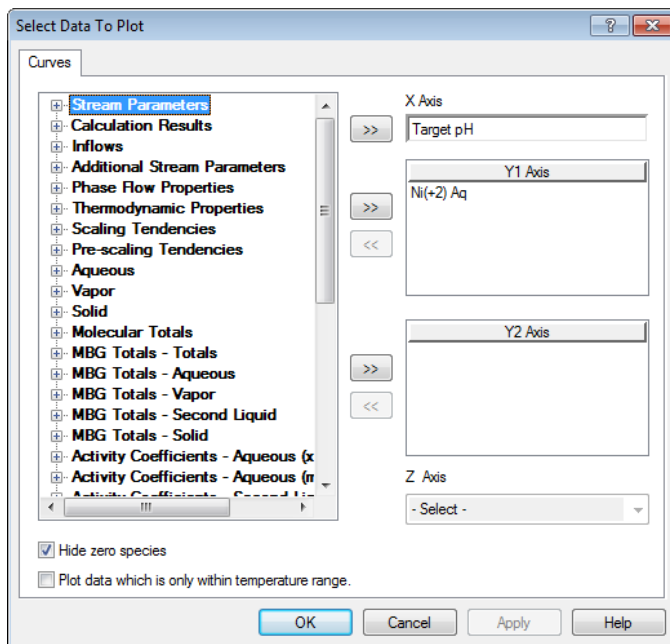
Figure 3-28 Selected variables

- 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.
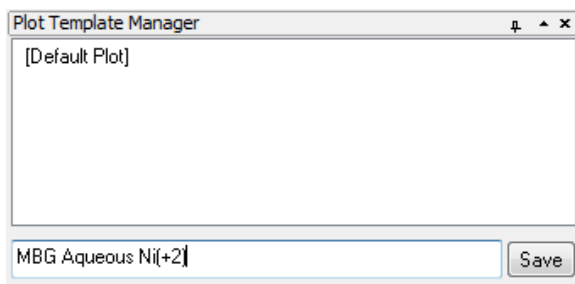
Figure 3-29 Saving a new template for plotting

- Click **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.
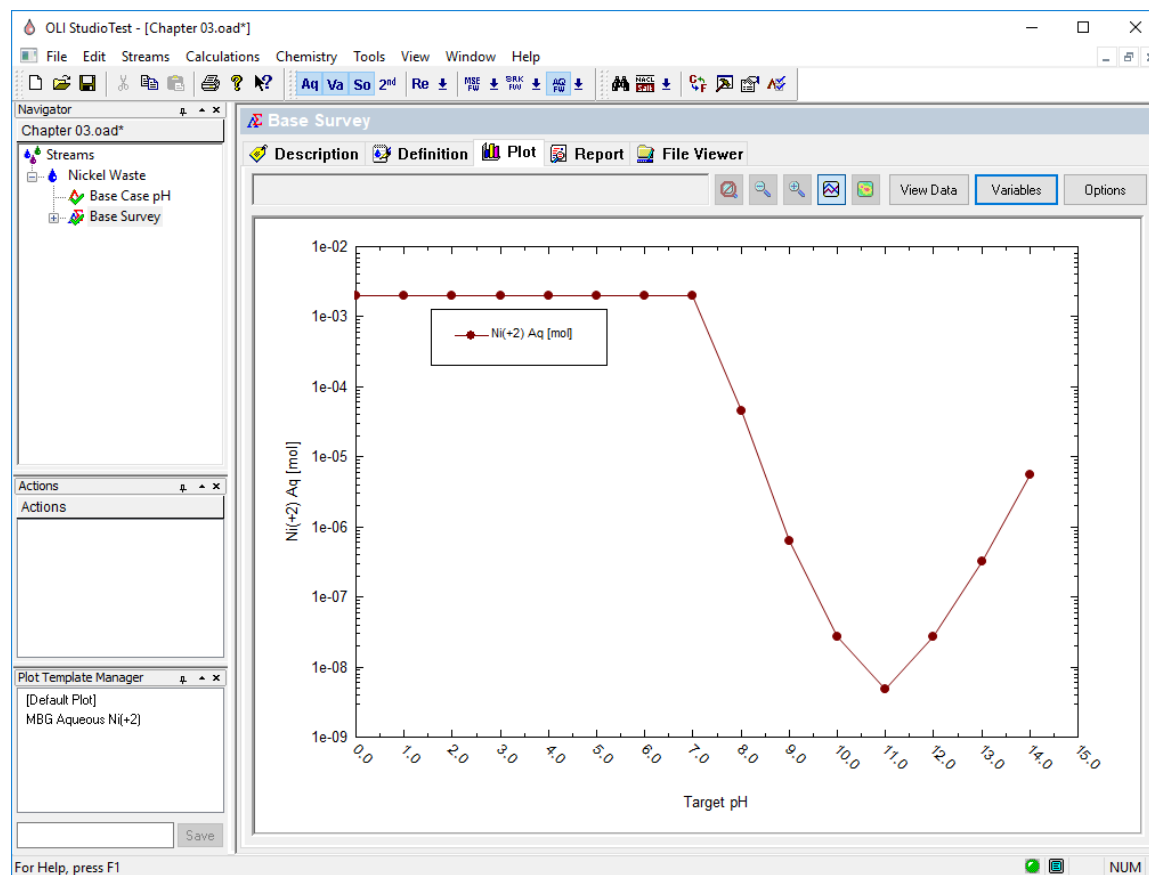
Figure 3-30 Newly added plot template in lower left-hand corner

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.
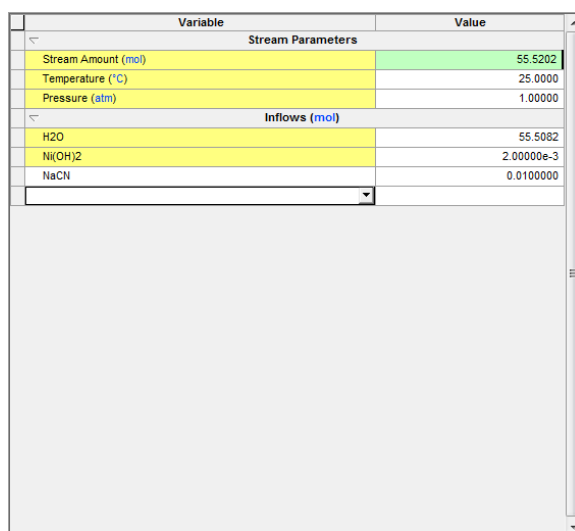
Step 1: Add a new Single Point calculation

- *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 3-31 Adding NaCN

When the **Calculate Button** light turns green, Click on the button.
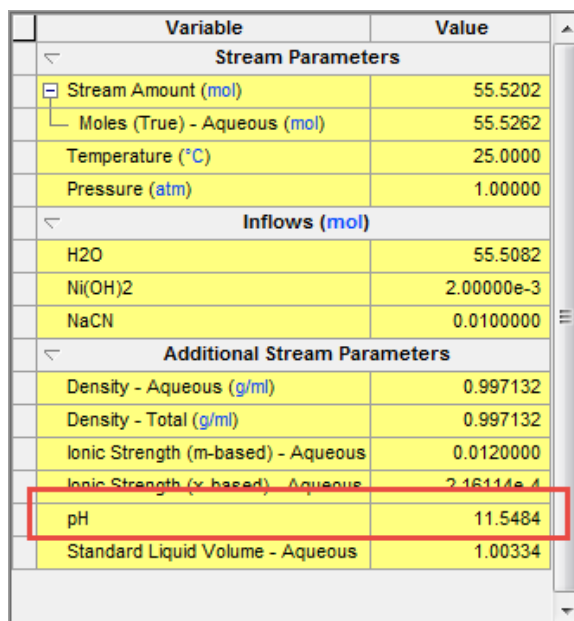
Step 2: Getting results of the Single Point Calculation.

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 3-13 on page 50).

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 3-32The 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.
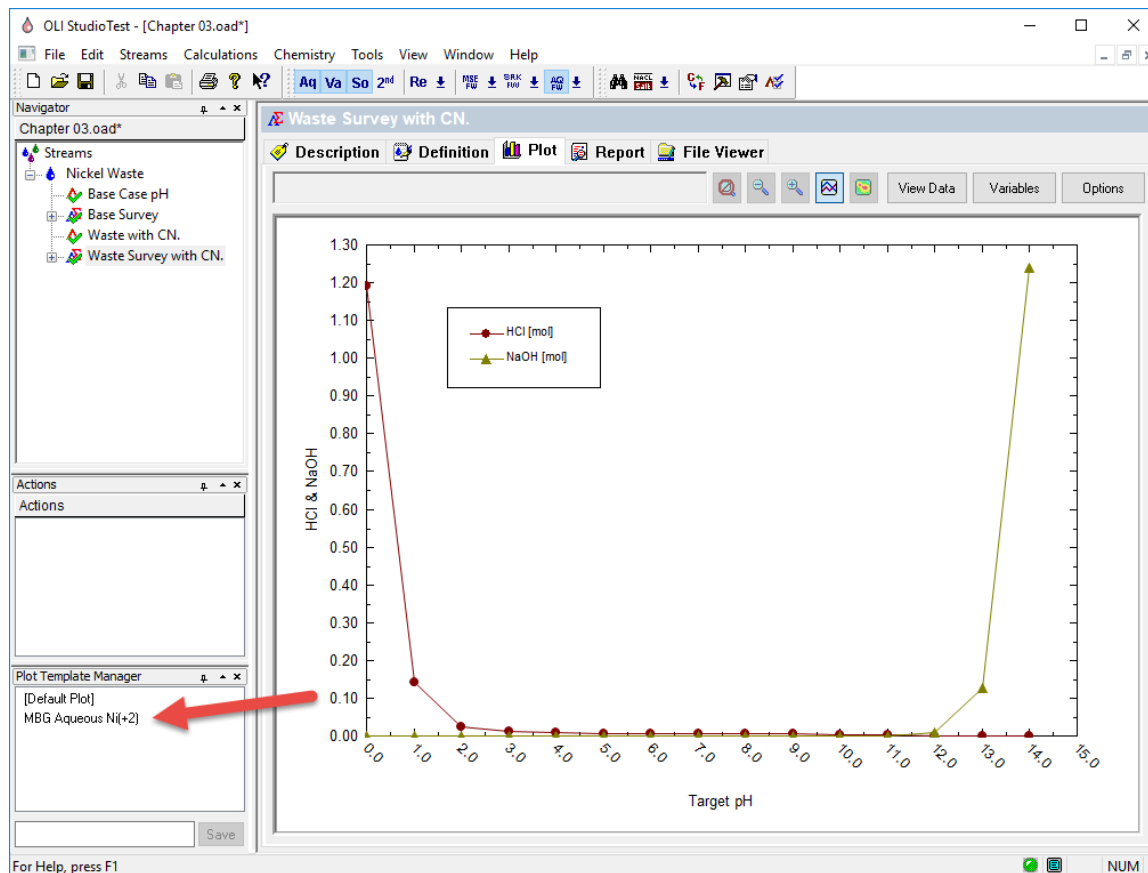
Figure 3-33 Select Plot Template

This will display the MBG Totals – Aqueous plot:
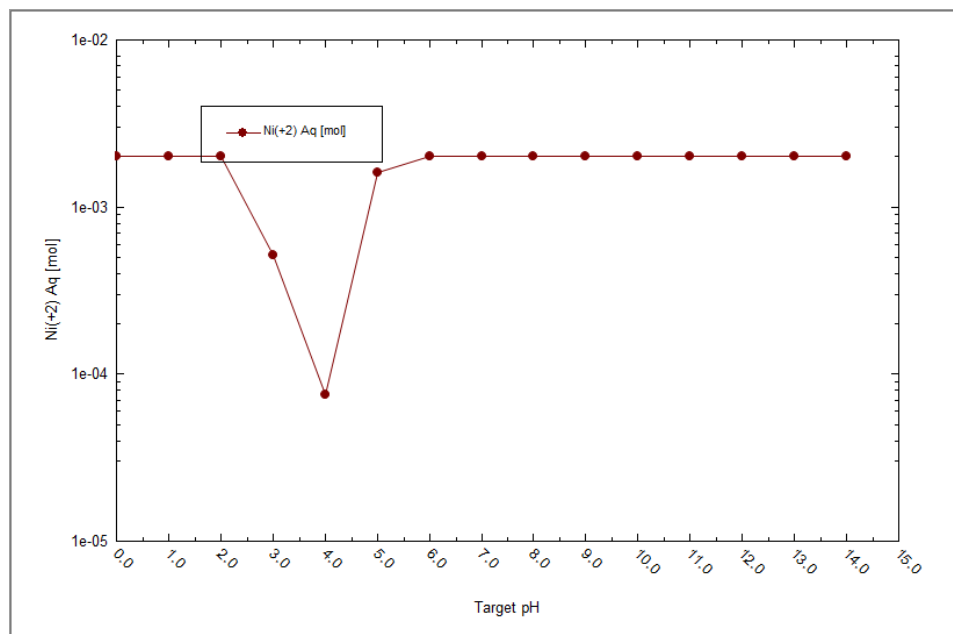
Figure 3-34 The result of the plot template

We can now modify this to display more variables.

Review the steps in **Scenario 1: Step 10** on page 3-53. 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
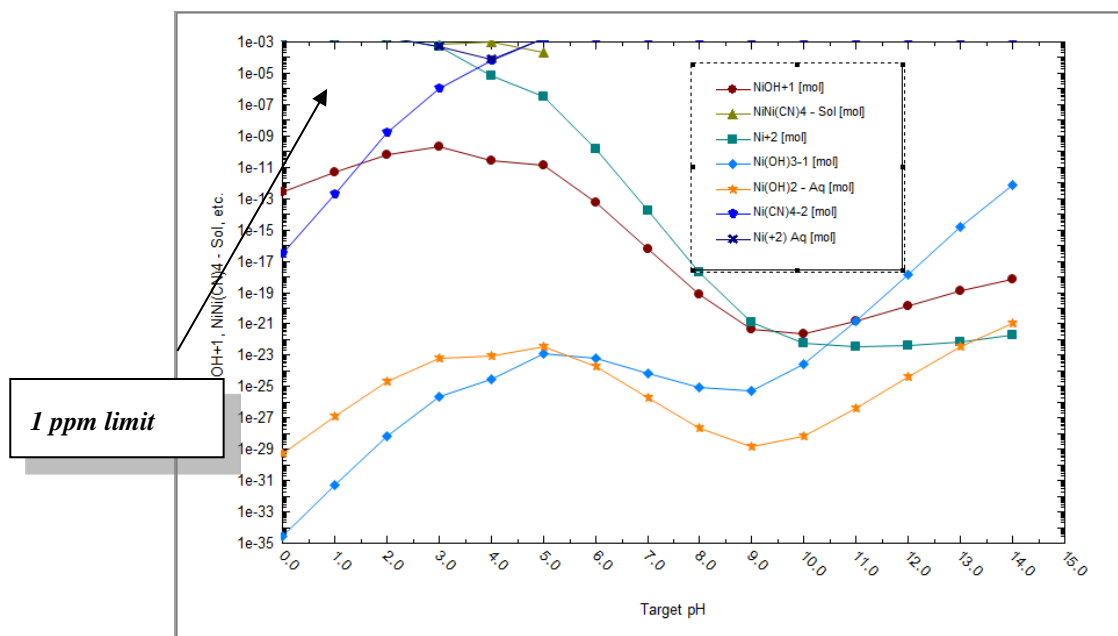
Figure 3-35 Nickel Waste Stream with NaCN added

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 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
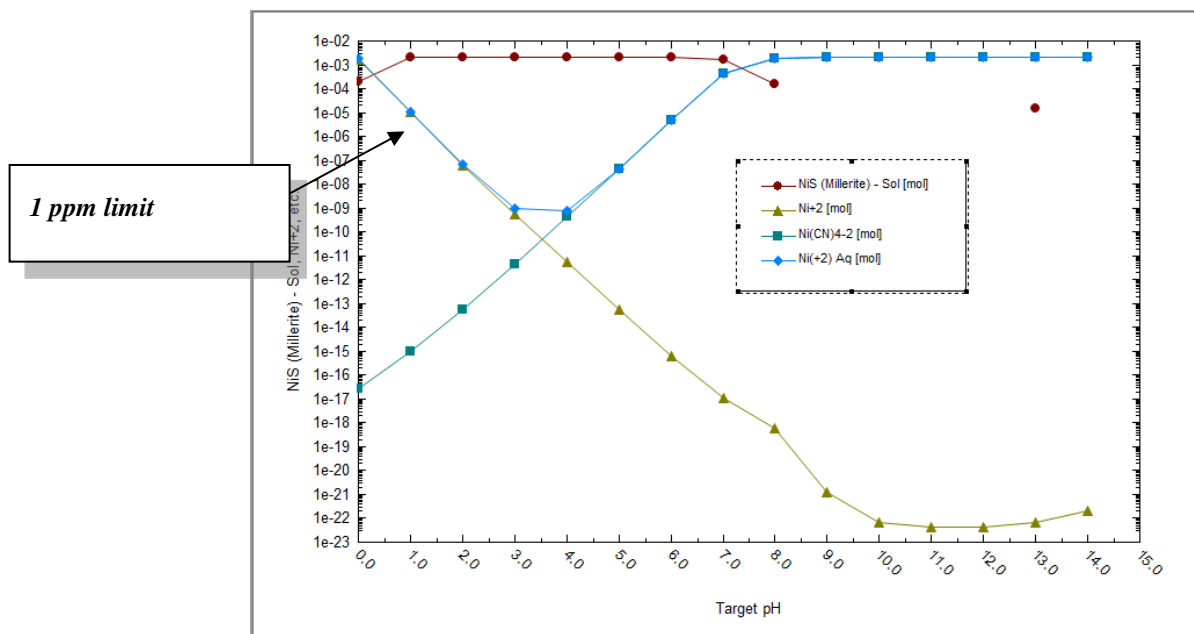
Figure 3-36 Waste Stream pH with both NaCN and H2S added

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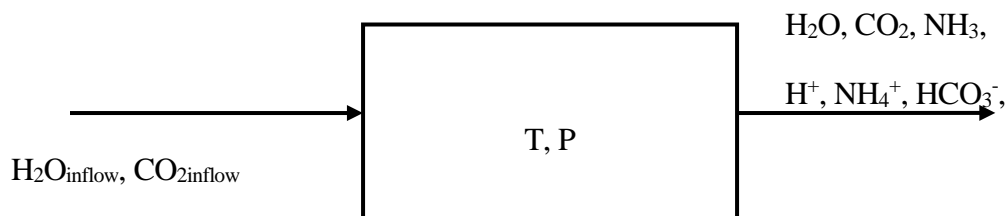
For the practical purposes of this section, we will take an actual problem and work it through. The problem is described as:

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.

$$H_2O_{(aq)} \quad = \quad H^+ + OH^-$$

$$CO_{2(aq)} + H_2O_{(aq)} \quad = \quad H^+ + HCO_3^-$$

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

$$NH_{3(aq)} + H_2O_{(aq)} \quad = \quad NH_4^+ + OH^-$$

$$NH_2CO_2^- + H_2O_{(aq)} \quad = \quad NH_{3(aq)} + HCO_3^-$$
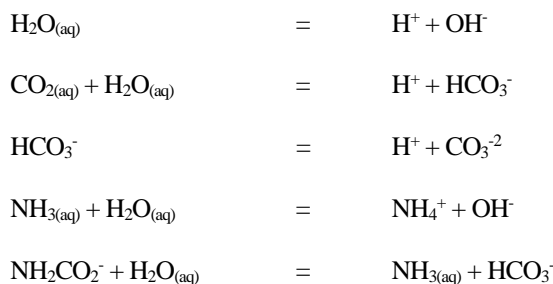
Step 1b: Write an equilibrium K-equation for all the independent aqueous intraphase equilibrium reactions.

For the example posed, these equations are:

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

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

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

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

---

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

* 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.

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

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

Step 2: Write an electroneutrality equation.

$$mH^+ + mNH_4^+ = mHCO_3^- + mNH_2CO_2^- + 2mCO_3^{-2} + mOH^-$$
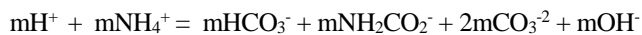
This gives us the sixth equation.

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

Step 3: Write enough 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:

$$2H_2O_{IN} + 3NH_{3IN} = 2H_2O + W(mH^+ + mOH^- + 3mNH_3 + 4mNH_4^+ + mHCO_3^- + 2mNH_2CO_2^-)$$
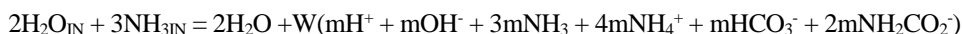
> For each balance, the amount of each species is multiplied by the number of atoms. In this case, for Hydrogen, we multiply by 4 for NH$_4^+$

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 4-1 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

---

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

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 ℃ (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.

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:

1. Vapor
2. Aqueous
3. 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.
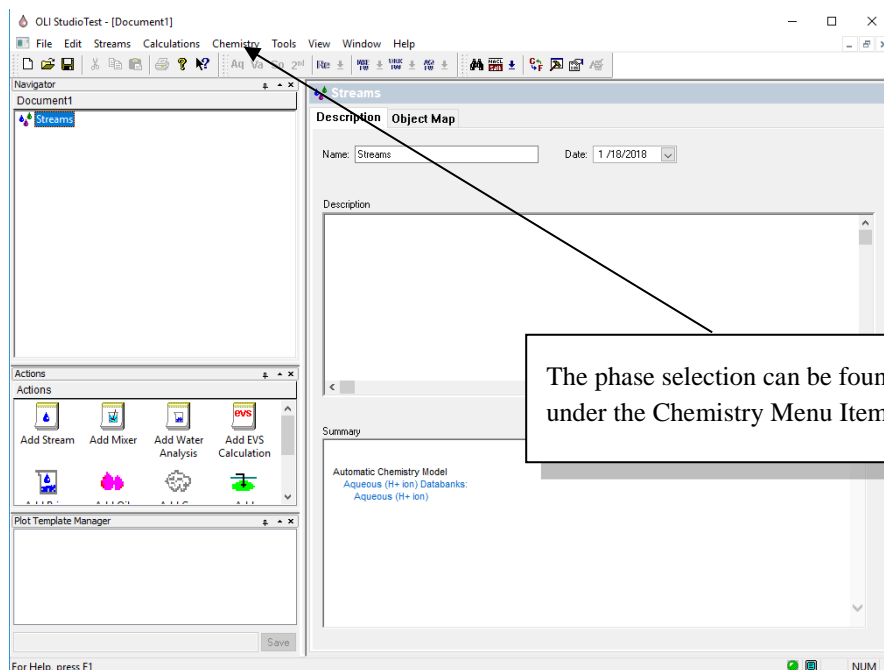
Figure 4-1 The Welcome window for OLI Studio
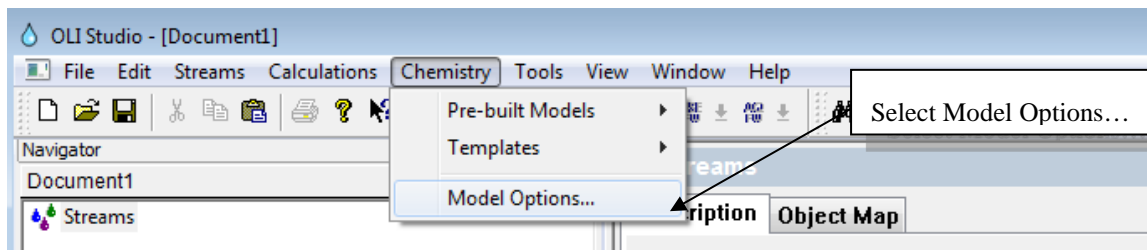
Figure 4-2 Chemistry Menu Items

.
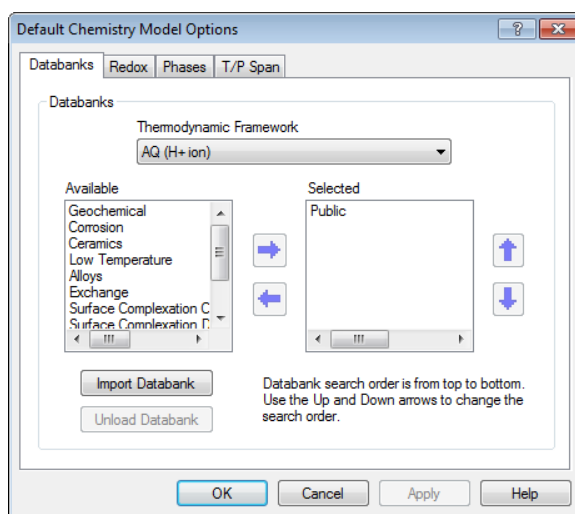
Figure 4-3 Model Options

Click on the **Phases** tab

Figure 4-4 Selecting phases

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

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.

Table 5-1 Chapter 5 Initial Values

Parameter/Component	Value	Units
Temperature	25	°C
Pressure	1.0	Atmosphere
H_2O	55.5082	Moles (this is the default value)
$CaCl_2$	0.1	Moles
$MgCl_2$	0.1	Moles
CO_2	0.01	Moles
$CaCO_3$	0.0	Moles

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

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
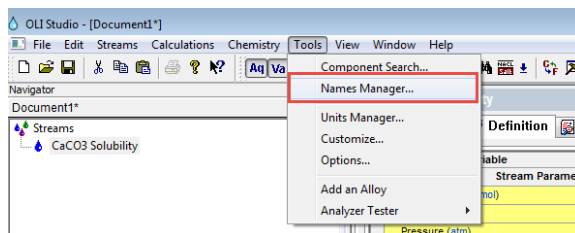
Figure 5-2 The Tools Menu

Selecting the **Names Manager** from the tools menu will display several options.
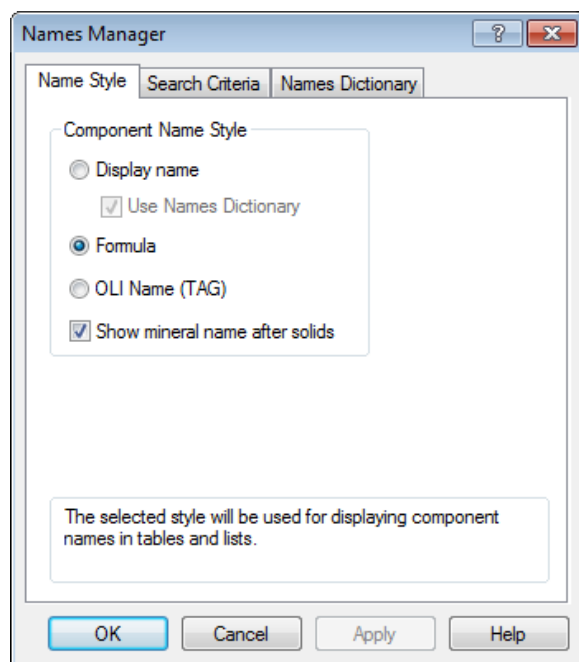
Figure 5-3 The Names Manager.

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.

Table 5-2 Names Manager Option

Parameter	Definition
Display name	This is the name 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 many 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	
Precipitant:	<select>
Adjusted Inflow:	<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 1.0×10^{-10} times the stream amount - a 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.
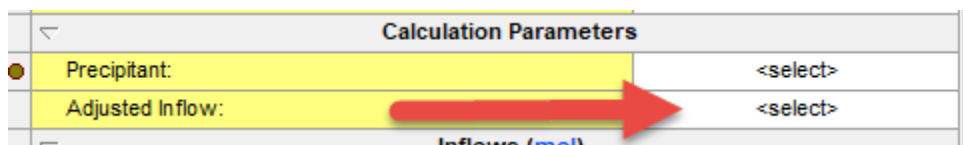
Figure 5-6

- select **CACO3**
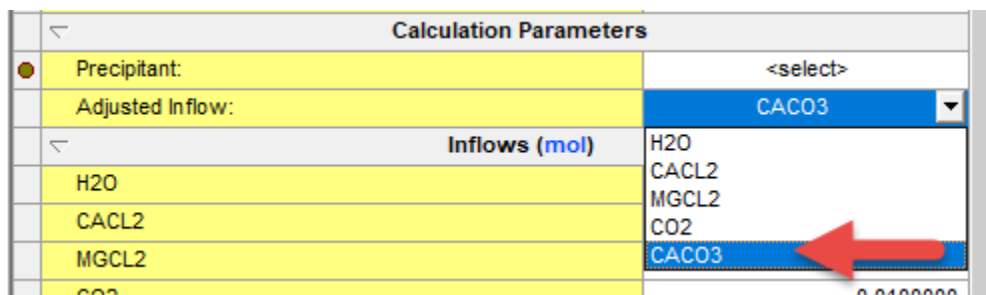
Figure 5-7

- Next *Click* in the ***Precipitant:*** box.
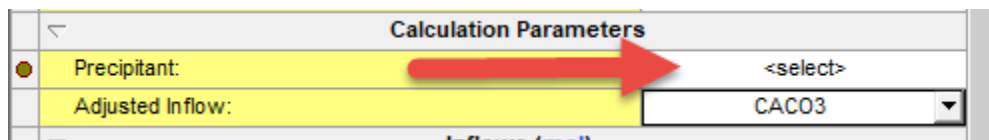
Figure 5-8

- And then select **CACO3 (Calcite)** you may need to scroll down to find it!
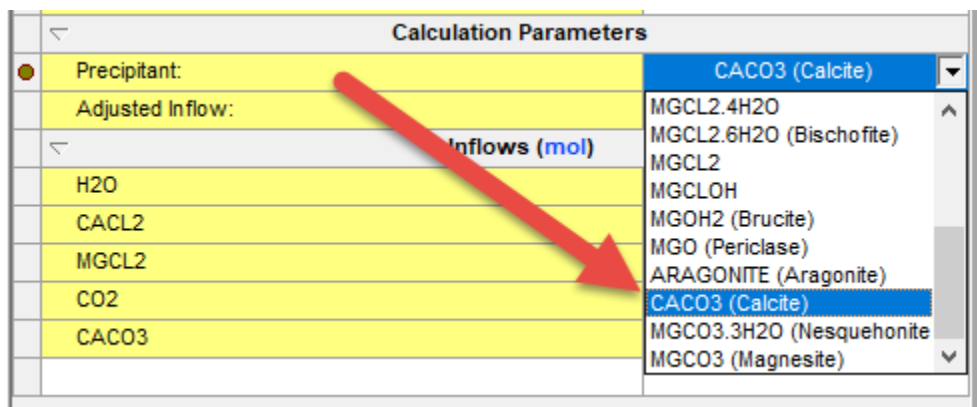
Figure 5-9

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
    Aqueous (H+ ion) Databanks:
        Aqueous (H+ ion)
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: 0.457 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:

Table 5-3 Databases used in this example

Databank	Description
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 (a/k/a CORROSIO)	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 **Chemistry** from the menu.

- Select **Model Options…** from the menu list.
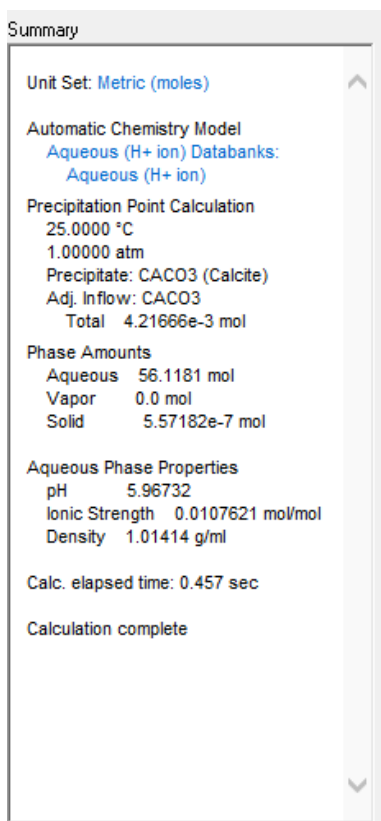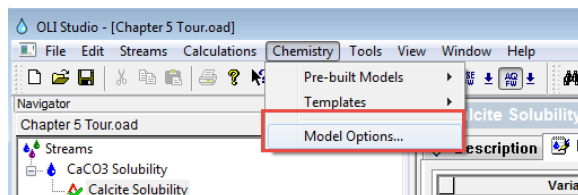

Figure 5-11 The Chemistry Menu

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

- Select **Geochemical** Databank and *click* the right arrow. *Click* **OK** 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.
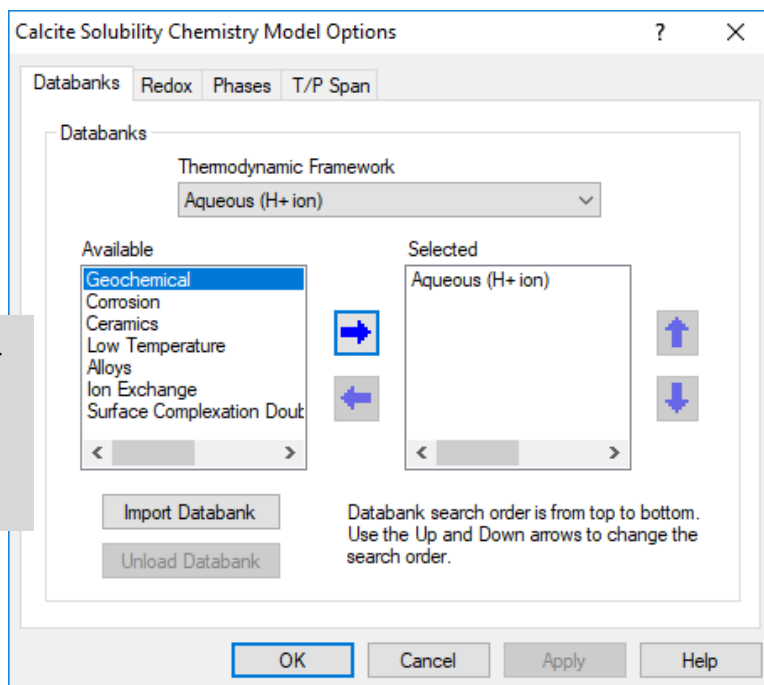
Figure 5-12 Selecting the Geochemical databank
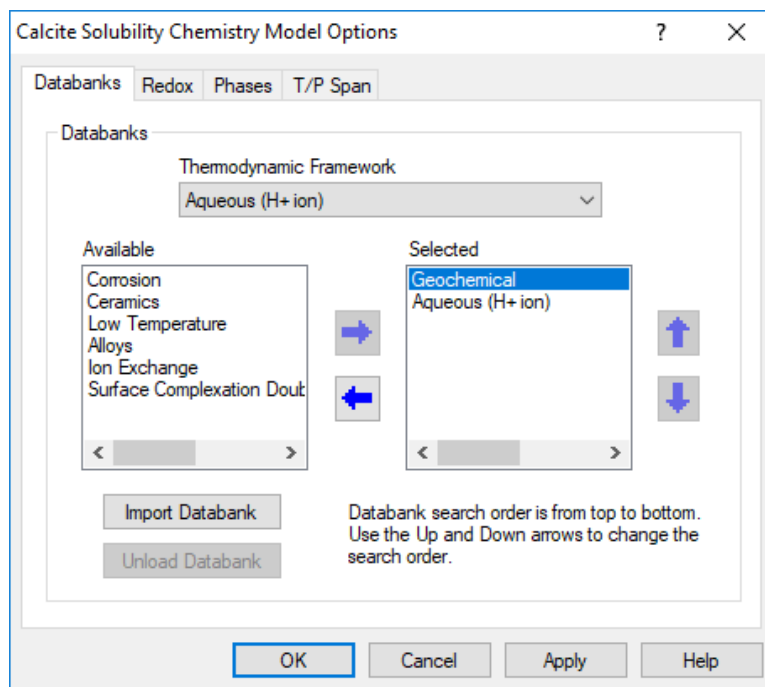
Figure 5-13 Geochemical databank selected

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:

<div style="margin-left: 4em;">

Calcite $CaCO_3$

Aragonite $CaCO_3$

Dolomite $CaMg(CO_3)_2$

</div>

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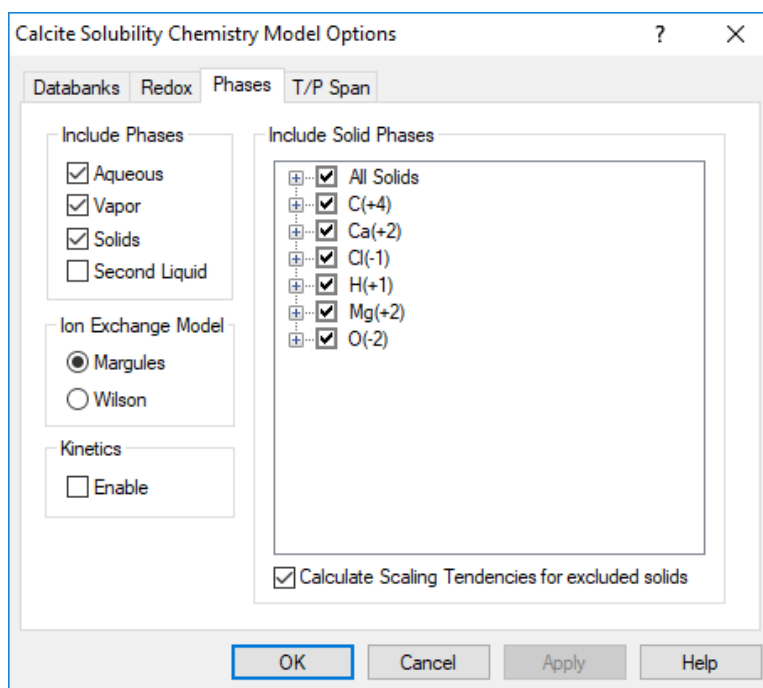
Figure 5-14 Removing Calcite (CaCO3) from the chemistry model

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
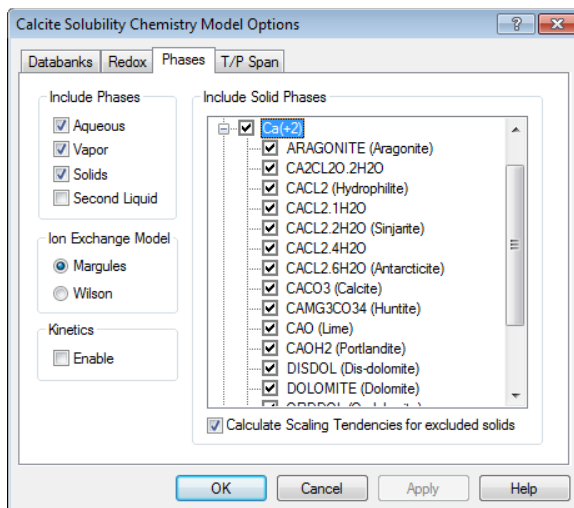
Figure 5-15 Expanding Calcium Solids

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:
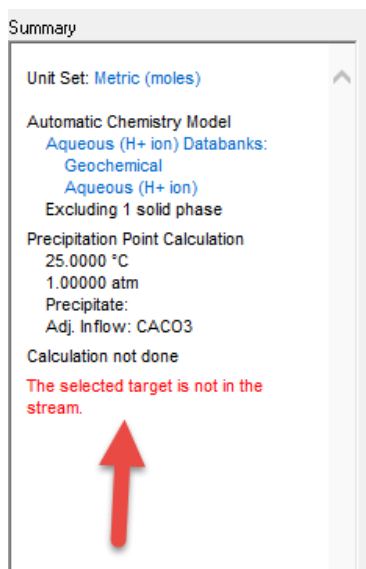
Figure 5-16

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.
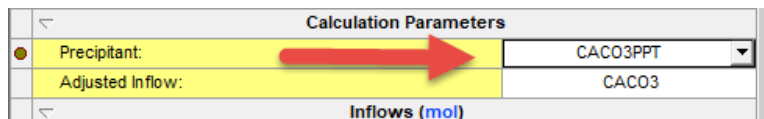
Figure 5-17

Change selection from CACO3PPT to **ARAGONITE (Aragonite)** from the solids list.
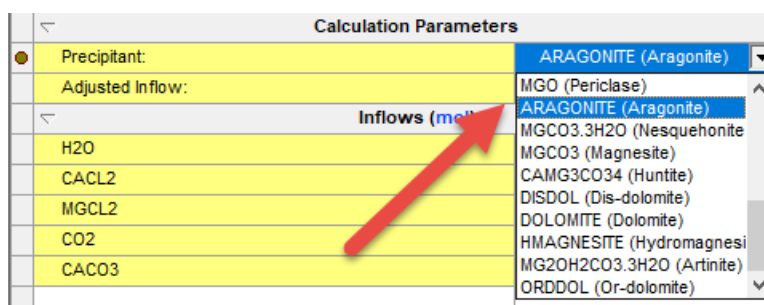
Figure 5-18

CACO3 remains as the **Adjusted Inflow.**

- 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

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	

Input Output

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.
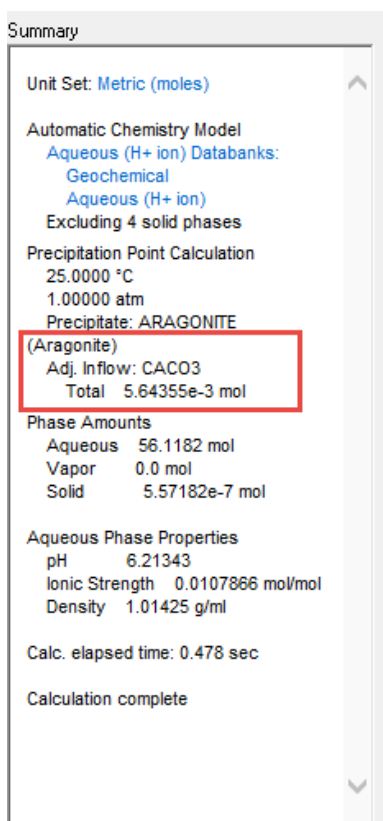
Figure 5-21 Solubility with Dolomite Turned off

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 Manager. One is through tools-> Units manager. Second is clicking on

this icon at the top toolbar. Both options should lead to the pop up window below.
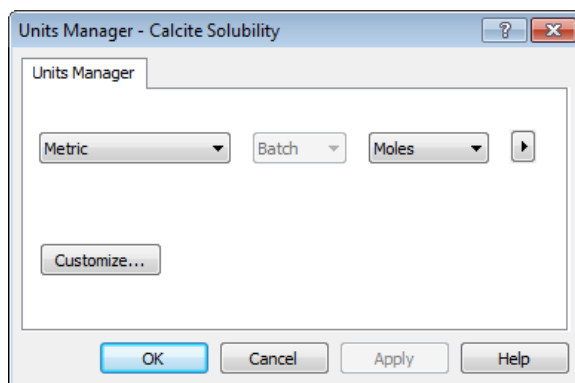
Figure 5-22 Units Manager

This Units manager gives more control at a higher level.

You can set your desired set of units from quick list option below.
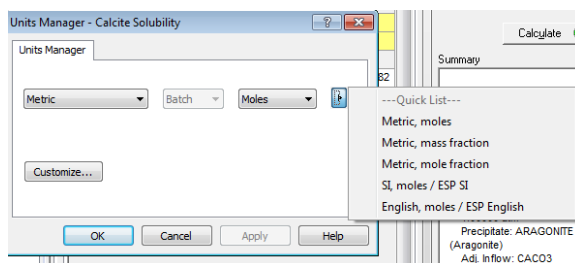
Figure 5-23 Using flyout menu for the units manager

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.

Figure 5-24 Customize units

Figure 5-25 Units Manager Dialog

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

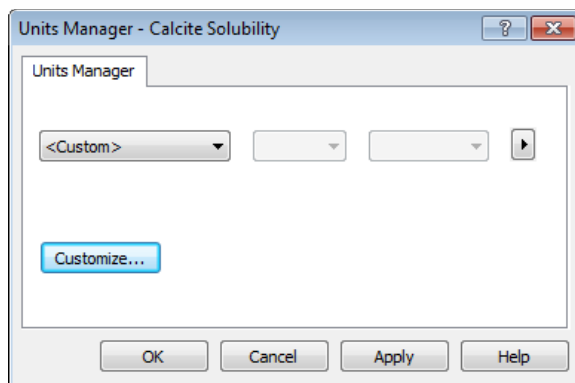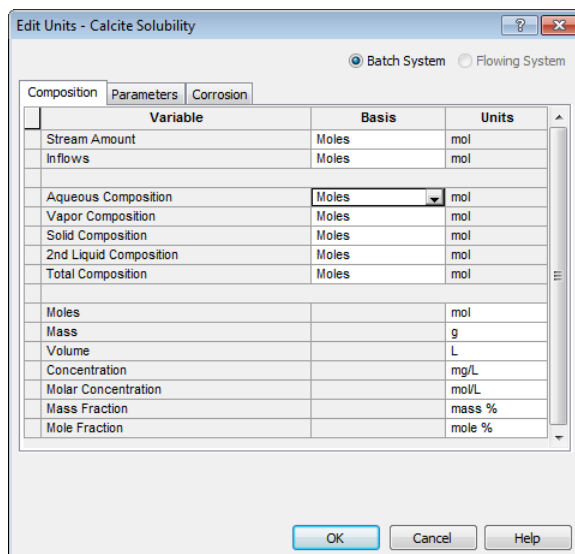The evaluation of the following equation is central to the OLI Software:

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

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 v_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 °C (298.15K)[11]?

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

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

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

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

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:

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

$$K^R = 0.34$$

---

[11] 25°C (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

[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**.

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 °).

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

$$\overline{S}_i = \overline{S}_i^{\,o} + \overline{S}_i^{\,E}$$

Partial Molal Heat Capacity

$$\overline{C}p_i = \overline{C}p_i^{\,o} + \overline{C}p_i^{\,E}$$

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

---

[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.

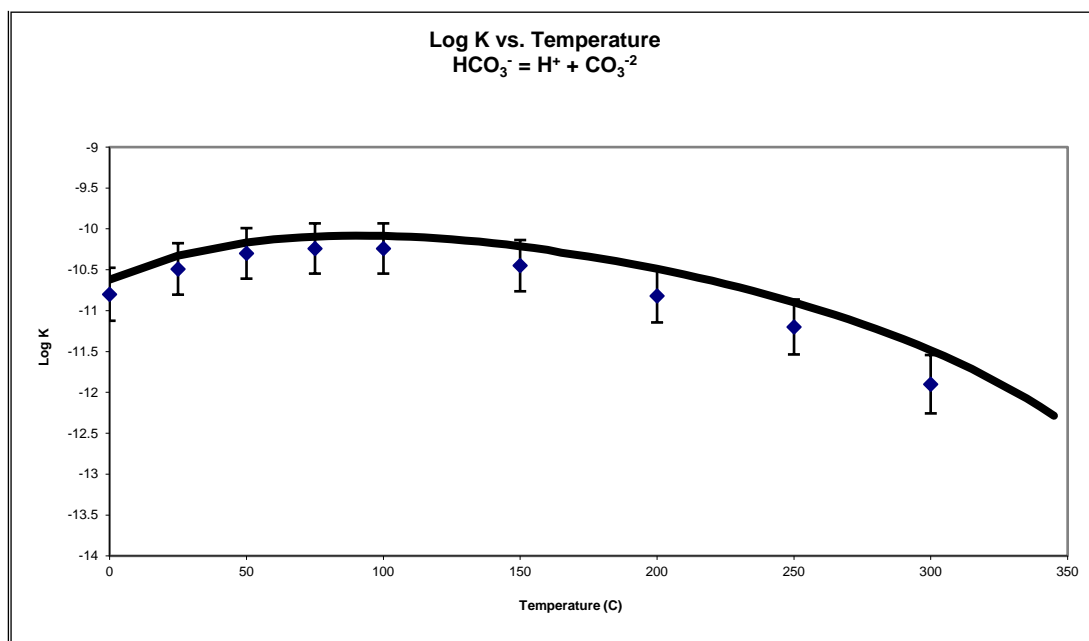The Helgeson Equation of State Parameters are used to predict equilibrium constants.

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.

---

[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)*

The Helgeson Equation of State

Enthalpy

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

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

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

Gibbs Free Energy

$$\overline{\Delta G^o_{P,T}} = \overline{\Delta G^o_f} - \overline{S^o_{Pr,Tr}}(T-T_r) - c_1\left[T\ln\left(\frac{T}{T_r}\right) - T + T_r\right] + a_1(P-P_r) + a_2\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\left(\frac{\Psi+P}{\Psi+P_r}\right)$$

$$+ \left[a_3(P-P_r) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right]\left(\frac{1}{T-\Theta}\right) - c_2\left[\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right)\right)\left(\frac{\Theta-T}{\Theta}\right) - \frac{T}{\Theta^2}\ln\left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right)\right]$$

$$+ \omega\left(\frac{1}{\varepsilon}-1\right) - \omega_{Pr,Tr}\left(\frac{1}{\varepsilon_{Pr,Tr}}-1\right) + \omega_{Pr,Tr}Y_{Pr,Tr}(T-T_r)$$

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

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

Entropy

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

$$+ \omega Y - \left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_P - \omega_{\mathrm{Pr},Tr}Y_{\mathrm{Pr},Tr}$$

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…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.
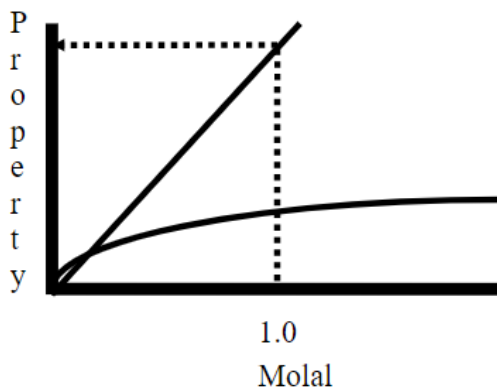
Vapor

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.

---

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

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:

$$a_i = \gamma_i m_i$$

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

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

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

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

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

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,

$\mathring{A}$ ion size parameter

$A(T)$, $B(T)$ Debye-Huckel parameters related to dielectric constant of water.

At 25 °C 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⁺:

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

where:

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.

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

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

---

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*

Each of the modern formulations are explained in more detailed below:

1. *Bromley*

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

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

2. *Meissner*

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

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

---

[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)

$$B = 0.75 - 0.065q$$

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

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

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

The family of q values are:
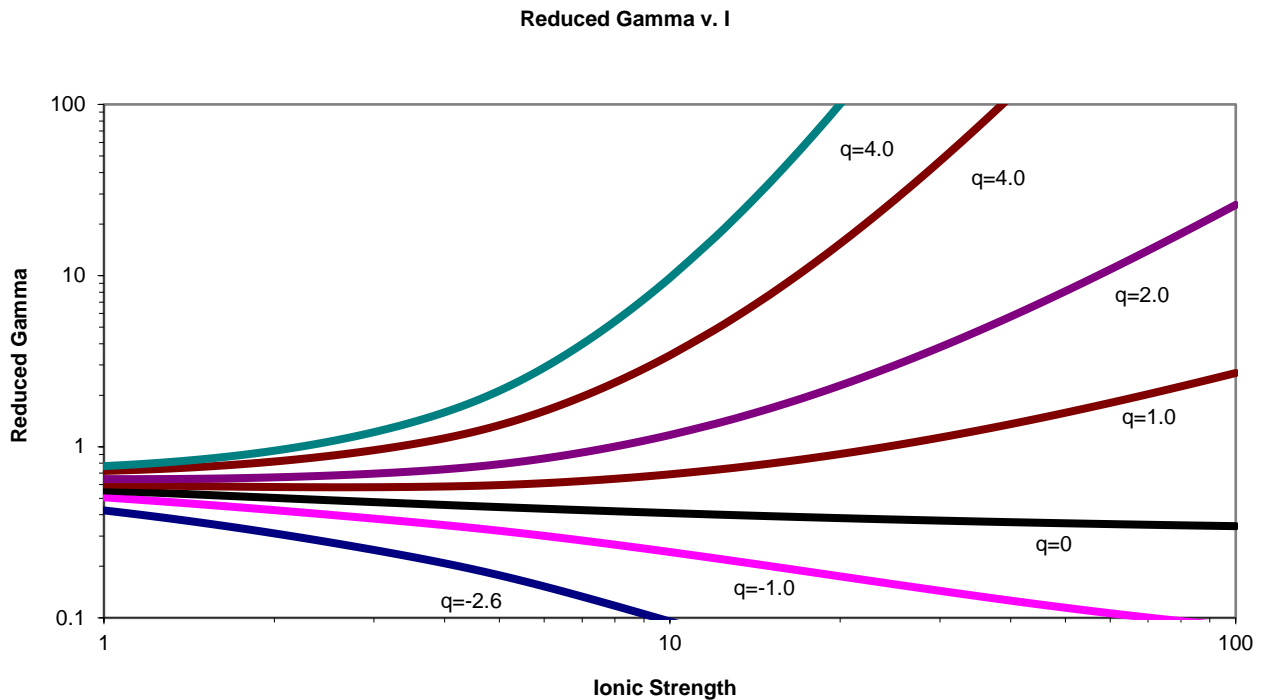
Figure 6-2 The Meissner q lines

3. 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:

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[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.

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

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

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

The other coefficients have the same form:

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

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

4. Pitzer

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

Where,

f^γ	=	The "Debye-Huckel" term.[28]
v_+	=	Stoichiometric coefficient for the cation
v_-	=	Stoichiometric coefficient for the anion
v	=	$v_+ + v_-$
m	=	Concentration in molal
$B_\pm^\gamma$	=	Pitzer B term, containing the adjustable parameters
$C_\pm^\gamma$	=	Pitzer C term, containing adjustable parameters

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[28] IBID, Page 74

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5. Helgeson

$$Log\ \overline{\gamma_{\pm}} = \frac{-A_{\gamma}\mid Z_i Z_l \mid \sqrt{\overline{I}}}{1 + a_0 B\gamma\sqrt{\overline{I}}} + \Gamma_{\gamma} + \left(\frac{\omega_k}{\nu_k}\sum_k b_k Y_k \overline{I} + \frac{\nu_{i,k}}{\nu_k}\sum_l \frac{b_{il}\overline{Y_l}\sqrt{\overline{I}}}{\Psi_l} + \frac{\nu_{l,k}}{\nu_k}\sum_i \frac{b_{il}\overline{Y_i}\sqrt{\overline{I}}}{\Psi_i} \right)$$

Where,

A_{γ}	=	Debye-Hückel 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-Hückel term according to Helgeson
$\overline{I}$	=	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

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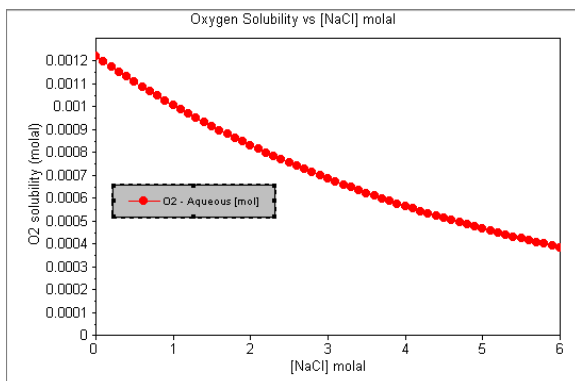
Figure 6-3 The solubility of oxygen in NaCl solutions at 25 C, 1 Atmosphere

1. Setschenow[29]

This characterizes a phenomenon 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.

2. Pitzer[30]

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

---

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

[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)

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

Where,

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

                (a function of temperature)

$\beta_{0(m\text{-}s)}$ =   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:

$$S_i = p_1\,P_1 + p_2\,P_2 + ...\ p_p\,P_p$$

Examples:

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

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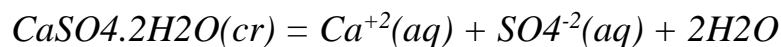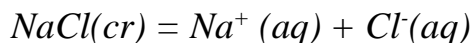
Solid Phase Thermodynamic Properties

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

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

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

$$V = b_1$$

$$\text{Log}_{10}\text{K}_{sp}(\text{T,P}) = \text{A} + \text{B/T}_\text{K} + \text{CT}_\text{K} + \text{DT}^2{}_\text{K} + \text{E} + \text{FP} + \text{GP}^2$$

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

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

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

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.

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

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

$$\overline{G_{Vi}^o} \; + \; RTln(\; f_{\,Li}) \; = \; \overline{G_{Aqi}^o} \; + \; RTln(\; a_{\,Aqi})$$

$$K \; = \; EXP[\frac{\overline{(G_{Aqi}^o \; - \; \overline{G_{Li}^o})}}{RT}] \; = \; \frac{a_{\,Aqi}}{f_{\,Li}}$$

Limitations of the Current OLI Thermodynamic Model[31]

Aqueous Phase

$X_{H2O} > 0.65$

$-50\ ^oC < T < 300\ ^oC$

$0\ atm < P < 1500\ atm$

$0 < I < 30$

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.

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[31] This refers only to the traditional OLI Aqueous Model and not the MSE model or MSE-SRK 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:
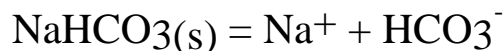
$$NaHCO_{3(s)} = Na^+ + HCO_3^-$$

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:

$$\gamma_{Na} \quad = \quad 1.0 \qquad\qquad \gamma_{HCO3} \quad = \quad 1.0$$

$$m_{na} \quad = \quad 1.0 \qquad\qquad m_{HCO3} \quad = \quad 1.0$$

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

$$IAP = 1.0$$

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.

---

[34] Based on the OLI PUBLIC databank version 9.2.6

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

$$ST = 1.0/0.265038$$

$$ST = 3.77$$

Was assuming ideal conditions valid??

The actual species concentration and activity coefficients are:

$$\gamma_{Na} = 0.566 \qquad \gamma_{HCO3} = 0.566$$

$$m_{Na} = 0.764 \qquad m_{HCO3} = 0.739$$

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:

$$CO_2^o \qquad = \qquad 0.014 \text{ molal}$$

$$NaHCO_3^o \qquad = \qquad 0.233 \text{ molal}$$

$$CO_3^{2-} \qquad = \qquad 0.011 \text{ molal}$$

$$NaCO_3^- \qquad = \qquad 0.003 \text{ molal}$$

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.

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
Na2CO3	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.
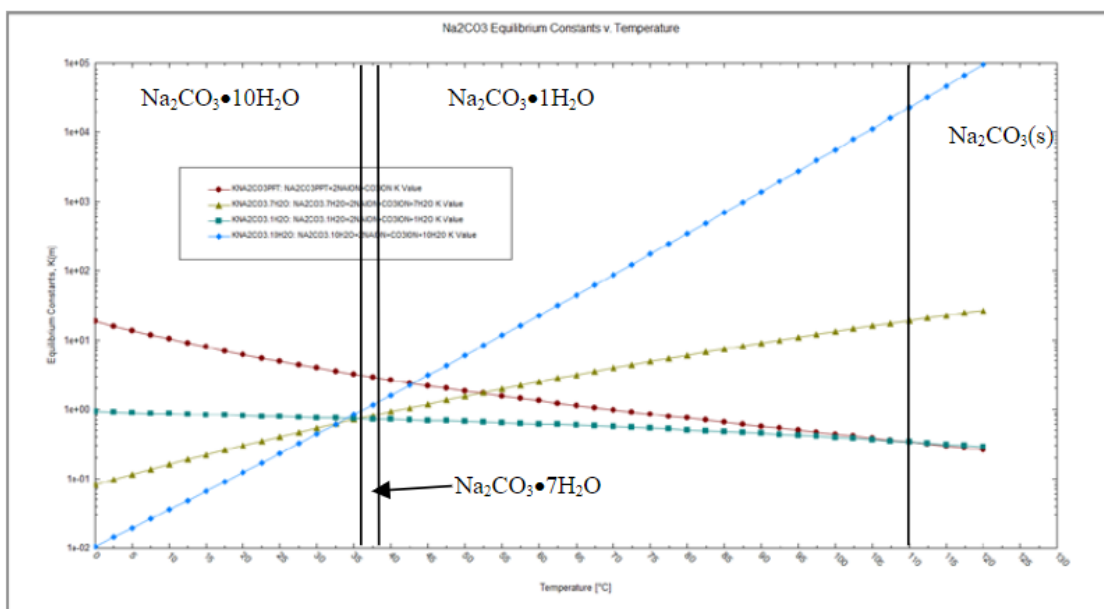
Figure 6-4 Plot of K vs. Temperature. The K's have been extrapolated.

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.

The mono-hydrate species does not extrapolate well to lower temperatures. In the range 35 to 37 °C, that the mono-hydrate equilibrium constant is smaller than the hepta-hydrate. If we concern ourselves with 36°C, we can see that if the mono-hydrate solid could 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 9.6.1 which can be found here Pre-scaling example (OAD, v9.6.1)

Let's look at an example. We have created a simple case in MSE.
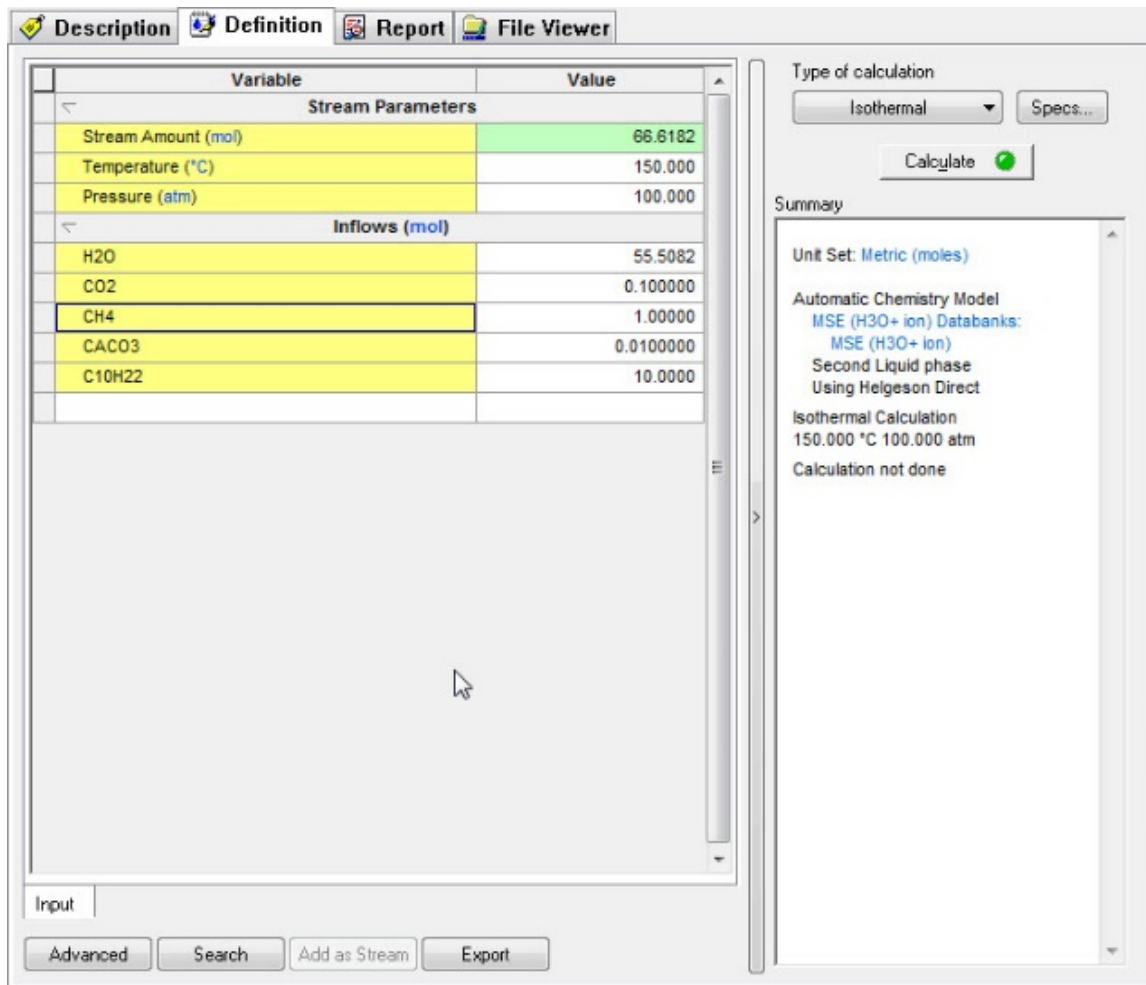
Figure 6-5 An MSE case, example of pre-scaling

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
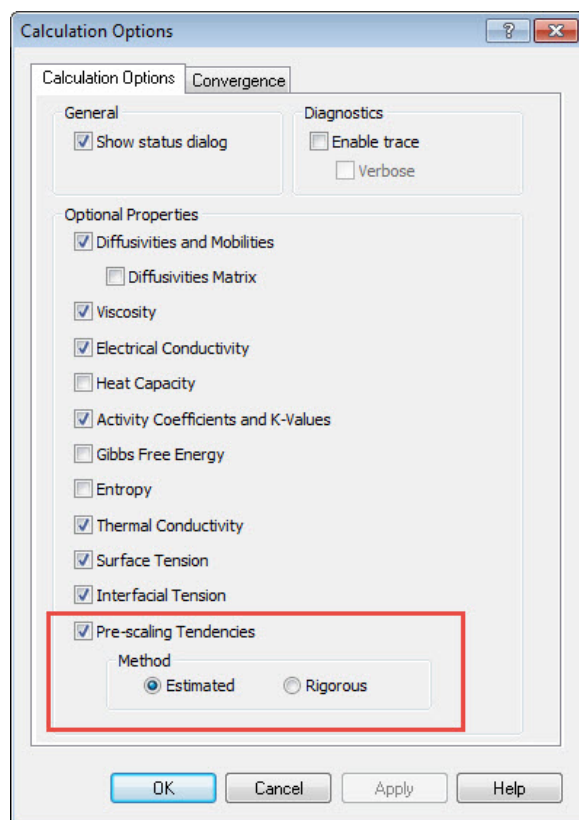
Figure 6-6 Calculation Options for a single point case

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

We will run this case and look at the output.
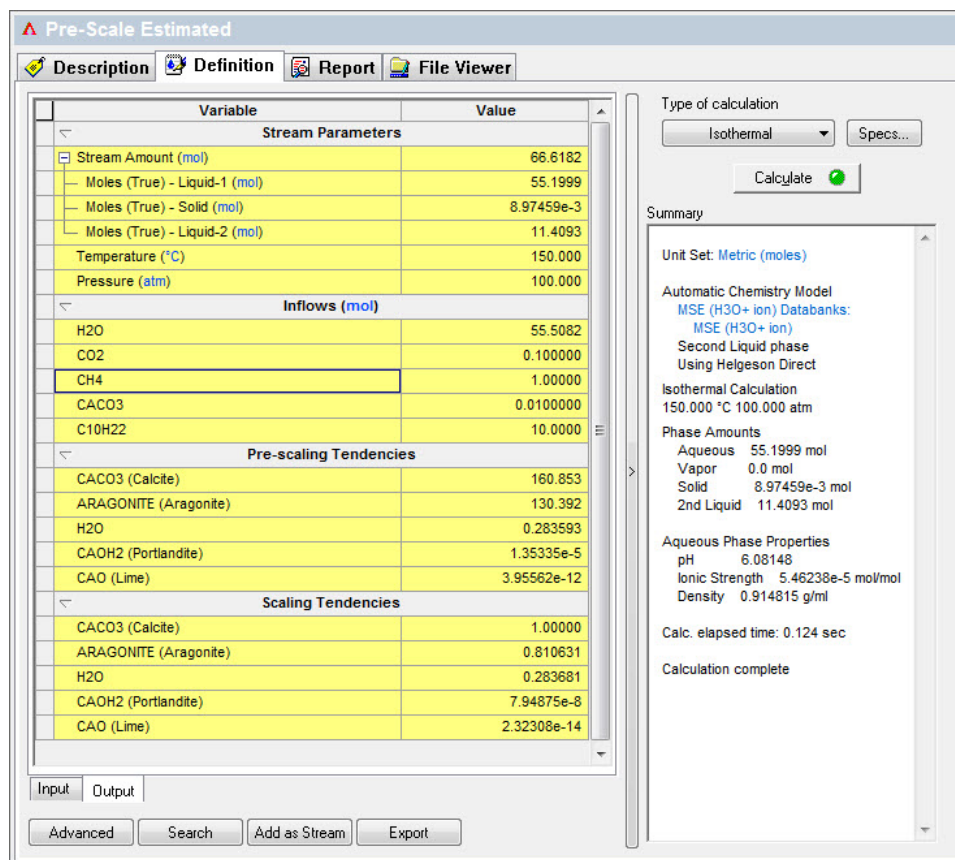
Figure 6-7 Results with estimated pre-scaling tendencies

Look the pre-scaling tendencies for CaCO₃(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

We have 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 CaCO₃and MgCO₃ in the same model or with very soluble species such as Na₂CO₃

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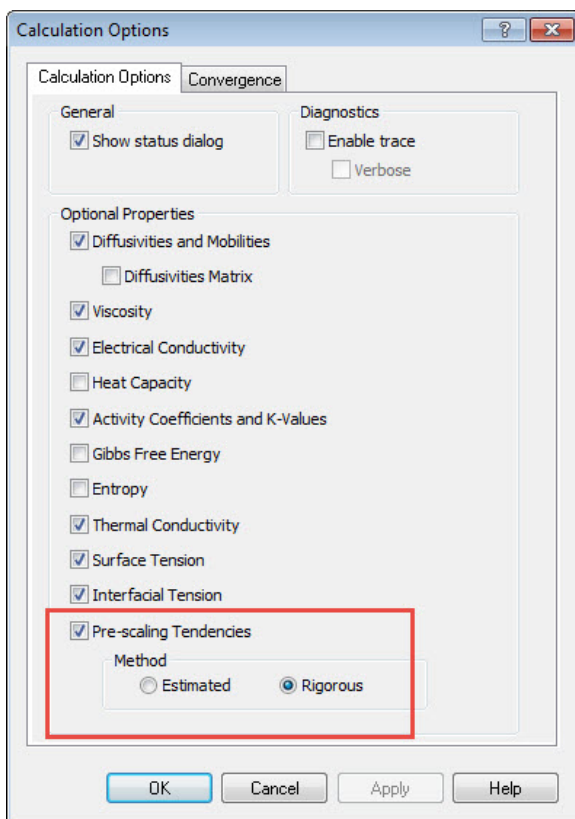
Figure 6-8 Calculation options for rigorous pre-scaling tendencies

Run the calculation
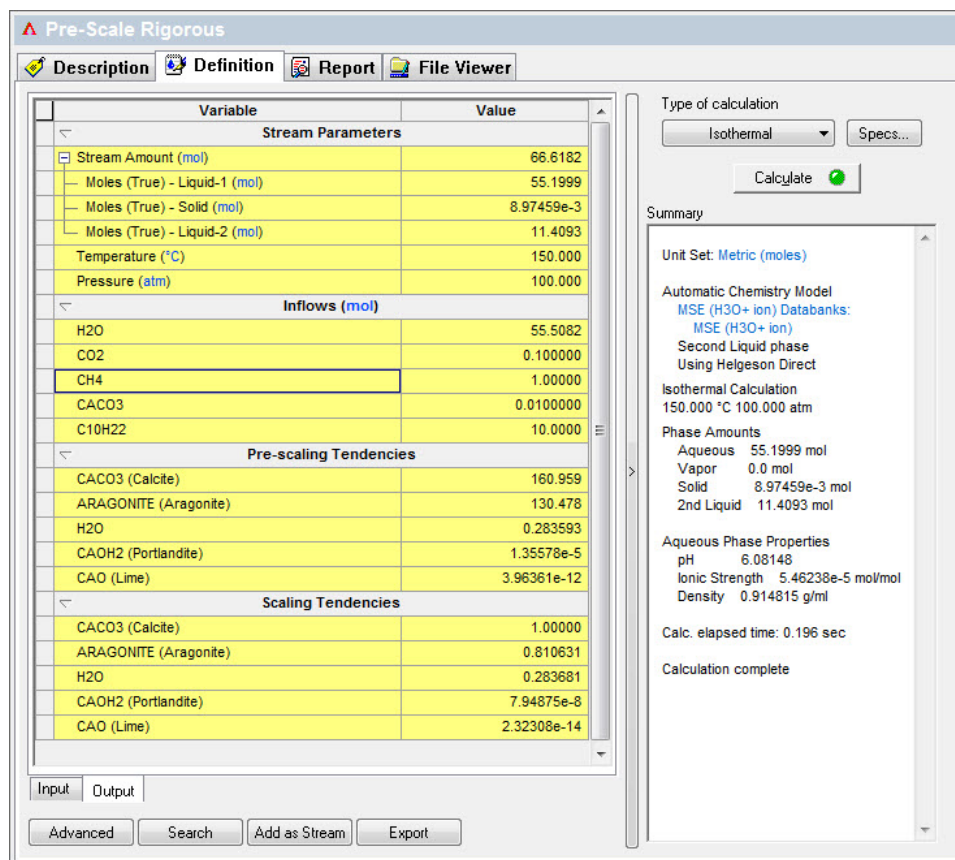
Figure 6-9 Results for rigorous pre-scaling tendencies

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 vs. Rigorous pre-scaling tendency for $CaCO_3$ is 160.853 vs. 160.959 which is small difference. The Estimated vs. 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
    a. Using Custom Units
2. Adiabatic Calculation
    a. Using the Names Manager
3. Bubble Point Calculations
    a. Using new custom units
    b. Modifying the report
4. Dew Point Calculations
    a. Modifying model options
5. Vapor Amount/Fraction Calculations
    a. Using custom report units

Since we have already used many of the features of the software, we will reduce the amount of text required to perform these simulations. We will only show you only the features not previously discussed.

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 °C 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.

Table 7-1 Isothermal Stream Conditions

Parameter	Value	Units
Stream Name	Acetic Acid Solutions	
Temperature	75.0	°C
Pressure	1.0	Atmospheres
H_2O	(Calculated)	
ACETACID (OLI Tag Name)	10	Mass %

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

1. From the **Tools** menu item, select **Units Manager.**
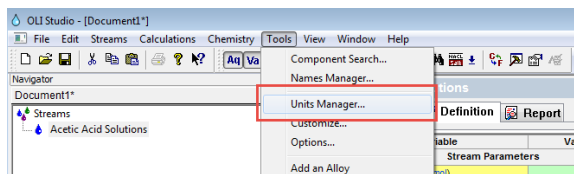
Figure 7-1 Menu Item/Tools/Units Manager

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.
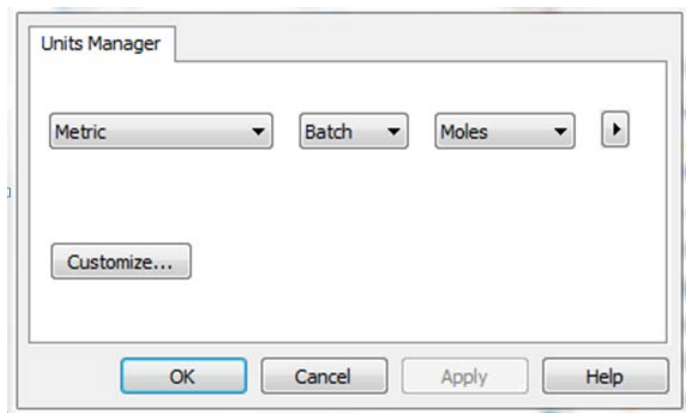
Figure 7-2 Units Manager Dialog

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

Figure 7-3

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

Figure 7-4 Selecting Mass Fraction

Figure 7-5

4. *Click* **OK** to close the **Units Manager** until you are back at the **Definition** tab.

5. 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 ºC, 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 7-6 the filled-out grid for 10 % Acetic Acid

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

7.   Select the default calculation type – **Isothermal.**

8.   *Right-click* the new object in the tree-view (usually with a name similar to SinglePoint1).
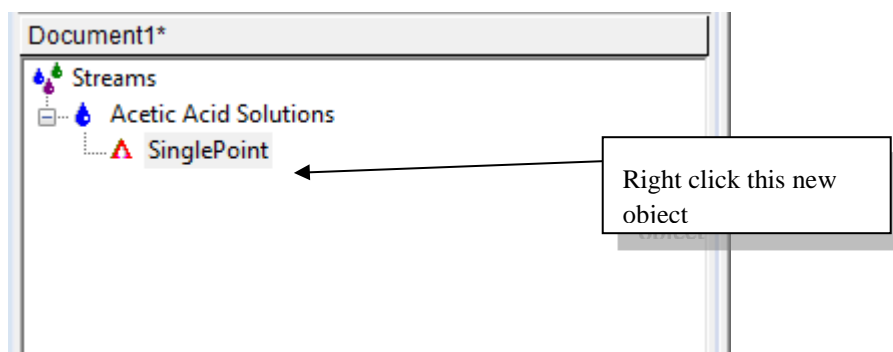
Figure 7-7 Right-click the new object

This will display a menu.
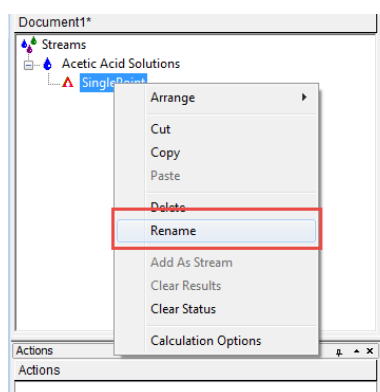
Figure 7-8 Right-click menu choices for the tree-view

Select **Rename** from the list. (Double click on the object name works too)
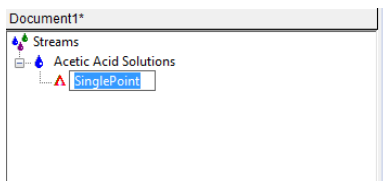
Figure 7-9 Renaming the object

The original text is now high-lighted, so you can edit this field. Rename the value to *pH.*
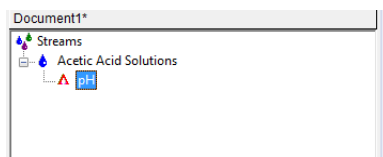
Figure 7-10 The renamed object

9. *Click* on the **Calculate** button to start the calculation.

10. After the calculation is complete you may:

   a. *Click* on the *Output* mini-tab display

   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 7-11 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.

Figure 7-12 Standard Stream Definition

3. *Click* on the __Tools/Names Manager__ menu item (see next figure).
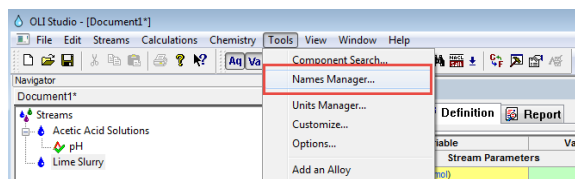
Figure 7-13 Menu Item/Tools/Names Manager

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)
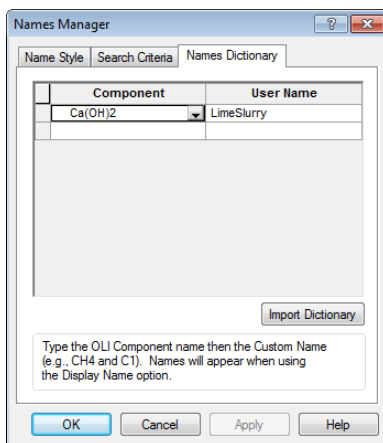
Figure 7-14 Defining Calcium Hydroxide as "Lime Slurry"

7. ***Click*** on **Apply** and then **OK.**

8. As you did in the previous example for the **"**Isothermal**"** calculation. Select ***Mass-Fraction*** units from the Units Manager for **inflows** and *Mass* for **Stream Amount**.

9. ***Enter the following conditions***:

Table 7-2 Stream Lime Slurry Conditions

Parameter	Value	Units
Stream Name	Lim Slurry	
Temperature	25.0	ºC
Pressure	1.0	Atmospheres

Stream Amount	1000	Grams
H$_2$O	(Calculated)	
LimeSlurry (a/k/a Ca(OH)$_2$)	10	Mass %
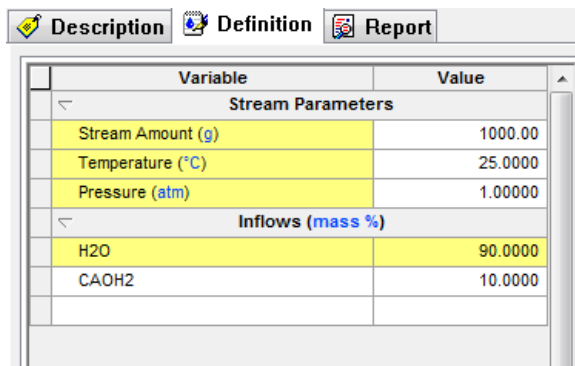
Figure 7-15 Lime Slurry Stream Definition (using display name from Names Manager Tool)

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.

Table 7-3 Stream "Acid" conditions

Parameter	Value	Units
Stream Name	Acid	
Temperature	25	ºC
Pressure	1.0	Atmospheres
Stream Amount	1000	grams
H$_2$O	(Calculated)	
HCl	10	Mass %

Figure 7-16 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.
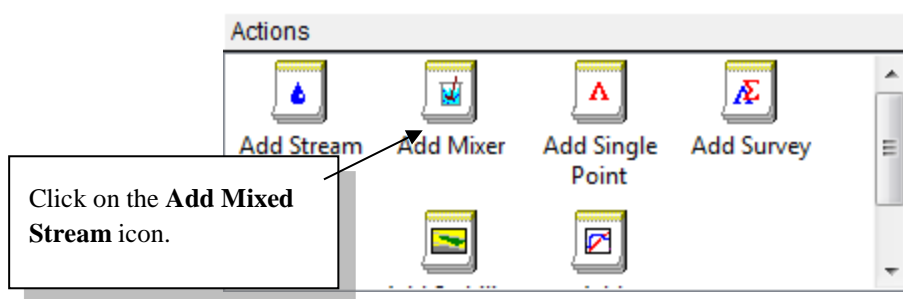
Figure 7-17 Adding a mixer calculation.

10. *Click* on the **Add Mixer** icon in the **Actions** 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.
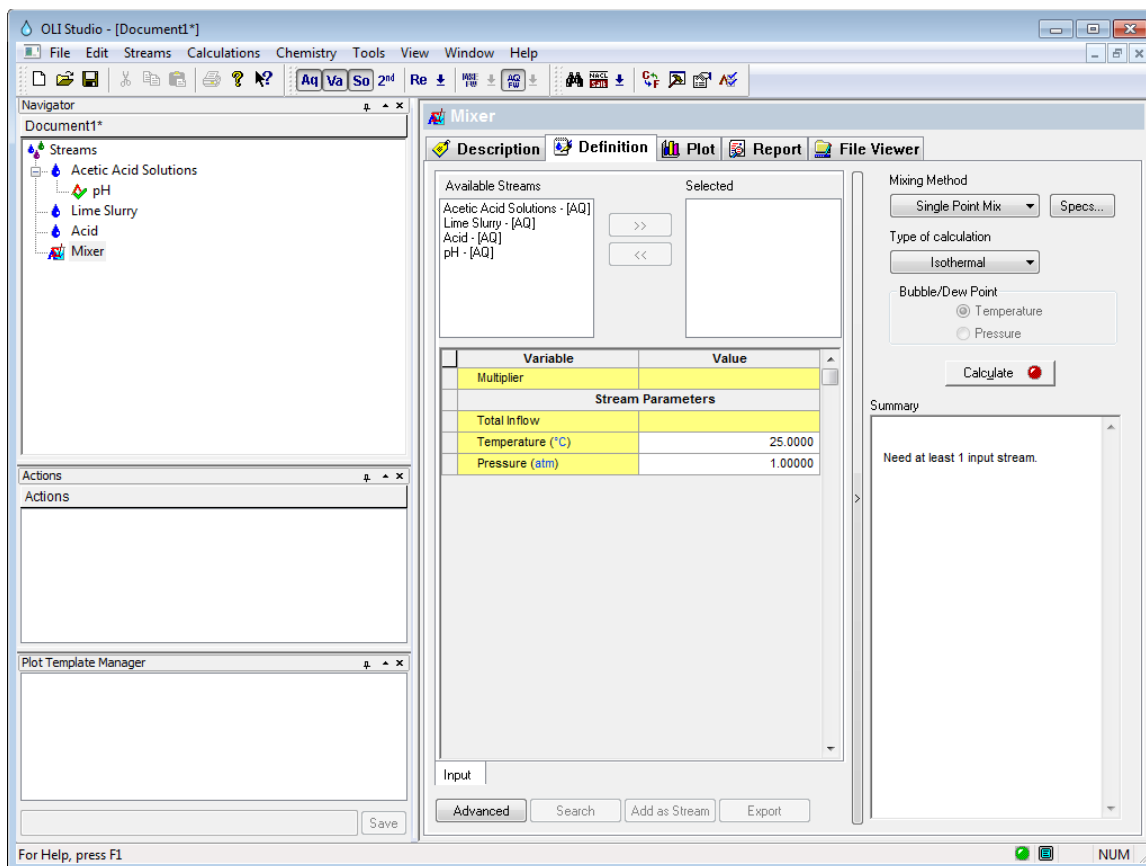
Figure 7-18 The input for the mix calculations.

11. Select the **Lime Slurry** stream from the available list and *click* on the **>>** button.

12. Select the **Acid** *stream* and *click* on the **>>** button. The display should look like this:
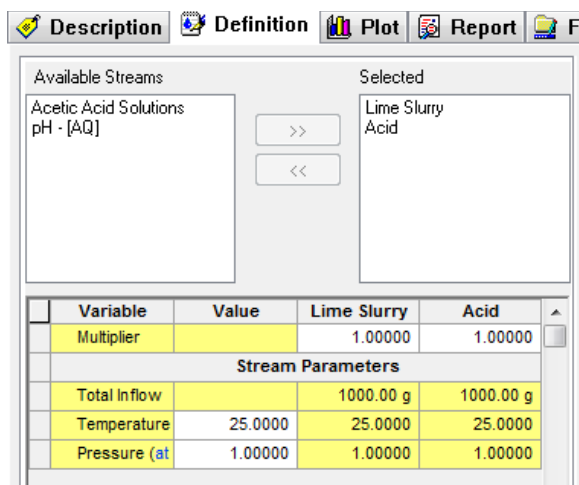
Figure 7-19 Selecting streams. You may have a different list.

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.

13. **Click** on the second **Type of Calculation** button.
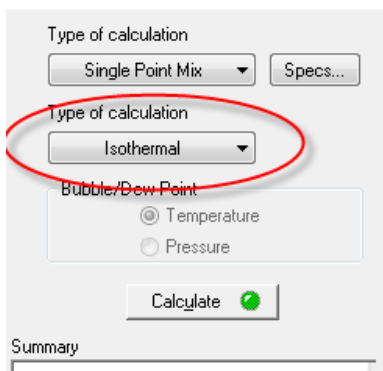
Figure 7-20 Changing the type of calculation
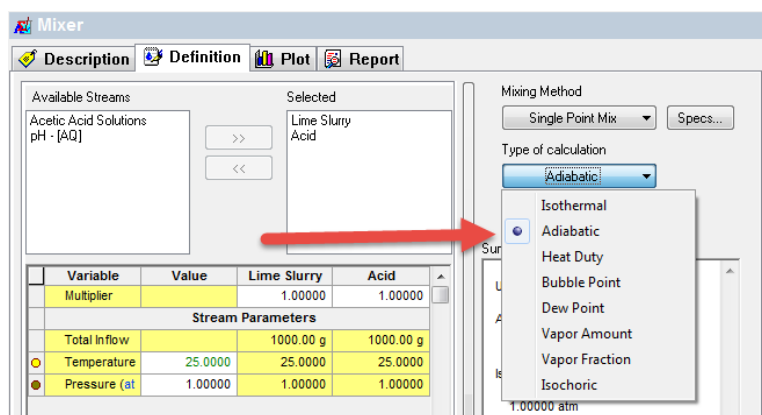
Figure 7-21 Selecting the mix calculation type.

14. **Select** **Adiabatic.**
15. **Click** on the **Calculate** button.
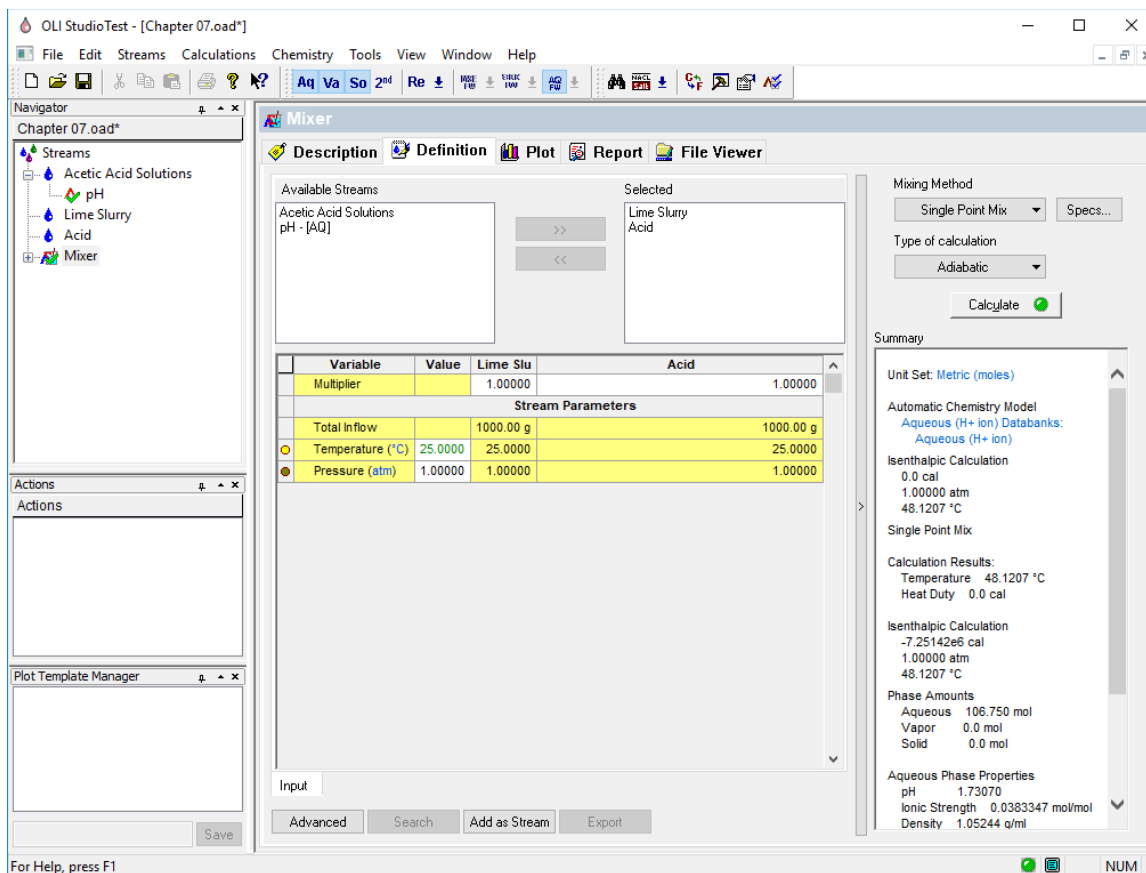
Figure 7-22 The results of the mix.

The **Summary Box** 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.

Table 7-4 Bubble Point Conditions

Parameter	Value	Units
Stream Name	Bubble	
Temperature	25.0	ºC
Pressure	1.0	Atmospheres
Stream Amount	1.0	L (requires a unit change see Figure 7-23)
H_2O	(Calculated)	
ACETONE	1.0	mol/L
Calculation Parameters	**Type**	**Sub-type**
Calculation Class	Single Point	
Calculation Type	Bubble Point	Temperature

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 7-23 Molar Concentration Units
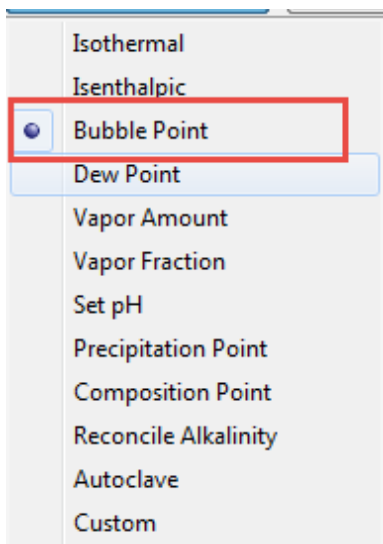
Figure 7-24 Selecting Bubble point calculations

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:

Figure 7-25

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

Figure 7-26

For this calculation select **Temperature**.

Notice the presence of a "Free Dot" next to **Temperature** to indicate that value will be adjusted.
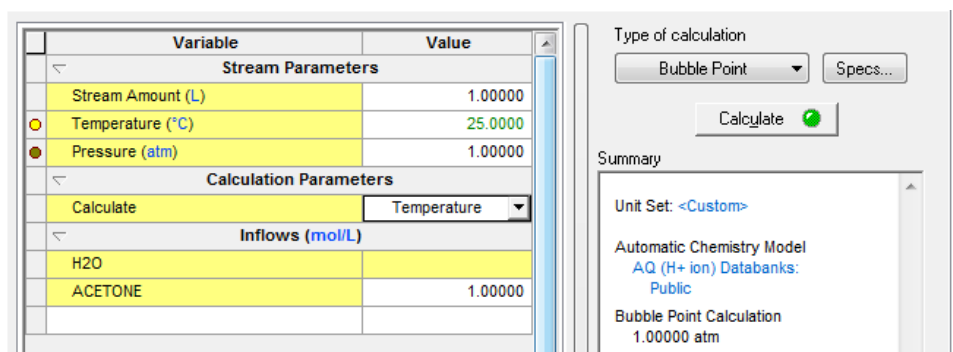
Figure 7-27 Bubble point temperatures are selected

- *Click* on the **Calculate** button.

- *Click* on the **Report** tab to see the results. The temperature is 89.4 C.

- Scroll down to see more information.

Figure 7-28 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.

- *Click on the Customize button.*

By default, all the options are selected. Clear all the **<u>Check Boxes</u>** leaving only **<u>Calculation Summary, </u><u>Stream Inflows</u>** and **<u>Stream Parameters</u>** selected.
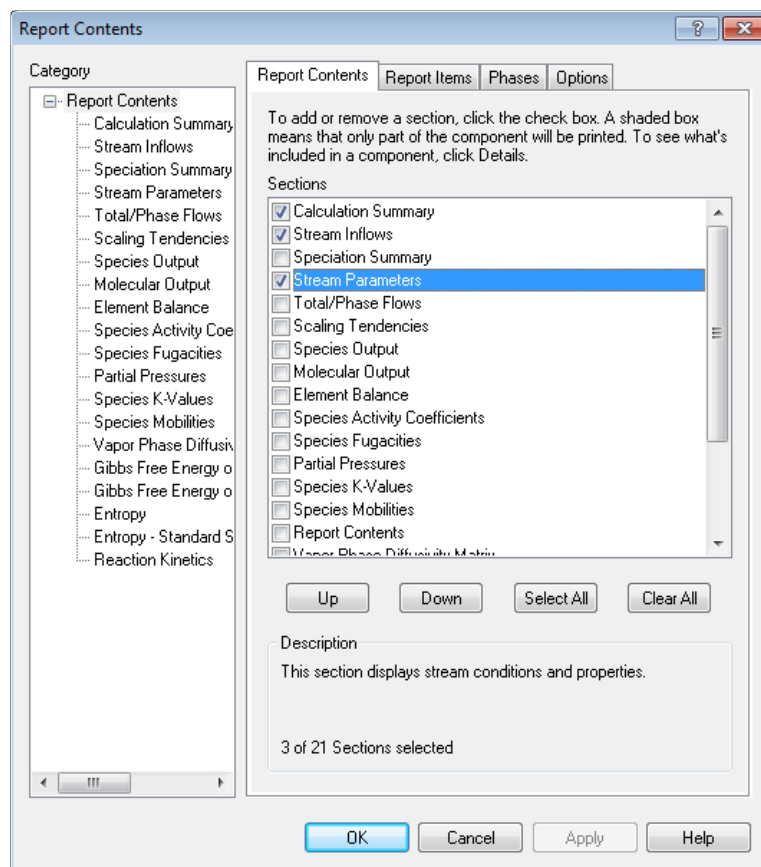
Figure 7-29 Customizing information displayed in a Report

- *Click* the **<u>OK</u>** *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:

Table 7-5 Dew Point Calculation Conditions

Parameter	Value	Units
Stream Name	Dew Point	
Temperature	25.0	ºC
Pressure	1.0	Atmospheres
Stream Amount	(Default)	Don't change this value
H_2O	1.0	Mole
CO_2	1.0	Mole
CH_4	95.0	Mole
H_2S	3	Mole
Calculation Parameters	**Type**	**Sub-type**
Calculation Class	Single Point	
Calculation Type	Dew Point	Temperature

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.*
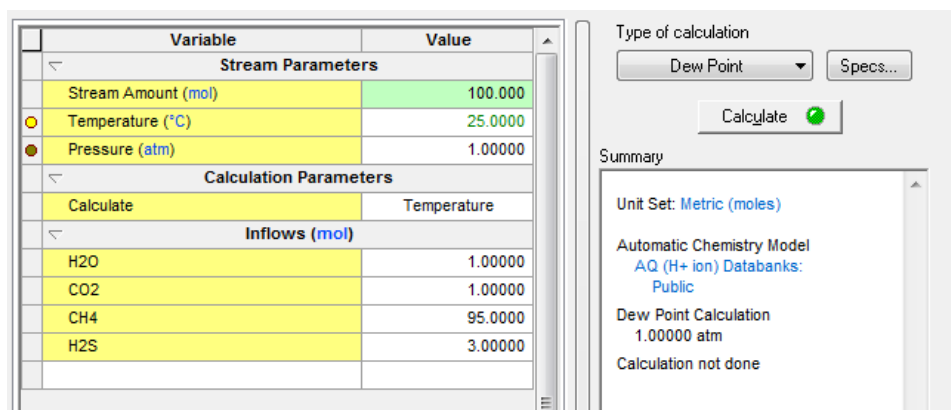
Figure 7-30 Bubble Point Temperature Stream Definition

After the calculation is complete, the resultant temperature is approximately 7.01483 C.
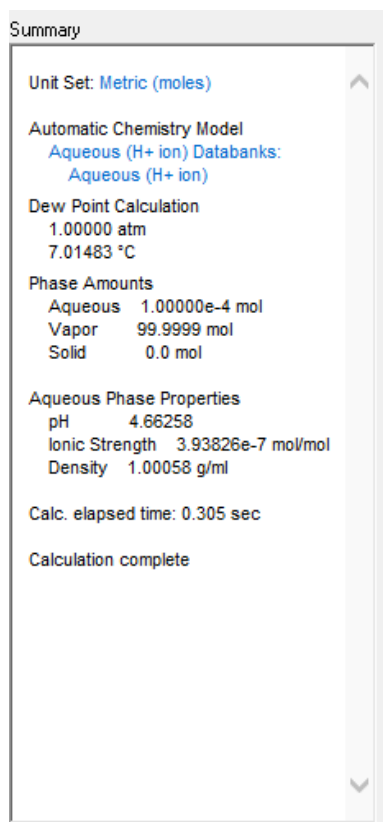
Figure 7-31 Results with standard model options

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:

Table 7-6 Vapor Fraction Conditions

Parameter	Value	Units
Stream Name	Vapor Fraction	
Temperature	25.0	ºC
Pressure	1.0	Atmospheres
Stream Amount	1.0	L (requires a unit change see Figure 7-23)
H_2O	(Calculated)	

NaCl	9.0	Mass %
CaSO₄	1.0	Mass %
Calculation Parameters	**Type**	**Sub-type**
Calculation Class	Single Point	
Calculation Type	Vapor Fraction-Type	Temperature
	Vapor Fraction Amount	95 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.

Figure 7-32 Vapor Fraction Stream Definition

Click on **Calculate** to start.

After the program finishes the calculation, the temperature is approximately 109 ºC. At this temperature, 95 percent of the system will be vapor.
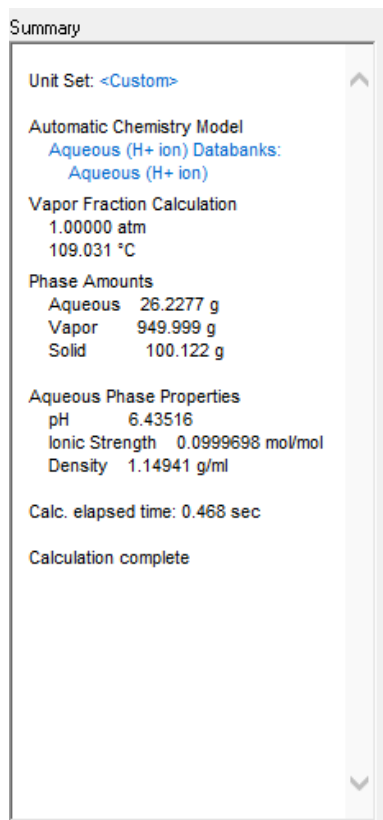
Figure 7-33 Summary of Vapor Fraction

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.
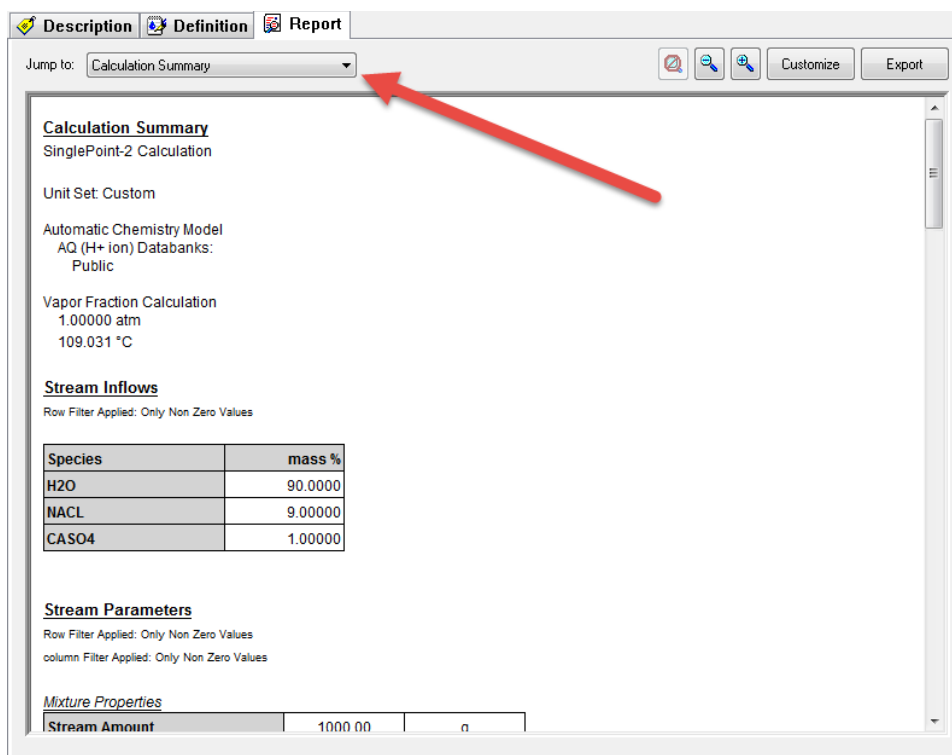
Figure 7-34

Use the drop-down box indicated in Figure 7-34 to find the **Species Output** section.
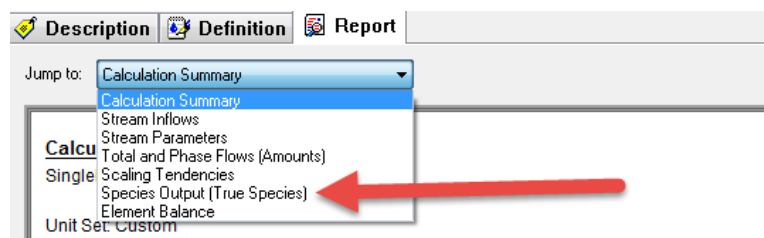
Figure 7-35

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.

Figure 7-36 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:

Table 8-1 Temperature Survey - Stream Data

Parameter	Value	Units
Stream Name	(Default Name)	
Temperature	25.0	ºC
Pressure	1.0	Atmospheres
Stream Amount	55.5082 (calculated – Default)	Mole
H_2O	55.5082	
Benzoic Acid	0	Mole
Calculation Parameters	Type	Specs…
Survey	Temperature	0 to 100 ºC with 5 ºC increments
Calculation Type	Precipitation Point	Solid Precipitate: Benzoic Acid – sol
		Adjusted Inflow: Benzoic Acid

Select **Survey** for the calculation type.

The **Definition** should look like the figure below.
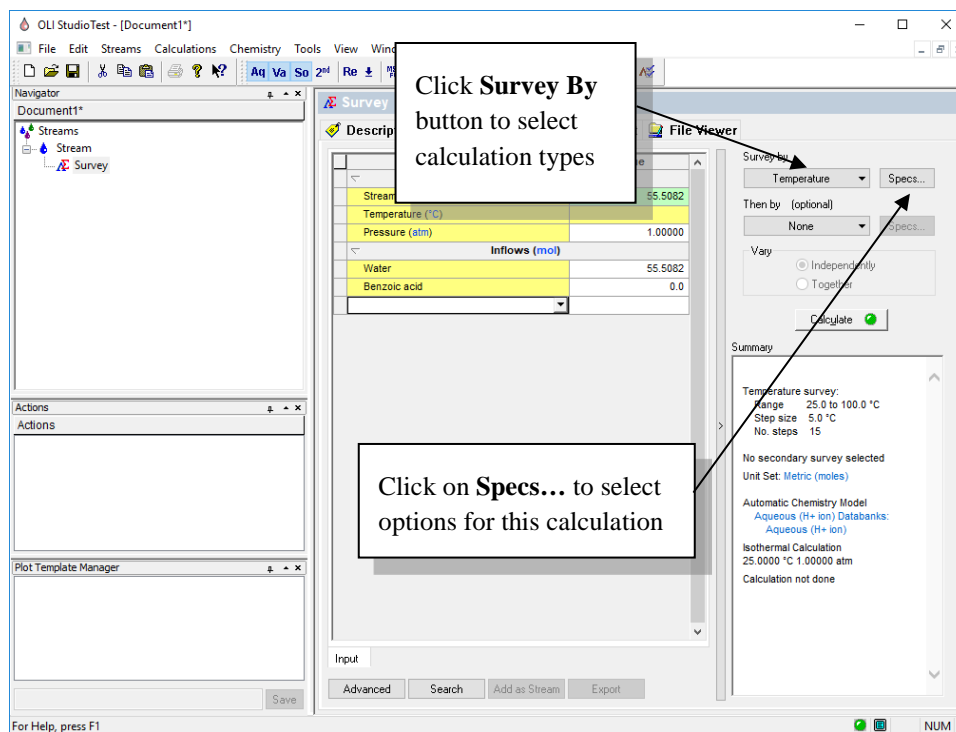
Figure 8-1 Stream Definition for Temperature survey

The temperature survey is the default. Now click on the **Specs** button to display this figure. We will be using a temperature range of 0 to 100 C.
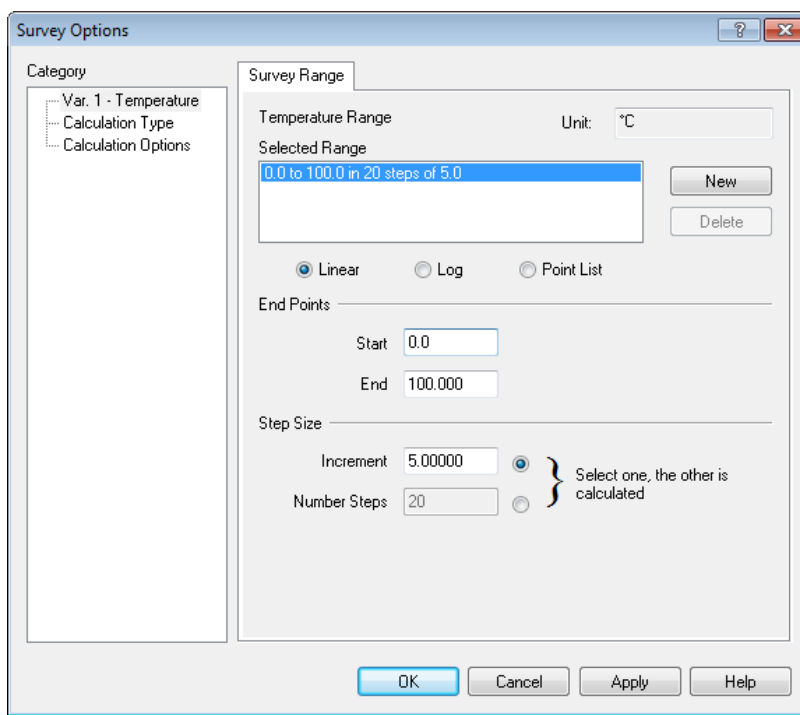
Figure 8-2 Spec Options - Range

- Make sure the **Increment** is set to 5 degrees C.

- Now *Click* on **Calculation Type**

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)
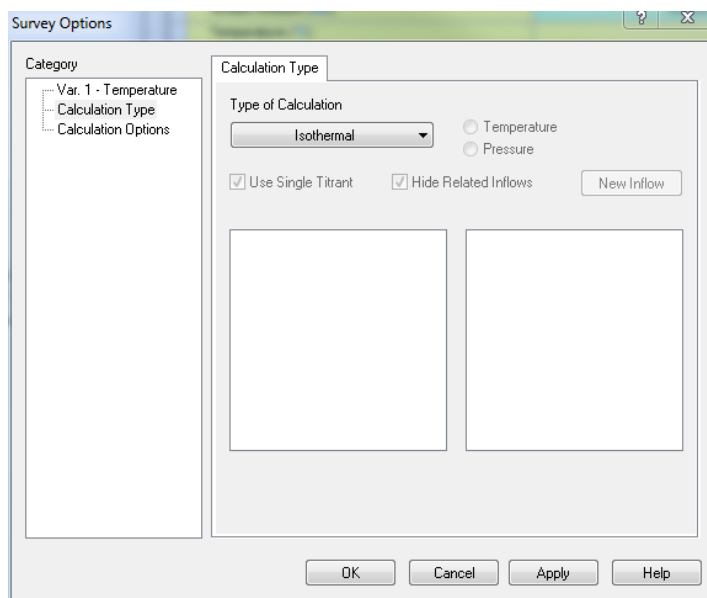
Figure 8-3 the default calculation type dialog.

- *Click* on the **Type of Calculation** button.

The list of calculations is like ones found in the single point calculations chapter (see chapter 7).
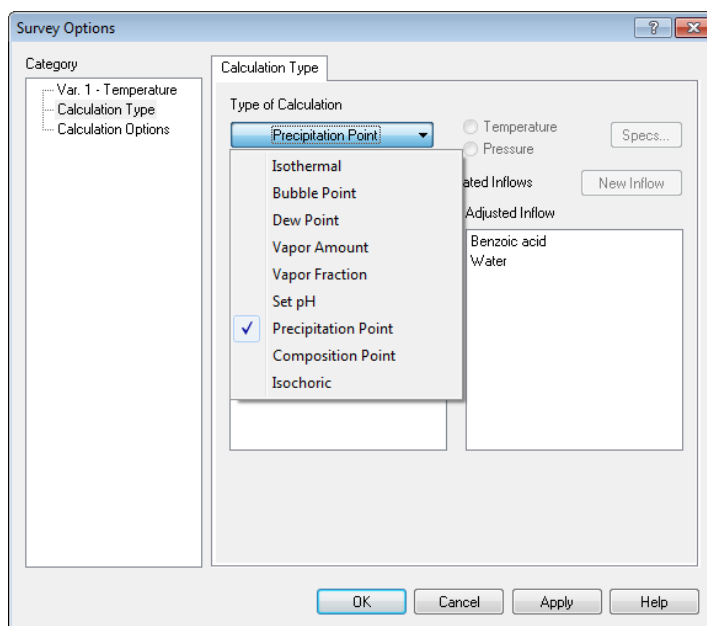
Figure 8-4 Specifying calculation type.

- 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.
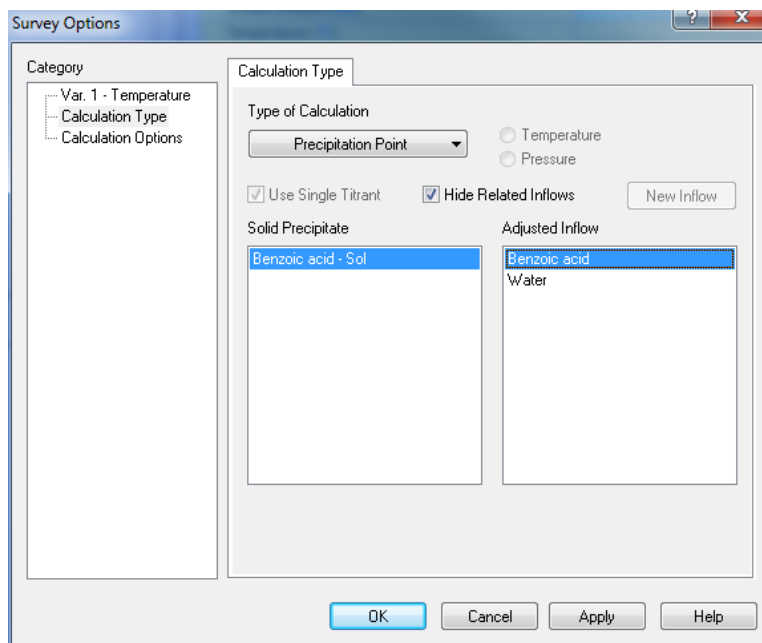
Figure 8-5 Selecting benzoic acid solid

- 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.
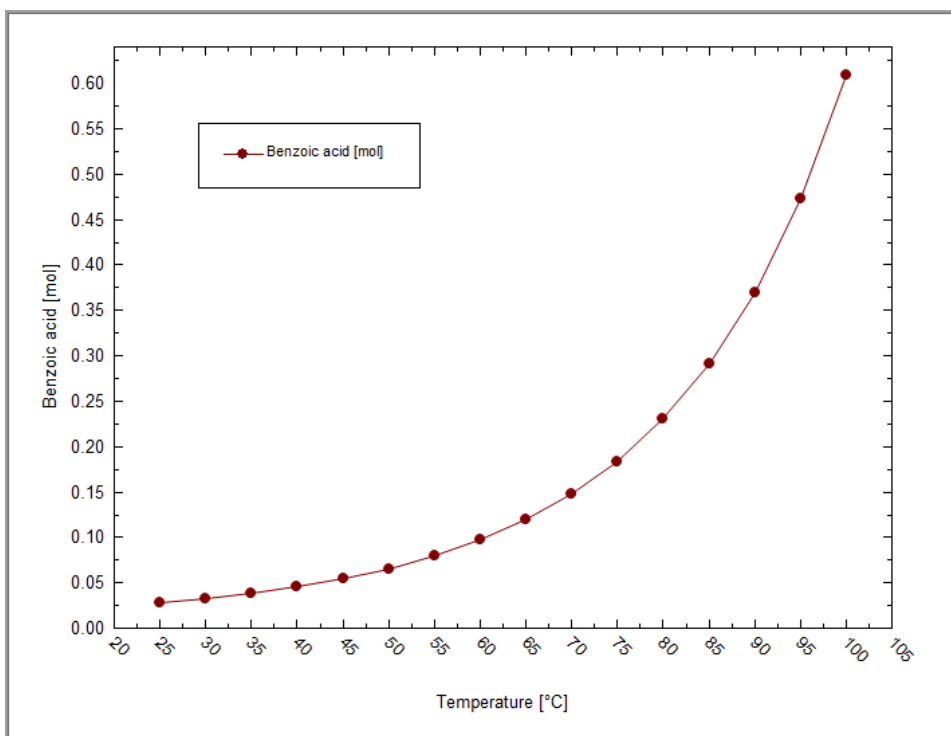
Figure 8-6 The Default Plot

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.
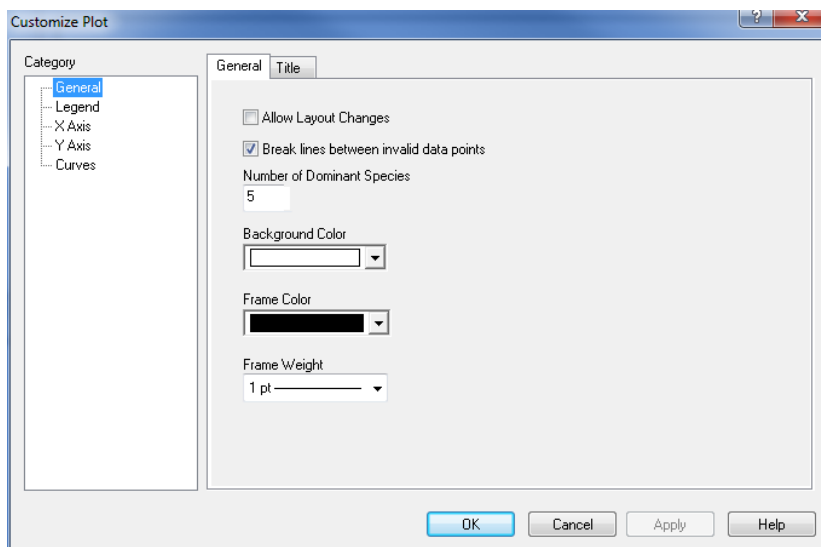
Figure 8-7 Plot Options

For example, you can *Click* on the **Y-Axis** category.
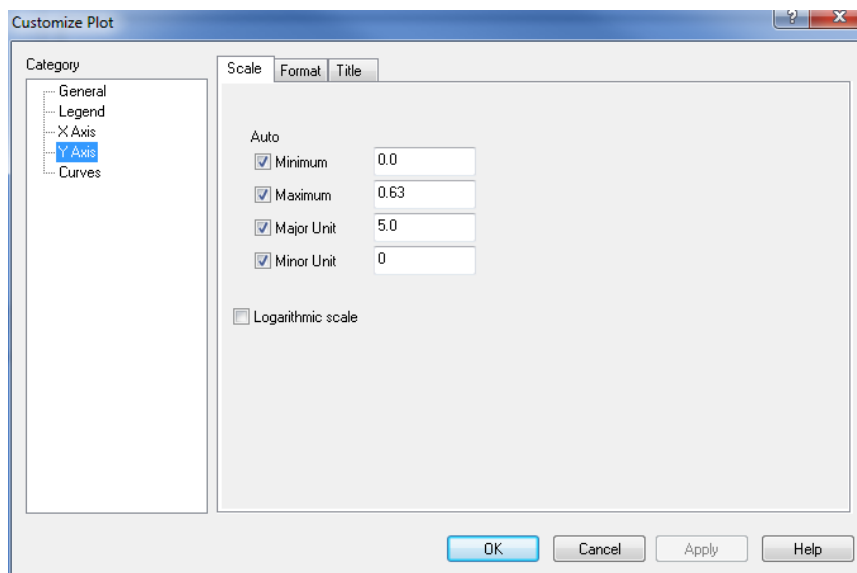
Figure 8-8 Y-axis options

To change the scale on the Y-axis.

- *Click* on the **Title** tab.
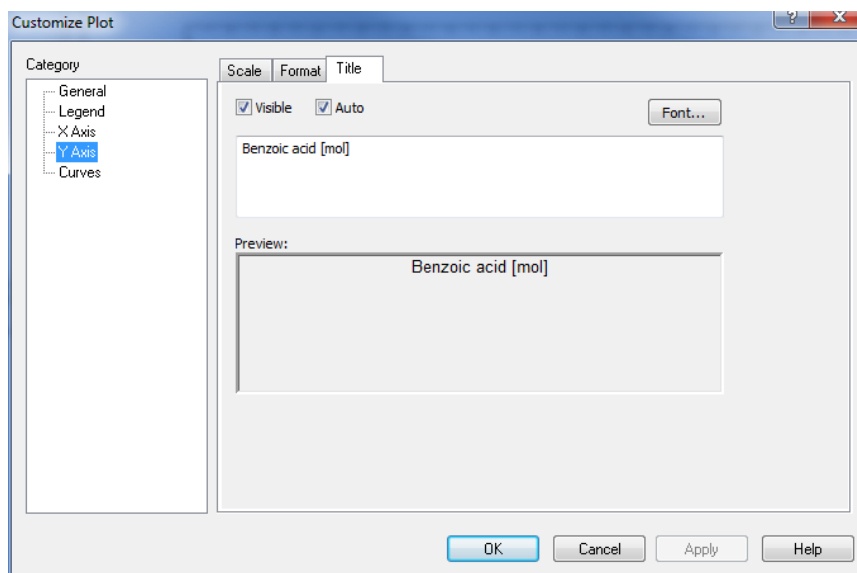
Figure 8-9 Y-Axis title

Enter the text in the below box. Click on **OK** when ready.
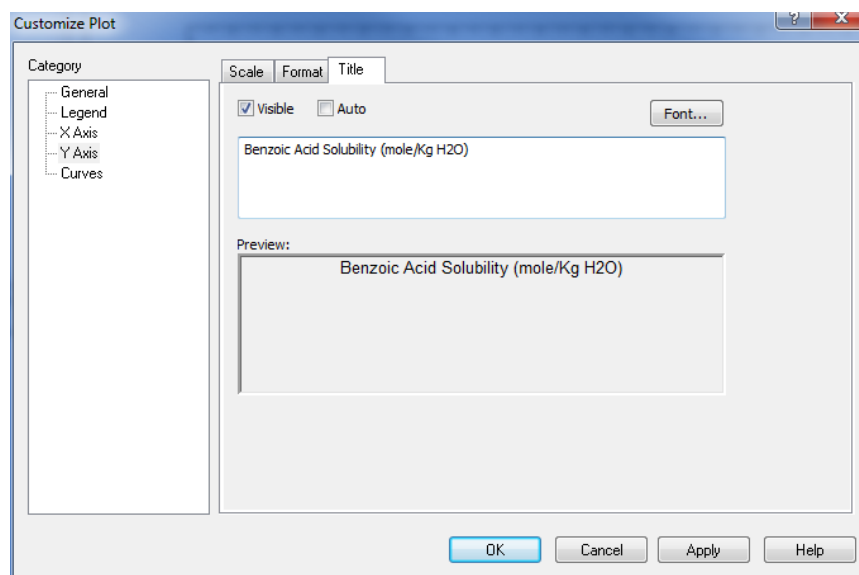
Figure 8-10 Entering a new Y-axis title.

You can see that the Preview box automatically updates with the new text and the **<u>Auto</u>** 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.
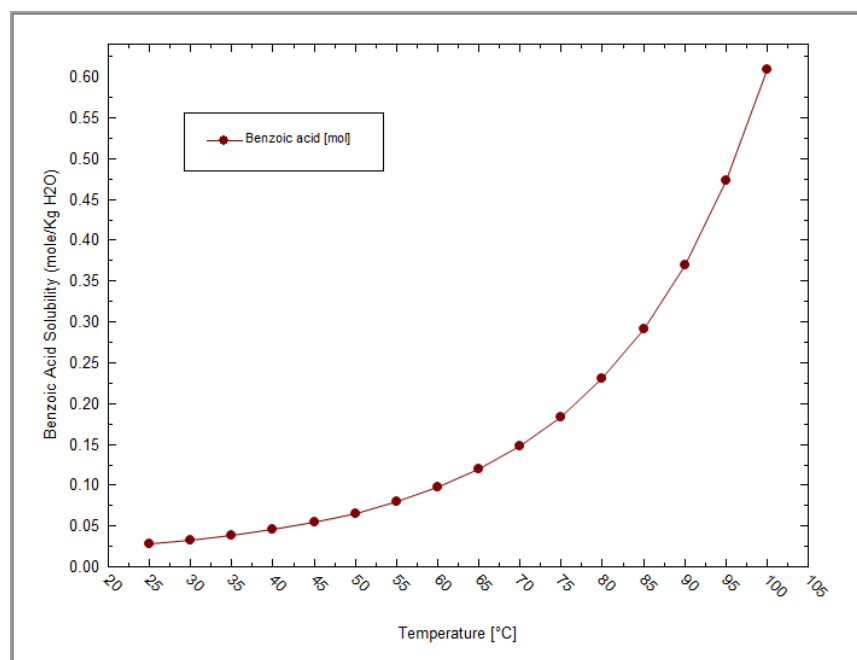
Figure 8-11 Revised Plot

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:
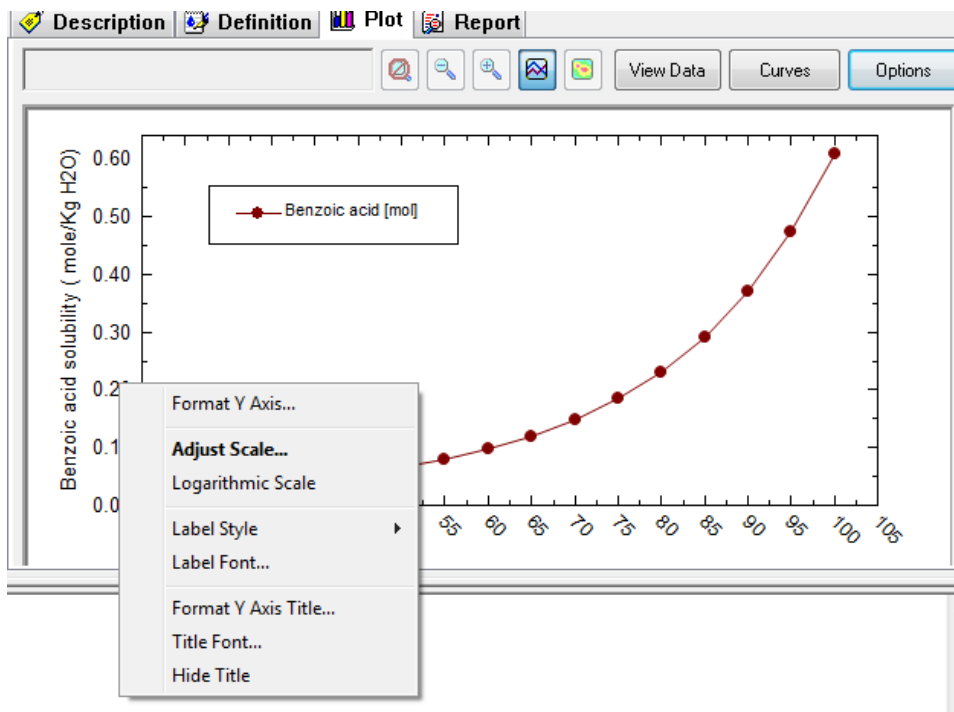
Figure 8-12Right-Click on axis and select Logarithmic
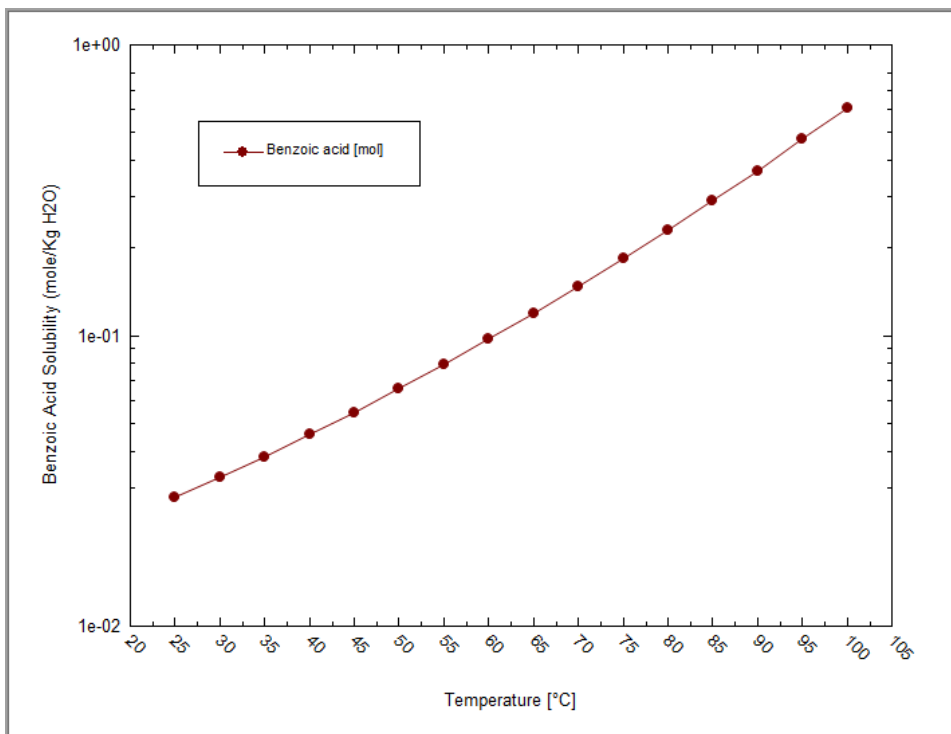
Figure 8-13 Now on a logarithmic scale

You can also display the data in table form. Click the **View Data** button:
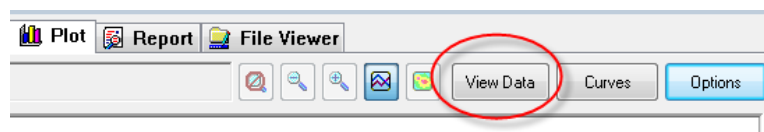
Figure 8-14 Select View Data

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:

Figure 8-16

Next use the Menu and select **Edit > Copy** to copy the data:
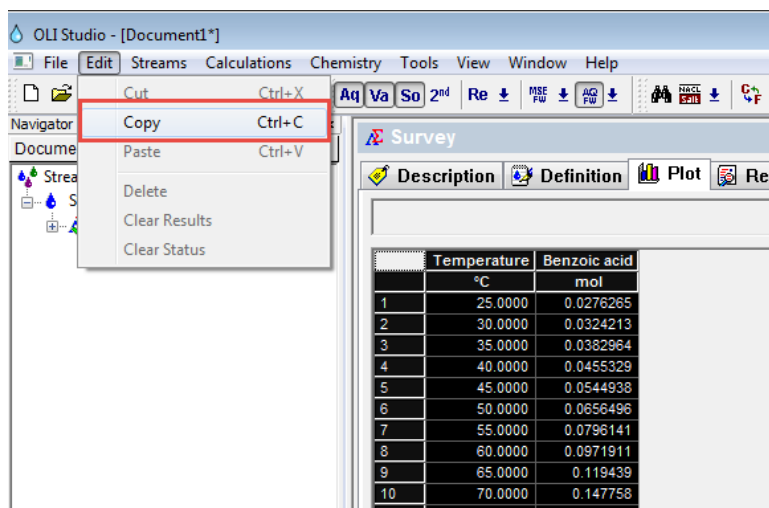
Figure 8-17

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.

Table 8-2 Pressure Survey Stream Data

Parameter	Value	Units
Stream Name	(Default Name)	
Temperature	25.0	^{o}C
Pressure	1.0	Atmospheres
Stream Amount	55.5082 (calculated – Default)	Mole

H₂O	55.5082	
CO₂	2	Mole
Calculation Parameters	Type	Specs…
Survey	Pressure	0 to 100 atm with 5 atm increments
Calculation Type	Default	
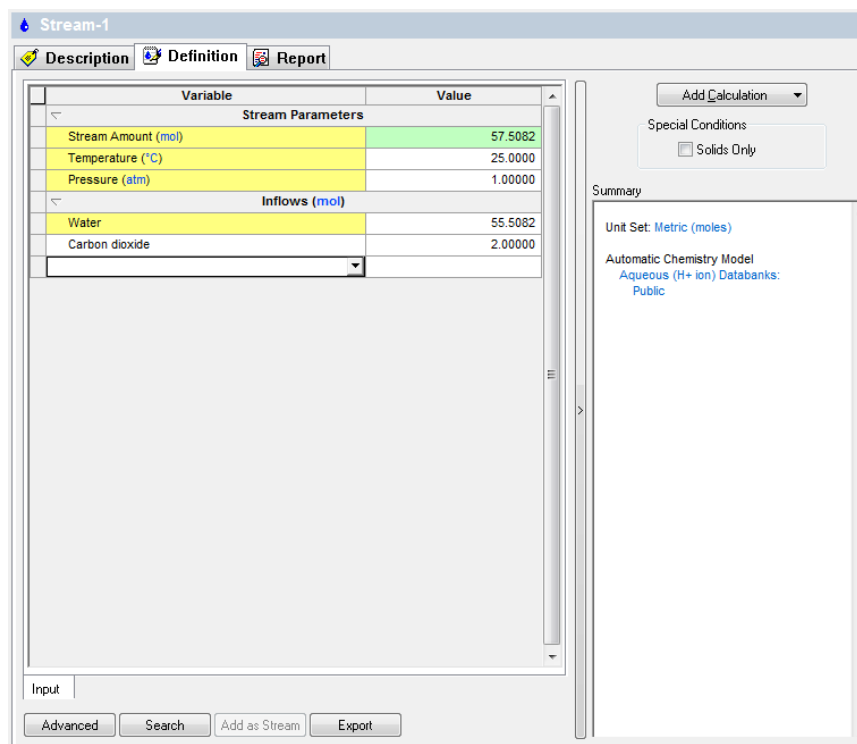
Figure 8-18 Stream Definition for Pressure Survey

- ***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.
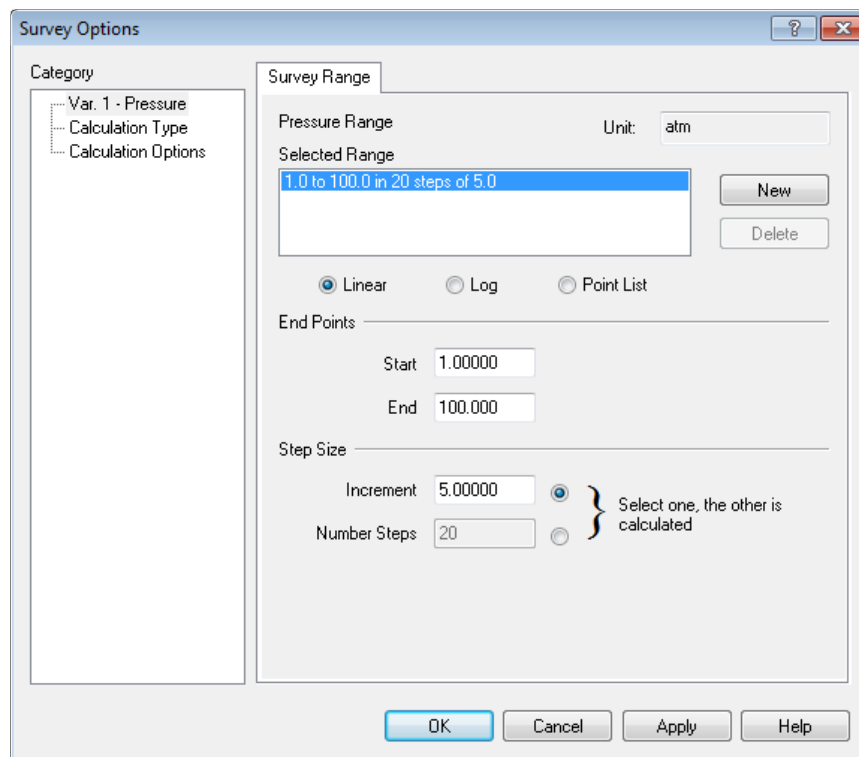
Figure 8-19 Changing the range

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.
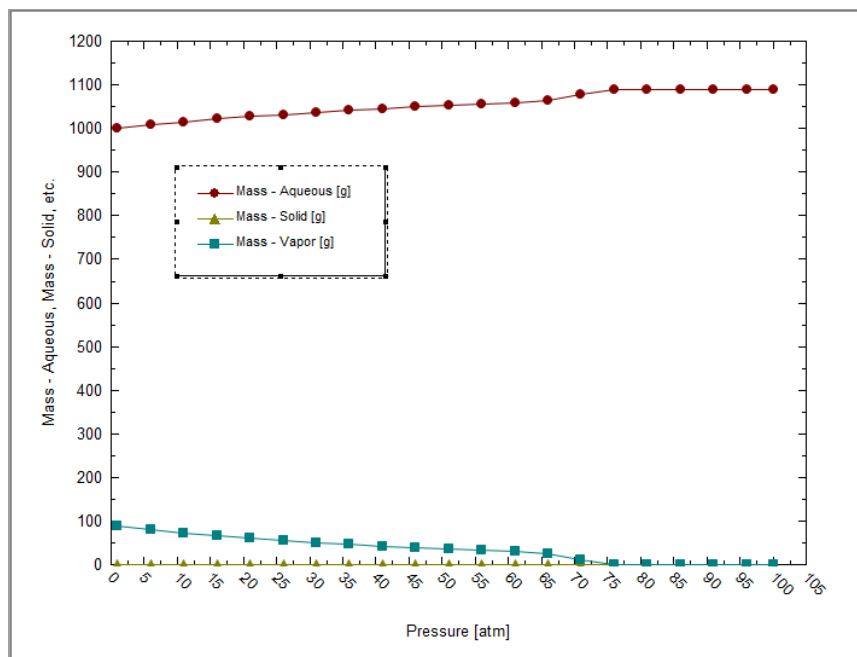
Figure 8-20 Default Dominant Aqueous species

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.**
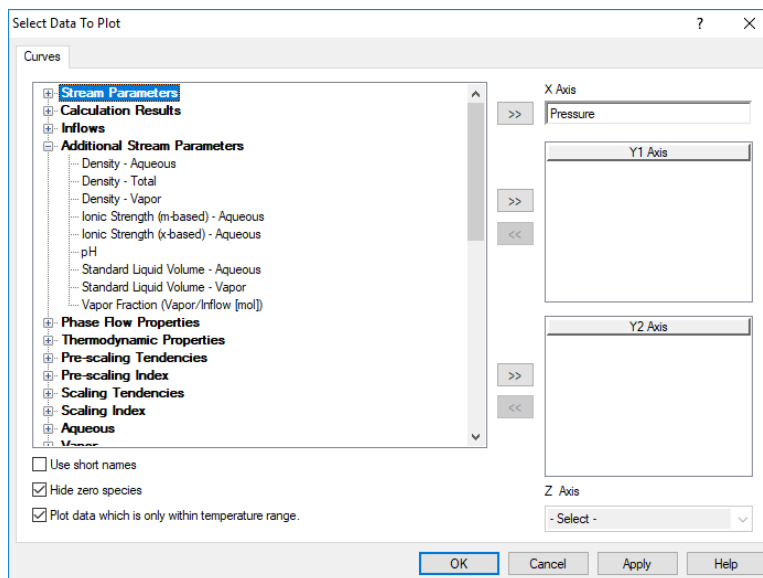
Figure 8-21 Classes of variables, select Additional Stream Parameters

From the new list, select **pH**
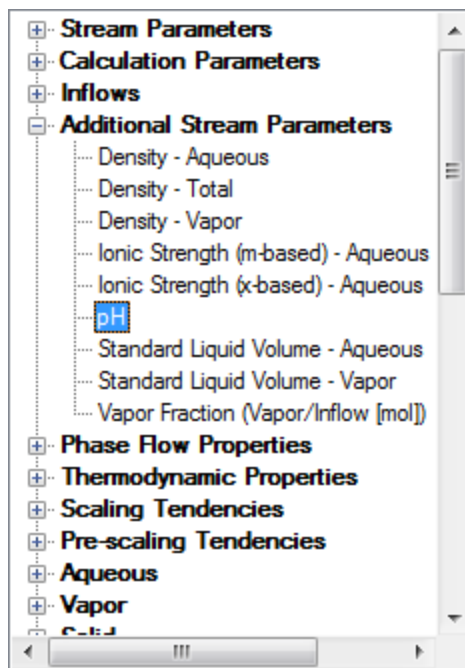
Figure 8-22 Locate and select pH

Then click on the **Right double-arrow** or *double click* the entry.
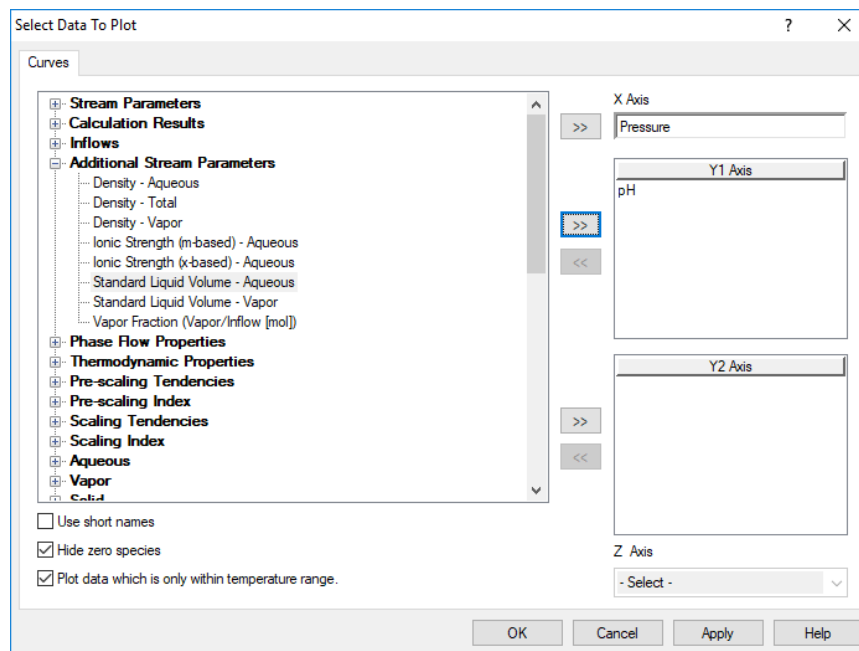
Figure 8-23 Final Variables selection

Click on the **OK** button to display pH as a function of pressure.
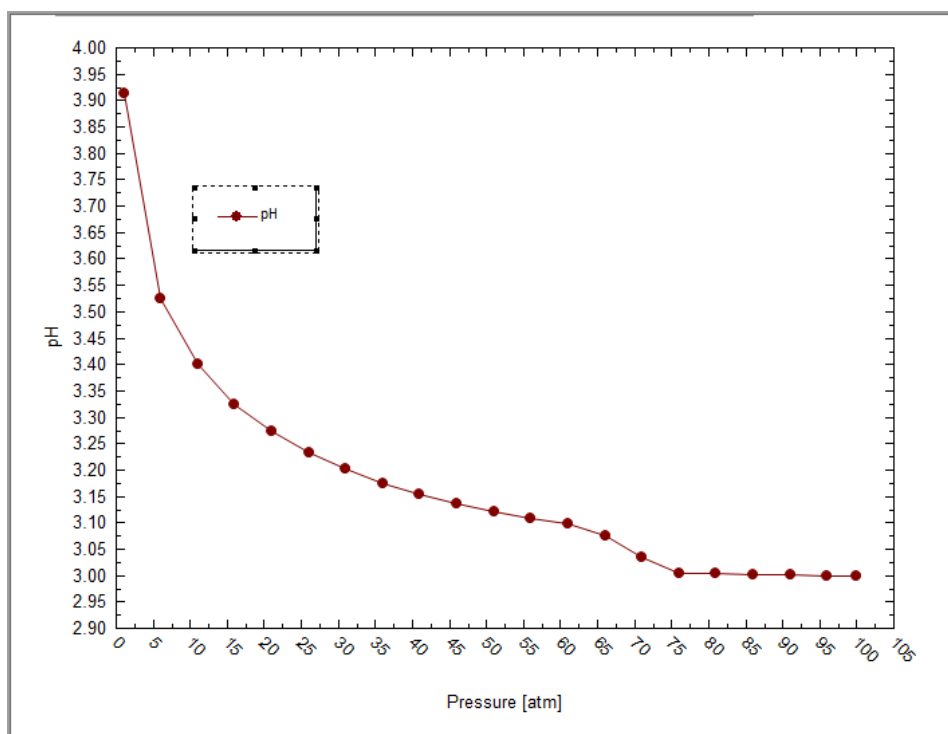
Figure 8-24 Final Plot

The pH decreases with pressure because of the increased solubility of carbon dioxide. Carbon dioxide is an acid gas. The pertinent equilibria are:

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

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

$$HCO_3^- = H^+ + CO_3^{2-}$$
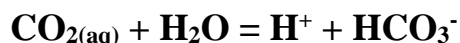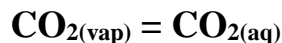
Thus, as the amount of carbon dioxide in the aqueous phase increases, more of it can dissociate producing hydrogen ions.

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:

Table 8-3 Composition Survey Data

Parameter	Value	Units
Stream Name	(Default Name)	
Temperature	25.0	ºC
Pressure	75.0	Atmospheres
Stream Amount[35]	55.5582	Mole
H_2O	55.5082	Mole
$CaCO_3$ (Calcite)	0.05	Mole
CO_2	0	Mole
Calculation Parameters	Type	Specs…
Survey	Composition	Component: CO2
		Survey Range: 0.0 to 1.0 mole with 0.05 mole increment
Calculation Type	Default	

---

[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.

The following figure is filled out for this example.

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**.
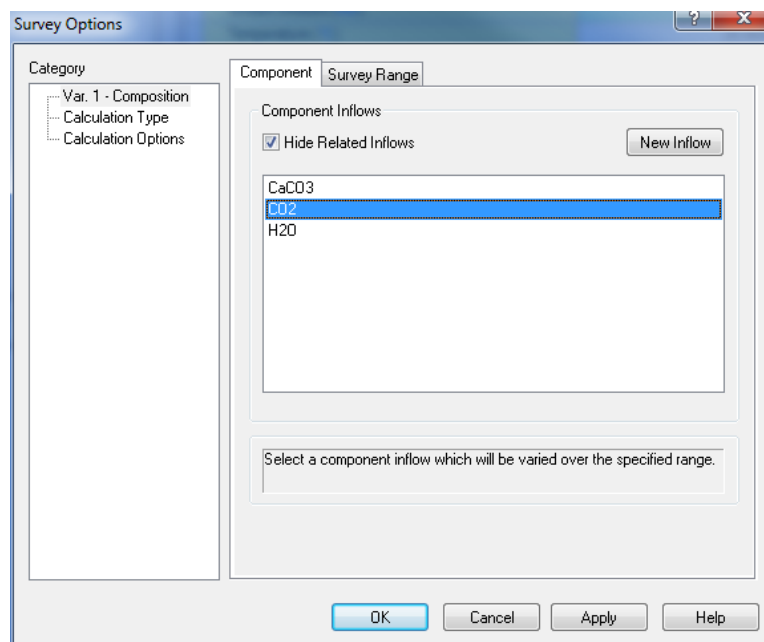
Figure 8-26 Selecting the component CO2

- Select *Carbon dioxide, CO₂* 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**.
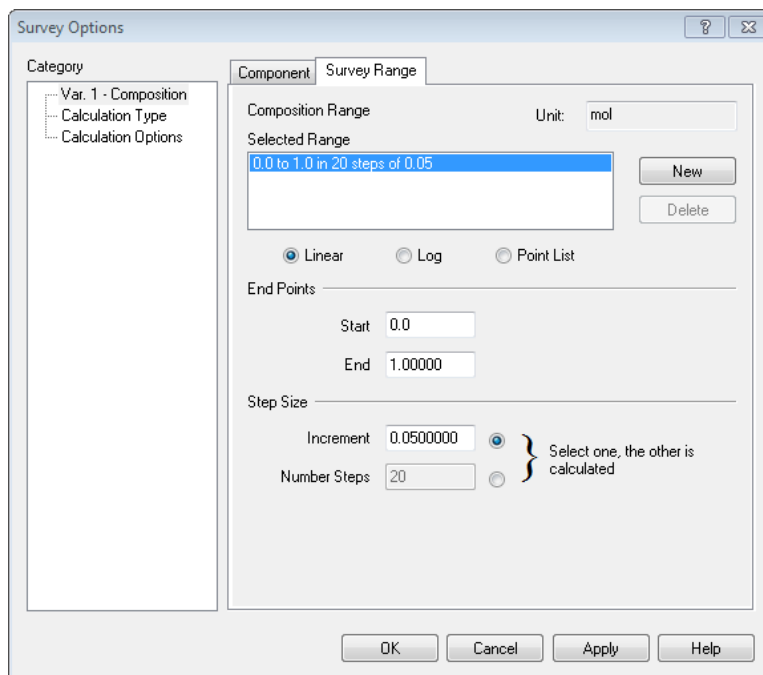
Figure 8-27 Narrowing the range of the calculation

- *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.
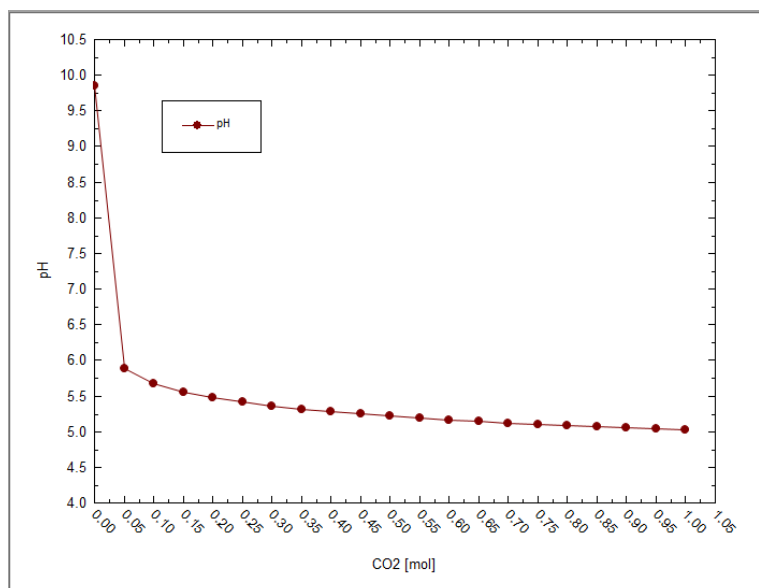
Figure 8-28 The default composition survey plot

Remove the existing entry. Scroll up or down to find and select **Solid**. Select **CaCO3 (Calcite) - Sol** from the list. Click on **OK** when ready.
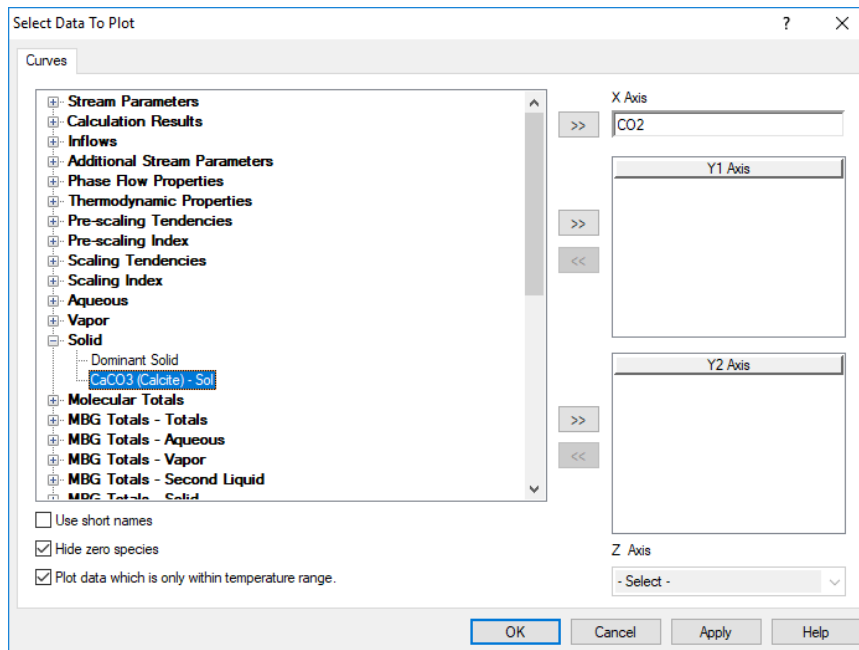
Figure 8-29 Removing default variable and replacing it with the solid CaCO3
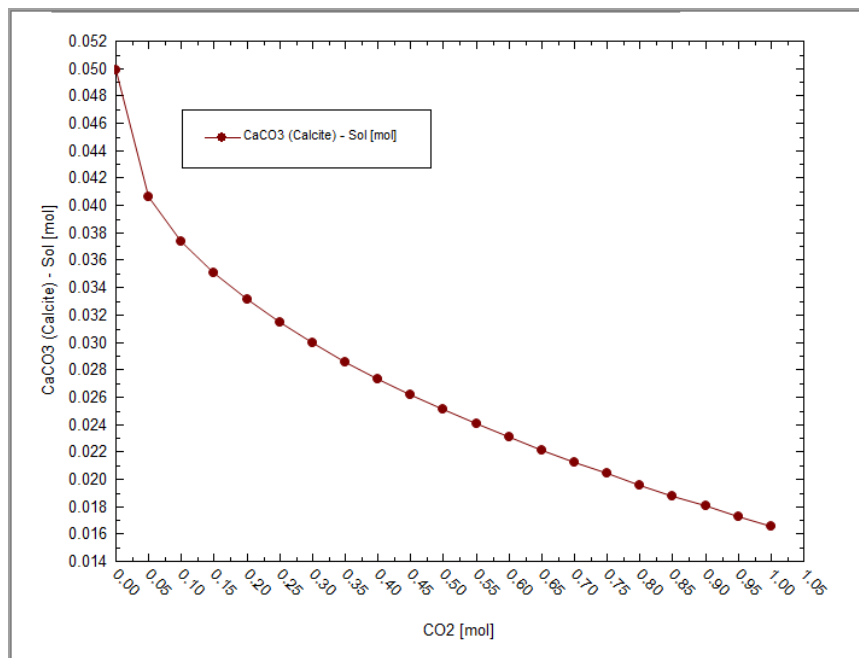
Figure 8-30 Our desired plot.

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:

OH

|

HOOC-CH2-C-CH2-COOH

|
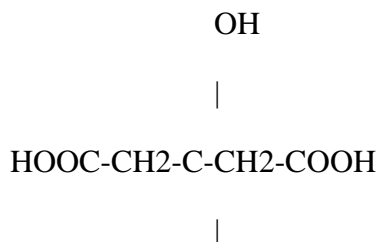
There are three acid hydrogen atoms and hence three pKa's.

We will use the **MIX** calculation to perform an actual titration curve.

We need to create two new streams. You have already done this step many times. Create the following two streams.

Table 8-4 Mixer Stream Data

Parameter	Value	Units
Stream Name	Citric Acid	
Temperature	25.0	ºC
Pressure	1.0	Atmospheres
Stream Amount	55.5082 (Default)	Mole
H_2O	55.5082	Mole
Citric Acid	0.1	Mole
Stream Name	NaOH	
H_2O	55.5082	Mole
NaOH	0.1	Mole

- Choose **Add Mixer** from the Action area.
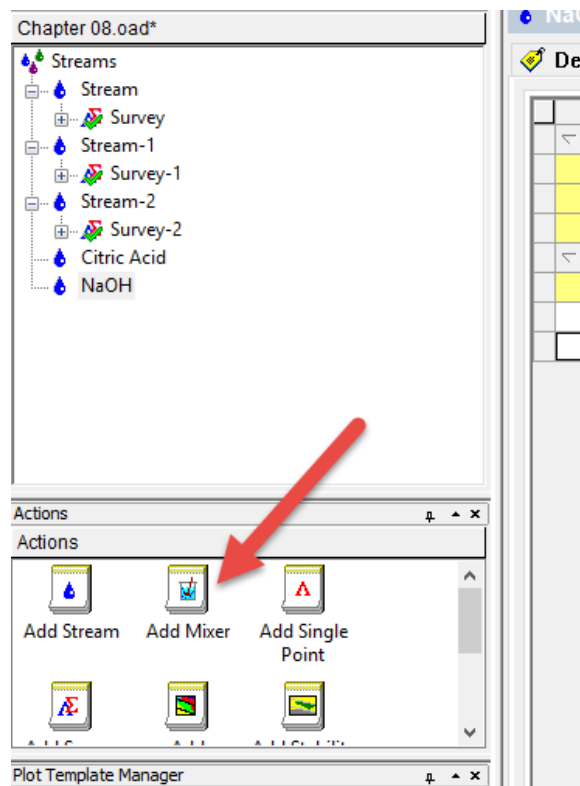
Figure 8-31 Adding a mixer (method 1)

Alternatively, you can add a calculation from the menu line:
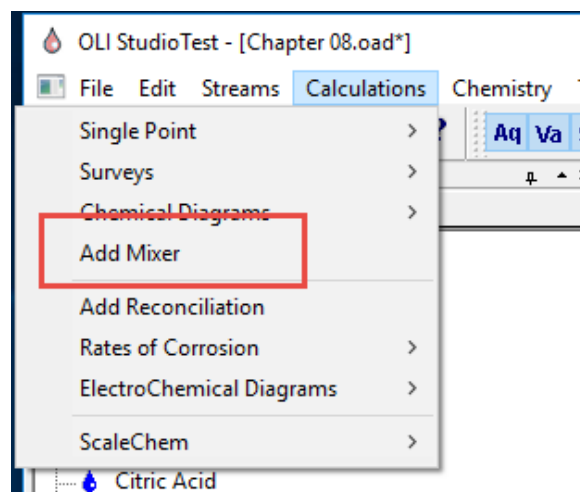
Figure 8-32 Adding a mixer (method 2)
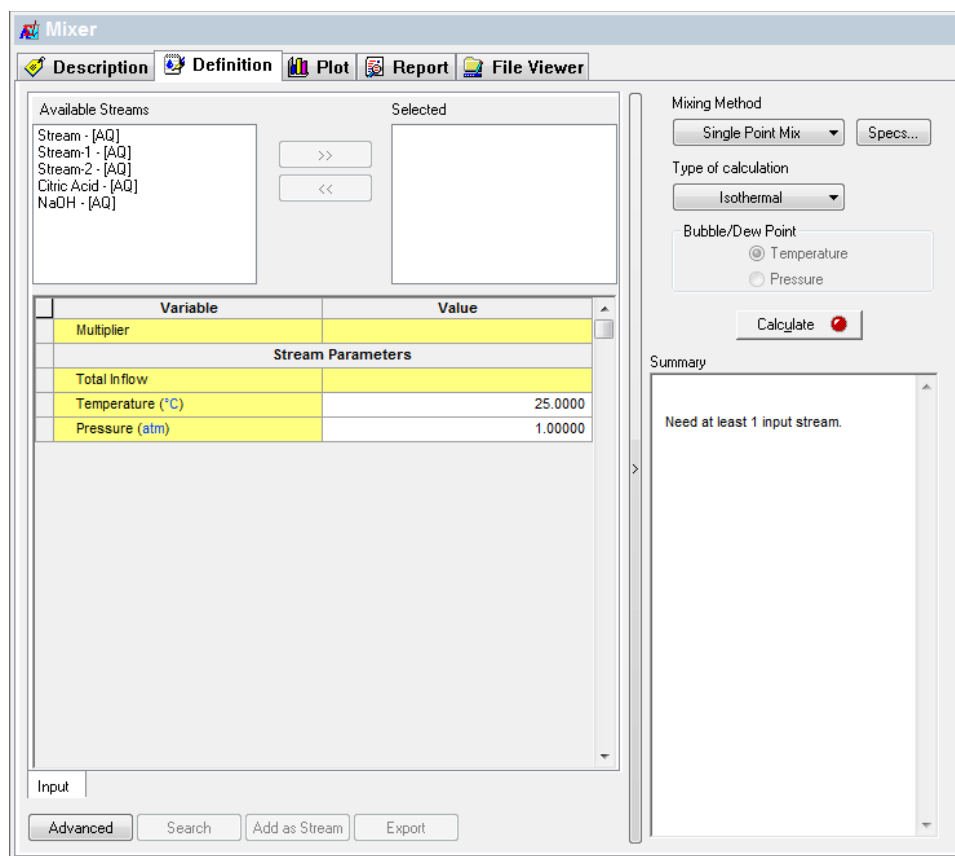
Figure 8-33 The Mixed Stream Input

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.
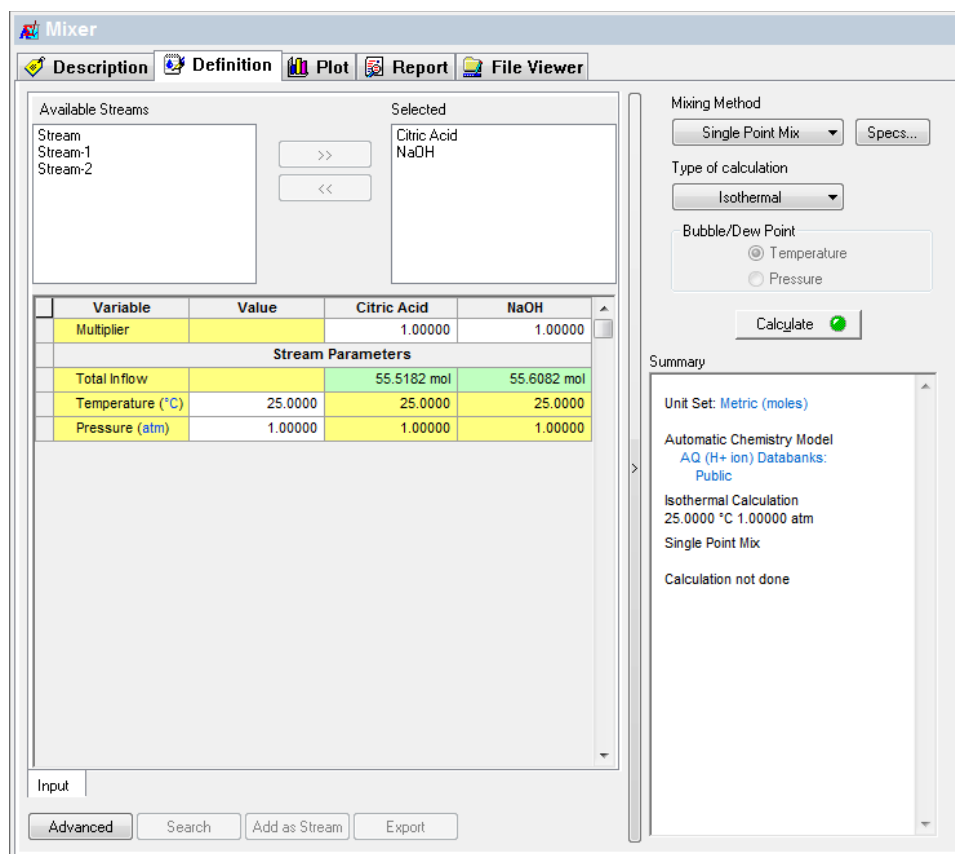
Figure 8-34 Selected Streams

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
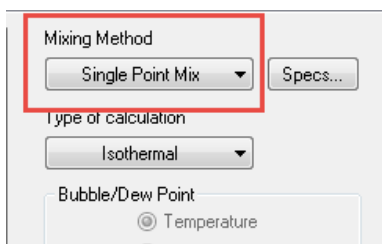
Figure 8-35

- Then select **Multiplier**.
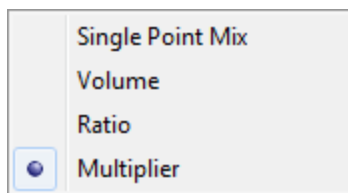
This will add the varied stream in a specific amount. Now select the **Specs…** button.
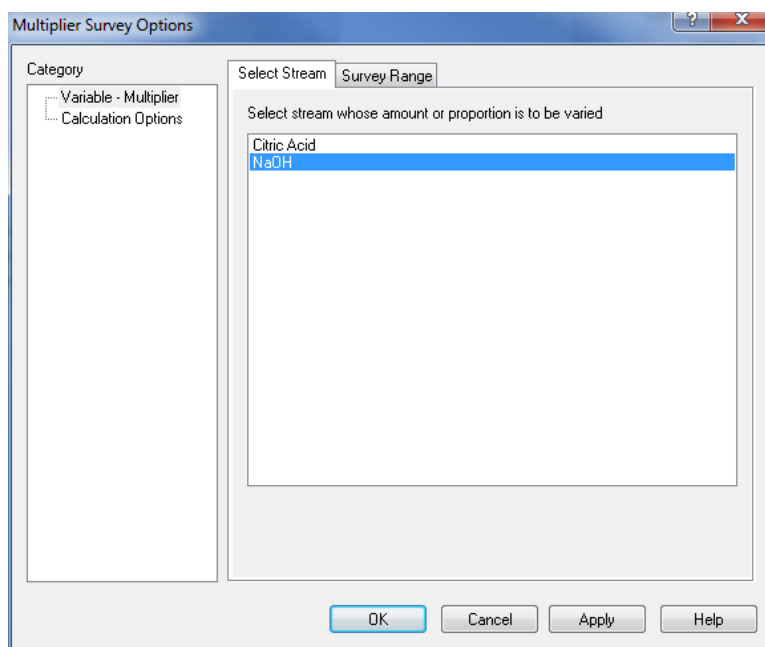
Figure 8-36 Selecting the NaOH stream.

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.
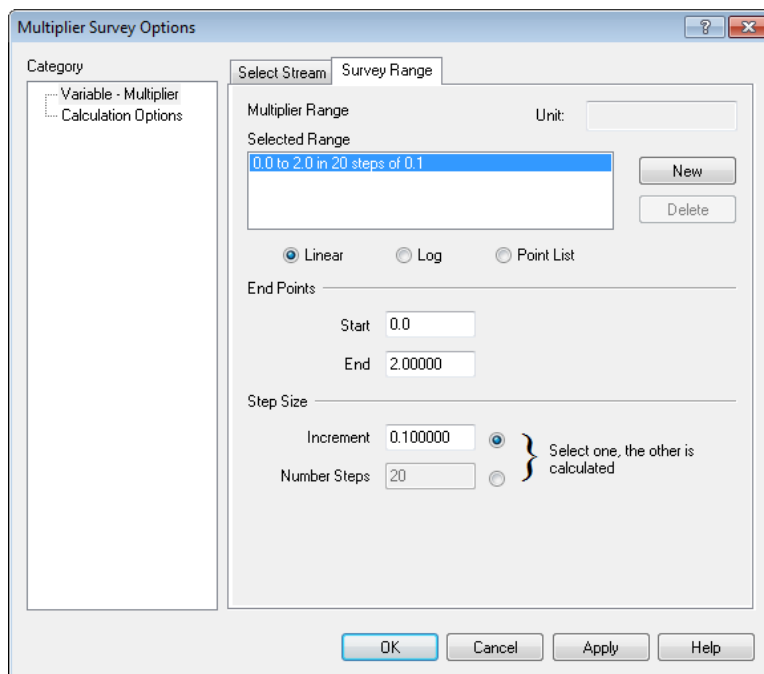
Figure 8-37 Setting the range of the ratio variable.

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.
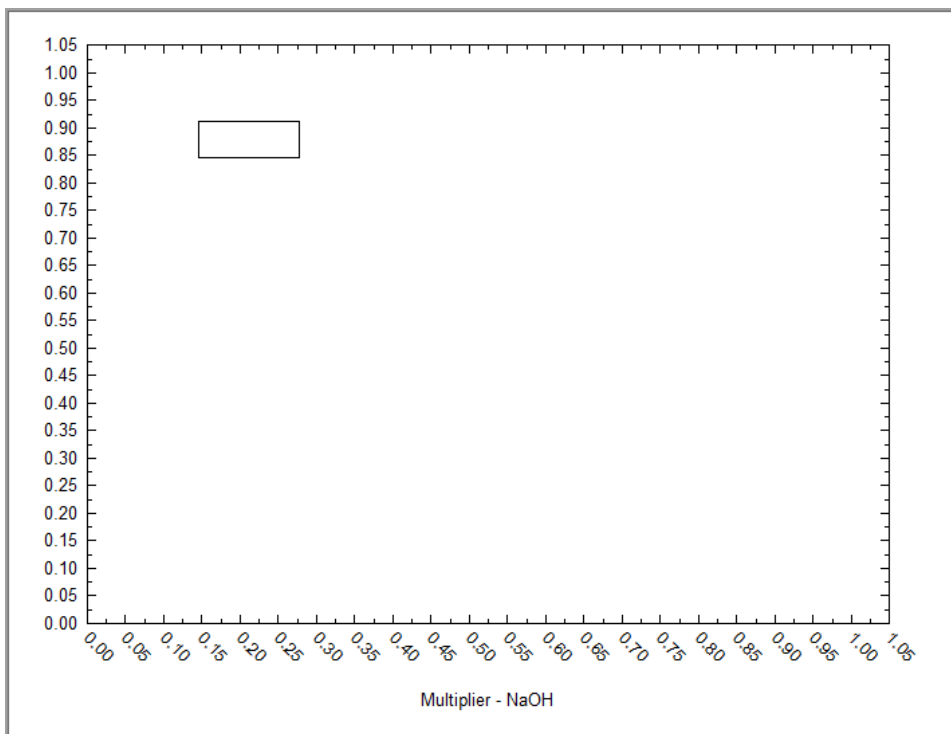
Figure 8-38 The default plot.

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.
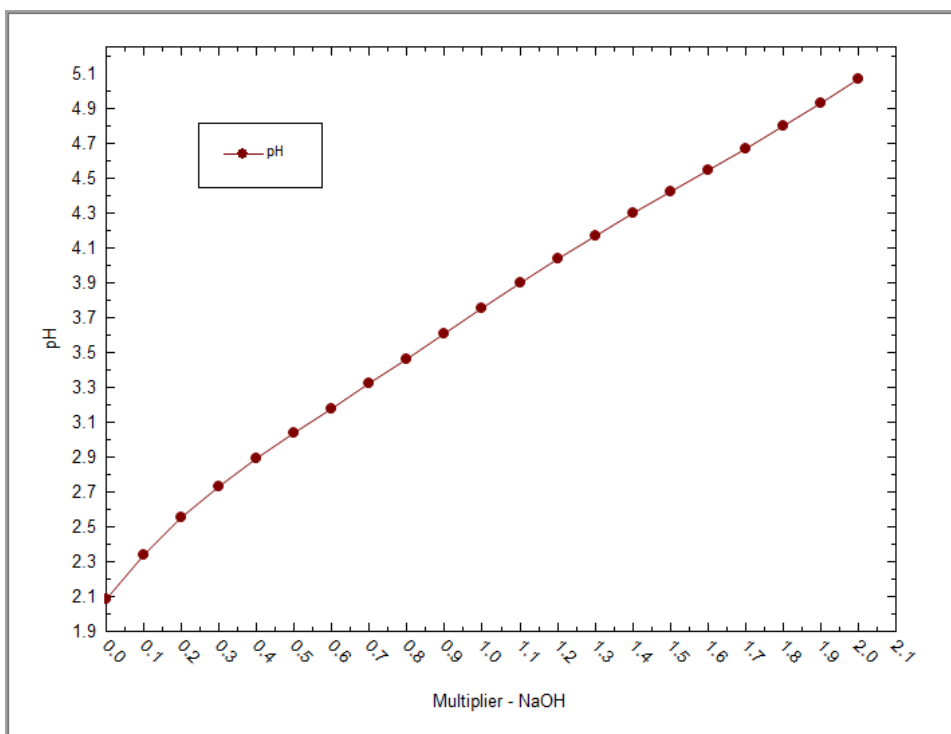
Figure 8-39 pH v. NaOH

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)
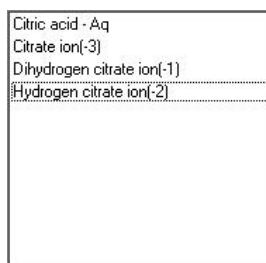
Figure 8-40 species to select
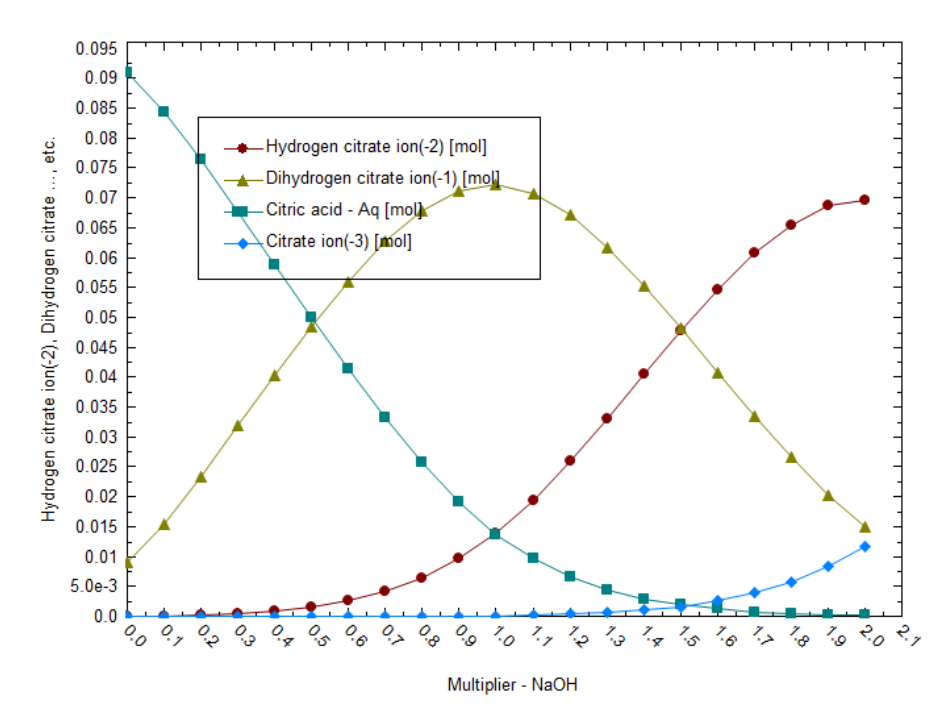
Figure 8-41 Citric Acid species v. NaOH

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_2citrate^{-1} to Hcitrate^{-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.

---

[37] You may find it easier to locate the ion names if you switch the Names Manager to Display Name.

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 8-42 below illustrates the layout.
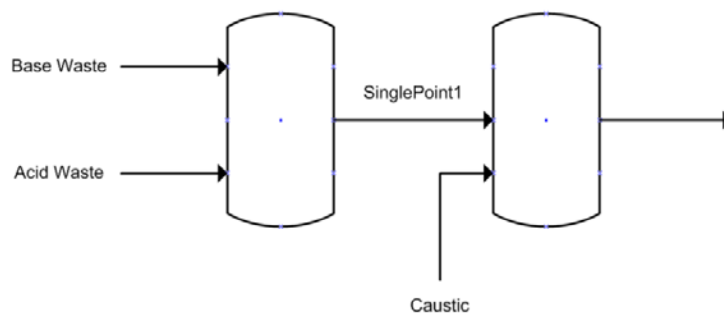
Figure 8-42 Schematic of cascading mixers

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)

Table 8-5 Cascading Mixer Stream Data

Parameter	Value	Units
Stream Name	Base Waste	
Temperature	25.0	ºC
Pressure	1.0	Atmospheres
Stream Amount	55.5082 (Default)	Mole
H_2O	55.5082	Mole
CO2	0.1	Mole
NH3	0.01	Mole
SO2	0.01	Mole
Stream Name	Acid Waste	
Temperature	25.0	ºC
Pressure	1.0	Atmospheres
H_2O	55.5082	Mole
HCl	0.1	Mole

H2SO4	1.0	Mole
Stream Name	Acid Waste	
Temperature	25.0	ºC
Pressure	1.0	Atmospheres
H_2O	55.5082	Mole
NaOH	1.0	Mole

To test that our streams are representing their respective names, perform a single point isothermal flash on each stream. When you are done you should have a window that looks like Figure 8-43 below:
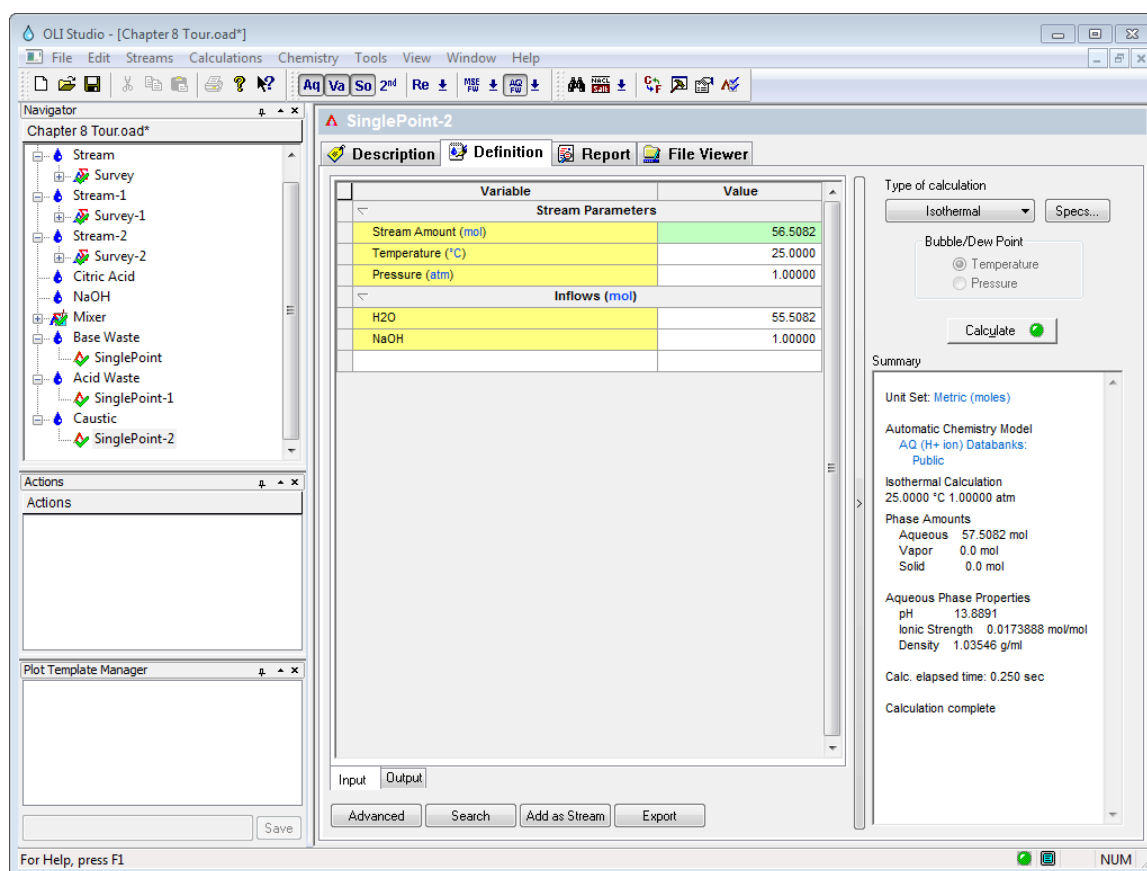
Figure 8-43 completed inputs for cascading mixer

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.
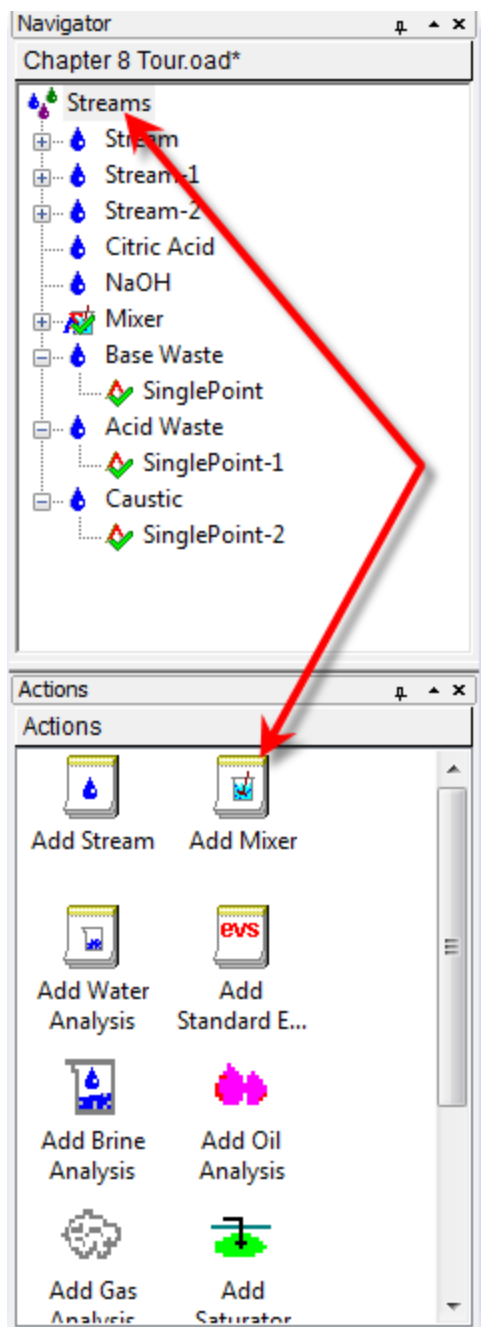
Figure 8-44 Adding a mixer

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.
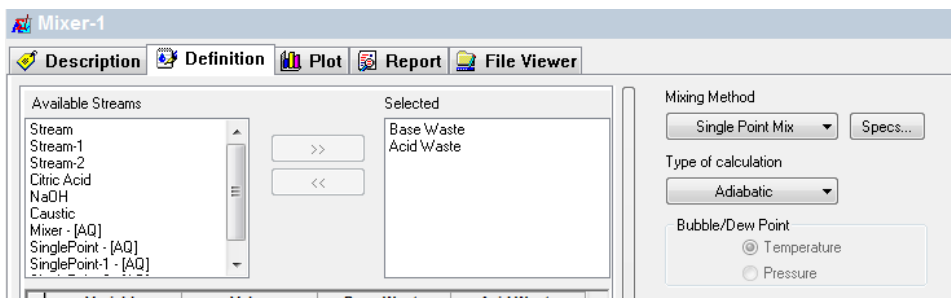
Figure 8-45 Selecting the Base and Acid waste stream

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.
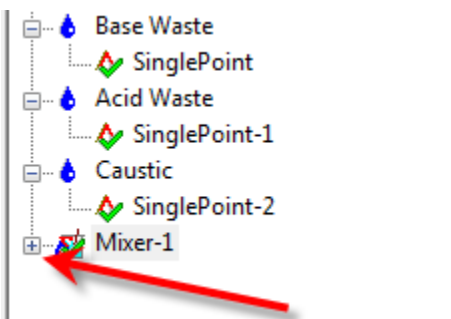
Figure 8-46 Click the "+" sign to expand the tree

Click the "+" sign to expand the tree.
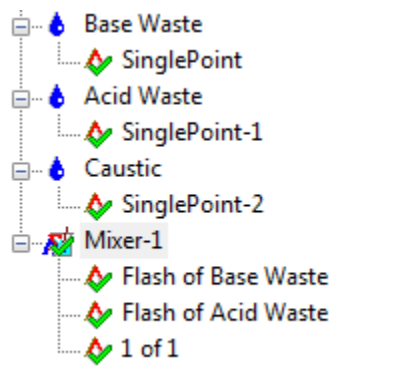
Figure 8-47 Expanded tree view

---

[38] You can use the Report Tab to find the pH value.

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.
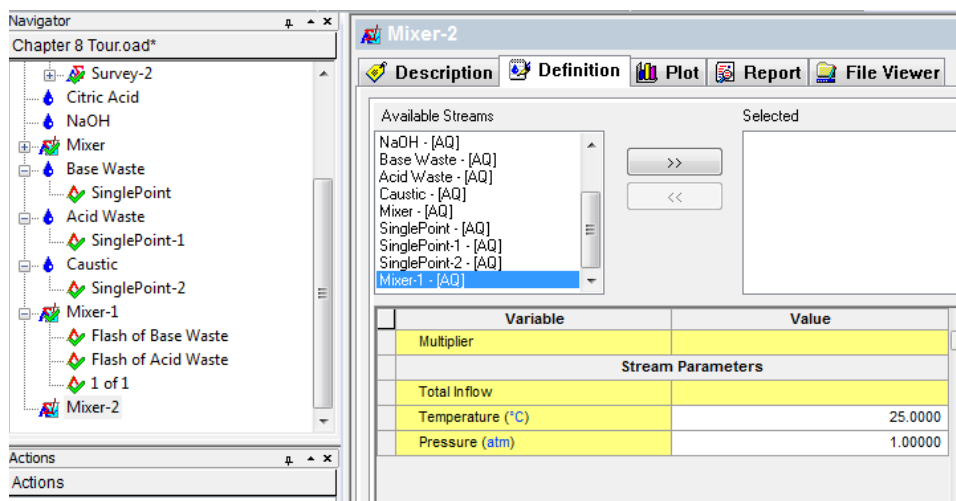
Figure 8-48 Adding the second mixer

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 OLI Flowsheet.) We want to connect the output from our first mixer (Mixer1) to the inlet of the **Caustic** stream. Click the object **Mixer-1-(AQ)** as highlighted in Figure 8-48 above.

Then add the Caustic Reagent. Select the type of calculation as Isothermal.
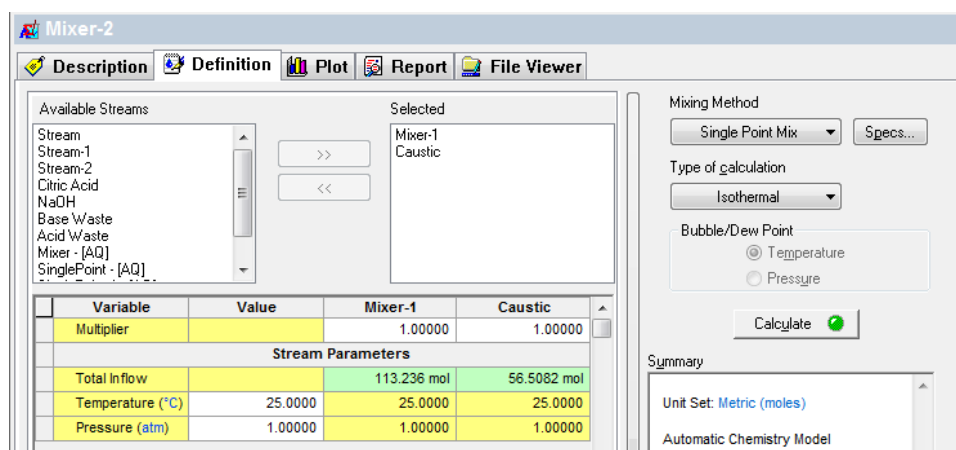
Figure 8-49 connecting the output of mixer 1 to the new mixer

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

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

Figure 8-50 Changing the multiplier value

Click the calculate button again. The new pH should be approximately 12.4.

The real value of the cascading mixer is the quick ability to re-calculate the objects if we want to change something. Let's add some diethanolamine to the series of calculations. Click the **Acid Waste** stream (not the single point calculation below it) and add the component DEXH[39] to the grid with a value of 10.0 moles.

Figure 8-51 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.

[39] This is the OLI Tag name for diethanolamine, which is easier to type if you know the name.

Figure 8-52

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 **<u>Definition</u>** below.
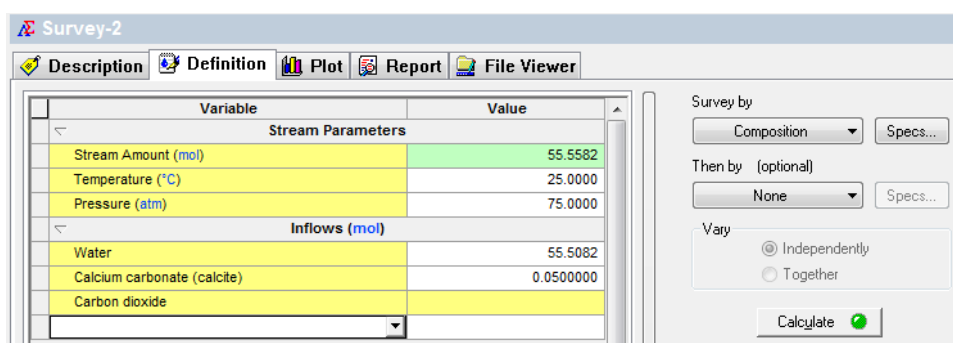
Figure 8-53 Composition survey definition

Select **<u>Composition</u>** from the **<u>Survey by</u>** button. Select the **<u>Specs</u>** button and then select ***CO2***.

Select the **<u>Range</u>** tab and adjust the increment to ***0.05***, the ending value is ***1.0.***

Starting from a saved case

> ***Click*** on the **<u>Definition</u>** tab for the survey.
>
> Now select the **<u>Then by</u>** button.
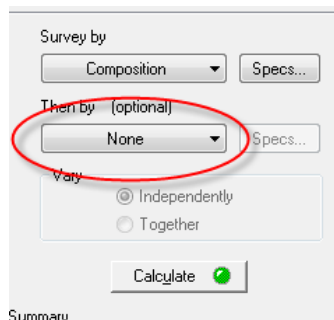
Figure 8-54
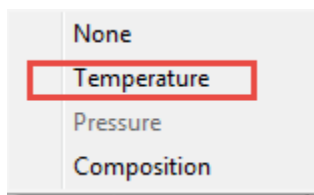
Figure 8-55 Selecting the Secondary Survey

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.
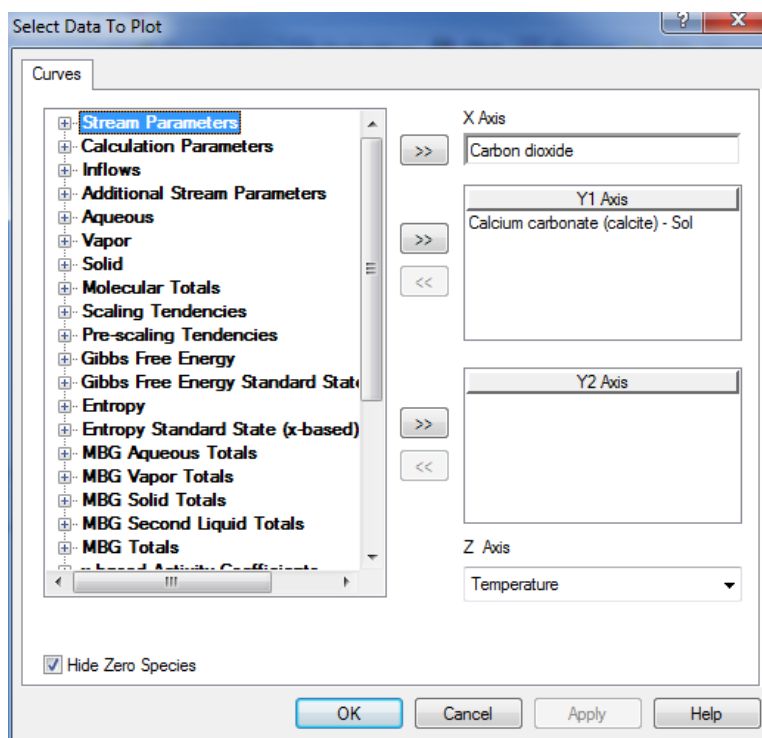
Figure 8-56 Setting the plot variables

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.
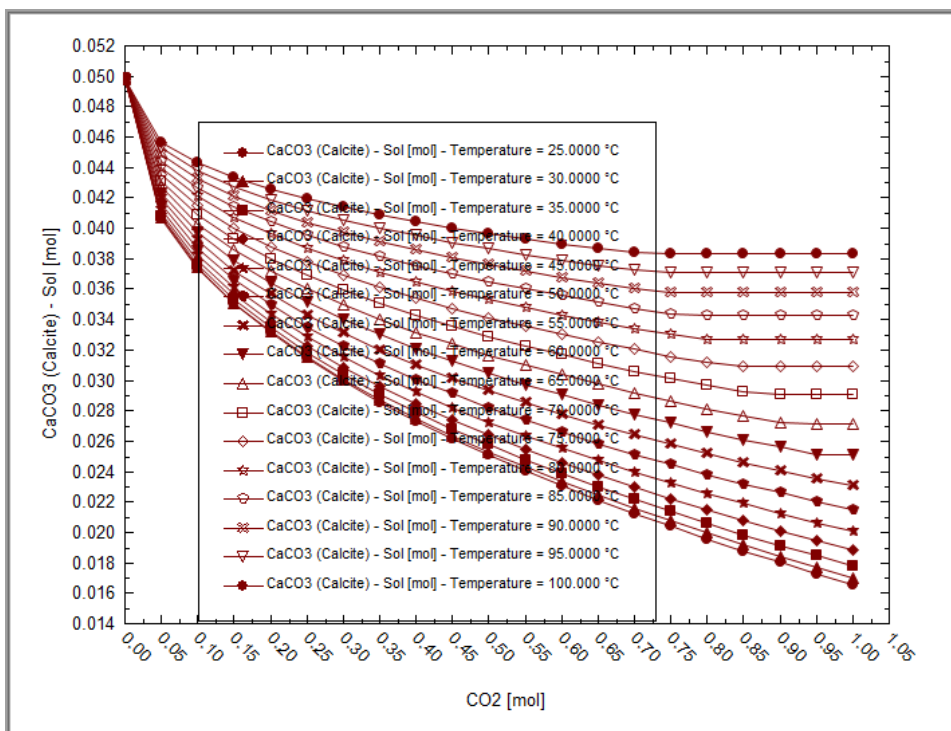
Figure 8-57 A family of Curves, the legend is in the way.

Right-clicking anywhere on the plot brings up the following menu:
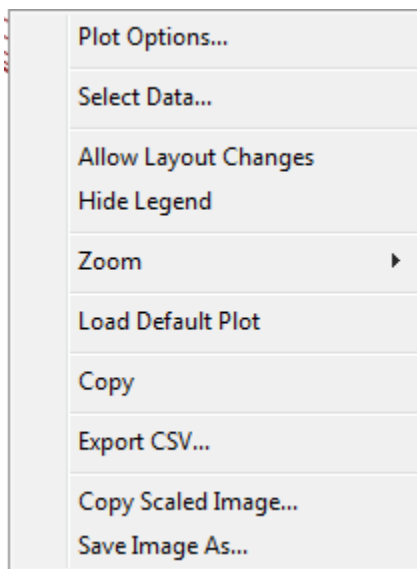
Figure 8-58 Right-Click on the plot to pop this up.

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.
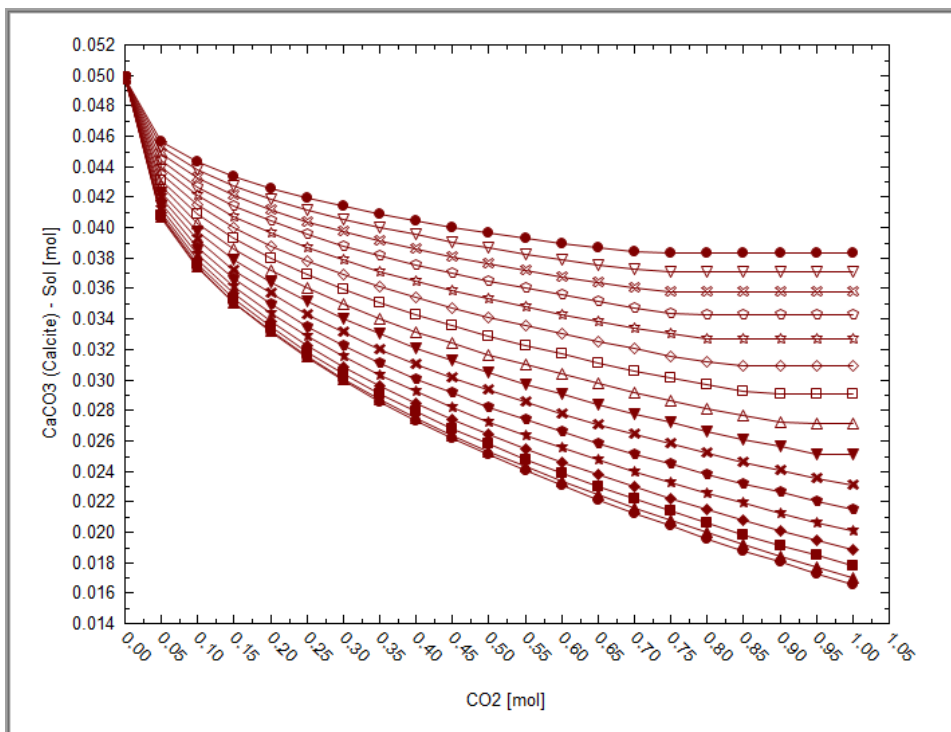
Figure 8-59 The uncluttered view.

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 8-60 the contour plot button

This dramatically changes the display.
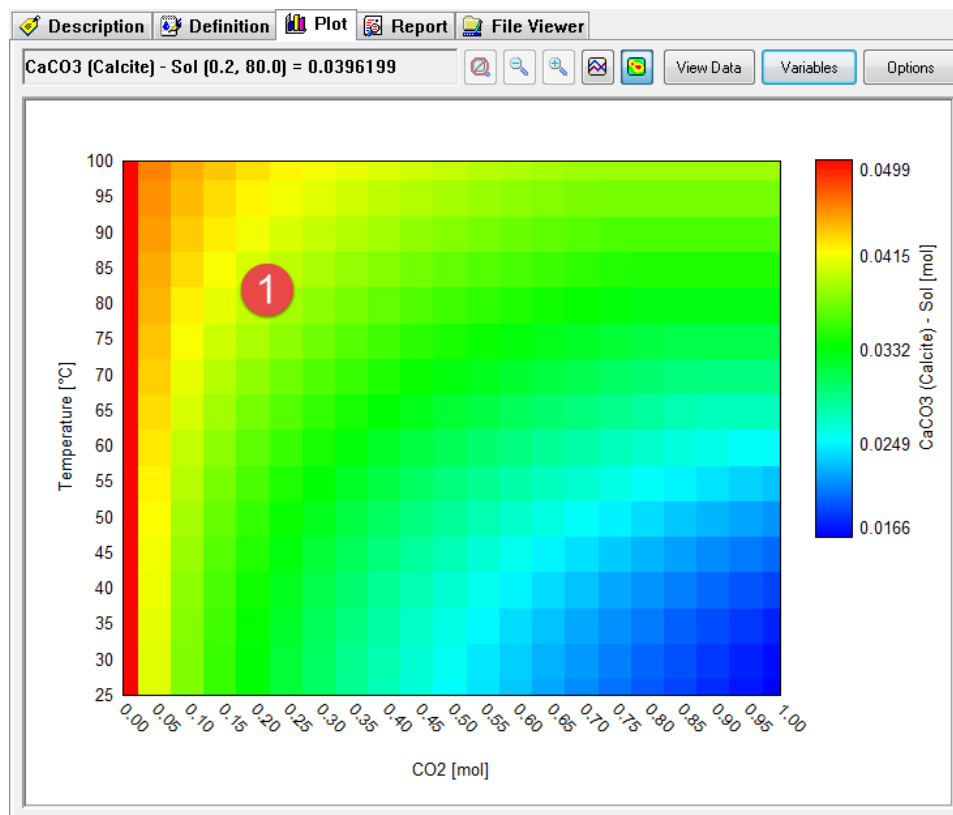
Figure 8-61 the contour plot

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 ºC 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:
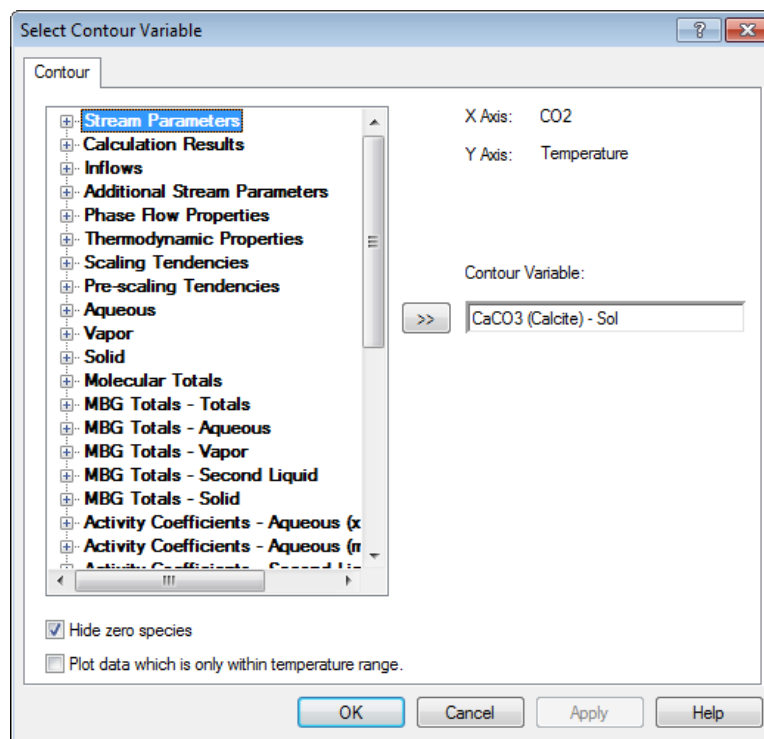
Figure 8-62 Contour variables

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:
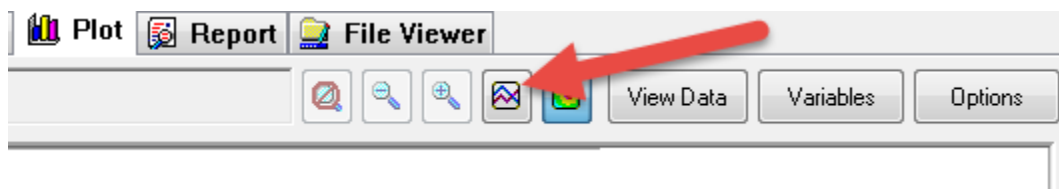
Figure 8-63 The standard plot button

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**	**mg/L**
Ba+2	0.46	Cl-	3896.00	**Gas**	
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.
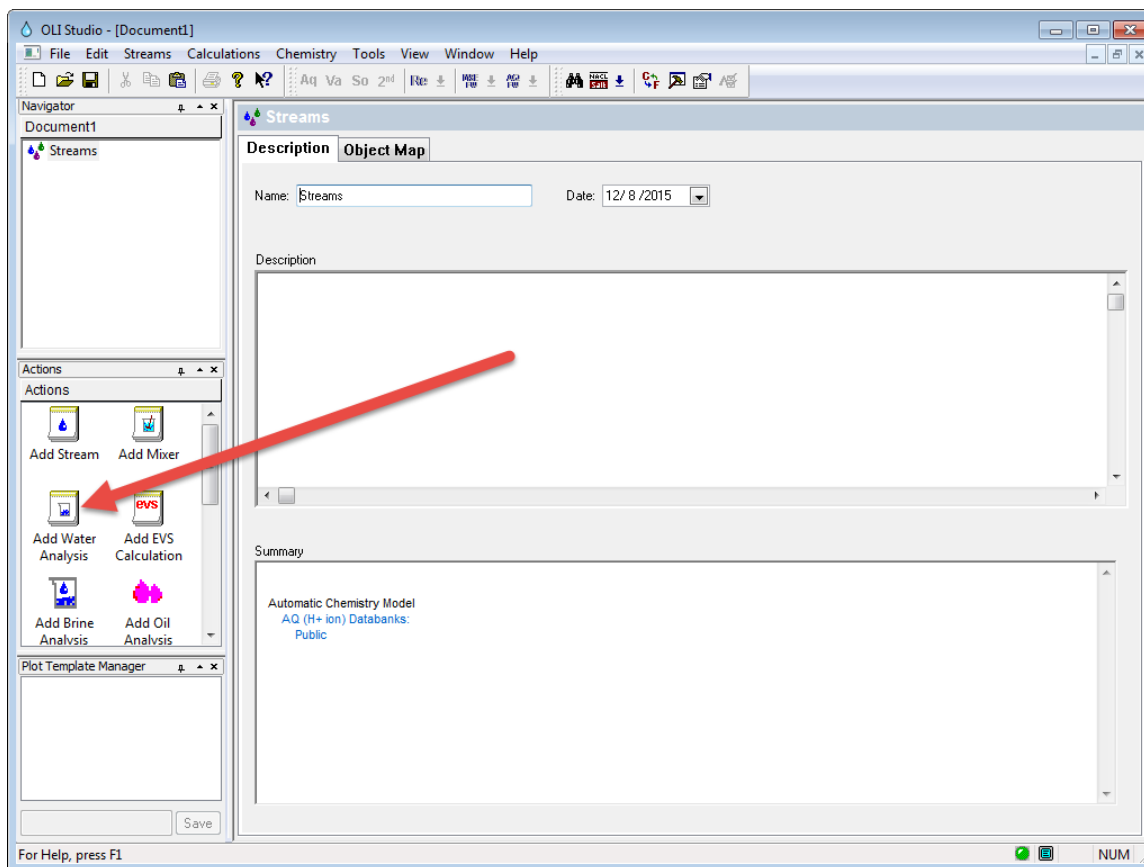
Figure 9-1 The main window.

As with the other Analyzer calculations, we start by define the conditions.

Figure 9-2 The icons available for the analysis

We will enter the concentrations listed on the previous page.

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.
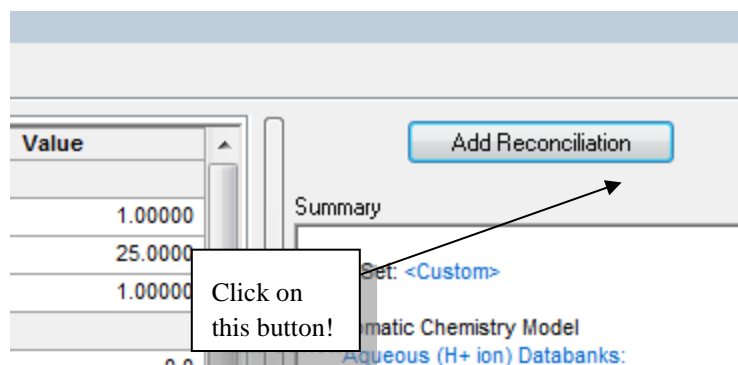
Figure 9-4 click on the Add Reconciliation button

This will automatically update the tree view on the left and place you in the description tab for the reconciliation.
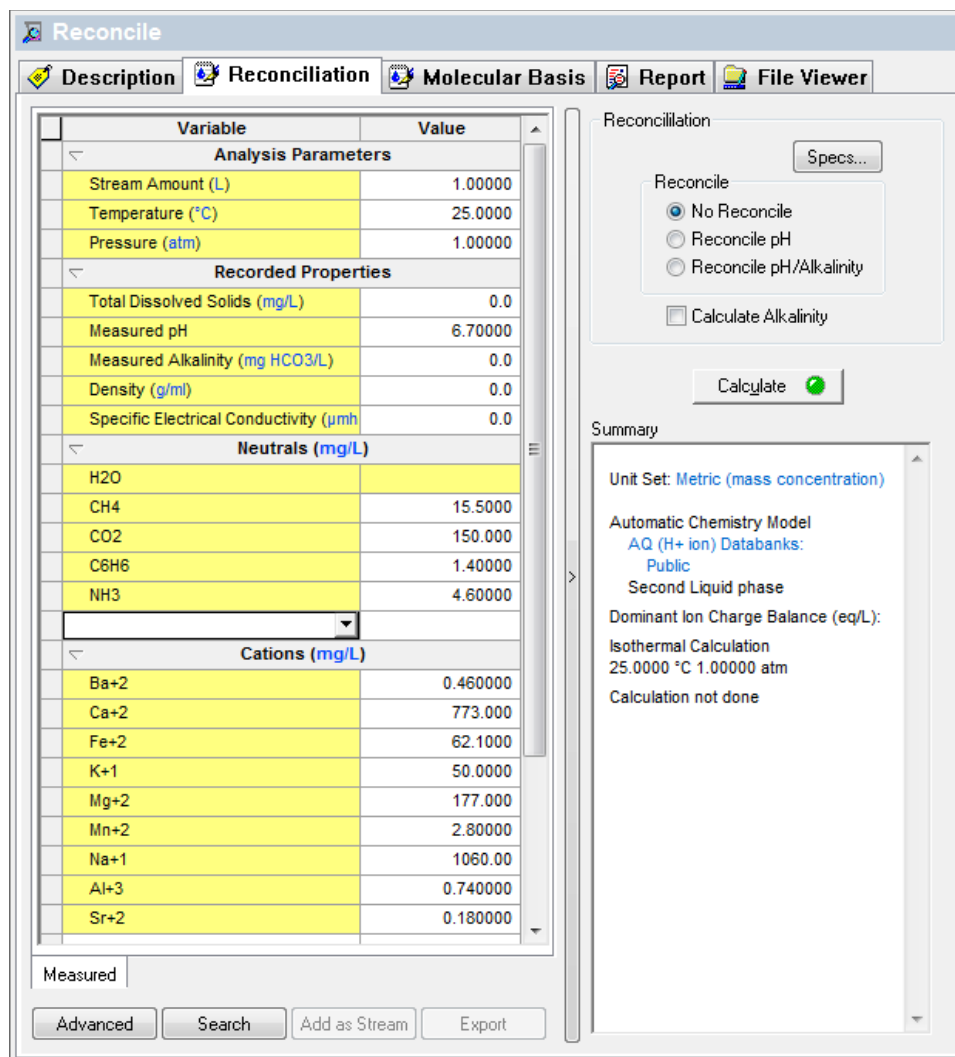
Figure 9-5 The reconciliation panel.

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.
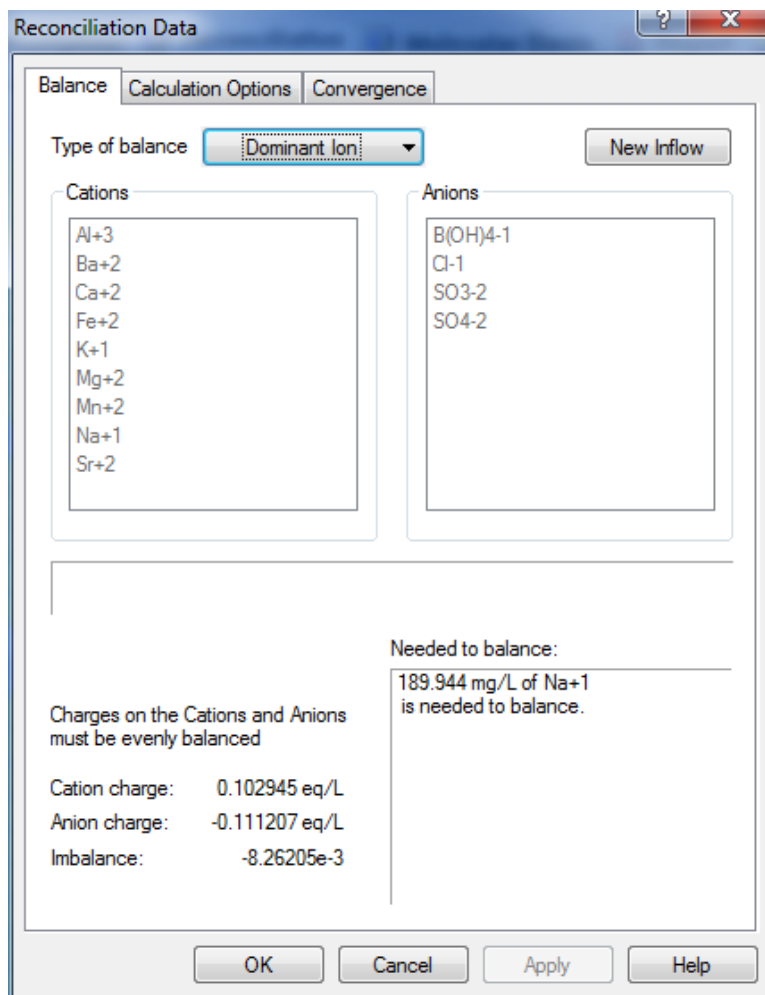
Figure 9-6 The Reconciliation Data dialog.

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.
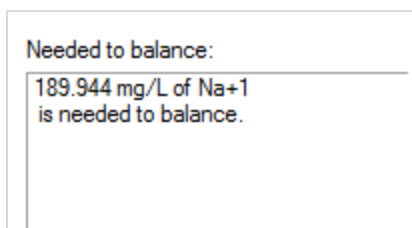
Figure 9-7 The largest concentration of cation to be entered.

We will now change the type of balance to **Na/Cl**.
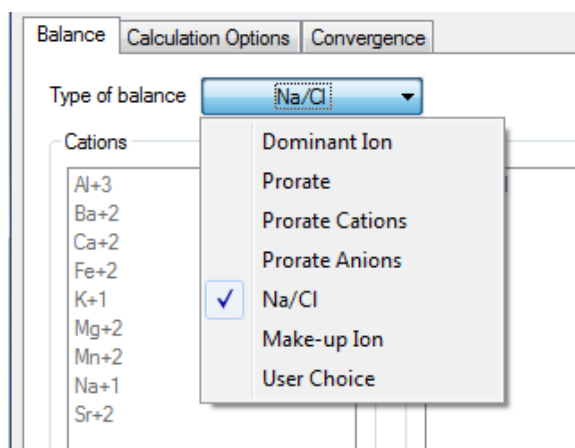
Figure 9-8 Na/Cl reconciliation method

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:

$$\left(0.007138\frac{eq}{L}\right)\left(\frac{1\,moleNa^+}{1eq}\right)\left(\frac{22.99\,gramsNa^+}{moleNa^+}\right)\left(\frac{10^3\,mgNa^+}{gramsNa^+}\right)=189.944\frac{mgNa^+}{L}$$

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.
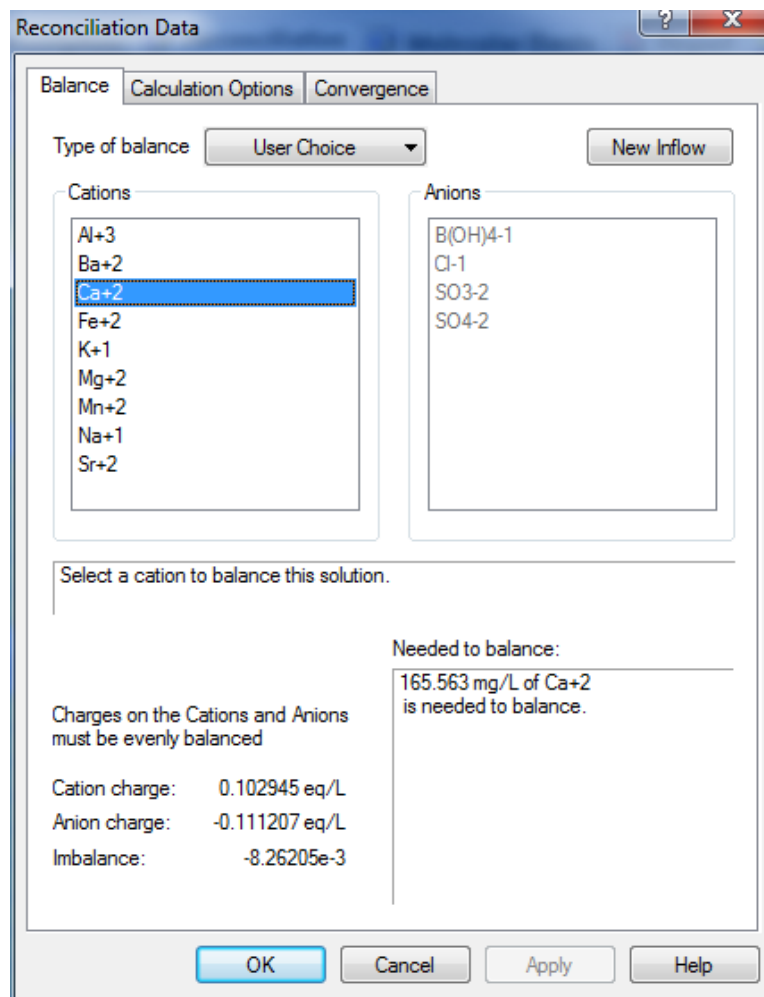
Figure 9-9 User choice option

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.
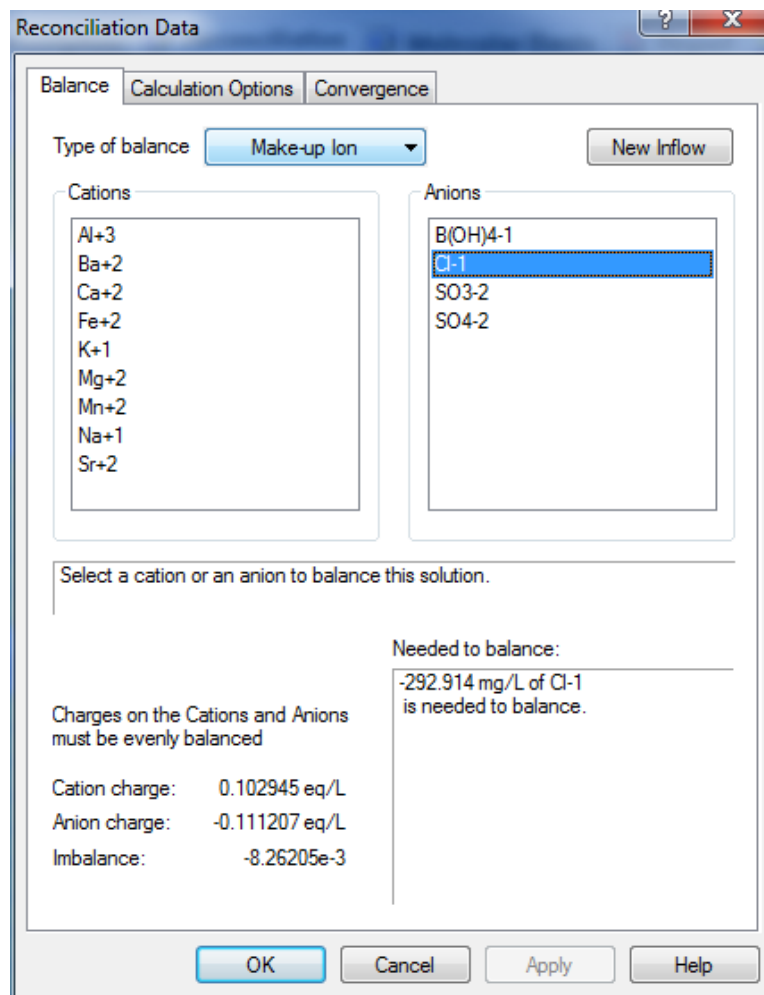
Figure 9-10 Make Up Ion Option

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.
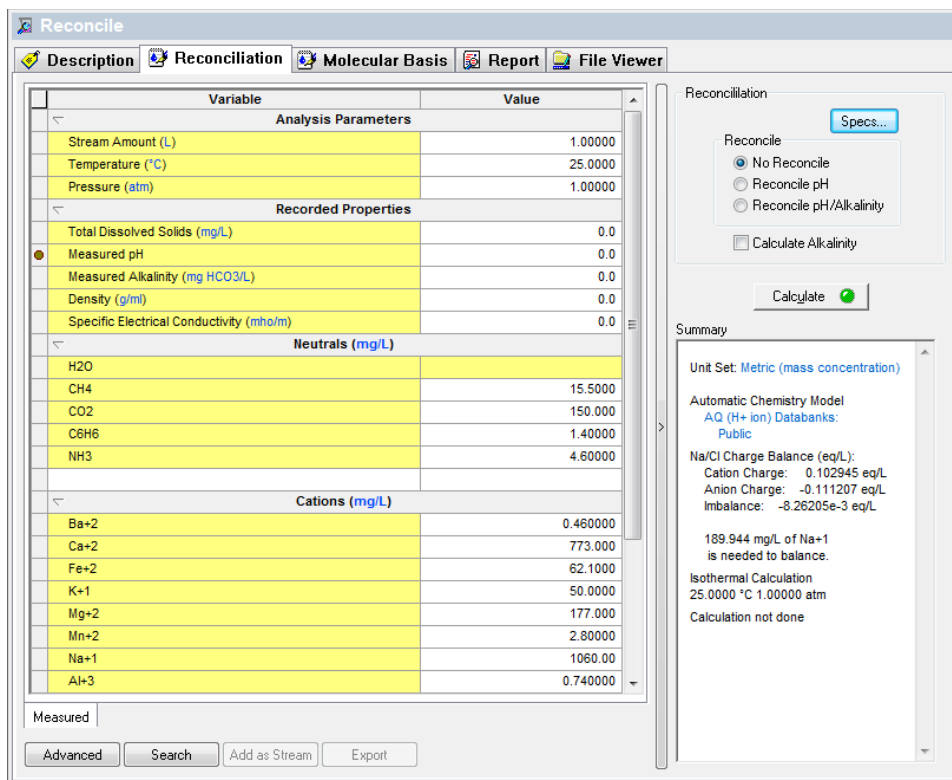
Figure 9-11 The updated summary box.

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.

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.
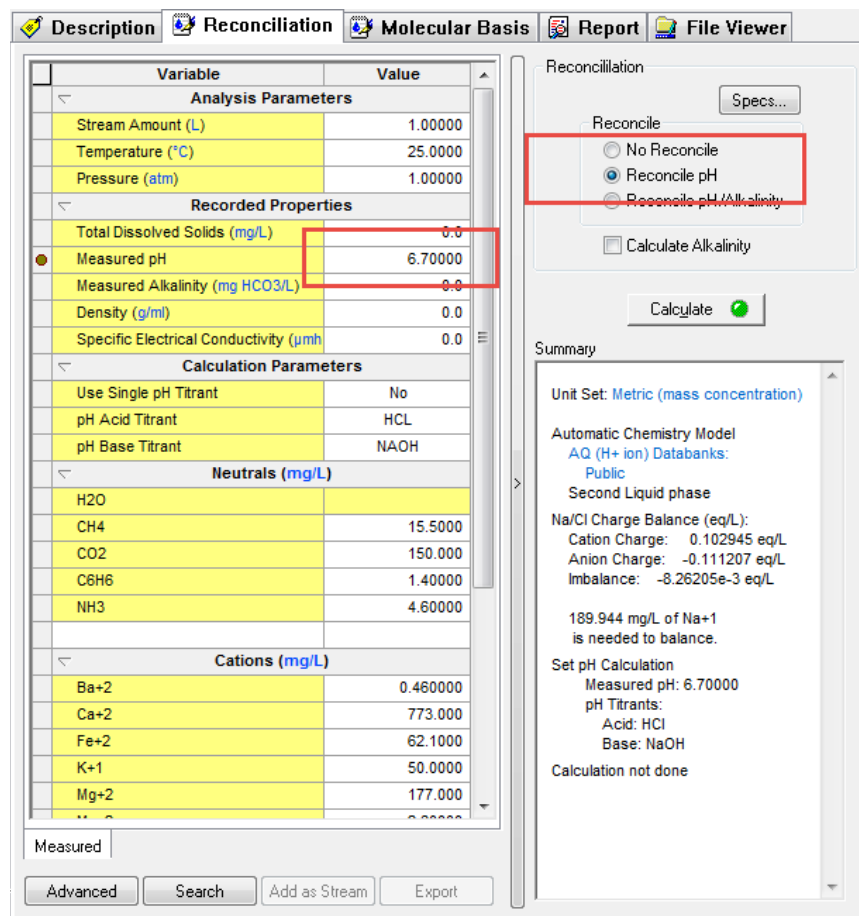
Figure 9-13 Choosing the Reconcile pH option.

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.
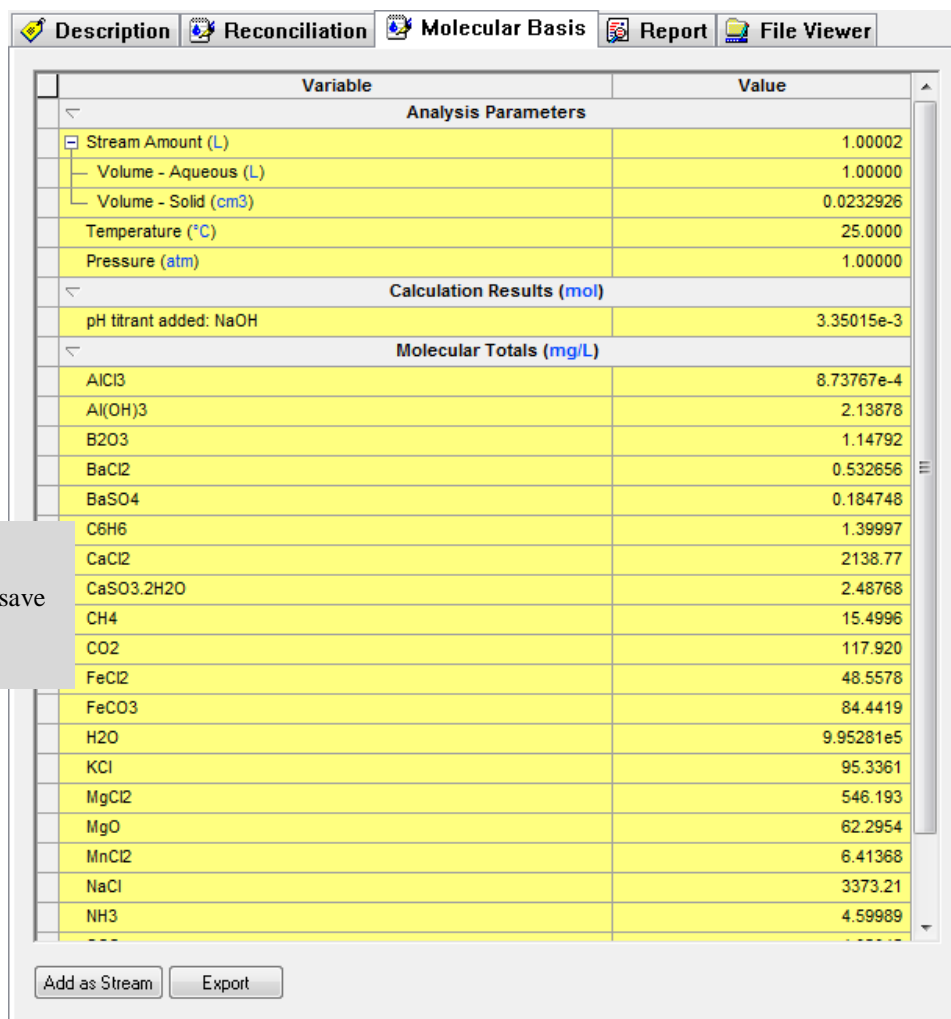
Figure 9-14 The amount of NaOH added.

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

Add as Stream   Export

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.
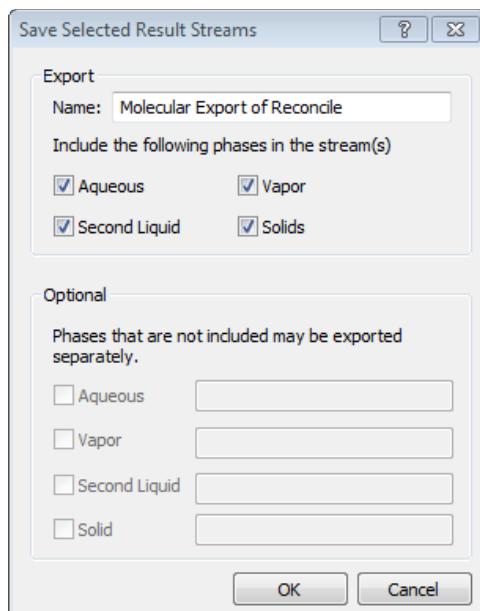
Figure 9-16 Save As Stream dialog

- 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 **Definition** tab.
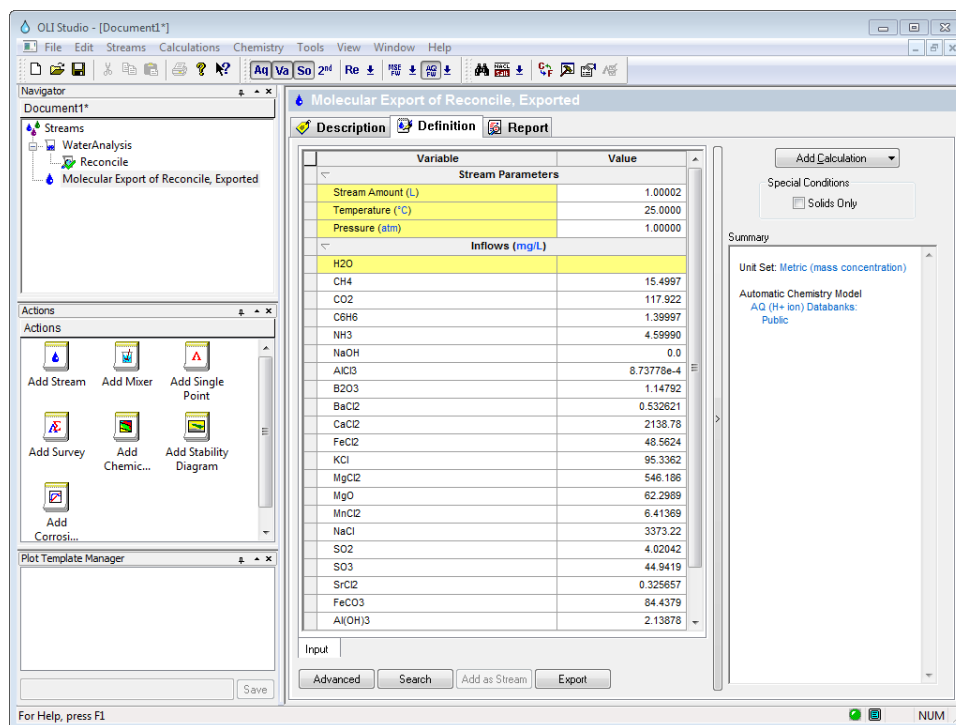
Figure 9-17 The molecular stream

Summary

OLI Studio provides for alternative feed stream definition based upon a "Raw" Laboratory Analysis:

Flagging of Inconsistencies

- o Determines the amount of imbalance with respect to electroneutrality
- o Calculates pH based upon sample information

Reconciliation of Inconsistencies

- o Adds or subtracts mass to balance electroneutrality
- o Adds and acid or base to adjust pH

Simulation Options

- o Surveys
- o Single Point Calculations
- o 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
Bold and Underlined	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 **Tree-view** or **Navigator** 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 **Actions** or the **Explorer** view and shows the icons of the objects.
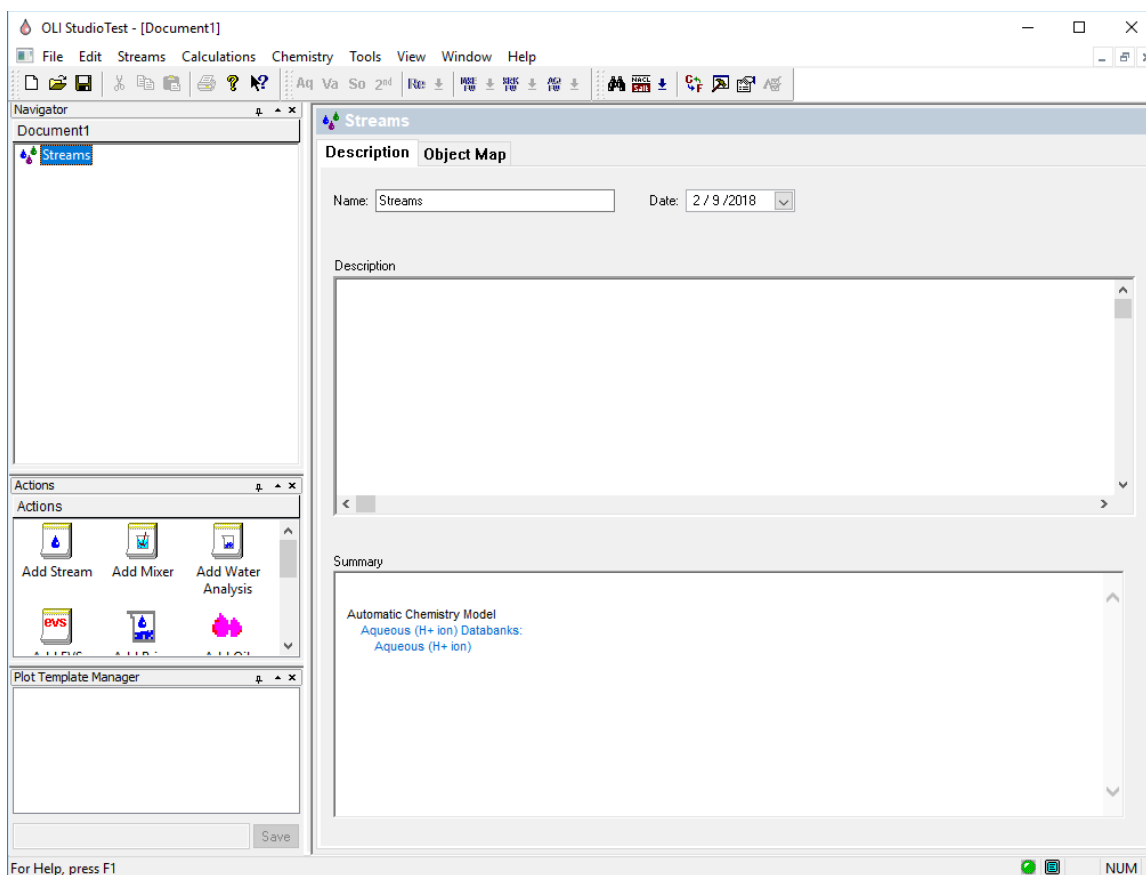
Figure 10-1 the main window.

To set up this tour, we need to change some settings. Please locate and ***click*** on the <u>**Tools**</u> 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 <u>**Names Manager**</u> by ***Clicking*** on the item.
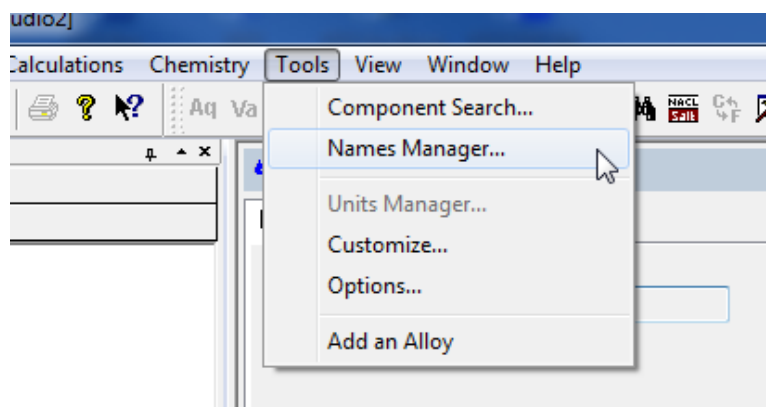
Figure 10-2 The Tools menu items.

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.
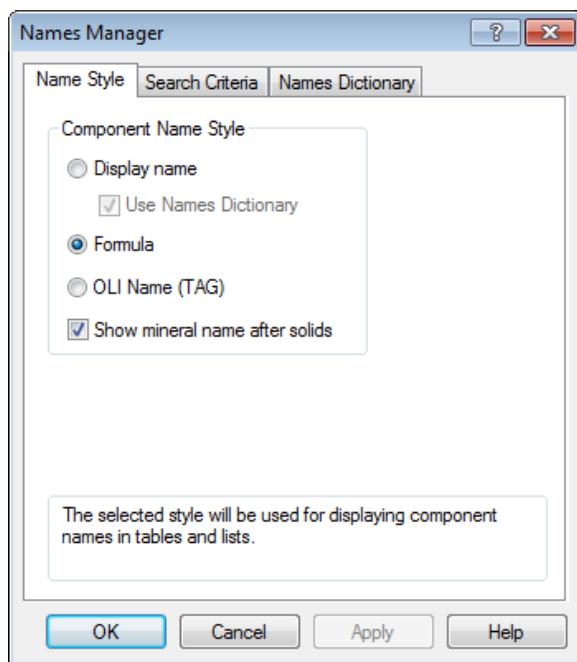
Figure 10-3 The Names Manager

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 show two 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.*
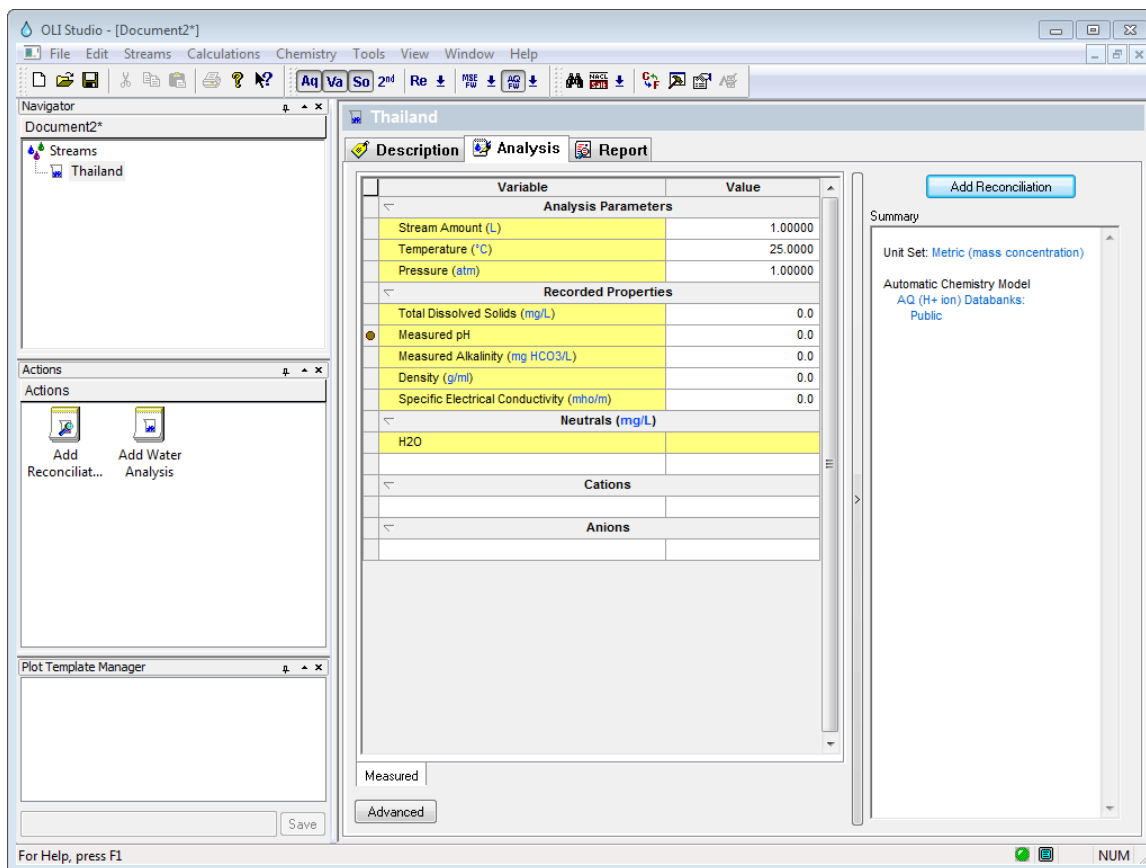
Figure 10-4 The Water Analysis Definition.

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.
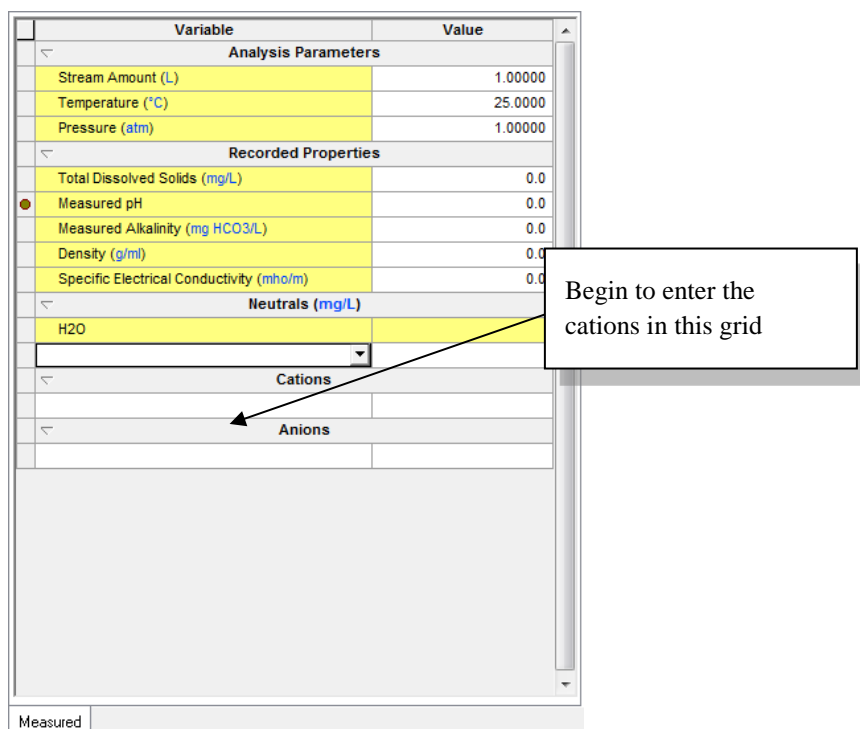
Cations

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.

Figure 10-5 Entering the cations

Scroll down the grid and enter the anions:

Figure 10-6 Entering the anions

We are now ready to perform some reconciliation calculations for this sample.
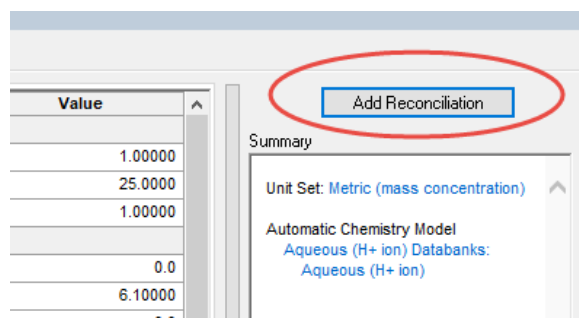
Figure 10-7 Finished data entry

Click on the **Add Reconciliation** Button.

This will display more tabs for entering data about the reconciliation. A new object will appear under the **Thailand** 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.
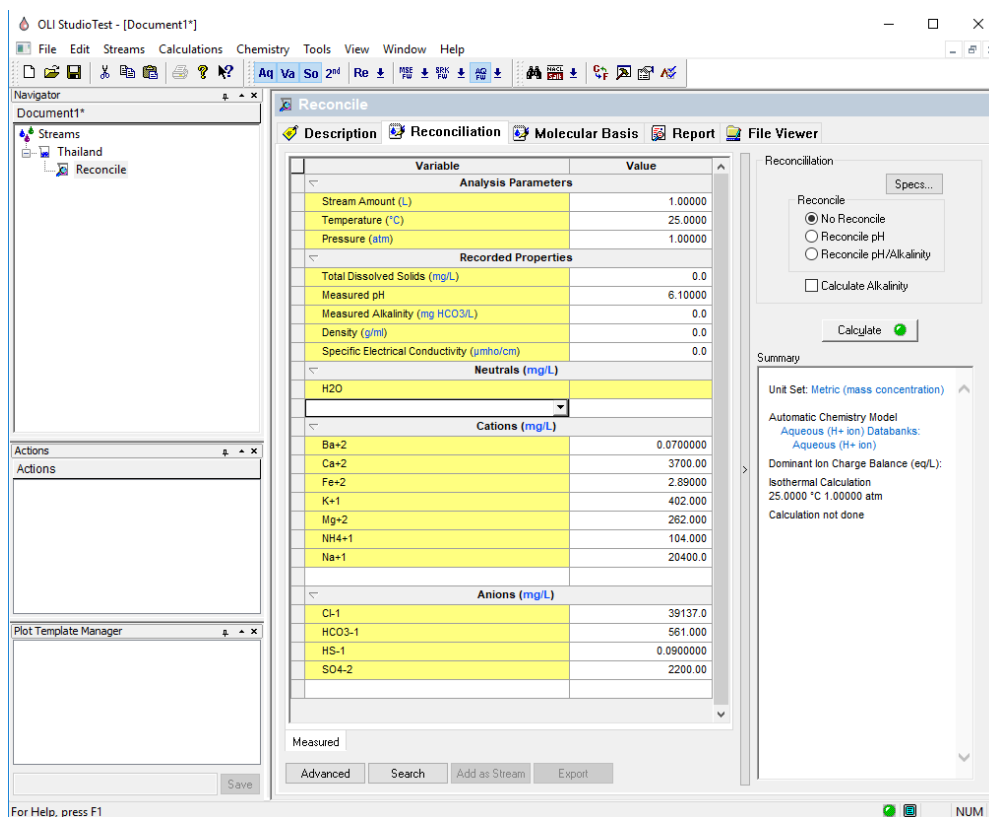
Figure 10-8 Starting the reconciliation.

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.
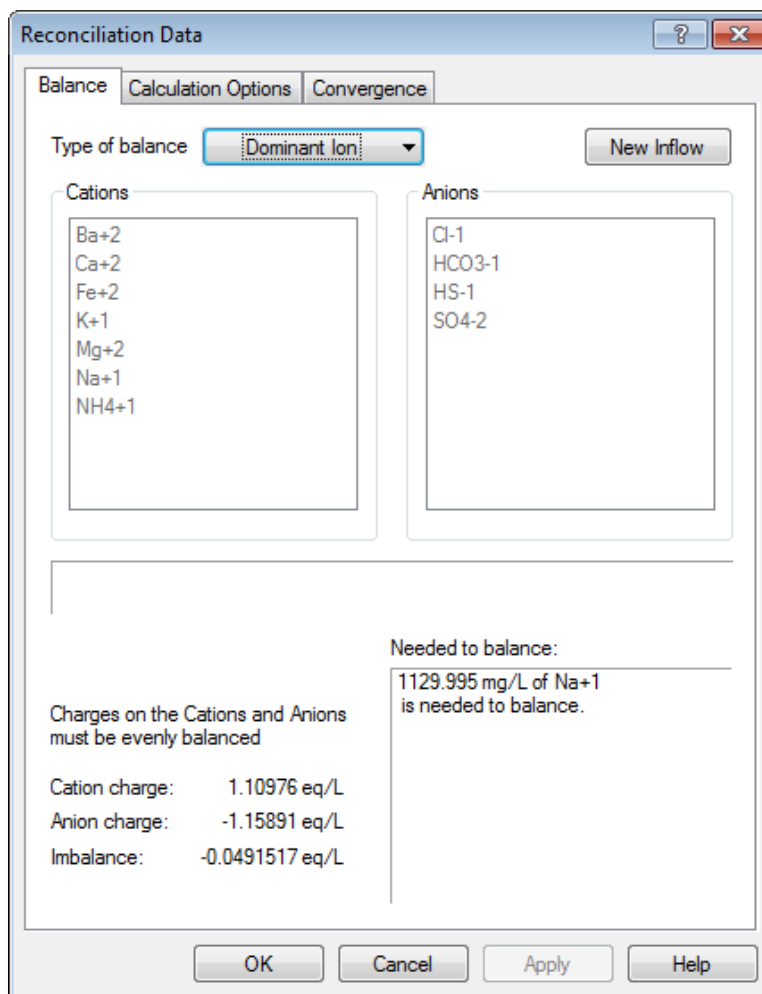
Figure 10-9 choosing electroneutrality

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.
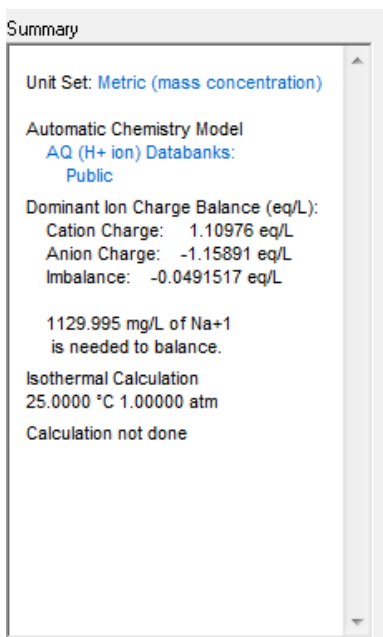
Figure 10-10 the summary box

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.

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.

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.
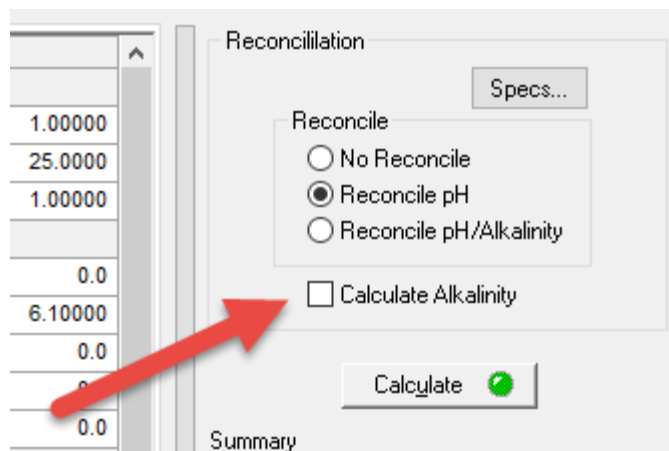
Figure 10-14 Calculate Alkalinity

Check the box

The input grid updates with a new set of parameters in the **Calc Parameters** section.

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:

Figure 10-16 Additional Alkalinity Titrants

The Alkalinity Titrant is defaulted to H_2SO_4 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 H_2SO_4) is being added to the stream.

Click the Calculate button.
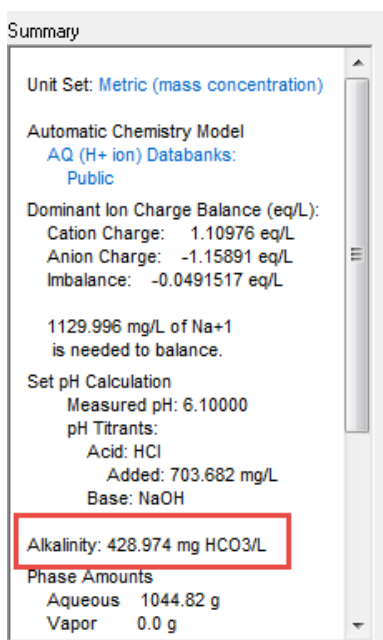
Figure 10-17 Calculated Alkalinity

From the summary box we can see that the solution's calculated alkalinity is approximately 429 mg/L as HCO3.

Now let's reconcile both pH and alkalinity.

Figure 10-18 reconciling both pH and alkalinity

Figure 10-19 User entered values note that the original pH of 6.1 is still used

Enter the measured alkalinity value of 425 mg HCO3/L, and then click the Calculate button.
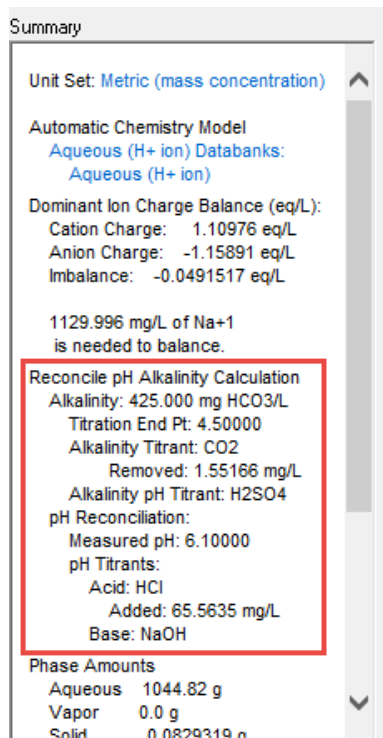
Figure 10-20 The red box shows the alkalinity values

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.
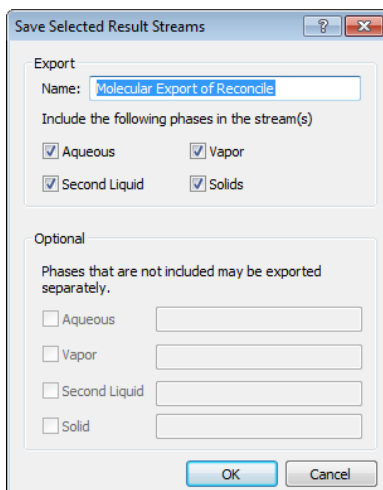
Figure 10-21 Save As Stream dialog, default options selected

Click the **OK** button to save all the phases as a new stream.

The tree-view will be updated to display a new stream.

Figure 10-22 A new stream object is displayed.

Click here for a worked example for this chapter: <u>Chapter 10 – Water Analysis Tour</u>

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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:

$$P * V = n * R * T$$

$$1\ atm * 1L = n * 0.082057\ \frac{L\ atm}{K\ mol} * 298.15\ K$$

$$n = 0.04087\ moles$$

- ✓ Start a new file and give it a name such as ***Chapter 11 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

---

[40] This chapter is authored by Anthony Gerbino of AQSim. Used with permission

✓ Add N2 as an inflow
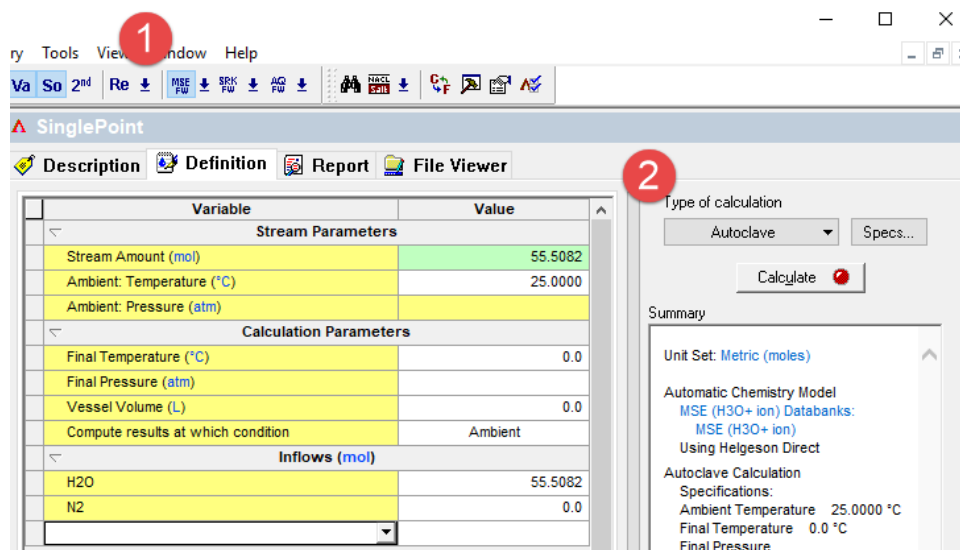
Figure 11-1 Initial Autoclave Setup

✓ Add a Single Point Calculation then select Autoclave as the calculation type. Click the Specs button

✓ Click the Specs button

✓ Highlight N2 in the gas field then press OK
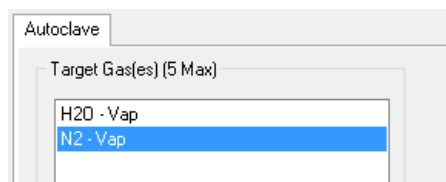
Figure 11-2 Selecting Nitrogen

✓ 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

Table 11-1Basic Autoclave Data

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+)						
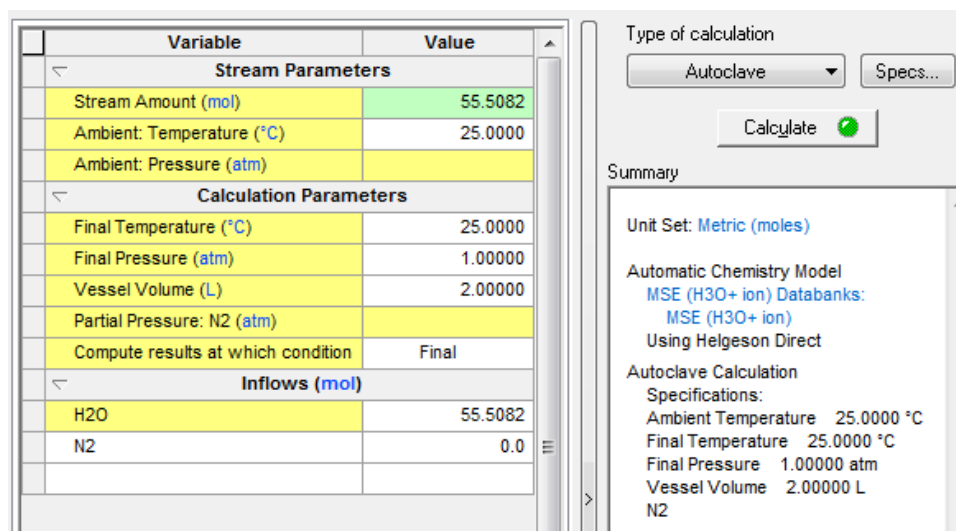
Figure 11-3 Setup complete

✓ Change the Compute results at which condition to Final

✓ Calculate

Figure 11-4 Computed output

✓ 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)	Total	Liquid-1	Vapor
Row Filter Applied: Only Non Zero Values			
column Filter Applied: Only Non Zero Values			
	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

Figure 11-5 Basic example repot output

✓ 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 Soave-Redlich-Kwong (SRK) cubic equation of state. The SRK equation for one mole gas looks like the following:

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b)}$$

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: $4L * 0.04087 \frac{moles}{L} = 0.1634 \; moles$ of gas.

Calculation Parameters	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	5.00000

Figure 11-6 Changing conditions

✓ 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
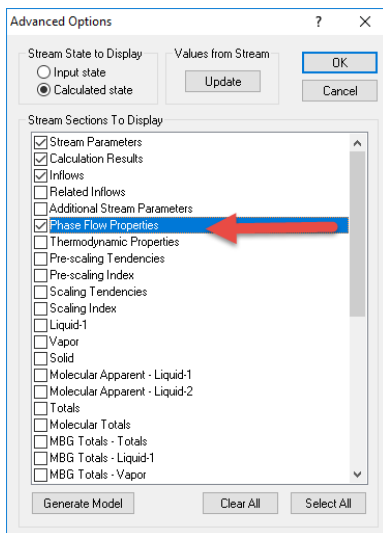
Figure 11-7 Advanced options

✓ Press OK

✓ 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:

$$n = \frac{1\ atm * 19L}{0.082057\ \dfrac{L\ atm}{Kmol^{-1}} * 298.15K} = 0.776\ moles$$

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
Moles (Apparent) - Liquid 1 (mol)	55.4845

Figure 11-8 Results with increased volume

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

Figure 11-9 Results at higher pressure

- ✓ Click on the Output tab and view the results

- ✓ Calculate the gas amount using the Ideal Gas Law

$$n = \frac{50\ atm * 19\ L}{0.082057 \frac{L\ atm}{K\ mol} * 298.15K} = 38.83\ moles$$

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

Figure 11-10 Results at 200 atmospheres pressure

The computed gas amount is 143.76 moles and is less than the 155.32 moles as per the Ideal Gas Law:

$$n = \frac{200 \; atm * 19 \; L}{0.082057 \frac{L \; atm}{K \; mol} * 298.15K} = 155.32 moles$$

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 100 °C and calculate

✓   View the results in the lower Output tab

✓   Compare the results to what the Ideal Gas equation would produce

$$n = \frac{200 \; atm * 19 \; L}{0.082057 \frac{L \; atm}{K \; mol} * 373.15K} = 124.104 \; moles$$

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

Figure 11-11 Results at 100 C

The difference is between 124.1 moles and 112.2 moles, or about 11% higher.

✓   Recalculate at 200C and compare the two equations of states

The Ideal Gas Law computes 97.87 moles of gas in the 19 liters.

$$n = \frac{200\ atm * 19\ L}{0.082057\ \frac{L\ atm}{K\ mol} * 473.15K} = 97.87\ moles$$

With enhanced SRK, the software computes 91.45 moles. Note also, that the Software computes a 19.04 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 computed for	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	
Moles (Apparent) - Total (mol)	137.024	
Mass - Total (g)	3283.52	
Mass - Liquid-1 (g)	822.358	
Mass - Vapor (g)	2461.17	
Volume - Total (L)	19.9998	
Volume - Liquid-1 (L)	0.959272	
Volume - Vapor (L)	19.0405	

Figure 11-12 Results at 200 C

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.

Table 11-2 Reactive test data

T	P	Vol	Ideal Gas Law	Calculated (total)	Calculated (vapor)	%Diff (vapor)
C	atmmm	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
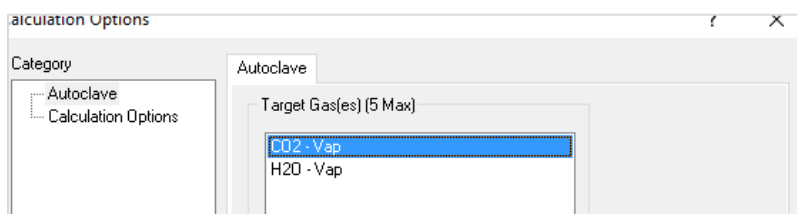
Figure 11-13 Selecting target gas = CO2

✓ 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

---

Table 11-3 Basic autoclave setup data

Basic Autoclave Setup							
Setup		Stream Parameters		Calculation		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+)						

The input should look like this:

Figure 11-14 Input data

Calculate

Figure 11-15 Results of reactive gas calculationClick 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.

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.

Table 11-4Comparison between a noble gas and a reactive gas

T	P	Vo	Ideal Gas	Calculated	Calculated	Calculated	Calculated
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

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	55.508	55.5067	1.29346e-3
CO2	0.0722846	0.0326549	0.0396297
H3O+1	1.23094e-4	1.23094e-4	
HCO3-1	1.23093e-4	1.23093e-4	
OH-1	8.41483e-11	8.41483e-11	
CO3-2	4.91026e-11	4.91026e-11	
Total (by phase)	55.5805	55.5396	0.0409232

Figure 11-16 Results report

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 and add 0.1 moles NaOH to the input grid

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

Figure 11-17 adding NaOH to the inflows

Click **Calculate**

When complete click on the **Output** mini-tab.

Figure 11-18 Results when adding NaOH

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
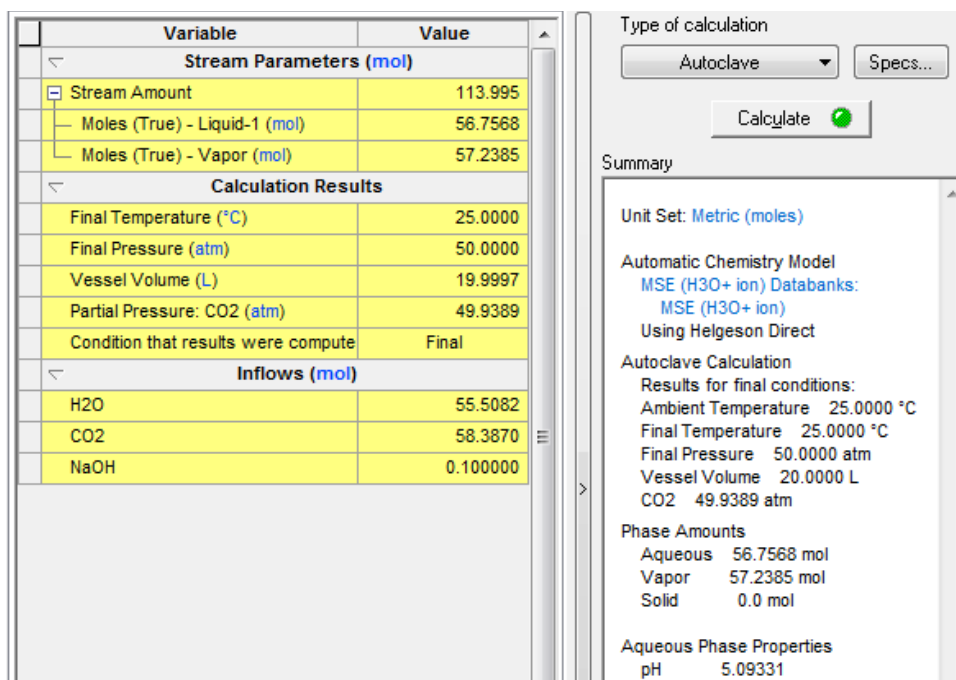
Figure 11-19 Results at higher pressure and volume

✓ 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

Figure 11-20 Species report at higher pressure and volume

The vapor amount is 57.2 moles, compared to ~39 for ideal gas and with N_2. The primary difference is the CO_2 fugacity.

Table 11-5 Comparing noble gas v. reactive gas

T	P	Vo	Ideal Gas	Calculated	Calculated	Calculated	Calculated
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

Figure 11-21 results at higher pressure

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 Flow table

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Solid
	mol	mol	mol
Mole (True)	466.719	466.669	0.0499978
Mole (App)	466.720	466.670	0.0499978
	g	g	g
Mass	19121.2	19106.9	14.3065
	L	L	cm3
Volume	20.0002	19.9904	9.79956

Figure 11-22 Phase flows

View **Thermodynamic Parameters** in the report

Thermodynamic Properties

	Unit	Total	Liquid-1	Solid
Density	g/ml	0.956048	0.955801	1.45991
Enthalpy	cal	-4.35332e7	-4.34845e7	-48729.4

Figure 11-23 Thermo properties

According to the calculation, the stream is two-phase with no vapor and the liquid density is 0.96. The software either computed the wrong results, or the system is truly no-vapor 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.
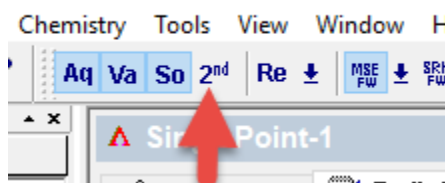
Figure 11-24 Click to enable the "organic" phase

Click **Calculate**

Figure 11-25 Results with 2nd-liquid is enabled

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	Liquid-1	Liquid-2
	mol	mol	mol
Mole (True)	454.848	55.5736	399.274
Mole (App)	454.848	55.5736	399.274
	g	g	g
Mass	18574.5	1040.89	17533.6
	L	L	L
Volume	20.0003	1.01720	18.9831

Figure 11-26 Report when 2nd liquid phase is enabled

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

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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 types

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Arrhenius type reaction kinetics

Arrhenius type reactions use a traditional form of a reaction rate constant. For the theoretical reaction of:

$$aA + bB \xrightarrow{k_f} cC + dD$$
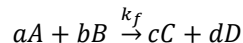
Where:

$$k_f = A_f e^{\frac{-E_a}{RT}}$$

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:

$$2NH_{3(aq)} + CO_{2(aq)} \rightarrow NH_2CONH_{2(aq)} + H_2O$$
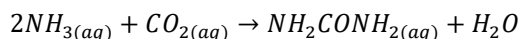
There is a forward and reverse reaction (a k_f and k_r) which we will have to define. We start by using OLI Studio and then entering the following components:

Table 12-1 Urea reaction kinetics inflow species

Standard Reaction Kinetics		
Thermodynamic Framework	Aqueous (H+ Ion)	
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.
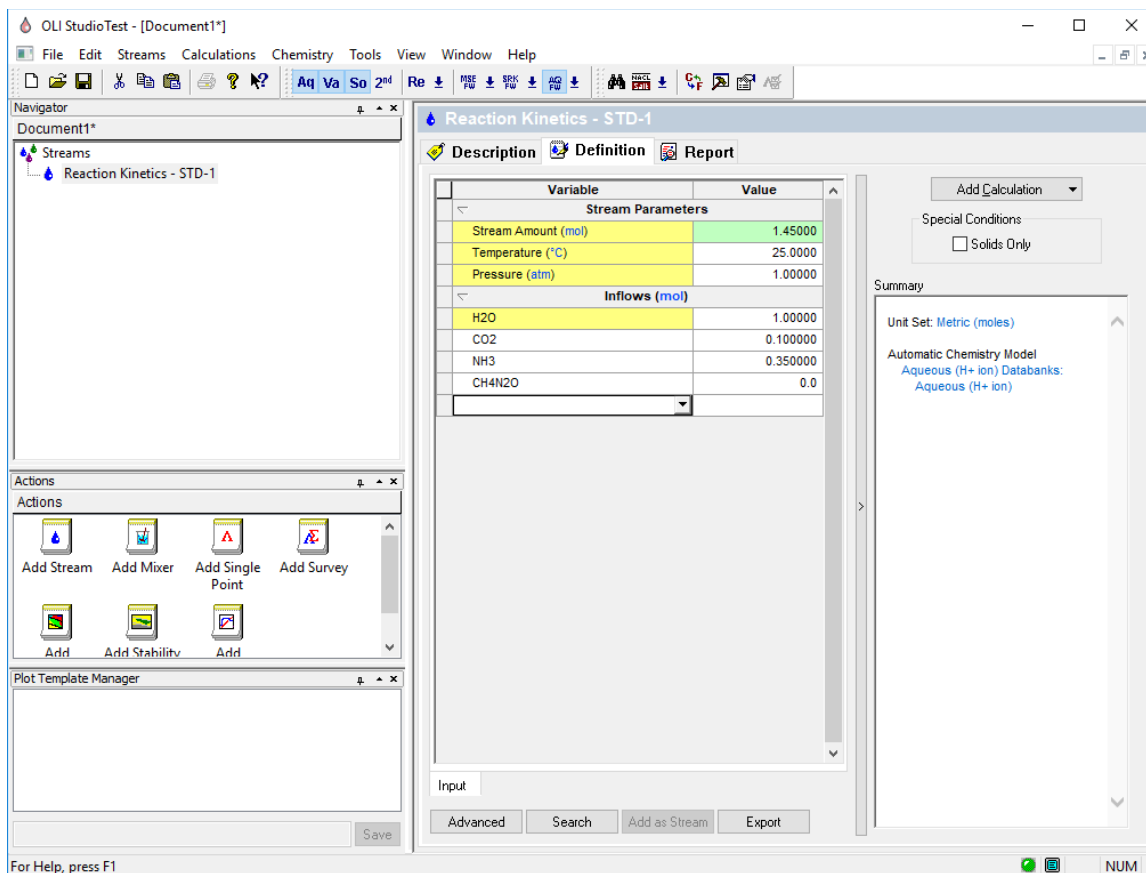
Figure 12-1 Input conditions

We now need to enable reaction kinetics. **Click** the **Chemistry** menu item, then **Model Options** and finally select the **Phases** tab.
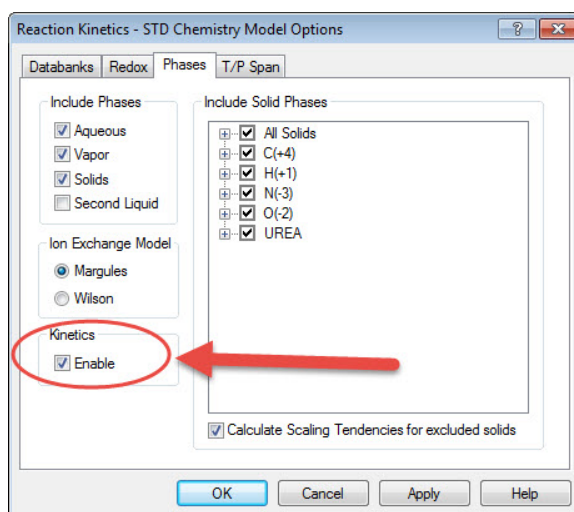
Figure 12-2 Check the indicated box

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 add the reaction kinetics via the **Specs…** button.
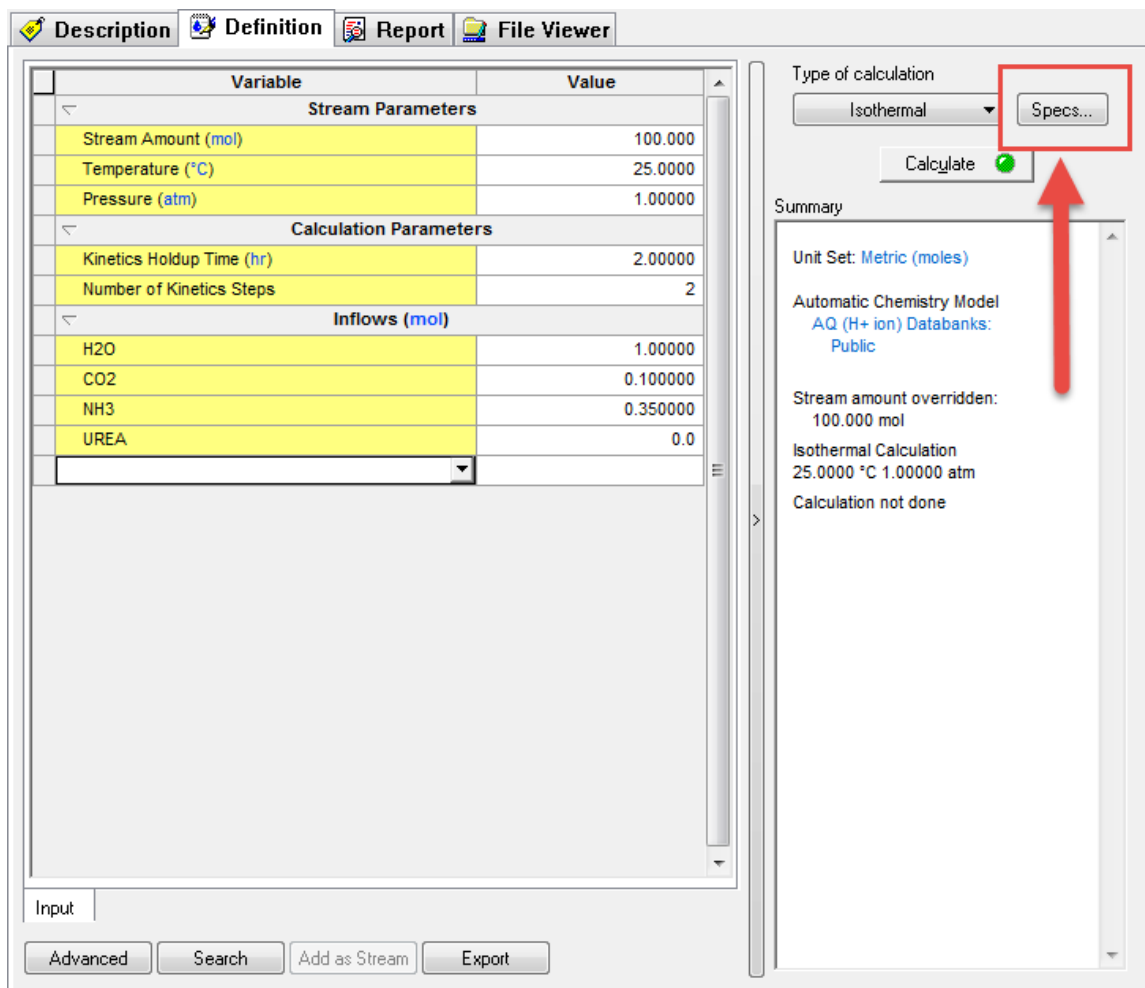
Figure 12-3 Click the specs... button

Click the **Specs…** button.

This will display options for this calculation.
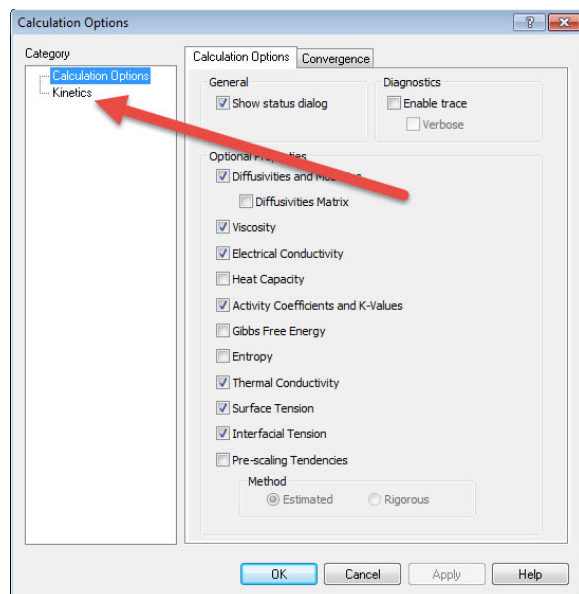
Figure 12-4 Calculation options

Click the category that says *Kinetics*.
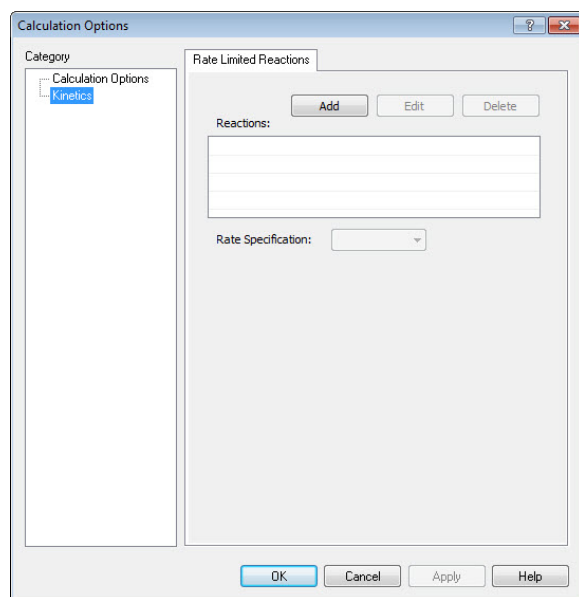
Figure 12-5 Kinetics Dialog

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:
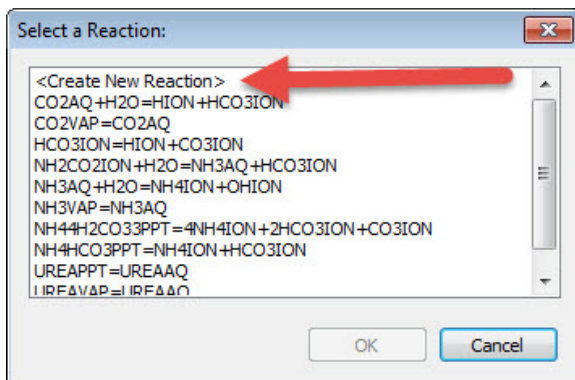
Figure 12-6 List of reactions

We will create a new reaction. Click the **<Create New Reaction>** line and then click **OK**.
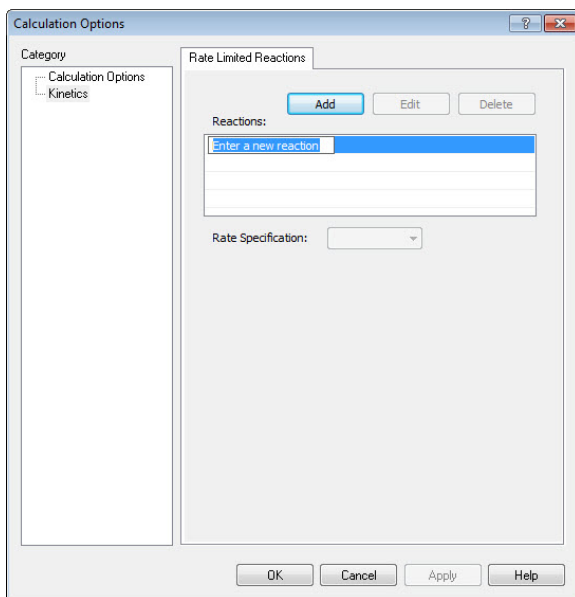
Figure 12-7 Adding a new reaction

You can now enter your reaction. You must use the OLI Tag Name for this step. Enter the following reaction:

2NH3AQ+CO2AQ=UREAAQ+H2O
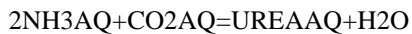
When you press the enter key the dialog will update:
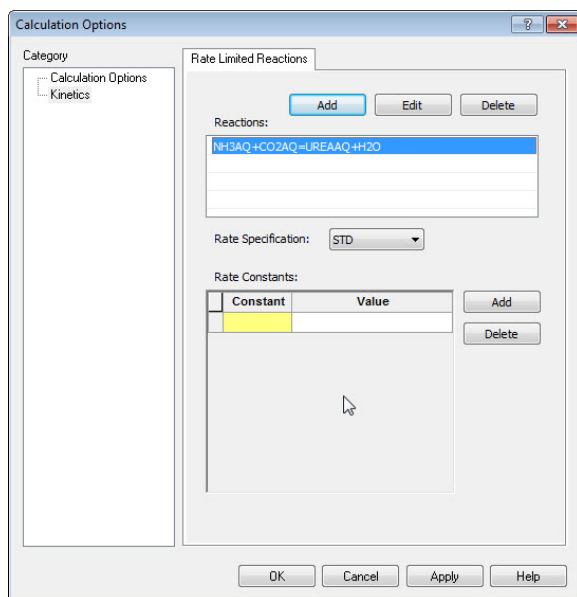
Figure 12-8 Added ammonia reaction

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:

$$Rate = k_f[NH_3]^2[CO_2] - k_r[NH_2CONH_2]$$

---

[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.

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]:

Table 12-2 Reaction Rate Parameters

Parameters	Value	Comment
k_f	20	forward rate constant
k_r	calculated	See above
A_r	1.2x10^{-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$_2$CONH$_2$]
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 252 above.

Now that we have the parameters we can add them. Click the **Add** button in Figure 12-8
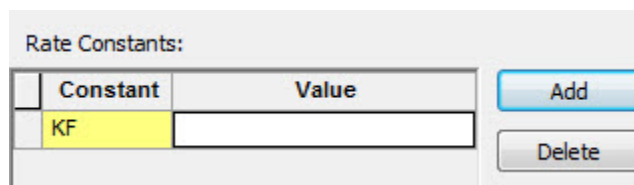
Figure 12-9 Select a parameter

---

[42] It is unknown from whence these parameters were obtained. Do not use them for any real design work.

Select **KF**
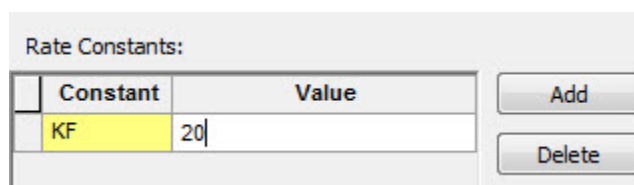
Figure 12-10 Selecting kf

Enter the value from the Table 12-2 Reaction Rate Parameters above:

Figure 12-11 Entered kf

Repeat these steps for the remaining parameters (not k_r, it does not need to be entered)

Click **OK** when done.

You will see that the input grid has changed to accommodate time parameters:
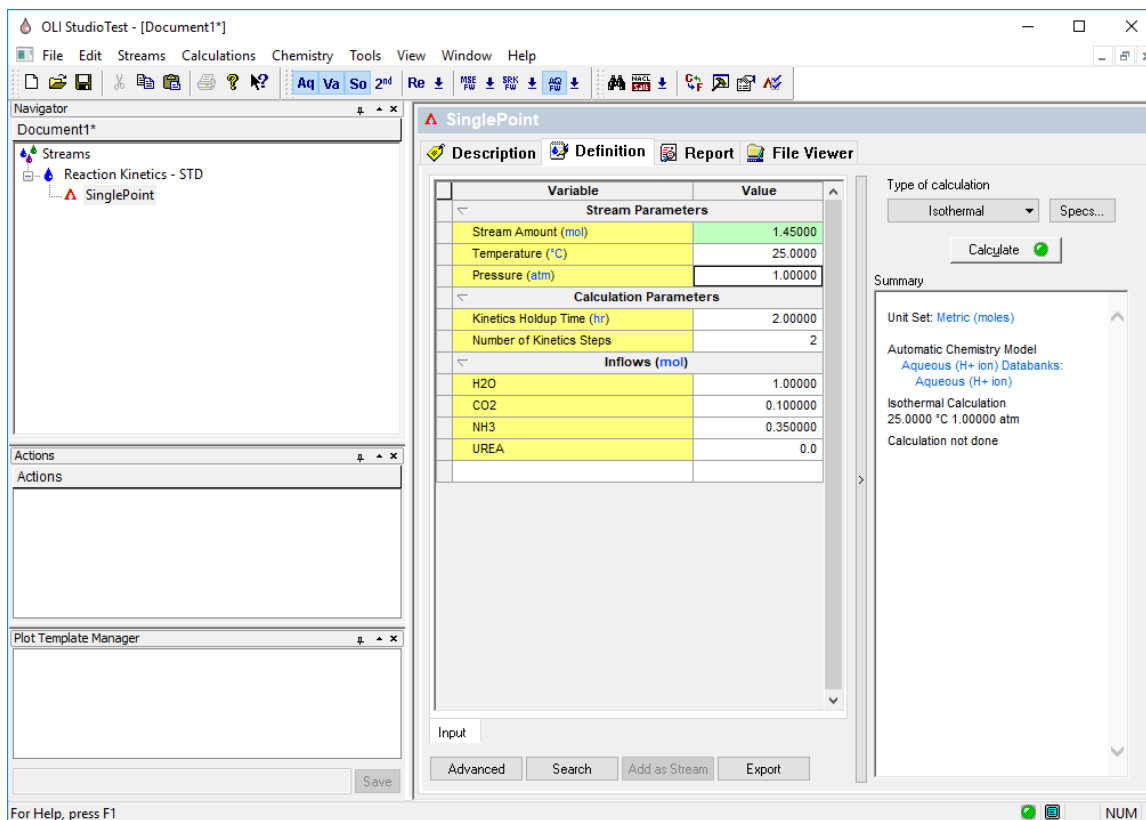
Figure 12-12 Updated time parameters

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 ºC.

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*.

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 at: Chapter 11 – Standard Reaction Kinetics

---

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:

$$NH_{3(aq)} + H_2O \rightleftharpoons NH_4^+ + OH^-$$
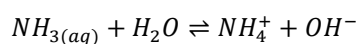
For this example, we know the forward rate constant but need to constrain the reverse reaction to the thermodynamic equilibrium constant. This implies that we are going to replace an existing equation.

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 ºC		
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:
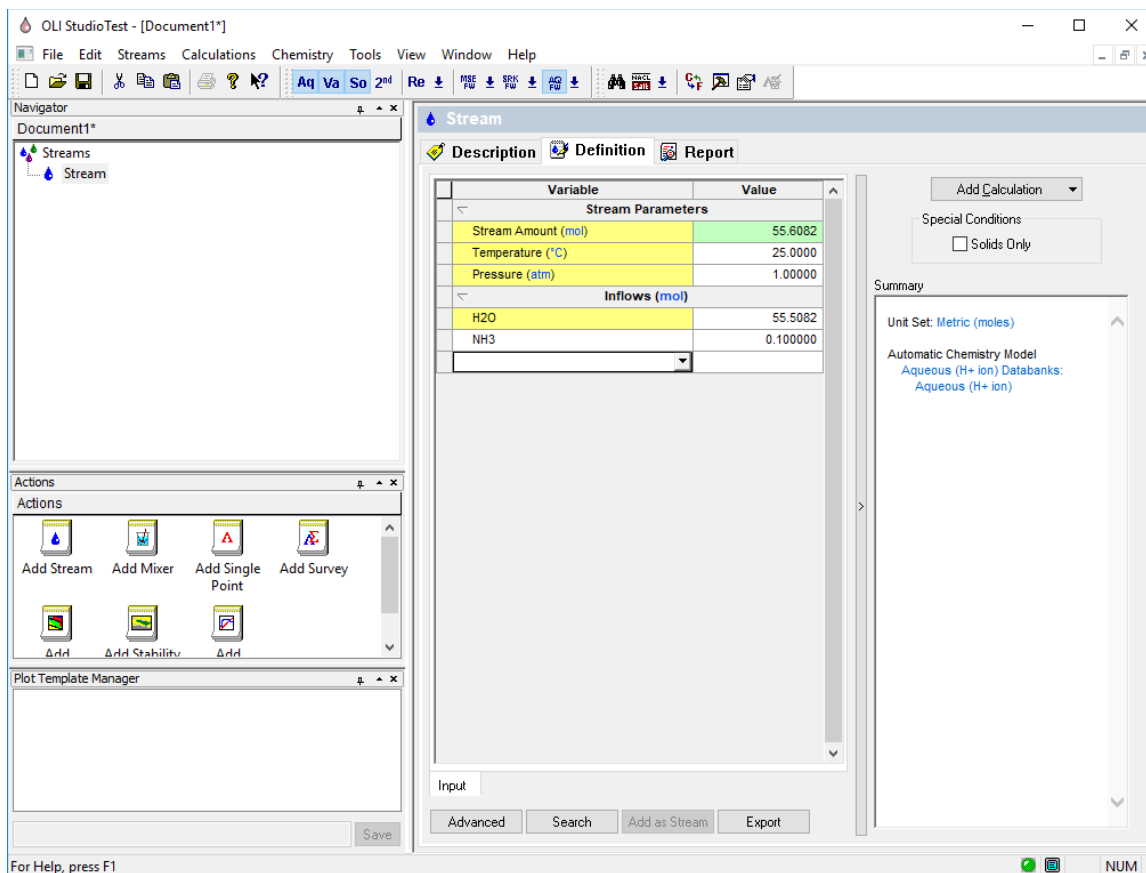
Figure 12-15 Non-standard kinetics stream

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 248.

Now we need to add a calculation, for the example we are adding a single point isothermal calculation.

As before we start with the **Specs…** button and then the **Kinetics** category.
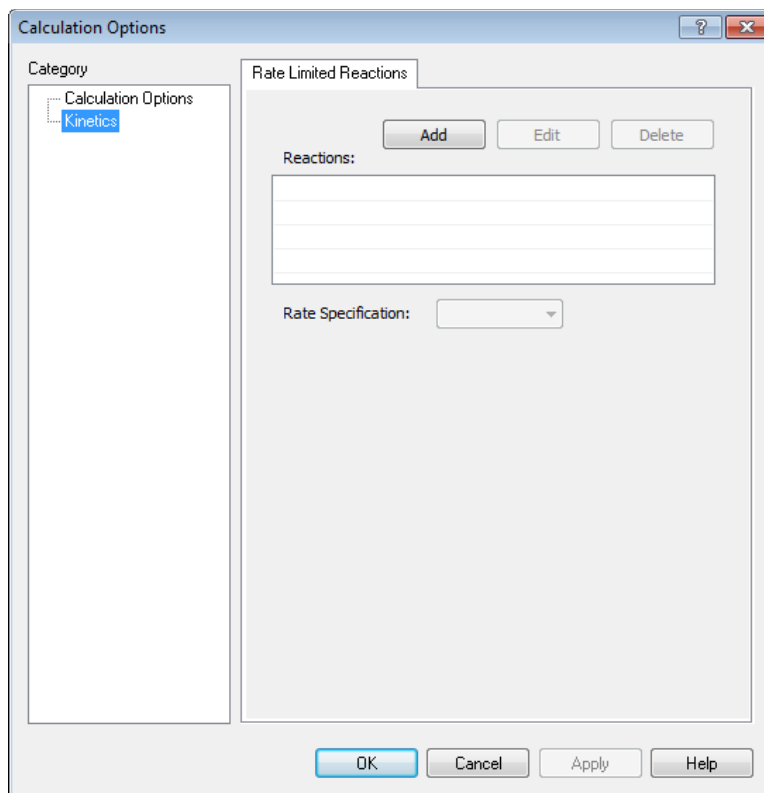
Figure 12-16 Adding a new reaction kinetics equation

Click the **Add** button

Once again we will see a list of equation in the OLI Tag Name format;
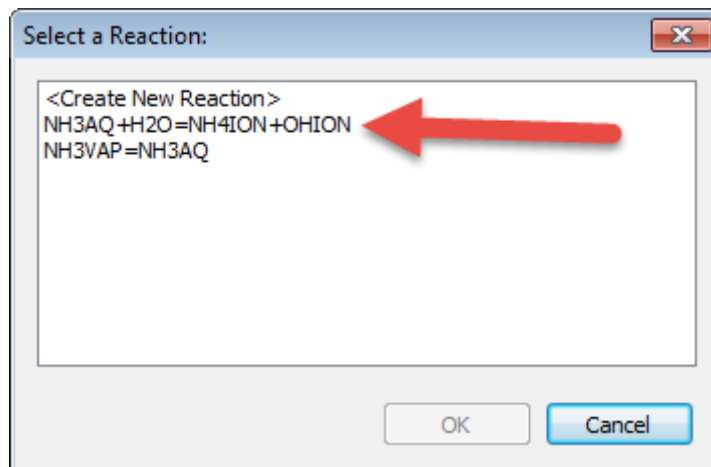
Figure 12-17 Possible reactions

In this case our desired reaction is the first reaction. Click it and then click the **OK** button.
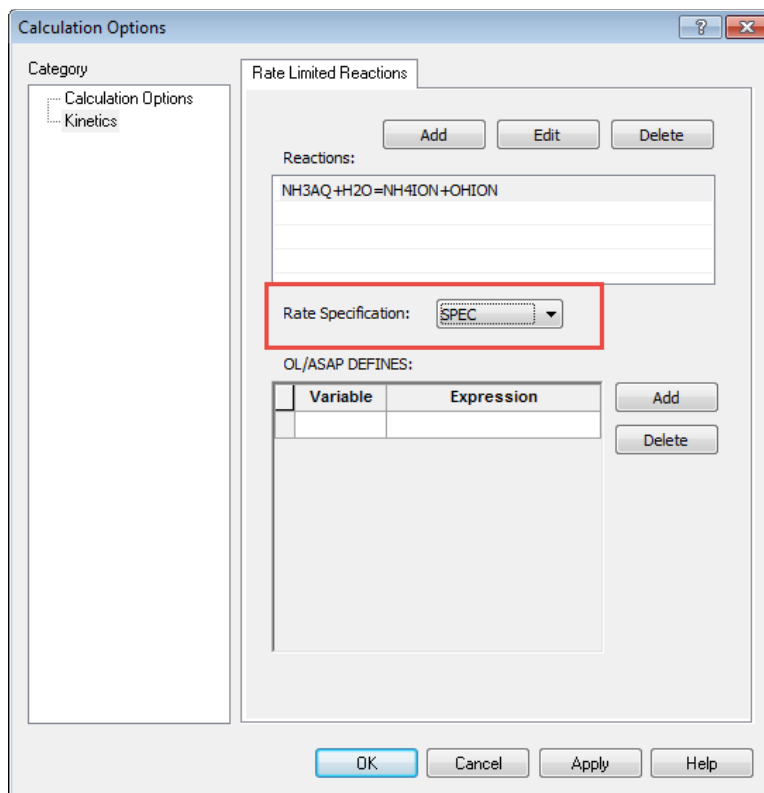
Figure 12-18 Clicking the SPEC type reaction.

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$_e$ γ_{OH^-} = AOHION.

KEQ is the thermodynamic equilibrium constant for the equation. AH2O is special in the Aqueous thermodynamic framework in that it is the variable Log$_e$(a$_{H2O}$).

We now need to add these variable to the kinetics window[44]:

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.
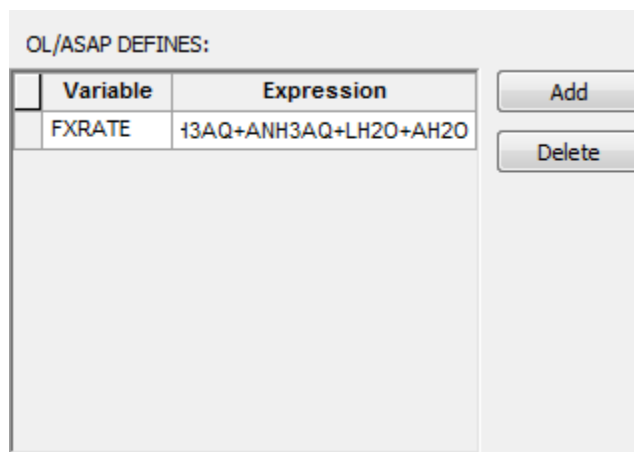
Figure 12-19 Adding variables

---

[43] Commonly referred to as ASAP variables.

[44] Copy and paste from this document can make this step easier

---

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

Complete the remainder of the variables.
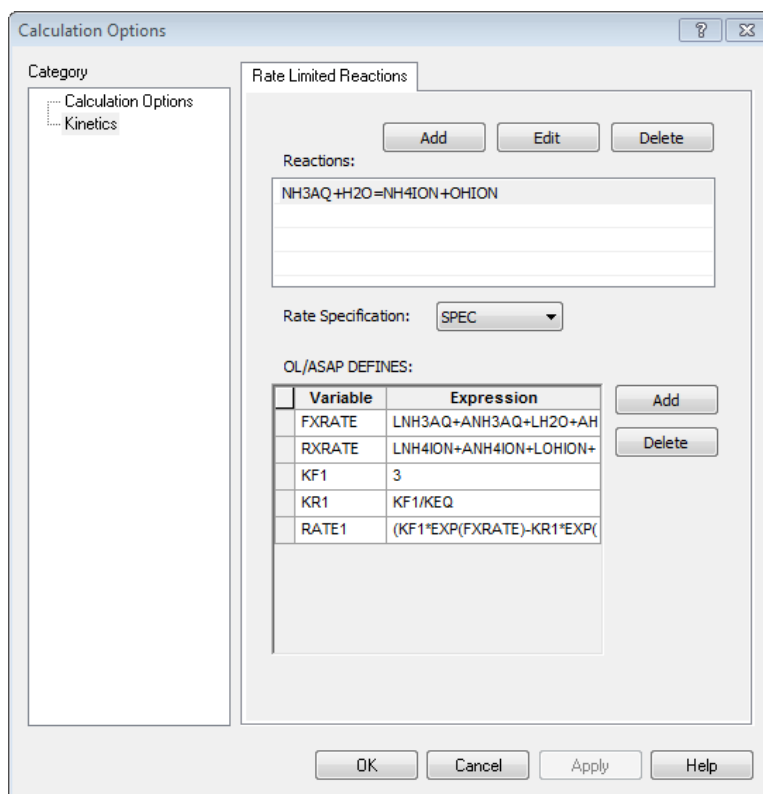
Figure 12-20 The completed equations

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.

Now **Calculate**
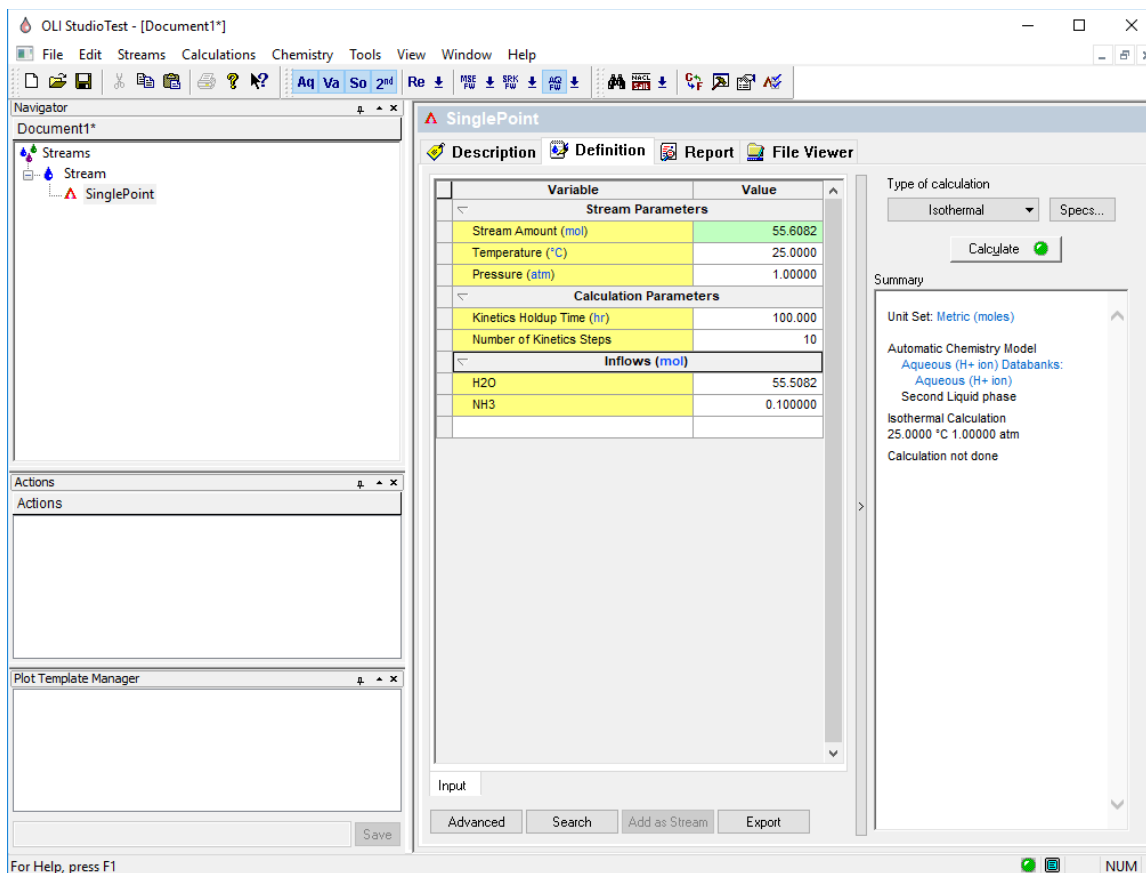
Figure 12-21 Setting up the calculation

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 aqueous):
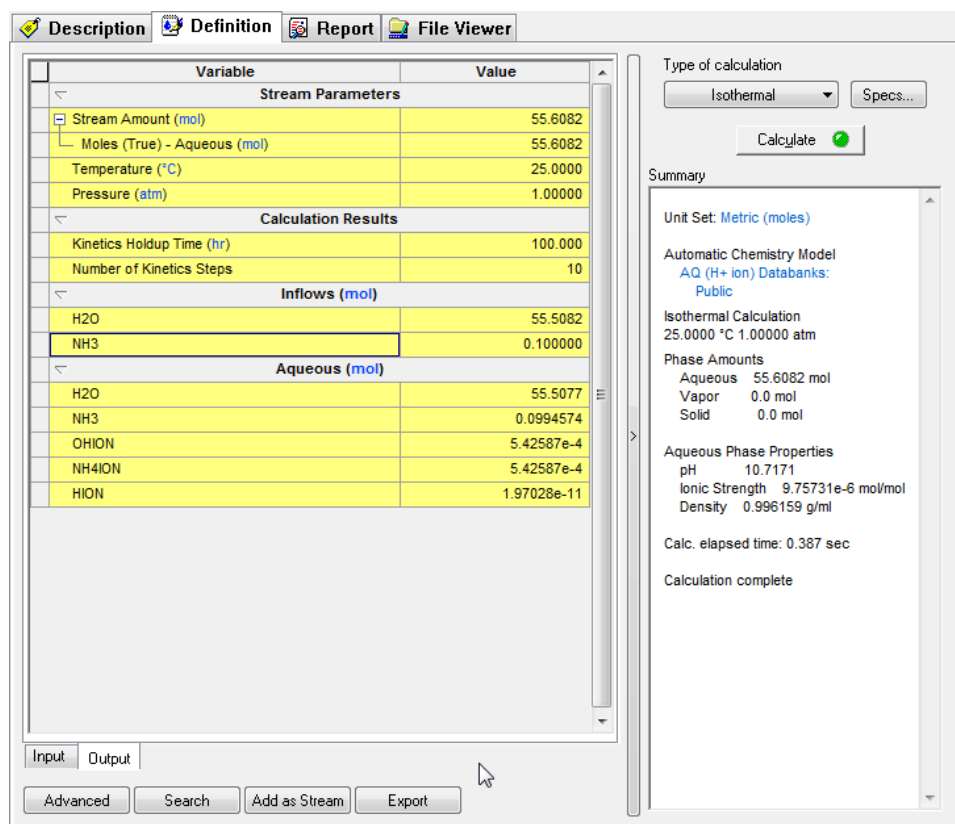
Figure 12-22 The results

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:

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 reactions, we allow the back reaction to take place and that only formed 5.4x10^{-4} moles of NH_4^+

You can find a completed and worked example here: Chapter 11 – Non-standard Reaction Kinetics

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 278 for a description of the distillation methods). The data for the distillation curve can be found in Table 13-1 on page 267.

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

Table 13-2 Crude Assay Stream Data (Assay information not yet complete)

Stream: Crudes			
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	5.0 mol
Assay	-	ASSAY	1000

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
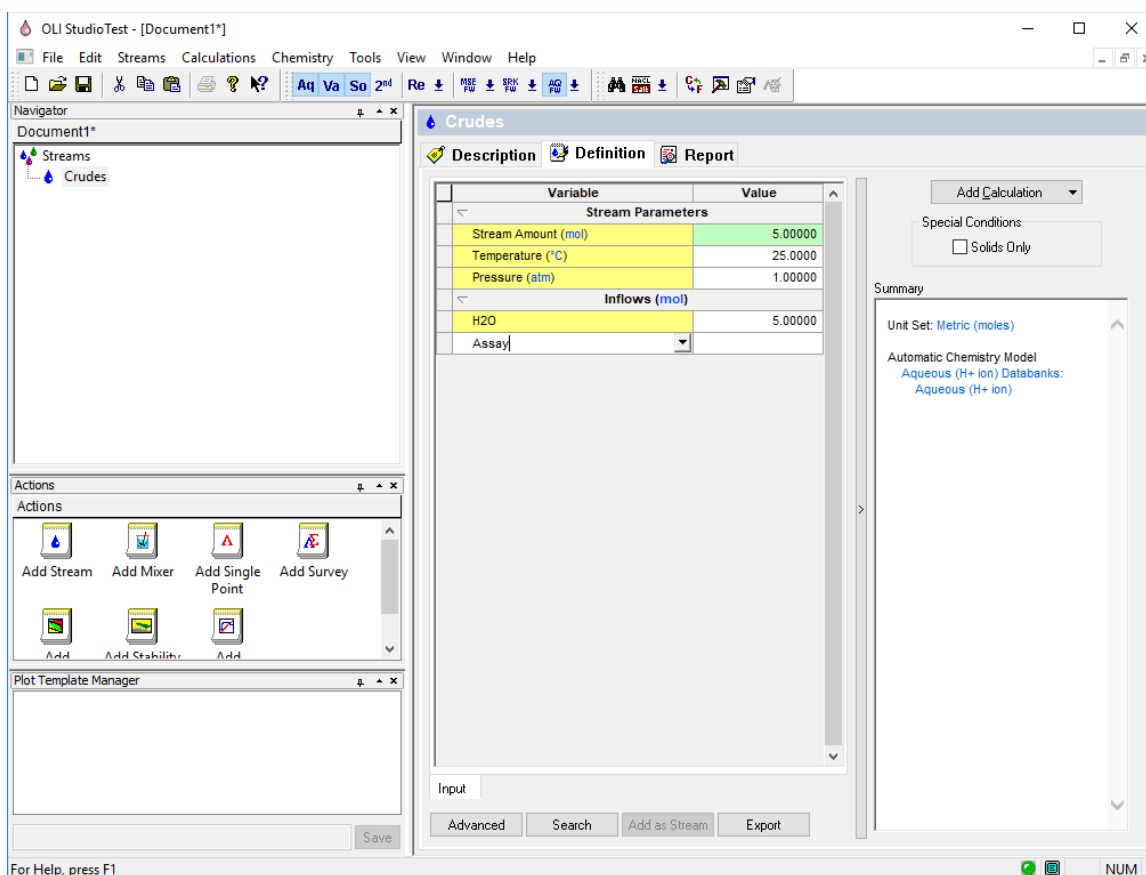
Figure 13-1 Entering a petroleum sample, Don't press ENTER yet!

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 keys together. You should be able to view the screen as shown in Figure 13-2 on page 269.

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.

Figure 13-3Assay Data Types

There are four types, select **ASTM D86** (See Hydrocarbon Petroleum Fractions on page 281 below)

Next click in the cell next to the **Average Bulk Density Type**

Figure 13-4 Average Bulk Density options

Select API Gravity

Finally, we need to select the thermodynamic method. Click in the cell next to **Thermo Method**
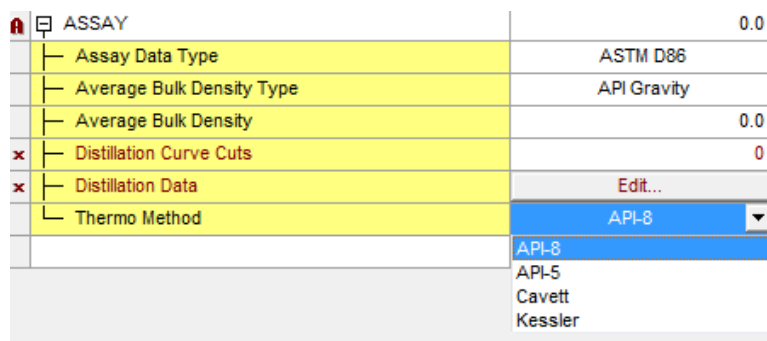
Figure 13-5 Thermodynamic methods

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
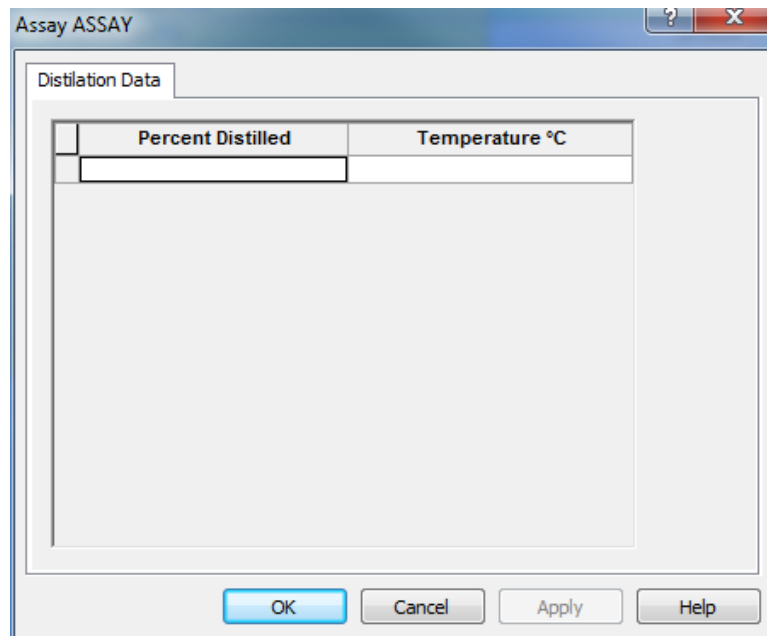
Figure 13-6 Blank Distillation Data, cut and paste works here!

Enter the data from Table 13-1on page 267[45]
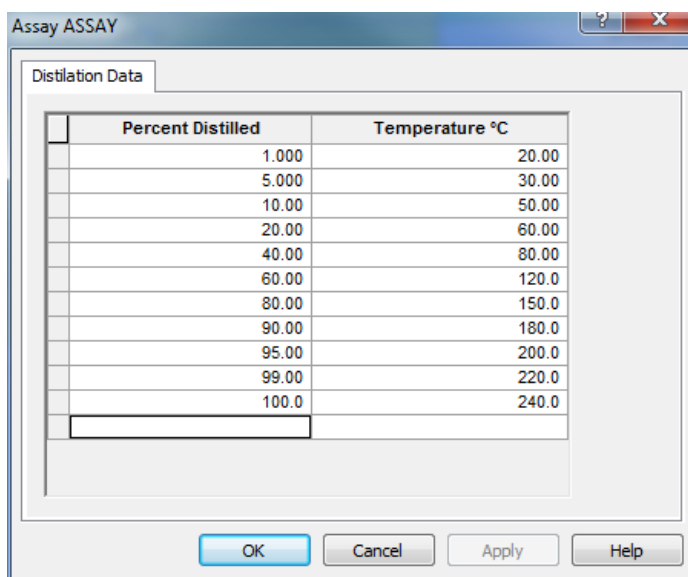
Figure 13-7 Completed Data

When done click the <u>OK</u> button.

We can now finish the entering of the data.

Table 13-3 Completed Stream Date including assay data

Stream: Crudes			
Thermodynamic Framework	Aqueous (H+ ion)		
Additional databanks	None		
Temperature	25 °C		
Pressure	1.0 atm		
Stream Value	automatic		
Assay Data Type	ASTM D86		
Density (API Gravity)	31		
Distillation Curve Cuts	5		
Thermo Method	API-8		
Inflows	Formula	OLI Tag Name	Value
Water	H_2O	H2O	5.0 mol
Assay	-	ASSAY	1000

[45] Copy and paste works here too

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.

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 after typing the name of the pseudocomponent.
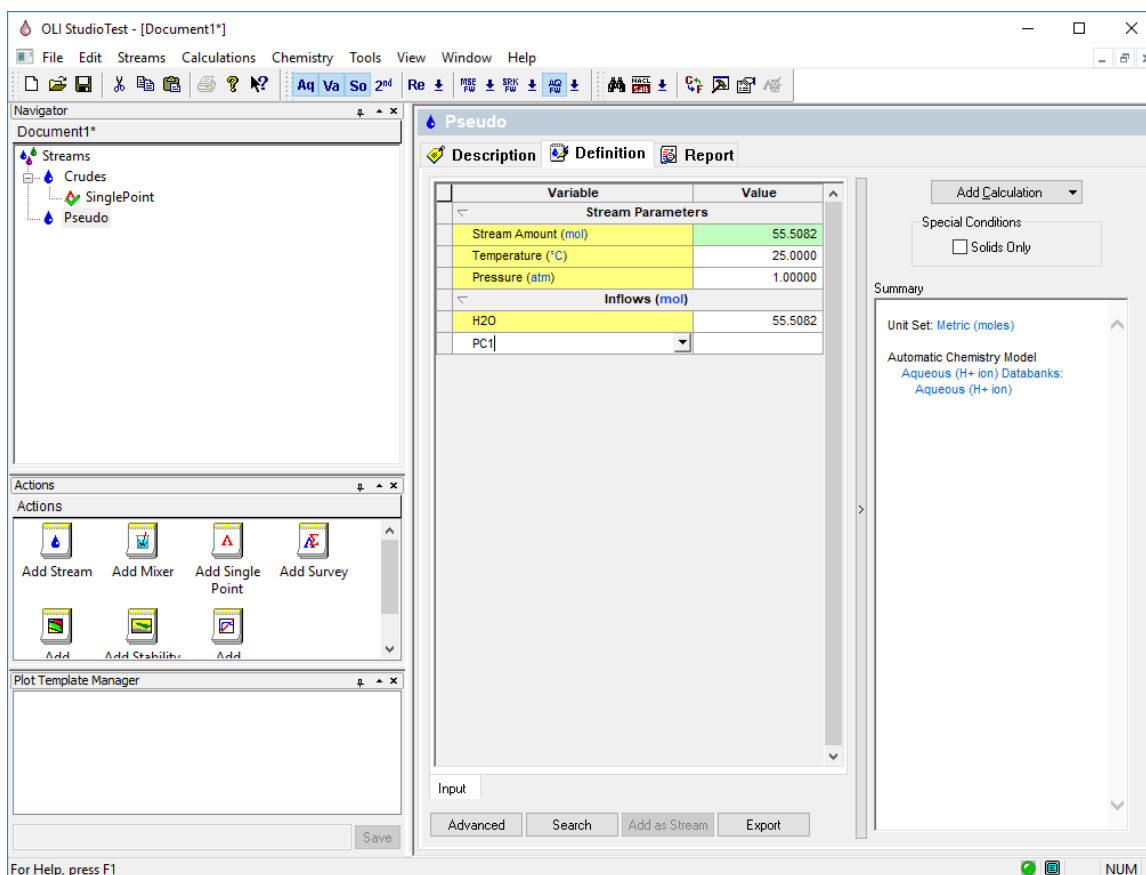
Figure 13-10 Starting to enter a pseudocomponent

This will create an empty data grid for the pseudocomponent. As with the assays, we need to enter some data for the pseudocomponent.

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 20°C 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.

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 13-4 below.

Table 13-4 Sample pseudocomponent data

Pseudocomponent	Amount (moles)	Method	Normal Boiling Point, ºC	Specific Gravity
PC1	100	API-8	20	0.72
PC2	200	API-8	60	0.76
PC3	250	API-8	100	0.8
PC4	250	API-8	140	0.85
PC5	180	API-8	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.

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 15°C and 1.0 atmospheres and press the calculate button.

Figure 13-15 PC Output

You can download a worked copy of this example from here:

14. ScaleChem Overview

Why Use ScaleChem?

Scaling 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, SiO_2, $B(OH)_3$, 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, NH4+, Fe+3, Al+3,
>**Anions:** OH-, F-, Br-, H2SiO4-, H3SiO4-, SO3-2, S-2, CO3-2, NO3-, NO2-, COOH-, C3H7COO- C4H9COO-
>> C5H11COO-
>
>**Organic acids:** formic, acetic, propanoic, butanoic, pentanoic
>**Alcohols:** methanol, ethanol, ethylene glycol,
>**Mineral Acids:** HF, HCl, H2SO4, HBr, HNO3
>**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 CO_2 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 CO_2 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 CO_2 gas fraction calculation by taking the PCO_2 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 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:

$$CaSO_4 \bullet 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$$
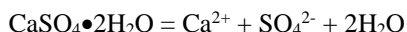
The activity product, Q, is defined as:

$$Q = a_{ca++} \, a_{so4-2} \, a^2_{H2O}$$

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:

$$
\begin{array}{lll}
[Ca^{+2}] & = & 0.008 \text{ molal} \\
[SO_4^{-2}] & = & 0.008 \text{ molal} \\
\gamma_{Ca} & = & 0.5 \\
\gamma_{SO4} & = & 0.5 \\
a_{H2O} & = & 0.99977 \\
K_{sp} & = & 2.68 \times 10^{-5}
\end{array}
$$

The Q value is:

$$Q = (0.5)(0.008)(0.5)(0.008)(0.99977)^2$$

The Scaling Tendency is Q/Ksp

$$ST = 0.000016/(2.68E\text{-}05) = 0.596$$

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:

$$\text{Scale Index (SI)} = \text{Log}_{10}(\text{ST}).$$

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 – A Tour

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.

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.
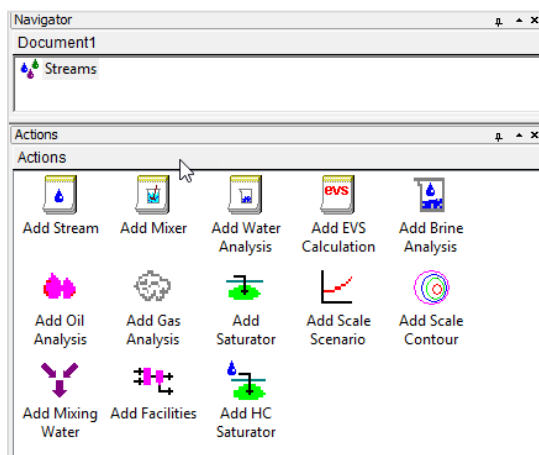
Figure 16-1 ScaleChem objects.

Task 1 – Create a Brine Analysis

In this tour we will show the main interface of a Brine Analysis, followed by an example of a brine (water analysis) and calculate its scale tendency. Let's begin. Steps for the simulation will be given with bullet points.

- Add Brine Analysis from Actions Panel.

Click on the description Tab. If the *__Description__* tab is not currently displayed, click on the tab.
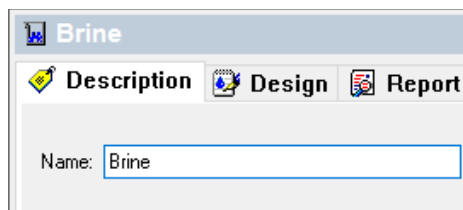
Figure 16-2 Brine description tab

The chemistry of the brine needs to be entered. This information includes concentrations, alkalinity, pH and density.

The table below describes the hypothetical water that we will create:

Table 16-1. Brine Analysis

Cations mg/L		Anions mg/L		Measured Properties	
Na+1	36000	Cl-	57000	Temperature	25 C
K+1	300	SO4-2	250	Pressure	1 atm
Ca2+	600	H3CO3-1	600	pH	7.67
Mg2+	150			Alkalinity	600
Sr+2	80			Density (mg/L)	1.064
Ba+2	5			Total Dissolved Solids (mg/L)	96280

- Go to the Design Tab.

Data Entry Tab

- Enter the information given in Table 16-1 in the Data Entry Tab, as is shown in the figure below:

Figure 16-2 Brine Analysis

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 like 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 effect on pH and alkalinity.

Entry Options

Different entry options are displayed in the Data Entry Tab.

Figure 16-3 Entry Options

You can use the Display drop-down menu to switch to *Display name, Formula, OLI Tag.*

Figure 16-4

- Select **Formula**

You can display an easier-to-read table by showing only the species that have actual concentrations.

- Select the Show **non-zero only** box

Figure 16-5 Show non-zero only box

Another thing to consider is which **Balance Option** to select.

It is highly unusual for the data to be electrically neutral. Therefore, samples are reconciled for Electroneutrality. After entering each species concentrations, you will notice that Balanced values show up in the column next to values. The Column header says **Balanced.**

Figure 16-6 Electroneutrality balance column

When adding or removing ions to balance charge, the solute mass is altered. We must decide as to whether we keep the mass of the solution constant (thereby adjusting the amount of water) or keeping the amount of water constant and adjusting the solution mass.

The user can select from a variety of balancing options:

Dominant Ions   The dominant ion of the deficient charge is added.

Proration Anion   The complete set of anions is prorated (all concentrations are multiplied by the same ratio.

Proration Cation   The complete set of cations is prorated

Make Up Ion   The selected ion is either added or removed to balance the solution.
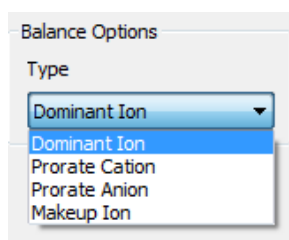
Figure 16-7

- Select **Dominant Ion** balance option type.

You can review the Dominant Ion Charge and Ions needed to balance in the tables presented in the Summary Box.
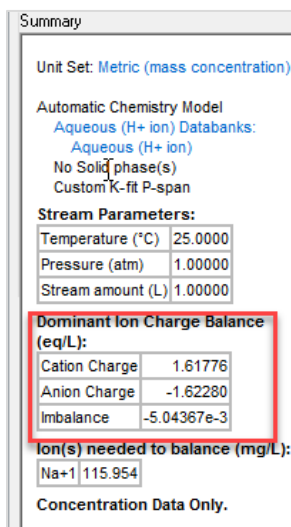
Figure 16-8

The summary box shows additional detail about the brine's chemistry and balance option. The stream parameters table shows default values. The Dominant Ion Charge Balance shows the total cations or anions, and the total imbalance.

Now is time to enter the measured property data in the ***Reconcile Tab.***

Reconcile Tab

In this Tab, we will tell the software how to reconcile the brine. Based on the Reconciliation Options and the brine's composition, the software will calculate the pH, osmotic pressure, speciation, activity coefficient, and the amount and type of formed solids.

Types of 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. This is default calculation.

Gas-Phase CO$_2$ Content

> The CO$_2$ 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.

Measured pH Only

> The pH of the solution can be specified by adjusting the titrant/s.

Properties

The following variables in the properties column are also 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.

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 (HCO_3^-). ScaleChem can reconcile on a measured alkalinity by adjusting the solution composition.

Alkalinity End Point pH

This is the end point for the experiment used by the lab to determine the Alkalinity. The default value is 4.5.

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.

Electrical Conductivity

This is the solution electrical conductivity. 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.

Added Titrant HCl

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.

For this example:

- Select *Concentration Data Only* Option
- Check the *Calculate Alkalinity* box
- Enter the measured pH (7.67), density (1.064 g/mL) and TDS (96280 mg/L)
- Leave the *Allow solids to form* unchecked.

We will leave the Allow solids to form unchecked because generally the industry uses acid to preserve water samples, which prevent solids to form. Acidified samples contain the unprecipitated ion concentration, which is what we entered into the brine. In this step, we will eliminate solids because allowing solids to form would change the brine's composition significantly.

See the example set-up in Figure 16-9.

Figure 16-10 Reconcile options

- Select the Calculate Button or press the <F9> key

Figure 16-11 Results

Once the calculation is done, the calculated column displays results based on the concentration that were entered in the Data Entry Tab. The calculated results of note are pH=7.43 and 564.26 mg/L as HCO3 in total alkalinity.

Experimental inaccuracies in sample measurement may, on occasion, result in a calculation that indicates that solid is supersaturated. This can normally be ignored providing that the super saturation is not excessive.

Figure 16-12 Super saturation warning.

More details of the Brine composition can be found in the **Report** Tab.

In the Report tab, scroll down to the Pre and Post Scaling Tendencies, where you will find the results of Scaling Tendencies with Solids off.

Figure 16-13 Scaling tendencies and Brine composition with solids off

If we would have allowed solids to form, these concentrations would not be as close to the initial values.

Note: If scaling tendencies did not show up in the Report Tab, follow these steps:

- Right click on the brine analysis icon

- Select *Calculation Options*
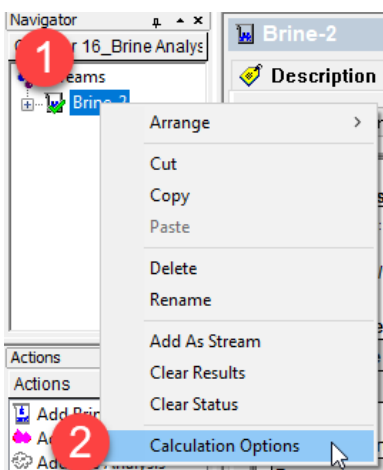
- Enable *Pre-scaling Tendencies*
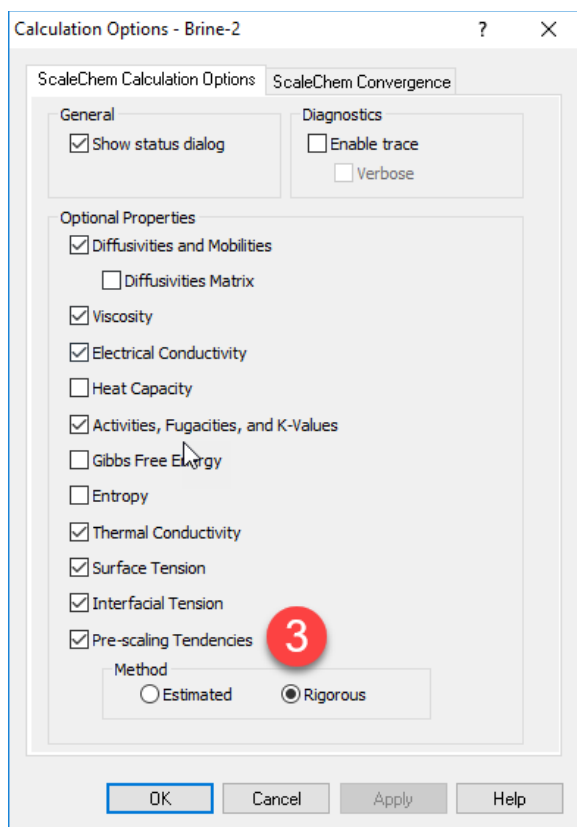
Task 2 – Create a Scaling Scenario

The next task is to calculate the brine scaling tendencies. Once the Brine Analysis data is entered and the sample reconciled, we can begin the **Scaling Scenario** calculation.

- Select **Add Scale Scenario** from Actions panel.
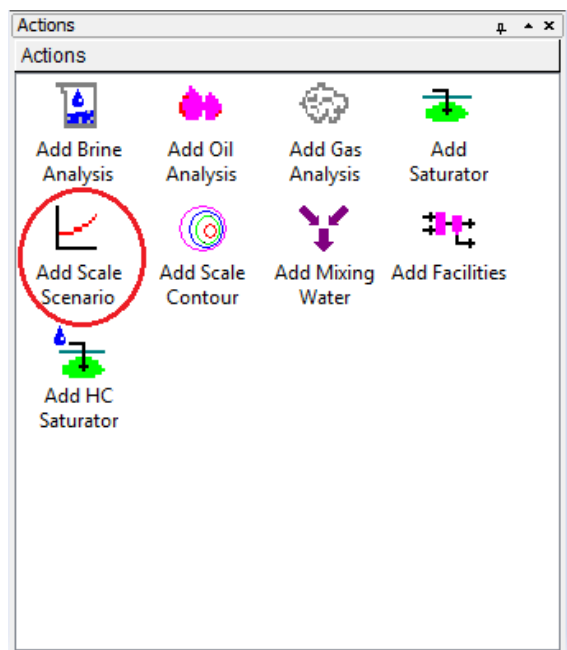
Figure 16-14 Scaling Scenario object

Once we add a **Scale Scenario** object, the software opens to a new **Design** screen containing three vertical tabs: **Inlets, Conditions**, and **Solid**. We will work in each of these sections to set up the scaling calculation.
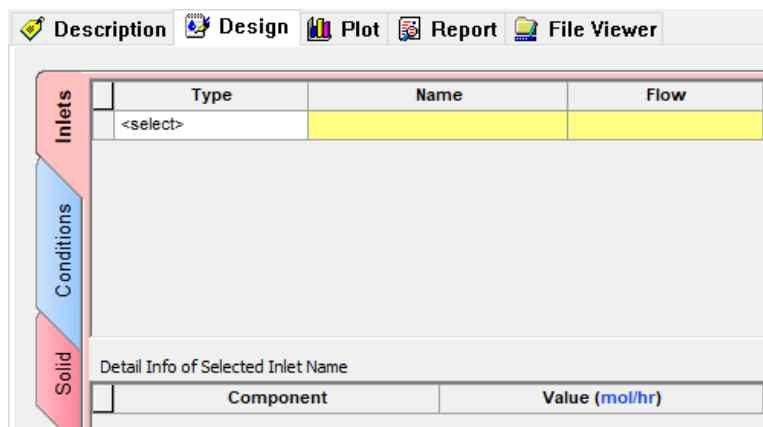
Figure 16-15 Design screen of a newly added Scale Scenario Object

Inlet Tab

Type   You can select the brine, gas or hydrocarbon of interest

Name   Click in the Name field. As you position the cursor in the field, a Down Arrow will appear. You can then select from a list of brines, gases or oils already entered into this ScaleChem document.

Flow   Enter the flow rate for the gas, hydrocarbon or brine.

- Click on the **Description** tab and rename the Scale Scenario as " Brine Scale Scenario".
- Then click the **Design** tab.

Your screen should now look like image **Error! Reference source not found.**
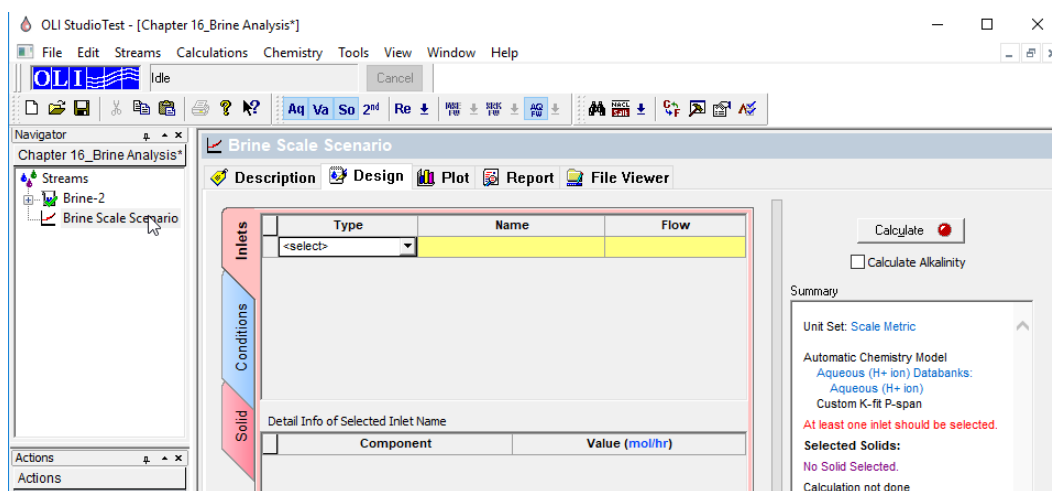
- Select the *Inlets* tab
- Select the right corner of the first cell in the Type column then select Brine (bbl/day)
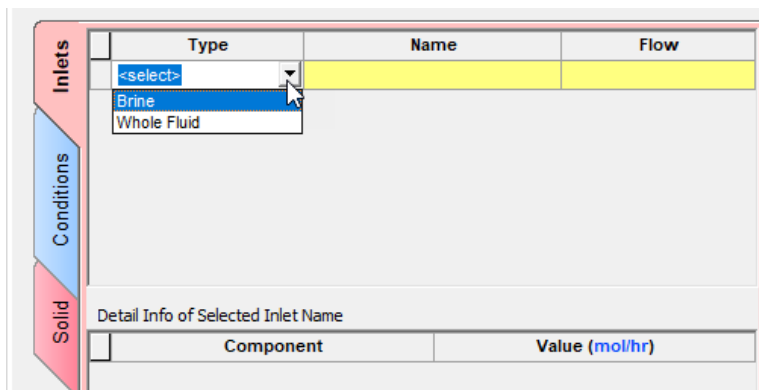
- Select Brine from the drop-down menu in the Name column.
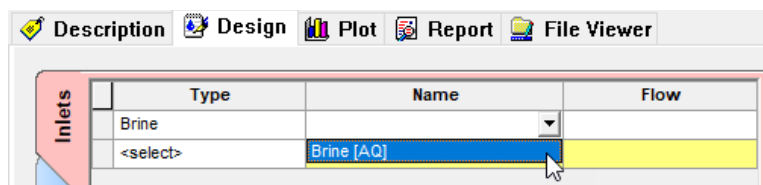
- Enter 1400 (bbl/day) in the Flow Column. Please change units if necessary.

Conditions Tab

- Select the **Conditions** Tab (vertical blue tab on the left-hand side of the Design screen)
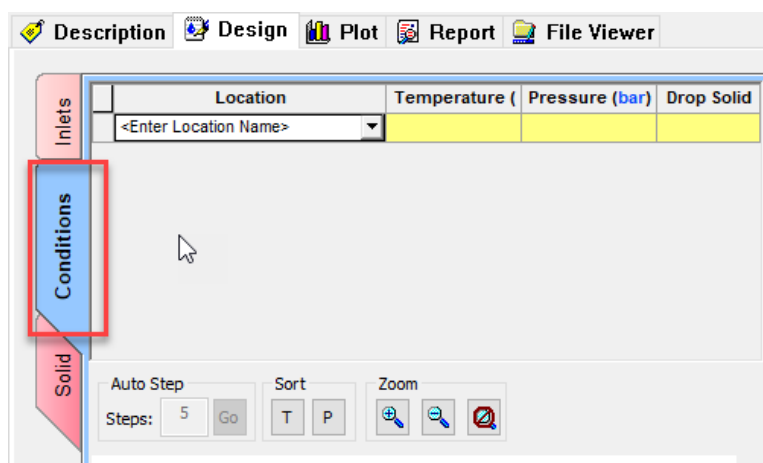
The **Conditions** section is where we enter points along the production scheme. The first column is Location. We can use the dropdown menu in each row to select a location or type in our own location name.

- Type in the following conditions or use the dropdown menu within the Location cells.

Table 16-2. Scale Scenario Locations

Location	Temperature (C)	Pressue (bar)
Reservoir	125	275
Bottomhole	125	280
Downhole	115	190
Midwell	105	130
Wellhead	100	100
Choke	90	80
Separator	60	30

The diagram within the Conditions screen and the list of locations in the Summary box both show the locations in the order that we entered. This screen has options for zooming, auto steps, sorting by temperature or pressure, and dropping solids at particular conditions.

Figure 16-16 List of locations entered

The graphical view clearly shows the five locations and their Temperature and pressure conditions.

The Drop Solids checkbox column at the very end of the grid is designed to help the users decide if they want to carry forward solids from certain locations or not.

Solid Tab

- Select the **Solid** Tab
- Make sure that the solid button in the menu bar is selected.

- Select the Standard checkbox
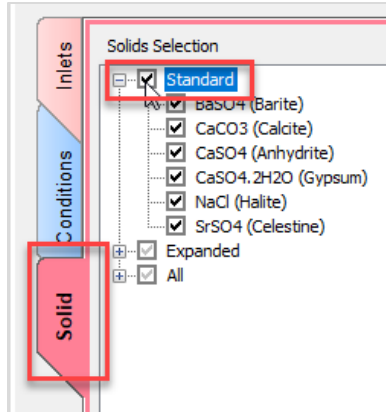
*Figure 16-17 **Solid** Tab Options*

- Press the **Calculate** Button of select the <F9> key
- Select the **Plot Tab**

You can customize which curves are visible by selecting the *Variables* button.
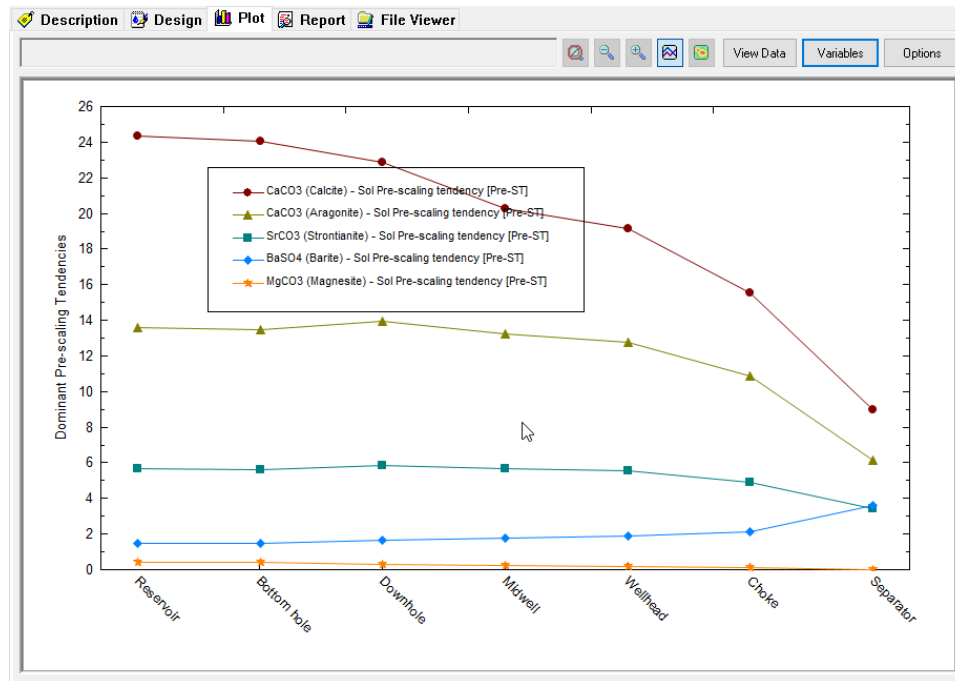
Figure 16-18 Plot Results

- Select the View Data button
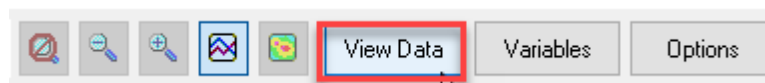
The *View Data* button shows the pre-scaling tendency at each location. We can copy the results of this table to a program like Excel by selecting the top left cell then selecting <Ctrl>+<C> on the keyboard.

Task 3 – Create a Gas Analysis

This Task introduces the Gas Analysis object. It is a very simple object with a limited number of functions. Its purpose is to provide a quick way to enter a pure-component hydrocarbon gas.

- Double click on the ***Add Gas Analysis*** object in the Actions Panel
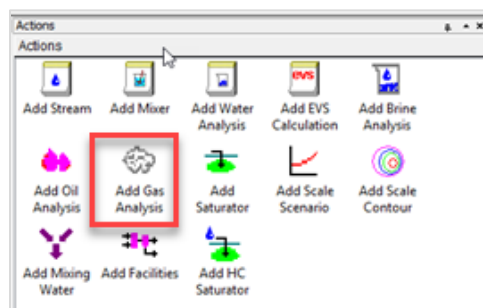
This adds a Gas object to the Navigator panel.

- Select the **Description** tab, then rename the object Gas Analysis.
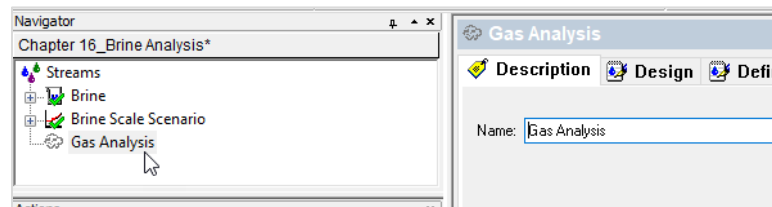
Enter the following composition and values in the Inflows grid:

Table 16-3. Gas Analysis

Formula	Component Name	mole %	Formula	Component Name	mole %
H2O	Water	1.80	C3H8	Propane	8.00
N2	Nitrogen	3.00	i-C4H10	Isobutane	1.00
CO2	Carbon dioxide	1.50	n-C4H10	n-Butane	3.00
H2S	Hydrogen sulfide	0.50	i-C5H12	Isopentane	0.50
CH4	Methane	65.5	n-C5H12	n-Pentane	0.70
C2H6	Ethane	14.0	n-C6H14	n-Hexane	0.50

The *Inflows* grid will look like one of the two below, depending on the Names view you select.
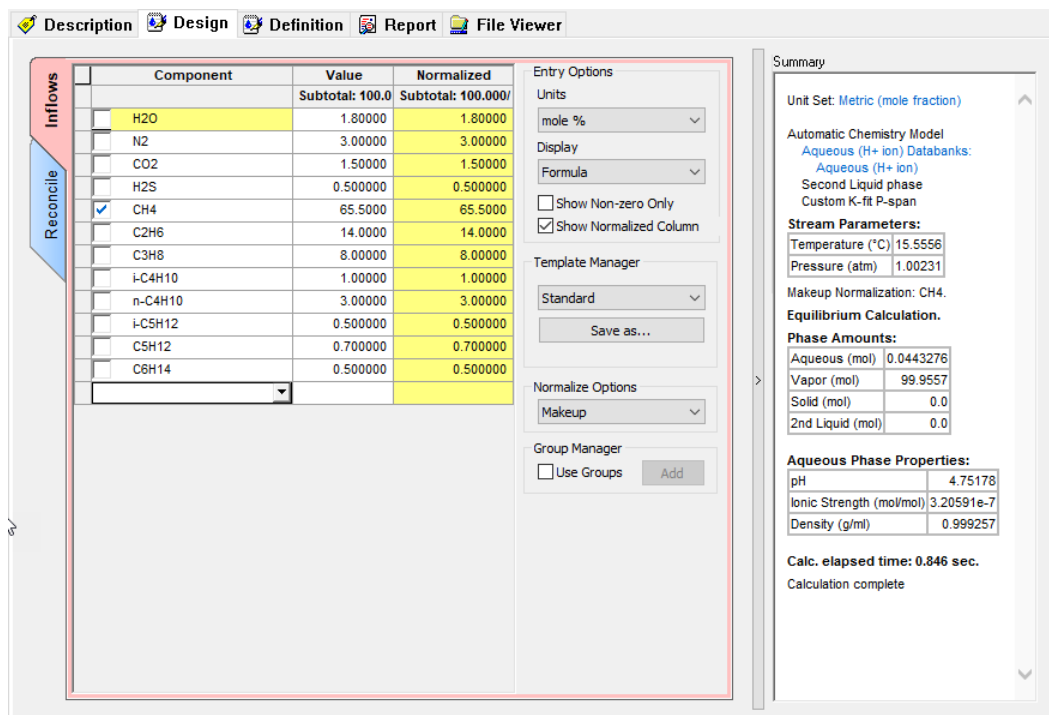
Figure 16-19 Inflows Tab

A brief description of the Inflows tab is given below:

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.

This is the extent of the gas entry step. There are modifications that can be part of the gas analysis entry step (in the Reconcile Tab), but in this case, they are not considered. Now that the gas is entered, the scale scenario considered in Task-2 will be recomputed.

In the *Reconcile* Tab, under Conditions, you can saturate the Gas with Water at determined conditions.

Saturated with 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).

Task 4 – Recalculate Scale Scenario with Gas

The gas analysis will be added to the Scale Scenario so that it is considered during the scale evaluation.

* Select the Brine Scale Scenario icon in the navigator panel
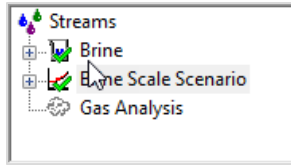
- Select the **Design** Tab (horizontal tab) if not automatically sent there
- Select the *Inlets* tab (vertical) if not automatically sent there
- In the *Type* Column Add *Gas*

- In the *Name* column select *Gas Analysis*

- Enter a flowrate of 250 std E3m3/day in the flow cell

- Calculate (Press <F9>)
- Select **Plot** Tab
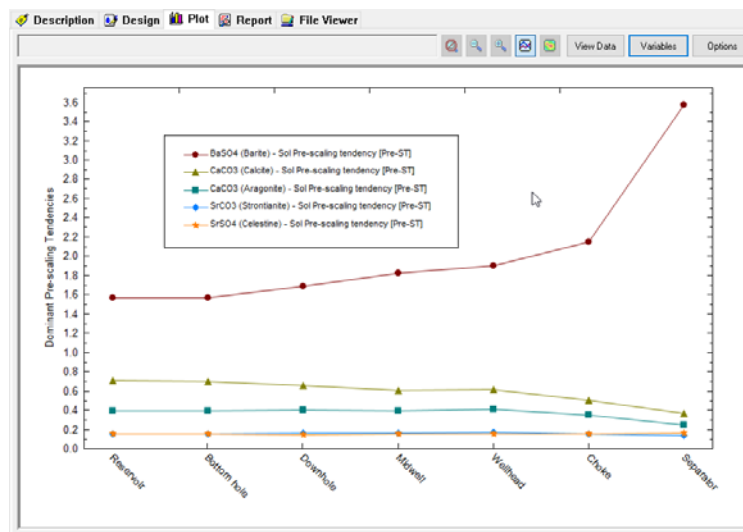
Figure 16-20 Plot Results

- Select Variables button
- Remove all the variables from the Y1 Axis and the Y2 axis by double-clicking on the variables (this removes then from the list). Alternatively, highlight each variable and click on the double-arrow.

You will replace the existing variables with the calcite pre-scaling tendency.

- Expand the Pre-scaling Tendencies button by clicking the + sign
- Double-click on the CaCO3 (Calcite) variable to move it to the Y1 Axis
- Expand the Additional Stream Parameters and add pH to the Y2 axis
- Click **OK**
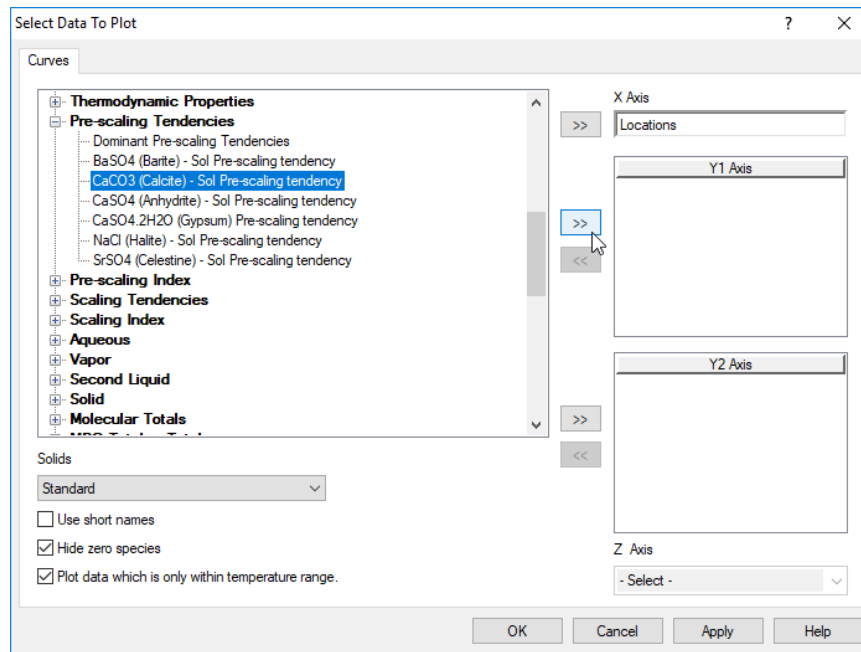
If you are in the *View Data* view, then the table should be similar to the one below.

	Locations	CaCO3 (Calcite) - Sol Pre-scaling tendency	pH
		Pre-ST	
1	Reservoir	0.705312	5.61211
2	Bottom hole	0.694891	5.60661
3	Downhole	0.655192	5.67654
4	Midwell	0.604697	5.74096
5	Wellhead	0.616784	5.79768
6	Choke	0.500689	5.81369
7	Separator	1.24448	6.14419

Calcite is sub-saturated (S<1) at all locations, except the separator.

- Select the *View plot* button

The decreasing calcite saturation trend and the increasing pH is easier to see from the plot view.
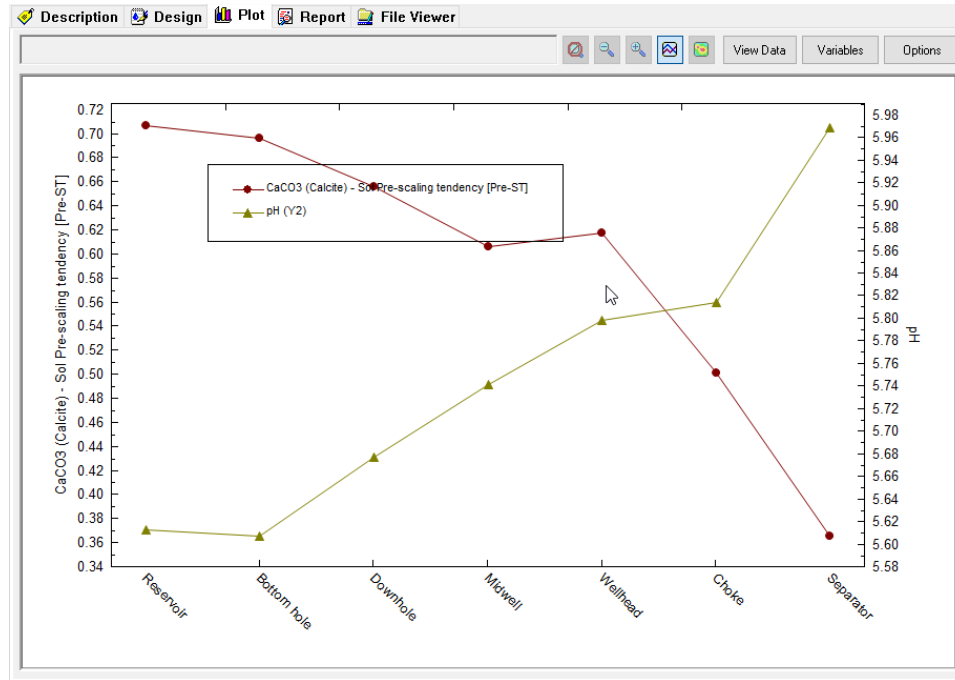
You are done with this Tour! Don't forget to save your file.

Task 5 – Creating a Saturator Object

You will use the *Saturator* object to set the reservoir minerals at equilibrium with the produced fluid. It is reasonable, in some cases, to saturate the produced fluid with common evaporite and secondary minerals like CaCO3, CaSO4.H2O, FeCO3, and NaCl. This is based on the assumption that as the reservoir fluid flows through the rock pores, there is sufficient time to interact with the surface minerals. This is based on a second assumption that the vertical column of liquid and gas are in complete equilibrium and that the saturating minerals are distributed throughout the reservoir matrix, such that complete water-mineral contact is possible.

In this case we are going to simulate a particular oil & gas well: ABC. This well produces from calcite-cemented sandstone. Barite is also present in minor quantities in the rock matrix. You will, therefore, create a reservoir called ABC Reservoir and saturate the Brine (previously calculated) with calcite and barite. You will then recalculate the Brine Scale Scenario.

- Add a Saturator Object.
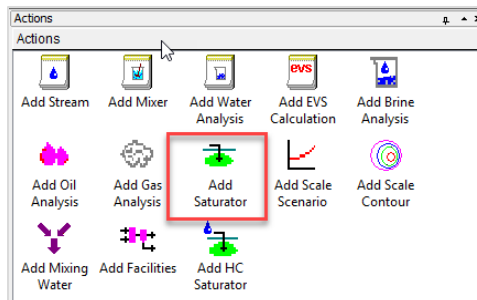
- Select the **<u>Description</u>** Tab to rename the Object **Reservoir**
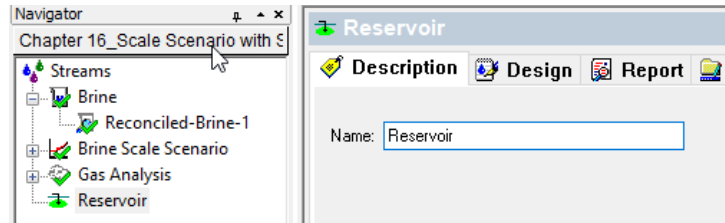
- Select the **<u>Design</u>** Tab
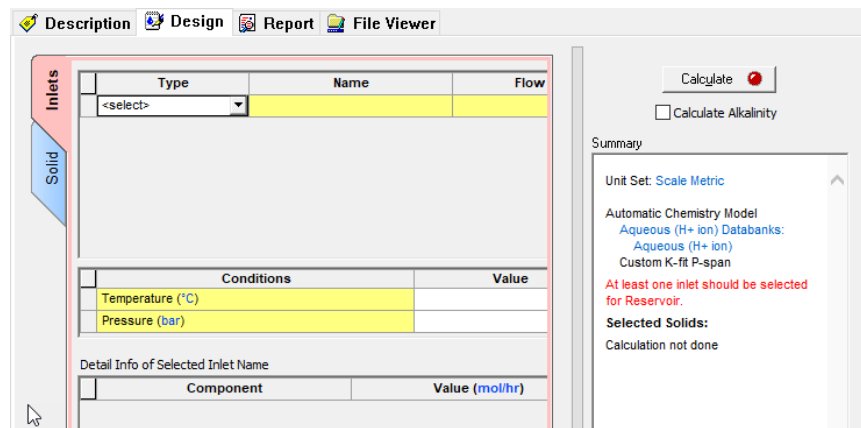
The Saturator has two vertical tabs: Inlets and Solid.

In the **<u>Inlets</u>** Tab the Fluids are entered in the top grid and the Conditions are entered in the bottom grid.

Solids are selected and saturated in the **<u>Solid</u>** Tab.

- Enter the Brine calculated in Task 1
- Enter the Gas calculated in Task 3
- Enter the Reservoir conditions: 125 C and 275 bar in the conditions section.
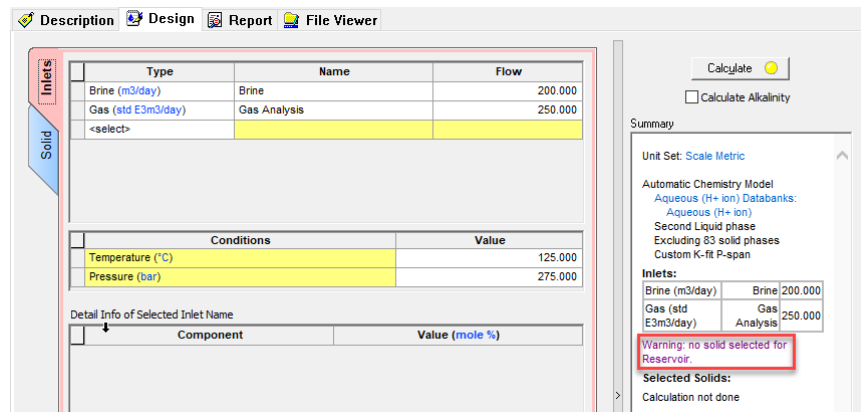
The Saturator's calculate button is yellow. This is because solids have not been selected yet. A warning also appears in the summary box. A yellow button is allowable, and a calculation may continue; it is merely a warning that the case is incomplete.

- Select the *Solid* Tab (vertical tab)
- Select the Standard checkbox

This last step instructs the software to allow the selected solids to precipitate – to include solid-liquid equilibrium equation in the calculation. It **does not** instruct the software to saturate these solids. Rather, if the phase is supersaturated, then it will precipitate. It is in the lower section that saturated solids are chosen.

This section contains two columns. The first (Solid) is the mineral to be saturated, and the second (inflow) is the cation and anion to be adjusted. If, for example, Barite is subsaturated in the existing fluid, then Ba+2 and SO4-2 are added. The amount of each added is stoichiometrically equivalent; one Ba+2 with one SO4-2, which maintains charge balance. If, for example, (again) Calcite is supersaturated, then equal mole amounts of Ca+2 and CO3-2 will be removed from the fluid. This inflow will be positive if the solid is subsaturated in the existing fluid, or it will be negative if the solid is supersaturated.

- Use the Solid drop-down menus to select BaSO4 (Barite) and CaCO3 (Calcite) as solids to saturate
- Use the Inflow drop-down menu to select BaSO4 and CaCO3 as solids to saturate (it should have been selected automatically).

Reservoir Mineral Saturation Section

	Mineral to saturate	Inflow to vary
	BaSO4 (Barite)	BaSO4
	CaCO3 (Calcite)	CaCO3
	<Select Solid>	
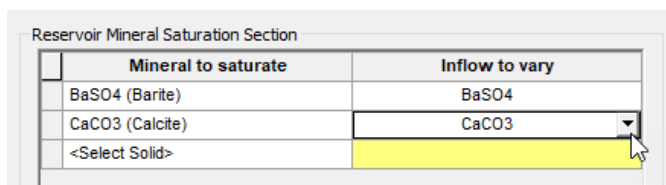
At this point, the Calculate button is green indicating that the specifications are complete.

- Calculate (or press the <F9> key)
- Click the **Report** tab

The Saturator Report tab contains several tables: Saturation Details, Inlet Summary, Stream/Phase Properties, Pre and Post Scaling Tendencies, Brine Composition, Gas Composition, and if selected an inlet summary.

- Scroll down to the Pre and Post Scaling Tendencies Table

Pre and Post Scaling Tendencies

Formula	Mineral	Excess Solute mg/L	Excess Solute lb/1000bbl	Pre-Scale S, ST	Pre-Scale SI, Index	Post-Scale S, ST	Post-Scale SI, Index
CaSO4.2H2O	Gypsum	0.0	0.0	0.0179366	-1.74626	0.0179365	-1.74626
SrSO4	Celestine	0.0	0.0	0.148191	-0.829178	0.148191	-0.829178
SrCO3	Strontianite			0.209852	-0.678087	0.209852	-0.678087
BaSO4	Barite	2.64658e-5	9.27644e-6	1.00000	1.82534e-6	1.00000	0.0
CaSO4	Anhydrite	0.0	0.0	0.0934633	-1.02936	0.0934633	-1.02936
CaCO3	Calcite	1.13495e-5	3.97806e-6	1.00000	-4.81593e-8	1.00000	0.0
Mg(OH)2	Brucite			4.98480e-4	-3.30235	4.98479e-4	-3.30235
NaCl	Halite	0.0	0.0	0.0245553	-1.60985	0.0245553	-1.60985
KCl	Sylvite			2.14382e-4	-3.66881	2.14382e-4	-3.66881

Excess solute or Max Scale: The solids amount forming at equilibrium.
Pre-Scale: The saturation ratio before solids precipitate.
Post-Scale: The saturation ratio AFTER solids precipitate (if solids are selected).
S, ST – Saturation, Scale Tendency: The ratio of the concentration (activity) to its solubility (S=1).
SI – Scale Index: Log(S).

The Max scale column shows that trace amounts of BaSO4 and CaCO3 are present in the water. These exceedingly small values (in the parts-per-trillion range) are the specifications or targets for the calculation. The software sets these target solid concentrations and then adjusts up or down, the BaSO4 and CaCO3 inflows until it reaches these targets. These part-per-trillion values may look arbitrary, but in fact the values are equivalent to 1e-10 moles of solid/kg water.

Notice also, that the pre-scale tendency for BaSO4 and CaCO3 are set to 1.0, by saturation definition. That is, these are not calculated, they are defined. The remaining scale tendencies are computed.

Task 6 – Recalculate the Scale Scenario with the Saturated Reservoir

Considerable time is spent creating what is hoped to be a more representative brine. The Brine is reconciled for charge balance, and where needed, alkalinity and pH; the gas is saturated with water as needed (though not done in this case), and lastly the fluids are set to equilibrium with important reservoir minerals. It is only after these steps are complete, and that there is confidence that the assumptions and calculations are representative of the process, that a final scaling calculation is run.

The **Reservoir** calculation contains the representative fluid. It is, therefore, the output of this calculation that will be used in all subsequent calculations. To access this output, a new Type of fluid, Whole Fluid is defined. The Whole Fluid type represents 100% of the contents of a previous calculation, regardless of phase.

You will use the Whole Fluid from the Reservoir to rerun the scaling calculations.

- Select *Brine Scale Scenario* in the Navigator Pane and rename it **Reservoir Scale Scenario**
- Select the **Design** tab
- In the *Inlets* tab in the **Type** column delete the Brine and Gas from the Type column
- Add *Whole Fluid*
- In the **Name** column select *Reservoir*
- In the **Flow** column select *<Automatic>*
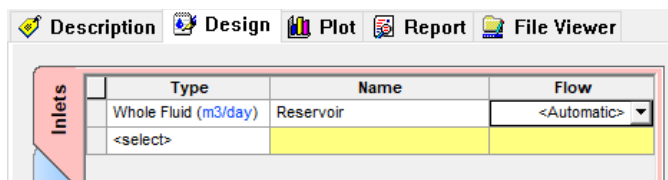
Note: The Whole Fluid type refers to all the phases within the fluid. The Automatic option takes the final flow rate phase of the separator and automatically enters this as the flow rate in the Scale Scenario calculation.

- Go to the *Solid* tab and make sure that the Standard box is checked

---
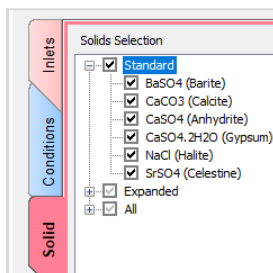
- Calculate (Press <F9>)
- Select **Plot** tab and select *View Plot*
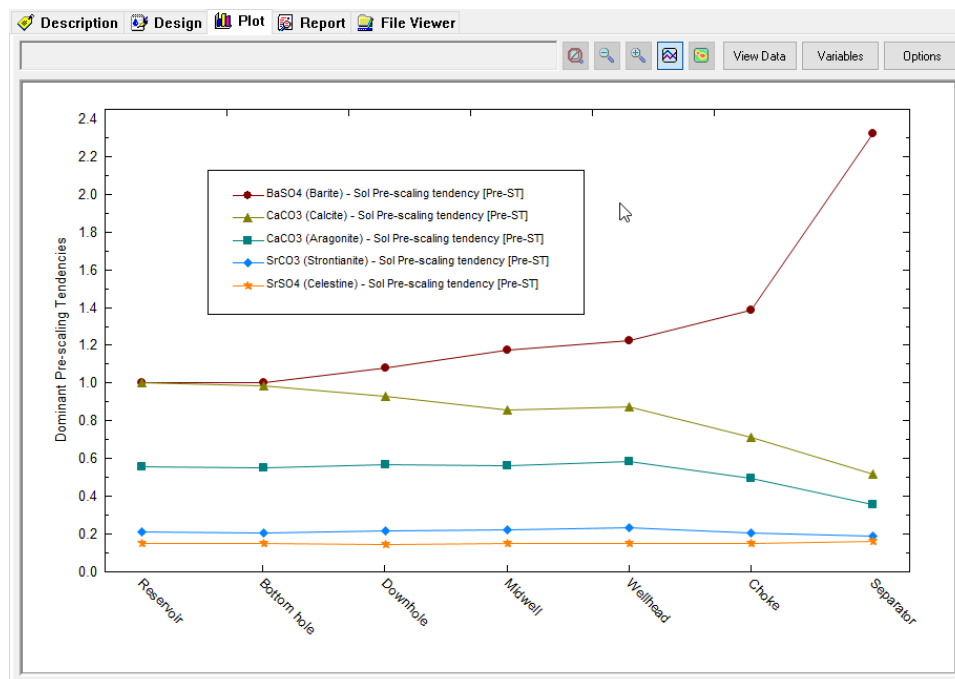
The Saturator is a tool for normalizing the thermodynamics of a reservoir system. The purpose of this calculation is to apply the constraint of solid-liquid equilibrium on a system to create a specific compositional starting point.

The basis of this calculation is that water in the pores of a rock matrix is at equilibrium with the mineral surface. Some questions to consider are whether it is reasonable to assume that a reservoir gas, oil, water, and rock are in equilibrium. Furthermore, we should also consider over what vertical and radial distance we can make this claim.

Regardless of the inconsistencies, the industry widely accepts this approach. It is up to the analyst to decide if the Saturator produces a more representative fluid than the original data.

Task 7 – Add a Contour Diagram

An alternative to the *Scale Scenario* calculation is the *Contour Diagram*. The conditions defined in the Scale Scenario are specific to production locations, and generally no more than ten are entered. By comparison, the conditions defined in the Contour Diagram are a range of temperatures and pressures. The object then computes a matrix of temperature and pressure conditions and creates a presentation-quality contour diagram.

- Add Scale Contour
- Rename the Object **Contour Reservoir**
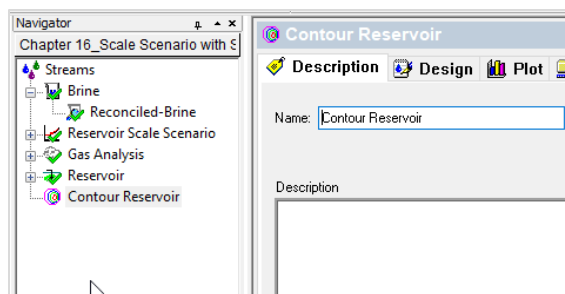
- Select the **Design** Tab
- Select the *Inlets* (vertical) tab
- Select the bottom right corner of the 1st cell in the Inlet grid and choose *Whole Fluid*
- Select *Reservoir* in the 2nd column
- Keep the *<Automatic>* flow rate option in the 3rd column
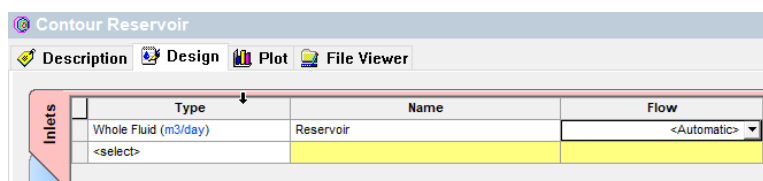
- Click Conditions (vertical) tab

The minimum and maximum conditions are at the Separator 60C, 30 bar and Reservoir 125C, 275 bar. These are the start and end range of the study. To create a reasonable number of calculations (~300) and to keep the matrix somewhat symmetric, we will use increments of 2 C and 10 bar.

- Change the Start to 60
- Change the End to 125
- Select the Increment radio button
- Enter 5 as the increment
- Uncheck the Log box (if it is checked)
- In the Pressure Range box, change the Start to 30
- Change the End to 275
- Select the Increment radio button (uncheck the Log box first)
- Change the Increment to 10
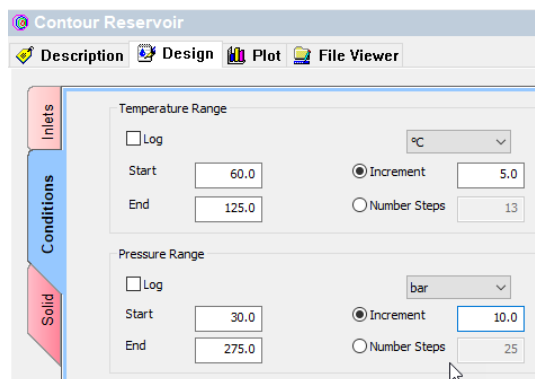
This produces a matrix of 13 temperature and 15 pressure steps. This produces a 14x16 matrix, or 224 calculations.

	Temperature	Pressure
Units	°C	bar
Start	60.0	1.01325
Stop	125.0	10.1325
Step Size	5.0	0.60795
No. Steps	13.0	15.0
Calculations	224	

- Select the *Solid* Tab
- Check the Standard box
- Calculate. The calculation should take less than 10 min to be complete
- When calculation is done, go to the **Plot** tab
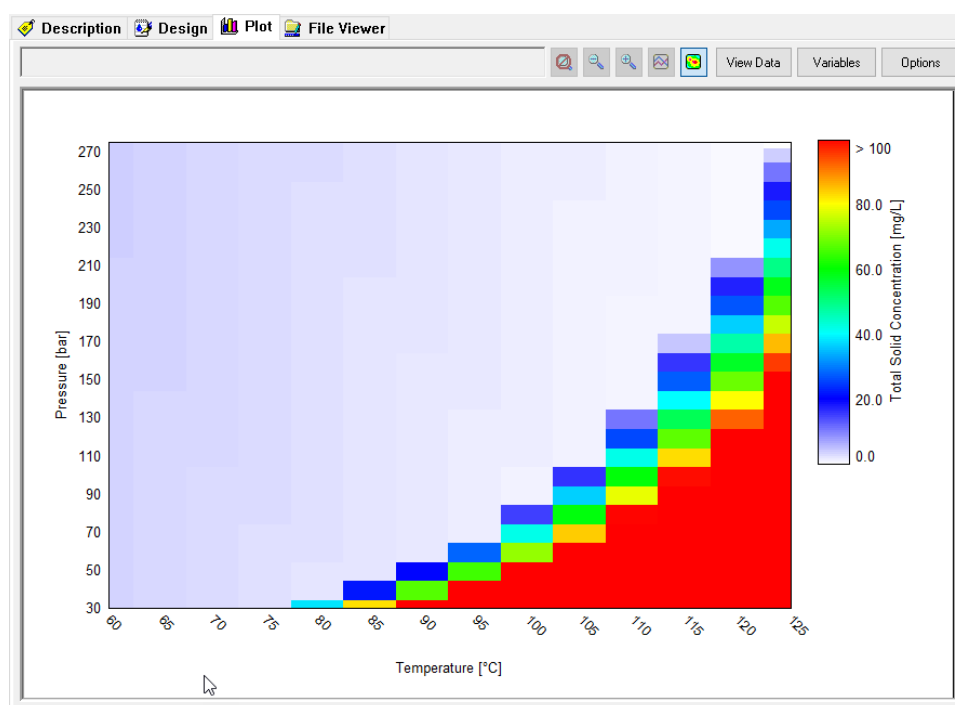
The default plot is the total solids forming. The color scale represents a different numerical range. The red cells indicate heavier solid precipitation, and the faint purple-white in the center and left of the screen indicate that little to no scale forms. The upper right corner is the Reservoir conditions (125C and 275 bar). The lower left represents Separator conditions (60C and 30 bar). At both points, minimal solids are computed to form. The fluid traveling through the piping traverses this plot as temperature and pressure decreases. Layering production conditions (e.g., early to late life) over this plot provides an indication as to whether production will be at risk now or in the future. For example, if the pressure decline is significant (e.g., 60 bar), then the fluid will be unstable at the higher temperatures (bottom of well).

This completes our Tour in ScaleChem.

You can download a worked example file for this tutorial from here: Chapter 16 – Basic ScaleChem.

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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 reviewed a scaling calculation in the ScaleChem Tour.

This chapter will cover the same calculation objects using fewer instructions and will introduce *Mixing* and *Facility* Calculations. Its purpose is to reinforce what was learned in the previous chapter and to promote the anticipating of next-steps when using the interface. This will be divided into different tasks.

Task 1 – Add a Brine

- Add a *Brine Analysis* from the Action Panel
- Rename the Brine in the **Description** Tab, and name it WTXWTR
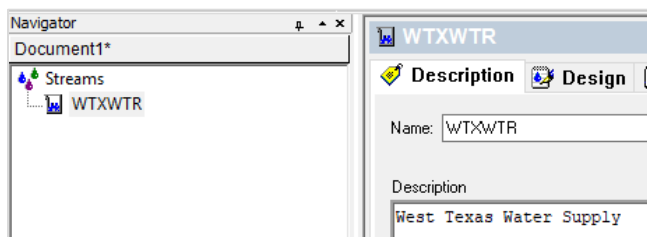
Figure 17-1 The default brine sample description

- Go to the **Design** Tab and enter the following composition in the *Data Entry* (vertical) tab:

Name	WTXWTR	
Type of water	Aquifer Water	
Comment:	West Texas Water Supply	
Species	Concentration	
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
HCO$_3^-$	439	mg/L
HS^{-1}	146.2	mg/L

- Check the *Show non-zero Only* box (under Entry Options)
- Go to the **Reconcile** (vertical) tab
- Select the measured pH and alkalinity Option
- Enter the following conditions (change units if necessary)
  - o To change units just click on the hyperlink next to the variable that you want to change.

Temperature (°F)
Pressure (psi)
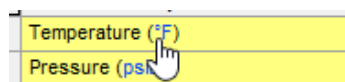
Temperature	77 F
Pressure	14.7 psia
pH	7.98
Alkalinity end Point pH	439 mg/L as HCO3-
Titration pH	4.5
Density	(will be estimated)

Figure 17-2 The calculated Brine WTXWTR

- Click the Calculate Button

Task 2 – Add a Second Brine

- Add a Brine Analysis
- Enter the composition given below in the **Data Entry** (vertical) Tab

Figure 17-4 Brine data entry

- Go to **Reconcile** tab
- Select *pH and Alkalinity* calculation type, and enter the information provided in the figure below:

Figure 17-4 Reconcile data entry

- Click the Calculate button

Task 3 – Add a Gas

- From the Actions Panel click on *Add Gas Analysis*
- Input the name in the **Description** tab. Name it *LightHC*
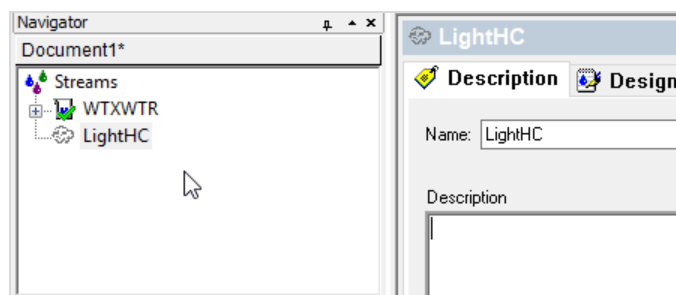
Figure 17-3 Entering a gas sample

- Go to the **Design** Tab and enter the following composition in the *Inflows* (vertical) tab,
- Enter the following composition:

Component	Composition
Carbon dioxide (CO2)	10 mole %
Water (H2O)	15 mole %
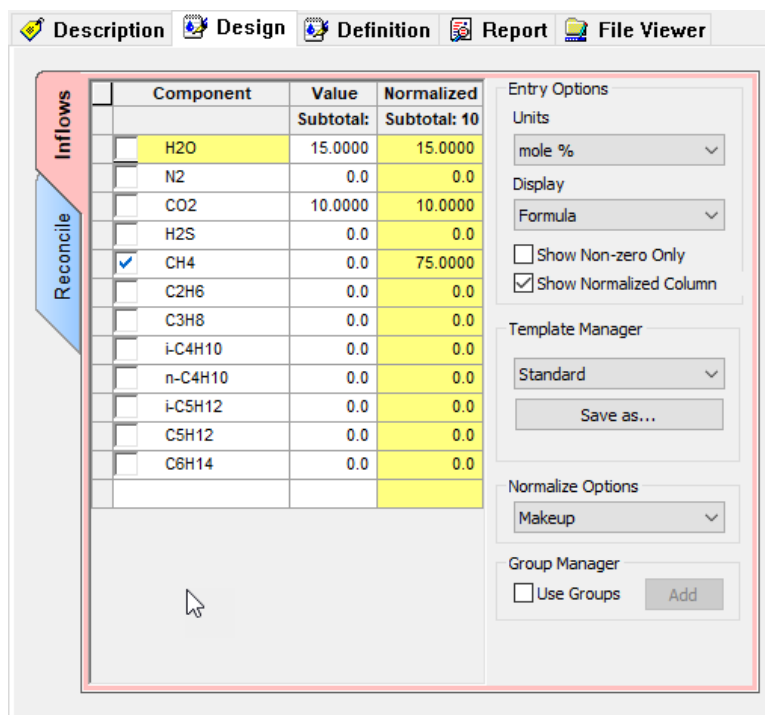
Figure 17-5 Entered gas.

ScaleChem will assume that all of the hydrocarbon gas is methane (CH_4). So, in this case the software normalizes the gas adding 75 mole% of CH_4.

- Go to the **Reconcile** (vertical) Tab
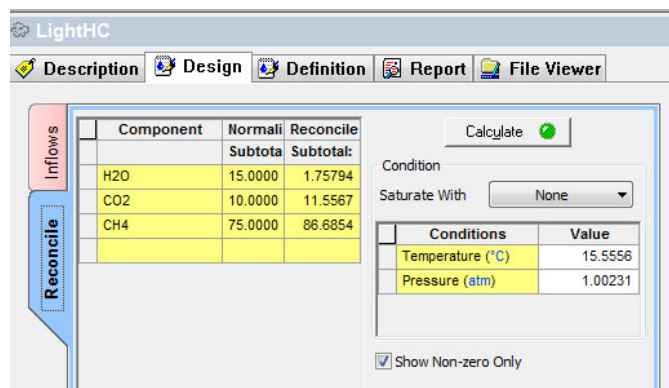
Figure 17-6 Reconcile tab

- Leave the default conditions for Temperature and Pressure
- Calculate

Task – Add an Oil

- From the Actions Panel click *Add Oil Analysis*.
- Enter the name in the **Description** Tab. Name it *OIL-1*
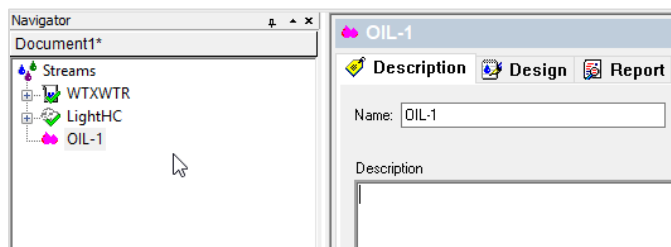
Figure 17-7 Input name for the Oil Analysis

- Go to the **Design** tab
  - This tab is divided into:
    - Combined Tab: Here pure components (organic and inorganic) are entered.
    - Pseudocomponent Tab
    - Assay Tab: Here distillation curves are entered.
    - Reconcile Tab

For this example, we will enter pure component and pseudocomponent data.

- Go to the **Combined** tab

- Enter the following composition:

Methane (CH4)	20.53mole %
Hexane (C6H14)	8.595mole %
CO2	6.09mole %

Note: You will have to scroll down to find the CO2 entry.
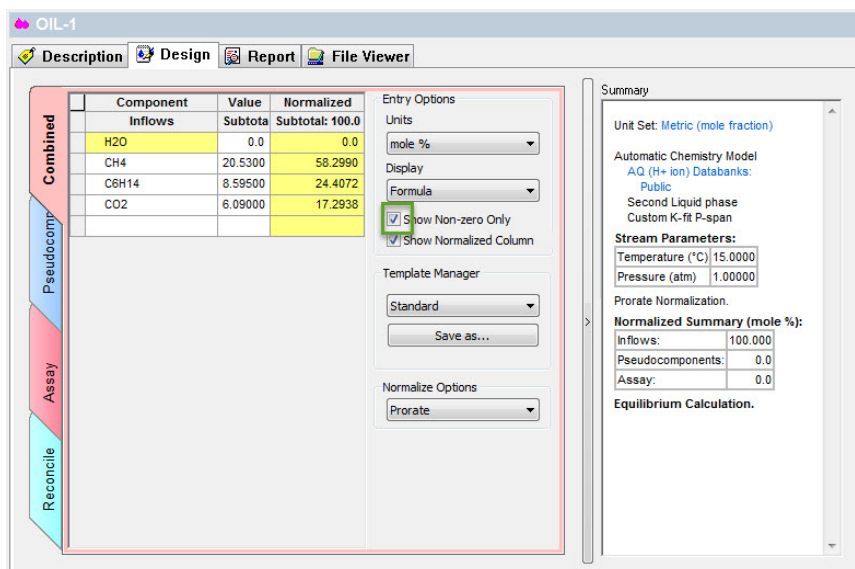
Figure 17-8 Starting to add compositions.

- Go to the **Pseudocomponent** tab
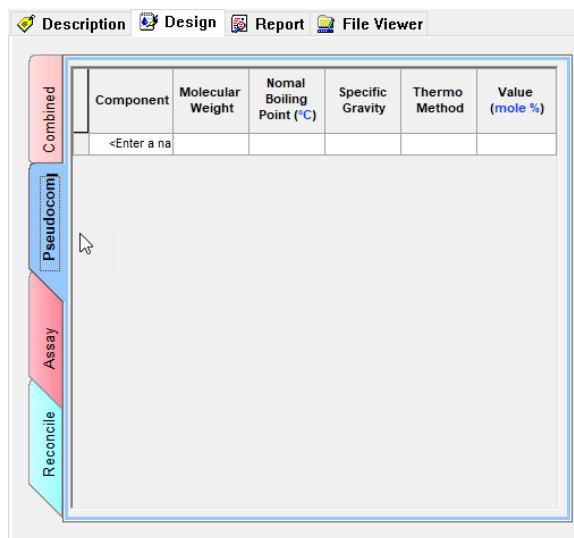
Figure 17-10 Entering pseudocomponents

- Add the following pseudocomponents:

Name	MW (g/mol)	nBP (F)	Thermo Method	Value mole %
PC1	98.43	100.21	API	27.57
PC2	170.34	216.32	API	29.35
PC3	282.55	343.78	API	7.19
PC4	506.0	645.00	API	0.68

The completed input looks like this:

Figure 17-12 Completed input

- Go to the **Reconcile** (vertical) tab
  Here you will see how well the pseudocomponent will predict the phase behavior of the hydrocarbon sample.
- In the Condition option (below calculate button) enter T=204 F and P=1 atm.
- Click on the *Add boiling point curve* (red square)

Figure 17-13 Reconciliation Tab

- A new calculation appears in the navigation panel below OIL1 Object.
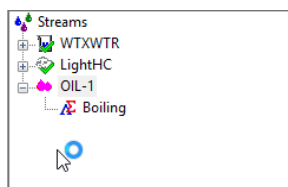
Figure 17-14 Boiling Point calculation

- This is a survey by Pressure. Click on the specs button and specify the conditions below. Change pressure units if necessary.
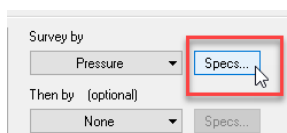
- Enter a pressure range:

Start	200 psia
End	2000 psia
Decrement	100 psia

- Click the *Calculate* button.

- Click on the plot tab, you will see the following graph: You could adjust the parameters by clicking on curves.
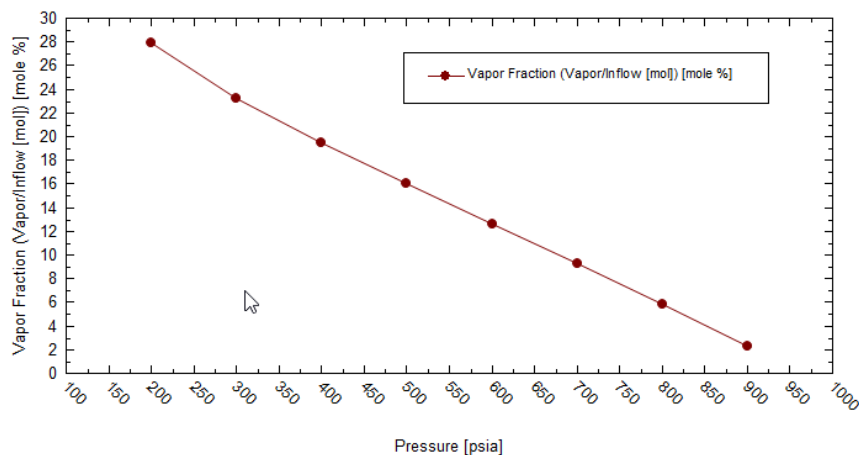
Figure 17-15 Boiling point curve

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.

	Pressure	Vapor Fraction (Vapor/Inflow [mol])
	psia	mole %
1	200.000	27.8711
2	300.000	23.1977
3	400.000	19.4660
4	500.000	16.0216
5	600.000	12.6532
6	700.000	9.26672
7	800.000	5.80919
8	900.000	2.24433
9	1000.00	
10	1100.00	
11	1200.00	
12	1300.00	
13	1400.00	
14	1500.00	
15	1600.00	
16	1700.00	
17	1800.00	
18	1900.00	
19	2000.00	

Frequently the hydrocarbon was saturated with water.

- Go back to OIL-1 in the Action panel
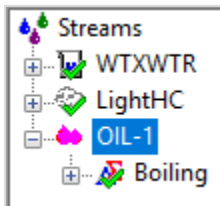
- Click on the **Design** tab
- Click on the _Saturate with_ drop down. Select H20

Figure 17-16 Saturate with H2O

- In the Conditions option use T= 77 F and 14.7 psia.

The software requires an initial "Guess" for the concentration of the water..

- Click on the *Calculate* button.

When done, the software will create a *Reconciled OIL-1* in the Navigator pane.

The Brine, Gas and Oil that we already calculated will be used for Mix, Saturator and Facilities Calculations.

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

- From the Actions Panel, click on the Add Mixing Water logo.

Add Mixing
Water

- After double clicking the logo, you will the object in the Navigation Panel.
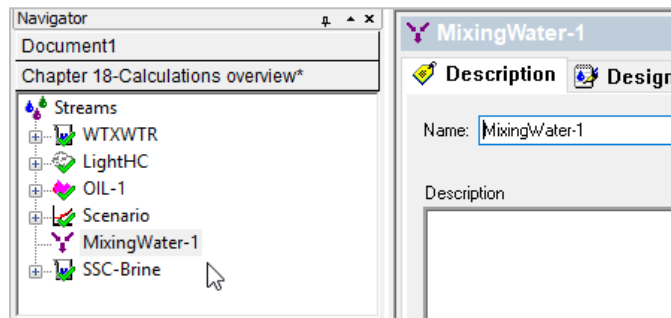
Figure 17-17 Input name for Mixing Water object

- Click on the **Design** tab to enter more information.
- Select your Brines, Gas and Oil s as shown in the figure below. Enter the indicated brine flow rate of 1000 bbl/day, gas flow of 230 stdMft3/day and oil flow of 7 bbl/day.

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.
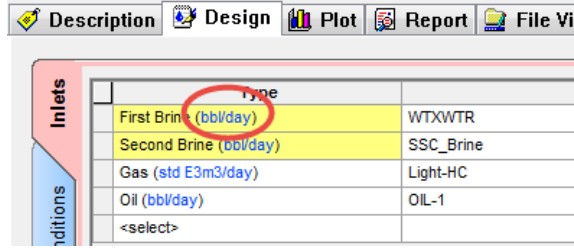
Figure 17-19 Changing units

This should pop the following window up. Click on Inlets tab and change the units.

Inlets tab looks like below. Changing units on Brine:
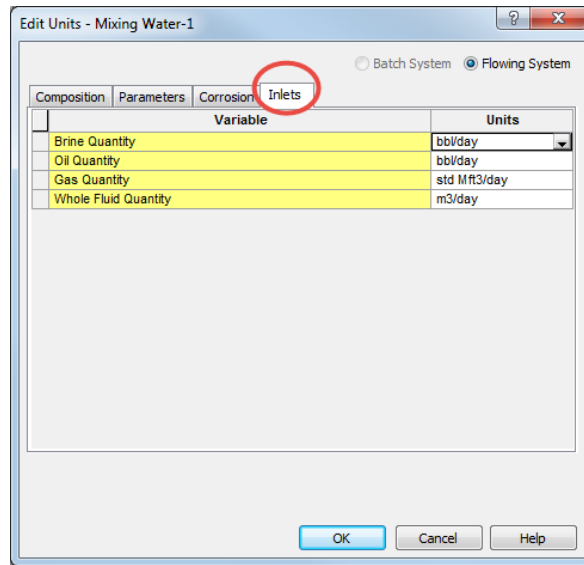
Figure 17-20 Units manager layering

Method 2   This can also be done in one other way, that is through the units manager button on the toolbar. which looks like .
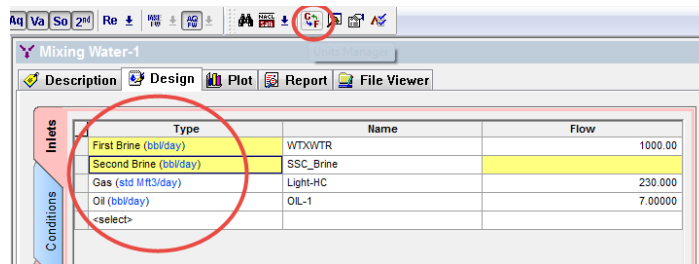
Figure 17-21 Units Manager accessibility

When you click on units manager, following windows pops up.
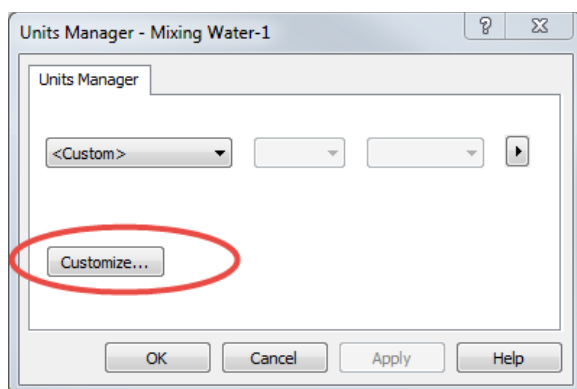
Figure 17-22 Units Manager first layer

Click on Customize. Change the individual parameters as shown below.
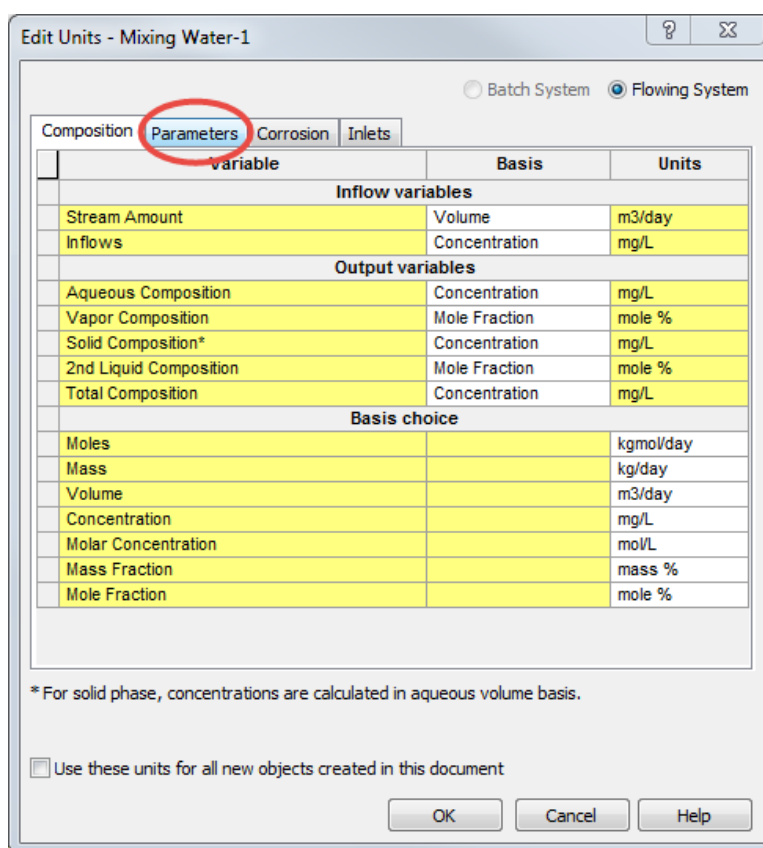
Figure 17-23 Changing units for parameters

The final Mixer with inflows entered should look like the image below:
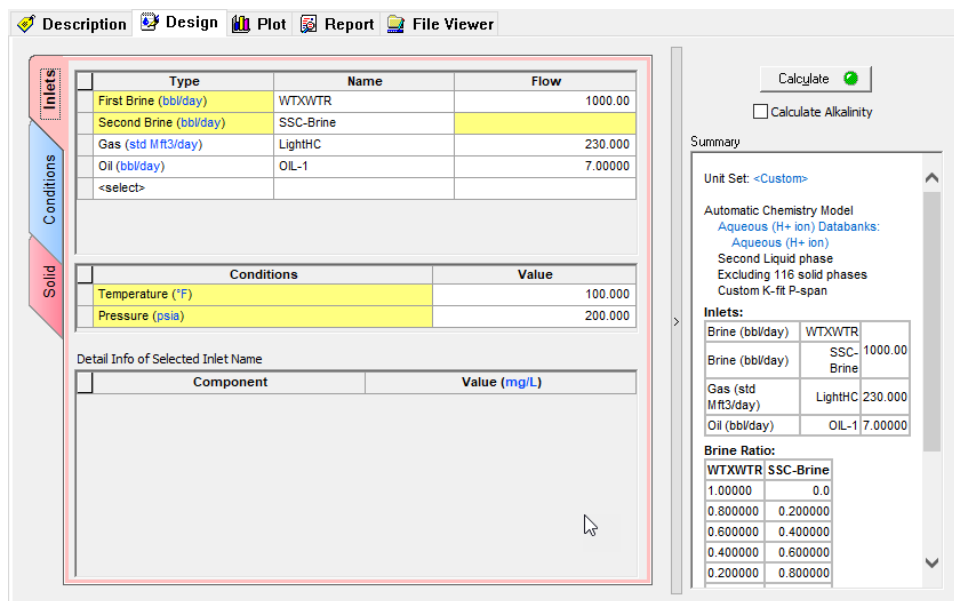
Figure 17-24 Mixer with inflows entered (Inlets Tab)

- Go to the **Conditions** tab

In this example, we are mixing the brines at 100 F and 200 psia. The first brine specified (WTXWTR) is the one we compare to when evaluating the ratios. In this case we start out with all brine WTXWTR and none of the SSC_Brine and end up with none of brine WTXWTR and all of the SSC_Brine.

- Leave the default values
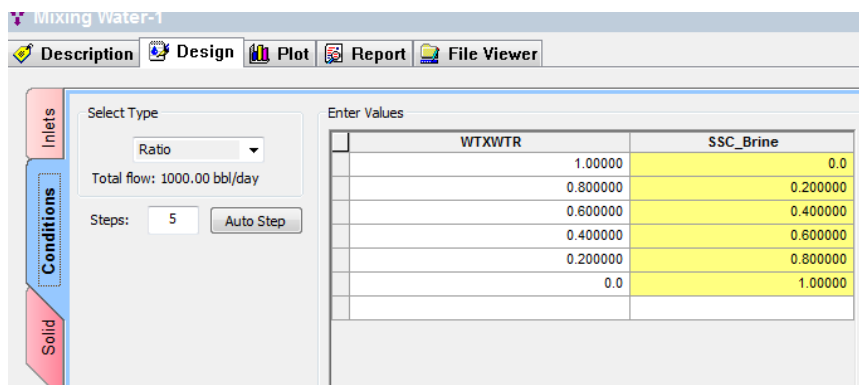
Figure 17-25 the mixing conditions (Conditions tab)

- Go to the **Solid** tab

For this calculation we are only selecting a few of the possible solids. Mark a check box next to desired solids (BaSO4, CaCO3, CaSO4.2H2O, NaCl).
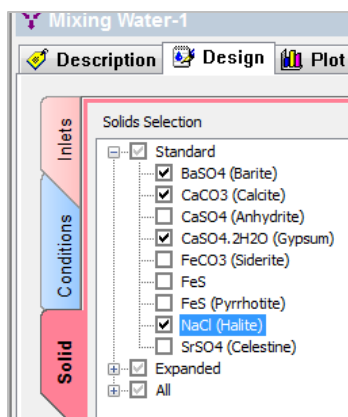
Figure 17-27 Selecting a few solids. (Solids tab)

- Click on the Calculate button.

- Click on the **Plot** tab.
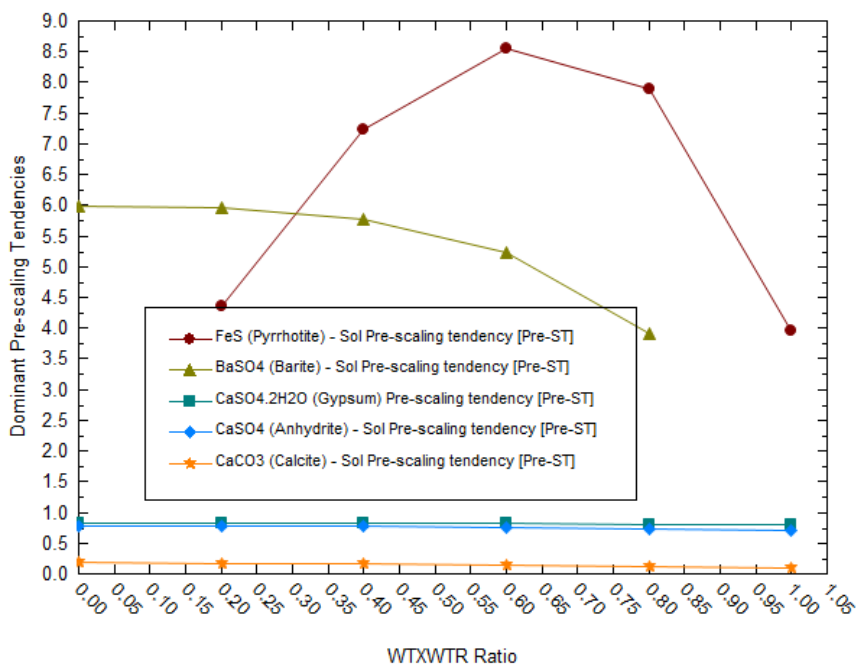
Figure 17-28 Default plot

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.
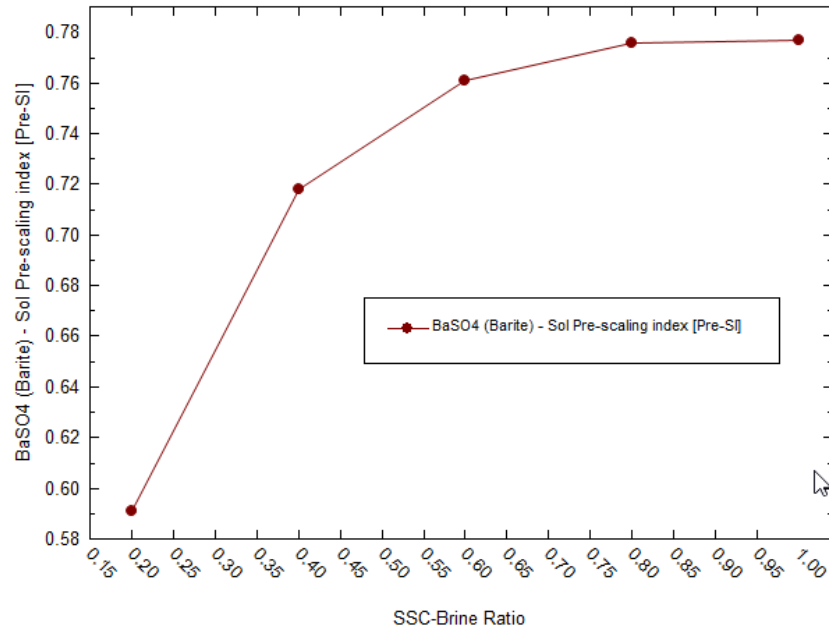
Figure 17-29 Mixing results

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.

- Select **Add Saturator** from the Actions Panel.

- Rename the object in the descriptions tab. Name it Saturator-1
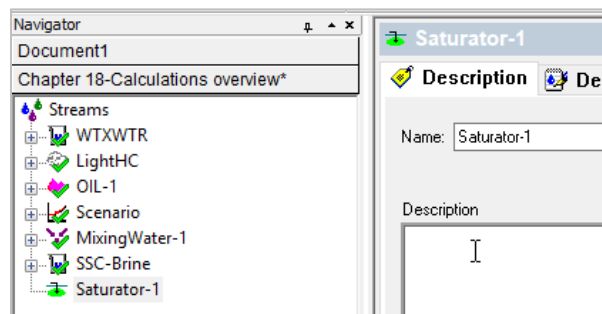
Figure 17-31 Description tab

- Go to **Design** tab
- And go to *Inlets* (vertical) tab

We will select objects that we have already defined.

- Enter a Brine flow of 1000 bbl/day
- Enter a Gas flow of 230 std Mft3/day
- Enter T=77 F and P=14.7 psia
- Set these units as custom units for all new objects in Units manager.
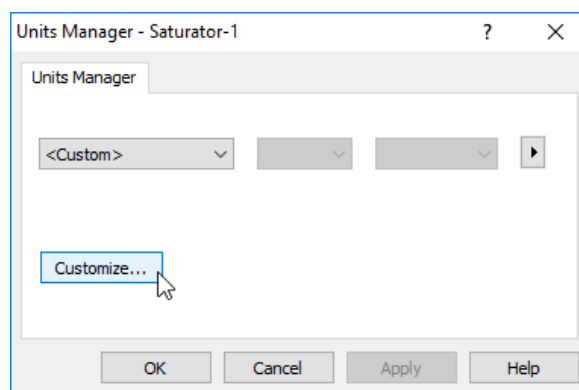
Figure 17-33 Customize the unit sets

The window should look like this:

- Go to **Solid** (vertical) tab
- Check the Standard box

We need to select solids inflow to vary for Saturator1. Under the table *Select Inflows to Vary*, choose the solid to vary from the dropdown list.

- Select BaSO4 (solid) and hit enter. Automatically the inflow to vary BaSO4 will appear.
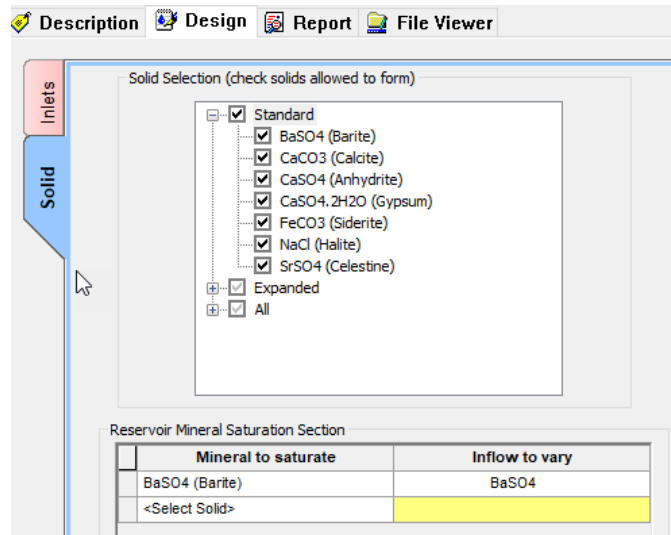
Figure 17-34 Selecting solids to vary

To study the Saturator-1 (Brine and Gas mix) at various locations we need to add a Scaling Scenario, as was performed in Chapter 16.
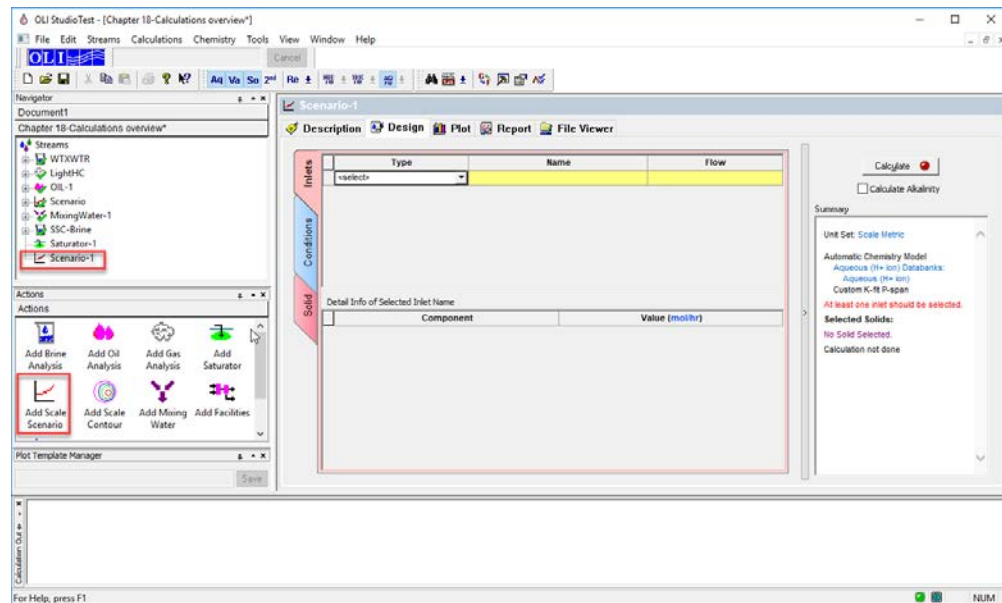
Figure 17-35 Adding a scaling Scenario

- Name the new Scale Scenario as *Saturator-1 Scale Scenario* under the **Description** tab.
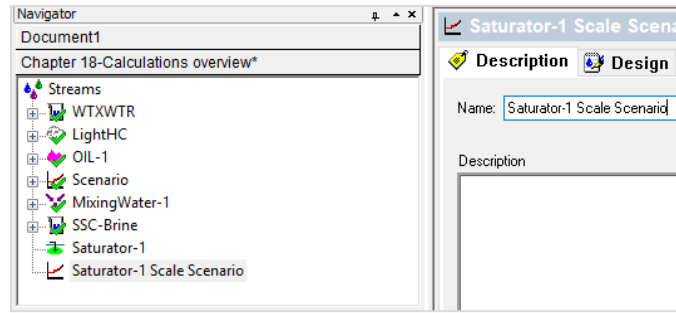
- Go to the **Design** Tab
- Under the *Inlets* (vertical) tab, select *Brine* under the *Type column*
- Make sure to select Saturator-1, as is shown in the picture below:
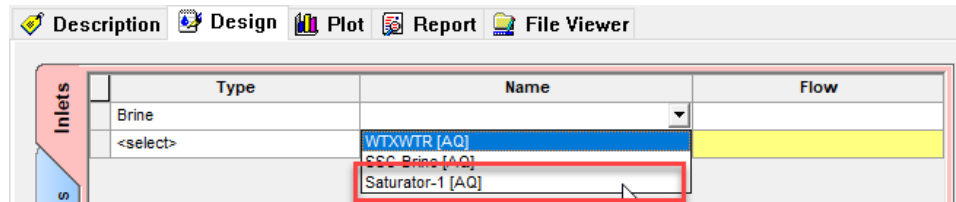
Flow will be automatically controlled. Locations can be input under the *Conditions* tab.

- Go to *Conditions* (vertical) tab, and enter the information provided in the figure below:
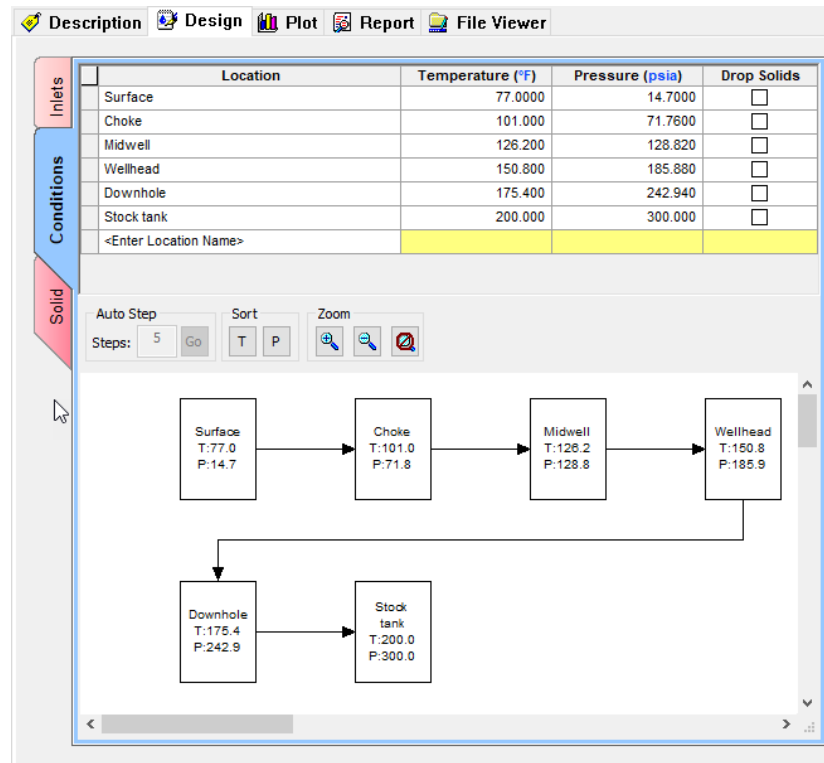
Figure 17-36 Conditions set up

- Go to *Solid* tab and check the Standard box
- Click the Calculate Button
- Go to **Plot** tab
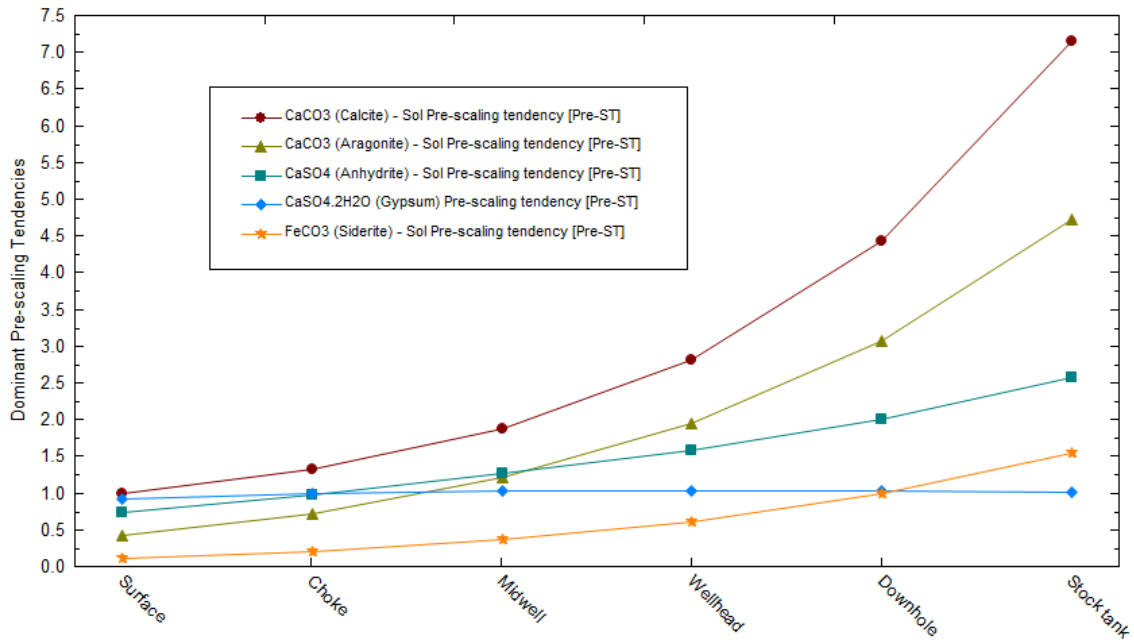
Figure 17-38 The plotted results

After the calculation is complete, the plot for scale scenario shows that other solids are appearing.

- Go to the Report tab, and look for Pre and Post Scaling Tendencies

Pre and Post Scaling Tendencies

Formula	Mineral	Excess Solute	Excess Solute	Pre-Scale	Pre-Scale	Post-Scale	Post-Scale
		mg/L	lb/1000bbl	S, ST	SI, Index	S, ST	SI, Index
CaSO4.2H2O	Gypsum	0.0	0.0	0.928262	-0.0323294	0.928262	-0.0323294
FeCO3	Siderite	0.0	0.0	0.114350	-0.941763	0.114350	-0.941763
SrSO4	Celestine	0.0	0.0	0.203747	-0.690908	0.203747	-0.690908
SrCO3	Strontianite			0.0120481	-1.91908	0.0120481	-1.91908
BaSO4	Barite	0.0	0.0	1.00000	-2.23307e-11	1.00000	0.0
CaSO4	Anhydrite	0.0	0.0	0.731753	-0.135635	0.731753	-0.135635
CaCO3	Calcite	0.0	0.0	1.00000	-1.46285e-11	1.00000	0.0
NaCl	Halite	0.0	0.0	0.0121174	-1.91659	0.0121174	-1.91659
KCl	Sylvite			6.71059e-4	-3.17324	6.71059e-4	-3.17324

Excess solute or Max Scale: The solids amount forming at equilibrium.

Pre-Scale: The saturation ratio before solids precipitate.

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

S, ST – Saturation, Scale Tendency: The ratio of the concentration (activity) to its solubility (S=1).

SI – Scale Index: Log(S).

Facility Calculation: Overview

This section presents a new calculation objects, *Facilities*. The Facilities is a simplified process simulator; it mixes and separates. ScaleChem has the ability to link together several individual calculations to create a flow sheet facility. An example of a facility calculation is shown in the figure below.
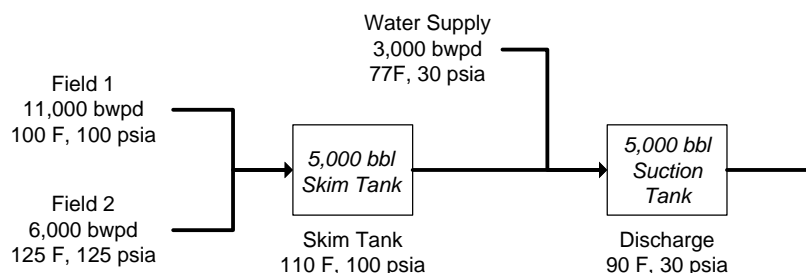
It is a simple process in which two field brines mix in a skim tank. The discharge from this tank then mixes with a water supply in a discharge tank. Below are the compositions and conditions of the inlet fluids.

Name	Field 1 mg/L	Field 2 mg/L	Water Supply mg/L
Na+	38209	27078	3074
Ca+2	6600	4480	910
Mg+2	1531	1191	249
Fe+2	120	6.6	0.77
Cl-1	73150	51134	4474
SO4-2	2453	1840	2960
HCO3-	421	677	439
HS-1	244	146.2	0
Conditions			
Temperature	100 F	125 F	77 F
Pressure	100 psia	125 psia	30 psia
pH	6.97	7.53	7.98
Alkalinity (As HCO3 mg/L)	421	677	439
Alkalinity End Point pH	4.5	4.5	4.5

Follow the steps below:

- Open a new Window for Simulation
- Create the above brines: Field 1, Field 2 and Water Supply
- Use the *Add Brine Analysis* object as you have done before to create them.

The *Data Entry* Windows should look like this:

- *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.

Figure 17-39 Reconcile for Field 1 Brine

- Select **Add Facilities** from the Action Panel.
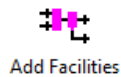
Add Facilities

- Go to the **Description** Tab and rename the object as Facilities-1
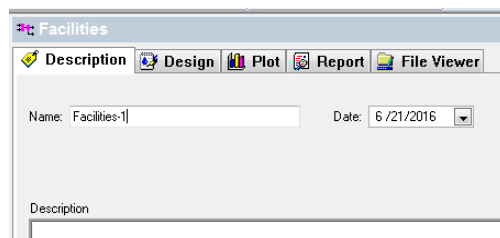
Figure 17-39 The Description tab for the Facilities

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.

- Go to the **Design** tab
- Go to the *Inflow Specs* (vertical tab)

Within *Inflow Specs*, we can add Nodes via Node input options. There will be one default node added.

- Double click on the node name (where it says: Node 1) and type "Skim Tank".
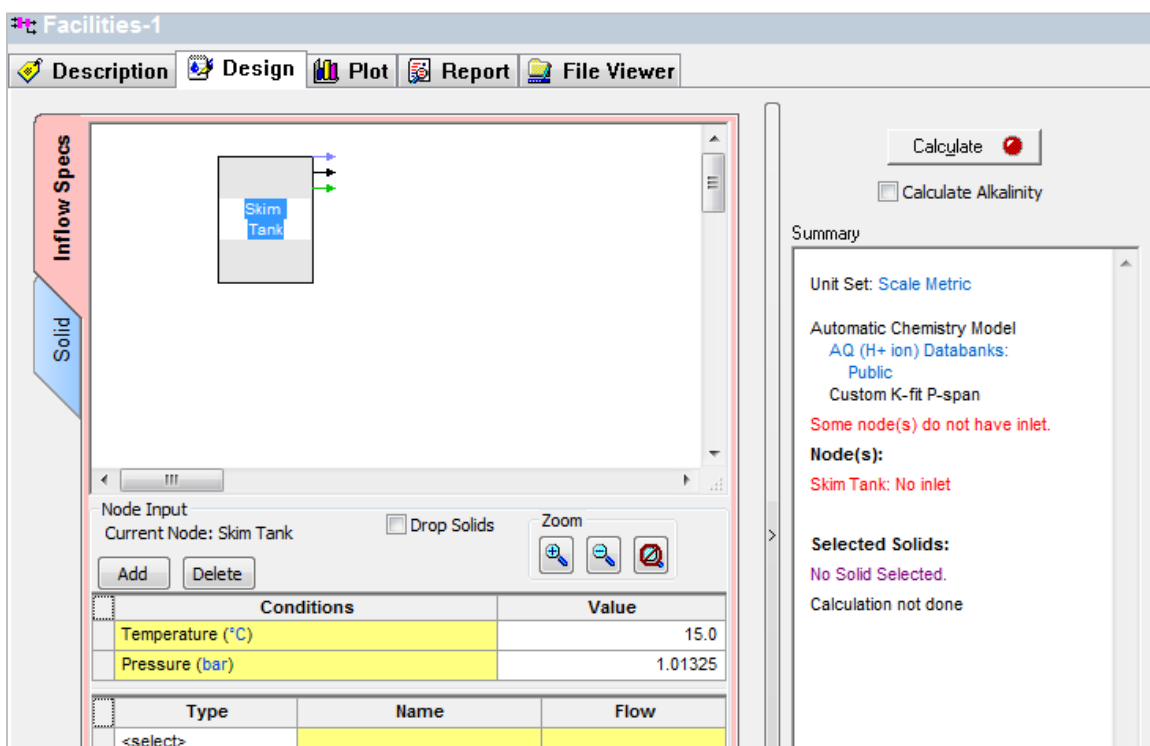
Figure 17-40 Node input Screen

- Enter the name, description, conditions, and streams for the Skim Tank shown in the table below:

	Flow	Temperature, F	Pressure, psia
Field 1	11000 bbl/day	100	100
Field 2	6000 bbl/day	125	125
Water Supply	3000 bbl/day	77	30
Skim Tank	5000 bbl/day	110	100
Suction Tank	5000 bbl/day	90	30

- Make sure to select drop solids checkbox at the Skim Tank node.

When complete, your screen should look like this.
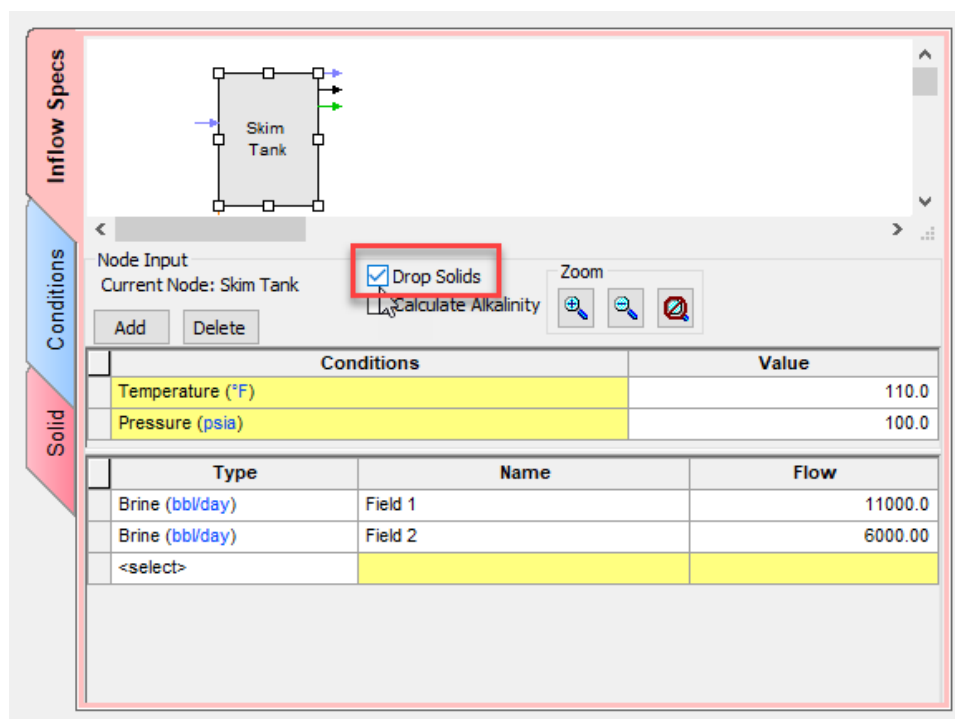
Figure 17-41 Node 1 is complete

The output of this calculation will go to the next node.

Next, enter the information for the second node, Suction Tank. We will select the output brine of the Skim tank, which is a ***brine from node.*** The temperature and pressure as well as the flow of the brine are calculated.

- Click on the Add button to add a second Node
- Change the name of the node to Suction Tank
- Change the conditions of this node to 90 F and 30 psia.

When complete your screen should look like this:
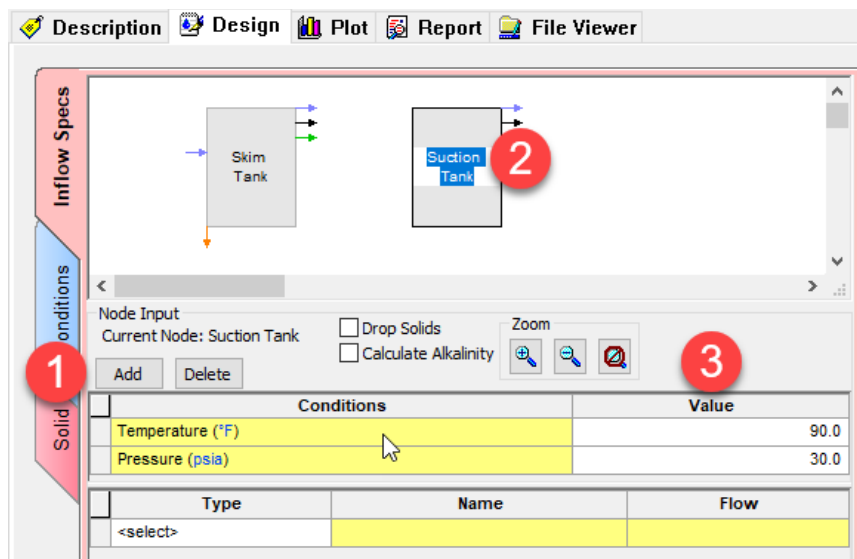
Figure 17-42 Node 2 is entered

When a brine is calculated in a facilities calculation, we have the option of allowing any produced solids to be considered (that is they traveled along with the brine) or to *eliminate* them as they precipitate out. We will eliminate the solids in this case. The orange downward arrow from Skim Tank indicate dropped solids.

We are also adding the **Water Supply** to this tank.

- In the Type column and first row select *Brine from*. In the Name column select *Skim Tank*. The *Flow* is calculated (since it comes from the Skim Tank).
- In the Type column and second row select *Brine*. In the Name column select *Water Supply*. Enter 3000 bbl/day in the Flow column.

When complete the screen should look like:
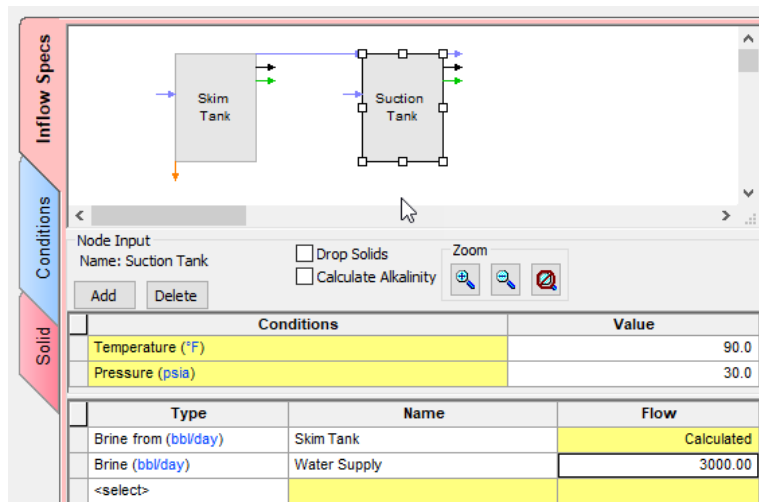
Figure 17-42 Suction Tank Definition

- Click on the Calculate button, or press <Ctrl+F9>
- Go to the **Report** tab, and check for the Pre-scaling Tendencies and Scaling Tendencies
- See the Results

Pre-Scaling Tendencies

Column Filter Applied: Values > 1.0e-4

Temperature Filter Applied: Active TRange Only.

Nodes	CaCO3 (Aragonite)	CaCO3 (Calcite)	CaSO4.2H2O (Gypsum)	CaSO4 (Anhydrite)	FeCO3 (Siderite)	Fe(OH)2 (Amakinite)
Temp Range °C	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
Skim Tank	5.20710	8.91186	1.24207	1.39847	0.165109	3.48775e-4
Suction Tank	4.83533	9.86145	1.18226	1.09089	0.147451	1.58132e-4

Nodes	FeS (Pyrrhotite)	FeS (Mackinawite)	MgCO3.3H2O (Nesquehonite)	MgCO3 (Magnesite)	Mg(OH)2 (Brucite)	MgSO4.7H2O (Epsomite)
Temp Range °C	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
Skim Tank	41958.3	906.834	4.47209e-3	9.15709e-3	1.05810e-3	1.11430e-3
Suction Tank	41552.1	781.107	3.37396e-3	4.74809e-3	3.15204e-4	1.21290e-3

Figure 17-43 the reports tab

Based on these results, it is clear to see that the software predicts the formation of several solids in this process. Solids with a Pre-Scaling Tendency > 1 are predicted to form.

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.

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.

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.

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.

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.

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.
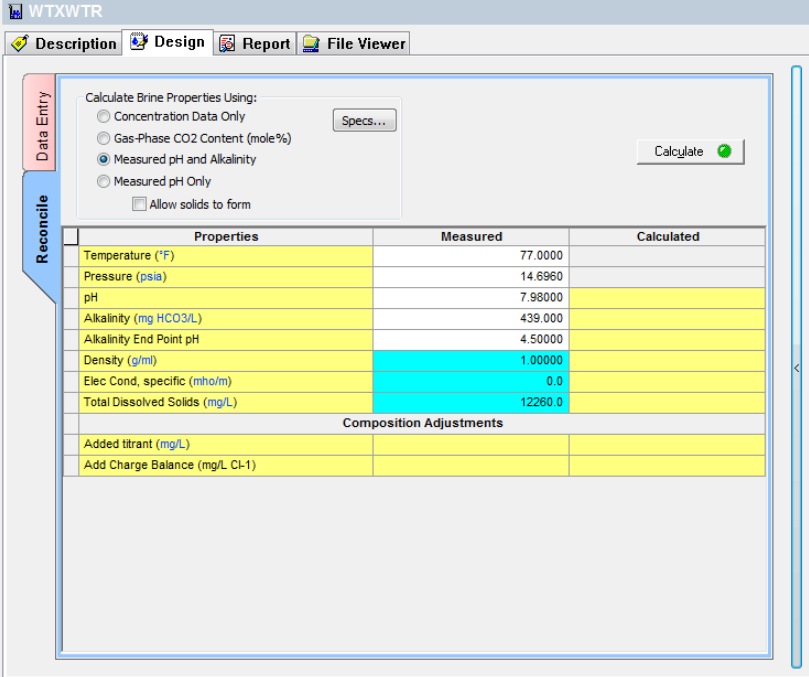
Titration pH   The titration pH is the end point of the actual alkalinity experiment. Normally this value is a pH of 4.5. The only requirement here is that the alkalinity pH must be less than the measured pH. An error will occur if this is not true.

Clicking on *Calculate* will execute the procedure.

When the calculation is complete, ScaleChem will report the values required to reconcile the sample.

The reconciled values are approximately 159 mg/l HCl added and 183 mg/l of CO$_2$ removed

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.

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 HCO₃⁻

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.
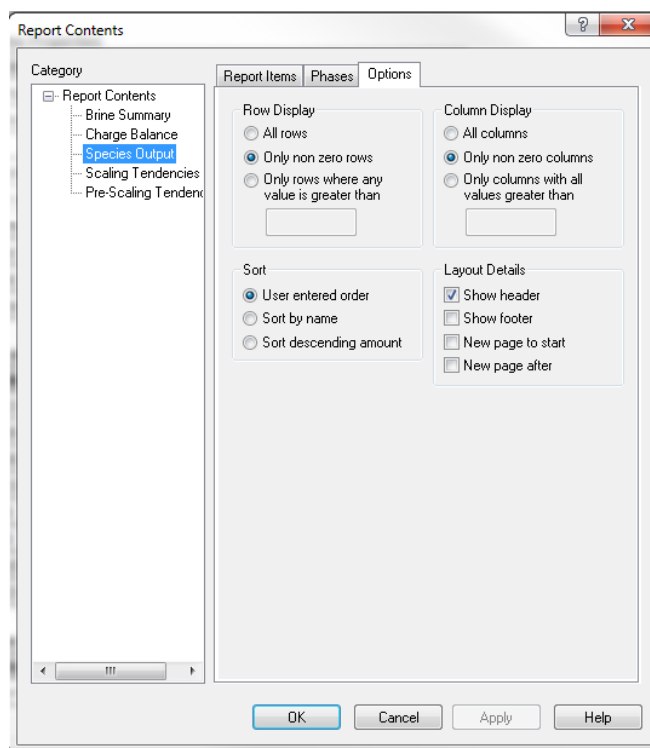
Figure 18-7 The default species display

Default Speciation Display

See **Chapter 15 ScaleChem Chemistry** for a more complete description of the standard chemistry.

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.
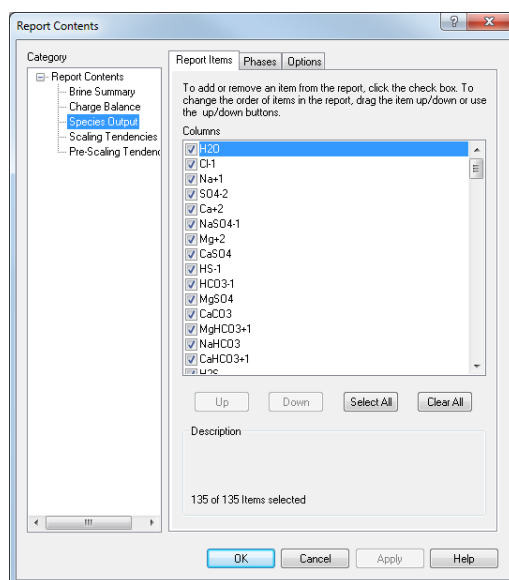
Figure 18-9 Displaying the Expanded Species lists

The complete list of the expanded ions can be found in **Chapter 15 ScaleChem Chemistry.**

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.
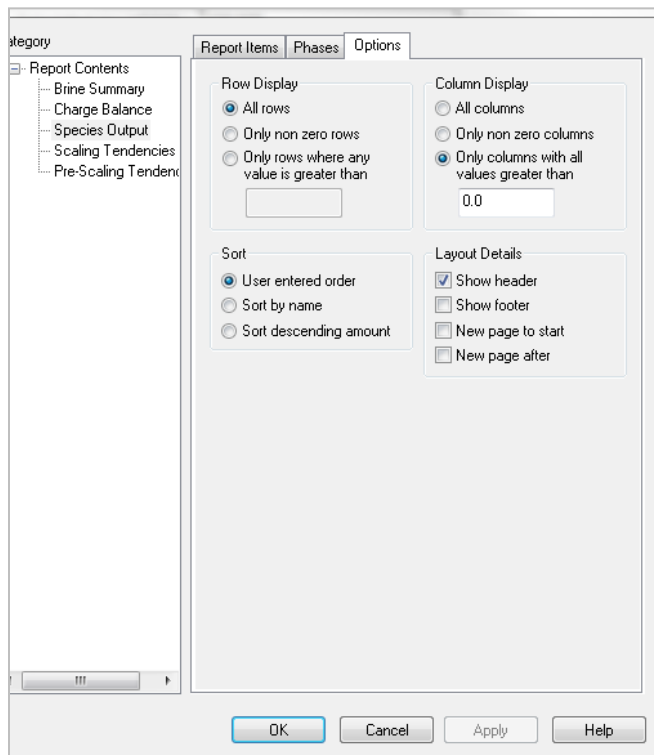
Figure 18-10 Water Analysis with zero values masked

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.

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.

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.

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.

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 <u>T</u>ools… <u>O</u>ptions 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 <u>T</u>ools.. <u>O</u>ption 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.
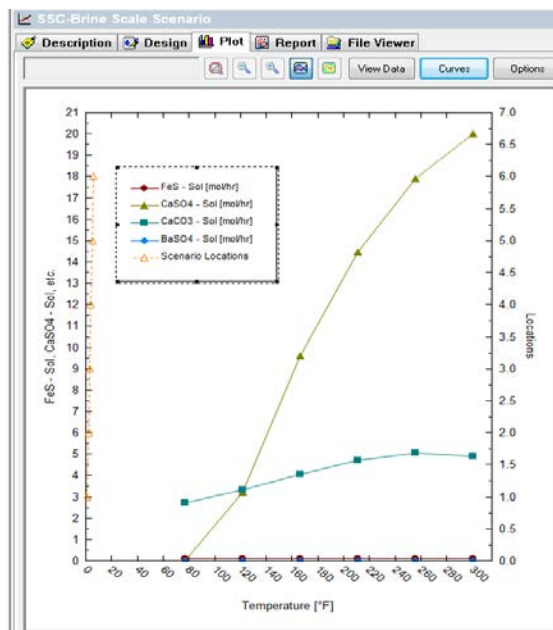
Figure 18-15 Displaying the Default plot

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	Y axis variable
If the temperature varying, use Temperature else if Pressure varying, use Pressure else use Case number or Mix Ratio	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.
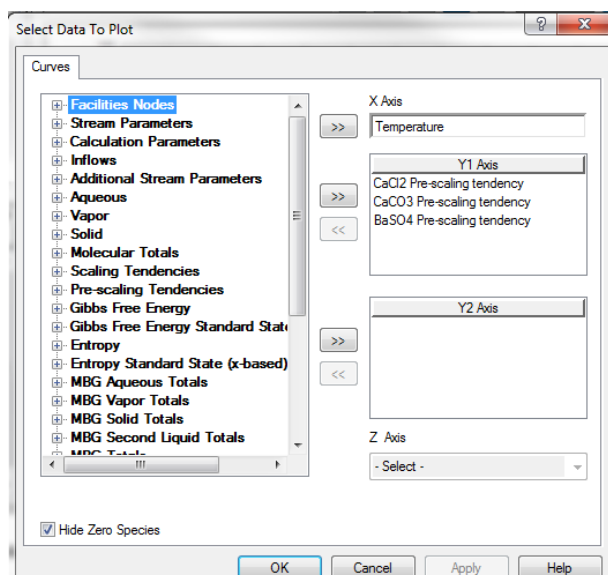
Figure 18-16 Selecting Data

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 corrosion rate 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:

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 $^\circ$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.
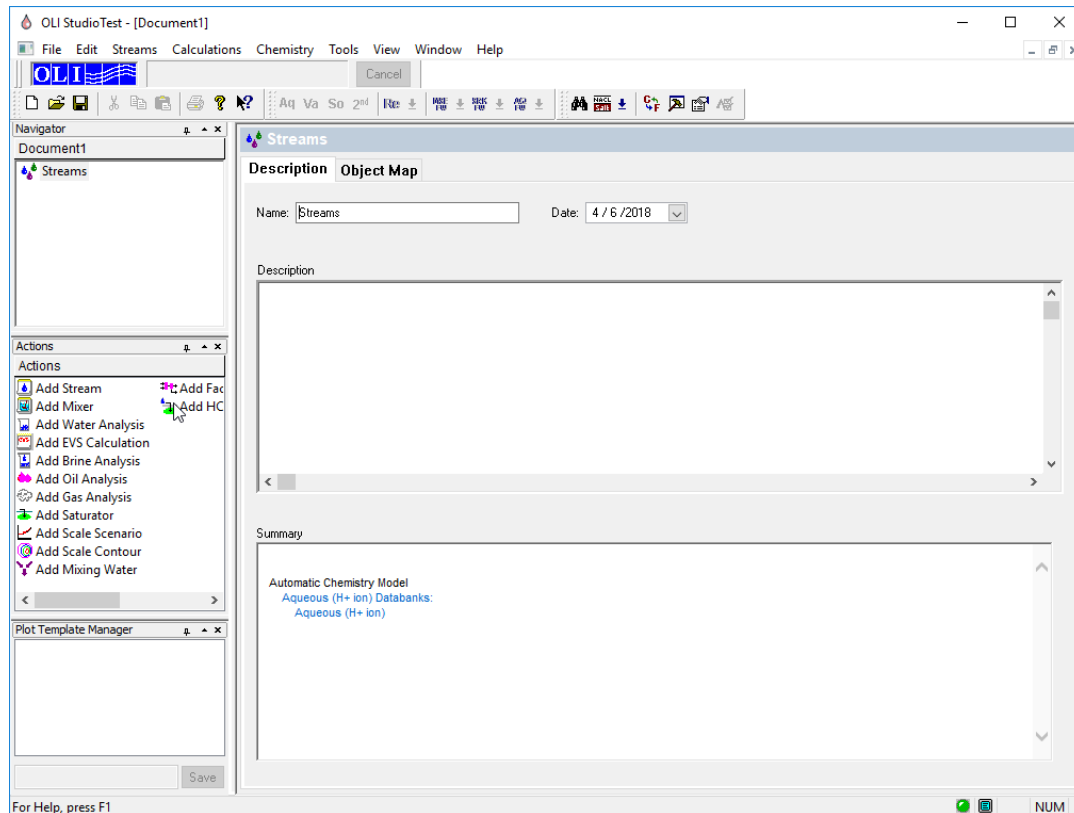
Figure 20-1 The OLI Studio main window.

- *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.
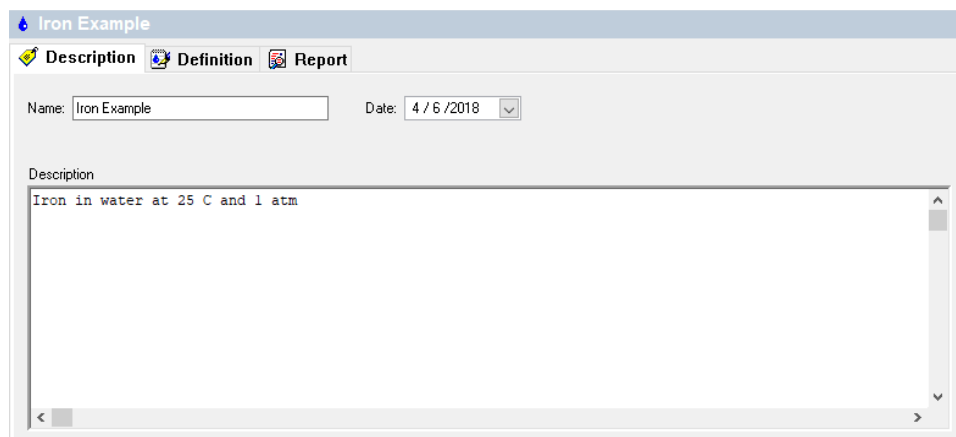
Figure 20-2 The Description tab.

- 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.
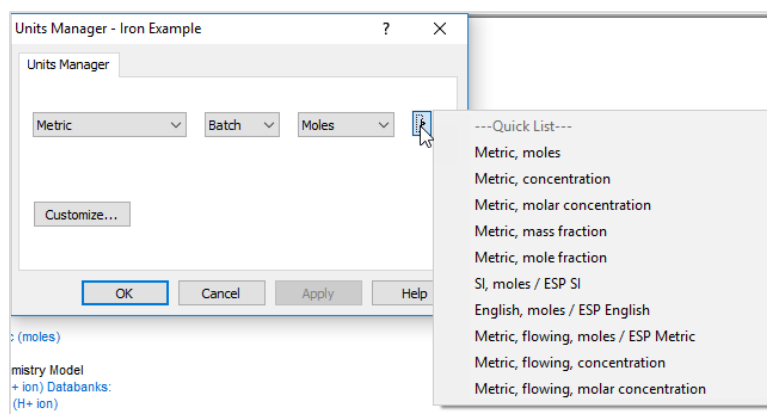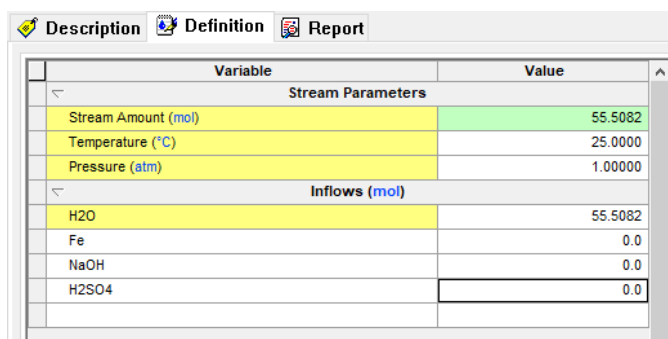
Figure 20-3 Units Manager

Enter *Iron, Sodium Hydroxide* and *Sulfuric Acid* to the grid as shown in Figure 20-4[46].

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.
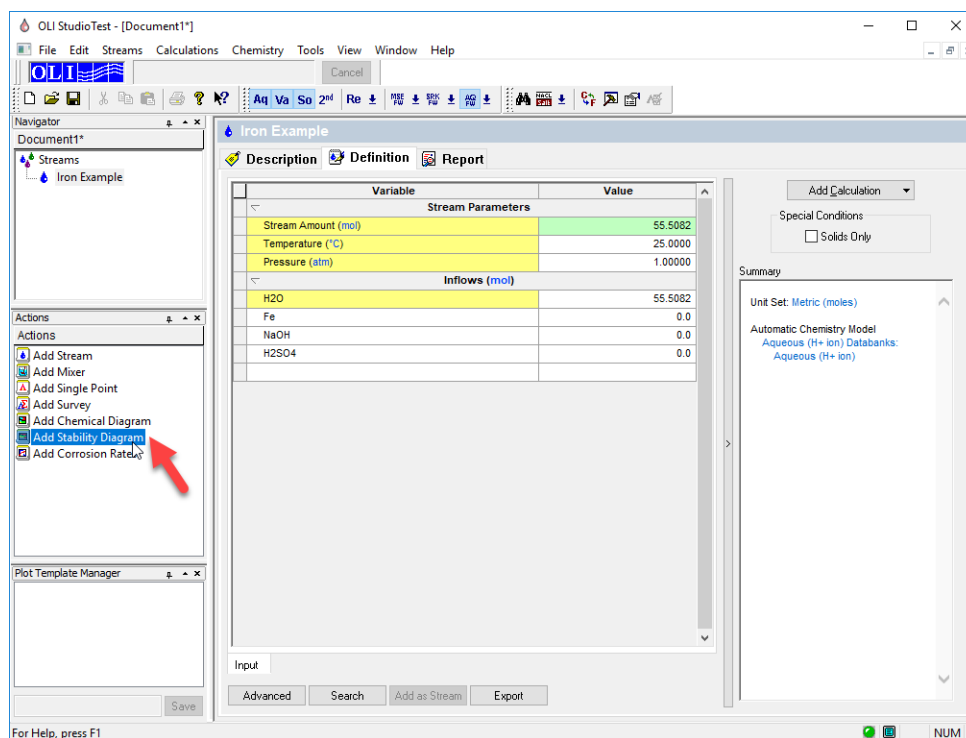
Figure 20-5 Adding a stability diagram.

---

[46] Depending on the settings for names manager, the displayed names may be formulas or names.

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**
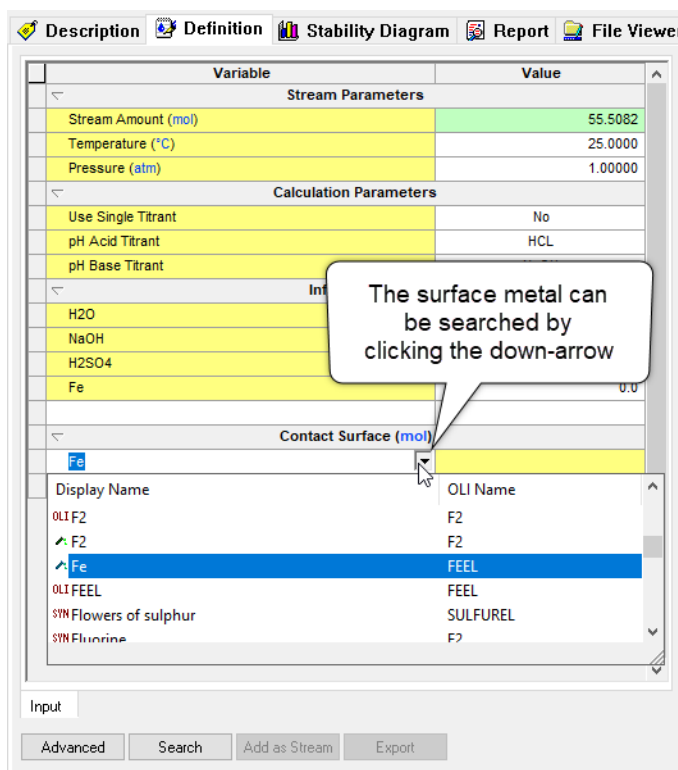
Figure 20-6 The stability diagram Definition tab.

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.

- Click on the **Display** category. Look for the **Display Choices** section.
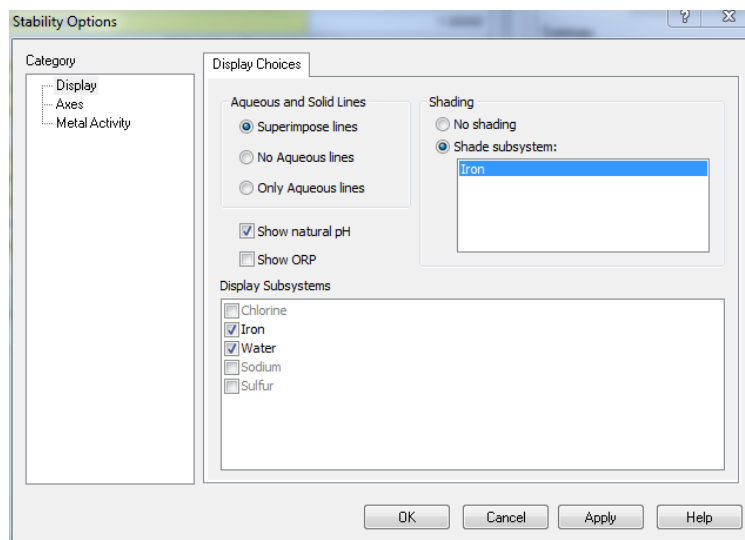
Figure 20-7 Selecting displayed subsystems (using defaults)

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 has some control over how the stability diagram will display. In this case we will accept the defaults.

- Click **OK**
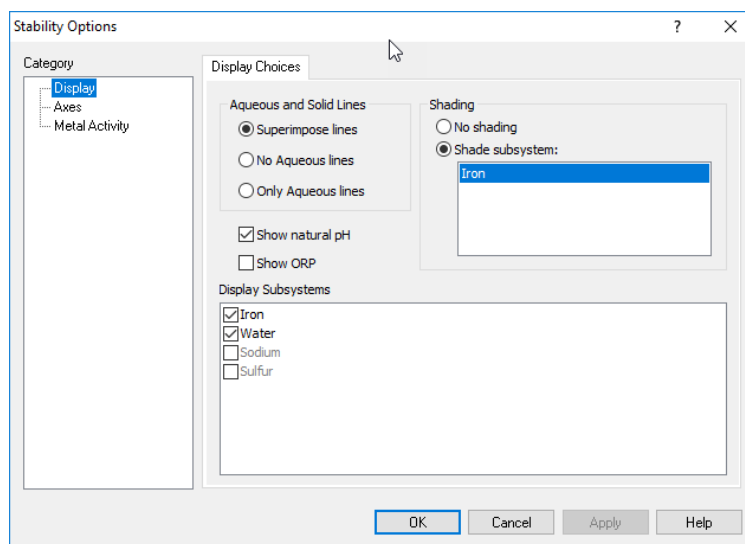
Figure 20-8 The X-variable Tab

- Click on the **Axes** category. Choose the **Select** radio button in the **Titrants** section. This will enable the **pH Titrants** button.
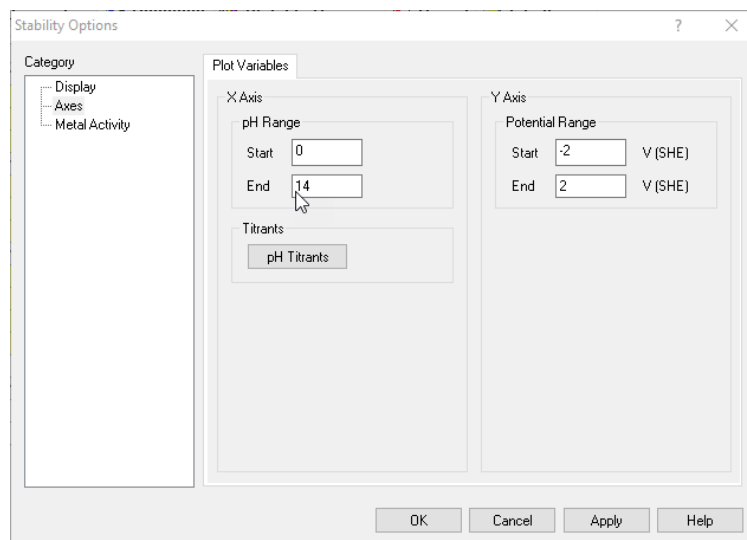
Figure 20-9 enabling the titrants button.

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
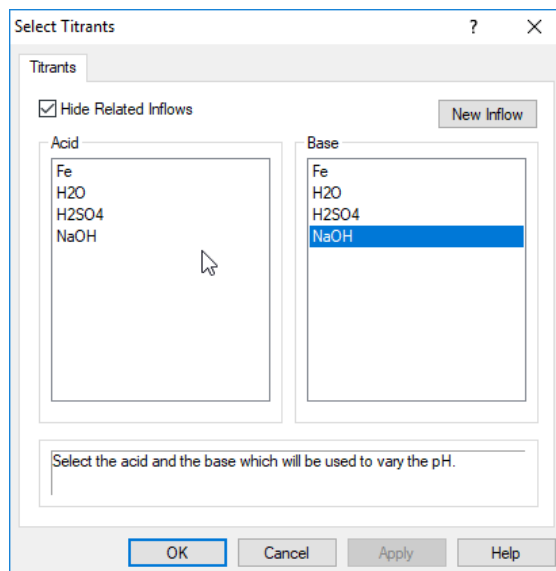
Figure 20-10 Selecting sulfuric Acid and sodium hydroxide as titrants

- Click on the **OK** button.

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 ºC and 1 atm. These diagrams are also referred to as Pourbaix diagrams.[47]
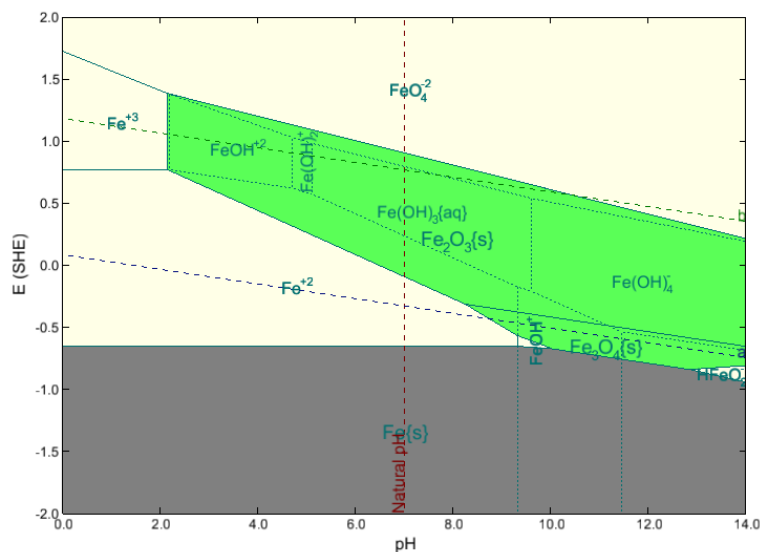
Figure 20-11 The finished stability diagram

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[47] Marcel Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions". Translated from the French by James. A. Franklin. Pergamon Press, Oxford (1965).

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^0, 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.

- 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.
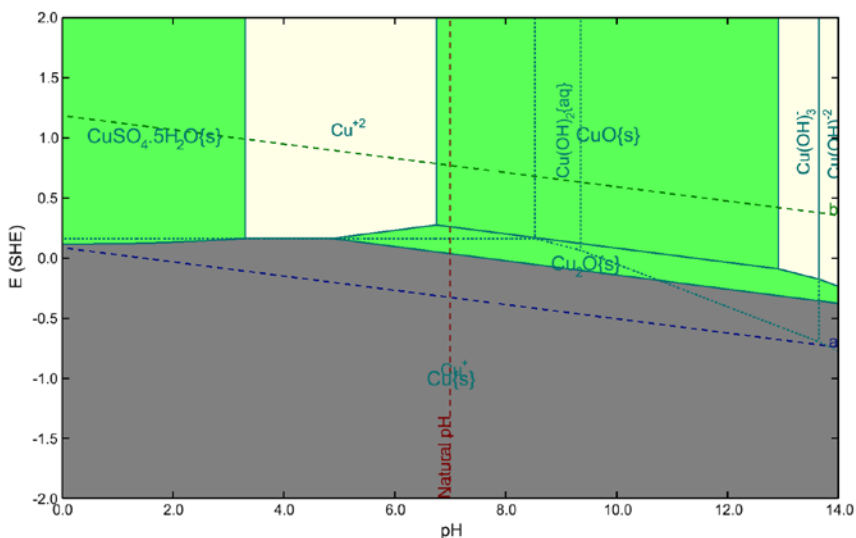
Figure 20-12 Stability diagram for Copper

Features of real-solution stability diagrams, as the one shown in *Figure 20-12 Stability diagram for Copper*.

- 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 more 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.
5. Determination of predominance areas.

Construction of equilibrium equations

For each pair of species X and Y in a particular redox subsystem:

$$\nu_X X + \sum_{i=1}^{k} \nu_i A_i = Y + \nu_e e^-$$
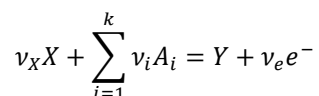
where:

A_i – basis species

General Formula:

$$X \equiv M_{X_1} H_{X_2} O_{X_3} C_{X_4} D_{X_5} E_{X_6}$$

$$Y \equiv M_{Y_1} H_{Y_2} O_{Y_3} C_{Y_4} D_{Y_5} E_{Y_6}$$
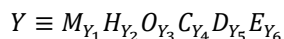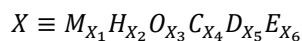
M-element associated with the redox system.

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:

$$X \equiv Cu_{X_1} H_{X_2} O_{X_3} N_{X_4}^{-3}$$

Basis species: H^+, H_2O, $NH_{3(aq)}$

For a system composed of Fe, H_2O and sulfur-bearing species:

$$X \equiv Fe_{X_1} H_{X_2} O_{X_3} S_{X_4}^{-2} S_{X_5}^0 S_{X_6}^{+6}$$

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 activity coefficients to calculate equilibrium lines.

Equilibrium lines for chemical reactions

Affinity of a reaction between X and Y:

$$\frac{A}{RT} = -\frac{1}{RT} \left(\overline{G_Y} - \nu_X \overline{G_X} - \sum_{i=1}^{k} \nu_i \, \overline{G_{A_i}} \right) = \ln K - \left(\ln a_Y - \nu_X - \sum_{i=1}^{k} \nu_i \ln a_{A_j} \right)$$

Construct a discrete function of the independent variable:

$A_p = f(var_p)$, $p = 1...N$

Find the root:

$f(var_0) = 0$

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:

$$E = E^0 + \frac{RT}{Fv_e}\left(\ln a_Y - v_X \ln a_X - \sum_{i=1}^{k} v_i \ln a_{A_i} \right)$$

$$E^0 = \frac{\overline{G_Y}^0 - v_X\overline{G_X}^0 - \sum_{i=1}^{k} v_i \overline{G_{A_i}}^0}{Fv_e}$$

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.*
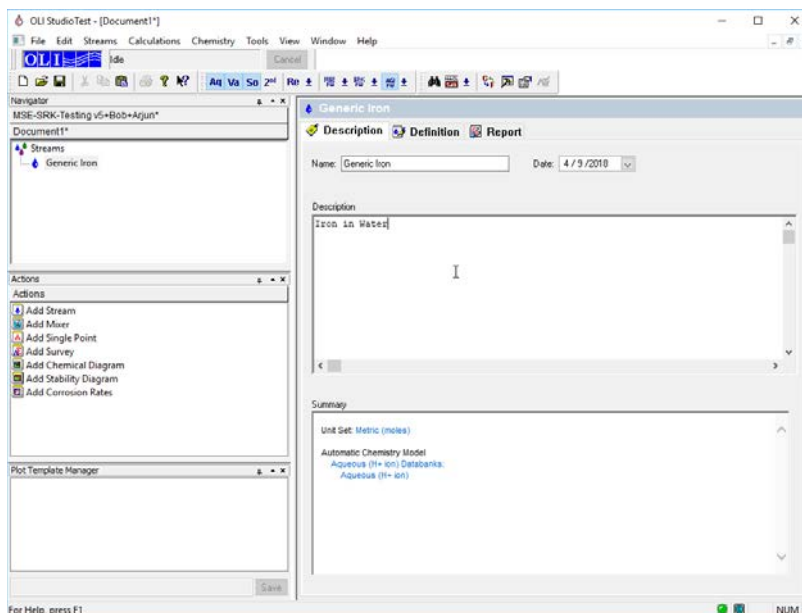
Figure 22-1 The Description tab.

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.
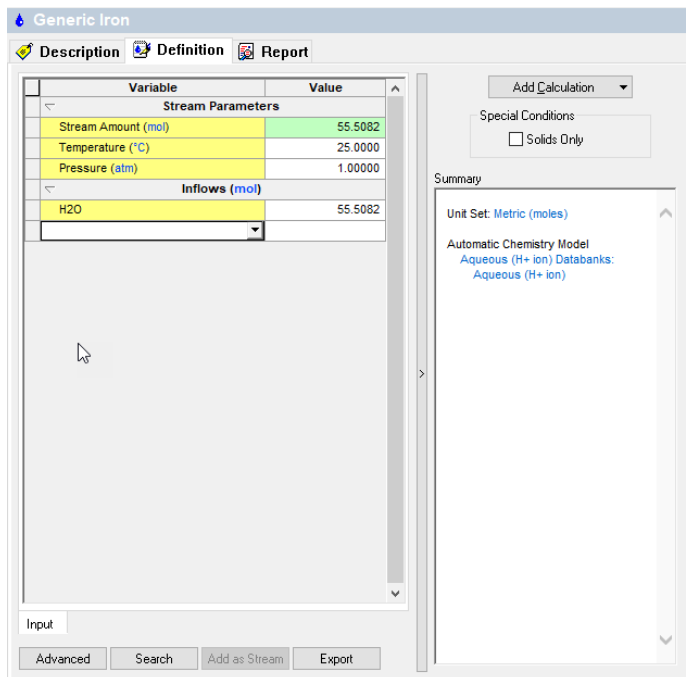
Figure 22-2 Default stream definition grid.

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.
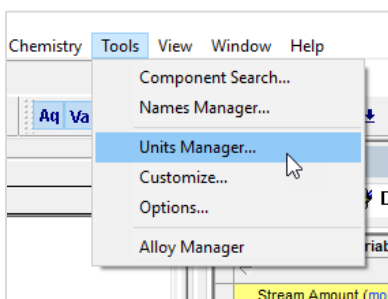
Figure 22-3 Tools Menu

We wish to use metric units. Click the down-arrow in the drop-down list box under the **Standard** radio button.
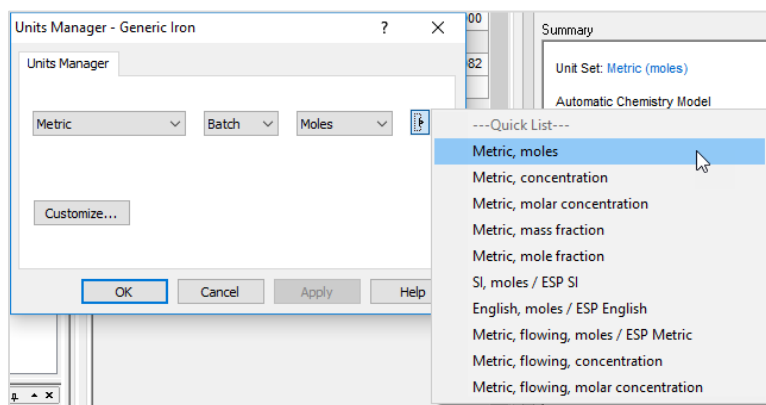
Figure 22-4 Default Units Manager

- Scroll down and select **Metric, moles**.

We now have the correct units for the tour. Enter the following species into the grid:

Fe

NaOH

H₂SO₄

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…**
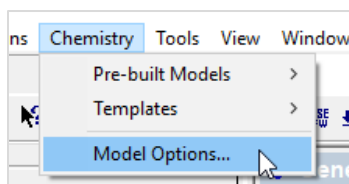
Figure 22-6 Chemistry Menu Items

This will display the model options.

Click on the **Redox** tab.
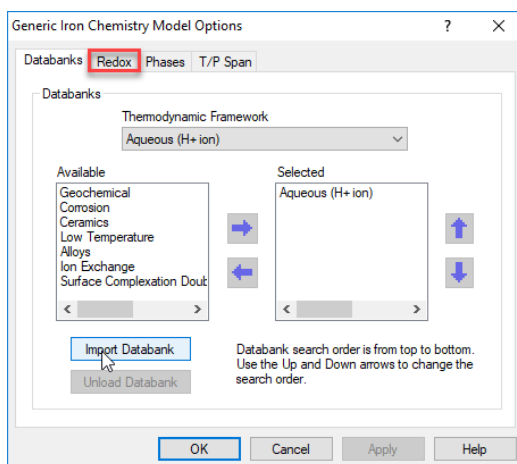
Figure 22-7 Model Options

We will now verify that the iron subsystems have been selected.
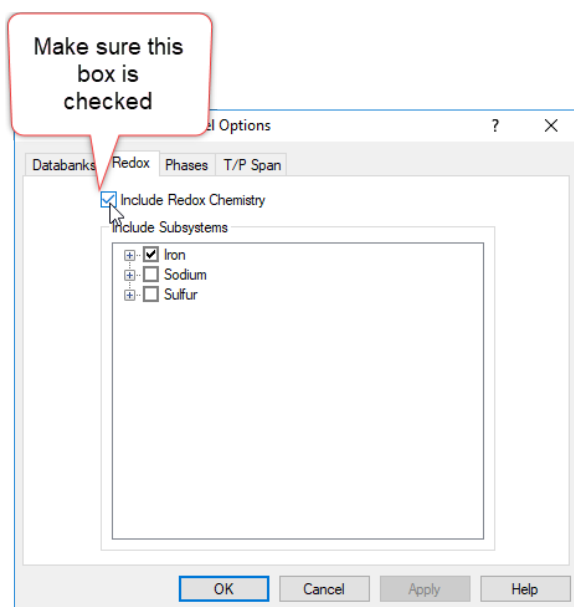
Figure 22-8 The selected redox subsystems.

Another way to make sure Redox is turned on is look at the top toolbar. Re button should be selected.
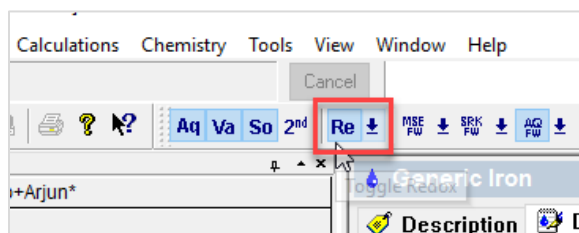
Figure 22-9 Shortcut to switch Redox On

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 **Actions** panel.

You can enter descriptive information if you want. Otherwise, click on the **Definition** tab.

Table 22-1. Changing 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	
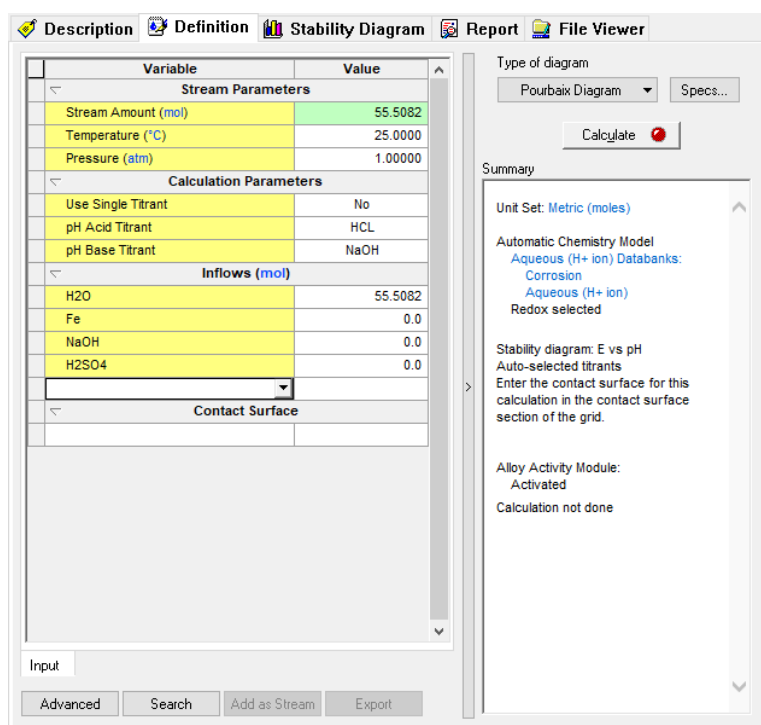
Figure 22-10 Diagram Definition

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)
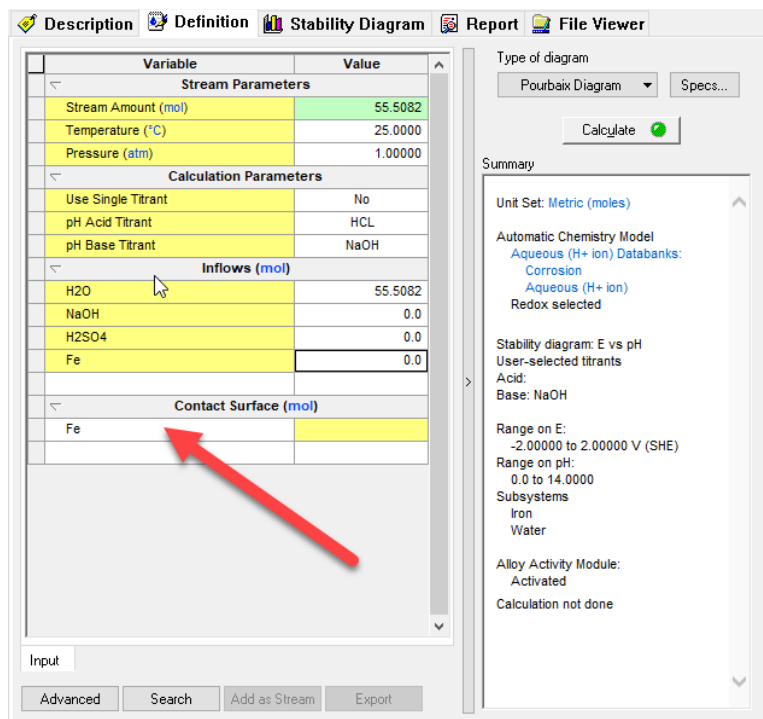
Figure 22-9 Adding Fe to the Contact Surface list.

- Click on the **Specs…** button to fill out the remaining information.

- Click on the **Axes** category.
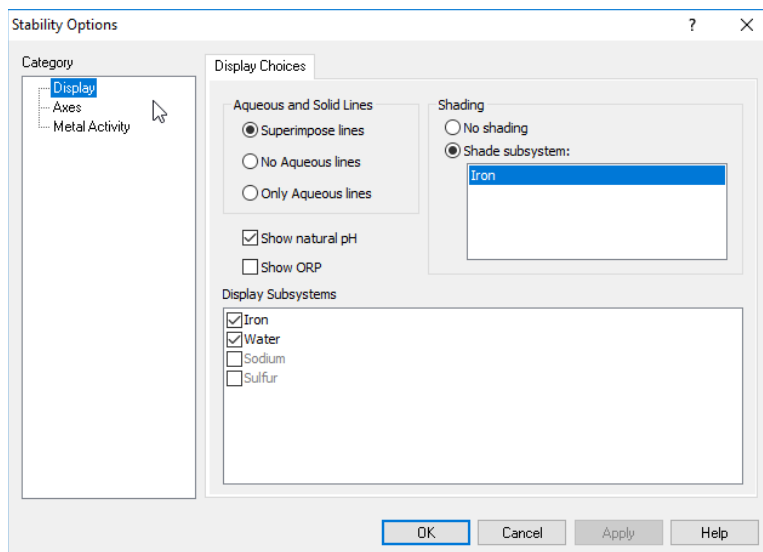
Figure 22-10 Select Titrants

- Choose the **Select** radio button in the **Titrants** box. This will enable the **pH Titrants** button.

We now need to select an acid and a base. Select *H₂SO₄* as the acid (Sulfuric Acid) and *NaOH* as the base (sodium hydroxide).
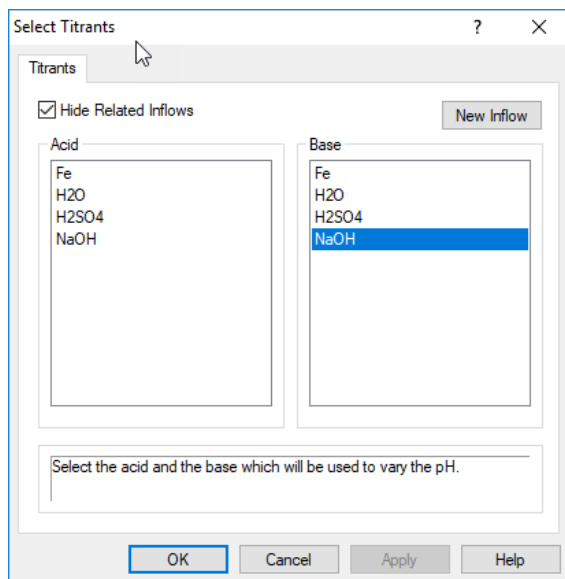
Figure 22-11 Choose an acid and base

Click OK

The Y-Variable specifies voltage (E) as the variable; we wish to continue using it so will skip the category.

Click on the **Display** category.
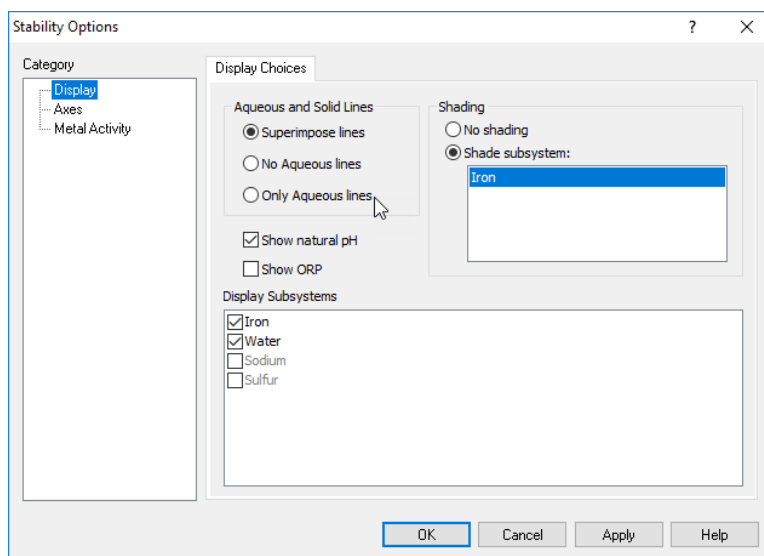
Figure 22-12 Make sure the Sulfur subsystem is unchecked.

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.
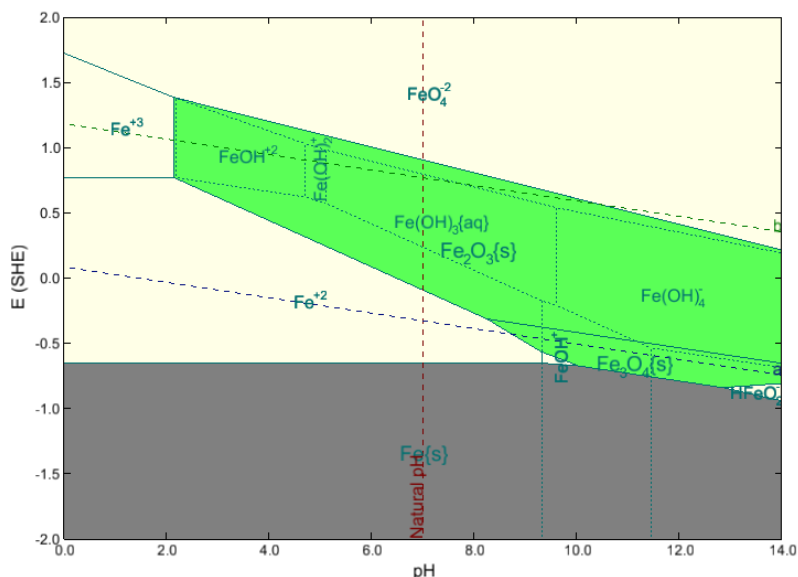
Figure 22-13 A Pourbaix diagram for iron

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_2O 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 H₂S** to the stream.

- Click on the **Definition** tab.

In the grid, add hydrogen sulfide (H₂S) to the stream at a rate of 1.0000E-04 moles.
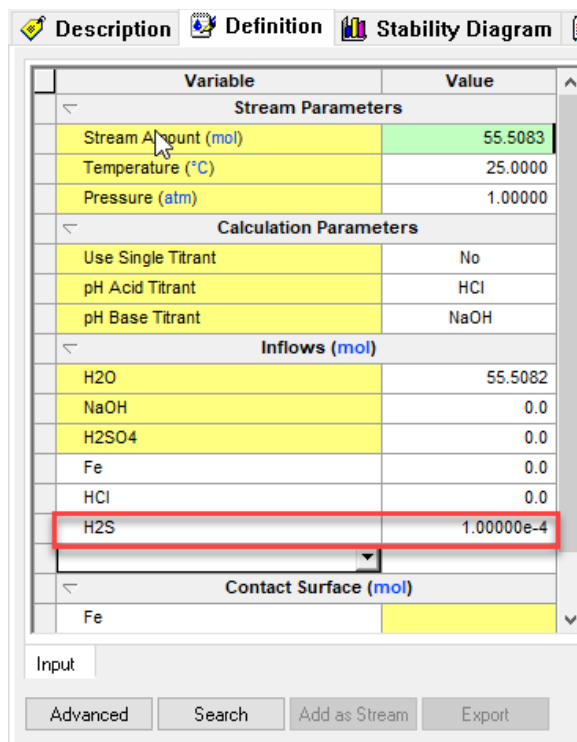
Figure 22-14 Add Hydrogen Sulfide

- 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.
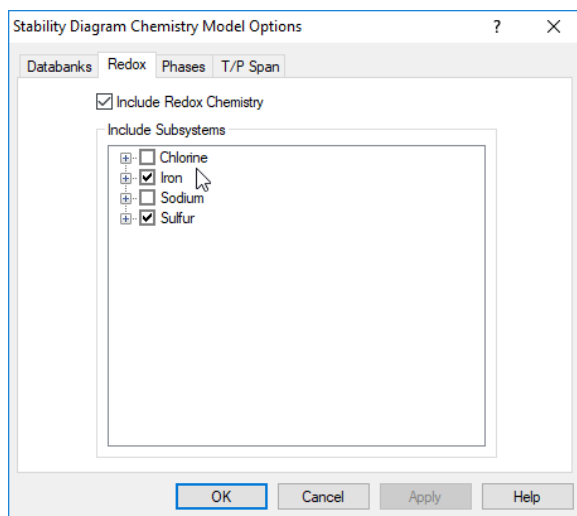
Figure 22-15 Enabling the sulfur redox subsystem.

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.
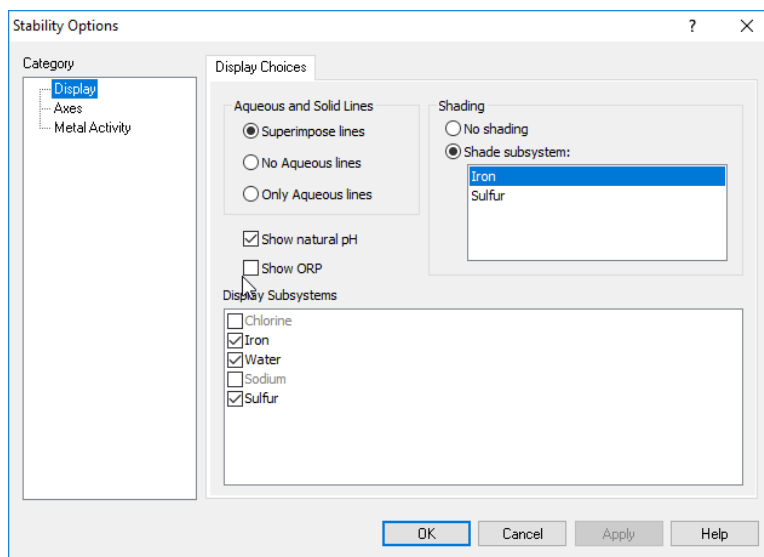
Figure 22-16 Turn on display on for Sulfur.

- Click the **OK** button

Click the Calculate button when you are ready. When the calculation finishes, click the **_Stability Diagram Tab_**.
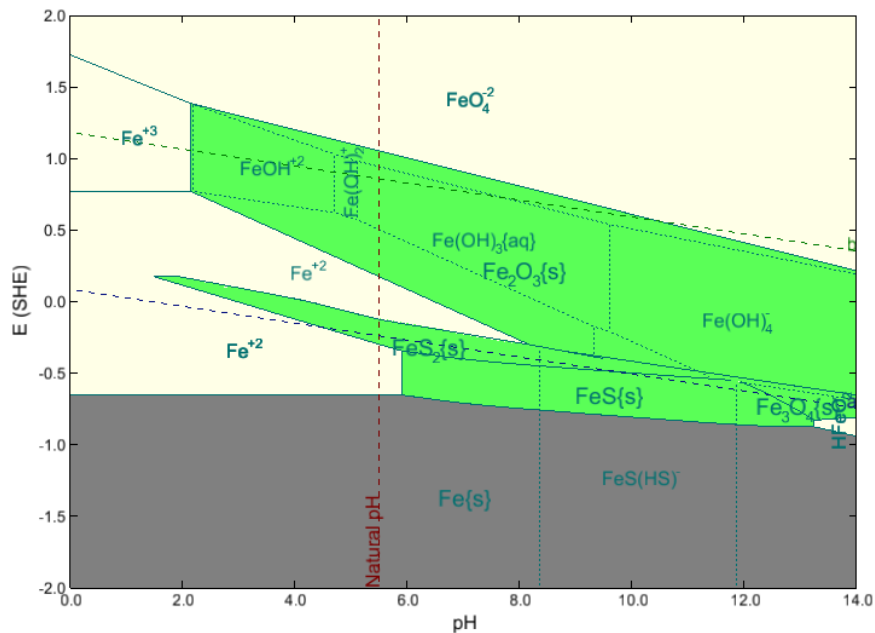
Figure 22-17 The stability diagram with Sulfur.

Inspection of the diagram reveals a profound effect of H$_2$S 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$_3$O$_4$ (magnetite) in the absence of H$_2$S. This has important implications for corrosion in refinery installations, where H$_2$S 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:

Figure 23-1 The stream definition.

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?[48]
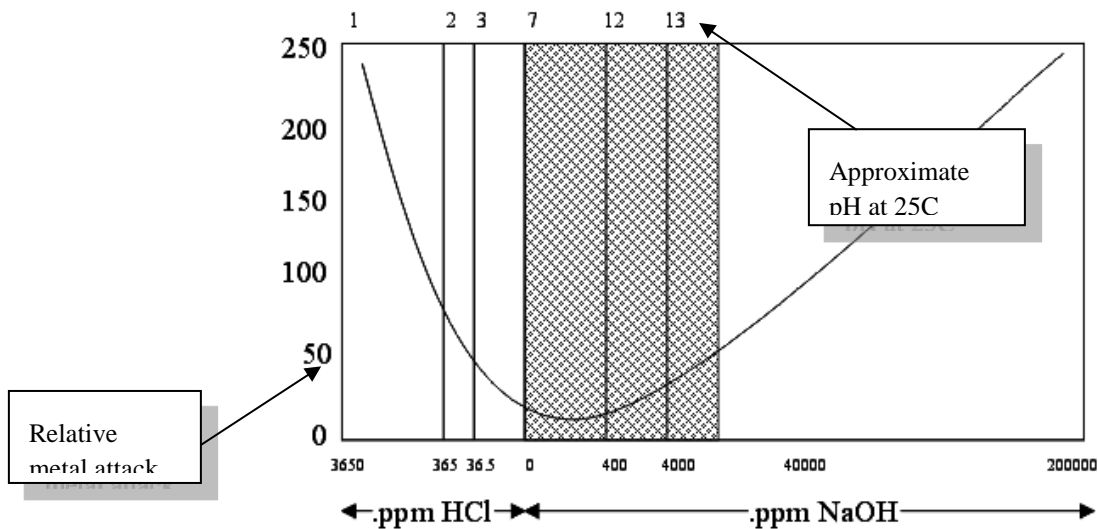
Figure 23-4 Relative metal attack v. pH and titrant concentration

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[48] 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)

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 (ºC)	50	
Pressure (atm)	1	
H2O (mol)	55.5082	Default Value
Acid Titrant	HCl	No initial value
Base Titrant	DEA[49]	No Initial Value
C8H18 (mol)	2E-07	
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:

---

[49] The "ESP" name for this species is DEXH, which can be used as an input to make your life easier. The formula name is: $HN(C_2H_4OH)_2$

Figure 23-5 Stream input grid.

Create a stability diagram as in previous chapters

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 that Sulfur is checked in the **Redox** section of the chemistry model options.
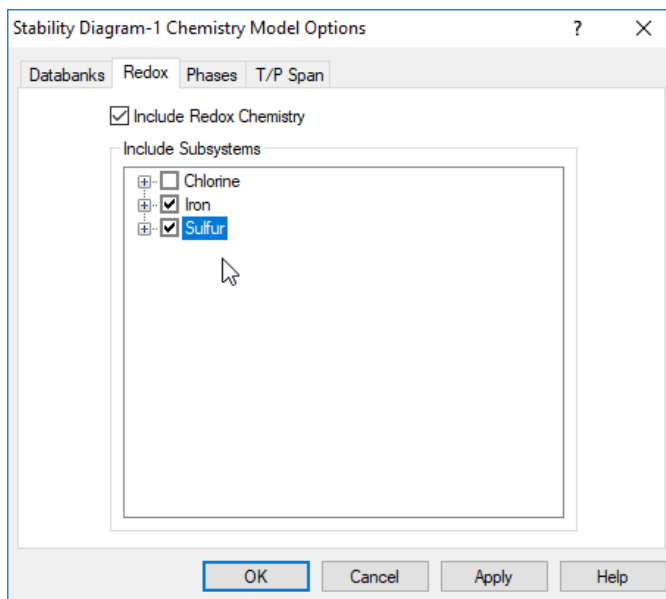
23-7: Selecting the redox subsystems from the chemistry model options.

- Click the **Calculate** button when you are ready. When the calculation finishes, click on the **Stability Diagram** tab.
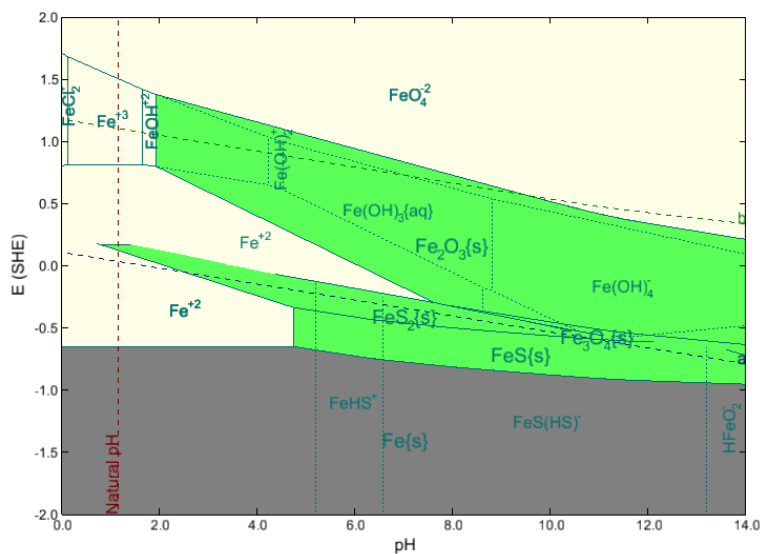
Figure 23-8 The stability of iron in DEA solutions.

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:

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.
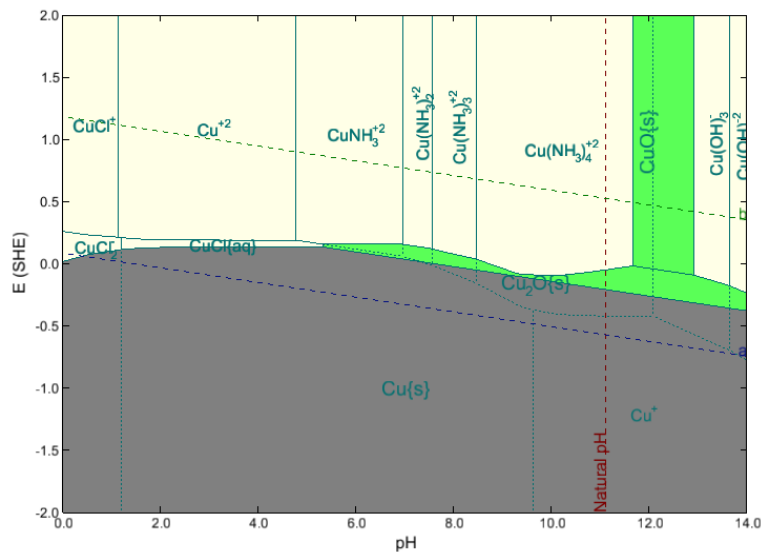
Figure 24-3 The effect of adding 0.1 moles of ammonia on the stability diagram.

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*.
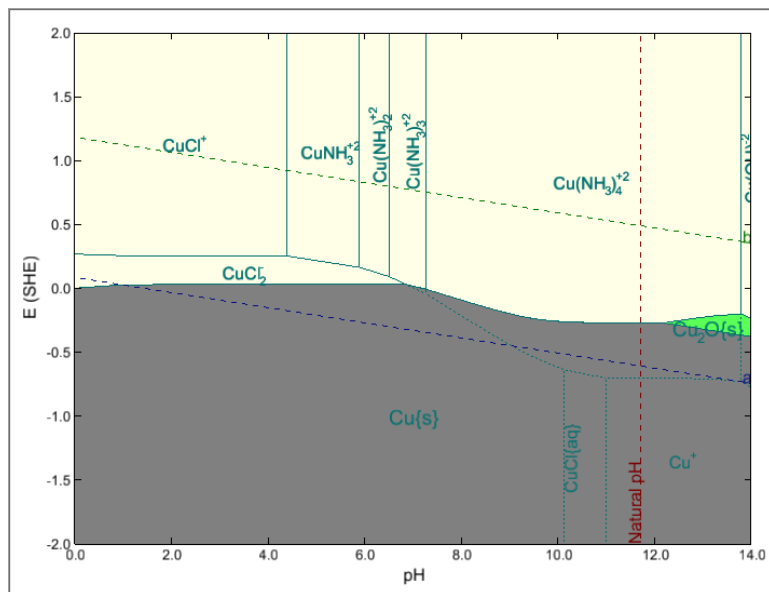
Figure 24-4 The effect of adding 1.5 moles of ammonia on the stability diagram.

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 (ºC)	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:

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:
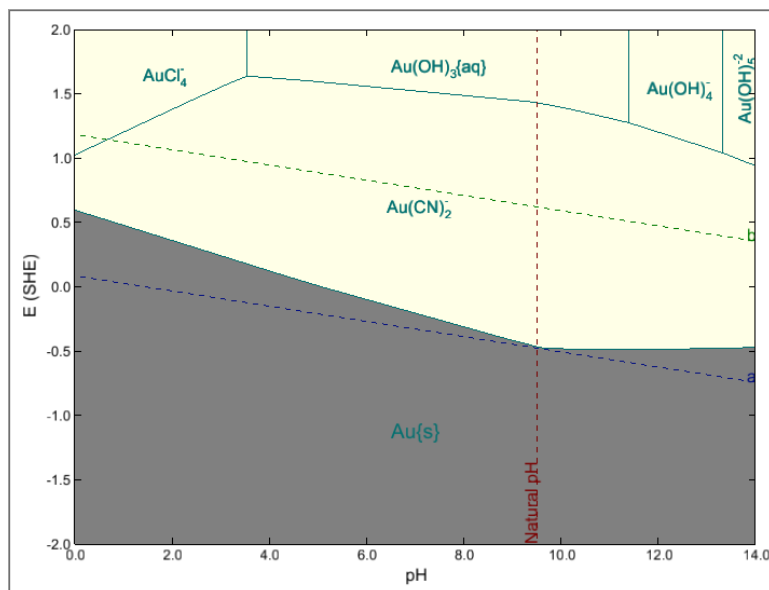
Figure 24-7 The effect of adding 1.0E-04 moles of NaCN on the stability diagram.

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.

The filled-out definition for the stability diagram should look like the following figure:
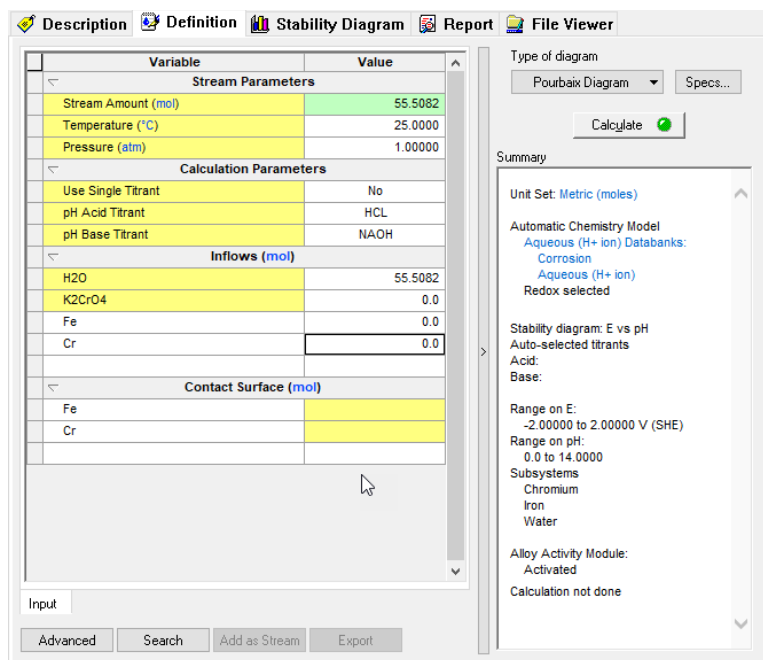
Figure 25-1 The filled-out grid. Note that two metals are used.

Use the **Chemistry** model item and **Model Options > Redox** to ensure that Chromium and Iron are selected in the **Included Subsystems** list.
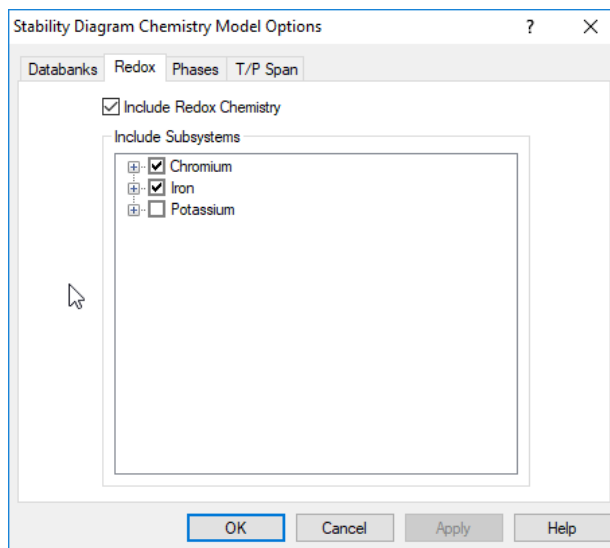
Figure 25-2 Selecting subsystems.

We want to shade the chromium subsystem instead of the default iron subsystem. Click the **Specs…** button and then select the **Display** category**.**
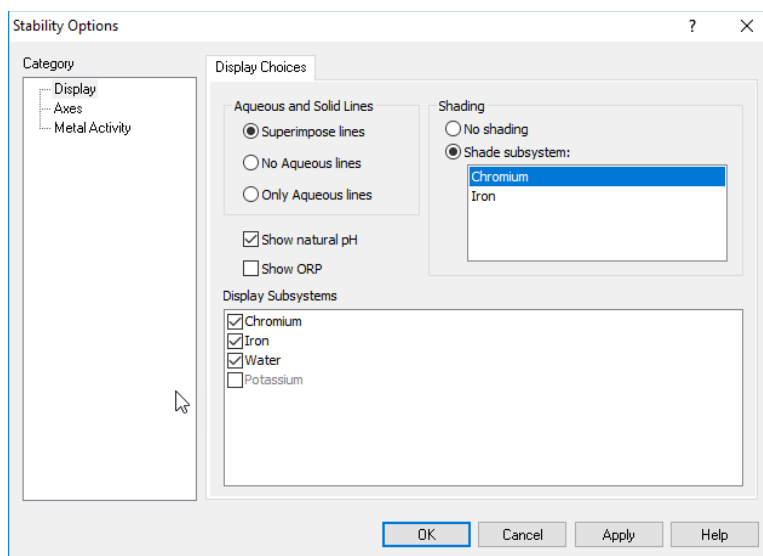
Figure 25-3 Selecting chromium to be shaded.

- Click on the **OK** button, and then click **Calculate**. When the calculation has finished, click the **Stability Diagram** tab.
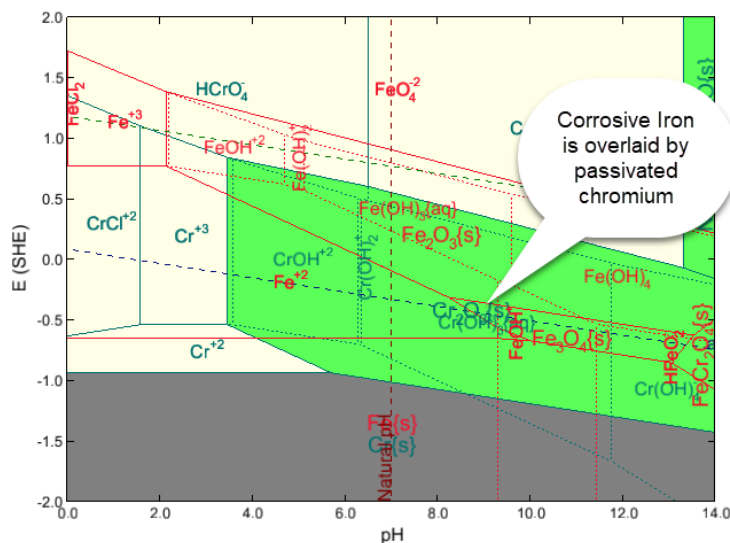
Figure 25-4 The stability diagram with both iron and chromium.

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:

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.
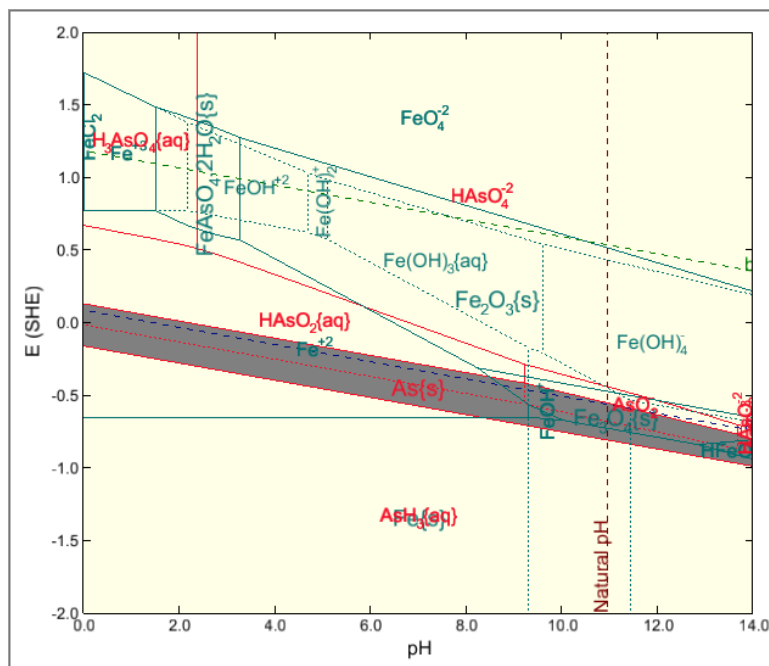
Figure 25-6 Iron with arsenates, arsenates are shaded

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* and the reduction of arsenates to elemental *As.* This promotes the deposition of a protective layer of *As*. This can only work in reducing environments; otherwise the protective layer of *As* will oxidize and dissolve.

You can download a worked example of this chapter from the OLI Wiki Page.

26. Implications of Stability Diagrams on Cathodic Protection

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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 °C
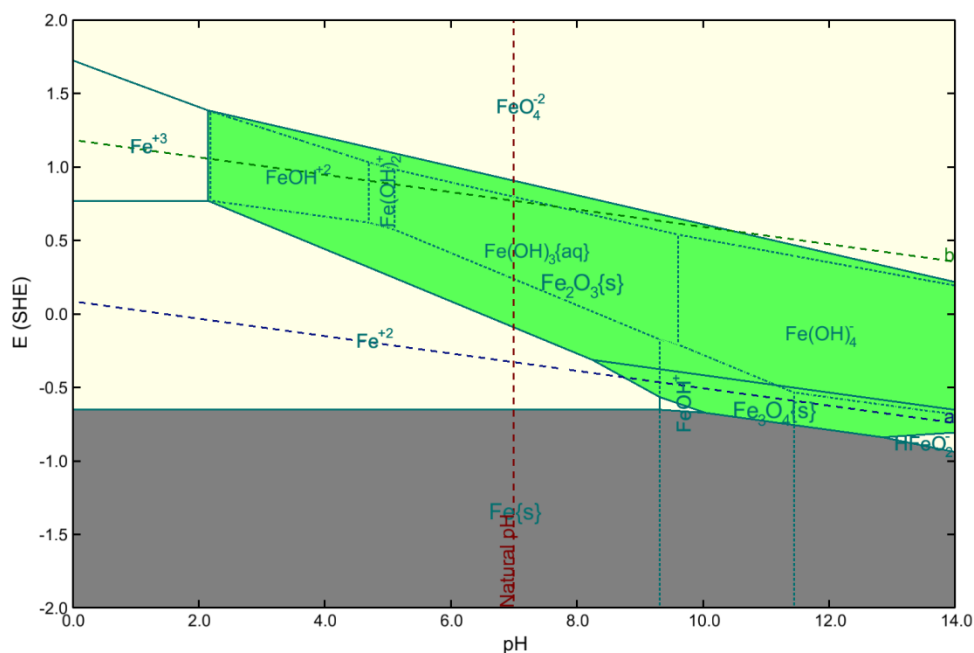
Figure 26-1 Iron in water at 25 °C and 1 Atm.

In the whole pH range, cathodic protection will require shifting the potential to moderately negative values.
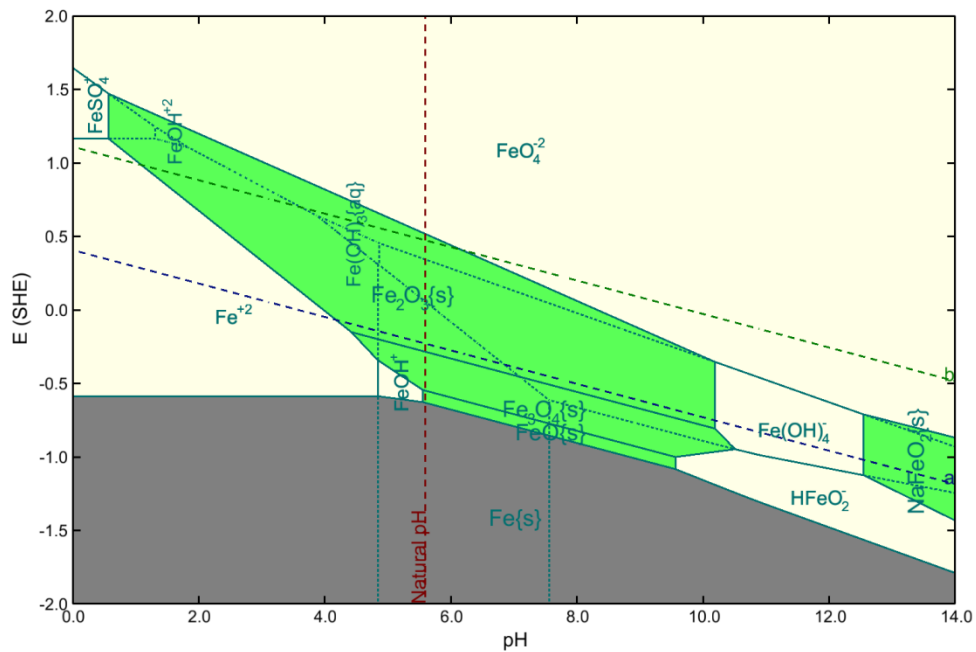
Figure 26-2 Iron in water at 300 °C and 100 atm.

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 Chapter 22 for details on how to create this stream. In Figure 27-1 we have created the input for our standard Iron stability diagram.

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[50].
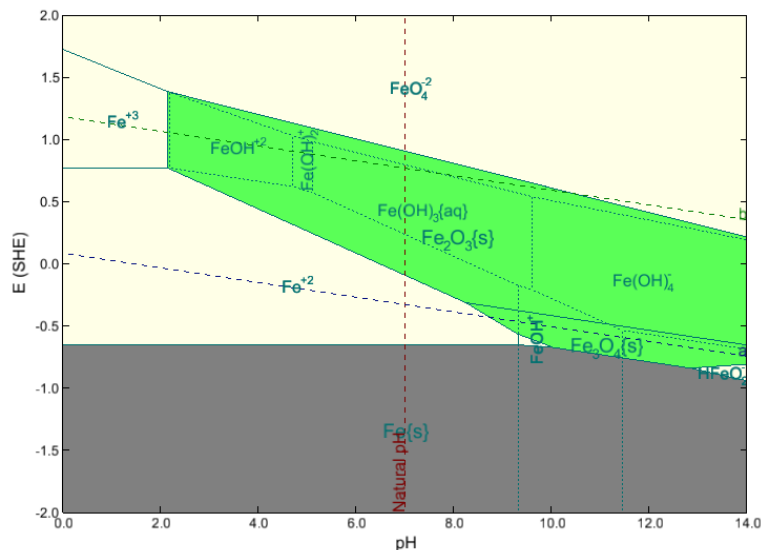
Figure 27-2 Standard OLI E-pH diagram for Iron

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…**

---
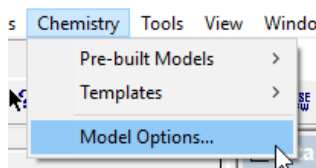
[50] Named after Marcel Pourbaix, who in the 1960's created a series of such diagrams. The latest reference is: Pourbaix, M., Atlas of electrochemical equilibria in aqueous solutions. 2d English ed. 1974, Houston, Tex.: National Association of Corrosion Engineers

Figure 27-3 Selecting Chemistry | Model Options

- Next select the **Redox** Tab.
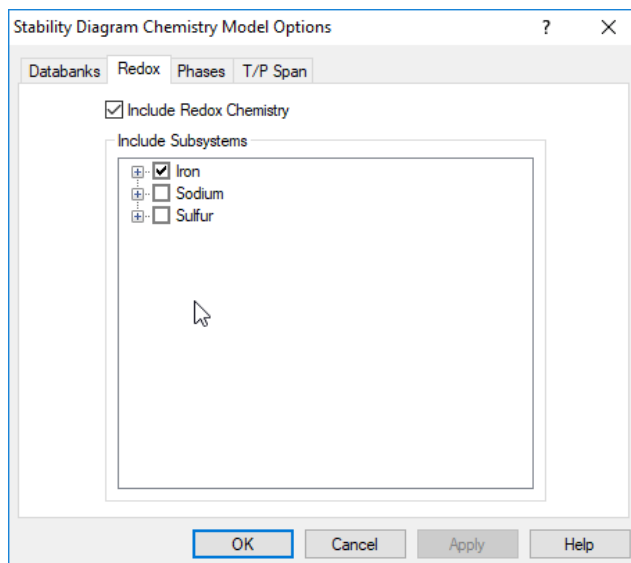
Figure 27-4 Selecting subsystems

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.
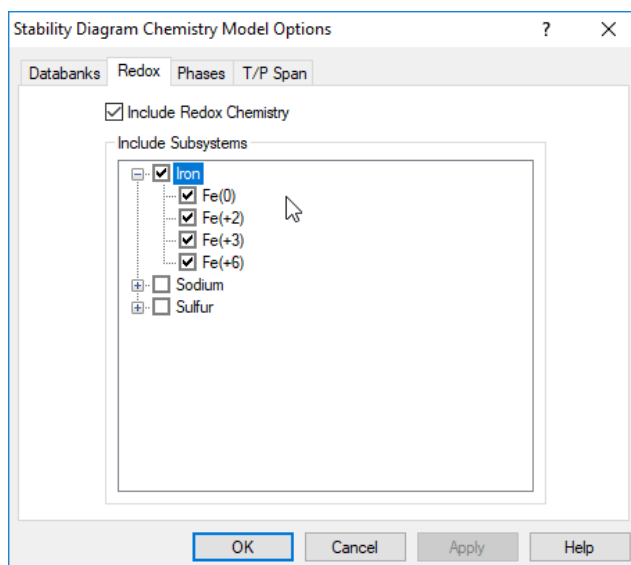
Figure 27-5 Expanding the individual oxidation states

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.
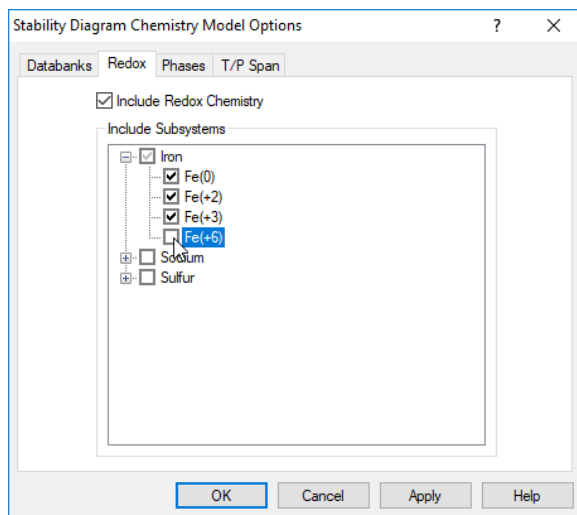
Figure 27-6 Unchecking the Fe(+6) oxidation state

- 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.
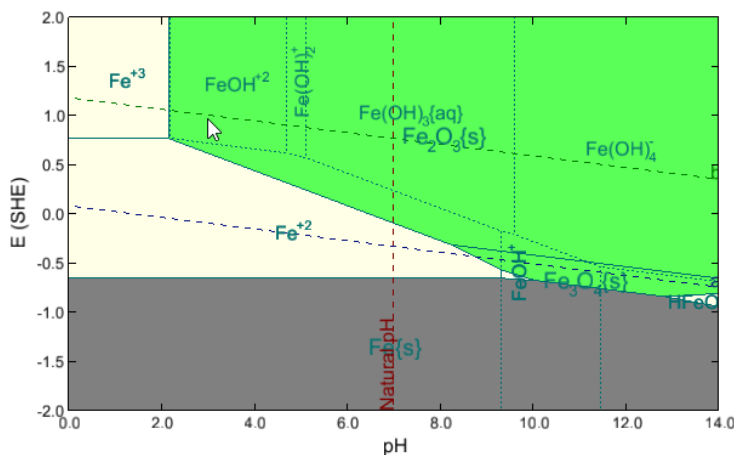
Figure 27-7 A more traditional Pourbaix diagram

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[51] 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.

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[51] These species are subject to change with time, most-likely to increase in number

---

pH Survey

This calculation is analogous to the pH Survey found in other OLI Studio components. The specification requires a titrant acid and base.

Temperature Survey

A survey in temperature can be performed. The default range is from 25 to 100 °C. Any range may be used by changing the **Range** option.

The user should consider that some points in the survey may not converge due to phase changes (e.g., boiling off of aqueous liquids).

Composition Survey

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 result.

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

$$i = i_O \, exp \left[\frac{\alpha z F}{RT} (E - E_O) \right]$$

Exchange current density depends on concentrations of active species

$$i_o = i^* a_K^k \, a_L^l \, a_M^m \, ...$$

Reaction orders depend on various mechanisms

$$E_0 = E_0{}^0 + \frac{RT}{zF} \prod a_i{}^{vi}$$

Activities of species that participate in the reaction

$$a_i \ (i = 1, 2 \, ...)$$

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

$$i_{lim} = zk_mF\,a_X\,(bulk)$$

The mass transfer coefficient k_m 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 (ºC)	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:
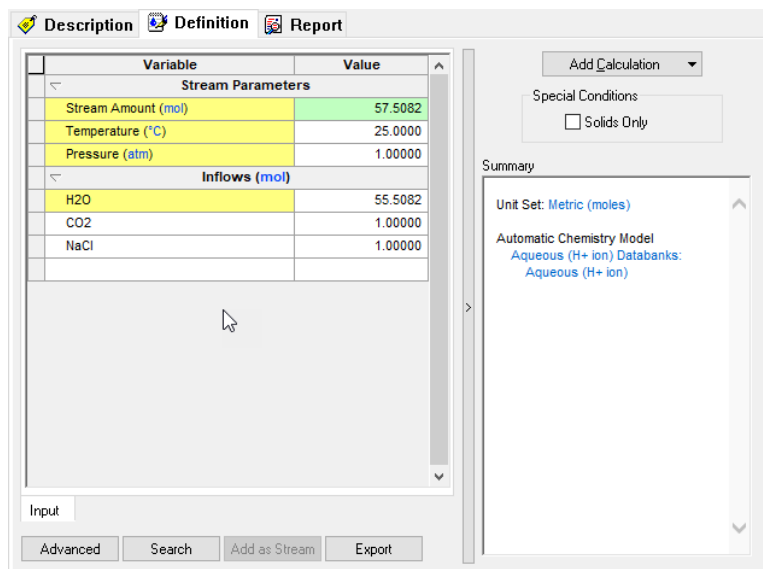
Figure 29-1 The stream definition.

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.
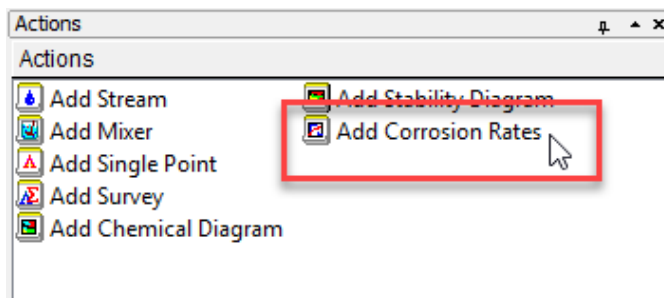
Figure 29-2 Click on the Add Corrosion Rates icon.

- 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. Pressure: 30 atm.

Click on the **Specs…** button. Select the *Var. 1 – Temperature* category.
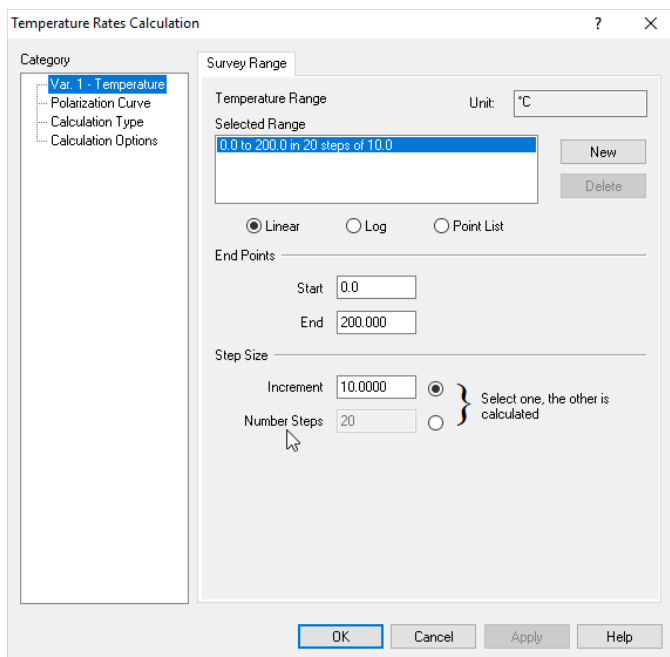
Figure 29-3 Specifying temperature range for the survey.

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.
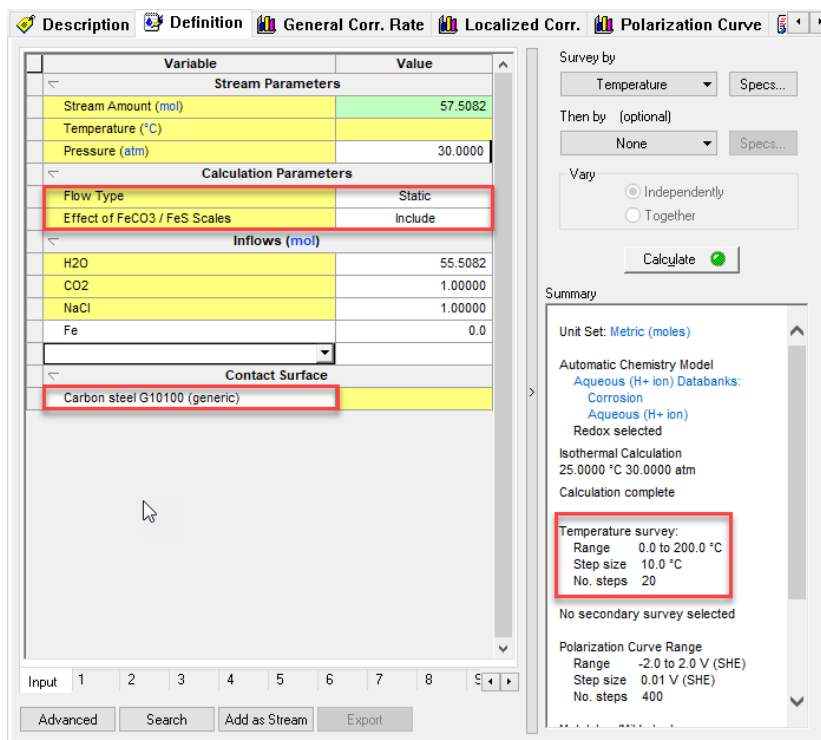
Figure 29-4 Specifying contact surface and flow conditions.

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.
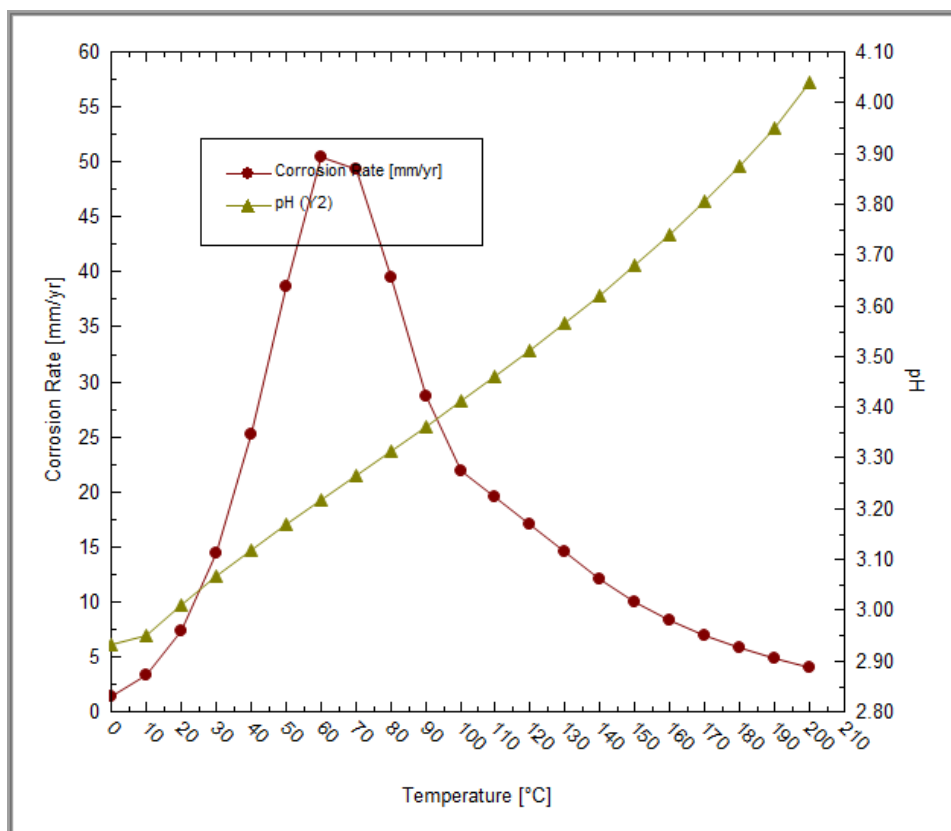
Figure 29-5 The rate of corrosion versus temperature plot.

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)
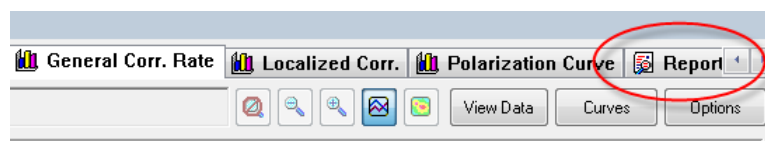
Figure 29-6 Locating Scroll Arrows
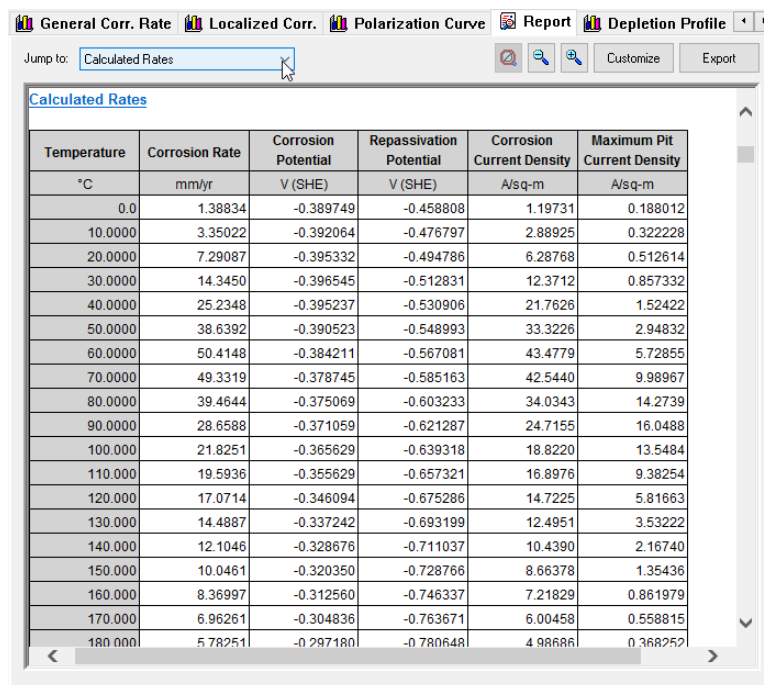
Figure 29-7 Tabulated results

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**
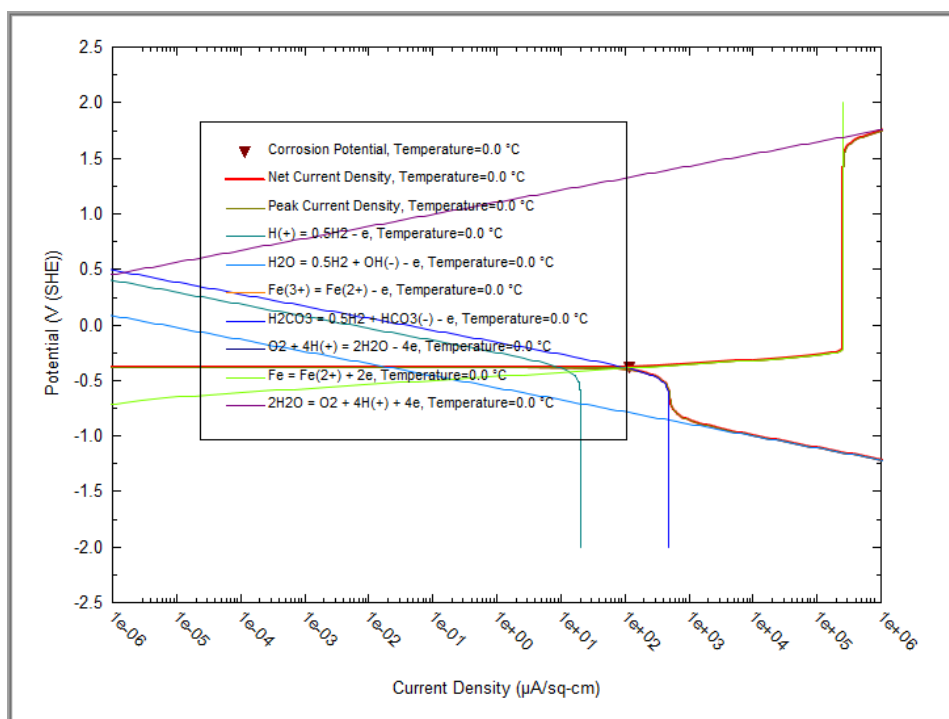
Figure 29-8 Polarization Curve at 0° C

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.*
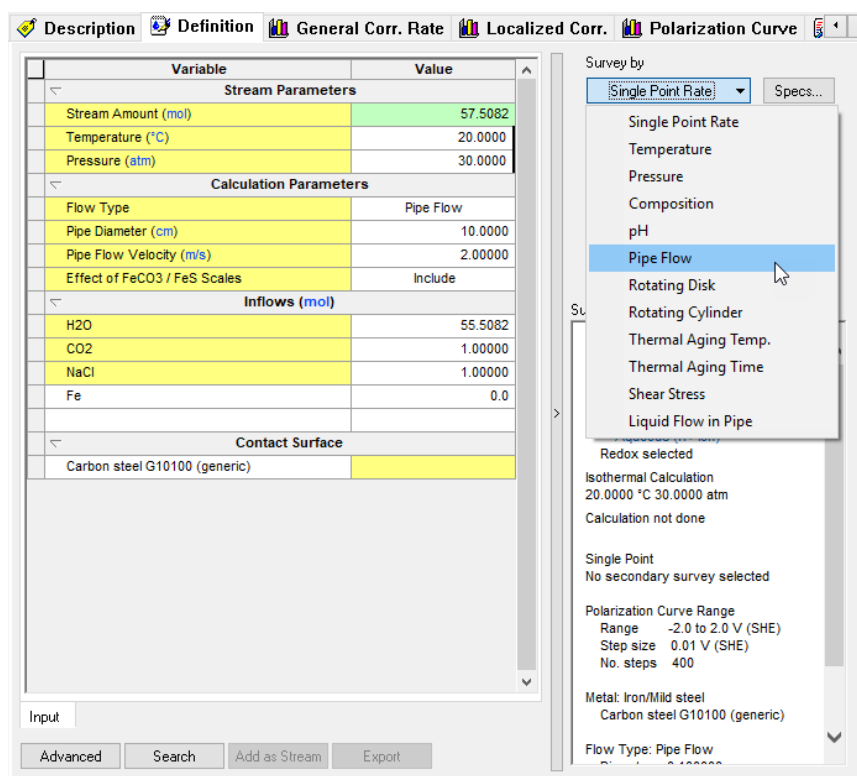
Figure 29-9 Selecting Pipe Flow

The flow specifications entered in the **Corrosion Values** section of the definition grid.

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.
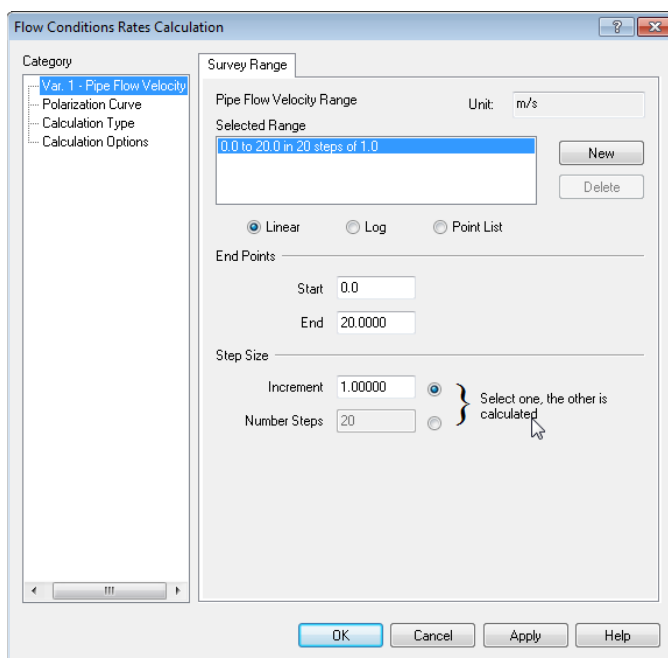
Figure 29-11 Range setting

The range of values indicates the lowest and highest velocity. The radio buttons in the <u>**Step Size**</u> section allow the user to perform quick conversion.

The <u>**Increment**</u> 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.
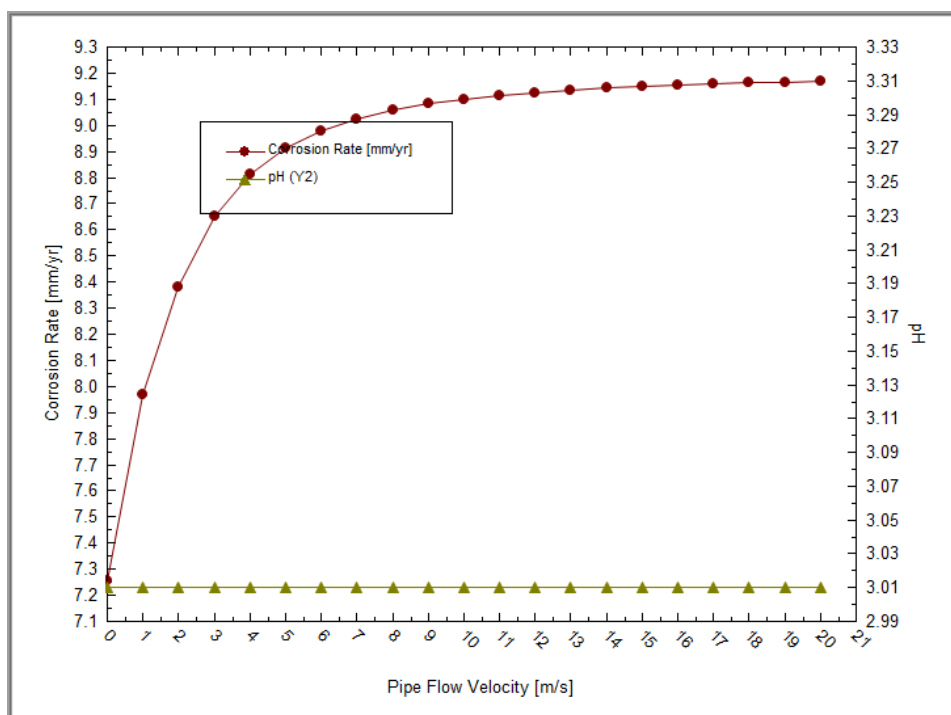
Figure 29-12 The flow survey

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.

(4)

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:
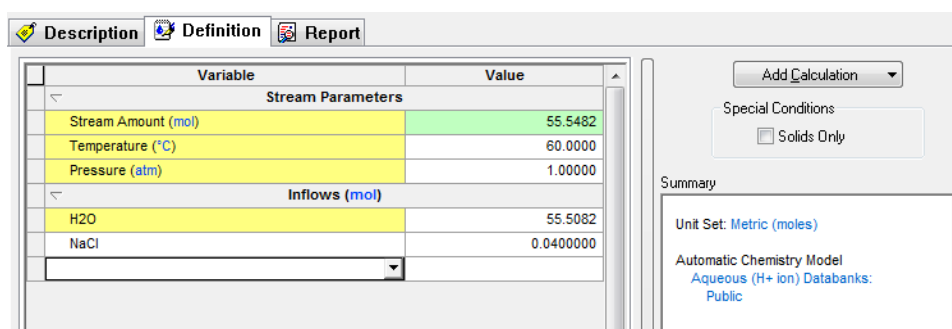
Figure 31-1: The stream definition.

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:

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.
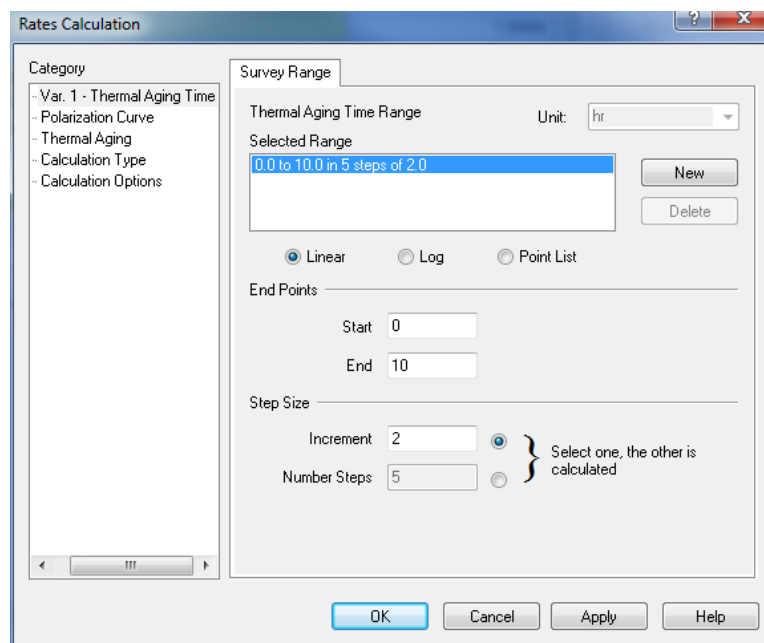
Figure 31-3 Default Thermal Aging Survey Range

- Then, click on the **Thermal Aging** category.
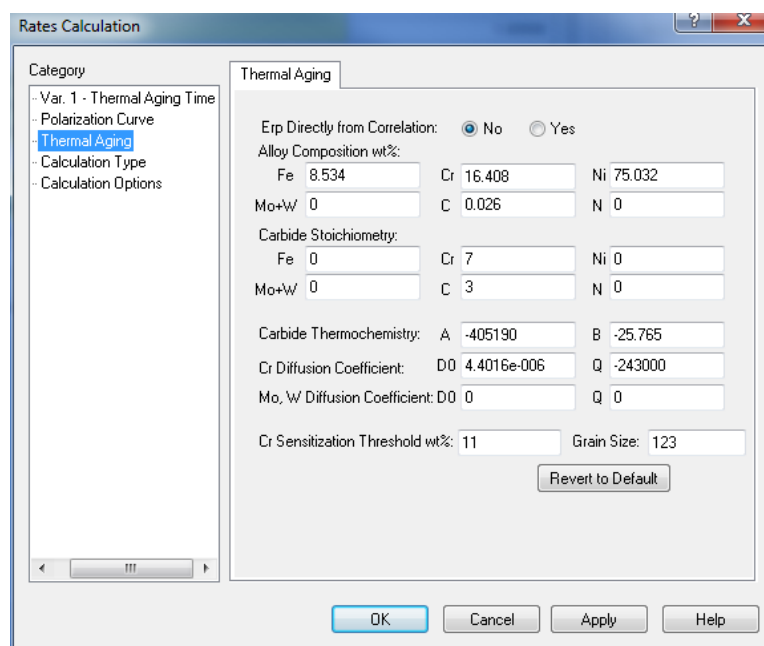
Figure 31-4 Thermal Aging Parameters

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 **<u>Calculate</u>** button.

Analyzing the results

When the calculations are finished, click on the **<u>Depletion Profile</u>** tab[52]. 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:

---

[52] Remember to use the scroll-arrows if necessary
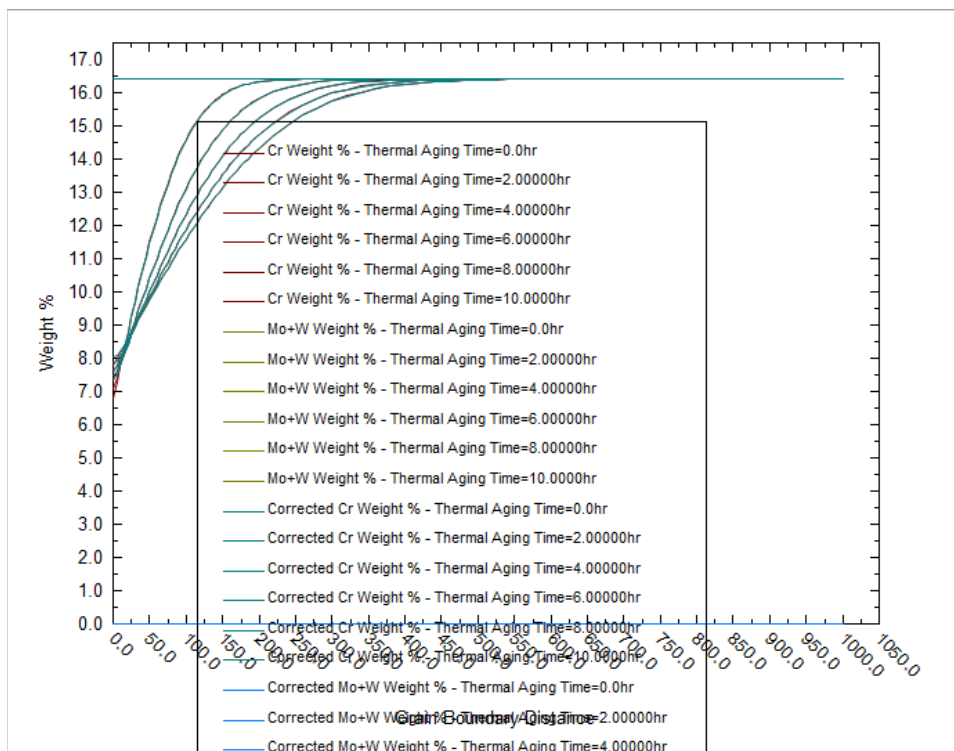
Figure 31-5 The plot of predicted depletion profiles for alloy 600 thermally aged at 700 °C as a function of time.

Let us customize the plot now by clicking on the **<u>Options</u>** button.

Since alloy 600 does not contain Mo or W, let us eliminate the Mo+W curves. To do this, select the **<u>Curves</u>** category from the left-hand side pane (**NOTE: this is not the same as the Curves Button!**)
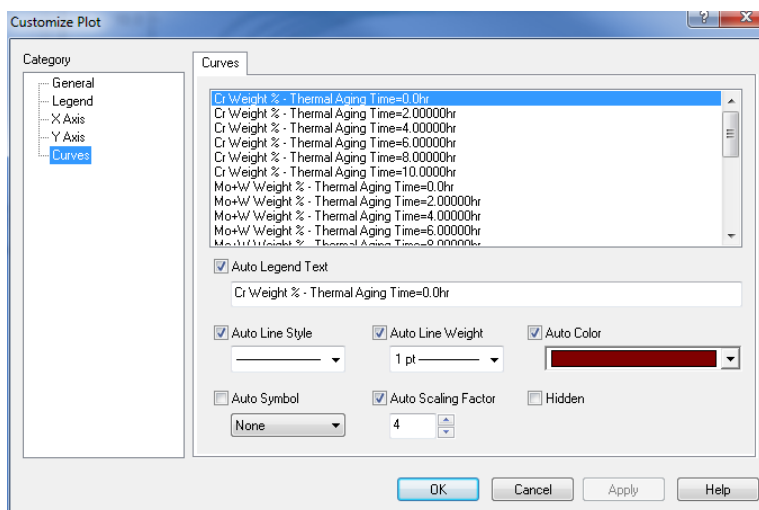
Figure 31-6 Plot Options | Curves Category

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:
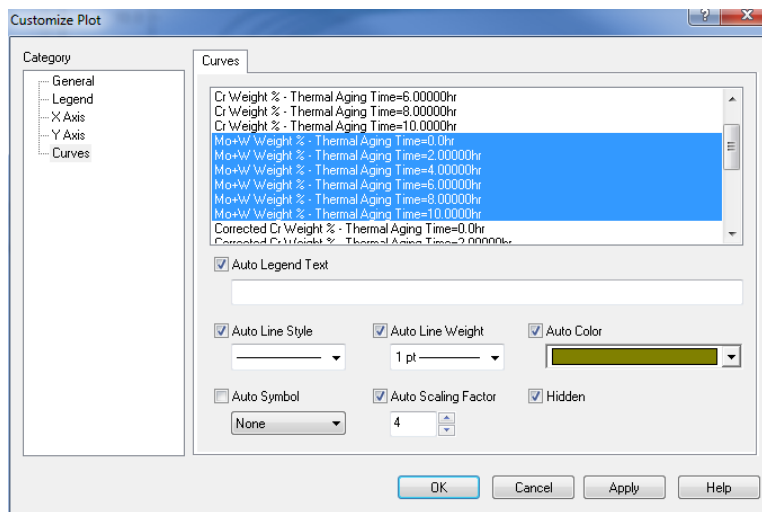
Figure 31-7 The window for customizing the display of depletion profiles.

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:
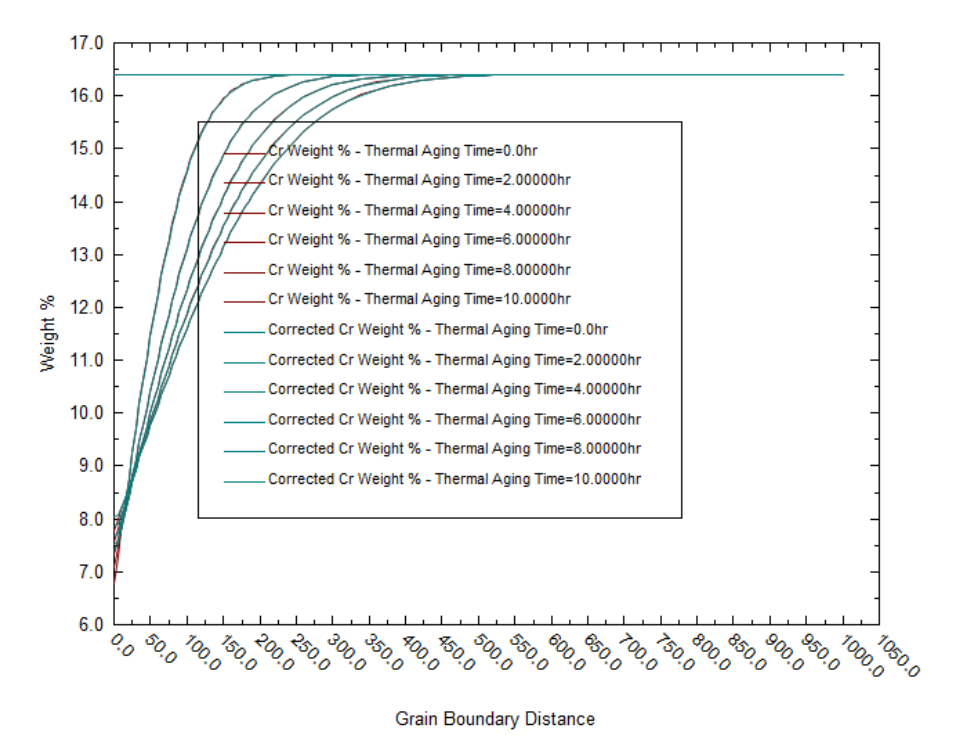
Figure 31-8 A customized depletion profile plot that shows only Cr depletion profiles

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:
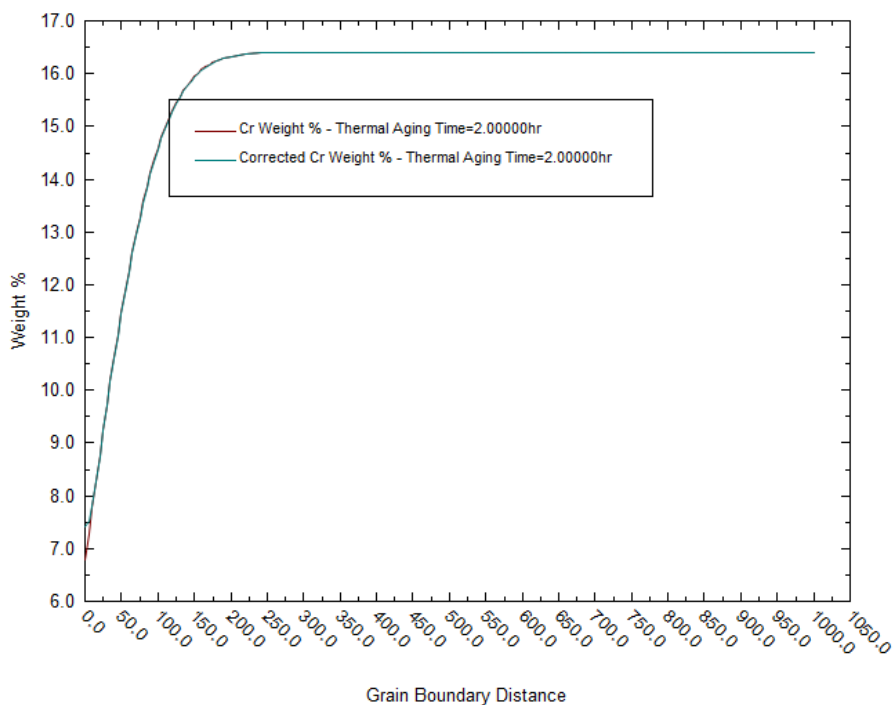
Figure 31-9 A customized depletion profile plot that shows uncorrected and corrected Cr depletion profiles only for 2 hours of thermal aging

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:
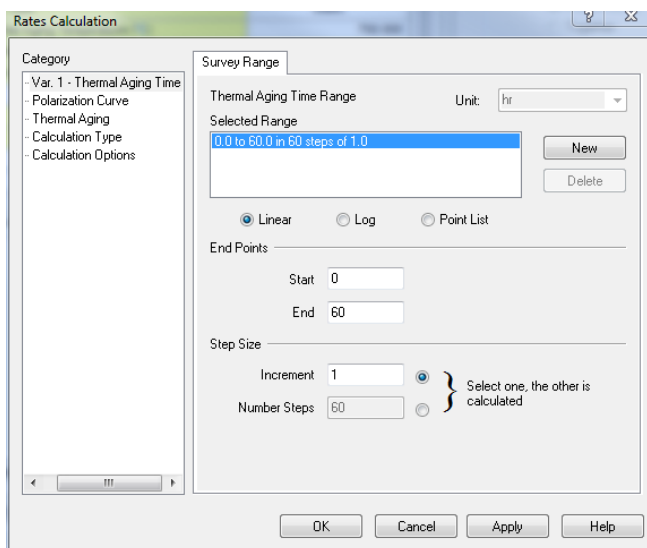
Figure 31-10 Changing the survey range for thermal aging.

- 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 **Variables**. 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:
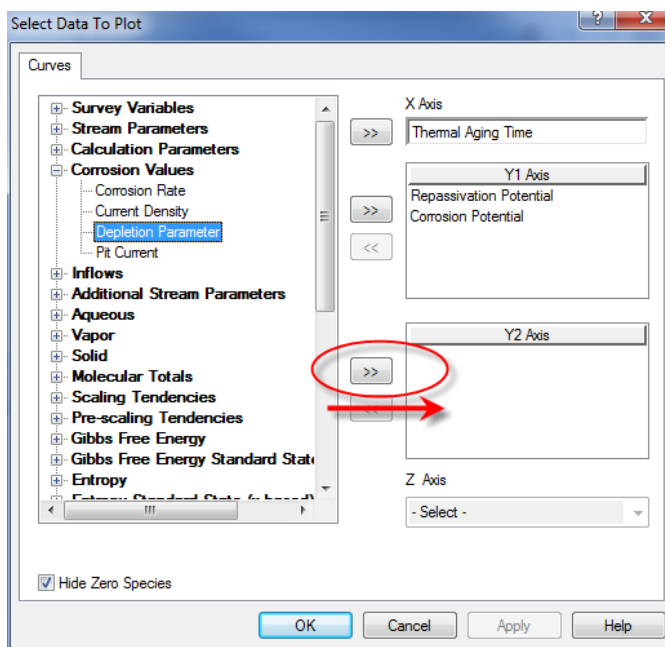
Figure 31-11 Including the depletion parameter in the plot on the Y2 axis.

- Click **OK**. You will see a plot that should look like:
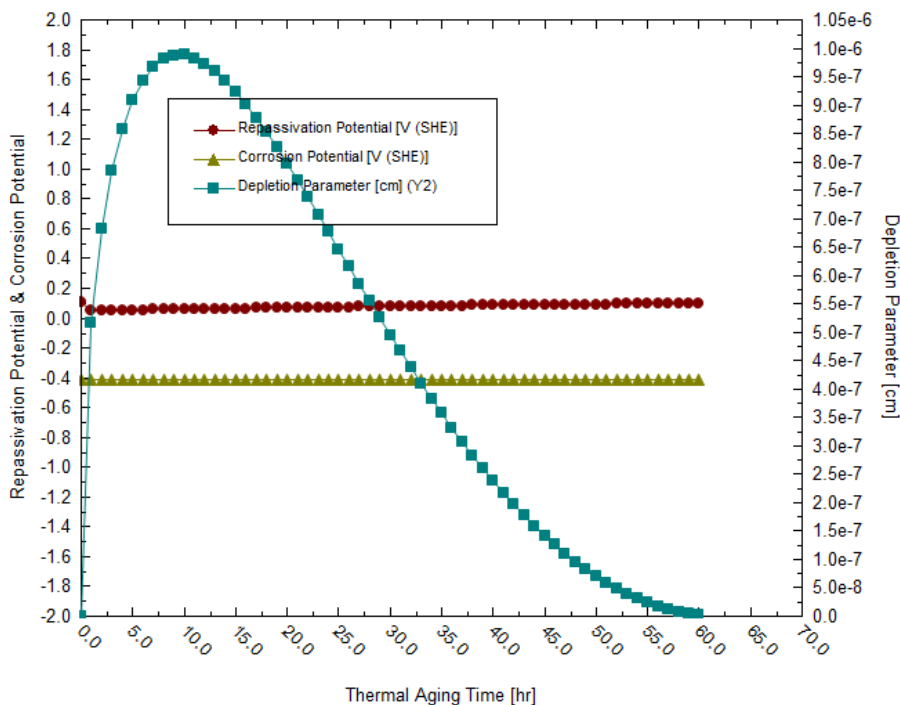
Figure 31-12 A plot of the repassivation potential and depletion parameter for thermally aged alloy 600 as a function of aging time.

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:
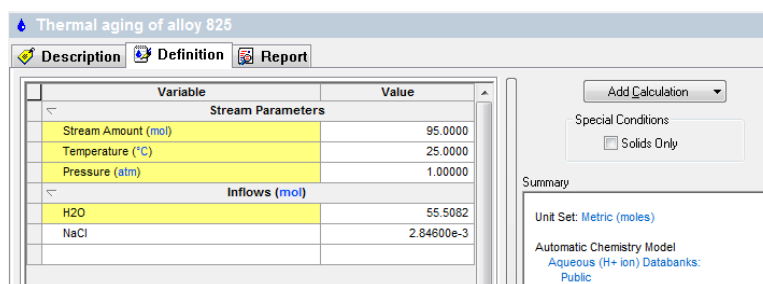
Figure 31-13 Stream definition for studying the effect of thermal aging on alloy 825.

- 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 Survey by 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 squares:
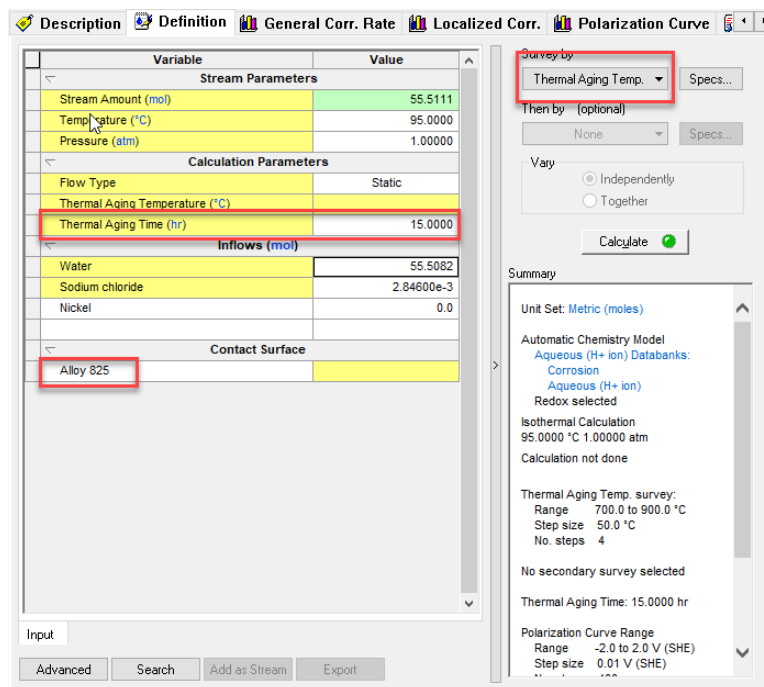
Figure 31-14 Specifying the type of calculation, thermal aging time, and contact surface.

- 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:
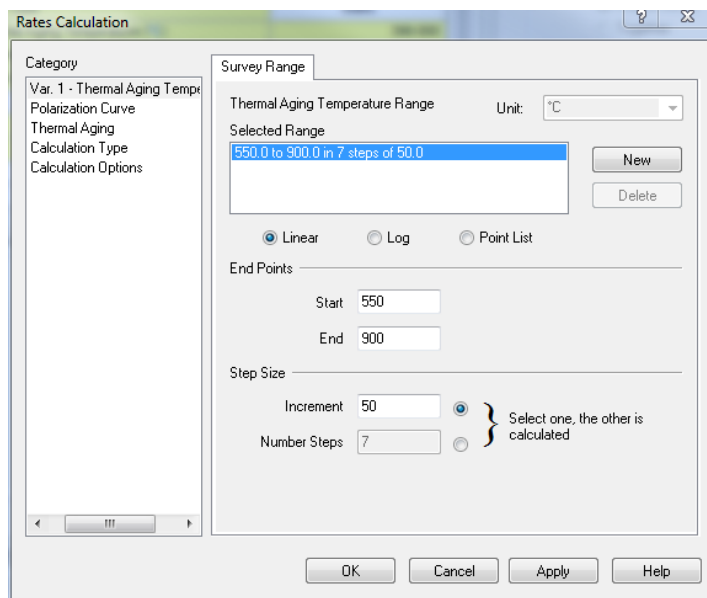
Figure 31-15 Defining the range for a thermal aging temperature survey.

- 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 **<u>Depletion Profile</u>** 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 **<u>Options</u>,** select the **<u>Curves</u>** 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:
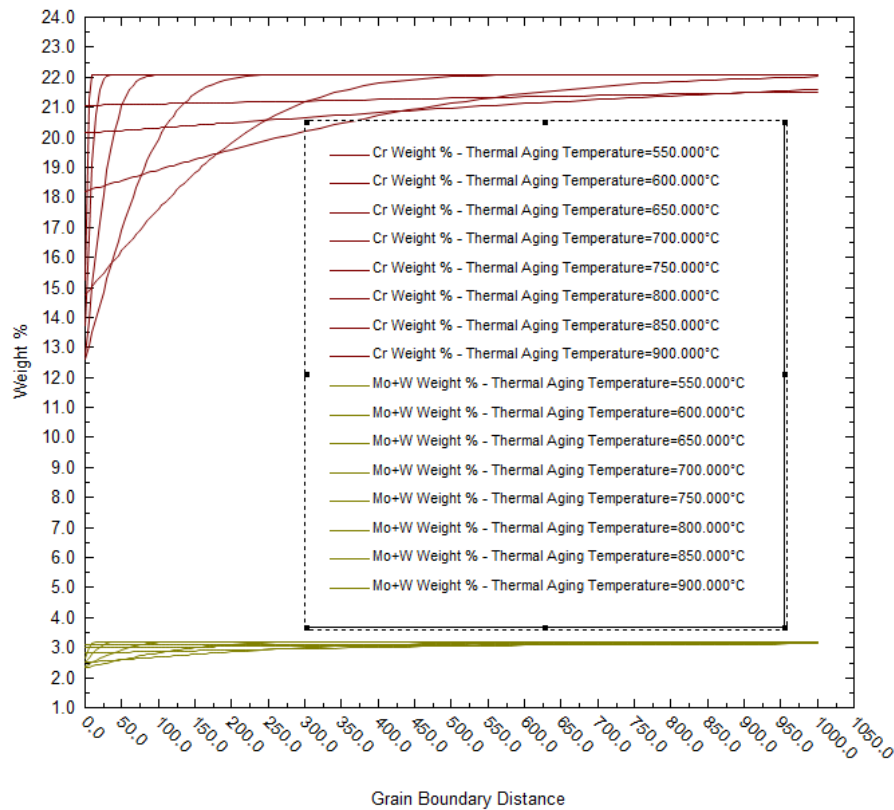
Figure 31-16 Predicted Cr and Mo depletion profiles for alloy 825 as a function of thermal aging temperature.

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:
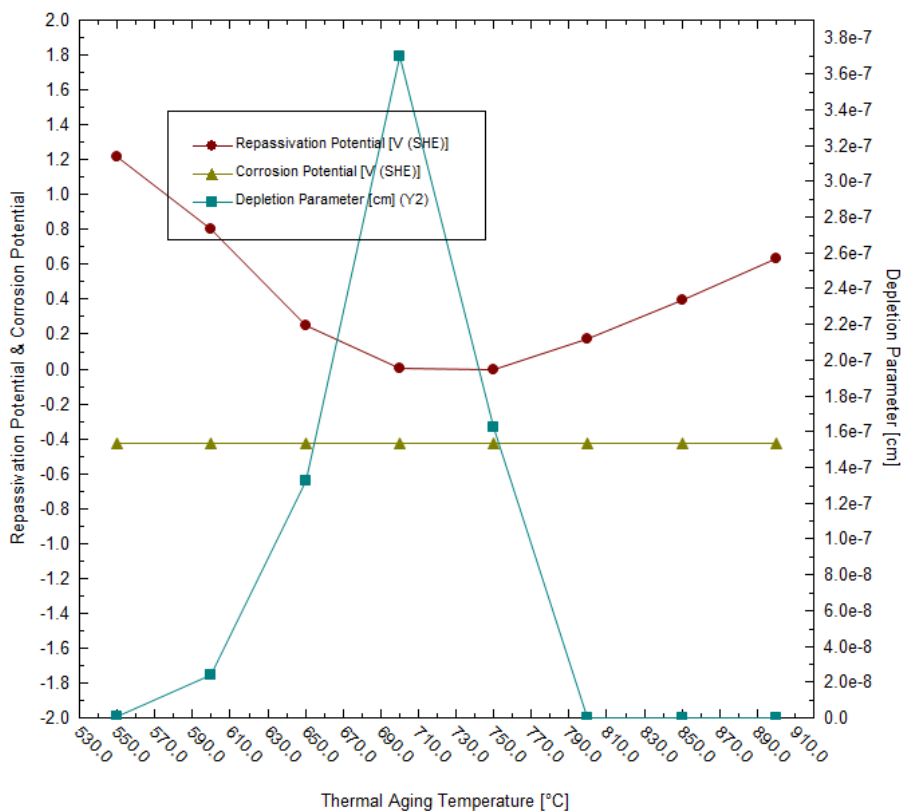
Figure 31-17 Calculated repassivation potential and depletion parameter for alloy 825 as a function of thermal aging temperature.

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 ($\gamma2$). 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.

Part a: Prediction of localized corrosion for alloy 2205

- 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:
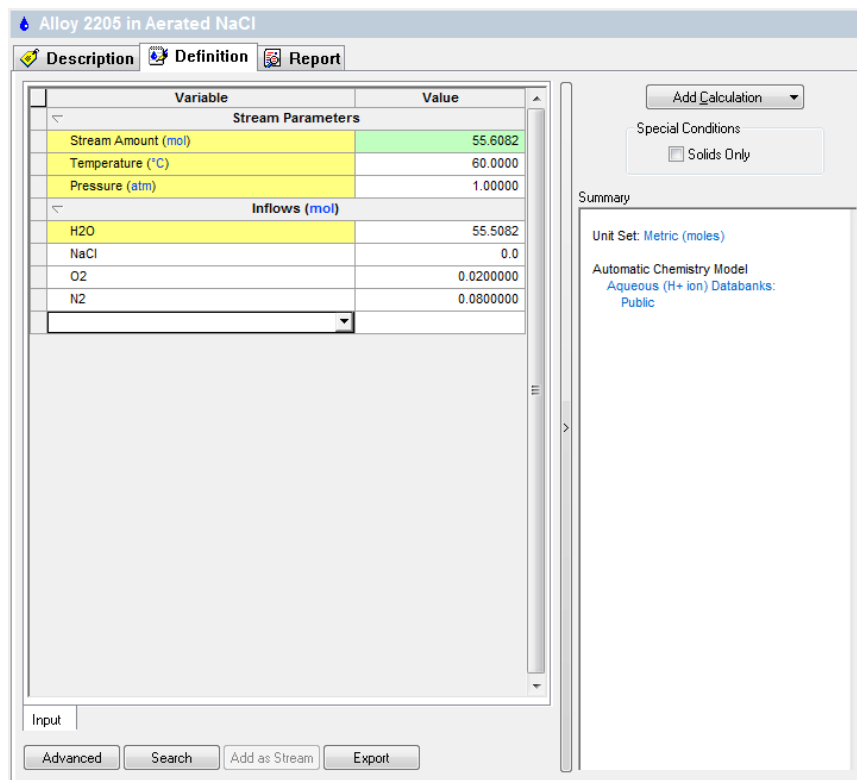
Figure 31-18 Stream composition for simulating localized corrosion of alloy 2205.

- Double-click on the **Add Corrosion Rates** icon in the **Actions** 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 in the **Survey by** button, use the drop-down and select **Composition**.

The definition grid for the Corrosion Rates should look similar to the figure below. The key specifications are highlighted using red ovals:
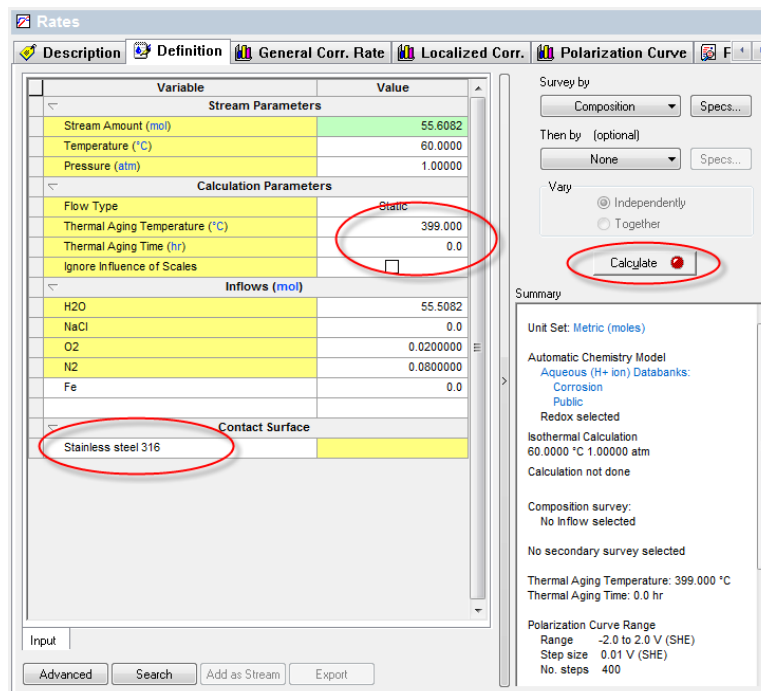
Figure 31-19 Selection of contact surface and survey type.

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…**
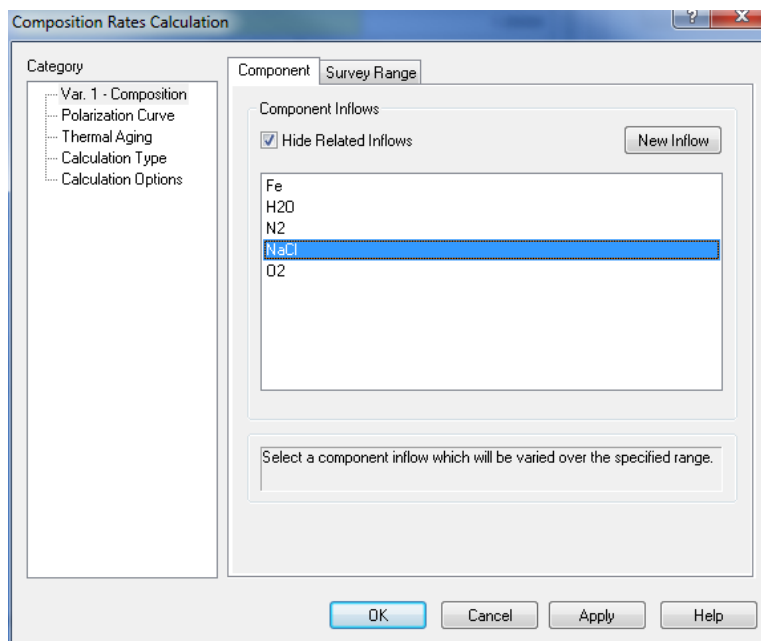
Figure 31-20 Selecting the component for the survey (NaCl)

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:
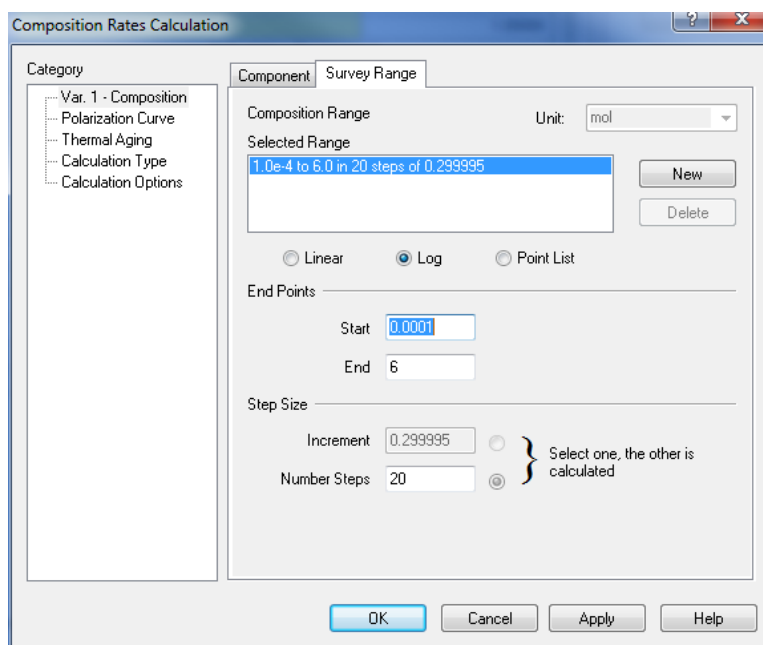
Figure 31-21 Defining the survey range for the NaCl concentration survey.

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:"*
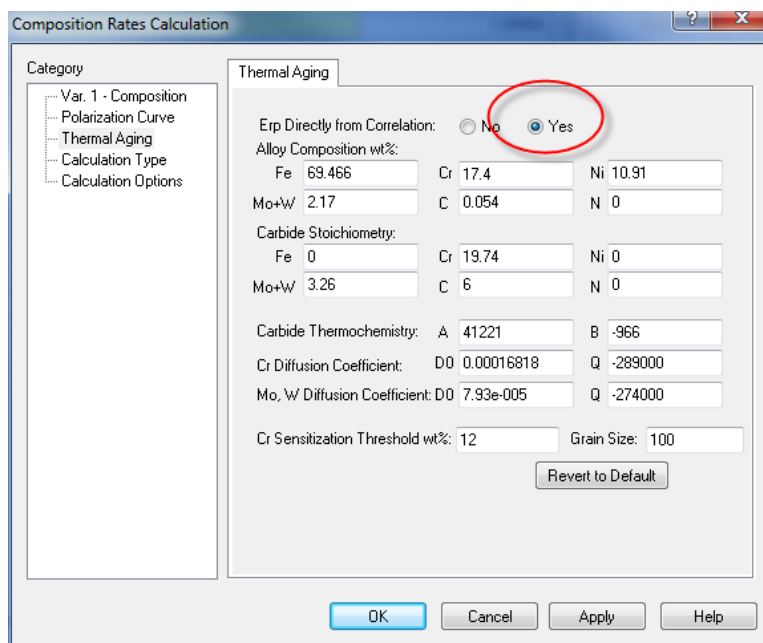
Figure 31-22 Thermal Aging Parameters

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:
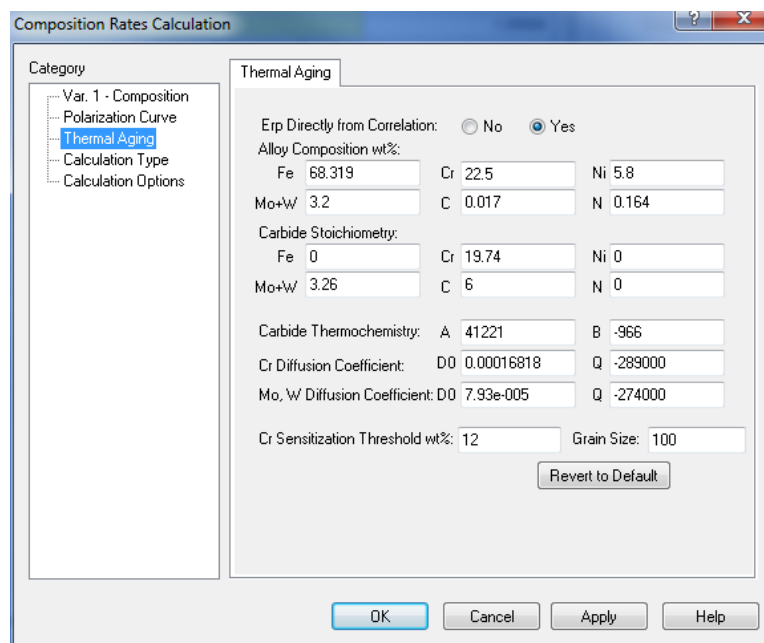
Figure 31-23 Defining the composition of alloy 2205 and specifying the direct use of the correlation for predicting the repassivation potential.

- 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. In the Y2 axis the Maximum Pit Current Density is also plotted. See figure below:
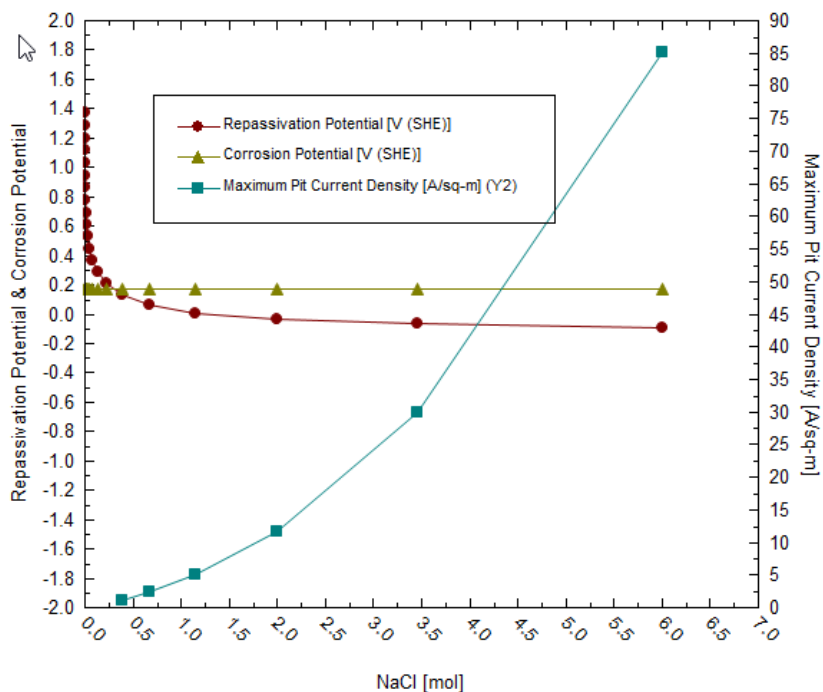
Figure 31-24 Predicted repassivation potential and corrosion potential for alloy 2205.

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**.
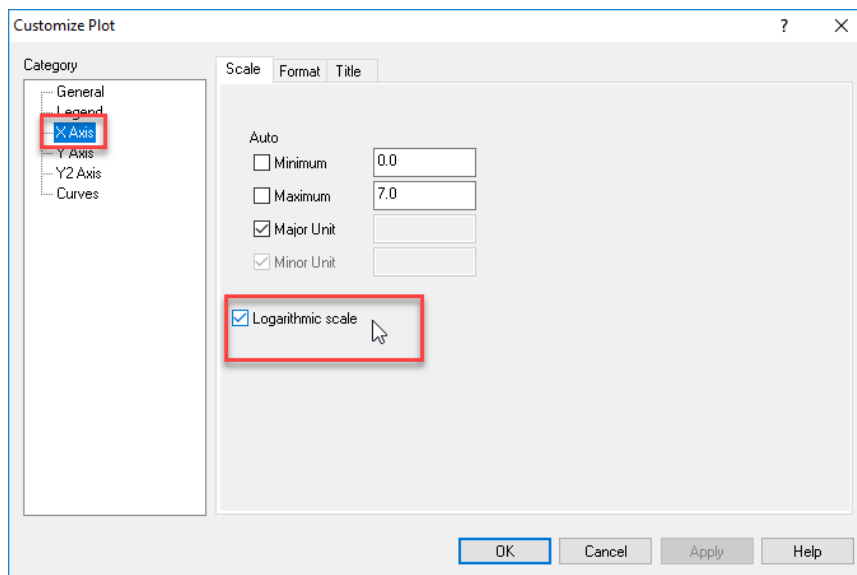
Figure 31-25 Changing the X-Axis to Log

Then, the plot should look similar to the following one:
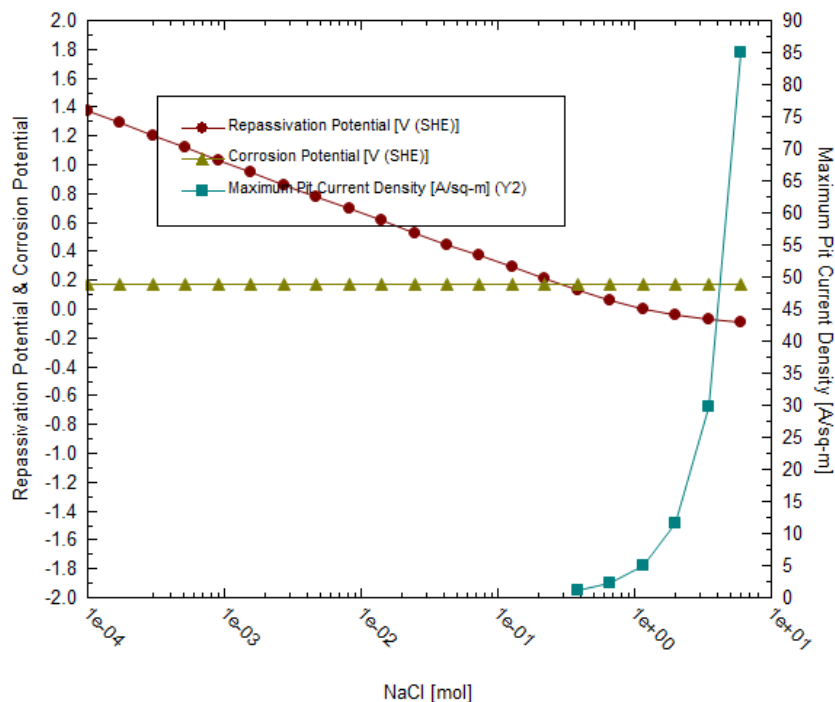
Figure 31-26 Predicted repassivation potential and corrosion potential for alloy 2205.

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.

Part b: Prediction of localized corrosion for alloy 2205 after thermal aging

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** pane and click on the **Definition** tab.

As in the previous simulation, select **316 Stainless Steel** from the drop-down **Contact Surface** menu.

From the Type of rates calculation in the **Survey by** button, use the drop-down and select **Composition**.

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 31-21 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.

- 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:

Figure 31-27 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**.

The plot should look similar to the following one:
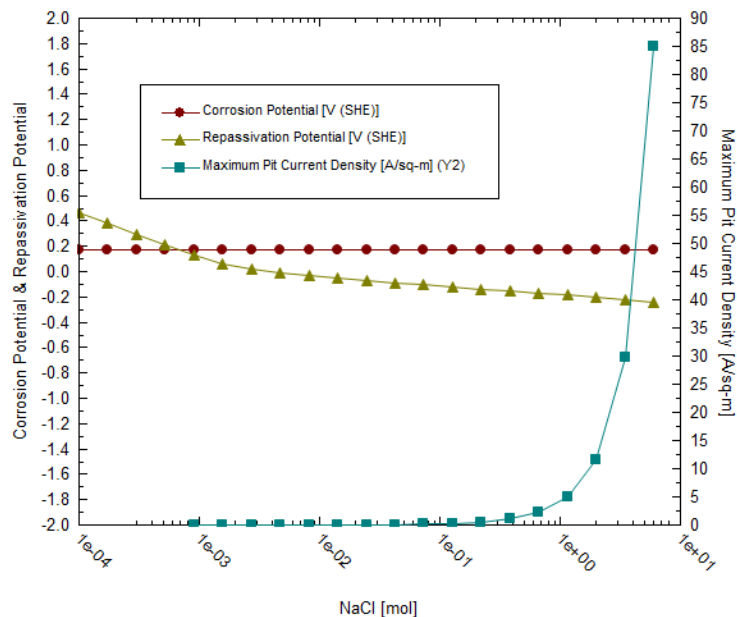
Figure 31-28 Predicted repassivation potential and corrosion potential for thermally aged alloy 2205. The calculations were made using the composition of the secondary austenite phase.

The obtained plot shows that the repassivation potential is much lower than that for bulk alloy 2205 (cf. Figure 31-26). 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:

1. The results of the analysis cannot be transferred for predicting corrosion damage to other systems (for example pipelines) due to the different technological and environmental conditions that generally exist. The results cannot be used for predicting damage in the same system if technological and environmental conditions change.
2. We can expect that when the depth of the pit increases some critical value, the nucleation of cracks can occur. It is clear that a purely statistical method cannot predict such a transition. This method also cannot predict any catastrophic event.
3. This method cannot be used for design of new constriction, because it relies upon calibration upon a 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

1. The depth of the deepest pit in the engineering structure or laboratory systems as a function of time and the surface area of the system;
2. Probability of failure for a given penetration depth and the area of the system as a function of observation time.
3. Probability of failure for a given observation time and the area of the system as a function of penetration depth.
4. Probability of failure for a given penetration depth and observation time as a function of the area of the system.

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
	7 days	30 days	90 days	180 days	365 days
1	180	460	480	620	640
2	266	500	578	620	680
3	290	510	610	620	700
4	306	580	610	680	760
5	334	580	610	680	800
6	340	640	660	720	810
7	340	654	690	740	820
8	410	680	718	740	840
9	410	692	760	760	840
10	545	692	798	760	900

- Double-Click the ***Add Standard EVS Calculation*** icon
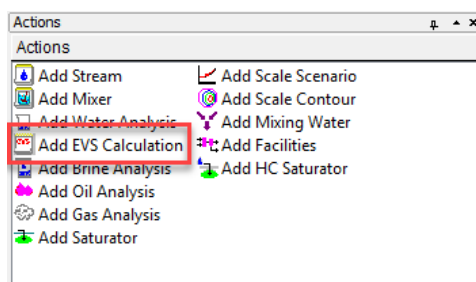
Figure 33-1 Starting EVS

- 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.

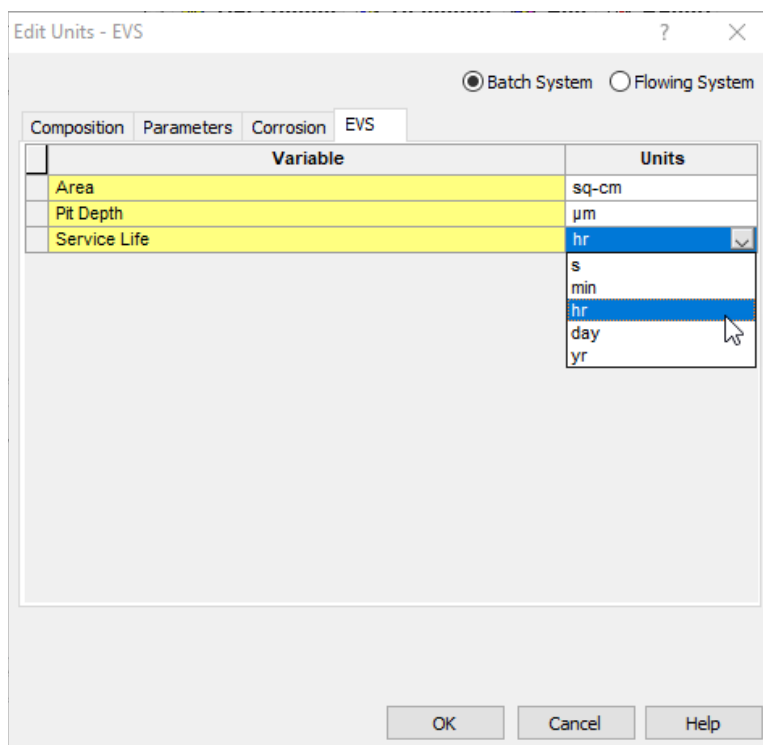The definition grid of the system should look like Figure 33-2.

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).
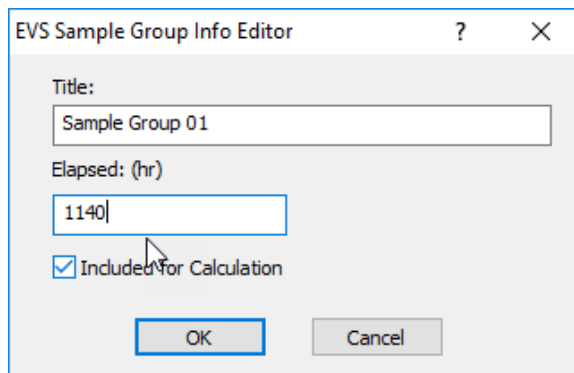

Figure 33-3: Drop down-table for adding groups.

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.
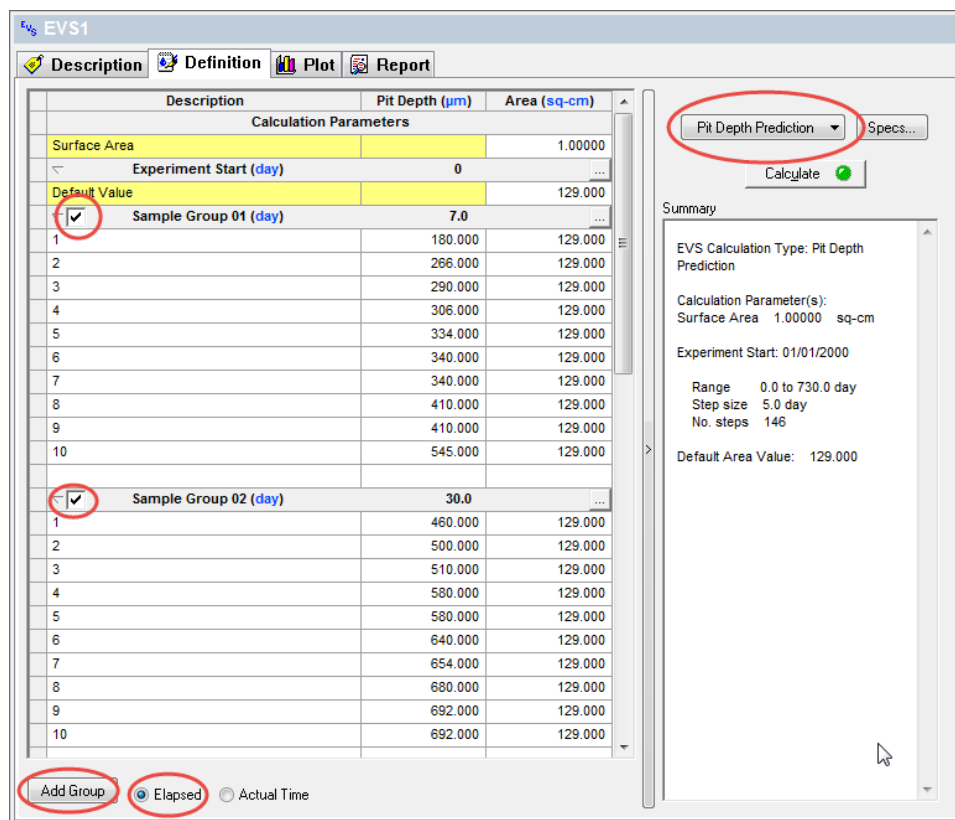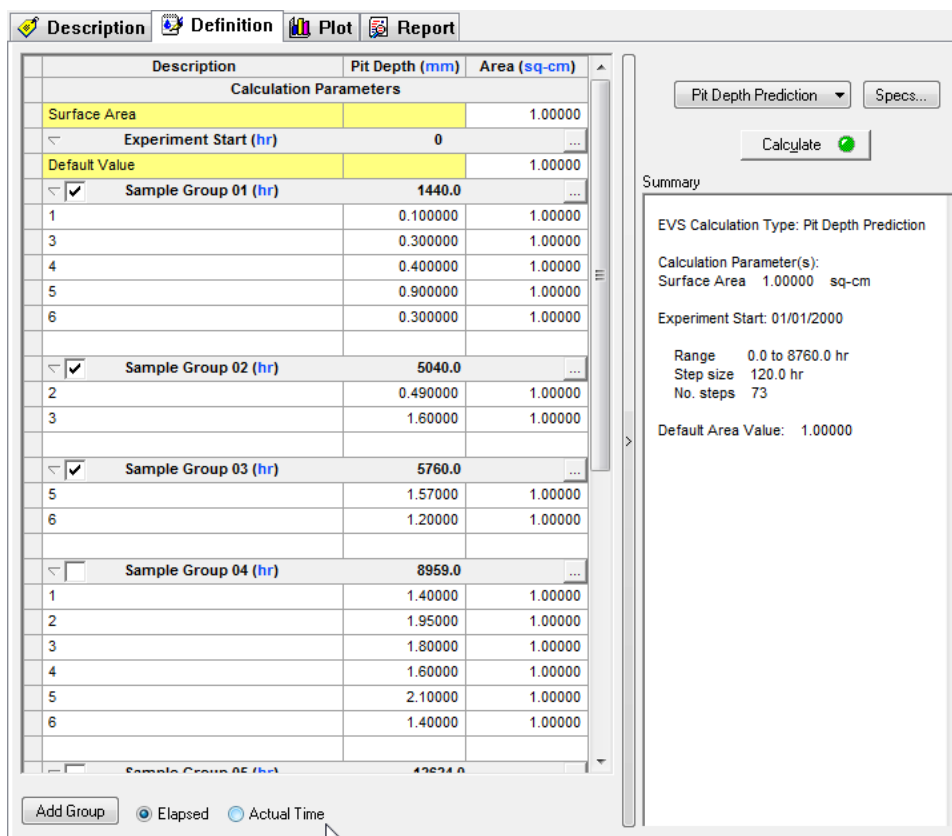
Figure 33-4: Specifying experimental data for depths of deepest pits (not completed)

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.

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 (red 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 groups (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**.

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.
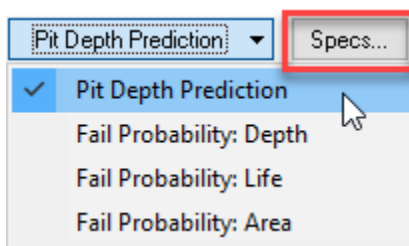
Figure 33-7 Selecting the type of calculation

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.
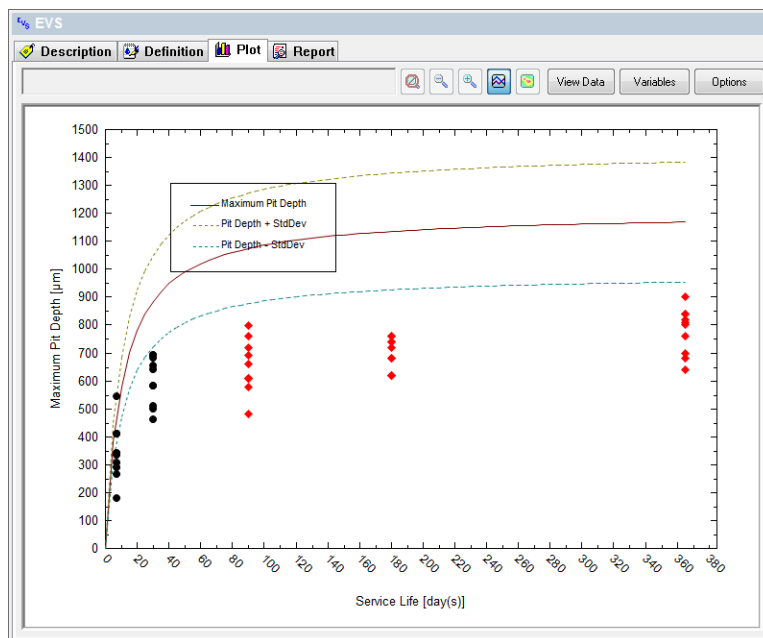
Figure 33-7: *Predicted depth of the deepest pit. The experimental data for t = 1 week and 1 month are included into consideration.   S = 129 cm².*

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**
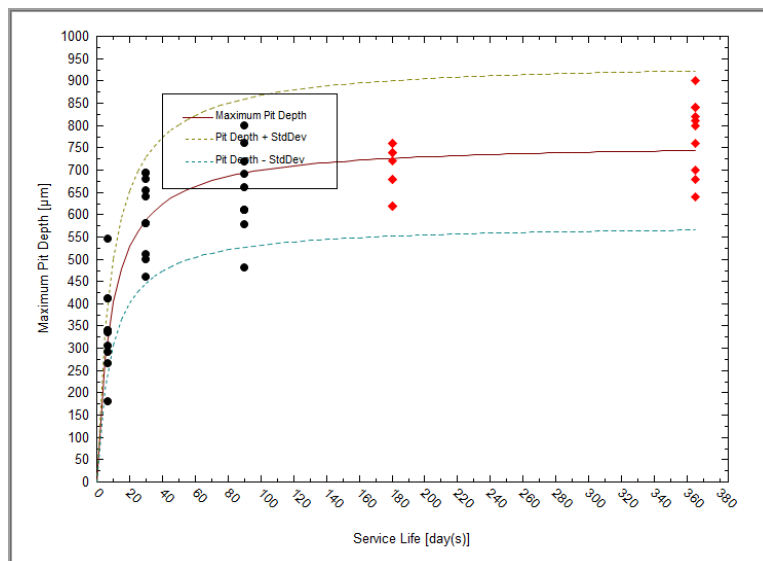
Figure 33-8:Predicted depth of the deepest pit. The experimental data for t = 1 week, 1 month, and 3 months are included into consideration.   S = 129 cm².

For predicting depth of the deepest pit in the system with a substantially larger area (say, 10 m²) for the period of observation time of 2 years we have to input S = 10 (m²) into **Surface Area** window and to specify the range [0, 2] (years) for observation time by clicking on **Specs…** button.
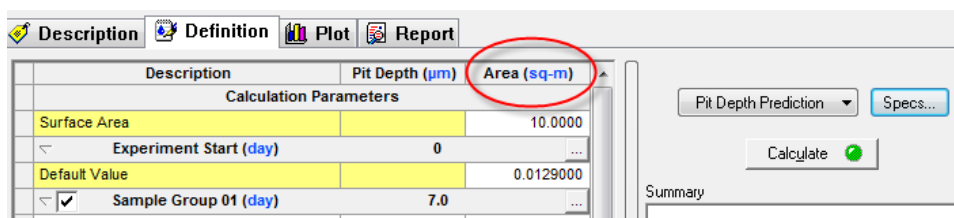
Figure 33-9 Changing the surface area, note the unit change from sq-cm to sq-m
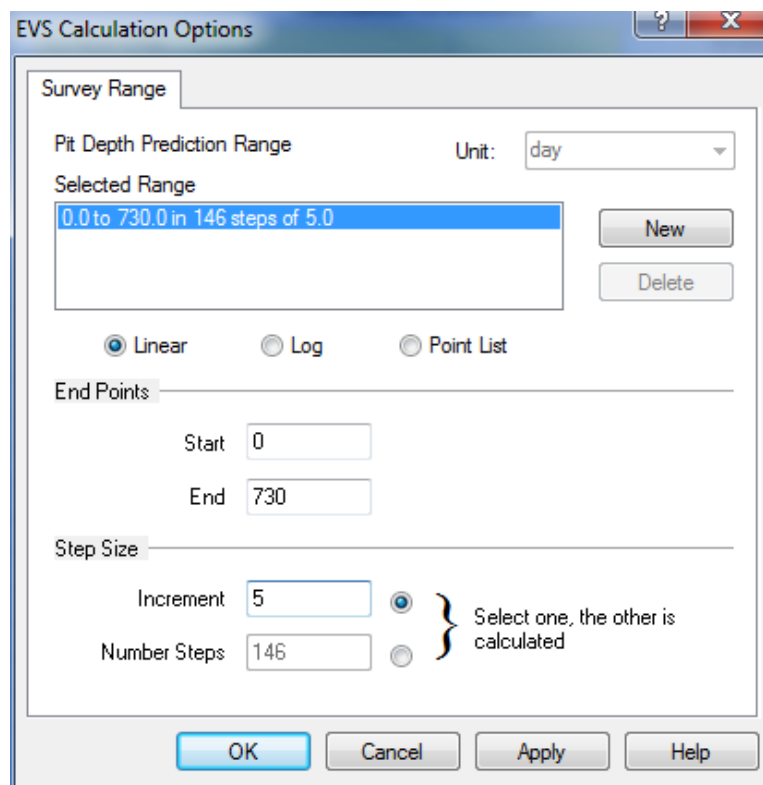
Figure 33-10 Changing the end time to 2 years (730 days)

The results of calculations are shown below.
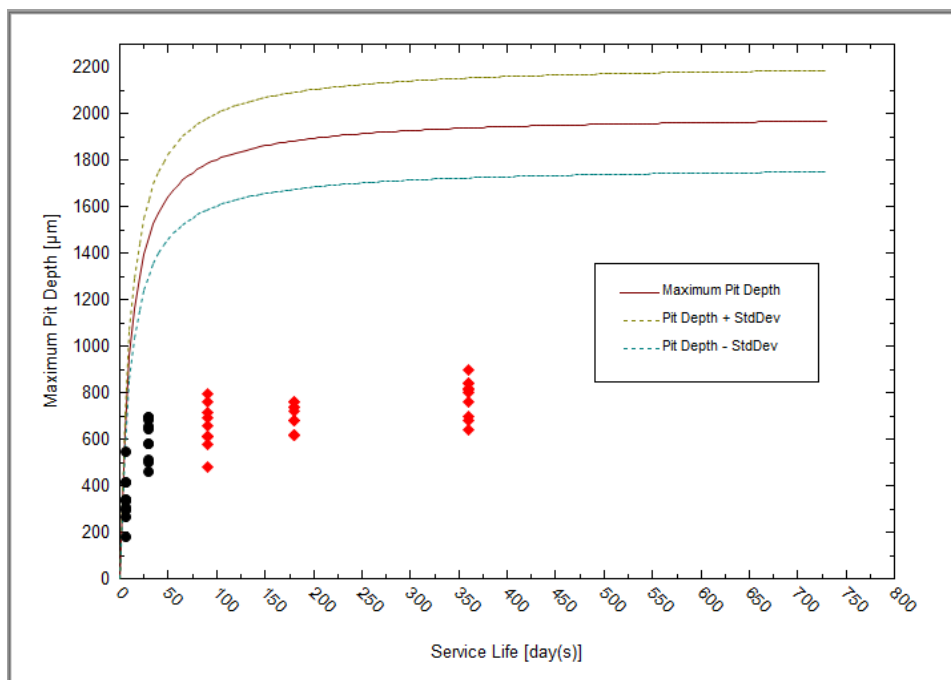
Figure 33-11: Predicted depth of the deepest pit. S = 10 m².

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 m²) 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 (m²) 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

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
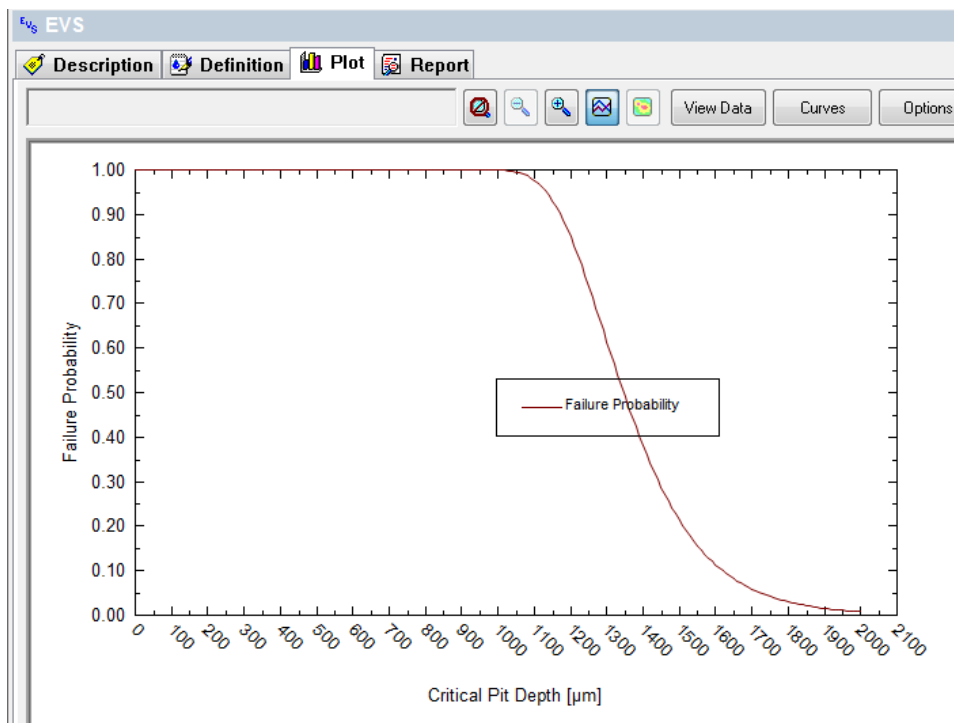
Figure 33-13: Probability of failure as a function of the width of the wall at given observation time and area of the pipe.

- 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 m²) 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 (m²) 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.
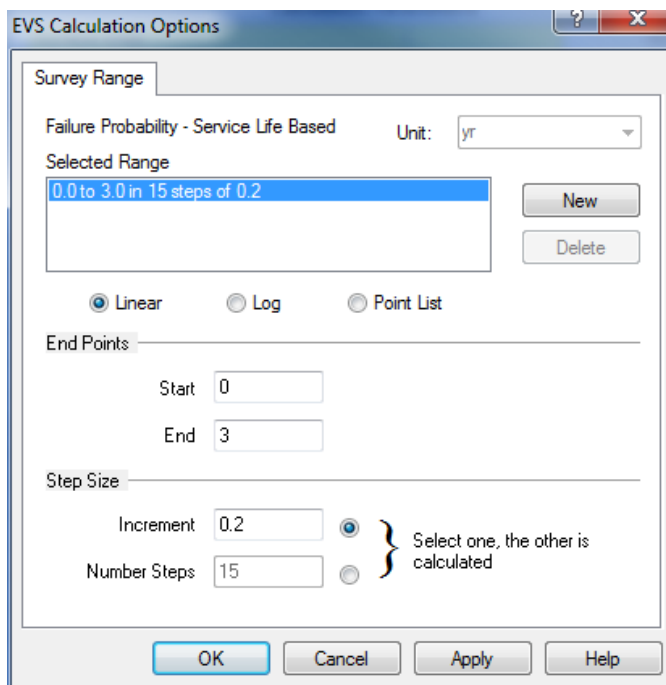
Figure 33-14 Changing the time to 3 years. Note the change in units from days to years

- Click **OK**

The definition grid for calculating the acceptable pipe wall width should look similar to Figure 33-15

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**)
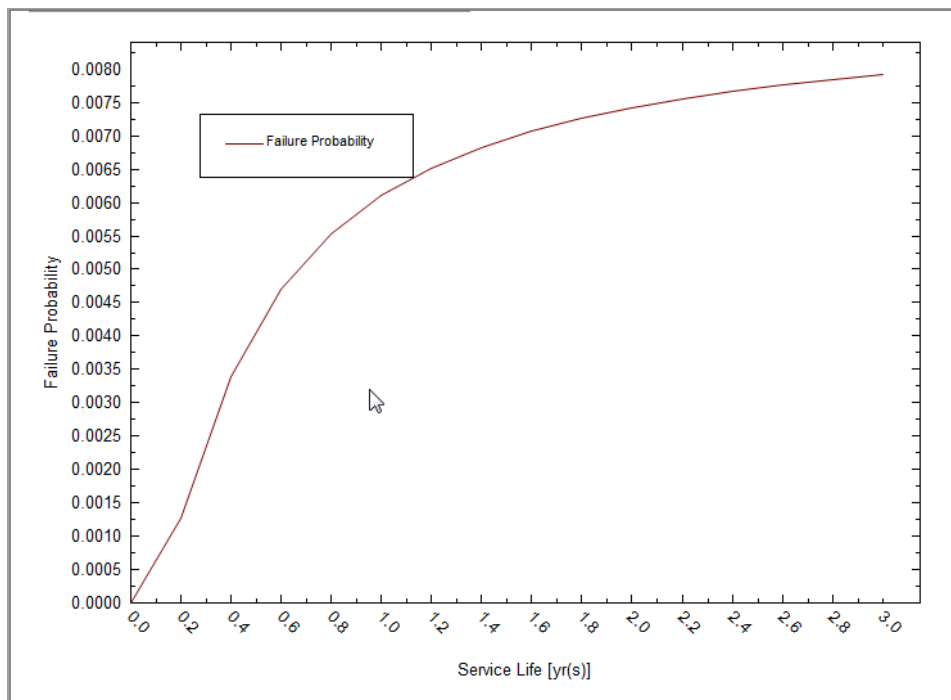
Figure 33-16: Probability of failure as a function of service life for a given width of the wall and given area of the pipe.

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.
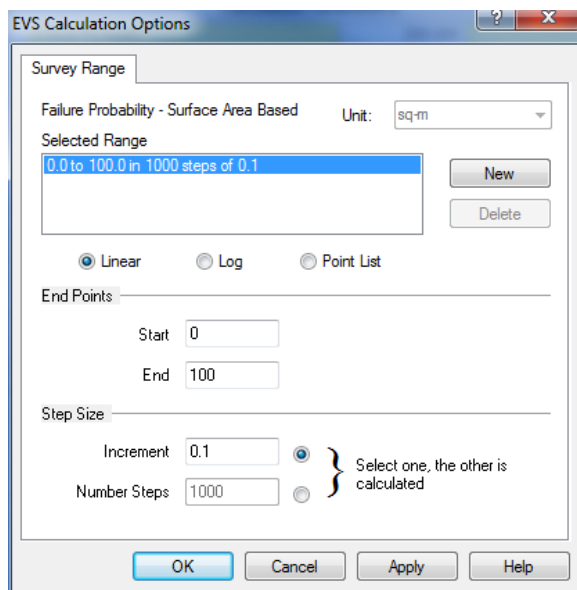
Figure 33-17 Setting the area range for Failure Probability

The definition grid for calculating the acceptable pipe wall width should look similar to Figure 33-18.

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).
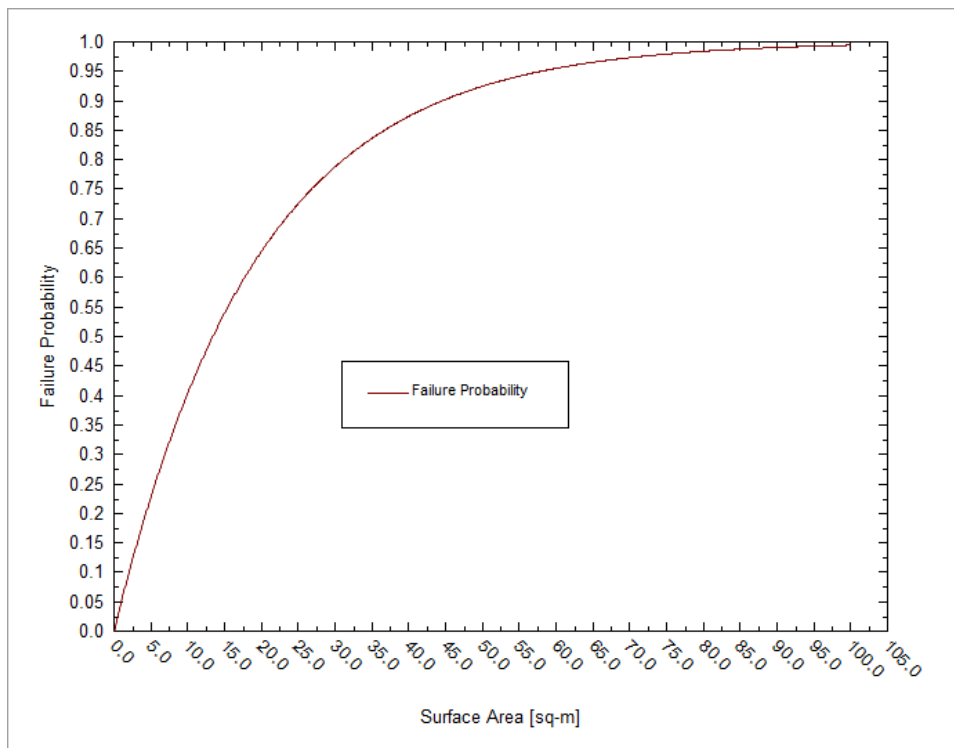
Figure 33-19: Probability of failure as a function of the area of the pipe at given width of the wall and given service life.

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 33-24 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	

- Double-Click the ***Add Standard EVS Calculation*** icon
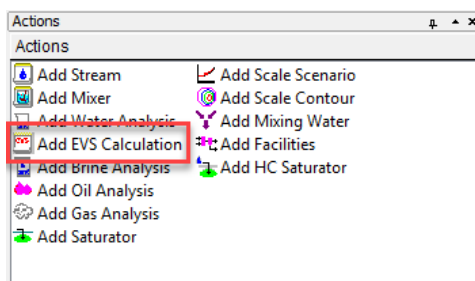
Figure 33-20: Starting EVS

- Click on **Definition** tab and start by inputting experimental data.

The grid should look like this:

Figure 33-21: The system definition.

Since the data is in hours, click on the link (**day**) and change it to hours (for both: the Experiment Start and the Sample Group. See figure below:

Figure 33-22: Changing units

There are experimental data for 8 different times (8 groups). Click on the button inside the red rectangle (see Figure 33-21) and type time 1140 hours in empty space below Elapsed, as is show below:

Figure 33-23: Drop down-table for adding groups.

Insert data from the second column in Table 33-2 into the Sample Group 01. Group 01 is representing 1140 hours.

After that, click on **Add Group** button, and in blank space type elapsed time = 5040 hours and insert all data from the third column for Sample Group 02. After inserting the data from Table 33-2 (from columns 1 and 8) the definition grid for EVS calculations should look like:

Figure 33-24: Specifying experimental data for depths of deepest pits for corrosion in pipelines. Only 3 observation times are used

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
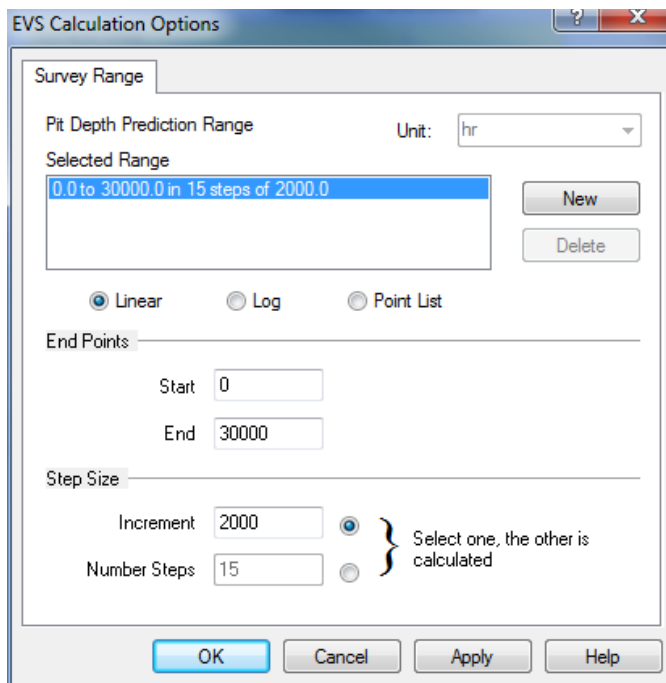
Figure 33-25 Setting the range to 30,000 hours, Note the units for time

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 33-24 are arbitrary.

- **Check** only Groups 1 through 3. They are the only ones we are going to use.
- Click the **Calculate** button.
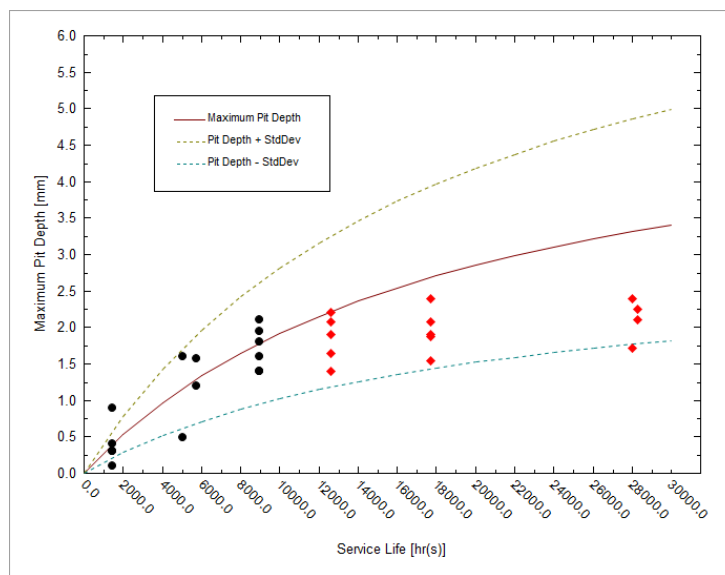
Figure 33-26: Predicted depth of the deepest pit with calibration on three observation times.

- **Click** on the <u>**Definition**</u> tab and **Check** Groups 1 through 5.

- Recalculate the diagram.
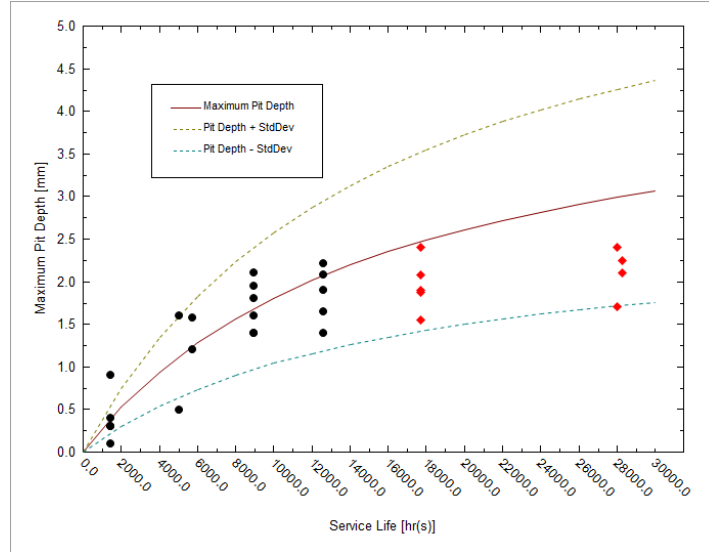
Figure 33-27: Predicted depth of the deepest pit with calibration on five observation times.

Figure 33-26 and Figure 33-27 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 33-29 and Figure 33-30).

Table 33-3. Pit 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	

Figure 33-28: 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.
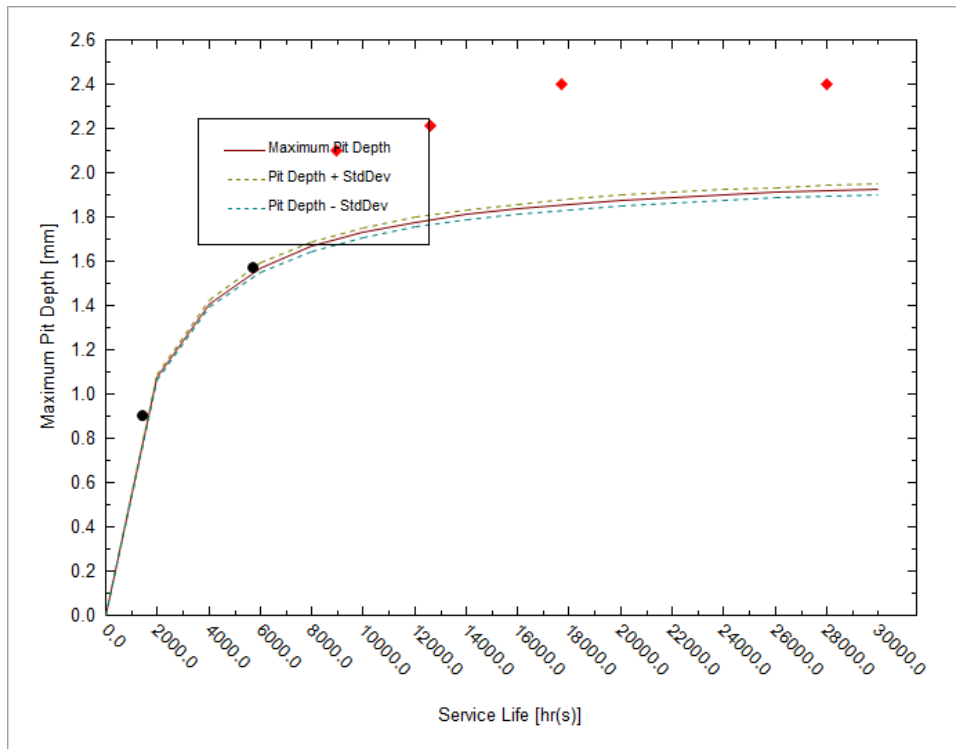
Figure 33-29: Predicted depth of the deepest pit with calibration on two observation times. Data are taken from one location on the pipe.
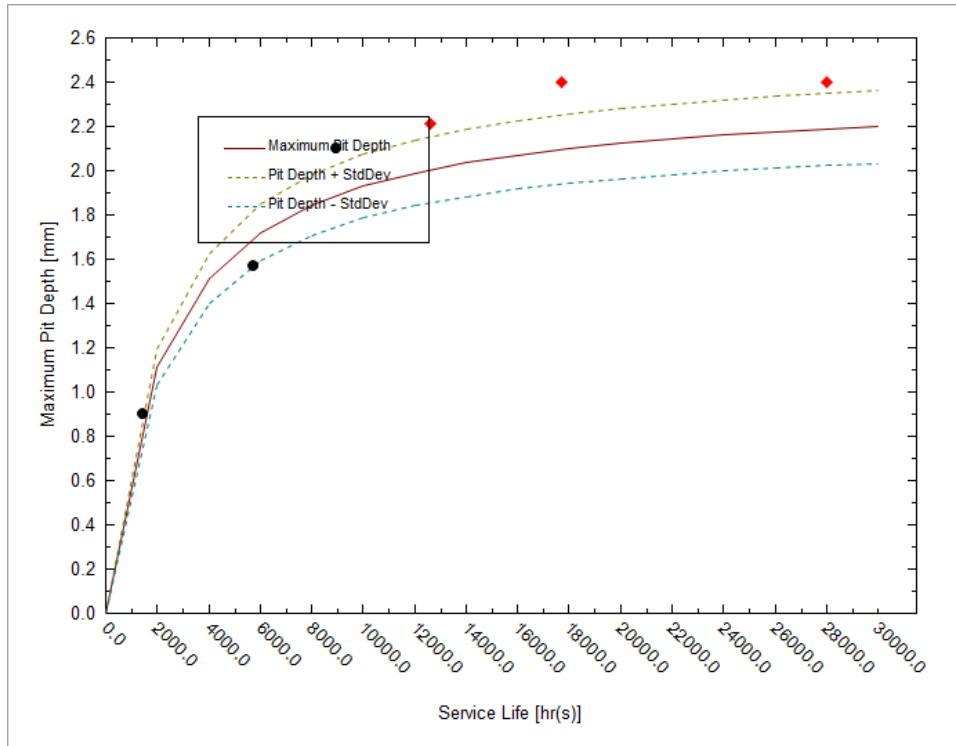
Figure 33-30: Predicted depth of the deepest pit with calibration on three observation times (groups 1,3 and 4). Data are taken from one location on the pipe.
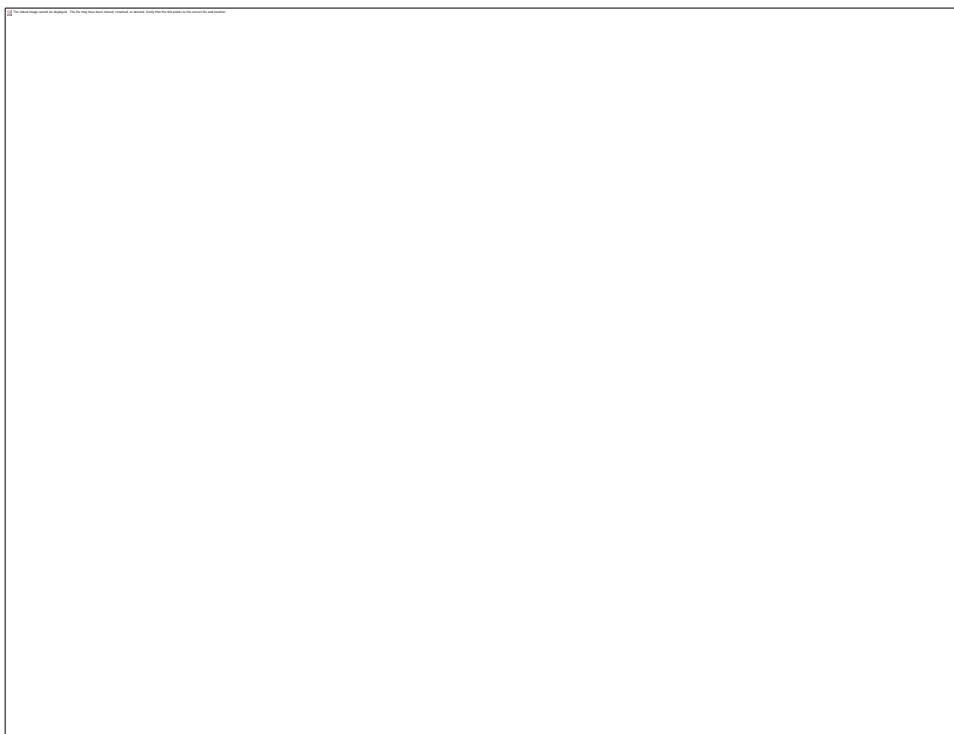
Figure 33-31: Predicted depth of the deepest pit with calibration on four observation times(groups 1, 3, 4, and 6). Data are taken from one location on the pipe.

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 33-32, which shows the predicted maximum pit depth for this system by using measurements at first three observation times.

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

Table 33-4 Pit depth data for 25.8 sq-cm, depth in micrometers
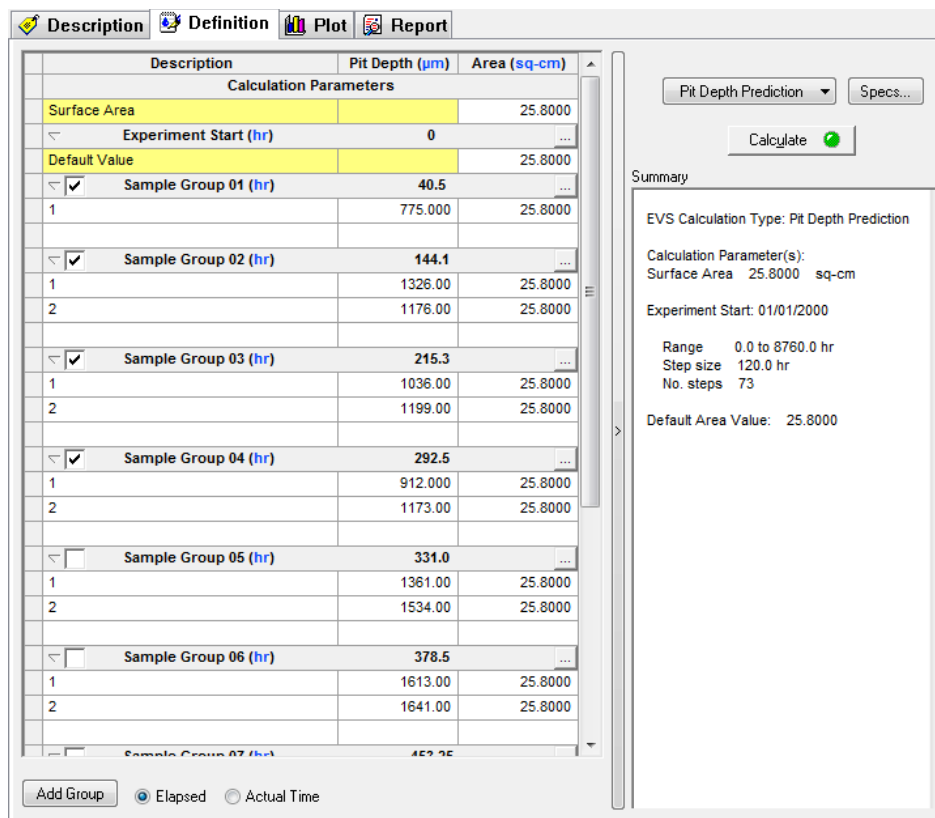
Figure 33-32: Specifying experimental data for depths of deepest pits for corrosion of 316L coupons in 10% ferric chloride solution.

We would like to simulate for 580 hours so we need to change the **Specs…** button.

Start 0.0 hrs

End 580 hrs

Number of Steps 50 hrs

The EVS Calculation Options should look like the image below:
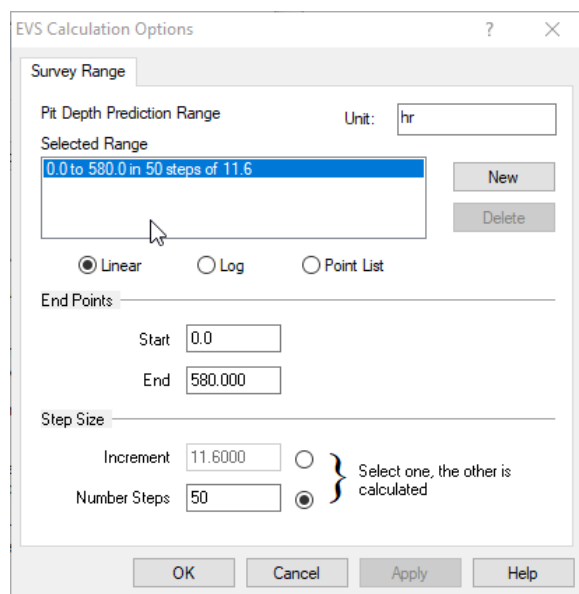
Figure 33-33: EVS Calculation Options
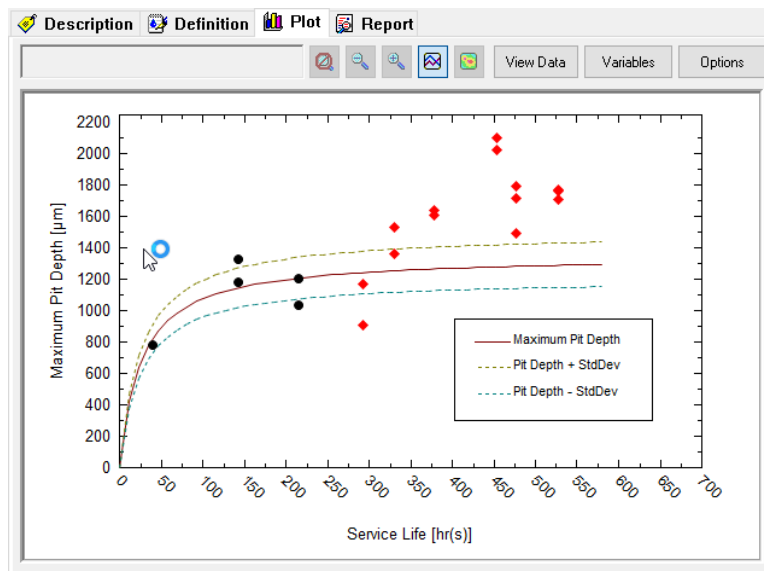
Figure 33-34: Predicted depth of the deepest pit on the stainless steel with calibration on the first four observation times (groups 1-4)

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 33-35 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.
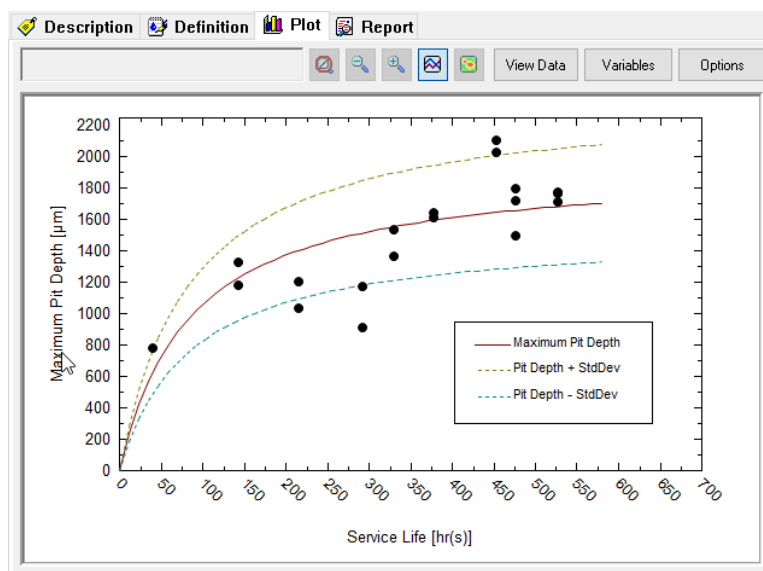
Figure 33-35: Predicted depth of the deepest pit on the stainless steel with calibration on full set of available data.

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 (°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.

Example 1: La(C₂H₃O₂)₃ - K₃PO₄ chemical diagram

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**
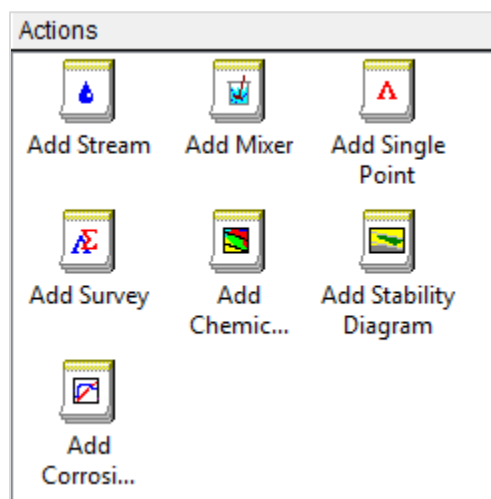
Figure 35-1 Selecting a new stream

We will not enter the conditions of the stream at this point. Don't worry, we can make modifications to the stream conditions later. At 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 ºC 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.
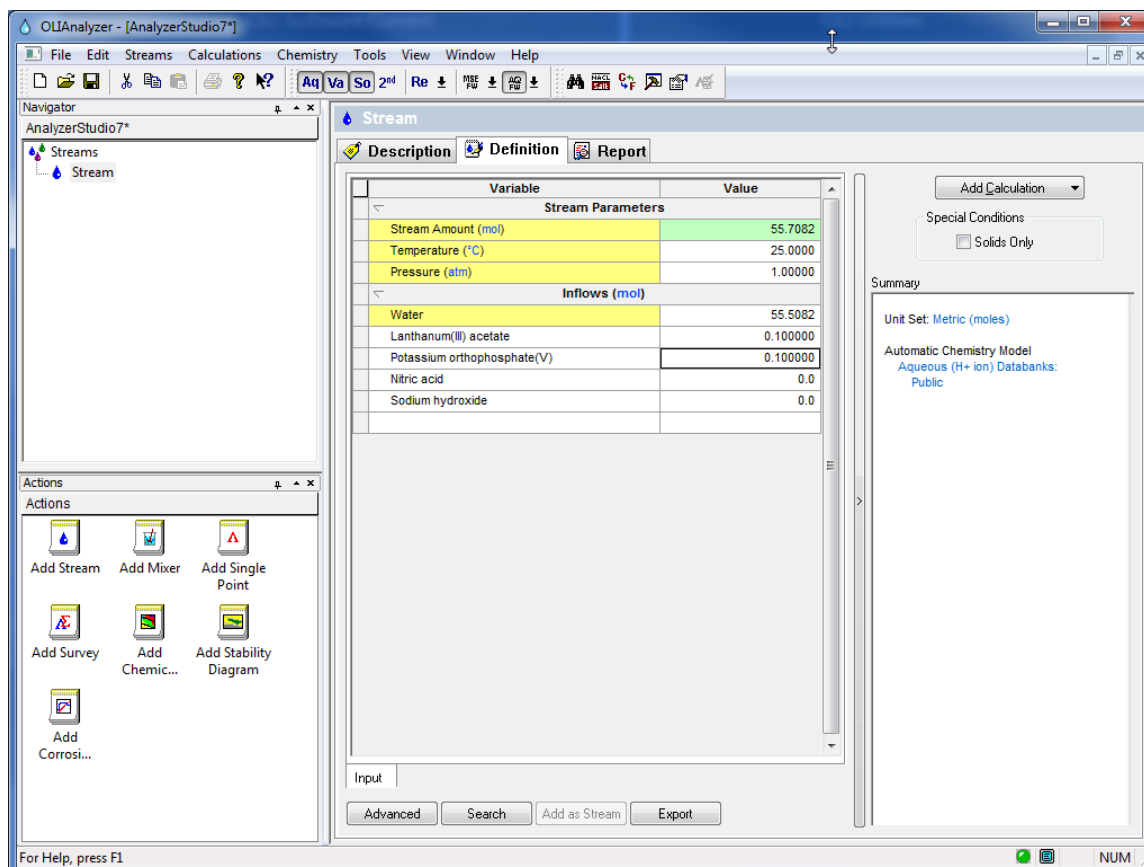
Figure 35-2 Entering starting conditions

As a side note, you could have also entered the chemical formula names for the species. The formula names are:

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*
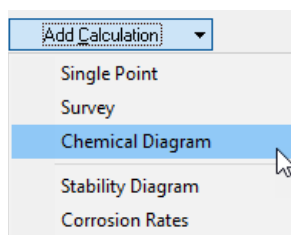
Figure 35-4 Selecting Chemical Diagrams

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.
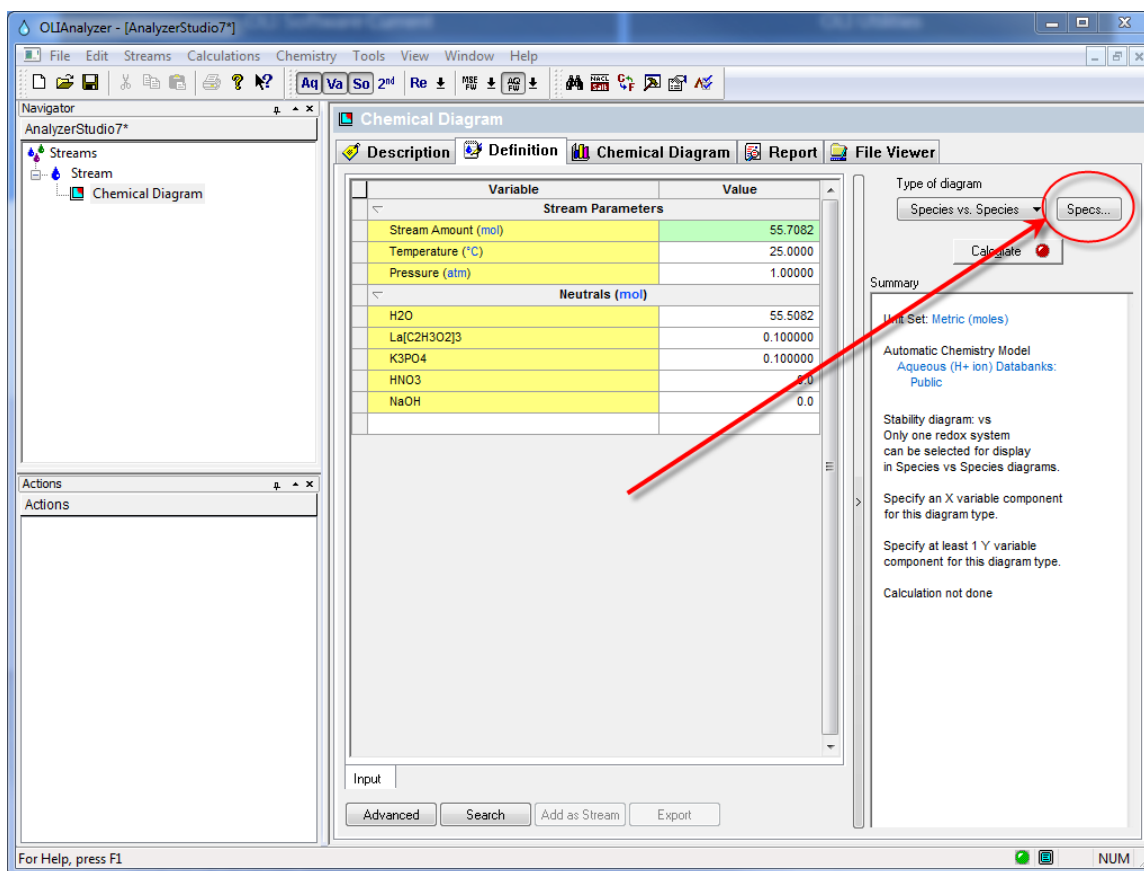
Figure 35-5 Selecting the Specs... button

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.
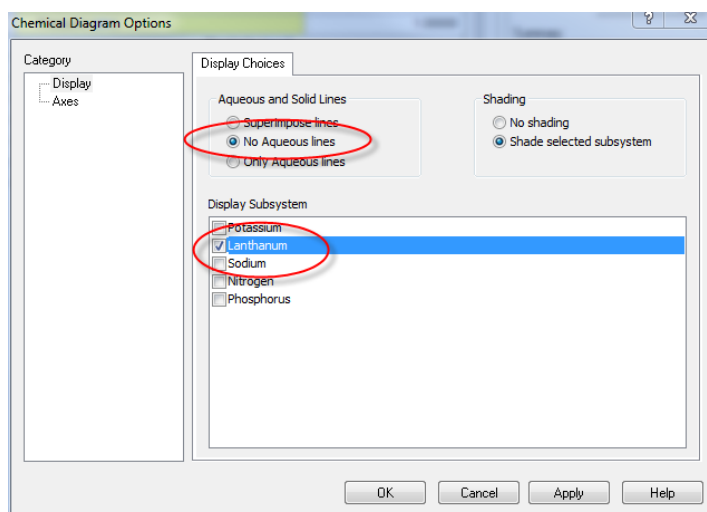
Figure 35-6

- 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.
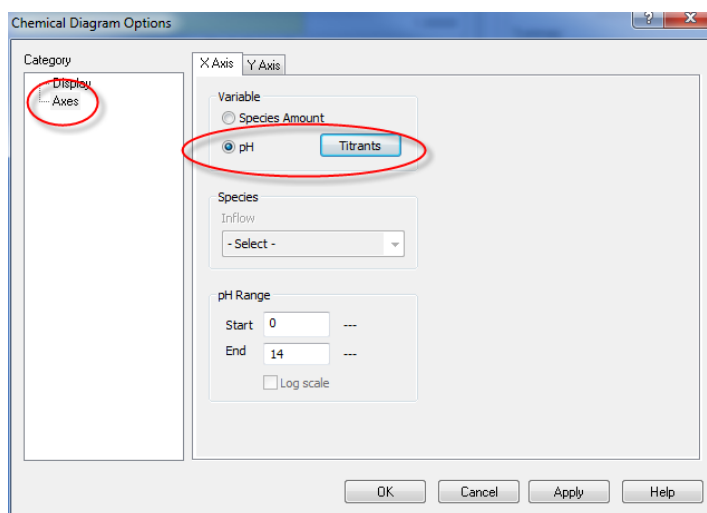
Figure 35-7

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.
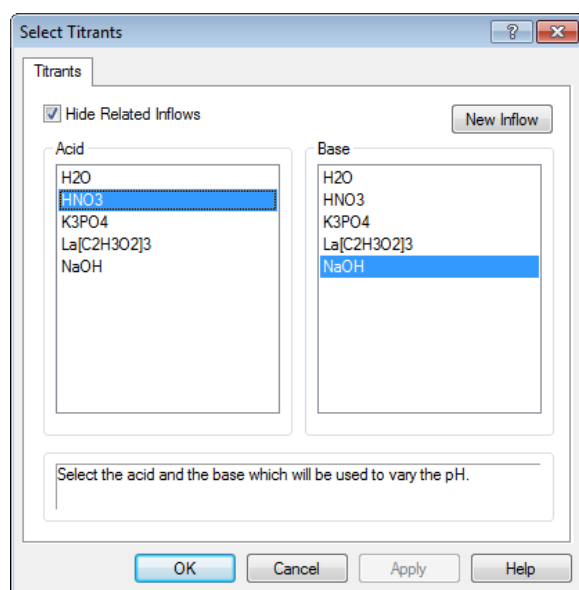
Figure 35-8

- 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.
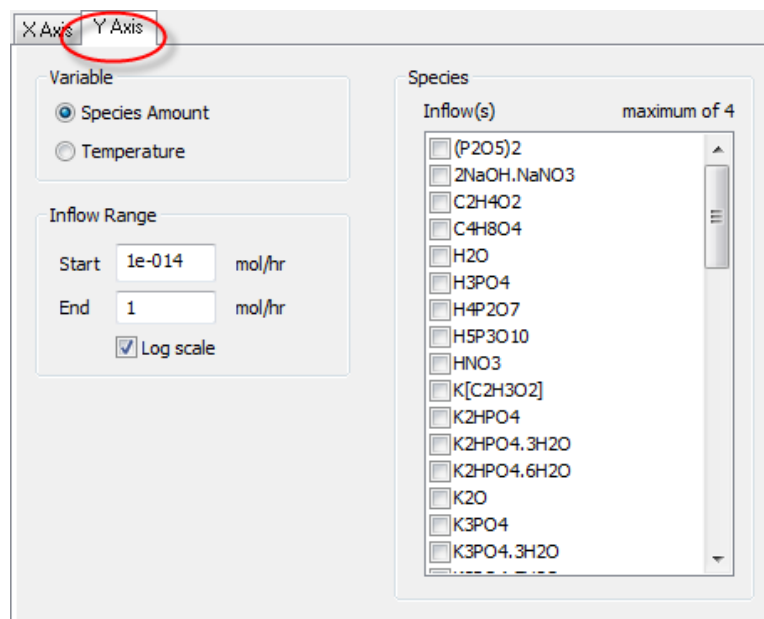
Figure 35-9

We will be adjusting the inflow species lanthanum acetate - La(C$_2$H$_3$O$_2$)$_3$ and potassium phosphate - K$_3$PO$_4$.

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$_2$H$_3$O$_2$)$_3$ and 1.0E-14 moles of K$_3$PO$_4$ increasing equally until we have 1.0 moles of each.
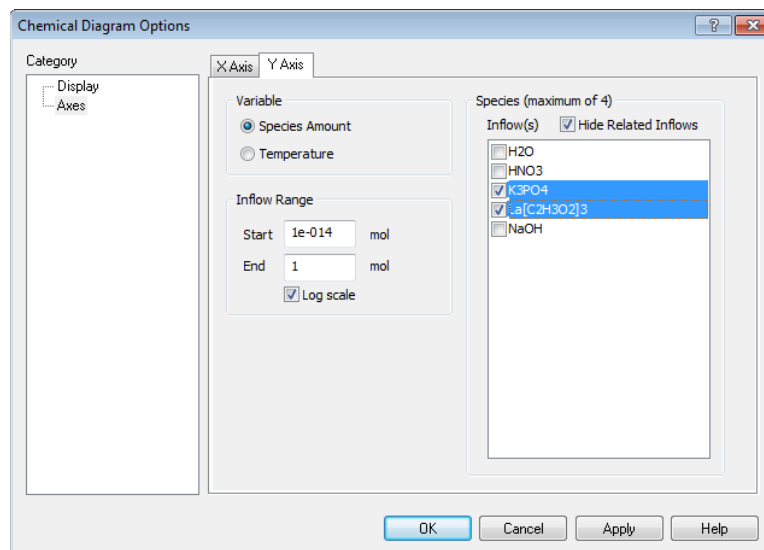
Figure 35-10

- **Check** the box next to lanthanum(III) acetate - or La(C$_2$H$_3$O$_2$)$_3$ and potassium phosphate - K$_3$PO$_4$.

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.
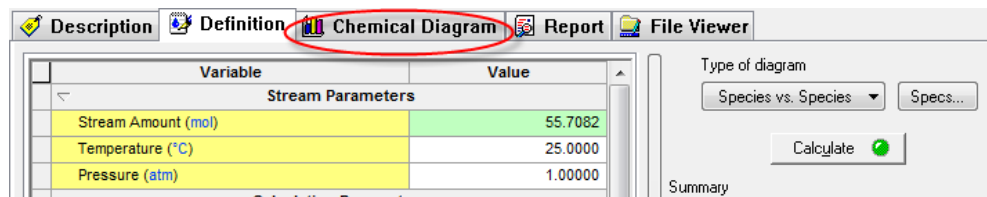
This displays the Species - pH diagram for this calculation.
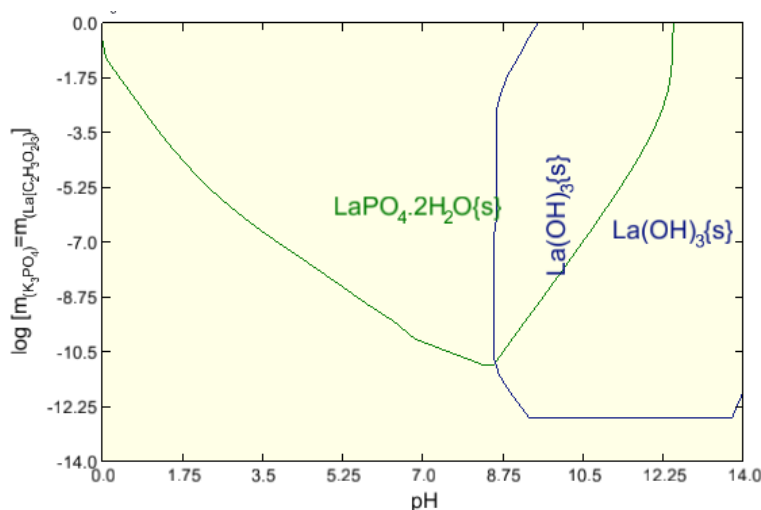
This diagram is very similar to the diagram in the above paper. It does different slightly since the author of the paper made some changes to the chemistry model that is not reflected here.

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.

Example 2: Adding 5% Lanthanum Acetate

To do this click back on the **Definition** tab and change the inflow amount for lanthanum acetate from 0.1000 to 0.10500.

Figure 35-11

- Re-Calculate and then click on the **Chemical Diagram** tab again.

Notice that the diagram is essentially the same. Only that the Y axis label has changed to reflect the increased amount of the lanthanum acetate.
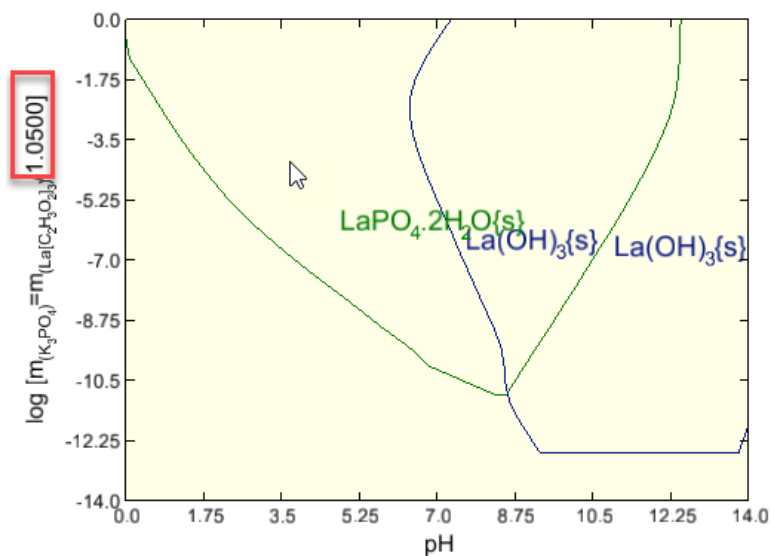
Figure 35-12

Example 3: Changing temperature and pressure

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.

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.
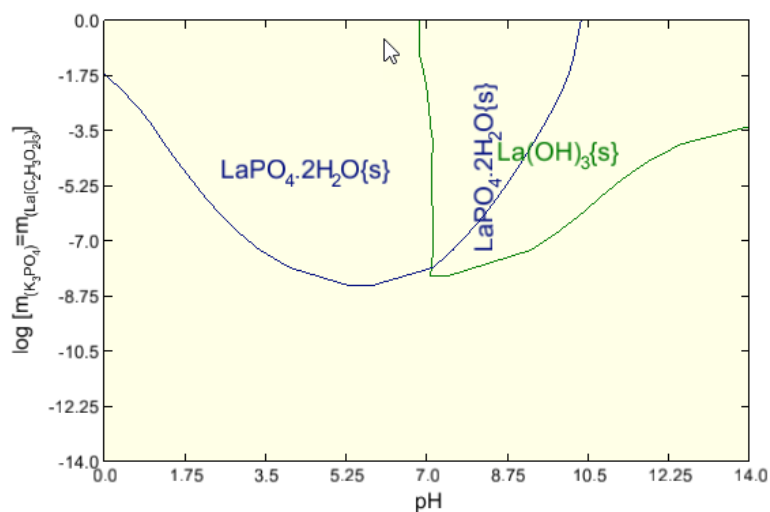
36. Managing Private Databases in the OLI Analyzer

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.
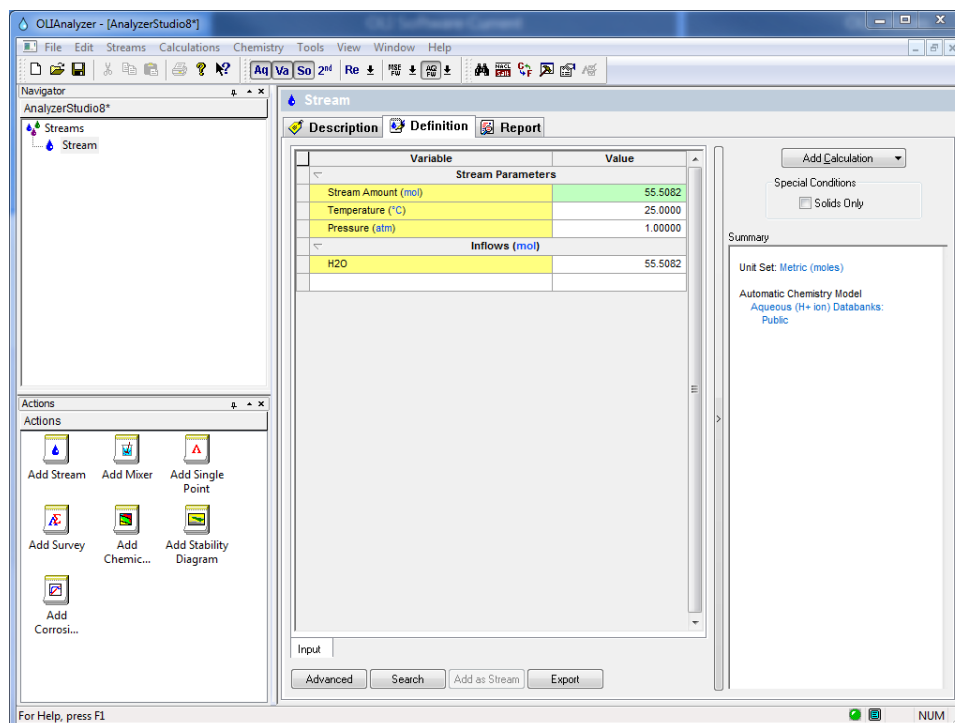
Figure 36-1

Click on the **Chemistry** menu item.

This will display the chemistry options. **Select Model Options…**
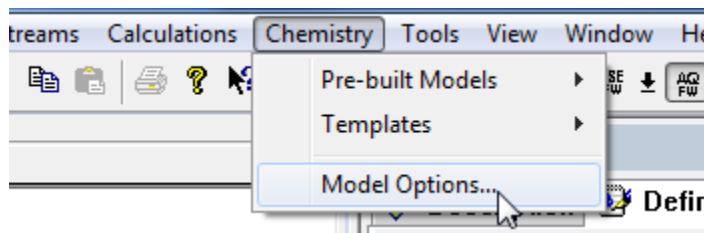
Figure 36-2

The currently loaded databases will be displayed as well as the current thermodynamic framework (AQ or MSE)
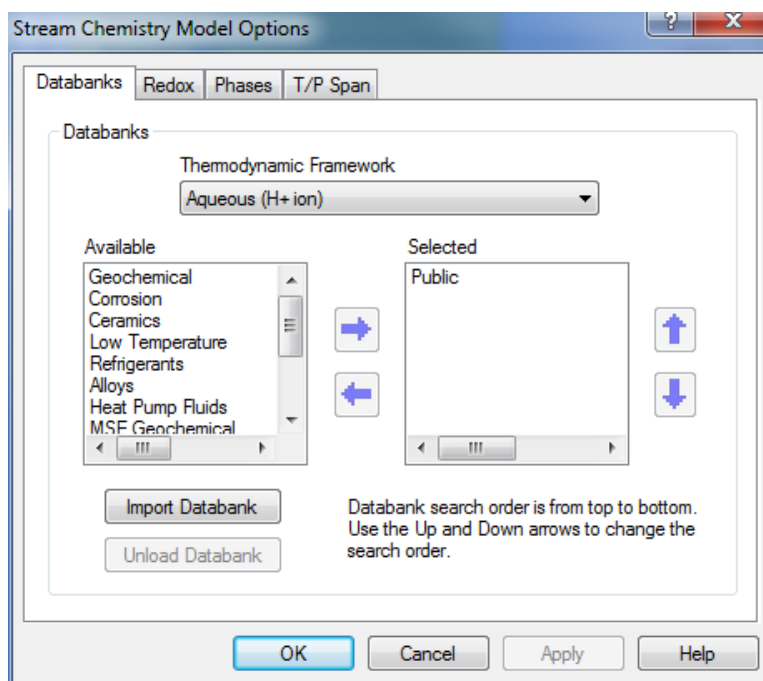
Figure 36-3

Highlight **Geochemical**
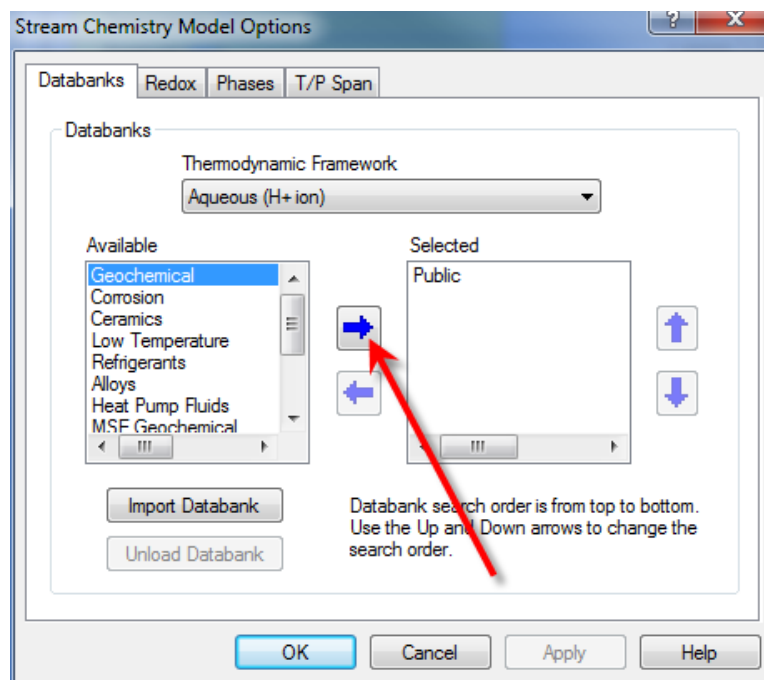
Figure 36-4

When the desired database is highlighted, click the right arrow to select it. We are also selecting the Corrosion Database for example purposes.
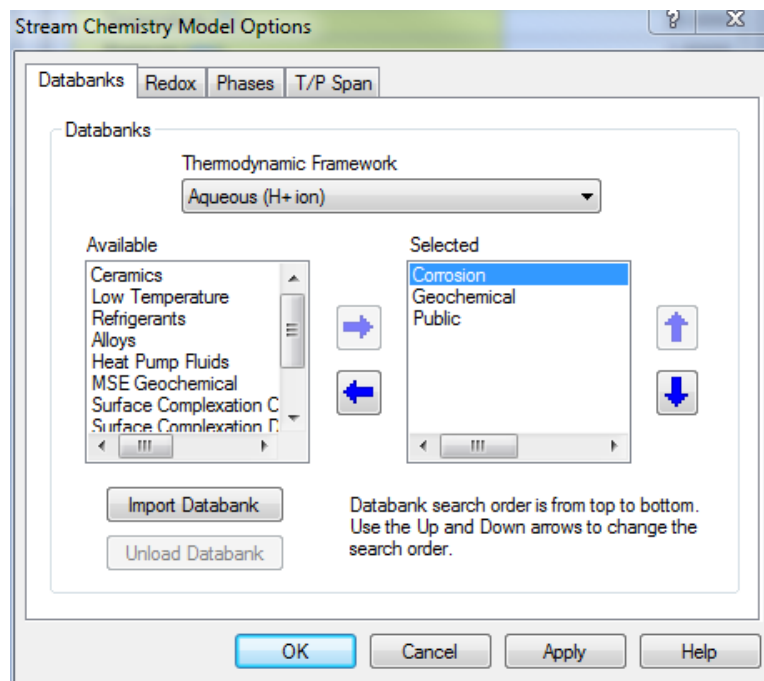
Figure 36-5

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.
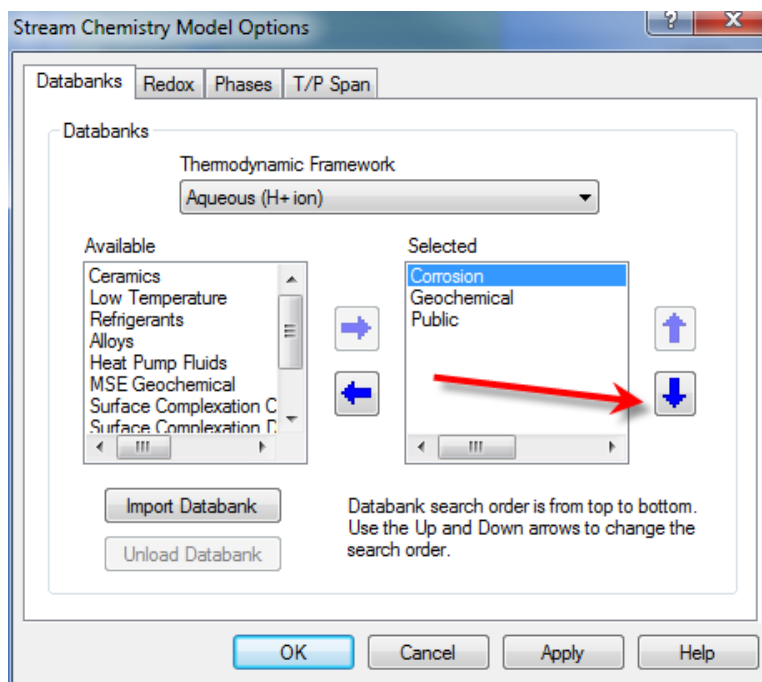
Figure 36-6

Click the down-arrow to reorder the list:
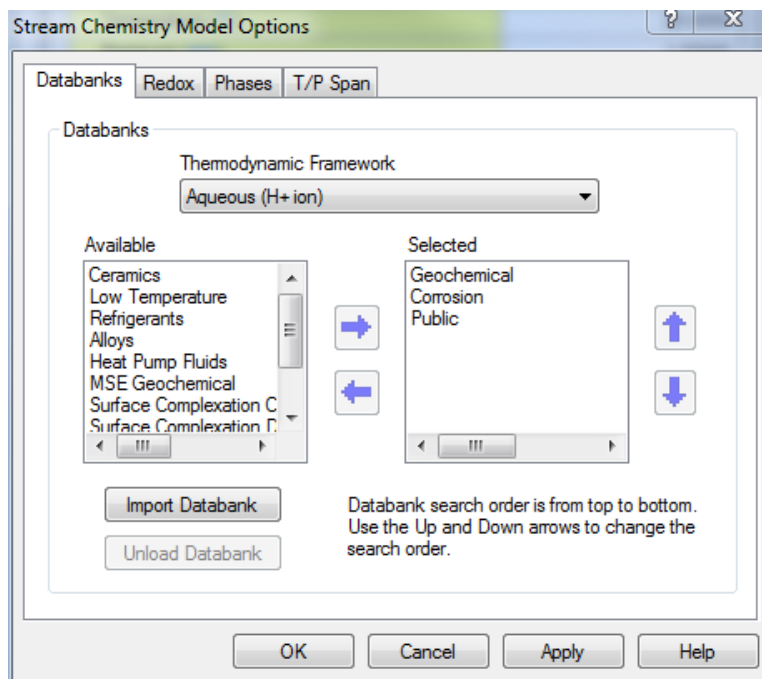
Figure 36-7

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.
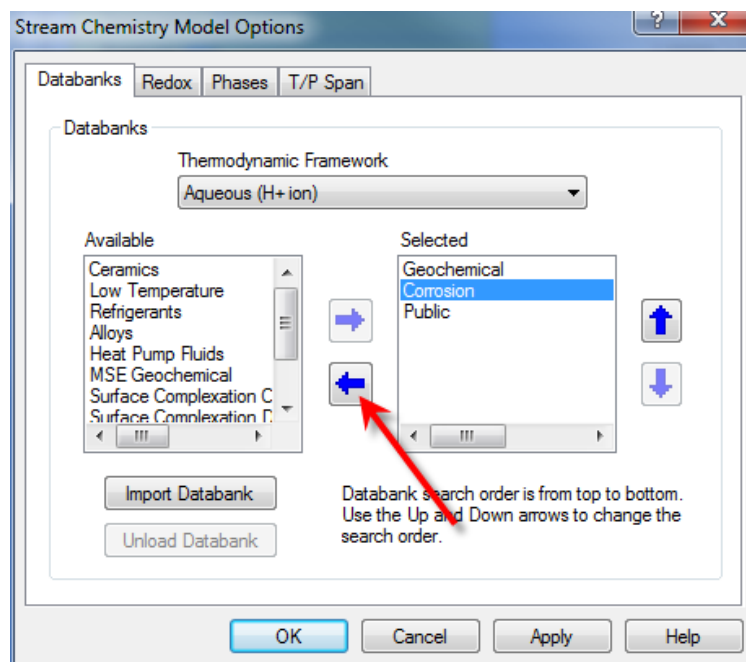
Figure 36-8

Click the left-arrow and the Corrosion database will not be used in this calculation.
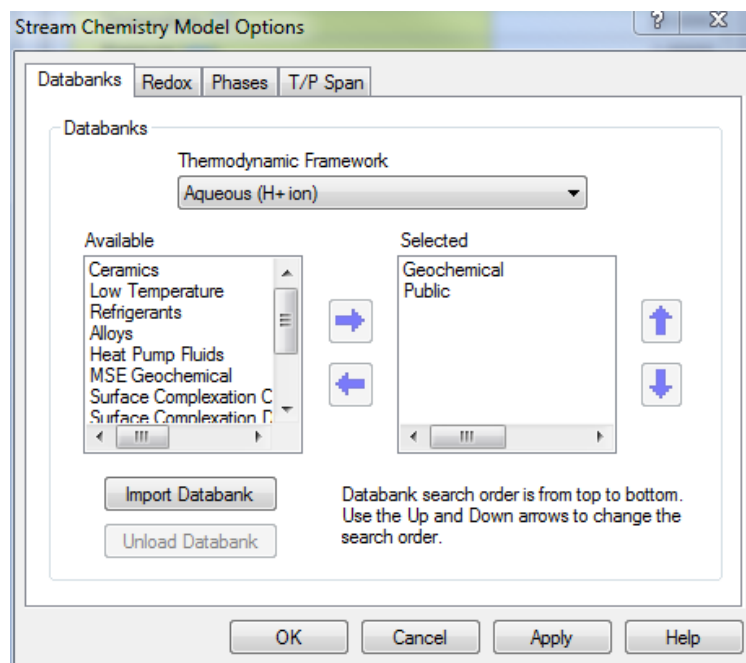
Figure 36-9

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**
-
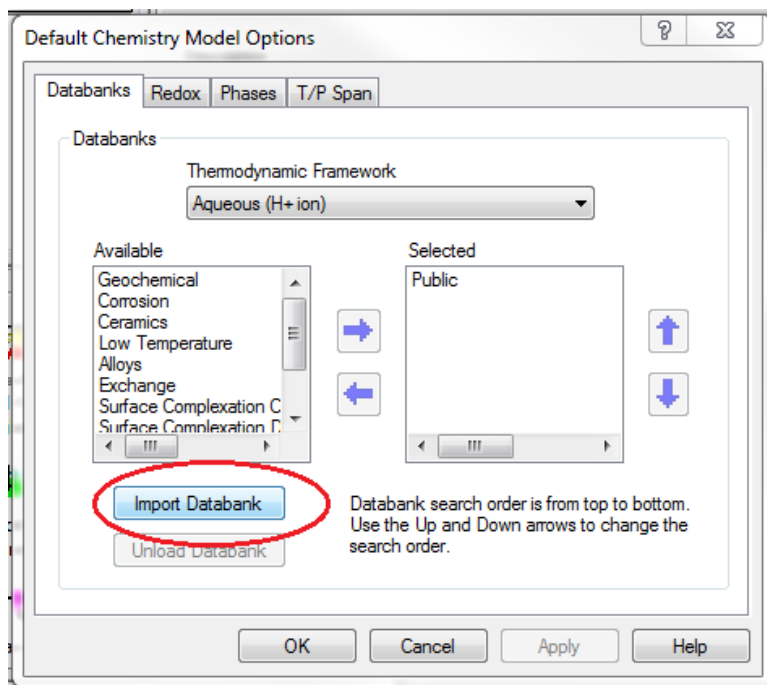
Figure 36-10

You can load both Aqueous databases and MSE databases from the same screen.

- Click the **Import Databank** button.
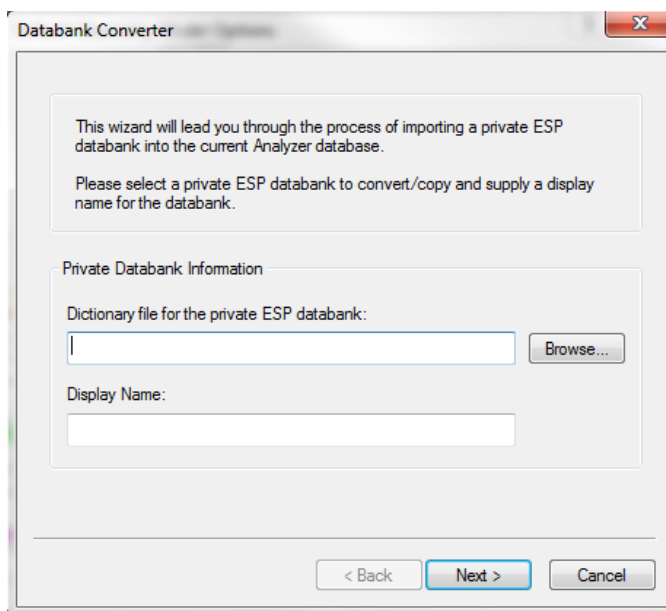
Figure 36-11

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.
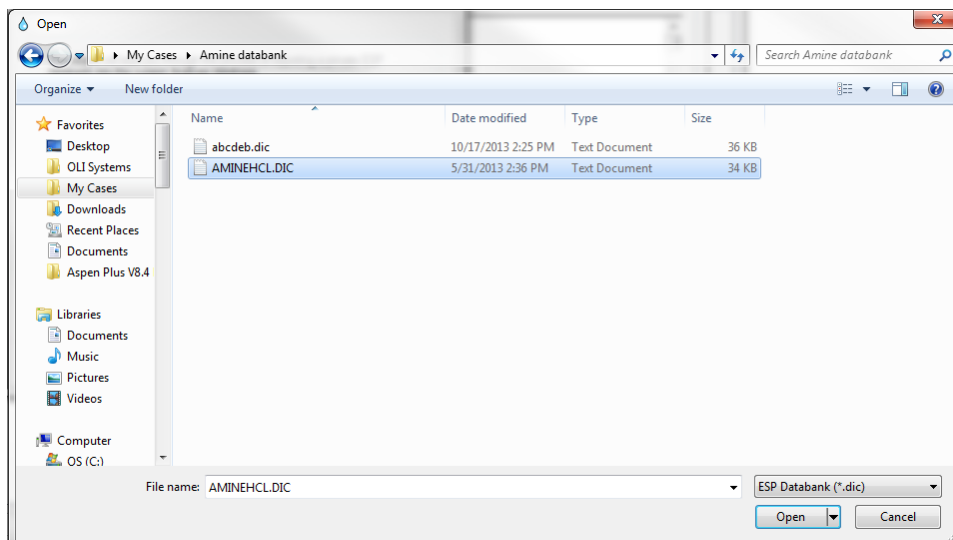
Figure 36-12

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.
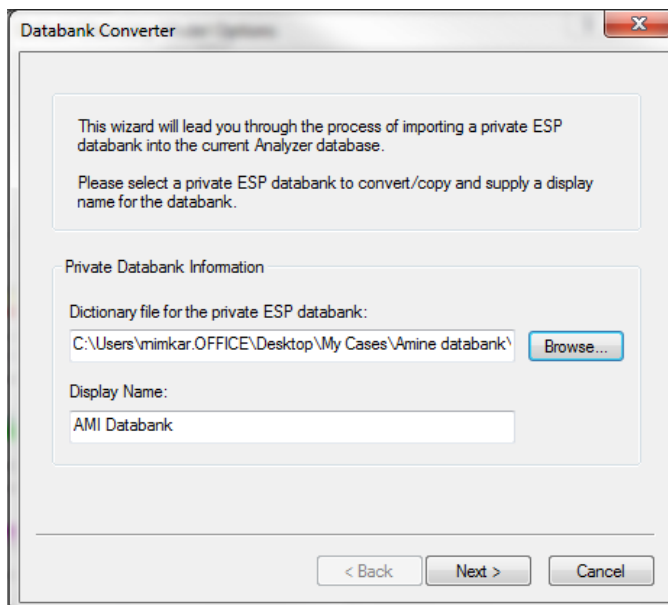
Figure 36-13

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.
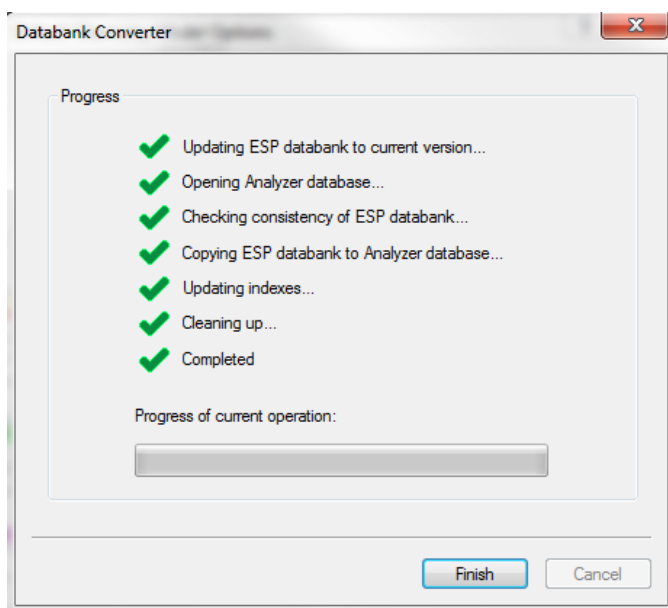
Figure 36-14

The process of converting and uploading the file starts.

If all the lines are checked, then click the **Finish** button
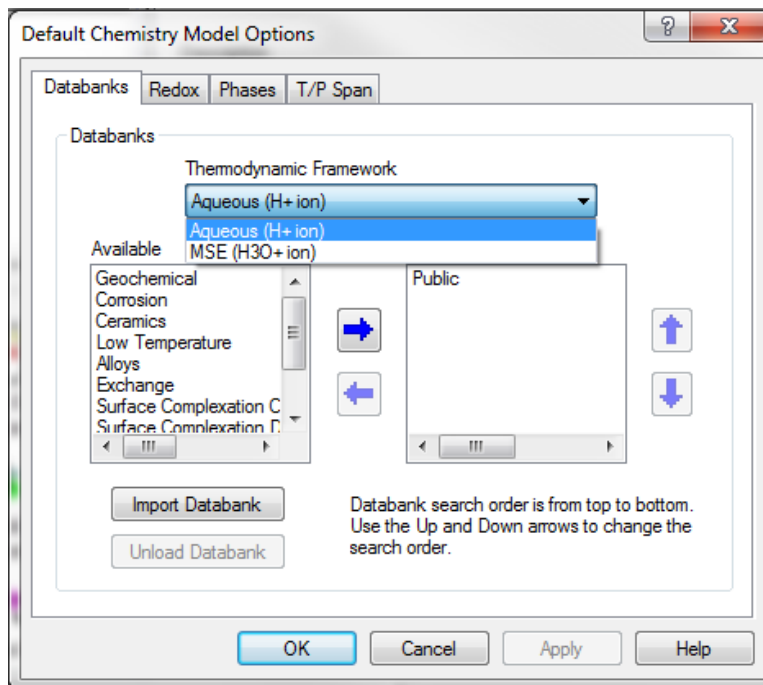
Figure 36-15

Your imported database is now ready for use. If your database was for the MSE framework, 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.
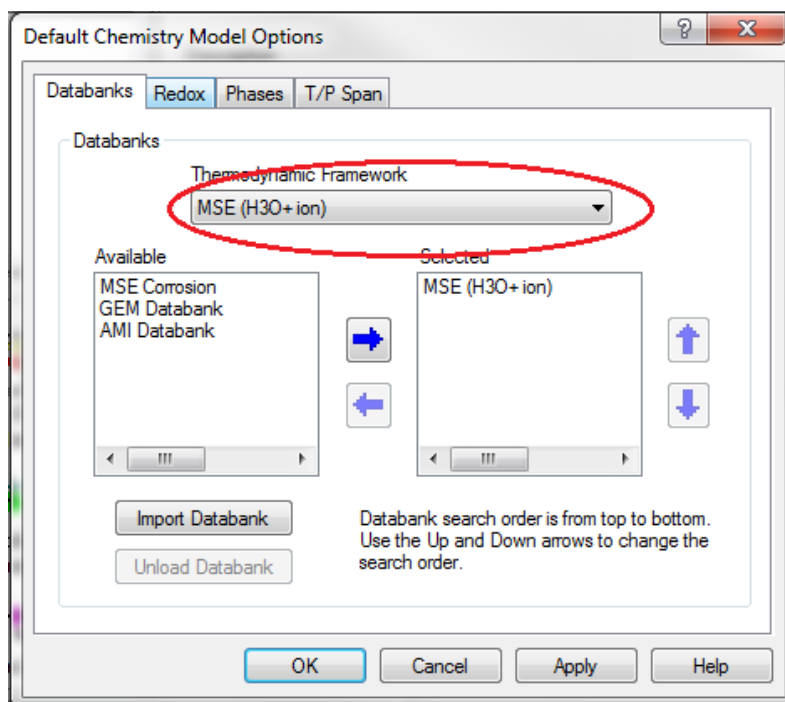
Figure 36-16
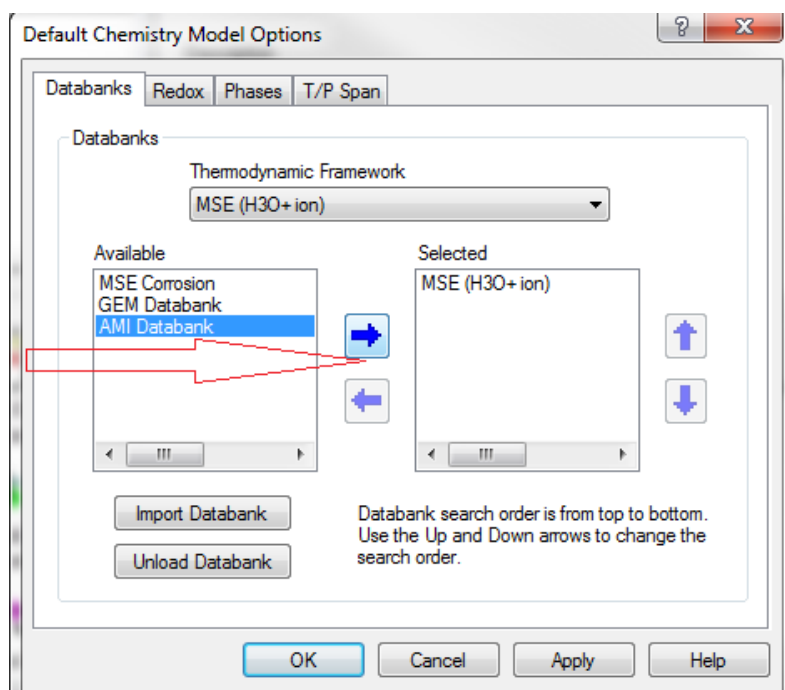
Figure 36-17

Click it to select it. Then click the right-arrow.
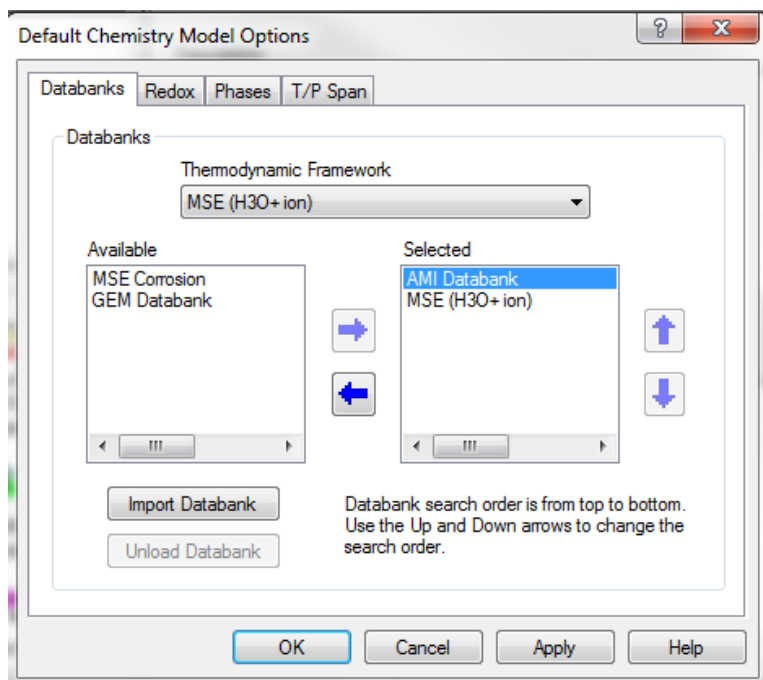
Figure 36-18

Click the OK button to continue.
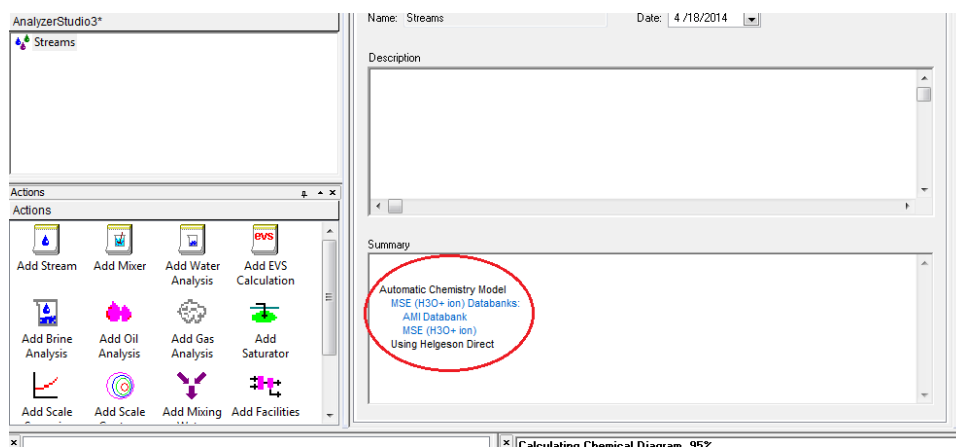
Figure 36-19

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.
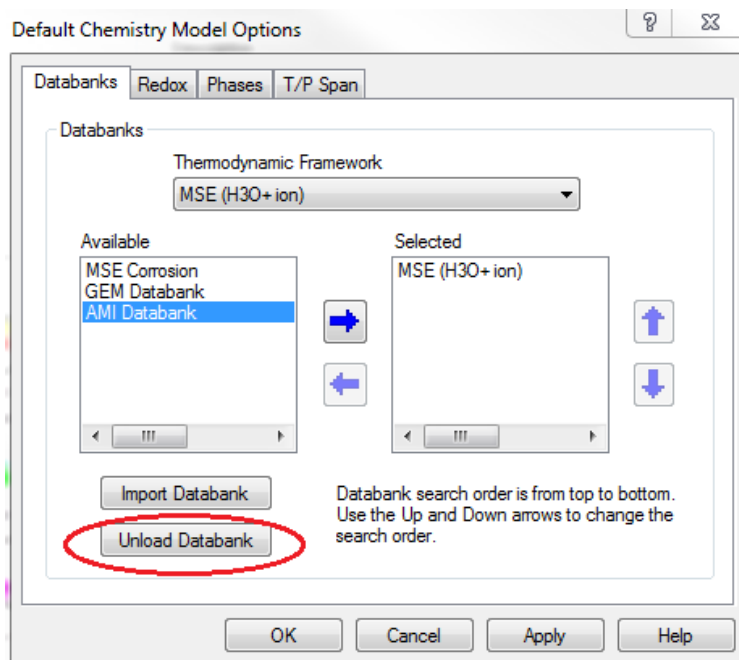
Figure 36-20

There is no pop up warning to make sure you want to do this. Be careful!

Click the **Unload Databank** button
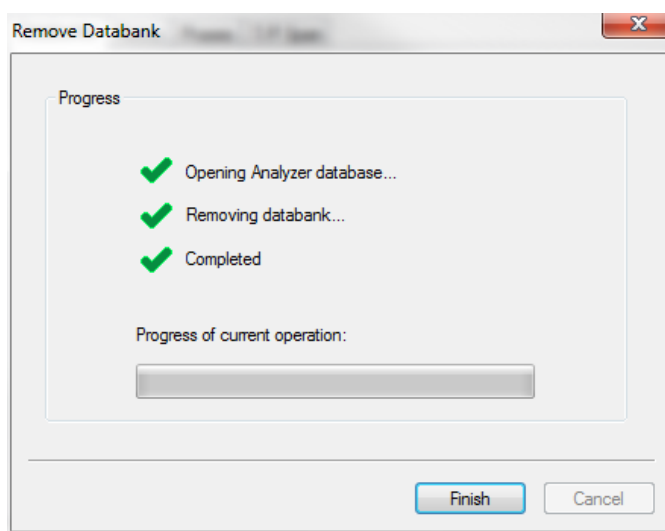
Figure 36-21

This removes the selected databank.
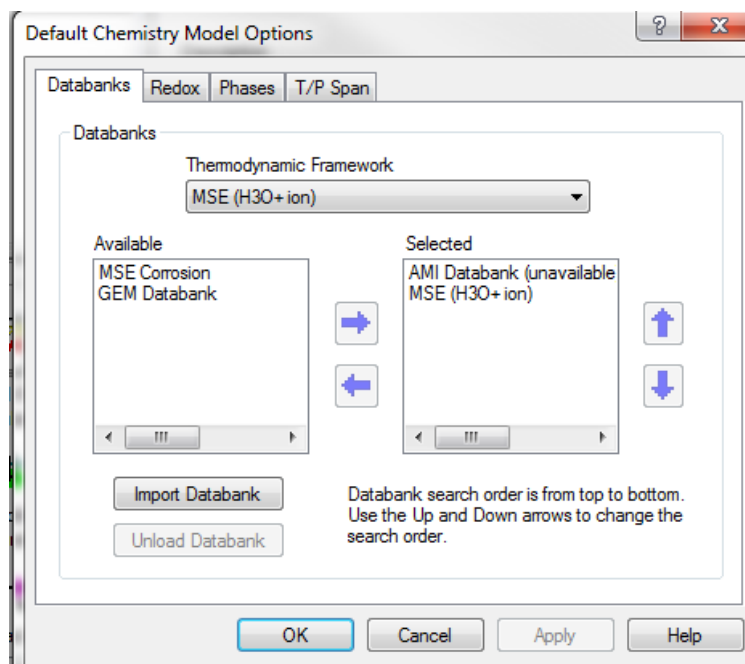
Figure 36-22

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.

Figure 37-1

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.

Figure 37-2

Click on the blue **ºC**
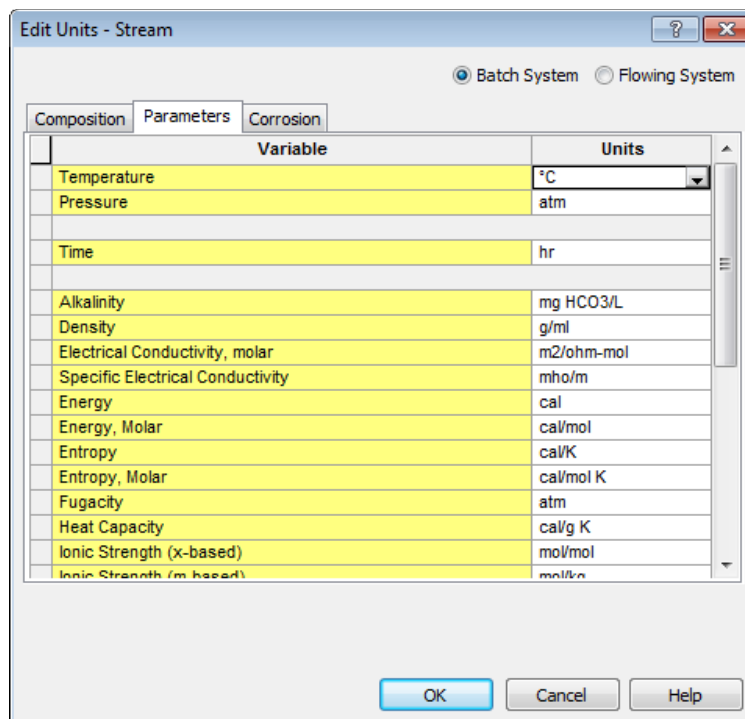
Figure 37-3

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.
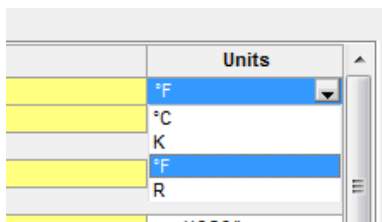
Figure 37-4

You can select from a range of units. For this example, we are choosing Fahrenheit.

As you can see the 25 ºC value is now 77 ºF.

Figure 37-5

It would be cumbersome to do this for 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.

Figure 37-6

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...**
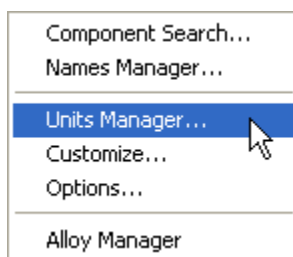
Figure 37-7

Below is the units manager dialog with the default standard units selected.
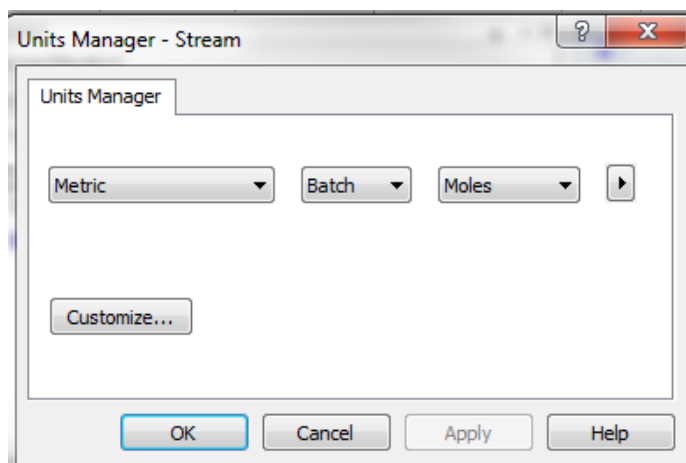
Figure 37-8

For a quick units change we can click one of the radio buttons. Click the **Customize** button
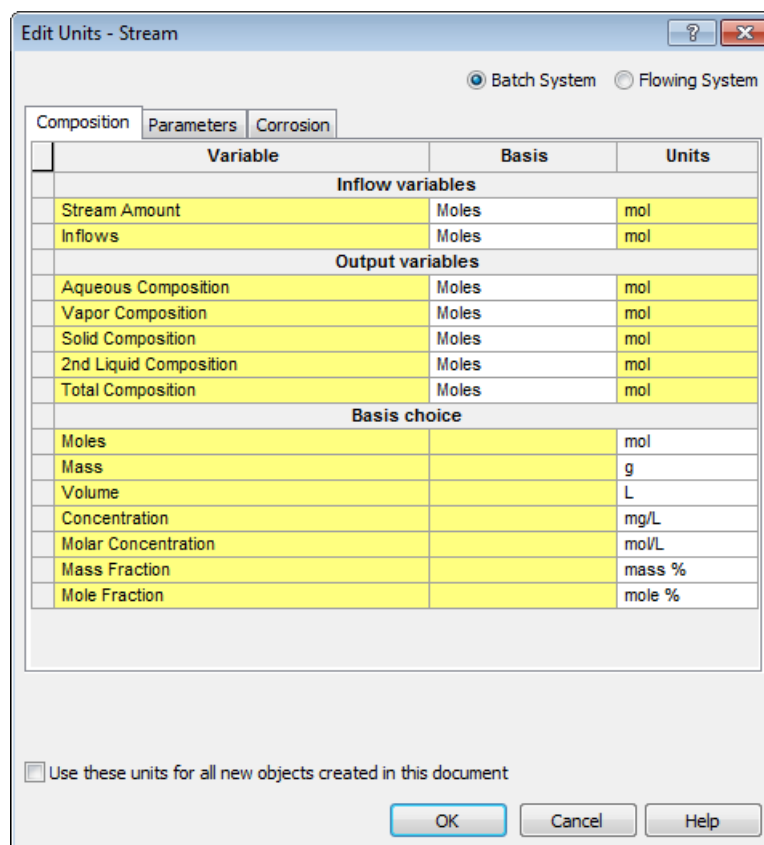
Figure 37-9

Click the drop-down menu next to **Inflows** under the basis column:
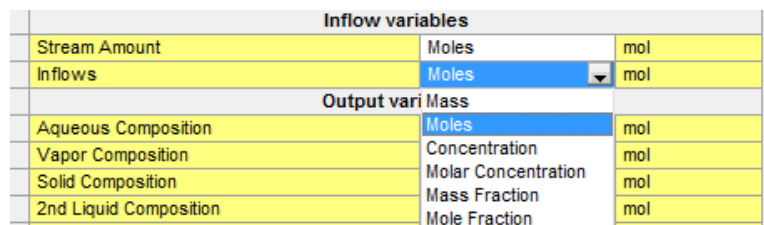
Figure 37-10

Next select **Mass Fraction** and the grid updates:
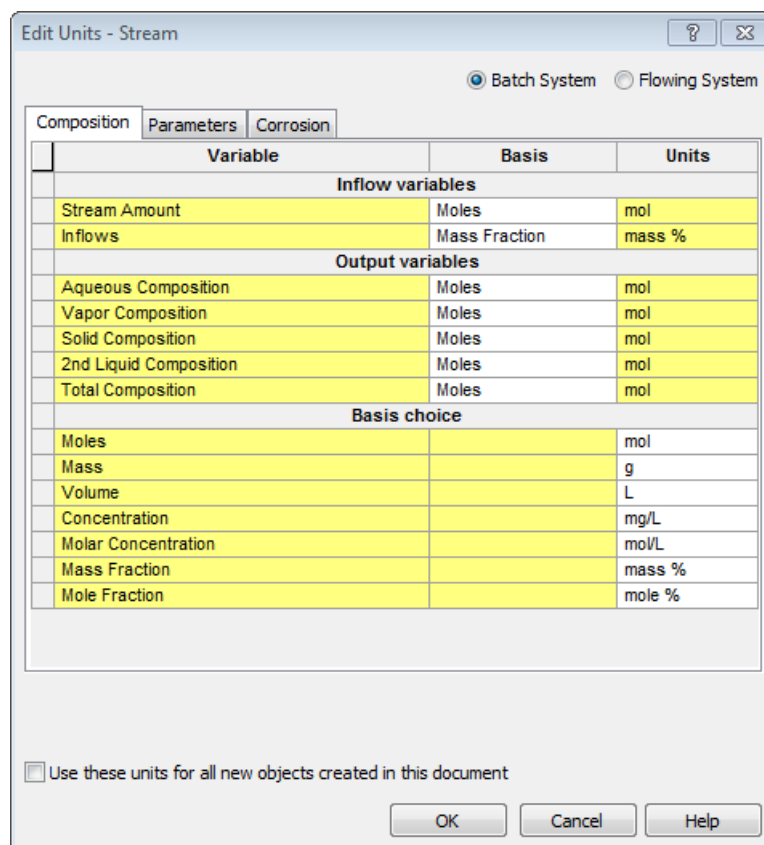
Figure 37-11

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.

Figure 37-12

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 back up 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.
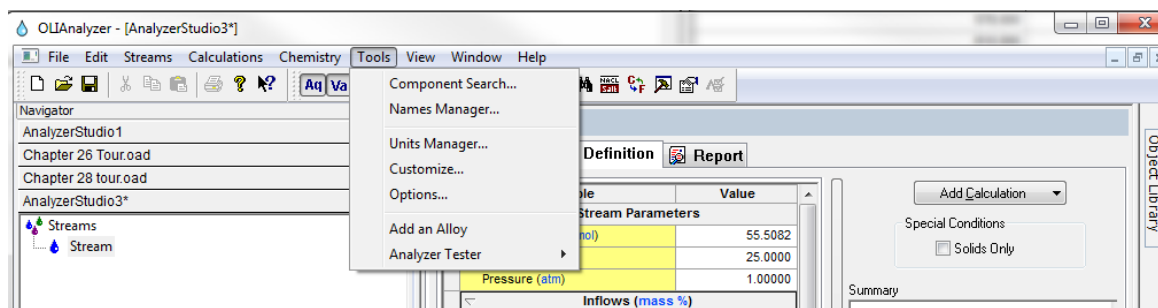
Figure 38-1

Next select **Options...**

Select the **General** category

By default, the OLI Analyzers will create a backup 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.
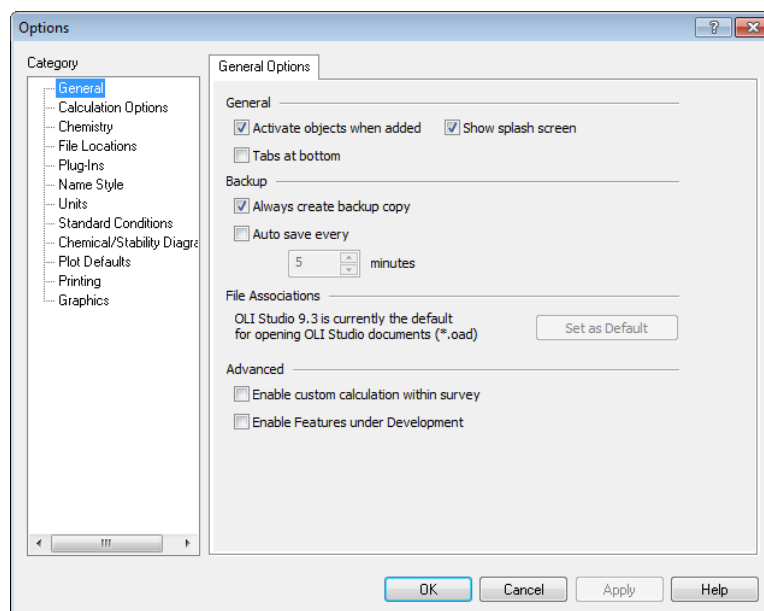
Figure 38-2

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.
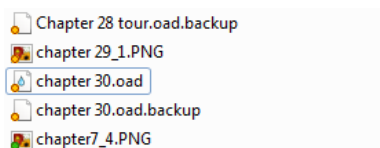
Figure 38-3

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:
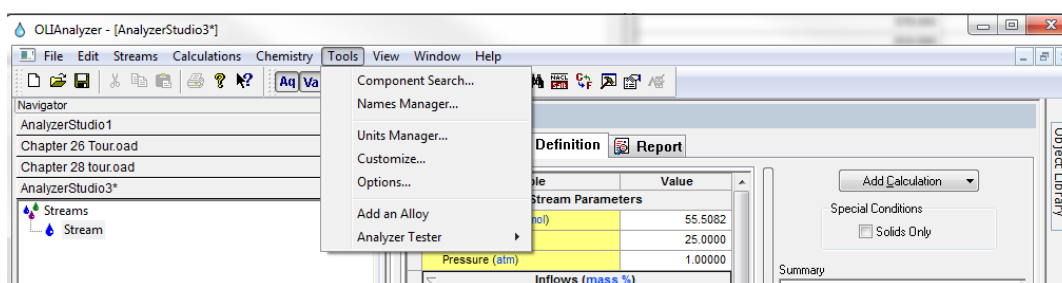
Figure 38-4

Next select *Options...*

Next select *File Locations* and then click on the *Configuration* tab.
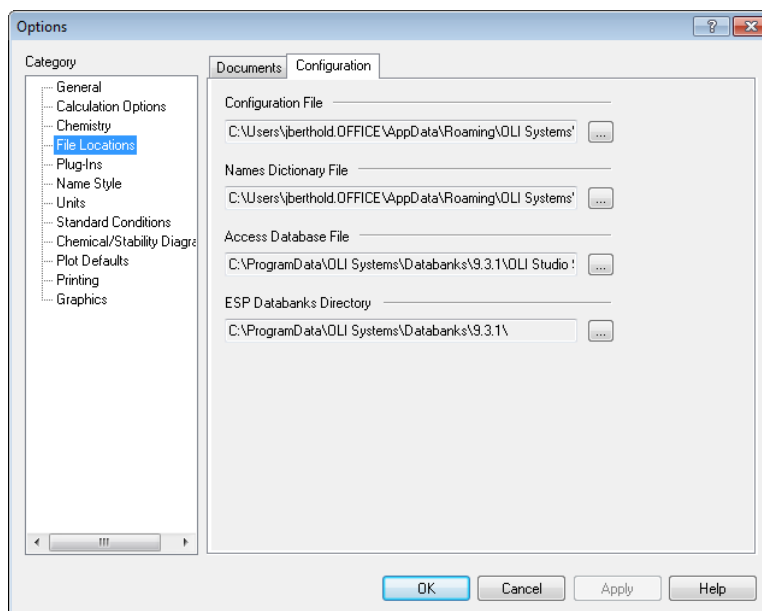
Figure 38-5

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.
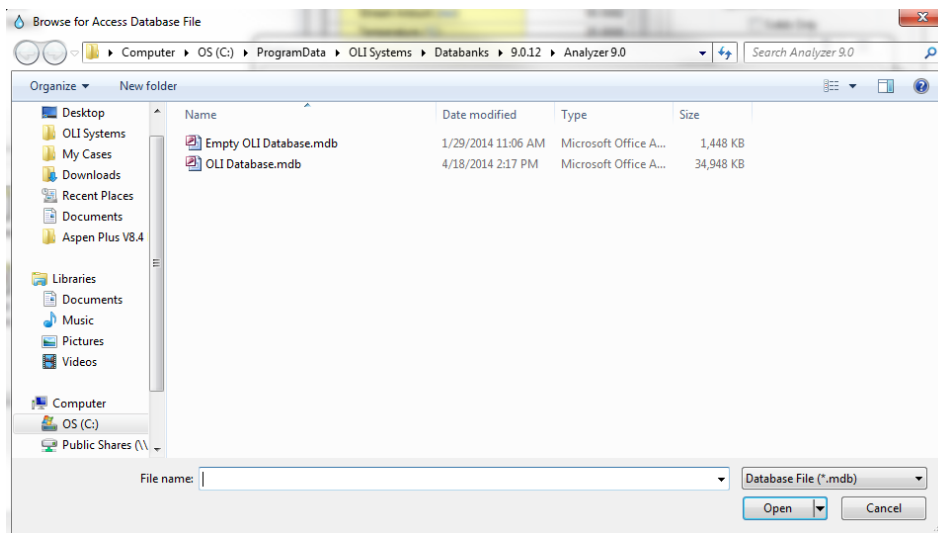
Figure 38-6

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.
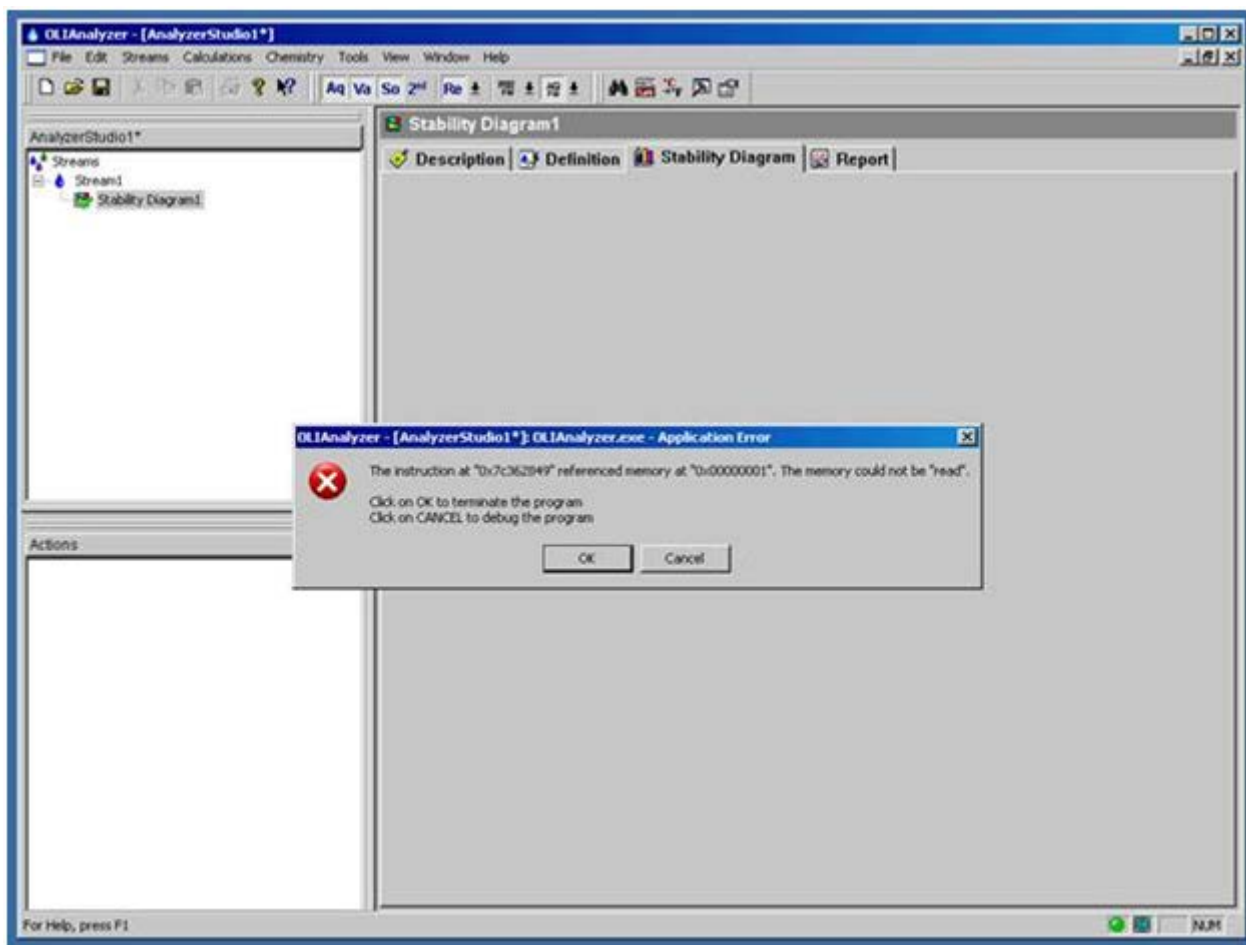
Figure 38-7

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.
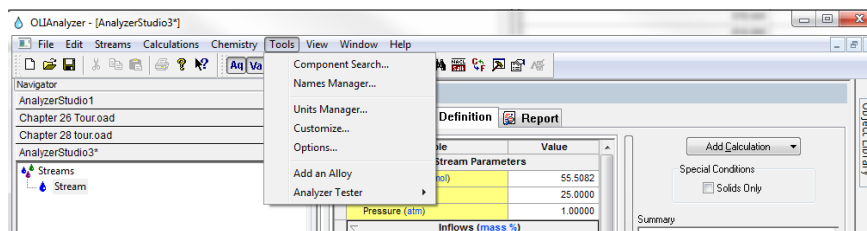
Figure 38-8

Then select Options from the drop-down menu.

This will display the options available for the Analyzers. Select Chemical/Stability diagrams.
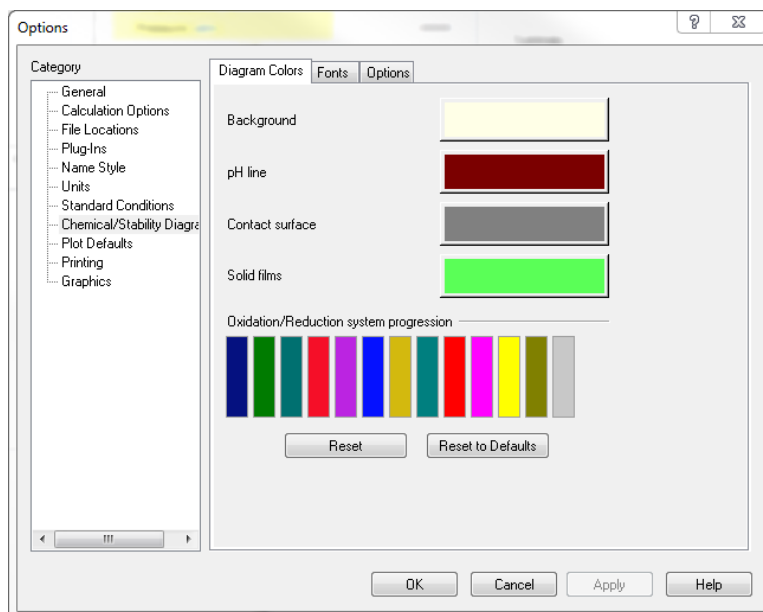
Figure 38-9

You can change the way your plots look. To turn off hardware acceleration click the Options tab.
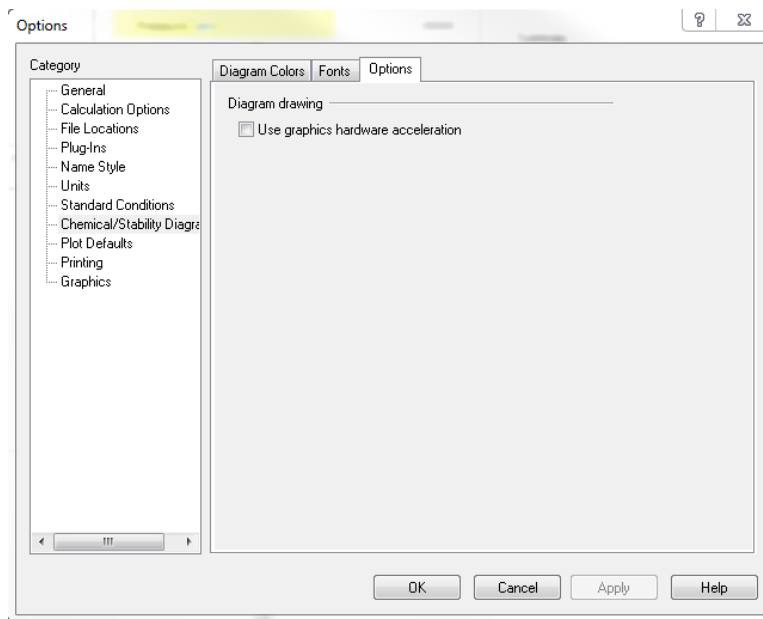
Figure 38-10

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.
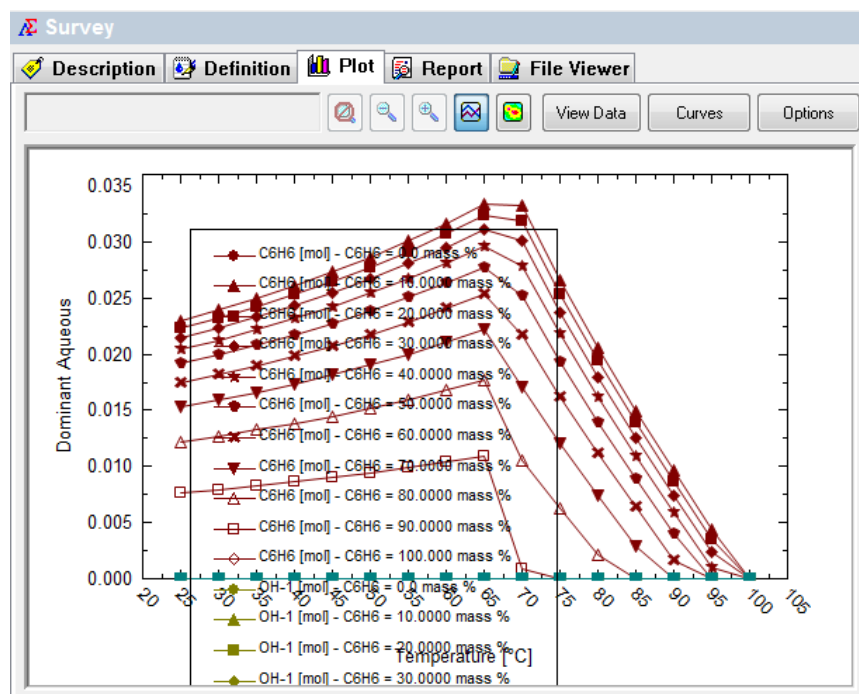
Figure 39-1

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.
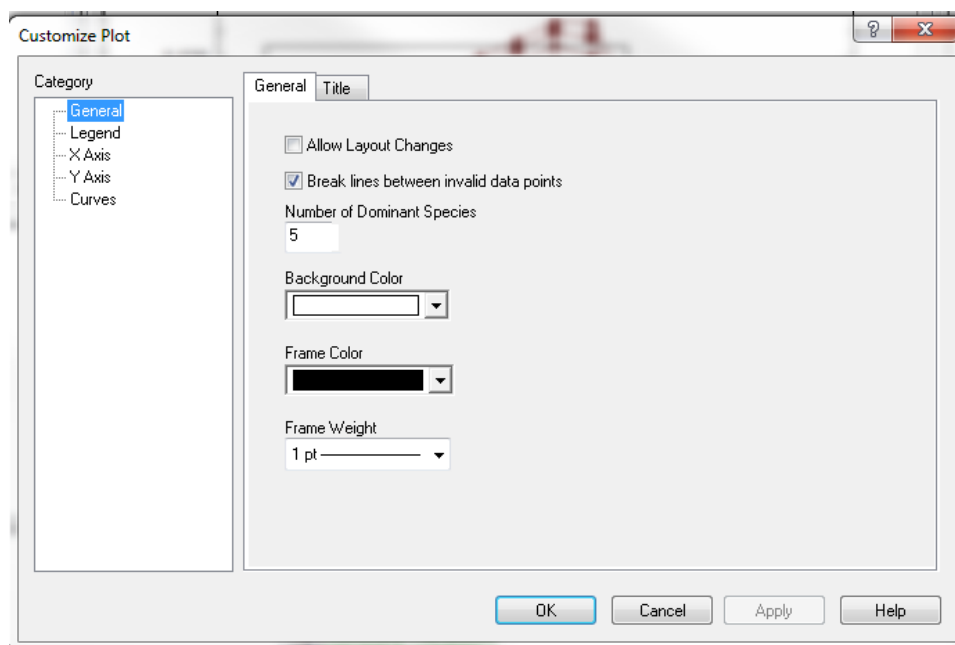
Figure 39-2

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.**
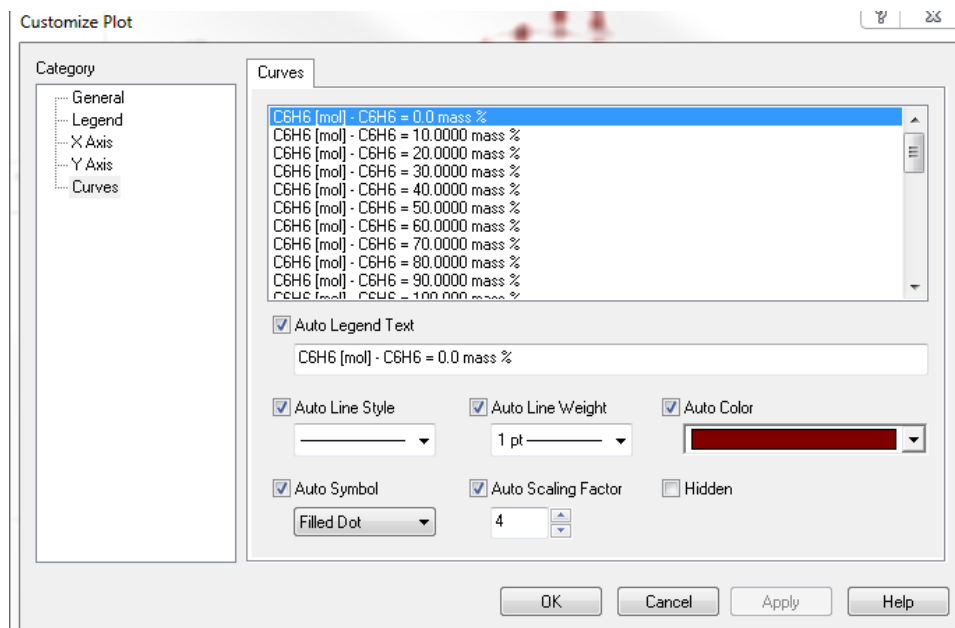
Figure 39-3

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 %

Figure 39-4

We have now selected all the items. Click the **Hidden** check box to hide these curves.
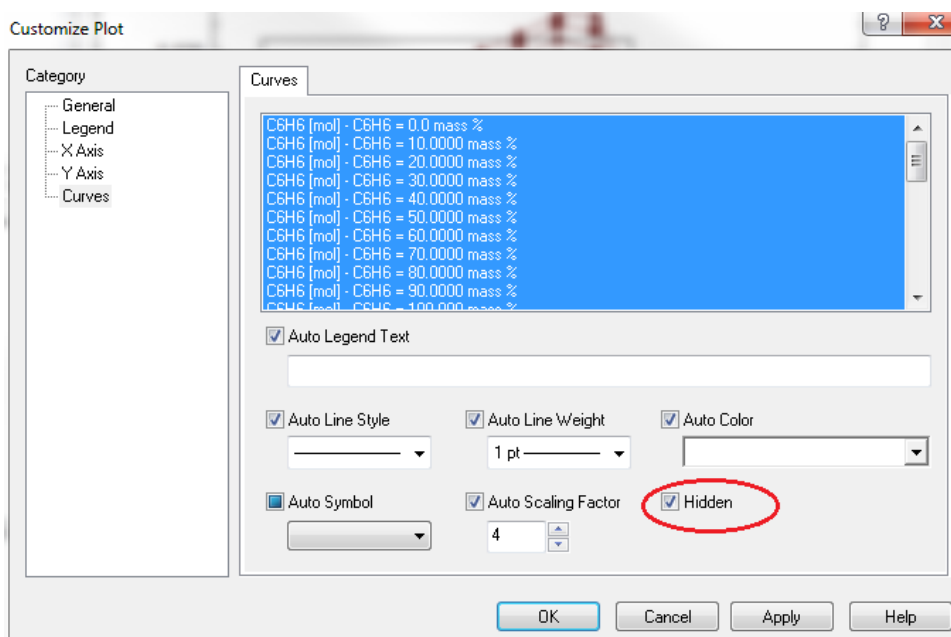
Figure 39-5

Click the **Apply** and then **OK** buttons to see the plot.
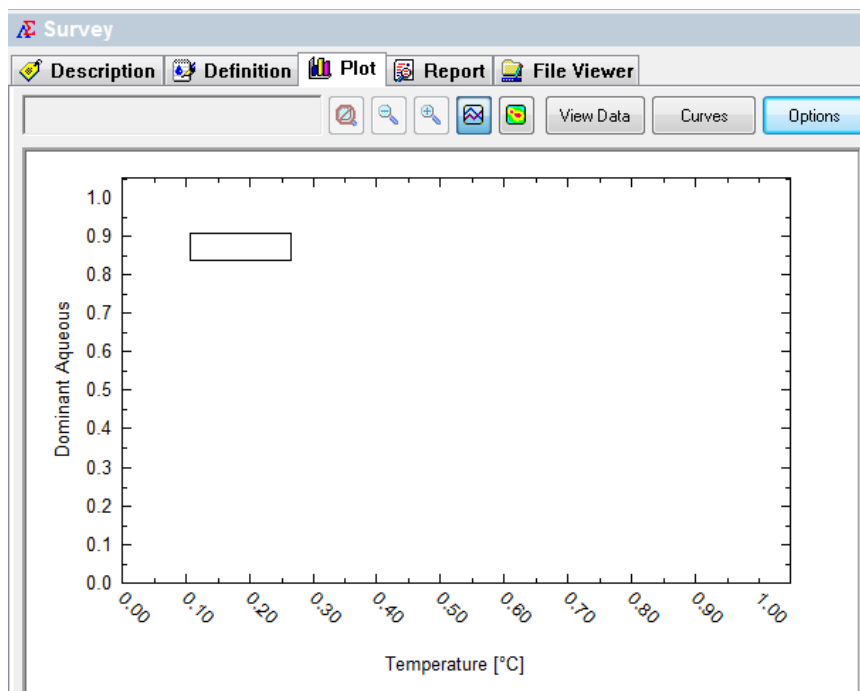
Figure 39-6

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.
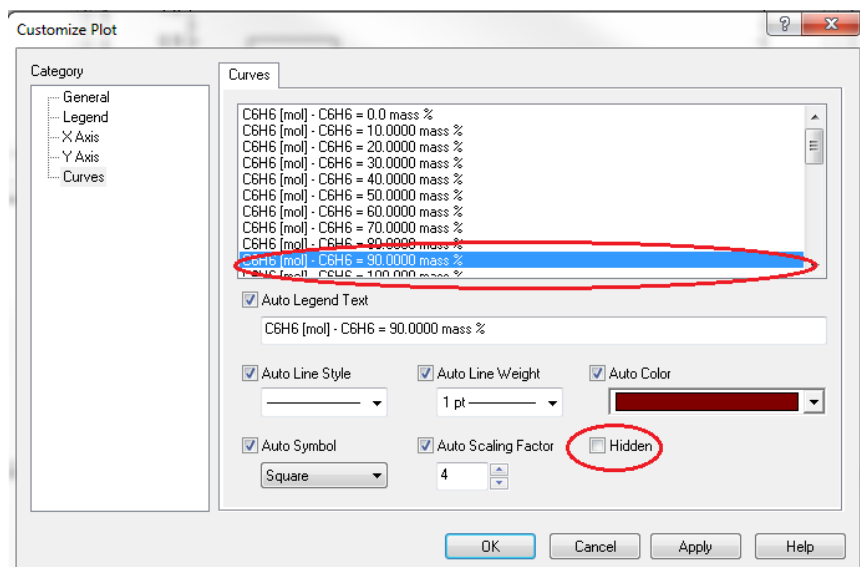
Figure 39-7

Click the **Apply** and **OK** buttons to display the plot.
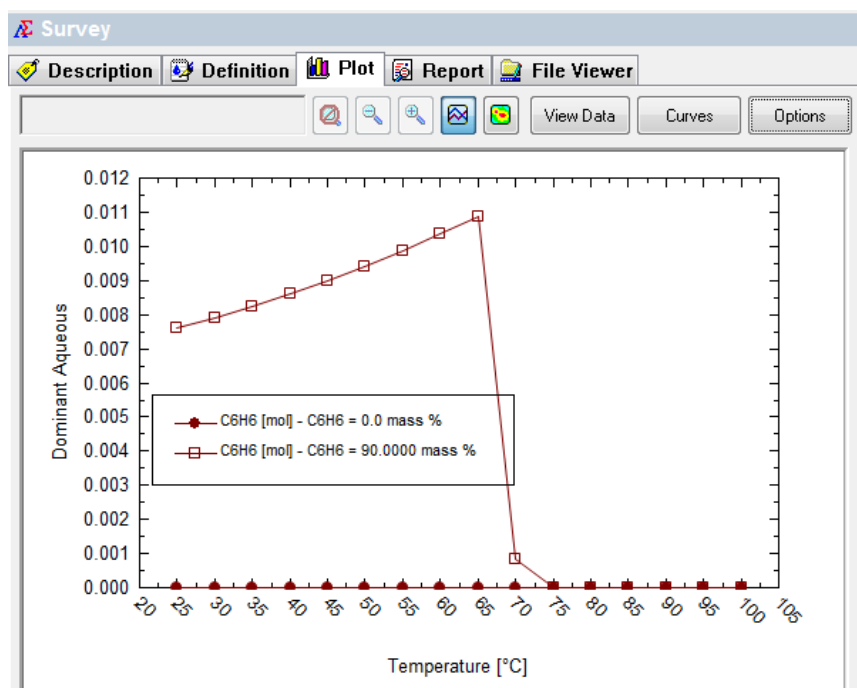
Figure 39-8

We now have our plot without all the clutter of extra points. We can now go back and add (or unhide) additional curves. Once again, click the **Options** button and then reselect the **Curves** category.
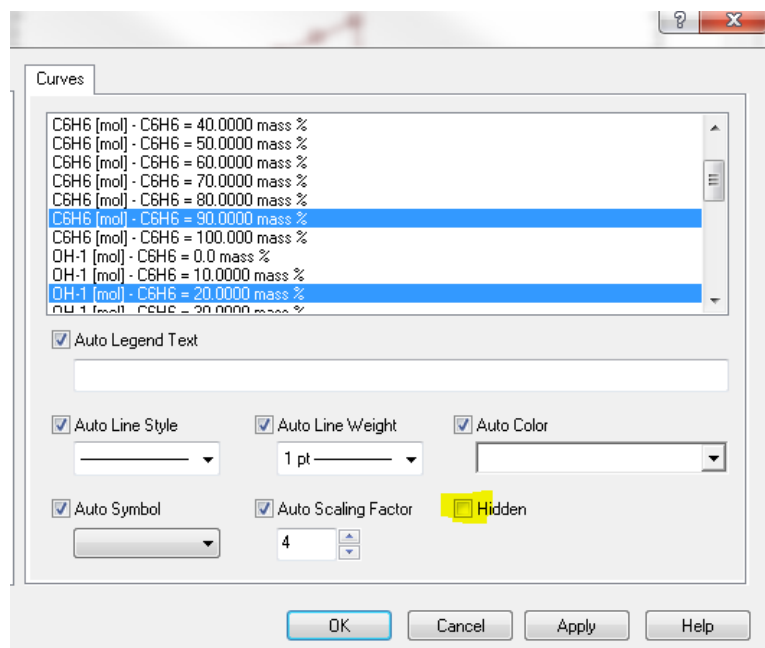
Figure 39-9

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.
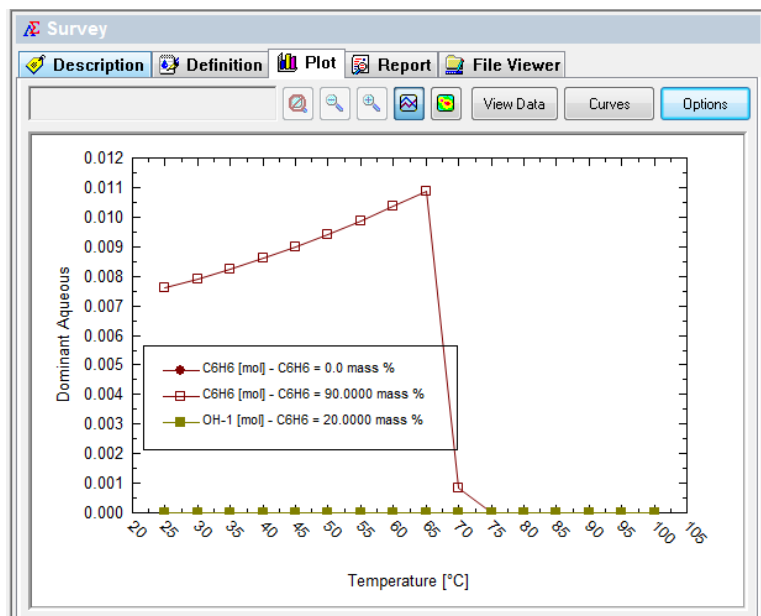
Figure 39-10

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.
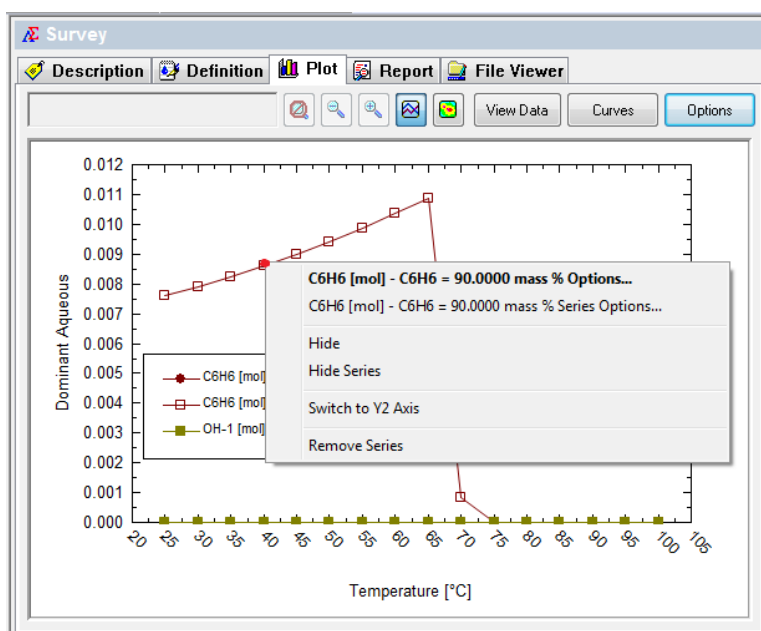
Figure 39-11

This will display a pop-up menu. The name of the series is displayed. Select **Hide Series.**

Hide
Hide Series

Switch to Y2 Axis

Remove Series

Figure 39-12

This removed the series from display. Unfortunately, the only method to "Unhide" the series is to use the Options button as we did above.
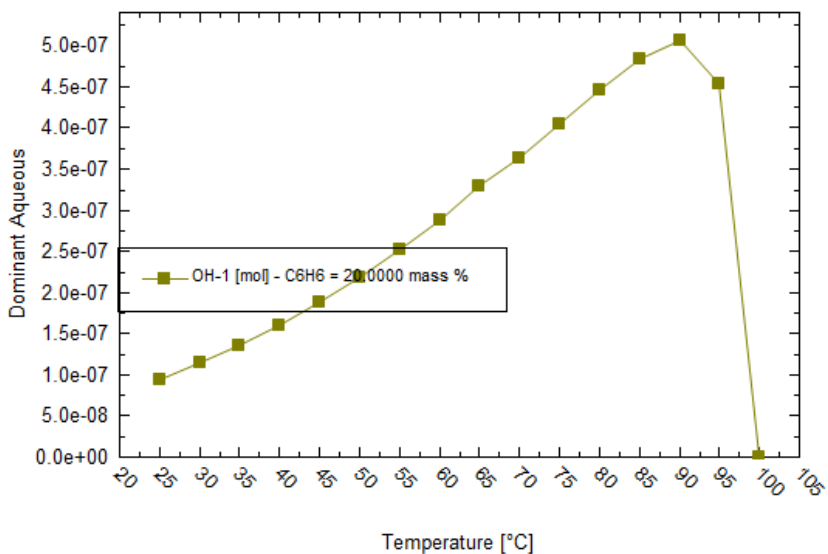
Figure 39-13

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 171 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:
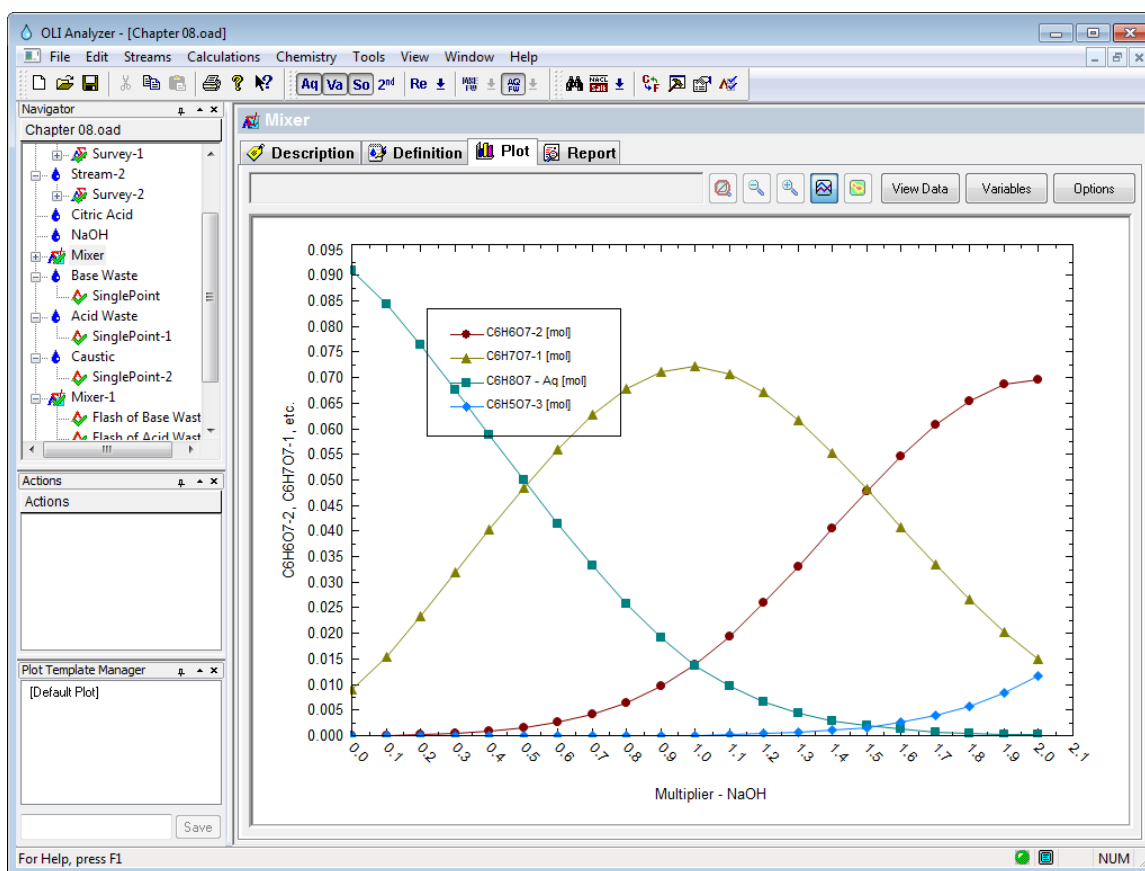
Figure 39-14 Chapter 8 citric acid survey

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.
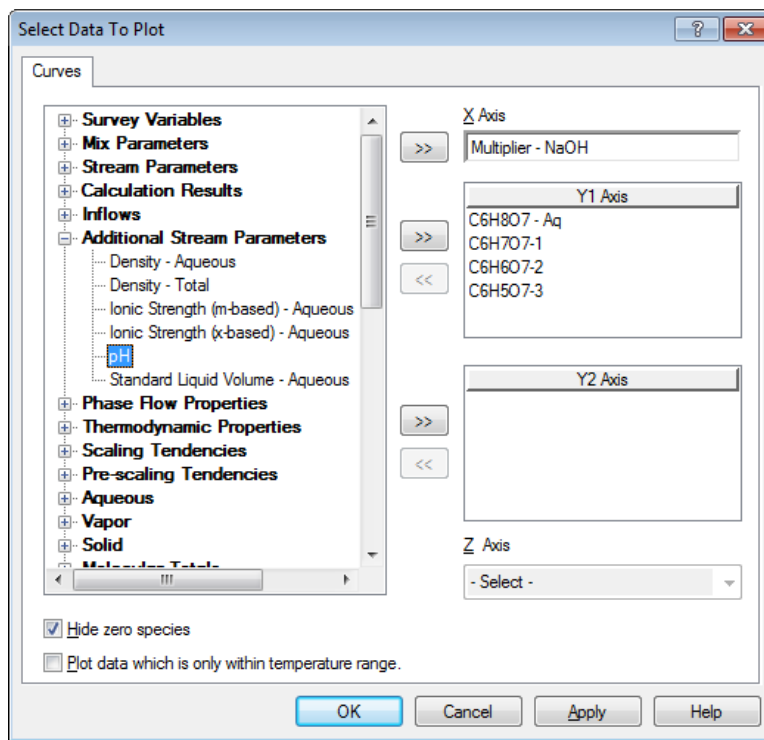
Figure 39-15 Selecting pH from the Additional Stream Parameters

This will put the pH on the Y1 axis by default. Here is the resultant plot:
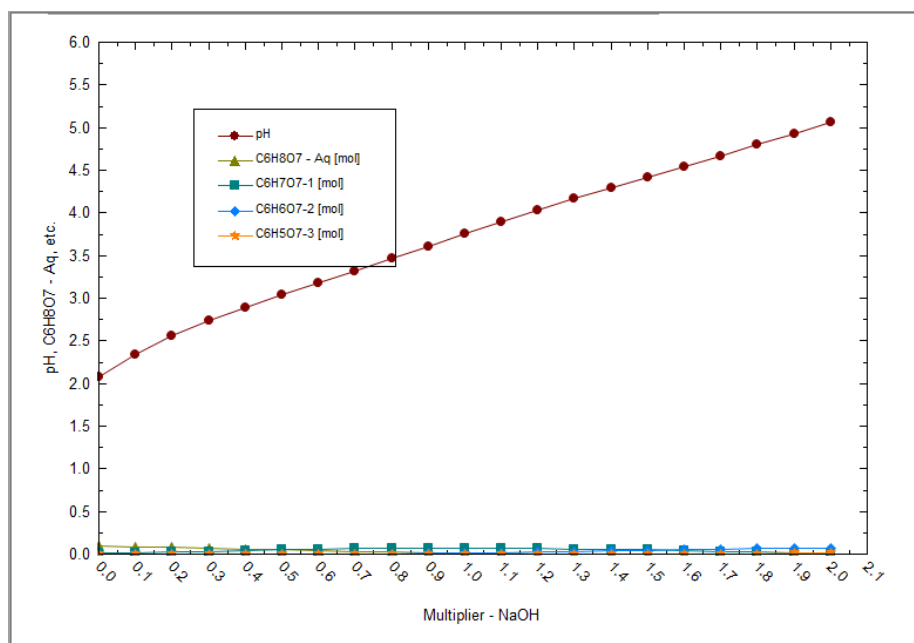
Figure 39-16 pH plotted, this skews the view

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.
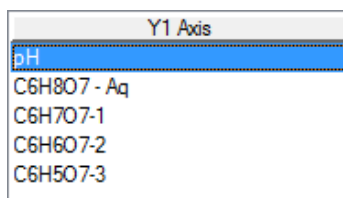
Figure 39-17

Now right-click the variable
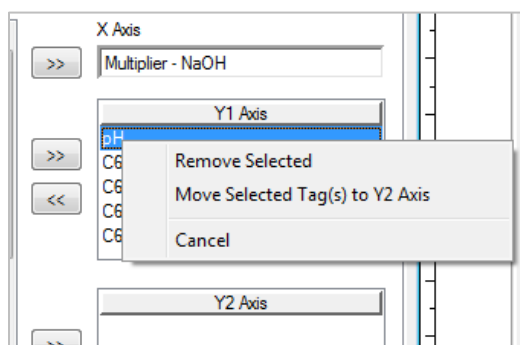
Figure 39-18 Right-clicking "pH"

Select **Move Selected Tag(s) to Y2 Axis**
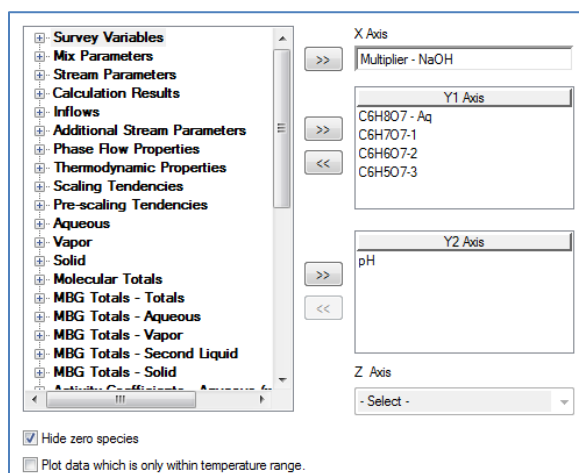
Figure 39-19 Variable moved

Here is the updated plot.
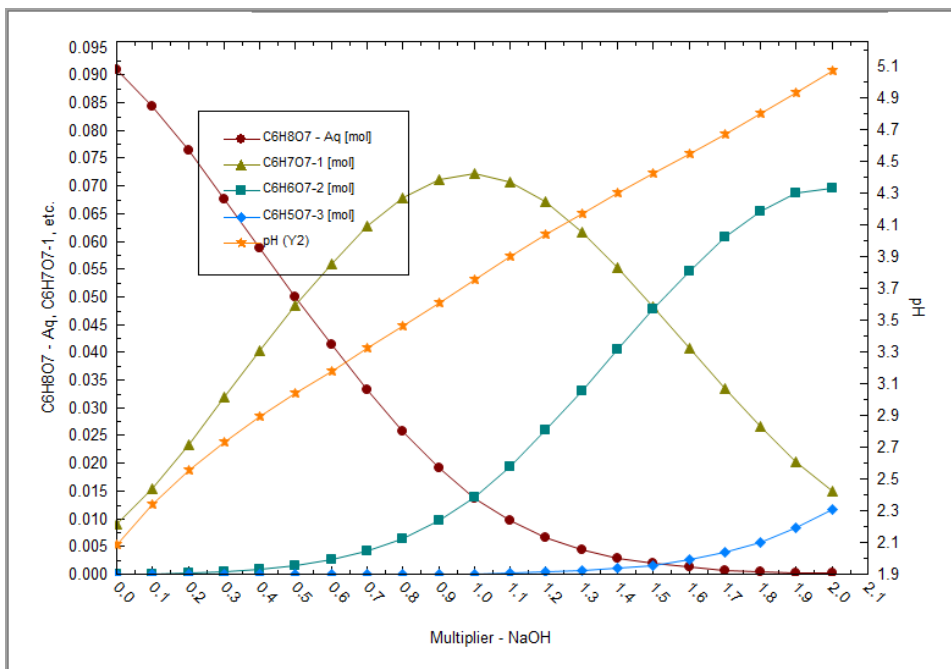
Figure 39-20 Updated plot with Y2 axis variable

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:
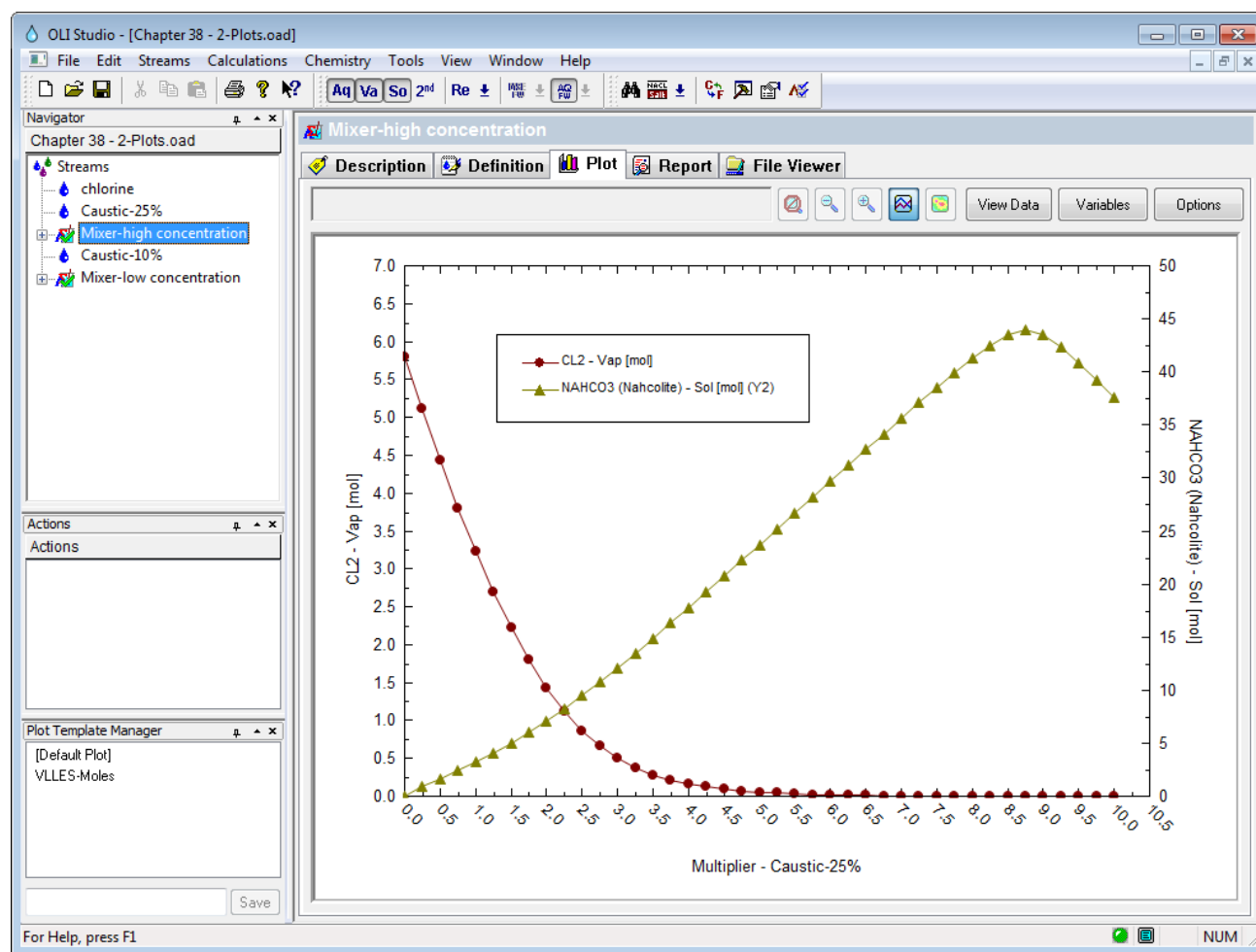
Figure 39-21 Our sample file

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**.
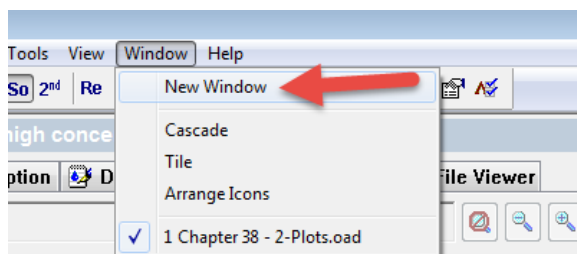
Figure 39-22 Creating a new window

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).
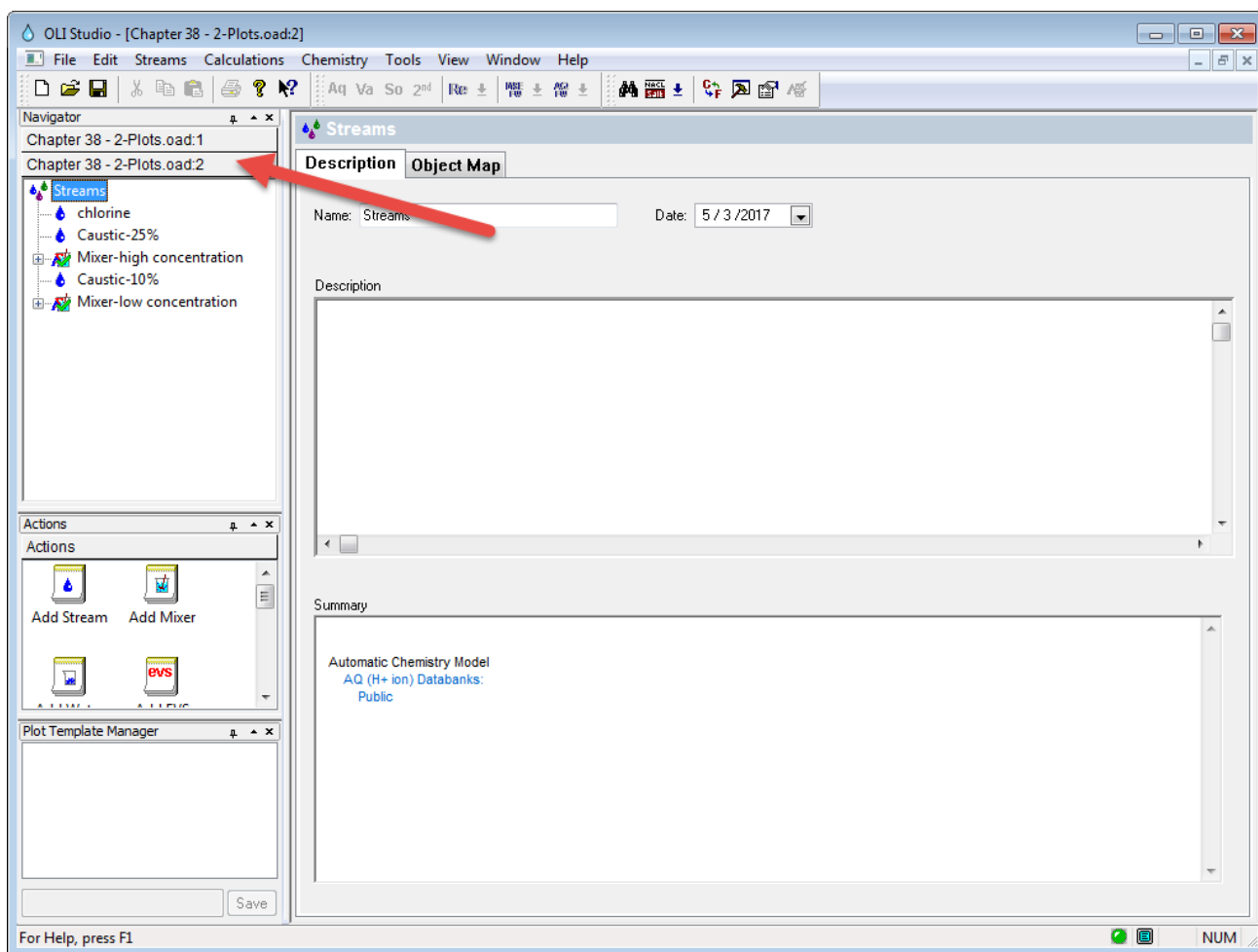
Figure 39-23 The new window

Now we select the other mixer and set up the plot with the same variables as the first plot:
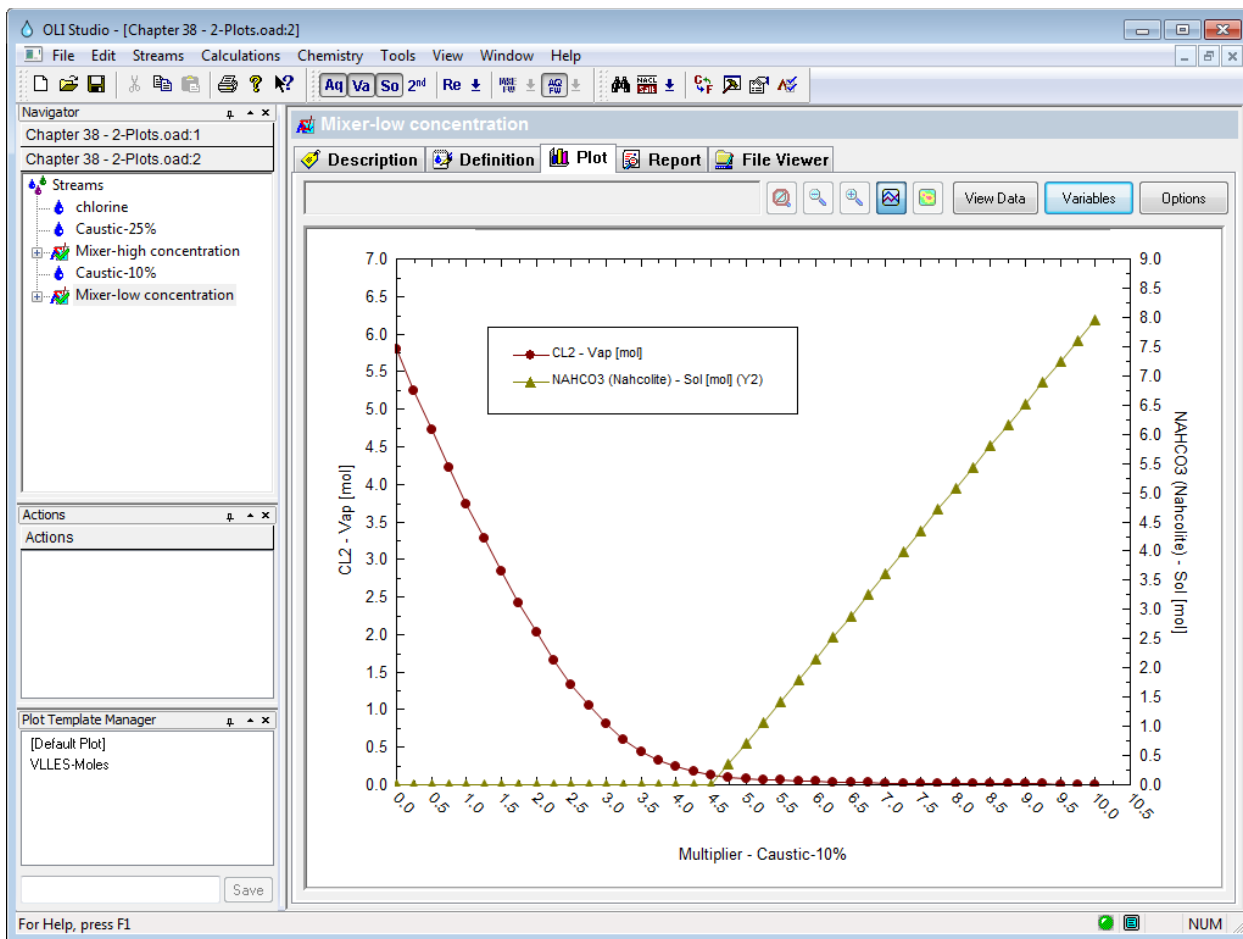
Figure 39-24 Plotting the low concentration case

Now we begin the process of putting both plots on the same display. Reselect **Window** and this time select **Tile**
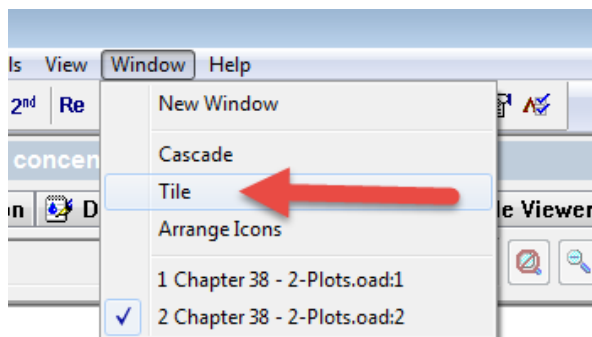
Figure 39-25 Tiling the images
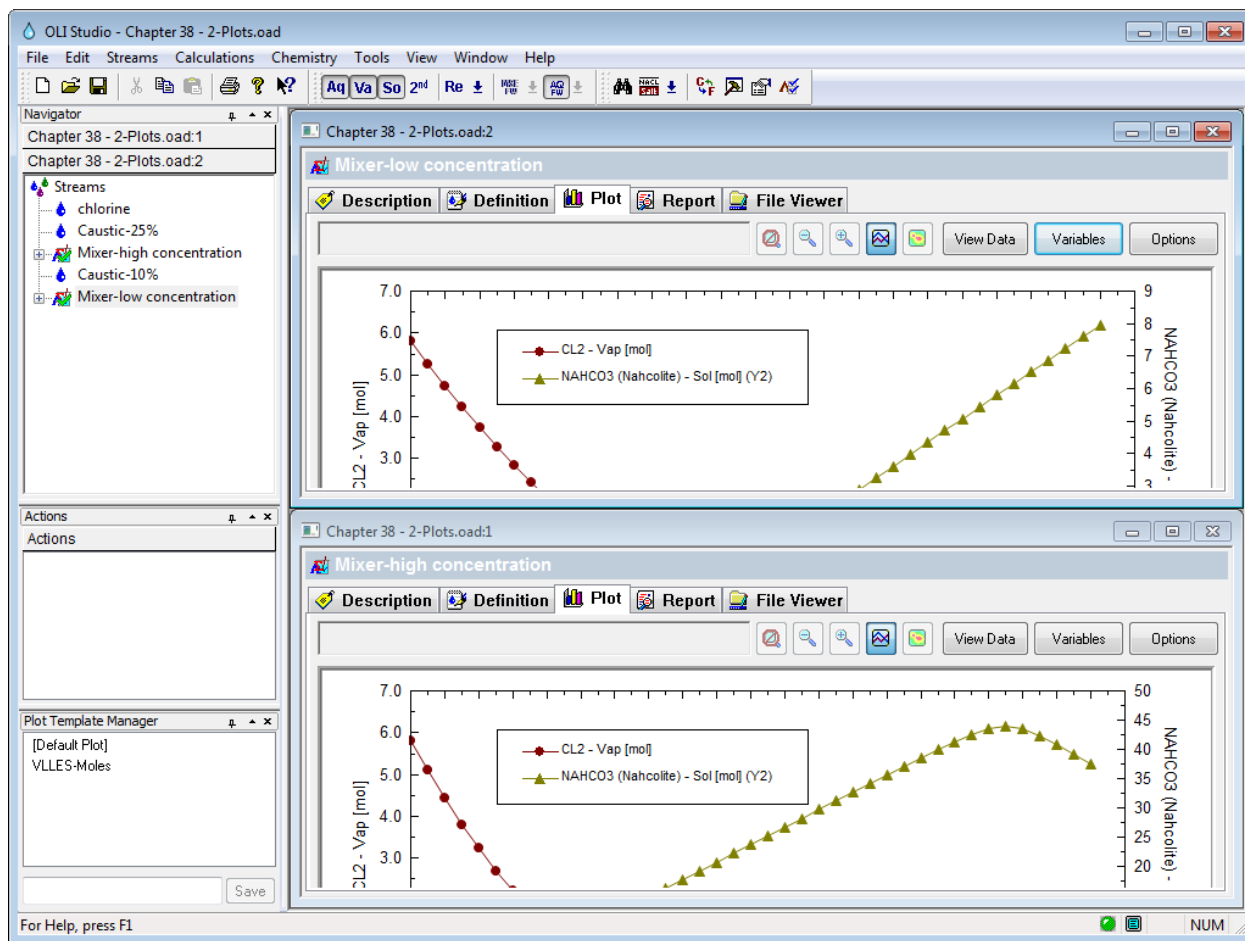
Figure 39-26 The tiled images

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.
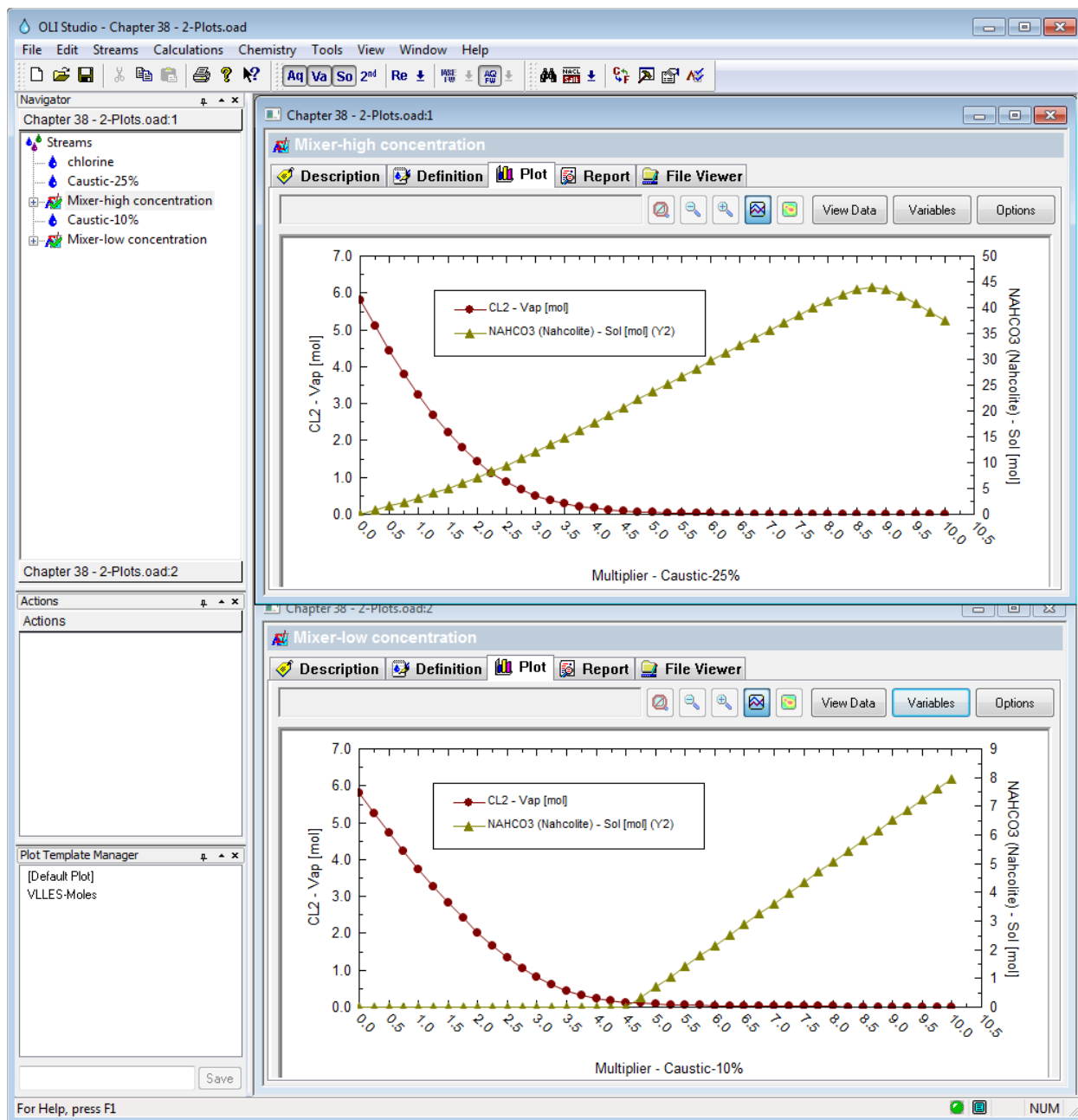
Figure 39-27 Resized Pictures

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.
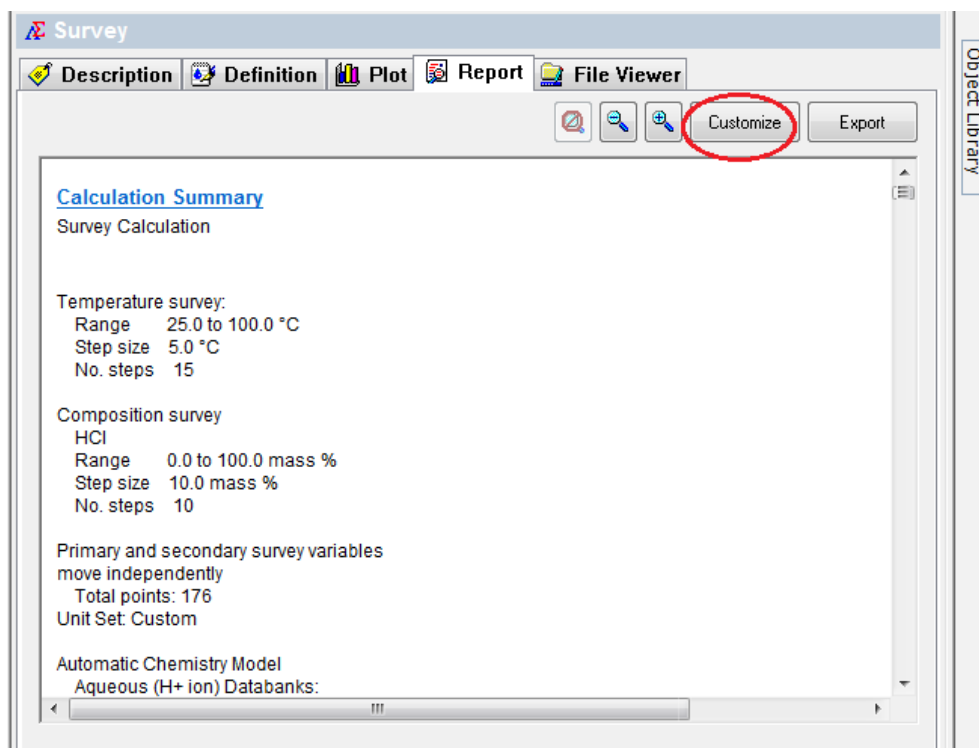
Figure 40-1

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.
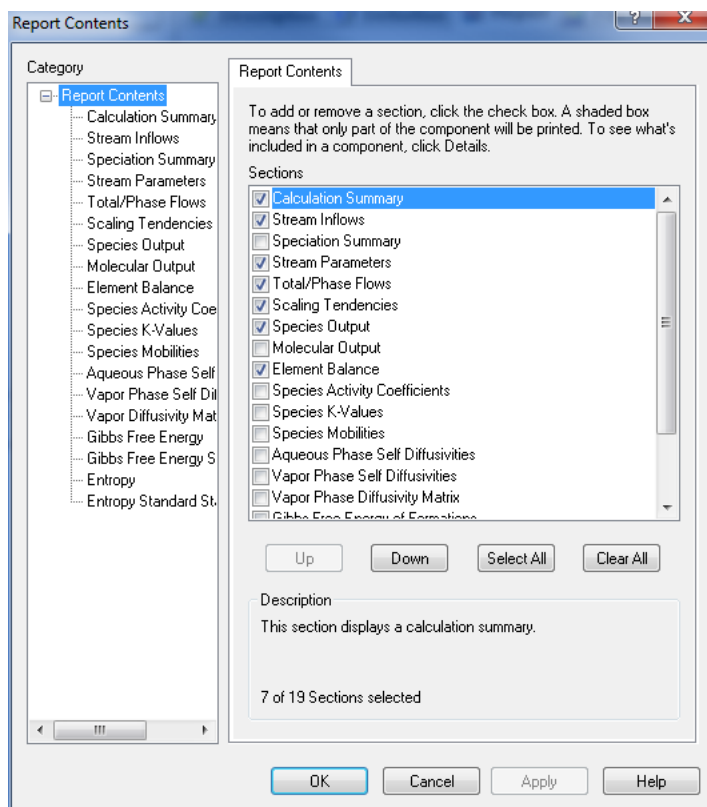
Figure 40-2

Eventually you will find the unchecked categories.

Check the boxes you wish to display and then click the **OK** button.
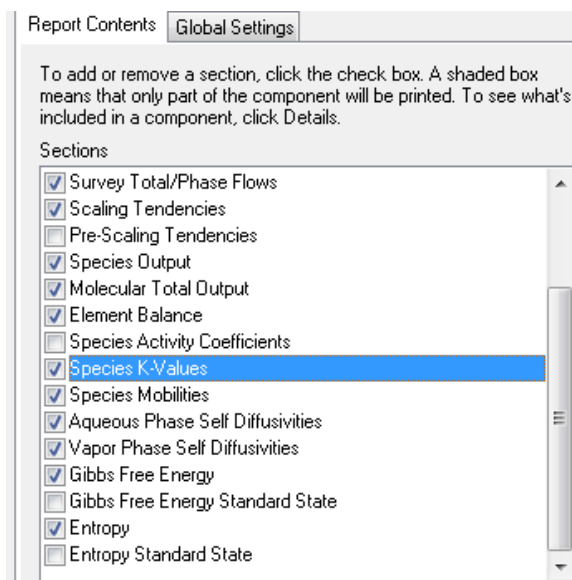
Figure 40-3

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
CI-1	-28310.5	
CO2	-88769.5	-90755.2
CO3-2	-1.24329e5	
H2O	-55476.1	-51465.6
H2S	-2711.37	-4391.58
HCI	-19568.4	-20258.9
HCO3-1	-1.3644e5	
H+1	1849.89	
HS-1	6335.04	
OH-1	-35503.2	
S-2	22876.6	

Figure 40-4

If you cannot see the above table, please right click on the single point calculation in the tree diagram under Navigator panel.
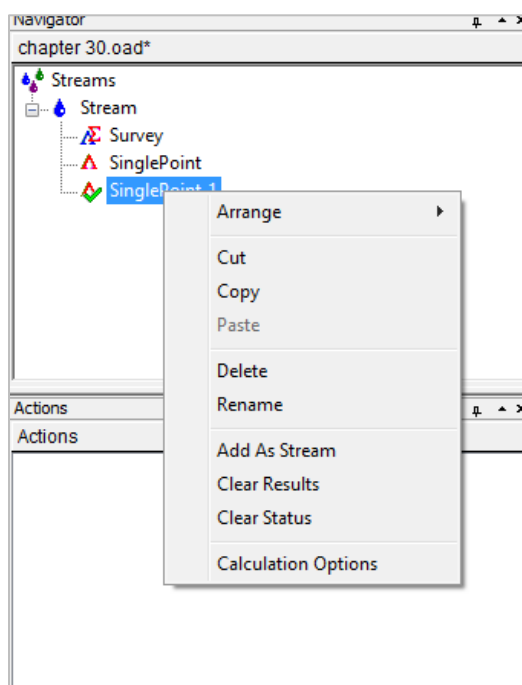
Figure 40-5

Click on calculation options
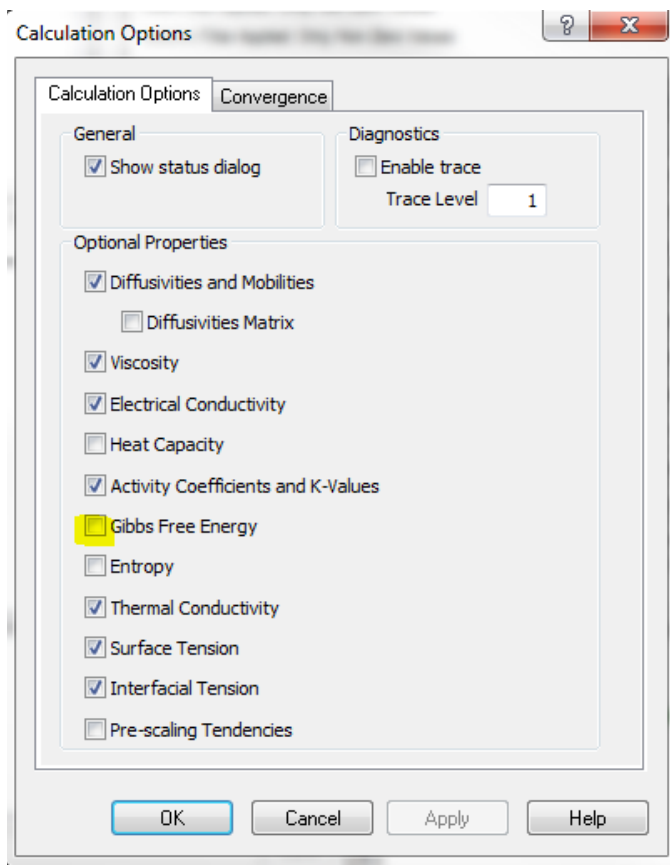
Figure 40-6

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.

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. See Chapter 2

Open the Mixer example that we used for determining the pH of $FeCl_3$ solutions

Click the **Specs...** button to enable the extra thermodynamic calculations.
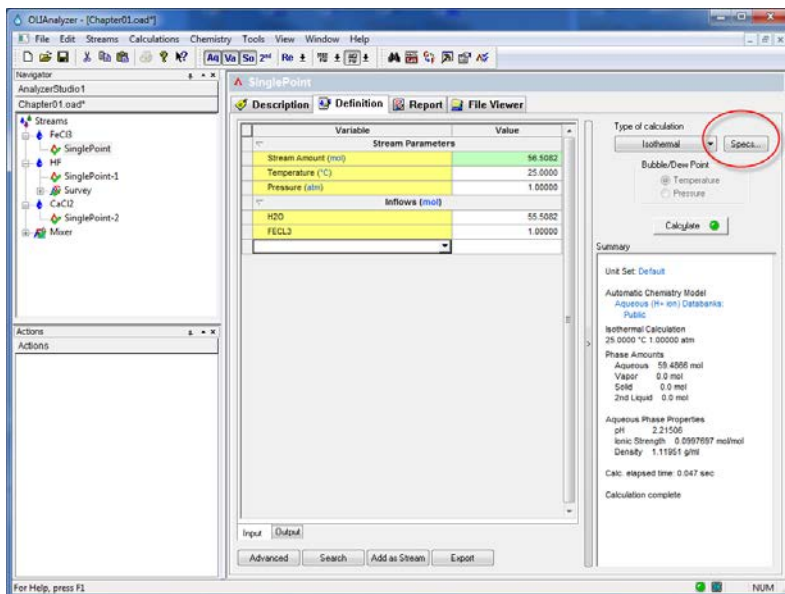
Figure 41-1

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.
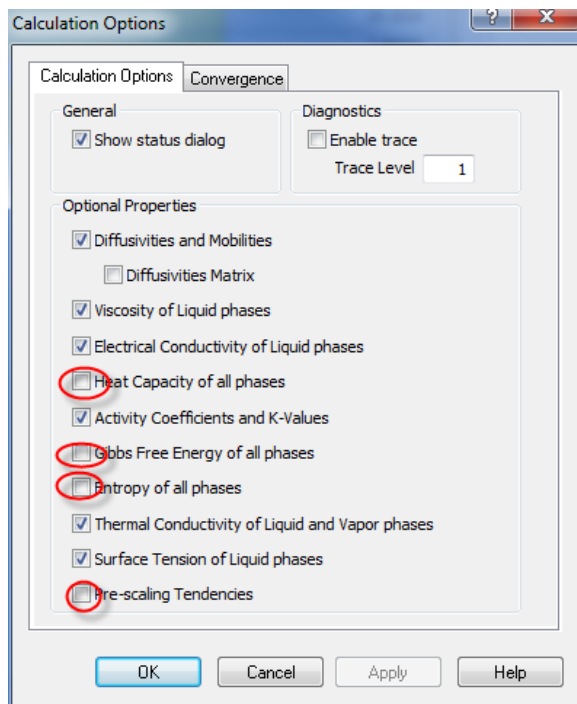
Figure 41-2

Here we have enabled all the extra calculations.
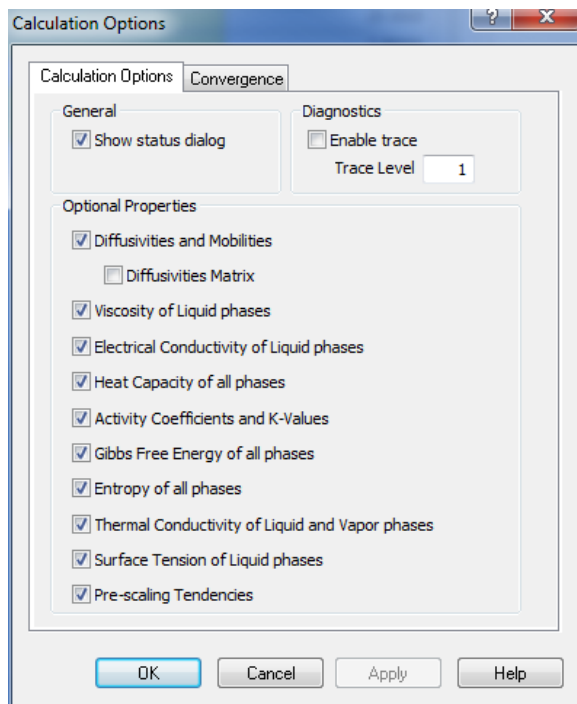
Figure 41-3

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.
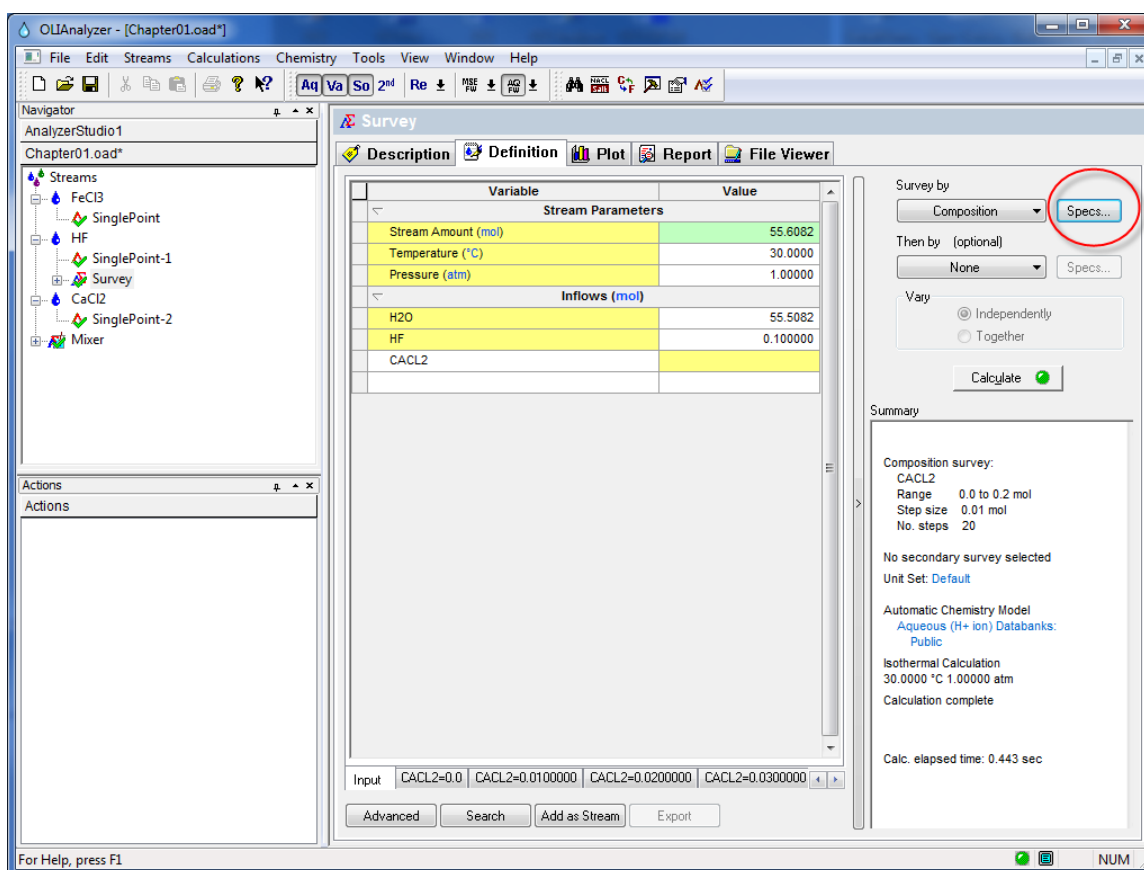
Figure 41-4

The Survey Options dialog is different from the single point dialog. You now must select **Calculation Options** to select the new calculations.
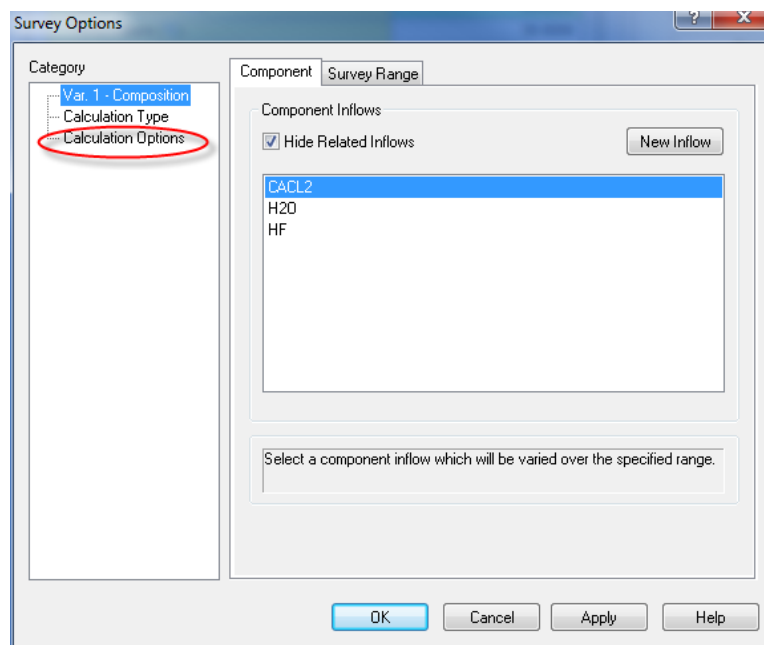
Figure 41-5

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.
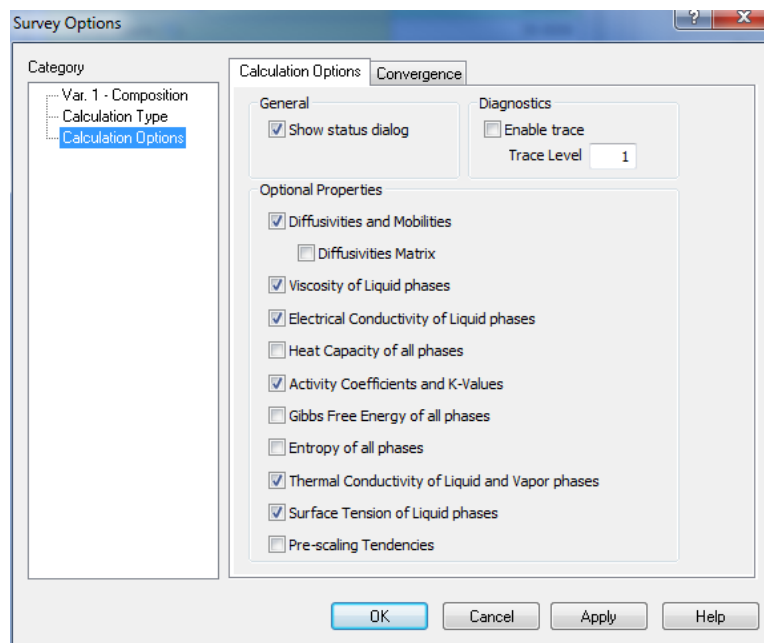
Figure 41-6

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**
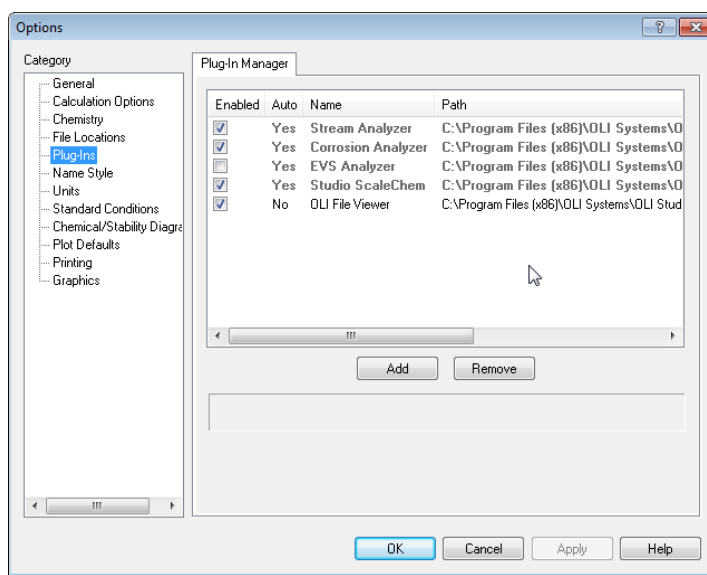
Figure 42-1 Default Plug-Ins menu

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.
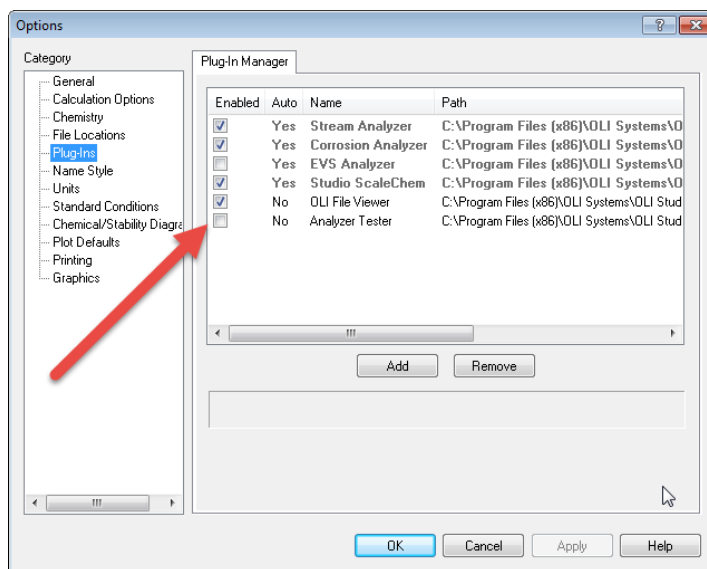
Figure 42-2 OLI Tester has been installed

Check the box to enable the OLI Tester.
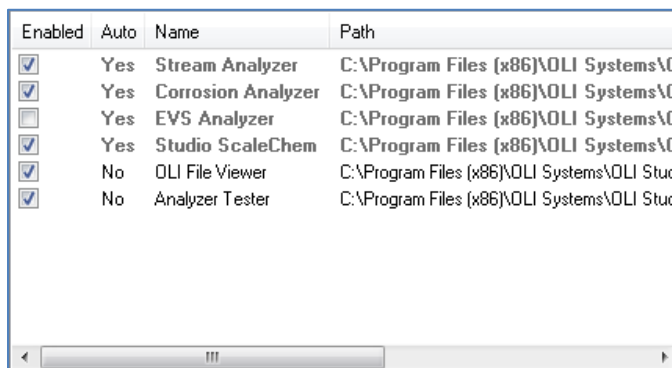
Figure 42-3 OLI Tester enabled

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.
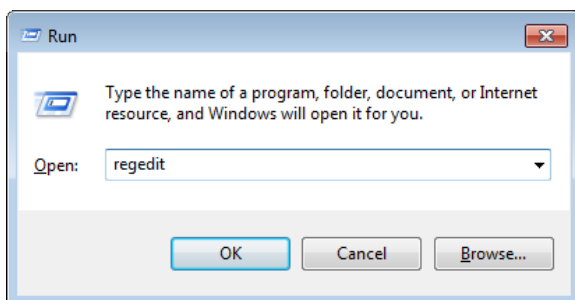
Figure 42-4 entering the registry editor command

This will display the registry editor

Navigate to the key:

HKEYCURRENT_USER\Software\OLI Systems\OLI Studio 9.5
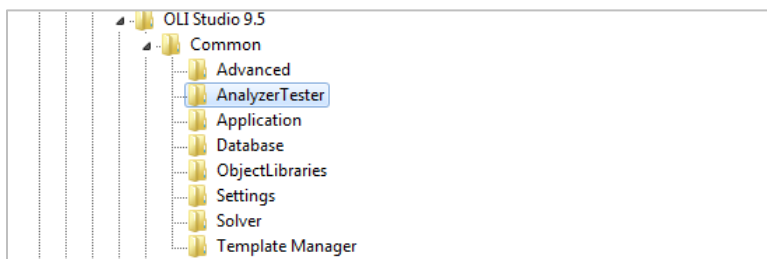
Figure 42-5 Navigating to the OLI Tester key

Click on the **AnalyerTester** key. In the right-hand window there should be only the default value:
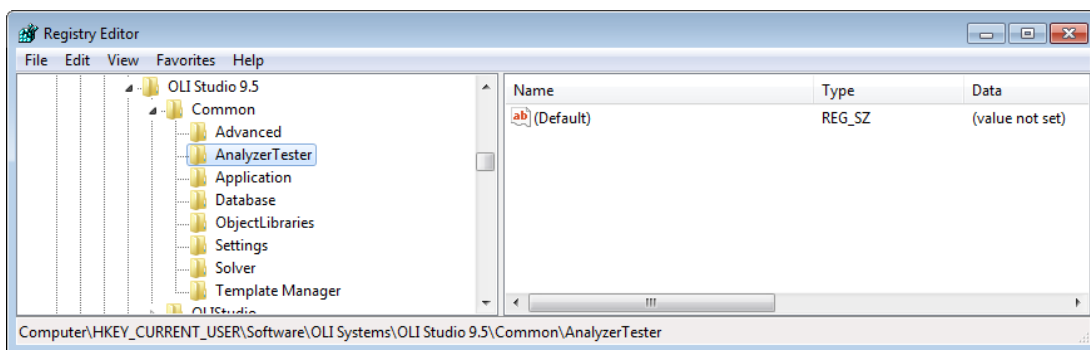
Figure 42-6 Default key value

Right-click in the right-hand windows and select **New | String Value**
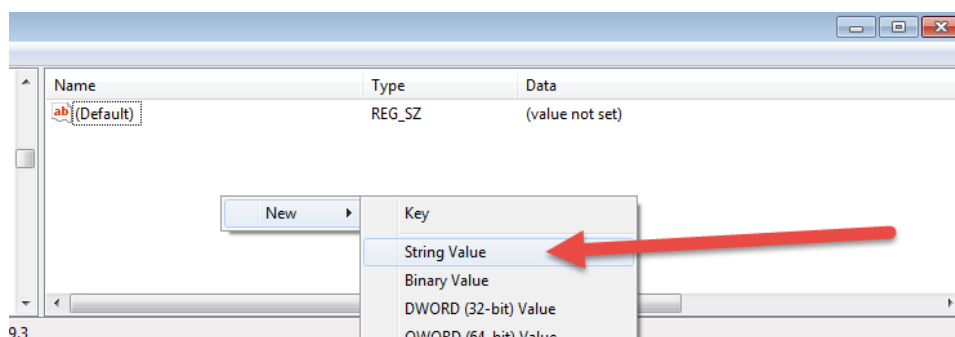
Figure 42-7 Selecting a new string value
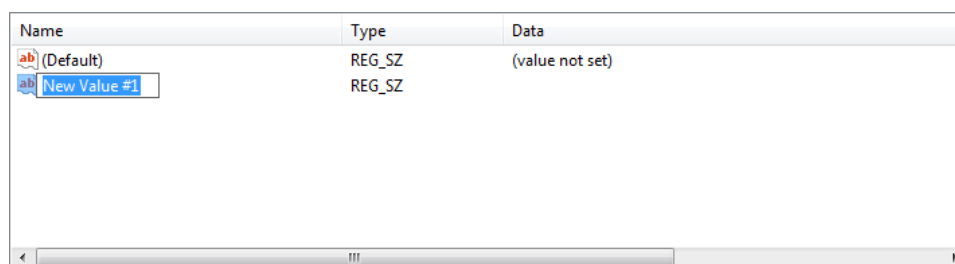
Figure 42-8 Creating a new variable

Rename the *New Value #1* variable to *AllowSurveyTesting*

Figure 42-9 Renamed variable, spelling counts!

Double-click the new variable name ***AllowSurveyTesting*** and this will display a new dialog:
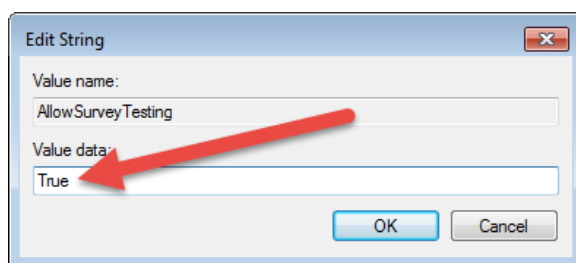
Figure 42-10 Enter "True" in the blank box

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.
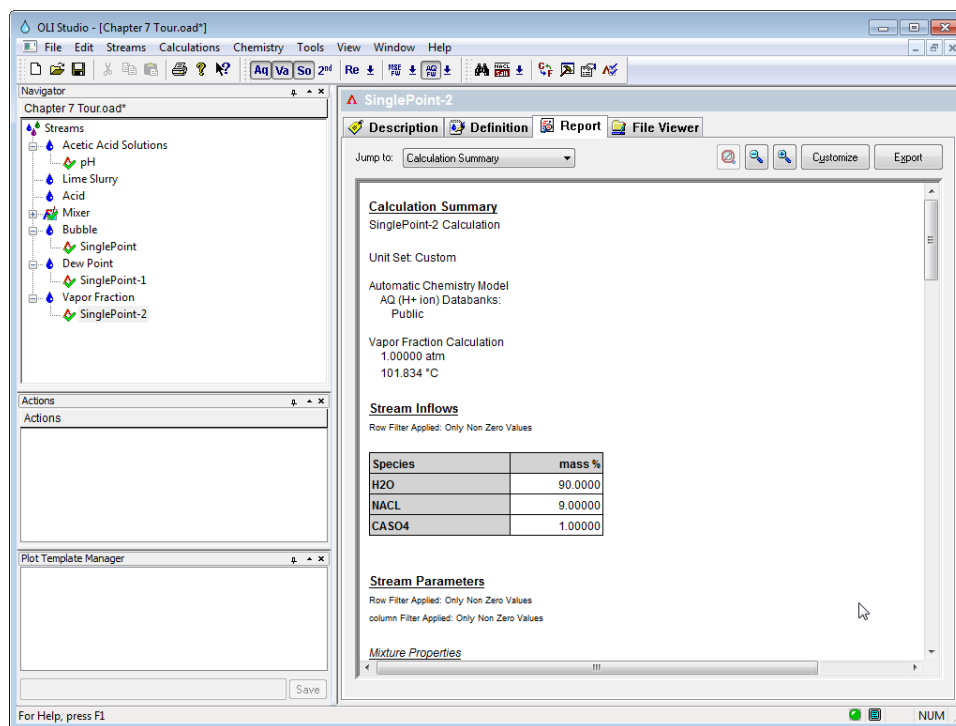
Figure 42-11 Starting a case

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**
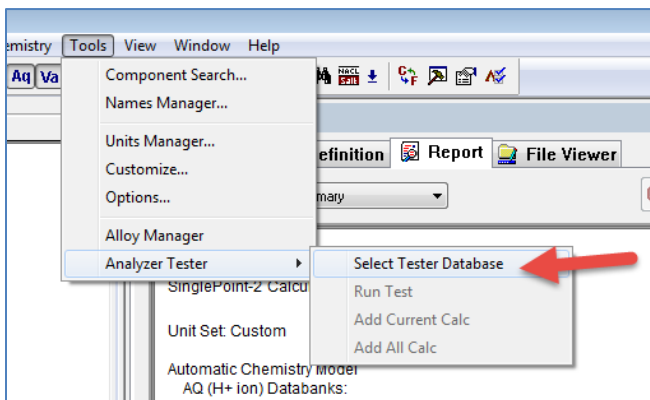
Figure 42-12 selecting the database

This will display a new dialog to either open a database or create a new database.
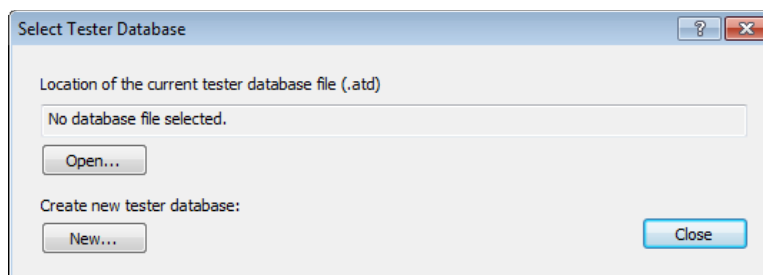
Figure 42-13 Database selection dialog

For this example, click the **New…** button.
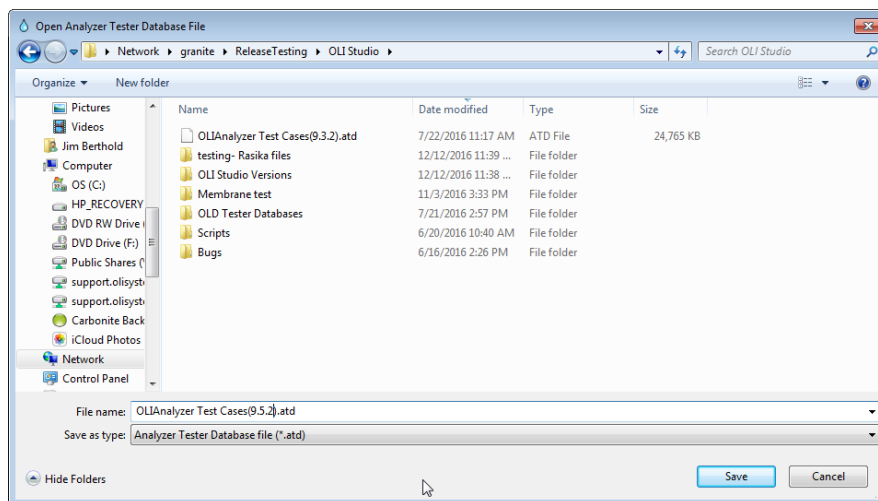
Figure 42-14 Determining a location for your database

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 547 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
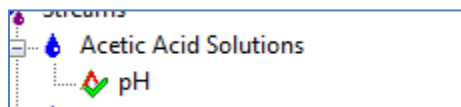
Figure 42-15 Clicking the object

Now select **Tools | Analyzer Tester | Add Current Calc**
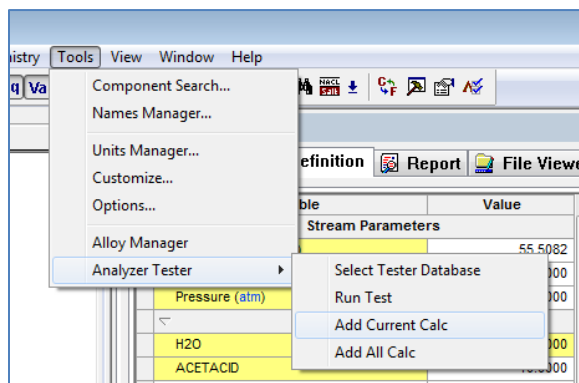
Figure 42-16 Adding the current calculation

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 <u>**Open…**</u> (refer to Figure 42-12 through Figure 42-14).

Here we are opening the 9.5.2 file we created earlier:
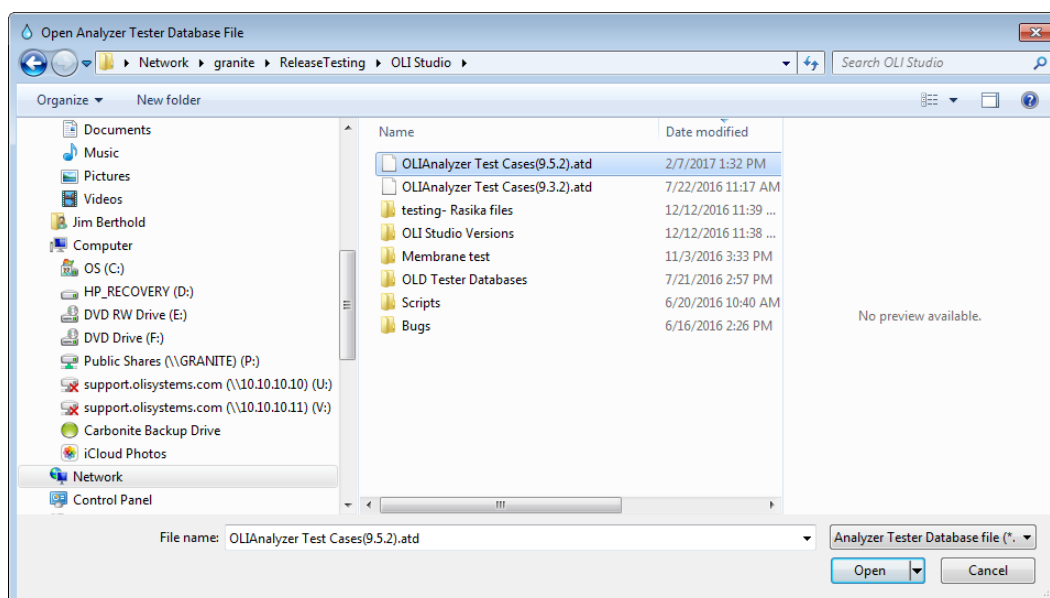
Figure 42-17 Opening an existing database

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:
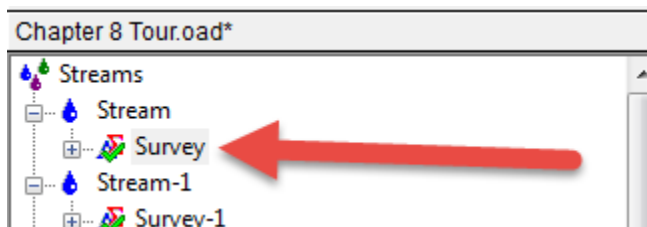
Figure 42-18 Selecting a survey

Now select **Tools | Analyzer Tester | Add Current Calc** (refer to Figure 42-16 on page 549).

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**
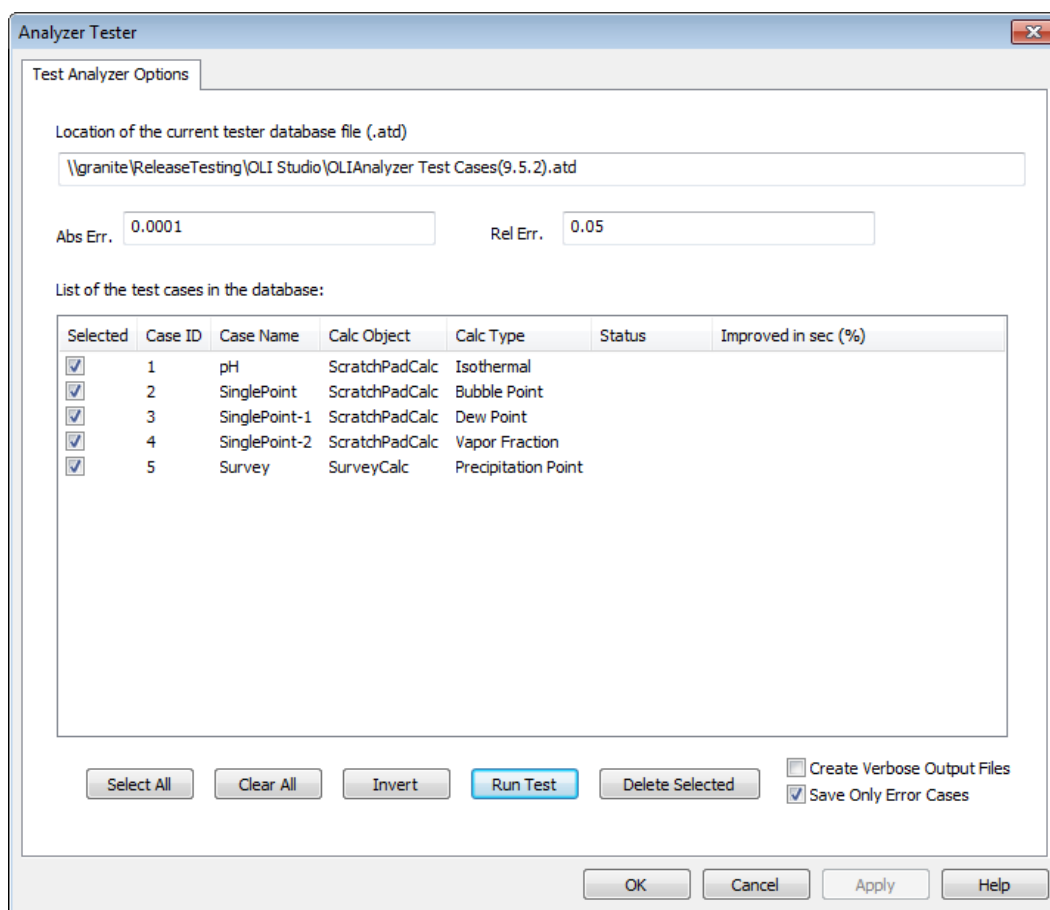
Figure 42-19 The Tester roster of tests

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.
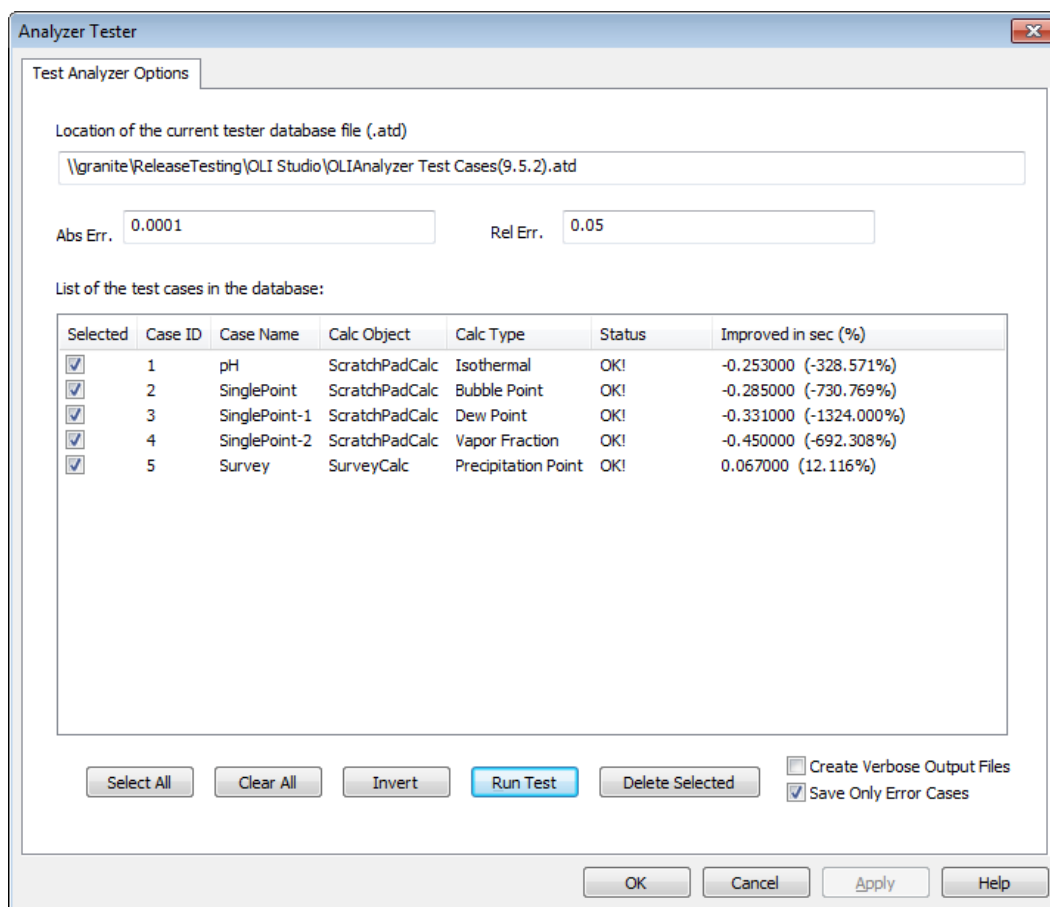
Figure 42-20 The completed test

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.
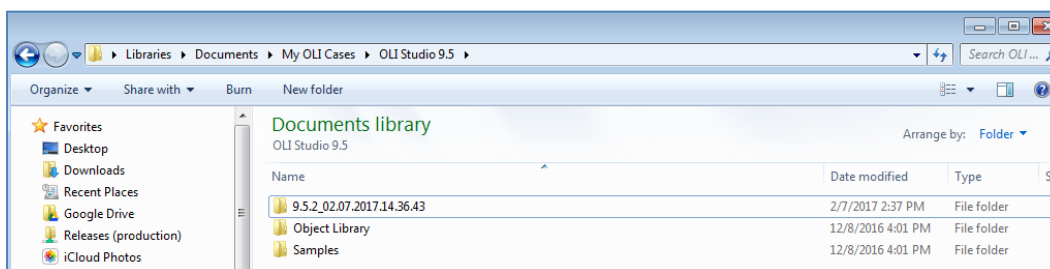
Figure 42-21 The results of the tests

This is a very strange name for the folder. The name includes the version number and the time and date. Expand this folder.
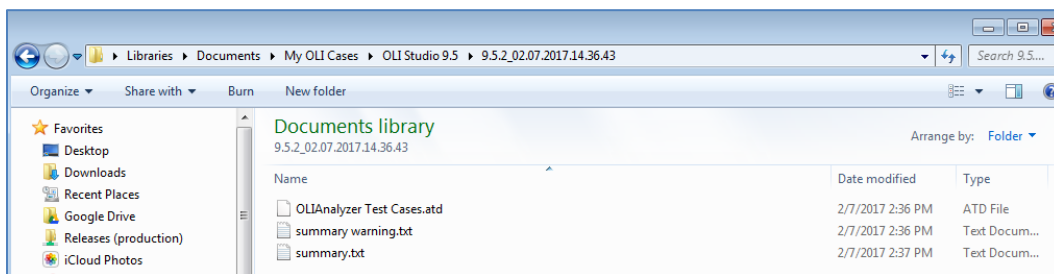
Figure 42-22 the results details

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:

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**.
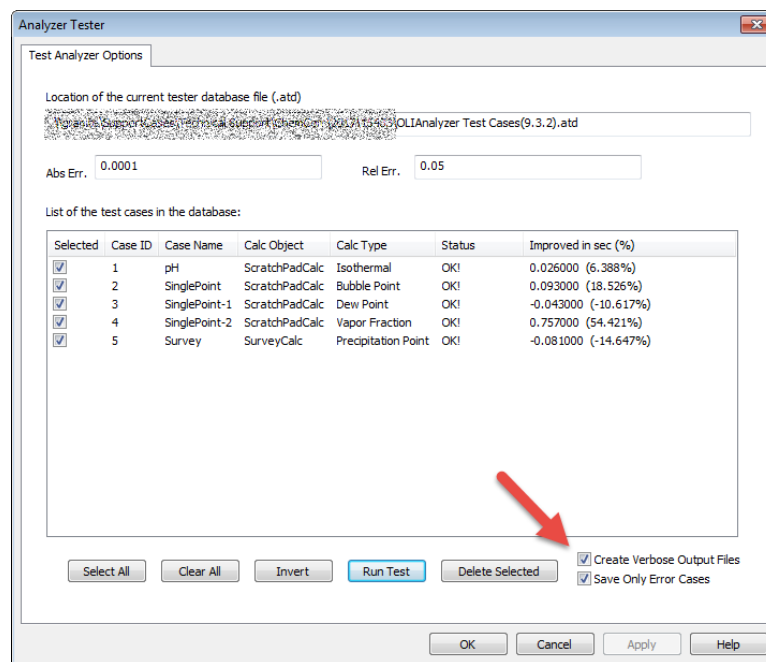
Figure 42-24 Completed test set from an earlier version

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.
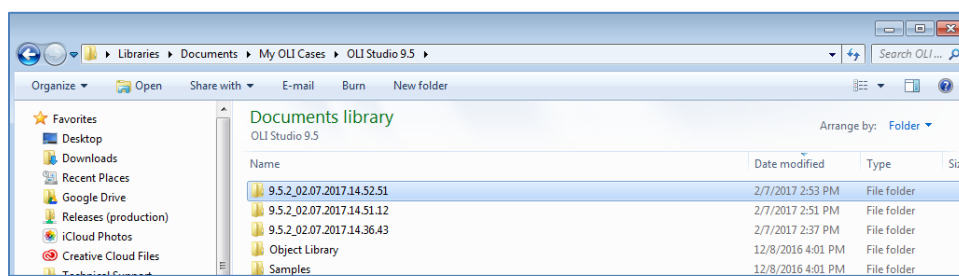
Figure 42-25 We want to look at the most recent set of results.

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.
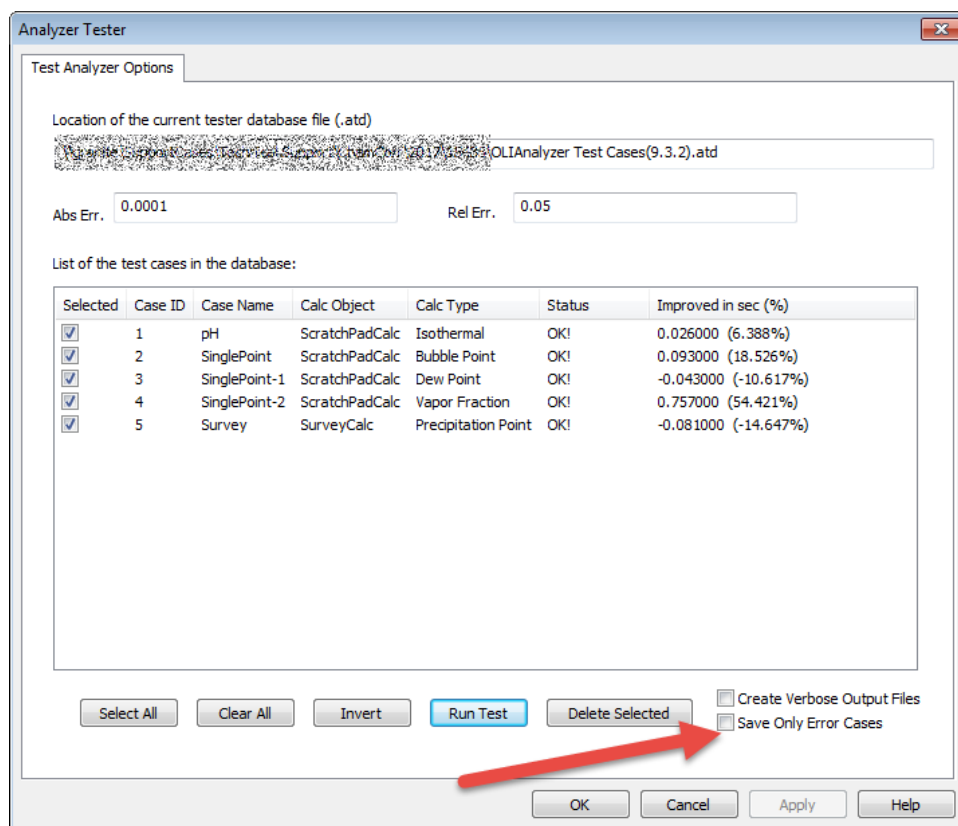
Figure 42-27 Unchecking the save option

Now review the results in yet another new folder (most recent) in the same general location at the other results:
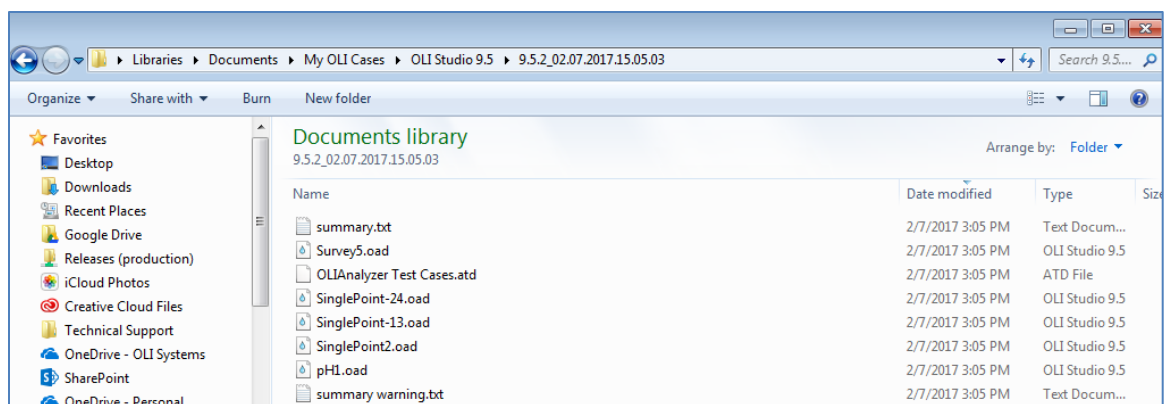
Figure 42-28 Individual tests are saved as files

Each of the test set cases are saved as individual files for further analysis if required.

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