

Chapter 11 Problems

1. Explain why coexisting nepheline and albite are said to “buffer” the concentration of silica in a coexisting solution.
2. This exercise will illustrate how PHREEQC handles input data with respect to the Phase Rule, in contrast to EQ3/6 and The Geochemist’s Workbench (program REACT). To do this we will consider an aqueous solution containing K, Al and Si, and then equilibrate this solution first with one mineral, then with two, three and four minerals, and observe what happens at each step.

- (a) Prepare an input file for PHREEQC with the following in mind. We want an aqueous solution at 25°C, 1 bar, containing K, Al and Si, but which is undersaturated with all possible minerals which might form from these elements. This can be accomplished using a concentration of 0.01 micro-moles/kg (giving 10^{-8} molal) for each element. In PHREEQC input, this is called SOLUTION 1.

Your input file should look something like this (spacing is unimportant):

```
TITLE Illustrating the Phase Rule
SOLUTION 1
      units      umol/kgw
      temp       25.
      pH         7.
      Si         .01
      Al         .01
      K          .01
END
```

(Note: The TITLE is optional, but it is good practice to use one. Also temp and pH are the default values, so they are optional too, but again it is good to put them in for clarity.)

- (b) Run PHREEQC using this input file, and look at the output. Satisfy yourself that everything is as it should be. The solution is undersaturated with all minerals, and the pH is 7.
- (c) Add Gibbsite (must be spelled exactly as it is in PHREEQC.DAT, with capitalization) as an EQUILIBRIUM_PHASE. Use a target Saturation Index of 0.0 and any number of moles. If you leave the number of moles blank, 10 moles is assumed. Look at the example problems in the PHREEQC documentation if you are puzzled as to how to do this.
- (d) In the output, note that Gibbsite is now saturated, the pH is different (charge balanced), and the total aqueous Al is now not 0.01 μ moles, but is fixed by the presence of Gibbsite.
- (e) Add Quartz as a second EQUILIBRIUM_PHASE, target SI 0.0. Run PHREEQC.

- (f) In the output, note that now both minerals are saturated, the pH is different (why only slightly?) and now the concentrations of both Al and Si are fixed. Also note that this is a metastable equilibrium. Gibbsite and quartz should react to form kaolinite, but PHREEQC does not know about kaolinite unless you tell it.
- (g) Add K-mica as a third EQUILIBRIUM_PHASE. Run PHREEQC.
- (h) In the output, note that now all three minerals are saturated, the pH is much different (why?) and all three elements are fixed.
- (i) Add K-feldspar as a fourth EQUILIBRIUM_PHASE. Use the Phase Rule to show that you should be expecting some kind of problem now. You should not be able to equilibrate four minerals with water (five phases) in this four component system at a given T and P . What is PHREEQC going to do? Run it and find out.
- (j) You see that PHREEQC does not crash, or even complain. It simply equilibrates the water with three minerals, and undersaturates the fourth one, in spite of your instructions about having four equilibrium minerals. The question is, how does PHREEQC decide which mineral to undersaturate?

Run the same problem using EQ3/6 and REACT from The Geochemist's Workbench™.

It is interesting to compare the results of various programs for various problems. A solution buffered by K-spar, K-mica and quartz at 25°C, 1 bar is a good example. The results for three programs are as follows (you should have the same PHREEQC results from the last run above).

Total molal element concentration and pH	PHREEQC	EQ3/6	REACT
K	3.981e-3	7.4046e-5	3.667e-5
Al	6.731e-7	7.2673e-8	1.914e-7
Si	2.510e-3	2.2105e-4	1.193e-4
pH	11.158	8.9277	9.231

Table 1: The composition of a solution buffered by microcline, muscovite and quartz. PHREEQC results are for database phreeqc.dat. Different results are obtained using llnl.dat.

After a few comparisons like this, you give up the idea of knowing anything *exactly*.