
AQSOL001 software

The installation package AQSOL001.zip contains

- the file you are reading now, AQSOL001.pdf.
- Excel Macro-Enabled Workbooks, AQSOL001.XLSM and AQSOL001_Validation.XLSM
- the AQSOL001_Setup.exe file.

Double click the AQSOL001_Setup.exe file and run the installation directly from the zip file. Copy the Excel files and this manual to the folder where you want to use the software. After the installation, you can run the software from the Excel files (AQSOL001.XLSM) or copies that you might create.

About the software

The software consists of a Microsoft Excel Macro-Enabled Workbook, AQSOL001.XLSM and its associated dynamic link libraries. The macro in this Excel file calls the Extended UNIQUAC thermodynamic routines required for equilibrium calculations in solutions with salts. If the Excel file does not respond to changes in input fields, #VALUE – error, it usually helps to restart the computer. Otherwise, please contact info@phasediagram.dk.

The Microsoft Excel file contains various calculation examples that demonstrate how the thermodynamic routines can be used. The calculation examples in the Excel file are compared with experimental data from the open literature so that the accuracy of the calculations can be evaluated.

This version of the software includes the ions Na^+ , H^+ , OH^- , Cl^- , SO_4^{2-} , and HSO_4^- . The program can be used for calculating phase diagrams and performing general phase equilibrium calculations and process simulations for aqueous solutions with these ions. 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 and more.

The software is the property of Aqueous Solutions ApS, Søborg, Denmark. This software license will expire after approximately one year. You can download a new version with a new one year license at www.phasediagram.dk any time. You can also contact info@phasediagram.dk to purchase a license for an extended version of this software including additional ions.

You are not allowed to sell this software, but you can pass it on for free.

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 info@phasediagram.dk.

How to use the software

The AQSOL001.xlsm file contains the sheets “props” and “calculation template”. The AQSOL001_Validation.xlsm file includes a number of sheets with application examples such as

calculated phase diagrams and calculated properties of salt solutions. In these sheets, the model is validated by comparing the calculated graphs to experimental values.

Calculation template sheet

In the calculation template sheet you can perform calculations for aqueous electrolyte solutions.

To create a new column for calculation, the easiest is to copy and paste an existing column, from the cell containing the input temperature to the cell that contains the calculated water activity. The input cells in the new column can then be modified to make a new calculation. The calculation template sheet can be copied and renamed within the same Excel file.

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 amount of cations does not match the amount of anions. This is for example often the case if the input data are the results of a laboratory analysis.

In order 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 so the charge becomes balanced. The two dummy ions have 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 you have input the ions 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 given:

- 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 H₂O). This is the ionic strength of the equilibrium solution calculated on the molality scale.
- Water activity

Property sheet, “props”

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. In addition, there is a column with “Factor to be multiplied with solubility product to stop a salt from precipitating”. Cell C32 contains a value for “Time out”. Cell B1 gives access to license information.

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

The molar masses, the heat capacity at 25°C and the enthalpy of formation at 25°C are given for your information. The molar masses are helpful in converting between moles and grams. The cells containing the molar mass of water and of ions are named. In order to retrieve the molar mass of for example the sodium ion, it is sufficient to write NaMW in a formula.

The heat capacity and the enthalpy of formation listed in the props sheet are identical to the ones used by the program at 25°C. At other temperatures, the program will calculate the values appropriate at that temperature. The program is not reading the data from the excel sheet. Even if you change the properties manually in the “props” sheet, it will not be reflected in the calculation.

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

Sometimes you might want to disable one salt from precipitating in the calculation. Then you can replace the factor one for that solid with a larger number and it will require a certain supersaturation before that species precipitates. 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 F prior to any calculation in order to include this factor.

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 10 seconds. If a calculation takes more than 10 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.

License information

By clicking cell B1 in the props sheet, you get information about the day the software license will expire.

Array formula/Array function

The function call that displays all the results is called "equilib". It is an array function and there is a specific procedure for calling it. You can for example write "=equilib(" in a cell. Then click on the *fx* symbol to the left of the address line. Then excel will prompt you for the input to the function. Remember to scroll down to give all the inputs. After finishing the input, you press enter, and the cell will display the first number in the solution vector. To display the complete solution, select the same cell again together with the 60 cells below. Then press F2 followed by pressing Ctrl+Shift+Enter simultaneously. The cells will then contain the results of the calculation.

Software Warranty

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