

SOFTWARE VALIDATION TEST PLAN FOR GEOCHEMIST'S WORKBENCH, VERSION 3.0.2

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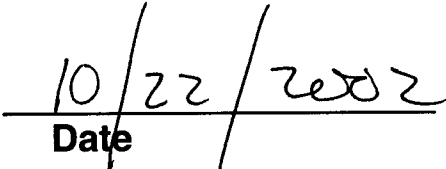
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1 SCOPE OF THE VALIDATION

This document establishes the Software Validation Test Plan for validating the installation and functionality of software tools in the code Geochemist's Workbench (Bethke, 1996). Geochemist's Workbench was developed by Craig Bethke at the University of Illinois at Urbana-Champaign, and acquired by the Center for Nuclear Waste Regulatory Analyses (CNWRA) to provide technical assistance to the U.S. Nuclear Regulatory Commission (NRC) in its high-level waste program.

This Software Validation Test Plan applies to Geochemist's Workbench Version 3.0.2, and is intended to validate the set of software tools used to evaluate chemical reactions, calculate phase stability and aqueous speciation, establish equilibrium conditions, and trace kinetic reaction pathways. All validation exercises will be performed using the thermo.dat database. The following software tools are used to perform these geochemical evaluations:

- * Rxn
- * Act2
- * Tact
- * React

Each of these software programs includes a large number of user options, including options to format and constrain data, depict modeling results, or control numerical processing methods. These options increase the diversity of site-specific geochemical applications that can be evaluated by the code, but do not alter the general functionality of the individual software tools. This Software Validation Test Plan has been designed to provide evidence of correct and successful implementation of the underlying theory and algorithms as outlined in the Geochemist's Workbench Version 3.0.2 User's Manual and required by the TOP-018 (CNWRA, 2001).

2 REFERENCES

The following documents are referenced or used as the basis for this Software Validation Test Plan.

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3 ENVIRONMENT

3.1 Software—Introduction

Geochemist's Workbench Version 3.0.2 (Bethke, 1998) is a package of interactive software programs that run on IBM-compatible personal computers. The main programs in Geochemist's Workbench are named Rxn, Act2, React, and Tact. These programs manipulate chemical reactions (e.g., Rxn), evaluate phase stability (e.g., Act2), calculate aqueous speciation, equilibrium conditions, and reaction pathways (e.g., React), and evaluate temperature-activity relationships (e.g., Tact). An additional software tool, called Gtplot, is also included in the Geochemist's Workbench Version 3.0.2 package to facilitate processing and visualization of the modeling results. This Geochemist's Workbench suite of programs was developed to support educational, scientific, and practical applications of geochemical modeling. Development of Geochemist's Workbench began in the mid-1980s, and was based on a simpler batch mode code named GT, which had been developed earlier by Bethke.

The program Rxn balances chemical reactions between dissolved species, minerals, and gases. The program Act2 calculates and plots information on mineral stabilities and predominant aqueous species for a given combination of dissolved components and

environmental conditions. Tact is a program that determines species activities and gas fugacities at different temperatures to show the effect of temperature on mineral stability and the predominance of aqueous species in specific chemical systems. The program React is the geochemical modeling program in the Geochemist's Workbench software package. React performs aqueous speciation calculations and calculates gas fugacities and fluid saturation states with respect to various minerals. This program allows the User to determine the equilibrium state of a chemical system or the influence of kinetic dissolution/precipitation reactions on species concentrations at various times along a reaction pathway.

3.2 Code Description

The following description of Geochemist's Workbench is based mainly on the User's manual (Bethke, 1998) provided with the Geochemist's Workbench Version 3.0.2 file. Additional information about the code was obtained from the associated textbook on geochemical reaction modeling (Bethke, 1996).

3.2.1 Input

Each of the four geochemical software programs in Geochemist's Workbench (i.e., Rxn, Act2, Tact, and React) are designed for interactive, rather than batch mode, use. This approach allows the User to configure each Geochemist's Workbench program interactively with a series of commands that modify, run, or save input files. The most current chemical system defined by the User can be saved into a dataset described by commands in the format of the specific program. These datasets can be recalled and used as input scripts later.

All the programs use an independent set of aqueous species, known as the basis, to write reactions. Table 3-1 shows the default list of independent basis species used in Geochemist's Workbench. Reactions described by basis species may include dissolved species only, or may also involve various combinations of interacting solid phases and gases. Basis species comprise a portion of all thermodynamic databases included with the Geochemist's Workbench installation package, and can be modified interactively by the User.

The same basic process is used to configure calculations in the Rxn, Act2, Tact, and React programs. Basis species can be "swapped" with other aqueous species, minerals, or gases that are anticipated to play an important role in the modeled system. Swapped species may, for example, constrain fugacity conditions or describe minerals co-existing with the system. The next step in the process is to set the system conditions. The User must set a temperature and assign values of concentration, activity, or fugacity to each default and/or swapped basis species in the model system. A variety of options are available to constrain the system. In React, for example, the User can apply a single temperature to the system or define a polythermal reaction pathway. Another option allows the User to linearly adjust gas fugacities or aqueous species activities within a User-defined range. There is a wide variety of different species concentration options, such as molality, molarity, or ppm.

Table 3-1. Basis Species in the Geochemist's Workbench Version 3.0.2 Database ^{*,†}		
H ₂ O	Eu ⁺⁺⁺	Pb ⁺⁺
Ag ⁺	F ⁻	PUO ₂ ⁺⁺
Al ⁺⁺⁺	H ⁺	Ra ⁺⁺
Am ⁺⁺⁺	HPO ₄ ⁻	Rb ⁺
As(OH) ₄ ⁻	Hg ⁺⁺	Ru ⁺⁺⁺
Au ⁺	I ⁻	SeO ₃ ⁻
B(OH) ₃	Fe ⁺⁺	SiO ₂ (aq)
Ba ⁺⁺	K ⁺	Sr ⁺⁺
Br ⁻	Li ⁺	SO ₄ ⁻
Ca ⁺⁺	Mg ⁺⁺	TcO ₄ ⁻
HCO ₃ ⁻	Mn ⁺⁺	Th ⁺⁺⁺⁺
Cs ⁺	NO ₃ ⁻	Sn ⁺⁺⁺⁺
Cl ⁻	Na ⁺	U ⁺⁺⁺⁺
Co ⁺⁺	Ni ⁺⁺	V ⁺⁺⁺
Cr ⁺⁺⁺	Np ⁺⁺⁺⁺	Zn ⁺⁺
Cu ⁺	O ₂ (aq)	

^{*}Johnson, J.W., E.H. Oelkers, and H.C. Helgeson. "SUPCRT92: A Software Package for Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous Species, and Reactions from 1 to 5000 Bars and 0° to 1000 °C." Livermore, California: Lawrence Livermore National Laboratory. 1991.

[†]Wolery, T.J. "EQ3/6, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0)." UCRL-MA-11066 Pt III. Livermore, California: Lawrence Livermore National Laboratory. 1992.

The Geochemist's Workbench Version 3.0.2 package includes the following thermodynamic databases:

thermo.dat (employs Debye-Huckel equation for calculating activity coefficients)

thermo.pdata (contains coefficients needed for Pitzer activity model)

thermo.hdata (contains coefficients needed for Harvie-Moller-Weare activity model)

thermo.phrqpitz (contains coefficients needed for modified Harvie-Moller-Weare activity model), which can be accessed by any of the Geochemist's Workbench software programs. All thermodynamic datasets contain properties of aqueous species, minerals, and gases. The datasets also include equilibrium constants for reactions to form these species, and information

required to calculate activity coefficients. When available, data are provided for the temperature range 0°–300 °C: at one atm pressure below 100 °C, and along the vapor pressure curve for water at higher temperatures. If information on equilibrium constants is missing at specific temperatures, the omissions are generally denoted by a “500” in the datasets. All thermodynamic databases in the Geochemist’s Workbench software package can be modified by the User, and new thermodynamic databases can be created.

At this time, it is expected that Geochemist’s Workbench calculations performed in support of the NRC high-level waste program will primarily access the thermo.dat database. The thermo.dat database is the default database in the Geochemist’s Workbench software package, because it is the one most commonly employed by Users. This dataset was compiled at Lawrence Livermore National Laboratory for use with the geochemical code EQ3/6 (Wolery, 1992), and is based mainly on the SUPCRT data compilation (Johnson, et al., 1991). Other databases included in the Geochemist’s Workbench installation package were largely designed to support calculations involving high ionic strength solutions, which are applicable to a smaller subset of geologic problems commonly addressed by thermodynamic and kinetic models. All validation exercises described in Section 6 of this plan will therefore be performed by the thermo.dat database. If a decision is made to use thermo.pdata, thermo.hdata, or thermo.phrqpitiz databases in the future in support of the NRC high-level waste program, then additional validation exercises should be performed.

3.2.2 Output

The results from the software packages React, Act2, and Tact are written to output files React.Output, Act2.Output and Tact.Output, respectively. In addition, the programs Act2 and Tact display a diagram on the User’s workstation screen, which can be modified interactively with standard pull-down menus. The program Rxn is usually run interactively, with the output written on the workstation screen. It is possible, however, to divert Rxn’s output to a file, by using the “output” command in place of “go”.

3.3 Hardware Requirements and Installation

The Geochemist’s Workbench is designed for IBM-compatible personal computers. Successful installation requires the following system features:

- Windows 98/ME/NT/2000/XP
- Pentium-level processor
- 32 MB RAM
- 20 MB free disk space.

In order to install the Geochemist’s Workbench programs and supporting data, it is first necessary to log in as the system administrator. The “Geochemist’s Workbench” CD is then inserted into the CDROM drive. After double-clicking on setup.exe, an interactive installation program provides the necessary instructions and guidance for completing the installation.

4 PREREQUISITES

Prerequisites for successful installation and application of the Geochemist's Workbench software include an appropriate level of hardware capabilities and compliance with Geochemist's Workbench installation process, as described in Section 3.3. Input files will be prepared for all validation tests, as necessary.

5 ASSUMPTIONS AND CONSTRAINTS

It is difficult, or perhaps even impossible (Oreskes, et al., 1994), to produce a quantitative representation of a complex earth science system that is unique. Assumptions, constraints, and limitations are unavoidable in quantitative geochemical models. This is, in part, because there are different, and yet often equally valid, equations to describe geochemical processes, such as reaction rates or nonideal speciation behavior. Two different modelers may conceptualize the same chemical system in different ways, electing to include different minerals and aqueous species in his or her model or to evaluate the same data with somewhat different equations. In addition, thermodynamic data for a given phase often vary from dataset to dataset. Bethke (1992) demonstrates how modelers may obtain different results due to the presence of multiple mathematical roots to a single set of governing equations by employing slightly different sets of initial assumptions and constraints to a model. There are thus assumptions and constraints involved in the algorithms, the mathematical formulations, the data, and the conceptual models generated by Geochemist's Workbench. Other geochemical codes, such as EQ3/6 (Wolery, 1992) or PHREEQC (Parkhurst and Appelo, 1999) have similar limitations. It is thus important to clarify what aspect of Geochemist's Workbench Version 3.0.2 is being validated here. This software validation test plan is designed to provide evidence only that the Geochemist's Workbench Version 3.0.2 software package successfully implements the main underlying theory and algorithms described in the Geochemist's Workbench User's manual, as required by TOP-018 (CNWRA, 2001).

6 TEST CASES

In some cases, it is appropriate to validate software functionality by direct comparison between modeling results with analytical solutions (Richardson and McSween, 1989). Comparison with analytical results is a useful test of whether or not the software is reproducing anticipated results for a specific problem evaluated under relatively simple conditions. If all geochemical applications could be treated analytically, however, it would not be necessary to write codes to obtain solutions numerically. Geochemical systems generally include a large number of species, gases, and solid phases that interact in complex ways that are difficult to represent analytically. To test the ability of the underlying theory and algorithms in the Geochemist's Workbench software package to represent accurately complex geochemical processes more representative of natural systems, validation of the Geochemist's Workbench software package is mainly based on comparisons with published geochemical data from field studies, experiments, and modeling exercises. One test for the program React will be performed by comparison with an analytical calculation. Validation tests for the programs Rxn and React will be more detailed than those for Act2 and Tact, because it is anticipated that Rxn and React will be the main Geochemist's Workbench programs used in support of the NRC high-level waste program. The following tests should, however, provide an adequate test of the basic underlying theory and algorithms of the full set of geochemical programs included in the Geochemist's

Workbench package. Installation of the Geochemist's Workbench software package will be considered to have been successful if the individual software packages are determined to function as expected.

6.1 Rxn

The software program Rxn balances chemical reactions among minerals, dissolved species, and gases, and provides thermodynamic data describing equilibrium conditions for that reaction at different temperatures. Through an iterative process of swapping basis species for other species, minerals, or gases, the User instructs the program to construct balanced reactions and present associated thermodynamic data for that reaction. To obtain the desired results, species stoichiometries may be manipulated by the program to calculate a transformation matrix that gives the desired balanced reaction and associated equilibrium constant. Alternatively, the RXN code may obtain this information by addition, subtraction, and multiplication of the balanced reactions described in the thermodynamic database until the desired reaction appears on the computer screen. Data used to balance reactions are thus sourced from the thermodynamic dataset that was selected by the User. A more detailed description of the underlying equations used to perform reaction balancing in Rxn are described in Chapter 9 of Bethke (1996).

Several tests will be performed to validate the primary capabilities of the Rxn program. These tests and anticipated results are:

- * accurate reproduction of Analcime dissolution reaction described in thermo.dat thermodynamic database
- * accurate reproduction of equilibrium constants for the Analcime dissolution reaction described in the thermo.dat thermodynamic database
- * construction of a reaction that is stoichiometrically and electrically balanced for the mineral pyrite using aqueous species other than the default basis species (e.g., swapped species).

6.2 Act2

In support of the NRC high-level waste program, it is expected that the main function of the software program Act2 will be to develop activity-activity plots. To test the ability of Geochemist's Workbench to calculate activity-activity diagrams, a test will be performed to determine if Act2 is capable of reproducing a series of activity-activity diagrams published on page 44 in Bethke (1998).

Successful validation of the Act2 program will require accurate reproduction (i.e., less than 5 percent difference) of the following redox-pH diagrams for uranium drawn at 25 °C assuming a species activity of 10^{-10} .

- * uranium speciation as a function of dissolved oxygen and pH
- * uranium speciation as a function of oxygen fugacity and pH
- * Eh and pH
- * oxygen fugacity as a function of the activity ratio of Fe^{+++} to Fe^{++} and pH

6.3 Tact

The program Tact calculates and plots mineral stabilities and the predominance of specific species or gases at different temperatures. To demonstrate the basic capabilities of Tact, the following tests will be performed:

- * a diagram will be constructed depicting stability regions for different phosphate species as a function of temperature and pH, and compared with the published temperature-pH relations for phosphate species show on page 80 in Bethke (1998)

- * a diagram depicting the solubility of quartz as a function of temperature will be constructed and the results will be compared with solubility data for quartz described in the thermo.dat database at discrete temperatures.

6.4 React

React is the primary equilibrium and kinetic reaction pathway modeling program in the Geochemist's Workbench Version 3.0.2 software package. The program calculates equilibrium aqueous speciation relationships, a fluid's saturation state with respect to solid phases, and gas fugacities. The program is extremely flexible, allowing the User to select, among other options, isothermal or polythermal, open or closed, and reversible or irreversible reaction pathways. The underlying theory and algorithms used in React are described in Bethke (1996), predominantly in Chapters 5, 7, and 14. React calculations have two different components: characterization of the initial system and the system's evolution after User-defined processes have altered it. Two tests of the React program will be performed to validate the underlying theory and algorithms for calculation of the equilibrium chemical system and a kinetic reaction pathway. The following tests were designed to evaluate the two fundamental components of React's calculations, as described above:

- * activity coefficients and fluid saturation state with respect to various minerals in seawater will be compared to those obtained from chemical models of seawater described in Bethke (1996). The seawater model described in Bethke (1996) generally follows the approach first undertaken by Garrels and Thompson (1962), and is constrained by the major element composition of seawater as determined by chemical analysis and by modeling assumptions described in Holland (1978), McDuff and Morel (1980) and others. Successful completion of these tests will validate React's calculation of the initial equilibrium component.

- * the reaction rate of quartz sand at 100 °C will be calculated according to the rate law described in Rimstidt and Barnes (1980), assuming a specific surface area of 1,000 cm²/g. Analytical calculations will be performed to determine the amount of quartz expected to dissolve under these conditions, and the results will be compared with the calculated volume losses for quartz.

7 TEST INPUTS

In all cases, test inputs will consist of a series of interactive commands described in the Geochemist's Workbench Version 3.0.2 User's Manual. Chemical conditions in the Geochemist's Workbench Version 3.0.2 input files such as temperature, component

concentration and mineral reaction rates will be set at values consistent with the problems described in Section 6 of this software validation test plan. In all test cases, thermodynamic data will be accessed from the thermo.dat database.

8 TEST PROCEDURES

The results of all Geochemist's Workbench validation test cases will be compared to analytical solutions and published data and analyses, as described in Section 6. Results of Act2 and Tact test cases will be presented as plots to facilitate comparisons with published plots. Output from the interactive program Rxn will be copied directly from the screen printouts, and output files from React will be used to perform validation exercises. Test results are documented in a software validation test report in accordance with TOP-018 Section 5.10.5. Scientific Notebook 331 may be used to store detailed data, etc.