Computational Chemical Equilibrium Model: MINTEQA (Minimization of Total Equilibrium Activity) for Solving Complex Aqueous Equilibrium Problems

The following problems are based on the class-lecture and demonstration of a computational chemical equilibrium program. These are simple problems that should be understood on the basis of known reactions and the model outcome is generally predictable. The purpose of this exercise is to introduce MINTEQA as a tool to solve much more complex and practical problems in geochemistry and environmental chemistry. Start with the tutorial to guide you through solving these problems.

Problem 1

Compute the pH of pure water in equilibrium with atmospheric CO_2(g). Find the concentration of all the species in solution. Explain the pH based on the nature of the species.

Problem 2

Natural groundwater has Ca^{2+} and CO_3^{2-} as the major components and closed to atmospheric CO_2. Reset and start new, select and enter 0.005 molal each of Ca^{2+} and CO_3^{2-}. Find the pH and concentrations of all the species in solution. Identify and write the chemical composition of the solid minerals formed from the saturation indices (SI). Why only some of the minerals are precipitated?

Problem 3

Run problem 2 with pH 2, 3, 4…12 by utilizing the 'Multi-problem/ Sweep' option of the program. Gather selected sweep results for H_2CO_3(aq), HCO_3^-, CO_3^{2-}, and Ca^{2+} in spread-sheet and plot the log(concentration) vs. pH. Also, record the CO_2(g) pressure as a function of pH. Explain the plot in chemical terms. Why Ca^{2+} has barely changed? Find the $K_{a1 \text{ and } a2}$ for carbonic acid from the plot. Record the minerals precipitated at different pH values. At what pH the minerals start to precipitate?

Problem 4

Arsenic is the 20th abundant element in earth's crust and a known carcinogen. Under certain geochemical redox conditions arsenic is mobilized by dissolution in groundwater. The presence of toxic levels of arsenic (> 50 ppb or ug/L) in groundwater used for drinking is a major public health concern worldwide.

One way to remove arsenic from groundwater is to treat water with dilute $FeCl_3$ and let it precipitate. Assume that arsenic in groundwater is present as its soluble salt at 1.0 x 10^{-6} molal Na_3AsO_4 and 2.0 x 10^{-4} molal $FeCl_3$ is added to it, find if arsenic can be removed by precipitation by using the MINTEQA model. Enter the following as components:

Components	Concentration (molal)
AsO_4^{3-}	1.0 x 10^{-6} (write 1e-6)
Na^+	3.0 x 10^{-6} (write 3e-6)
Fe^{3+}	2.0 x 10^{-4} (write 2e-4)
Cl^-	6.0 x 10^{-4} (write 6e-4)

a) Identify all the species. Write pertinent reactions for the formation of Fe containing species. Explain why the pH has decreased to the acidic side.
b) Did the free concentration of arsenic species (total soluble arsenic) decrease to less than 50 ug/L? How about free iron concentration? Check the SI indices and find which minerals are precipitated.
c) Run the same program with a fixed pH =7 (more palatable) and examine the concentration of total free arsenic. Propose a mechanism by which arsenic species is decreased to a safe level. Could this be modeled by MINTEQA?

A Short MINTEQA Tutorial

1. Open MINTEQA
2. Run MINTEQA without inputs. MINTRUN window appears. After few iterations, click OK. The OUTPUT window shows with species concentrations, pH, charge balance etc. The pH value should be 6.998. It shows that the default solvent pure water.
3. Go BACK TO INPUT MENU, click GASES on the top menu bar, click SPECIFY GASES, and click ADD. Accept the defaults. CO_2 is added at 1 atm. This is equivalent to exposing water to air atmosphere containing CO_2. Click BACK TO MAIN MENU, then click VIEW EDIT/LIST. CO_3^{2-} is shown as a component. Press RUN.
4. Compare the pH with that of the homework problem.
5. Reset and start a new worksheet. Enter the following:

   Click COMPONENT NAME Ca^{2+}
   Enter TOTAL CONCENTRATION 0.005 MOLAL

Click ADD TO LIST

This is how you enter components and concentrations. Do the same for CO_3^{2-}.

6. Press RUN. Find species, concentration, SI, and minerals precipitated. You have solved problem 2.
7. For problem 3, click MULTIPROBLEM/ SWEEP in top menu bar. Activate SWEEP - ONLY ONE COMPONENT VARIED. Enter 10 in STATE THE NUMBER OF PROBLEMS. Click pH under SWEEP COMPONENT. Select START VALUE 2 and INCREMENT 1. In the third block (the bottom part) select ADD COMPONENT/ SPECIES TYPE and select from the drop-down menu: Click Ca^{2+}, Click CONCENTRATION, Click ADD. Do the same for H_2CO_3, HCO_3^-, and CO_3^{2-}. Click SAVE AND BACK. RUN. Click SELECTED SWEEP RESULTS and click PRESS TO EXCEL. Plot log of species concentrations. An example plot is shown here.