Problem Set 1.
12.741 2022

Part 1: Chemical Speciation

Ocean acidification is an emerging environmental problem with largely unknown impacts on marine biogeochemistry, ecology, and biochemistry. Estimates predict decreases in pH in the range of several tenths of a pH unit, which being on a log scale reflects a considerable change in proton abundance. The influence of ocean acidification marine bioinorganic chemistry can be complex due to complexation chemistry. Here we will calculate the influence of pH on the speciation of iron and zinc. While we do not yet know the structure and acid-base constants for natural ligands in seawater, we can use EDTA as a model ligand.

1. Write the equation for inorganic speciation of ferric iron (Fe(III)) at pH 8.1 and pH 7.3, using abundant major inorganic species for iron in seawater as listed in Table 6.3 of Morel and Hering (ignore solid phases), and using the seawater concentrations of abundant ions provided in class (also page 291 of Morel and Hering). Use a total iron concentration of 200pM. Calculate the concentrations and percentages contribution of the iron chemical species and Fe'. You can ignore organic complexes and ionic strength corrections for this problem. Show your handwritten calculations and equations.

2. Iron has an unusual inorganic speciation relative to other metals. Repeat question 1 for zinc at 1nM.

3. For the iron question in part 1, incorporate the EDTA complexes with a total EDTA of 10μM, and seawater Ca and Mg abundances. Estimate the concentration of Fe' at pH 8.1 and 7.3.

4. Work up problems #1 and #3 in Visual Minteq and make plots of Fe^{3+} and and Fe' from pH 4 to 10 (0.5 unit resolution is sufficient). Incorporate seawater's major ions for ionic strength correction. Describe what is happening in each system in a few sentences. Then incorporate iron solid phases into the problem (using the possible solids function) at pH 8, first ferrihydrite then add aged ferrihydrite. What percentage of the iron remains in solution in each case? Which solubility product constant is the "more accurate" one to use (if either)? You can use Visual Minteq's sweep function or conduct single runs and plot up in Excel. Visual minteq available at: http://vminteq.lwr.kth.se/ and will run on Windows and Windows emulators for Macs.

Part 2: Orbital Geometries

A. Draw all five of the d orbitals. Please include where they sit along the x, y, z plane

B. Draw the coordination chemistry for the following geometries. Include the bond angle.

a. Trigonal planar
b. Square planar
c. Tetrahedral
d. Octahedral

C. Below are three compounds

1. $[Zn(H_2O)_6]^{2+}$
2. $CoCl_4^{2-}$
3. $Ni(CN)_4^{2-}$

For each compound, do the following:

a. Give the coordination geometry

b. Give the oxidation state of the central metal

c. Give the d electron count

d. Note whether the ligand is a strong or weak ligand

e. Draw the field splitting diagrams and provide a rationale for orbital placement

Hint: Pay special attention to whether the ligand is strong or weak as that will help you to place the electrons in the correct orbitals

f. Note whether the compound is paramagnetic or diamagnetic.