

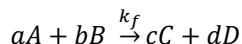
12. Reaction Kinetics

Overview

In this chapter we discuss reaction kinetics. Most of the chemistry in OLI Studio/Analyzer assumes equilibrium. This means the forward and reverse reactions are considered to be very fast. OLI considers two types of reaction kinetics; 1-Arrhenius and 2-User defined. This chapter will consider both type.

Arrhenius type reaction kinetics

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



Where:

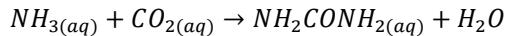
$$k_f = A_f e^{\frac{-E_a}{RT}}$$

| | | |
|-------|---|------------------------|
| k_f | = | Forward rate constant |
| A_f | = | Pre-exponential factor |
| E_a | = | Energy of Activation |
| R | = | Gas constant |
| T | = | Temperature |

The user is required to supply these values. OLI does not maintain a database of these parameters.

Reaction of Ammonia and Carbon Dioxide

For our example, we are going to consider the reaction of ammonia and carbon dioxide to form urea and water. We will also be using the AQ thermodynamic framework. Here is our reaction:



There is a forward and reverse reaction (k_f and k_r) which we will have to define. We start by using OLI Studio and then entering the following components:

Table 2 Urea reaction kinetics inflow species

| Standard Reaction Kinetics | | |
|----------------------------|-----------------------------------|--------------|
| Thermodynamic Framework | Aqueous (H+ Ion) | A |
| Additional Databanks | None | |
| Phases | Default | |
| Inflows | Formula | OLI Tag Name |
| Water | H ₂ O | H2O |
| Carbon Dioxide | CO ₂ | CO2 |
| Ammonia | NH ₃ | NH3 |
| Urea | NH ₂ CONH ₂ | UREA |

Here is the OLI Studio/Analyzer input screen.

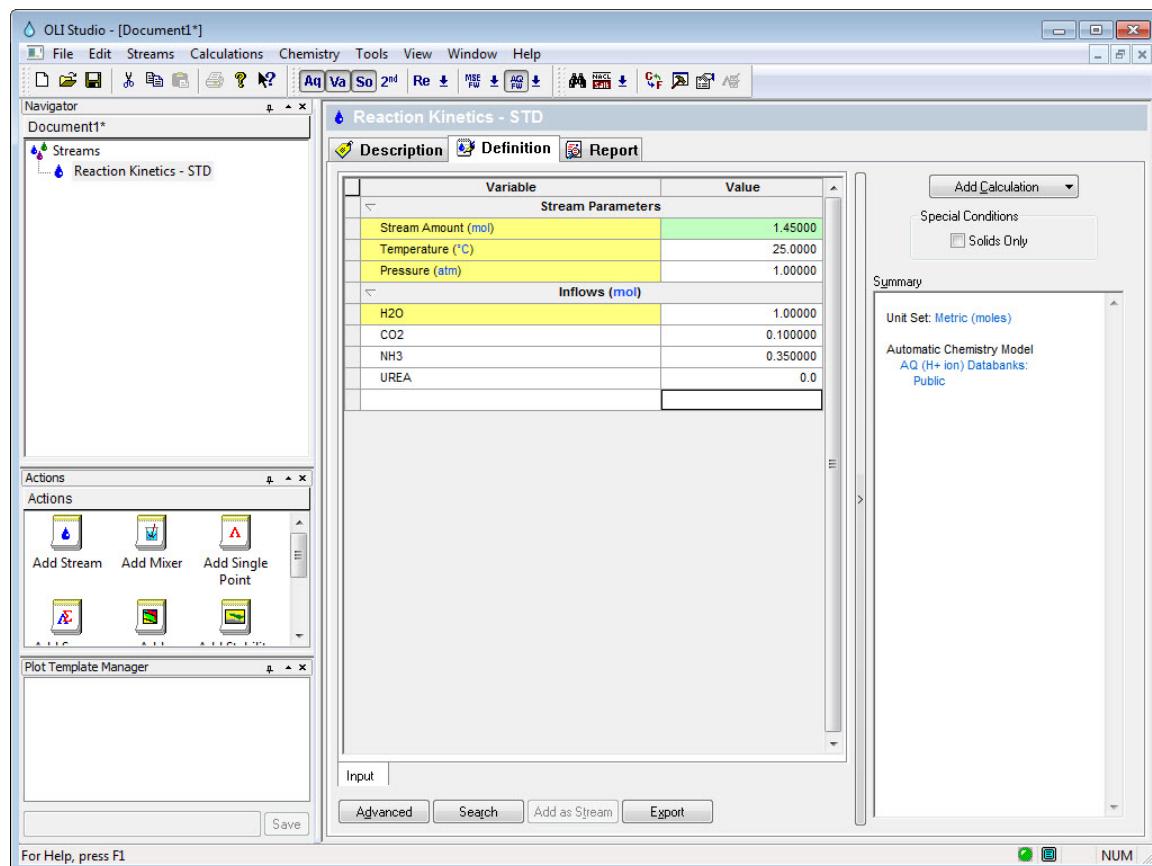


Figure 12-1 Input conditions

We now need to enable reaction kinetics. Click the Chemistry menu item, then Model Options and finally select the Phases tab.

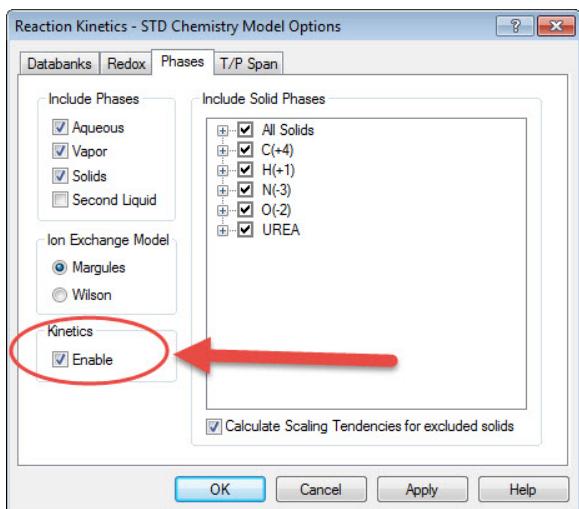


Figure 12-2 Check the indicated box

Check the Kinetics/Enable box to turn on reaction kinetics.

We add the actual reaction kinetics in the calculation. For our example, add an isothermal single point calculation.

We will the reaction kinetics via the Specs... button.

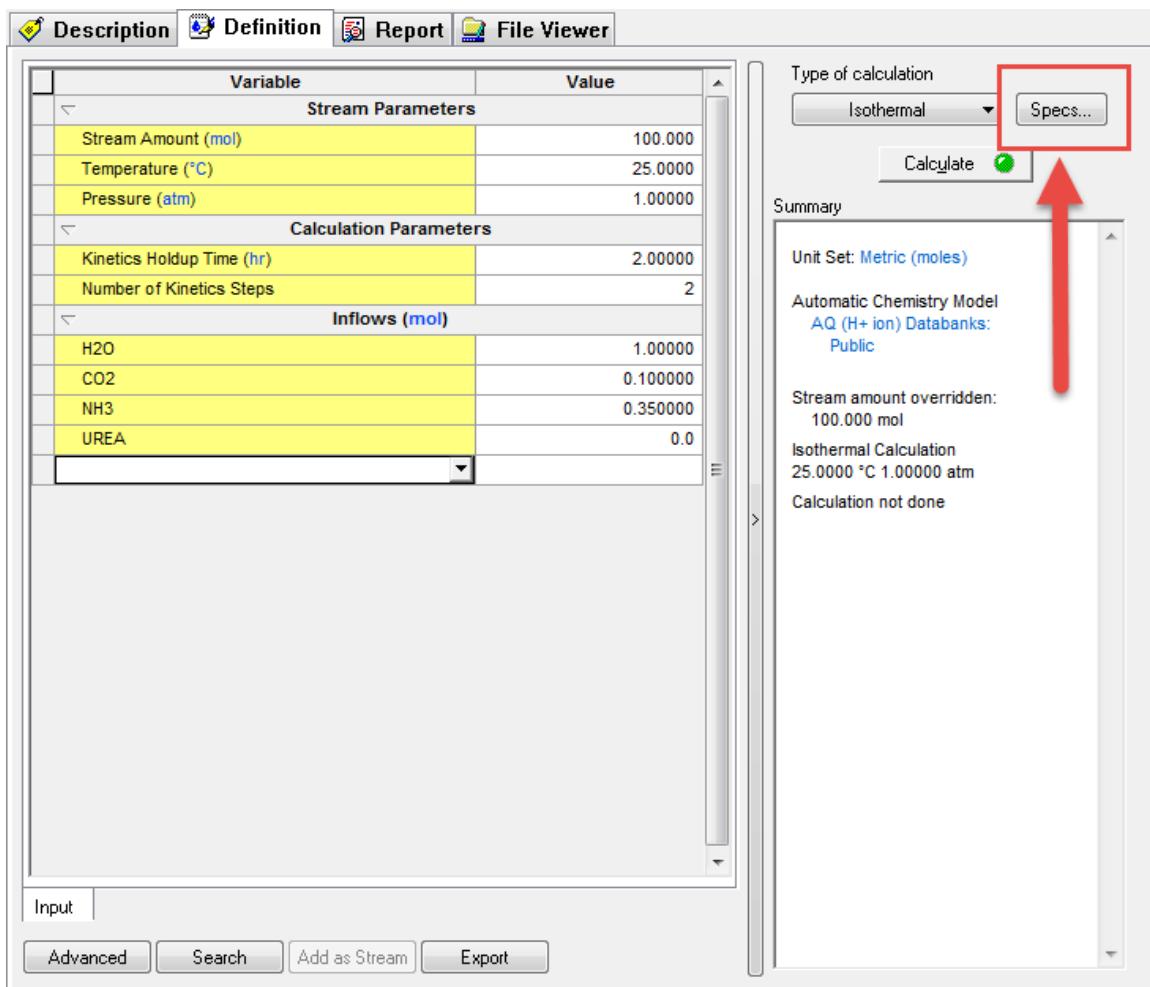


Figure 12-3 Click the specs... button

Click the Specs... button.

This will display options for this calculation.

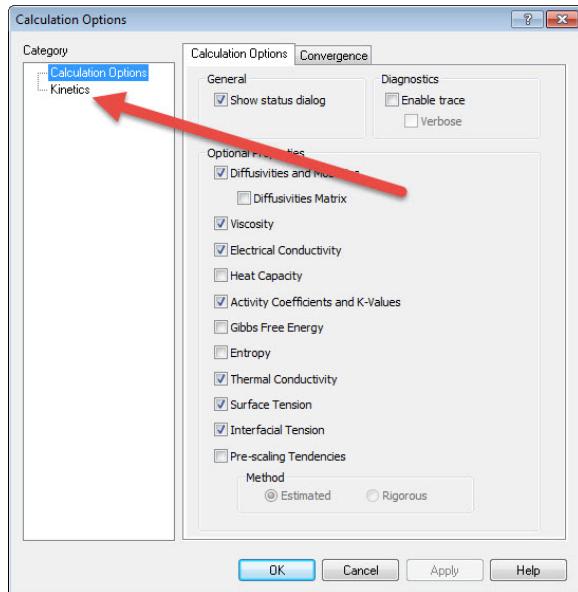


Figure 12-4 Calculation options

Click the category that says Kinetics.

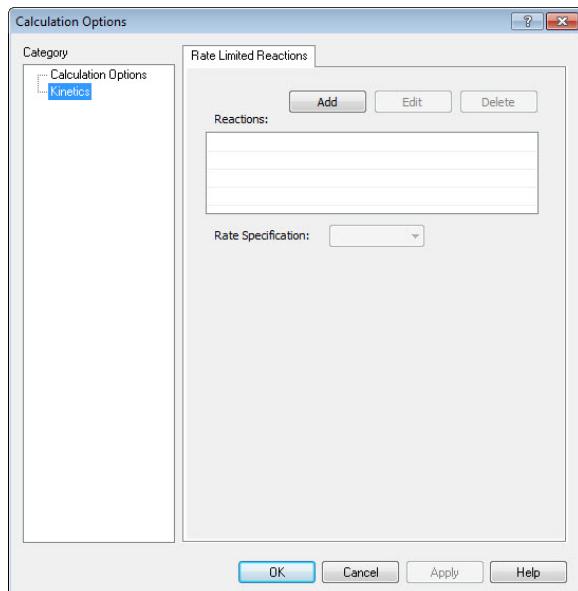


Figure 12-5 Kinetics Dialog

Click the Add button to start adding our reaction kinetics.

You will be given a list of reactions which are already in the chemistry model. These can be replaced if you require it. For our example, the reaction we need is not in the list:

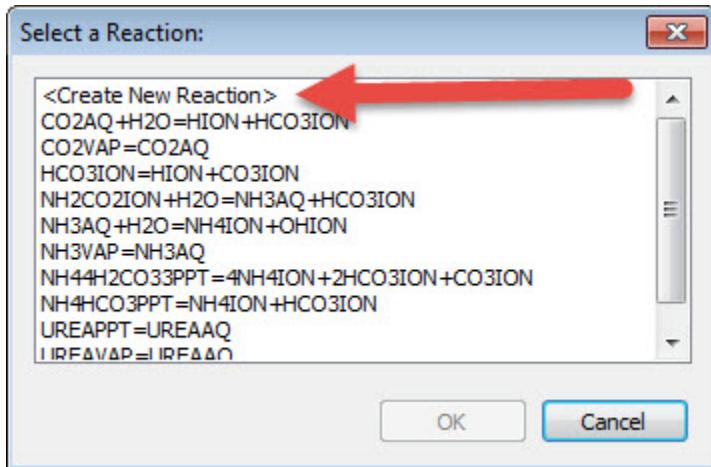


Figure 12-6 List of reactions

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

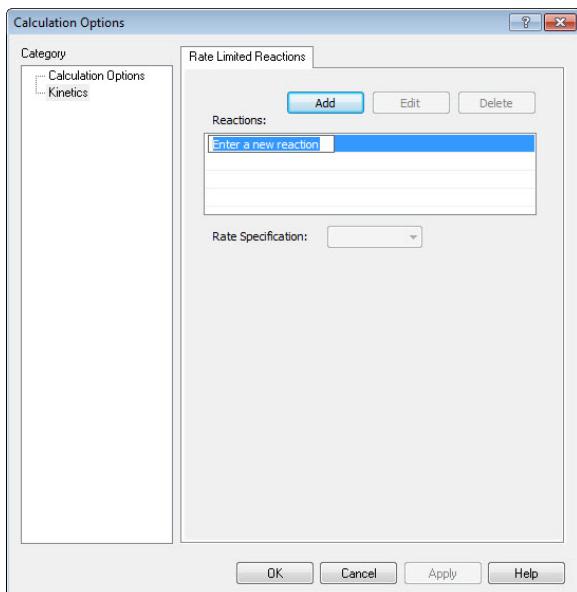
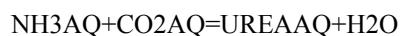


Figure 12-7 Adding a new reaction

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



When you press the enter key the dialog will update:

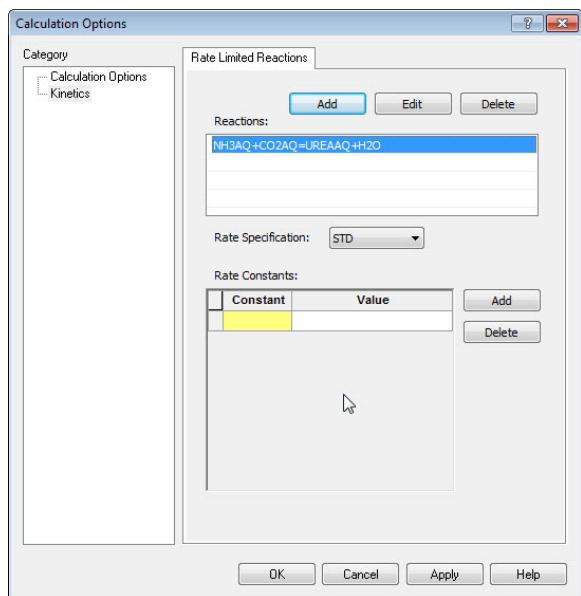


Figure 12-8 Added ammonia reaction

There are two types of Rate Specification. For this example, we are using the standard or **STD** type. Leave the button **Rate Specification** as *STD*.

We can now add our rate constant parameters.

The first comment we need to make is that we have combined some of the terms in the standard Arrhenius equation. The gas constant and the energy of activation are constant, so OLI had decided to make them another constant.⁴¹

$$B = \frac{E_a}{R}$$

The forward and reverse reactions have the same format. The mechanism of the rate is the following:

$$\text{Rate} = k_f [NH_3]^2 [CO_2] - k_r [NH_2CONH_2]$$

The forward rate constant is fixed in value, but the reverse is:

$$k_r = A_r e^{\frac{-B_r}{T}} = 1.2 \times 10^{-6} e^{\frac{3480.78}{T}}$$

Here are the parameters⁴²

⁴¹ The reason for this is lost to antiquity. Rather than upset the developers we have kept the format the same as when Marshall Rafal wrote the original program.

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

Table 3 Reaction Rate Parameters

| Parameters | Value | Comment |
|------------|----------------------|---|
| k_f | 20 | forward rate constant |
| k_r | calculated | See above |
| A_r | 1.2×10^{-6} | |
| B_r | 3480.78 | Determined from $B_r = -(-28939.9 / 8.3142)$ |
| EP1 | 1 | This is the exponent of product 1 in the mechanism. In this case $[NH_2CONH_2]$ |
| EP2 | 0 | H ₂ O does not partake in the reaction |
| ER1 | 2 | This is the exponent of reactant 1 $[NH_3]^2$ |
| ER2 | 1 | This is the exponent of reactant 2 $[CO_2]$ |

The values of EP and ER are based on the added reaction in Figure 12-8 on page 215 above.

Now that we have the parameters we can add them. Click the Add button in Figure 12-8

Rate Limited Reactions

| | | | |
|--|------------------------------------|-------------------------------------|---------------------------------------|
| | <input type="button" value="Add"/> | <input type="button" value="Edit"/> | <input type="button" value="Delete"/> |
|--|------------------------------------|-------------------------------------|---------------------------------------|

Reactions:

Rate Specification:

Rate Constants:

| Constant | Value |
|----------|-------|
| | |

Figure 12-9 Select a parameter

Select KF

Rate Constants:

| | Constant | Value |
|--|----------|-------|
| | KF | |

Add Delete

Figure 12-10 Selecting kf

Enter the value from the Table 3 Reaction Rate Parameters above:

Rate Constants:

| | Constant | Value |
|--|----------|-------|
| | KF | 20 |

Add Delete

Figure 12-11 Entered kf

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

Click **OK** when done.

You will see that the input grid has changed accommodate time parameters:

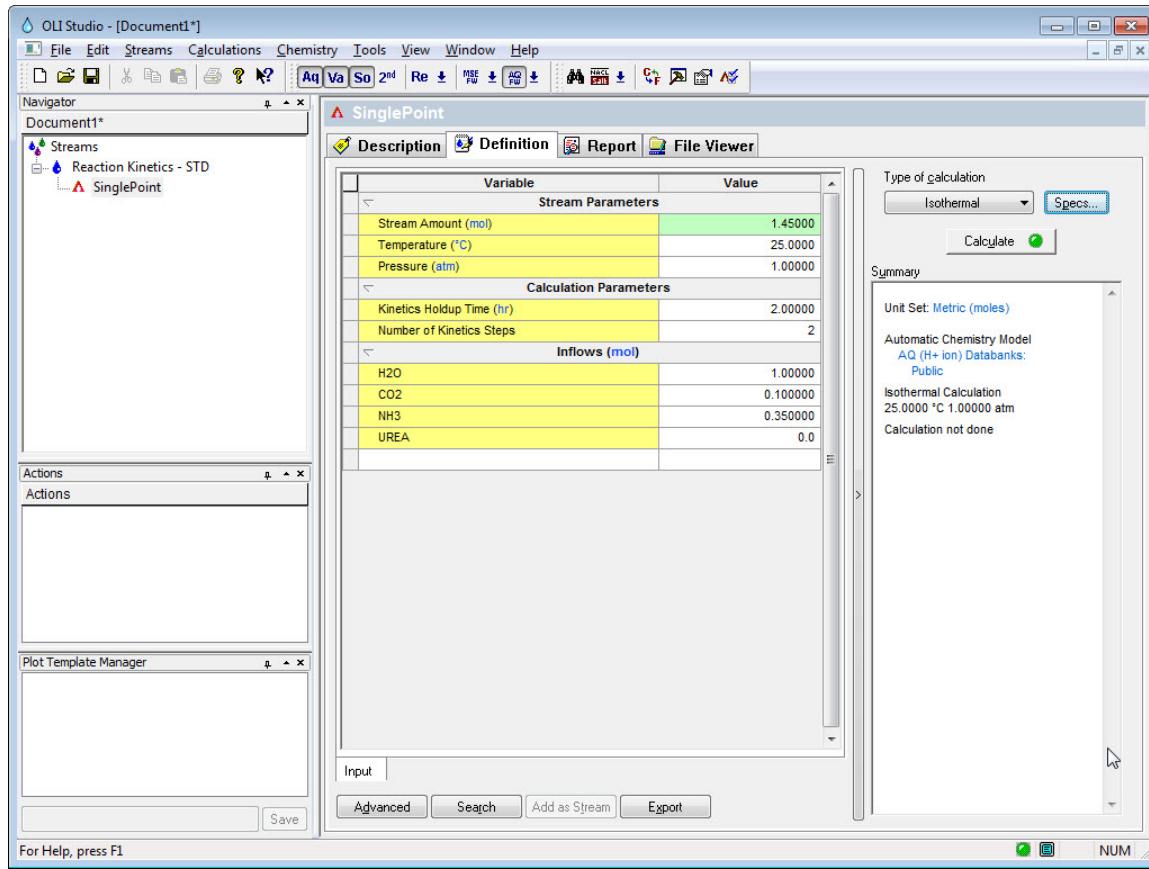


Figure 12-12 Updated time parameters

This example is simulating a chemical reactor with a residence time of 100 hours. We call this in OLI Studio/Analyzer Kinetics Holdup Time. We are also going to simulate this as a plug-flow reactor and divide the simulation into 10 stages (or plugs). Finally, we will increase the temperature to 35 °C.

| Variable | Value |
|-------------------------------|----------|
| Stream Parameters | |
| Stream Amount (mol) | 1.45000 |
| Temperature (°C) | 35.0000 |
| Pressure (atm) | 1.00000 |
| Calculation Parameters | |
| Kinetics Holdup Time (hr) | 100.000 |
| Number of Kinetics Steps | 10 |
| Inflows (mol) | |
| H2O | 1.00000 |
| CO2 | 0.100000 |
| NH3 | 0.350000 |
| UREA | 0.0 |

Figure 12-13 Input conditions are filled out.

OLI recommends that you save the file at this time!

Click the **Calculate** button.

When the program calculation is complete click on the **Output** mini-tab and then add a section for Molecular Apparent – Aqueous.

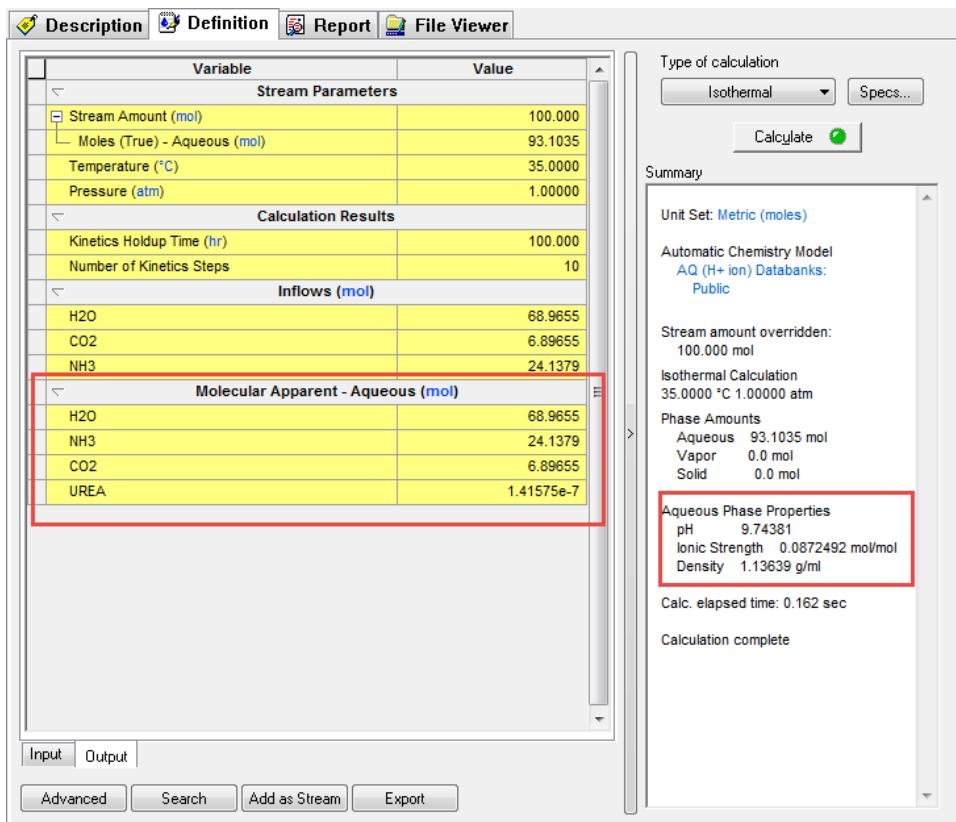


Figure 12-14 The results

So, it seems we have created some urea. Not much but some. The user is left to make changes to the holdup time and/or steps to see if the results change.

You can find this worked example file on our wiki page at:

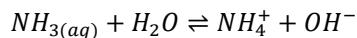
http://wiki.olisystems.com/wiki/OLI_Studio_Stream_Analyzer_User_Guide_v9.5

Non-standard SPEC type reaction kinetics

These reactions do not necessarily follow Arrhenius kinetics or require a more complicated mechanism than can be represented by the standard OLI implementation of reaction kinetics.

Ammonia Hydrolysis

In this example we are using simpler chemistry. The hydrolysis reaction we are using is the following:



For this example, we know the forward rate constant but need to constrain the reverse reaction to the thermodynamic equilibrium constant. This implies that we are going to replace an existing equation.

We are going to start off by creating a stream with the following parameters:

| Non-standard Reaction Kinetics | | | |
|--------------------------------|------------------|--------------|------------------|
| Thermodynamic Framework | | | Aqueous (H+ ion) |
| Additional databanks | | | None |
| Temperature | | | 25 °C |
| Pressure | | | 1.0 atm |
| Stream Value | | | automatic |
| Inflows | Formula | OLI Tag Name | Value |
| Water | H ₂ O | H2O | 55.5087 mol |
| Ammonia | NH ₃ | NH3 | 0.1 mol |

The stream should look like this:

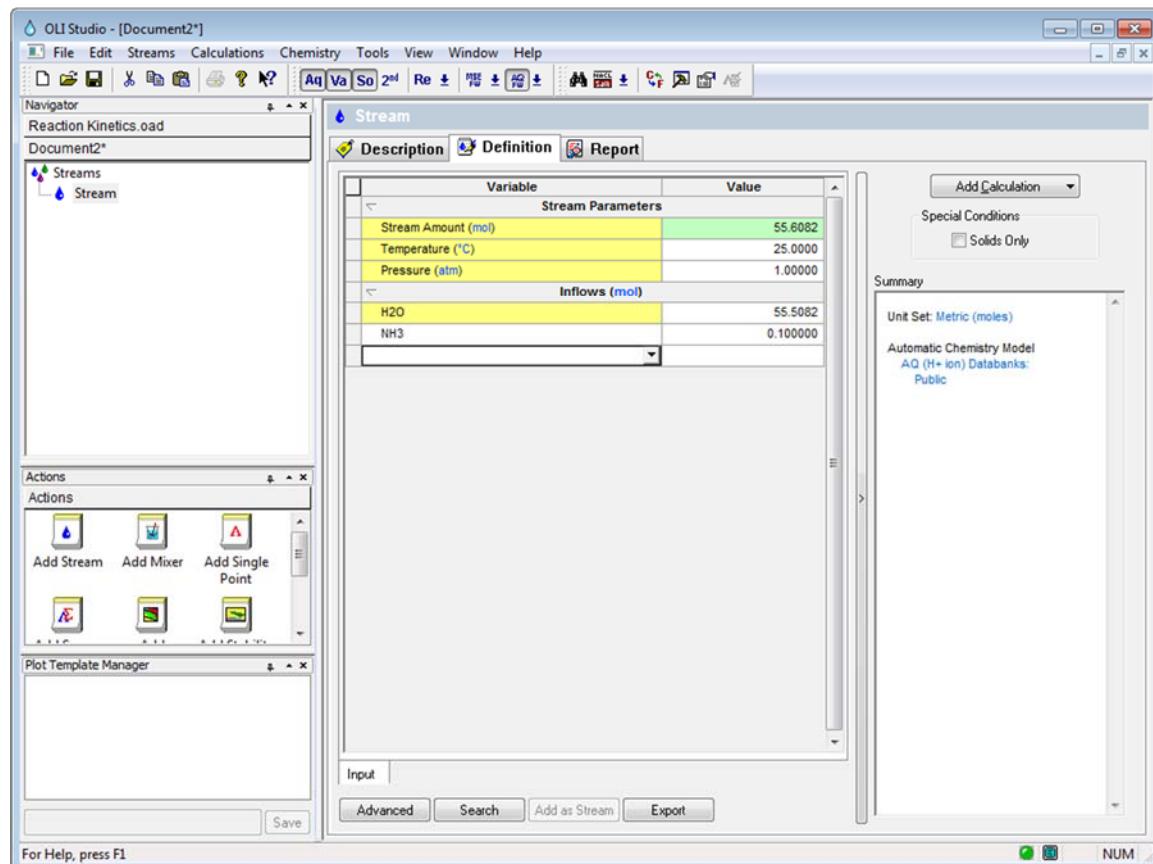


Figure 12-15 Non-standard kinetics stream

As with the previous example, we need to first enable kinetics via the **Chemistry | Model Options | Phases** menu items.

Review the steps illustrated in Figure 12-1 and Figure 12-2 on page 211.

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

As before we start with the **Specs...** button and then the **Kinetics** category.

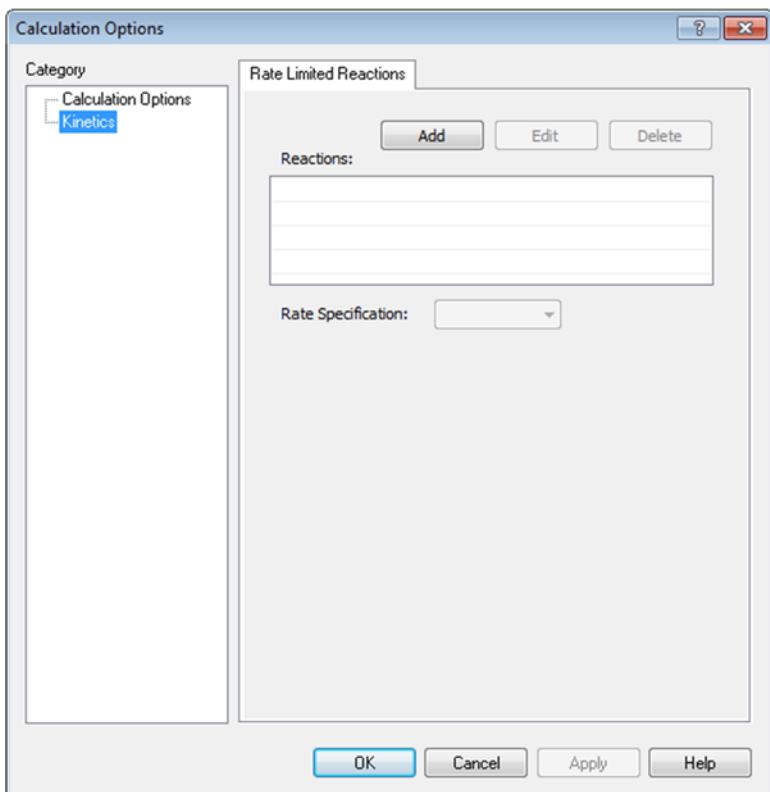


Figure 12-16 Adding a new reaction kinetics equation

Click the **Add** button

Once again we will see a list of equation in the OLI Tag Name format;

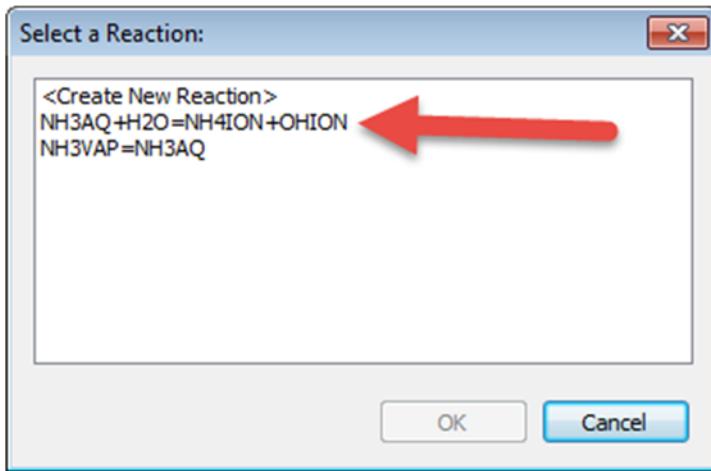


Figure 12-17 Possible reactions

In this case our desired reaction is the second one. Click it and then click the **OK** button.

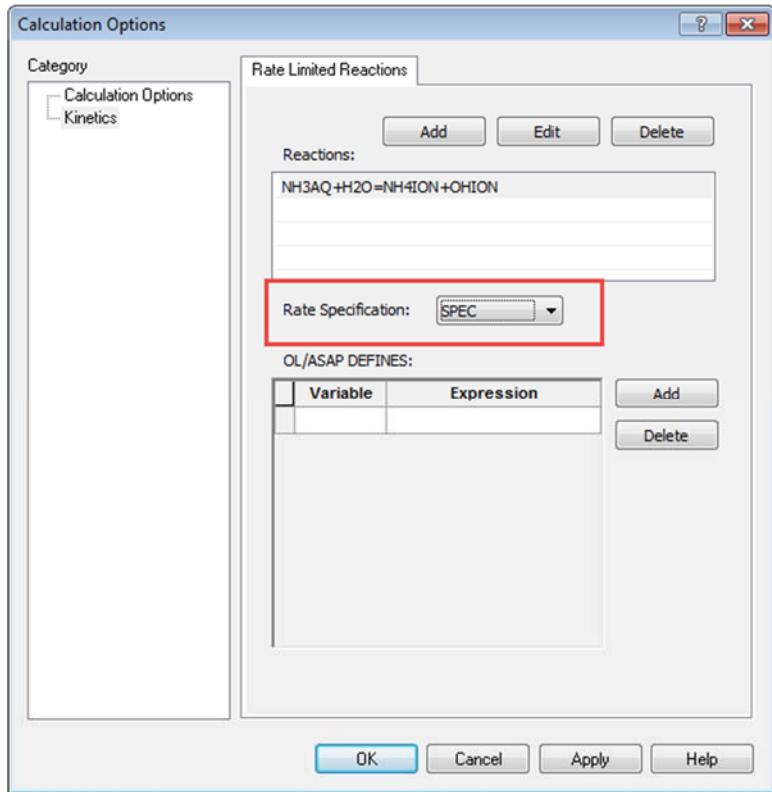


Figure 12-18 Clicking the SPEC type reaction.

These is where things get difficult. You now need to speak “OLI”. We have some rules for SPEC type equations. First we will show you the rate equations were using:

$$\text{Rate}_{\text{forward}} = k_f \gamma_{\text{NH}_3(\text{aq})} [\text{NH}_3(\text{aq})] \gamma_{\text{H}_2\text{O}} [\text{H}_2\text{O}]$$

$$\text{Rate}_{\text{reverse}} = k_r \gamma_{\text{NH}_4^+} [\text{NH}_4^+] \gamma_{\text{OH}^-} [\text{OH}^-]$$

$$k_f = 3$$

$$k_r = \frac{k_f}{K_{eq}}$$

$$\text{rate} = (k_f e^{\text{Rate}_{\text{forward}}} - k_r e^{\text{Rate}_{\text{reverse}}}) \frac{\text{Volume}}{1000}$$

We now need to turn these values into “OLI” terms⁴³.

We can define any variable we want. We have some variables that you will need to use. Any concentration variable such as $[\text{NH}_3\text{aq}]$ is defined as the natural log and is designated with the letter “L”. So $[\text{NH}_3\text{aq}]$ is used as $\text{Log}_e[\text{NH}_3\text{aq}] = \text{LNH3AQ}$,

Similarly, activity coefficients (γ) are also taken as the natural log so γ_{OH^-} is used as $\text{Log}_e \gamma_{\text{OH}^-} = \text{AOHION}$.

KEQ is the thermodynamic equilibrium constant for the equation. AH2O is special in the Aqueous thermodynamic framework in that it is the variable $\text{Log}_e(a_{\text{H}_2\text{O}})$.

⁴³ Commonly referred to as ASAP variables.

We now need to add these variable to the kinetics window:

```
FXRATE=LNH3AQ+ANH3AQ+LH2O+AH2O  
RXRATE=LNH4ION+ANH4ION+LOHION+AOHION  
KF1=3  
KR1=KF1/KEQ  
RATE1=(KF1*EXP(FXRATE)-KR1*EXP(RXRATE))*VOLLIQ/1000.
```

Start with the first line and keep going, in the variable field add FXRATE and in the expression, add the rest.

OL/ASAP DEFINES:

| | Variable | Expression |
|--|----------|-----------------------|
| | FXRATE | t3AQ+ANH3AQ+LH2O+AH2O |

Add **Delete**

Figure 12-19 Adding variables

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

Complete the remainder of the variables.

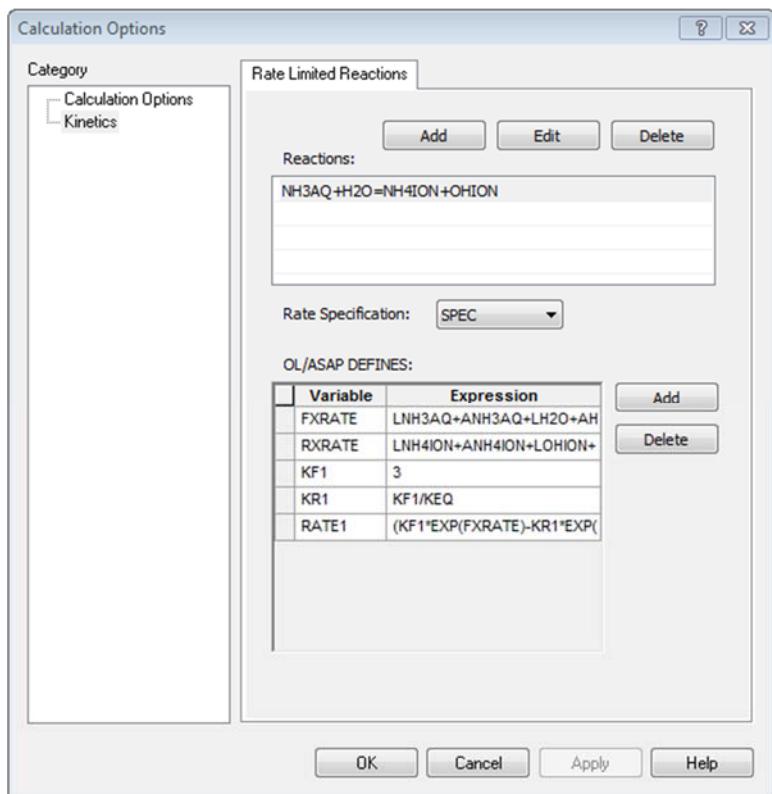


Figure 12-20 The completed equations

The variable VOLLIQ is the volume of the liquid phase in Liters. OLI requires the rate to be in mol/m³ we need to divide by 1000.

Click the **OK** button.

Like the previous example, this is a plug-flow reactor with a holdup time of 100 hours and 10 steps.

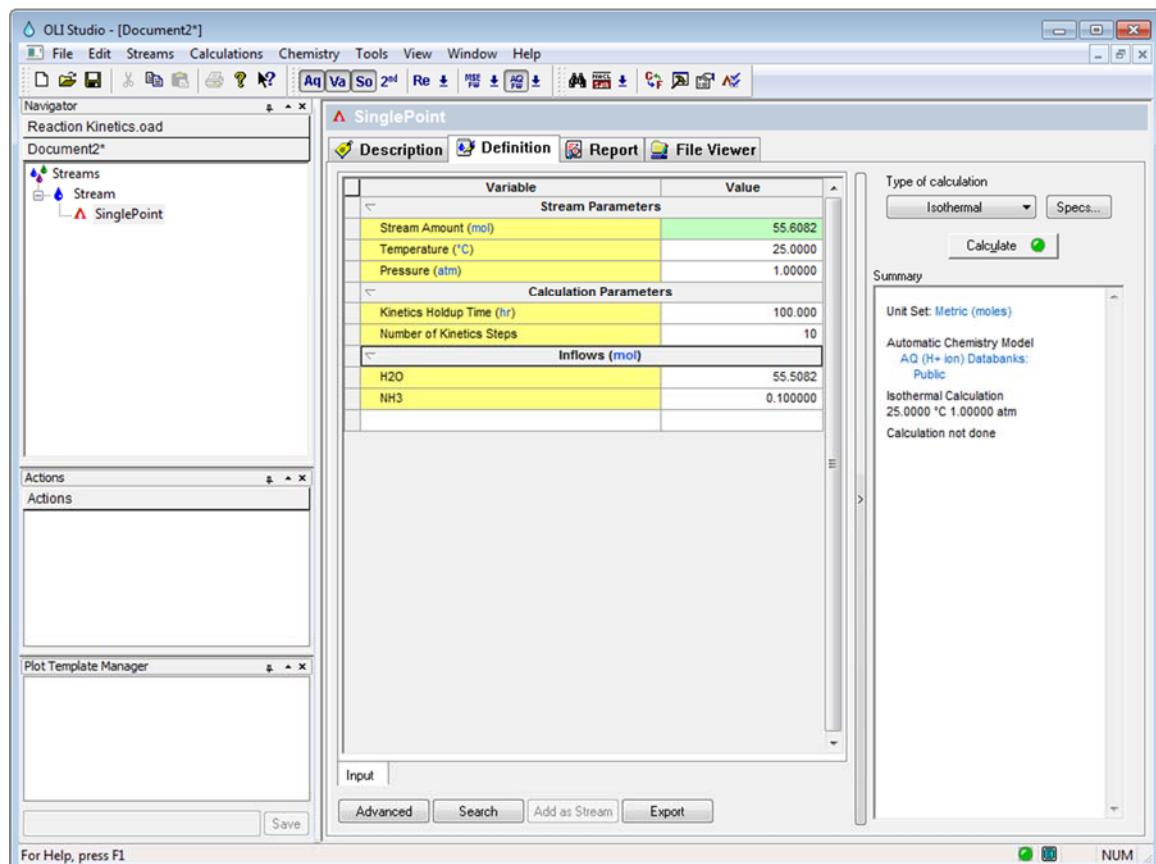


Figure 12-21 Setting up the calculation

OLI recommends you save the file at this time:

Once the calculation is complete you can click the **Output** mini tab and add the Aqueous section (not molecular aqueous):

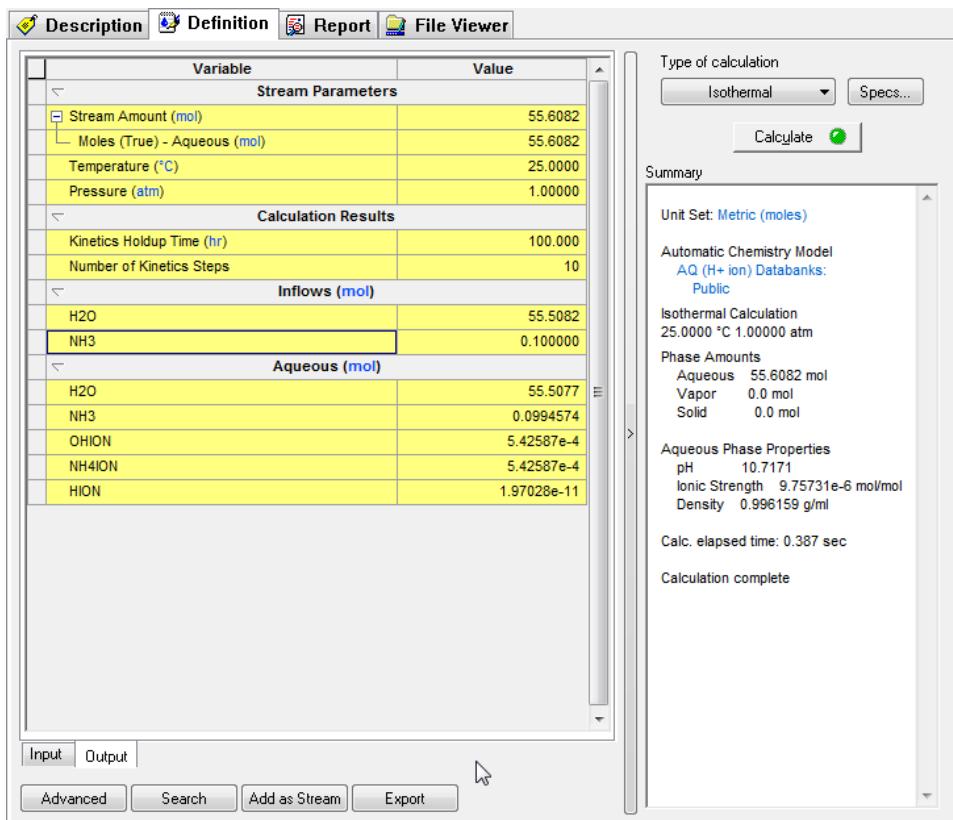


Figure 12-22 The results

You can see that some ammonium ion has been created. It is interesting to see what the equilibrium condition would be.

Create another single point isothermal calculation and run it without any reaction kinetics. Here are results below:

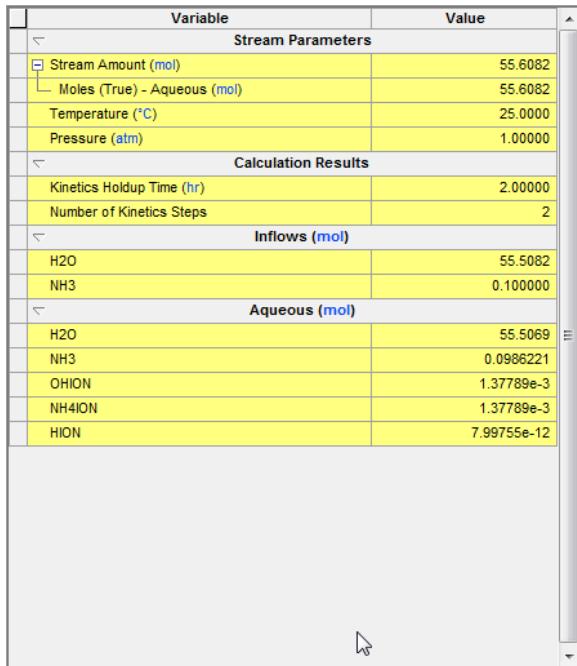


Figure 12-23 No kinetics, only equilibrium results

The reaction kinetics have forced the back reaction to be dominant. In the equilibrium case, approximately 1.3×10^{-3} moles of NH_4^+ have been created. By limiting the forward reaction we allow the back reaction to take place and that only formed 5.4×10^{-4} moles of NH_4^+