Analytical Chemistry Cumulative Exam

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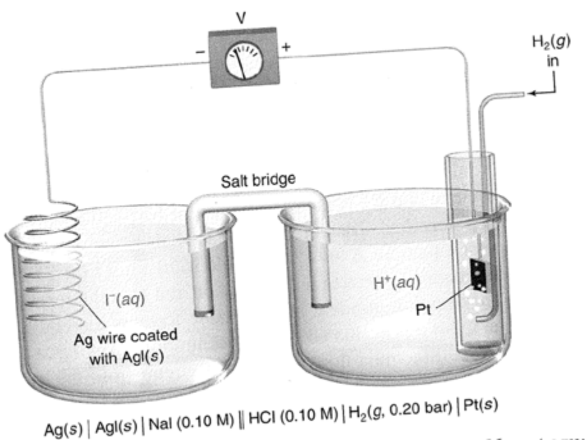
A few rules:

- You may use a calculator for this exam.
- Please read the questions fully and carefully before answering.
- One the critical aspects of a successful scientific article is conciseness. This is your opportunity to prepare. Please explain steps and/or justify your answers ***adequately, but concisely***.
- Please **print legibly!**
- Last but not least, I will borrow two lines,
    - one from Prof. Snee: ***<u>DON'T PANIC!</u>***
    - one from Forest Gump: *Life is like a box of chocolates*.

The questions amount to <u>150 points</u>. The pass line is at <u>80 points</u>.

1) **(20)** At standard conditions, will Cr^{3+} spontaneously reduce to Cr by oxidizing Cu to Cu^{2+}, or will Cu^{2+} spontaneously reduce to Cu by oxidizing Cr to Cr^{3+}? Write the full reaction in the spontaneous direction and calculate ΔE° for a cell made of these species, in equilibrium.

2) Consider the following cell:



The left half reaction can be written as:

$AgI_{(s)} + e^- \leftrightarrow Ag_{(s)} + I^-$ (1)

$Ag^+_{(aq)} + e^- \leftrightarrow Ag_{(s)}$ (2)

The right half reaction is:

$H^+_{(aq)} + e^- \leftrightarrow H_{2(s)}$ (3)

a. **(15)** Using reactions 2 and 3, calculate ΔE^0 and write the Nernst Equation for the cell. Assume the spontaneous direction, and activity coefficients of 1.

b. **(15)** Knowing that K_{sp} (AgI) = 1.5×10^{-16}, you can use equations 2 and 3 to describe this cell. **Compute** $[Ag^+]$ and find the cell voltage. Note the concentrations provided in the footnote of the figure.

c. **(15)** Now let's describe the cell using reactions 1 and 3. The cell voltage should be the same regardless of what reaction we use for $Ag^+_{(aq)}$ to $Ag_{(s)}$. **Write** the Nernst Equation for reactions 1 and 3 and use it to find E^0 for reaction 1. Compare your result with tabulated values.

3) **(15)** The ferricyanide molecule, $[Fe(CN)_6]^{3-}$, shows tremendous (yuge!) chemical versatility. It is a food additive. It is a component of the Prussian blue, a widely used pigment and antidote for heavy metal poisoning. It has also been the object of many electrochemical studies because it is robust and presents rapid kinetics. In fact, in a groundbreaking paper in *Science* in 2015 (volume 349, page 1529), Lin *et al.* report its use as an electrode in a flow battery for applications in grid storage. The redox reaction of this molecule is as follows:

$$[Fe(CN)_6]^{3-} + e^- \leftrightarrow [Fe(CN)_6]^{2-} \qquad E^o = 0.356 \text{ V}$$

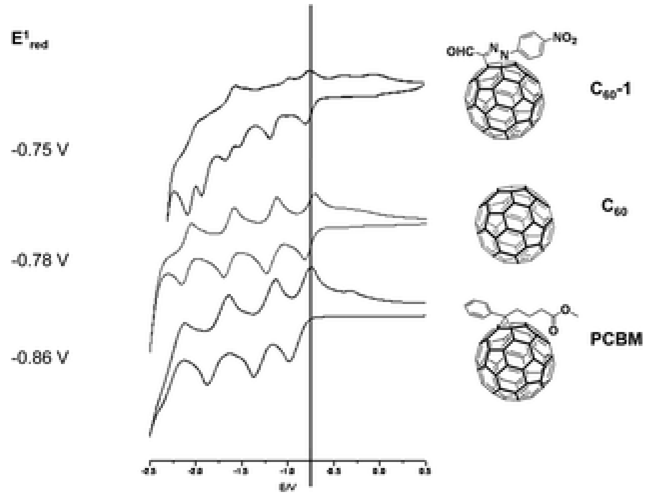
Compare this value with the redox potential of the ferric/ferrous ions only coordinated by water:

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+} \qquad E^o = 0.77 \text{ V}$$

[here, Fe^{3+} is, in reality, $[Fe(H_2O)_6]^{3+}$]

This change in values for the same formal oxidation states of the cations tells you something about their changes in stability by changing ligands. Which ion, Fe(III) or Fe(II), is stabilized more by complexing with CN^-? **Justify** your answer.

4) In a paper in *Energy and Environmental Science* (**2010**, 3, 971), Shoaee *et al.* state that "[t]he observation of efficient photoinduced electron transfer from a semiconducting polymer to a fullerene in blend films has motivated extensive studies of the application of such films for photovoltaic solar energy conversion". To understand these interactions, they probe electron transfer (a.k.a. redox reactions) of a number of fullerene (C_{60}) derivatives with different functional groups using an electrochemical cell. The paper discusses the following graph:



a. **(10)** What is the name of the technique used to produce these data?

b. **(15)** Let's focus on non-functionalized C_{60} (molecule in the middle). How many redox states were detected in this experiment? **Why?**

5) In a paper in *Chemical Communications* (**2010**, 46, 1661), Zhang *et al.* describe the design of a novel battery based on lithium metal and oxygen electrodes, in an aqueous electrolyte at acidic pH. This design is impressive because it uses really cheap materials (Li, O_2, H_2O) to build an energy storage device with twice the capability of a commercial Li-ion battery (yep, the one in your cell phone). The battery is based on the two following half reactions:

$$Li^+ + e^- \leftrightarrow Li \qquad (1)$$

$$1/2O_2 + 2H^+ + 2e^- \leftrightarrow H_2O \qquad (2)$$

a. **(10)** Upon discharge, the battery proceeds in the spontaneous direction. **Write** the overall reaction occurring between the two electrodes in the spontaneous direction.

b. **(15) Explain** whether the thermodynamic potential of the reaction will increase or decrease if the pH is increased (i.e., basic).

Bonus questions (20 pts.)

1) (5) **Name** one speaker in Seminars of the Department of Chemistry during academic year 2016-2017 whose talk had a significant component of research in Analytical Chemistry.
2) (5) **Name** the steps you have to follow when you want to use a fire extinguisher to put out a small fire in your lab.
3) (5) When should you wear safety glasses in a lab?
4) (5) What is Gold Open Access in the context of scientific publishing?

Supplementary Data

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathscr{E}°$ (V)	Half-Reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3-} + e^- \rightarrow Co^{2-}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^- + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Constants:

R = 8.3144598(48) J/mol·K

F = 96500 C/mol e^-