

Chapter 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 ₂ O	=	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.

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.

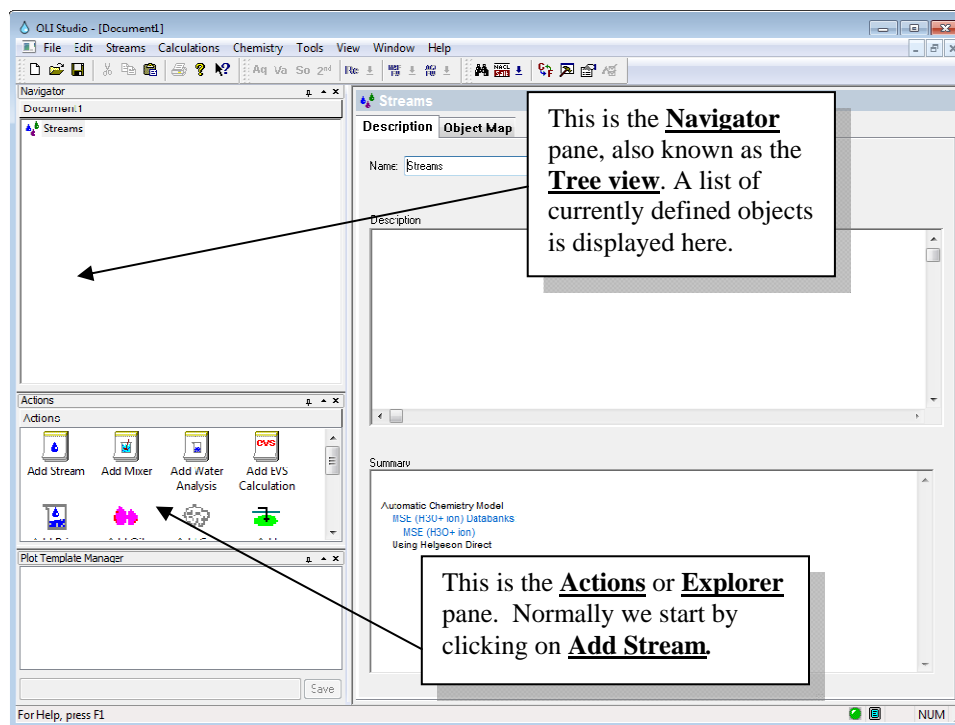


Figure 2-1 The main OLI Studio window

Click on the Add Stream icon.

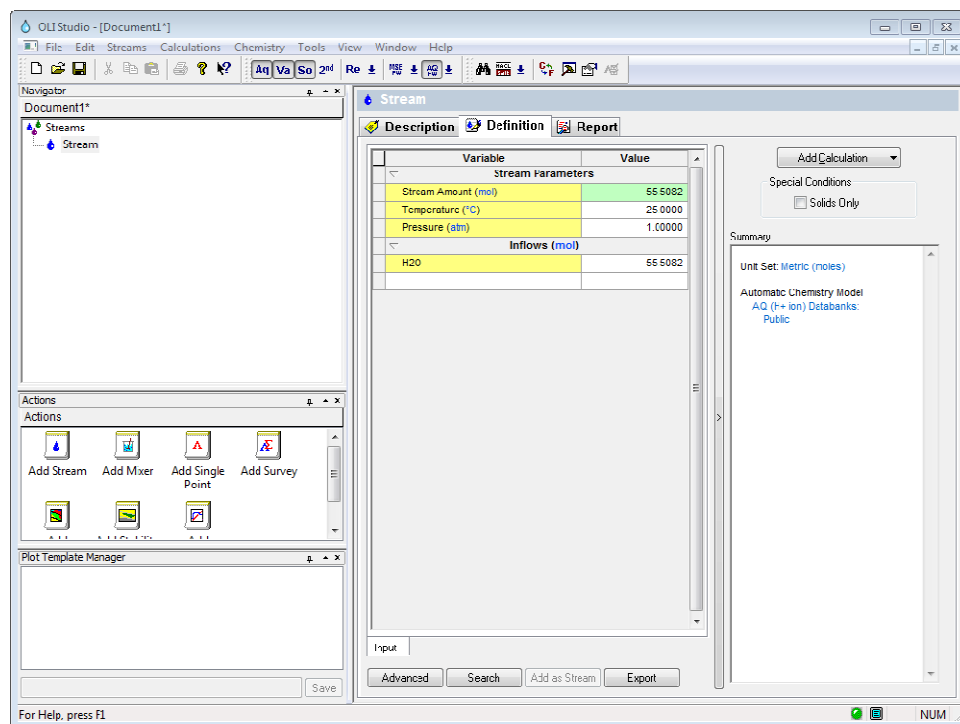


Figure 2-2 Adding a new stream

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

1. **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.
2. **Mixed Solvent Electrolyte / MSE (H_3O^+ ion):** The MSE framework is OLI's newly developed model capable of reproducing speciation, chemical, and phase equilibria applicable to water-organic-salt systems in the full range of concentrations as well as aqueous electrolytes from dilute solutions to the fused salt limit.

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

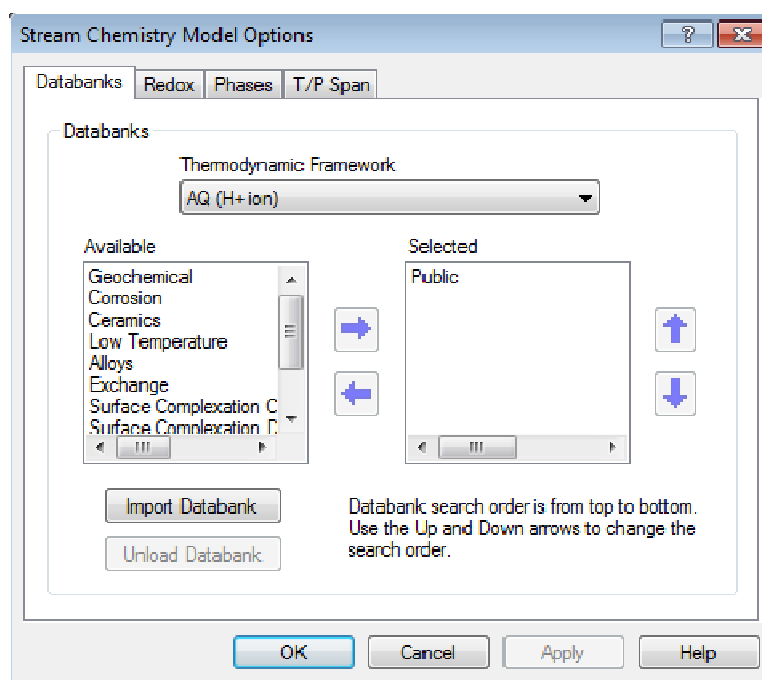


Figure 2-3: Selecting the thermodynamic framework used for simulation.

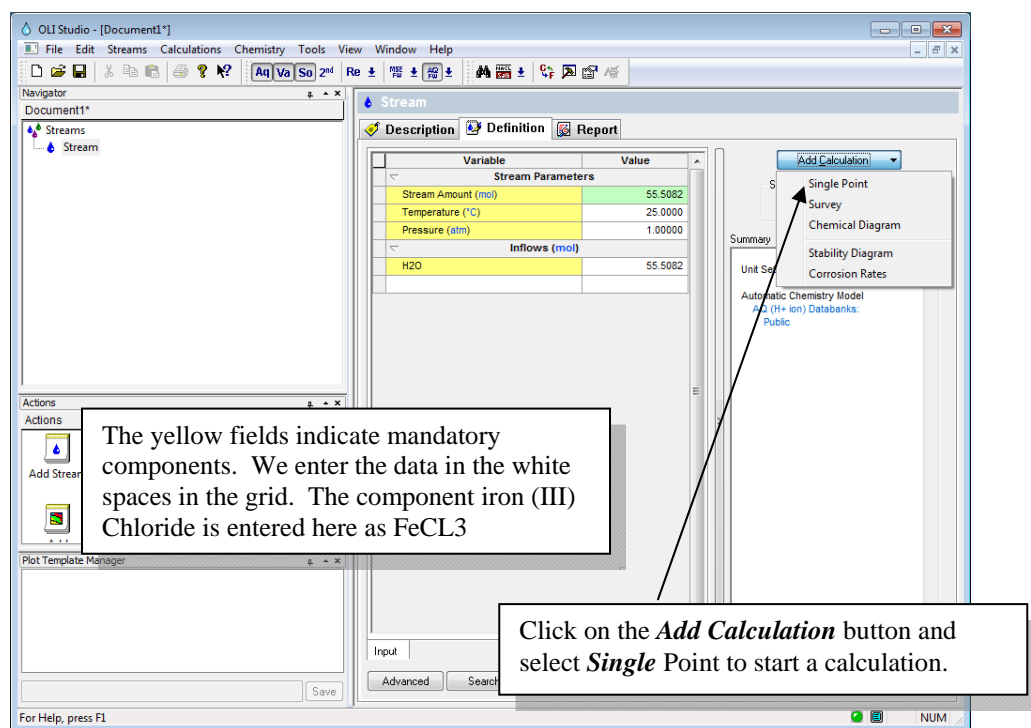


Figure 2-4 Entering Stream Information

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

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

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

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

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

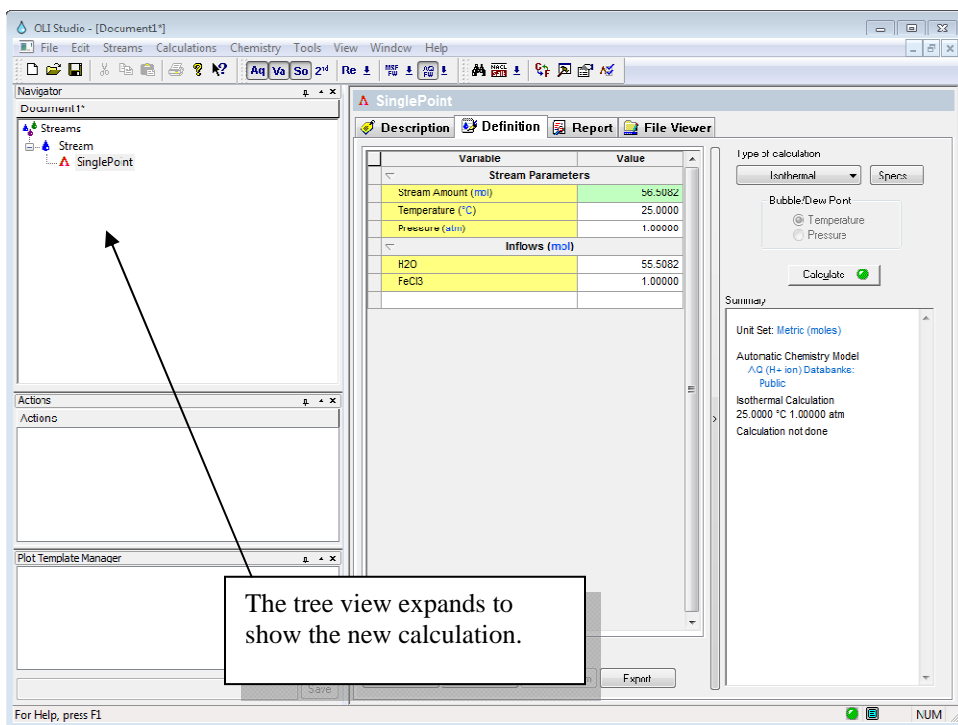


Figure 2-5 Starting the calculation

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

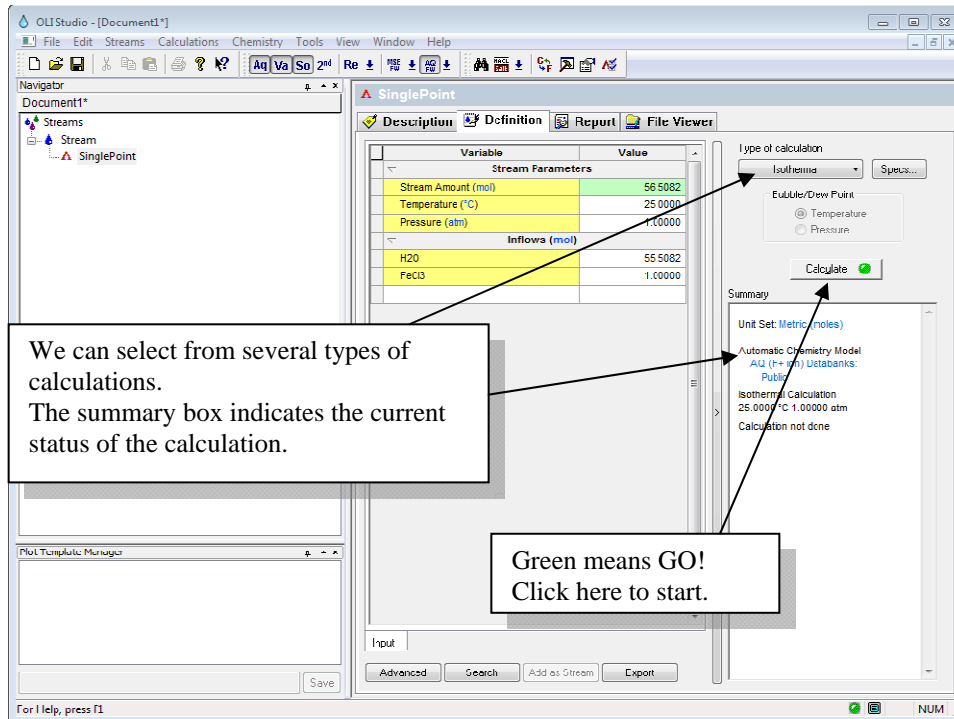


Figure 2-6 Entering the calculation conditions.

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

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

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

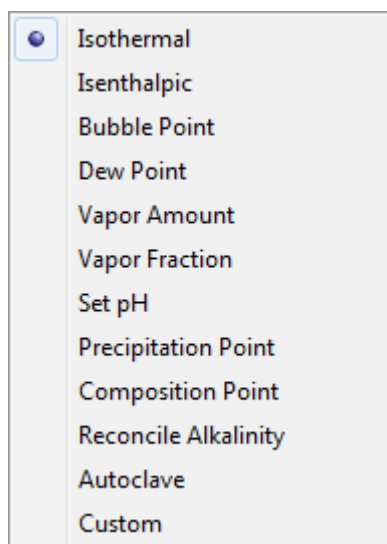


Figure 2-7 Single Point Calculation Types

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

<i>Isothermal</i>	A constant temperature and pressure calculation.
<i>Isenthalpic</i>	A constant heat loss/gain is applied to the calculation and a temperature or pressure can be adjusted to meet this new heat content.
<i>Bubble Point</i>	The temperature or pressure is adjusted to reach a condition where a small amount of vapor begins to appear.
<i>Dew Point</i>	The temperature or pressure is adjusted to reach a condition where a small amount of aqueous liquid appears.
<i>Vapor Amount</i>	The temperature or pressure is adjusted to produce a specified amount of vapor.
<i>Vapor Fraction</i>	The temperature or pressure is adjusted to produce a specified amount of vapor as a fraction of the total quantity.
<i>Set pH</i>	The pH of the solution can be specified by adjusting the flowrate of species.
<i>Precipitation Point</i>	The amount of a solid (solubility point) may be specified by adjusting the flowrate of a species.
<i>Composition Point</i>	The aqueous concentration of a species may be specified by adjusting the flowrate of a species.
<i>Reconcile Alkalinity</i>	The alkalinity of a solution can be specified by adjusting the flowrate of species.
<i>AutoClave</i>	This simulates a closed pressure vessel. ²
<i>Custom</i>	Combinations of the above calculations can be created.

² You may have to enable this calculation from Tools | Options

Select **Isothermal** calculations.

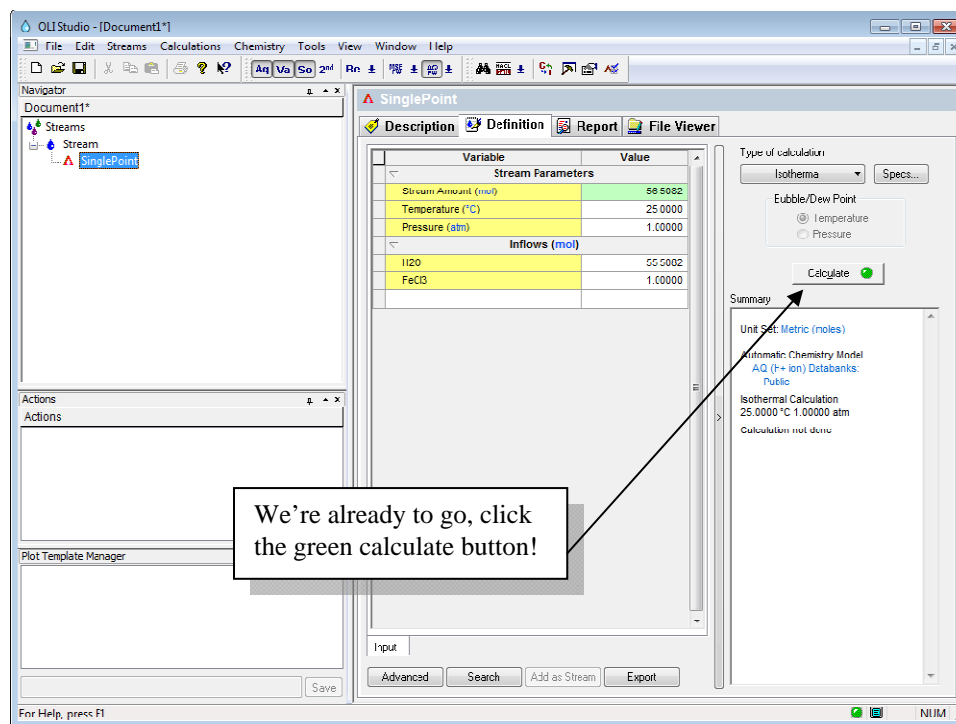


Figure 2-8 Let's GO! Click the Calculate button!

Click the green **Calculate** button.

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

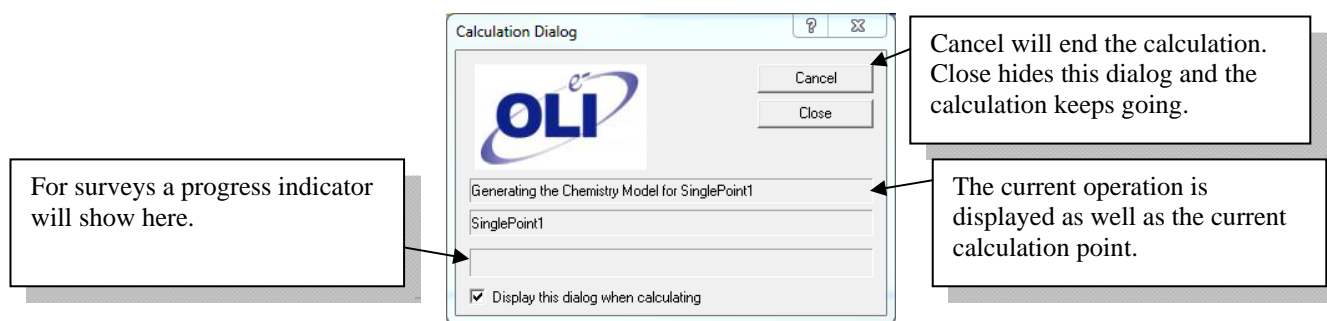


Figure 2-9 The OLI Calculation Status Dialog

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.

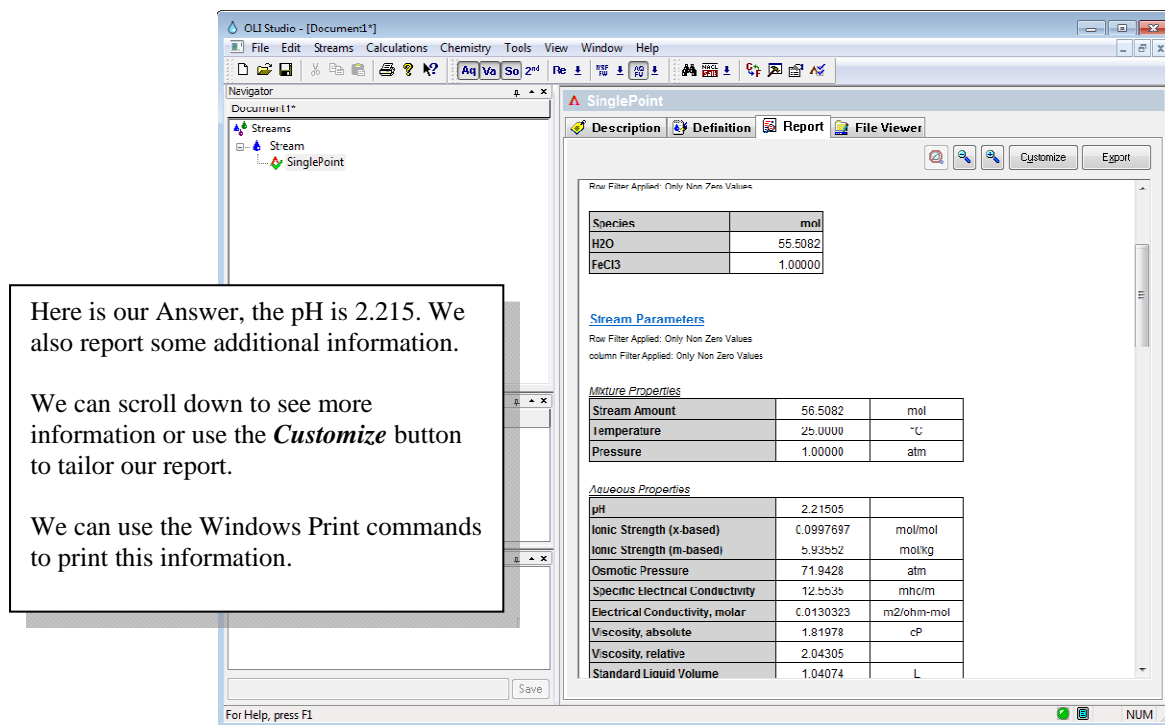


Figure 2-10 The Answer to our question

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

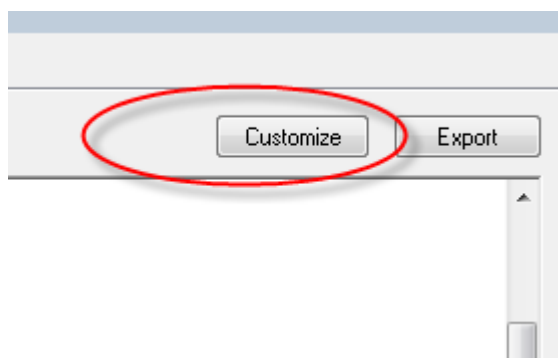


Figure 2-11 Click on the customize button

Click on the **Customize** button.

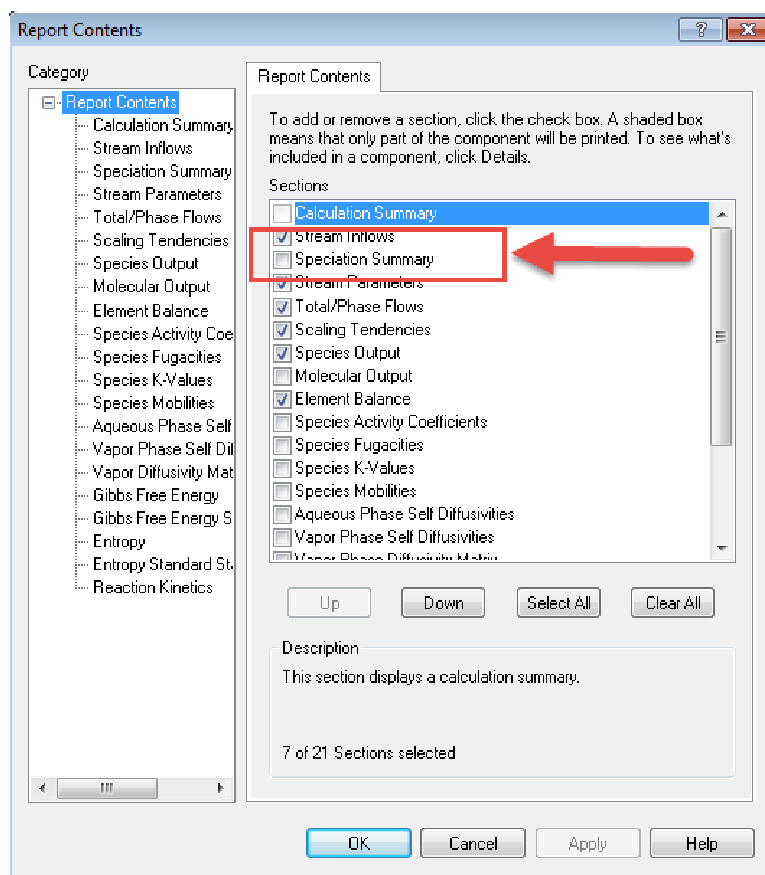


Figure 2-12 Report content options

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

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

FeCl3	1.00000
-------	---------

Speciation Summary

Total number of species: 24

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

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

Figure 2-13 Modifying the report

Answer:

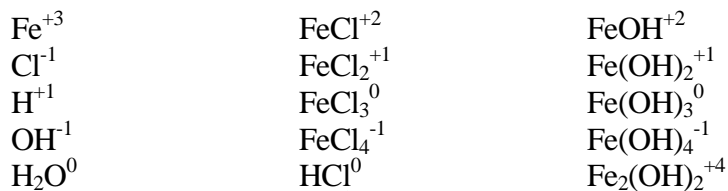
$$\text{pH} = 2.215$$

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 ions³. 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:



Speciation:



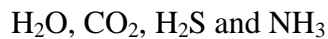
This is a weak species at 25°C.

Speciation in Sour Water

Now we will look at a different system; the sour water system ($\text{NH}_3/\text{H}_2\text{S}/\text{CO}_2/\text{H}_2\text{O}$).

Sour Water Species

Vapor Species:



Aqueous Neutral Species:



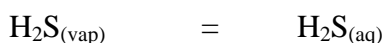
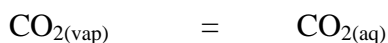
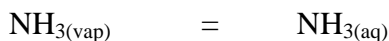
³ Le Châtelier's principle. P.W. Atkins. Physical Chemistry. W.H. Freeman and Company, San Francisco (1982) p 269.

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:

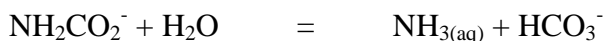


Chemistry Summary (Electrolyte Equilibrium)

Additional electrolyte reactions needed



Notice that this is the hydrolysis of an ion.



Calculating Partial Pressures

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

We now want to calculate the partial pressures of 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 %)

H₂S: 0.040 - 0.407 molal

(0.1- 1.3 wt %)

H₂O: Balance

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

Temp (C)	Liquid Concentration (molality)			Partial Pressure (mmHg)								
	NH3	CO2	H2S	NH3			CO2			H2S		
				Experim- ental	OLI	VLE	Experim- ental	OLI	VLE	Experim- ental	OLI	VLE
60	2.076	1.516	0.064	14.744	12.388	121.6	751.48 8	592.192	79594.8	31.616	36.936	1033.6
	2.098	1.601	0.052	13.604	10.792	129.2	738.11 2	744.572	84762.8	23.256	35.112	843.6
	1.954	1.471	0.04	11.476	11.172	114	691.90 4	638.4	76820.8	22.8	25.004	638.4
	2.16	1.581	0.05	13.68	12.92	129.2	705.28	590.52	83524	22.42	28.12	813.2
20	1.231	0.424	0.196	4.104	3.648	12.16	1.444	1.672	8580.4	3.192	3.04	1292
	1.236	0.507	0.201	2.888	2.66	12.16	3.496	3.42	10290.4	5.092	4.484	1325.44
	1.45	0.517	0.407	2.432	2.736	14.44	3.724	4.028	10526	12.54	10.944	2690.4
	1.439	0.665	0.396	1.52	1.444	14.44	13.072	13.148	13611.6	26.98	20.672	2634.16
	1.132	0.681	0.1	1.368	1.216	11.4	12.16	13.984	13892.8	5.32	4.94	663.48
	1.234	0.694	0.199	1.292	1.216	12.16	13.072	16.036	14181.6	11.172	11.096	1322.4
	1.238	0.712	0.203	1.292	1.064	12.16	19	18.62	14561.6	15.276	12.464	1345.2
	1.234	0.725	0.199	0.912	0.988	12.16	20.444	20.672	14835.2	15.96	13.072	1079.2
	1.235	0.771	0.2	0.912	0.836	12.16	29.184	30.324	15808	27.36	17.024	1333.04
	1.126	0.794	0.095	0.684	0.684	11.4	35.188	36.252	16271.6	12.236	8.892	633.08

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

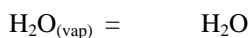
The data contained in **Table 2-1** compares the experimental partial pressures of carbon dioxide, ammonia and hydrogen sulfide against a VLE only model and the full OLI speciated model.

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)

Considering only the Vapor-Liquid equilibria

Only the following equilibria are considered in these calculations:



Partial Pressures of Gases (VLE only)

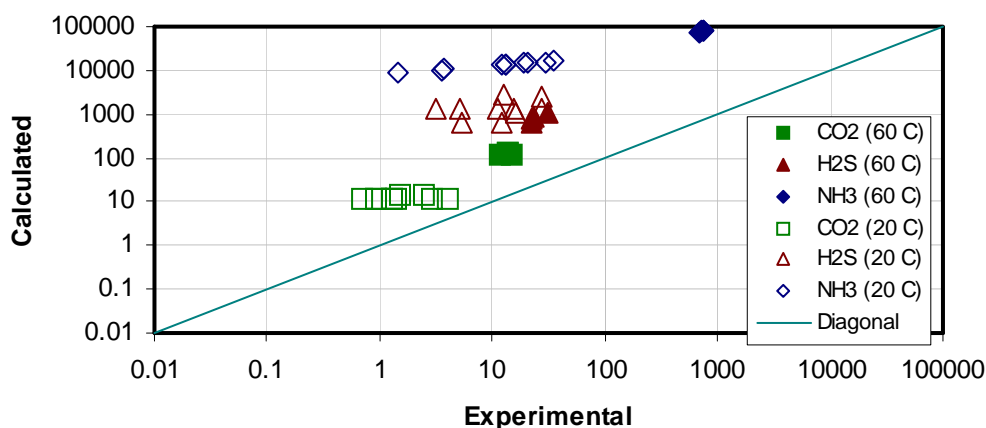


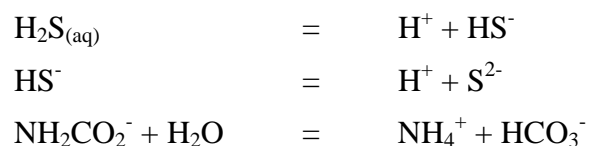
Figure 2-14 Parity plot of the partial pressures of gases without aqueous reactions

In Figure 2-14, 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 desired conditions other than the conditions in these series of calculations, then perhaps the corrections will over-correct.

Considering the full OLI Speciation Model

All of these equilibria are now considered in these new series of calculations:





Partial Pressure of Gases (Full OLI Model)

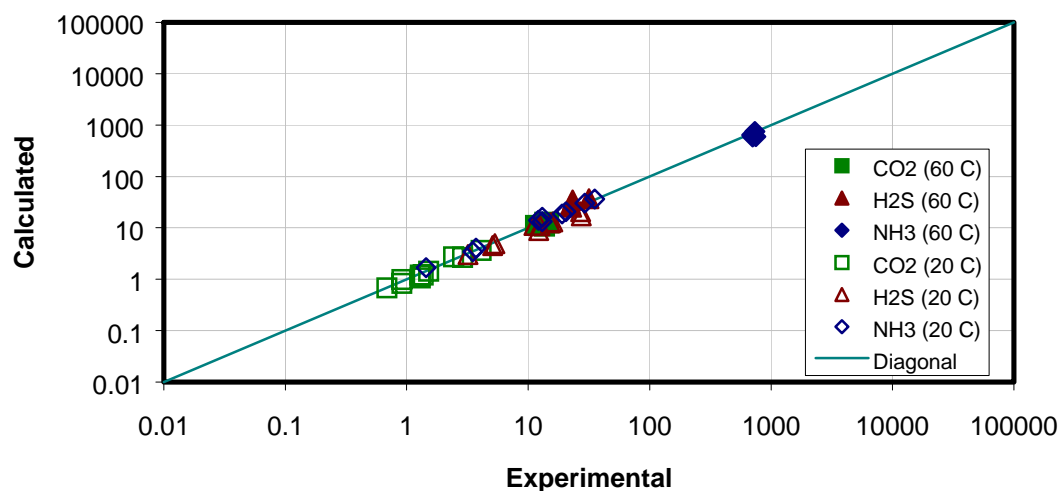


Figure 2-15 Parity plot of the partial pressures of gases with aqueous reactions

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 H₂O) hydrofluoric acid sample is to be titrated with calcium chloride (CaCl₂). What will the titration curve look like?

a)

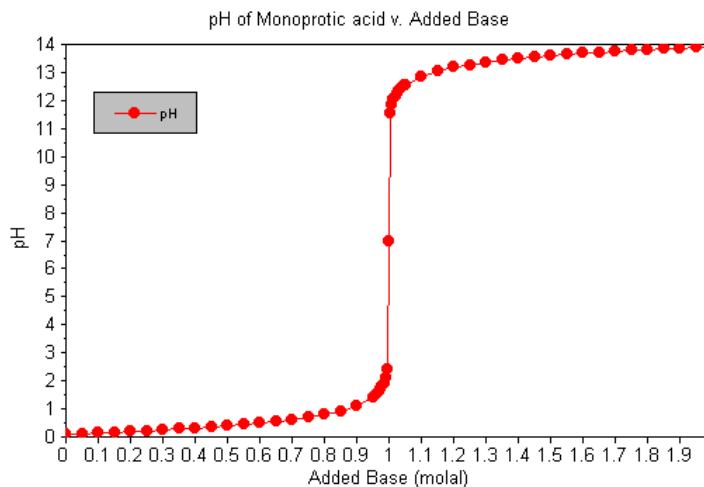


Figure 2-16 a mono protic acid titration curve

b)

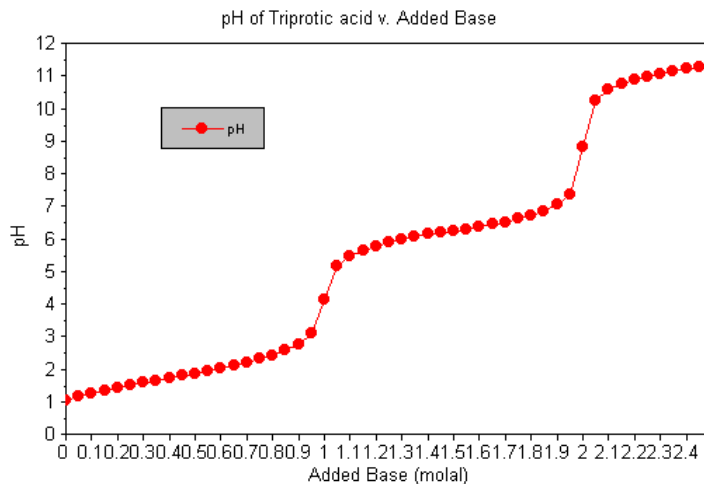


Figure 2-17 a triprotic acid titration curve

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 °C? Let’s use the OLI Studio to find out.

The Stream definition would be:

Temperature	=	30 °C
Pressure	=	1 Atmosphere
H2O	=	55.5082 moles
HF	=	0.1

The input should look like this:

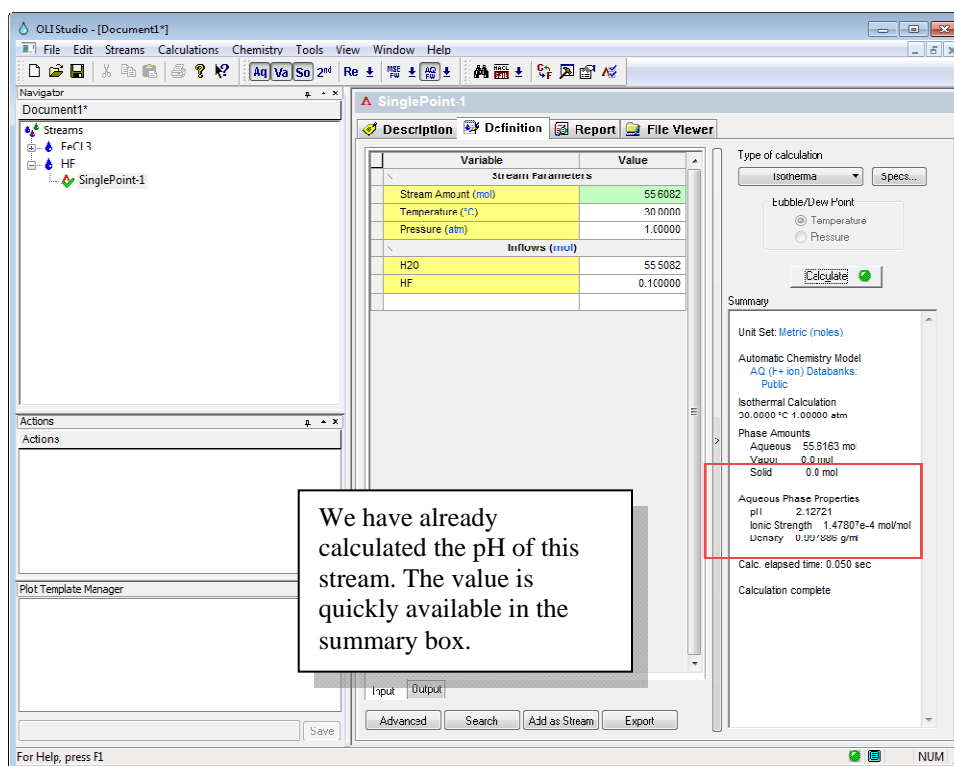


Figure 2-18 the pH of the HF stream

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 ₂ O	=	55.5082 moles
CaCl ₂	=	0.1

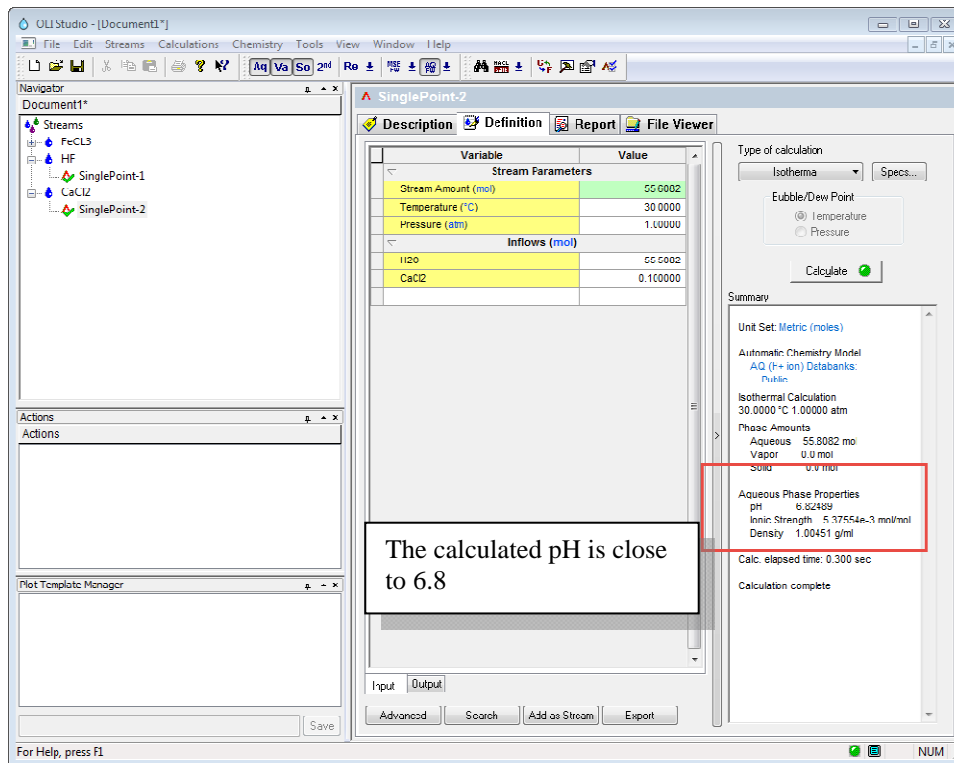


Figure 2-19 The pH of the Calcium chloride stream.

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.

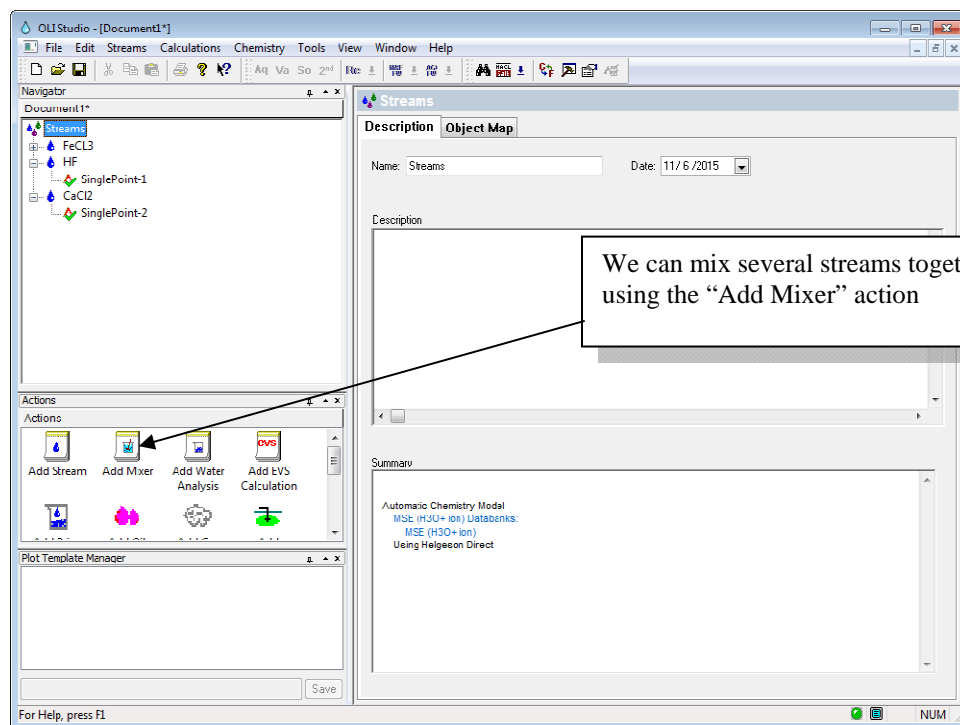


Figure 2-20 The main explorer window. Locating the Mix calculation.

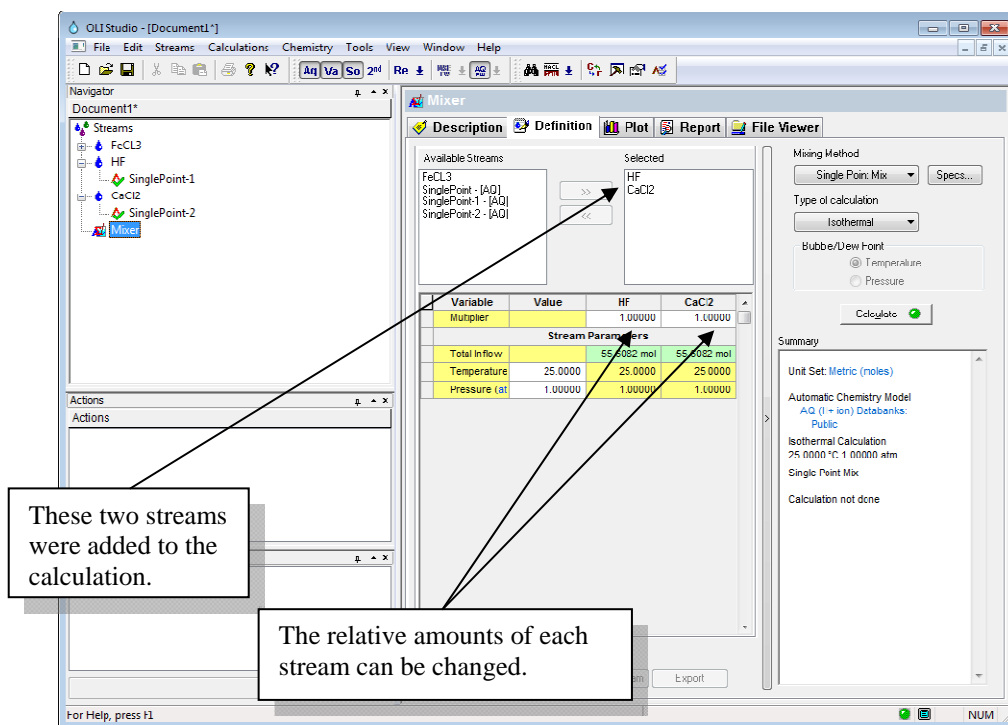


Figure 2-21 The completed mix calculation.

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

Stream Parameters

Row Filter Applied: Only Non Zero Values

Column Filter Applied: Only Non Zero Values

Mixture Properties

Stream Amount	111.216	mol
Temperature	25.0000	°C
Pressure	1.00000	atm

Aqueous Properties

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

Solid Properties

Standard Liquid Volume	1.30476e-3	L
------------------------	------------	---

The resultant pH is 1.44. How can this be? An acid stream (the HF stream had a pH of approximately 2.13) and a nominally basic stream (the CaCl₂ 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 CaCl₂.

OLI Studio - [Document1]

File Edit Streams Calculations Chemistry Tools View Window Help

Navigator
Document1
Streams
HCl
HF
SinglePoint-1
Survey
CaCl2
SinglePoint-2
Mixer

Survey

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

Survey by
Composition
Then by (optional)
None
Vary
☐ Independently
☐ Together
Calculate

Summary
Composition survey:
CaCl2
Range: 0.0 to 0.2 mol
Step size: 0.01 mol
No. steps: 20
No secondary survey selected
Unit Set: Metric (molca)
Automatic Chemistry Model
A/Q (H+ Ion) Databases:
Public
Isothermal Calculation
30.0000 °C 1.00000 atm
Calculation not done

Input
Advanced Search Add as Stream Export

For Help, press F1

NUM

We have switched back to the HF stream and added a survey. We also added the inflow of CaCl2

Figure 2-22 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.

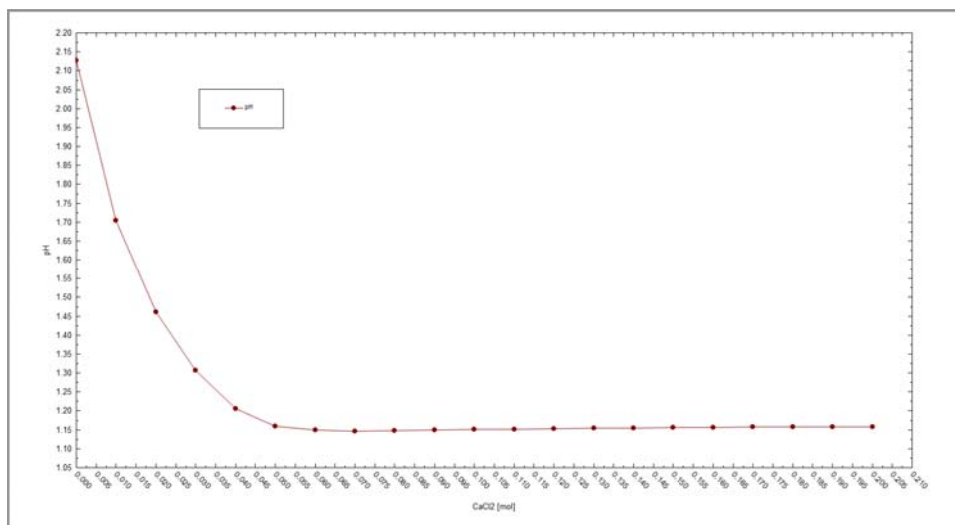


Figure 2-23 pH response to CaCl_2 titration

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, $\text{CaF}_{2(\text{cr})}$. This effectively removes fluoride ion from solution according to the following equation:

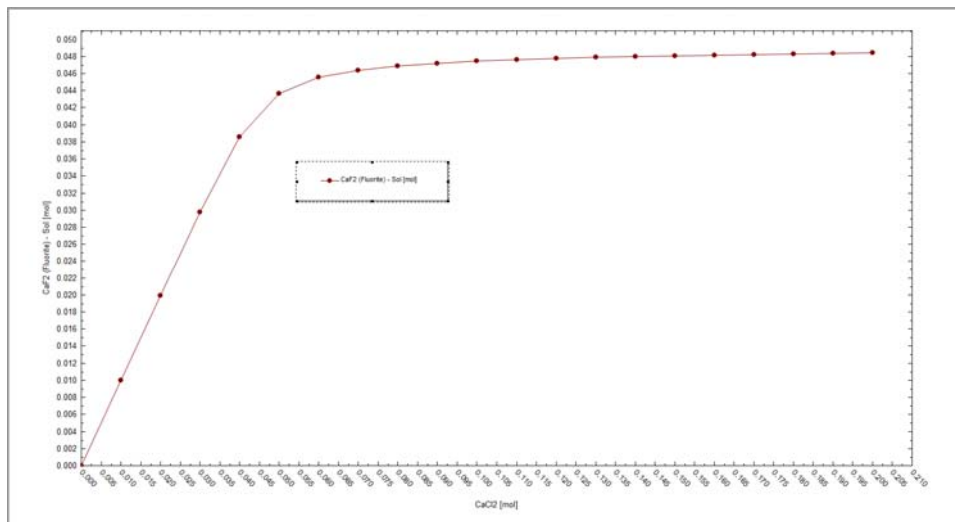
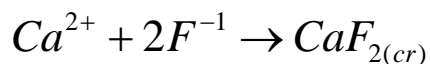


Figure 2-24 the formation of CaF_2

This shifts the following equilibrium to the right.

Is Hydrofluoric Acid a strong Acid?

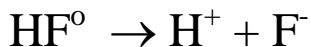
No, HF is a weak acid with a $pK_a = 3.45$.

Compare this to other weak acids:

Acetic Acid: $pK_a=4.75$

Citric Acid: $pK_{a1}=3.14$

HF is between these values.



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

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

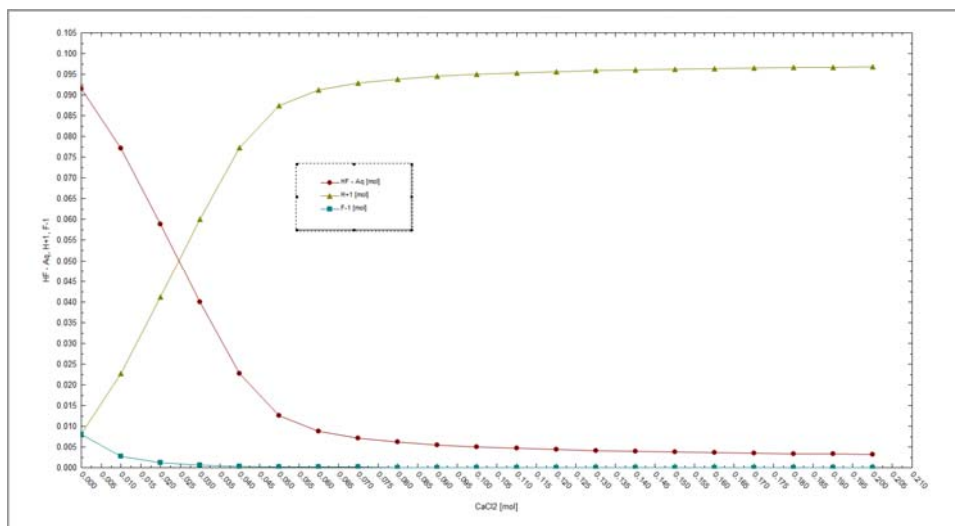


Figure 2-25 The dominant fluoride species in solution.

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.