CHM 106
Exam III

1. An unknown metal M forms a soluble compound $M(NO_3)_2$.

a) A 0.50 L solution of $M(NO_3)_2$ of unknown concentration is electrolyzed. A constant current of 2.50 amperes is applied for 35.0 minutes, after which 3.06 grams of the metal M is deposited and the reaction is complete. Calculate the molar mass of M and identify the metal.

b) A galvanic cell is constructed with the metal M and a 1.0 M solution of $M(NO_3)_2$ in one half-cell and zinc metal and 1.0 M $ZnSO_4$ in the other half-cell. Write the net ionic equation for the cell reaction and calculate the cell potential $\mathscr{E}^0$.

c) What is the standard free energy change ΔG^0 for this reaction?

d) A galvanic cell is constructed with the metal M and a fresh portion of the $M(NO_3)_2$ solution from part (a) in one half-cell and zinc metal and 1.0 M $ZnSO_4$ in the other half cell. What is the cell potential $\mathscr{E}$ for this galvanic cell?

2. At 25 °C, ΔH_C^0 = -2183.6 kJ / mol for the combustion of butyric acid, shown below:

$$C_3H_7COOH(l) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 4\ H_2O(l)$$

Substance	ΔH_f^0 (kJ / mol)	S^0 (J / mol · K)
$C(s)$	0	5.7
$CO_2(g)$	-393.5	213.8
$H_2(g)$	0	205.2
$H_2O(l)$	-285.8	70.0
$O_2(g)$	0	205.2
$C_3H_7COOH(l)$	?	222.2

a) From the data above, calculate the standard enthalpy of formation ΔH_f^0 for butyric acid.

b) Write a correctly balanced equation for the formation of butyric acid from its elements.

c) Entropy values for substances are typically tabulated as absolute entropy (S^0) rather than entropy of formation (ΔS_f^0), which is different from any other energy quantity in thermodynamics. What property of thermodynamics allows us to do this?

d) We do, however, need the entropy of formation to calculate the free energy of formation. Calculate the standard entropy of formation ΔS_f^0 for butyric acid.

e) Calculate the standard free energy of formation ΔG_f^0 for butyric acid.

3. The lithium-sulfuryl chloride cell is one type of disposable lithium battery used in many applications that require a small, lightweight battery with relatively high energy density. In this galvanic cell, lithium reacts with liquid sulfuryl chloride (SO_2Cl_2) to produce lithium ions, chloride ions, and sulfur dioxide.

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 in this reaction.

d) Using the method of half-reactions, balance this chemical equation. Show your work.

e) The standard cell potential for this battery is $\mathscr{E}^0 = 3.9$ V. What is the standard reduction potential of the sulfuryl chloride half-reaction?

f) In this cell, the sulfuryl chloride is a liquid that is a poor conductor so an inert graphite electrode is used. What is the line notation for this cell?

g) One commercial lithium-sulfuryl chloride cell can supply a constant current of 0.020 A for 80 hours before being completely discharged. If the sulfuryl chloride is the limiting reagent in this battery, what mass of sulfuryl chloride does the battery contain?

4. Dinitrogen trioxide exists in an equilibrium between nitric oxide and nitrogen dioxide:

$$N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g)$$

Substance	ΔH_f^0 (kJ / mol)	S^0 (J / mol · K)
$N_2O_3(g)$	?	308.5
$NO(g)$	90.3	210.7
$NO_2(g)$	33.1	240.0

a) A flask initially containing 0.0400 M of pure $N_2O_3(g)$ at 0 °C has an equilibrium concentration of [NO] = 0.0371 M. What is the value of the equilibrium constant at 0 °C?

b) What is the value of ΔG at 0 °C?

c) What is the value of ΔS^0 for this reaction at 25 °C?

d) Assuming that ΔH^0 and ΔS^0 do not depend on temperature, what is ΔH^0 at 25 °C?

e) What is ΔH_f^0 for $N_2O_3(g)$ at 25 °C?

5. Explain each of the following phenomena:

a) When an aqueous solution of NaCl is electrolyzed, $Cl_2(g)$ is produced at the anode, but no Na(s) is produced at the cathode.

b) The mass of Fe(s) produced when 1 Faraday (96,485 C) is used to reduce a solution of $FeSO_4$ is 1.5 times the mass of Fe(s) when 1 Faraday of charge is used to reduce a solution of $FeCl_3$.

c) Chlororoform ($CHCl_3$) has a boiling point of 61.7 °C. The condensation of chloroform is exergonic for all temperatures less than 61.7 °C.

d) The galvanic cell Zn $\vert$ Zn^{2+} (1.0 $\underline{M}$) $\Vert$ Pb^{2+} (1.0 $\underline{M}$) $\vert$ Pb has the same potential as the galvanic cell $\vert$ Zn^{2+} (0.010 $\underline{M}$) $\Vert$ Pb^{2+} (0.010 $\underline{M}$) $\vert$ Pb.

e) A real process with ΔG = -100 kJ / mol can only do less than 100 kJ / mol of useful work.

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

6. Which of the following reagents is the strongest oxidizing agent?

(A) Br_2
(B) Ce^{3+}
(C) H_2
(D) Li^+
(E) Zn

7. Which one of the following reagents is the strongest reducing agent?

(A) Br^-
(B) Ce^{4+}
(C) H^+
(D) Li
(E) Zn^{2+}

8. A strip of copper is placed in a 1.0 M solution of copper nitrate and a strip of silver is placed in a solution of 1.0 M silver nitrate. The two metal strips are connected to an electrical load by wires and the two solutions are connected by a salt bridge. Which of the following does not take place?

(A) The silver electrode increases in mass as the cell operates.
(B) There is a net movement of silver ions through the salt bridge to the copper half-cell.
(C) Electrons flow in the external circuit from the copper electrode to the silver electrode.
(D) Negative ions pass through the salt bridge from the silver half-cell to the copper half-cell.
(E) Some positive copper ions pass through the salt bridge from the copper half-cell to the silver half-cell.

9. When a stable diatomic molecule spontaneously forms from its atoms, what are the signs of ΔH^0, ΔS^0, and ΔG^0, respectively?

(A) +, +, +
(B) −, −, −
(C) −, +, +
(D) +, −, −
(E) −, −, +

10. Suppose that the system Al $\mid Al^{3+} \parallel Cu^{2+} \mid$ Cu is to be utilized as a galvanic cell. Which of the following statements is *true*?

I. Copper is the anode and aluminum is the cathode.
II. Electrons will flow from the aluminum electrode to the copper electrode.
III. The cell potential $\mathscr{E}^0$ can be increased by increasing the concentration of $[Cu^{2+}]$.
IV. The cell potential $\mathscr{E}^0$ will be at a minimum when the system reaches equilibrium.
V. The reaction is spontaneous when aluminum is reduced and copper is oxidized.

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

11. Which of the following reactions has the largest positive value of ΔS per mol of Cl_2?

(A) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
(B) $Cl_2(g) + ½\ O_2(g) \rightarrow Cl_2O(g)$
(C) $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
(D) $2\ NH_4Cl(s) \rightarrow N_2(g) + 4\ H_2(g) + Cl_2(g)$
(E) $Cl_2(g) \rightarrow 2\ Cl(g)$

12. The following reaction occurs in basic solution: $F_2 + H_2O \rightarrow O_2 + F^-$. When the equation is balanced, the sum of the coefficients for all species is:

(A) 10
(B) 11
(C) 12
(D) 13
(E) none of the above

13. A particular reaction has a negative ΔH and a negative ΔS. Which of the following statements is true?

(A) The reaction is spontaneous at all temperatures.
(B) The reaction is nonspontaneous at all temperatures.
(C) The reaction becomes spontaneous as temperature increases.
(D) The reaction becomes spontaneous as temperature decreases.
(E) The reaction is always at equilibrium.

14. A mixture of hydrogen and chlorine remains unreacted until it is exposed to ultraviolet light, at which point the following reaction occurs very rapidly:

$$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$$

For this reaction, ΔG = -45.54 kJ / mol, ΔH = -44.12 kJ / mol, and ΔS = -4.76 J / mol · K. Which statement best explains this behavior?

(A) The reaction has a small equilibrium constant.
(B) The reactants are thermodynamically more stable than the products.
(C) The ultraviolet light raises the temperature of the system and makes the reaction more favorable.
(D) The negative value for ΔS slows the reaction down.
(E) The reaction is spontaneous, but the reactants are kinetically stable.

15. Which of the following statements are *true*?

I. Exothermic reactions are always spontaneous
II. Exergonic reactions are always spontaneous.
III. Exentropic reactions are always spontaneous.
IV. A reaction with a negative ΔS cannot be spontaneous.
V. Free energy is dependent on temperature.

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

Equations and Constants

$$PV = nRT$$

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

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

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

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

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

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

$$ax^2 + bx + c = 0$$

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

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

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

$$pH + pOH = 14.00$$

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

$$K_a \cdot K_b = K_w$$

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

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

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

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

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

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

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

$R = 8.314$ J / mol · K $= 0.0821$ L · atm / mol · K

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

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		