

SOFTWARE RELEASE NOTICE

1. SRN Number: 326		
2. Project Title: Radionuclide Transport Key Technical Issue	Project No. 20.06002.01.141	
3. SRN Title: PhreeqcI Version 2.8		
4. Originator/Requestor: Miriam R. Juckett	Date: 09/03/2004	
5. Summary of Actions		
<input checked="" type="checkbox"/> Release of new software <input type="checkbox"/> Change of access software <input type="checkbox"/> Release of modified software: <input type="checkbox"/> Software Retirement <input type="checkbox"/> Enhancements made <input type="checkbox"/> Corrections made		
6. Validation Status		
<input type="checkbox"/> Validated <input type="checkbox"/> Limited Validation <input checked="" type="checkbox"/> Not Validated Explain: <u>Scheduled for validation in FY2004</u>		
7. Persons Authorized Access		
Name	Read Only/Read-Write	Addition/Change/Delete
David R. Turner	Read-Write	
F. Paul Bertetti	Read-Write	
Miriam R. Juckett	Read-Write	
Jude McMurry	Read-Write	
8. Element Manager Approval:		Date: 9/7/2004
9. Remarks:		

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

QA VERIFICATION REPORT

FOR

→ ACQUIRED SOFTWARE NOT TO BE MODIFIED ←

Software Title/Name: PHREEQCI
Version: 2.8
Demonstration workstation: PC
Operating System: WINDOWS 95, 98, NT 4.0, ME, 2000 or XP
User: M. JUCKETT

NOTE: Acquired software may or may not meet all requirements and will be evaluated on a case-by-case basis.

Installation Testing [TOP-018, Section 5.6]

Has installation testing been conducted for each intended computer platform and operating system?
Yes: No: N/A:

Computer Platforms: PC Operating Systems: WIN
Location of Acceptance Test Results: SEE SCR 538 (REGRESSION TESTING VS PHREEQCI 2.6)
Comments: 7/3/02

Software Output [TOP-018, Section 5.5.4]

Is software designed so that individual runs are uniquely identified by date, time, name of software and version?
Yes: No: N/A:

Date and Time Displayed: _____
Name/Version Displayed: _____
Comments:

NOTE: Output identification content and format is typically taken as is.

Medium Documentation [TOP-018, Section 5.5.6]

The physical labeling of software medium (tapes, disks, etc.) contains: Program Name, Module/Name/Title, Module Revision, File type (ASCII, OBJ, EXE), Recording Date, and Operating System(s)?
Yes: No: N/A:

Comments:

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User Documentation [TOP-018, Section 5.5.7]

Is there a Users' Manual for the software and is it up-to-date?

Miriam Fickett, D. Turner have copies.

Yes: No: N/A:

User's Manual Version and Date: *2.8, 4/15/2003*

Comments:

Available on USGS website www.brr.cr.usgs.gov/projects/GWR-completed/proc/eg/indup.html

Are there basic instructions for the *installation* and use of the software?

Yes: No: N/A:

Location of Instructions: *User Manual (see above)*

Comments:

Configuration Control [TOP-018, Section 5.7, 5.9.3]

Is the Software Summary Form (Form TOP-4-1) completed and signed?

Yes: No: N/A:

Date of Approval: *9/3/2004*

Is the list of files attached to the Software Summary Form complete and accurate?

Yes: No: N/A:

Comments:

Is the source code available or, is the executable code available in the case of (acquired/commercial codes)?

Yes: No: N/A:

Location of Source Code: *@Accounts - CD*

Comments:

Have all the script/make files and executable files been submitted to the Software Custodian?

Only the executable files are being submitted.

Yes: No: N/A:

Location of executable files: *@Accounts - CD*

Comments:

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

QA VERIFICATION REPORT

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Software Release [TOP-018, Section 5.9]

Upon acceptance of the software as verified above, has a Software Release Notice (SRN), Form TOP-6 been issued and does the version number of the software match the documentation?

Yes: No: N/A:

SRN Number: 326

Comments:

Software Validation [TOP-018, Section 5.10]

Has a Software Validation Test Plan (SVTP) been prepared for the *range of application* of the software?

Yes: No: N/A:

Version and Date of SVTP: See SCR 538

Date Reviewed and Approved via QAP-002: _____

Comments: SCR 538 - REGRESSION TESTING V2. VALIDATED
PREVIOUS RELEASE 2.4

Has a Software Validation Test Report (SVTR) been prepared that documents the results of the validation cases, interpretation of the results, and determination if the software has been validated?

Yes: No: N/A:

Version and Date of SVTR: _____ See SCR 538

Date Reviewed and Approved via QAP-002: _____

Comments.:

Additional Comments:

Miriam Jewett 9/7/04
Software Evaluator/User/Date

Software Custodian/Date

SOFTWARE CHANGE REPORT (SCR)

1. SCR No. (Software Developer Assigns): SCR-538	2. Software Title and Version: Phreeqcl 2.8	3. Project No: 20.06002.01.141
4. Affected Software Module(s), Description of Problem(s): New software version: update from PHREEQC 2.6 to Phreeqcl 2.8		
5. Change Requested by: Miriam R. Juckett Date: September 2, 2004	6. Change Authorized by (Software Developer): Miriam R. Juckett Date: September 2, 2004	
7. Description of Change(s) or Problem Resolution (If changes not implemented, please justify): Bugs from previous versions fixed, and a few new keywords have been added. See attached list for a full description of changes.		
8. Implemented by:	Date:	
9. Description of Acceptance Tests: Regression testing was completed by running Installation tests and validation tests from the last validation (for PHREEQC v. 2.6) using Phreeqcl 2.8. The result files were compared for discrepancies. Files with no unexplainable discrepancies are considered successful tests. The comparison files for old and new results are contained in the attached CD. Acceptable discrepancies in the files consisted of the following types: 1) Small changes in value as a result of rounding differences, e.g. 2.345 changed to 2.347. Most files contained differences of this type, possibly as a result of use of a different operating system (Windows XP vs. Windows NT) or calculation methods. These differences are insignificant. (Example: ex2 Comparison) 2) Changes in format such as spaces, tabs, minor text differences, etc. are considered insignificant differences. (Example: Example 1 Comparison) 3) Changes in values such as iteration numbers, electrical balances, etc. which do not impact the final data are considered insignificant. (Example: Barite2 comparison) 4) Some changes were made to the database used for this validation after the version 2.6 validation was completed. This caused some anomalies that are insignificant in the final data, as they do not affect major values important in the analyses. (Example: u_phrq2 comparison) 5) Example 14 has significant changes, but are due to a change in the database used, as noted in the output files.		
10. Tested by: 	Date: 9/7/04	

Features not documented in WRIR 99-4259.

 Version 2.8:

No new features.

 Version 2.7:

Changed format of selected output file:

Removed quotations surrounding strings in headings.
 Removed quotations surrounding strings in state variable.
 All fields are 12 or 20 places depending on
 -high_precision.
 Headings are not truncated even if longer than
 specified precision.
 For isotopes, missing value is -9999.9
 Selected output is updated each simulation.
 If a species or phase is defined
 subsequent to the simulation where SELECTED_OUTPUT
 was defined it will appear in the selected output
 file in the simulation in which it is defined and
 in subsequent simulations.

Added strings for each file, which can be extracted from the
 executable file with the "ident" command.

Fixed null pointer for isotope_ratios if Basic routine
 was undefined.

Fixed problem in C++ if structure name is same as member name.
 logk member of logk structure was renamed to log_k.

Added identifier -add_constant to PHASES, EXCHANGE_SPECIES,
 SOLUTION_SPECIES, and SURFACE_SPECIES.

-add_constant -0.301

log K is augmented by the specified constant.

Theory and implementation of isotopes in PHREEQC is documented in:

Thorstenson, D.C., and Parkhurst, D.L., 2002, Calculation of
 individual isotope equilibrium constants for implementation in
 geochemical models: U.S. Geological Survey Water-Resources
 Investigations Report 02-4172, 129 p.

Added KEYWORDS:

ISOTOPES

Element
 -isotope isotope_name units standard_ratio
 -total_is_major T/F (OPTION IS DISABLED!!)

CALCULATE_VALUES

Name
 -start
 Basic statements, must have SAVE

-end

ISOTOPE_RATIOS (for printing)
 Name=Calculate_values_name Isotope_name

ISOTOPE_ALPHAS (for printing)
 Name=Calculate_values_name Named_logk=named_expression_name

Basic functions:

calc_value("calc_value_name")	evaluates a definition of CALCULATE_
lk_named("name")	log10(K) of definition in NAMED_EXPR
lk_phase("name")	log10(K) of definition in PHASES
lk_species("name")	log10(K) of definition in (SOLUTION,
sum_gas("template","element")	Sum of element in gases with specifi
	template="{C,[13C],[14C]}{O,[18O]}2"
sum_species("template","element")	Sum of element in aqueous, exchange,
	specified template
sum_s_s("s_s_name","element")	Sum of element in a specified solid

PRINT keyword:

-initial_isotopes	T/F	
-isotope_ratios	T/F	
-isotope_alphas	T/F	
-censor_species	1e-8	# omit species from Distribution of Species if les
		# relative minimum of an element or element redox
		# total concentration

SELECTED_OUTPUT keyword:

-calculate_values	name1 name2 ...
-isotopes	minor_isotope1 minor_isotope2

Added functions LK_SPECIES, LK_NAMED, LK_PHASE for Basic interpreter. LK_SPECIES("CaHCO3+") returns the log k for the association reaction for the ion pair CaHCO3+ at the current temperature. The log K is for the reaction as defined in the database or input file. Similarly, LK_NAMED("Log_alpha_18O_CO2(aq)/CO2(g)") returns the value for the log K at the current temperature using expressions defined in NAMED_LOG_K data block; LK_PHASE("Calcite") returns the value of log K for calcite at the current temperature for the dissociation reaction defined in the database or input file. Values are "log10" values.

Example for Basic program:

```
10 PRINT "Log10 KCalcite: ", LK_PHASE("Calcite")
20 PRINT "Log10 KCaHCO3+: ", LK_SPECIES("CaHCO3+")
30 PRINT " 1000ln(alpha): ", LK_NAMED("Log_alpha_18O_CO2(aq)/CO2(g)")*LOG(10
```

NAMED_EXPRESSION--New keyword data block.

This data block was implemented to facilitate isotopic calculations. It allows analytical expressions that are functions of temperature to be defined. The purpose is to separate the fractionation factors from the log K, so that the fractionation factor or its temperature dependence can be easily modified. The named expression can be added to a log K for a species or phase by the -add_logk identifier in SOLUTION_SPECIES EXCHANGE_SPECIES, SURFACE_SPECIES, or PHASES data

block. Log K, Delta H, and analytical expressions for a log K can be defined with identifiers -log_k, -delta_h, and -analytical_expression as described in SOLUTION_SPECIES in WRIR 99-4259. Fractionation factors are often defined as $1000 \cdot \ln(\alpha)$. The identifier -ln_alpha1000 can be used to enter data in this form. The analytical expression is the same as defined in SOLUTION_SPECIES, but the result of the expression is converted to $\log_{10}(\alpha)$ by dividing by $1000 \cdot \ln(10)$ before it is summed into log K values.

NAMED_EXPRESSIONS

Log_K_calcite	#	CaCO3 + 2H3O+ = Ca+2 + 3H2O + CO2			
log_k	8.201				
delta_h	-8.035	kcal			
-analytic	292.29	0.015455	-24146.841	-94.16451	
Log_alpha_180_CO2(aq)/Calcite					
-ln_alpha1000	3.8498	0.0	10.611e3	0.0	-1.8034e6
Log_alpha_13C_CO2(aq)/Calcite					
-ln_alpha1000	2.72	0.0	0.0	0.0	-1.1877e6

 Added identifier -add_logk to SOLUTION_SPECIES EXCHANGE_SPECIES, SURFACE_SPECIES, and PHASES data block.

Allows a named expression to be added to the definition of the log K for a species or phase. In the following example, the log K for the phase Ca[14C][18O]3 is summed from four parts, one defined with the log_k identifier and the other three parts from expressions defined in NAMED_EXPRESSIONS. The named expression is multiplied by the coefficient at the end of the line before it is summed into the log K. A missing coefficient is 1.0 by default.

PHASES

Ca[13C][18O]3				
Ca[13C][18O]3 + 3CO2 + 2H3O+ = Ca+2 + 3H2O + 3CO[18O] + [13C]O2				
log_k	0.903089986991			# 3*log10(2)
-add_logk	Log_K_calcite			1.0
-add_logk	Log_alpha_13C_CO2(aq)/Calcite			1.0
-add_logk	Log_alpha_180_CO2(aq)/Calcite			3.0

SOLUTION keyword:

At present, can only define isotopes in the units defined in ISOTOPES.

Version 2.6:

 No new features.

Version 2.5:

 Added the capability to use square brackets to define an "element" name. The brackets act like quotation marks in that any character string can be used within the

brackets as an element name. For example, [Fe3], [13C], and [N5] are now legal "element" names. All element names without brackets must begin with a capital letter, followed by zero or more lower case letters and underscores.

Added identifier `-activity_water` for a species in SOLUTION_SPECIES data block. This identifier has been added for future updates that will allow isotopic calculations. It is intended to be used only for isotopic variations of H2O, like D2O or H2[O18]. It forces the activity coefficient for the species to be `activity(water)/55.5`. This effectively sets the activity of the species to the mole fraction in solution.

Added identifier `-bad_step_max` to KINETICS data block. An integer following `-bad_step_max` gives the maximum number of times a rate integration may fail before execution of the program is terminated. Default is 500.

Version 2.4:

Added identifier `-warnings` to PRINT keyword.

An integer following `-warnings` gives the maximum number of warnings to print into the output file. A negative number allows all warnings to be printed.

Example: `-warnings 20`

Changed the results of the function CELL_NO in Basic programs.

Function `cell_no` in Basic now prints a number equivalent to `-solution` in SELECTED_OUTPUT data block. It gives the solution number for initial solution calculations and the solution being used in batch reaction calculations. Result is the same as previous versions for ADVECTION or TRANSPORT calculations.

Version 2.3:

DATABASE--New keyword data block

It must be the first keyword in the input file. The character string following the keyword is the pathname for the database file to be used in the calculation. The file that is specified takes precedence over any default database name, including environmental variable PHREEQC_DATABASE and command line arguments.

LLNL_AQUEOUS_MODEL_PARAMETERS--New keyword data block

Added new keyword to make aqueous model similar to EQ3/6 and Geochemists Workbench when using `llnl.dat` as the database file. Values

of Debye-Huckel a and b and bdot (ionic strength coefficient) are read at fixed temperatures. Linear interpolation occurs between temperatures.

New options for SOLUTION_SPECIES are

-llnl_gamma a , where a is the ion-size parameter.
 -co2_llnl_gamma , indicates the temperature dependent function for the bdot term given in -co2_coefs of LLNL_AQUEOUS_MODEL_PARAMETERS will be used. Applies to uncharged species only.

LLNL_AQUEOUS_MODEL_PARAMETERS

-temperatures

0.0100	25.0000	60.0000	100.0000
150.0000	200.0000	250.0000	300.0000

#debye huckel a (adh)

-dh_a

0.4939	0.5114	0.5465	0.5995
0.6855	0.7994	0.9593	1.2180

#debye huckel b (bdh)

-dh_b

0.3253	0.3288	0.3346	0.3421
0.3525	0.3639	0.3766	0.3925

-bdot

0.0394	0.0410	0.0438	0.0460
0.0470	0.0470	0.0340	0.0000

#cco2 (coefficients for the Drummond (1981) polynomial)

-co2_coefs

-1.0312	0.0012806
255.9	0.4445
-0.001606	

 Added function SURF to Basic.

SURF("element", "surface") gives the amount of element sorbed on "surface". "surface" should be the surface name, not the surface-site name (that is, no underscore).

 Allow decimals in definition of secondary master species.

Some redox states do not average to integers, for convenience in identifying them, decimal numbers may be used within the parentheses that define the redox state, example S(0.3) could be used in the MASTER_SPECIES data block for the valence state of aqueous species S6-2.

 Eliminate echo of input file in PRINT data block.

-echo_input T/F turns echoing on and off. Default is true, initial value is true.

 Added option for an equilibrium-phase to dissolve only.

"dis" is added at the end of a line defining an equilibrium-phase. No data fields may be omitted. Should not

be used when adding an alternative reaction.
 Example:
 EQUILIBRIUM_PHASES
 Dolomite 0.0 0.001 dis

 Version 2.2:

Added function EDL to Basic.

EDL("element", "surface") gives the amount of element in the diffuse layer for "surface", not including sorbed species. "surface" should be the surface name, not the surface-site name (that is, no underscore).

Special values for "element" include:

- "charge" - gives surface charge, equivalents.
- "sigma" - surface charge density, C/m**2.
- "psi" - potential at the surface, Volts.
- "water" - mass of water in the diffuse layer, kg.

 End of Features not documented in WRIR 99-4259.

 Revisions and bug fixes

Version 2.8 Date: Tue April 15, 2003

Updated arsenic data in wateq4f.dat to be consistent with Archer and Nordstrom (2002).

Revised Basic interpreter to allow lines of any length and character strings of any length.

Renumbering basic statement that included the function SURF in PhreeqcI caused SURF to be omitted and generated a syntax error. SURF and other functions had not been implemented in PhreeqcI.

Fixed a bug in the Basic Interpreter. If elements of a dimensioned variable (character or number) were used on both sides of an equation, the result was erroneously stored in the last element of the variable used on the right-hand side instead of the element specified on the left-hand side.

Using comma in some fields caused an infinite loop.

Fixed bug with SOLUTION_SPREAD, Phreeqc was not calculating solution numbers for solution_spread solutions without solution numbers.

Fixed bug with stagnant zone calculations. If solutions not defined for stagnant cells, PhreeqcI crashed.

Added new state for calculations, PHAST. Previously phast used the state TRANSPORT, which caused some erroneous results with temperature when TRANSPORT was

used in the PHREEQC part of the calculation.

Trying to define dump file in TRANSPORT caused a file opening error. Fixed logic so now can open a file and the name can include blanks.

Version 2.7 Date: Fri February 14, 2003

Initialized gfw in elements structure.

Fixed bug where "time" would be wrong for initial solution calculation. Needed to initialize rate variables for PhreeqcI.

Added print of simulation number to error file for phreeqci

Limited printing of cell numbers to output file in advection calculations. Cell numbers only printed if results for cell are going to be printed.

PhreeqcI captured status messages for kinetics, which made a very large error file in some cases and a long wait to view the output file in PhreeqcI. Now PhreeqcI does not capture these intermediate status messages.

Removed old code related to redirecting error file

Corrected error in transport where wrong time step was used for integration.

Changes to speed up transport algorithm.

Allow file names with spaces in selected_output file name and dump_file name.

Modifications to work with RC1 phast log file.

Allow any characters in square brackets for element name.
- and + and perhaps others caused problems before.

Fixed log molality of water in species printout, was equal to log activity of water. Also fixed basic function for LM.

Changed solid solution prints to print 0 if solid solution is not present.

Fixed bug if no rate name was defined before options in RATES.

Fixed warning on Mac compilation in fpunchf.

Fixed bug if isotopes were used but H and O isotopes were not defined.

Fixed bug where special initial solution calculations were done at later calculation stages.

Needed to set `initial_solution_isotopes = FALSE;`

Fixed problem in C++ if structure name is same as member name.
`logk` member of `logk` structure was renamed to `log_k`.

Added identifier `-add_constant` to `PHASES`, `EXCHANGE_SPECIES`,
`SOLUTION_SPECIES`, and `SURFACE_SPECIES`.

`-add_constant -0.301`

`log K` is augmented by the specified constant.

Added `punch_isotopes` and `punch_calculate_values` to allow
printing isotope ratios and any `CALCULATE_VALUES` result.

Added KEYWORDS:

ISOTOPES

Element

`-isotope isotope_name units standard_ratio`

`-total_is_major T/F (OPTION IS DISABLED!!)`

CALCULATE_VALUES

Name

`-start`

Basic statements, must have `SAVE`

`-end`

ISOTOPE_RATIOS (for printing)

Name=`Calculate_values_name` Isotope_name

ISOTOPE_ALPHAS (for printing)

Name=`Calculate_values_name` Named_logk=`named_expression_name`

Basic functions:

`calc_value("calc_value_name")` evaluates a definition of `CALCULATE_`

`lk_named("name")` `log10(K)` of definition in `NAMED_EXPR`

`lk_phase("name")` `log10(K)` of definition in `PHASES`

`lk_species("name")` `log10(K)` of definition in `(SOLUTION,`

`sum_gas("template","element")` Sum of element in gases with specifi
`template="{C,[13C],[14C]}{O,[18O]}2"`

`sum_species("template","element")` Sum of element in aqueous, exchange,
specified template

`sum_s_s("s_s_name","element")` Sum of element in a specified solid

PRINT keyword:

`-initial_isotopes T/F`

`-isotope_ratios T/F`

`-isotope_alphas T/F`

`-censor_species 1e-8 # Omits print of species if less than relative cri`

SELECTED_OUTPUT keyword:

`-calculate_values name1 name2 ...`

`-isotopes minor_isotope1 minor_isotope2`

Added functions `LK_SPECIES`, `LK_NAMED`, `LK_PHASE` for Basic
interpreter. `LK_SPECIES("CaHCO3+")` returns the
`log k` for the association reaction for the ion pair
`CaHCO3+` at the current temperature. The `log K` is

for the reaction as defined in the database or input file. Similarly, LK_NAMED("Log_alpha_180_CO2(aq)/CO2(g)") returns the value for the log K at the current temperature using expressions defined in NAMED_LOG_K data block; LK_PHASE("Calcite") returns the value of log K for calcite at the current temperature for the dissociation reaction defined in the database or input file. Values are "log10" values.

Example for Basic program:

```
10 PRINT "Log10 KCalcite: ", LK_PHASE("Calcite")
20 PRINT "Log10 KCaHCO3+: ", LK_SPECIES("CaHCO3+")
30 PRINT " 1000ln(alpha): ", LK_NAMED("Log_alpha_180_CO2(aq)/CO2(g) "
```

Added NAMED_EXPRESSIONS data block. This data block was implemented to facilitate isotopic calculations. It allows analytical expressions that are functions of temperature to be defined. The purpose is to separate the fractionation factors from the log K, so that the fractionation factor or its temperature dependence can be easily modified. The named expression can be added to a log K for a species or phase by the -add_logk identifier in SOLUTION_SPECIES, EXCHANGE_SPECIES, SURFACE_SPECIES, or PHASES data block.

Version 2.6 Date: Mon April 22, 2002

PhreeqcI released.

All selected_output is routed through a single routine.

Allow "_" inside square brackets, [A_bcd].

Fixed bug match_elts_in_species, check for "e-" was wrong.

Modified minteq.dat to put CuS4S5-3, Cu(S4)2-3 in in Cu(1) mole balance equations instead of Cu(2). Before the change, the program would not converge if Cu(2) were defined in an initial solution.

Made revisions hopefully to improve SOLID_SOLUTIONS convergence with small numbers of moles of solids.

Made changes related to dump file and PhreeqcI.

Iterations now sums iterations in all kinetics calculations

Fixed bug with LA("H2O"), which was returning natural log of activity of water.

Version 2.5 Date: Mon October 1, 2001

In llnl.dat, fixed sign errors in RRE (rare earth elements) for some redox reactions and removed some redundant species, generally ReeO2- was retained and Ree(OH)4- was removed.

Added the capability to use square brackets to define an "element" name. The brackets act like quotation marks in that any character string can be used within the brackets as an element name. This was introduced to simplify expansion of the model to isotopic species. [13C], [14C], and [18O] are legal element names.

Added identifier -activity_water for a species in SOLUTION_SPECIES data block. This identifier has been added for future updates that will allow isotopic calculations. It is intended to be used only for isotopic variations of H2O, like D2O or H2[O18]. It forces the activity coefficient for the species to be activity(water)/55.5. This effectively sets the activity of the species to the mole fraction in solution.

Fixed bug in checking solid solutions for presence or absence of elements in the system. Programming error caused segmentation fault if an error was detected under certain conditions.

Changed return value of MOL to be molality of water if argument is "H2O". Also changed return value of LA to be activity of water if argument is "H2O".

Diffuse layer calculation was incorrect if aqueous phase did not have 1 kilogram of water. Eq. 74 of manual has molality, but code used moles. The code was corrected by adding the mass of water to the formulation.

Stagnant zones with first-order exchange approximation (1 stagnant cell, exchange factor, and porosities defined) did not work correctly if mobile and immobile cells did not have equal volumes of water. The mixing factors were revised to account for the masses of water in the stagnant and mobile zones.

A fatal error was erroneously detected if the database file had a DATABASE data block. DATABASE data block is now ignored while reading the database file.

Added identifier -bad_step_max to KINETICS data block. An integer following -bad_step_max gives the maximum number of times a rate integration may fail before execution of the program is terminated. Default is 500.

Version 2.4.2: Date: Fri June 15, 2001

Fixed spreadsheet bug. Program was not ignoring columns that could not be identified as either element names or allowed data (ph, pe, number, description, etc). Also, the program failed if a spreadsheet solution number was negative.

Version 2.4.1: Date: Mon June 4, 2001

Fixed spreadsheet bugs with isotopes.

Version 2.4: Date: Fri June 1, 2001

Added structure for spreadsheet for use by PhreeqcI.

Isotope value initialized incorrectly if only an -uncertainty was defined in SOLUTION_SPREAD.

Fixed segmentation violation when primary and secondary master species were defined improperly.

Corrected enthalpies of reaction in llnl.dat. Previous release had erroneously had enthalpies of formation in -delta_H parameter; the values should be enthalpies of reaction. Enthalpies of reaction were calculated from the enthalpies of formation and these values are now included in the -delta_H parameter. This change will have very little impact on calculations because the analytical expression has precedence over -delta_H in calculating temperature dependence of log K, and nearly all species and minerals have an analytical expression or lack both an analytical expression and an enthalpy of reaction.

Corrected bugs in punch of solid solution components that caused both selected output and output file errors: moles were incorrect in selected output, and total moles and mole fraction were incorrect in output file.

Added surface complexation constants for Fe+2; two complexes for weak sites and one complex for strong sites. phreeqc.dat and wateq4f.dat modified.

Comment for units of parameters for calcite rate equation was wrong. Rate equation now uses cm^2/L for area parameter. Previously the correct units would have been 1/decimeter. phreeqc.dat and wateq4f.dat modified.

Fixed a bug when rates were equal within tolerance, but negative concentrations occurred because of small initial concentrations.

Added -warnings to PRINT keyword for specification of maximum number of warnings to print. Negative number allows all warnings to be printed.

Function CELL_NO in Basic now prints a number equivalent to -solution in SELECTED_OUTPUT data block. This does not change printing for ADVECTION or TRANSPORT calculations.

Kinetics time is halved for advective part of reaction in transport; time incorrectly accounted for before.

-punch_ identifiers printed -1 instead of the correct solution number for batch-reaction calculations.

-high_precision is no longer reset to false with every SELECTED_OUTPUT data block.

SELECTED_OUTPUT file name stored for use by PhreeqI.

Alkalinity for NH3 corrected to 1.0 in llnl.dat.

Fixed bug with USER_PRINT of kinetics. Did not find correct kinetics information in some cases.

Fixed bug in default values for SOLUTION_SPREAD. Cannot use phase name and SI for pH or pe, and bug did not allow PHREEQC to run. Now PHREEQC runs, but warns that this is not allowed.

Version 2.3: Date: Tue January 2, 2001

Added new keyword DATABASE. It must be the first keyword in the input file. The character string following the keyword is the pathname for the database file to be used in the calculation. The file that is specified takes precedence over any default database name, including environmental variable PHREEQC_DATABASE and command line arguments.

Fixed bug in SOLUTION_SPREAD. If first heading in the spread-sheet input was an identifier--pH, pe, units, etc--then the headings were interpreted as an identifier and bad things happened.

Added new keyword to make aqueous model similar to LLNL and Geochemists Workbench when using llnl.dat as the database file. Values of Debye-Huckel a and b and bdot (ionic strength coefficient) are read at fixed temperatures. Linear interpolation occurs between temperatures.

New options for SOLUTION_SPECIES are

-llnl_gamma a , where a is the ion-size parameter.
 -co2_llnl_gamma , indicates the temperature dependent function for the bdot term given in -co2_coefs of LLNL_AQUEOUS_MODEL_PARAMETERS will be used. Applies to uncharged species only.

LLNL_AQUEOUS_MODEL_PARAMETERS

-temperatures

0.0100	25.0000	60.0000	100.0000
150.0000	200.0000	250.0000	300.0000

#debye huckel a (adh)

-dh_a

0.4939	0.5114	0.5465	0.5995
0.6855	0.7994	0.9593	1.2180

#debye huckel b (bdh)

-dh_b

0.3253	0.3288	0.3346	0.3421
0.3525	0.3639	0.3766	0.3925

-bdot

0.0394	0.0410	0.0438	0.0460
0.0470	0.0470	0.0340	0.0000

#cco2 (coefficients for the Drummond (1981) polynomial)

-co2_coefs

-1.0312	0.0012806
255.9	0.4445
-0.001606	

Fixed bug in basic interpreter. A number like ".524" would cause an infinite loop.

Added function SURF to Basic.

SURF("element", "surface") gives the amount of element sorbed on "surface". "surface" should be the surface name, not the surface-site name (that is, no underscore).

Fixed option to "runge_kutta" from "runge-kutta" to match documentation for KINETICS.

Fixed UO2+2 and Mn+2 reaction stoichiometry for Hfo surface complexation in wateq4f.dat.

Added option for an equilibrium-phase to dissolve only.
"dis" is added at the end of a line defining an equilibrium-phase. No data fields may be omitted. Should not be used when adding an alternative reaction.

Example:

```
EQUILIBRIUM_PHASES
      Dolomite 0.0  0.001 dis
```

R-K integration failed when only the final rate generated negative concentrations.

Allow decimals in definition of secondary master species, for example S(0.3).

Fixed bug if description was more than about 85 characters; now allows about 400 characters.

Fixed bug for surface/exchange sites related to phases. Was checking internal copies of surfaces/exchange with negative numbers.

Fixed bug in quick prep that did not set the correct pointer for gas phases.

Fixed segmentation fault that occurred if all elements for phase-boundary mineral were not in the solution.
Only applied to a phase used to define concentration in an initial solution calculation.

Added option to eliminate echo of input file in PRINT data block. -echo_input T/F turns echoing on and off. Default is on.

Release 2.2: Date: Wed March 1, 2000

Fixed bug in MIX if no solutions are defined.

Changed printout for surface.

Only gives net surface charge for diffuse layer calculation.

Prints correct value for the surface charge and surface charge density for diffuse-layer calculation.

Added function EDL to Basic.

EDL("element", "surface") gives the amount of element in the diffuse layer for "surface". not including sorbed species. "surface" should be the surface name, not the surface-site name (that is, no underscore).

Special values for "element" include:

"charge" - gives surface charge, equivalents.

"sigma" - surface charge density, C/m**2.

"psi" - potential at the surface, Volts.
"water" - mass of water in the diffuse layer, kg.
Changed distribution to be more consistent with other USGS
water-resources applications.

Release 2.1: Date: Wed January 19, 2000

Added additional #ifdef's for PhreeqcI.
Fixed problem with formats for USER_PUNCH and
others with Microsoft C++ 3 digit
exponents.

Initial Release 2.0: Date: Wed December 15, 1999

Version: C_54 = Version 2.0