

**Electronic Scientific Notebook
826E
Software Validation for Geochemist's
Workbench 6.0 (GWB 6.0)**

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Notebook 826E

6/28/06

Software Validation for Geochemist's Workbench 6.0 (GWB 6.0)

By Lynn Sabido LS

Objective: To test GWB 6.0 to make sure that the output of this updated model matches that of its previous form GWB 5.0. This will be achieved by running the same problems (from the GWB 5.0 validation) to see the degree of accuracy.

Training: In order to perform said mentioned validation one needs to be familiar with the GWB 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.

Hypothesis: Although GWB has been updated to version 6.0, most of the modifications have been done to the professional version and minimal changes have occurred to the standard version. I expect the results for version 6.0 to be exactly the same as they were for 5.0.

Approach: To use the same set of validation problems used in the validation of GWB 5.0 (which is under TOP_018 control) to see if the results are the same when run on GWB 6.0. At this time GWB 6.0 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 four instruction manuals that accompany the program to determine theory and assumptions employed by the program.

Input Files: The input files used will accompany the validation report (and the version 5.0 report) or see below for file location.

File Location: D:\My Documents\GWB 6.0 Validation

LS

6/22/06-LS

I am currently working on GWB 6.0 validation. Looking at the RXN module example one called RXN_test1; the program seems to read the databases correctly, such as the log K values, reaction formula.

Ran the other validation input files by either using the interactive screen (for most) or typing in the commands. I had no problems.

Going through examples in the book; page 24 Activity coefficients says to change the IS=3 in the basis screen by config-variables- stoich_IS. You just put the 3 in the spot for Ionic strength (IS).

6/29-LS

It has been decided that the current validation be expanded to include several other problems from the PHREEQC manual (some comparison to analytical data) to demonstrate that GWB can simulate similar results as can other models, in this case PHREEQC was chosen.

The example problems include high ionic strength seawater that requires use of the Pitzer equations, sorption, reaction path, speciation, solubility, mixing of waters, and evaporation.

Worked on the mixing problem, having hard time figuring out how to react pure water in GWB, skipped that step and went to mixing portion of the problem. Did not get similar results, will take closer look (may be a units problem).

Also started the evaporation problem, similar results for most species except the Cl⁻ and some Ca⁺⁺ and Cl⁻ species were off by more than 10%.

6/30-LS

GWB can mix pure water with a solid phase if you enter Cl in as a small amount 1e-9 to use for charge balance. However, Cl⁻ concentration increase due to fix in charge balance, which throws the concentration of other ions in species off compared to that of PHREEQC

7/3-LS

I ran the GWB mix_A where calcite is dissolved in pure water with Cl⁻ being defined as a small concentration. I then took the resultant amount of Cl⁻ (after charge balance) and entered it in PHREEQC. The results are still off. There is a way to turn off charge balance in react, I did and deleted the Cl⁻ term, slight improvement.

For the evaporate problem I used the Thermo. V8 R6 that was suggested by Bobby, however, the Nitrogen species are not listed the same in that database, so I used NH₃ neutral instead of NH₄⁺. The results not much better.

For the speciate problem I used the Wateq.dat database, and created an excel spreadsheet that compared the results to Phreeqc using the Phreeqc.dat. File-Speciate. Most species were within a 10% difference for species with a concentration of greater than 1e-7, except HnSio4 species, because SiO₂ was entered in as H₄SiO₄. Also the Uranium species were off- different species were predicted in the outcome

7/5-LS

For the evaporation problem I ran the phreeqc model using the LLNL.dat, the results didn't change much from when the Phreeqc.dat was used. For GWB there were not that many changes in the output when using either the thermo.dat or thermoV8.dat or Phreeqc.dat. The major differences between the models remained unchanged no matter what database was used.

For the speciate with uranium problem, I ran Phreeqc with the LLNL.dat, no improvement in comparison to the GWB therm.dat. I also ran GWB with Phreeqc.dat, Thermo.V6r8, and again with Wateq (Uranium as UO_2^{++}). The best results seem to be the last mentioned run. The majority of major ions species didn't change, however when using the WATEQ database and entering in uranium as UO_2^{++} , many more uranium species were predicted. Also noticed that the Mn speciation is off, most likely due to the fact in Phreeqc the user specified that the Mn^{+} species control redox, not sure how to specify that for GWB. When I calculated the moles of H_4SiO_4 from the 4.28ppm of Si I came up with 14.417 ppm. When this value was entered into the model the results were worse for $HnSiOn$ species.

Started setting up Sorption example, try to figure a way to run a series of pH values in one run and work out kinks of not being able to enter the problem in the same way.

Started reaction path problem.

7/6

Could not get or find keywords in GWB to duplicate what was done in various Phreeqc problems. Will re-evaluate problems being used to more simple chemical systems.

7/13/06

Solubility problem resolved using Phreeqc database, and the Evaporation problem was fixed by was using the Thermo.dbs and turning off the charge balance.

The sorption problem seems to agree with the lower concentration of Zn^{+} ($1e-7$) more so than with the results for the Zn^{+} concentration of ($1e-4$). It was done in the react module to allow a change in pH from 5 to 8.

Trying to get the mixing problem to agree with the Phreeqc program. I entered the seawater composition into the react program and hand calculated the 70-30 percent of initial species before entering in the data. The pure water that reacts with calcite was all entered into the reactants pane. Note: not a great match in data, but I believe the concentrations were calculated incorrectly. Not sure how to equilibrate the answer above with calcite, other then taking the output and entering it in again in a different react window.

The reaction path examples doesn't like the activities for K^{+} and H^{+} in the output file, even though 10moles of Gibbsite dissolved (however, I was unable to find a way to use

the alternative chemical formula, used by PHREEQC, in order to put in the GWB problem).

In order to make a better match between models for the speciation with Uranium problem, I used the Wateq4f database in the GWB program. Few species greater than $1e-8$ concentration vary more than 10%. High percentages of differences between programs are between species with very low concentrations $1e-12$. This holds true for the U species also, however, more species variance was predicted with GWB than with Phreeqc.

LS

7/14/06

I re-ran the sorption problem with the two corrected concentrations $1e-4$ and .1, then I created a graph of pH vs Zn sorbed fraction and the results were much closer to those of Phreeqc (see Sorption spreadsheet). The % Sorbed is a guess taken off the graph.

LS

7/17/06

Speciation problem was run with three databases, WATEQ4F, Thermo, and Thermo Revision8. The Wateq4F database is the closest match. However, I went back to the files and made sure alkalinity was entered as HCO_3 and that all other U species, except those present in the PHREEQC output file were suppressed. The only complex not in the databases- was $\text{U}(\text{OH})_5^-$. When the other U species were suppressed the comparison improved, however even with the Wateq4f database the % difference was still high, however the concentrations are $10e-9$ or smaller. As stated before the other species in the problem show good agreement.

The mixing problem needs to be entered differently, you have to take the resultant of calcite dissolving in pure water (calculate 70%) and enter the components, in moles, as a reactant. I tried a few different ways of adding the reactants, as calcite, switching calcite for Ca. However, this didn't work because you are then reacting moles of calcite with a brine-which is not what the example in PHREEQC specified.

The reaction path seems to be off, even if I react only 10 moles of microcline, gibbsite, kaoline, or muscovite the activity of H_2SiO_4 , K, and H are all off. Can't constrain system to just the four components. The SI for the minerals is below the limit of what is printed in the output file.

LS

7/18/06

For the reaction path problem the system can be constrained by using the suppress function. However, the other problems with the input parameters, I'm not sure how to handle. Also there is the problem of not getting the desired information in the output files, even after adjusting the print options.

LS

7/20/06

Tried an alternative mixing problem, two well water data from Chapelle article. Didn't turn out the way I wanted.

LS

7/24/06

Took the sorption graphs of pH vs. Zn concentration and pulled the spreadsheet data and loaded it into excel to pull regression curves. None of the curves matched well at all to either graph. So I took the raw data and pulled the Zn Concentrations at pH values as close to the desired values as possible. The match up between Phreeqc and GWB is rather well. See file named spreadsheet_1 and spreadsheet_4 in D:\My Documents\GWB\GWB_compare\sorpton.

Also, I took part A of the Phreeqc mixing problem, entered the results (at 70%) into the reactant pane of Geochemist workbench, with (30%) solution of the seawater in the basis pane, the results are not as close as they should be considering the Phreeqc database was used in the GWB run. The same problem was run using the thermo database that comes with GWB. When changing the database, some of the basis components must be altered; for example, in the phreeqc DB H4SiO4, and in the Thermo SiO2. The results are in spreadsheet form. I also looked at the Phreeqc databases in the PHREEQC and GWB programs to compare the log K values. There are differences which contribute to the differences in output, for example, the CH4 concentrations are vastly different this is due to the log Ks which also affect other Carbon species

					-	Log K in	Log K in
CH4 -		CH4 -		%difference		GWB	Phreeqc
GWB	1.46E-05	Phreeqc	2.87E-25	5.1E+21		145.0792	41.071

LS

7/25/06

Made a few adjustments to the mixing problem, the one that used the Thermo database, specified HCO3 as mg/kg instead of alkalinity. These changes made little difference.

Working on the reaction path problem, I broke up the problem into a similar manner as the Phreeqc example problem #6 and created input files for both. The first four runs had 10 moles of K-spar, Gibbsite, muscovite, or Kaolinite. The next two runs were 1-10 moles of Gibbsite reacting along with 1 mol of kaolinite 2- 10 moles of Kaolinite with one mol of K-mica. I wanted to graph the activity of H3SiO4 vs the activity of K+/H+, however with the way the runs were set up the (GWB only reporting species with values above 1e-8) the required species were not reported in the output for both programs.

LS

7/26/06

I created a spreadsheet called reaction path that's in the directory D:\My Documents\GWB for the above reaction path runs (see 7/25/06).

The reaction path problem is set up differently than the Phreeqc example because GWB can't set the problem up in the same manner. The Phase and equilibrium keywords in Phreeqc were changed, (instead of having the 10 moles in equilibrium, I added the react keyword). Also I reran the runs by altering the log K's in the Phase keyword to match those of GWB. This made the results worse.

Using the Thermo database, the results are off because GWB doesn't contain H₄SiO₄, and doesn't report aq species under 1e-8 concentration. I tried to alter Phreeqc to suppress H₄SiO₄, and have the dominate species be H₃SiO₄. These attempts didn't work, nor improve the results.

LS

7/27/06

I then ran the GWB with the Phreeqc database; once again the results were off. I also tried various reactants (1mol gibbsite with 10 moles kaolinite), just to basically get results that included K and H in solution in concentrations above 1e-8. I wasn't getting the same trends much less similar numbers.

LS

7/31/06

I found a mistake with the initial sea water composition and recalculated part C of the Mixing problem. I then recalculated part A in GWB, two ways, one allowing calcite in solution as a basis species and another using calcite as a reactant. When using part A info from GWB in part C the results are not as good as when the calcite water chemistry (part A) from Phreeqc is used. However, the results are still considerably off. The pH of the Phreeqc part C was run with a fix pH that matches that of the GWB results, this if little improved the results.

LS

8/1/06

For the Mixing problem I adjusted the alkalinity, due to the pH being off, I first took the difference of the carbonate alkalinity of the two programs and added it to the carbonate water (which is only 70% of the system), I also tried adding/subtracting various amounts of HCO₃ to adjust the pH. The closest I came to achieving the same pH as the Phreeqc program was within 0.6% difference; however the speciation was still considerably off.

LS

8/2/06

For the reaction path problem I used the print option, aqueous species- long, to print species with concentrations smaller than 1e-8. However, because the difference in H₄SiO₂ species in both programs (thermo.dat database in GWB and Phreeqc.dat in Phreeqc), I tried to add the H₄SiO₄ species by cut and paste from the thermo_phreeqc.dat database to the Thermo.dat database, however, I had to save the file in an alternative location on the D drive, and when using the file, which was altered a few times, I received an error "corrupt file" message.

LS

8/10/06

I renamed and resaved the Phreeqc's Phreeqc.dat database after making a few changes. I made H3SiO4 the basis species (instead of H4SiO4) and altered the SiO2 species and made H3SiO4 a product of SiO2 and water. When the database was used the following error messages were displayed:

```
ERROR: Elements in species have not been tabulated, H4SiO4.  
ERROR: Reaction for species has not been defined, H4SiO4.  
ERROR: Calculations terminating due to input errors.  
Stopping.
```

I tried to properly define H4SiO4, however, I continued to get the same error message.
LS

11/1/06

Spent some time reviewing the problems I've had with the last two examples, mixing and reaction path. It is relevant that GWB was not meant to perform these calculations in the manner I'd like, so if I'd had a mixing problem I'd use Phreeqc not GWB. I would like to come up with another problem or two to complete the validation. These would be problems that a user would actually employ GWB to solve. I looked at a temperature problem; however it's very close to what I used as a solubility problem. I will look at other program validations for ideas.

LS

11/2/06

I looked at the various problems used in the Minteqa2 validations and tried to apply them to GWB. The barite solubility problem hasn't worked out because I'm not sure exactly how to enter it and what GWB databases to use. I'm having trouble on how to enter specific parameters into GWB for the gas chemistry and redox problems and these are important pieces of information that can't be neglected.

LS

11/3/06

The Barite solubility problem has been worked out, it shows barite is more soluble in a dilute solution than in pure water. See the spreadsheet named Barite in D:\My Documents\GWB\GWB_compare\Solubility. I ran the problem with three different databases, the thermo R6, Minteq, and Phreeqc. All the databases are compatible and show the proper trend, however, the Minteq database, gives the closest concentration results. I worked on the redox problem, however, in Phreeqc and Minteqa you can specify pH, pE, and partial pressure of a gas. I'm unsure how to do all in the same run for GWB. The simplest problem with Fe⁺⁺/Fe⁺⁺⁺ concentrations specified to see the resultant pE, I was unable to get the desired results, GWB requires O2 be entered as a species.

LS

11/6/06

For the redox example there are three sections to part A- Fe⁺⁺/Fe⁺⁺⁺ with a pH of 7, PO₂=.22 atm with a fixed pH of 7.5, and lastly Mn⁺² in equilibrium with pyrolusite. The first section, Fe example, was able to be worked out to match that of Phreeqc. However, the redox couple had to be turned off in GWB in order to enter concentrations for both Fe⁺² and⁺³, However this required the PO₂ to be entered as part of the input file. The value used, I took from the Phreeqc output file. If no value was supplied for PO₂, pE was not reported. The pE that was calculated closely matched that of Phreeqc (GWB 3.9805- Phreeqc 4.0), However the value is off from Stumm and Morgan (1996). Equilibrium constants (log K) differ in GWB database (Fe redox couple = 8.4878) from the values provided in Stumm and Morgan (1996) (Fe redox couple = 13). The second part provided PO₂ information, so no alteration to the input was done in order to get a comparable result. In the third section once again the PO₂ was provided in order for the problem to solve, the value was taken from the corresponding Phreeqc output file. The second part, B, of the redox problem involves sliding the pE from -9 to -4 while holding the pH. At this time I am unable to create a working file.

LS

11/7/06

In Phreeqc the O₂ concentration and PO₂ are calculated for you, in GWB that information must be supplied. Part B of the redox problem, It is difficult to get a working file, however, when the pE is made to Slide from -9 to -4, there are no increments specified, So each pE value would need to be a different file. Again the PO₂ would need to be specified also and the HS⁻/SO₄²⁻—may need to be turned off in order to get the problem to run.

I also tried to work on the Aqueous and Gas Phase Carbonate chemistry problem. In GWB, you can't specify a mineral to be in equilibrium with the system. SO I entered Calcite in a molar quantity, however, that supersaturated the results. If calcite is removed from the input, there is a non-convergence error.

LS

11/8/06

Tried looking for a problem different from what plan on using for the validation, however, there are a few things I need to figure out on how to add input to the interface of the React module. How to slide pE and pH in a specific number of steps, how to enter both pE and pH to the same input and how to set up redox problems. It is not clear in the manual on how to incorporate all your input, or alter it to fit the program. However the variables (step sizes) can be specified.

LS

11/9/06

Working on how to slide the pE and have the output from specified steps reported. There are a few variables, delxi = step size in reaction process and dxprint are the intervals in between printing results. However, the problem is not converging and the fugacity taken from the end result of Phreeqc is most likely causing errors.

LS

11/10/06

Have decided to keep the barite solubility problem and then abandon the redox, mixing, and reaction path problems completely. Have received the last problem for the Pitzer/HMW database.

LS

11/14 /06

I have entered the Pitzer problem in exactly how it was set up and run in GWB 4.0.3. The problem isn't converging with the thermo_hmw.dat. I have tried to change the database and reached convergence, however, the other databases are not able to handle the Ionic strength. The output is off from where it should be. I have altered the inputs and still no convergence. I have also been looking at the variables, to see what can be changed.

LS

11/15/06

I tried to change the number of iterations, number of iterations per reaction step, delxi-step size. The only thing that worked was changing the step size in the reaction progress, however that means larger quantities of water were evaporated quicker and the steps would not match that to the comparison example.

LS

11/16/06

Tried a combination of variables and options, however, I couldn't get the file to run properly. Bobby Pablan got did the problem on his computer and it worked fine. He changed the delxi to .00001.

LS

12/5/06

Taking another look at the seawater speciation with Uranium, I decided to alter the Phreeqc input file because GWB can't specify both the pH and pE in the same file using SPEC8. Also I entered o2(g) correctly into GWB, the files are much more comparable.

LS

12/7/06

The original Phreeqc evaporation problem also looked at redox. I tried various was of entering in the Nitrogen species (convert all to NO3+ while allowing redox couple to remain). None of the changes worked.

LS

12/8/06

When using the PHREEQC database and/or altering the Phreeqc input file, an agreement on redox could not be reached. This has something to with the fact in the GWB databases The formula for NH4+ is $\text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} = \text{NH}_4^+ + 2\text{O}_2$. In Phreeqc the formula is $\text{NH}_4^+ = \text{NH}_3 + \text{H}^+$. Also as noted above, GWB has not correctly handled redox in the other examples, unless a specific pE was entered. This problem specifies pH and only one of the two variables can be specified.

LS

3/20/07

Last week my GWB program was re-installed, however when I ran the unaltered file for the Pitzer problem given to me from Bobby P, it still failed to converge. The only changed made was the path to the database, but the same one was used.

LS

3/20/07

Bobby P sent me his version of the Pitzer file and using the proper database, the file still did not converge.

LS

3/28/07

I transferred a untouched version of Bobby's pitzer file to Jim Myers computer and still was unable to run the file using the thermo_hmw.dat. However, when I ran it using the thermo.dat file it converged, but unable to handle the high ionic strengths.

LS

4/2/07

I ended up redoing some of the validation files, because using the swap function some files worked out better. Also, some of the Phreeqc 2.12..5 example files were rerun with the phreeqc.dat database. Initially I had pulled the data from the validation of that version, which had used a specific database other than phreeqc.dat. All the checked Phreeqc validation files that will be used were put into a separate folder and the unused trial files are in separate folders and all files will be included with this notebook on a cd.

For the GWB validation files, the evaporation of rain water was redone. The script was changed and the database used. This was a closer set up to Phreeqc which was also modified to specify NO₃⁻ and NH₄⁺ for N(5) and N(-3). Various alternatives were tried with turning of certain redox couples and using the thermo.v8 database. With the GWB program if specific redox couples were turned off all N species were converted to either N₂ or NO₃⁻. The script below gave the best results.

```
# React script, saved Mon Apr 02 2007 by Isabido
data = "c:\program files\gwb\gtdata\thermo.dat" verify
temperature = 25
swap CO2(g) for HCO3-
swap NH4+ for O2(aq)
1 kg H2O
-3.5 log fugacity CO2(g)
.384 mg/l Ca++
.043 mg/l Mg++
.141 mg/l Na+
.036 mg/l K+
.236 mg/l Cl-
4.5 pH
1.3 mg/l SO4--
.237 mg/l NO3-
.208 mg/l NH4+
balance off
react -52.73 mol of H2O
printout species = long minerals = long
```

I tried to work out part two of the evaporation problem by multiplying the results of part one by 20 to show the water mass would return to 1kg, the moles of each element would be 20x greater and the concentrations would remain the same. I was unable to achieve this, only because I'm not sure how to enter it into the react program.

At the end of part one GWB predicted 1.535e-005 moles of nitrogen and log (f) of N2(g) -0.807 and the molality of N species as N2(aq) 0.0001019 and NH4+ 1.03E-04 and NH3 8.685e-011 and NH4SO4- 1.880e-007 . GWB lists the moles and mg/kg of Nitrogen in fluid are 1.535e-005 4.296

However the moles don't add up. SO there must be free N(0).

Phreeqc reports the same values (NH4SO4) off a bit, but phreeqc reports 1.535e-005 moles of nitrogen element and gives the total N(0) 2.038e-004 molality Attributing to N2 1.019e-004. So the rest of N(0)? Total Nitrogen is 3.07e-4 mol/l and 1.535e-005 moles but the Distribution only reports only 2.05e-4 mol/kg a difference of 1.02e-4? The molality and moles of N element are N 3.070e-004, 1.535e-005 so this is 4.296 mg/kg.

For step 2 in GWB I reacted the outcome (seen in the 4aevaprainwater excel file) I took the moles of the elements *19 (because the 20 solution is initial) and entered the actual chemistry output to part 1, this made a 20 fold solution with a water mass of 1kg. The moles of each element should be 20xs the initial moles, but the concentrations of the species should remain the same. I can not get this to work, all mole values worked out for the elements except N, with a few changes all work except H and O are doubled (see 4aevaprainwater spreadsheet).

```
# React script, saved Mon Apr 02 2007 by Isabido
data = "c:\program files\gwb\gtdata\thermo.dat" verify
temperature = 25
swap CO2(g) for HCO3-
swap N2(aq) for NO3-
.05 kg H2O
-2.194 log fugacity CO2(g)
-64 log activity O2(aq)
.000191 molality Ca++
3.53e-5 molality Mg++
.000123 molality Na+
1.84e-5 molality K+
.000133 molality Cl-
.000623 molality H+
.00027 molality SO4--
.000168 molality N2(aq)
balance off
react .95 kg of H2O
react .000182 mol of Ca++
react 3.36e-5 mol of Mg++
react .000117 mol of Na+
react 1.75e-5 mol of K+
react .000126 mol of Cl-
react .000257 mol of SO4--
react .000292 mol of N2(aq)
react .000215 mol of CO3--
printout species = long minerals = long
```

LS

4/3/07

The data from the last run (see script above) was pulled into tables in the excel spreadsheet. The total element moles match (what they should be), but the concentrations are off, mainly the CO2 may be incorrectly entered. Also the moles of Nitrate when entered as N2 are divided in half (react pane).

```
# React script, saved Tue Apr 03 2007 by Isa
data = "c:\program files\gwb\gtdata\thermo.d
temperature = 25
swap CO2(g) for HCO3-
swap NH4+ for NO3-
swap N2(aq) for O2(aq)
.05 kg H2O
-2.194 log fugacity CO2(g)
.000103 molality NH4+
.000102 molality N2(aq)
.000191 molality Ca++
3.53e-5 molality Mg++
.000123 molality Na+
1.84e-5 molality K+
.000133 molality Cl-
.000623 molality H+
.00027 molality SO4--
balance off
react .95 kg of H2O
react .000182 mol of Ca++
react 3.36e-5 mol of Mg++
react .000117 mol of Na+
react 1.75e-5 mol of K+
react .000126 mol of Cl-
react .000257 mol of SO4--
react .000146 mol of N2(aq)
react .000215 mol of CO3--
printout species = long minerals = long
```

Carbonate is still supersaturated, concentrations off. I then unswapped HCO3 and CO2, no better. I reacted HCO3 instead of Co3 because it was a greater concentration of Carbon. This was an Improvement, so I changed the reactant to CO2

```
# React script, saved Tue Apr 03 2007 by Isabido
data = "c:\program files\gwb\gtdata\thermo.dat" verify
temperature = 25
swap NH4+ for NO3-
swap N2(aq) for O2(aq)
swap CO2(aq) for HCO3-
.05 kg H2O
.000103 molality NH4+
.000102 molality N2(aq)
.000191 molality Ca++
3.53e-5 molality Mg++
.000123 molality Na+
```

```

1.84e-5 molality K+
.000133 molality Cl-
.000623 molality H+
.00027 molality SO4--
.000226 molality CO2(aq)
balance off
react .95 kg of H2O
react .000182 mol of Ca++
react 3.36e-5 mol of Mg++
react .000117 mol of Na+
react 1.75e-5 mol of K+
react .000126 mol of Cl-
react .000257 mol of SO4--
react .000146 mol of N2(aq)
react .000215 mol of CO2(aq)
printout species = long minerals = long

```

This is a big improvement now that I have the correct values in for Carbon, however the SI of the minerals are off, possibly due to so4. The CaSO4 in solution 3 is higher than it should be and the HCO3 is an order of magnitude higher than it should be.

Basically the file repeats the same as Phreeqc, I'm sure its how I'm entering the problem. If I can't fine tune it enough to create a table, I'll scrap it.
LS

4/4/07

Evaporation part 2, put all Nitrogen (reported as moles) and entered it as NH4+

```

# React script, saved Thu Apr 05 2007 by Isabido
data = "C:\Program Files\Gwb\Gtdata\thermo.dat" verify
temperature = 25
swap NH4+ for NO3-
swap e- for O2(aq)
swap CO2(aq) for HCO3-
.05 kg H2O
.000256 molality NH4+
1.5192 pe
.000226 molality CO2(aq)
.000191 molality Ca++
3.53e-5 molality Mg++
.000123 molality Na+
1.84e-5 molality K+
.000133 molality Cl-
.000636 molality H+
.00027 molality SO4--
balance off
react .95 kg of H2O
react .000182 mol of Ca++
react 3.36e-5 mol of Mg++
react .000117 mol of Na+
react 1.75e-5 mol of K+

```

```
react .000126 mol of Cl-
react .000257 mol of SO4--
react .000146 mol of N2(aq)
react .000215 mol of CO2(aq)
printout species = long minerals = lon
```

This did improve the results, however moles/L of nitrogen species still off, I tried entering Nitrogen in both the react and basis pane while turning off various redox couples. This made the results worse.

**The pitzer problem worked with my hmw database and my file. I had to decrease the time step to .0001 for delxi
LS

4/5/07

I multiplied the moles of elements in sol 2, and added that to the react pane and all species in the basis pane had a conc 1e-10, pe specified. I tried with basis water mass of .01 and 0.05, this gives me almost the exact same results as yesterday.

```
# React script, saved Thu Apr 05 2007 by Isabido
data = "C:\Program Files\Gwb\Gtdata\thermo.dat" verify
temperature = 25
swap CO3-- for HCO3-
.01 kg H2O
1e-10 mg/l O2(aq)
1e-10 mg/l CO3--
1e-10 mg/l NO3-
1e-10 mg/l Ca++
1e-10 mg/l Mg++
1e-10 mg/l Na+
1e-10 mg/l K+
1e-10 mg/l Cl-
1e-10 mg/l H+
1e-10 mg/l SO4--
balance off
react .95 kg of H2O
react .000192 mol of Ca++
react 3.54e-5 mol of Mg++
react .000123 mol of Na+
react 1.84e-5 mol of K+
react .000133 mol of Cl-
react .000271 mol of SO4--
react .000154 mol of N2(aq)
react .000226 mol of CO2(aq)
kinetic redox-1
printout species = long minerals = long
```

I see in the react pane, you can specify the kinetic redox reaction, I will look that up to see if that's the problem.

LS

4/6/07

The redox couple is not the problem if solution 2 of GWB and Phreeqc predict the same. I tried to fix pe, and specify pH as concentration of H+. I then tried to specify fugacity of O₂, and enter a pH, both options made the results worse. The results improved by specifying NH₄ for all nitrogen with a 3.07e-4 concentration and H+ as molality and reporting the pE. However the Nitrogen concentrations for solution 3 are still off, but the moles of each element are ok, the SI of gyp, cal, dol are also slightly off.

LS

4/9/07

I specified pH and pE in the basis pane then fixed them in the reactant pane. When reacting the .95 kg of water, it was reacting a pure water with a pH of 7, this is what was throwing the nitrogen concentrations off, the distribution of nitrogen wasn't being preserved. This was added to the report and the validation was handed in.

LS

ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK NO. 826E

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GEOSCIENCES AND ENGINEERING DIVISION

SCIENTIFIC NOTEBOOK REVIEW CHECKLIST RECORD

Scientific Notebook No. 826 E Project Numbers: 20. 06002. 01-222

Accomplished

- 1. Initial entries per QAP-001
- 2. Dating of entries
- 3. Corrections (crossed out, one line through w/initials/date)
- 4. No White out used
- 5. Page number visible on copy or original notebook
- 6. In process entries per QAP-001
- 7. Figure information present
- 8. Text readable
- N/A 9. Copyrighted material is identified
- 10. Permanent ink or type only
- 11. Signing of entries (not required on each page)
- 12. Electronic media in the scientific notebook properly labeled
- 13. NRC Supplementary Scientific Notebook Questions are addressed.
- 14. The independent, two person verification required by AP-019, Section 5.2.1.2(b) is complete

Any discrepancies must be resolved before notebook closeout.

I have reviewed this scientific notebook and find it in agreement with QAP-001.

E. C. [Signature]
Manager's Signature

7/2/2007
Date

Attach this completed form to the last page of the notebook.