CHEM 105 – Sample Comprehensive Problems for Extra Credit – Due by 5 PM Thurs., December 5, 2019

A. Carbonic Acid and Blood pH

Carbonic acid is formed from the reaction of carbon dioxide and water and has important effects on pH in aqueous solutions, including our bodily fluids.

1. Carbonic acid is a diprotic acid (containing two H^+ ions) related to the carbonate ion.
    a. Please draw the best Lewis structure(s) for carbonate, indicating the formal charge on each atom.
    b. Based on your structure(s) and formal charges above, show where the two H^+ ions bond to carbonate to form carbonic acid. Consider formal charges again to justify your proposed structure.

2. Please write and balance a chemical reaction for the formation of aqueous carbonic acid from liquid water and gaseous carbon dioxide. Then, please determine oxidation numbers for each atom. Is this an oxidation-reduction reaction? If so, identify what is oxidized and what is reduced.

3. Is your reaction in Question 2 above spontaneous under standard conditions? (Show your work. You will need values from Appendix 4; in addition, the standard Gibbs free energy of formation for aqueous carbonic acid is -699.65 kJ/mol.)

4. As a weak, diprotic acid, carbonic acid undergoes two successive acid-ionization reactions, each involving transfer of one proton. Please write these two reactions, and write expressions for the two K_a values, Ka_1 and Ka_2.

5. You can find numeric values for the K_a's in Question 4 in Appendix 5. Given the value of Ka_1:
    a. Do reactants or products dominate at equilibrium?
    b. Please calculate ΔG° for this acid-ionization step (i.e., for the donation of the first proton by carbonic acid).

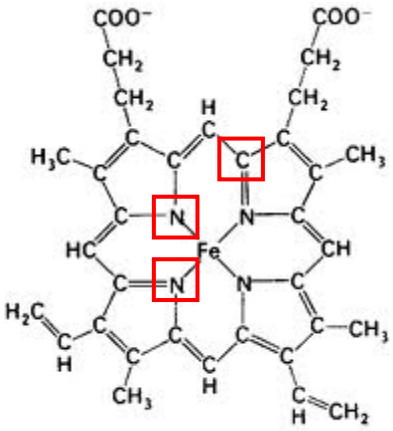
6. The reactions described above form a set of equilibria that maintain physiological pH very near 7.40.
    a. Given the pH value above, what is the normal molar concentration of H_3O^+ in the blood?
    b. Write the reactions for formation of carbonic acid (from Question 2) and the first acid-ionization of carbonic acid (from Question 4) as two joined equilibria. (You should have two sets of equilibrium arrows, with carbonic acid in the middle, as it is simultaneously the product of one reaction and the reactant of the other. See below.)

        water and carbon dioxide $\rightleftharpoons$ carbonic acid $\rightleftharpoons$ products of first acid ionization

    c. If someone is having difficulty breathing, the concentration of dissolved carbon dioxide increases; if this situation is prolonged, it results in a condition called respiratory acidosis – a decrease of physiological pH. Use the equilibria from part (b) and your understanding of Le Chatelier's Principle to explain this phenomenon.

B. Hemoglobin and Oxygen Transport

Oxygen transport by the protein hemoglobin is also linked to blood pH, and controlled by an equilibrium. Hemoglobin consists of four identical subunits, each of which contains a heme group (shown below), with an iron(II) ion surrounded by what is called a porphyrin ring. Each of the four iron ions can bind one oxygen molecule.



Heme
(Fe-protoporphyrin IX)

7. Write the ground-state electron configuration for iron(II) and give the orbital "box" diagram.

8. For each of the atoms in boxes above, please determine the following. [**Note:** This structure does not show lone pairs. Before you answer these questions, you'll need to consider whether there are any nonbonding electrons on these atoms.]
   a. The estimated bond angles around the atom
   b. The type of hybrid orbitals it will use in bonding

9. When oxygen is bound to the iron ion, it has a steric number of six, as it is also bonded to an amino acid in the protein (not shown above). Name and sketch the predicted geometry for the iron, and estimate the bond angles.

10. Heme gives (oxygenated) blood its red color, due to strong absorbance of visible light near 420 nm. What is the energy (in Joules) of a photon with this wavelength?

11. The equilibrium that controls oxygen transport is shown below. Four hemoglobin subunits (Hb) each bind one molecule of oxygen.

$$4\ Hb + 4\ O_2 \rightleftharpoons 4\ Hb\text{-}O_2$$

Use your understanding of Le Chatelier's Principle to explain how O_2 transport works: why does hemoglobin bind oxygen in the lungs and release it in the tissues of your body?