1. Define or explain of the following:

12% (a) Zeeman effect (b). Configuration interaction

(c). Quantum yield (d). Standard hydrogen electrode

2. Determine the point group of the following:

8% (a) NO_2^- (b) CO_3^{-2} (c) PCl_3F_2 (d) $NiCl_4^{-2}$

3. The charge-to-mass (e/m) ratio of the proton, H^+, is 9.65×10^4 coulomb/g.

5% The proton has a charge equal to 1.60×10^{-19} coulomb. Calculate the value of Avogadros' number.

4. A beam of electrons is accelerated through a potential difference

8% of 8000 V. Calculate the energy, the speed, the linear momentum, and the wavelength of these electrons.

($h = 6.63\times10^{-34}$ J·s, mass of electron $= 9.11\times10^{-31}$ kg, $1\,eV = 1.60\times10^{-19}$ J)

5. Sketch the radial distribution functions for the 3S, 3p, and

6% 3d electrons of hydrogen. Label the axes clearly.

6. Given three hybrid orbitals, as follows:

$\Psi_1 = \sqrt{\frac{2}{5}}\psi_s + \sqrt{\frac{3}{5}}\psi_{px}$, $\Psi_2 = a_2\psi_s + b_2\psi_{px} + c_2\psi_{py}$, $\Psi_3 = a_3\psi_s + b_3\psi_{px} + c_3\psi_{py}$.

6% (a). Determine a_2, b_2, and c_2 so that Ψ_1 and Ψ_2 will be equivalent and mutually orthogonal.

6% (b). Determine a_3, b_3, and c_3 so as to use up the original atomic orbitals and to make Ψ_3 orthogonal to the other two. Will Ψ_3 then be equivalent to the other two?

7. How can one identify experimentally which electrode in a

4% galvanic cell is the anode and which is the cathode?

8. Write equations for the half-reactions for the oxidation and

4% reduction of water.

9. (a) Calculate the standard potential for

5% $Mn^{++} + 3e^- \rightarrow Mn(s)$

given that

$Mn^{++} + 2e^- \rightarrow Mn(s)$, $E^\circ = -1.19$ V.

$Mn^{+++} + e^- \rightarrow Mn^{++}$, $E^\circ = +1.51$ V.

5% (b) Does Mn^{++} disproportionate in acid solution? Explain.

(c). Given that $Fe^{++} + 2e^- \rightarrow Fe(s)$, $E^\circ = -0.41$ V.

6% $Fe(CN)_6^{-4} + 2e^- \rightarrow Fe(s) + 6CN^-$, $E^\circ = -1.51$ V.

Calculate the equilibrium constant of the reaction

$$Fe^{++} + 6CN^- \rightarrow Fe(CN)_6^{-4}.$$

10. A mechanism proposed for the reaction in which 2-methylpropene, $(CH_3)_2C=CH_2$, is converted to tert-butyl alcohol, $(CH_3)_3COH$, is

8% Step 1 $(CH_3)_2C=CH_2 + H^+ \rightarrow (CH_3)_2\overset{\oplus}{C}-CH_3$ (slow)

Step 2 $(CH_3)_2\overset{\oplus}{C}-CH_3 + H_2O \rightarrow (CH_3)COH + H^+$ (fast)

(a). What is the intermediate species in this mechanism? (b) Is this a catalyzed reaction? If so, what is the catalyst? (c) What is the rate law for this reaction? (d). If the reaction is run in aqueous acidic solution, what will the observed rate law be?

11. The decomposition of dinitrogen pentoxide, $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$, is first order in N_2O_5. The following mechanism has been proposed.

10% Step 1 $N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$ (rapid equilibrium)

Step 2 $NO_2 + NO_3 \xrightarrow{k_2} NO_2 + O_2 + NO$ (slow)

Step 3 $NO + NO_3 \xrightarrow{k_3} 2NO_2$ (fast)

(a) Show that this mechanism is consistent with rate law. (b) If the experimental rate constant equal $5.0 \times 10^{-4}\ s^{-1}$ at a certain temperature, how long does it take for the concentration of N_2O_5 to fall to one tenth its original value at this temperature?

12. The reaction between aqueous thallous and ceric ions in acidic solution, $Tl^+(aq) + 2Ce^{4+}(aq) \rightarrow 2Ce^{3+}(aq) + Tl^{3+}(aq)$, is very slow at

7% room temperature, even though the equilibrium constant is very large. The stoichiometry represents an elementary process. The reaction is catalyzed by Mn^{2+} ion, with the following mechanism:

$$Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$$
$$Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$$
$$Mn^{4+} + Tl^+ \rightarrow Te^{3+} + Mn^{2+}$$

Suggest a reason for the fact that the catalyzed mechanism is faster than the uncatalyzed pathway.