CHM 106
Exam III

1. Suppose we are interested in the following galvanic cell:

$$Ag \mid Ag^{+} \parallel Cr^{3+} \mid Cr$$

a) Write the spontaneous, balanced chemical equation for this reaction.

b) What is the standard cell potential for this reaction? A table of standard reduction potentials is provided at the end of this exam.

c) Suppose the concentration of $[Ag^{+}] = 5.00$ M and the concentration of $[Cr^{3+}] = 1.00$ M. Should the value of $\mathscr{E}$ for this cell be higher or lower than $\mathscr{E}^{0}$? Explain.

d) Calculate the potential of this cell.

2. Acetic acid reacts with thionyl chloride to produce acetyl chloride, hydrogen chloride, and sulfur dioxide:

$$CH_3COOH(l) + SOCl_2(l) \rightarrow CH_3COCl(l) + HCl(g) + SO_2(g)$$

Substance	ΔH_f^0 (kJ / mol)	S^0 (J / mol · K)
$CH_3COOH(l)$	-484.5	159.8
$SOCl_2(l)$	-245.6	309.8
$CH_3COCl(l)$	-273.8	200.8
$HCl(g)$	-92.3	186.9
$SO_2(g)$	-296.8	248.2

a) What is the value of ΔH^0 for this reaction?

b) What is the value for ΔS^0 for this reaction?

c) What is the value for ΔG^0 for this reaction?

d) Is this reaction spontaneous at 25 °C?

e) What is the value of the equilibrium constant for this reaction?

3. Electroplating is an electrochemical technique for depositing a layer of metal on a solid surface. Suppose we are interested in gold plating an object using the following half-reaction:

$$Au^{3+}(aq) + 3e^{-}(aq) \rightarrow Au(s)$$

a) Suppose we plate a large object with 1.50 g Au(*s*). How many moles of electrons does this require?

b) How long does this process take at a current of 5.0 A? Recall that 1 A ≡ 1 C / s.

4. Permanganate reacts with chloride to produce manganese (II) and chlorine in the following unbalanced equation:

$$MnO_4^-(aq) + Cl^-(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g)$$

a) Assign oxidation states to all atoms involved in this reaction.

b) Identify which atom is being oxidized and which atom is being reduced.

c) Identify the oxidizing agent and the reducing agent.

d) Using the method of half-reactions, write a balanced chemical equation for this reaction.

e) What is the standard cell potential for this reaction?

f) Is this reaction spontaneous?

g) What is ΔG^0 for this reaction?

h) Sketch an electrochemical cell for this process. In your sketch, identify the anode, the cathode, and the direction of electron flow.

i) Write the line notation shorthand for this cell.

j) If 0.100 mol of $Cl^-(aq)$ is consumed during the operation of this cell, how many Coulombs of charge pass through the wire?

k) If the discharge in part j occurs over 1.00 hour, how many amperes of current flows through the wire?

5. In the gas phase, oxygen isomerizes to ozone:

$$3\ O_2(g) \rightleftharpoons 2\ O_3(g)$$

Substance	ΔG_f^0 (kJ / mol)
$O_2(g)$	-61.2
$O_3(g)$	163.2

a) What is the value for ΔG^0 for this reaction?

b) Is this reaction spontaneous at 25 °C?

c) What is the value of the equilibrium constant for this reaction?

d) Suppose a particular system contains oxygen at a partial pressure of 0.98 atm and ozone at a partial pressure of 0.02 atm. What is the value of ΔG at 25 °C under these conditions?

6. Consider an aqueous solution containing $Cu^{2+}(aq)$, $Mg^{2+}(aq)$, and $Ni^{2+}(aq)$.

Half-reaction	$\mathscr{E}^0$ (V)
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$2H^+ + 2e^- \rightarrow H_2$	-2.23
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23

a) Suppose we put this solution in an electrochemical cell and begin to increase the cell voltage. In what order do these four half-reactions occur?

b) Assuming no overvoltage effects, which metals plate out of solution? Explain.

c) Rank these four cations in order of increasing oxidizing strength.

For the remaining questions, choose the letter that corresponds to the best answer.

7. Consider the vaporization of bromine, which occurs at 58.7 °C:

$$Br_2(l) \rightarrow Br_2(g)$$

Which of the following statements are *true*?

I. $\Delta S_{system} > 0$ because a gas has greater positional entropy than a liquid
II. $\Delta S_{system} < 0$ because a gas uniformly filling its container is more ordered than a liquid
III. $\Delta S_{surroundings} > 0$ because the process is endothermic
IV. $\Delta S_{surroundings} < 0$ because the process is endothermic
V. $\Delta S_{universe} > 0$ for all temperatures less than 58.7 °C.

A) **I** and **III**
B) **II** and **III**
C) **I**, **IV**, and **V**
D) **V** only
E) **I** and **IV**

8. Which of the following statements is *false*?

A) A system has the lowest possible free energy at equilibrium.
B) If $\Delta H < 0$ and $\Delta S > 0$, a process is spontaneous at all temperatures.
C) If a process has $\Delta G < 0$, it will spontaneously proceed to completion.
D) A system with the equilibrium constant $K > 1$ will be spontaneous.
E) The maximum useful work a process can generate is ΔG.

9. Which of the following can be utilized to increase the value of $\mathscr{E}_{cell}$ for a galvanic cell?

I. Choose a reagent with a more positive value of $\mathscr{E}^0$ for the reduction half-reaction
II. Choose a reagent with a more positive value of $\mathscr{E}^0$ for the oxidation half-reaction
III. Increase the concentrations of the aqueous reactants
IV. Increase the mass of the anode and cathode
V. Decrease the temperature of the cell

A) **I**, **III**, and **V**
B) **II** and **III**
C) **II**, **III**, and **IV**
D) **I** and **III**
E) **III** and **V**

10. Gas A reacts with gas B to form the product C:

$$A(g) + B(g) \rightarrow C(g)$$

The bond energies in C are much greater than the bond energies in both A and B (i.e. C is more stable than A and B).

Which of the following statements are *true*?

I. $\Delta S_{system} > 0$
II. $\Delta H < 0$
III. $\Delta G < 0$ for all temperatures
IV. $\Delta S_{surroundings} > 0$
V. This process is spontaneous for all temperatures.

A) **I**, **III**, and **V**
B) **II** and **IV**
C) **III** and **V**
D) **I** only
E) all of the above

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	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.34
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	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		

Equations and Constants

$PV = nRT$

$\ln [A] = -kt + \ln [A]_0$

$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

$[A] = -kt + [A]_0$

$K_p = K(RT)^{\Delta n}$

$pH = -\log [H^+]$

$pOH = -\log [OH^-]$

$pH = pK_a + \log \frac{[A^-]}{[HA]}$

$\Delta G = \sum n_p \cdot \Delta G_p - \sum n_r \cdot \Delta G_r$

$\Delta G^0 = -RT \ln K$

$\mathscr{E} = \mathscr{E}^0 - \frac{RT}{nF} \ln Q$

$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$

$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$ax^2 + bx + c = 0$

$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

$pH + pOH = 14.00$

$K_a \cdot K_b = K_w$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = \Delta G^0 + RT \ln Q$

$\Delta G^0 = -nF\mathscr{E}^0$

$R = 8.314 \text{ J / mol} \cdot \text{K} = 0.0821 \text{ L} \cdot \text{atm / mol} \cdot \text{K}$

$F = 96{,}485 \text{ C / mol } e^-$