Chapter VI – Scaling Inhibition

Introduction

OLI has developed a rigorous Nucleation and Inhibition tool for mineral scaling formation. The two tools help users predict the onset of precipitation in a process environment and also how to delay it. Both tools are built on OLI's fundamental thermodynamic framework and extends these predictions into kinetics using the Classical Nucleation Theory [1]. This theory use the energetics of the solution and the solid to predict the time needed for a supersaturated solution to start precipitating. This is the transition time between when a metastable solution finally starts to precipitate.

What is a mineral scale?

Mineral scaling occurs when there are changes in process conditions, such as pressure and temperature changes, dissolved gases, or when mixing incompatible waters. When scales accumulate in fixed diameter volumes, like membrane pores, production tubing, or process piping, flow is restricted. Action is then needed to remove the scale and restore flow.

A scale deposit may occur as single mineral phases, but more commonly, it is a combination of different elements. Common scales include $CaCO_3$ (calcite) and $BaSO_4$ (barite) in oil and gas production, $CaCO_3$, struvite, $Ca_3(PO_4)_2$, Mg-Silicates, and silica in water treatment, Jarosite, $CaSO_4$, and $CaCO_3$ (calcite) in mineral processing, and additional scale types in other chemical processes.

Scale deposition involves two distinct steps. The first is the nucleation step, this is the time between when a supersaturated water goes from no solids to forming the stable, microscopic crystals. The second is the crystal growth step. In this step, the microscopic crystals grow until the concentration in the water reduces to the point where the solution is no longer supersaturated.

The duration of this nucleation step is known as the “induction time”. It is the time that passes from the creation of supersaturated solution to the detection of first solids. This time is critical, because the longer this time can be delayed the greater chance that the solids do not form in an area that affects operations.

Scale formation - how OLI predicts this induction time?

OLI has developed a state-of-the-art tool that predicts this induction time. This enables users to assess the risk of mineral scale forming more accurately in their process. This is a major advancement compared to existing technology, in which the scaling tendency value plus empirical rules of thumb are used to assess scale risk in a process.

Figure 2 is a plot showing the output of the new model. The x-axis is the inverse square of the Scale Index. The scale index is a base-10, logarithm of the scale tendency.

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[1] See: https://en.wikipedia.org/wiki/Classical_nucleation_theory

$$SI^{-2} = \left(log10(ST)\right)^{\frac{1}{2}}$$

A lower SI^{-2} value (left side of the plot) means a higher supersaturation.

The Y-axis is the time it takes before stable crystals begin to form (in seconds). As the liquid supersaturation increases (increasing the driving force for precipitation), the time it takes for the solids to form shrinks.

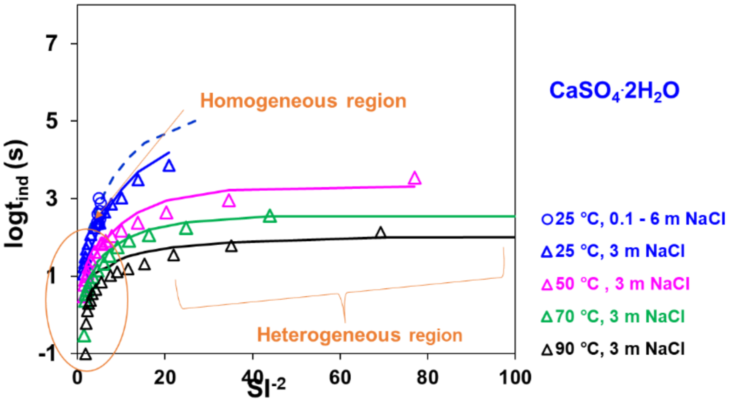

Figure 0-1 - Calculated and experimental gypsum ($CaSO_4.2H_2O$) induction times in the $CaSO_4$-NaCl solution at 25, 50, 70, and 90 °C. Symbols are experimental data, whereas lines represent MSE+CNT model calculations

There are two distinct slopes to the plot, the far-left slope is the Homogeneous nucleation region, while the right slope is the heterogeneous region. The homogeneous nucleation region represents a liquid that is highly supersaturated, and where little time elapses before solids start precipitating. The heterogeneous region is where the liquid is only slightly saturated, and solids only start to form if there is dust or other types of particles in the water that makes it easier for the solids to form. Both time regions are important to modeling induction time properly, and the OLI database contains the required parameters for these calculations.

OLI Nucleation Induction Time model

OLI has created a database that will predict the induction time for four of the most common scales, calcite ($CaCO_3$), barite ($BaSO_4$), gypsum ($CaSO_4.2H_2O$), and Celestine ($SrSO_4$). In future releases, the predictions will be extended to other solids.

Scale Inhibition - how is OLI used to predict treatment?

Scale inhibitors are a type of chemical that interacts with the nascent crystallites and prevents them from becoming stable. They effectively delay the formation of a stable crystal by poisoning its surface. Scale inhibitors are an essential part of engineering, because when added to the process water, they delay the formation of these crystals, allowing a process to remain free of solids. Scale inhibitors are used in many applications, including cooling tower water, as a pre-treatment to RO membranes, and oil and gas production wells.

Because scale inhibitors represent the key solution to unwanted mineral scaling, OLI created a database that predicts this time delay. Thus, an OLI Studio user can now predict a more accurate scale risk analysis for their process and simultaneously develop a chemical treatment plan. Six of the most common scale inhibitors are included; NTMP/ATMP, DTPMP, HEDP, EDTPMP, PPCSA, and PMA (see footnote for chemical names)[2].

Using the Nucleation Model in OLI Studio

The nucleation model is a post-process to all OLI calculations. Therefore, the only impact on any calculation is that a new table will be available in the Report tab, or a new set of categories will be available in the Plots tab. When scale inhibitors are added, then its speciation is included in the calculation. Usually the inhibitor concentrations are low (in the parts per million) so there will be minimal performance difference. There will be the same changes to the report and plot, since the inhibitor speciation will be added to the output, and its effects on nucleation will also be shown.

Performing induction time calculations in OLI

The OLI software contains nucleation induction times (t_{ind}) for four mineral phases; $CaCO_3$ (calcite), $BaSO_4$ (barite), $SrSO_4$ (celestine), and $CaSO_4.2H_2O$ (Gypsum). Also included are the inhibition induction times, t_{ind}, for six scale inhibitors, HEDP, NTMP/ATMP, DTPMP, EDTMP, PMA, and PBTC. The nucleation model is developed in the MSE framework (database) and its prediction range extends across the range of this framework.

OLI Tag Name	Chemical Formula	IUPAC Names
DTPMP	C9H28N3O15P5	Diethylenetriamine penta(methylene phosphonic acid)
HEDP	C2H8O7P2	1-hydroxyethane 1,1-diphosphonic acid
NTMP/ATMP	C3H12NO9P3	Nitrilotris(methylenephosphoric acid)
PMLA	C40H40O40	Poly maleic acid
PBTC	C7H11O9P	2-phosphono-butane-1,2,4-tricarboxylic acid
EDTMP	C6H20N2O12P4	Ethylenediamine tetra(methylene phosphonic acid)

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[2] 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), amino tris (methylenephosphonic acid) (NTMP), diethylenetriamine penta (methylene phosphonic acid) DTPMP, ethylenediamine tetra (methylene phosphonic acid) (EDTPMP), and polymaleic acid (PMA)

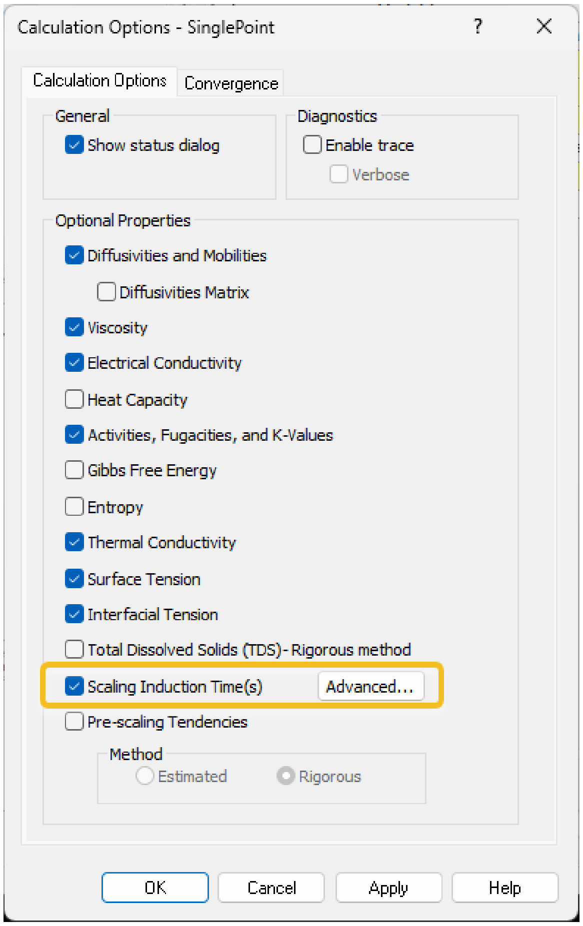
Setting up the automatic calculation

Induction time calculations are activated within the **Calculation Options** popup window (shown below). When checked, the model sub-routine is included as a post process to the calculation being run. The induction time calculation is available for the Single Point and Survey calculation of a Stream, in a Mixer calculation, and in the five ScaleChem calculations (Saturator, Scale Scenario, Facilities, Contour, Mixing Waters).

Start the software. There should be no streams or calculations in the Navigator panel

Select **Tools > Options > Calculation Options**

Check the **Scaling Induction Time(s)** box at the bottom of the popup window. Then press OK to close the window.



General

☑ Show status dialog

Diagnostics

☐ Enable trace

☐ Verbose

Optional Properties

☑ Diffusivities and Mobilities

  ☐ Diffusivities Matrix

☑ Viscosity

☑ Electrical Conductivity

☐ Heat Capacity

☑ Activities, Fugacities, and K-Values

☐ Gibbs Free Energy

☐ Entropy

☑ Thermal Conductivity

☑ Surface Tension

☑ Interfacial Tension

☐ Total Dissolved Solids (TDS)- Rigorous method

☑ Scaling Induction Time(s)

☐ Pre-scaling Tendencies

Method

○ Estimated ● Rigorous

Calculation Options window showing the Scaling Induction Time(s) check box

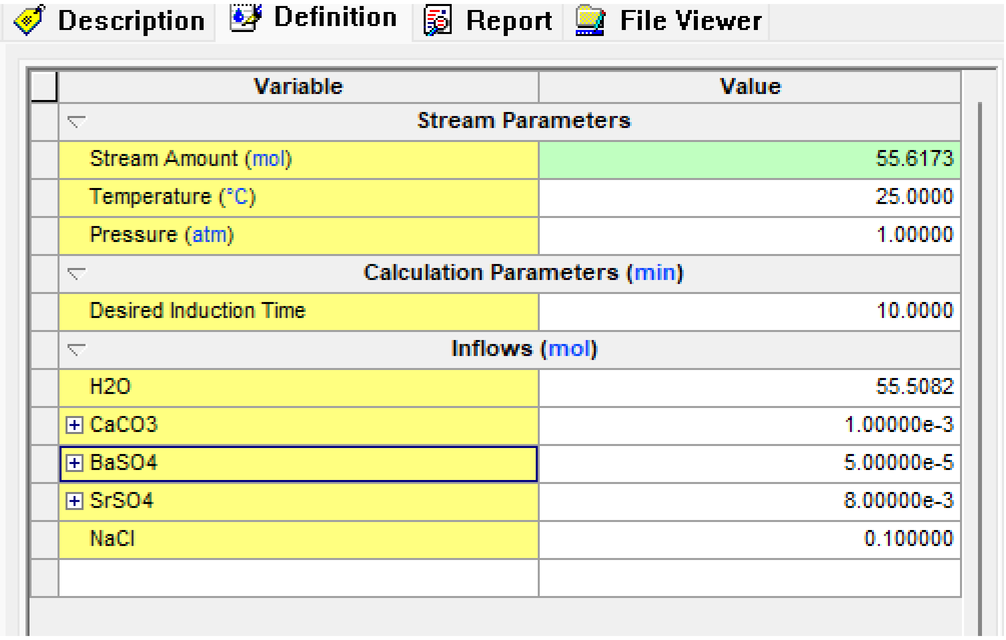
Example #1 – Induction times for $CaCO_3$, $BaSO_4$, and $SrSO_4$ in a Stream

The following stream contains low concentrations of $CaCO_3$, $BaSO_4$, and $SrSO_4$ in a NaCl brine at 25°C. We will use a few single point, isothermal calculations to show how the model works.

Step #1 – Create a basic induction time calculation

Add a stream and label it Basic Calculation (MSE model)

Add the four inflows and mole amounts: $CaCO_3$ – 0.001; $BaSO_4$ – 0.00005; $SrSO_4$ – 0.008; and NaCl – 0.1.



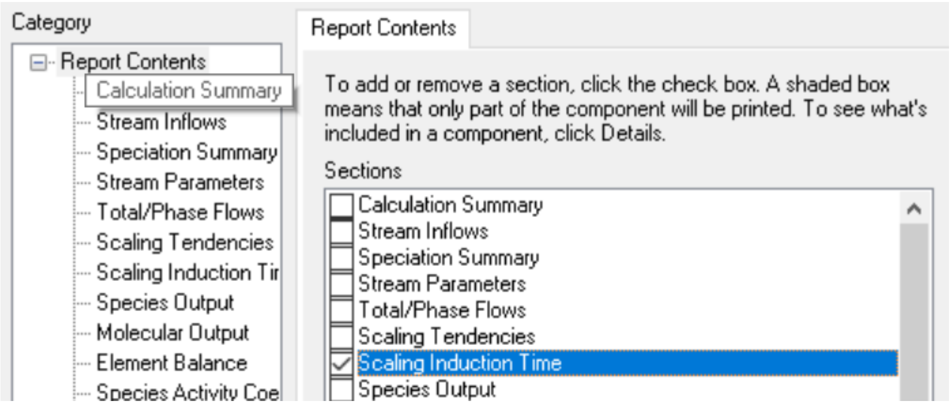
Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6173
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters (min)	
Desired Induction Time	10.0000
Inflows (mol)	
H2O	55.5082
⊞ CaCO3	1.00000e-3
⊞ BaSO4	5.00000e-5
⊞ SrSO4	8.00000e-3
NaCl	0.100000

New Stream containing low concentrations of CaCO3, BaSO4, and SrSO4 in a 0.1 NaCl electrolyte solution.

Add a single point calculation and label it *No Inhibitor*

When the calculation is complete, click on the **Report** tab. Then click on the **Customize** button in the upper right of the screen.

Clear All boxes and then check the **Scaling Induction Time** box only



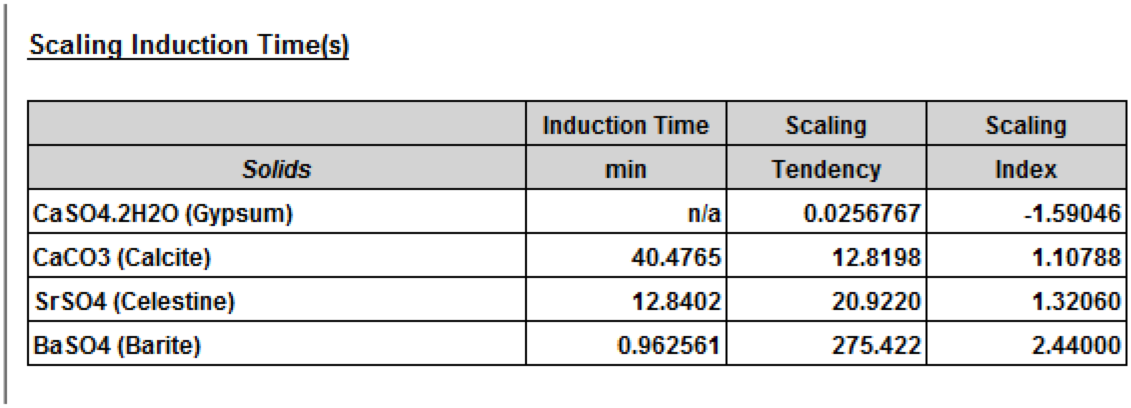
To add or remove a section, click the check box. A shaded box means that only part of the component will be printed. To see what's included in a component, click Details.

Sections

☐ Calculation Summary
☐ Stream Inflows
☐ Speciation Summary
☐ Stream Parameters
☐ Total/Phase Flows
☐ Scaling Tendencies
☑ Scaling Induction Time
☐ Species Output

The Report's Customize popup window showing where the Scaling Induction Time category is located

Review the column data in the Scale Induction Time(s) table



Scaling Induction Time(s)

	Induction Time	Scaling	Scaling
Solids	min	Tendency	Index
CaSO4.2H2O (Gypsum)	n/a	0.0256767	-1.59046
CaCO3 (Calcite)	40.4765	12.8198	1.10788
SrSO4 (Celestine)	12.8402	20.9220	1.32060
BaSO4 (Barite)	0.962561	275.422	2.44000

The three solid phases are supersaturated as shown in the Scaling Tendency column, and their induction times vary from 1.0 to 40.5 minutes. This means that barite will form in about 60 seconds while the other solids will take several minutes longer before they start to precipitate.

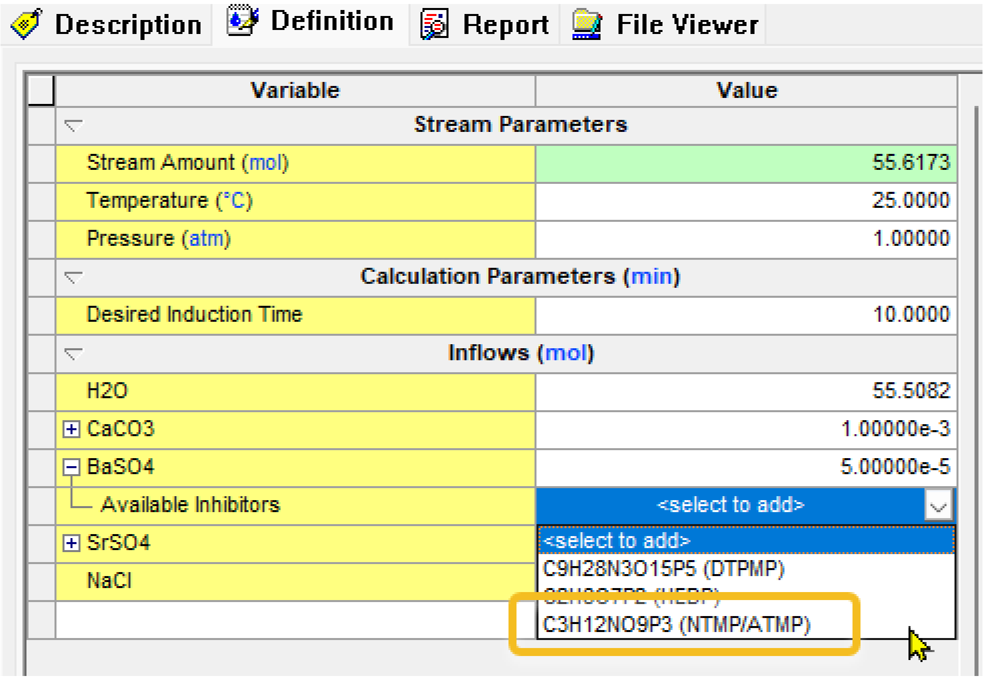
Step #2 – Adding scale inhibitors

Add a new single point calculation and label it *With Inhibitor*

You may have noticed already that there are + boxes to the left of $CaCO_3$, $BaSO_4$ and $SrSO_4$. These boxes expose a sub grid containing the available scale inhibitors for that specific mineral.

Click on the + sign adjacent to $BaSO_4$ to expose the sub grid.

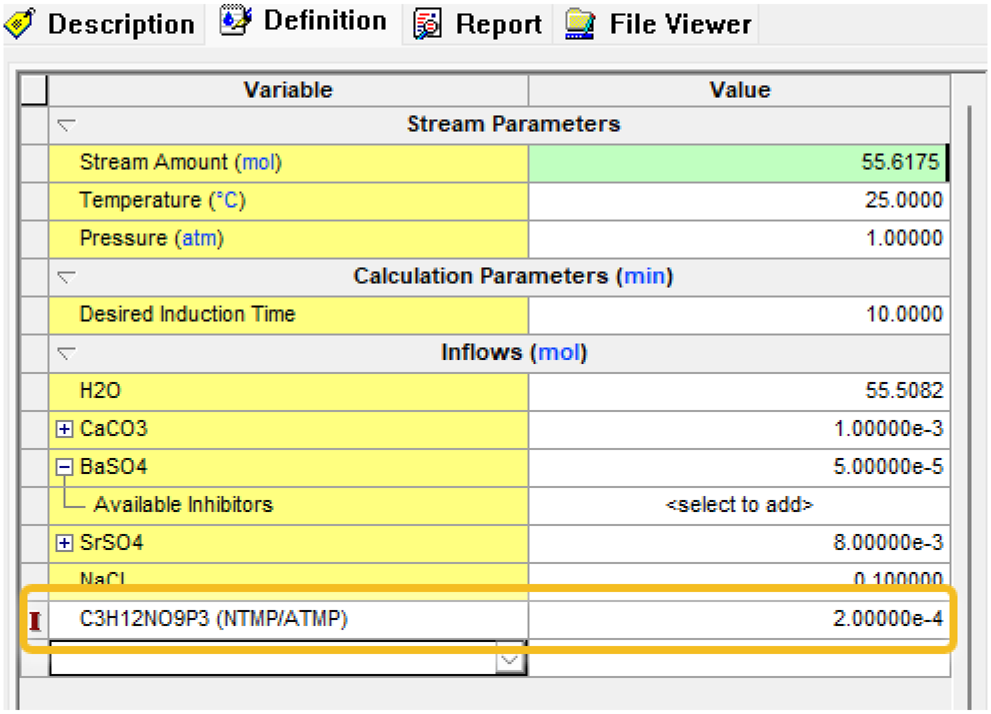
Click on the <select to add> box and select the **C3H12NO9P3 (NTMP/ATMP)** inhibitor.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6173
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters (min)	
Desired Induction Time	10.0000
Inflows (mol)	
H2O	55.5082
⊞ CaCO3	1.00000e-3
⊟ BaSO4	5.00000e-5
Available Inhibitors	<select to add>
⊞ SrSO4	
NaCl	

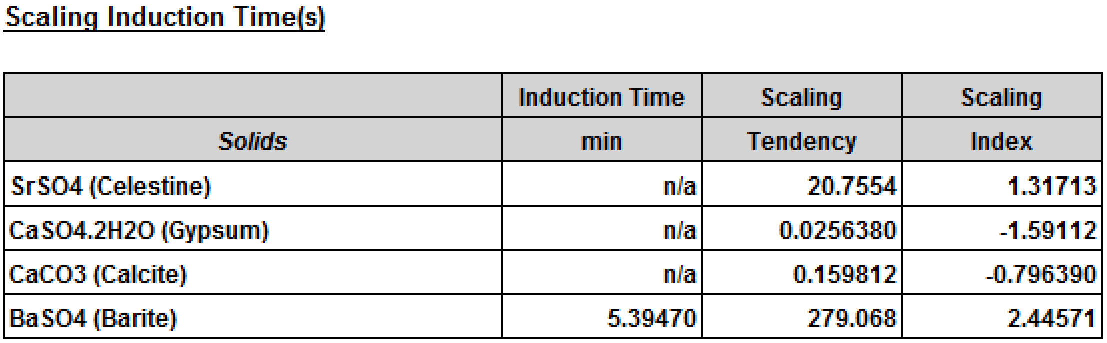
It will now appear at the bottom of the grid

Give it an amount of 2e-4 moles (this is about 60 mg/l) and calculate



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.6175
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters (min)	
Desired Induction Time	10.0000
Inflows (mol)	
H2O	55.5082
⊞ CaCO3	1.00000e-3
⊟ BaSO4	5.00000e-5
Available Inhibitors	<select to add>
⊞ SrSO4	8.00000e-3
NaCl	0.100000
C3H12NO9P3 (NTMP/ATMP)	2.00000e-4

Click on the **Report** tab and once again, turn on only the **Scaling Induction Time** table using the **Customize** window

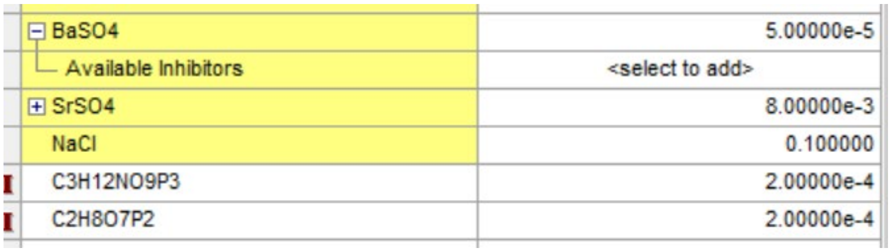


Scaling Induction Time(s)

	Induction Time	Scaling	Scaling
Solids	**min**	**Tendency**	**Index**
SrSO4 (Celestine)	n/a	20.7554	1.31713
CaSO4.2H2O (Gypsum)	n/a	0.0256380	-1.59112
CaCO3 (Calcite)	n/a	0.159812	-0.796390
BaSO4 (Barite)	5.39470	279.068	2.44571

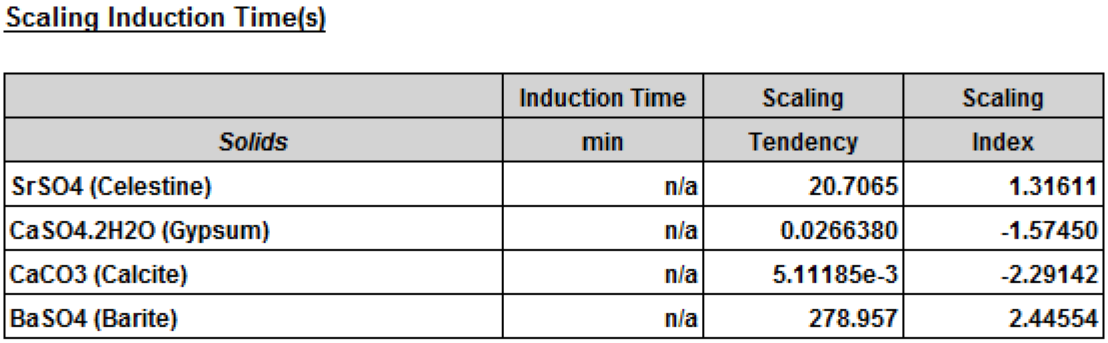
The induction time for $BaSO_4$ increased to 5.4 minutes, a time that would likely prevent the solid from precipitating in the process. The calcite and celestine induction times now show n/a, which means that the compute time exceeds the maximum limit of 10,000 hours.

Return to the Definition tab and select the + adjacent to $SrSO_4$. Select the C2H8O7P2 (HEDP) inhibitor and give it a value of 2e-4 (~41 mg/l).



⊟ BaSO4	5.00000e-5
Available Inhibitors	<select to add>
⊞ SrSO4	8.00000e-3
NaCl	0.100000
C3H12NO9P3	2.00000e-4
C2H8O7P2	2.00000e-4

Re-calculate and view the Report table



Scaling Induction Time(s)

	Induction Time	Scaling	Scaling
Solids	min	Tendency	Index
SrSO4 (Celestine)	n/a	20.7065	1.31611
CaSO4.2H2O (Gypsum)	n/a	0.0266380	-1.57450
CaCO3 (Calcite)	n/a	5.11185e-3	-2.29142
BaSO4 (Barite)	n/a	278.957	2.44554

The HEDP inhibited both $SrSO_4$ and $BaSO_4$. At these concentrations, the water would now be considered inhibited (and possibly overdosed!).

Step #3 – Using a concentration survey to compute the best inhibitor concentration

In the previous steps, you created a supersaturated solution and then reduced its propensity to precipitate by adding a scale inhibitor. The inhibitor concentrations used were not optimized. You will use the survey calculation to vary the inhibitor concentration and find a reasonable value.

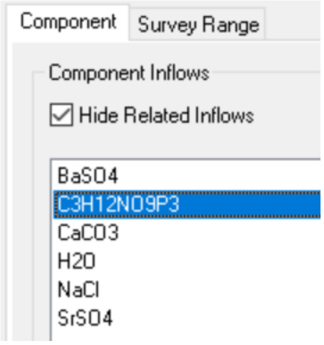
Add a **Survey** calculation and label it *Inhibitor survey*

Expand the BaSO4 box and select C3H12NO9P3 (NTMP/ATMP) again

Change the Survey by from Temperature to Composition

Open the **Specs** window, select NTMP/ATMP as the component

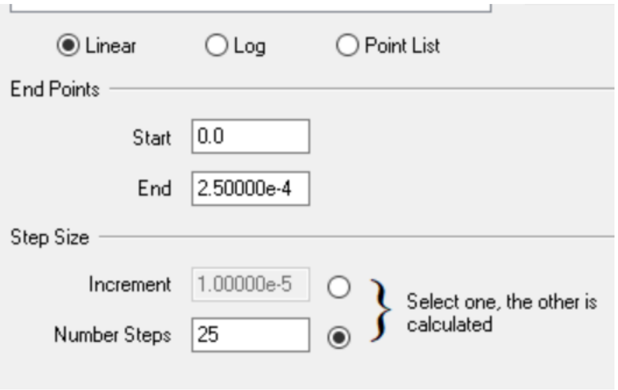
Set the concentration range to star start at 0, end at 2.5e-4, and have 25 steps



Component Inflows

☑ Hide Related Inflows

BaSO4
C3H12NO9P3
CaCO3
H2O
NaCl
SrSO4



● Linear ○ Log ○ Point List

End Points

Start 0.0

End 2.50000e-4

Step Size

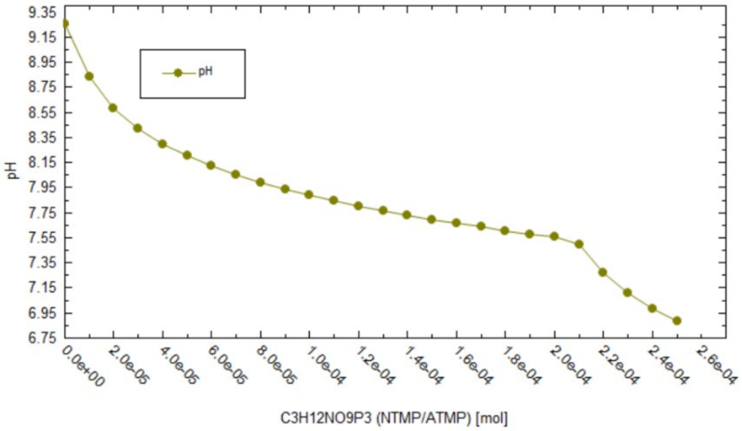
Increment 1.00000e-5 ○

Number Steps 25 ●

Select one, the other is calculated

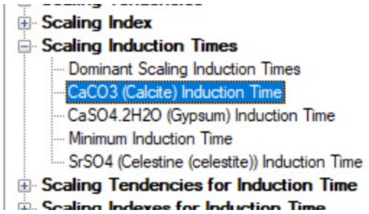
Calculate and select the **Plot** tab

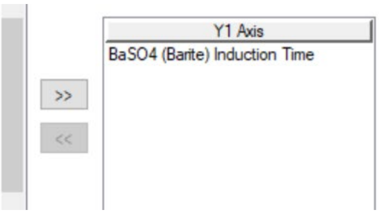
The scale inhibitor has a significant impact on the pH because NTMP is a hexavalent acid. This will affect scale tendencies for carbonate solids if added in this way. Right now, we are looking at $BaSO_4$, and so we will ignore the impact on calcite



Click the **Variables** button to open the **Curves** window

Remove the pH from the Y1 axis and add the $BaSO_4$ induction time from the **Scaling Induction Times** category



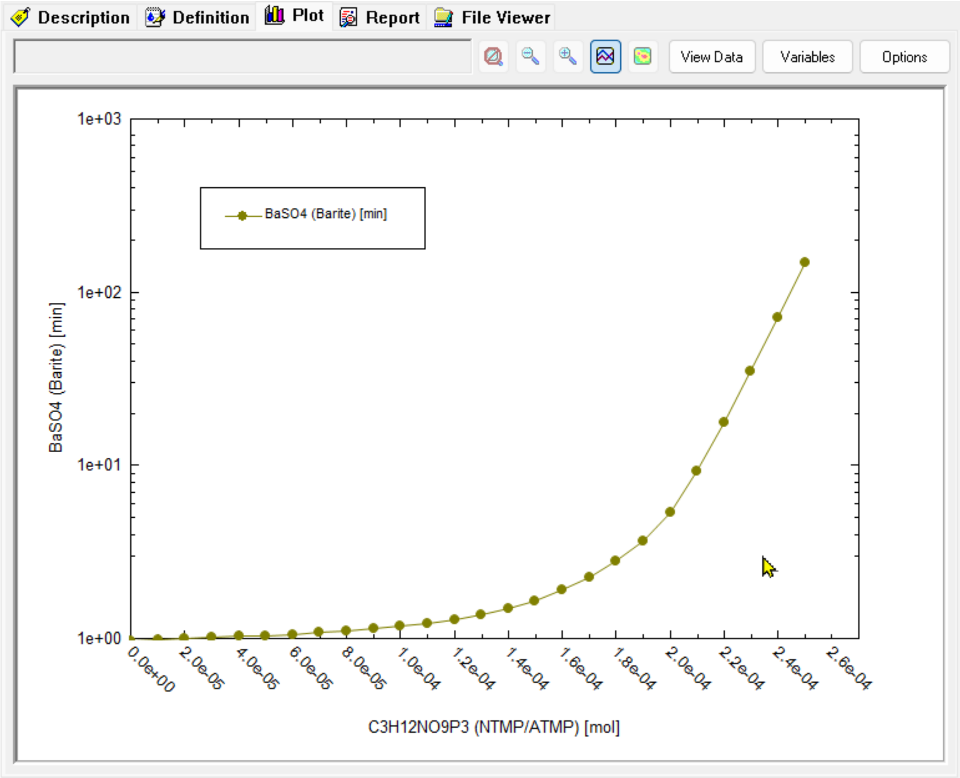


Y1 Axis

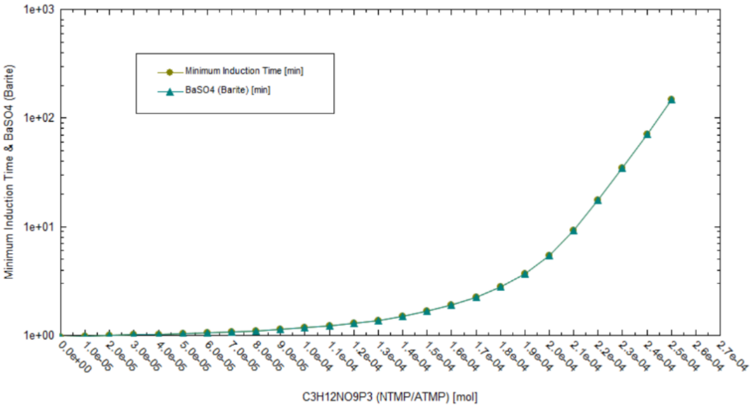
BaSO4 (Barite) Induction Time

Set the Y-axis to log scale

The plot now shows the barite induction times as the inhibitor is added. The induction times increase from 1 minute to 148 minutes when the concentration increases from 1.3e-4 to 2.0e-4 moles (52 to 80 mg/L). Somewhere in this rage would be the optimal inhibitor concentration.



You will notice that the plot does not extend to the final concentration of 2.5e-4 NTMP. It is because at this point the induction time exceeded the 10,000 hr maximum value.



Step #4 - Using a temperature survey to test induction times

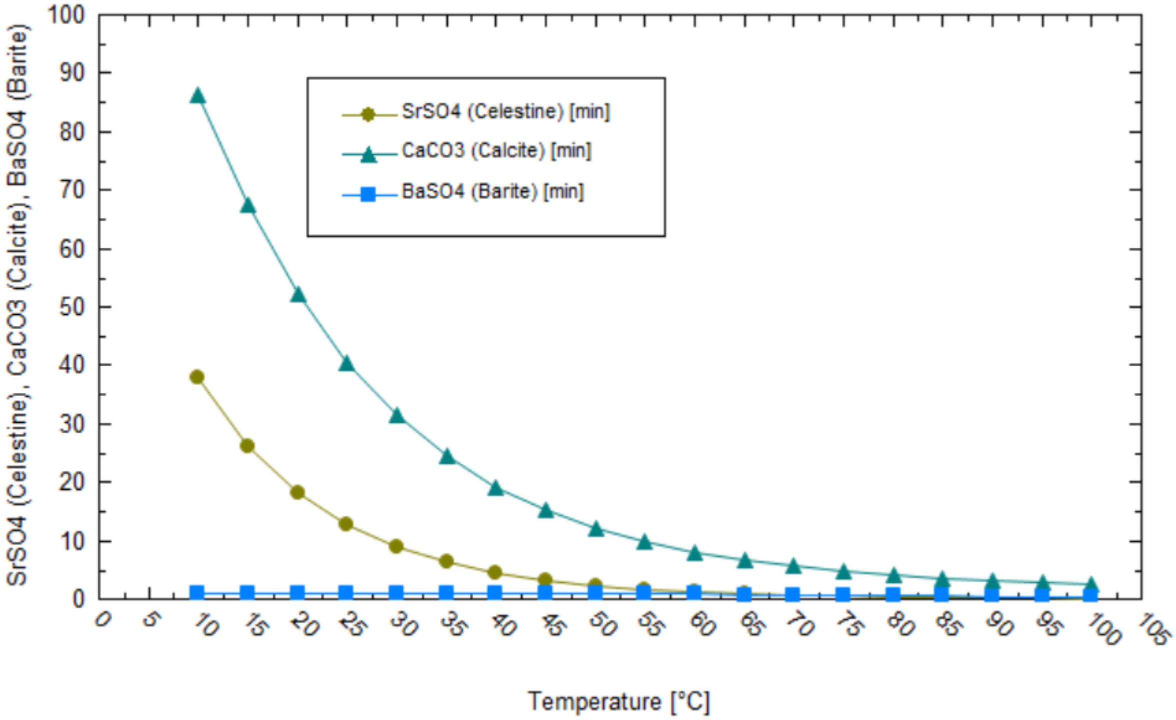
Induction times depend on both the scaling tendency of the solid (driving force for precipitation) and the temperature (reaction rates). Therefore, changes to either will result in different induction times for the solid.

Add a new **Survey** calculation and label it *t_ind vs T*

Set the temperature range from 10 to 100 °C by 5 °C increments, click **OK** and then and **calculate**

Select the **Plot** tab and plot the induction times for the three solids, $CaCO_3$, $BaSO_4$, and $SrSO_4$

The plot shows how temperature affects induction times. At 10 °C, $CaCO_3$ and $SrCO_3$ induction times are at 86 and 38 minutes, respectively. At 100 °C, the induction times for the 3 of them are less than 1 minute.

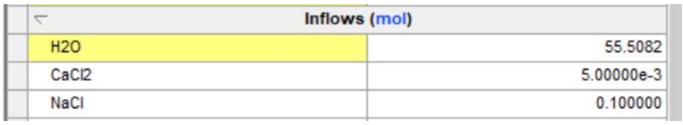


Example #2 – Using induction times in a Mixer calculation

A common cause of scaling is when two incompatible streams are mixed together. For example, one stream containing a high calcium concentration and the other containing high concentrations of carbonate. The software will compute the induction times during the time of mixing using the Mixer block. This next example shows this.

1) Add a stream and label it *Cations*

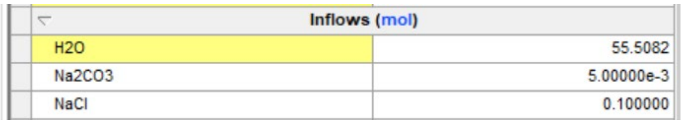
2) Add $CaCl_2$ and NaCl to the grid. Set the values to 0.005 and 0.1 moles, respectively



Inflows (mol)	
H2O	55.5082
CaCl2	5.00000e-3
NaCl	0.100000

3) Add a second stream and label it *Anions*

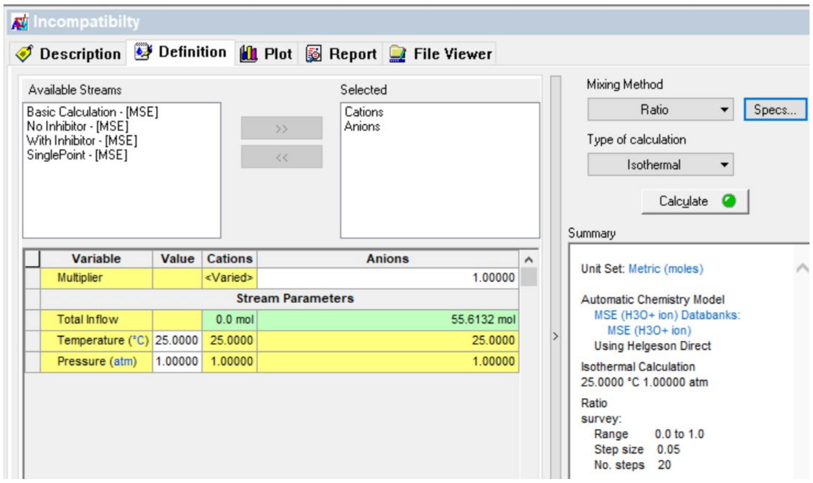
4) Add Na_2CO_3 and NaCl to the grid. Set the values at 0.005 and 0.1 moles, respectively



Inflows (mol)	
H2O	55.5082
Na2CO3	5.00000e-3
NaCl	0.100000

5) Add a Mixer calculation and label it *Incompatibility*

6) Move the Cations and Anions streams to the **Selected** Section
7) Set the **Mixing Method** to **Ratio**
8) Open the **Specs** window and select Cations as the Ratio stream.
9) Under the **Survey Range** tab set the steps to 20



Available Streams
Basic Calculation - [MSE]
No Inhibitor - [MSE]
With Inhibitor - [MSE]
SinglePoint - [MSE]

Selected
Cations
Anions

Mixing Method: Ratio

Type of calculation: Isothermal

Variable	Value	Cations	Anions
Multiplier		<Varied>	1.00000
Stream Parameters			
Total Inflow		0.0 mol	55.6132 mol
Temperature (°C)	25.0000	25.0000	25.0000
Pressure (atm)	1.00000	1.00000	1.00000

Summary

Unit Set: Metric (moles)

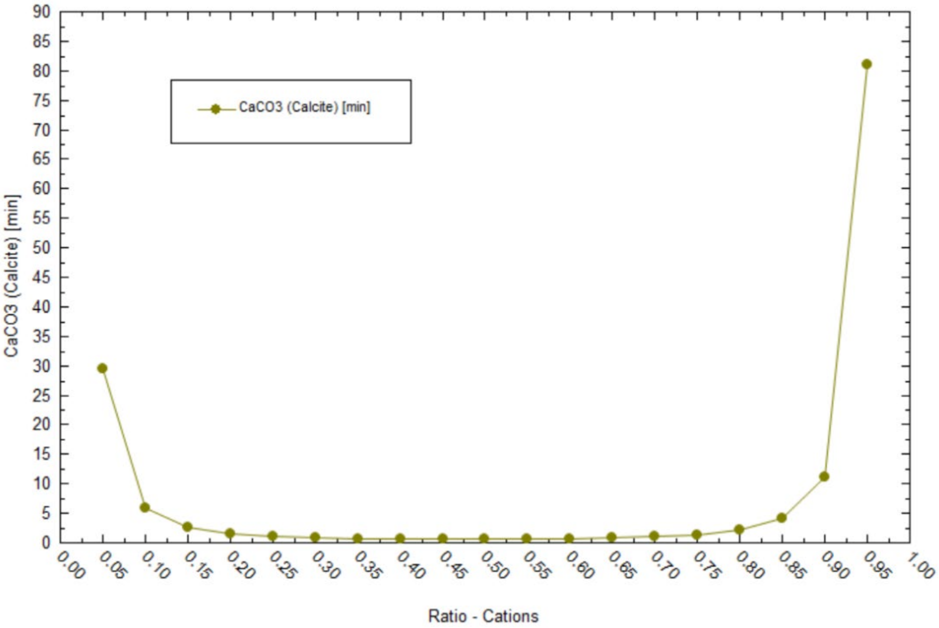
Automatic Chemistry Model
MSE (H3O+ ion) Databanks:
MSE (H3O+ ion)
Using Helgeson Direct

Isothermal Calculation
25.0000 °C 1.00000 atm

Ratio
survey:
Range 0.0 to 1.0
Step size 0.05
No. steps 20

10) **Calculate** and go to the **Plot** tab
11) Plot the $CaCO_3$ induction times

The plot shows that induction times are lowest (fastest to form) at a 50:50 mixture and highest at the far ends of the plot. In fact, at the 0 and 100% points, no induction times are shown because there is no calcium in the 0% calculation and no carbonate in the 100% calculation.

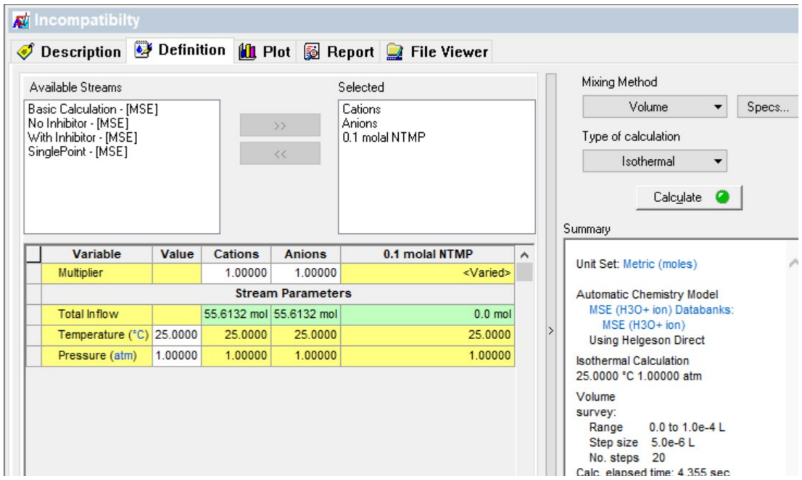


Scale inhibitors can also work in the mixer calculation, but to do this, the user must create a separate stream and add it to the mixer like it would occur in a process.

12) Create a new stream and label it 0.1 molal NTMP

Again, we are disregarding practical units in this example so that we can focus on the procedure of studying induction times.

1) Add NTMP to the grid and give it a value of 0.1 mole
2) Return to the Incompatibility mixer and add the 0.1 molal NTMP stream to the Selected window
3) Change the mixing type from Ratio to Volume
4) Open the **Specs** window and select the 0.1 molal NTMP as the adjustable stream
5) Set the start and end to 0 L and 1e-4 L, respectively. Set the steps to 20.



Available Streams
Basic Calculation - [MSE]
No Inhibitor - [MSE]
With Inhibitor - [MSE]
SinglePoint - [MSE]

Selected
Cations
Anions
0.1 molal NTMP

Mixing Method: Volume

Type of calculation: Isothermal

Variable	Value	Cations	Anions	0.1 molal NTMP
Multiplier		1.00000	1.00000	<Varied>
Stream Parameters				
Total Inflow		55.6132 mol	55.6132 mol	0.0 mol
Temperature (°C)	25.0000	25.0000	25.0000	25.0000
Pressure (atm)	1.00000	1.00000	1.00000	1.00000

Summary

Unit Set: Metric (moles)

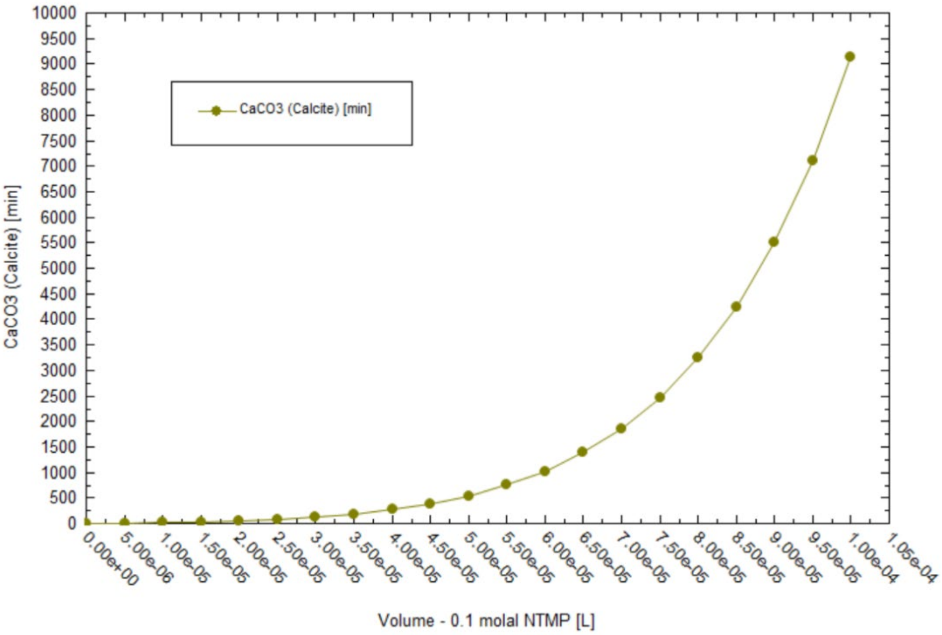
Automatic Chemistry Model
MSE (H3O+ ion) Databanks:
MSE (H3O+ ion)
Using Helgeson Direct

Isothermal Calculation
25.0000 °C 1.00000 atm

Volume
survey:
Range 0.0 to 1.0e-4 L
Step size 5.0e-6 L
No. steps 20
Calc. elapsed time: 4.355 sec

6) **Run** the calculation and click on the **Plot** tab when done
7) Add the CaCO3 induction time to the plot and click OK

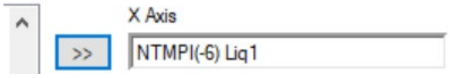
As NTMP is added to the mixture, the calcite induction time increases from less than one minute to over 1600 minutes. Somewhere in this addition would be the optimal treatment value, and that would depend on how long the solid needs to remain in solution. For example, 200 minutes is over three hours, a time that would probably be enough for a fluid to exit any process unit, like an RO or mixing tank. This would correlate with a 6e-5 L or 0.060 mL dosage per the two liters of mixed material.



An alternative way to plot this would be to use the MBG-Liquid 1 variables. Instead of plotting the volume of the NTMP added, you can plot the concentration of NTMP in solution. This concentration would be the minimum inhibitor concentration desired, or perhaps the residual concentration that you want to keep in solution.

8) Open the **Variables** button and expand the MBG Totals - Liquid 1 category

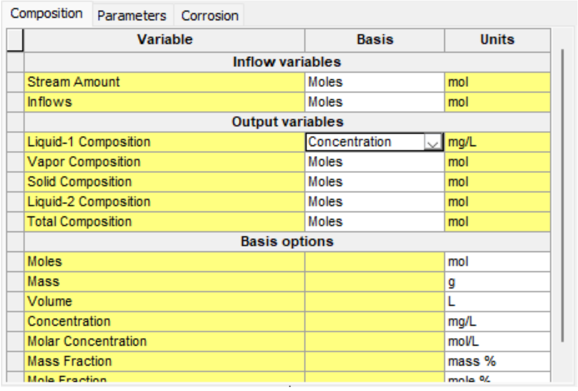
9) Move NTMP(-6) to the X-axis



X Axis: NTMPI(-6) Liq1

10) Close the **Variables** window and open the Units Manager ( )

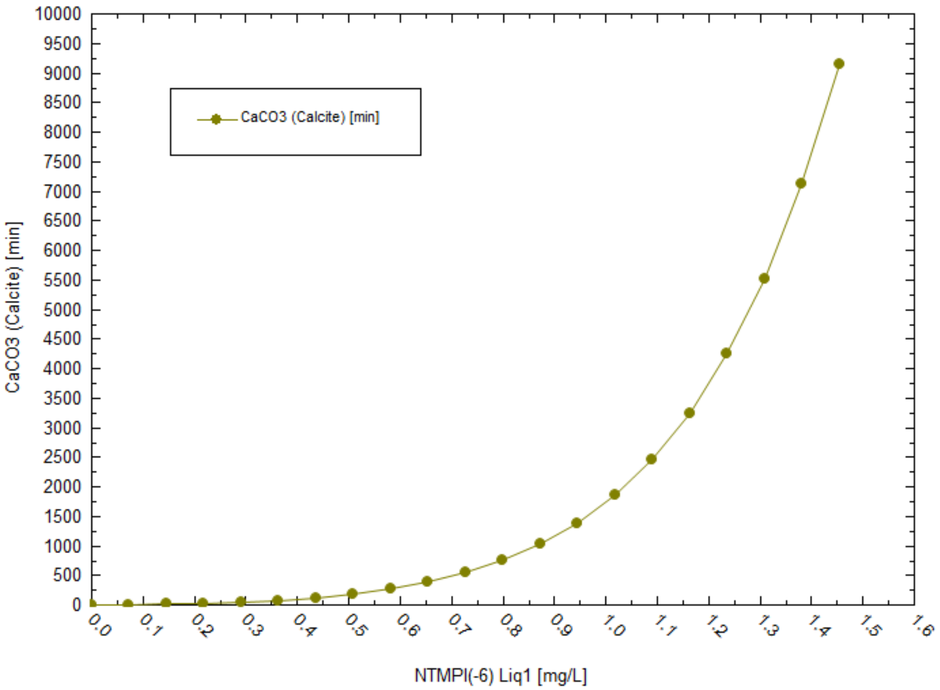
11) Click on the **Customize** button and change the *Liquid-1 Composition* from moles to Concentration



Variable	Basis	Units
Inflow variables		
Stream Amount	Moles	mol
Inflows	Moles	mol
Output variables		
Liquid-1 Composition	Concentration	mg/L
Vapor Composition	Moles	mol
Solid Composition	Moles	mol
Liquid-2 Composition	Moles	mol
Total Composition	Moles	mol
Basis options		
Moles		mol
Mass		g
Volume		L
Concentration		mg/L
Molar Concentration		mol/L
Mass Fraction		mass %

12) Close the units manager and review the plot

According to the calculation, a residual NTMP concentration of about 0.3 mg/l will keep $CaCO_3$ from precipitating for 60 minutes. A concentration of 1 mg/L will inhibit precipitation for about 32 hours (1856 minutes).



More Induction time options

The induction time calculation is a post-process calculation, meaning that it calculates the scale tendencies and t_{ind} after the system converges to equilibrium. This means that the software will keep the target solids in solution so that it can calculate its supersaturation. Competing solids that remove precipitating ions from the water can impact the induction times. For example, $BaSO_4$ is supersaturated, but $CaSO_4$ also precipitates, and in doing so, removes sulfate from solution. This sulfate removal affects the final $BaSO_4$ induction time. The software must be able to accommodate conditions where such mass actions impact the calculation. It does this in the **Calculation Options** window.

Click on any of the calculations you created using this chapter

Select the **Specs** button and then the **Calculation Options** tab (or category)

Click on the Advanced button adjacent to the Scaling Induction Times(s) check box


☐ Total Dissolved Solids (TDS)- Rigorous method

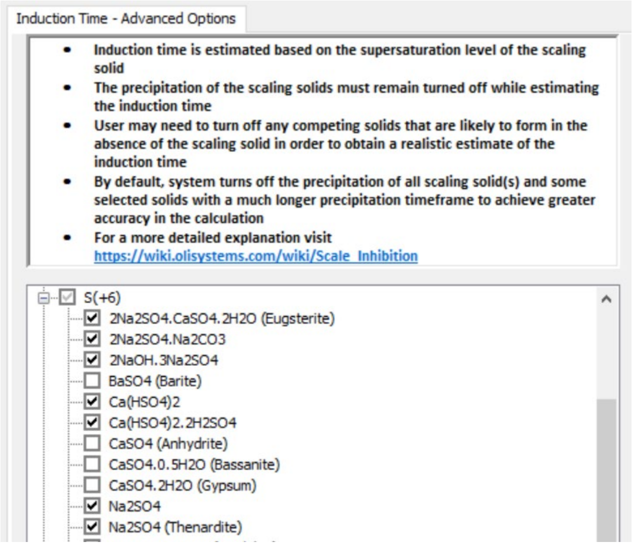
☑ Scaling Induction Time(s)

☑ Pre-scaling Tendencies

Expand the S(+6) category in the window

The text in the upper section of the window explains how the induction times work. It explains that the induction times are based on the supersaturation level of the specific solid and that for this solid to be supersaturated, it must not precipitate during the induction time calculation. In addition to the target solid, any competing solids that might change the concentration in the supersaturation equation (Ba and SO_4 if the calculation is for $BaSO_4$) also need to be turned off. Otherwise, the supersaturation of the target solid will be lowered and a less accurate induction time value will be computed.

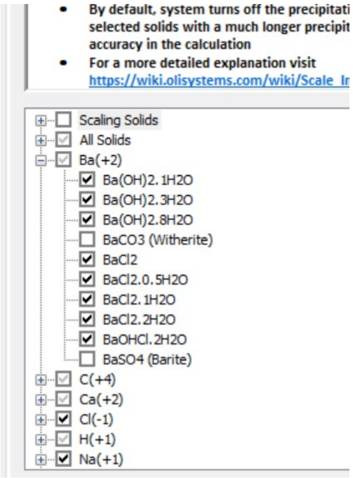
So, in this case, potential competing solids for $BaSO_4$ include three $CaSO_4$ phases and $BaCO_3$. These are turned off by default. There are many other Ba- and SO4-containing solids that can form, and if you see them forming in your induction time calculation, you can go to this window and turn them all off.



Induction Time - Advanced Options

- Induction time is estimated based on the supersaturation level of the scaling solid
- The precipitation of the scaling solids must remain turned off while estimating the induction time
- User may need to turn off any competing solids that are likely to form in the absence of the scaling solid in order to obtain a realistic estimate of the induction time
- By default, system turns off the precipitation of all scaling solid(s) and some selected solids with a much longer precipitation timeframe to achieve greater accuracy in the calculation
- For a more detailed explanation visit https://wiki.olisystems.com/wiki/Scale_Inhibition

☑ S(+6)
  - ☑ 2Na2SO4.CaSO4.2H2O (Eugsterite)
  - ☑ 2Na2SO4.Na2CO3
  - ☑ 2NaOH.3Na2SO4
  - ☐ BaSO4 (Barite)
  - ☑ Ca(HSO4)2
  - ☑ Ca(HSO4)2.2H2SO4
  - ☐ CaSO4 (Anhydrite)
  - ☐ CaSO4.0.5H2O (Bassanite)
  - ☐ CaSO4.2H2O (Gypsum)
  - ☑ Na2SO4
  - ☑ Na2SO4 (Thenardite)



- By default, system turns off the precipitati
selected solids with a much longer precipit
accuracy in the calculation
- For a more detailed explanation visit
https://wiki.olisystems.com/wiki/Scale_Ir

☐ Scaling Solids
☑ All Solids
☑ Ba(+2)
  - ☑ Ba(OH)2.1H2O
  - ☑ Ba(OH)2.3H2O
  - ☑ Ba(OH)2.8H2O
  - ☐ BaCO3 (Witherite)
  - ☑ BaCl2
  - ☑ BaCl2.0.5H2O
  - ☑ BaCl2.1H2O
  - ☑ BaCl2.2H2O
  - ☑ BaOHCl.2H2O
  - ☐ BaSO4 (Barite)

☑ C(+4)
☑ Ca(+2)
☑ Cl(-1)
☑ H(+1)
☑ Na(+1)

You may also decide that these competing solids <u>should</u> affect the induction time of your target solid. In that case, you turn those solids on. When that happens, reduced concentration of the target solid's ions will be used to compute the induction time.

Scale Kinetics Inhibitor Optimization Tool

The Scale Kinetics Inhibitor Optimization Tool in OLI Studio is designed to reconcile the user's experimental scale inhibition data by adjusting OLI's literature-based model parameters. With this feature, users can add experimental data of inhibitor concentration vs observed induction time (time to see formation of first visible crystal solid), from which the software will optimize the relevant OLI Databook kinetic parameters for the selected solid and applied inhibitor(s). After running the optimization, the re-parametrized scaling solid and inhibitor(s) can be saved to a private database. This will override the existing parameters for these species in OLI's underlying databank when users employ the private database in other calculations. That way, users can remain confident that OLI's scaling predictions are well-aligned with their observations and tailored to their system.

Scaling solids and inhibitors in OLI's databank:

<u>Target scaling solids:</u> Barite, Celestine, Gypsum, Calcite

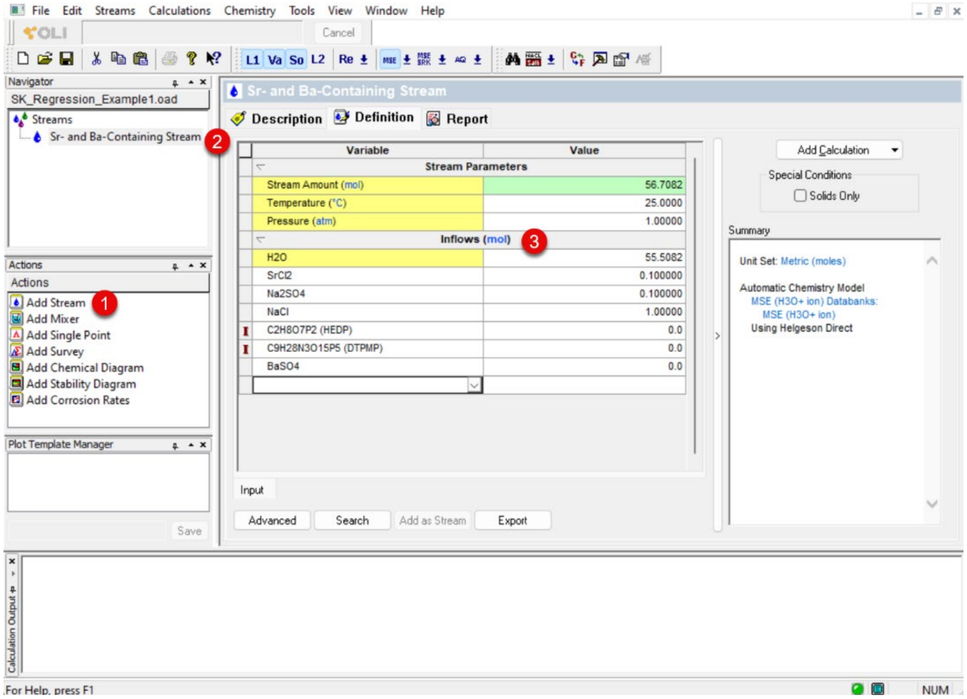
<u>Comprehensive scaling inhibitors:</u> HEDP, NTMP, DTPMP, PMLA, PBTC

Notably, the tool is not limited to the scaling solids and inhibitors already existing in OLI's databank; if users have the required data for a proprietary inhibitor or scaling solid not listed above, they can create a private databank in OLI Databook with these species. Then, they can utilize the Scale Kinetics Inhibitor Optimization Tool in OLI Studio to re-parametrize their model. For more information on this process, please visit our Support Center.

Example 1

In this example, we will prepare a scale kinetics optimization case. First, with the global stream selected, be sure that Induction Time calculations are enabled. This can be confirmed by navigating to Tools > Options... > Calculation Options, and checking that the Scaling Induction Time(s) checkbox is selected.

Now, we will add a new stream, label it "Sr and Ba-Containing Stream," and add the Inflows as shown in the image below.

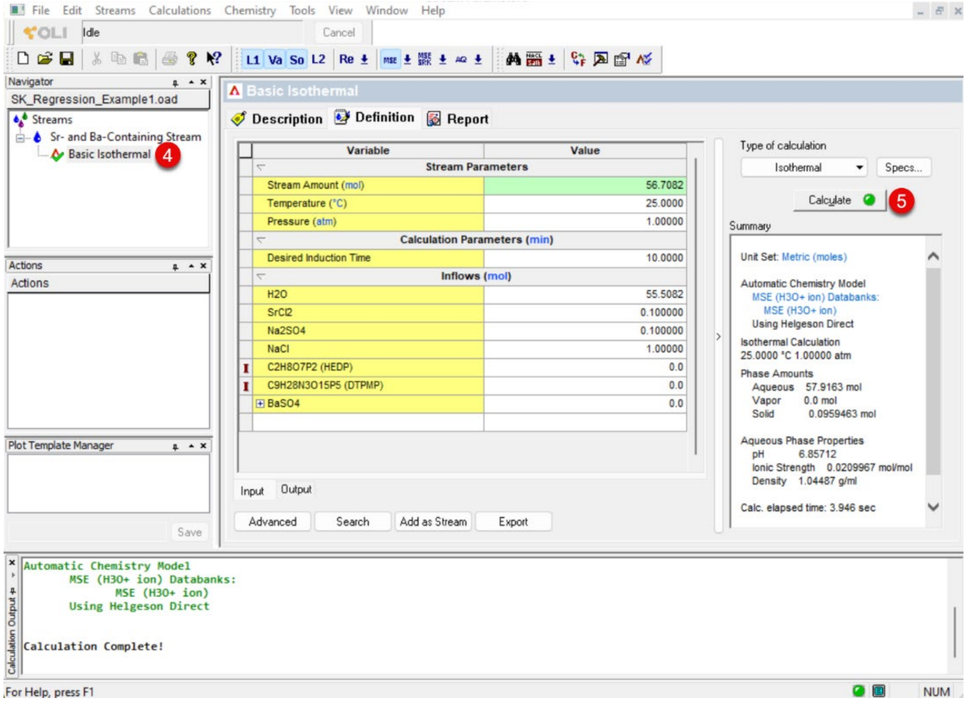


Variable	Value
Stream Parameters	
Stream Amount (mol)	56.7082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
SrCl2	0.100000
Na2SO4	0.100000
NaCl	1.00000
C2H8O7P2 (HEDP)	0.0
C9H28N3O15P5 (DTPMP)	0.0
BaSO4	0.0

Unit Set: Metric (moles)

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

Next, we will add a Single Point Isothermal calculation, change its name to "Basic Isothermal," and run the calculation.



Variable	Value
Stream Parameters	
Stream Amount (mol)	56.7082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters (min)	
Desired Induction Time	10.0000
Inflows (mol)	
H2O	55.5082
SrCl2	0.100000
Na2SO4	0.100000
NaCl	1.00000
C2H8O7P2 (HEDP)	0.0
C9H28N3O15P5 (DTPMP)	0.0
BaSO4	0.0

Summary

Unit Set: Metric (moles)

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

Isothermal Calculation
25.0000 °C 1.00000 atm

Phase Amounts
Aqueous 57.9163 mol
Vapor 0.0 mol
Solid 0.0959463 mol

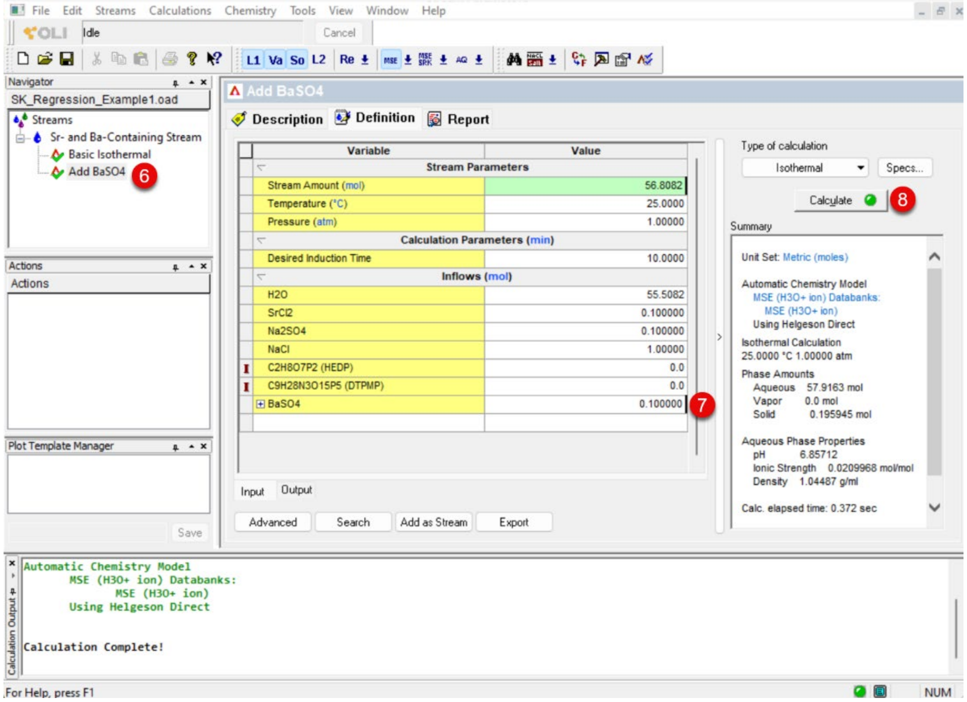
Aqueous Phase Properties
pH 6.85712
Ionic Strength 0.0209967 mol/mol
Density 1.04487 g/ml

Calc. elapsed time: 3.946 sec

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


Calculation Complete!
```

Having successfully executed the Basic Isothermal run, we will select the ”Sr and Ba-Containing Stream” level in the Navigator Panel, and add another Single Point Isothermal calculation and label it “Add BaSO4.” Here, we will change the BaSO4 Inflow to 0.1 moles, and run the calculation.



Variable	Value
Stream Parameters	
Stream Amount (mol)	56.8082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Calculation Parameters (min)	
Desired Induction Time	10.0000
Inflows (mol)	
H2O	55.5082
SrCl2	0.100000
Na2SO4	0.100000
NaCl	1.00000
C2H8O7P2 (HEDP)	0.0
C9H28N3O15P5 (DTPMP)	0.0
BaSO4	0.100000

Summary

Unit Set: Metric (moles)

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

Isothermal Calculation
25.0000 °C 1.00000 atm

Phase Amounts
Aqueous 57.9163 mol
Vapor 0.0 mol
Solid 0.195945 mol

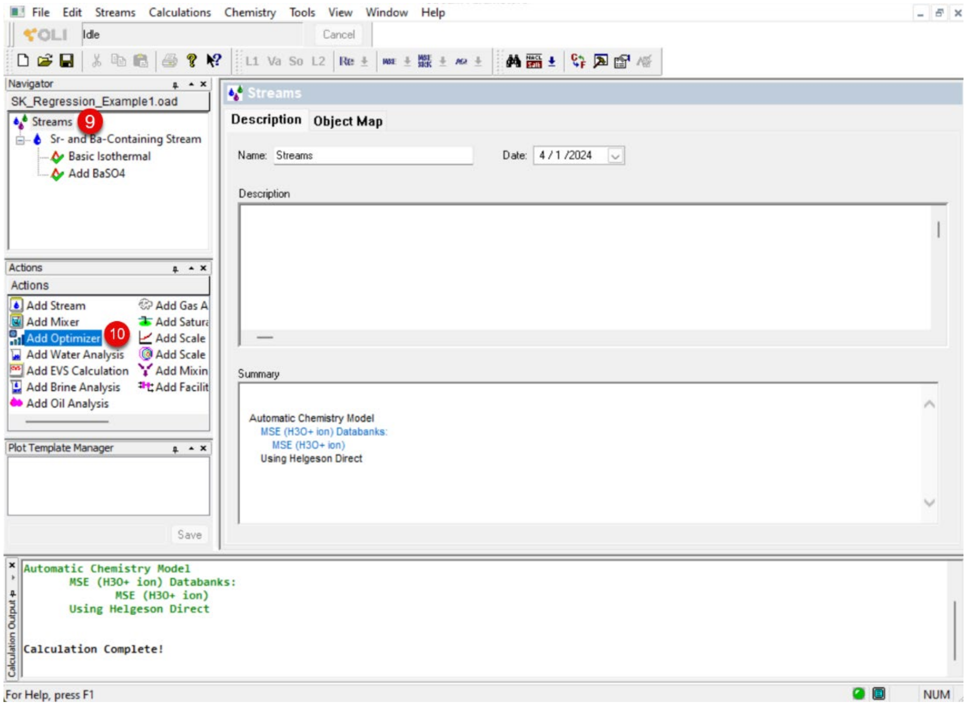
Aqueous Phase Properties
pH 6.85712
Ionic Strength 0.0209968 mol/mol
Density 1.04487 g/ml

Calc. elapsed time: 0.372 sec

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


Calculation Complete!
```

Once the second isothermal calculation is complete, we can select the Global Stream level in the Navigator Panel, and select the action, “Add Optimizer.”



Name: Streams

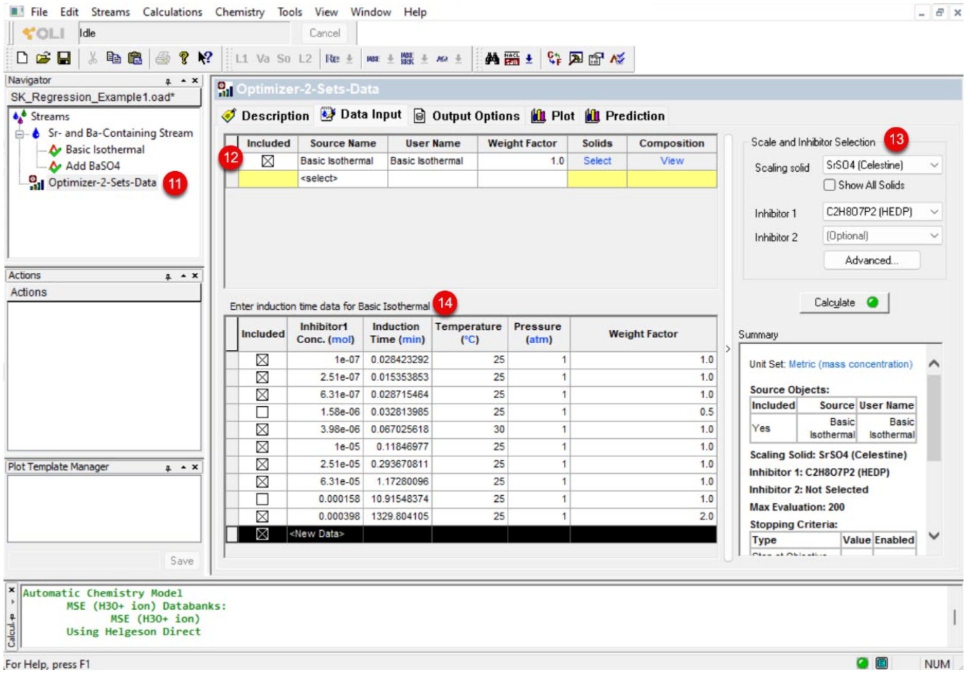
Date: 4 / 1 /2024

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

```
Automatic Chemistry Model
      MSE (H30+ ion) Databanks:
            MSE (H30+ ion)
      Using Helgeson Direct


Calculation Complete!
```

From here, we can label the object “Optimizer-2-Sets-Data." We can select “Basic Isothermal” as the first Source Name. In the Scale and Inhibitor Selection section, we can choose Celestine as the Scaling solid, and HEDP as Inhibitor 1. Next, we can enter all the induction time data for this calculation as shown below.



Included	Source Name	User Name	Weight Factor	Solids	Composition
☒	Basic Isothermal	Basic Isothermal	1.0	Select	View
	<select>				

Scale and Inhibitor Selection

Scaling solid: SrSO4 (Celestine)

☐ Show All Solids

Inhibitor 1: C2H8O7P2 (HEDP)

Inhibitor 2: (Optional)

Enter induction time data for Basic Isothermal

Included	Inhibitor1 Conc. (mol)	Induction Time (min)	Temperature (°C)	Pressure (atm)	Weight Factor
☒	1e-07	0.028423292	25	1	1.0
☒	2.51e-07	0.015353853	25	1	1.0
☒	6.31e-07	0.028715464	25	1	1.0
☐	1.58e-06	0.032813985	25	1	0.5
☒	3.98e-06	0.067025618	30	1	1.0
☒	1e-05	0.11846977	25	1	1.0
☒	2.51e-05	0.293670811	25	1	1.0
☒	6.31e-05	1.17280096	25	1	1.0
☐	0.000158	10.91548374	25	1	1.0
☒	0.000398	1329.804105	25	1	2.0
☒	<New Data>				

Unit Set: Metric (mass concentration)

Source Objects:

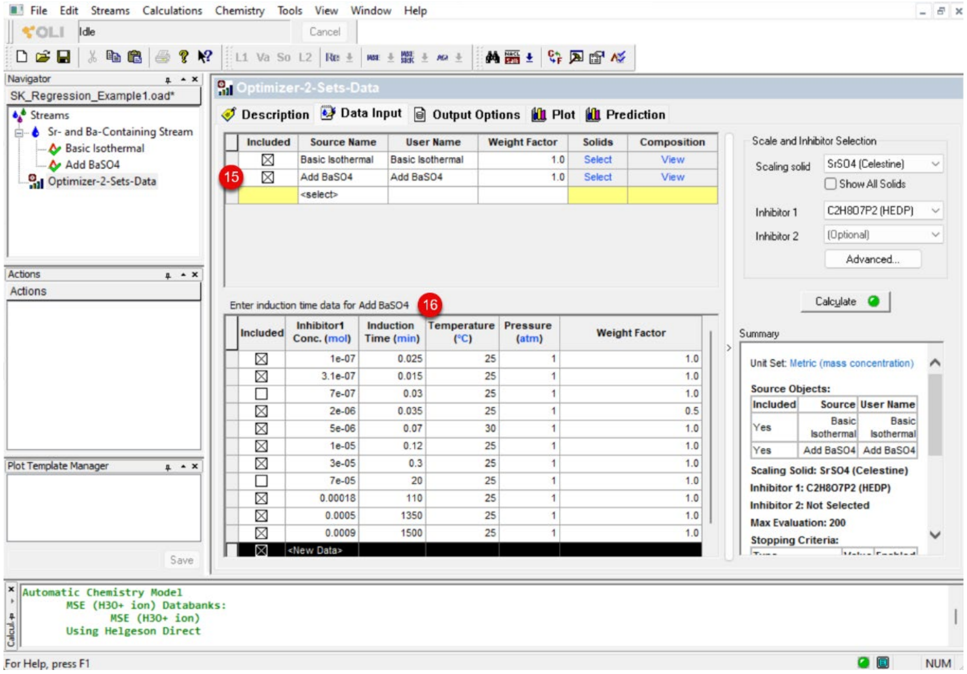
Included	Source	User Name
Yes	Basic Isothermal	Basic Isothermal

Scaling Solid: SrSO4 (Celestine)
Inhibitor 1: C2H8O7P2 (HEDP)
Inhibitor 2: Not Selected
Max Evaluation: 200
Stopping Criteria:

Type	Value	Enabled

```
Automatic Chemistry Model
      MSE (H30+ ion) Databanks:
            MSE (H30+ ion)
      Using Helgeson Direct
```

We will repeat the same process by selecting the next cell in the Source Name grid and choosing the “Add BaSO4” stream. Then, we will add the induction time data for this stream. You will notice that certain points have been selected to be excluded from the regression; this demonstrates how the user has agency to decide which data points to leverage or omit as outliers, etc.



Included	Source Name	User Name	Weight Factor	Solids	Composition
☒	Basic Isothermal	Basic Isothermal	1.0	Select	View
☒	Add BaSO4	Add BaSO4	1.0	Select	View
	<select>				

Enter induction time data for Add BaSO4

Included	Inhibitor1 Conc. (mol)	Induction Time (min)	Temperature (°C)	Pressure (atm)	Weight Factor
☒	1e-07	0.025	25	1	1.0
☒	3.1e-07	0.015	25	1	1.0
☐	7e-07	0.03	25	1	1.0
☒	2e-06	0.035	25	1	0.5
☒	5e-06	0.07	30	1	1.0
☒	1e-05	0.12	25	1	1.0
☒	3e-05	0.3	25	1	1.0
☐	7e-05	20	25	1	1.0
☒	0.00018	110	25	1	1.0
☒	0.0005	1350	25	1	1.0
☒	0.0009	1500	25	1	1.0
☒	<New Data>				

Scale and Inhibitor Selection

Scaling solid: SrSO4 (Celestine)

☐ Show All Solids

Inhibitor 1: C2H8O7P2 (HEDP)

Inhibitor 2: (Optional)

Advanced...

Summary

Unit Set: Metric (mass concentration)

Source Objects:

Included	Source	User Name
Yes	Basic Isothermal	Basic Isothermal
Yes	Add BaSO4	Add BaSO4

Scaling Solid: SrSO4 (Celestine)

Inhibitor 1: C2H8O7P2 (HEDP)

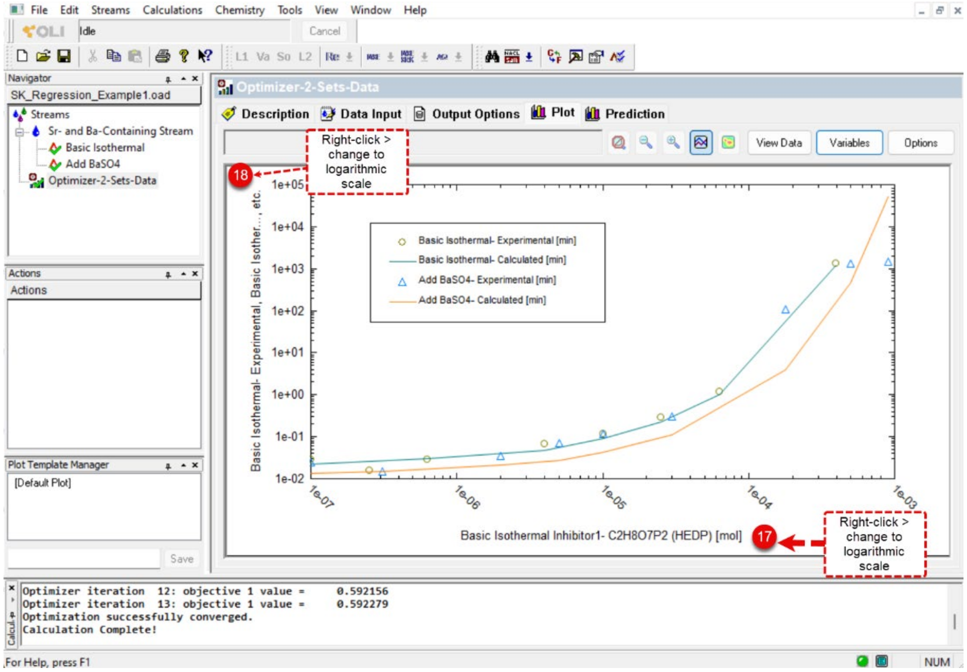
Inhibitor 2: Not Selected

Max Evaluation: 200

Stopping Criteria:

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

Now, we are ready to hit Calculate; during the runtime, we should see the Optimizer iteration number and objective value populate in the Calculation Output window. Once the optimization successfully converges, we can enter the plot tab to visualize the results. By default, the software plots the “Basic Isothermal” Inhibitor amount vs experimental and predicted results. We will right-click on the x- and y-axes to change to logarithmic scale to better visualize the outputs.

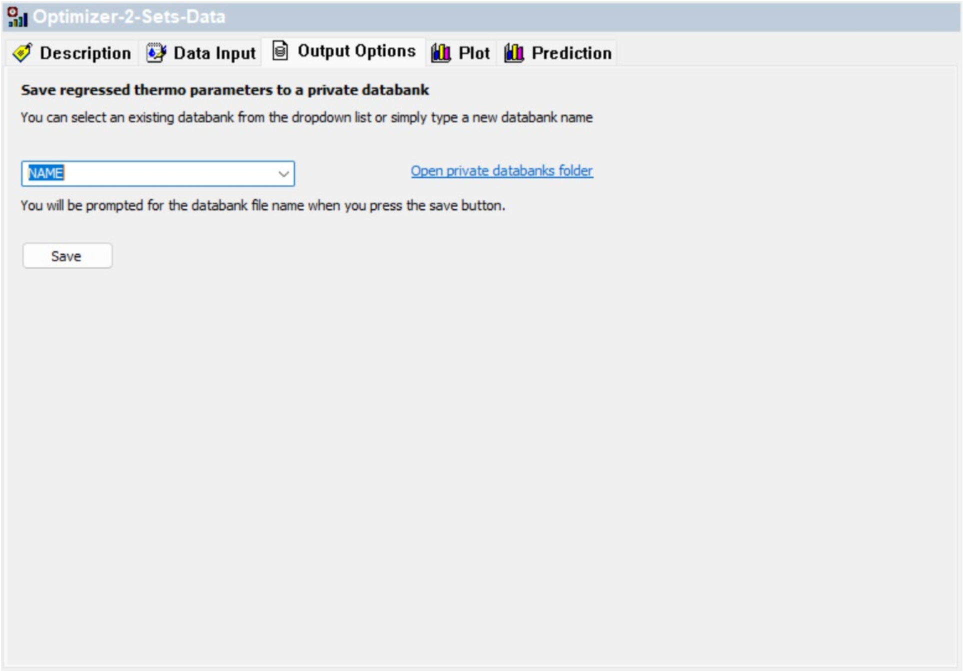


18 Right-click > change to logarithmic scale

17 Right-click > change to logarithmic scale

```
Optimizer iteration  12: objective 1 value =     0.592156
Optimizer iteration  13: objective 1 value =     0.592279
Optimization successfully converged.
Calculation Complete!
```

To save these re-parametrized species to a private database, we can navigate to the Output Options tab. Here, we can provide a name to a new private database and click the “Save” button. This database can be loaded into OLI Studio for future calculations to leverage the newly parametrized scaling solid and inhibitor.



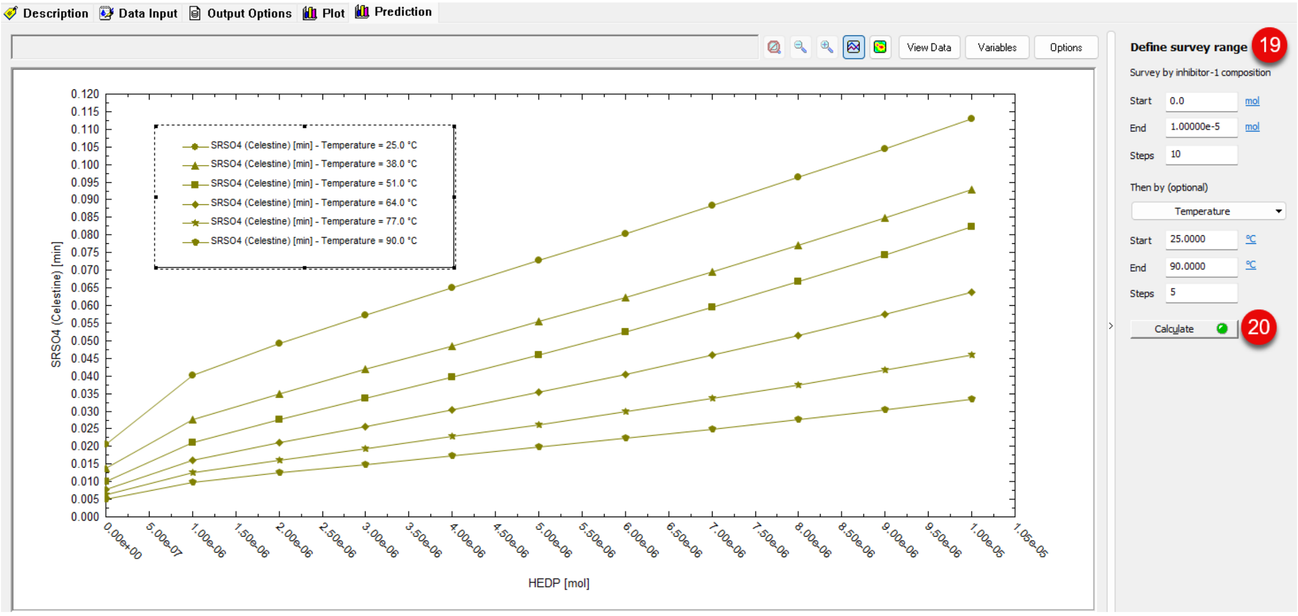
Save regressed thermo parameters to a private databank

You can select an existing databank from the dropdown list or simply type a new databank name

NAME

You will be prompted for the databank file name when you press the save button.

Lastly, in the Prediction tab, we can leverage the newly regressed kinetic parameters to evaluate the predicted celestine induction time based on HEDP loading and temperature. We can enter the survey ranges shown below and press the calculate button to arrive at the following plot.



Define survey range

Survey by inhibitor-1 composition

Start 0.0 mol
End 1.00000e-5 mol
Steps 10

Then by (optional)

Temperature

Start 25.0000 °C
End 90.0000 °C
Steps 5

Chapter VII – Naming Conventions in OLI Studio and Definitions

OLI naming conventions are important to understand as they become critical in performing advanced features in OLI Studio. The following chapter explains OLI naming conventions, when they're important, and provides key definitions for understanding these conventions.

Naming the Phases of Species

Let's say for example you want to type the following reaction in the OLI reaction kinetics tool:

$$2NH_{3(AQ)}+CO_{2(AQ)}=CH4N2O_{(AQ)}+H2O$$

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

As a general rule:

For an aqueous phase: AQ
For a vapor/gas phase: VAP

For a solid phase: PPT
For a hydrated solid: SOLIDNAME.nH2O, where n is the hydration number
For an ion: ION

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

In OLI terminology the above reaction will look like:

2NH3AQ+CO2AQ=UREAAQ+H2O

Ionic Strength

Ionic Strength (molal based or m-based)

The ionic strength is a quantity representing the strength of the electric field in a solution, and it is equal to the sum of the molalities of each type of ion present multiplied by the square of their charges, as represented by the following equation:

$$I = \frac{1}{2}\sum_{i=1}^{n}(z_i^2 m_i)$$

Where n is the number of charged species

For example, a 1.0 molar solution of NaCl has 1.0 moles of Na^{+}ions and 1.0 moles of Cl^{-} ions in 1 kg of H_2O. Therefore, the ionic strength is 1.0 molal.

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

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

Now, consider a 1.0 molal solution of $CaCl_2$. This solution has 1.0 mole of Ca^{+2} ions and 2.0 moles of Cl^{-} ions in 1 kg of H_2O. Therefore, the ionic strength is 3.0 molar, or it can be said that a 1.0 molal solution of $CaCl_2$ behaves similar to a 3.0 molar solution of NaCl.

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

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

Ionic Strength (mole fraction based or x-based)

In this case the ionic strength is calculated using the mole fraction rather than the molality:

$$I = \frac{1}{2}\sum_{i=1}^{n}(z_i^2 x_i)$$

Where n is the number of charged species.

Material Balance Group (MBG)

MGB is an abbreviation for Material Balance Groups. The **MGB** variable is a sum of all the species with the same oxidation state. OLI gives this information as Total or for the specific phase requested (Aqueous, Vapor, Solid, and Organic) or as absorbed to the surface.

For example, if we have the following system:

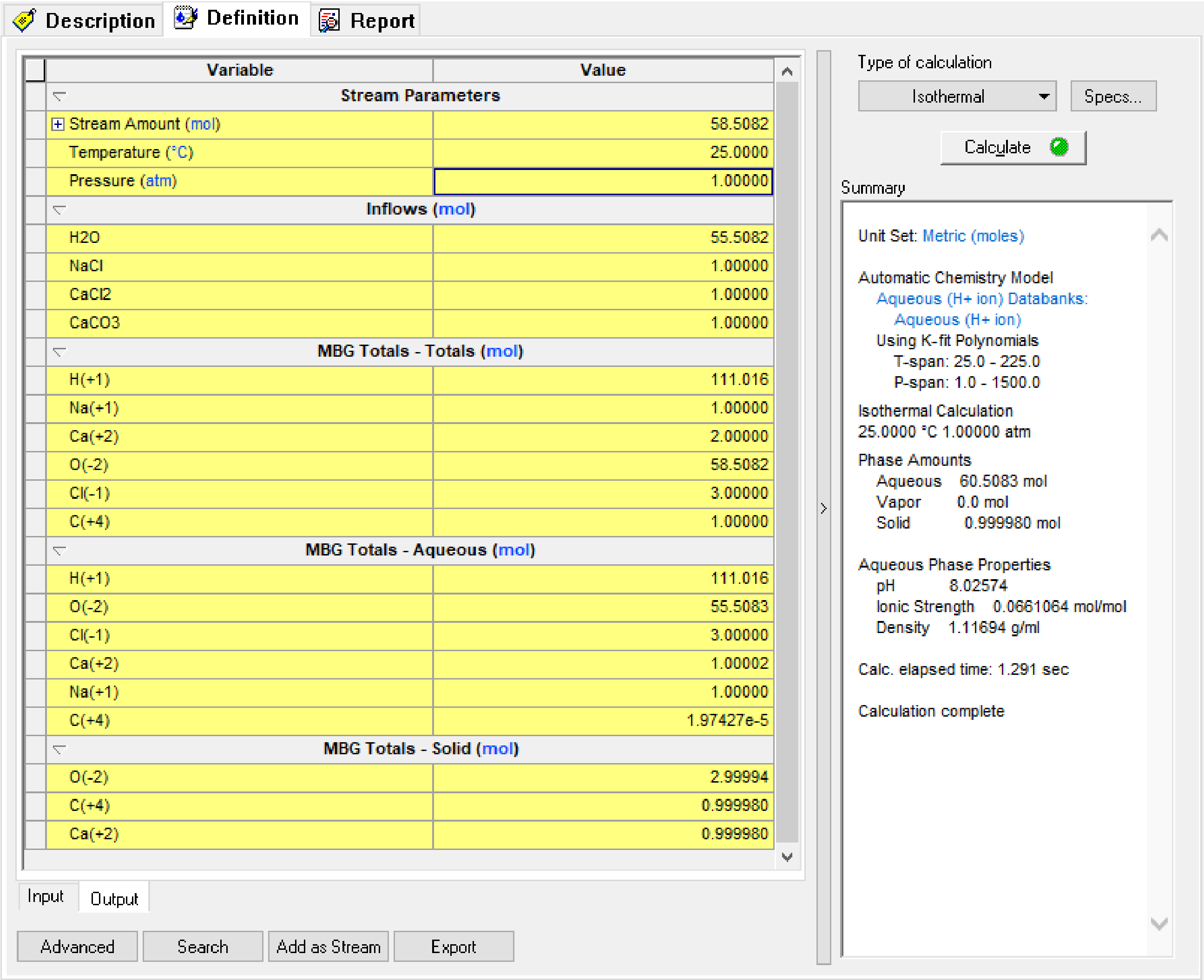
55.5082 moles of H_2O

1 mol of NaCl

1 mol of $CaCl_2$

1 mol of $CaCO_3$

The distribution of the elements with their respective oxidation states are given as MBG for the total system, and for the phases that are predicted to form, as shown in the image below.



Type of calculation: Isothermal

Variable	Value
Stream Parameters	
Stream Amount (mol)	58.5082
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
NaCl	1.00000
CaCl2	1.00000
CaCO3	1.00000
MBG Totals - Totals (mol)	
H(+1)	111.016
Na(+1)	1.00000
Ca(+2)	2.00000
O(-2)	58.5082
Cl(-1)	3.00000
C(+4)	1.00000
MBG Totals - Aqueous (mol)	
H(+1)	111.016
O(-2)	55.5083
Cl(-1)	3.00000
Ca(+2)	1.00002
Na(+1)	1.00000
C(+4)	1.97427e-5
MBG Totals - Solid (mol)	
O(-2)	2.99994
C(+4)	0.999980
Ca(+2)	0.999980

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model
Aqueous (H+ ion) Databanks:
Aqueous (H+ ion)
Using K-fit Polynomials
T-span: 25.0 - 225.0
P-span: 1.0 - 1500.0

Isothermal Calculation
25.0000 °C 1.00000 atm

Phase Amounts
Aqueous 60.5083 mol
Vapor 0.0 mol
Solid 0.999980 mol

Aqueous Phase Properties
pH 8.02574
Ionic Strength 0.0661064 mol/mol
Density 1.11694 g/ml

Calc. elapsed time: 1.291 sec

Calculation complete

Volume vs. Volume at Standard Conditions vs. Standard Liquid Volume

Volume

This is the volume of the system at a specified temperature, pressure, and composition.

Volume at Standard Conditions

It is also known as the Standard Volume. This is the calculated volume of each phase (using the composition of each phase) at standard conditions. The standard conditions for each phase: vapor, liquid-1, and liquid-2 are predefined in the software, and can be changed.

The standards conditions are:

Vapor: Temperature: 15ºC and Pressure: 1.0023 atm

Liquid-1: Temperature: 25ºC and Pressure: 1 atm

Liquid-2: Temperature: 15ºC and Pressure: 1 atm

Standard Liquid Volume

This is a transport unit. Standard liquid volume is the calculated standard liquid volume based on true species. You can see it as the contribution of volume of each true species to the total liquid volume.

An example

Standard liquid volume calculation of Liquid-1 phase (MSE), H_2O: 55.5082 mole, NaCl: 1 mole, 25ºC, 1 atm (using OLI Studio 9.5.4).

Standard liquid volume of material balance group (MBG) (accessible through Databank > literature >Material codes > VOLU).

MBG name	Standard liquid volume of MBG, VOLU (m^3)
H(+1)	1.41E-05
Na(+1)	1.82E-05
O(-2)	-1.02E-05
Cl(-1)	1.72E-05

True species composition after speciation:

True species (Name)	Composition (COMP), mole
H2O	55.5082
Cl-1	1
Na+1	1
H3O+1	1.33E-07
OH-1	1.33E-07
NaOH	5.30E-14
HCl	2.07E-15

Standard liquid volume of the phase calculation, considering MBG group contribution in each true species:

MBG Name	Contribution	Contribution Value
H(+1)	1.41E-05×(55.5082×2 + 1.33E-07×3 + 1.33E-07×1 + 5.30E-14×1 + 2.07E-15×1)	1.57E-03
Na(+1)	1.82E-05× (1×1 + 5.30E-14×1)	1.82E-05
O(-2)	-1.02E-05× (55.5082×1 + 1.33E-07×1 + 1.33E-07×1 + 5.30E-14×1)	-5.65E-04
Cl(-1)	1.72E-05× (1×1 + 2.07E-15×1)	1.72E-05
	Volume (m^3)	0.00103827
	Volume (L)	1.03827

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