

Project # 20.06002.01.212 LS 3/5/07

Notebook # 827E

7/12/06

Software Validation for MINTEQA2, Version 4.03

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Objective: To test MINTEQA2 VERSION 4.03 to make sure that the output of this updated model matches that of its previous form MINTEQA2 VERSION 4.02. This will be achieved by running the same problems (from the MINTEQA2 VERSION 4.02 validation) to see the degree of accuracy.

Training: In order to perform said mentioned validation one needs to be familiar with the MINTEQA2 program and have a basic understanding of various aqueous systems and graphs and tools to interpret such systems. I personally read the instruction manuals and became acquainted with the program by performing examples from the books. The User-manual and other reference documents are located on disk and in D:\MyDocuments\Minteqa2_4.03_dos\Minteqa2_4.03_validation\4.03_MINTEQA2_Configuration\Documents.

This covers the algorithm and some assumptions made by the code.

Hypothesis: Although MINTEQA2 has been updated to version 4.03, most of the modifications have been to additions to the program; see the file names 4.03 changes.wpd in the directory D:\My Documents\Minteqa2_4.03_dos. I expect the results for version 4.03 to match closely to those from the 4.02 version.

Approach: To use the same set of Installation(example)/validation problems used in the validation of MINTEQA2 VERSION 4.02 (which is under TOP_018 control) to see if the results are the same when run on MINTEQA2 VERSION 4.03. At this time MINTEQA2 VERSION 4.03 will not be compared to other models or analytical data for validation, but may be so in the future. When that time arises modifications to the validation will be noted.

Mathematical and other model assumptions: The user is referred to the instruction manual that accompanies the program to determine theory and assumptions employed by the program.

Input Files: The input files used will accompany the validation report or see below for file location.

File Location: D:\My Documents\Minteqa2_4.03_dos\Minteqa_4.03_validation

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Ran all example files with no problem, however when running the validation files there were a few problems that need to be worked out with the validation files. For the three

files that test the cnwra updated databases, I need to find a usable database for these files that can be used in the new version. Also the temperature effect problems 67A and B need to be looked at to see why the output files are not the same as those from version 4.02. For problems valid62 and Valid 64a the U and Sr species vary between versions however the rest of the file seems to match rather well, with some rounding differences.
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7/11

I have the DBS formats of the CNWRA updated databases and tried to run them through the unformat program that comes with version 4.03; however I got an error-file too long. Reading the updates **for 4.03 specifies using the .unf version of databases and then with the executables in 4.03 run it through the format then unformat programs.** This did not work either, got a similar error message trying to format the .unf version of the CNWRA databases.

For the temperature effect problem, I used the files used in the MINTEQA2 for windows validation. The only difference there was the pH was constrained to 7. Valid 67a worked and matched the output file for the Minteqa2 for windows program, however 67b was off, and Gypsum appeared super saturated. SO I went back into the files and allowed all solids to precipitate, however that didn't work either. I also took the original 67b (no pH constraint) and allowed solids to precipitate, but gypsum still appeared oversaturated.
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I got the thermo4_nea.dbs and type6.dbs to convert to the unformatted form. I didn't do anything different, just cleaned out the "make databases" folder and copied in the files then renamed them to thermo and type6 and ran the unformat executable. I then reran all the validation files using those databases and the comp4_rad database. The files were in much better agreement than previously and there is much less cross outs in the comparison files. The U_mint2 and3 files were off, mostly rounding, and the valid67A+B were still off course.

I couldn't get the file thermo4rad_nea.dbs to convert, there was an error that I'm not sure what it meant. This may make the U-mint2 and 3 files better fit the 4.02 output, however I'm not sure what database was really used in the 4.02 validation.
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7/14/06

I still can't get the file thermo4rad_nea.dbs to convert.

Worked on valid 67a and b, by 1 constraining pH, if you do that with the interactive prodefa2 file, you must add another component, NO3, to balance the equations. This really throws off the output, so I copied the valid67a and b from the Minteqa2 for windows validation folder and pasted them into the 4.03 document shell. I also went in and specified all solids are to be allowed to precipitate after they form. I also further modified the files by breaking up part b into two separate files. Each version was run

with the 1999 and 2002 databases. None matched that of the 4.02 version and gypsum still appeared supersaturated, even though it was allowed to precipitate. However, for 67a with the pH constrained the results matched those, with the 1999 databases, of Minteqa2 for Windows, valid67a-wind.out.doc, see comparison of all output files in D:\My Documents\Minteqa2_4.03_dos\4.03_validation\Validation_test\Comparison_validation LS

7/15/06

Re-did valid67a+b with the same ideas above-but tried not to use prodefa2. Even though I'm allowing precipitates to form and adding another component to the system, the output still shows supersaturation.

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7/19/06

For some reason when I use Prodefa2 to update the input files, I can't match the original input files from 4.02 (meaning the heading under the temperature that specifies edit level 1 parameters). So I copied the input files from the MINTEQA2 for windows validation and got the same results. All the files are listed in D:\My Documents\Minteqa2_4.03_dos\4.03_validation and are broken into installation and validation folders.

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7/20/06

I gave up on altering valid67a-b using Prodefa2, it just wasn't correcting all the errors. So I matched the input file to those of the windows version and I had to break up part B into two problems. I did get the results to match what I had during the windows validation.

What I think Turner did, which I tried in the windows program, was calculate the log K (minerals) based on Phreeqs polynomial (I have that somewhere) and alter the K at each temperature step, which each temperature step in dos version is a different problem. This couldn't be done in windows because the temperature can vary within one problem-and you can't specify more than one log K for any mineral for one run. Now that I have it at least matching the windows version I'll go back and see if I can use prodefa2 and/or cut and paste to input in what I think Turner did to get the problem to work.

For 4.03 I manually and I used Prodefa2 to change the log K's for anhydrite and gypsum at each temperature along with making the enthalpy = 0. Both input files reached the same SI for all temperatures. I also did a test sample of 5 or so in windows, (which I did before-I found reference to it in my notebook) and the results were the same as the 4.03 version. However, they were not the same as the output for 4.02. Michelle just re-installed windows version so the database is untouched. I'm thinking this is not what Turner did, because if it were, his input files would look like mine- O delta H and various log K values (see attachment).

I'm not sure what he did, but the above seems to make sense. Maybe there is another catch that I'm missing. Well at least 4.03 and windows match!

I tried deleting enthalpy instead of entering 0, the file failed. I also took the log K's calculated using the Phreeqc polynomial equation and entered those log K's at temps from 25-75 degrees C into the van't hoff equation to solve for enthalpy. I took that enthalpy and entered it into Minteqa2, example 40 degrees, using the original log K to see if the Phreeqc results could be duplicated, and they were not.

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10/26/06

I tried looking for an alternative temperature problem that would be also used in the Minteqa2 for Windows validation. Modeling seawater to see the affects of temperature on silica precipitation didn't work due to the low temperature range of Minteqa2, and the usable temperature range didn't produce the desired results. An attempt to model the original temperature problem 67a-b in another solution other than pure water failed. The two programs Minteqa2 and Phreeqc still calculate log K's differently at elevated temperatures.

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10/31/06

I looked online for a calcite problem that can be applied to the temperature range of 25-75 to demonstrate the code capabilities. However, most problems were too complex or lacked all the needed information.

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11/1/06

In preparing printouts for a meeting, I did discover a reference to a power factor (polynomial). I was looking back through the manuals and discovered that on page 17 of the users' manual under "temperature corrections of equilibrium constants" that in fact Minteqa2 used a power function to correct for temperature when the constants were provided in the thermodynamic database, although for only 25 of the 1000 species. However, when I looked at the explanation of the Thermodynamic database I don't believe these constants are mentioned. In the supplement, page 31, only mentions the Van't Hoff equation for temperature correction of log K and the explanation of the Thermodynamic database is pretty much the same. After some searching through files I decided to email the EPA at CEAM@epamail.epa.gov.

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11/2/06

I sent an email to the EPA and the response indicates that the power factor (polynomial) is still used by Minteqa2 and that the constants needed for the equation are in ANALYT.DBS. I went back through the manuals and saw no mention of this file and how to update it, in the response email it was mentioned no documentation could be found. A copy of the email will be included after all responses have been completed.

I updated the file based on how the file appeared to be set up. However, it didn't produce the desired results.

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11/3/06

The EPA sent another response that verifies what I had done; even the spacing sequence they told me to use is what I had followed when updating the file. I also updated the ANALYT.DBS for the Minteqa2 for Windows and it produced the same results. When I originally updated the file I added Anhydrite and Gypsum's constants to the top portion of the file, where I believe the minerals should be added. I went back and then cut out what I added and pasted it to the lower portion of the file. This however, did not work. I sent another email questioning if there is another file that needs to be updated in order for Minteqa2 to properly read the polynomial constants.

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11/7/06

I tried to alter the Windows and Dos ANALYT.DBS by cutting and pasting existing lines and then altering those lines. The results were the same when changes were made manually entering line data.

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11/13/06

In order to update the MINTEQA2 for Windows the user needs to update the database file named ANALYT.DBS. The procedure for updating this file is not mentioned in either user manual and will briefly be discussed here. The file should be opened in a text editor program (Textpad, Wordpad). The program reads "110 read (1un07,9070) idt,at,bt,ct,dt,et,ft,gt," this line of code reads a "record". Where at-gt corresponds to A1-A7 equation 3-7 and the first variable, idt, is MINTEQA2 identifier that occupies the first 7 spaces then it skips a space, and reads the next seven variables, at,bt,ct,dt,et,ft,gt, as decimal numbers, each occupying 10 spaces with one space after each number. Each will be stored with 3 digits to the right of the decimal point (whether the decimal point is specified or not; if more than three digits to the right are specified they are ignored). If the constants are being added for a mineral or a aqueous species they are added to the top or bottom, respectively, of the file that is separated by a single 0 character. Note that if the polynomial constants are taken from PHREEQC they must be multiplied by (-1) before they are entered into MINTEQA2's database. MINTEQA2 (all versions) assumes solid phase reactions in its database are written as formation reactions, but the solid phase reactions in PHREEQC's database are written as solubility products. There is a slight discrepancy between the SI values calculated by MINTEQA2, Version 4.02 and MINTEQA2 for Windows; this is likely due to an accumulation of rounding errors. For the most part the output is comparable.

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Scientific Notebook No.: 827E Project Numbers: 20.06002-01.212

Accomplished

- 1. Initial entries per QAP-001
- 2. Dating of entries
- 3. Corrections (crossed out, one line through w/initials/date)
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Any discrepancies must be resolved before notebook closeout.

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3/8/2007
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ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK NO. 827E

Document Date:	07/12/2006
Availability:	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, Texas 78228
Contact:	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, TX 78228-5166 Attn.: Director of Administration 210.522.5054
Data Sensitivity:	<input checked="" type="checkbox"/> "Non-Sensitive" <input type="checkbox"/> Sensitive <input type="checkbox"/> "Non-Sensitive - Copyright" <input type="checkbox"/> Sensitive - Copyright
Date Generated:	12/10/1999
Operating System: (including version number)	Windows
Application Used: (including version number)	MINTEQA2, Version 4.03
Media Type: (CDs, 3 1/2, 5 1/4 disks, etc.)	1 CD
File Types: (.exe, .bat, .zip, etc.)	txt, pdf, exe, for, dbs, unf
Remarks: (computer runs, etc.)	Media contains: software validation