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# AQSOL001 software

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## How to install the software

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To install the software:

- Log in to the computer with administrator rights.
- Run the AQSOL001setup.exe file directly from the AQSOL001setup.zip file, without extracting any files from the zip file.
- Copy the Excel files, AQSOL001.xlsm and AQSOL001\_Validation.xlsm and AQSOL001manual to a user folder.
- Do not open the Excel files until you have run AQSOL001setup.exe.
- In some cases, a restart of the computer is required before the dynamic link between the Excel file and the DLL file can be established.

The software is operated from the Microsoft Excel macro-enabled workbooks (\*.xlsm files) based on the AQSOL001.xlsm file, which can be copied and renamed.

After you open the AQSOL001.xlsm file, make sure to enable content (macros).

You can save the Excel file under any name you choose. It is important to save it as an “Excel macro-enabled workbook” (\*.xlsm file).

The AQSOL001\_Validation.xlsm file contains a number of calculated phase diagrams compared with experimental data. There are also sheets with density calculations at different temperatures plotted together with experimental values.

## About the software

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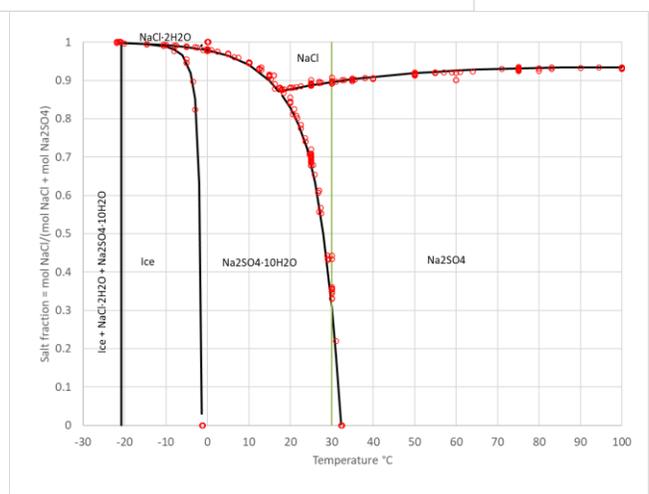
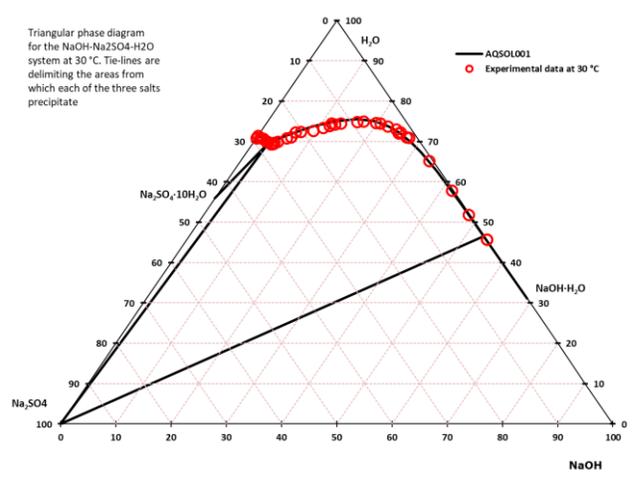
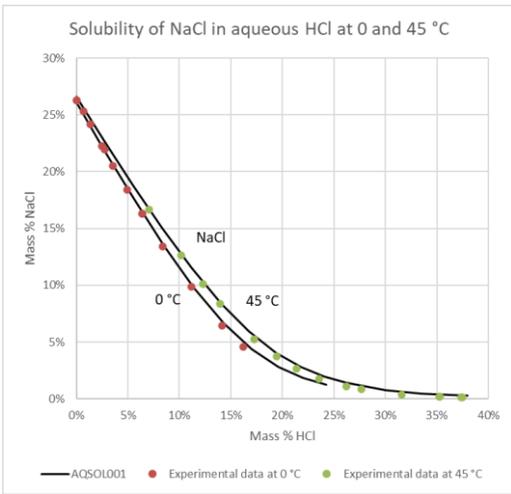
The software consists of 32-bit and 64-bit Dynamic Link Libraries and two Microsoft Excel Macro-Enabled Workbooks. The DLL files contain the Extended UNIQUAC thermodynamic routines required for equilibrium calculations in solutions with salts.

The program can be used for calculating phase diagrams and performing general phase equilibrium calculations for aqueous solutions with salts. The program also gives information on the speciation of the solution, the enthalpy of formation, the heat capacity, the ionic strength, the bubble point pressure of the solution, density, and more.

The software is the property of Aqueous Solutions ApS., Søborg, Denmark.

You are not allowed to sell this software to others.

If you find problems or errors with this software or if you have suggestions for improvements, you are encouraged to send this information as detailed as possible to [kaj@phasediagram.dk](mailto:kaj@phasediagram.dk).



**Phase diagram for the NaCl - Na<sub>2</sub>SO<sub>4</sub> - H<sub>2</sub>O system as a function of temperature.**

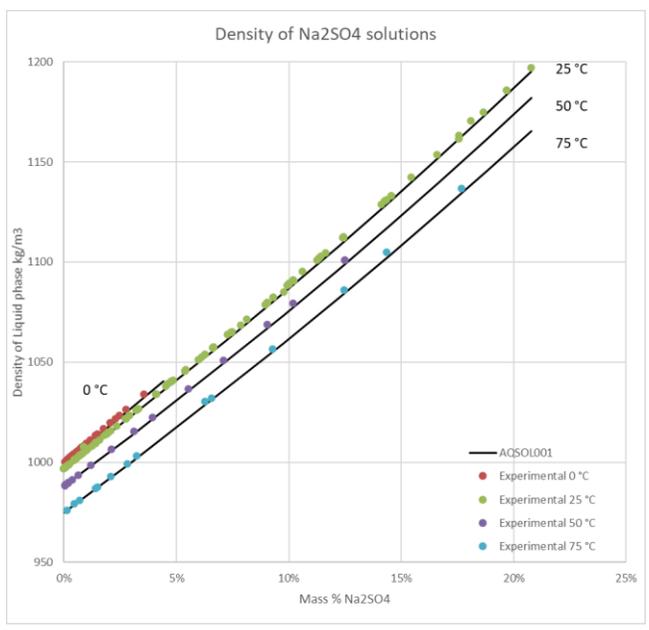
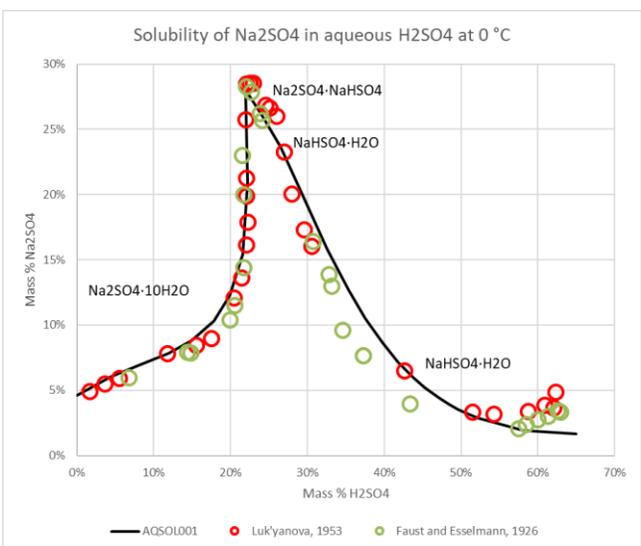
The phase diagram to the left has temperature on the x-axis and "Salt fraction" on the y-axis.

The lines mark solutions that are in equilibrium with two salts simultaneously. The water content of the solutions can't be inferred from the diagram. From this type of diagram, the temperature range and the salt composition range for the precipitation of a specific salt can quickly be determined.

The red circles indicate experimental data for solutions saturated with two solids. These data were reported in the literature.

According to the model, the ternary eutectic temperature is -20.7 °C. In literature, this temperature is reported slightly lower, -21.9 °C (Chrétien, Caliche, 9(1928)248-257).

The green vertical line at 30 °C marks the 30 °C isotherm. It passes through an area where Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O precipitates, then an area where Na<sub>2</sub>SO<sub>4</sub> precipitates, and finally an area where NaCl precipitates.



## How to use the software

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The AQSOL001.xlsm file contains the sheets “props” and “calculation\_template”.

### Calculation sheet

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The “Calculation\_template” sheet is meant as a template for performing calculations. You can make copies of the “Calculation\_template” sheet and perform your calculations in these sheets.

The program accepts input in degree centigrade for the temperature and grams of each of the aqueous species. When you input amounts of ions in grams you will sometimes experience that the amounts of cations do not match the amounts of anions. This is for example often the case if the input data are the results of a laboratory analysis.

To minimize the effect of an unbalanced charge, the program contains two dummy ions,  $NN^+$  and  $NN^-$ . The program will automatically use one of these ions to balance the charges. The two dummy ions have been given properties that minimize their interactions with other ions.

If your input data are supposed to be electrically balanced, the amounts of  $NN^-$  and  $NN^+$  are both zero. You can watch the amounts of  $NN^+$  and  $NN^-$  to check that the ions are present in stoichiometric proportions.

After you finish writing your input, you can right away read the results:

The first part of the results is a statement on the speciation. The amounts of aqueous species are given in grams of each species. Next, the amounts of solids precipitated are stated. In the following rows, the “Saturation index before equilibrium” is given. Further down, “Saturation index after equilibrium” is given.

The saturation index is defined as the ionic activity product divided by the solubility product. At equilibrium, the saturation index is therefore equal to one. If a salt is unsaturated, its saturation index is less than one. If the salt is supersaturated, its saturation index is larger than one. Any salt with a saturation index higher than one can precipitate if it has favorable kinetic conditions. At thermodynamic equilibrium, which can take ages to achieve, the solids with the lowest Gibbs energy form the precipitate. The “Saturation index before equilibrium” can be used to evaluate which salts might precipitate from a certain solution. The “Saturation index after equilibrium” gives the saturation index after thermodynamic equilibrium is achieved.

In the last paragraph, the following properties are provided:

- Enthalpy of liquid, J/g. This is the enthalpy of formation of the aqueous solution at the given composition and temperature.
- Enthalpy of solid, J/g. This is the enthalpy of formation of the precipitated solids at the given temperature.
- Heat capacity of liquid, J/(g·K). This is the heat capacity of the aqueous solution at the given composition and temperature.
- Bubble point pressure, bar. This is the bubble point pressure of the solution in thermodynamic equilibrium.
- pH – calculated as minus the logarithm base 10 of the hydrogen ion activity (molality scale). The hydrogen ion activity is calculated as the molality of the hydrogen ion times the mean ionic molal activity coefficient. pH-meters are usually calibrated to very dilute solutions. At

increasing ionic strength, there will therefore be an increasing difference between the calculated pH and the measured pH.

- Mean ionic molal activity coefficient.
- Ionic strength, mol/(kg H<sub>2</sub>O). This is the ionic strength of the equilibrium solution calculated on the molality scale.
- Water activity
- Density of aqueous phase
- Density of solid phase

### Property sheet, “props”

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In the sheet “props”, some properties of the species are listed. These properties are molar mass, heat capacity at 25°C and enthalpy of formation at 25°C.

The cells with molar masses of the ions have been named so that you for example can refer to the molar mass of the sodium ion by writing “=NaMW”. The cell will be given the value 22.9897693, the molar mass of the sodium ion

In the first row of the “props” sheet, there is a button for “License information”. By pressing this button, you can see when the software expires. Then you can return to the website ([www.phasediagram.dk](http://www.phasediagram.dk)) and download a new version.

In addition, there is a column with “Factor to be multiplied with solubility product to stop a salt from precipitating”. A cell contains a value for “Time out”. It is explained below how to use these cells.

### Molar mass, heat capacity at 25°C and enthalpy of formation at 25°C

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The molar masses, the Gibbs energy of formation, the enthalpy of formation, and the heat capacity at 25°C used by the program are given for your information. The molar masses are helpful in converting between moles and grams. The program is not reading the data from the props sheet. Even if you change the properties manually in the “props” sheet, it will therefore not be reflected in the calculation.

### Factor to be multiplied with solubility product to stop a salt from precipitating

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Sometimes you might want to disable one salt from precipitating in the calculation due to for example kinetic considerations. Then you can replace the factor 1 in column G for that solid with a larger number and it will require a certain supersaturation before that species precipitates. The solubility product of each salt is multiplied with this factor.

Some thermodynamic conditions need to be fulfilled before a certain salt can precipitate. Kinetics often plays a role in determining which one of the supersaturated salts actually precipitate. If you have knowledge about which salt actually precipitates in your system, you can disable the precipitation of another salt by increasing its factor. The program will read column G prior to any calculation in order to include this factor. This feature is for example useful in connection with gypsum-anhydrite-hemihydrate precipitation

## Time out

The calculation of equilibrium in multi-component solutions can sometimes take a considerable amount of time, especially in solutions from which 4-5 or more solid phases precipitate. In order to limit the time you have to wait for the calculation to be completed, a time out value is set. The default value is 25 seconds. If a calculation takes more than 25 seconds to complete, the calculation will be interrupted and a dialog box appear to inform you that the calculation was stopped due to time out. In order to complete the calculation, you can increase the time out value.

## Software Warranty

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