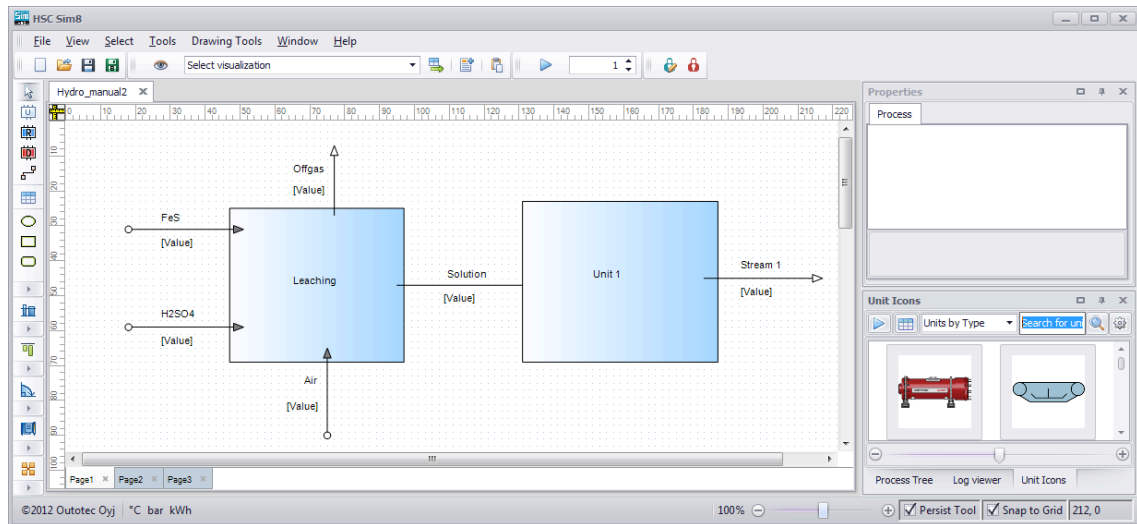# 43. Sim Reactions (Hydro) Unit

The Reactions unit calculates chemical reactions based on unit operations in solid, liquid, and gas systems. This unit was originally made for hydrometallurgical process calculations, but can be used for almost any process, especially those that can be modeled with chemical reactions.

43.1.   Steps to Successful Sim Reactions Simulation

It is important to add the necessary information before the simulation can be started. It is good to follow this list while making your Sim Reactions models. Steps 3 to 9 are explained in more detail below.

1.   Draw units and streams, see Chapter 40 (section 40.1.)
2.   Save Process (see step 8)
3.   Create variable list
4.   Add reaction equations
5.   Specify distributions
6.   Set controls
7.   Specify raw material amounts
8.   Save Process and Save Backup
9.   Run process

43.2.   Creating a Variable List

A variable list editor is shown in **Fig. 1**. The user should at least add some species to phases in this editor. In this simple (cooler) example, only H_2O has been added to the water phase (row 13) and just the amount has been checked (cell E12), which automatically creates row 17. Default system variables are also shown in rows 3-9 and default phases in rows 10, 12, and 15.
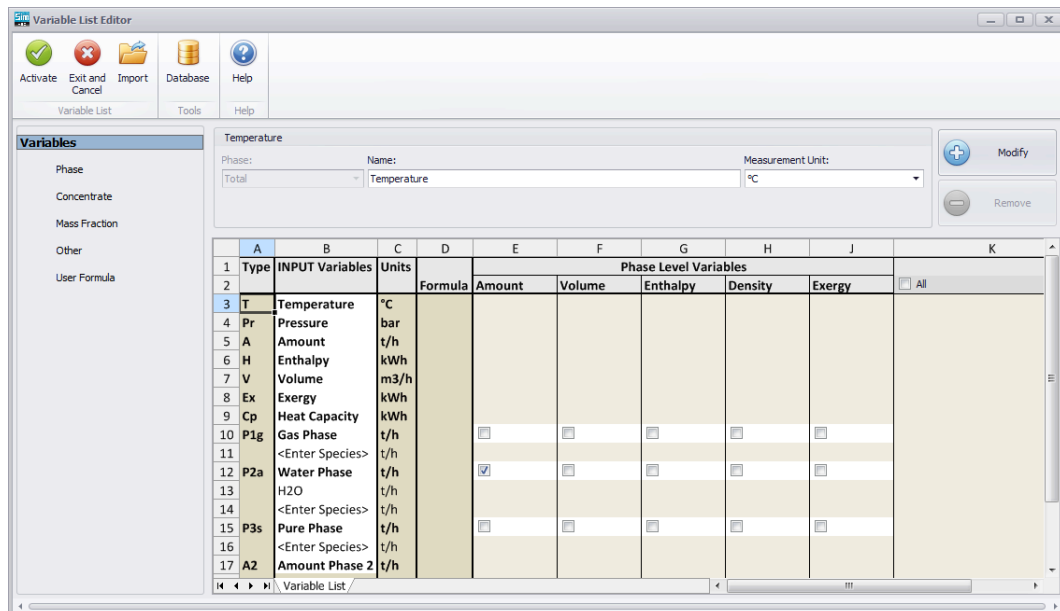

Fig. 1. Variable List Editor where user specifies the variables needed in the simulation.

43.2.1.   Filling Variable List Manually

Specify the Species

First you need to specify the species you are using in your calculation. The species can be any combination of elements (like Fe, Ag, O, etc.), solid species ($CaCO_3$, Na_2S, CuS, etc.),

gases (CO_2(g), O_2(g), N_2(g), etc.), or liquids (H_2SO_4(a), $CuSO_4$(a), etc. or Cu(+2a), SO$_4$(-2a), H(+a), etc.).

Special case: species that are not found in HSC database

If the compound is not found from the HSC database. To use the compound you need to add it to the own database.

Here are instructions what you need to take into account when you add the compound:

The compound needs to have a chemical formula. Molecular weight is calculated from the formula. For mixtures use formula that gives average molecular weight and if you do not know the exact formula use formula that has correct molecular weight.

For example organic compound with average molecular weight of 350 g/mol can be put to the database as: C29(MPEG350).

Note that the last character in brackets defines the phase so it cannot be any of the following characters: a, g, l, s, + or -.

You can add properties to the compound manually, for example enthalpy (kJ/mol), entropy (J/(mol*K)), heat capacity (J/(mol*K)) and density (kg/l). For heat capacity you can fit data for different temperature ranges.

If you know the chemical formula for the compound the enthalpy, entropy and heat capacity values can be estimated with H, S and Cp estimates module.

Example

Organic compound

In copper solvent extraction you have unloaded reagent, loaded reagent and diluent that are not found from the HSC database. You know the density and molecular weight of the compounds. This is one way how you add the compounds to the database.

Type the compound name to the variable list editor. It will open the database editor automatically and copy the compound name to editor if compound is not found from the database.

Type the data for the compound (name and density in units kg/l):

C42H2(unloaded reagent), 0.96
C42Cu(loaded reagent), 1.00
C14(diluent), 0.79

If you know enthalpy, entropy or heat capacity values you can add them for the compounds.

After adding compounds to the database and the densities you can use these organic compounds in your model. The density for the organic phase is calculated automatically from the fed data. The compounds can be used in chemical reactions just like other compounds.

Divide the Species into Phases

Divide the species into meaningful phases, because only this will enable you to calculate phase properties like densities and compositions, **Fig. 1**. Species can be typed manually or they can be imported from the database.

A) Type species formulae manually into <enter species> cells.
B) Go to cell <enter species>, click database button, select species and click Import items button in Database Browser.

Specify the Variables

Phase
Measurement units of different phases
- Gas (Nm^3/h, t/h, kg/h)
- Water, Particles, Organic, Solid (t/h, kg/h)

Default phases are "Gas Phase", "Water Phase", and "Pure Phase". The user can change phase names and add new phases as well using the **Modify** button or delete phases using **Remove**.

Concentrate (Concentration)
Measurement units of different phases
- Gas (wt %, vol % or ppm)
- Water (wt %, g/l or ppm)
- Pure (wt % or ppm)

Mass Fraction
To calculate mass fractions of the Water phase, the user has to give
- A compound which is found in Density Database ($Al_2(SO_4)_3$…$ZnSO_4$)
- A compound (aqueous ion) which is found in the variable list (Al(+3a)…Zn(+2a))

Other
Specify Name (e.g. Solid concentration)
Specify Unit (e.g. g/l)

User Formula
Specify Name (e.g. Solid concentration)
Specify Unit (e.g. g/l)
Insert an Excel-type formula in Column D (e.g. =D13/D7/1000. HSC functions like Molecular weight, MW("H2O"), can also be used in the formulae)

43.2.2.   Importing Ready-Made Variable List

A custom-made variable list allows you to utilize the HSC Sim module in many different types of simulation applications, such as mineralogical, chemical, hydrometallurgical, pyrometallurgical, economic, biological, etc. Only your imagination sets the limits! The custom-made variable list gives a lot of flexibility but the drawback is that the users have to know what they are doing.

This is also the main reason why the specification of the variable list is one of the most important tasks in the new model development stage. It is easy to add/delete/modify the

variable list later on, but it may still be best to try to specify a complete variable list right at the beginning or at least before you start to create the calculation models.

If you have a ready-made variable list available you can use the **Import** button in the Variable list editor and choose the *.xls or *.xlsx file that includes your variable list. Some example files can be found in the HSC Chemistry installation folder …\Flowsheet_Hydro.

43.2.3.   Activating Variable List

After filling the variable list manually or importing it, the next thing is to click **Activate**.

43.2.4.   Summary of Columns

The meaning of the Input, Output, and Dist sheet columns can be summarized as follows:

<u>**Column A - Type:**</u> Specifies the row type:

- **T** Temperature
- **Pr** Pressure
- **A** Amount
- **H** Enthalpy
- **V** Volume
- **Ex** Exergy
- **Cp** Heat Capacity
- **P** Phase
-    Species
- **D** Density (mass fractions also need to be specified for water phase species)
- **C** Concentration (concentrate)
- **F** Mass Fraction (base species must be specified)
- **O** Other
- **U** User formula

The number section in the row type parameter refers to the phase number. For example: A2 = Amount of phase 2, H3 = enthalpy of phase 3, etc.

<u>**Column B - Variable:**</u> Specifies the variable name.

<u>**Column C - Unit:**</u> Specifies the measurement unit. Use the same measurement units within all the process unit models.

<u>**Column D - Formula:**</u> Specifies the Excel-type cell formula which will automatically be added into model Input and Output sheets in Column D and in all the stream columns. HSC AddIn functions can also be used, e.g. MW("H2O").

The HSC AddIn function =Units ("C";"MJ") will check whether the temperature and energy units are as specified in the formula. The user may change the measurement units only in the variable list editor.

<u>**Columns E - Streams:**</u> Each stream has a column of its own.

43.3.   Adding Reaction Equations to Create Calculation Model

In the reactions unit, the mathematical connection (model) between the Input and Output streams is created using Chemical Reactions Wizard. This model transforms the raw materials into products by using chemical reactions given by the user, see **Fig. 3**.

Fig. 2. In Chemical Reactions Wizard the user specifies reaction equations and their progress.

The first step is to enter the reactions that happen in the process unit in the Chemical Reactions Wizard, **Fig. 2**. The species used in the reactions must exist in the variable list.

The first species of each reaction is assumed to be the "raw material" which is consumed in this reaction according to the progress %. For example, FeS is the raw material in reaction 1. You must keep in mind that more than 100% of the raw materials cannot be consumed. The sum of Progress % cannot be more than 100% for the same raw material, although it may be less than 100%. The other species in the reaction equations will automatically be taken into account when a model is created based on the reaction stoichiometry. However, it is still recommended to check whether there are negative amounts on the Model sheet and remove them, for example, by decreasing the Progress %.

The second step is to test the balances by pressing the Balance button. This gives an OK in the Balance column, showing that everything is acceptable. The balance test will also give enthalpy H and equilibrium constant K for the reaction at 25 °C if all the species are found in the active HSC databases. Negative H values mean that heat is released in the reaction, whereas positive values mean that more heat is needed. Large K values (>1) mean that the reaction tends to go to the right and small values (<1) mean that the reaction tends to go to the left in the equilibrium state.

The third step is to **Activate** the reaction equations. After that the reactions can be seen on the model sheet. This sheet contains a list of the reactions with progress percentages. The user may change the Progress % cells (H7 and H11) manually or by using a control, see **Fig. 3.** NB! The species name is **red** if it is not found in the variable list. This will lead to material balance errors since the missing species will not be copied to the output sheet.

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Fig. 3. Model sheet shows user-defined chemical reactions.

43.3.1.   Unit Model Editor - Excel Wizards

Ready-made Excel wizards for some units like **Filter** and **Thickener** were used in HSC7. These wizards are also available in HSC8; however, they will no longer be supported in the future so we recommend users not to use them any more. New dll units can be used for this purpose.

Unit model editor is activated from the **Tools menu** in the main flowsheet window (or right mouse click over any unit). In the editor, the user can choose a unit, double-click the wizard and click OK. The user then specifies the streams and after that the model is ready to be used, see also Chapter 40 (section 40.2.2).

43.4.   Distributions

The Dist sheet is filled because the user must divide the products into the output streams. If there is only one output stream then 100% of the products enter this stream. The example in **Fig. 4** shows a distribution where all the gas species enter the Offgas stream (type 100 in cell F14) and all the water and pure species go to the solution phase (type 100 in cells E18 and E24).

	Type	Dist Variables	Units	Total % Sum	Solution	Offgas
14	P1g	Gas Phase	Nm3/h	100.00	0.00	100.00
15		H2O(g)	Nm3/h	100.00	0.00	100.00
16		O2(g)	Nm3/h	100.00	0.00	100.00
17		N2(g)	Nm3/h	100.00	0.00	100.00
18	P2a	Water Phase	t/h	100.00	100.00	0.00
19		H2O	t/h	100.00	100.00	0.00
20		H2SO4	t/h	100.00	100.00	0.00
21		Fe(+2a)	t/h	100.00	100.00	0.00
22		H(+a)	t/h	100.00	100.00	0.00
23		SO4(-2a)	t/h	100.00	100.00	0.00
24	P3s	Pure Phase	t/h	100.00	100.00	0.00
25		FeS	t/h	100.00	100.00	0.00
26		S	t/h	100.00	100.00	0.00

Fig. 4. Dist sheet is usually filled with given distribution percentages.

43.5.   Creating Controls

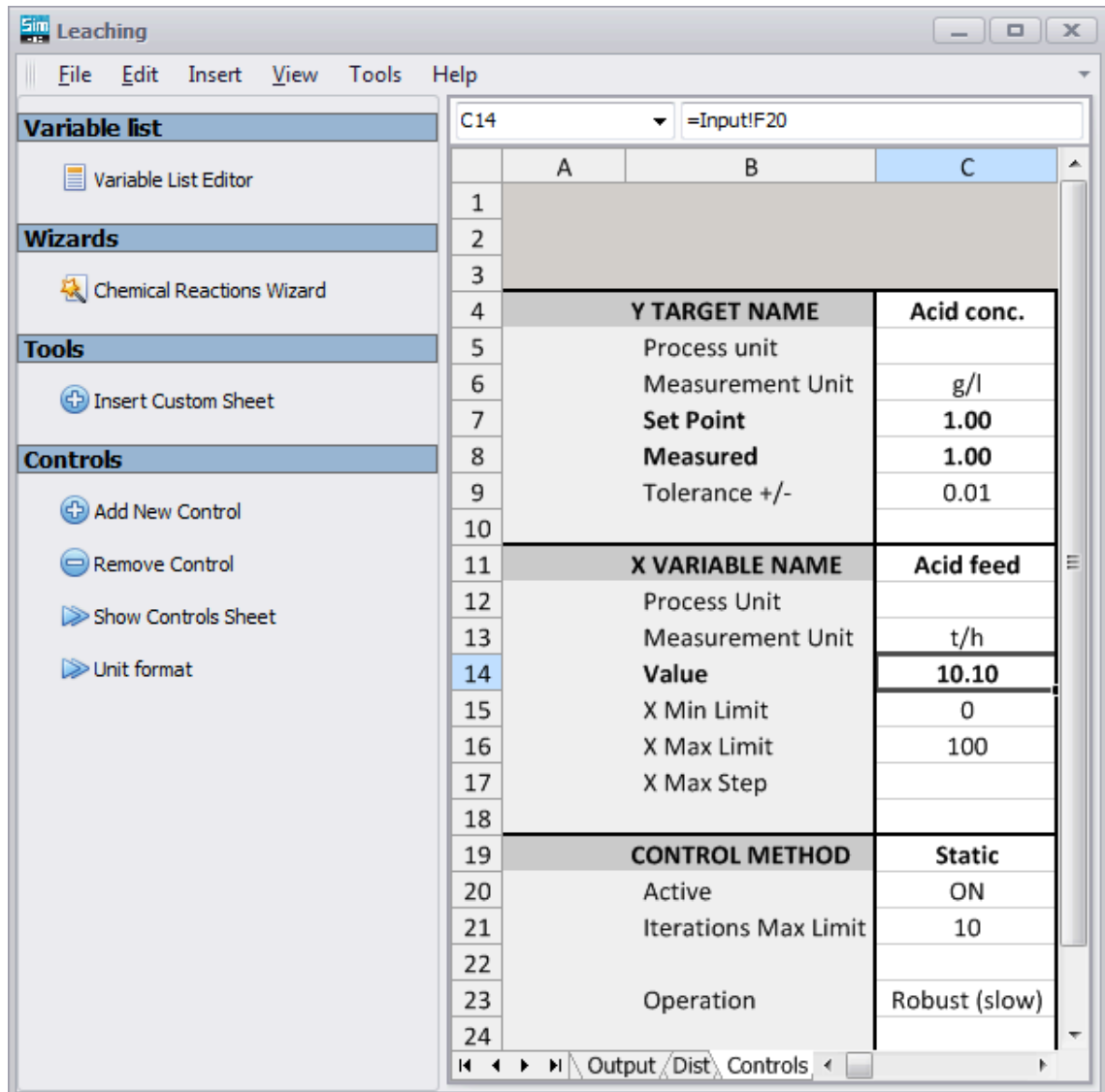Controls can be added, removed and seen using quick links on the left column, see **Fig. 5**.

Fig. 5. The calculation model "Controls sheet" with one control.

The HSC Sim Controls sheet makes it possible to create controls that regulate the target parameter cell value using another variable cell value, see **Fig. 5**. In principle, Sim Control works exactly like a real process control. For example, in a real process unit you can assign a set point to the process unit temperature and regulate the temperature by changing the fuel oil feed.

To create a control on the Controls sheet, you have to set at least the set point, the Target cell reference, the Variable cell reference, the limits for the variable, and the tolerance. You can type this information on the Controls sheet using the following procedure:

1. Type the name and the unit of measure in Control sheet cells C4 to C6 (optional).
2. Type Target set value in cell C7.
3. Locate the Target cell from your active unit and right mouse click "Copy cell reference".

4. Go to Control sheet cell C8 and right mouse click "Paste cell reference".

5. Give the tolerance of the calculation in cell C9. When the difference between the Set Point and the Measured value is smaller than the Tolerance, the control is in balance and will not be calculated further.

6. Type the name and the unit of measure in cells C12 and C13 (optional).

7. Locate the Variable cell from your active unit and select "Copy cell reference".

8. Go to Control sheet cell C14 and right mouse click "Paste cell reference".

9. Type **Limit Min** and **Max** in cells C15 and C16; a narrow numerical range speeds up the calculations.

The default **Tolerance** is +/-. A small tolerance increases the calculation time and a large tolerance increases errors. Some 2% of the target value may be a good compromise. The control will not be taken into account if the value is within the tolerance.

Sim Controls have exactly the same **limitations** as real process controls, for example:

- If the target cell does not depend on the variable cell value, the iterations will fail.
- If an external variable cell is used, there may be a long delay before the effect on the target value becomes visible. In these cases a lot of iteration rounds might be needed to reach the set point. This increases the calculation time.

Table 1. Information on the Control sheet.

Row	Name	Description
4	Y Target Name	Name of Y (optional)
5	Process Unit	Unit name (optional)
6	Measurement Unit	Name of the unit of measure (optional)
7	**Set Point**	**Set point of Y (obligatory)**
8	**Measured**	**Y cell reference (obligatory)**
9	**Tolerance +/-**	**Y tolerance (obligatory**)
11	X Variable Name	Name of X (optional)
12	Process Unit	Unit name (optional)
13	Measurement Unit	Name of the unit of measure (optional)
14	**Value**	**X cell reference (obligatory)**
15	**X Min Limit**	**Min limit of the X range (obligatory)**
16	**X Max Limit**	**Max limit of the X range (obligatory)**
17	X Max Step	Maximum X Step (optional, default = empty)
19	Control Method	Iteration method (optional, default = Auto[1])
20	Active	Set control ON/OFF (optional, default = empty = ON)
21	Iterations max limit	Max number of iterations (optional, default = 10)
22	Iterations min limit	Min number of iterations (optional, default = empty)
23	Operation	Control calculation operation (optional, default = Light[2])

[1]**Auto** (Solves the control with information on rows 20 - 23), **Auto Smart** (Same as Auto except changes X Max Step and Iterations max limit when needed), **PID** (not in use, will be added to HSC8 version).

[2]**Light** (Solves the control with modified tangent method, fast), **Robust** (Solves the control with modified Newton method, slow), **Simple direct** (Increases X value when Measured value is too small. The step used can be specified in X max step.), **Simple reverse** (Decreases X value when Measured value is too small. The step used can be specified in X max step.).

43.5.1.   Internal and External Controls

1. Internal control in which the target and variable cells exist in the same process unit (FAST).

2. External control in which the target and variable cells exist in different process units (SLOW).

Calculation of an internal control is <u>fast</u> because only one unit is calculated. Usually you can create a large number of **internal controls** in a process without a dramatic drop in calculation speed because they do not increase the number of calculation rounds of the process.

Calculation of an external control might <u>take more time</u> because material must be recirculated within the whole process several times to reach a stable target value. Usually only a few **external controls** can be used in one process without a considerable decrease in the calculation speed because external controls might multiply the calculation rounds of the process.

Sometimes it is easier to set controls using additional sheets, where some calculations may be done. You can insert new sheet using left column quick link Insert Custom Sheet or by using menu Insert…Sheet.

43.5.2.   Advices When Using Controls

- It is recommended to moderate large changes of the variable with the use of **X Max Step** when using external controls with slow responses.

- If you want to keep some concentration lower than a set point (8 g/l), change the bleed stream amount (valve 0 - 100%). Please use an external control since the bleed amount will not change the concentration unless the whole process is calculated. This is possible when the bleed and concentration cells are in different units.

- The **RecoveryX** add-in function cannot be used in the Target cell, because it is recalculated only after all the calculation rounds have been completed.

- The large number of thermochemical add-in functions (**StreamH**, StreamS, etc.) may reduce the calculation speed if the argument value changes in each control iteration round, because the data search from the H, S, and Cp database takes time. Use these add-in functions only when needed.

43.6. Adding Raw Materials

In both input and output sheets if the cells are white it means that the user can edit them.

43.6.1. Input Sheet

In the input sheet, temperature row 7, pressure row 8, and the raw material amounts are given. In the example in **Fig. 6,** the amount of H_2O and FeS is known and the $O_2(g)$ and $N_2(g)$ amounts are calculated using equations, whereas the H_2SO_4 amount is calculated using the control. The user can give an initial guess of the sulfuric acid value in cell F20 or it can also be empty before the simulation is started.

If the flowsheet contains more than one unit and the units are connected, intermediate stream properties cannot be edited since these values are calculated, see **Fig. 7**.

		A	B	Units	D Total Sum	E FeS	F H2SO4	G Air
5	Type	INPUT						
6		Variables						
7	T	Temperature	°C		25.00	25.00	25.00
8	Pr	Pressure	bar		1.00	1.00	1.00
9	A	Amount	t/h	84.16	60.00	10.10	14.06
10	H	Enthalpy	kWh	-246798.99	-223520.49	-23278.49	0.00
11	V	Volume	m3/h	60.11	50.15	10.13	0.00
12	Ex	Exergy	kWh	33512.47	28640.61	4681.93	189.93
13	Cp	Heat Capacity	kWh				
14	P1g	Gas Phase	Nm3/h	10927.08	0.00	0.00	10927.08
15		H2O(g)	Nm3/h	0.00			
16		O2(g)	Nm3/h	2294.69			2294.69
17		N2(g)	Nm3/h	8632.40			8632.40
18	P2a	Water Phase	t/h	60.10	50.00	10.10	0.00
19		H2O	t/h	50.00	50.00		
20		H2SO4	t/h	10.10		10.10	
21		Fe(+2a)	t/h	0.00			
22		H(+a)	t/h	0.00			
23		SO4(-2a)	t/h	0.00			
24	P3s	Pure Phase	t/h	10.00	10.00	0.00	0.00
25		FeS	t/h	10.00	10.00		
26		S	t/h	0.00			
27	A1	Amount Phase 1	t/h	14.06	0.00	0.00	14.06
28	A2	Amount Phase 2	t/h	60.10	50.00	10.10	0.00
29	A3	Amount Phase 3	t/h	10.00	10.00	0.00	0.00
30	V1	Volume Phase 1	m3/h				
31	V2	Volume Phase 2	m3/h	60.11	50.15	10.13	0.00
32	V3	Volume Phase 3	m3/h				
33	D2	Density Phase 2	kg/m3	999.80	996.95	996.95	996.95
34	F2	FeSO4	Fe(+2a)	0.00	0.00	0.00	0.00
35	F2	H2SO4	H(+a)	0.00	0.00	0.00	0.00
36	U	H2SO4 concentration	g/l	0.00	0.00	0.00	0.00

Fig. 6. Input sheet, raw material amounts.

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Fig. 7. Input streams of the second unit cannot be edited.

43.6.2.   Output Sheet

In the output sheet, temperature row 7 and pressure row 8 are given, see **Fig. 8**. Values in the output sheet are calculated according to the settings in the Dist and Model sheets.

Fig. 8. Output sheet, temperature and pressure of the streams can be changed.

43.7.   Save and Run simulation and visualize results

It is good to Save Process and Backup often. It is good habit to save process after each step. Remember to save at least before starting the simulation, see **Fig. 9** and **Fig. 10**. There are many ways to visualize the simulation results, see **Fig. 11** and Chapter 40 (section 40.3.).

Fig. 9. Save Process and Save Backups icons.

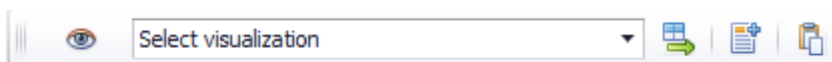**Fig. 10.** Run simulation and give iteration rounds to calculations.

Fig. 11. Visualize results and add stream tables, header or copy flowsheet to clipboard.