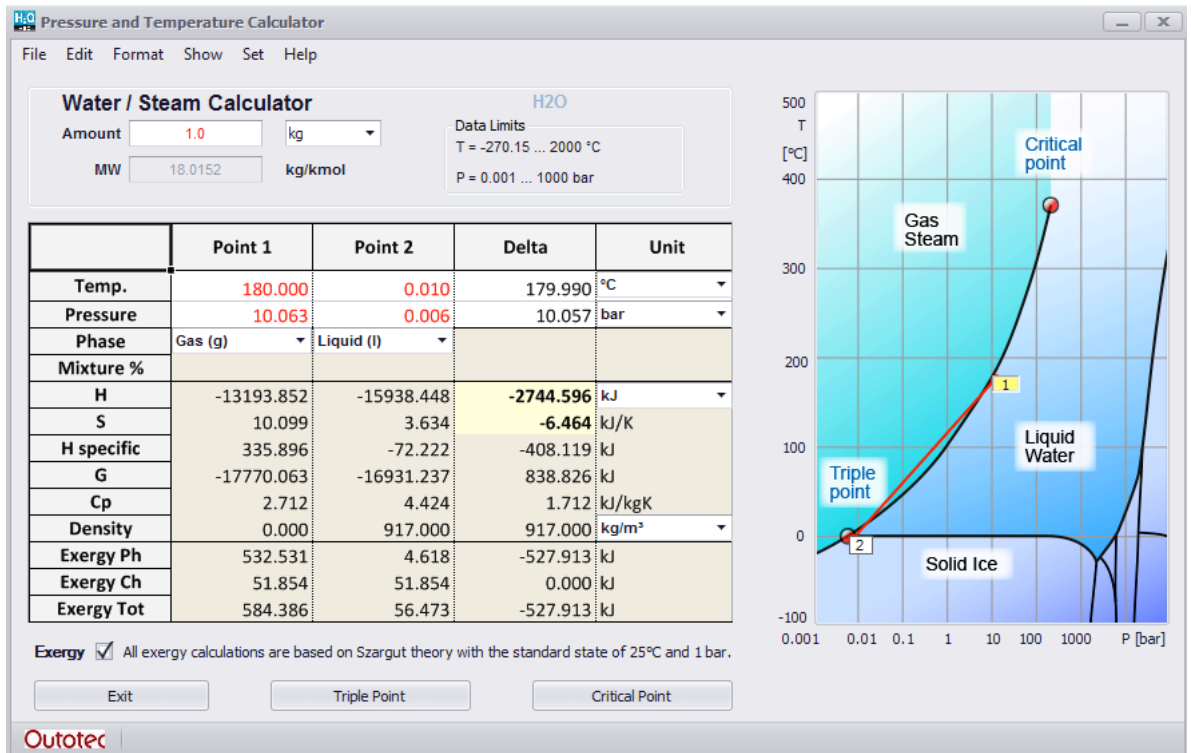# 25. Water Module

Fig. 1. Pressure-Temperature calculator for water.

The Pressure and Temperature calculator enables a complete thermodynamic description for a species, by allowing the user to specify not only the temperature, but also the pressure (partial). This calculator is currently only available for water, since the properties of steam, in particular, deviate significantly from those of an ideal gas, i.e. the heat capacity is purely a temperature-dependent function. In allowing the user to specify water/steam pressure, cases where pressure is of extreme importance can easily be calculated.

This calculator is a very useful replacement for **steam table books** and **Mollier diagrams**. By directly typing the pressure and temperature of the process points, or by simply clicking on the diagram, the process enthalpy and entropy are calculated along with several other useful thermodynamic data. The module is also available through the Heat and Material Balances module (Chapter *11. Heat and Material Balance*), where the pressure correction may be inserted into the worksheet as a cell formula.

25.1.   Basic Calculation Procedure

The calculator lets the user specify two *process points*; point 1 being the starting point and point 2 the end point. The calculator then calculates the *absolute values* for the two points and then the *difference* between them. The absolute values are mostly useful for density and heat capacity data, whereas the difference or delta values are useful for enthalpy and entropy data. A line between the two points may be drawn by selecting *Show/Line* from the menu. However, this line *does not necessarily represent the actual process path*, instead it makes the visualization of the two points easier. There are two basic ways of specifying the process points, which may also be combined:

Specifying points using the mouse:

1.   Specify the appropriate units from the comboboxes and the amount (kmol or kg) in the textbox.
2.   Activate one of the points by clicking on the appropriate box in the diagram. A yellow box indicates the active point and a white box the inactive point.
3.   Click on a position in the diagram and the selected point will move to that position and the data will automatically be recalculated. Note that if a *saturated state* is selected, the point will jump to the appropriate saturated curve if possible. It is also possible to use the drag-and-drop technique to move the selected point.
4.   Repeat steps 2 and 3 for the other point.
5.   If a point is on a saturated curve, the user may specify the Mixture %, i.e. the percentage of the *first* of the two phases in the mixture shown in the combobox in row 3 of the worksheet. The default value is 50 %.

Specifying points manually:

1.   Specify the appropriate units from the comboboxes and the amount (kmol or kg) in the textbox.
2.   Specify pressures and temperatures for the two points by simply typing them into the cells in columns 1 and 2. Note that if a *saturated state* is selected, the temperature or pressure will be calculated automatically. The values that are automatically calculated are indicated in a black font.
3.   If a point is on a saturated curve, the user has to specify the Mixture %, i.e. the percentage of the *first* of the two phases in the mixture given in the combobox in row 3. The default value is 50 %.
4.   If a point is on a saturated curve, the user may specify the Mixture %, i.e. the percentage of the *first* of the two phases in the mixture shown in the combobox in row 3 of the worksheet. The default value is 50 %.

Explanation of the p,T diagram:

The p,T diagram to the right of the window contains a few labels. These are explained below:

1. Triple Point

The triple point refers to the point where all three phases of water may exist simultaneously. This point is at T = 0.01 °C and p = 0.0061 bar. Most steam tables use this as the reference point, i.e. the absolute enthalpy and absolute entropy are set to zero. By selecting *Edit/Point 2 = Triple Point* from the menu, the second process point will automatically be set

to the triple point, which is also the default setting. This means that the enthalpy and entropy differences will have the same values as those found in most steam tables if the phase is set to *liquid* at the triple point.

2. Critical Point

When the temperature rises above the critical point, it is no longer possible to clearly distinguish between the liquid and the gaseous phase. Such a condition is referred to as *supercritical*. The critical point for water is at T = 373.946 °C and p = 220.64 bar. It is important to know that above this point the program still specifies the phase of the point, although there are no longer any actual phase transitions between the phases.

3. Saturated Curves

There are three saturated curves in the diagram. These are *gas/liquid*, *gas/solid,* and *liquid/solid*. A point located on any one of these curves indicates that the two phases are in equilibrium. The three curves join at the *triple point*, which is where all three phases can exist simultaneously. The user may force a point onto the saturated curve by selecting either **Sat. (g,l)**, **Sat. (g,s)** or **Sat. (l,s)** from one of the phase comboboxes in row 3.

4. Solid Ice

A stability area consisting of several solid ice phases, with different crystal structures, some of which are shown in the diagram. However, there are no data available for the high pressure solid phases.

Calculation worksheet:

The calculation worksheet is to the left of the window. The first four rows are input rows and the last six rows show the results. The input rows are explained below:

1. Temperature

The temperature unit may be either °C or K, depending on the temperature unit combobox. The temperature is automatically calculated when the Sat. (l,s) state is selected.

2. Pressure

The pressure unit may be either bar or MPa, depending on the pressure unit combobox. The pressure is automatically calculated when the Sat. (g,l) or the Sat. (g,s) state is selected.

3. Phase

There are three different pure phases available for water: Solid (s), Liquid (l), and Gas (g). These three phases may be combined on the *saturated curves* and they are specified as: Sat. (g,l), Sat. (g,s) and Sat. (l,s). At the triple point a mixture of all of these is possible, however, only a mixture of two is possible in this module. When a *pure phase* is selected, the actual phase is automatically selected according to the user input (manually or with the mouse). When a *saturated state* is selected, the temperature or pressure is automatically calculated, which is then indicated in a black font. For gas/liquid and gas/solid mixtures the pressure is calculated automatically and for liquid/solid mixtures the temperature is calculated automatically. Note that when moving outside the limits of the saturation curve,

the phase will automatically change into the corresponding pure phase of the specified point.

4. Mixture %

It is possible here to enter the mixture percentage of the saturated state. This is the same as the *dryness percentage* of steam when the point is on the saturated gas/liquid curve. The percentage always refers to the amount of the first phase in the total mixture, e.g. the gas percentage in a gas/liquid mixture. This is set to 50 % by default and only visible when a saturated state is specified.

The results of the calculation are shown in the same table below the input. The data calculated includes:

1. Enthalpy (H) and Entropy (S)

The enthalpies and entropies for the two process points are calculated using the reference point T = 25 °C and p = 1 bar. This differs from what is normally found in steam tables, where the reference point is T = 0.01 °C and p = 0.0061 bar (triple point for water). This means that only the *differences in enthalpy and entropy are of importance*, since they are independent of the choice of reference points. Point 2 is therefore *by default set to the triple point*, which means that the enthalpy and entropy differences, indicated by a yellow background, give the values normally found in steam tables.

2. Specific Enthalpy (H specific)

The specific enthalpies are the enthalpies when the phase transformations are ignored. In other words, the enthalpy released/gained when water is cooled/heated to 25 °C at constant pressure. Therefore, the specific enthalpy is zero at 25 °C.

3. Gibbs Energy (G)

These cells show the Gibbs Energy for the two points.

4. Heat Capacity (Cp)

These cells show the specific heat capacity at constant pressure for the two points.

5. Density

These cells give the densities for the two points. The densities are interpolated or extrapolated from the Excel file Density_H2O.xls located in the .\HSC8\Databases directory. Please do not modify this file.

Other important terms:

1. Isentropic process

If the entropy is constant through a process, i.e. the entropy difference is zero, the process is called *isentropic*. An isentropic process is an ideal process and real processes are often compared to the corresponding isentropic process.

2. Isentropic efficiency

An isentropic process generates no entropy and may therefore be considered an ideal process. It is useful to compare real processes to that of the isentropic through the isentropic efficiency. The isentropic efficiency for a *compressor* or *pump* is defined as
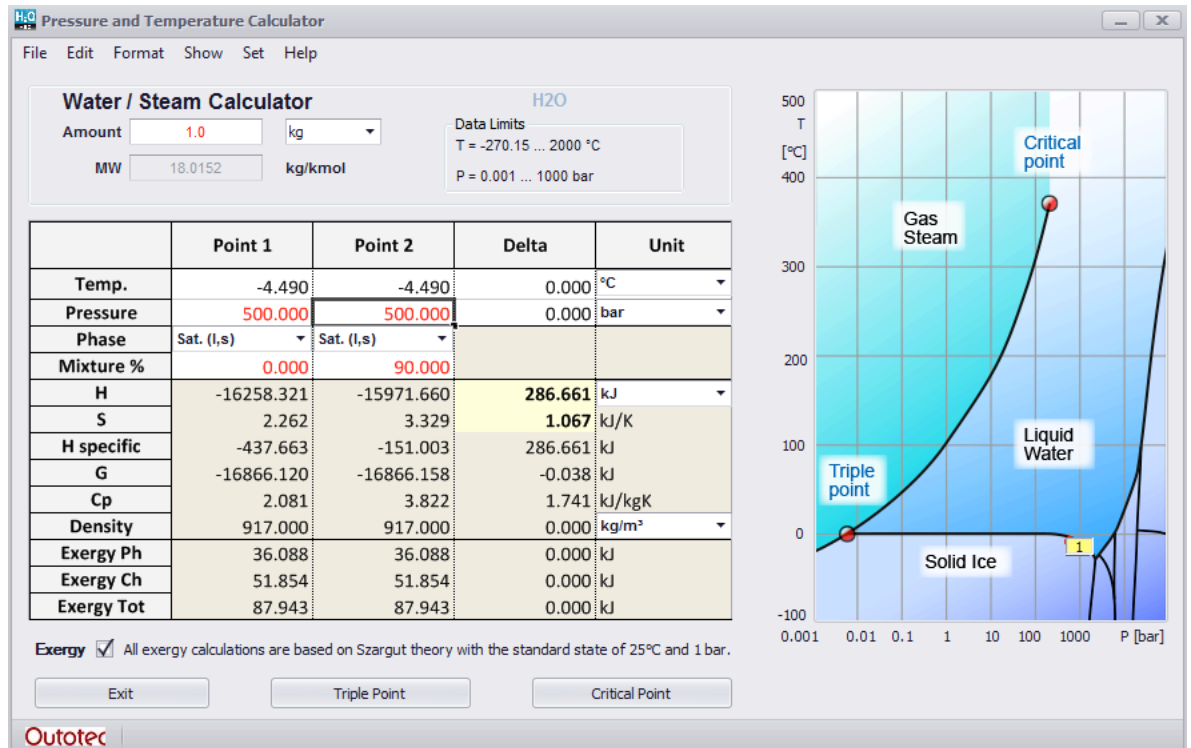
$$\eta_{s,c} = \frac{\Delta h_s}{\Delta h},$$
(1)

where Δh is the *real enthalpy difference* and Δh_s is the *isentropic enthalpy difference*. The isentropic efficiency for a *turbine* is defined as

$$\eta_{s,t} = \frac{\Delta h}{\Delta h_s}.$$
(2)

An isentropic process is always *adiabatic*, although an adiabatic process is not necessarily isentropic.

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25.2. Calculation Examples

25.2.1. Ice Melting at High Pressure

Fig. 2. Melting of ice at a pressure of 500 bar.

The example in **Fig. 2** shows the enthalpy and entropy change of 1 kg of solid ice melting at a constant pressure of 500 bar, until 90 % of the *total* mixture is liquid water. The enthalpy difference is ~290 kJ and the process therefore endothermic. The entropy difference is ~1.079 kJ/°C and the process therefore generates entropy. The melting point of ice at 500 bar is calculated automatically, since the point is on the saturated liquid/solid curve, and it is roughly –4.5 °C. This pressure is achieved, for example, when pressing a sharp object against an icy surface, which then melts due to the decreased melting point temperature.

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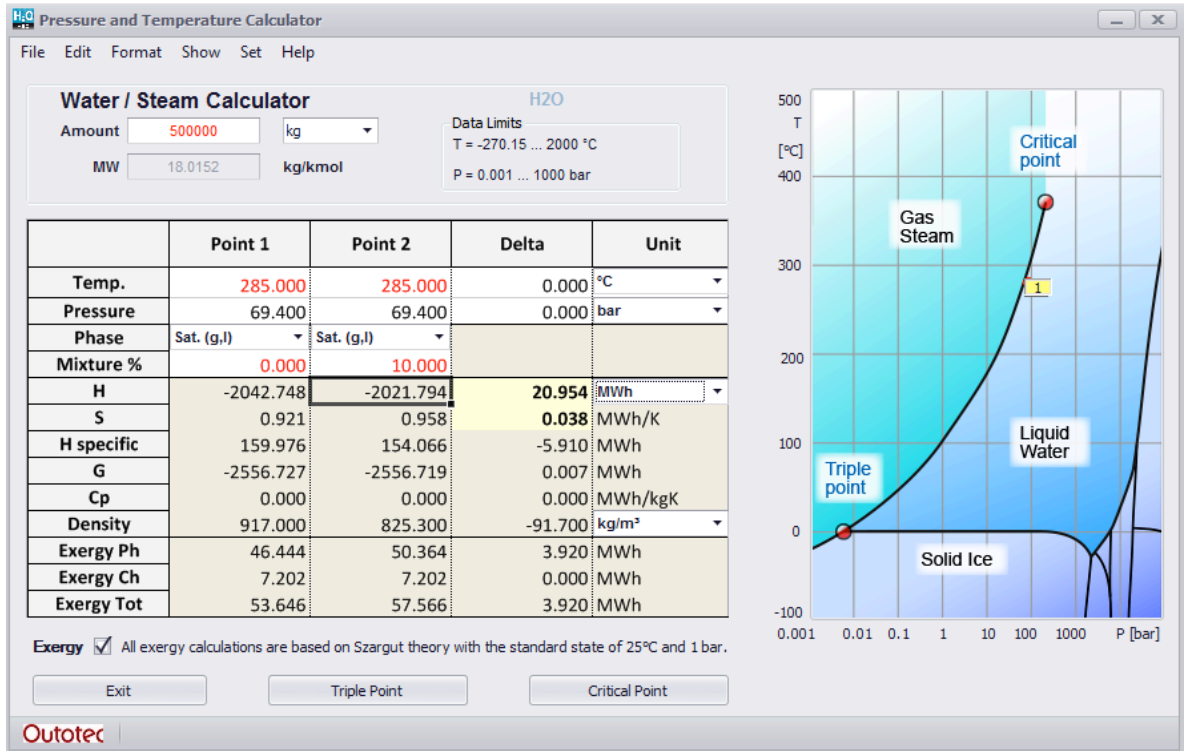### 25.2.2.   Evaporation Process in a Heat Recovery Boiler

Fig. 3. Evaporation process.

The example in **Fig. 3** shows the evaporation process in a heat recovery boiler, when the mass flow is 500 t/h (Amount: 500000 kg, Unit: MWh). The temperature is 285 °C and the pressures are calculated automatically, since the saturated gas/liquid state is selected. The transferred heat is ~21 MW, when 10 % of the *total* water flow evaporates. This is equivalent to a water/steam ratio of 90%/10% = 9. The entropy generation of ~0.038 MW/°C indicates that the process is not isentropic.
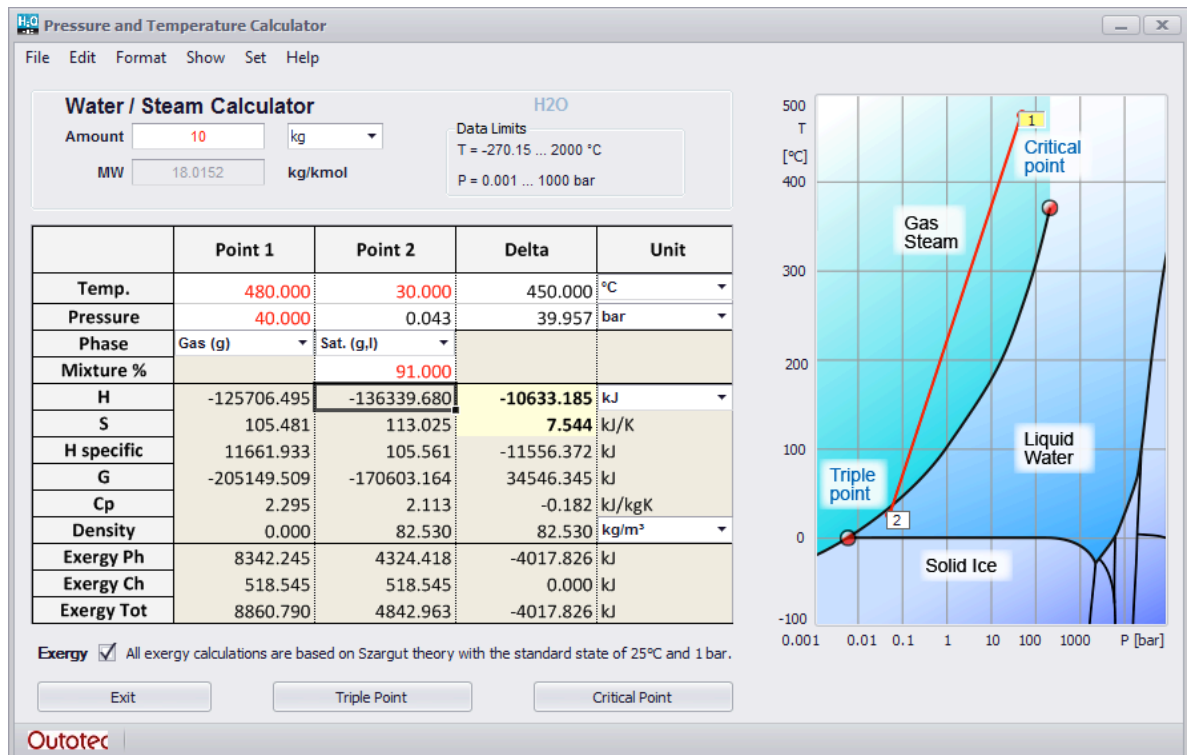
25.2.3. Steam Turbine Process

Fig. 4. Steam turbine process.

A simple steam turbine process is shown in **Fig. 4**. The calculation shows that the net enthalpy for a mass flow of 10 kg/s is –10633 kW and thus exothermic, i.e. the enthalpy is released in the form of work on the shaft. The entropy generation is 7.5 kW/°C and the process is therefore not isentropic. By decreasing the Mixture % (in this case ~81.7 %), the process may be compared with the ideal isentropic process for which there is no entropy generation. The enthalpy released in the isentropic process is –12903 kW and the isentropic efficiency is therefore, according to Equation (2), $\eta_{s,t}$ = -10633 kW / -12903 kW = 0.82.

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25.3.   Detailed Description

25.3.1.   Pressure Correction in the Database

The pressure-corrected calculations are based on new pressure-specific species in the database. They are of the form S(**X**bar**P**), where S denotes the species, **X** the pressure (partial) in bars and **P** the phase. The phase is only specified for gaseous species. The only currently available species is H_2O (water), and the pressure-corrected species are found in the database as $H_2O(0.01bar)$, $H_2O(0.01barg)$, $H_2O(100bar)$, $H_2O(100barg)$, etc.; see **Table 1**. Note that if the phase is not specified, it may be either solid or liquid depending on the temperature. For *supercritical steam*, that is for T μ 373.946 °C, a gaseous phase is used for p < 220.64 bar and a liquid phase for p μ 220.64 bar, although the two phases are impossible to separate in reality.

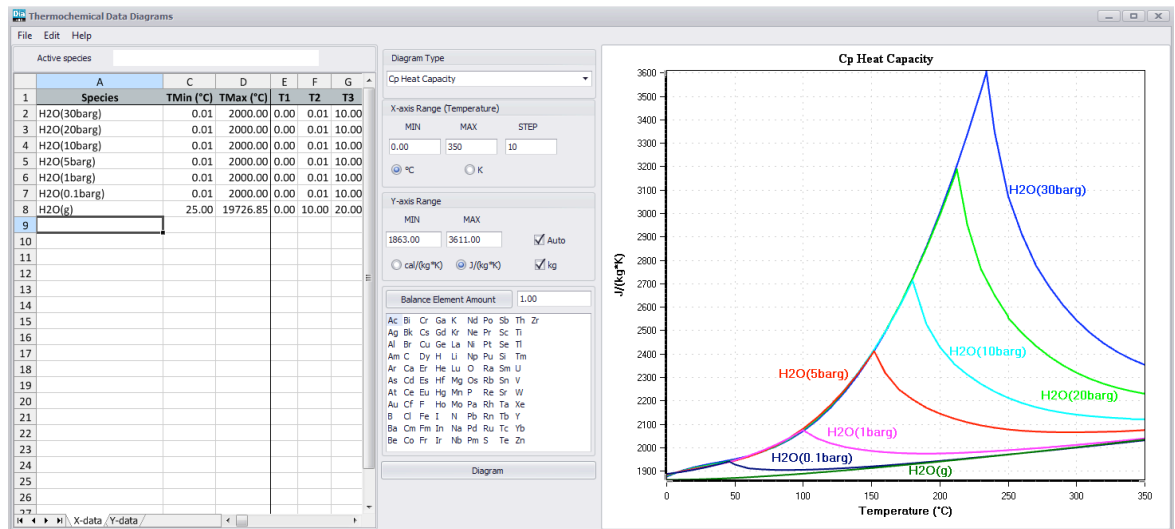**Table 1.** Pressure-corrected species currently available in the HSC database.

Pressure / bar	Solid/liquid species (ice/water)	Gaseous species (steam)
0.01	H2O(0.01bar)	H2O(0.01 barg)
0.05	H2O(0.05bar)	H2O(0.05 barg)
0.1	H2O(0.1bar)	H2O(0.1 barg)
0.5	H2O(0.5bar)	H2O(0.5 barg)
1	H2O(1bar)	H2O(1 barg)
5	H2O(5bar)	H2O(5 barg)
10	H2O(10bar)	H2O(10 barg)
20	H2O(20bar)	H2O(20barg)
30	H2O(30bar)	H2O(30barg)
40	H2O(40bar)	H2O(40barg)
50	H2O(50bar)	H2O(50barg)
60	H2O(60bar)	H2O(60barg)
70	H2O(70bar)	H2O(70barg)
80	H2O(80bar)	H2O(80barg)
90	H2O(90bar)	H2O(90barg)
100	H2O(100bar)	H2O(100barg)
200	H2O(200bar)	H2O(200barg)
300 *	H2O(300bar) *	
400 *	H2O(400bar) *	
500 *	H2O(500bar) *	
600 *	H2O(600bar) *	
700 *	H2O(700bar) *	
800 *	H2O(800bar) *	
900 *	H2O(900bar) *	
1000 *	H2O(1000bar) *	

 * Supercritical pressures

Since water is in a liquid form at the reference temperature of 25 °C for pressures higher than 0.032 bar, the Cp functions for steam follow the *saturated steam curve* below the boiling point. This means that *the pressure is not kept constant below this point* and thus the pressure value in the species name, i.e. **X** in H_2O(**X**barg), is no longer valid for these temperatures. This may be seen in **Fig. 5**, where the Cp functions of steam at different pressures are shown. When the temperature drops below the boiling point, the Cp functions follow the saturation curve, where the partial pressure also reduces with the temperature. This also means that the *total enthalpy* and *entropy* curves below the boiling point will not join as expected and therefore these curves are *comparable with each other only for values above or equal to the boiling point*. This is, however, not an issue when studying only one pressure-corrected species at a time since the enthalpy/entropy differences are then still valid. Naturally, this is never a problem in the Pressure and Temperature calculator, since it automatically chooses the liquid phase when the temperature drops below the boiling point for a constant pressure.

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For the solid/liquid phases, i.e. $H_2O(Xbar)$, this reference point does not cause any problems, since at least one of the two phases (liquid and/or solid) exist below 25 °C and at pressure X. They can therefore easily be extrapolated up to 25 °C when necessary. Extrapolation above the boiling/sublimation points at different pressures are shown as dotted curves in the diagrams, which also means that the liquid/solid phase does not exist at these temperatures.

Fig. 5 also shows that the ideal gas approximation, indicated by the label $H_2O(g)$, is generally more accurate for low pressures and high temperatures. The ideal gas curve can be seen below the constant pressure curves. The rule of thumb is that the accuracy of the ideal gas approximation increases the further away you move from the critical point.

Fig. 5. Cp functions for steam at different pressures.

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25.3.2.   Basic Theory

In order to calculate the enthalpy and entropy at different pressures, slight modifications have to be made to the enthalpy of formation and standard entropy at 25 °C, i.e. the H_f term of equations 1 and 3 in Chapter *8. Introduction*. Most steam tables use the *triple point* of water (T = 0.01 °C, p = 0.0061 bar), instead of the standard reference point used in HSC (T = 25 °C, p = 1 bar), therefore the *absolute* enthalpies and entropies will be different from those found in steam tables. However, since point 2 is by default set to the triple point, the enthalpy and entropy differences (cells C5 and C6) are the same as the absolute values found in steam tables and diagrams. This is achieved by selecting *Edit/Point 2 = Triple Point* from the menu and choosing the *liquid* phase.

The pressure-corrected enthalpy at temperature T and pressure p is calculated as

$$H(T,p) = H_f^{'}(298.15K,p) + \int_{298.15K}^{T} Cp(T,p)dT + \sum H_{tr} , \qquad (3)$$

where H'_f(298.15K, p) is the modified enthalpy of formation at pressure p, and H_{tr} is the enthalpy of a phase transformation. The entropy at pressure p may be calculated in a similar manner as

$$S(T,p) = S_0^{'}(298.15K,p) + \int_{298.15K}^{T} \frac{Cp(T,p)}{T}dT + \sum \frac{H_{tr}}{T_{tr}} , \qquad (4)$$

where S'_0 (298.15K, p) is the modified standard entropy at pressure p, and H_{tr} is the enthalpy of a phase transformation at temperature T_{tr}.

The Cp function still utilizes the Kelley equation, but the coefficients are now pressure-dependent according to

$$Cp(T,p) = A(p) + B(p) \cdot 10^{-3} + C(p) \cdot 10^{5} \cdot T^{-2} + D(p) \cdot 10^{-6} \cdot T^{2} , \qquad (5)$$

where A(p), B(p), C(p), and D(p) are the coefficients fitted at different pressures p. See **Table 1** for a list of the current pressures available.

The temperature or pressure of a saturated curve is calculated through one of Equations (6)-(8). The pressure for a saturated *gas/liquid mixture* is

$$p(T) = 0.1 \cdot \exp\left(\frac{11.78 \cdot (T - 372.79)}{(T - 43.15)} \right), \qquad (6)$$

where T is the temperature in K and p the pressure in MPa. The pressure for a saturated *gas/solid mixture* is

$$p(T) = \frac{10^{10.5380997 - \frac{2663.91}{T + 0.01}}}{10000} , \qquad (7)$$

where T is the temperature in K and p the pressure in MPa. The temperature for a saturated *liquid/solid mixture* is

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$$T(p) = -0.009p + 273.16 \qquad (8)$$

where T is the temperature in K and p the pressure in MPa. These equations correspond to the saturated curves in the p,T diagram and are utilized in the module whenever a saturated state is selected.

In order to calculate the influence of pressure on the enthalpy and entropy below the freezing point, a pressure correction term is used. The correction term is

$$\Delta h_{T=const} = \left(1 - T_f \alpha_{v,ice}\right) v_{ice}\left(p_f - p_0\right) \qquad (9)$$

where T_f is the temperature at the freezing point, p_f is the pressure at the freezing point, $\alpha_{v,ice}$ is the coefficient of thermal expansion, and v_{ice} is the specific volume.

25.4.   Limitations

- The current temperature and pressure range is –200 °C to 2000 °C and 0.001 bar to 1000 bar.
- Accuracy in c_p values and density values decreases close to the critical point.
- Accuracy in saturated liquid/gas pressure decreases close to the critical point.
- Uncertainties in c_p values for ice at different pressures.
- The high temperature and pressure region (800 °C - 2000 °C and 100 bar - 1000 bar) is extrapolated.
- The low pressure region (0.001 bar - 0.01 bar) is extrapolated.