μQL "Portable MICROQL" Summary of Mathematics — Version 1.9

Michael Gfeller   **October 27, 1998**

gfeller@ito.umnw.ethz.ch
ETH/ITÖ, Grabenstrasse 3, CH-8952 Schlieren, Switzerland

Contents

1 Introduction

This report contains a summary of the mathematical framework used in μQL, an extended version of MICROQL (Westall 1979Westall 1986).

2 Symbols

All symbols correspond to the ones used in Westall (1979) and Westall (1986) except the symbol for the solid concentration (here: q, Westall: a) and the symbols used for features specific to μQL.

2.1 Scalars

scalar	description
C_i	free activity of species i
F	number of components with fixed, i.e., known, free activity
G	number of solid phases
I	ionic strength
K_i	stability constant of species i
Lp_g	solubility product of solid phase g
M	number of components
N	number of species
$P_{i\alpha}$	normalised sensitivity coefficient of species i with respect to equilibrium constant α
Q_i	stability constant of species i calculated from K_i using the Davies-Equation
S_{gj}	stochiometric coefficient of component j in solid phase g
T_j	total analytical concentration of component j
U	number of components with unknown free activity ($U = M - F$)
W_j	value used to check convergence
X_j	free activity of of component j
Y_j	residual in material balance equation of component j
α	index for any equilibrium constant ($\longrightarrow P_{i\alpha}$)
a	factor a in Davies-Equation
a_{ij}	stochiometric coefficient of component j in species i
b	factor b in Davies-Equation
g	index for any solid phase (oversaturation calculation)
i	index for any species
j, k	indices for any component
z_{jk}	partial derivative $\partial Y_j / \partial X_k$, i.e., an element of the Jacobian

2.2 Vectors and matrices

vector/matrix	description
A	matrix of a_{ij}
C	vector of C_i
$C^\star$	vector of $\log C_i$
K	vector of K_i
$K^\star$	vector of $\log K_i$
L	matrix for the transformation of an old set of components (columns) to a new set of components (rows)
Lp	vector of Lp_g
S	matrix of S_{gj}
T	vector of T_j
W	vector of W_j
X	vector of X_j
$X^\star$	vector of $logX_j$
Y	vector of Y_j
Z	Jacobian of Y with respect to X (matrix of z_{jk})

2.3 Surface complexation models

The following lists correspond to Tables 3.2 to 3.5 in Westall (1979). Note that the names given in the column "Variable" correspond to the variables used in the programs. The symbols given

in the column "Explanation" are used in the formulae in this report.

2.3.1 Fundamental constants

variable	symbol or formula	description	value	units
	ϵ	dielectric constant of water	82	
	ϵ_0	permittivity of vacuum	$8.85\ 10^{-12}$	$C^2\ m^{-1}\ J^{-1}$
	R	gas constant	8.314	$J\ mol^{-1}\ K^{-1}$
	T	temperature	298.15	K
B1	N_A	Avogardo's constant	$6.022\ 10^{23}$	mol^{-1}
B2	$(8\epsilon\epsilon_0 RT)^{1/2}$		0.1174	$C\ m^{-2}\ (mol\ L^{-1})^{1/2}$
B3	$F/(2RT)$		19.46	V^{-1}
B4	RT/F		0.0256	V
B5	$\ln 10 RT/F$		0.05916	V
B6	F	Faraday	96487	$C\ mol^{-1}$

2.3.2 Adjustable parameters

variable	symbol	description	units
C1	N_S	surface site density	sites m^{-2}
C2	s	specific surface area	$m^2\ g^{-1}$
C3	q	concentration of solid	$g\ L^{-1}$
	$(a$	Westall (1979))	
C4	I	ionic strength	
C5	C_1	capacitance (inner)	$F\ m^{-2}$
C6	C_2	capacitance (outer)	$F\ m^{-2}$

2.3.3 Computed electrostatic quantities

variable	symbol	definition	units
D0	Ψ_0	surface potential	V
D1	Ψ_1	surface potential	V
D2	Ψ_2	surface potential	V
D3	s	$(8\epsilon\epsilon_0 RT)^{1/2}\sinh(F\Psi/(2RT))$ charge computed by Poisson-Boltzman for a monovalent electrolyte.	$C\ m^{-2}$
D4		sq/F conversion factor from electrostatic quantities ($[\sigma] = Cm^{-2}$) to concentration ($[T_\sigma] = molL^{-1}$): $T_\sigma = \sigma sq/F$	$m^2\ C^{-1}\ mol\ L^{-1}$

2.3.4 Surface component identification

variable	identifies	description
L0	Ψ_0, σ_0	surface potential, charge
L1	Ψ_1, σ_1	surface potential, charge
L2	Ψ_2, σ_2	surface potential, charge
L3	SOH	surface component

3 Solution speciation

A modified Newton-Raphson algorithm (no negative free activities are allowed) is used to solve the system of the U mass-balance equations, which are generally non-linear, by optimising the free activities X_j of the components.

The residual Y_j is calculated by

$$Y_j = T_{j,\text{calc}} - T_j \ j = 1\ldots U \tag{1}$$

Using

$$T_{j,\text{calc}} = \sum_{i=1}^{N} a_{ij} C_i \ j = 1 \dots M \tag{2}$$

Equation 1 can be written as

$$Y_j = \sum_{i=1}^{N} a_{ij} C_i - T_j \ j = 1 \dots M \tag{3}$$

or, in matrix notation

$$Y = {}^t AC - T \tag{4}$$

where ${}^t A$ is the transpose of matrix A. The problem is solved when $Y = 0$.

The concentrations of the species, C_i, are calculated by

$$C_i = K_i \prod_{j=1}^{M} X_j^{a_{ij}} \qquad i = 1 \dots N \tag{5}$$

Taking the logarithm of Equation 5 yields

$$\log C_i = \log K_i + \sum_{j=1}^{M} a_{ij} \log X_j \qquad i = 1 \dots N \tag{6}$$

or, in matrix notation,

$$C^\star = K^\star + AX^\star \tag{7}$$

The derivatives $z_{jk} = \partial Y_j / \partial X_k$ needed in the Newton-Raphson algorithm can be calculated from Equation 3:

$$\frac{\partial Y_j}{\partial X_k} = \sum_{i=1}^{N} a_{ij} \frac{\partial C_i}{\partial X_k} - \frac{\partial T_j}{\partial X_k} \qquad j, k = 1 \dots U \tag{8}$$

Since T_j is constant:

$$\frac{\partial T_j}{\partial X_k} = 0 \tag{9}$$

From Equation 5, we obtain

$$\frac{\partial C_i}{\partial X_k} = a_{ik} \frac{C_i}{X_k} \tag{10}$$

Substituting Equations 9 and 10 in Equation 8 yields

$$z_{jk} = \frac{\partial Y_j}{\partial X_k} = \sum_{i=1}^{N} \frac{a_{ij} a_{ik} C_i}{X_k} \qquad j, k = 1 \dots U \tag{11}$$

The set of equations to be solved can be expressed in matrix notation as

$$Z \Delta X = Y \tag{12}$$

where

$$\Delta X = X_{\text{original}} - X_{\text{improved}} \tag{13}$$

4

If $X_{\text{improved}} < 0$, then it is calculated according to

$$X_{\text{improved}} = \frac{X_{\text{original}}}{f} \tag{14}$$

where f is an empirical constant (e.g. 10).

Convergence is reached when

$$W_j = \frac{|Y_j|}{\sum_{i=1}^{N} |a_{ij} C_i| + |T_j|} < \epsilon \qquad \text{for all } j; j = 1 \ldots U \tag{15}$$

ϵ[1] is a small number, e.g. $1.E - 6$.

4 Transformation of components

It is sometimes easier to transform a set of "old" components to a set of "new" components by specifying a transformation matrix L than to formulate a new MICROQL problem. The transformations of the vectors T, $X^\star$, and $K^\star$ and the matrix A are given by

$$
\begin{aligned}
T_{\text{new}} &= {}^t L^{-1} T_{\text{old}} & (16) \\
X_{\text{new}}^\star &= L X_{\text{old}}^\star & (17) \\
K_{\text{new}}^\star &= K_{\text{old}}^\star & (18) \\
A_{\text{new}} &= A_{\text{old}} L^{-1} & (19)
\end{aligned}
$$

where L^{-1} is the inverse of the transformation matrix L.

5 Davies-Equation (model 1)

Equilibrium constants adjusted for ionic strength, Q_i, are calculated using the Davies-Equation (Baes & Mesmer 1976):

$$\log Q_i = \log K_i + a \frac{\sqrt{I}}{1 + \sqrt{I}} + bI \tag{20}$$

6 Surface complexation models

This section describes the modifications necessary to compute adsorption of chemical species on charged surfaces. It is based on the report published by Westall (1979).

Consider the proton transfer reactions at an amphoteric surface

$$
\begin{aligned}
\text{SOH} + \text{H}^+ &\rightleftharpoons \text{SOH}_2^+ \\
\text{SOH} - \text{H}^+ &\rightleftharpoons \text{SO}^-
\end{aligned}
$$
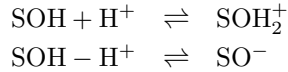
where SOH represents a surface hydroxyl group. Since the surface may be at a potential Ψ with respect to the bulk of the solution, the coulombic energy of charged surface groups, $zF\Psi$, must be accounted for in the mass action equations for the two reactions:

$$
\begin{aligned}
[\text{SOH}][\text{H}^+] e^{-F\Psi/RT} K_+ &= [\text{SOH}_2^+] \\
[\text{SOH}][\text{H}^+]^{-1} (e^{-F\Psi/RT})^{-1} K_- &= [\text{SO}^-]
\end{aligned}
$$

It is apparent that that the electrostatic potential term, $\exp(-F\Psi/RT)$, in these equations appears in the same form as the chemical concentration. This suggests that it is be appropriate to include the electrostatic potential in the set of components.

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[1]symbol-clash: not the same as the dielectric constant of water

The charge on the surface can be defined as the excess of positive groups over negative groups

$$T_\sigma = [\text{SOH}_2^+] - [\text{SO}^-] \qquad [\text{mol L}^{-1}] \tag{21}$$

or, in electrostatic quantities

$$\sigma = T_\sigma \frac{F}{sq} \qquad [\text{C m}^{-2}] \tag{22}$$

In addition, the charge may be defined from an electrostatic relationship (e.g. a Helmholtz constant capacitance):

$$\sigma = C\Psi \qquad [\text{C m}^{-2}] \tag{23}$$

The "total concentration" or charge of the surface is, in the case of the constant capacitance model, given by the independent electrostatic charge-potential relationship of Equation 22. In molar quantities, this is

$$T_\sigma = \sigma \frac{sq}{F} = C\Psi \frac{sq}{F} \qquad [\text{mol L}^{-1}] \tag{24}$$

The subscript "σ" or "Ψ" is used to denote the electrostatic components (e.g. T_σ, X_Ψ). Since T_σ is not experimentally determined, but a function of the potential, the derivative of T_σ with respect to X_Ψ is not zero and must be attached to the expression given by Equation 11 for a Jacobian element:

$$z_{\Psi\Psi} = \frac{\partial Y_\sigma}{\partial X_\Psi} = \sum_{i=1}^{N} \frac{a_{i\Psi} a_{i\Psi} C_i}{X_\Psi} - \frac{\partial T_\sigma}{\partial X_\Psi} \tag{25}$$

$$\frac{\partial T_\sigma}{\partial X_\Psi} = -C\frac{sq}{F}\frac{RT}{FX_\Psi} \tag{26}$$

Equation 26 has been derived using

$$\frac{\partial T_\sigma}{\partial X_\Psi} = \frac{\partial T_\sigma}{\partial \Psi}\frac{d\Psi}{dX_\Psi} \tag{27}$$

The convergence criteria have to be changed for some of the electrostatic models. In the following sections, all electrostatic models implemented in μQL are summarised. The symbol $\sum_{\Psi\Psi}$ (with indices where necessary) denotes the sum in the Jacobian element $z_{\Psi\Psi}$ (Equation 11). If only one electrostatic component is used, no indices (for C, Ψ, and σ) are used.

6.1   Constant capacitance model (model 2)

Total concentrations:

$$T_{\text{SOH}} = \frac{N_S sq}{N_A} \tag{28}$$

$$T_\sigma = C\Psi\frac{sq}{F} \tag{29}$$

Jacobian:

$$z_{\Psi\Psi} = \sum_{\Psi\Psi} + C\frac{RT}{FX_\Psi}\frac{sq}{F} \tag{30}$$

Convergence test:

no change necessary

6.2 Diffuse layer model (model 3)

Total concentrations:

$$T_{\text{SOH}} = \frac{N_S sq}{N_A} \tag{31}$$

$$T_\sigma = \sqrt{8\epsilon\epsilon_0 RTI}\,\sinh\left(\frac{F\Psi}{2RT}\right)\frac{sq}{F} \tag{32}$$

Jacobian:

$$z_{\Psi\Psi} = \sum_{\Psi\Psi} +\sqrt{8\epsilon\epsilon_0 RTI}\,\cosh\left(\frac{F\Psi}{2RT}\right)\frac{sq}{FX_\Psi} \tag{33}$$

Convergence test:

no change necessary

6.3 Basic Stern layer model (model 4)

Total concentrations:

$$T_{\text{SOH}} = \frac{N_S sq}{N_A} \tag{34}$$

$$T_{\sigma_0} = C(\Psi_0 - \Psi_1)\frac{sq}{F} \tag{35}$$

$$T_{\sigma_1} = C(\Psi_1 - \Psi_0)\frac{sq}{F} + \sqrt{8\epsilon\epsilon_0 RTI}\,\sinh\left(\frac{F\Psi}{2RT}\right)\frac{sq}{F} \tag{36}$$

Jacobian:

$$z_{\Psi_0\Psi_0} = \sum_{\Psi_0\Psi_0} +C\frac{RT}{FX_{\Psi_0}}\frac{sq}{F} \tag{37}$$

$$z_{\Psi_0\Psi_1} = \sum_{\Psi_0\Psi_1} -C\frac{RT}{FX_{\Psi_1}}\frac{sq}{F} \tag{38}$$

$$z_{\Psi_1\Psi_0} = \sum_{\Psi_1\Psi_0} -C\frac{RT}{FX_{\Psi_0}}\frac{sq}{F} \tag{39}$$

$$z_{\Psi_1\Psi_1} = \sum_{\Psi_1\Psi_1} +\left[C + \frac{F}{2RT}\sqrt{8\epsilon\epsilon_0 RTI}\,\cosh\left(\frac{F\Psi_1}{2RT}\right)\right]\frac{RT}{FX_{\Psi_1}}\frac{sq}{F} \tag{40}$$

Convergence test:[2]

$$\sigma_1 : \frac{|Y_{\sigma_1}|}{\sum_{i=1}^{N}|a_{ij}C_i| + |T_{\sigma_0}| + \left|\sigma_d\frac{sq}{F}\right|} < \epsilon \tag{41}$$

where σ_d is the diffuse layer charge given by

$$\sigma_d = \sqrt{8\epsilon\epsilon_0 RTI}\,\sinh\left(\frac{F\Psi_d}{2RT}\right) \tag{42}$$

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[2]This formula is taken from Westall (1979). However, in the source code (MIC7.BAS, 2/7/87) the denominator is set to ABS(-T[L0])+ABS(D3*D4). In μQL, the same denominator is used.

6.4 Triple layer model (model 5)

Total concentrations:

$$T_{\text{SOH}} = \frac{N_S sq}{N_A} \tag{43}$$

$$T_{\sigma_0} = C_1(\Psi_0 - \Psi_1)\frac{sq}{F} \tag{44}$$

$$T_{\sigma_1} = [C_1(\Psi_1 - \Psi_0) + C_2(\Psi_1 - \Psi_2)]\frac{sq}{F} \tag{45}$$

$$T_{\sigma_2} = C_2(\Psi_2 - \Psi_1)\frac{sq}{F} \tag{46}$$

Jacobian:

$$z_{\Psi_0\Psi_0} = \sum_{\Psi_0\Psi_0} +C_1\frac{RT}{FX_{\Psi_0}}\frac{sq}{F} \tag{47}$$

$$z_{\Psi_0\Psi_1} = \sum_{\Psi_0\Psi_1} -C_1\frac{RT}{FX_{\Psi_1}}\frac{sq}{F} \tag{48}$$

$$z_{\Psi_1\Psi_0} = \sum_{\Psi_1\Psi_0} -C_1\frac{RT}{FX_{\Psi_0}}\frac{sq}{F} \tag{49}$$

$$z_{\Psi_1\Psi_1} = \sum_{\Psi_1\Psi_1} +(C_1 + C_2)\frac{RT}{FX_{\Psi_1}}\frac{sq}{F} \tag{50}$$

$$z_{\Psi_1\Psi_2} = -C_2\frac{RT}{FX_{\Psi_2}}\frac{sq}{F} \tag{51}$$

$$z_{\Psi_2\Psi_1} = -C_2\frac{RT}{FX_{\Psi_1}}\frac{sq}{F} \tag{52}$$

$$z_{\Psi_2\Psi_2} = \left[C_2 + \frac{F}{2RT}\sqrt{8\epsilon\epsilon_0 RTI}\cosh\left(\frac{F\Psi_2}{2RT}\right)\right]\frac{RT}{FX_{\Psi_2}}\frac{sq}{F} \tag{53}$$

$$z_{\Psi_2\Psi_0} = 0 \tag{54}$$

$$z_{\Psi_0\Psi_2} = 0 \tag{55}$$

$$\tag{56}$$

Convergence test:[3]

$$\sigma_2 : \frac{\left|\sigma_d\frac{sq}{F}\right| - |T_{\sigma_2}|}{|T_{\sigma_2}|} < \epsilon \tag{57}$$

where σ_d is given by Equation 42.

7 Normalised sensitivity coefficients

7.1 General

The normalised sensitivity coefficients[4] are defined in Furrer et al. (1989) as

$$P_{i\alpha} = \frac{d\ln C_i}{d\ln K_\alpha} \qquad i, \alpha = 1\dots N \tag{58}$$

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[3]This formula is taken from Westall (1979). However, in the source code (MIC8.BAS, 2/7/87) the denominator is set to ABS(T[L2])+ABS(D3*D4). In μQL, the same denominator is used.

[4]In μQL, the calculation of normalised sensitivity coefficients is implemented for models 0, 1, and 2.

They can be interpreted for practical purposes in the following way: a one percent change in the equilibrium constant α will cause a $P_{i\alpha}$ percent change in in the concentration of species i. This interpretation is based on a finite-difference approximation to the derivatives in Equation 58:

$$P_{i\alpha} = \frac{d\ln C_i}{d\ln K_\alpha} = \frac{dC_i}{dK_\alpha}\frac{K_\alpha}{C_i} \approx \frac{\Delta C_i}{\Delta K_\alpha}\frac{K_\alpha}{C_i} \tag{59}$$

Using the chain rule, dC_i/dK_α can be expressed as

$$\frac{dC_i}{dK_\alpha} = \sum_{j=1}^{U}\frac{\partial C_i}{\partial X_j}\frac{\partial X_j}{\partial K_\alpha} + \frac{\partial C_i}{\partial K_\alpha} \tag{60}$$

Note that the summation runs from $j = 1$ to $j = U$ since $X_{j>U}$ is fixed (i.e. constant).

From Equation 5 we obtain

$$\frac{\partial C_i}{\partial K_\alpha} = \frac{C_i}{K_\alpha} \qquad i = \alpha \tag{61}$$

and

$$\frac{\partial C_i}{\partial K_\alpha} = 0 \qquad i \neq \alpha \tag{62}$$

$\partial C_i/\partial X_j$ has already been derived (Equation 10).

$\partial X_j/\partial K_\alpha$ can be found by applying the chain rule to dY_j/dK_α:

$$\frac{dY_j}{dK_\alpha} = \sum_{k=1}^{U}\frac{\partial Y_j}{\partial X_k}\frac{\partial X_k}{\partial K_\alpha} + \frac{\partial Y_j}{\partial K_\alpha} \tag{63}$$

Now,

$$\frac{dY_j}{dK_\alpha} = 0 \tag{64}$$

because $Y = 0$ when the μQL-problem is solved. Therefore,

$$\sum_{k=1}^{U}\frac{\partial Y_j}{\partial X_k}\frac{\partial X_k}{\partial K_\alpha} + \frac{\partial Y_j}{\partial K_\alpha} = 0 \tag{65}$$

$\partial Y_j/\partial X_k$ corresponds to the elements of the Jacobi matrix, z_{jk}, derived above. $\partial Y_j/\partial K_\alpha$ can be calculated using Equations 3 and 5 to yield

$$\frac{\partial Y_j}{\partial K_\alpha} = a_{\alpha j}\frac{C_\alpha}{K_\alpha} \tag{66}$$

This means that for every equilibrium constant α, there is a set of U equations with the unknowns $\partial X_k/\partial K_\alpha$ to be solved. In matrix notation, this is

$$ZX' = C' \tag{67}$$

where

$$X_k' = \frac{\partial X_k}{\partial K_\alpha} \tag{68}$$

and

$$C_j' = -\frac{\partial Y_j}{\partial K_\alpha} \tag{69}$$

7.2 Constant capacitance model

In the constant capacitance model, all of the above remains valid. We can extend the computation of the normalised sensitivity coefficients by including the sensitivity of the species with respect to the total concentration of the surface component SOH

$$P_{i\text{SOH}} = \frac{d \ln C_i}{d \ln T_{\text{SOH}}} \tag{70}$$

and with respect to the capacitance

$$P_{iC} = \frac{d \ln C_i}{d \ln C} \tag{71}$$

The procedure to obtain the derivatives necessary is analogous to the computations for the equilibrium constants, in Equations 60 and 65 the variable K_α has to be replaced by T_{SOH} and C, respectively. $\partial C_i / \partial T_{\text{SOH}}$ and $\partial C_i / \partial C$ are always zero.

For the sensitivity coefficients with respect to T_{SOH}, the elements of the vector C' (Equation 67) are calculated as follows

$$\frac{\partial Y_j}{\partial T_{\text{SOH}}} = 1 \qquad j = \text{SOH} \tag{72}$$

and

$$\frac{\partial Y_j}{\partial T_{\text{SOH}}} = C\Psi \frac{N_A}{FN_S} \qquad j = \alpha \tag{73}$$

using Equations 28 and 29, and

$$\frac{\partial Y_j}{\partial T_{\text{SOH}}} = 0 \qquad j \neq \text{SOH}, j \neq \sigma \tag{74}$$

For the sensitivity coefficients with respect to C, the elements of the vector C' (Equation 67) are calculated according to

$$\frac{\partial Y_j}{\partial C} = \frac{T_\sigma}{C} \qquad j = \sigma \tag{75}$$

using Equation 29, and

$$\frac{\partial Y_j}{\partial C} = 0 \qquad j \neq \sigma \tag{76}$$

8 Saturation ratio

The vector Ξ obtained by multiplying the matrix S by the (final) vector $X^\star$ ($\Xi = SX^\star$) can be used to calculate the saturation ratio Ω with respect to the different solid phases. The saturation ratio Ω_s for the solid s is defined by

$$\Omega_s = \frac{\text{IAP}_s}{10^{Lp_s}} = \frac{10^{\Xi_s}}{10^{Lp_s}} \tag{77}$$

where IAP_s is the ion activity product (i.e. the product of the actual activities in the solution) and Lp_s the solubility product (base 10 logarithm). If the solution is oversaturated, $\Omega \geq 1$. Note that the values of Ω are not identical for a solid represented by A_aB_b and $A_{2a}B_{2b}$, i.e. the saturation ratio is not "normalised" (Stumm 1992).

9 Percentage distribution

The amount of component j in species i (in % of the component's total concentration) can be calculated by

$$\frac{a_{ij}C_i}{T_j}100 \qquad j \leq U \tag{78}$$

and

$$\frac{a_{ij}C_i}{Y_j}100 \qquad j > U \tag{79}$$

These %-values can be used to determine whether a species is relevant in the system considered. A species can be considered relevant if it contains more than e.g. 1 % of at least one component (since the %-values can also be negative, the absolute value should be taken).

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