Reactor Block

Standard Reaction Kinetics

For this example, we will show you the standard reaction kinetics implementation. This is for the hydrolysis of urea. You will need to create a flowsheet with the following input chemistry:

Table 1 Standard Reaction Kinetics Example - chemistry model

Species	Formula	OLI Tag Name
Water	H_2O	H2O
Carbon dioxide	CO_2	CO2
Ammonia	NH_3	NH3
Urea	NH_2CONH_2	UREA

Use the AQ thermodynamic framework. When complete your chemistry model section should look like the following.

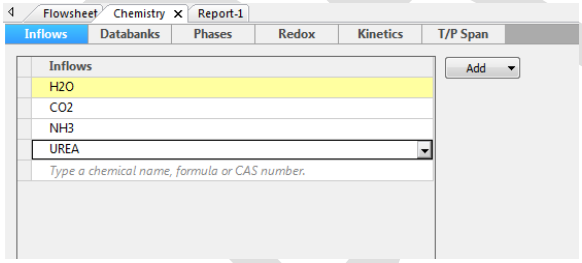


Figure 1 Standard Reaction Kinetics Chemistry

Click on the **Kinetics** tab.

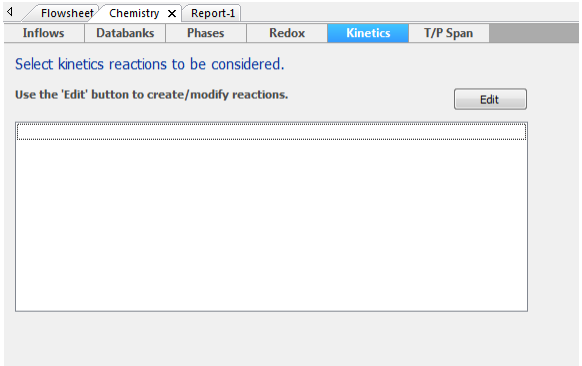
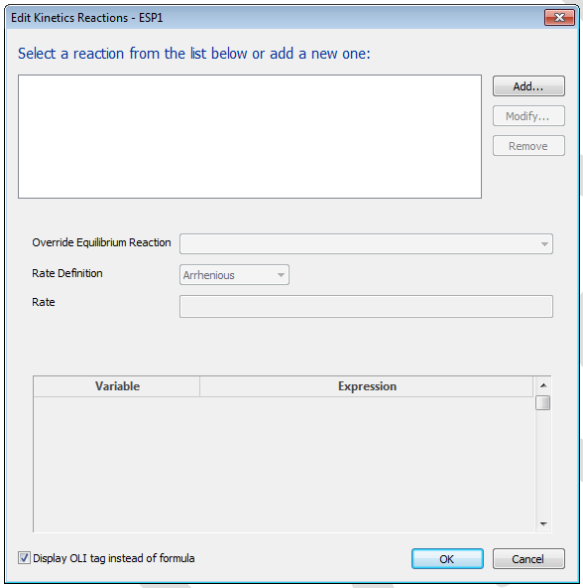


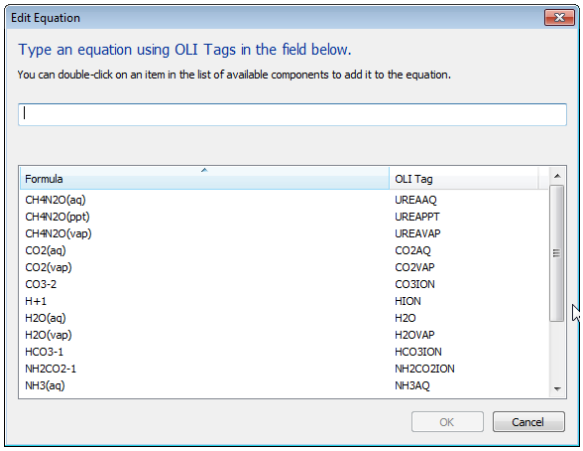
Figure 2 Starting to add reaction kinetics

This will display the reaction kinetics editor. At the moment, there is nothing displayed.

Click the **Edit** button.



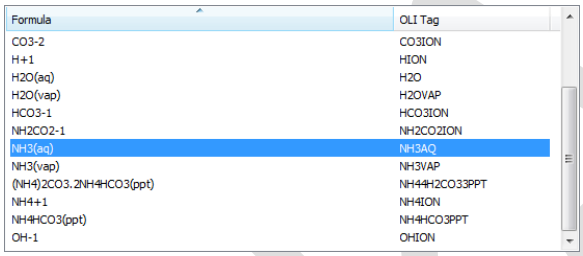
This is the reaction kinetics editor. To add the hydrolysis of urea we need to click the **Add** button.



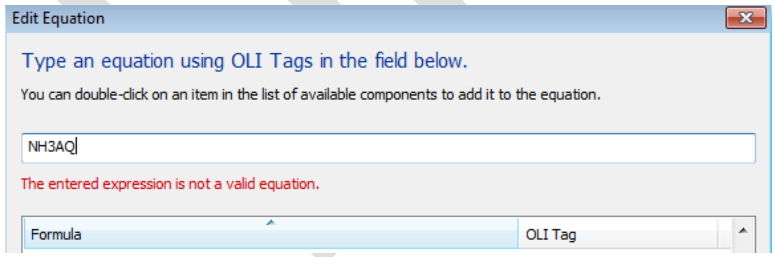
These are all the components currently in the chemistry model. Our reaction equation must contain these species. The reaction we want is the following:

2NH3AQ + CO2AQ = NH2CONH2AQ + H2O

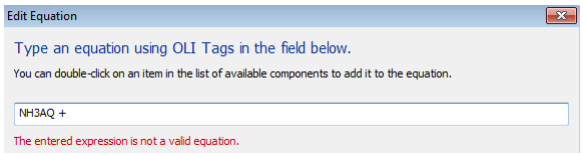
Let's start by locating NH3(AQ) from the list:



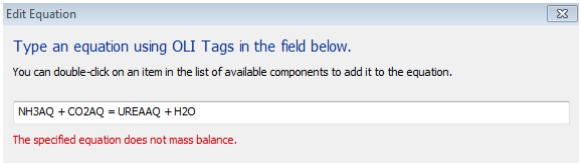
Double-click the component to add it to the equation.



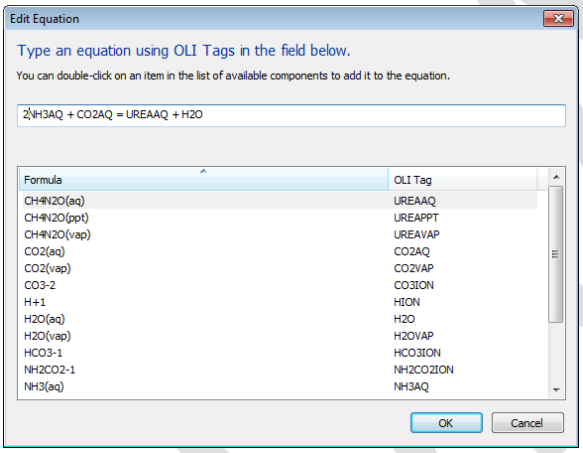
You can see that we have entered the component but there is an error message. This is ok for now since we haven't completed the equation. We now need to add the plus sign "+" to add the next component:



Now locate CO2(AQ) from the list and add it in the same manner. After that complete the equation so it looks like the following:

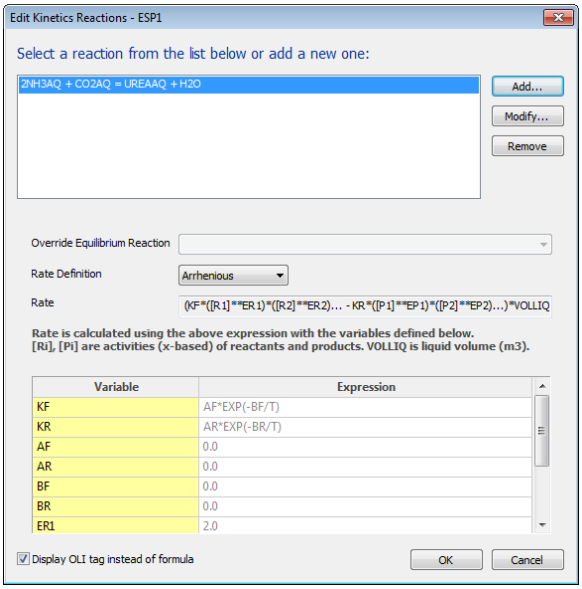


There seems to be a problem. The program will check to see if the equation mass-balances and in this case, it does not. This is because it takes two molecules of ammonia to make urea. You can add the "2" in front of the NH3AQ variable:



Click the OK button to close the editor.

We now have a reaction in the model. We now must change some constants which we get from the literature.



We do have some data to enter. The rate function has been determined to be:

Rate = $Kf[NH3]^2$ [CO2] - Kr [NH2CONH2]

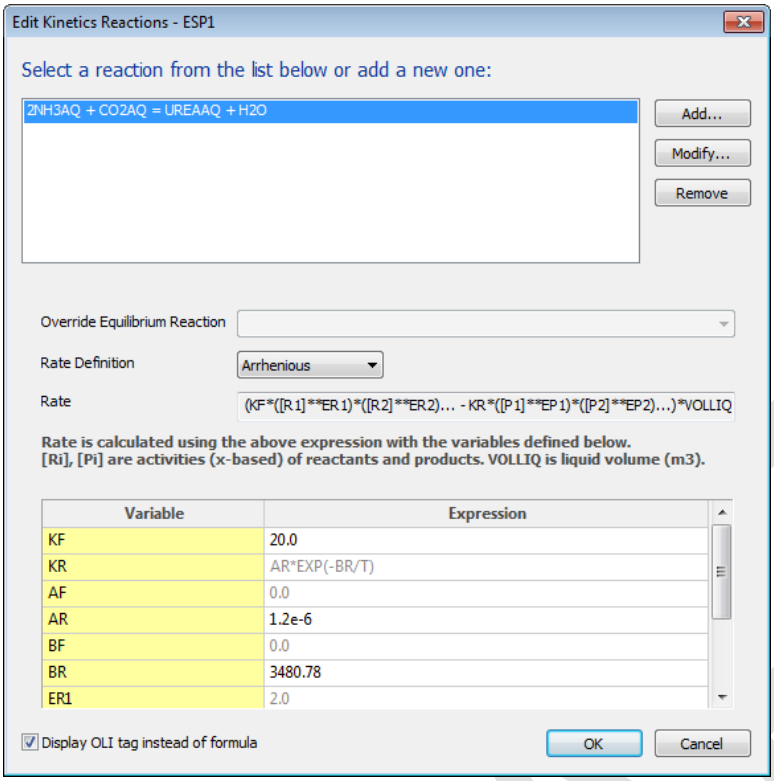
Where:

Rate = moles/hr

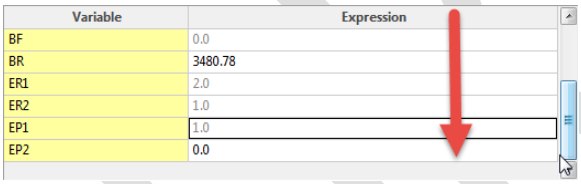
Kf = forward reaction equilibrium constant = 20

[a] = concentration of species a
Kr = reverse reaction equilibrium constant determined by Arrhenius Equation
= 1.2E-06 exp [-28939.9/8.3142 x T]

Where BR = -(-28939.9/8.3142) = 3480.78

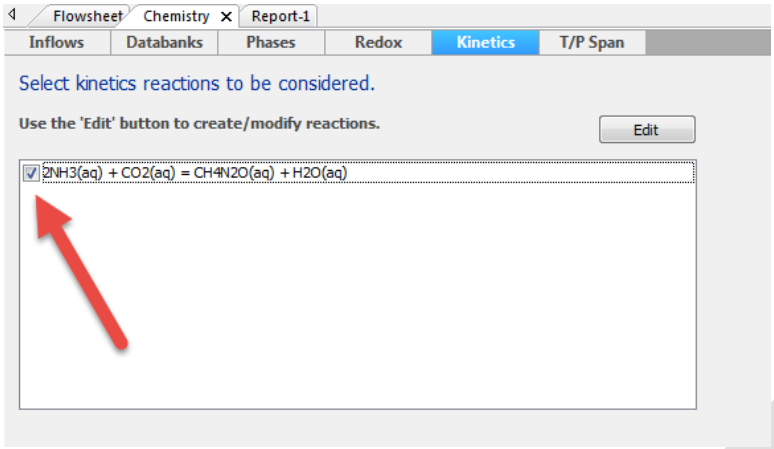


You will need to scroll down to enter EP2



Click OK when done.

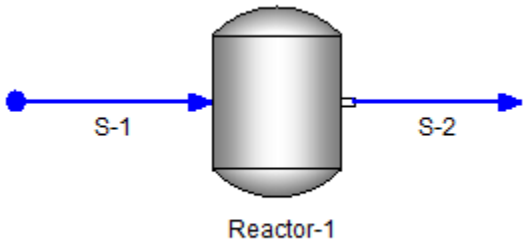
You will now need to enable the added reaction kinetics.



Check the box if it is not already checked.

Now click on the **Flowsheet** tab to begin entering the blocks and streams.

Create a flowsheet with a rector block with a single feed stream and a single product stream such as the following:



Enter the following parameters:

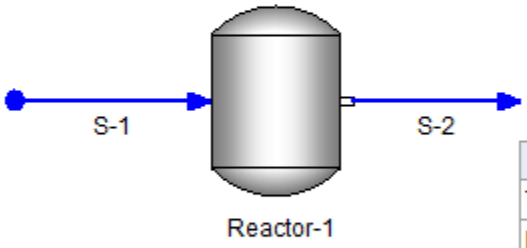
Feed Stream Parameters	
Feed Stream Name	S-1
Temperature	25 °C
Pressure	1 atmosphere

Total Flow	100 mole/hr
H2O	1.0 mole/hr
CO2	0.1 mole/hr
NH3	0.35 mole/hr
Urea	0.0 mole/hr

Reactor Block Parameters		
Reactor Type		Kinetics
Kinetic Parameters		
	Number of Stages	10
	Residence Time (Hr)	100
Calculation Type		Isothermal
Pressure Spec.		Min. Inlet Pressure
Temperature (°C)		35.0
Chemistry Model		Default

Once entered, run the process and then review the output. We have added call-outs to show you the formation of urea (albeit a small amount):

S-1	
T (°C)	25.0
P (atm)	1.0
pH	10.0567
UREAAq (mol/hr)	0.0



S-2	
T (°C)	35.0
P (atm)	1.0
pH	9.74381
UREAAq (mol/hr)	1.41575e-7

Non-Standard (User Defined) Reaction Kinetics

In this example, we are using non-standard reaction kinetics to hydrolyze ammonia. The overall reaction is:

Equation 1

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

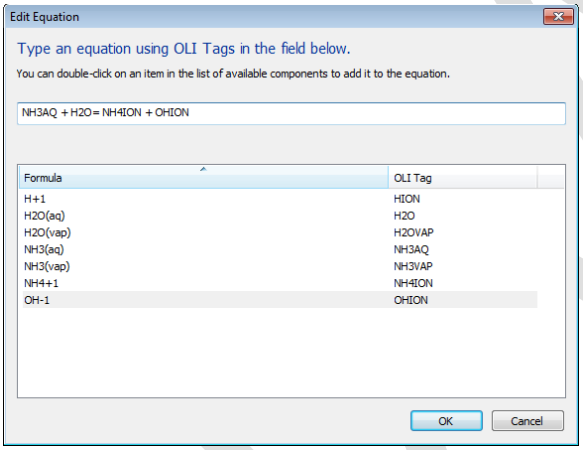
We know the forward rate constant (and hence the forward reaction rate) but we wish to constrain the forward and reverse reaction rates to the thermodynamic equilibrium constant stored in the OLI Databases.

Create a chemistry section with the following information:

Non-Standard Reaction Kinetics	
Thermodynamic Framework	Aqueous (H+ Ion)

Additional Databanks	None	
Phases	Default	
Redox	Off	
Inflows	Formula	OLI Tag Name
Water	H_2O	H2O
Ammonia	NH_3	NH3

Using the techniques from the previous section, add the kinetics reaction from Equation 1.



The reaction mechanism has been previously determined. It is beyond the scope of the document to instruct you how to determine that mechanism, only to add the mechanism to the program.

$$Rate_{forward} = k_f \gamma_{NH_{3(aq)}} [NH_{3(aq)}] \gamma_{H_2O} [H_2O] \quad \textbf{Equation 2}$$

$$Rate_{reverse} = k_r \gamma_{NH_4^+} [NH_4^+] \gamma_{OH^-} [OH^-] \quad \textbf{Equation 3}$$

$$k_f = 3 \quad \textbf{Equation 4}$$

$$k_r = \frac{k_f}{K_{eq}}$$ **Equation 5**

$$rate = \left(k_f e^{Rate_{forward}} - k_r e^{Rate_{reverse}}\right)\frac{Volume}{1000}$$ **Equation 6**

We now need to turn these values into "OLI" terms[1].

FXRATE=LNH3AQ+ANH3AQ+LH2O+AH2O

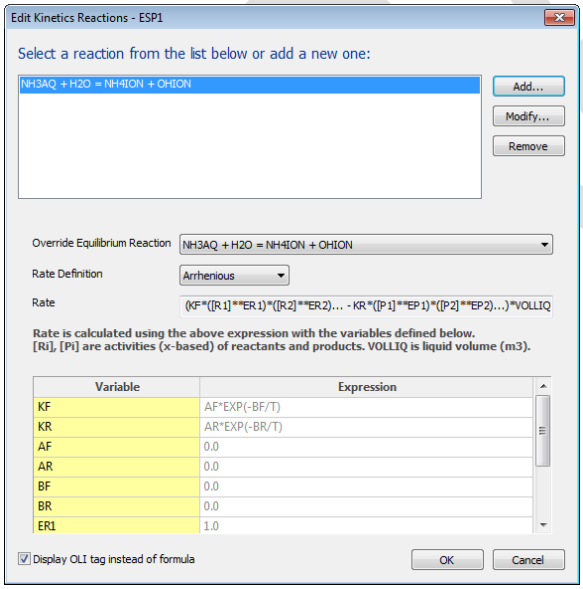
RXRATE=LNH4ION+ANH4ION+LOHION+AOHION

KF1=3

KR1=KF1/KEQ

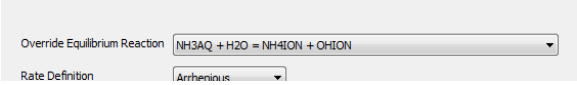
RATE=(KF1*EXP(FXRATE)-KR1*EXP(RXRATE))*VOLLIQ/1000.

Clicking OK will return you to the editor:

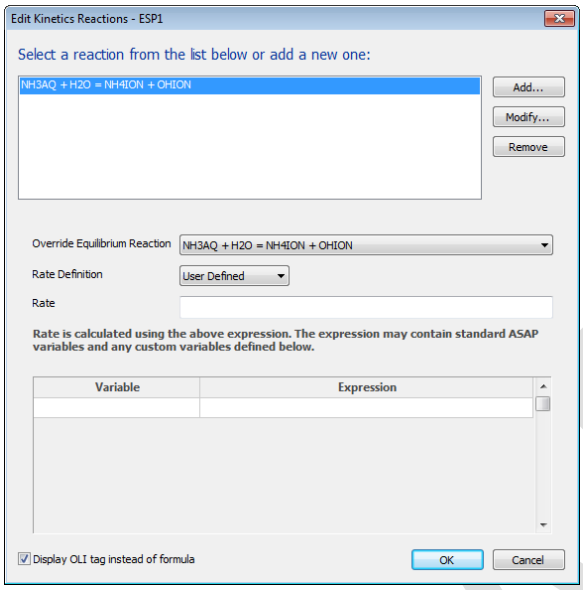


You will notice that we replacing an existing equilibrium equation with reaction kinetics (unlike the previous example where we created a new equation.)

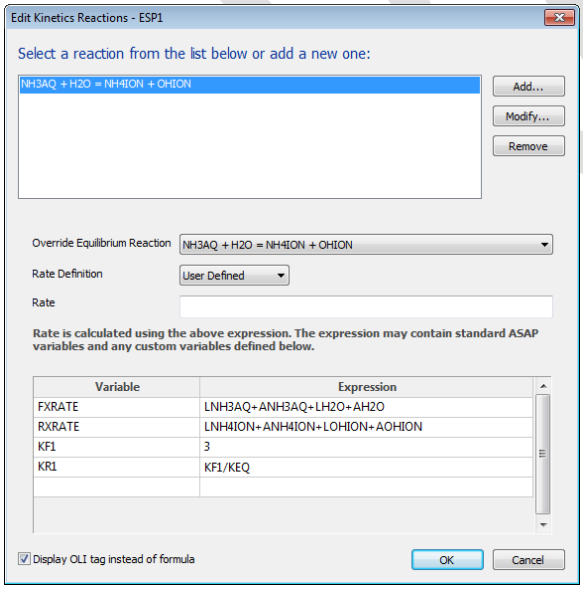
[1] Commonly referred to as ASAP variables.



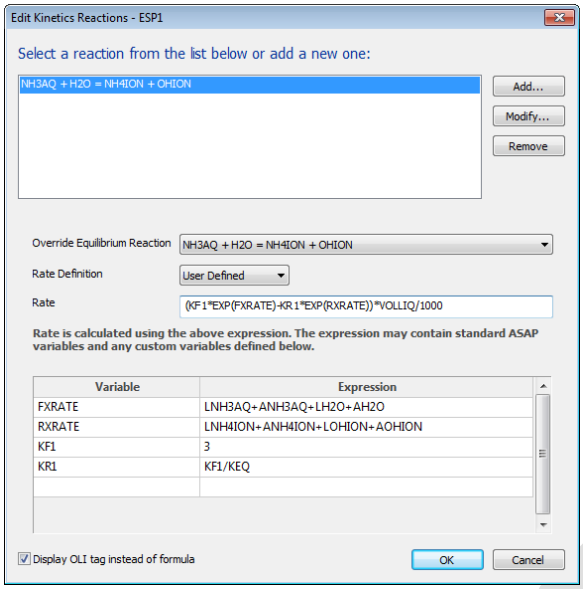
The reaction kinetics we have for this example is not Arrhenius. Change the **Rate Definition** button to **User Defined.**



We first must enter our variables and expressions in the lower half of the dialog. Each variable must be on a separate row.

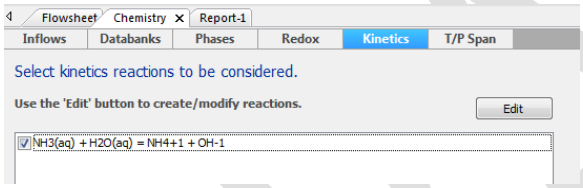


You now must enter the overall rate expression in the box marked **Rate**.



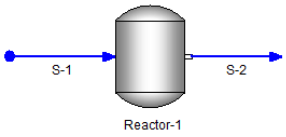
Click ok to accept this information.

Enable the kinetics reaction by checking the box.



Return now to the flowsheet.

Create a flowsheet with a rector block with a single feed stream and a single product stream such as the following:



Enter the following parameters:

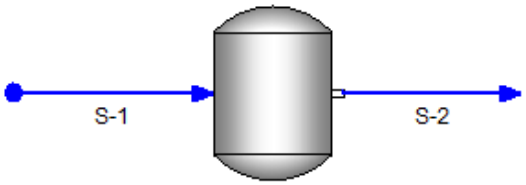
Feed Stream Parameters	
Feed Stream Name	S-1

Temperature	25 °C
Pressure	1 atmosphere
Total Flow	Automatic
H2O	55.5087 mole/hr
NH3	0.1 mole/hr

Reactor Block Parameters		
Reactor Type		Kinetics
Kinetic Parameters		
	Number of Stages	10
	Residence Time (Hr)	100
Calculation Type		Isothermal
Pressure Spec.		Min. Inlet Pressure
Temperature (°C)		25.0
Chemistry Model		Default

Run the process.

Here we have displayed the output of the process using callouts:



S-1	
T (°C)	25.0
P (atm)	1.0
pH	6.99709
NH3 Aq, True (mol/hr)	0.1
NH4ION Aq (mol/hr)	0.0
OHION Aq (mol/hr)	1.0071e-7
HION Aq (mol/hr)	1.0071e-7

S-2	
T (°C)	25.0
P (atm)	1.0
pH	10.6921
NH3 Aq, True (mol/hr)	0.0994881
NH4ION Aq (mol/hr)	5.11867e-4
OHION Aq (mol/hr)	5.11867e-4
HION Aq (mol/hr)	2.08544e-11

The stream S-1 represents the equilibrium condition. The stream pH is approximately 7.0. The stream S-2 represents the condition with reaction kinetics limiting the reforming of ammonia from the ammonium ion. The pH is much higher at approximate 10.7 which shows that it is not at equilibrium.

Stoichiometric Reactors (CONV)

Stoichiometric reactors in the ESP Original program were called CONV reactors (conversion). These reactors used a simple stoichiometric relationship between reactants and products. There is no time factor for these reactions.

In this example, we will mimic the bio-remediation of phenol (C_6H_5OH) using aerobic degradation. The reaction we are simulating is:

$$C_6H_5OH + 7O_2 \rightarrow 3H_2O + 6CO_2$$ **Equation 7**

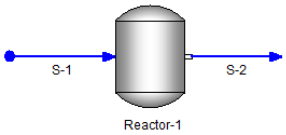
Start OLI Flowsheet and create the following chemistry:

Stoichiometric Reactor	
Thermodynamic Framework	Aqueous (H+ Ion)
Additional Databanks	None

Phases	Default	
Redox	Off	
Inflows	Formula	OLI Tag Name
Water	H_2O	H2O
Phenol	C_6H_5OH	C6H5OH
Oxygen	O_2	O2
Carbon Dioxide	CO_2	CO2

Unlike previous reactors, we do not define the stoichiometric parameters in the chemistry section. Create a flowsheet with the following block and streams:

Create a flowsheet with a rector block with a single feed stream and a single product stream such as the following:



Enter the following parameters:

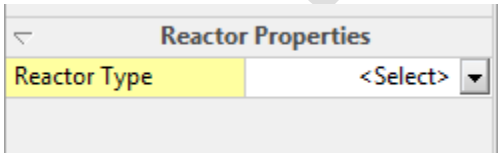
Feed Stream Parameters	
Feed Stream Name	S-1
Temperature	25 °C

Pressure	200.0 atmosphere
Total Flow	Automatic
H2O	55.0 mole/hr
C6H5OH	1.0 mole/hr
O2	7.0 mole/hr

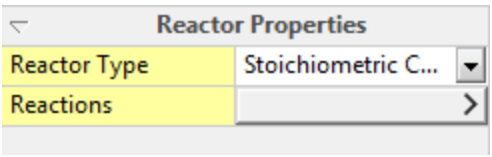
Now enter the block parameters:

Reactor Block Parameters		
Reactor Type		Stoichiometric Conversion
Reactions		
	Conversion Reaction (edit)	C6H5OH + 7O2 = 3H2O + 6CO2
	Key Component	C6H5OH
	Conversion factor	0.4
Calculation Type		Isothermal
Pressure Spec.		Min. Inlet Pressure
Temperature (°C)		25.0
Chemistry Model		Default

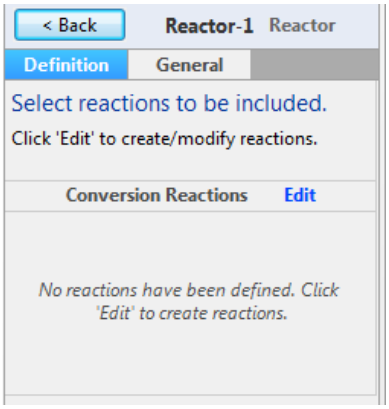
Here are the individual steps for this type of reactor. Click on the reactor you have added. This will display the properties dialog for the block:



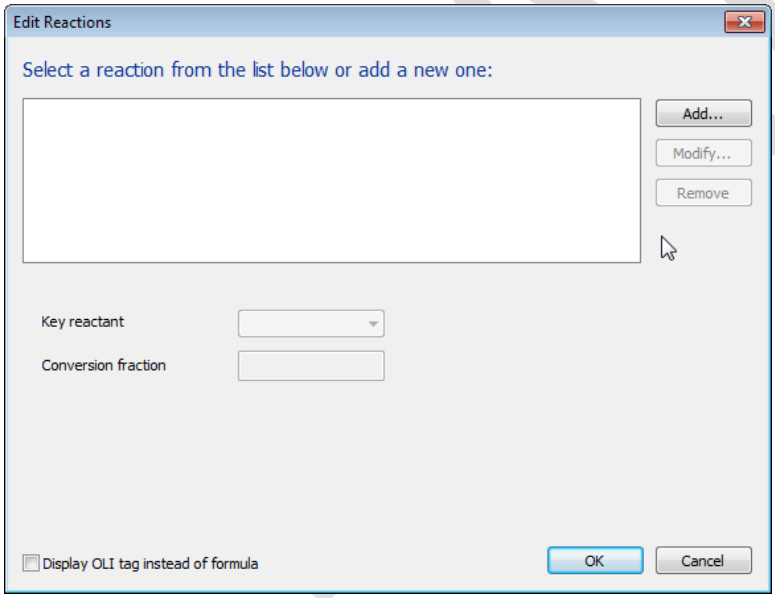
Change the type of reactor to **Stoichiometric Conversion**.



Click on the **Reactions** button. This will display a fly-out dialog.

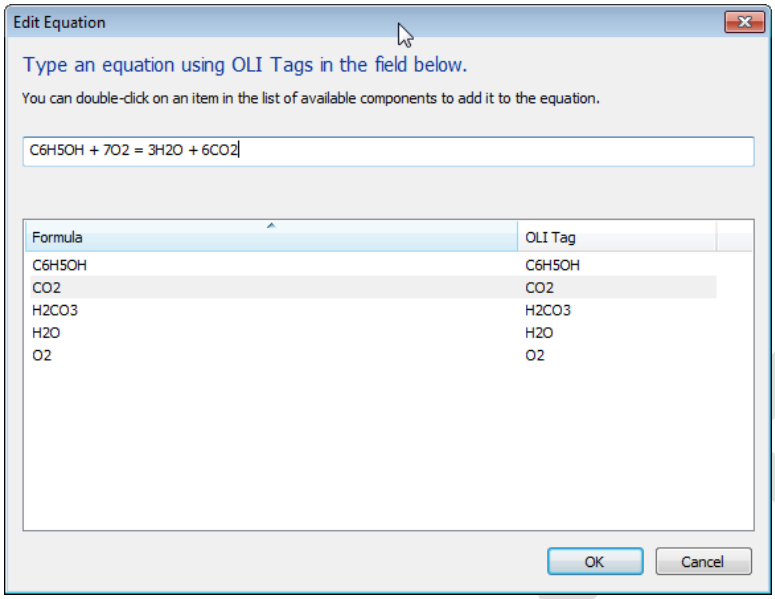


This brings up a familiar dialog. Normally we used this dialog in the chemistry section but now we are using the same dialog in the block.

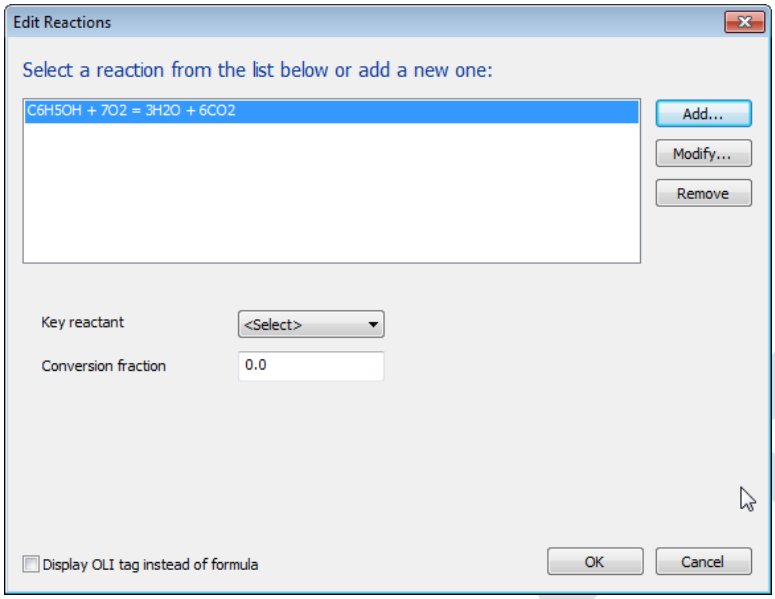


Click the **Add** button.

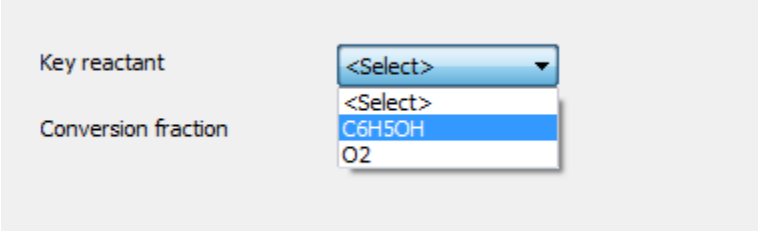
As we did in the previous section, we will now add the equation from above (see $\boldsymbol{C_6H_5OH + 7O_2 \rightarrow 3H_2O + 6CO_2}$ Equation 7)



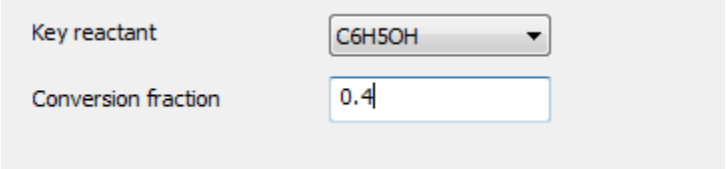
Click **OK**



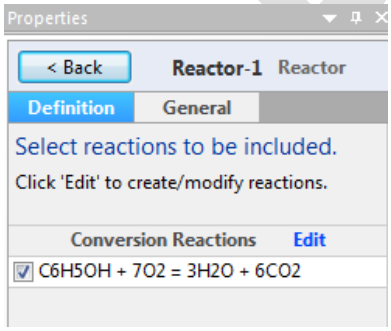
We now must define the key reactant. This is what the conversion is based on. Select phenol (C_6H_5OH).



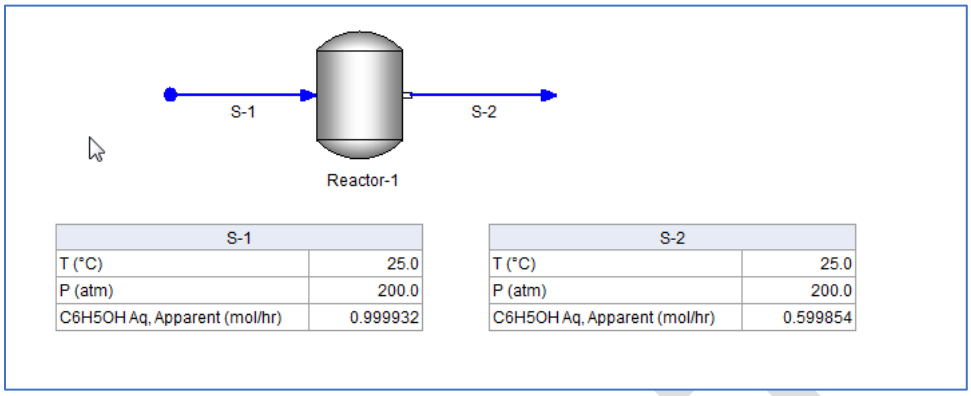
For our purposes we are converting 40% (on a mole basis) so enter 0.4



Click **OK** to continue.



We have run our sample process at very high pressure to force the oxygen into solution. Here are the results:



S-1	
T (°C)	25.0
P (atm)	200.0
C6H5OH Aq, Apparent (mol/hr)	0.999932

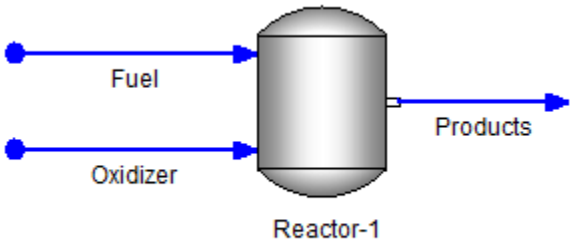
S-2	
T (°C)	25.0
P (atm)	200.0
C6H5OH Aq, Apparent (mol/hr)	0.599854

We started with 1.0 mole of phenol (0.999932 is close to 1.0 moles) and have 0.599854 moles. This is means we have reacted 40% of the phenol which is exactly to what the conversion factor was set.

Gibbs Reactor

A Gibbs reactor is a special type of reaction in OLI Flowsheet in that it does not evaluate the standard equilibrium equations found in the chemistry model. Rather it minimizes the Gibbs Free Energy at a given temperature and pressure or maximizes entropy at a given pressure and enthalpy. The latter is usually what is calculated in OLI Flowsheet.

Create a flowsheet with the following configuration:



Now create the chemistry model with the following parameters:

Gibbs Reactor		
Thermodynamic Framework	MSE (H3O+ Ion)	
Additional Databanks	None	
Phases	Default	
Redox	Off	
Inflows	Formula	OLI Tag Name
Water	H_2O	H2O
Methane	CH_4	CH4
Oxygen	O_2	O2
Carbon Dioxide	CO_2	CO2
Nitrogen	N_2	N2
Carbon Monoxide	CO	CO

Now enter the parameters for each inlet stream:

Feed Stream Parameters

Feed Stream Name	Fuel	
Temperature	25	^{o}C
Pressure	1.0	Atm
Total Flow	1 m3/hr	m3/hr
H2O	0.0 mole/hr	mole/hr
CH4	100.0	mole/hr
O2	0	mole/hr
CO2	0	mole/hr
N2	0	mole/hr
CO	0	mole/hr

Feed Stream Parameters		
Feed Stream Name	Oxidizer	
Temperature	25	^{o}C
Pressure	1.0	Atm
Total Flow	0.1 m3/hr	m3/hr

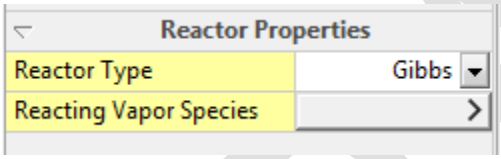
H2O	0.0 mole/hr	mole/hr
CH4	0.0	mole/hr
O2	20	mole/hr
CO2	0	mole/hr
N2	80	mole/hr
CO	0	mole/hr

Now enter the block parameters for the reactors. We will describe the details about the new parameters after the table.

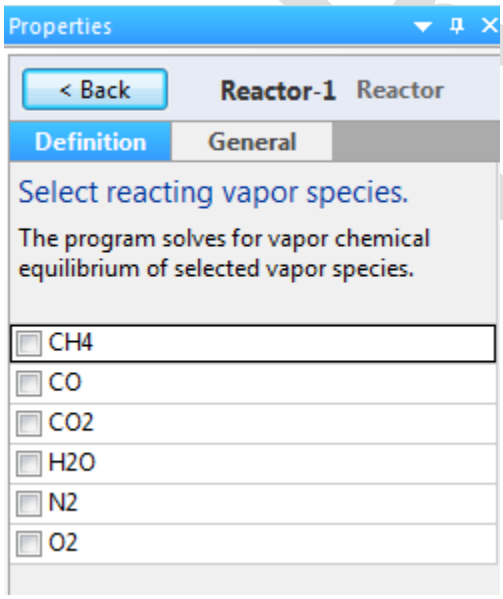
Reactor Block Parameters		
Reactor Type		Gibbs
Reacting Vapor Species		
	CH4	Enabled
	CO	Enabled
	CO2	Enabled
	H2O	Enabled
	N2	Disabled

O2	Enabled
Calculation Type	Adiabatic
Pressure Spec.	Min. Inlet Pressure
Heat Duty	0.0
Chemistry Model	Default

This the type of reactor you need to specify which vapor species can react. In this case, we are simulating a combustion reaction so we do not require Nitrogen gas to be reactive. After specifying the reactor type we need to enable the gasses:



Click the fly-out button next to **Reacting Vapor Species**.



Check the components:

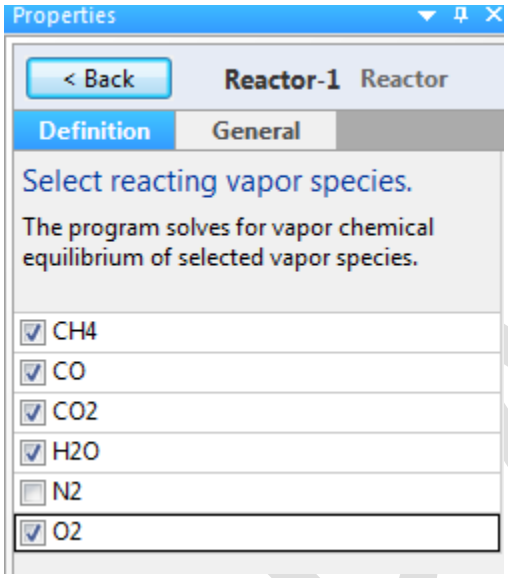
CH4CO

CO2

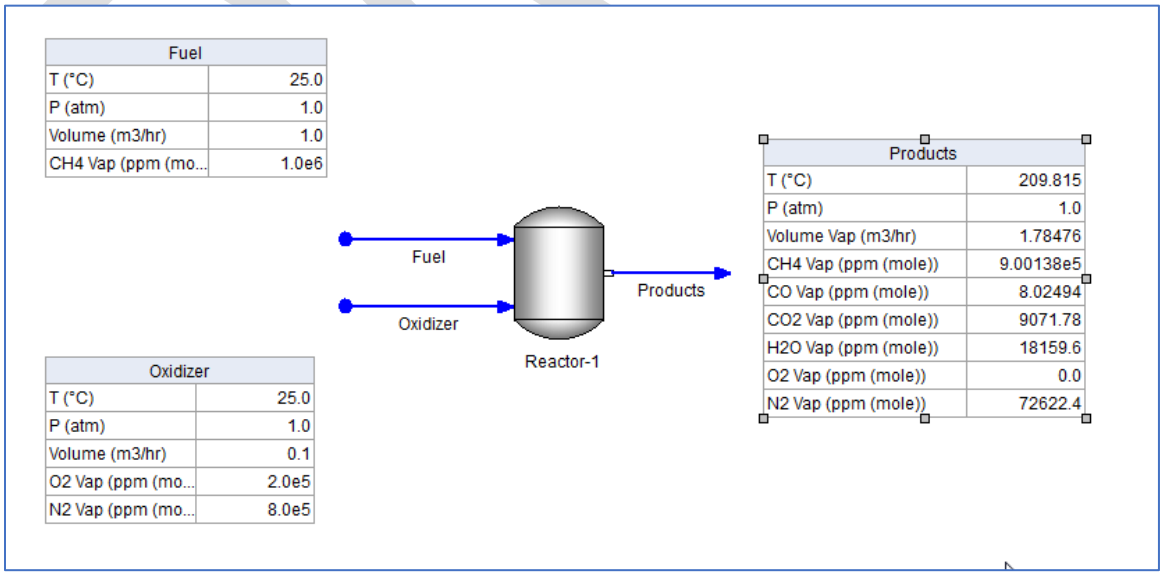
H2O

O2

Skip N2



Click the **Back** button and then run the calculation.



You can see that we have reacted methane with oxygen and have formed the traditional combustion products of carbon dioxide and water. We also have some incomplete combustion and have formed some carbon monoxide at approximately 8 ppm. There has also been a temperature increase.