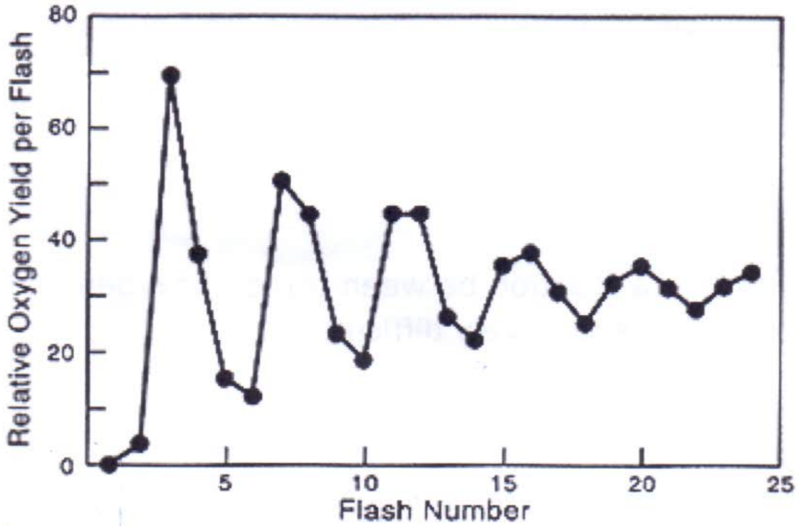
Bioinorganic Calalysis

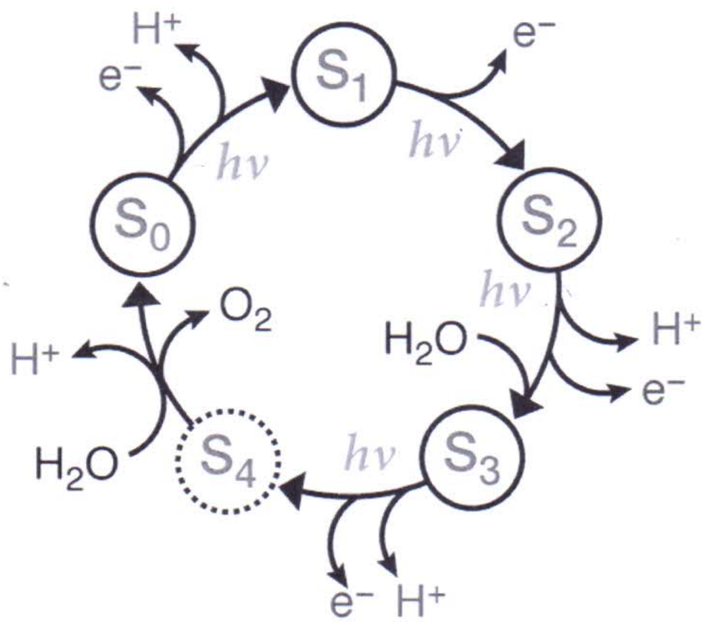
EXAM

This exam consists out of 5 problems and 6 pages. ***Write your name and student number on every page containing answers.*** *It is not allowed to use your notes, books, mobile phone, etc. Read the questions carefully before you answer them. Answer the question precisely, make sure your answer is complete, and clearly indicate how you got to your answer. When a justification is asked, it counts as least as many points as the answer itself. If your argumentation contains a lot of nonsense besides the correct answer points will be deducted. The number of points (total = 90) is indicative and may be re-evaluated.*

1) Explain why a reaction between triplet dioxygen and a diamagnetic metal center is relatively difficult. – *5 points*

2) Given below is a photochemical experiment wherein photosystem II is irradiated with very short and very intense light flashes that allow exclusively for one-electron oxidation of the oxygen evolving center. On the x-axis the number of flashes is depicted. On the y-axis the relative amount of oxygen that is formed is depicted. Based on the figure below assign which of the S-states in the Kok cycle is the resting state. Explain your answer. *- 5 points*

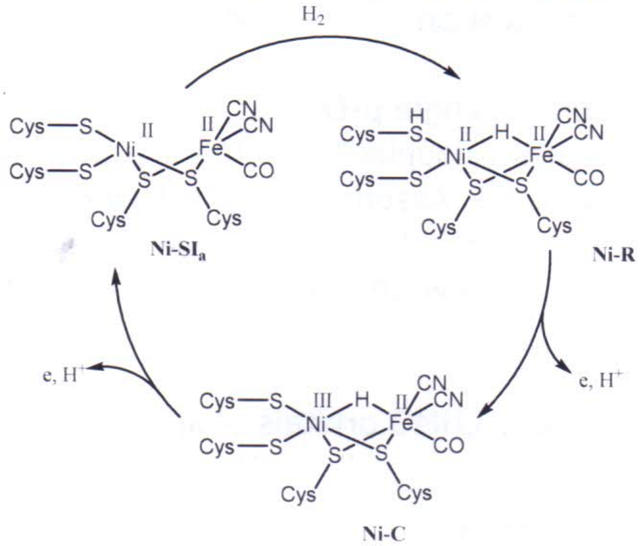




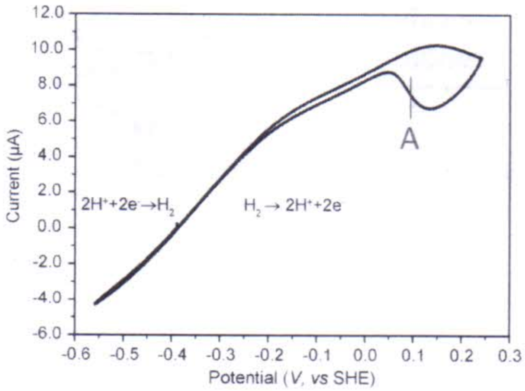
3) [NiFe] Hydrogenases comprise a large family of enzymes that catalyze the oxidation of dihydrogen as illustrated in the scheme below. Some variants of [NiFe] Hydrogenases are tolerant to small amounts of dioxygen.

a. What is the most important structural difference between oxygen tolerant [NiFe] Hydrogenases and regular [NiFe] Hydrogenases? What is the advantage of this structural difference? Why/how is this important? – *5 points*

b. Describe (you may use words) the reaction path how dioxygen reacts with the oxygen tolerant [NiFe] Hydrogenase and how it is eventually removed to regenerate any of the catalytic species **Ni-SIa**, **Ni-R** or **Ni-C**.– *8 points*



c. In the figure below is given the cyclic voltammetry diagram of a hydrogenase. Explain the general shape of the voltammogram and in particular feature A. – *7 points*



4) The dinuclear diiron complex **A** is a precursor for the mononuclear water oxidation catalyst **B**. Both **A** and **B** are depicted below.

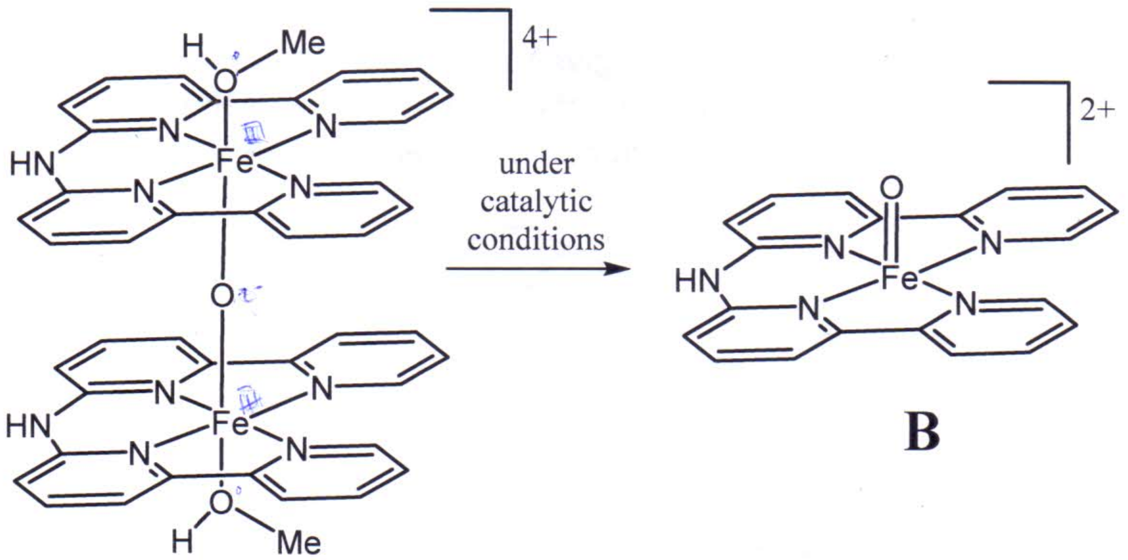
a. Give the crystal field splitting of the mononuclear Fe=O species **B**. Give the proper labeling of all orbitals. What is the bond order of the Fe-O bond? Does the Fe-O bond have radical character? – *10 points*

b. In the water oxidation reaction a kinetic isotope effect of $k(H_2O)/k(D_2O)=3.5$ is found. Give a possible reason for this kinetic isotope effect and propose a reasonable mechanism for the O-O bond formation step. – *5 points*

c. Describe another experiment that could support or disprove the hypothesis for the O-O bond formation that you provided in the answer of question 4b). – *5 points*

d. Metal centers with a single μ-O bridge are often antiferromagnetically coupled. Give the crystal field splitting diagram for species **A**. Assume that Δ is large and that the Fe-O-Fe interaction is ionic. What is the spin state (S) of the dinuclear species **A**? Give the proper labels for all orbitals. – *10 points*

e. Draw the HOMO and LUMO orbitals of species **A**. – *5 points*



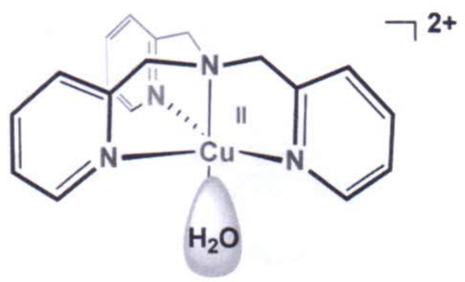
A

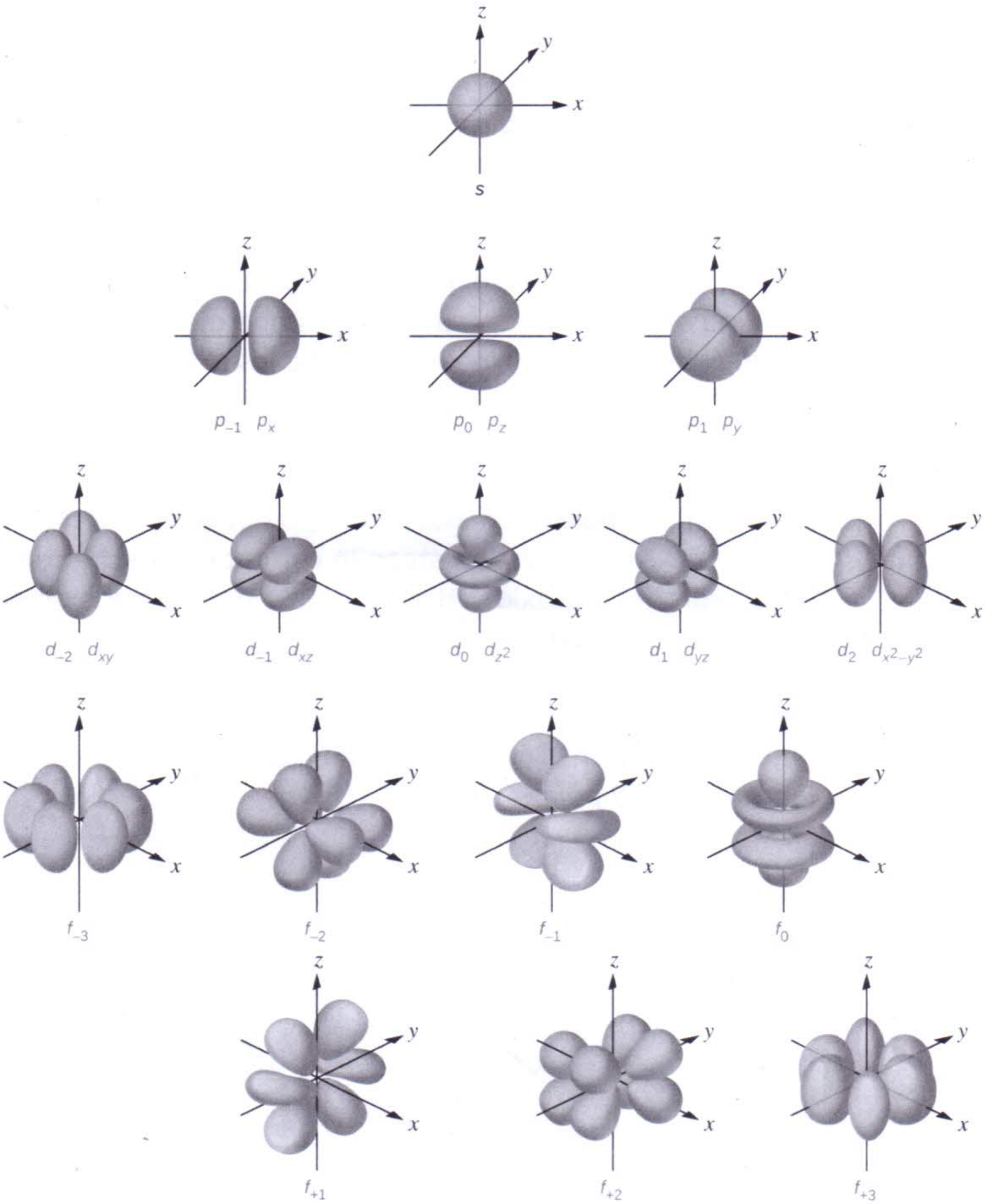
5) The $[Cu(tpa)(OH_2)]^{2+}$ complex depicted below is capable of reducing dihydrogen peroxide in an electrochemical reaction. The reaction was found to be second order in copper(II) and first order in H_2O_2.

a. Give a reasonable mechanism for the reduction of peroxide. You may only move one proton and one electron at the same time. Note that dihydrogen peroxide loses both its protons when it coordinates to copper before any redox reaction occurs. – *8 points*

b. The same complex can also reduce dioxygen via a mechanism that has several reaction steps in common with the reduction of dihydrogen peroxide. How do you envision the oxygen reduction reaction to occur? – *7 points*

c. Give the oxidation states of Cu <u>and</u> O for all catalytic intermediates that take part in the reaction mechanisms of 4a) and 4b). – *10 points*




s
p−1 px
p0 pz
p1 py
d−2 dxy
d−1 dxz
d0 dz2
d1 dyz
d2 dx2−y2
f−3
f−2
f−1
f0
f+1
f+2
f+3