Technical Report WinSGW

# The WinSGW Program – A Powerful Tool for Equilibrium Calculations in Multi Component and Multi Phase Systems

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# Technical Report WinSGW 2.x – 2002

## The WinSGW Program – A Powerful Tool for Equilibrium Calculations in Multi Component and Multi Phase Systems

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More information about the program can be found at the WinSGW website:
http://www.chem.umu.se/dep/inorgchem/

## Updated 2012 to match WINSGW 4.x.

More information is available at http://WWW.WINSGW.SE

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# 1 Introduction

SolGasWater was elaborated at the Department of inorganic chemistry at Umeå University (Eriksson 1979). The program was developed in a DOS environment and enabled computerised calculations of large and complicated chemical equilibrium systems. The program made it possible to carry out these types of calculations on an ordinary computer and therefore became an appreciated tool for analyses of equilibrium systems. During the years a number of modifications of the original code was carried out aiming for a more powerful and flexible program. Due to the evolution of computer technology during the last decade and the wish for a user-friendlier interface, adapted to teaching and non-specialist scientists, an initiative to a new Windows based SolGasWater (WinSGW) was taken in 1999. This initiative together with the results of continuous tests with the program by students and scientists at Umeå University lead to even further development of the original SolGasWater code in cooperation with Gunnar Eriksson. Parallel to this work new models were incorporated to adapt to the present requirements of the scientific world.

# 2 Theory

All equilibrium analytical calculations are in principle based on the same fundamental concepts and formulaes. These concepts form the general computational basis in WinSGW and are described below.

## 2.1 The equilibrium reaction

The equilibrium reaction states the type of chemical equilibria that will be used for describing a given chemical system. It gives the relationship between components A, B, C, ... and formed complexes $A_pB_qC_r...$:

$$pA + qB + rC \ldots \rightleftarrows A_pB_qC_r\ldots \qquad [1]$$

where $p, q, r, \ldots$ are the stoichiometric coefficients in the reaction. The phase notations in reaction [1] have been omitted but will be commented on below. Depending on how the components have been chosen, the *pqr*-values may attain positive or negative values, which means that the component in question is consumed or formed. Negative values are for instance found when component A represents the proton and a deprotonation or hydrolysis reaction is considered. The components A, B, C in [1] can be denoted (1,0,0), (0,1,0) and (0,0,1). This formalism has been shown to be a very convenient basis for the general mathematical-numerical treatment of complicated equilibrium systems. Sillén and his co-workers (Dyrssen 1961) were the first to use it and numerous examples can, for instance, be found in publications from the Departments of Inorganic Chemistry at KTH, Stockholm and at Umeå University.

Following a commonly used nomenclature, both components and complexes will be denoted as species. As a rule, chemically well characterised, preferably mononuclear, species should be chosen as components. The number of components is defined as the smallest number of species by which all other species can be expressed; i.e. the components are the independent variables being used when solving the mass balance equations. For example when $H^+$ is chosen as a component, $OH^-$ is considered as a complex and vice versa. In WinSGW even solid phases, gas molecules, and active sites on a particle surface will be referred to as species.

In most common cases all species are present in an aqueous phase (aq). However, the WinSGW program can handle other fluid phases as well as coupled equilibria between aqueous species, species in a gas phase, solid phases, species at the surfaces of solid phases (commonly referred to as surface complexes) and species in a Donnan phase. The program can handle up to 300 species formed from a maximum of 15 components, of which 5 can be surface components. Within the calculations a maximum of 31 solid phases are allowed.

## 2.2 The Law of Mass Action and the Formation Constant

The Law of mass action determines the activity relations between components and formed complexes. Provided that the activity coefficients are kept constant, the concentration of each species, x, can then be calculated from:

$$[x] = \beta \cdot a^p b^q c^r \ldots \tag{2}$$

where [x] and a, b, c,… are the equilibrium concentrations of the formed species and components respectively, and $\beta$ is the formation (equilibrium) constant for the species formed. The formation constant is dependent on temperature ($T$ ), ionic strength ($I$ ) and, in the case of surface complexes, also the charge at the surface ( *cf.* paragraphs 2.4, 2.5 and 2.6).

## 2.3 Mass balance equations

The total concentration of each component is given by the mass balance equations:

$$A = a + \sum p \cdot \beta \cdot a^p b^q c^r \ldots = \sum_x p \cdot [x] \tag{3}$$

$$B = b + \sum q \cdot \beta \cdot a^p b^q c^r \ldots = \sum_x q \cdot [x] \tag{4}$$

$$C = c + \sum r \cdot \beta \cdot a^p b^q c^r \ldots = \sum_x r \cdot [x] \tag{5}$$

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## 2.4 Temperature dependency of the formation constant

In WinSGW it is possible to perform calculations at other temperatures than the one for which the formation constants are given by using the van’t Hoff equation. The van’t Hoffs equation can be derived from basic thermodynamic relationships relating the Gibbs free energy and the equilibrium constant. The deviation from a given reference temperature at which the formation constant is given can, accordingly, be calculated:

$$\log \beta_{T_2} = \log \beta_{T_1} - \frac{\Delta H^o}{R \cdot \ln 10}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{6}$$

Here $\beta_T$ is the formation constant at temperature $T$ (K), $R$ is the molar gas constant and $\Delta H^o$ (J/mole) is the molar enthalpy for the reaction. Equation [6] can be used provided that the temperature dependency in $\Delta H^o$ can be neglected.

## 2.5 Ionic strength dependency of the formation constant

The activity of a species, x, is defined as:

$$\{x\} = [x] \cdot f_x \qquad [7]$$

where $f_x$ is the activity coefficient for species x. This activity coefficient is dependent on the ionic strength of the solution and, as a consequence, the formation constant is dependent on the ionic strength as:

$$\log \beta = \log \beta^0 + p \log f_a + q \log f_b + r \log f_c + \ldots - \log f_x \qquad [8]$$

In this equation $\beta^0$ is the formation constant at infinite dilution (ionic strength equal to zero). To model the ionic strength behaviour of activity coefficients, different relationships can be used (Stumm, Morgan 1996). In WinSGW the following five equations are available:

$$\log f = -Az^2\sqrt{I} \qquad \text{Debye-Hückel} \quad [9]$$

$$\log f = -Az^2\left(\frac{\sqrt{I}}{1+B\cdot a\sqrt{I}} - b\cdot I\right) \qquad \text{Extended Debye-Hückel} \quad [10]$$

$$\log f = -Az^2\frac{\sqrt{I}}{1+\sqrt{I}} \qquad \text{Güntelberg} \quad [11]$$

$$\log f = -Az^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - d\cdot I\right) \qquad \text{Davies} \quad [12]$$

$$\log f = -Az^2\left(\frac{\sqrt{I}}{1+B\cdot a\cdot\sqrt{I}}\right) + e\cdot I \qquad \text{Specific Ion interaction Theory} \quad [13]$$

The SIT-model is sometimes also referred to as the Brønsted-Guggenheim-Scatchard (Brönsted 1922; Guggenheim 1935; Scatchard 1936) model and is the preferred model within the NEA Thermochemical Data Base (TDB) project, *e.g.,* (Wanner and Forest, eds. 1992, Olin et al. 2005). In these equations $z$ is the charge of a species and $I$ is the molar ionic strength of the solution. $b$ and $d$ are constants supplied by the user as well as $a$ and $e$ which are species specific constants. $A$ and $B$ are given by the following equations:

$$A = 1.82\cdot 10^6 \cdot (\varepsilon T)^{-3/2} \qquad [14]$$

$$B = 50.3\cdot(\varepsilon T)^{-1/2} \qquad [15]$$

where $\varepsilon$ is the dielectric constant of the solvent at the absolute temperature $T$. In WinSGW is not equation [15] used in combination with equation [13], instead is the user asked to give a value for $B\cdot a$.

The ionic strength, $I$ (M), is calculated through an iterative process in WinSGW from the resulting species distribution as:

$$I = \frac{1}{2}\sum[x]\cdot z^2 \qquad [16]$$

where the electric charge balance requirement is fulfilled via the "Background electrolyte" information supplied. For details, see paragraph 5.4.

In addition to these five relationships between the activity coefficient and the ionic strength (*i.e.*, eqs. [9] to [13]), it is also possible to use the Pitzer theory (simplified) in WinSGW. Details and advantages of this method are described in detail by Harvie and Weare (1980).

## 2.6 Surface charge dependency of the formation constant

Reactions at the surface/solvent interface will result in charge accumulation at the surface, and the apparent equilibrium constants for the reactions will not be constant. To mathematically model this effect, a handful of electrostatic expressions have been developed according to the theories for electric double layers at such interfaces.

In WinSGW six different electrostatic models can be chosen; the Constant Capacitance Model (CCM), the Extended Constant Capacitance Model (ECCM), the Diffuse Layer Model (DLM), the Stern Model (Stern), the Triple Layer Model (TLM) and the Three Plane Model (TPM). These models describe the relationship between the surface potential, $\psi$, and the density of charge at a particle surface. Depending on the model, the charge can be distributed over one, two or three planes (*cf.* Figures 1-6). In addition to these planes a diffuse layer of electrolyte ions (with surface potential $\psi_{diff}$) is present in the DLM, Stern, TLM and TPM models.

The effect of charge accumulation on the formation constant of an individual species can be calculated from:

$$\Delta G_{app} = \Delta G_{\text{int}} + \Delta Q_0 F\psi_0 + \Delta Q_1 F\psi_1 + \Delta Q_2 F\psi_2 \qquad [17]$$

where $\Delta G_{app}$ and $\Delta G_{int}$ are the apparent and intrinsic Gibbs free energies of surface complex formation, respectively. $\Delta Q_n$ and $\psi_n$ (mV) are the changes in charges and the surface potential at the 0-, 1- and 2-planes, respectively ($\Delta Q_n$ is often referred to as $\Delta Z_n$ in the literature). To calculate the overall equilibrium constant the coulombic correction term and the intrinsic equilibrium constant are required. The apparent formation constants, $\beta_{app}$, are corrected for coulombic energy to obtain intrinsic constants $\beta_{int}$ according to:

$$\beta_{(\text{int})} = \beta_{(app)}\cdot e^{\Delta Q_0 F\psi_0/RT}\cdot e^{\Delta Q_1 F\psi_1/RT}\cdot e^{\Delta Q_2 F\psi_2/RT} \qquad [18]$$

where $F$ is Faraday's constant. The molar concentration of charge at surface plane $n$, $T(\sigma_n)$, (mol·dm$^{-3}$), can be calculated from:

$$T(\sigma_n) = \sum Q_n\cdot[x] \qquad [19]$$

and expressed as density of charge at the surface, $\sigma_n$, (C·m$^{-2}$):

$$\sigma_n = \frac{T(\sigma_n)\cdot F}{SolCon \cdot SpArea} \qquad [20]$$

where *SolCon* is the concentration of solid ($g\cdot dm^{-3}$) and *SpArea* is the specific surface area of the solid ($m^2\cdot g^{-1}$).
In the case of the CCM (Schindler, Gamsjäger 1972), $\psi_1$, $\psi_2$ and $\psi_{diff}$ are not defined and $\psi_0$ is given by:

$$\psi_0 = \frac{\sigma_0}{C} \qquad [21]$$

where $C$ is the specific capacitance ($C\cdot V^{-1}\cdot m^{-2}$). By inserting this value into equation [18] the equilibrium constant can be corrected for electrostatic forces. In Figure 1 the relationship between the potential and the distance from the surface is illustrated.

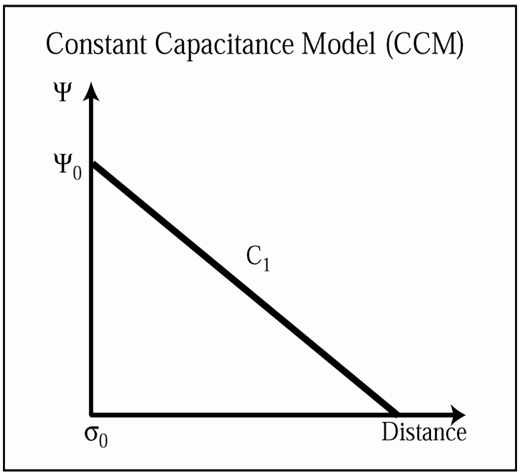


Figure 1. An illustration of the electrostatic behaviour at the surface/water interface according to the Constant Capacitance Model

For the ECCM (*cf.* Figure 2) (Nilsson *et al.* 1996) in which two planes are present ($\psi_2$ and $\psi_{diff}$ not defined) the overall specific capacitance, $C$, is given by $C_1$ (between the 0-plane and the 1-plane) and $C_2$ (between the 1-plane and the bulk solution) according to:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \qquad [22]$$

The following equations are valid for the relations between the potentials and the charges at the 0-plane and the 1-plane respectively:

$$\psi_1 = \frac{\sigma_0 + \sigma_1}{C_2} \qquad [23]$$

$$\psi_0 - \psi_1 = \frac{\sigma_0}{C_1} \qquad [24]$$

Using these results in equation [18] makes it possible to determine the apparent equilibrium constant.

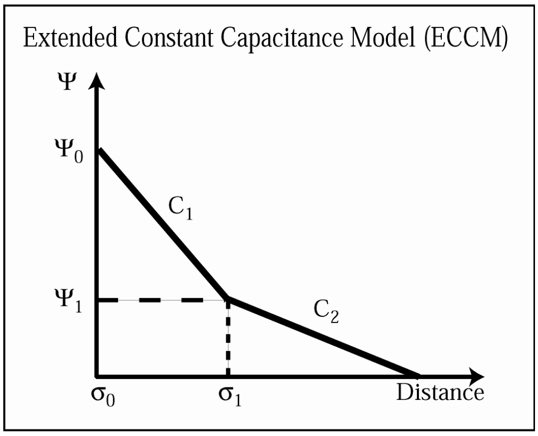


Figure 2. An illustration of the electrostatic behaviour at the surface/water interface according to the Extended Constant Capacitance Model

In the electrostatic models including a diffuse layer, the charge, $\sigma_{diff}$, is obtained from the electro neutrality condition for the particles:

$$\sigma_0 + \sigma_1 + \sigma_2 + \sigma_{diff} = 0 \qquad [25]$$

and the potential in the diffuse layer is given by the Gouy-Chapman equation:

$$\psi_{diff} = \frac{2 \cdot R \cdot T}{F} \sinh^{-1}\left(\sigma_{diff} \cdot \sqrt{8000 \cdot \varepsilon \cdot \varepsilon_0 \cdot R \cdot T \cdot I}\right) \qquad [26]$$

In this equation $I$ is the ionic strength of the solution (*cf.* Eq. [16]) and $\varepsilon_0$ is the permittivity of vacuum.

The DLM (Figure 3) (Stumm *et al.* 1970; Huang, Stumm 1973) involves one plane (the 0-plane) and a diffuse layer. The surface charge densities, $\sigma_0$ and $\sigma_{\mathrm{diff}}$, are given by equations [20] and [25]. The potential $\psi_{diff}$ is calculated using equation [26] and the potential at the 0-, 1- and 2-planes are equal to the potential at the diffuse layer ($\psi_0 = \psi_1 = \psi_2 = \psi_{diff}$). By inserting these values into equation [18] the apparent equilibrium constant, $\beta_{app}$, can be calculated.

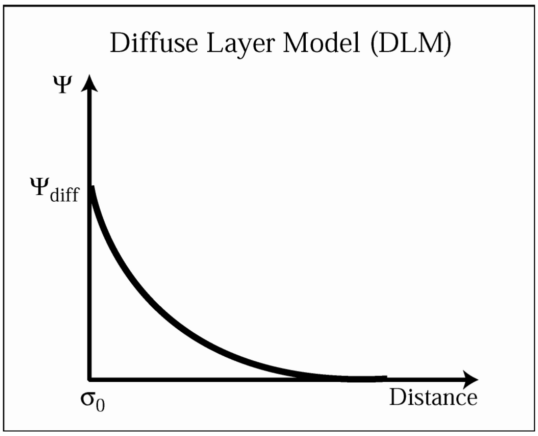


Figure 3. An illustration of the electrostatic behaviour at the surface/water interface according to the Diffuse Layer Model

In the Stern model two planes (the 0-plane and the 2-plane) (Stern 1924; Westall, Hohl 1980) and a diffuse layer are used (Figure 4). As in the DLM case the surface charge densities are given by equations [20] and [25] and the potential in the diffuse layer is given by equation [26]. The surface potential at the 1- and 2-planes are equal to the potential at the head end of the diffuse layer and $\psi_0$ is obtained from:

$$\psi_0 - \psi_2 = \frac{\sigma_0}{C} \qquad [27]$$

By inserting these values into equation [18] the apparent equilibrium constant can be corrected for the charge dependence.

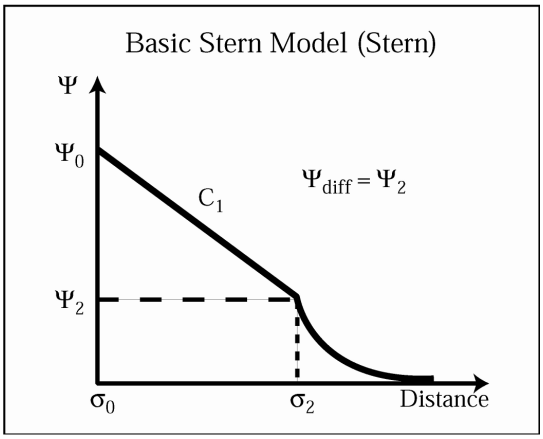


Figure 4. An illustration of the electrostatic behaviour at the surface/water interface according to the Basic Stern Model

The Triple Layer Model (TLM) (Figure 5) (Yates *et al.* 1974; Davis *et al.* 1978) involves two planes (the 0-plane and the 1-plane) and a diffuse layer. The surface charge densities are given in analogy to the previously presented models and surface potentials ($\psi_0$, $\psi_1$, $\psi_{diff}$) are obtained using equations [23], [24] and [26]. $\psi_2$ is given by:

$$\psi_2 = \psi_{diff} \qquad [28]$$

Using these potentials the charge dependence for the equilibrium constant can be determined.

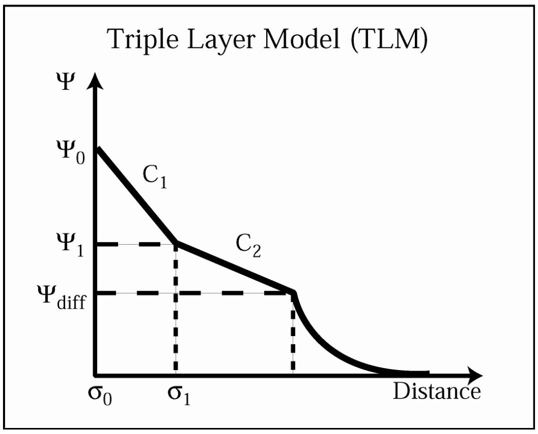


Figure 5. An illustration of the electrostatic behaviour at the surface/water interface according to the Triple Layer Model

Finally, in the TPM (Hiemstra, Van Riemsdijk 1996) three planes of absorbed ions and a diffuse layer of electrolyte ions are used. The surface charge densities are given by equations [20] and [25], and from equations [23], [24], [26] and [28] the surface potentials are obtained (Figure 6). Inserting these potentials into equation [18] makes it possible to correct the $\beta_{app}$-constant for the build-up of electrostatic charges at the surface.

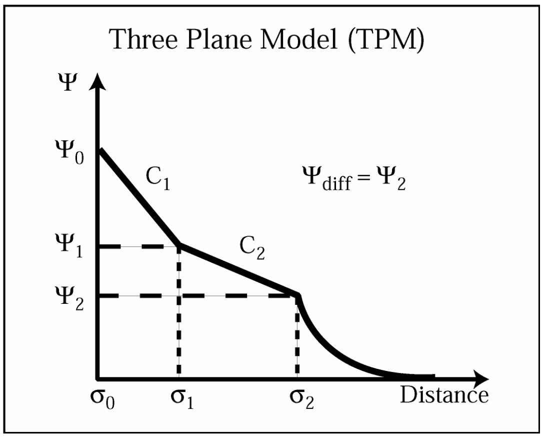


Figure 6. An illustration of the electrostatic behaviour at the surface/water interface according to the Three Plane Model

## 2.7 Unspecific interactions according to Donnan ion exchange theory

The Donnan equations (Donnan, Harris 1911) used in WinSGW were derived to describe the distribution of ions between a water volume confined to a wood fibre and a suspension liquid in a pulp suspension. Therefore it is assumed that at least one negatively charged surface species ($Q_0 < 0$) is present. It is also assumed that this charged surface species has access to the fibre volume (commonly referred to as the Donnan volume) and gives rise to a potential, which results in an uneven distribution of ions between the two sub-volumes. In WinSGW it is also possible to define two charged surface species giving rise to this potential and to calculate the distribution of ions with charge from –5 to +7. According to the Donnan theory (Towers, Scallan 1996), the distribution of an ion $x$ between the Donnan volume (f) and the suspension liquid (s) is given by:

$$\lambda = \left( \frac{[x^z]_f}{[x^z]_s} \right)^{1/z} \qquad [29]$$

where λ is the distribution coefficient and $z$ is the charge ($-5 \le z \le 7$). In both of the aqueous volumes, the requirement of electric neutrality must be met, i.e. the total positive charge must equal the total negative charge. This can be expressed as:

$$\sum_{z=-5}^{-1} |z| \cdot [x^z]_s = \sum_{z=1}^{7} z \cdot [x^z]_s \qquad [30]$$

$$\sum |Q_0| \cdot [\equiv x]_f + \sum_{z=-5}^{-1} |z| \cdot [x^z]_f = \sum_{z=1}^{7} z \cdot [x^z]_f \qquad [31]$$

where $\equiv x$ is the $Q_0$ charged surface species giving rise to the Donnan potential. By combining these equations with the mass balance equation an expression that contains the total concentrations, total aqueous volume, specific Donnan volume, the mass of fibre and λ is obtained. The following equation is an example of this relationship

$$\begin{aligned} &(\lambda^2 - 1)\cdot[H^+]_s + (\lambda^2-1)\cdot\frac{\sum [x^+]_{TOT}\cdot V_{TOT}}{V_{TOT} + D\cdot m_f \cdot(\lambda - 1)} + 2\cdot(\lambda^3-1)\cdot\frac{\sum [x^{2+}]_{TOT}\cdot V_{TOT}}{V_{TOT} + D\cdot m_f\cdot(\lambda^2-1)} + \\ &3\cdot(\lambda^4-1)\cdot\frac{\sum [x^{3+}]_{TOT}\cdot V_{TOT}}{V_{TOT} + D\cdot m_f\cdot(\lambda^3-1)} - \lambda\cdot\frac{[\equiv x^-]\cdot V_{TOT}}{D\cdot m_f} = 0 \end{aligned} \qquad [32]$$

Equation [31] is valid in a system where only protons, monovalent anions and mono-, di- and trivalent cations are present. Furthermore, only one type of site is present on the fibre. In the equation, $[x^{z+}]_{TOT}$ denotes the total concentration of cations with charge $z$, $V_{TOT}$ is the total volume, $m_f$ is the mass of fibre used in the experiment and $D$ denotes the specific Donnan volume per unit weight. The Donnan ion exchange theory applied to pulp systems has been described in detail in the literature, *e.g.* Lindgren *et al.* 2001, Norberg *et al.* 2001, Norberg *et al.* 2002.

# 3 Calculations

The calculation in WinSGW follows the equations described above. The calculations are performed by an updated version of the SOLGASWATER (Eriksson 1979) program in which the free-energy minimisation method is applied to systems containing fluid (aqueous), gaseous, solid, surface and Donnan phases.

The requested input to the program is:
a) a coherent description of all the equilibrium reactions that operates in the system and
b) an instruction with regard to the actual chemical conditions under which the system is to be simulated.

With respect to the first issue, a set of components are chosen (*cf.* paragraph 2.1) and, from these, the stoichiometric compositions and equilibrium constants for all appearing species logically follows. A series of numerical examples illustrating this procedure are presented in paragraphs 5.1, 5.2, 5.4, 5.5, and 5.6. Also illustrated in paragraphs 5.1 and 5.6 is the fact that this choice can be made in several ways, especially when the system includes weak acids and/or redox reactions.

With respect to the second issue many options are available to the user, including both discrete point calculations and serial calculations. The options are designed to allow for the user to calculate the equilibrium composition when the total or free concentrations of the components are known, or to calculate the composition necessary to reach a given point, but they are also designed to make it possible to simulate titration curves, Z-curves, logarithmic diagrams, distribution diagrams, predominance area diagrams (so-called "Pourbaix diagrams" when describing redox systems), and so on. Many of these latter options are exemplified in paragraph 5.

When numerically defining the total concentration corresponding to a certain discrete point an intellectual challenge is sometimes met since, depending on the choice of components, the total concentration of $H^+$ (and $e^-$) can attain a negative value. This follows mathematically from the fact that $OH^-$, and species which are more deprotonated than the chosen weak acid(s) component(s), are assigned negative proton stoichiometric coefficients in the chemical matrix. (With respect to the electron content, this same holds for redox species which are more oxidized than the component chosen.)

A numerical example illustrating the situation is presented in the latter part of paragraph 5.1. The interconnection between the component choice and the numerical value of the total proton (electron) concentration, and the independence of the equilibrium composition, is of utmost importance to realize.

Also vitally important to keep in mind when dealing with redox systems, is that $\{e^-\}$ denotes a formal activity and not a chemical concentration. Therefore, this component should always be assigned "Not Use" in the input matrix, *cf.* paragraph 5.4. By this, the program correctly calculates the activity but puts the chemical concentration to zero.

## *3.1 Options for simulation*

The list presented below shows the available choices open to the user. For each component in the system, one of the options is chosen on the “Variation for Each Component” tab. Depending on the choices made, different information is requested on the “Input data: Each component” tab and, if surfaces are being included, the “Input data: Surfaces” tab.

**Tc**: Total Concentration for the actual component
**a**: Activity for the free amount of the actual component

*Option 1*: **Tc** varies irregularly between each point
*Option 2*: **Tc** is constant
*Option 3*: **Tc** varies with constant steps
*Option 4*: **Tc** varies through varied volume-additions
*Option 5*: **Tc** varies through constant volume-additions
*Option 6*: log **Tc** varies with constant steps
*Option 7*: log **Tc** is dependent variable in predominance diagram
*Option 8*: log **a** varies irregularly
*Option 9*: log **a** is constant
*Option 10*: log **a** varies with constant steps
*Option 11*: log **a** is dependent variable in predominance diagram

**For surface components the following options are available**

*Option 20*: Conc. of **solid phase** is constant
*Option 21*: Conc. of **solid phase** varies with constant steps
*Option 22*: Conc. of **solid phase** varies through titration with constant volume-additions
*Option 23*: Conc. of **solid phase** varies irregularly

## 3.2 Results

The calculations result in a matrix of data containing all necessary information about the equilibrium composition of the actual system. This information includes total concentrations of all components, concentrations of all species and corresponding activities. The matrix also includes the volume added, the total volume and the amounts of solids formed etc.

This data is used within WinSGW to calculate all optional quantities in the "Display Calculation Results" window.

The different options are:

| | |
|---|---|
| [x] (mM) Conc. | Concentration of the selected species or component in milli molar units ($10^{-3}\cdot mol\cdot dm^{-3}$). |
| log ([x]/M) | Logarithm of the selected species or component concentration in molar units ($mol\cdot dm^{-3}$). |
| - log ([x]/M) | The negative logarithm of the selected species or component concentration in molar units ($mol\cdot dm^{-3}$). Use this option to display pH. |
| {a} Activity | Activity of the selected species or component.<br>(*cf.* paragraph 2.5.) |
| log {a} | Logarithm of the activity. |
| Tc (mM) Total conc. | Total concentration of selected component in the system ($10^{-3}\cdot mol\cdot dm^{-3}$). |
| log ( \|Tc\| / M ) | Logarithm of the absolute total concentration Tc. Total concentration in molar units ($mol\cdot dm^{-3}$). |
| Tf (mM) Total Conc. In Fluid | Total concentration of selected component in the fluid (aqueous) phase (excluding solid phases) in milli molar units ($10^{-3}\cdot mol\cdot dm^{-3}$). |
| log ( \|Tf\| / M ) | Logarithm of the absolute total concentration Tf ($mol\cdot dm^{-3}$). |
| Ts (mM) Total Conc. in Solution | Total concentration of selected component in fluid (aqueous) phase (excluding solid and surface phases) in milli molar units ($10^{-3}\cdot mol\cdot dm^{-3}$). |
| Fi (aq) | The distribution of a component between the species. Solid phases are not included.<br>$F_x$ (aq) = $n\cdot[x] / T_f$.<br>where n is the stoichiometric coefficient (*cf.* paragraph 2.1) for the component in species x, *i.e.* Fi (aq) is corrected for polynuclearity (n > 1). |

| | |
|---|---|
| Fi (s) | The distribution of a component between the species. Solid phases included<br>$F_x$ (s) = n·[x] / $T_c$.<br>where n is the stoichiometric coefficient (*cf.* paragraph 2.1) for the component in species x, *i.e.* Fi (s) is corrected for polynuclearity (n > 1). |
| Z | The average number of component A bound to another component (B). *E.g.*: Number of protons (component A) bound to component B is calculated as<br>$Z = \frac{A_{TOT} - [H^+] + [OH^-]}{B_{TOT}}$ |
| n-bar | The average number of one component, regarded as a ligand, bound to unit amount of another component, regarded as the central atom. *E.g.*: Number of component B bound to component C is calculated as<br>$\overline{n} = \frac{\sum q[A_p B_q C_r ...]}{C_{TOT}}$ |
| Vt ($cm^3$) | Added volume in a simulated titration ($cm^3$). |
| Vtot / Donnan volume ($cm^3$) | Total volume in $cm^3$ if "None" is chosen. The Donnan volume is obtained if the Donnan active surface component is chosen. |
| Dominating species | The species with the highest concentration containing the chosen component. *N.B.* this function is not corrected for polynuclearity (n > 1), *cf.* calculation of Fi (aq). |
| Conc. Surface Phase ($g/dm^3$) | The solid phase concentration of the chosen surface component (*cf.* Eq [20]). |
| Surface Pot. (mV) | The surface potential ($\psi$) for the chosen surface component at the specified plane or diffuse layer (Eq [18]). |
| Surf. Cha. ($mol/dm^3$) | The surface charge, $T(\sigma_n)$, for the chosen surface component at the specified plane (Eq [19]). |
| Ionic strength (mM) | The ionic strength of the solution Eq [16]. |
| log B / lambda | The apparent log $\beta$ value [8] for the chosen species or, if no species is chosen, the Donnan distribution coefficient $\lambda$, equation [29]. |
| Empty | Clears the chosen column. |

## *3.3 Diagrams*

The results shown in the “Display Calculation Results” window (described above), and chosen by the user, can be plotted in a diagram. For the construction of diagrams of various types, such as distribution diagrams, pH diagrams, solubility diagrams, n-bar diagrams, titration curves and so forth, the proper dependent (y-axis) and independent variables (x-axis) are combined. The user makes these choices on the “Define Columns to Plot” window. It is furthermore possible to enter a restriction for the plotting (low limit value), *i.e.* a curve is not plotted if its highest y-value is below the limit value.

### 3.3.1 Predominance area diagrams

In addition to the user defined diagrams it is possible to make predominance area diagrams where the species of the highest concentration are shown. The input for this type of diagram is made before the calculation at the right on the “Variation for each component” tab in the “Input for Solgaswater Calculation” window. There it is possible to chose for which component the diagram should be constructed, if solids should be included, and if polynuclearity (formula units) should be considered (*cf.* paragraph 5.4).

# 4 Literature

**Brønsted, J.N**. (1922): J. Am. Chem. Soc. 44 877.

**Davis, J.A., James, R.O. and Leckie, J.O.** (1978): Surface ionization and complexation at oxide/water interface. I: Computation of electrical double layer properties in simple electrolytes, *J. Colloid Interface Sci.* 63, 480.

**Donnan, F. and Harris, A.** (1911): The osmotic pressure and conductivity of aqueous solutions of Congo-red, and reversible membrane equilibria. *J. Chem. Soc*. 99**:** 1554.

**Dyrssen, D., Ingri, N. and Sillén, L.G.** (1961): "Pit-mapping" – a general approach for computer refining of equilibrium constants, *Acta Chem. Scand.* 15, 694.

**Eriksson, G.** (1979): An algorithm for the computation of aqueous multicomponent, multiphase equilibria, *Anal. Chim. Acta* 112, 375.

**Guggenheim, E.A.** (1935): Philos. Mag. 19 588.

**Harvie, C.E. and Weare, J.H.** (1980): The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-Cl-$SO_4$-$H_2O$ system from zero to high concentration at 25$^o$C, *Geochim. Cosmochim. Acta* 44, 981.

**Hiemstra, T. and Van Riemsdijk, W.H.** (1996): A surface structural approach to ion adsorption: The charge distribution (CD) model, *J. Colloid Interface Sci.*, 179, 488.

**Huang, C.P. and Stumm, W.** (1973): Specific adsorption of cations on hydrous $\alpha$-$Al_2O_3$, *J. Colloid Interface Sci.* 22, 231.

**Lindgren, J., Wiklund, L. and Öhman, L.-O.** (2001): The contemporary distribution of cations between bleached softwood fibres and the surrounding bulk solution, as a function of -log[$H^+$], ionic strength and temperature,*Nordic Pulp Paper Res. J.*, 16(1), 24.

**Nilsson, N., Persson, P., Lövgren, L. and Sjöberg, S.** (1996): Competitive surface complexation of o-phthalate and phosphate on goethite ($\alpha$-FeOOH) particles, *Geochim. Cosmochim. Acta* 60, 4385.

**Norberg, C., Lidén J., Lindgren, J. and Öhman, L.-O.** (2002): Some practical aspects of the metal ion chemistry in pulp processes, SPCI 7th International Conference on New Available Technologies, Stockholm.

**Norberg, C., Lidén, J. and Öhman, L.-O.** (2001). Modelling the distribution of "free", complexed and precipitated metal ions in a pulp suspension using Donnan equilibria*, J. Pulp Paper Sci.* 27(9): 296.

**Olin, Å, Noläng, B., Osadchii, G., Rosen, E. and Öhman, L.-O. (2005):** Chemical Thermodynamics of Selenium, Elsevier.

**Scatchard, G.** (1936): Chem. Rev. 19 309.

**Schindler, P.W. and Gamsjäger, H.** (1972): Acid-base reactions of the $TiO_2$(Anatase) - water interface and the point of zero charge of $TiO_2$ suspensions, *Kolloid Z. u. Z. Polymere* 250, 759.

**Stern, O.**, (1924): Zur theory der electrolytischen doppelschicht, *Z. Electrochem.*, 30, 508.

**Stumm, W., Huang, C.P. and Jenkins, S.R.** (1970): Specific chemical interactions affecting the stability of dispersed systems, *Croat. Chem. Acta* 42, 223.

**Stumm, W. and Morgan, J.J.** (1996): *"Aquatic Chemistry"* 3rd ed., John Wiley & Sons Inc., New York.

**Towers, M. and Scallan, A.** (1996): Predicting the ion-exchange of kraft pulps using Donnan theory, *J. Pulp Paper Sci.* 22**:** 332.

**Wanner, H. and Forest, I**., eds. (1992): Chemical Thermodynamics of Uranium, North Holland.

**Westall, J. and Hohl, H.** (1980): A comparison of electrostatic models for the oxide/solution interface, *Adv. Colloid Interface Sci.*, 12, 265.

**Yates, D.E., Levine, S. and Healy, T.W.** (1974): Site-binding model of the electrical double layer at the oxide/water interface*, J. Chem. Soc., Faraday Trans. 1.* 70, 1807.

# 5 Examples*

The majority of the equilibrium constants employed have been collected from Stumm, W. and Morgan, J. J., *Aquatic Cemistry*, 3rd ed.. “pH” is regularly used to denote –log[$H^+$].

## 5.1 Create a distribution diagram for the ($H^+$-$H_3PO_4$) system

**Task:** Plot a diagram showing the distribution of phosphate species as a function of pH at a total phosphoric acid concentration of 10 mM.

1. The following four equilibrium reactions describe a dilute phosphoric acid system.

| | | log β* |
|---|---|---|
| 1 | $H_2O \rightleftarrows H^+ + OH^-$ | -14.00 |
| 2 | $H_3PO_4 \rightleftarrows H_2PO_4^- + H^+$ | -2.15 |
| 3 | $H_2PO_4^- \rightleftarrows HPO_4^{2-} + H^+$ | -7.20 |
| 4 | $HPO_4^{2-} \rightleftarrows PO_4^{3-} + H^+$ | -12.35 |

*Equilibrium constants valid at infinite dilution and at 25°C.

2. Define chemical components that can describe all species present ($H^+$, $OH^-$, $H_3PO_4$, $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$). Components: a) $H^+$ and $H_3PO_4$; b) $H^+$ and $PO_4^{3-}$

3. Write a chemical matrix using the components and the equilibrium reactions.

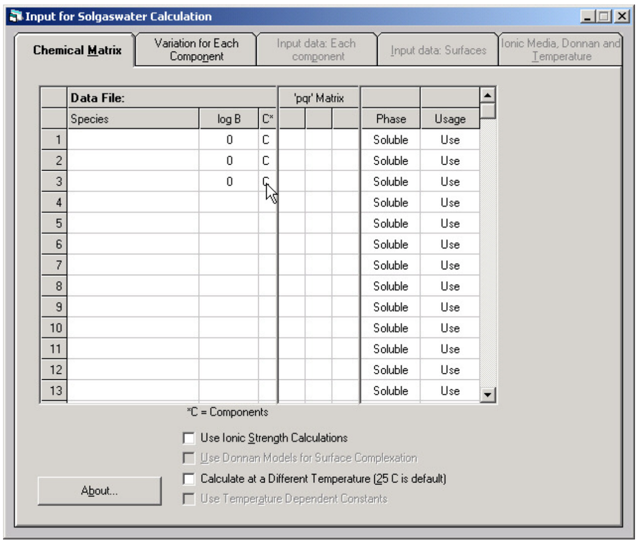
| a) | log β | $H^+$ | $H_3PO_4$ | Equilibria Nos. |
|---|---|---|---|---|
| $H^+$ | 0 | 1 | 0 | |
| $H_3PO_4$ | 0 | 0 | 1 | |
| $OH^-$ | -14.00 | -1 | 0 | 1 |
| $H_2PO_4^-$ | -2.15 | -1 | 1 | 2 |
| $HPO_4^{2-}$ | -9.35 | -2 | 1 | 2 + 3 |
| $PO_4^{3-}$ | -21.70 | -3 | 1 | 2 + 3 + 4 |

| b) | log β | $H^+$ | $PO_4^{3-}$ | Equilibria Nos. |
|---|---|---|---|---|
| $H^+$ | 0 | 1 | 0 | |
| $PO_4^{3-}$ | 0 | 0 | 1 | |
| $OH^-$ | -14.00 | -1 | 0 | 1 |
| $HPO_4^{2-}$ | 12.35 | 1 | 1 | - 4 |
| $H_2PO_4^-$ | 19.55 | 2 | 1 | - 4 - 3 |
| $H_3PO_4$ | 21.70 | 3 | 1 | - 4 - 3 - 2 |

---

*Due to a continous development of the program, the screen captures in this section will not always be identical to those appearing in the latest version of the WinSGW software.

4. Start WinSGW and choose “New Chemical Matrix” from the “File” menu. Since WinSGW has three components as default value, remove one by clicking on a “C” in the “C*” column.

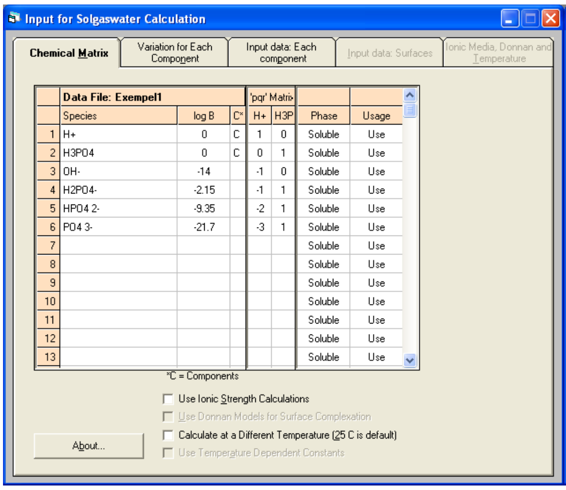


|  | Data File: |  |  | 'pqr' Matrix |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  | Species | log B | C* |  |  |  | Phase | Usage |
| 1 |  | 0 | C |  |  |  | Soluble | Use |
| 2 |  | 0 | C |  |  |  | Soluble | Use |
| 3 |  | 0 | C |  |  |  | Soluble | Use |
| 4 |  |  |  |  |  |  | Soluble | Use |
| 5 |  |  |  |  |  |  | Soluble | Use |
| 6 |  |  |  |  |  |  | Soluble | Use |
| 7 |  |  |  |  |  |  | Soluble | Use |
| 8 |  |  |  |  |  |  | Soluble | Use |
| 9 |  |  |  |  |  |  | Soluble | Use |
| 10 |  |  |  |  |  |  | Soluble | Use |
| 11 |  |  |  |  |  |  | Soluble | Use |
| 12 |  |  |  |  |  |  | Soluble | Use |
| 13 |  |  |  |  |  |  | Soluble | Use |

*C = Components

☐ Use Ionic Strength Calculations
☐ Use Donnan Models for Surface Complexation
☐ Calculate at a Different Temperature (25 C is default)
☐ Use Temperature Dependent Constants

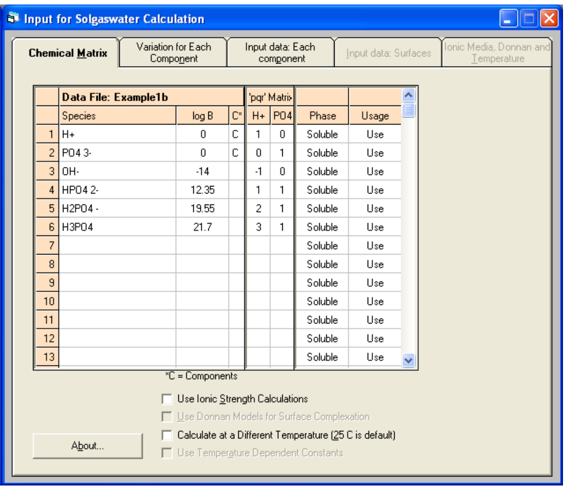
5. Enter the matrix. Blanks in the matrix will be interpreted as zeros by the program. By clicking the right mouse button in the brownish line number column it is possible to insert, clear and/or delete rows in the matrix.



|  | Data File: Exempel1 |  |  | 'pqr' Matrix |  |  |  |
|---|---|---|---|---|---|---|---|
|  | Species | log B | C* | H+ | H3P | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 0 | Soluble | Use |
| 2 | H3PO4 | 0 | C | 0 | 1 | Soluble | Use |
| 3 | OH- | -14 |  | -1 | 0 | Soluble | Use |
| 4 | H2PO4- | -2.15 |  | -1 | 1 | Soluble | Use |
| 5 | HPO4 2- | -9.35 |  | -2 | 1 | Soluble | Use |
| 6 | PO4 3- | -21.7 |  | -3 | 1 | Soluble | Use |
| 7 |  |  |  |  |  | Soluble | Use |
| 8 |  |  |  |  |  | Soluble | Use |
| 9 |  |  |  |  |  | Soluble | Use |
| 10 |  |  |  |  |  | Soluble | Use |
| 11 |  |  |  |  |  | Soluble | Use |
| 12 |  |  |  |  |  | Soluble | Use |
| 13 |  |  |  |  |  | Soluble | Use |

*C = Components

☐ Use Ionic Strength Calculations
☐ Use Donnan Models for Surface Complexation
☐ Calculate at a Different Temperature (25 C is default)
☐ Use Temperature Dependent Constants

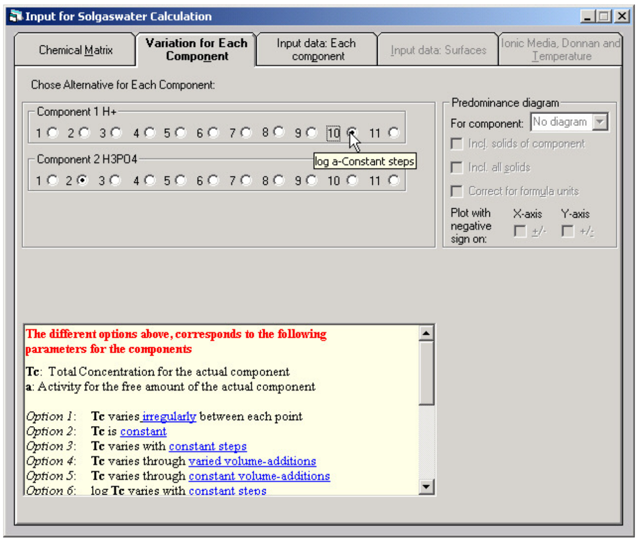


|  | Data File: Example1b |  |  | 'pqr' Matrix |  |  |  |
|---|---|---|---|---|---|---|---|
|  | Species | log B | C* | H+ | PO4 | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 0 | Soluble | Use |
| 2 | PO4 3- | 0 | C | 0 | 1 | Soluble | Use |
| 3 | OH- | -14 |  | -1 | 0 | Soluble | Use |
| 4 | HPO4 2- | 12.35 |  | 1 | 1 | Soluble | Use |
| 5 | H2PO4 - | 19.55 |  | 2 | 1 | Soluble | Use |
| 6 | H3PO4 | 21.7 |  | 3 | 1 | Soluble | Use |
| 7 |  |  |  |  |  | Soluble | Use |
| 8 |  |  |  |  |  | Soluble | Use |
| 9 |  |  |  |  |  | Soluble | Use |
| 10 |  |  |  |  |  | Soluble | Use |
| 11 |  |  |  |  |  | Soluble | Use |
| 12 |  |  |  |  |  | Soluble | Use |
| 13 |  |  |  |  |  | Soluble | Use |

*C = Components

☐ Use Ionic Strength Calculations
☐ Use Donnan Models for Surface Complexation
☐ Calculate at a Different Temperature (25 C is default)
☐ Use Temperature Dependent Constants

6. Move to next tab “Variation for each component”. At this tab we choose which kind of calculation we aim at. There is a description of the possible choices in the yellow text box. For this example we would like to vary pH in constant steps (Component 1 $H^+$, option 10) and to keep the total phosphoric acid concentration constant (Component 2 $H_3PO_4$, option 2).



Chose Alternative for Each Component:

Component 1 H+
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ● 11 ○

log a-Constant steps

Component 2 H3PO4
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

For component: No diagram

☐ Incl. solids of component

☐ Incl. all solids

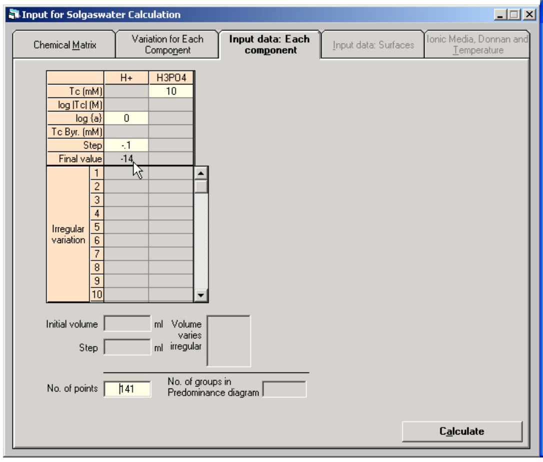
☐ Correct for formula units

**The different options above, corresponds to the following parameters for the components**

**Tc**: Total Concentration for the actual component
**a**: Activity for the free amount of the actual component

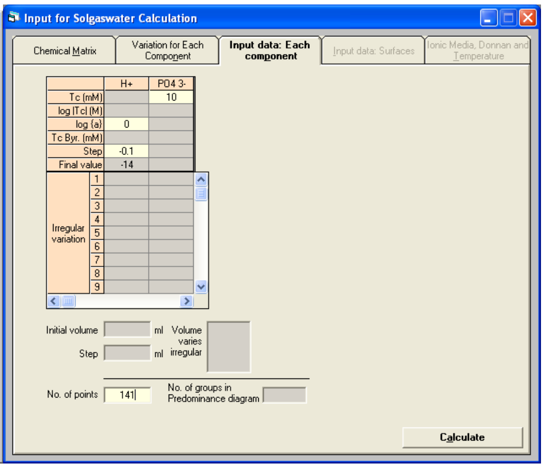
*Option 1*: **Tc** varies irregularly between each point
*Option 2*: **Tc** is constant
*Option 3*: **Tc** varies with constant steps
*Option 4*: **Tc** varies through varied volume-additions
*Option 5*: **Tc** varies through constant volume-additions
*Option 6*: log **Tc** varies with constant steps

7. Move to next tab “Input data: Each component”. Enter Start value “log {a}”, Step length “Step” for the first component ($H^+$), total concentration of phosphoric acid “Tc” and the number of points. The program will calculate the log {a} value in the last calculated point. In this position, it is advisable to save and/or print the matrix and the input on the File menu.



| | | H+ | H3PO4 |
|---|---|---|---|
| Tc (mM) | | | 10 |
| log \|Tc\| (M) | | | |
| log {a} | | 0 | |
| Tc Byr. (mM) | | | |
| Step | | -.1 | |
| Final value | | -14 | |
| Irregular variation | 1 | | |
| | 2 | | |
| | 3 | | |
| | 4 | | |
| | 5 | | |
| | 6 | | |
| | 7 | | |
| | 8 | | |
| | 9 | | |
| | 10 | | |

Initial volume ml
Step ml
Volume varies irregular
No. of points 141
No. of groups in Predominance diagram



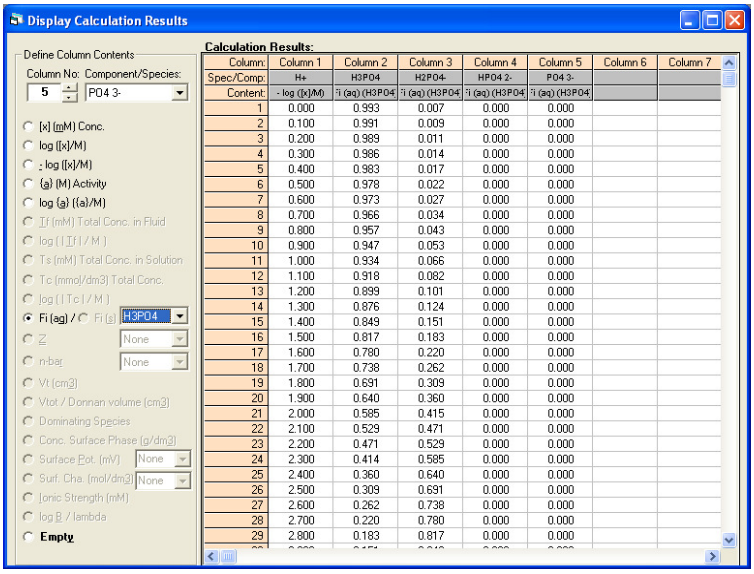
| | | H+ | PO4 3- |
|---|---|---|---|
| Tc (mM) | | | 10 |
| log \|Tc\| (M) | | | |
| log {a} | | 0 | |
| Tc Byr. (mM) | | | |
| Step | | -0.1 | |
| Final value | | -14 | |
| Irregular variation | 1 | | |
| | 2 | | |
| | 3 | | |
| | 4 | | |
| | 5 | | |
| | 6 | | |
| | 7 | | |
| | 8 | | |
| | 9 | | |

Initial volume ml
Step ml
Volume varies irregular
No. of points 141
No. of groups in Predominance diagram

8. Start the calculation by pressing the “Calculate” button or use the Calculate menu.

9. Viewing the result.

Choose $H^+$ in the Component/Species box and then "-log {[x]/M}" to view pH in column 1. Move to the next column. To display the distribution of $H_3PO_4$ choose a "phosphorus containing species" in the Component/Species box, "Fi (aq)" and $H_3PO_4$ in the box next to "Fi (aq)". Repeat these steps for the remaining phosphate species.

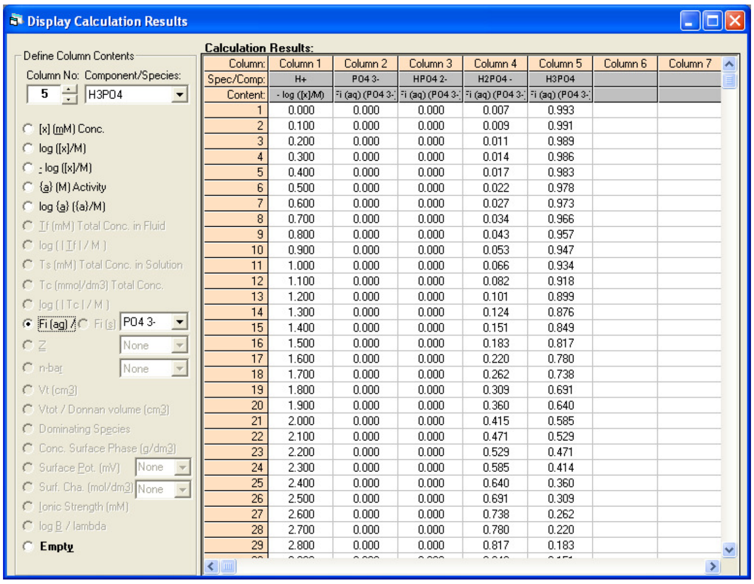


Column No: 5 Component/Species: PO4 3-

● Fi (aq) / ○ Fi (s) H3PO4

Calculation Results:

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | H3PO4 | H2PO4- | HPO4 2- | PO4 3- | | |
| Content: | - log ([x]/M) | Fi (aq) (H3PO4 | Fi (aq) (H3PO4 | Fi (aq) (H3PO4 | Fi (aq) (H3PO4 | | |
| 1 | 0.000 | 0.993 | 0.007 | 0.000 | 0.000 | | |
| 2 | 0.100 | 0.991 | 0.009 | 0.000 | 0.000 | | |
| 3 | 0.200 | 0.989 | 0.011 | 0.000 | 0.000 | | |
| 4 | 0.300 | 0.986 | 0.014 | 0.000 | 0.000 | | |
| 5 | 0.400 | 0.983 | 0.017 | 0.000 | 0.000 | | |
| 6 | 0.500 | 0.978 | 0.022 | 0.000 | 0.000 | | |
| 7 | 0.600 | 0.973 | 0.027 | 0.000 | 0.000 | | |
| 8 | 0.700 | 0.966 | 0.034 | 0.000 | 0.000 | | |
| 9 | 0.800 | 0.957 | 0.043 | 0.000 | 0.000 | | |
| 10 | 0.900 | 0.947 | 0.053 | 0.000 | 0.000 | | |
| 11 | 1.000 | 0.934 | 0.066 | 0.000 | 0.000 | | |
| 12 | 1.100 | 0.918 | 0.082 | 0.000 | 0.000 | | |
| 13 | 1.200 | 0.899 | 0.101 | 0.000 | 0.000 | | |
| 14 | 1.300 | 0.876 | 0.124 | 0.000 | 0.000 | | |
| 15 | 1.400 | 0.849 | 0.151 | 0.000 | 0.000 | | |
| 16 | 1.500 | 0.817 | 0.183 | 0.000 | 0.000 | | |
| 17 | 1.600 | 0.780 | 0.220 | 0.000 | 0.000 | | |
| 18 | 1.700 | 0.738 | 0.262 | 0.000 | 0.000 | | |
| 19 | 1.800 | 0.691 | 0.309 | 0.000 | 0.000 | | |
| 20 | 1.900 | 0.640 | 0.360 | 0.000 | 0.000 | | |
| 21 | 2.000 | 0.585 | 0.415 | 0.000 | 0.000 | | |
| 22 | 2.100 | 0.529 | 0.471 | 0.000 | 0.000 | | |
| 23 | 2.200 | 0.471 | 0.529 | 0.000 | 0.000 | | |
| 24 | 2.300 | 0.414 | 0.585 | 0.000 | 0.000 | | |
| 25 | 2.400 | 0.360 | 0.640 | 0.000 | 0.000 | | |
| 26 | 2.500 | 0.309 | 0.691 | 0.000 | 0.000 | | |
| 27 | 2.600 | 0.262 | 0.738 | 0.000 | 0.000 | | |
| 28 | 2.700 | 0.220 | 0.780 | 0.000 | 0.000 | | |
| 29 | 2.800 | 0.183 | 0.817 | 0.000 | 0.000 | | |



Column No: 5 Component/Species: H3PO4

● Fi (aq) / ○ Fi (s) PO4 3-

Calculation Results:

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | PO4 3- | HPO4 2- | H2PO4 - | H3PO4 | | |
| Content: | - log ([x]/M) | Fi (aq) (PO4 3- | Fi (aq) (PO4 3- | Fi (aq) (PO4 3- | Fi (aq) (PO4 3- | | |
| 1 | 0.000 | 0.000 | 0.000 | 0.007 | 0.993 | | |
| 2 | 0.100 | 0.000 | 0.000 | 0.009 | 0.991 | | |
| 3 | 0.200 | 0.000 | 0.000 | 0.011 | 0.989 | | |
| 4 | 0.300 | 0.000 | 0.000 | 0.014 | 0.986 | | |
| 5 | 0.400 | 0.000 | 0.000 | 0.017 | 0.983 | | |
| 6 | 0.500 | 0.000 | 0.000 | 0.022 | 0.978 | | |
| 7 | 0.600 | 0.000 | 0.000 | 0.027 | 0.973 | | |
| 8 | 0.700 | 0.000 | 0.000 | 0.034 | 0.966 | | |
| 9 | 0.800 | 0.000 | 0.000 | 0.043 | 0.957 | | |
| 10 | 0.900 | 0.000 | 0.000 | 0.053 | 0.947 | | |
| 11 | 1.000 | 0.000 | 0.000 | 0.066 | 0.934 | | |
| 12 | 1.100 | 0.000 | 0.000 | 0.082 | 0.918 | | |
| 13 | 1.200 | 0.000 | 0.000 | 0.101 | 0.899 | | |
| 14 | 1.300 | 0.000 | 0.000 | 0.124 | 0.876 | | |
| 15 | 1.400 | 0.000 | 0.000 | 0.151 | 0.849 | | |
| 16 | 1.500 | 0.000 | 0.000 | 0.183 | 0.817 | | |
| 17 | 1.600 | 0.000 | 0.000 | 0.220 | 0.780 | | |
| 18 | 1.700 | 0.000 | 0.000 | 0.262 | 0.738 | | |
| 19 | 1.800 | 0.000 | 0.000 | 0.309 | 0.691 | | |
| 20 | 1.900 | 0.000 | 0.000 | 0.360 | 0.640 | | |
| 21 | 2.000 | 0.000 | 0.000 | 0.415 | 0.585 | | |
| 22 | 2.100 | 0.000 | 0.000 | 0.471 | 0.529 | | |
| 23 | 2.200 | 0.000 | 0.000 | 0.529 | 0.471 | | |
| 24 | 2.300 | 0.000 | 0.000 | 0.585 | 0.414 | | |
| 25 | 2.400 | 0.000 | 0.000 | 0.640 | 0.360 | | |
| 26 | 2.500 | 0.000 | 0.000 | 0.691 | 0.309 | | |
| 27 | 2.600 | 0.000 | 0.000 | 0.738 | 0.262 | | |
| 28 | 2.700 | 0.000 | 0.000 | 0.780 | 0.220 | | |
| 29 | 2.800 | 0.000 | 0.000 | 0.817 | 0.183 | | |

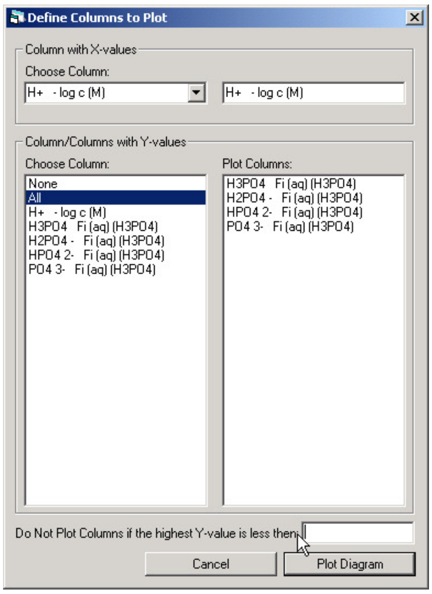
Note that the results employing the two different choices of components, of course, are identical.

## 10. Plotting the results

Choose “Plot calculation data” from the “Diagrams” menu.

The default setting is that the first column in the Calculation Result grid contains X-values and all remaining columns will be plotted on the Y-axis. It is possible to remove a series from the Plot Columns list by clicking on the series. As an option you can choose to exclude all curves that never exceed a given minimum value.

Continue by pressing “Plot diagram”.



Column with X-values

Choose Column: H+ - log c (M) | H+ - log c (M)

Column/Columns with Y-values

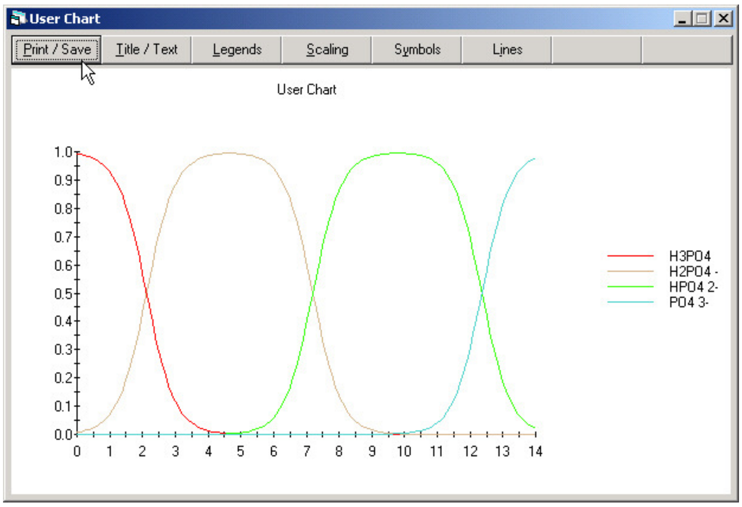
Choose Column:
None
All
H+ - log c (M)
H3PO4 Fi (aq) (H3PO4)
H2PO4 - Fi (aq) (H3PO4)
HPO4 2- Fi (aq) (H3PO4)
PO4 3- Fi (aq) (H3PO4)

Plot Columns:
H3PO4 Fi (aq) (H3PO4)
H2PO4 - Fi (aq) (H3PO4)
HPO4 2- Fi (aq) (H3PO4)
PO4 3- Fi (aq) (H3PO4)

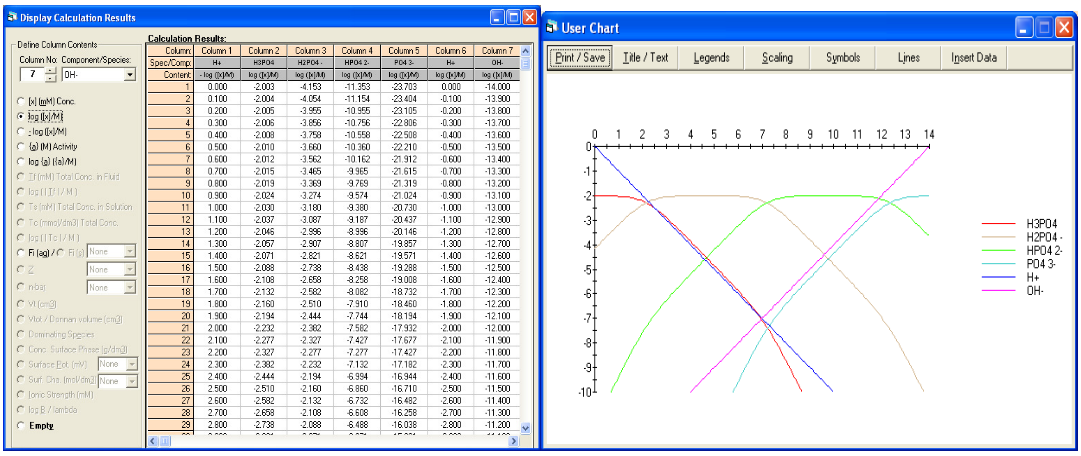
Do Not Plot Columns if the highest Y-value is less then

## 11. The diagram

You can modify your chart by using the top buttons, e.g. change the scale, labels, lines and symbols, or print your diagram.



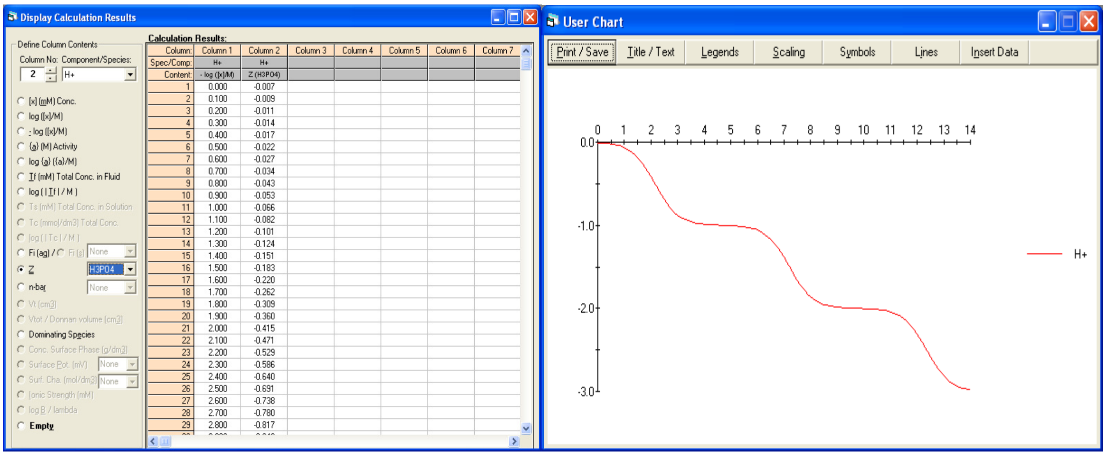
12. Without any renewed calculation, it is also possible to generate other relevant diagrams describing the system. This is made by returning to the "Display Calculation Results", changing the column contents to the new information of interest, and plotting these as described above.



Column No: 7
Component/Species: OH-
● log ([x]/M)

Calculation Results:

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | H3PO4 | H2PO4 - | HPO4 2- | PO4 3- | H+ | OH- |
| Content: | - log ([x]/M) | log ([x]/M) | log ([x]/M) | log ([x]/M) | log ([x]/M) | log ([x]/M) | log ([x]/M) |
| 1 | 0.000 | -2.003 | -4.153 | -11.353 | -23.703 | 0.000 | -14.000 |
| 2 | 0.100 | -2.004 | -4.054 | -11.154 | -23.404 | -0.100 | -13.900 |
| 3 | 0.200 | -2.005 | -3.955 | -10.955 | -23.105 | -0.200 | -13.800 |
| 4 | 0.300 | -2.006 | -3.856 | -10.756 | -22.806 | -0.300 | -13.700 |
| 5 | 0.400 | -2.008 | -3.758 | -10.558 | -22.508 | -0.400 | -13.600 |
| 6 | 0.500 | -2.010 | -3.660 | -10.360 | -22.210 | -0.500 | -13.500 |
| 7 | 0.600 | -2.012 | -3.562 | -10.162 | -21.912 | -0.600 | -13.400 |
| 8 | 0.700 | -2.015 | -3.465 | -9.965 | -21.615 | -0.700 | -13.300 |
| 9 | 0.800 | -2.019 | -3.369 | -9.769 | -21.319 | -0.800 | -13.200 |
| 10 | 0.900 | -2.024 | -3.274 | -9.574 | -21.024 | -0.900 | -13.100 |
| 11 | 1.000 | -2.030 | -3.180 | -9.380 | -20.730 | -1.000 | -13.000 |
| 12 | 1.100 | -2.037 | -3.087 | -9.187 | -20.437 | -1.100 | -12.900 |
| 13 | 1.200 | -2.046 | -2.996 | -8.996 | -20.146 | -1.200 | -12.800 |
| 14 | 1.300 | -2.057 | -2.907 | -8.807 | -19.857 | -1.300 | -12.700 |
| 15 | 1.400 | -2.071 | -2.821 | -8.621 | -19.571 | -1.400 | -12.600 |
| 16 | 1.500 | -2.088 | -2.738 | -8.438 | -19.288 | -1.500 | -12.500 |
| 17 | 1.600 | -2.108 | -2.658 | -8.258 | -19.008 | -1.600 | -12.400 |
| 18 | 1.700 | -2.132 | -2.582 | -8.082 | -18.732 | -1.700 | -12.300 |
| 19 | 1.800 | -2.160 | -2.510 | -7.910 | -18.460 | -1.800 | -12.200 |
| 20 | 1.900 | -2.194 | -2.444 | -7.744 | -18.194 | -1.900 | -12.100 |
| 21 | 2.000 | -2.232 | -2.382 | -7.582 | -17.932 | -2.000 | -12.000 |
| 22 | 2.100 | -2.277 | -2.327 | -7.427 | -17.677 | -2.100 | -11.900 |
| 23 | 2.200 | -2.327 | -2.277 | -7.277 | -17.427 | -2.200 | -11.800 |
| 24 | 2.300 | -2.382 | -2.232 | -7.132 | -17.182 | -2.300 | -11.700 |
| 25 | 2.400 | -2.444 | -2.194 | -6.994 | -16.944 | -2.400 | -11.600 |
| 26 | 2.500 | -2.510 | -2.160 | -6.860 | -16.710 | -2.500 | -11.500 |
| 27 | 2.600 | -2.582 | -2.132 | -6.732 | -16.482 | -2.600 | -11.400 |
| 28 | 2.700 | -2.658 | -2.108 | -6.608 | -16.258 | -2.700 | -11.300 |
| 29 | 2.800 | -2.738 | -2.088 | -6.488 | -16.038 | -2.800 | -11.200 |



Column No: 2
Component/Species: H+
● Z H3PO4

Calculation Results:

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | H+ | | | | | |
| Content: | - log ([x]/M) | Z (H3PO4) | | | | | |
| 1 | 0.000 | -0.007 | | | | | |
| 2 | 0.100 | -0.009 | | | | | |
| 3 | 0.200 | -0.011 | | | | | |
| 4 | 0.300 | -0.014 | | | | | |
| 5 | 0.400 | -0.017 | | | | | |
| 6 | 0.500 | -0.022 | | | | | |
| 7 | 0.600 | -0.027 | | | | | |
| 8 | 0.700 | -0.034 | | | | | |
| 9 | 0.800 | -0.043 | | | | | |
| 10 | 0.900 | -0.053 | | | | | |
| 11 | 1.000 | -0.066 | | | | | |
| 12 | 1.100 | -0.082 | | | | | |
| 13 | 1.200 | -0.101 | | | | | |
| 14 | 1.300 | -0.124 | | | | | |
| 15 | 1.400 | -0.151 | | | | | |
| 16 | 1.500 | -0.183 | | | | | |
| 17 | 1.600 | -0.220 | | | | | |
| 18 | 1.700 | -0.262 | | | | | |
| 19 | 1.800 | -0.309 | | | | | |
| 20 | 1.900 | -0.360 | | | | | |
| 21 | 2.000 | -0.415 | | | | | |
| 22 | 2.100 | -0.471 | | | | | |
| 23 | 2.200 | -0.529 | | | | | |
| 24 | 2.300 | -0.586 | | | | | |
| 25 | 2.400 | -0.640 | | | | | |
| 26 | 2.500 | -0.691 | | | | | |
| 27 | 2.600 | -0.738 | | | | | |
| 28 | 2.700 | -0.780 | | | | | |
| 29 | 2.800 | -0.817 | | | | | |

### 5.1.1 Calculate the equilibrium compositions for a series of phosphate solutions

A series of solutions were prepared by mixing equal volumes of:

i) 10 mM HCl and 10 mM $H_3PO_4$
ii) 10 mM NaOH and 10 mM $H_3PO_4$
iii) 10 mM $H_3PO_4$ and 10 mM $NaH_2PO_4$
iv) 5 mM NaOH and 10 mM $Na_2HPO_4$
v) 10 mM $NaH_2PO_4$ and 10 mM $Na_3PO_4$
vi) 10 mM NaOH and 10 mM $Na_3PO_4$

**Task:** Calculate the equilibrium pH and the distribution between different phosphate species.

1a). With $H^+$ and $H_3PO_4$ as components, the total concentrations in the 6 solutions are:

i) $[H]_{tot} = (1\cdot10 + 0)/2$ mM = 5 mM; $[P]_{tot} = (0 + 10)/2$ mM = 5 mM
ii) $[H]_{tot} = (-1\cdot10 + 0)/2$ mM = -5 mM; $[P]_{tot} = (0 + 10)/2$ mM = 5 mM
iii) $[H]_{tot} = (0 + (-1)\cdot10)/2$ mM = -5 mM; $[P]_{tot} = (10 + 10)/2$ mM = 10 mM
iv) $[H]_{tot} = (-1\cdot5 + (-2)\cdot10)/2$ mM = -12.5 mM; $[P]_{tot} = (0 + 10)/2$ mM = 5 mM
v) $[H]_{tot} = (-1\cdot10 + (-3)\cdot10)/2$ mM = -20 mM; $[P]_{tot} = (10 + 10)/2$ mM = 10 mM
vi) $[H]_{tot} = (-1\cdot10 + (-3)\cdot10)/2$ mM = -20 mM; $[P]_{tot} = (0 + 10)/2$ mM = 5 mM

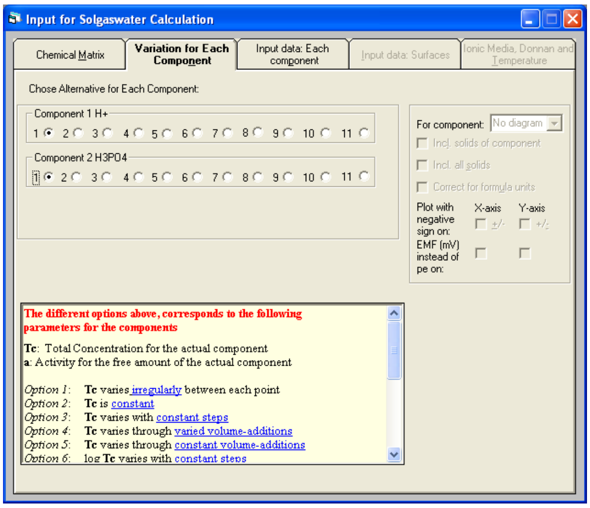
1b). With $H^+$ and $PO_4^{3-}$ as components, the total concentrations are:

i) $[H]_{tot} = (1\cdot10 + 3\cdot10)/2$ mM = 20 mM; $[P]_{tot} = (0 + 10)/2$ mM = 5 mM
ii) $[H]_{tot} = (-1\cdot10 + 3\cdot10)/2$ mM = 10 mM; $[P]_{tot} = (0 + 10)/2$ mM = 5 mM
iii) $[H]_{tot} = (3\cdot10 + 2\cdot10)/2$ mM = 25 mM; $[P]_{tot} = (10 + 10)/2$ mM = 10 mM
iv) $[H]_{tot} = (-1\cdot5 + 1\cdot10)/2$ mM = 2.5 mM; $[P]_{tot} = (0 + 10)/2$ mM = 5 mM
v) $[H]_{tot} = (2\cdot10 + 0)/2$ mM = 10 mM; $[P]_{tot} = (10 + 10)/2$ mM = 10 mM
vi) $[H]_{tot} = (-1\cdot10 + 0)/2$ mM = -5 mM; $[P]_{tot} = (0 + 10)/2$ mM = 5 mM

Note that the multiplication factors for calculating $[H]_{tot}$ are exactly the same as those appearing in the chemical matrix, *cf.* p. 19.

2. Start WinSGW and choose ”Open” from the ”File” menu. Retrieve the file “Example1a.cti” which was (hopefully) saved in the previous session. Otherwise, choose “New Chemical Matrix” and re-enter the matrix.

3. Move to the tab “Variation for each component”. This time we want to enter 6 discrete data points where both total concentrations varies irregularly between the points (Component 1 $H^+$, option 1; Component 2 $H_3PO_4$, option 1).



Chose Alternative for Each Component:

Component 1 H+
1 ● 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

Component 2 H3PO4
1 ● 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

For component: No diagram
☐ Incl. solids of component
☐ Incl. all solids
☐ Correct for formula units

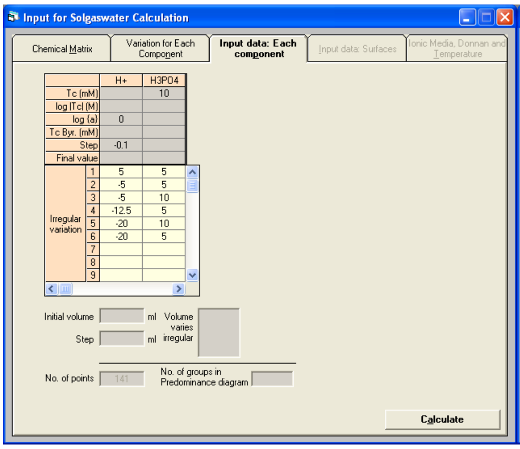
| | X-axis | Y-axis |
|---|---|---|
| Plot with negative sign on: | ☐ +/- | ☐ +/- |
| EMF (mV) instead of pe on: | ☐ | ☐ |

**The different options above, corresponds to the following parameters for the components**

**Tc**: Total Concentration for the actual component
**a**: Activity for the free amount of the actual component

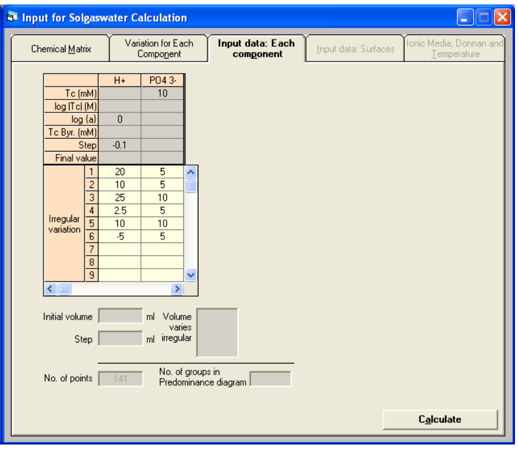
*Option 1*: **Tc** varies irregularly between each point
*Option 2*: **Tc** is constant
*Option 3*: **Tc** varies with constant steps
*Option 4*: **Tc** varies through varied volume-additions
*Option 5*: **Tc** varies through constant volume-additions
*Option 6*: log **Tc** varies with constant steps

4. Move to next tab “Input data: Each component” and enter the numerical values of $H_{tot}$ and $P_{tot}$.



| | | H+ | H3PO4 |
|---|---|---|---|
| Tc (mM) | | | 10 |
| log \|Tc\| (M) | | | |
| log {a} | | 0 | |
| Tc Byr. (mM) | | | |
| Step | | -0.1 | |
| Final value | | | |
| Irregular variation | 1 | 5 | 5 |
| | 2 | -5 | 5 |
| | 3 | -5 | 10 |
| | 4 | -12.5 | 5 |
| | 5 | -20 | 10 |
| | 6 | -20 | 5 |
| | 7 | | |
| | 8 | | |
| | 9 | | |

Initial volume ml
Step ml
Volume varies irregular
No. of points 141
No. of groups in Predominance diagram

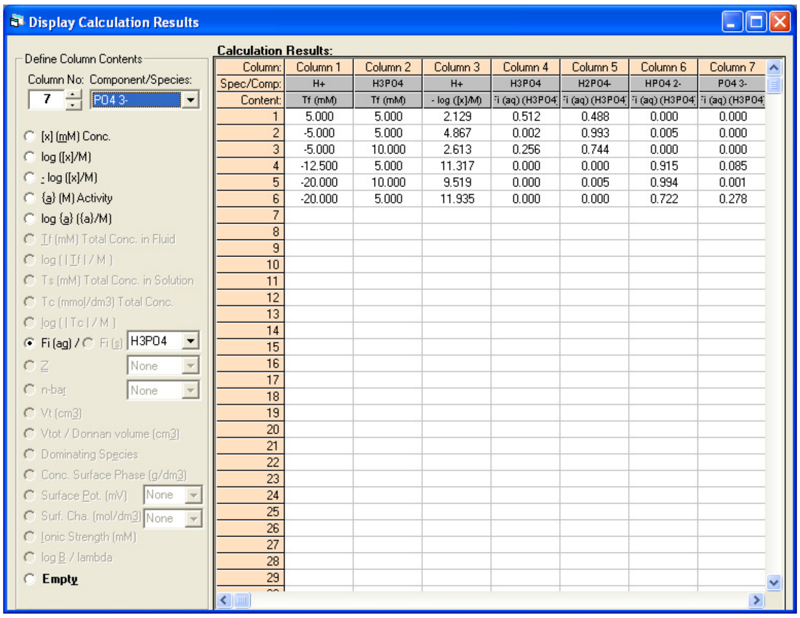


| | | H+ | PO4 3- |
|---|---|---|---|
| Tc (mM) | | | 10 |
| log \|Tc\| (M) | | | |
| log {a} | | 0 | |
| Tc Byr. (mM) | | | |
| Step | | -0.1 | |
| Final value | | | |
| Irregular variation | 1 | 20 | 5 |
| | 2 | 10 | 5 |
| | 3 | 25 | 10 |
| | 4 | 2.5 | 5 |
| | 5 | 10 | 10 |
| | 6 | -5 | 5 |
| | 7 | | |
| | 8 | | |
| | 9 | | |

Initial volume ml
Step ml
Volume varies irregular
No. of points 141
No. of groups in Predominance diagram

5. Calculate

6. Choose $H^+$ in the Component/Species box and then “Tf (mM) Total Conc in Fluid” to display $H_{tot}$ in column 1. Move to the next column and display $P_{tot}$. The resulting $–\log[H^+]$ and the distribution between the different phosphate species are displayed as in previous session.



Column No: 7

Component/Species: PO4 3-

● Fi (aq) / ○ Fi (s): H3PO4

Calculation Results:

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | H3PO4 | H+ | H3PO4 | H2PO4- | HPO4 2- | PO4 3- |
| Content: | Tf (mM) | Tf (mM) | - log ([x]/M) | Fi (aq) (H3PO4 | Fi (aq) (H3PO4 | Fi (aq) (H3PO4 | Fi (aq) (H3PO4 |
| 1 | 5.000 | 5.000 | 2.129 | 0.512 | 0.488 | 0.000 | 0.000 |
| 2 | -5.000 | 5.000 | 4.867 | 0.002 | 0.993 | 0.005 | 0.000 |
| 3 | -5.000 | 10.000 | 2.613 | 0.256 | 0.744 | 0.000 | 0.000 |
| 4 | -12.500 | 5.000 | 11.317 | 0.000 | 0.000 | 0.915 | 0.085 |
| 5 | -20.000 | 10.000 | 9.519 | 0.000 | 0.005 | 0.994 | 0.001 |
| 6 | -20.000 | 5.000 | 11.935 | 0.000 | 0.000 | 0.722 | 0.278 |
| 7 | | | | | | | |
| 8 | | | | | | | |
| 9 | | | | | | | |
| 10 | | | | | | | |
| 11 | | | | | | | |
| 12 | | | | | | | |
| 13 | | | | | | | |
| 14 | | | | | | | |
| 15 | | | | | | | |
| 16 | | | | | | | |
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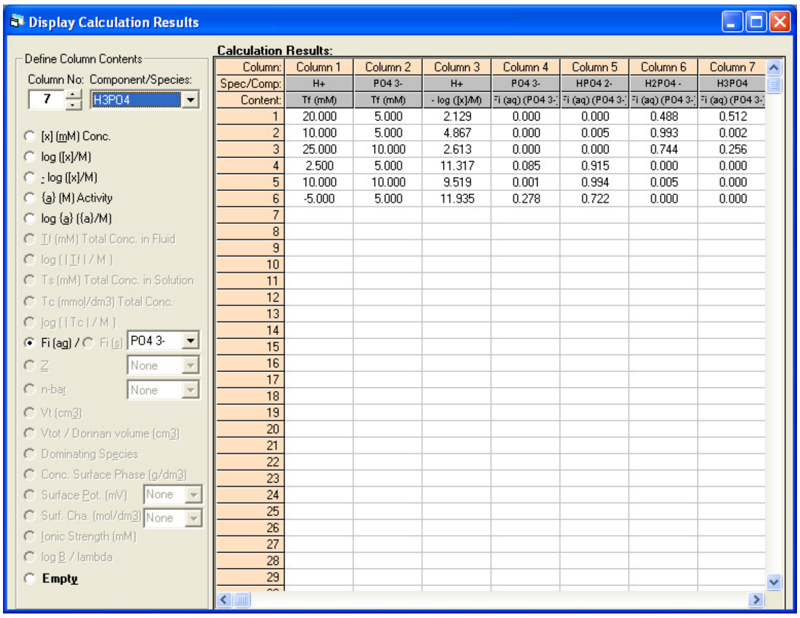
| 23 | | | | | | | |
| 24 | | | | | | | |
| 25 | | | | | | | |
| 26 | | | | | | | |
| 27 | | | | | | | |
| 28 | | | | | | | |
| 29 | | | | | | | |



Column No: 7

Component/Species: H3PO4

● Fi (aq) / ○ Fi (s): PO4 3-

Calculation Results:

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | PO4 3- | H+ | PO4 3- | HPO4 2- | H2PO4 - | H3PO4 |
| Content: | Tf (mM) | Tf (mM) | - log ([x]/M) | Fi (aq) (PO4 3- | Fi (aq) (PO4 3- | Fi (aq) (PO4 3- | Fi (aq) (PO4 3- |
| 1 | 20.000 | 5.000 | 2.129 | 0.000 | 0.000 | 0.488 | 0.512 |
| 2 | 10.000 | 5.000 | 4.867 | 0.000 | 0.005 | 0.993 | 0.002 |
| 3 | 25.000 | 10.000 | 2.613 | 0.000 | 0.000 | 0.744 | 0.256 |
| 4 | 2.500 | 5.000 | 11.317 | 0.085 | 0.915 | 0.000 | 0.000 |
| 5 | 10.000 | 10.000 | 9.519 | 0.001 | 0.994 | 0.005 | 0.000 |
| 6 | -5.000 | 5.000 | 11.935 | 0.278 | 0.722 | 0.000 | 0.000 |
| 7 | | | | | | | |
| 8 | | | | | | | |
| 9 | | | | | | | |
| 10 | | | | | | | |
| 11 | | | | | | | |
| 12 | | | | | | | |
| 13 | | | | | | | |
| 14 | | | | | | | |
| 15 | | | | | | | |
| 16 | | | | | | | |
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| 18 | | | | | | | |
| 19 | | | | | | | |
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| 22 | | | | | | | |
| 23 | | | | | | | |
| 24 | | | | | | | |
| 25 | | | | | | | |
| 26 | | | | | | | |
| 27 | | | | | | | |
| 28 | | | | | | | |
| 29 | | | | | | | |

7. Repeat steps 2 – 6 with $H^+$ and $PO_4^{3-}$ as components, *i.e.* Example 1b), and note that the results, of course, becomes exactly the same.

## 5.2 Create a pH-diagram for the heterogeneous water-carbon dioxide system

**Task:** Construct a pH diagram, plot the logarithmic concentrations of all species as function of pH ($0<pH<10$), for the heterogeneous water - carbon dioxide system. Set the partial carbon dioxide pressure to 1 atm.

1. The following four equilibrium reactions describe the water - carbon dioxide system.

| | | log β* |
|---|---|---|
| 1 | $H_2O \rightleftarrows H^+ + OH^-$ | -14.00 |
| 2 | $CO_2(g) + H_2O \rightleftarrows H_2CO_3(aq)$ | -1.47 |
| 3 | $H_2CO_3\,(aq) \rightleftarrows HCO_3^- + H^+$ | -6.35 |
| 4 | $HCO_3^- \rightleftarrows CO_3^{2-} + H^+$ | -10.33 |

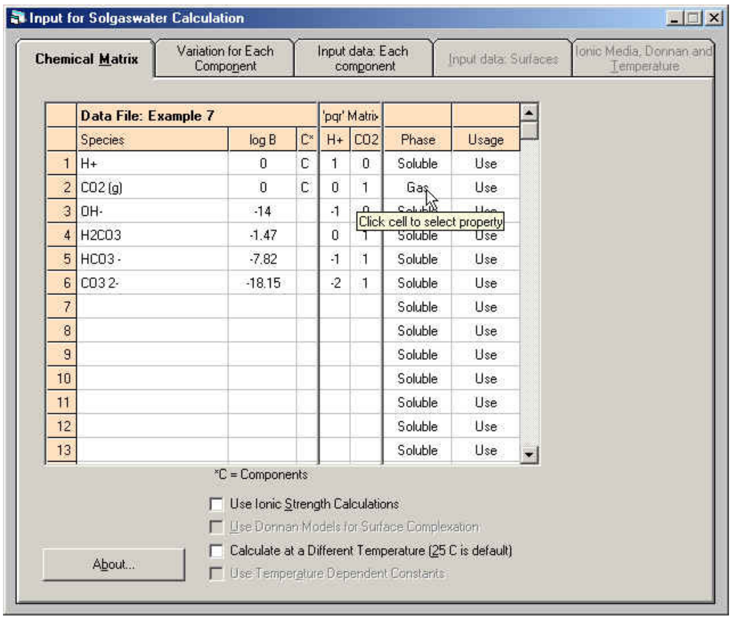
*Equilibrium constants valid at infinite dilution and 25°C.

2. Define chemical components that can describe all species present ($H^+$, $OH^-$, $CO_2(g)$, $H_2CO_3(aq)$, $HCO_3^-$, $CO_3^{2-}$).
   Components: $H^+$ and $CO_2(g)$

3. Write a chemical matrix using the components and the equilibrium reactions.

| | log β | $H^+$ | $CO_2(g)$ | Equilibria Nos. |
|---|---|---|---|---|
| $H^+$ | 0 | 1 | 0 | |
| $CO_2(g)$ | 0 | 0 | 1 | |
| $OH^-$ | -14.00 | -1 | 0 | 1 |
| $H_2CO_3\,(aq)$ | -1.47 | 0 | 1 | 2 |
| $HCO_3^-$ | -7.82 | -1 | 1 | 2 + 3 |
| $CO_3^{2-}$ | -18.15 | -2 | 1 | 2 + 3 + 4 |

4. Enter the matrix. Blanks in the matrix will be interpreted as zeros by the program. By clicking the right mouse button in the first column it is possible to insert, clear and delete rows in the matrix. Change the phase properties for $CO_2$(g) to Gas.



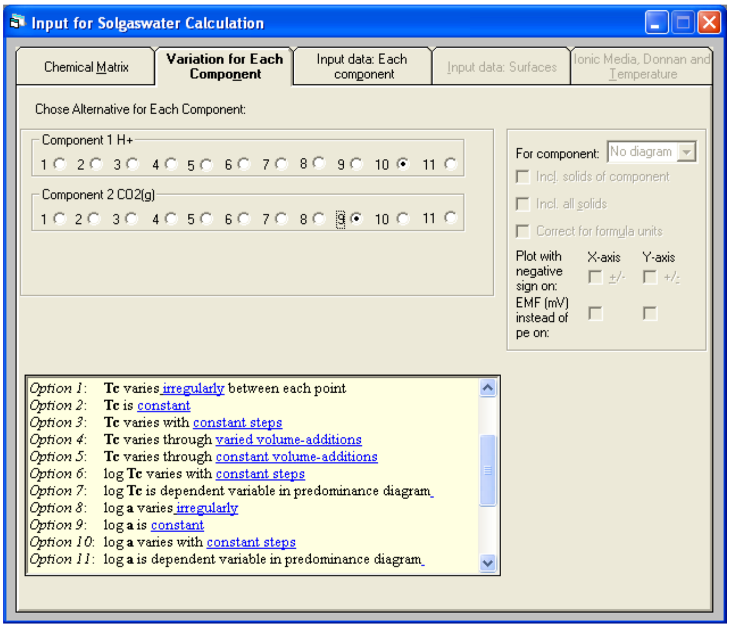
| | Data File: Example 7 | | | 'pqr' Matrix | | | |
|---|---|---|---|---|---|---|---|
| | Species | log B | C* | H+ | CO2 | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 0 | Soluble | Use |
| 2 | CO2 (g) | 0 | C | 0 | 1 | Gas | Use |
| 3 | OH- | -14 | | -1 | 0 | Soluble | Use |
| 4 | H2CO3 | -1.47 | | 0 | 1 | Soluble | Use |
| 5 | HCO3 - | -7.82 | | -1 | 1 | Soluble | Use |
| 6 | CO3 2- | -18.15 | | -2 | 1 | Soluble | Use |
| 7 | | | | | | Soluble | Use |
| 8 | | | | | | Soluble | Use |
| 9 | | | | | | Soluble | Use |
| 10 | | | | | | Soluble | Use |
| 11 | | | | | | Soluble | Use |
| 12 | | | | | | Soluble | Use |
| 13 | | | | | | Soluble | Use |

Click cell to select property

*C = Components

☐ Use Ionic Strength Calculations
☐ Use Donnan Models for Surface Complexation
☐ Calculate at a Different Temperature (25 C is default)
☐ Use Temperature Dependent Constants

5. Move to next tab “Variation for each component”. At this tab we choose which kind of calculation we should do. For this example we would like to step pH (Component 1 $H^+$, option 10) and to keep the carbon dioxide activity (logarithmic) constant (Component 2 $CO_2$(g), option 9).



Chose Alternative for Each Component:

Component 1 H+
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ● 11 ○

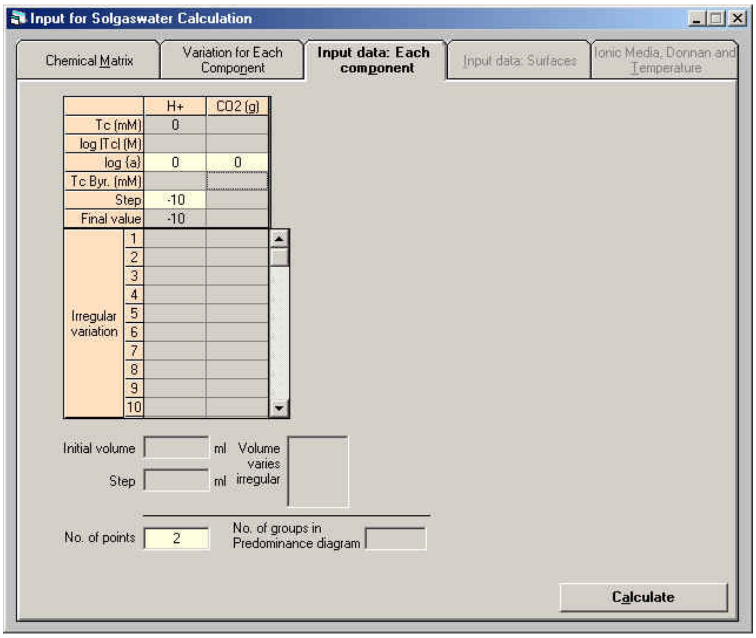
Component 2 CO2(g)
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ● 10 ○ 11 ○

For component: No diagram
☐ Incl. solids of component
☐ Incl. all solids
☐ Correct for formula units

Plot with negative sign on: X-axis ☐ +/- Y-axis ☐ +/-
EMF (mV) instead of pe on: ☐ ☐

*Option 1:* Tc varies irregularly between each point
*Option 2:* Tc is constant
*Option 3:* Tc varies with constant steps
*Option 4:* Tc varies through varied volume-additions
*Option 5:* Tc varies through constant volume-additions
*Option 6:* log Tc varies with constant steps
*Option 7:* log Tc is dependent variable in predominance diagram
*Option 8:* log a varies irregularly
*Option 9:* log a is constant
*Option 10:* log a varies with constant steps
*Option 11:* log a is dependent variable in predominance diagram

6. Move to next tab “Input data: Each component”. Enter Start value “log {a}”, Step length “Step” for the first component ($H^+$), the logarithmic carbon dioxide activity and the number of points. Since the activity of a gas species is equal to its partial pressure, the logarithmic activity will be 0.

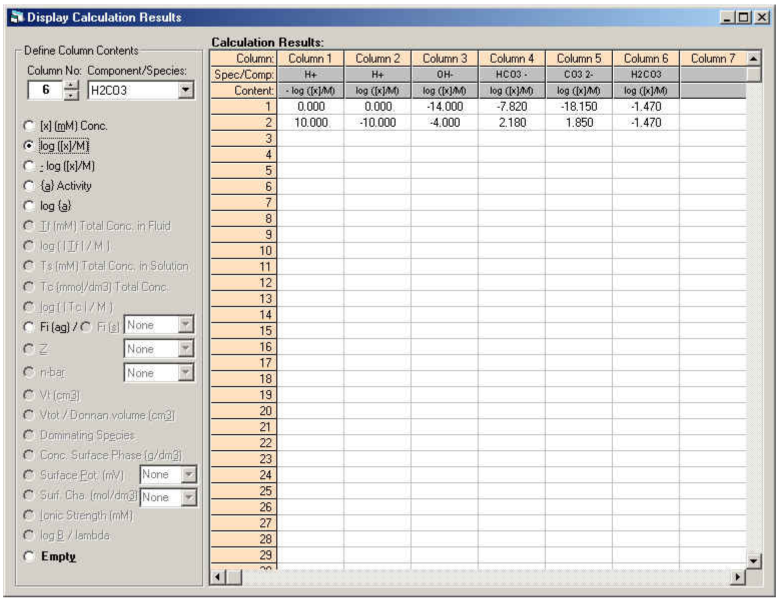


|  | H+ | CO2 (g) |
|---|---|---|
| Tc (mM) | 0 |  |
| log [Tc] (M) |  |  |
| log {a} | 0 | 0 |
| Tc Byr. (mM) |  |  |
| Step | -10 |  |
| Final value | -10 |  |

No. of points 2

7. Start the calculation by pressing the “Calculate” button or use the Calculate menu.

8. Viewing the result.
Choose $H^+$ in the Component/Species box and then “-log {[x]/M}” to view pH in column 1. Display the logarithmic concentration of all soluble species present in the following columns.



Column No: 6 Component/Species: H2CO3

Calculation Results:

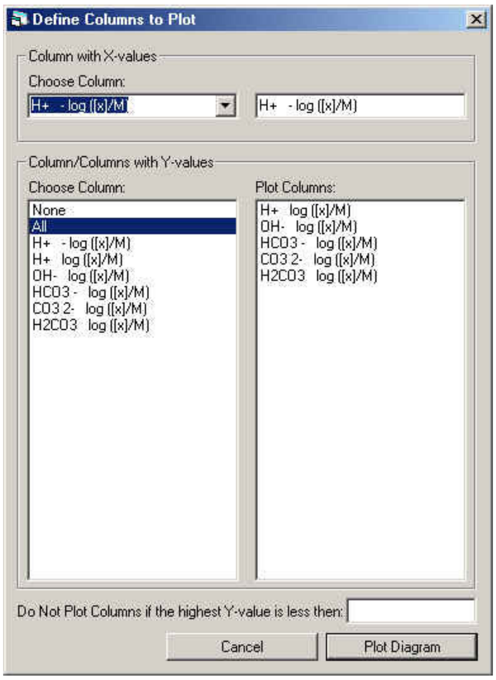
| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | H+ | OH- | HCO3 - | CO3 2- | H2CO3 |  |
| Content: | - log ([x]/M) | log ([x]/M) | log ([x]/M) | log ([x]/M) | log ([x]/M) | log ([x]/M) |  |
| 1 | 0.000 | 0.000 | -14.000 | -7.820 | -18.150 | -1.470 |  |
| 2 | 10.000 | -10.000 | -4.000 | 2.180 | 1.850 | -1.470 |  |
| 3 |  |  |  |  |  |  |  |
| 4 |  |  |  |  |  |  |  |
| 5 |  |  |  |  |  |  |  |
| 6 |  |  |  |  |  |  |  |
| 7 |  |  |  |  |  |  |  |
| 8 |  |  |  |  |  |  |  |
| 9 |  |  |  |  |  |  |  |
| 10 |  |  |  |  |  |  |  |
| 11 |  |  |  |  |  |  |  |
| 12 |  |  |  |  |  |  |  |
| 13 |  |  |  |  |  |  |  |
| 14 |  |  |  |  |  |  |  |
| 15 |  |  |  |  |  |  |  |
| 16 |  |  |  |  |  |  |  |
| 17 |  |  |  |  |  |  |  |
| 18 |  |  |  |  |  |  |  |
| 19 |  |  |  |  |  |  |  |
| 20 |  |  |  |  |  |  |  |
| 21 |  |  |  |  |  |  |  |
| 22 |  |  |  |  |  |  |  |
| 23 |  |  |  |  |  |  |  |
| 24 |  |  |  |  |  |  |  |
| 25 |  |  |  |  |  |  |  |
| 26 |  |  |  |  |  |  |  |
| 27 |  |  |  |  |  |  |  |
| 28 |  |  |  |  |  |  |  |
| 29 |  |  |  |  |  |  |  |

9. Plotting the results

Choose “Plot calculation data” from the “Diagrams” menu.

The default setting is that the first column in the Calculation Result grid contains X-values and all remaining columns will be plotted on the Y-axis. It is possible to remove a series from the Plot Columns list by clicking on the series. As an option you can choose to exclude all curves that never exceed a given value.

Continue by pressing “Plot diagram”.


Define Columns to Plot

Column with X-values

Choose Column: H+ - log ([x]/M)

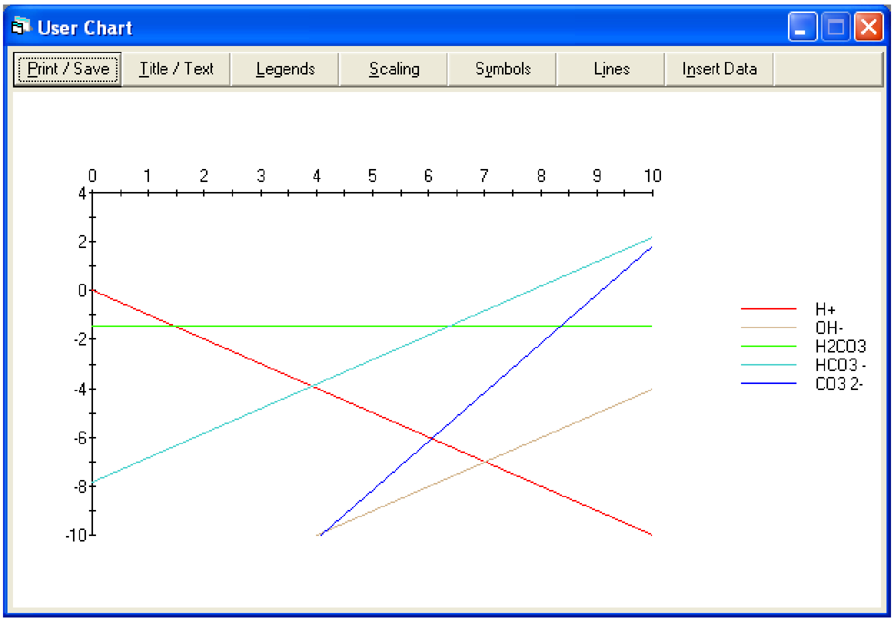
H+ - log ([x]/M)

Column/Columns with Y-values

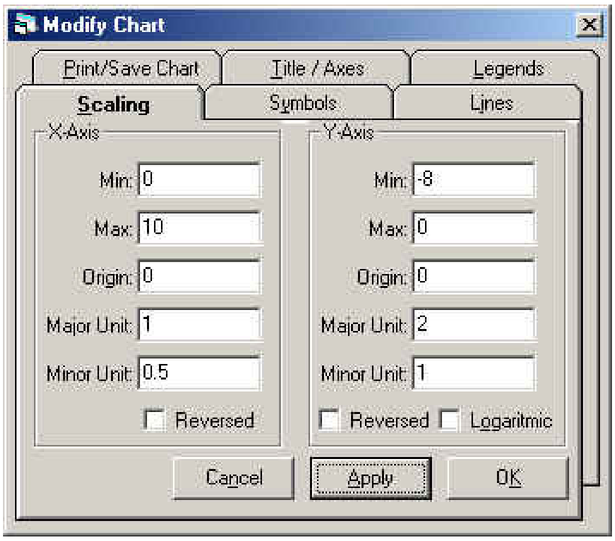
Choose Column:
None
All
H+ - log ([x]/M)
H+ log ([x]/M)
OH- log ([x]/M)
HCO3 - log ([x]/M)
CO3 2- log ([x]/M)
H2CO3 log ([x]/M)

Plot Columns:
H+ log ([x]/M)
OH- log ([x]/M)
HCO3 - log ([x]/M)
CO3 2- log ([x]/M)
H2CO3 log ([x]/M)

Do Not Plot Columns if the highest Y-value is less then:

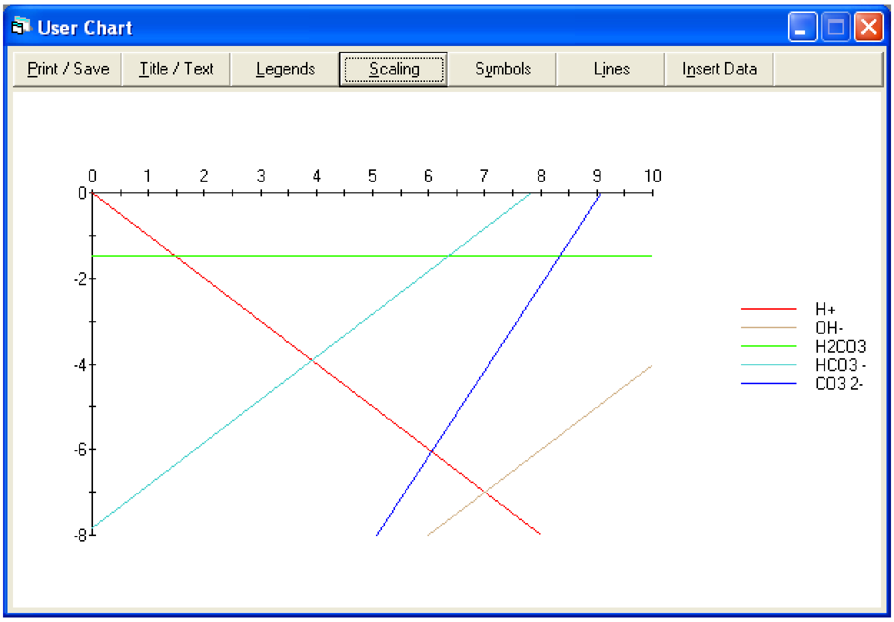


10. The diagram
You can modify your chart using the top buttons, e.g. change the scale, labels, lines and symbols, or print your diagram. For example rescale Y-axis (min –8, max 0, origin 0).



X-Axis
Min: 0
Max: 10
Origin: 0
Major Unit: 1
Minor Unit: 0.5
☐ Reversed

Y-Axis
Min: -8
Max: 0
Origin: 0
Major Unit: 2
Minor Unit: 1
☐ Reversed ☐ Logaritmic



## 5.3 Surface complexation models ($H^+$-goethite)

**Task:** Compare experimental data points with a model calculation by plotting a diagram showing the protonation of a goethite surface as a function of pH.

1. The following equilibrium reactions and electrostatic information describe the actual chemical system.

| | | log β* |
|---|---|---|
| 1 | $H_2O \rightleftarrows H^+ + OH^-$ | -13.775 |
| 2 | $\equiv FeOH + H^+ \rightleftarrows \equiv FeOH_2^+$ | 7.47 |
| 3 | $\equiv FeOH \rightleftarrows \equiv FeO^- + H^+$ | -9.51 |

| Additional information about the goethite system: | |
|---|---|
| Surface site concentration | 1.2 mmol/dm$^3$ |
| Solid phase concentration | 11 g/dm$^3$ |
| Specific surface area | 39.9 m$^2$/g |
| Specific capacitance | 1.28 C/V·m$^2$ * |

*Constants valid at 25°C and 100mM ($NaNO_3$).

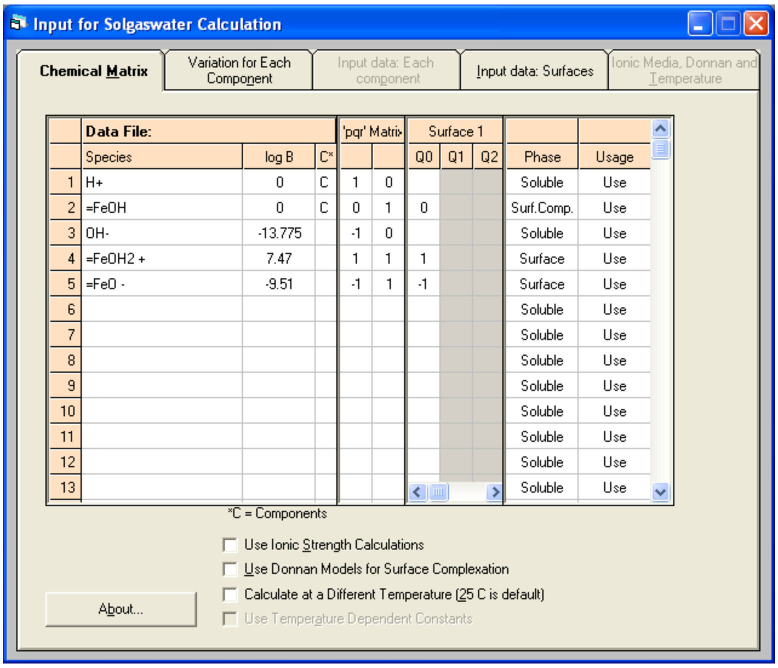
2. Two components: $H^+$ and ≡FeOH

3. The chemical matrix and the surface charges.

| | log β | $H^+$ | ≡FeOH | $Q_0$ | $Q_1$ | $Q_2$ |
|---|---|---|---|---|---|---|
| $H^+$ | 0 | 1 | 0 | | | |
| ≡FeOH | 0 | 0 | 1 | 0 | 0 | 0 |
| $OH^-$ | -13.775 | -1 | 0 | | | |
| $\equiv FeOH_2^+$ | 7.47 | 1 | 1 | 1 | 0 | 0 |
| $\equiv FeO^-$ | -9.51 | -1 | 1 | -1 | 0 | 0 |

WinSGW can simultaneously model inner-sphere complexes in the 0-plane (the plane of the surface sites), outer-sphere complexes in the 1-plane, electrolyte ion pairs in the 2-plane, and the diffuse layer of electrolyte ions.

4. Start WinSGW and enter the matrix. By changing the Phase properties of ≡FeOH from “Soluble” to “Surf.Comp.” the surface charge columns become visible. It is only possible to enter surface charge for species with “Surf.Comp.” or “Surface” as the Phase property. The default model in WinSGW is CCM and, to open the columns for $Q_1$ and $Q_2$, the relevant surface charge model is chosen on the tab “Input data: Surfaces”.

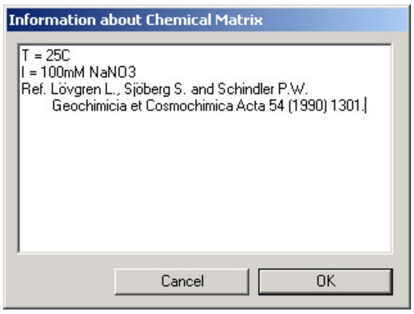


| | Data File: | | | 'pqr' Matrix | | Surface 1 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Species | log B | C* | | | Q0 | Q1 | Q2 | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 0 | | | | Soluble | Use |
| 2 | =FeOH | 0 | C | 0 | 1 | 0 | | | Surf.Comp. | Use |
| 3 | OH- | -13.775 | | -1 | 0 | | | | Soluble | Use |
| 4 | =FeOH2 + | 7.47 | | 1 | 1 | 1 | | | Surface | Use |
| 5 | =FeO - | -9.51 | | -1 | 1 | -1 | | | Surface | Use |
| 6 | | | | | | | | | Soluble | Use |
| 7 | | | | | | | | | Soluble | Use |
| 8 | | | | | | | | | Soluble | Use |
| 9 | | | | | | | | | Soluble | Use |
| 10 | | | | | | | | | Soluble | Use |
| 11 | | | | | | | | | Soluble | Use |
| 12 | | | | | | | | | Soluble | Use |
| 13 | | | | | | | | | Soluble | Use |

*C = Components

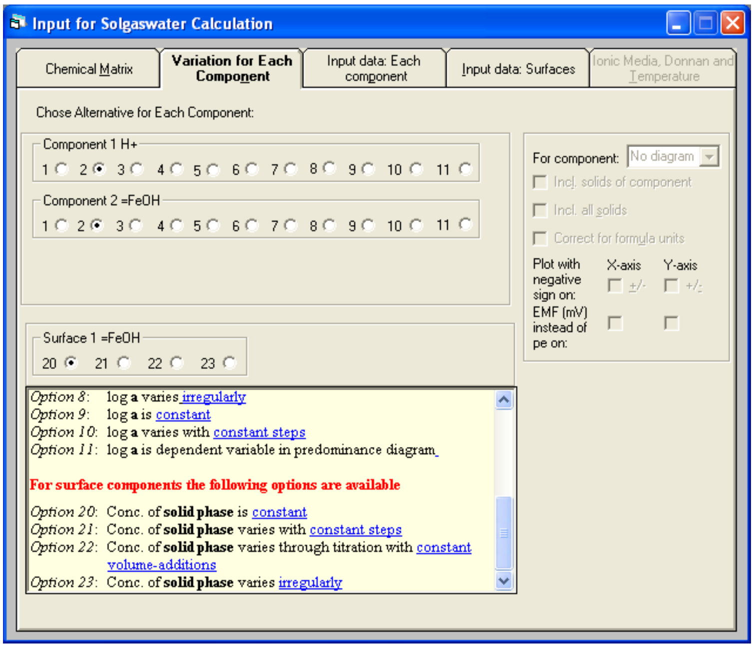
☐ Use Ionic Strength Calculations
☐ Use Donnan Models for Surface Complexation
☐ Calculate at a Different Temperature (25 C is default)
☐ Use Temperature Dependent Constants

5. Under “About…” it is possible to enter information about the chemical system e.g. temperature, ionic strength and references.



T = 25C
I = 100mM NaNO3
Ref. Lövgren L., Sjöberg S. and Schindler P.W.
Geochimicia et Cosmochimica Acta 54 (1990) 1301.

6. Move to next tab “Variation for each component”.
Choose to make constant steps in pH and to keep the total concentration of goethite constant. (Component 1 $H^+$, option 10; Component 2 ≡FeOH, option 2; Surface 1 ≡FeOH, option 20).



Chose Alternative for Each Component:

Component 1 H+
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

Component 2 =FeOH
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

Surface 1 =FeOH
20 ● 21 ○ 22 ○ 23 ○

For component: No diagram
☐ Incl. solids of component
☐ Incl. all solids
☐ Correct for formula units

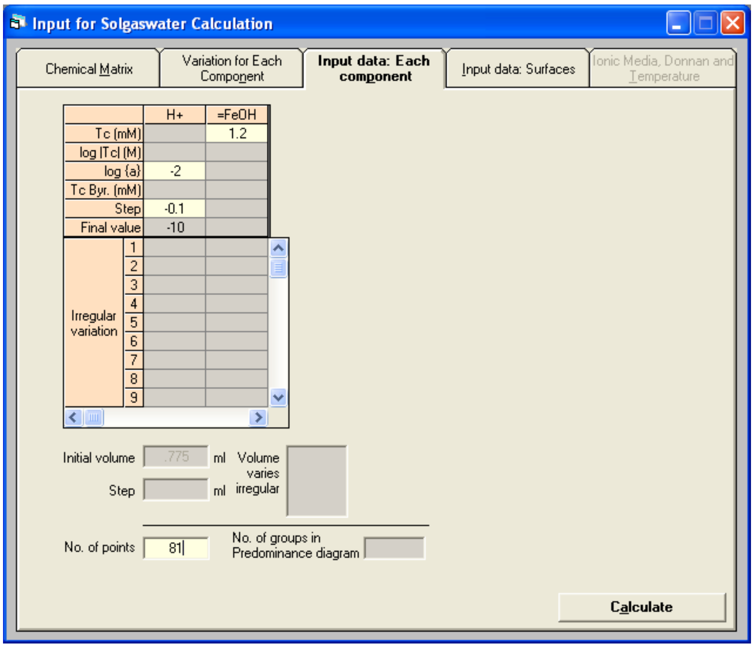
Plot with negative sign on: X-axis ☐ +/- Y-axis ☐ +/-
EMF (mV) instead of pe on: ☐ ☐

*Option 8*: log **a** varies irregularly
*Option 9*: log **a** is constant
*Option 10*: log **a** varies with constant steps
*Option 11*: log **a** is dependent variable in predominance diagram

**For surface components the following options are available**

*Option 20*: Conc. of **solid phase** is constant
*Option 21*: Conc. of **solid phase** varies with constant steps
*Option 22*: Conc. of **solid phase** varies through titration with constant volume-additions
*Option 23*: Conc. of **solid phase** varies irregularly

7. On the “Input data: Each component” tab, enter the start value of “log {a}”, the step length “Step” for the first component $H^+$, the total concentration of goethite “Tc” and the number of points.



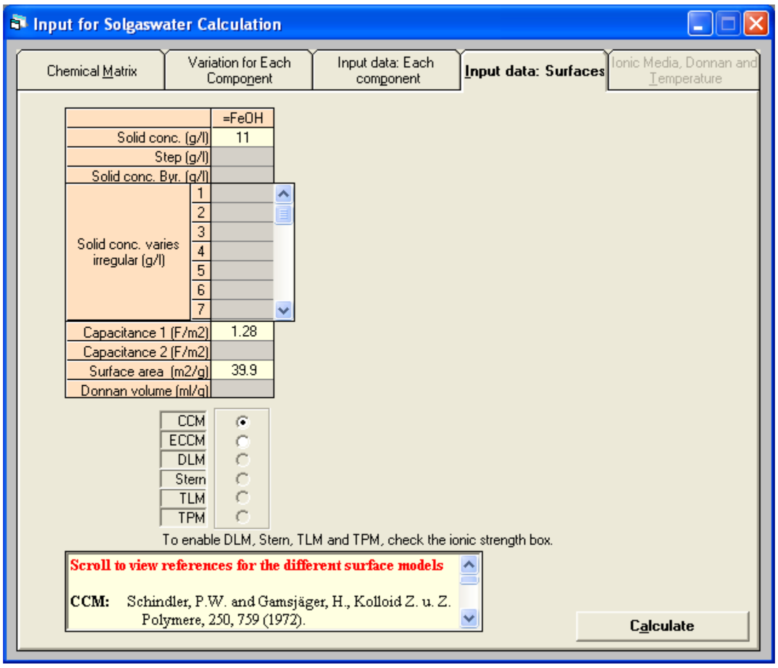
|  | H+ | =FeOH |
|---|---|---|
| Tc (mM) |  | 1.2 |
| log [Tc] (M) |  |  |
| log {a} | -2 |  |
| Tc Byr. (mM) |  |  |
| Step | -0.1 |  |
| Final value | -10 |  |

Irregular variation: 1, 2, 3, 4, 5, 6, 7, 8, 9

Initial volume .775 ml
Step ml
Volume varies irregular

No. of points 81
No. of groups in Predominance diagram

8. Move to next tab “Input data: Surfaces”. WinSGW can apply different electrostatic models to describe the double layer at the surface. Depending on the model, different charge columns (Q0, Q1 and Q2) will be activated on the Chemical Matrix tab and the program will prompt for one or two capacitance values. To activate the ionic strength dependent electrostatic models, the ionic strength check box on tab “Chemical Matrix” must be marked. In this example the Constant Capacitance Model is to be used. Enter values for solid phase concentration, capacitance 1 and the specific surface area.
N.B. In the yellow text box references describing the different models are listed.



| | | =FeOH |
|---|---|---|
| Solid conc. (g/l) | | 11 |
| Step (g/l) | | |
| Solid conc. Bvr. (g/l) | | |
| Solid conc. varies irregular (g/l) | 1 | |
| | 2 | |
| | 3 | |
| | 4 | |
| | 5 | |
| | 6 | |
| | 7 | |
| Capacitance 1 (F/m2) | | 1.28 |
| Capacitance 2 (F/m2) | | |
| Surface area (m2/g) | | 39.9 |
| Donnan volume (ml/g) | | |

CCM ●
ECCM ○
DLM ○
Stern ○
TLM ○
TPM ○

To enable DLM, Stern, TLM and TPM, check the ionic strength box.

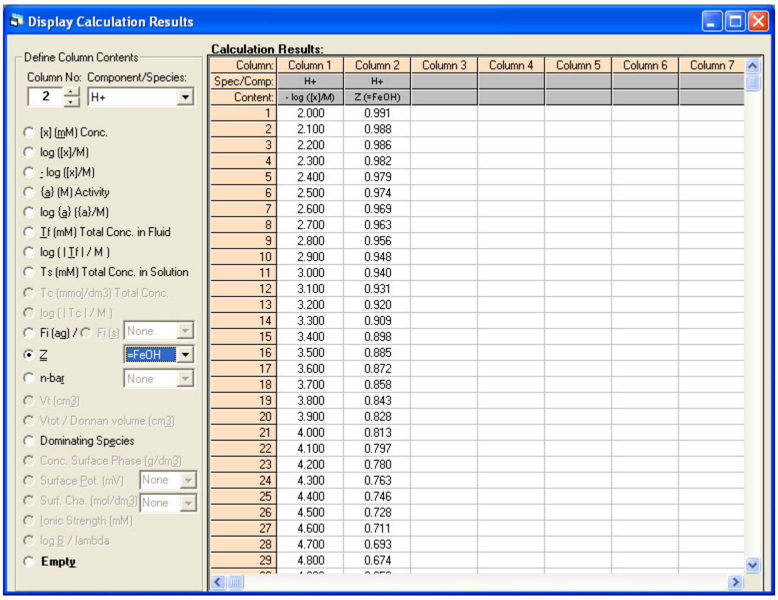
**Scroll to view references for the different surface models**

**CCM:** Schindler, P.W. and Gamsjäger, H., Kolloid Z. u. Z. Polymere, 250, 759 (1972).

9. Start the calculation.

## 10. Viewing the result

View pH in the first column and Z in the second column (Choose $H^+$ in the Component/Species box, “Z” and ≡FeOH in the box next to “Z”). Z is calculated as the average number of protons taken up by ≡FeOH.



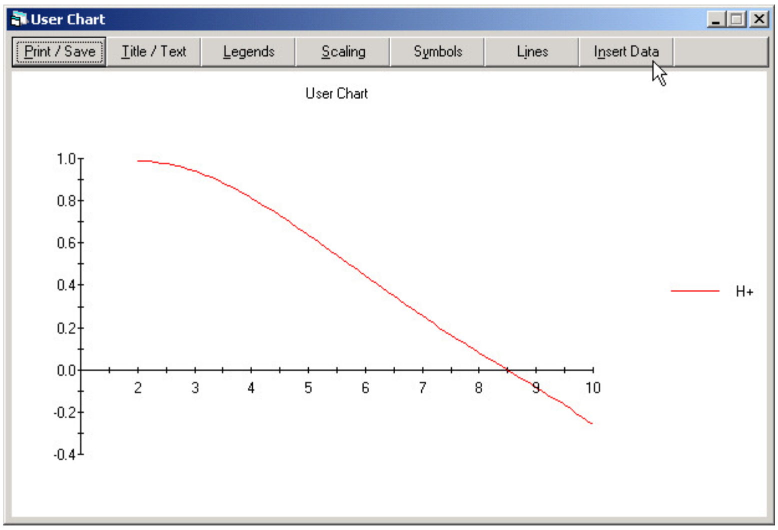
Column No: 2
Component/Species: H+
Z: =FeOH

Calculation Results:

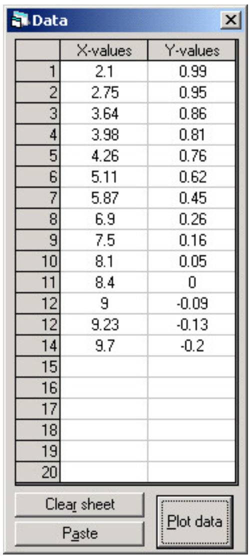
| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | H+ | | | | | |
| Content: | - log ([x]/M) | Z (=FeOH) | | | | | |
| 1 | 2.000 | 0.991 | | | | | |
| 2 | 2.100 | 0.988 | | | | | |
| 3 | 2.200 | 0.986 | | | | | |
| 4 | 2.300 | 0.982 | | | | | |
| 5 | 2.400 | 0.979 | | | | | |
| 6 | 2.500 | 0.974 | | | | | |
| 7 | 2.600 | 0.969 | | | | | |
| 8 | 2.700 | 0.963 | | | | | |
| 9 | 2.800 | 0.956 | | | | | |
| 10 | 2.900 | 0.948 | | | | | |
| 11 | 3.000 | 0.940 | | | | | |
| 12 | 3.100 | 0.931 | | | | | |
| 13 | 3.200 | 0.920 | | | | | |
| 14 | 3.300 | 0.909 | | | | | |
| 15 | 3.400 | 0.898 | | | | | |
| 16 | 3.500 | 0.885 | | | | | |
| 17 | 3.600 | 0.872 | | | | | |
| 18 | 3.700 | 0.858 | | | | | |
| 19 | 3.800 | 0.843 | | | | | |
| 20 | 3.900 | 0.828 | | | | | |
| 21 | 4.000 | 0.813 | | | | | |
| 22 | 4.100 | 0.797 | | | | | |
| 23 | 4.200 | 0.780 | | | | | |
| 24 | 4.300 | 0.763 | | | | | |
| 25 | 4.400 | 0.746 | | | | | |
| 26 | 4.500 | 0.728 | | | | | |
| 27 | 4.600 | 0.711 | | | | | |
| 28 | 4.700 | 0.693 | | | | | |
| 29 | 4.800 | 0.674 | | | | | |

## 11. Plotting the results

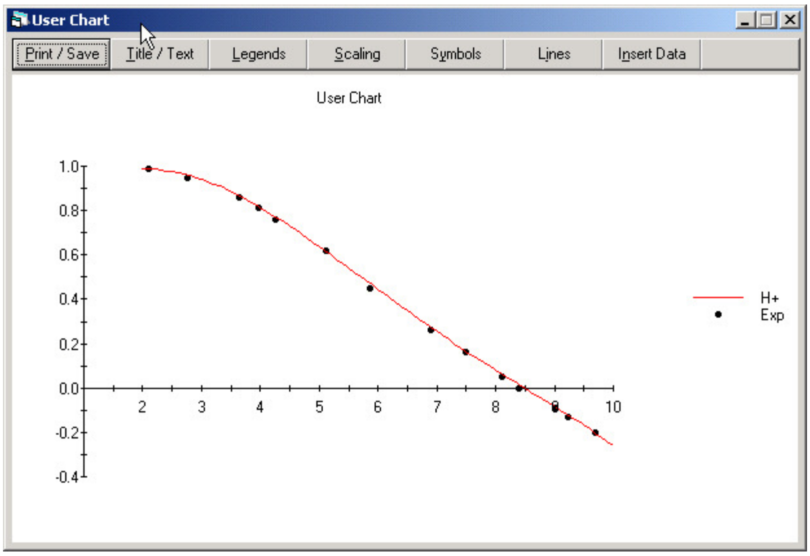
Plot Z as a function of pH.



12. Insert experimental data points in the chart
Choose Insert Data at the top of the chart and enter your experimental values or paste them using the Windows Clipboard.



|  | X-values | Y-values |
|---|---|---|
| 1 | 2.1 | 0.99 |
| 2 | 2.75 | 0.95 |
| 3 | 3.64 | 0.86 |
| 4 | 3.98 | 0.81 |
| 5 | 4.26 | 0.76 |
| 6 | 5.11 | 0.62 |
| 7 | 5.87 | 0.45 |
| 8 | 6.9 | 0.26 |
| 9 | 7.5 | 0.16 |
| 10 | 8.1 | 0.05 |
| 11 | 8.4 | 0 |
| 12 | 9 | -0.09 |
| 12 | 9.23 | -0.13 |
| 14 | 9.7 | -0.2 |
| 15 |  |  |
| 16 |  |  |
| 17 |  |  |
| 18 |  |  |
| 19 |  |  |
| 20 |  |  |



## *5.4 Create a predominance area diagram ($H^+$-$Fe^{2+}$-$e^-$)*

**Task:** Plot a diagram showing the predominating iron species as a function of pH and pe for the $H^+$-$Fe^{2+}$-$e^-$ system. This type of plot is commonly referred to as a predominance area diagram.

NB. pe is the negative logarithm of the formal electron activity and can be correlated to the NHE (normal hydrogen electrode) electrode potential ($E_H$, mV) with the following equations:
pe = $E_H$ / g    g =RT ln(10) / F
(R: molar gas constant, T: absolute temperature in Kelvin, F: Faradays constant)
With $E_H$ plotted on the Y-axis, the diagram is usually referred to as a Pourbaix diagram.

1. The following equilibrium reactions describe the actual chemical system.

| | | log β* |
|---|---|---|
| 1 | $H_2O \rightleftarrows H^+ + OH^-$ | -14.00 |
| 2 | $Fe^{2+} + OH^- \rightleftarrows FeOH^+$ | 4.5 |
| 3 | $Fe^{2+} + 2OH^- \rightleftarrows Fe(OH)_2(aq)$ | 7.4 |
| 4 | $Fe^{2+} + 3OH^- \rightleftarrows Fe(OH)_3^-$ | 11.0 |
| 5 | $Fe^{2+} + 2OH^- \rightleftarrows Fe(OH)_2(s)$ | 15.1 |
| 6 | $Fe^{3+} + OH^- \rightleftarrows Fe(OH)^{2+}$ | 11.8 |
| 7 | $Fe^{3+} + 2OH^- \rightleftarrows Fe(OH)_2^+$ | 22.3 |
| 8 | $Fe^{3+} + 4OH^- \rightleftarrows Fe(OH)_4^-$ | 34.4 |
| 9 | $2Fe^{3+} + 2OH^- \rightleftarrows Fe_2(OH)_2^{4+}$ | 25.0 |
| 10 | $Fe^{3+} + 3OH^- \rightleftarrows Fe(OH)_3(am)$ | 38.8 |
| 11 | $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$ | 13.0 |
| 12 | $Fe^{2+} + 2e^- \rightleftarrows Fe(s)$ | -13.8 |

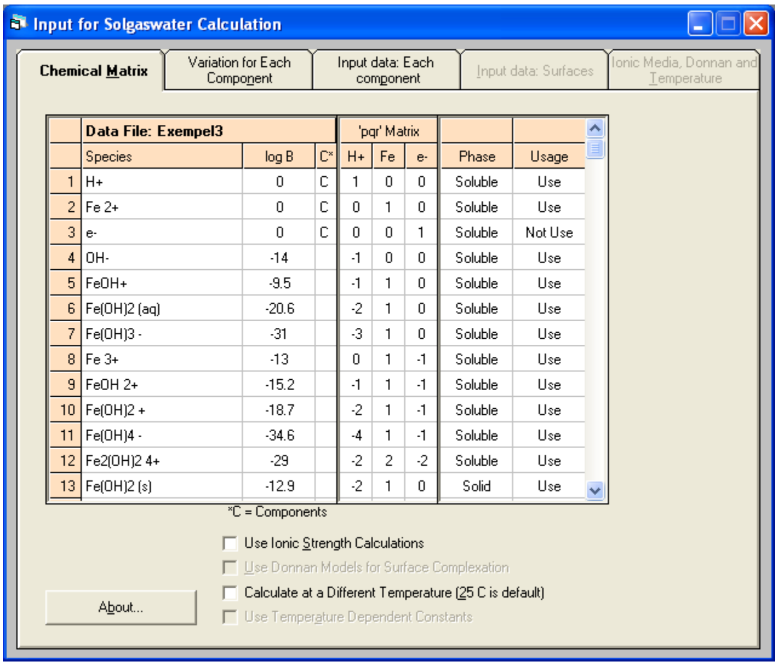
*Constants valid at 25°C and at infinite dilution.

2. Three components: $H^+$, $Fe^{2+}$ and $e^-$.

3. The chemical matrix.

| | log β | $H^+$ | $Fe^{2+}$ | $e^-$ | Equilibria Nos. |
|---|---|---|---|---|---|
| $H^+$ | 0 | 1 | 0 | 0 | |
| $Fe^{2+}$ | 0 | 0 | 1 | 0 | |
| $e^-$ | 0 | 0 | 0 | 1 | |
| $OH^-$ | -14.0 | -1 | 0 | 0 | 1 |
| $FeOH^+$ | -9.5 | -1 | 1 | 0 | 1 + 2 |
| $Fe(OH)_2(aq)$ | -20.6 | -2 | 1 | 0 | $2 \cdot 1 + 3$ |
| $Fe(OH)_3^-$ | -31.0 | -3 | 1 | 0 | $3 \cdot 1 + 4$ |
| $Fe^{3+}$ | -13.0 | 0 | 1 | -1 | -11 |
| $FeOH^{2+}$ | -15.2 | -1 | 1 | -1 | 1 + 6 - 11 |
| $Fe(OH)_2^+$ | -18.7 | -2 | 1 | -1 | $2 \cdot 1 + 7 - 11$ |
| $Fe(OH)_4^-$ | -34.6 | -4 | 1 | -1 | $4 \cdot 1 + 8 - 11$ |
| $Fe_2(OH)_2^{4+}$ | -29.0 | -2 | 2 | -2 | $2 \cdot 1 + 9 - 2 \cdot 11$ |
| $Fe(OH)_2(s)$ | -12.9 | -2 | 1 | 0 | $2 \cdot 1 + 5$ |
| $Fe(OH)_3(am)$ | -16.2 | -3 | 1 | -1 | $3 \cdot 1 + 10 - 11$ |
| Fe(s) | -13.8 | 0 | 1 | 2 | 12 |

4. Start WinSGW and enter the matrix. Remember to change "Usage" to Not Use for the component $e^-$ (*cf.* p. 12) and "Phase" to Solid for the three solids.

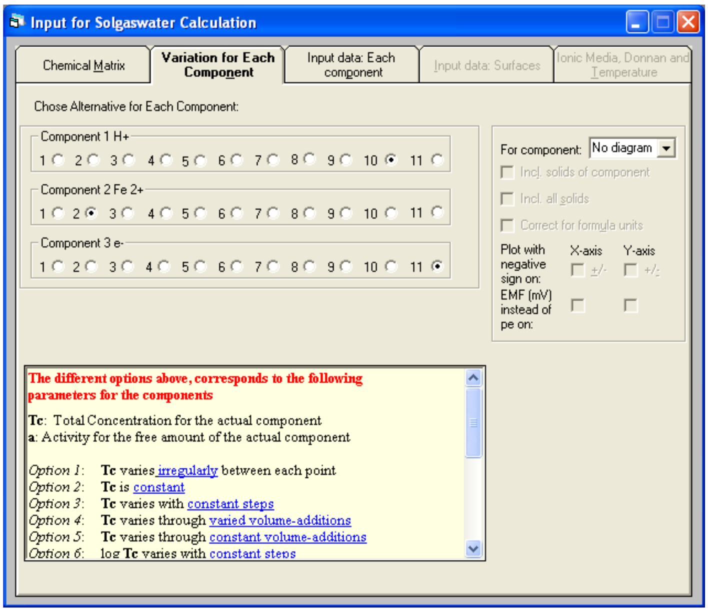


| | Data File: Exempel3 | | | 'pqr' Matrix | | | | |
|---|---|---|---|---|---|---|---|---|
| | Species | log B | C* | H+ | Fe | e- | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 0 | 0 | Soluble | Use |
| 2 | Fe 2+ | 0 | C | 0 | 1 | 0 | Soluble | Use |
| 3 | e- | 0 | C | 0 | 0 | 1 | Soluble | Not Use |
| 4 | OH- | -14 | | -1 | 0 | 0 | Soluble | Use |
| 5 | FeOH+ | -9.5 | | -1 | 1 | 0 | Soluble | Use |
| 6 | Fe(OH)2 (aq) | -20.6 | | -2 | 1 | 0 | Soluble | Use |
| 7 | Fe(OH)3 - | -31 | | -3 | 1 | 0 | Soluble | Use |
| 8 | Fe 3+ | -13 | | 0 | 1 | -1 | Soluble | Use |
| 9 | FeOH 2+ | -15.2 | | -1 | 1 | -1 | Soluble | Use |
| 10 | Fe(OH)2 + | -18.7 | | -2 | 1 | -1 | Soluble | Use |
| 11 | Fe(OH)4 - | -34.6 | | -4 | 1 | -1 | Soluble | Use |
| 12 | Fe2(OH)2 4+ | -29 | | -2 | 2 | -2 | Soluble | Use |
| 13 | Fe(OH)2 (s) | -12.9 | | -2 | 1 | 0 | Solid | Use |

*C = Components

☐ Use Ionic Strength Calculations
☐ Use Donnan Models for Surface Complexation
☐ Calculate at a Different Temperature (25 C is default)
☐ Use Temperature Dependent Constants

5. Move to next tab “Variation for each component”.
Choose to step pH, to keep the total concentration of iron constant and to step pe (as dependent variable).
(Component 1 $H^+$, option 10; Component 2 $Fe^{2+}$, option 2; Component 3 $e^-$, option 11).



Chose Alternative for Each Component:

Component 1 H+
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ● 11 ○

Component 2 Fe 2+
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

Component 3 e-
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ●

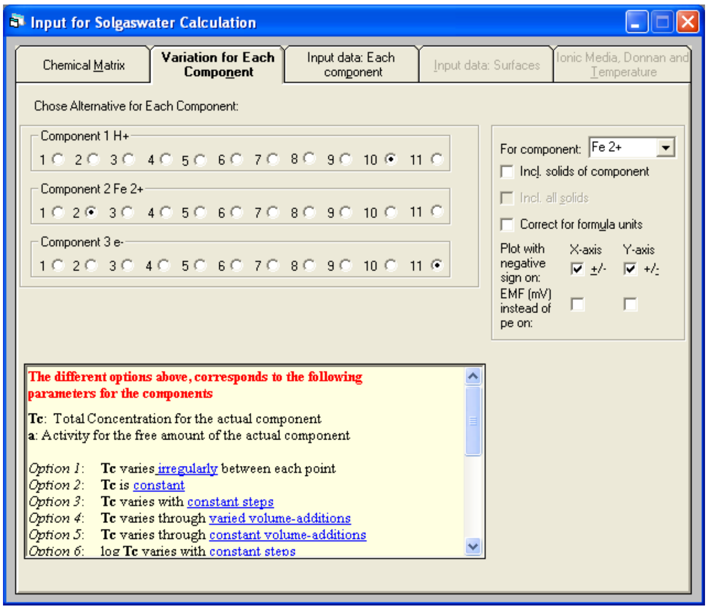
For component: No diagram
☐ Incl. solids of component
☐ Incl. all solids
☐ Correct for formula units
Plot with negative sign on: X-axis ☐ +/- Y-axis ☐ +/-
EMF (mV) instead of pe on: ☐ ☐

**The different options above, corresponds to the following parameters for the components**

**Tc**: Total Concentration for the actual component
a: Activity for the free amount of the actual component

*Option 1*: **Tc** varies irregularly between each point
*Option 2*: **Tc** is constant
*Option 3*: **Tc** varies with constant steps
*Option 4*: **Tc** varies through varied volume-additions
*Option 5*: **Tc** varies through constant volume-additions
*Option 6*: log **Tc** varies with constant steps

6. Choose the component ($Fe^{2+}$) for which the predominance area diagram should be constructed. Check the sign boxes to plot pH and pe instead of log[$H^+$] and log{$e^-$} on the axis.



Chose Alternative for Each Component:

Component 1 H+
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ● 11 ○

Component 2 Fe 2+
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

Component 3 e-
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ●

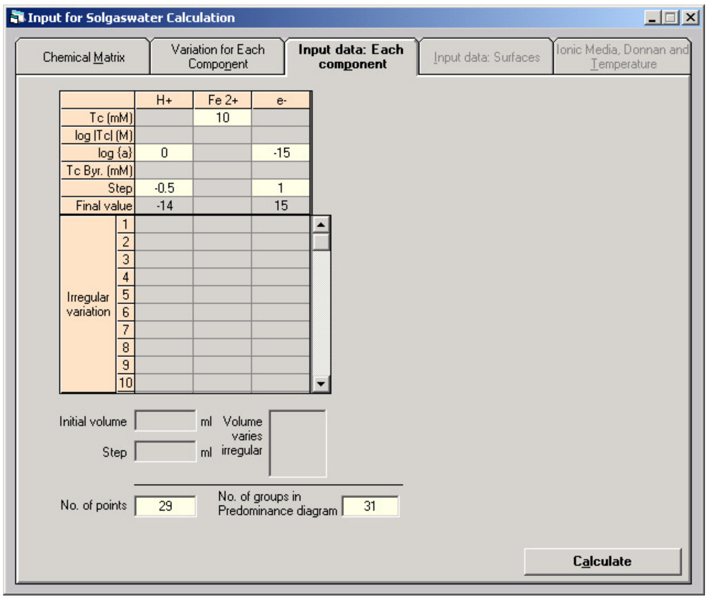
For component: Fe 2+
☐ Incl. solids of component
☐ Incl. all solids
☐ Correct for formula units
Plot with negative sign on: X-axis ☑ +/- Y-axis ☑ +/-
EMF (mV) instead of pe on: ☐ ☐

**The different options above, corresponds to the following parameters for the components**

**Tc**: Total Concentration for the actual component
a: Activity for the free amount of the actual component

*Option 1*: **Tc** varies irregularly between each point
*Option 2*: **Tc** is constant
*Option 3*: **Tc** varies with constant steps
*Option 4*: **Tc** varies through varied volume-additions
*Option 5*: **Tc** varies through constant volume-additions
*Option 6*: log **Tc** varies with constant steps

7. On the “Input data: Each component” tab, enter start value “log {a}”, step length “Step” for the first and third components ($H^+$ and $e^-$), the total concentration of $Fe^{2+}$ “Tc” and the number of points and groups. In this example 899 (29 times 31) equilibrium points will calculated, which might take some time depending on the actual computer performance. In WinSGW there is a limit for the maximum calculation time (default 30 seconds) that can be changed. This can be done at “Preferences” (Option tab) on the “File” menu.

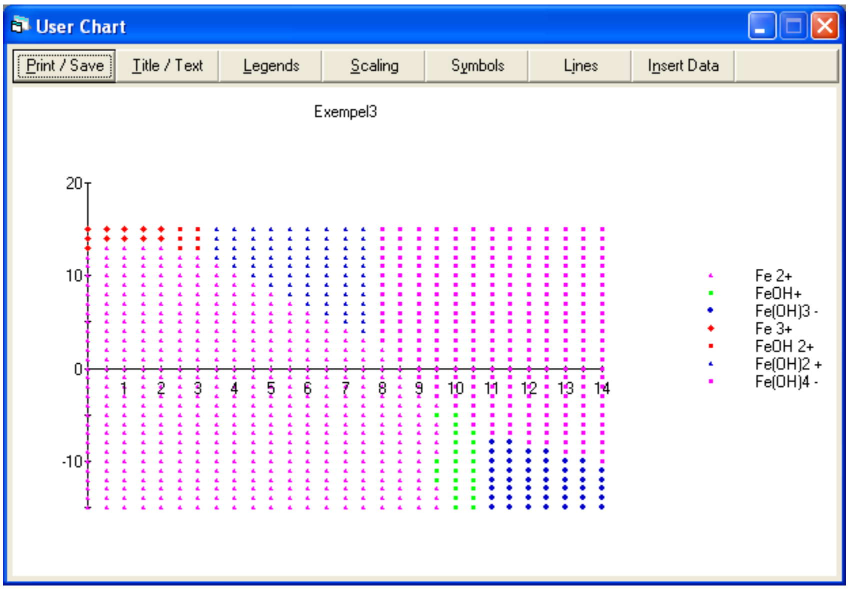


| | H+ | Fe 2+ | e- |
|---|---|---|---|
| Tc (mM) | | 10 | |
| log \|Tc\| (M) | | | |
| log {a} | 0 | | -15 |
| Tc Byr. (mM) | | | |
| Step | -0.5 | | 1 |
| Final value | -14 | | 15 |
| Irregular variation 1 | | | |
| 2 | | | |
| 3 | | | |
| 4 | | | |
| 5 | | | |
| 6 | | | |
| 7 | | | |
| 8 | | | |
| 9 | | | |
| 10 | | | |

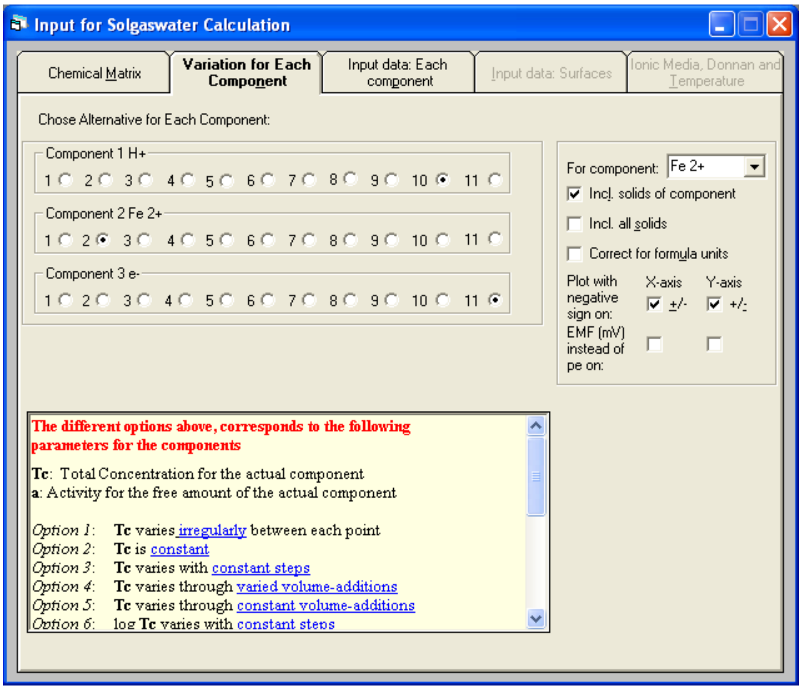
Initial volume ml
Step ml
Volume varies irregular
No. of points 29
No. of groups in Predominance diagram 31

8. Start the calculation.

9. Viewing the results.
Choose “Predominance diagram” from the “Diagrams” menu.



10. To include solids in the diagram return to the input (activate “Chemical Matrix” on the “View” menu) and, on the “Variation for each component” tab, mark “Incl. solids of component”. This implies that if a solid forms it will be plotted. It is also possible to include all solids (*i.e.* also solids not containing the specified component, $Fe^{2+}$) and to correct for formula units (poly-nuclear complexes).



Chose Alternative for Each Component:

Component 1 H+
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ● 11 ○

Component 2 Fe 2+
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

Component 3 e-
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ●

For component: Fe 2+
☑ Incl. solids of component
☐ Incl. all solids
☐ Correct for formula units

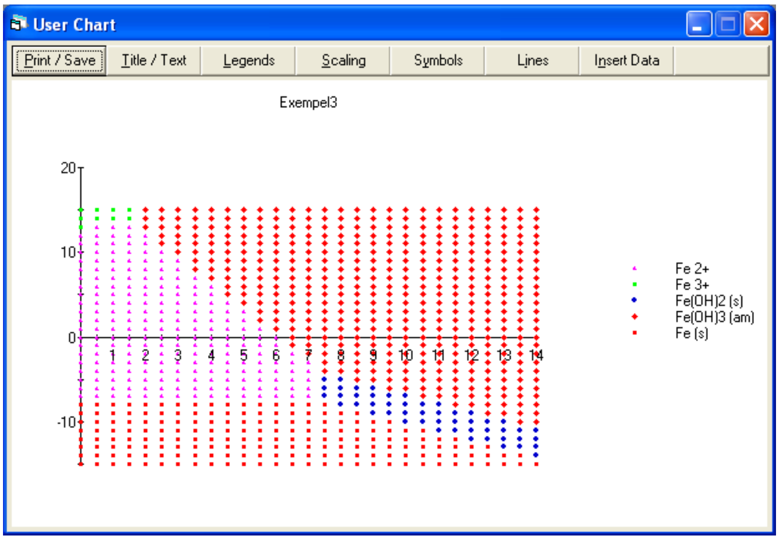
Plot with negative sign on: X-axis ☑ +/- Y-axis ☑ +/-
EMF (mV) instead of pe on: ☐ ☐

**The different options above, corresponds to the following parameters for the components**

**Tc**: Total Concentration for the actual component
**a**: Activity for the free amount of the actual component

*Option 1*: **Tc** varies irregularly between each point
*Option 2*: **Tc** is constant
*Option 3*: **Tc** varies with constant steps
*Option 4*: **Tc** varies through varied volume-additions
*Option 5*: **Tc** varies through constant volume-additions
*Option 6*: log **Tc** varies with constant steps

11. Start the calculation (Short-cut key, <F9>) and plot the new predominance area diagram.



## 5.5 Ionic strength dependent constants

**Task 1:** Calculate log{$H^+$} of 1, 5 and 10mM HCl and NaOH solutions in 500mM (NaCl) at 50°C using the Güntelberg, Davies, and Pitzer equations to calculate the activity coefficients at the actual ionic strength. The (NaCl) notation is used to imply that the solution, in addition to the HCl or NaOH added, also contain dissolved sodium chloride salt of the given concentration.

1. One equilibrium reaction describes the actual chemical system.

| | | log β |
|---|---|---|
| 1 | $H_2O \rightleftarrows H^+ + OH^-$ | -13.24 |

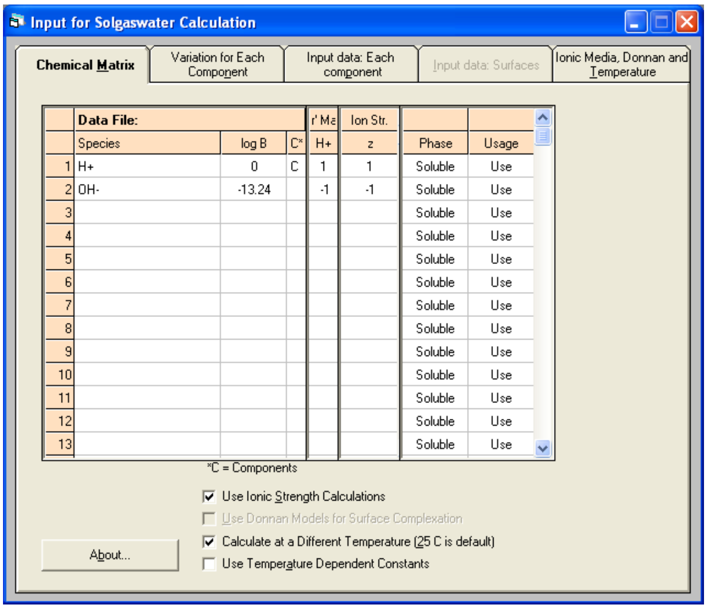
This constant is valid at 50°C and at infinite dilution. For WinSGW calculations involving activity coefficients, the log β constants must be given at infinite dilution.
At 50°C the dielectric constant for water is 69.90 (ε is needed to calculate the activity coefficients, *cf.* paragraph 2.5).

2. One component: $H^+$

3. The chemical matrix and the charge of the component (z)

| | log β | $H^+$ | z |
|---|---|---|---|
| $H^+$ | 0 | 1 | 1 |
| $OH^-$ | -13.24 | -1 | |

4. Start WinSGW and enter the matrix. Mark the “Use ionic strength calculations” box which activates the charge column (z) and the “Calculate at a different temperature” box. Only the charge of the components needs to be given.

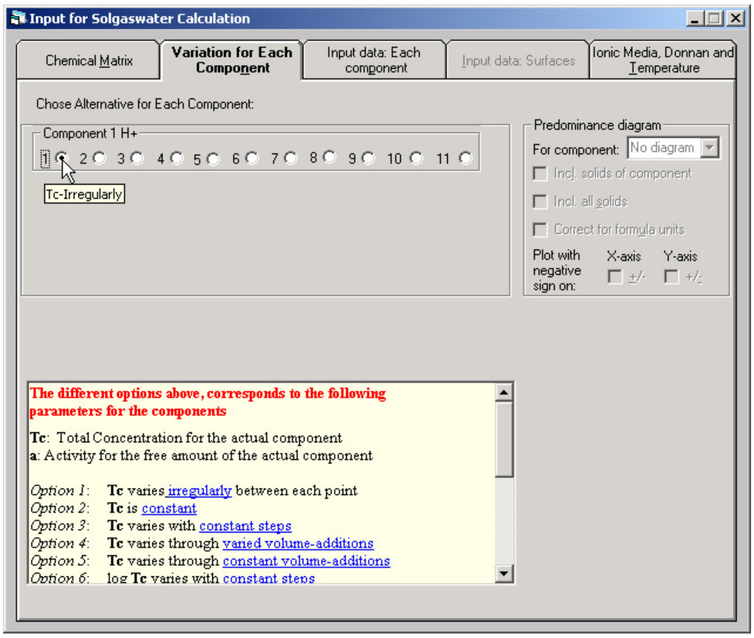


| | Data File: | | | r' Ma | Ion Str. | | |
|---|---|---|---|---|---|---|---|
| | Species | log B | C* | H+ | z | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 1 | Soluble | Use |
| 2 | OH- | -13.24 | | -1 | -1 | Soluble | Use |
| 3 | | | | | | Soluble | Use |
| 4 | | | | | | Soluble | Use |
| 5 | | | | | | Soluble | Use |
| 6 | | | | | | Soluble | Use |
| 7 | | | | | | Soluble | Use |
| 8 | | | | | | Soluble | Use |
| 9 | | | | | | Soluble | Use |
| 10 | | | | | | Soluble | Use |
| 11 | | | | | | Soluble | Use |
| 12 | | | | | | Soluble | Use |
| 13 | | | | | | Soluble | Use |

*C = Components

☑ Use Ionic Strength Calculations
☐ Use Donnan Models for Surface Complexation
☑ Calculate at a Different Temperature (25 C is default)
☐ Use Temperature Dependent Constants

5. On the “Variation for each component” tab choose to vary the total concentration of $H^+$ irregularly (Component 1 $H^+$, option 1).

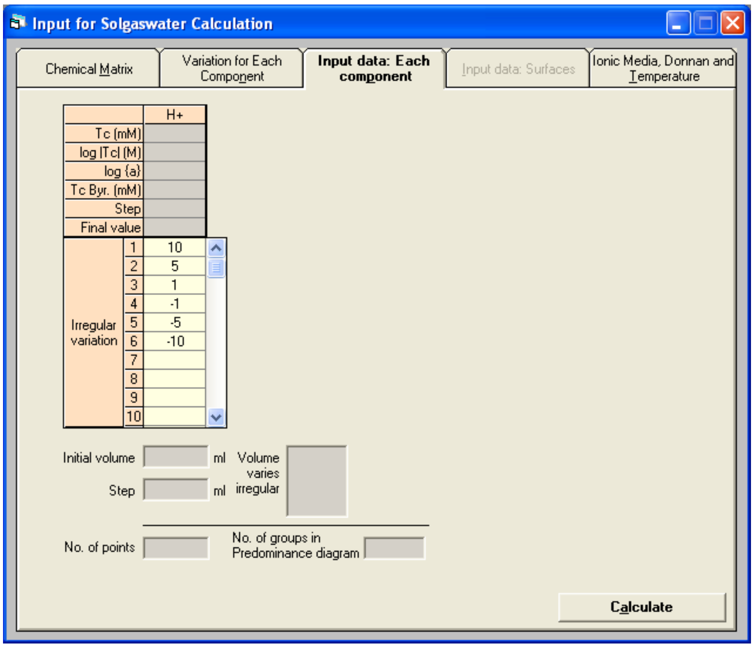


**The different options above, corresponds to the following parameters for the components**

**Tc**: Total Concentration for the actual component
**a**: Activity for the free amount of the actual component

*Option 1*: **Tc** varies irregularly between each point
*Option 2*: **Tc** is constant
*Option 3*: **Tc** varies with constant steps
*Option 4*: **Tc** varies through varied volume-additions
*Option 5*: **Tc** varies through constant volume-additions
*Option 6*: log **Tc** varies with constant steps

6. On the “Input data: Each component” tab enter the total concentrations of $H^+$.

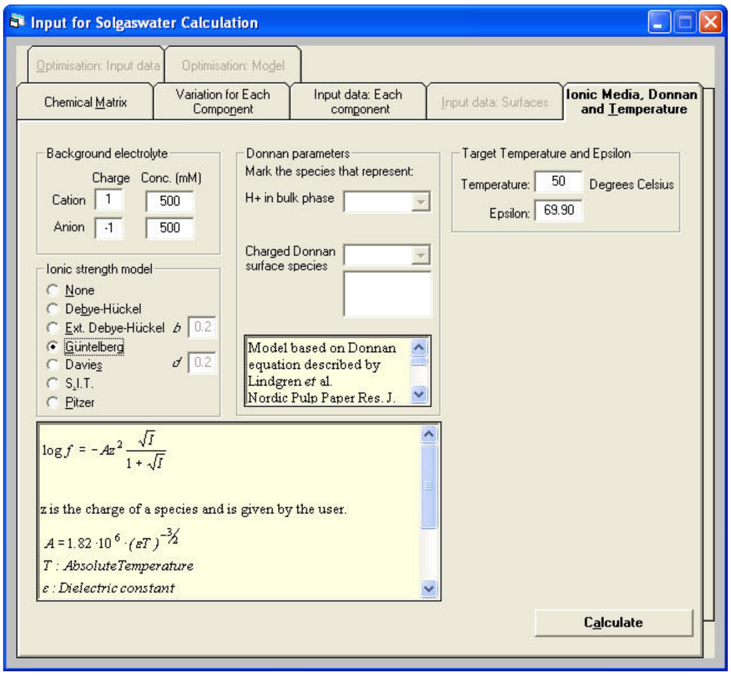


| | | H+ |
|---|---|---|
| Tc (mM) | | |
| log [Tc] (M) | | |
| log {a} | | |
| Tc Byr. (mM) | | |
| Step | | |
| Final value | | |
| Irregular variation | 1 | 10 |
| | 2 | 5 |
| | 3 | 1 |
| | 4 | -1 |
| | 5 | -5 |
| | 6 | -10 |
| | 7 | |
| | 8 | |
| | 9 | |
| | 10 | |

7. Move to the “Ionic Media, Donnan and Temperature” tab and enter the temperature (in degrees Celsius), the dielectric constant of water (ε), and information with respect to the background electrolyte concentration.

Here, three different situations can be distinguished. Thus, the solutions can be prepared to contain a given salt concentration in addition to the system of interest, or they can be made to contain either a constant cation, or anion, concentration of the ionic medium. The notations for these three options are (XZ), X(Y), and(X)Y, respectively (*e.g.* 0.1 M ($Na_2SO_4$), 0.5 M K(Cl), 3 M (Na)$ClO_4$).

In the first case, the charge and concentration of both ions are entered, and WinSGW solves for the charge balance by “adding” an extra amount of cations or anions with the charge given. This is made also in the second (and third) case, but here the input concentration of the anion (cation) is given as zero.



Background electrolyte

| | Charge | Conc. (mM) |
|---|---|---|
| Cation | 1 | 500 |
| Anion | -1 | 500 |

Ionic strength model
○ None
○ Debye-Hückel
○ Ext. Debye-Hückel b 0.2
● Güntelberg
○ Davies d 0.2
○ S.I.T.
○ Pitzer

Donnan parameters
Mark the species that represent:
H+ in bulk phase
Charged Donnan surface species

Model based on Donnan equation described by Lindgren *et* al.
Nordic Pulp Paper Res. J.

Target Temperature and Epsilon
Temperature: 50 Degrees Celsius
Epsilon: 69.90

$$\log f = -Az^2 \frac{\sqrt{I}}{1+\sqrt{I}}$$

z is the charge of a species and is given by the user.

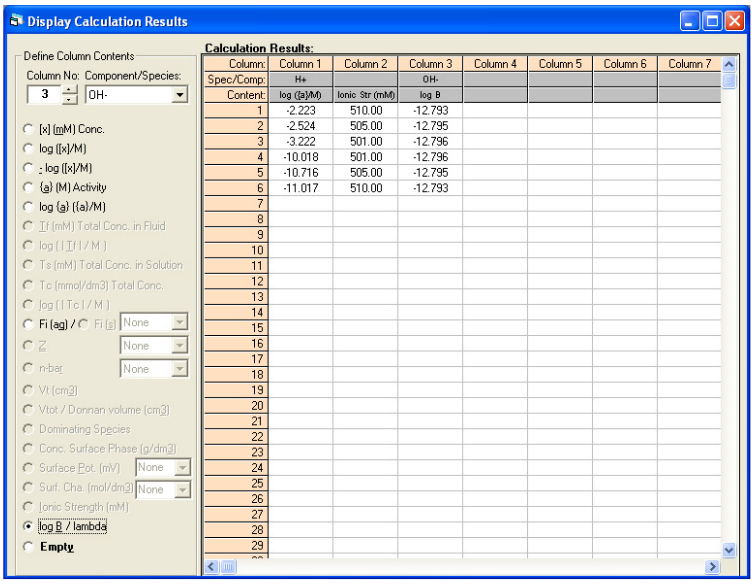
$A = 1.82 \cdot 10^6 \cdot (\varepsilon T)^{-3/2}$

$T$ : Absolute Temperature

$\varepsilon$ : Dielectric constant

8. Calculate

9. Results
View log{H$^+$}, the ionic strength and log β for the formation of OH$^-$ in columns.
(Col. 1: H$^+$, log{a}; Col. 2: None, Ionic strength; Col. 3: OH$^-$, log β/lambda)



Display Calculation Results

Define Column Contents

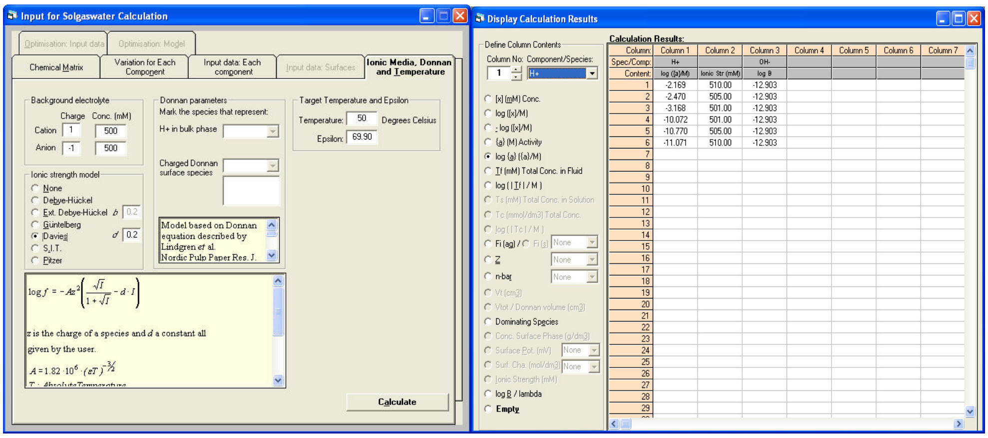
Column No: 3 Component/Species: OH-

● log B / lambda

Calculation Results:

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | | OH- | | | | |
| Content: | log ({a}/M) | Ionic Str (mM) | log B | | | | |
| 1 | -2.223 | 510.00 | -12.793 | | | | |
| 2 | -2.524 | 505.00 | -12.795 | | | | |
| 3 | -3.222 | 501.00 | -12.796 | | | | |
| 4 | -10.018 | 501.00 | -12.796 | | | | |
| 5 | -10.716 | 505.00 | -12.795 | | | | |
| 6 | -11.017 | 510.00 | -12.793 | | | | |

10. Change "Ionic strength model" to Davies (To activate the input again, choose Chemical matrix in the View menu) and recalculate.



Input for Solgaswater Calculation

Background electrolyte

| | Charge | Conc. (mM) |
|---|---|---|
| Cation | 1 | 500 |
| Anion | -1 | 500 |

Ionic strength model: ● Davies, d 0.2 (Ext. Debye-Hückel b 0.2)

Donnan parameters
Mark the species that represent:
H+ in bulk phase
Charged Donnan surface species

Model based on Donnan equation described by Lindgren *et al.* Nordic Pulp Paper Res. J.

Target Temperature and Epsilon
Temperature: 50 Degrees Celsius
Epsilon: 69.90

$$\log f = -Az^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - d\cdot I\right)$$

z is the charge of a species and d a constant all given by the user.

$$A = 1.82\cdot 10^6\cdot(\varepsilon T)^{-3/2}$$

T : Absolute Temperature

Display Calculation Results

Define Column Contents

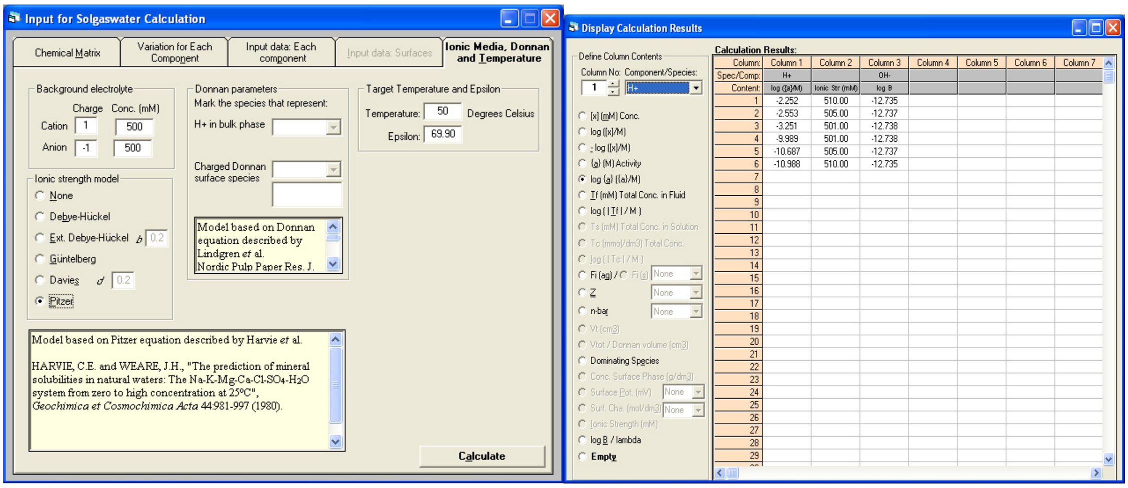
Column No: 1 Component/Species: H+

● log {a} ({a}/M)

Calculation Results:

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | | OH- | | | | |
| Content: | log ({a}/M) | Ionic Str (mM) | log B | | | | |
| 1 | -2.169 | 510.00 | -12.903 | | | | |
| 2 | -2.470 | 505.00 | -12.903 | | | | |
| 3 | -3.168 | 501.00 | -12.903 | | | | |
| 4 | -10.072 | 501.00 | -12.903 | | | | |
| 5 | -10.770 | 505.00 | -12.903 | | | | |
| 6 | -11.071 | 510.00 | -12.903 | | | | |

11. Change “Ionic strength model” to Pitzer and make a new calculation.



Background electrolyte

| | Charge | Conc. (mM) |
|---|---|---|
| Cation | 1 | 500 |
| Anion | -1 | 500 |

Ionic strength model: ○ None ○ Debye-Hückel ○ Ext. Debye-Hückel b 0.2 ○ Güntelberg ○ Davies d 0.2 ● Pitzer

Temperature: 50 Degrees Celsius

Epsilon: 69.90

Model based on Donnan equation described by Lindgren *et* al. Nordic Pulp Paper Res. J.

Model based on Pitzer equation described by Harvie *et* al.

HARVIE, C.E. and WEARE, J.H., "The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-Cl-SO4-H2O system from zero to high concentration at 25ºC", *Geochimica et Cosmochimica Acta* 44:981-997 (1980).

Column No: 1 Component/Species: H+ ● log {a} ({a}/M)

Calculation Results:

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | | OH- | | | | |
| Content: | log ({a}/M) | Ionic Str (mM) | log B | | | | |
| 1 | -2.252 | 510.00 | -12.735 | | | | |
| 2 | -2.553 | 505.00 | -12.737 | | | | |
| 3 | -3.251 | 501.00 | -12.738 | | | | |
| 4 | -9.989 | 501.00 | -12.738 | | | | |
| 5 | -10.687 | 505.00 | -12.737 | | | | |
| 6 | -10.988 | 510.00 | -12.735 | | | | |

**Task 2:** Calculate, as a function of log{H$^+$}, the hydrolysis of aluminium(III) at 25 °C in a river water and in sea-water.

1. The following equilibrium reactions define the chemical system at infinite dilution:

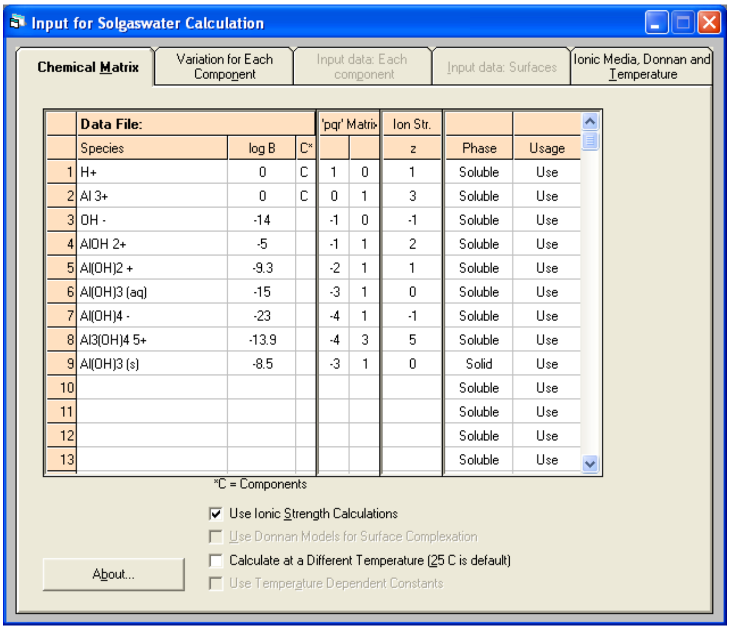
| | | log β |
|---|---|---|
| 1. | $H^+ + OH^- \rightleftarrows H_2O$ | 14.00 |
| 2. | $Al^{3+} + OH^- \rightleftarrows AlOH^{2+}$ | 9.0 |
| 3. | $Al^{3+} + 2\ OH^- \rightleftarrows Al(OH)_2^+$ | 18.7 |
| 4. | $Al^{3+} + 3\ OH^- \rightleftarrows Al(OH)_3(aq)$ | 27.0 |
| 5. | $Al^{3+} + 4\ OH^- \rightleftarrows Al(OH)_4^-$ | 33.0 |
| 6. | $3\ Al^{3+} + 4\ OH^- \rightleftarrows Al_3(OH)_4^{5+}$ | 42.1 |
| 7. | $Al^{3+} + 3\ OH^- \rightleftarrows Al(OH)_3(s)$ | 33.5 |

2. Two components, H$^+$ and Al$^{3+}$.

3. The chemical matrix and the charge of the components.

| | log β | $H^+$ | $Al^{3+}$ | z | Equilibria nos. |
|---|---|---|---|---|---|
| $H^+$ | 0 | 1 | 0 | 1 | |
| $Al^{3+}$ | 0 | 0 | 1 | 3 | |
| $OH^-$ | -14.00 | -1 | 0 | | -1 |
| $AlOH^{2+}$ | -5.0 | -1 | 1 | | 2 - 1 |
| $Al(OH)_2^+$ | -9.3 | -2 | 1 | | 3 – 2 x 1 |
| $Al(OH)_3(aq)$ | -15.0 | -3 | 1 | | 4 – 3 x 1 |
| $Al(OH)_4^-$ | -23.0 | -4 | 1 | | 5 – 4 x 1 |
| $Al_3(OH)_4^{5+}$ | -13.9 | -4 | 3 | | 6 – 4 x 1 |
| $Al(OH)_3(s)$ | -8.5 | -3 | 1 | | 7 – 3 x 1 |

4. Start WinSGW, chose “New Chemical Matrix” from the “File” menu, and activate the “Use ionic strength calculations” box. Enter the matrix with the charges of the components and remember to change “Phase” to Solid for $Al(OH)_3(s)$. The correct charges of all species will be calculated on entering the next tab. Don´t worry!

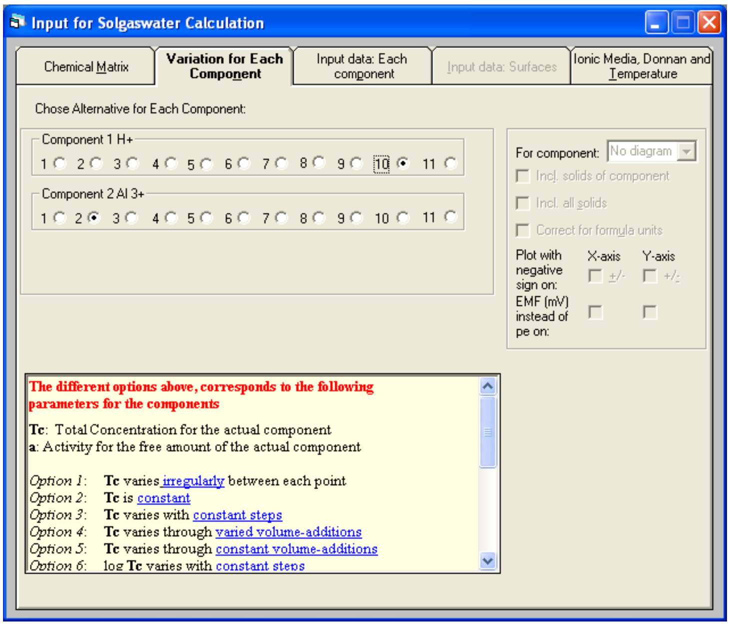


| | Data File: | | | 'pqr' Matri | | Ion Str. | | |
|---|---|---|---|---|---|---|---|---|
| | Species | log B | C* | | | z | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 0 | 1 | Soluble | Use |
| 2 | Al 3+ | 0 | C | 0 | 1 | 3 | Soluble | Use |
| 3 | OH - | -14 | | -1 | 0 | -1 | Soluble | Use |
| 4 | AlOH 2+ | -5 | | -1 | 1 | 2 | Soluble | Use |
| 5 | Al(OH)2 + | -9.3 | | -2 | 1 | 1 | Soluble | Use |
| 6 | Al(OH)3 (aq) | -15 | | -3 | 1 | 0 | Soluble | Use |
| 7 | Al(OH)4 - | -23 | | -4 | 1 | -1 | Soluble | Use |
| 8 | Al3(OH)4 5+ | -13.9 | | -4 | 3 | 5 | Soluble | Use |
| 9 | Al(OH)3 (s) | -8.5 | | -3 | 1 | 0 | Solid | Use |
| 10 | | | | | | | Soluble | Use |
| 11 | | | | | | | Soluble | Use |
| 12 | | | | | | | Soluble | Use |
| 13 | | | | | | | Soluble | Use |

*C = Components

☑ Use Ionic Strength Calculations
☐ Use Donnan Models for Surface Complexation
☐ Calculate at a Different Temperature (25 C is default)
☐ Use Temperature Dependent Constants

5. On the “Variation for each component” tab, chose to step log{$H^+$}with constant steps at a constant total concentration of Al(III). (Component 1 $H^+$, option 10; Component 2 $Al^{3+}$, option 2)



Chose Alternative for Each Component:

Component 1 H+
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ● 11 ○

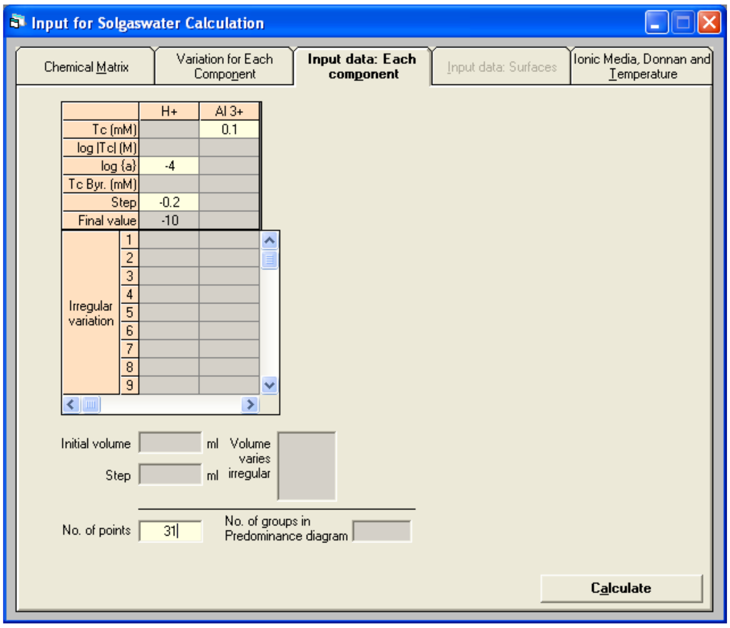
Component 2 Al 3+
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

**The different options above, corresponds to the following parameters for the components**

**Tc**: Total Concentration for the actual component
**a**: Activity for the free amount of the actual component

*Option 1*: **Tc** varies irregularly between each point
*Option 2*: **Tc** is constant
*Option 3*: **Tc** varies with constant steps
*Option 4*: **Tc** varies through varied volume-additions
*Option 5*: **Tc** varies through constant volume-additions
*Option 6*: log **Tc** varies with constant steps

6. On next tab, “Input data: Each component”, enter the start and step values for log{$H^+$}, the total concentration of $Al^{3+}$, and the number of points to be calculated.
To simulate a system which is always saturated with respect to $Al(OH)_3(s)$, Tc for $Al^{3+}$ is given as a high, fortuitous, value, *e.g.* 10 000 mM.

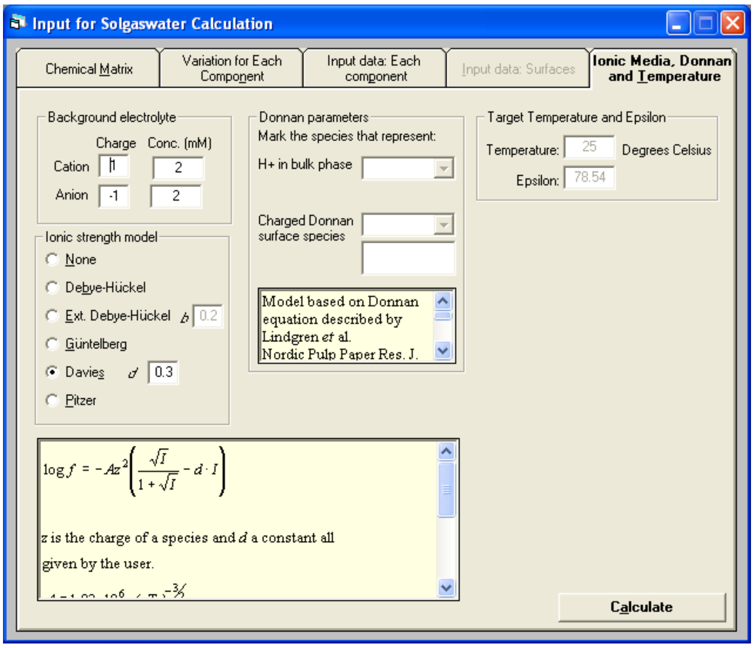


| | H+ | Al 3+ |
|---|---|---|
| Tc (mM) | | 0.1 |
| log \|Tc\| (M) | | |
| log {a} | -4 | |
| Tc Byr. (mM) | | |
| Step | -0.2 | |
| Final value | -10 | |

| Irregular variation | | H+ | Al 3+ |
|---|---|---|---|
| | 1 | | |
| | 2 | | |
| | 3 | | |
| | 4 | | |
| | 5 | | |
| | 6 | | |
| | 7 | | |
| | 8 | | |
| | 9 | | |

No. of points 31

7. Simulate, on the tab “Ionic Media, Donnan and Temperature”, a river water by entering a +1/-1 background electrolyte of 2 mM, and chose the Davies ionic strength model with *d* = 0.3.



**Input for Solgaswater Calculation**

Background electrolyte

| | Charge | Conc. (mM) |
|---|---|---|
| Cation | 1 | 2 |
| Anion | -1 | 2 |

Ionic strength model
- ○ None
- ○ Debye-Hückel
- ○ Ext. Debye-Hückel $b$ 0.2
- ○ Güntelberg
- ● Davies $d$ 0.3
- ○ Pitzer

$$\log f = -Az^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - d\cdot I\right)$$

$z$ is the charge of a species and $d$ a constant all given by the user.

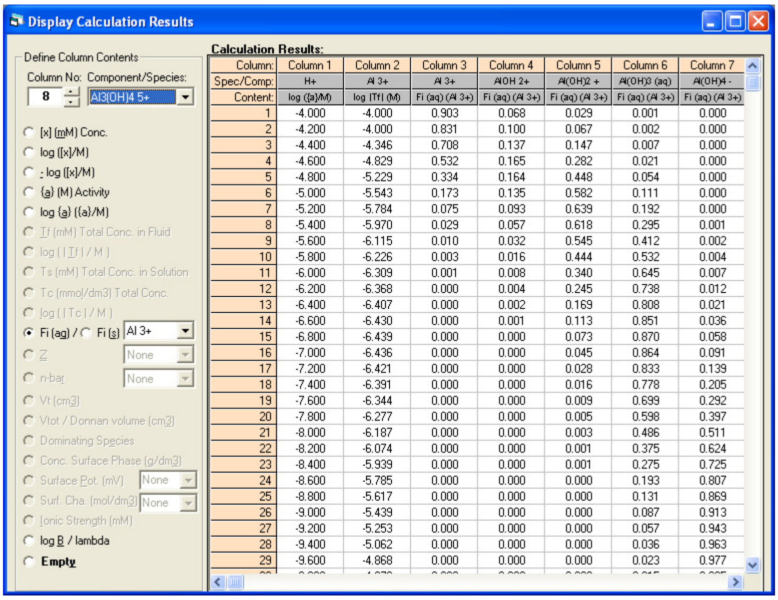
Donnan parameters
Mark the species that represent:
H+ in bulk phase
Charged Donnan surface species

Model based on Donnan equation described by Lindgren *et al.* Nordic Pulp Paper Res. J.

Target Temperature and Epsilon
Temperature: 25 Degrees Celsius
Epsilon: 78.54

8. Calculate

9. View log{H$^+$}, log S$_{Al}$, and the fraction of different aqueous aluminium species in columns. (Col. 1: H$^+$, log {a}; Col. 2: Al$^{3+}$, log (|Tf|/M); Col. 3: Al$^{3+}$, “F$_i$ of selected component in all species in solution” in the Column-Contents menu)



**Display Calculation Results**

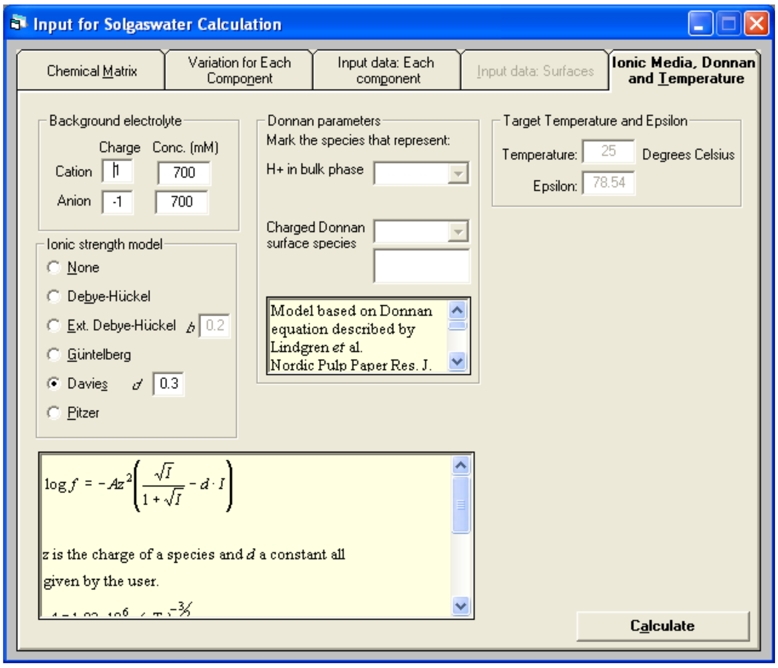
Define Column Contents
Column No: 8 Component/Species: Al3(OH)4 5+

- ○ [x] (mM) Conc.
- ○ log ([x]/M)
- ○ - log ([x]/M)
- ○ {a} (M) Activity
- ○ log {a} ({a}/M)
- ○ Tf (mM) Total Conc. in Fluid
- ○ log ( |Tf| / M )
- ○ Ts (mM) Total Conc. in Solution
- ○ Tc (mmol/dm3) Total Conc.
- ○ log ( |Tc| / M )
- ● Fi (aq) / ○ Fi (s) Al 3+
- ○ Z None
- ○ n-bar None
- ○ Vt (cm3)
- ○ Vtot / Donnan volume (cm3)
- ○ Dominating Species
- ○ Conc. Surface Phase (g/dm3)
- ○ Surface Pot. (mV) None
- ○ Surf. Cha. (mol/dm3) None
- ○ Ionic Strength (mM)
- ○ log B / lambda
- ○ **Empty**

Calculation Results:

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | Al 3+ | Al 3+ | AlOH 2+ | Al(OH)2 + | Al(OH)3 (aq) | Al(OH)4 - |
| Content: | log ({a}/M) | log \|Tf\| (M) | Fi (aq) (Al 3+) | Fi (aq) (Al 3+) | Fi (aq) (Al 3+) | Fi (aq) (Al 3+) | Fi (aq) (Al 3+) |
| 1 | -4.000 | -4.000 | 0.903 | 0.068 | 0.029 | 0.001 | 0.000 |
| 2 | -4.200 | -4.000 | 0.831 | 0.100 | 0.067 | 0.002 | 0.000 |
| 3 | -4.400 | -4.346 | 0.708 | 0.137 | 0.147 | 0.007 | 0.000 |
| 4 | -4.600 | -4.829 | 0.532 | 0.165 | 0.282 | 0.021 | 0.000 |
| 5 | -4.800 | -5.229 | 0.334 | 0.164 | 0.448 | 0.054 | 0.000 |
| 6 | -5.000 | -5.543 | 0.173 | 0.135 | 0.582 | 0.111 | 0.000 |
| 7 | -5.200 | -5.784 | 0.075 | 0.093 | 0.639 | 0.192 | 0.000 |
| 8 | -5.400 | -5.970 | 0.029 | 0.057 | 0.618 | 0.295 | 0.001 |
| 9 | -5.600 | -6.115 | 0.010 | 0.032 | 0.545 | 0.412 | 0.002 |
| 10 | -5.800 | -6.226 | 0.003 | 0.016 | 0.444 | 0.532 | 0.004 |
| 11 | -6.000 | -6.309 | 0.001 | 0.008 | 0.340 | 0.645 | 0.007 |
| 12 | -6.200 | -6.368 | 0.000 | 0.004 | 0.245 | 0.738 | 0.012 |
| 13 | -6.400 | -6.407 | 0.000 | 0.002 | 0.169 | 0.808 | 0.021 |
| 14 | -6.600 | -6.430 | 0.000 | 0.001 | 0.113 | 0.851 | 0.036 |
| 15 | -6.800 | -6.439 | 0.000 | 0.000 | 0.073 | 0.870 | 0.058 |
| 16 | -7.000 | -6.436 | 0.000 | 0.000 | 0.045 | 0.864 | 0.091 |
| 17 | -7.200 | -6.421 | 0.000 | 0.000 | 0.028 | 0.833 | 0.139 |
| 18 | -7.400 | -6.391 | 0.000 | 0.000 | 0.016 | 0.778 | 0.205 |
| 19 | -7.600 | -6.344 | 0.000 | 0.000 | 0.009 | 0.699 | 0.292 |
| 20 | -7.800 | -6.277 | 0.000 | 0.000 | 0.005 | 0.598 | 0.397 |
| 21 | -8.000 | -6.187 | 0.000 | 0.000 | 0.003 | 0.486 | 0.511 |
| 22 | -8.200 | -6.074 | 0.000 | 0.000 | 0.001 | 0.375 | 0.624 |
| 23 | -8.400 | -5.939 | 0.000 | 0.000 | 0.001 | 0.275 | 0.725 |
| 24 | -8.600 | -5.785 | 0.000 | 0.000 | 0.000 | 0.193 | 0.807 |
| 25 | -8.800 | -5.617 | 0.000 | 0.000 | 0.000 | 0.131 | 0.869 |
| 26 | -9.000 | -5.439 | 0.000 | 0.000 | 0.000 | 0.087 | 0.913 |
| 27 | -9.200 | -5.253 | 0.000 | 0.000 | 0.000 | 0.057 | 0.943 |
| 28 | -9.400 | -5.062 | 0.000 | 0.000 | 0.000 | 0.036 | 0.963 |
| 29 | -9.600 | -4.868 | 0.000 | 0.000 | 0.000 | 0.023 | 0.977 |

10. Return to the input by choosing “Chemical matrix” in the View menu and simulate a sea-water by changing the background electrolyte concentration to 700 mM.



Background electrolyte

| | Charge | Conc. (mM) |
|---|---|---|
| Cation | 1 | 700 |
| Anion | -1 | 700 |

Ionic strength model
○ None
○ Debye-Hückel
○ Ext. Debye-Hückel b 0.2
○ Güntelberg
● Davies d 0.3
○ Pitzer

Donnan parameters
Mark the species that represent:
H+ in bulk phase
Charged Donnan surface species

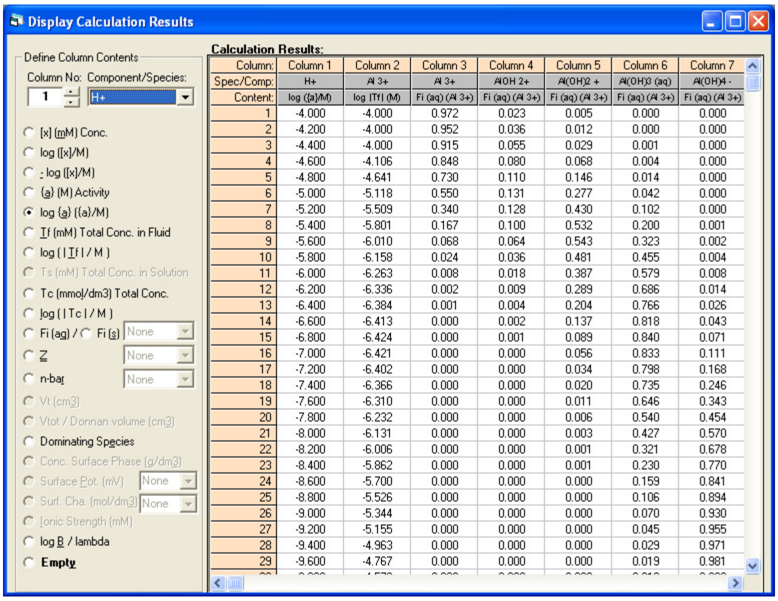
Model based on Donnan equation described by Lindgren *et* al. Nordic Pulp Paper Res. J.

Target Temperature and Epsilon
Temperature: 25 Degrees Celsius
Epsilon: 78.54

$$\log f = -Az^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - d \cdot I\right)$$

z is the charge of a species and d a constant all given by the user.

11. Calculate, and note that the previously defined column contents are automatically used to report the results. If desired, these contents can of course be exchanged.



Calculation Results:

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | Al 3+ | Al 3+ | AlOH 2+ | Al(OH)2 + | Al(OH)3 (aq) | Al(OH)4 - |
| Content: | log ({a}/M) | log \|Tf\| (M) | Fi (aq) (Al 3+) | Fi (aq) (Al 3+) | Fi (aq) (Al 3+) | Fi (aq) (Al 3+) | Fi (aq) (Al 3+) |
| 1 | -4.000 | -4.000 | 0.972 | 0.023 | 0.005 | 0.000 | 0.000 |
| 2 | -4.200 | -4.000 | 0.952 | 0.036 | 0.012 | 0.000 | 0.000 |
| 3 | -4.400 | -4.000 | 0.915 | 0.055 | 0.029 | 0.001 | 0.000 |
| 4 | -4.600 | -4.106 | 0.848 | 0.080 | 0.068 | 0.004 | 0.000 |
| 5 | -4.800 | -4.641 | 0.730 | 0.110 | 0.146 | 0.014 | 0.000 |
| 6 | -5.000 | -5.118 | 0.550 | 0.131 | 0.277 | 0.042 | 0.000 |
| 7 | -5.200 | -5.509 | 0.340 | 0.128 | 0.430 | 0.102 | 0.000 |
| 8 | -5.400 | -5.801 | 0.167 | 0.100 | 0.532 | 0.200 | 0.001 |
| 9 | -5.600 | -6.010 | 0.068 | 0.064 | 0.543 | 0.323 | 0.002 |
| 10 | -5.800 | -6.158 | 0.024 | 0.036 | 0.481 | 0.455 | 0.004 |
| 11 | -6.000 | -6.263 | 0.008 | 0.018 | 0.387 | 0.579 | 0.008 |
| 12 | -6.200 | -6.336 | 0.002 | 0.009 | 0.289 | 0.686 | 0.014 |
| 13 | -6.400 | -6.384 | 0.001 | 0.004 | 0.204 | 0.766 | 0.026 |
| 14 | -6.600 | -6.413 | 0.000 | 0.002 | 0.137 | 0.818 | 0.043 |
| 15 | -6.800 | -6.424 | 0.000 | 0.001 | 0.089 | 0.840 | 0.071 |
| 16 | -7.000 | -6.421 | 0.000 | 0.000 | 0.056 | 0.833 | 0.111 |
| 17 | -7.200 | -6.402 | 0.000 | 0.000 | 0.034 | 0.798 | 0.168 |
| 18 | -7.400 | -6.366 | 0.000 | 0.000 | 0.020 | 0.735 | 0.246 |
| 19 | -7.600 | -6.310 | 0.000 | 0.000 | 0.011 | 0.646 | 0.343 |
| 20 | -7.800 | -6.232 | 0.000 | 0.000 | 0.006 | 0.540 | 0.454 |
| 21 | -8.000 | -6.131 | 0.000 | 0.000 | 0.003 | 0.427 | 0.570 |
| 22 | -8.200 | -6.006 | 0.000 | 0.000 | 0.001 | 0.321 | 0.678 |
| 23 | -8.400 | -5.862 | 0.000 | 0.000 | 0.001 | 0.230 | 0.770 |
| 24 | -8.600 | -5.700 | 0.000 | 0.000 | 0.000 | 0.159 | 0.841 |
| 25 | -8.800 | -5.526 | 0.000 | 0.000 | 0.000 | 0.106 | 0.894 |
| 26 | -9.000 | -5.344 | 0.000 | 0.000 | 0.000 | 0.070 | 0.930 |
| 27 | -9.200 | -5.155 | 0.000 | 0.000 | 0.000 | 0.045 | 0.955 |
| 28 | -9.400 | -4.963 | 0.000 | 0.000 | 0.000 | 0.029 | 0.971 |
| 29 | -9.600 | -4.767 | 0.000 | 0.000 | 0.000 | 0.019 | 0.981 |

## 5.6 Temperature dependent constants ($H^+$-$Cu^{2+}$-acetic acid)

**Task:** Calculate the distribution of species containing acetic acid between pH 2 and 5 in an acetic acid-copper(II) system at 60°C using the formation constants evaluated at 25°C and reaction enthalpy values.

1. The following equilibrium reactions describe the actual chemical system (Critical Stability Constants, Volume 6). The constants are valid at 25°C. The corresponding reaction enthalpy values are listed in the last column.

| | | log β | ΔH (kJ/mole) |
|---|---|---|---|
| 1 | $H_2O \rightleftarrows H^+ + OH^-$ | -14.00 | 55.9 |
| 2 | $H^+ + Ac^- \rightleftarrows HAc$ | 4.76 | 0.42 |
| 3 | $Cu^{2+} + Ac^- \rightleftarrows CuAc^+$ | 2.21 | 4.18 |
| 4 | $Cu^{2+} + 2Ac^- \rightleftarrows CuAc_2(aq)$ | 3.63 | 5.86 |

2. Three components: a) $H^+$, HAc and $Cu^{2+}$ , b) $H^+$, $Ac^-$ and $Cu^{2+}$

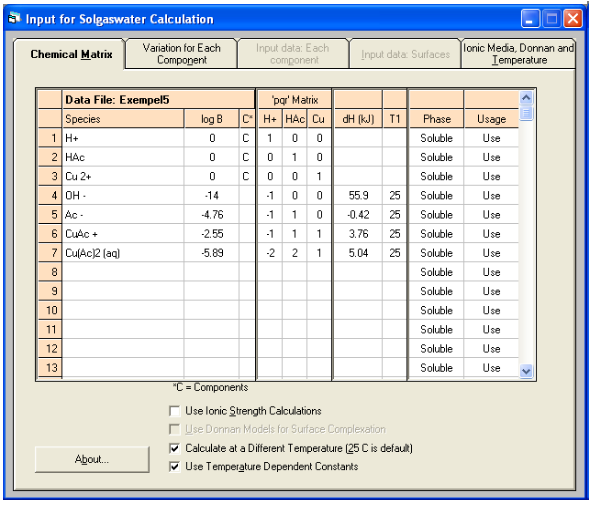
3. The chemical matrix and the reaction enthalpy of each species

| a) | log β | $H^+$ | HAc | $Cu^{2+}$ | ΔH | $T_1$ | Equilibria Nos. |
|---|---|---|---|---|---|---|---|
| $H^+$ | 0 | 1 | 0 | 0 | | | |
| HAc | 0 | 0 | 1 | 0 | | | |
| $Cu^{2+}$ | 0 | 0 | 0 | 1 | | | |
| $OH^-$ | -14.00 | -1 | 0 | 0 | 55.9 | 25 | 1 |
| $Ac^-$ | -4.76 | -1 | 1 | 0 | -0.42 | 25 | -2 |
| $CuAc^+$ | -2.55 | -1 | 1 | 1 | 3.76 | 25 | 3 - 2 |
| $Cu(Ac)_2(aq)$ | -5.89 | -2 | 2 | 1 | 5.04 | 25 | 4 - 2 · 2 |

| b) | log β | $H^+$ | $Ac^-$ | $Cu^{2+}$ | ΔH | $T_1$ | Equilibria Nos. |
|---|---|---|---|---|---|---|---|
| $H^+$ | 0 | 1 | 0 | 0 | | | |
| $Ac^-$ | 0 | 0 | 1 | 0 | | | |
| $Cu^{2+}$ | 0 | 0 | 0 | 1 | | | |
| $OH^-$ | -14.00 | -1 | 0 | 0 | 55.9 | 25 | 1 |
| HAc | 4.76 | 1 | 1 | 0 | 0.42 | 25 | 2 |
| $CuAc^+$ | 2.21 | 0 | 1 | 1 | 4.18 | 25 | 3 |
| $Cu(Ac)_2$ (aq) | 3.63 | 0 | 2 | 1 | 5.86 | 25 | 4 |

The temperature ($T_1$) is the temperature at which the log β constants are valid. Enthalpy values are set to zero for the components. Enthalpy values should be given in kJ per mole and $T_1$ in degrees Celsius.

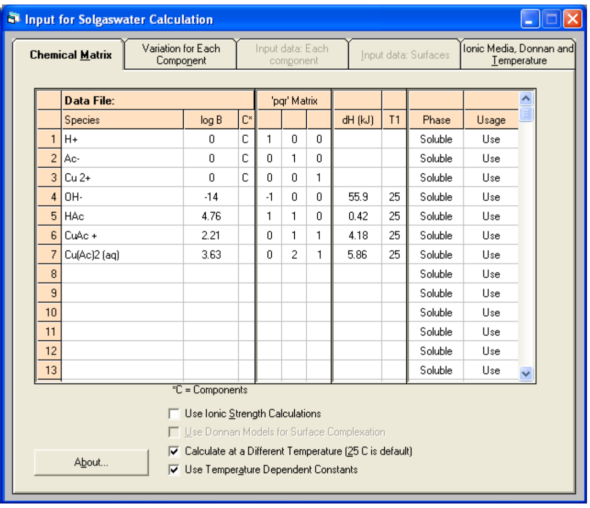
4. Start WinSGW and enter the chemical matrix. Mark the “Use temperature dependent constants” box which will activate the enthalpy and temperature columns.



| | Data File: Exempel5 | | | 'pqr' Matrix | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Species | log B | C* | H+ | HAc | Cu | dH (kJ) | T1 | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 0 | 0 | | | Soluble | Use |
| 2 | HAc | 0 | C | 0 | 1 | 0 | | | Soluble | Use |
| 3 | Cu 2+ | 0 | C | 0 | 0 | 1 | | | Soluble | Use |
| 4 | OH - | -14 | | -1 | 0 | 0 | 55.9 | 25 | Soluble | Use |
| 5 | Ac - | -4.76 | | -1 | 1 | 0 | -0.42 | 25 | Soluble | Use |
| 6 | CuAc + | -2.55 | | -1 | 1 | 1 | 3.76 | 25 | Soluble | Use |
| 7 | Cu(Ac)2 (aq) | -5.89 | | -2 | 2 | 1 | 5.04 | 25 | Soluble | Use |
| 8 | | | | | | | | | Soluble | Use |
| 9 | | | | | | | | | Soluble | Use |
| 10 | | | | | | | | | Soluble | Use |
| 11 | | | | | | | | | Soluble | Use |
| 12 | | | | | | | | | Soluble | Use |
| 13 | | | | | | | | | Soluble | Use |

*C = Components

☐ Use Ionic Strength Calculations
☐ Use Donnan Models for Surface Complexation
☑ Calculate at a Different Temperature (25 C is default)
☑ Use Temperature Dependent Constants

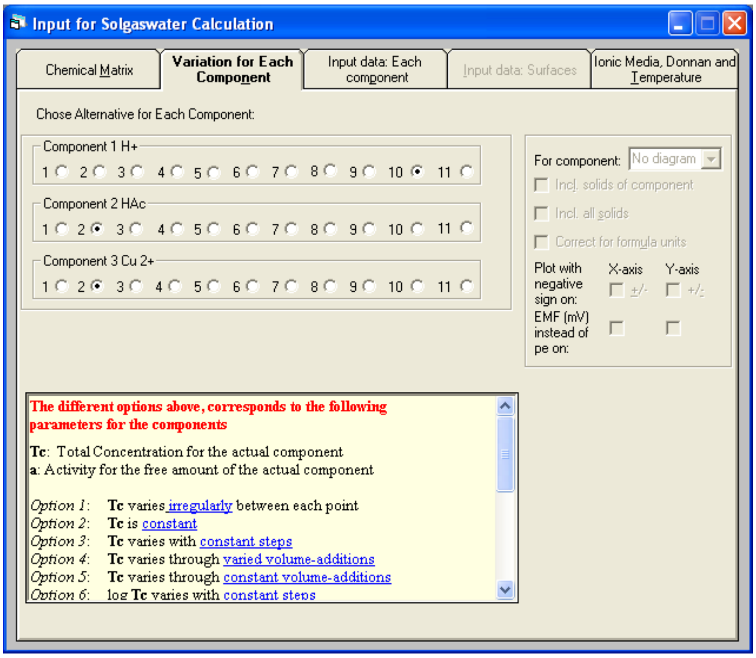


| | Data File: | | | 'pqr' Matrix | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Species | log B | C* | | | | dH (kJ) | T1 | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 0 | 0 | | | Soluble | Use |
| 2 | Ac- | 0 | C | 0 | 1 | 0 | | | Soluble | Use |
| 3 | Cu 2+ | 0 | C | 0 | 0 | 1 | | | Soluble | Use |
| 4 | OH- | -14 | | -1 | 0 | 0 | 55.9 | 25 | Soluble | Use |
| 5 | HAc | 4.76 | | 1 | 1 | 0 | 0.42 | 25 | Soluble | Use |
| 6 | CuAc + | 2.21 | | 0 | 1 | 1 | 4.18 | 25 | Soluble | Use |
| 7 | Cu(Ac)2 (aq) | 3.63 | | 0 | 2 | 1 | 5.86 | 25 | Soluble | Use |
| 8 | | | | | | | | | Soluble | Use |
| 9 | | | | | | | | | Soluble | Use |
| 10 | | | | | | | | | Soluble | Use |
| 11 | | | | | | | | | Soluble | Use |
| 12 | | | | | | | | | Soluble | Use |
| 13 | | | | | | | | | Soluble | Use |

*C = Components

☐ Use Ionic Strength Calculations
☐ Use Donnan Models for Surface Complexation
☑ Calculate at a Different Temperature (25 C is default)
☑ Use Temperature Dependent Constants

5. Move to next tab “Variation for each component”.
Choose to step pH and to keep the total concentrations of acetic acid and copper constant. (Component 1 $H^+$, option 10; Component 2 HAc, option 2; Component 3 $Cu^{2+}$, option 2).



Chose Alternative for Each Component:

Component 1 H+
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ● 11 ○

Component 2 HAc
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

Component 3 Cu 2+
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

For component: No diagram
☐ Incl. solids of component
☐ Incl. all solids
☐ Correct for formula units

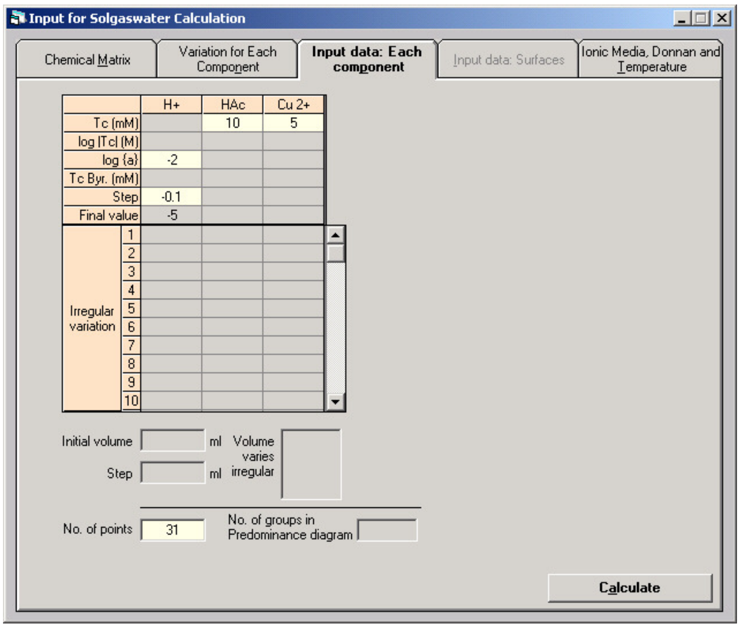
| | X-axis | Y-axis |
|---|---|---|
| Plot with negative sign on: | ☐ +/- | ☐ +/- |
| EMF (mV) instead of pe on: | ☐ | ☐ |

**The different options above, corresponds to the following parameters for the components**

**Tc**: Total Concentration for the actual component
**a**: Activity for the free amount of the actual component

*Option 1*: **Tc** varies irregularly between each point
*Option 2*: **Tc** is constant
*Option 3*: **Tc** varies with constant steps
*Option 4*: **Tc** varies through varied volume-additions
*Option 5*: **Tc** varies through constant volume-additions
*Option 6*: log **Tc** varies with constant steps

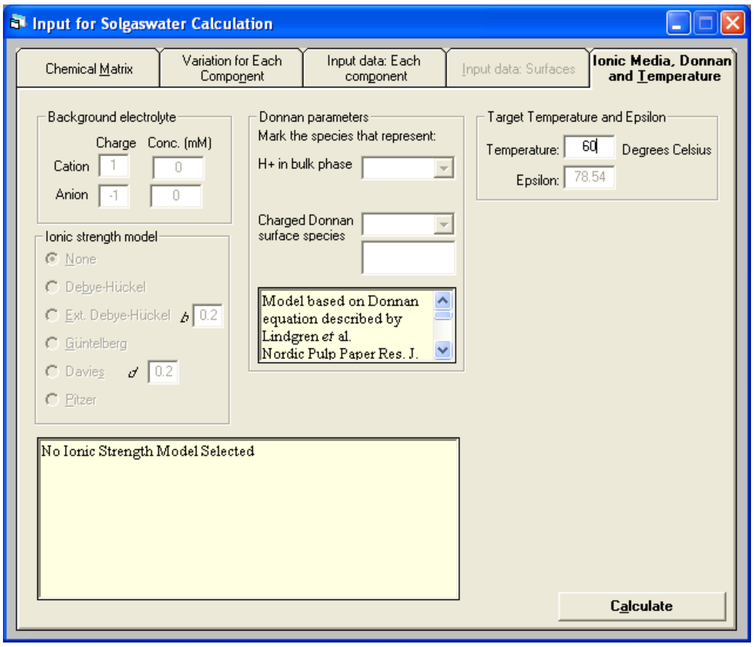
6. On the “Input data: Each component” tab, enter the start value “log {a}”, step length “Step” for the first component $H^+$, the total concentration of acetic acid and copper “Tc” and the number of points.



| | H+ | HAc | Cu 2+ |
|---|---|---|---|
| Tc (mM) | | 10 | 5 |
| log [Tc] (M) | | | |
| log {a} | -2 | | |
| Tc Byr. (mM) | | | |
| Step | -0.1 | | |
| Final value | -5 | | |

No. of points 31

7. Move to the “Ionic Media, Donnan and Temperature” tab and enter the target temperature.



| | Charge | Conc. (mM) |
|---|---|---|
| Cation | 1 | 0 |
| Anion | -1 | 0 |

Ionic strength model: ● None

Temperature: 60 Degrees Celsius

Epsilon: 78.54

Model based on Donnan equation described by Lindgren *et* al. Nordic Pulp Paper Res. J.

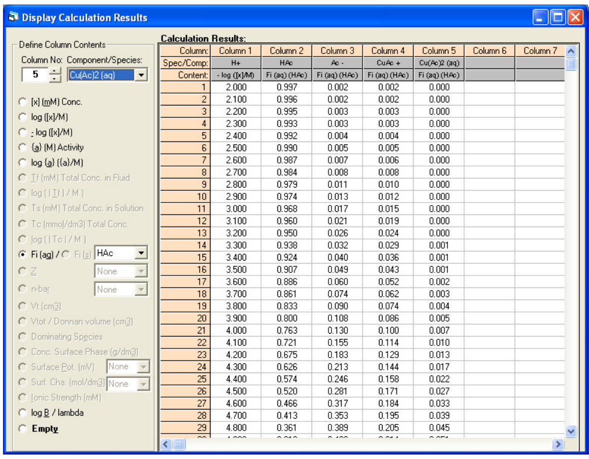
No Ionic Strength Model Selected

8. Calculate

9. Results

View -log[$H^+$] and the distribution (Fi) of the acetic acid containing species (HAc, $Ac^-$, $CuAc^+$ and $Cu(Ac)_2(aq)$ ). (Col. 1: $H^+$, -log{[x]/M}; Col. 2: HAc, Fi (aq) HAc; Col. 3: $Ac^-$, Fi (aq) HAc; Col. 4: $CuAc^+$, Fi (aq) HAc; Col. 5: $Cu(Ac)_2(aq)$ , Fi (aq) HAc).

There is a short-cut to view the distribution of all species containing a specific component. By choosing the actual component in the Component/species box and "Fi of selected component in all species in solution" from the Column Contents menu the distribution of all species containing the component is shown. The short-cut key for this is "<CTRL> + F".

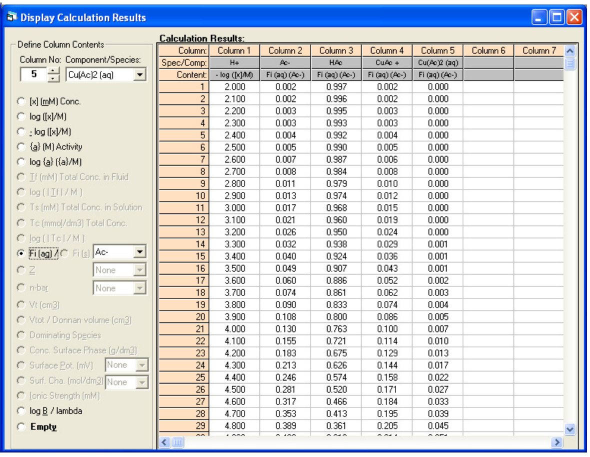


Column No: 5 Component/Species: Cu(Ac)2 (aq)

● Fi (ag) / ○ Fi (s) HAc

**Calculation Results:**

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | HAc | Ac - | CuAc + | Cu(Ac)2 (aq) | | |
| Content: | - log ([x]/M) | Fi (aq) (HAc) | Fi (aq) (HAc) | Fi (aq) (HAc) | Fi (aq) (HAc) | | |
| 1 | 2.000 | 0.997 | 0.002 | 0.002 | 0.000 | | |
| 2 | 2.100 | 0.996 | 0.002 | 0.002 | 0.000 | | |
| 3 | 2.200 | 0.995 | 0.003 | 0.003 | 0.000 | | |
| 4 | 2.300 | 0.993 | 0.003 | 0.003 | 0.000 | | |
| 5 | 2.400 | 0.992 | 0.004 | 0.004 | 0.000 | | |
| 6 | 2.500 | 0.990 | 0.005 | 0.005 | 0.000 | | |
| 7 | 2.600 | 0.987 | 0.007 | 0.006 | 0.000 | | |
| 8 | 2.700 | 0.984 | 0.008 | 0.008 | 0.000 | | |
| 9 | 2.800 | 0.979 | 0.011 | 0.010 | 0.000 | | |
| 10 | 2.900 | 0.974 | 0.013 | 0.012 | 0.000 | | |
| 11 | 3.000 | 0.968 | 0.017 | 0.015 | 0.000 | | |
| 12 | 3.100 | 0.960 | 0.021 | 0.019 | 0.000 | | |
| 13 | 3.200 | 0.950 | 0.026 | 0.024 | 0.000 | | |
| 14 | 3.300 | 0.938 | 0.032 | 0.029 | 0.001 | | |
| 15 | 3.400 | 0.924 | 0.040 | 0.036 | 0.001 | | |
| 16 | 3.500 | 0.907 | 0.049 | 0.043 | 0.001 | | |
| 17 | 3.600 | 0.886 | 0.060 | 0.052 | 0.002 | | |
| 18 | 3.700 | 0.861 | 0.074 | 0.062 | 0.003 | | |
| 19 | 3.800 | 0.833 | 0.090 | 0.074 | 0.004 | | |
| 20 | 3.900 | 0.800 | 0.108 | 0.086 | 0.005 | | |
| 21 | 4.000 | 0.763 | 0.130 | 0.100 | 0.007 | | |
| 22 | 4.100 | 0.721 | 0.155 | 0.114 | 0.010 | | |
| 23 | 4.200 | 0.675 | 0.183 | 0.129 | 0.013 | | |
| 24 | 4.300 | 0.626 | 0.213 | 0.144 | 0.017 | | |
| 25 | 4.400 | 0.574 | 0.246 | 0.158 | 0.022 | | |
| 26 | 4.500 | 0.520 | 0.281 | 0.171 | 0.027 | | |
| 27 | 4.600 | 0.466 | 0.317 | 0.184 | 0.033 | | |
| 28 | 4.700 | 0.413 | 0.353 | 0.195 | 0.039 | | |
| 29 | 4.800 | 0.361 | 0.389 | 0.205 | 0.045 | | |



Column No: 5 Component/Species: Cu(Ac)2 (aq)

● Fi (ag) / ○ Fi (s) Ac-

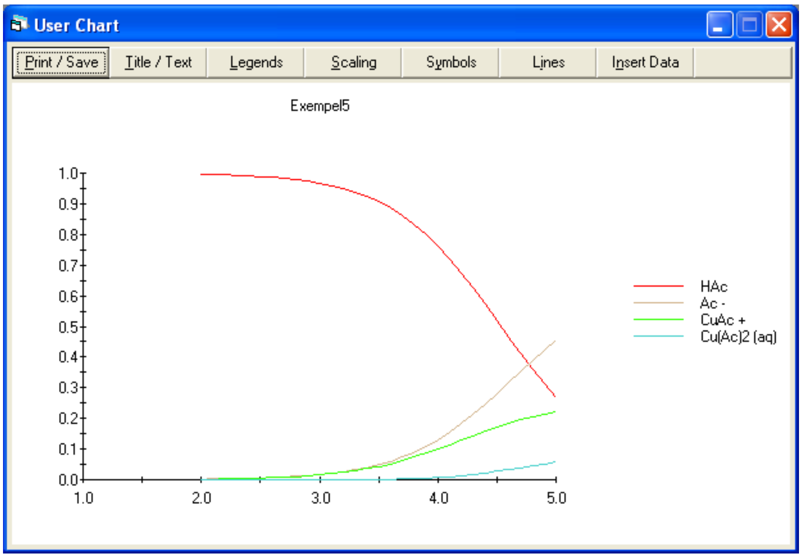
**Calculation Results:**

| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | Ac- | HAc | CuAc + | Cu(Ac)2 (aq) | | |
| Content: | - log ([x]/M) | Fi (aq) (Ac-) | Fi (aq) (Ac-) | Fi (aq) (Ac-) | Fi (aq) (Ac-) | | |
| 1 | 2.000 | 0.002 | 0.997 | 0.002 | 0.000 | | |
| 2 | 2.100 | 0.002 | 0.996 | 0.002 | 0.000 | | |
| 3 | 2.200 | 0.003 | 0.995 | 0.003 | 0.000 | | |
| 4 | 2.300 | 0.003 | 0.993 | 0.003 | 0.000 | | |
| 5 | 2.400 | 0.004 | 0.992 | 0.004 | 0.000 | | |
| 6 | 2.500 | 0.005 | 0.990 | 0.005 | 0.000 | | |
| 7 | 2.600 | 0.007 | 0.987 | 0.006 | 0.000 | | |
| 8 | 2.700 | 0.008 | 0.984 | 0.008 | 0.000 | | |
| 9 | 2.800 | 0.011 | 0.979 | 0.010 | 0.000 | | |
| 10 | 2.900 | 0.013 | 0.974 | 0.012 | 0.000 | | |
| 11 | 3.000 | 0.017 | 0.968 | 0.015 | 0.000 | | |
| 12 | 3.100 | 0.021 | 0.960 | 0.019 | 0.000 | | |
| 13 | 3.200 | 0.026 | 0.950 | 0.024 | 0.000 | | |
| 14 | 3.300 | 0.032 | 0.938 | 0.029 | 0.001 | | |
| 15 | 3.400 | 0.040 | 0.924 | 0.036 | 0.001 | | |
| 16 | 3.500 | 0.049 | 0.907 | 0.043 | 0.001 | | |
| 17 | 3.600 | 0.060 | 0.886 | 0.052 | 0.002 | | |
| 18 | 3.700 | 0.074 | 0.861 | 0.062 | 0.003 | | |
| 19 | 3.800 | 0.090 | 0.833 | 0.074 | 0.004 | | |
| 20 | 3.900 | 0.108 | 0.800 | 0.086 | 0.005 | | |
| 21 | 4.000 | 0.130 | 0.763 | 0.100 | 0.007 | | |
| 22 | 4.100 | 0.155 | 0.721 | 0.114 | 0.010 | | |
| 23 | 4.200 | 0.183 | 0.675 | 0.129 | 0.013 | | |
| 24 | 4.300 | 0.213 | 0.626 | 0.144 | 0.017 | | |
| 25 | 4.400 | 0.246 | 0.574 | 0.158 | 0.022 | | |
| 26 | 4.500 | 0.281 | 0.520 | 0.171 | 0.027 | | |
| 27 | 4.600 | 0.317 | 0.466 | 0.184 | 0.033 | | |
| 28 | 4.700 | 0.353 | 0.413 | 0.195 | 0.039 | | |
| 29 | 4.800 | 0.389 | 0.361 | 0.205 | 0.045 | | |

As seen, identical results are obtained regardless of component choice.

10. Plotting the results

Plot Fi as a function of pH.



## 5.7 Donnan equilibrium ($H^+$-$Na^+$-$Ca^{2+}$-fibre)

**Task:** Calculate the concentrations of sodium (1mM) and calcium (1mM) ions in the fibre volume and in the suspension liquid (according to the Donnan theory) between pH 2 and 7. (The Donnan theory applied to wood fibre systems has been described in detail in the work by Lindgren, Wiklund and Öhman (Nordic Pulp Paper Res. J. 16(1), 24).

1. The following equilibrium reactions describe the actual chemical system.

| | | log β |
|---|---|---|
| 1 | $H_2O \rightleftarrows H^+ + OH^-$ | -14 |
| 2 | $\equiv COOH \rightleftarrows H^+ + \equiv COO^-$ | -3.40 |

| Additional information about the fibre system: | |
|---|---|
| Surface site concentration | 0.31mM |
| Solid phase concentration | $10 g/dm^3$ |
| Specific surface area | $100 m^2/g$ |
| Specific capacitance | $0.27 F/m^2$ |
| Specific Donnan volume | 1.4ml/g |

In this example the Constant Capacitance Model is used to describe the electric double layer at the fibre/water interface.

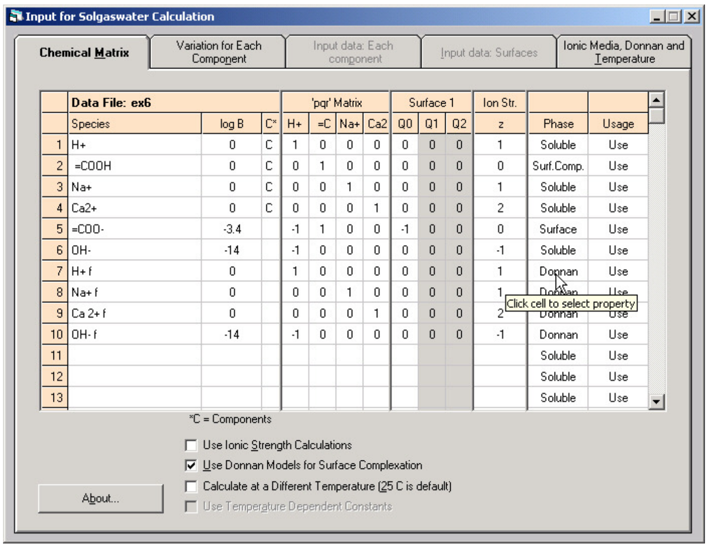
2. Four components: $H^+$, $\equiv COOH$, $Na^+$ and $Ca^{2+}$.

3. The chemical matrix with species charge(z) and surface charges (Q0, Q1 and Q2). Index "f" represents ions in the fibre phase (Donnan phase) and "s" ions in the surrounding suspension liquid.

| | log β | $H^+$ | $\equiv COOH$ | $Na^+$ | $Ca^{2+}$ | $Q_0$ | $Q_1$ | $Q_2$ | z |
|---|---|---|---|---|---|---|---|---|---|
| $H^+_s$ | 0 | 1 | 0 | 0 | 0 | | | | 1 |
| $\equiv COOH$ | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | |
| $Na^+_s$ | 0 | 0 | 0 | 1 | 0 | | | | 1 |
| $Ca^{2+}_s$ | 0 | 0 | 0 | 0 | 1 | | | | 2 |
| $OH^-_s$ | -14 | -1 | 0 | 0 | 0 | | | | -1 |
| $\equiv COO^-$ | -3.40 | -1 | 1 | 0 | 0 | -1 | 0 | 0 | |
| $H^+_f$ | 0 | 1 | 0 | 0 | 0 | | | | 1 |
| $Na^+_f$ | 0 | 0 | 0 | 1 | 0 | | | | 1 |
| $Ca^{2+}_f$ | 0 | 0 | 0 | 0 | 1 | | | | 2 |
| $OH^-_f$ | -14 | -1 | 0 | 0 | 0 | | | | -1 |

All mobile species (not surface complexes) should be entered twice, in both suspension liquid phase and Donnan phase, in the matrix. The log β for a species in the fibre phase should be the same as the log β in the suspension liquid phase.

4. Start WinSGW and enter the matrix. Mark the “Use Donnan models for surface calculation” box which will activate the species charge column (z) and the “Ionic media, Donnan and Temperature” tab. In WinSGW calculations it is only possible to involve Donnan equilibrium if a surface is present. Remember to change the Phase properties for the species in the fibre phase to “Donnan”.



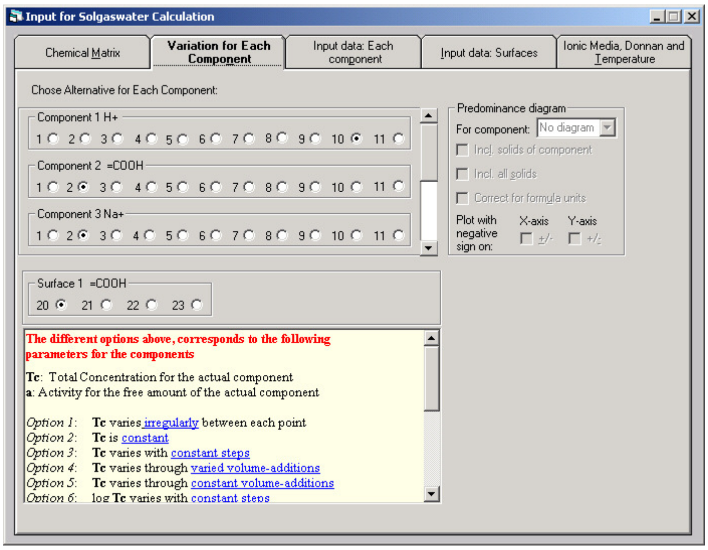
| | Data File: ex6 | | | 'pqr' Matrix | | | | Surface 1 | | | Ion Str. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Species | log B | C* | H+ | =C | Na+ | Ca2 | Q0 | Q1 | Q2 | z | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | Soluble | Use |
| 2 | =COOH | 0 | C | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | Surf.Comp. | Use |
| 3 | Na+ | 0 | C | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | Soluble | Use |
| 4 | Ca2+ | 0 | C | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 2 | Soluble | Use |
| 5 | =COO- | -3.4 | | -1 | 1 | 0 | 0 | -1 | 0 | 0 | 0 | Surface | Use |
| 6 | OH- | -14 | | -1 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | Soluble | Use |
| 7 | H+ f | 0 | | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | Donnan | Use |
| 8 | Na+ f | 0 | | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | Donnan | Use |
| 9 | Ca 2+ f | 0 | | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 2 | Donnan | Use |
| 10 | OH- f | -14 | | -1 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | Donnan | Use |
| 11 | | | | | | | | | | | | Soluble | Use |
| 12 | | | | | | | | | | | | Soluble | Use |
| 13 | | | | | | | | | | | | Soluble | Use |

Click cell to select property

*C = Components

☐ Use Ionic Strength Calculations
☑ Use Donnan Models for Surface Complexation
☐ Calculate at a Different Temperature (25 C is default)
☐ Use Temperature Dependent Constants

5. Move to next tab “Variation for each component”.
Choose to step pH and to keep the total concentration of remaining components constant.
(Component 1 $H^+$, option 10; Component 2 ≡COOH, option 2;
Component 3 $Na^+$, option 2; Component 4 $Ca^{2+}$, option 2; Surface 1 ≡COOH, option 20).



Chose Alternative for Each Component:

Component 1 H+
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ● 11 ○

Component 2 =COOH
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

Component 3 Na+
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

Surface 1 =COOH
20 ● 21 ○ 22 ○ 23 ○

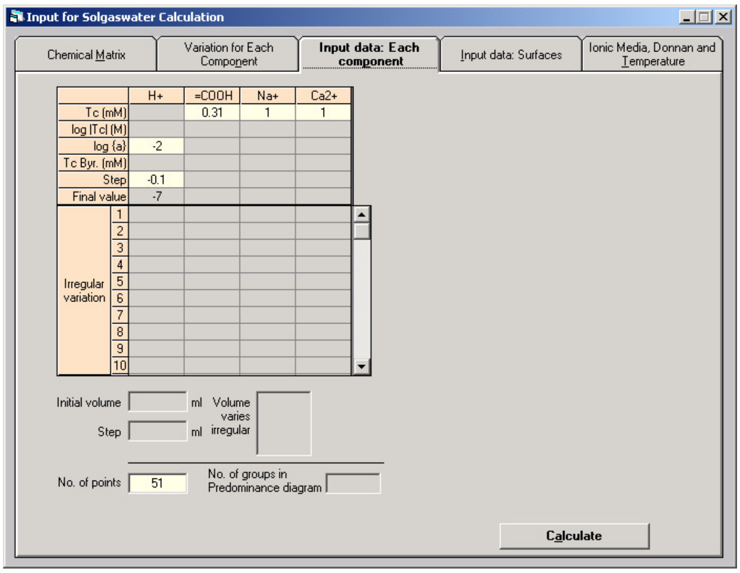
Predominance diagram
For component: No diagram
☐ Incl. solids of component
☐ Incl. all solids
☐ Correct for formula units
Plot with negative sign on: X-axis ☐ +/- Y-axis ☐ +/-

**The different options above, corresponds to the following parameters for the components**

**Tc**: Total Concentration for the actual component
**a**: Activity for the free amount of the actual component

*Option 1*: **Tc** varies irregularly between each point
*Option 2*: **Tc** is constant
*Option 3*: **Tc** varies with constant steps
*Option 4*: **Tc** varies through varied volume-additions
*Option 5*: **Tc** varies through constant volume-additions
*Option 6*: log **Tc** varies with constant steps

6. On the “Input data: Each component” tab, enter the start value “log {a}”, step length “Step” for the first component $H^+$, the total concentration of fibre sites, sodium and calcium “Tc” and the number of points.



| | | H+ | =COOH | Na+ | Ca2+ |
|---|---|---|---|---|---|
| Tc (mM) | | | 0.31 | 1 | 1 |
| log [Tc] (M) | | | | | |
| log {a} | | -2 | | | |
| Tc Byr. (mM) | | | | | |
| Step | | -0.1 | | | |
| Final value | | -7 | | | |
| Irregular variation | 1 | | | | |
| | 2 | | | | |
| | 3 | | | | |
| | 4 | | | | |
| | 5 | | | | |
| | 6 | | | | |
| | 7 | | | | |
| | 8 | | | | |
| | 9 | | | | |
| | 10 | | | | |

Initial volume ml

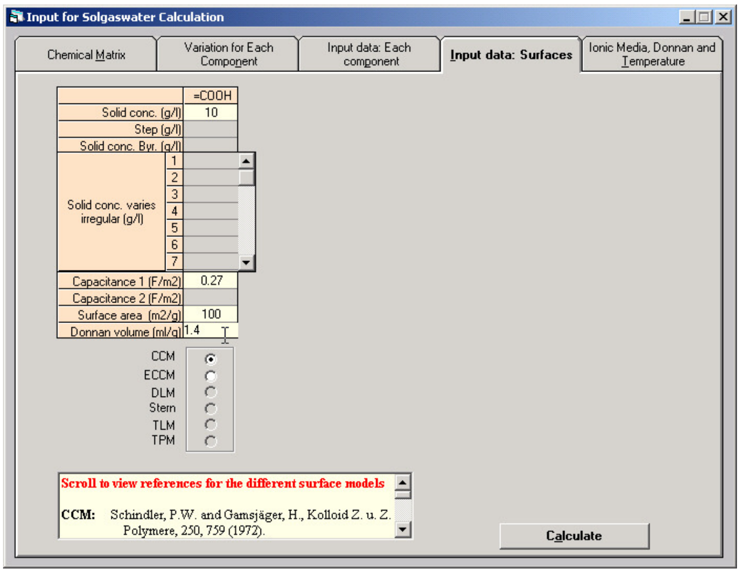
Step ml

Volume varies irregular

No. of points 51

No. of groups in Predominance diagram

7. Move to next tab “Input data: Surfaces”. Enter values for solid phase concentration, capacitance 1, surface area and the specific Donnan volume.



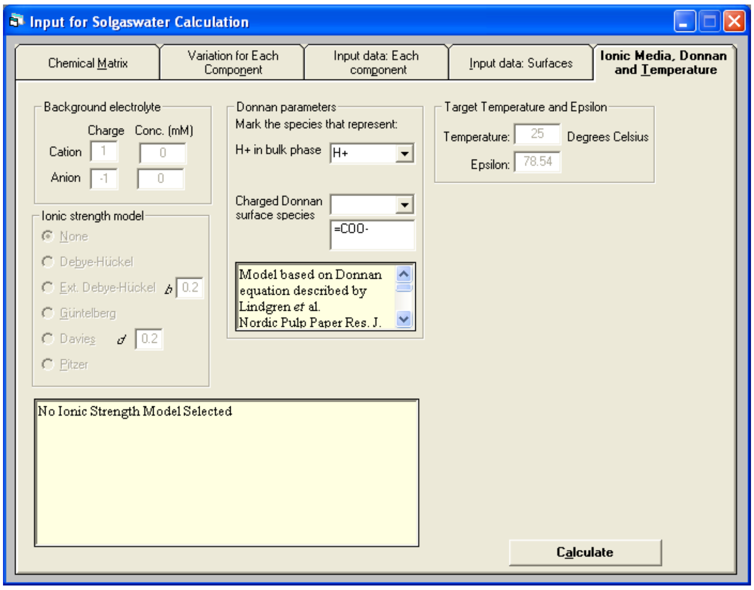
| | | =COOH |
|---|---|---|
| Solid conc. (g/l) | | 10 |
| Step (g/l) | | |
| Solid conc. Byr. (g/l) | | |
| Solid conc. varies irregular (g/l) | 1 | |
| | 2 | |
| | 3 | |
| | 4 | |
| | 5 | |
| | 6 | |
| | 7 | |
| Capacitance 1 (F/m2) | | 0.27 |
| Capacitance 2 (F/m2) | | |
| Surface area (m2/g) | | 100 |
| Donnan volume (ml/g) | | 1.4 |

CCM ●
ECCM ○
DLM ○
Stern ○
TLM ○
TPM ○

**Scroll to view references for the different surface models**

**CCM:** Schindler, P.W. and Gamsjäger, H., Kolloid Z. u. Z. Polymere, 250, 759 (1972).

8. Move to the "Ionic Media, Donnan and Temperature" tab and mark the species in the suspension liquid phase that represent the proton and the charged surface species causing the Donnan potential.



Background electrolyte

| | Charge | Conc. (mM) |
|---|---|---|
| Cation | 1 | 0 |
| Anion | -1 | 0 |

Ext. Debye-Hückel b: 0.2
Davies d: 0.2

Donnan parameters
Mark the species that represent:
H+ in bulk phase: H+
Charged Donnan surface species: =COO-

Model based on Donnan equation described by Lindgren *et al.* Nordic Pulp Paper Res. J.

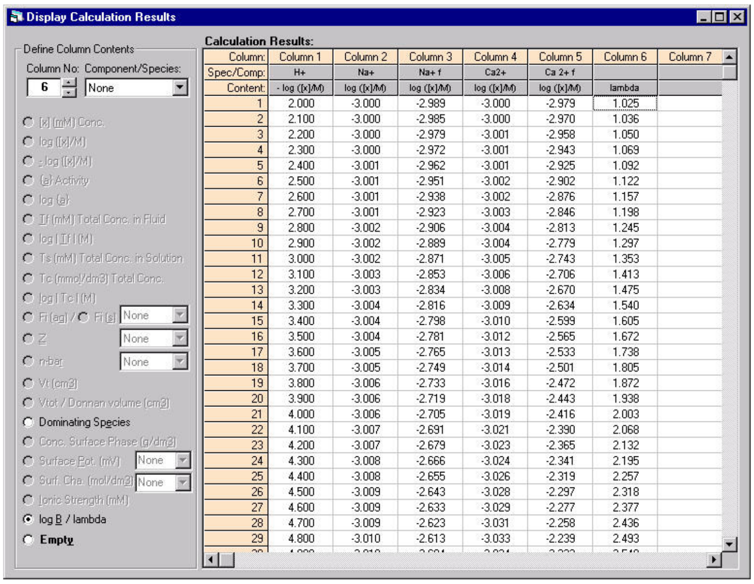
Target Temperature and Epsilon
Temperature: 25 Degrees Celsius
Epsilon: 78.54

No Ionic Strength Model Selected

9. Start the calculation

10. Results

View -log[$H^+$] and log c for all sodium and calcium species. In the sixth column view lambda ($\lambda = [H^+]_f / [H^+]_s = [Na^+]_f / [Na^+]_s = ([Ca^{2+}]_f / [Ca^{2+}]_s)^{½} = [OH^-]_s / [OH^-]_f$ ).
(Col. 1: $H^+$, -log{[x]/M}; Col. 2: $Na^+$, log{[x]/M}; Col. 3: $Na^+{}_f$, log{[x]/M}; Col. 4: $Ca^{2+}$, log{[x]/M}; Col. 5: $Ca^{2+}{}_f$, log{[x]/M}; Col. 6: None, lambda).



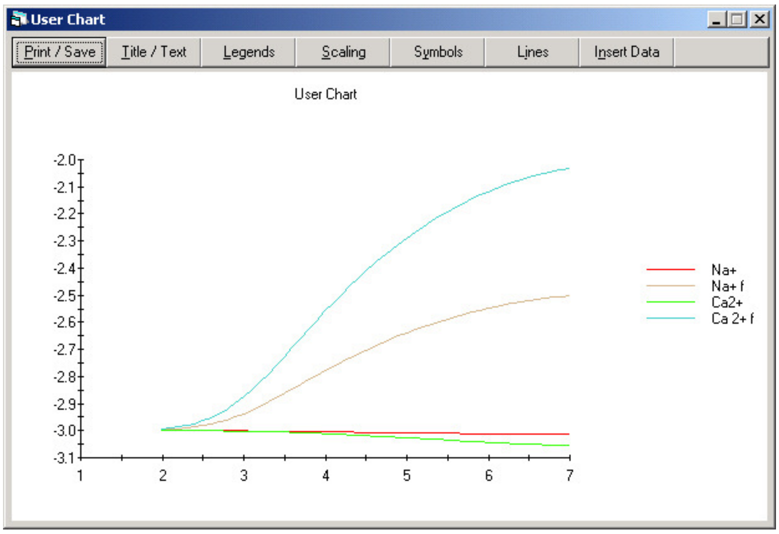
Column No: 6
Component/Species: None
● log B / lambda

Calculation Results:

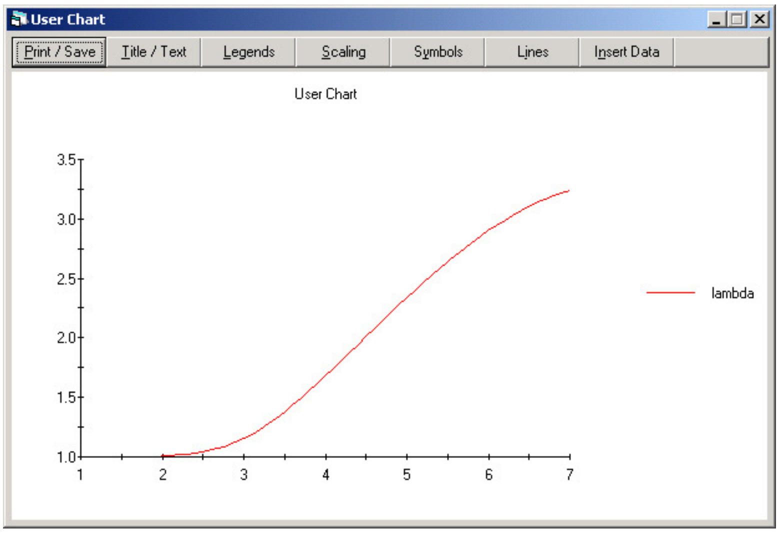
| Column: | Column 1 | Column 2 | Column 3 | Column 4 | Column 5 | Column 6 | Column 7 |
|---|---|---|---|---|---|---|---|
| Spec/Comp: | H+ | Na+ | Na+ f | Ca2+ | Ca 2+ f | | |
| Content: | - log ([x]/M) | log ([x]/M) | log ([x]/M) | log ([x]/M) | log ([x]/M) | lambda | |
| 1 | 2.000 | -3.000 | -2.989 | -3.000 | -2.979 | 1.025 | |
| 2 | 2.100 | -3.000 | -2.985 | -3.000 | -2.970 | 1.036 | |
| 3 | 2.200 | -3.000 | -2.979 | -3.001 | -2.958 | 1.050 | |
| 4 | 2.300 | -3.000 | -2.972 | -3.001 | -2.943 | 1.069 | |
| 5 | 2.400 | -3.001 | -2.962 | -3.001 | -2.925 | 1.092 | |
| 6 | 2.500 | -3.001 | -2.951 | -3.002 | -2.902 | 1.122 | |
| 7 | 2.600 | -3.001 | -2.938 | -3.002 | -2.876 | 1.157 | |
| 8 | 2.700 | -3.001 | -2.923 | -3.003 | -2.846 | 1.198 | |
| 9 | 2.800 | -3.002 | -2.906 | -3.004 | -2.813 | 1.245 | |
| 10 | 2.900 | -3.002 | -2.889 | -3.004 | -2.779 | 1.297 | |
| 11 | 3.000 | -3.002 | -2.871 | -3.005 | -2.743 | 1.353 | |
| 12 | 3.100 | -3.003 | -2.853 | -3.006 | -2.706 | 1.413 | |
| 13 | 3.200 | -3.003 | -2.834 | -3.008 | -2.670 | 1.475 | |
| 14 | 3.300 | -3.004 | -2.816 | -3.009 | -2.634 | 1.540 | |
| 15 | 3.400 | -3.004 | -2.798 | -3.010 | -2.599 | 1.605 | |
| 16 | 3.500 | -3.004 | -2.781 | -3.012 | -2.565 | 1.672 | |
| 17 | 3.600 | -3.005 | -2.765 | -3.013 | -2.533 | 1.738 | |
| 18 | 3.700 | -3.005 | -2.749 | -3.014 | -2.501 | 1.805 | |
| 19 | 3.800 | -3.006 | -2.733 | -3.016 | -2.472 | 1.872 | |
| 20 | 3.900 | -3.006 | -2.719 | -3.018 | -2.443 | 1.938 | |
| 21 | 4.000 | -3.006 | -2.705 | -3.019 | -2.416 | 2.003 | |
| 22 | 4.100 | -3.007 | -2.691 | -3.021 | -2.390 | 2.068 | |
| 23 | 4.200 | -3.007 | -2.679 | -3.023 | -2.365 | 2.132 | |
| 24 | 4.300 | -3.008 | -2.666 | -3.024 | -2.341 | 2.195 | |
| 25 | 4.400 | -3.008 | -2.655 | -3.026 | -2.319 | 2.257 | |
| 26 | 4.500 | -3.009 | -2.643 | -3.028 | -2.297 | 2.318 | |
| 27 | 4.600 | -3.009 | -2.633 | -3.029 | -2.277 | 2.377 | |
| 28 | 4.700 | -3.009 | -2.623 | -3.031 | -2.258 | 2.436 | |
| 29 | 4.800 | -3.010 | -2.613 | -3.033 | -2.239 | 2.493 | |

### 11. Plotting the results

Plot log {[x]/M}for sodium and calcium in both suspension liquid and fibre phase as a function of pH.



In a new diagram, plot lambda (the distribution coefficient) as a function of pH.



## 5.8 Find the best fitting model for the ($H^+$-$H_3PO_4$) system

**Task:** Optimise the formation constant for $PO_4^{3-}$ using experimental data. The total concentration of $H_3PO_4$ is constant during the experiment (10mM) and the following pH values (-log $\{H^+\}$)and $[PO_4^{3-}]$ are available.

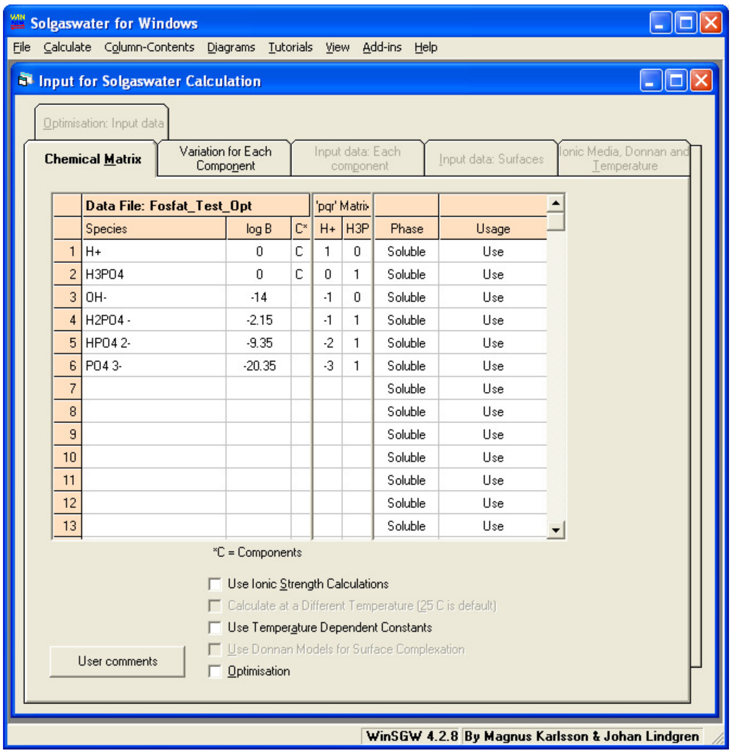
| pH | $[PO_4^{3-}]$ (mM) |
|---|---|
| 9 | 4E-03 |
| 9.8 | 0.03 |
| 10.2 | 0.07 |
| 10.5 | 0.12 |
| 11 | 0.25 |
| 11.2 | 0.66 |
| 11.8 | 2.2 |
| 12 | 3.2 |

1. The following model was entered into WinSGW in the first example in this manual.

| | | log β* |
|---|---|---|
| 1 | $H_2O \rightleftarrows H^+ + OH^-$ | -14.00 |
| 2 | $H_3PO_4 \rightleftarrows H_2PO_4^- + H^+$ | -2.15 |
| 3 | $H_2PO_4^- \rightleftarrows HPO_4^{2-} + H^+$ | -7.20 |
| 4 | $HPO_4^{2-} \rightleftarrows PO_4^{3-} + H^+$ | -12.35 |

*Equilibrium constants valid at infinite dilution and at 25°C.

2. Enter the model following the first five steps in the previous example. Change the formation constant for $PO_4^{3-}$ from -12.35 to -11. This entail that the chemical matrix in WinSGW will have the following content.

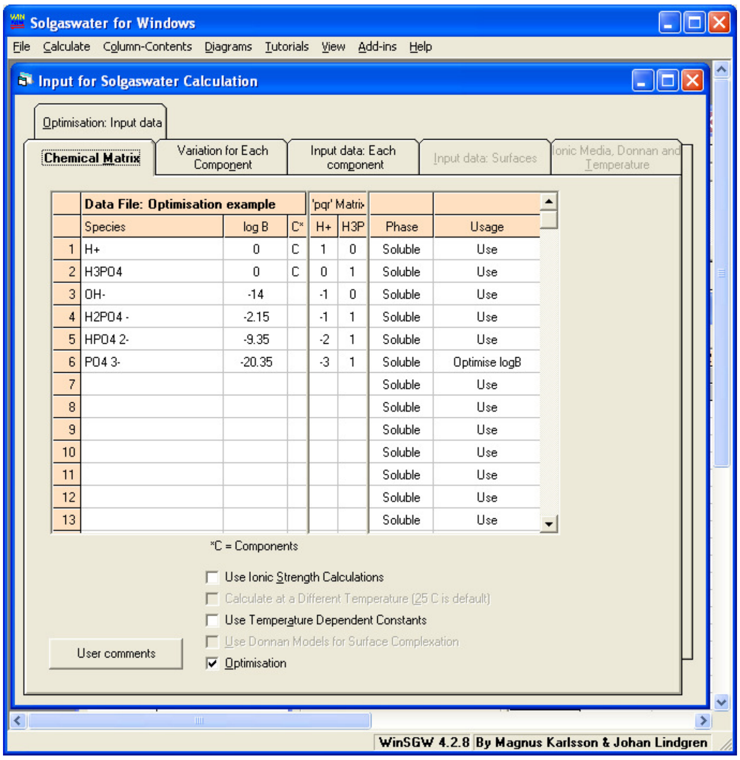


| | Data File: Fosfat_Test_Opt | | | 'pqr' Matrix | | | |
|---|---|---|---|---|---|---|---|
| | Species | log B | C* | H+ | H3P | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 0 | Soluble | Use |
| 2 | H3PO4 | 0 | C | 0 | 1 | Soluble | Use |
| 3 | OH- | -14 | | -1 | 0 | Soluble | Use |
| 4 | H2PO4 - | -2.15 | | -1 | 1 | Soluble | Use |
| 5 | HPO4 2- | -9.35 | | -2 | 1 | Soluble | Use |
| 6 | PO4 3- | -20.35 | | -3 | 1 | Soluble | Use |
| 7 | | | | | | Soluble | Use |
| 8 | | | | | | Soluble | Use |
| 9 | | | | | | Soluble | Use |
| 10 | | | | | | Soluble | Use |
| 11 | | | | | | Soluble | Use |
| 12 | | | | | | Soluble | Use |
| 13 | | | | | | Soluble | Use |

*C = Components

☐ Use Ionic Strength Calculations
☐ Calculate at a Different Temperature (25 C is default)
☐ Use Temperature Dependent Constants
☐ Use Donnan Models for Surface Complexation
☐ Optimisation

3. Mark the “Optimisation” check box and change the Usage-value for $PO_4^{3-}$ from “Use” to “Optimise logB”.



| | Data File: Optimisation example | | | 'pqr' Matrix | | | |
|---|---|---|---|---|---|---|---|
| | Species | log B | C* | H+ | H3P | Phase | Usage |
| 1 | H+ | 0 | C | 1 | 0 | Soluble | Use |
| 2 | H3PO4 | 0 | C | 0 | 1 | Soluble | Use |
| 3 | OH- | -14 | | -1 | 0 | Soluble | Use |
| 4 | H2PO4 - | -2.15 | | -1 | 1 | Soluble | Use |
| 5 | HPO4 2- | -9.35 | | -2 | 1 | Soluble | Use |
| 6 | PO4 3- | -20.35 | | -3 | 1 | Soluble | Optimise logB |
| 7 | | | | | | Soluble | Use |
| 8 | | | | | | Soluble | Use |
| 9 | | | | | | Soluble | Use |
| 10 | | | | | | Soluble | Use |
| 11 | | | | | | Soluble | Use |
| 12 | | | | | | Soluble | Use |
| 13 | | | | | | Soluble | Use |

*C = Components

☐ Use Ionic Strength Calculations

☐ Calculate at a Different Temperature (25 C is default)

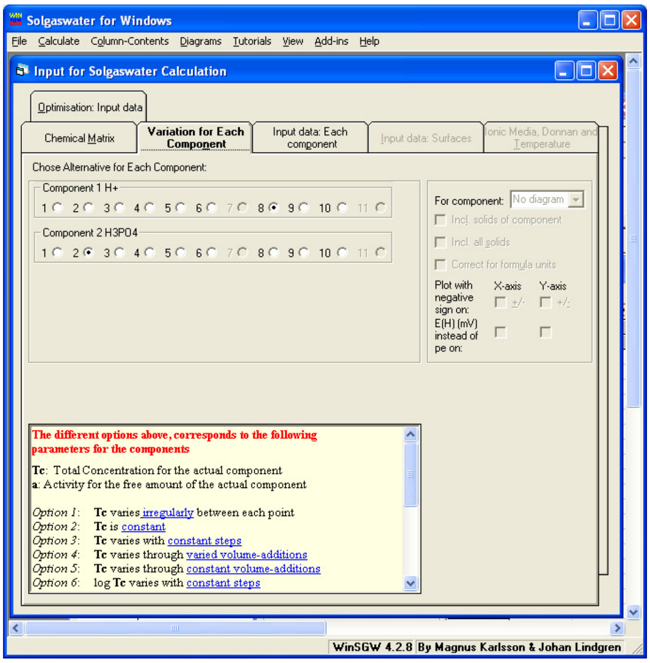
☐ Use Temperature Dependent Constants

☐ Use Donnan Models for Surface Complexation

☑ Optimisation

Up to 10 formation constant and/or capacitance figures could be optimised at the same time.

4. Change to next tab “Variation for each component”. For this example we would like to vary pH irregularly (Component 1 $H^+$, option 8) and to keep the total phosphoric acid concentration constant (Component 2 $H_3PO_4$, option 2).



Chose Alternative for Each Component:

Component 1 H+
1 ○ 2 ○ 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ● 9 ○ 10 ○ 11 ○

Component 2 H3PO4
1 ○ 2 ● 3 ○ 4 ○ 5 ○ 6 ○ 7 ○ 8 ○ 9 ○ 10 ○ 11 ○

For component: No diagram
☐ Incl. solids of component
☐ Incl. all solids
☐ Correct for formula units

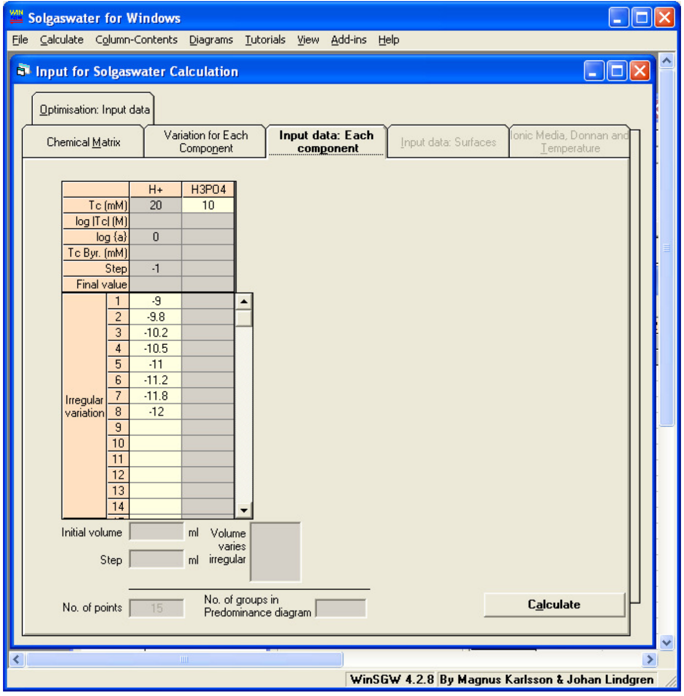
| | X-axis | Y-axis |
|---|---|---|
| Plot with negative sign on: | ☐ +/- | ☐ +/- |
| E(H) (mV) instead of pe on: | ☐ | ☐ |

**The different options above, corresponds to the following parameters for the components**

**Tc**: Total Concentration for the actual component
**a**: Activity for the free amount of the actual component

*Option 1*: **Tc** varies irregularly between each point
*Option 2*: **Tc** is constant
*Option 3*: **Tc** varies with constant steps
*Option 4*: **Tc** varies through varied volume-additions
*Option 5*: **Tc** varies through constant volume-additions
*Option 6*: log **Tc** varies with constant steps

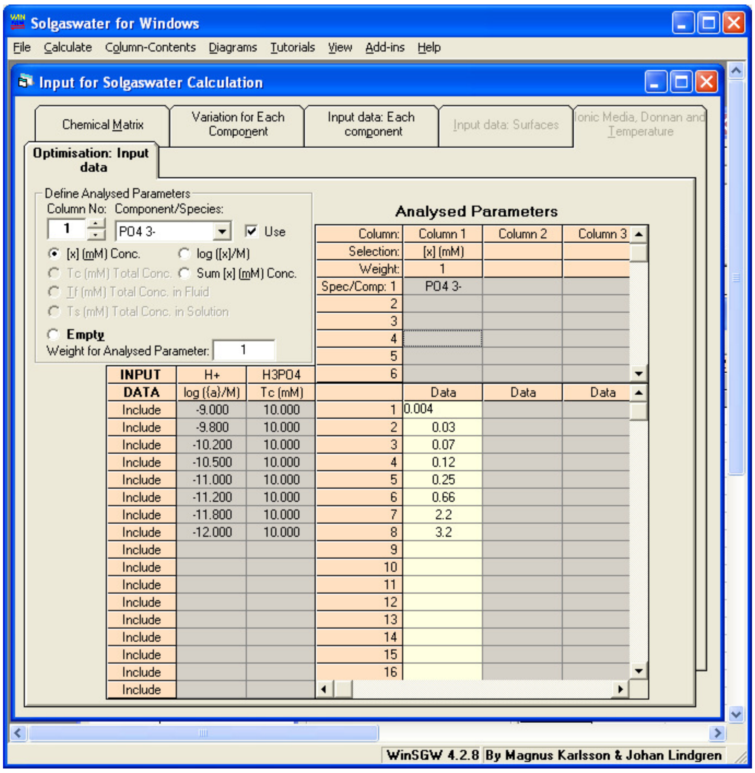
5. Move to next tab “Input data: Each component”. Enter the “log {a}” values and the total concentration of phosphoric acid “Tc”.



| | | H+ | H3PO4 |
|---|---|---|---|
| Tc (mM) | | 20 | 10 |
| log \|Tc\| (M) | | | |
| log {a} | | 0 | |
| Tc Byr. (mM) | | | |
| Step | | -1 | |
| Final value | | | |
| Irregular variation | 1 | -9 | |
| | 2 | -9.8 | |
| | 3 | -10.2 | |
| | 4 | -10.5 | |
| | 5 | -11 | |
| | 6 | -11.2 | |
| | 7 | -11.8 | |
| | 8 | -12 | |
| | 9 | | |
| | 10 | | |
| | 11 | | |
| | 12 | | |
| | 13 | | |
| | 14 | | |

Initial volume ml
Step ml
Volume varies irregular
No. of points 15
No. of groups in Predominance diagram

6. Move to “Optimisation: Input data” tab. Choose $PO_4^{3-}$ in the “Component/Species” box, mark the radio button for free species concentration ( [x] (mM) Conc. ) and enter the measured $PO_4^{3-}$ concentration into the matrix marked in yellow.



Define Analysed Parameters

Column No: 1

Component/Species: P04 3-

☑ Use

● [x] (mM) Conc.

○ log ([x]/M)

○ Tc (mM) Total Conc.

○ Sum [x] (mM) Conc.

○ Tf (mM) Total Conc. in Fluid

○ Ts (mM) Total Conc. in Solution

○ **Empty**

Weight for Analysed Parameter: 1

| **INPUT** | H+ | H3P04 |
|---|---|---|
| **DATA** | log ({a}/M) | Tc (mM) |
| Include | -9.000 | 10.000 |
| Include | -9.800 | 10.000 |
| Include | -10.200 | 10.000 |
| Include | -10.500 | 10.000 |
| Include | -11.000 | 10.000 |
| Include | -11.200 | 10.000 |
| Include | -11.800 | 10.000 |
| Include | -12.000 | 10.000 |
| Include | | |
| Include | | |
| Include | | |
| Include | | |
| Include | | |
| Include | | |
| Include | | |
| Include | | |
| Include | | |

**Analysed Parameters**

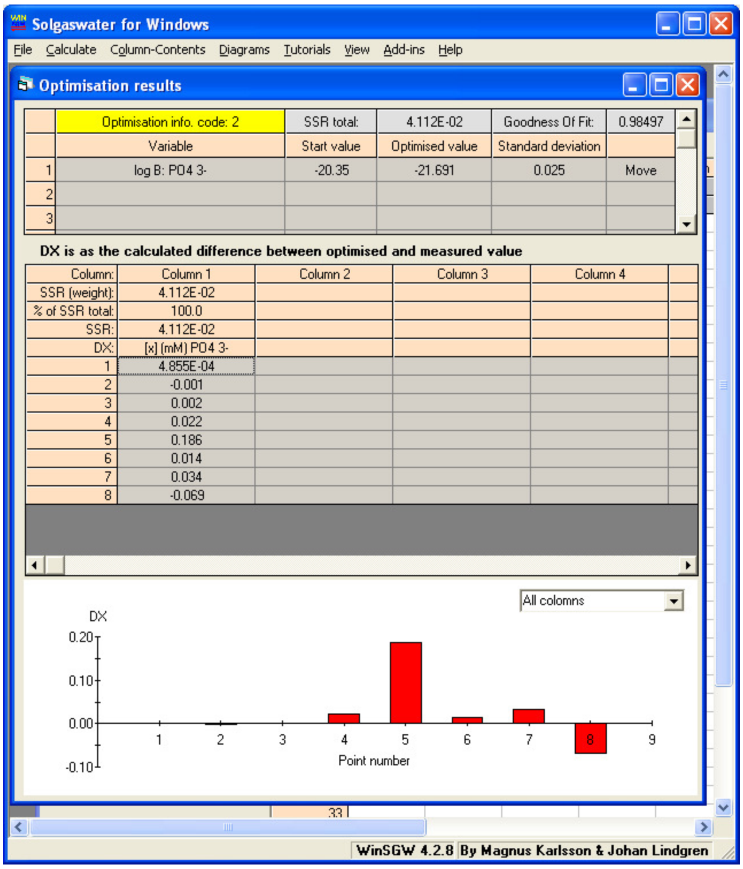
| Column: | Column 1 | Column 2 | Column 3 |
|---|---|---|---|
| Selection: | [x] (mM) | | |
| Weight: | 1 | | |
| Spec/Comp: 1 | P04 3- | | |
| 2 | | | |
| 3 | | | |
| 4 | | | |
| 5 | | | |
| 6 | | | |

| | Data | Data | Data |
|---|---|---|---|
| 1 | 0.004 | | |
| 2 | 0.03 | | |
| 3 | 0.07 | | |
| 4 | 0.12 | | |
| 5 | 0.25 | | |
| 6 | 0.66 | | |
| 7 | 2.2 | | |
| 8 | 3.2 | | |
| 9 | | | |
| 10 | | | |
| 11 | | | |
| 12 | | | |
| 13 | | | |
| 14 | | | |
| 15 | | | |
| 16 | | | |

If you have measured more than one type of data you could add up to fifteen data sets using the remaining columns. If a data point is missing in a data set the abbreviation NaN (Not a Number) could be used to exclude the missing data. Different weights could be applied to the data sets, which will move the resulting model closer to the data set given the highest weight.

7. Start the calculation by pressing a “Calculate” button, using the Calculate menu or the short cut key <F9>.

8. Two windows for the result will open, the normal grid for viewing results from a WinSGW calculation and a window called “Optimisation results”.



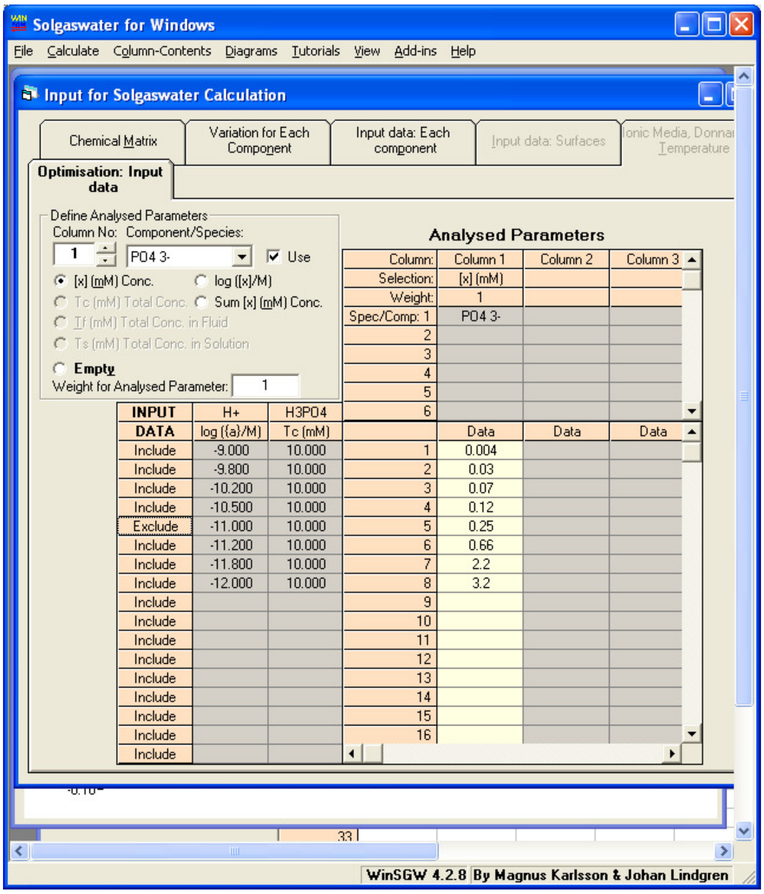
| | Optimisation info. code: 2 | SSR total: | 4.112E-02 | Goodness Of Fit: | 0.98497 |
|---|---|---|---|---|---|
| | Variable | Start value | Optimised value | Standard deviation | |
| 1 | log B: PO4 3- | -20.35 | -21.691 | 0.025 | Move |
| 2 | | | | | |
| 3 | | | | | |

**DX is as the calculated difference between optimised and measured value**

| Column: | Column 1 | Column 2 | Column 3 | Column 4 |
|---|---|---|---|---|
| SSR (weight): | 4.112E-02 | | | |
| % of SSR total: | 100.0 | | | |
| SSR: | 4.112E-02 | | | |
| DX: | [x] (mM) PO4 3- | | | |
| 1 | 4.855E-04 | | | |
| 2 | -0.001 | | | |
| 3 | 0.002 | | | |
| 4 | 0.022 | | | |
| 5 | 0.186 | | | |
| 6 | 0.014 | | | |
| 7 | 0.034 | | | |
| 8 | -0.069 | | | |

The upper table shows the best fitting model found by WinSGW and the overall fit to the experimental data. Sum of Squared Residuals (SSR) is the difference between the model and the experimental data and should be as low as possible. The Goodness of fit value close to one indicates that the resulting model has a good fit to the data. The starting value, the optimised value and the standard deviation for each optimised variable is then listed. By pressing on “Move” in the last column is the optimised value moved to the “Chemical matrix” and will then be used as the starting value in the next optimisation.
In the lower part is the DX figures, the difference between the model and the experimental data, for each data point listed and plotted. The squared sum of the DX figures is equal to the SSR.

9. It is obvious that data point number 5 is strongly deviating from the model. Move back to the Input window (View Chemical matrix) and Click in the first column for data point 5. This will change the value for this point from INCLUDE to EXCLUDE.



Define Analysed Parameters

Column No: 1

Component/Species: PO4 3-

☑ Use

● [x] (mM) Conc.

○ log ([x]/M)

○ Tc (mM) Total Conc.

○ Sum [x] (mM) Conc.

○ Tf (mM) Total Conc. in Fluid

○ Ts (mM) Total Conc. in Solution

○ Empty

Weight for Analysed Parameter: 1

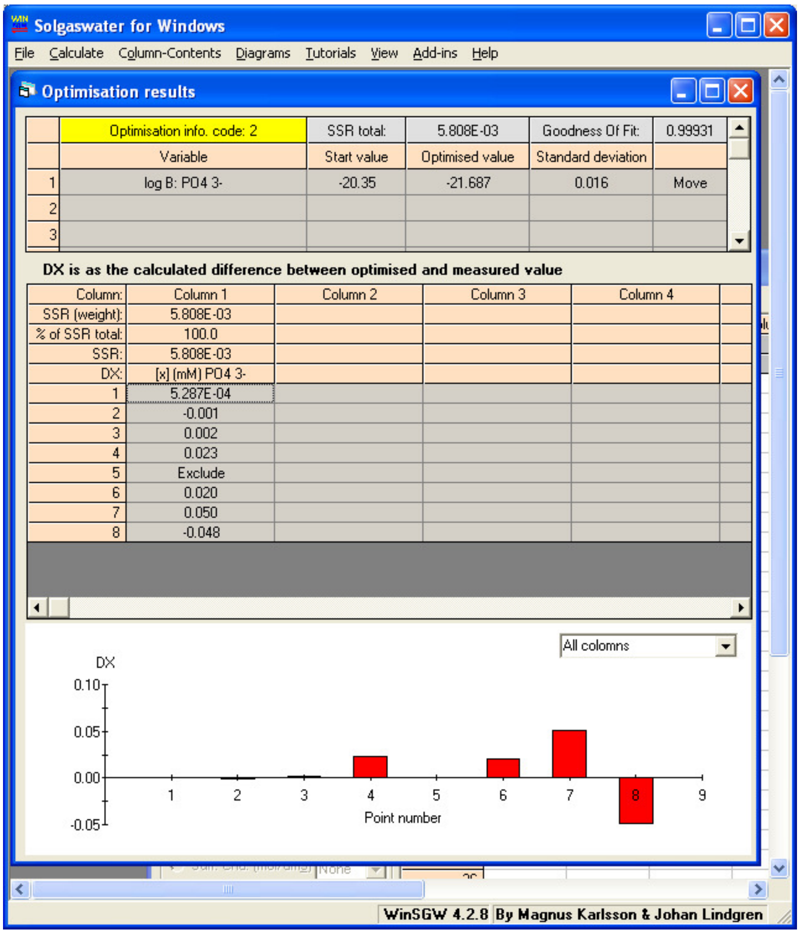
| INPUT | H+ | H3PO4 |
|---|---|---|
| DATA | log ({a}/M) | Tc (mM) |
| Include | -9.000 | 10.000 |
| Include | -9.800 | 10.000 |
| Include | -10.200 | 10.000 |
| Include | -10.500 | 10.000 |
| Exclude | -11.000 | 10.000 |
| Include | -11.200 | 10.000 |
| Include | -11.800 | 10.000 |
| Include | -12.000 | 10.000 |
| Include | | |
| Include | | |
| Include | | |
| Include | | |
| Include | | |
| Include | | |
| Include | | |
| Include | | |
| Include | | |

Analysed Parameters

| Column: | Column 1 | Column 2 | Column 3 |
|---|---|---|---|
| Selection: | [x] (mM) | | |
| Weight: | 1 | | |
| Spec/Comp: 1 | PO4 3- | | |
| 2 | | | |
| 3 | | | |
| 4 | | | |
| 5 | | | |
| 6 | | | |

| | Data | Data | Data |
|---|---|---|---|
| 1 | 0.004 | | |
| 2 | 0.03 | | |
| 3 | 0.07 | | |
| 4 | 0.12 | | |
| 5 | 0.25 | | |
| 6 | 0.66 | | |
| 7 | 2.2 | | |
| 8 | 3.2 | | |
| 9 | | | |
| 10 | | | |
| 11 | | | |
| 12 | | | |
| 13 | | | |
| 14 | | | |
| 15 | | | |
| 16 | | | |

10. Start the calculation by pressing a “Calculate” button, using the Calculate menu or the short cut key <F9>.



| | Optimisation info. code: 2 | SSR total: | 5.808E-03 | Goodness Of Fit: | 0.99931 |
|---|---|---|---|---|---|
| | Variable | Start value | Optimised value | Standard deviation | |
| 1 | log B: PO4 3- | -20.35 | -21.687 | 0.016 | Move |
| 2 | | | | | |
| 3 | | | | | |

DX is as the calculated difference between optimised and measured value

| Column: | Column 1 | Column 2 | Column 3 | Column 4 |
|---|---|---|---|---|
| SSR (weight): | 5.808E-03 | | | |
| % of SSR total: | 100.0 | | | |
| SSR: | 5.808E-03 | | | |
| DX: | [x] (mM) PO4 3- | | | |
| 1 | 5.287E-04 | | | |
| 2 | -0.001 | | | |
| 3 | 0.002 | | | |
| 4 | 0.023 | | | |
| 5 | Exclude | | | |
| 6 | 0.020 | | | |
| 7 | 0.050 | | | |
| 8 | -0.048 | | | |

Excluding data point 5 reduced the SSR total figure and changed the Goodness of fit value closer to 1.

Detailed information about the optimisation calculation (convergence criteria etc.) can be found under “Help and Show optimisation information codes”. The convergence criteria could be changed under “File, Preferences and Optimisation options”.