μQL "Portable MICROQL" Manual

Version 1.9

Report BS.96.1

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Contents

1 Introduction

This manual explains the use of μQL, an extended version of MICROQL (see Westall (1979) and Westall (1986)). It is assumed that the user knows the MICROQL formalism. The mathematics of μQL is explained in detail in Gfeller (1995).

2 Installation and Usage

2.1 Getting and installing μQL

The preferred way of obtaining μQL is via the ftp site of the Institute of Terrestrial Ecology at ftp://ftp.ito.umnw.ethz.ch/outdata/SoilProtection/microql/, where binaries, source, and documentation are accessible. It is recommended that, in addition to the executable file for the target platform, the manual and the examples are downloaded. The core source code is also available, but some more source files are necessary in order to compile the programm. You can obtain them by sending an e-mail to the author. After downloading the archives, extract them and move the resulting files and directories somewhere convenient. The binaries do not require to be in a specific directory.

2.2 Usage

μQL requires an input file and generates an output file. The input file can e.g. be generated with EXCEL or WORD. The input file must be in ASCII format (i.e. saved as TEXT).

Using μQL on an Apple Macintosh:

μQL is started by double clicking it's icon. Its name is microql. For every calculation, μQL needs to be started again. Then a dialog window is opened with which standard input and standard output can be redirected from and to files by clicking the "File" radio buttons.

Using μQL on command-line operating systems:

On the command line, type

```
microql < INPUT_FILE > OUTPUT_FILE
```

where `INPUT_FILE` and `OUTPUT_FILE` are the names of the input and output data files, respectively.

In the Microsoft Windows operating systems, a command line window (MS-DOS Prompt) is open by selecting *Start:Programs:Command Prompt* (*Start:Programme:MS-DOS-Eingabeaufforderung* for German versions of the operating system).

3 Input file format

3.1 General

The input file is organised in different blocks which start with at least one comment line. Some blocks are required for all types of calculations, others are included only for specific types of calculations. It is important that the input file format appears exactly as explained in this manual. However, it is irrelevant how many spaces or tabs appear between different entries on the same line. The input file format consists of several blocks, their sequence is determined by the block number. No empty lines are allowed between different blocks. Abbreviations of variables used are explained in Section 3.3. The **sequence of the components** is important: components **!** for which the free concentration is known must appear at the end of the component list. The number of species and components used in a specific calculation is only restricted by memory.

3.2 Units

Units for concentrations are mol L^{-1} except for solids, where it is g L^{-1}. Surface site density is given in mol g^{-1}g, specific surface area in m^2 g^{-1}g, and capacitance in F m^{-2}.

3.3 Variables

A Matrix A contains the stochiometric coefficients of the components in the species (components in columns, species in rows).

AFac, BFac For model 1, the vectors AFac and BFac are used to calculate ionic strength dependent equililibrium constants according to Baes & Mesmer (1976). They contain the a- and b-factors defined in Baes & Mesmer (1976).

Cap Capacitance for models 2 and 4

CompNames The names of the components (see also SpecNames)

convVal The convergence criterion. The iteration is stopped if the value W (defined in Westall (1979) and Westall (1986)) for all components is below convVal. Usually, a value of 1.E-6 is sufficient. If debugFlag=1, W is printed to standard output for all components.

debugFlag If debugFlag=1, the value of W is printed to standard output for every iteration step for all components. For single calculations only.

EXP1CompName The name of the component which designates the first potiental term in models 2, 3, 4, and 5 (in models 2 and 3, this is the only potential term required).

EXP2CompName The name of the component which designates the second potiental term in models 4 and 5 (in model 4, two potential terms are required).

EXP3CompName The name of the component which designates the third potiental term in model 5.

I Ionic strength. Required for models 1, 3, 4, and 5.

InnerCap Inner capacitance for model 5.

LMatFlag If LMatFlag=1, then the matrix L must be defined (block 7) which transforms the "old" set of components to the "new" set of components.

logK The vector logK contains the equilibrium constants for the reactions defined in matrix A describing the formation of the species from the components.

logX The vector logX contains the initial guess values of the free concentration of the components (e.g. -6). For components with fixed activity, the value corresponds to the fixed activity (e.g. if the pH is fixed at 10, then logX(H+)=-10).

Lp The vektor Lp contains the log10(solubility products) of the solid phases specified if satFlag=1.

manualXTFlag If LMatFlag=1, the transformation of the vectors logX and T is either performed by the program (manualXTFlag=0) or specified by the user in the input file (manualXTFlag=1).

maxIter The maximum number of iterations used to reach convergence. A value of 30 is usually sufficient.

model Model, which is one of

0 Solution Speciation

1 Davies-Equation (for 1:1 electrolyte)

2 Constant Capacitance Model by Schindler and Stumm

3 Diffuse Layer Model by Gouy and Chapman

4 Basic Stern Layer Model

5 Triple Layer Model

nComp Number of components

nFix Number of components with fixed activity

nSolid Number of solid phases (if satFlag=1)

nSpec Number of species

nTitrPoints Number of steps between xMin and xMax (incl.) for a titration.

OuterCap Outer capacitance for model 5

precipFlag The value of precipFlag should always be set to 0. In a later version, precipitation of solid phases will be taken into account if precipFlag=1.

Q stability constant calculated from K using the Davies-Equation

S The matrix S has nSolid rows and nComp columns and specifies the composition of the solids in terms of the components.

satFlag If satFlag=1, the saturation ratio (Stumm 1992) is calculated with respect to the solid phases specified in block 10.

SOHCompName The name of the surface component for models 2 to 5.

SolidConc Concentration of solid for models 2 to 5.

SolidNames The names of the solid phases for satFlag=1 (see also SpecNames)

SpecNames The names of the species. The length of the name is not restricted, but output is nicest if it is smaller than 12 characters. The names must not contain spaces/tabs.

SurfArea Specific surface area

SurfDens Surface site density

T The vector T contains the total concentration of the components.

Title The title of the MICROQL problem.

titrCompName The name of the component used in a titration. This name must correspond to the name of a component specified earlier.

titrFlag If a titration shall be calculated, titrFlag=1, otherwise titrFlag=0. A titration is a series of MICROQL calculations in which the free activity or total concentration of one component is varied in nTitrPoints steps between a minimal (xMin) and a maximal (xMax) value.

totalTitrFlag If, in a titration, the total concentration of a component is varied, then totalTitrFlag=1, else totalTitrFlag=0.

verifFlag If verifFlag=1 then the input data is printed to standard output for verification.

xMin, xMax Minimal and maximal values of the free activity or total concentration of the component varied in a titration. If the free activity is varied (totalTitrFlag=0), then xMin=log(Xmin) and xMax=log(Xmax). If the total concentration is varied, then xMin = Tmin and xMax = Tmax. In both cases, xMin < xMax.

Y residual of material balance

3.4 Block format

This section explains the format of the different blocks. Lines beginning with * contain comments. The values in the blocks are sample values and not consistent within the different blocks.

Block 1 (title):

```
*(1)  Title
      Speciation of acetic acid at  pH 4.76
```

Block 2 (dimensions):

```
*(2)  nComp   nSpec   nFix
      2       4       1
```

Block 3 (control 1):

```
*(3)  model titrFlag totalTitrFlag satFlag precipFlag LMatFlag manualXTFlag
      0     1        0             0       0          0        0
```

Block 4 (control2):

```
*(4)  debugFlag verifFlag maxIter convVal
      0         1         30      1.e-6
```

Block 5 (species, logK, matrix A):

```
*(5)  SpecNames   logK    Matrix A
*                         Ac-   H+
      H+           0.0    0     1
      OH-        -14.0    0    -1
      HAc          4.76   1     1
      Ac-          0.0    1     0
```

Block 6 (components, logX, T):

```
*(6)  CompNames   logX    T
      Ac-         -6      1.E-4
      H+          -4.76   0.0
```

Block 7 (new components, matrix L, if manualXTFlag=1: new vectors logX andT):

```
*(7)  new CompNames   Matrix L  new logX  new T
*                     Ac-   H+
      HAc             1     1   -6        1.E-4
      H+              0     1   -4.76     0.0
```

Block 8 (titration):

```
*(8)  titrCompName  xMin  xMax  nTitrPoints
      H+            -12   -2    21
```

Block 9 (models):

Block 9 contains model specific data, i.e. for each model, block 9 has another format. Model 0 doesn't require a block 9.

Model 1 (Davies-Equation):

```
*(9)  I (ionic strength)
      0.1
* AFac    BFac
  1.0     0.1
  2.1     1.5
  3.0     1.0
  0.5     2.0
```

Model 2 (Constant Capacitance):

```
*(9)  SOHCompName EXP1CompName
      SOH         EXP
*     SurfDens  SurfArea  SolidConc Cap
      2.E-3     50        10        1.6
```

Model 3 (Diffuse Layer):

```
*(9)  SOHCompName EXP1CompName
      SOH         EXP
*     SurfDens  SurfArea  SolidConc I
      2.E-3     50        10        0.1
```

Model 4 (Basic Stern Layer):

```
*(9)  SOHCompName EXP1CompName    EXP2CompName
      SOH         EXP1            EXP2
*     SurfDens  SurfArea  SolidConc I     Cap
      2.E-3     50        10        0.1   1.5
```

Model 5 (Triple Layer):

```
*(9)  SOHCompName EXP1CompName  EXP2CompName  EXP3CompName
      SOH         EXP1          EXP2          EXP3
*     SurfDens    SurfArea    SolidConc   I     InnerCap  OuterCap
      2.E-3       50          10          0.1   1.5       0.4
```

Block 10 (solid phases):

```
*(10) nSolid
    1
*     SolidNames  Lp    Matrix S
*                       Al3+    H+
      Gibbsite    -39   1       -3
```

4 Examples

The example input files are part of the program distribution.

4.1 Speciation of acetic acid at pH 4.76 (HAC.DAT)

Input file:

```
*(1)  Title
      Speciation of acetic acid at  pH 4.76
*(2)  nComp nSpec nFix
      2     4     1
*(3)  model titrFlag  totalTitrFlag satFlag precipFlag  LMatFlag  manualXTFlag
      0     0         0             0       0           0         0
*(4)  debugFlag verifFlag maxIter convVal
      0         1         30      1.00E-06
*(5)  Species Names   logK    Matrix A
*                             Ac-   H+
      H+              0       0     1
      OH-           -14       0    -1
      HAc             4.76    1     1
      Ac-             0       1     0
*(6)  CompNames logX    T
      Ac-       -6      1.00E-04
      H+        -4.76   0
```

Output file:

```
Portable MICROQL 1.8

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Title: Speciation of acetic acid at pH 4.76

Input data for verification:
============================

Number of components:                         2
Number of components with fixed activity:     1 ( H+ )
Number of species:                            4
Model:                                        0 (Solution speciation)
A matrix and logK:
                      logK          Ac-           H+
H+                   0.000        0.000        1.000
OH-                -14.000        0.000       -1.000
HAc                  4.760        1.000        1.000
Ac-                  0.000        1.000        0.000

logX and T vector:
                      logX            T
Ac-            -6.0000e+00   1.0000e-04
H+             -4.7600e+00   0.0000e+00



--------------------------------
```

```
Results of equilibrium system:
******************************

Species:
                    C(i)      logC(i)      logK(i)
H+            1.7378e-05  -4.7600e+00        0.000
OH-           5.7544e-10  -9.2400e+00      -14.000
HAc           5.0000e-05  -4.3010e+00        4.760
Ac-           5.0000e-05  -4.3010e+00        0.000

Components:
                 logX(j)         X(j)         T(j)            Y
Ac-          -4.3010e+00   5.0000e-05   1.0000e-04   2.9138e-19
H+           -4.7600e+00   1.7378e-05   0.0000e+00   6.7377e-05


-----------------------------------

Normalised sensitivity coefficients:

Rows:     species' concentrations
Columns:  equilibrium constants (K)

                      H+          OH-          HAc          Ac-
H+                 1.000        0.000        0.000        0.000
OH-                0.000        1.000        0.000        0.000
HAc                0.000        0.000        0.500       -0.500
Ac-                0.000        0.000       -0.500        0.500


-----------------------------------

Percentage p of component j contained in species i with respect
to the total concentration of component j. If the components
activity is fixed, Y(j) is taken as its total concentration.
If a component with unknow free activity has T[j]==0.0 then a 'total'
concentration is calculated as the sum of A(i,j)*C(i) (0 < i < # species),
seperately for A(i,j) > 0 and A(i,j) < 0.

Percentage level (pl): species i contains at least one component
with p in the % range given (ABSOLUTE).
  *    0.01 <= p <    0.1 %
  **   0.1  <= p <    1   %
  ***  1    <= p <= 100   %

                     Ac-           H+           pl
H+                 0.000       25.792          ***
OH-                0.000       -0.001
HAc               50.000       74.209          ***
Ac-               50.000        0.000          ***
```

4.2 Titration of acetic acid (HACT.DAT)

```
*(1)  Title
      Speciation of acetic acid as a function of pH
*(2)  nComp nSpec nFix
```

```
     2     4     1
*(3)  model titrFlag  totalTitrFlag satFlag precipFlag  LMatFlag  manualXTFlag
     0     1         0             0       0           0         0
*(4)  debugFlag verifFlag maxIter convVal
     0         1         30      1.00E-06
*(5)  Species Names   logK    Matrix A
*                             Ac-   H+
     H+              0       0     1
     OH-           -14       0    -1
     HAc             4.76    1     1
     Ac-             0       1     0
*(6)  CompNames logX    T
     Ac-       -6      1.00E-04
     H+        -4.76   0
*(8)  titrCompName  xMin  xMax  nTitrPoints
     H+            -9    -2    40
```

4.3 Constant Capacitance Model (MIC5.DAT)

```
*(1)  Title
     MIC5 BY J.C.WESTALL: CONSTANT CAPACITANCE MODEL
*(2)  nComp nSpec nFix
     3     5     1
*(3)  model titrFlag  totalTitrFlag satFlag precipFlag  LMatFlag  manualXTFlag
     2     0         0             0       0           0         0
*(4)  debugFlag verifFlag maxIter convVal
     0         1         30      1.00E-06
*(5)  Species Names   logK    Matrix A
                              SOH   EXP   H+
     H+              0       0     0     1
     OH-           -13.8     0     0    -1
     SOH2+           7.4     1     1     1
     SOH             0       1     0     0
     SO-           -9.24     1    -1    -1
*(6)  compNames     logX    T
     SOH           -6      0
     EXP            0      0
     H+            -7      0
*(9)  SOHCompName EXP1CompName
     SOH         EXP
*     SiteDens    SurfArea    SolidConc   Cap
     1.37E-04    129         8.174       1.06
```

4.4 Diffuse Layer Model (MIC6.DAT)

```
*(1)  Title
     MIC6 BY J.C.WESTALL: DIFFUSE LAYER MODEL
*(2)  nComp nSpec nFix
     3     5     1
*(3)  model titrFlag  totalTitrFlag satFlag precipFlag  LMatFlag  manualXTFlag
     3     0         0             0       0           0         0
*(4)  debugFlag verifFlag maxIter convVal
     0         1         30      1.00E-06
*(5)  Species Names   logK    Matrix A
                              SOH   EXP   H+
     H+              0       0     0     1
```

```
      OH-           -13.8     0     0    -1
      SOH2+           7.66    1     1     1
      SOH             0       1     0     0
      SO-            -8.98    1    -1    -1
*(6)  compNames     logX    T
      SOH           -3      0
      EXP            0      0
      H+            -7      0
*(9)  SOHCompName EXP1CompName
      SOH         EXP
*(10) SiteDens    SurfArea  SolidConc   I
      1.28E-04    129       8.174       0.1
```

4.5 Basic Stern Layer Model (MIC7.DAT)

```
*(1)  Title
      MIC7 BY J.C.WESTALL: BASIC STERN LAYER MODEL
*(2)  nComp   nSpec   nFix
      4       5       1
*(3)  model titrFlag  totalTitrFlag satFlag precipFlag  LMatFlag  manualXTFlag
      4     0         0             0       0           0         0
*(4)  debugFlag verifFlag maxIter convVal
      0         1         30      1.00E-06
*(5)  Species Names   logK    Matrix A
                              SOH   EXP1    EXP2    H+
      H+              0       0     0       0       1
      OH-           -13.8     0     0       0      -1
      SOH2+           8.16    1     1       0       1
      SOH             0       1     0       0       0
      SO-            -8.46    1    -1       0      -1
*(6)  compNames logX    T
      SOH       -3      0
      EXP1      -1      0
      EXP2      -0.5    0
      H+        -7      0
*(9)  SOHCompName EXP1CompName  EXP2CompName
      SOH         EXP1          EXP2
*     SiteDens  SurfArea  SolidConc   I     Cap
      1.33E-04  129       8.174       0.1   2.4
```

4.6 Triple Layer Model (MIC8.DAT)

```
*(1)  Title
      MIC8 BY J.C.WESTALL: TRIPLE LAYER MODEL
*(2)  nComp   nSpec   nFix
      5       7       1
*(3)  model titrFlag  totalTitrFlag satFlag precipFlag  LMatFlag  manualXTFlag
      5     0         0             0       0           0         0
*(4)  debugFlag verifFlag maxIter convVal
      0         1         30      1.00E-06
*(5)  Species Names   logK    Matrix A
                              SOH   EXP1  EXP2  EXP3  H+
      H+              0       0     0     0     0     1
      OH-           -13.8     0     0     0     0    -1
      SOH2+           7.33    1     1     0     0     1
      SOH             0       1     0     0     0     0
```

```
      SO-            -9.31    1    -1     0     0    -1
      SOH+2CLO4-      7.33    1     1    -1     0     1
      SO-Na+         -9.31    1    -1     1     0    -1
*(6)  compNames   logX    T
      SOH         -3      0
      EXP1        -1      0
      EXP2        -0.5    0
      EXP3         0      0
      H+          -7      0
*(9)  SOHCompName EXP1CompName  EXP2CompName  EXP2CompName
      SOH         EXP1          EXP2          EXP3
*     SurfDens  SurfArea  SolidConc   I     InnerCap  OuterCap
      1.32E-04  129       8.174       0.1   1.2       0.2
```

4.7 Oversaturation of an Al-OH solution with respect to gibbsite (SAT.DAT)

```
*(1)  Title
      Speciation of Al-OH solution as a function of pH, oversaturation w respect to Gibbsite
*(2)  nComp nSpec nFix
      2     6     1
*(3)  model titrFlag  totalTitrFlag satFlag precipFlag  LMatFlag  manualXTFlag
      0     1         0             1       0           0         0
*(4)  debugFlag verifFlag maxIter convVal
      0         1         30      1.00E-06
*(5)  Species Names   logK    Matrix A
                              Al3+    H+
      H+               0      0        1
      OH-            -14      0       -1
      Al               0      1        0
      AlOH            -5      1       -1
      Al(OH)2         -9.3    1       -2
      Al(OH)3        -15      1       -3
*(6)  compNames logX  T
      Al3+      -6    1.00E-04
      H+        -2    0
*(8)  titrCompName  xMin  xMax  nTitrPoints
      H+            -10   -2    100
*(10) nSolid
      1
*     SolidNames  Lp    Matrix  S
*                       Al3+    H+
      Gibbsite    8.5   1       -3
```

5 History

Version	Changes in current version
1.3	Added calculation of normalised sensitivity coefficients (presently for model 0 and 2 only) and percentage distribution of components in species. No change to input file format.
1.6	Instead of determining whether a solution is over- or undersaturated, the saturation ratio (Gfeller 1995) is now calculated and printed.
1.8	The code now complies to the C++ (Draft) Standard. In particular, instead of using my own string class, the standard string class is now used. μQL was compiled for Macintosh with Metrowerks CodeWarrior Professional Release 2 (only for PowerPC so far), for SunOS4.1.4 with g++ 2.7.2.3, and WinNT/95 with djgpp 2.7.2.1.
1.9	Some minor corrections and enhancements, including a few fixes to allow μQL to be called from a cgi-script (see CMQL.h).

6 Suggestions, corrections, and bugs

Please feel free to send me suggestions on how I could improve both the manual and the program.

Unfortunately, no program is free of bugs. Should μQL behave unexpectedly and give unrealistic results, please send me a short report (incl. input file). However, please make sure that the input file format is correct before reporting a bug.

References

Baes, C. F. & Mesmer, R. F. (1976), Hydrolysis of Al^{3+}, *in* C. F. Baes & R. F. Mesmer, eds, 'Hydrolysis of Cations', Publishing Company Malabar, Florida, pp. 112–123.

Gfeller, M. (1995), Portable MICROQL: Summary of mathematics, Technical Report 96.2, Institute of Terrestrial Ecology, Swiss Federal Institute of Technology, Zürich.

Stumm, W. (1992), *Chemistry of the Solid-Water Interface*, Wiley-Interscience, New York.

Westall, J. C. (1979), MICROQL - II. Computation of Adsorption Equilibria in BASIC, Technical report, EAWAG, 8600 Dübendorf, Switzerland.

Westall, J. C. (1986), MICROQL - I. A Chemical Equilibrium Program in BASIC, Version 2 for PC's, Technical Report 86-02, Oregon State University, Corvallis, Oregon 97331.