This exercise considers the evolution of the chemical composition of water as it travels from rain into groundwater.

1. Assume that rainwater is distilled water in equilibrium with the atmosphere at $P_{CO_2} = 10^{-3.5}$ atm. List the pH and the concentration of all chemical species present (i.e., $H^+$, $OH^-$ and the various carbonate species.) Recall that you can get the carbonic acid concentration $[H_2CO_3]$ from the $P_{CO_2}$ by multiplying $P_{CO_2}$ by Henry’s Law constant of $10^{-1.5}$ M/atm. What is the speciation of rainwater at 25 degrees C?

2. When the rain penetrates the soil it comes into equilibrium with soil vapor $P_{CO_2}$ which, due to root and microbe respiration, has a higher $P_{CO_2} = 10^{-1.5}$ atm. Assume no other chemical reactions occur in the shallow soil zone. List the pH and the concentration of all chemical species present at 25 degrees C. Re-calculate the problem for the more realistic, cooler soil temperature of 15 degrees C. What is the percent difference in each species concentration at the cooler temperature.

3. The soil water percolates down into a limestone formation where the water can be assumed to equilibrate with calcite at 12 degrees C. Assume the $P_{CO_2}$ is still at the soil value of $10^{-1.5}$ atm. What is the total speciation of the water? Highlight the major species that account for about 90% or more of each component. (For example, what are the important Ca species compare to the very minor Ca species).

4. The hardness of water is defined as the total of all the divalent metal cations present, expressed in meq/L. In this system, Ca$^{2+}$ is the only divalent cation, but it may occur in several soluble species. What is the hardness of the groundwater in question 3, in meq/L?

5. Suppose the groundwater is pumped to the surface and used for a domestic water supply. Furthermore, assume that in a water heater at 70 degrees C, essentially all of the hardness precipitates out as CaCO$_3$ (calcite). If the house uses 100 gallons of hot water per day, how many mg of CaCO$_3$ precipitates inside the water heater each day? How much calcite will precipitate in one year?

   **NOTE:** This is just a simple mass balance problem, and does not require the use of Vismint or any other equilibrium calculations, because you assume 100% precipitation of calcite from the water.