11. Autoclaves[40]

Overview

An autoclave is a high pressure, high temperature hydrometallurgy unit with carefully controlled conditions. In this chapter, we will simulate an autoclave using two different approaches. Some use a manual approach where the *Mixer* pressure or gas inflows is adjusted manually to match final volume. Others use the Custom calculation where pressure and total volume are linked, and lastly, some applications use the automatic *Autoclave* Calculation in which the partial pressures are fixed and the inflow composition is computed.

Basic Autoclave #1 – Ideal Gas Law, Inert Gas

In this section, we will add 1 kg water to a 2L autoclave then fill the void with N_2. The conditions are ambient, 25C and 1 atm. The amount of N_2 added is a combination of the dissolved N_2 (N_2 aqueous) and N_2 vapor filling the 1L void. N_2 has a low solubility in water, so nearly all the N_2 will remain in the vapor phase. H_2O will also evaporate to its vapor pressure, so the entire void will not contain N_2 alone. Since we know all the input parameters, we can use the Ideal Gas Law to estimate the amount of N_2 needed:

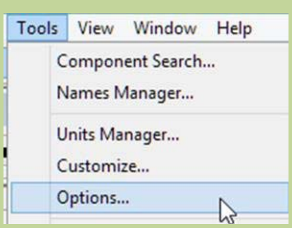
$$P * V = n * R * T$$

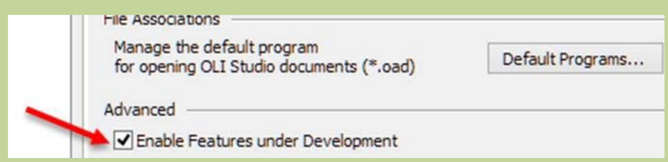
$$1\ atm * 1\ L = n * 0.082057\ \frac{L-atm}{K-mol} * 298.15\ K$$

$$n = 0.04087\ moles$$

Getting Started

Before adding a stream, some clients may have to enable the Autoclave feature. The steps below also require us to restart the software, so please save any open work.





- ✓ Press OK then Restart the software

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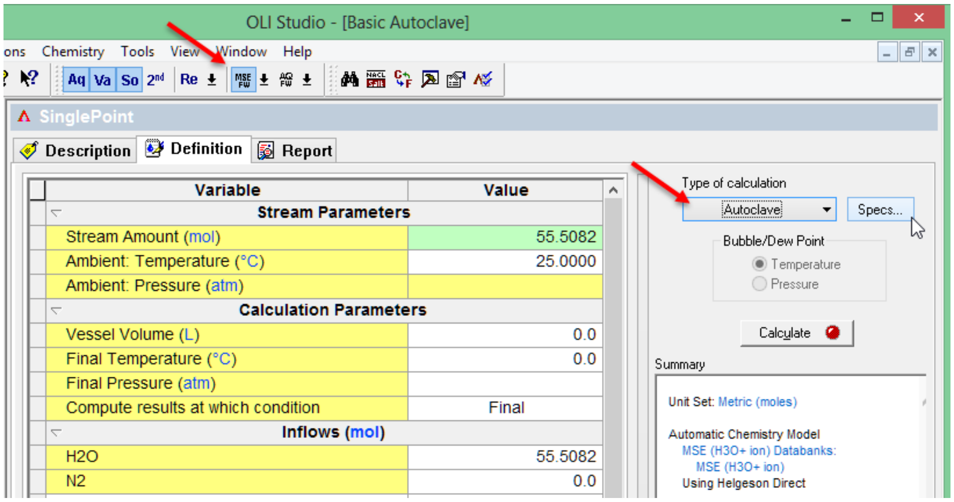
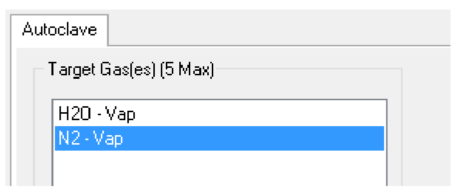
- ✓ Start a new file and give it a name such as ***Chapter 9 Autoclaves***
- ✓ Create a new stream and rename it ***Basic Autoclave – Inert Gas***
- ✓ Change the framework to MSE
- ✓ Make sure the units are set to Metric-Batch-Moles
- ✓ Add N2 as an inflow
- ✓ Add a Single Point Calculation then select Autoclave as the calculation type. Click the Specs button

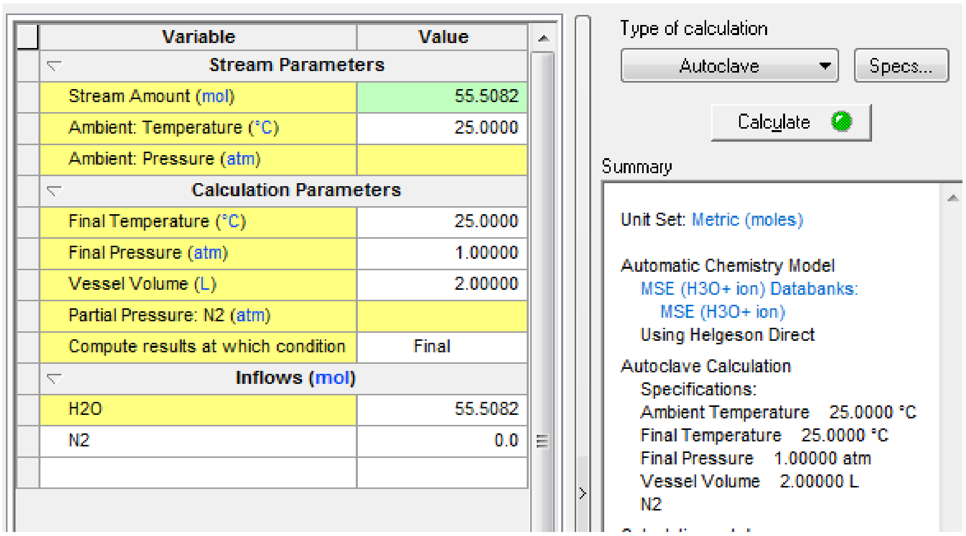


- ✓ Click the Specs button
- ✓ Highlight N2 in the gas field then press OK

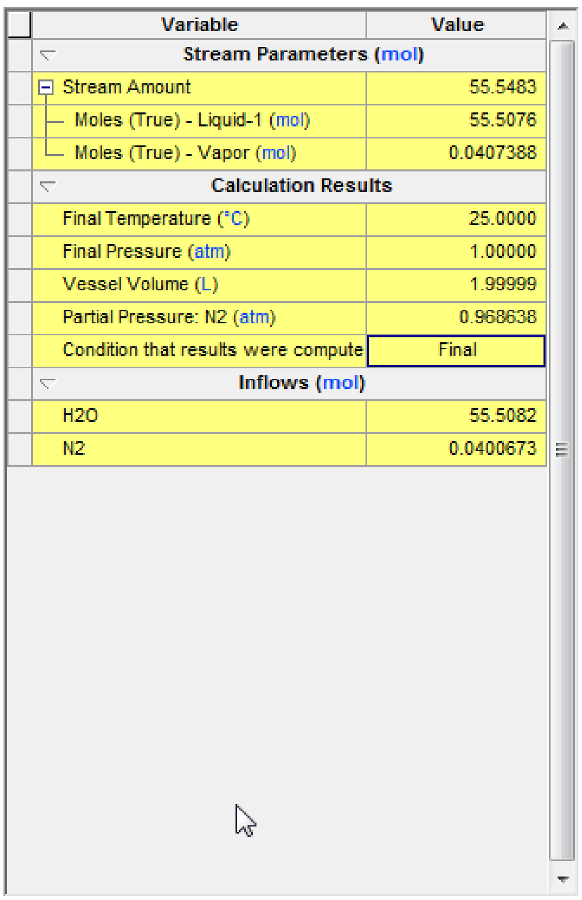


- ✓ Change the Vessel volume to 2L
- ✓ Change the final temperature to 25C and Final Pressure to 1 atm
- ✓ Confirm that the values in the grid match the information in the table below
- ✓

Basic Autoclave - Inert Gas Setup							
Setup		Stream Parameters		Calculation Parameters		Inflows (mol)	
Stream Name	Basic Autoclave – Inert Gas	Stream Amt	Calculated	Vessel Vol	2 L	H2O	55.508
Unit Set	Metric-Batch-Moles	Ambient T	25 C	Final T	25 C	N2	0
Unit Customize	none	Ambient P	calculated	Final P	1 atm		
Names Style	Formula			Gas : N2			
Framework	MSE (H3O+)						



- ✓ Change the Compute results at which condition to Final
- ✓ Calculate



- ✓
- ✓ Click on the Output tab at the bottom of the grid

The computed N_2 inflow is 0.04007 moles. This compares to the Ideal Gas value of 0.0409 moles, a 2% deviation.

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor
	mol	mol	mol
H2O	55.5082	55.507	1.27766e-3
N2	0.0400673	6.0619e-4	0.0394612
H3O+1	1.00624e-7	1.00624e-7	0.0
OH-1	1.00624e-7	1.00624e-7	0.0
Total (by phase)	55.5483	55.5076	0.0407388

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

The software computes 0.03946 moles of N_2 in vapor. This is now 3.4% lower than the ideal gas value. When we include H_2O, the total gas amount ($N_2 + H_2O$) is 0.04074 moles, a 0.3% difference. Thus, a rigorous calculation (including fugacity) is consistent with a simple ideal gas calculation when computing total gas amount of an unreactive, low soluble gas.

Setting the Vessel volume to 5L and 20L

The OLI Software computes gas properties and composition using an Enhanced Suave-Redlich-Kwong (SRK) cubic equation of state. The SRK equation for one mole gas looks like the following:

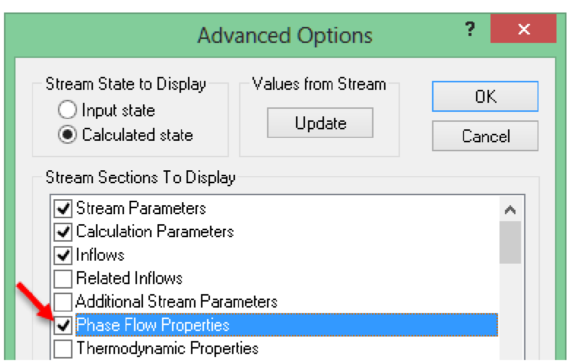
$$P = \frac{RT}{V-b} - \frac{a}{V(V+)}$$

When ‘a’ and ‘b’ are set to zero, SRK equation collapses to the Ideal Gas equation.

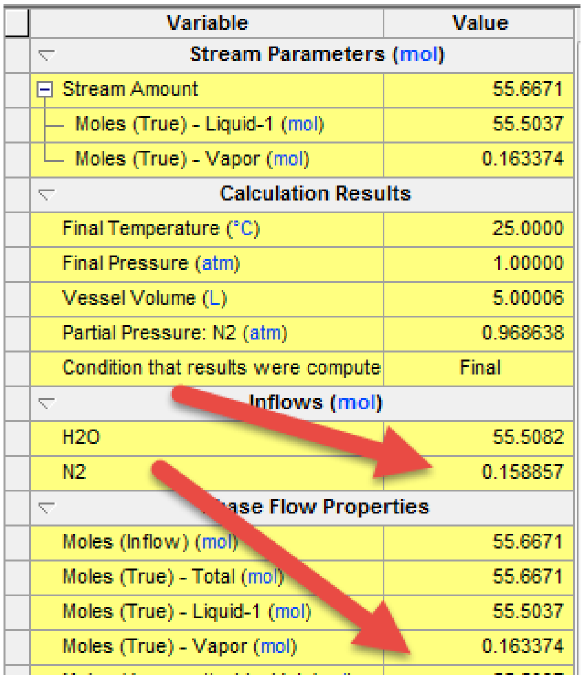
We will run the same calculation, except now the vessel volume will be five liters, that is, four liters of vapor. The ideal gas equation will predict: $4\ L * 0.04087\ {}^{moles}/_{L} = 0.1634\ moles$ of gas.

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

- ✓ Select the Definition tab then change the Vessel volume to 5 L then Calculate
- ✓ Click on the Output tab at the bottom of the grid
- ✓ Click on the Advanced button below the grid and check the Phase Flow Properties box



- ✓ Press OK



Variable	Value
Stream Parameters (mol)	
Stream Amount	55.6671
Moles (True) - Liquid-1 (mol)	55.5037
Moles (True) - Vapor (mol)	0.163374
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	5.00006
Partial Pressure: N2 (atm)	0.968638
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	0.158857
Phase Flow Properties	
Moles (Inflow) (mol)	55.6671
Moles (True) - Total (mol)	55.6671
Moles (True) - Liquid-1 (mol)	55.5037
Moles (True) - Vapor (mol)	0.163374

✓

✓ Review the N2 input and total Gas moles values

The calculated value is 0.1589 moles about 2.9% lower than predicted using Ideal Gas Law. The total gas amount is 0.1633 moles, nearly identical to the gas amount computed using Ideal Gas Law.

✓ Click the Input tab at the bottom of grid

✓ Change the Vessel Volume to 20L

✓ Calculate

✓ Click the Output tab and view N2 inflow and Moles Vapor

The N_2 inflow is 0.7527 moles and total vapor is 0.7766 moles. The Ideal Gas Law predicts:

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

The result from the equation matches the calculated result. Therefore, it appears that the Ideal Gas Law, will work at ambient conditions as well as when the vapor phase volume is much larger than the liquid phase volume

Variable	Value
Stream Parameters (mol)	
Stream Amount	56.2610
Moles (True) - Liquid-1 (mol)	55.4845
Moles (True) - Vapor (mol)	0.776528
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	1.00000
Vessel Volume (L)	19.9998
Partial Pressure: N2 (atm)	0.968638
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	0.752781
Phase Flow Properties	
Moles (Inflow) (mol)	56.2610
Moles (True) - Total (mol)	56.2610
Moles (True) - Liquid-1 (mol)	55.4845
Moles (True) - Vapor (mol)	0.776528
Moles (Apparent) - Liquid-1 (mol)	55.4845

Testing a higher pressure

The software computes that the Ideal Gas Law works well at ambient conditions. It also works when the gas phase is larger than the water phase. The next test is to see how it works at elevated conditions.

- ✓ Click the Input tab at the bottom of the grid
- ✓ Change the Final Pressure to 50 atm then Calculate

Variable	Value
Stream Parameters (mol)	
Stream Amount	94.1439
Moles (True) - Liquid-1 (mol)	55.5108
Moles (True) - Vapor (mol)	38.6331
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	50.0000
Vessel Volume (L)	19.9998
Partial Pressure: N2 (atm)	49.9654
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	38.6356
Phase Flow Properties	
Moles (Inflow) (mol)	94.1439
Moles (True) - Total (mol)	94.1439
Moles (True) - Liquid-1 (mol)	55.5108
Moles (True) - Vapor (mol)	38.6331

- ✓
- ✓ Click on the Output tab and view the results
- ✓ Calculate the gas amount using the Ideal Gas Law

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

The ideal gas value is 38.83 moles compared to 38.66 moles computed by the software. The deviation is small, 0.4%.

✓ Select the Input tab, change the Final Pressure to 200 atm, recalculate, then select Output

Variable	Value
Stream Parameters (mol)	
Stream Amount	199.269
Moles (True) - Liquid-1 (mol)	55.5720
Moles (True) - Vapor (mol)	143.697
Calculation Results	
Final Temperature (°C)	25.0000
Final Pressure (atm)	200.000
Vessel Volume (L)	19.9998
Partial Pressure: N2 (atm)	199.956
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	143.761
Phase Flow Properties	
Moles (Inflow) (mol)	199.269
Moles (True) - Total (mol)	199.269
Moles (True) - Liquid-1 (mol)	55.5720
Moles (True) - Vapor (mol)	143.697

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

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

Testing at High Temperature

Next, we will test the Ideal Gas Law against the Enhanced-SRK at higher temperatures.

✓ Select the Input tab then set the Final Temperature to 100C and calculate

✓ View the results in the lower Output tab

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

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

Variable	Value
Stream Parameters (mol)	
Stream Amount	167.051
Moles (True) - Liquid-1 (mol)	54.6927
Moles (True) - Vapor (mol)	112.358
Calculation Results	
Final Temperature (°C)	100.000
Final Pressure (atm)	200.000
Vessel Volume (L)	19.9998
Partial Pressure: N2 (atm)	198.415
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	111.543
Phase Flow Properties	
Moles (Inflow) (mol)	167.051
Moles (True) - Total (mol)	167.051
Moles (True) - Liquid-1 (mol)	54.6927
Moles (True) - Vapor (mol)	112.358

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

- ✓ Recalculate at 200C and compare the two equation of states

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

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

With enhanced SRK, the software computes 91.64 moles. Note also, that the Software computes a 19.02 L vapor volume.

Variable	Value
Stream Parameters (mol)	
Stream Amount	137.024
Moles (True) - Liquid-1 (mol)	45.5787
Moles (True) - Vapor (mol)	91.4450
Calculation Results	
Final Temperature (°C)	200.000
Final Pressure (atm)	200.000
Vessel Volume (L)	19.9998
Partial Pressure: N2 (atm)	178.011
Condition that results were compute	Final
Inflows (mol)	
H2O	55.5082
N2	81.5155
Phase Flow Properties	
Moles (Inflow) (mol)	137.024
Moles (True) - Total (mol)	137.024
Moles (True) - Liquid-1 (mol)	45.5787
Moles (True) - Vapor (mol)	91.4450
Moles (Apparent) - Liquid-1 (mol)	45.5787

Normalizing the moles to 19 L results in a value of 91.45 moles. This is 8% lower than the Ideal Gas predictions.

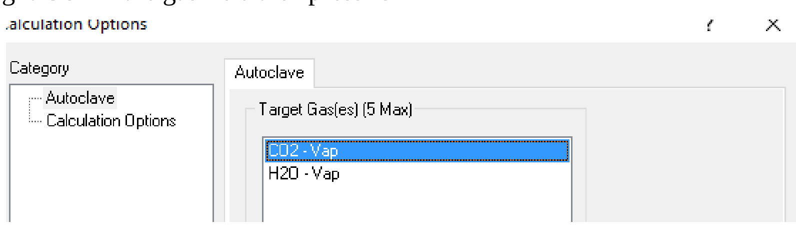
Basic Autoclave #2 – Ideal Gas Law, Reactive Gas

We will modify the approach taken in previous example by using a reactive gas, CO_2, to fill the headspace. In addition, you will modify the chemistry by adding NaOH to the water so that CO_2 reacts to form bicarbonate, changing the amount of CO_2 that is needed to fill the headspace. We will use the same Ideal Gas Law calculations amount of CO_2 needed, if the assumption was that no CO_2 dissolved or reacted.

T	P	Vol	Ideal Gas Law	Calculated (total)	Calculated (vapor)	%Diff (vapor)
C	atm	L	Moles of inert gas mixed with 1L H2O			
25	1	1	0.041	0.040	0.039	3.4%
25	1	5	0.163	0.159	0.158	3.1%
25	1	20	0.78	0.75	0.75	3.1%
25	50	20	38.83	38.64	38.61	0.6%
25	200	20	255.32	143.76	143.67	43.7%

Getting Started

- ✓ Create a new stream and rename it ***Basic Autoclave – Reactive Gas***
- ✓ Change the framework to MSE
- ✓ Make sure the units are set to Metric-Batch-Moles
- ✓ Add CO_2 and NaOH to the inflow list
- ✓ Add a Single Point Calculation then select Autoclave as the calculation type
- ✓ Click the Specs button
- ✓ Highlight CO_2 in the gas field then press OK

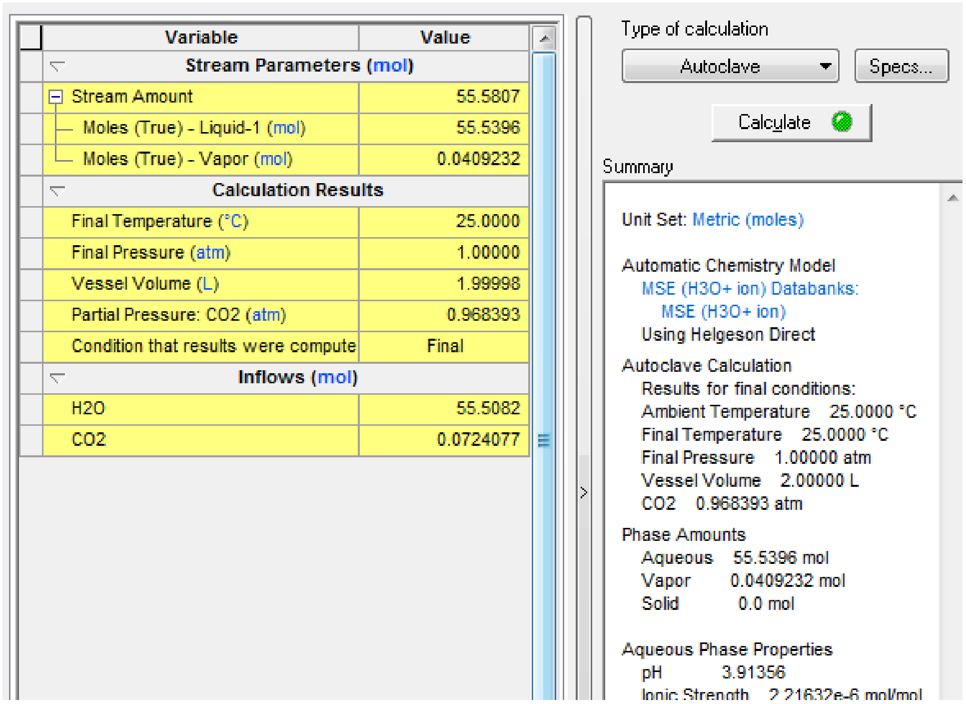


- ✓ Change the Vessel volume to 2L
- ✓ Change the final temperature to 25C and Final Pressure to 1 atm
- ✓ Confirm that the values in the grid match the information in the table below

Basic Autoclave Setup							
Setup		Stream Parameters		Calculation Parameters		Inflows (mol)	
Stream Name	Basic Autoclave – Reactive Gas	Stream Amt	Calculated	Vessel Vol	2 L	H2O	55.508
Unit Set	Metric-Batch-Moles	Ambient T	25 C	Final T	25 C	N2	0
Unit Customize	none	Ambient P	calculated	Final P	1 atm	NaOH	
Names Style	Formula			Gas : CO2			
Framework	MSE (H3O+)						

- ✓

✓ Calculate



✓

✓ Click on the Output tab at the bottom of the grid

The computed CO_2 inflow is 0.0724 moles. This compares to the Ideal Gas value of 0.0409 moles, a 2% deviation.

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

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

column Filter Applied: Only Non Zero Values

	Total	Aqueous	Vapor
	mol	mol	mol
H2O	55.508	55.5067	1.29227e-3
OH-1	8.41456e-11	8.41456e-11	0.0
H3O+1	1.23094e-4	1.23094e-4	0.0
CO2	0.0722526	0.0326206	0.039632
CO3-2	4.9102e-11	4.9102e-11	0.0
HCO3-1	1.23093e-4	1.23093e-4	0.0
Total (by phase)	55.5805	55.5396	0.0409242

The software computes 0.0396 moles of CO_2 in vapor, consistent with the ideal gas value. The difference is that about 45% of the CO_2 added dissolved in water.

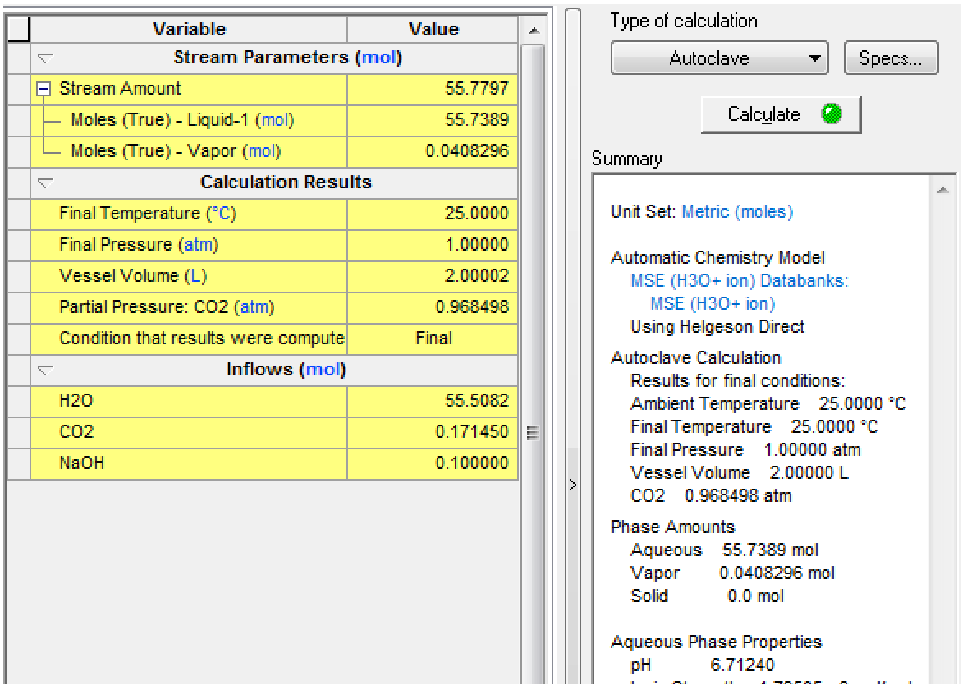
T	P	Vol	Ideal Gas Law	Calculated (total)	Calculated (vapor)	Calculated (total)	Calculated (vapor)
C	atm	L	Moles of N2 mixed with 1L H2O			Moles of CO2 mixed with 1L H2O	
25	1	1	0.041	0.040	0.039	0.073	0.040

Testing with 0.1m NaOH

You will repeat the study with NaOH added to the water. NaOH reacts with CO_2 to form HCO_3^{-1} and CO^{-} 3

[2], increasing overall CO_2 solubility.

- ✓ Click on the Input tab
- ✓ Add 0.1 moles NaOH to the input grid



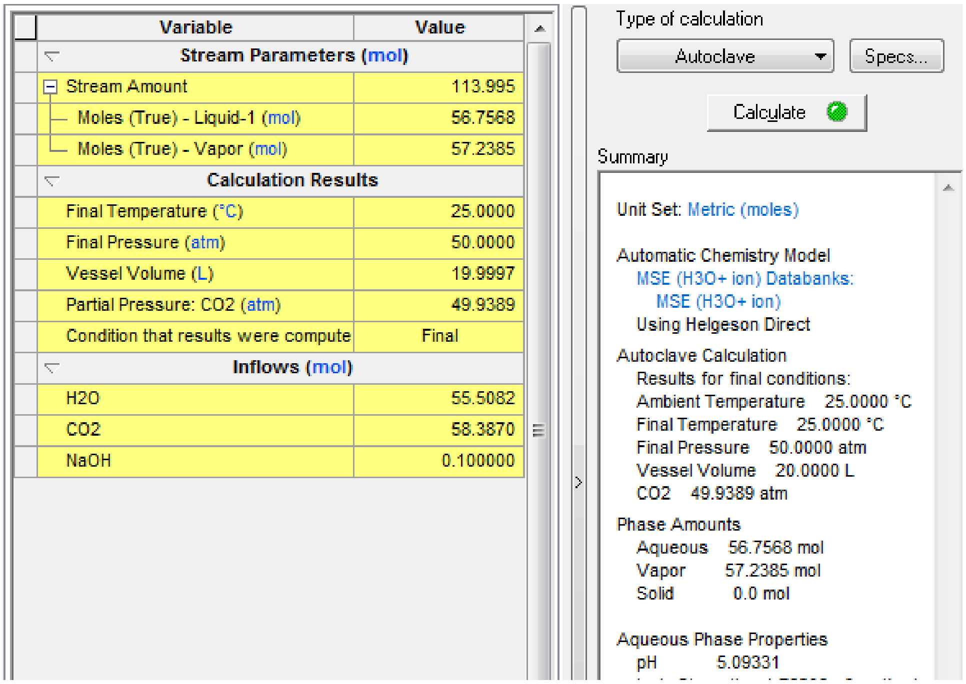
- ✓
- ✓ Calculate

The CO_2 inflow is approximately 0.1 moles greater than calculation without the NaOH, which is consistent with the CO_2 absorption and reaction by a base.

Testing a higher pressure

You will repeat the solubility calculations at 50atm.

- ✓ Click the Input tab at the bottom of the grid
- ✓ Change the Vessel volume to 20 L
- ✓ Change the Final Pressure to 50 atm
- ✓ Calculate



- ✓ Click on the Output tab and view the results

The ideal gas value is 38.83 moles compared to 58.3 moles computed by the software.

- ✓ Click on the Report and view the Species Output

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

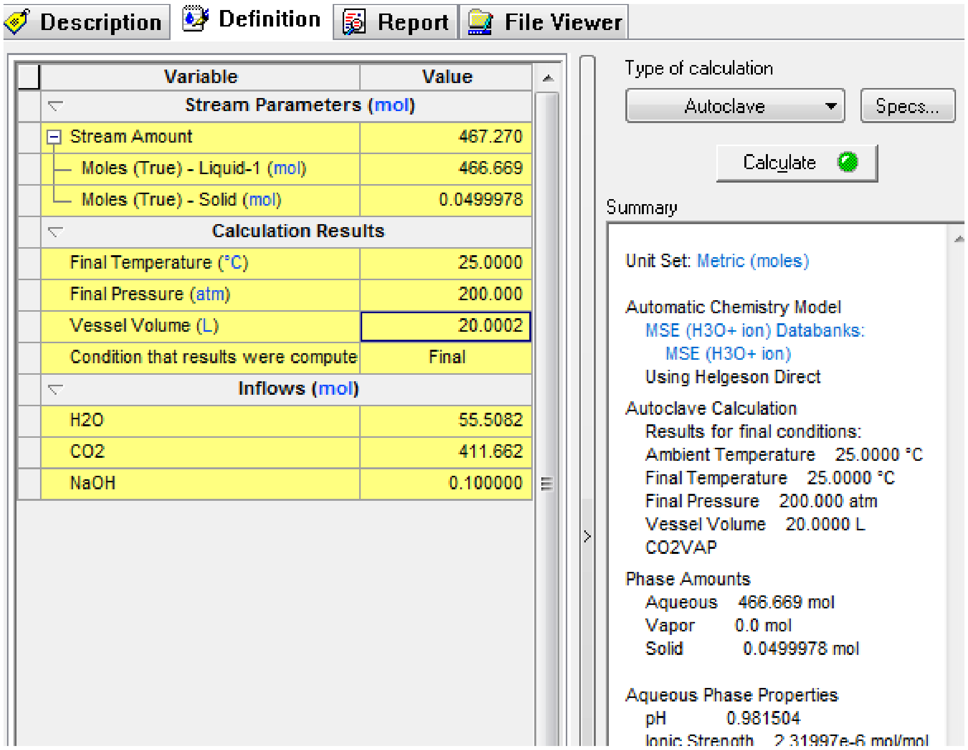
column Filter Applied: Only Non Zero Values

	Total	Liquid-1	Vapor
	mol	mol	mol
CO2	58.287	1.1185	57.1685
H2O	55.5082	55.4382	0.0699887
HCO3-1	0.100006	0.100006	0.0
Na+1	0.1	0.1	0.0
H3O+1	8.74885e-6	8.74885e-6	0.0
CO3-2	1.37355e-6	1.37355e-6	0.0
OH-1	1.85647e-9	1.85647e-9	0.0
NaOH	1.2057e-16	1.2057e-16	0.0
NaOHCO3-2	2.33697e-17	2.33697e-17	0.0
Total (by phase)	113.995	56.7568	57.2385

The vapor amount is 57.2 moles, compared to ~39 for ideal gas and with N_2. The primary difference is the CO2 fugacity.

T	P	Vol	Ideal Gas Law	Calculated (total)	Calculated (vapor)	Calculated (total)	Calculated (vapor)
C	atm	L	Moles of N2 mixed with 1L H2O			Moles of CO2 mixed with 1L H2O	
25	50	20	38.83	38.64	38.61	58.3	57.2

- ✓ Change the Final Pressure to 200 atm.
- ✓ Recalculate



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	Aqueous
	mol	mol
Mole (True)	467.250	467.250
Mole (App)	467.251	467.251
	g	g
Mass	19120.8	19120.8
	L	L
Volume	20.0002	20.0002

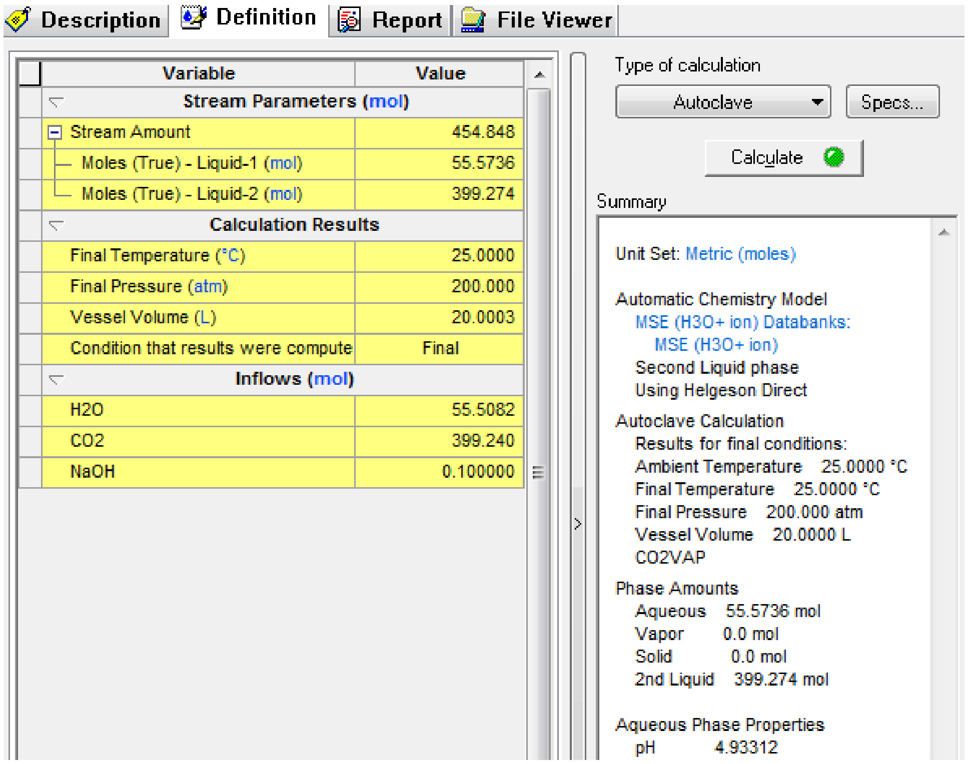
Thermodynamic Properties

	Unit	Total	Aqueous
Density	g/ml	0.956029	0.956029
Enthalpy	cal	-4.40425e7	-4.40425e7

According to the calculation, the stream is monophasic and the liquid density is 0.95. The software either computed the wrong results, or the system is monophasic under these conditions.

There is a setting that is off by default, the 2nd liquid phase. Normally a 2nd liquid is organic, but in this case it will be a supercritical CO2 phase. The software computed the wrong results, because this button is not on by default. OLI does not provide an automatic adjustment for this.

- ✓ Click on the 2nd button in the ribbon ad then calculate.



When the 2nd liquid phase is selected, the software compute a large 2nd liquid phase, and the CO_2 amount is slightly lower, 399 moles.

✓ Click on the Report tab and review the Total and Phase Flows table.

Total and Phase Flows (Amounts)

column Filter Applied: Only Non Zero Values

	Total	Aqueous	2nd Liquid
	mol	mol	mol
Mole (True)	454.704	55.4912	399.213
Mole (App)	454.705	55.4920	399.213
	g	g	g
Mass	18568.6	1036.46	17532.2
	L	L	L
Volume	20.0002	1.01801	18.9822

The calculated phases are 1.01 liters of water and 19 liters of critical CO_2. The Autoclave filled the void space (~19 liters) with sufficient critical CO_2 to match the specified vessel volume.

Click here for the final worked examples from this chapter: Chapter 11 - Autoclaves