START 8:05am
END 11:15am

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.

$2e^- + M^{2+} \rightarrow M$

4 $\frac{2.50\ C}{s} \cdot \frac{60\ s}{min} \cdot 35.0\ min \cdot \frac{mol\ e^-}{96485\ C} \cdot \frac{1\ mol\ M}{2\ mol\ e^-} = 0.0272\ mol\ M$

$\frac{3.06\ g\ M}{0.0272\ mol\ M} = \boxed{112.47\ \frac{g}{mol}}$ metal is $\boxed{Cd}$

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 $\mathscr{E}^0$.

$Zn^{2+} + 2e^- \rightarrow Zn \quad \mathscr{E}^0 = -0.76V$

$Cd^{2+} + 2e^- \rightarrow Cd \quad \mathscr{E}^0 = -0.40V$

4 $Zn + Cd^{2+} \rightarrow Zn^{2+} + Cd \quad \mathscr{E}^0 = 0.76 - 0.40V$

$\boxed{\mathscr{E}^0 = 0.36V}$

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

3 $\Delta G^0 = -nF\mathscr{E}^0 = -2\ mol\ e^- \cdot \frac{96485\ C}{mol\ e^-} \cdot \frac{0.36\ J}{C}$

$= \boxed{-69.47\ kJ/mol}$

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?

$[M^{2+}] = \frac{0.0272\ mol\ M}{0.5\ L\ M} = 0.0544\ M$ $\quad Q = \frac{[Zn^{2+}]}{[M^{2+}]} = \frac{1}{0.0544} = 18.382$

4 $\mathscr{E} = \mathscr{E}^0 - \frac{RT}{nF}\ln Q = 0.36V - \frac{8.314 \cdot 298.15\ K}{2 \cdot 96485}\ln 18.382$

$= \boxed{0.32V}$

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2. At 25 °C, ΔH^0_C = -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^0_f (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^0_f for butyric acid.

$$\Delta H_c^\circ = -2183.6 \frac{kJ}{mol} = [4(-393.5) + 4(-285.8)] - [\Delta H_f^\circ + 5(0)]$$

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$$\Delta H_f^\circ = \boxed{-533.6\ kJ/mol}$$

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

3 $4C(s) + 4H_2(g) + O_2(g) \longrightarrow C_3H_7COOH(l)$

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

THE THIRD LAW OF THERMODYNAMICS: THE ENTROPY

3 OF A PERFECT CRYSTAL AT 0K IS ZERO.

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

$$\Delta S_f^\circ = [222.2] - [4(5.7) + 4(205.2) + 205.2] = \boxed{-826.6\ J/mol \cdot K}$$

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

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ = -533.6 \frac{kJ}{mol} - 298.15\,K \cdot \left(-826.6 \frac{J}{mol \cdot K} \cdot \frac{1\,kJ}{1000\,J}\right)$$

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$$= \boxed{-287.1\ kJ/mol}$$

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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.

$$\overset{0}{Li} + \overset{+6\ -2\ -1}{SO_2Cl_2} \rightarrow \overset{+1}{Li^+} + \overset{-1}{Cl^-} + \overset{+4\ -2}{SO_2}$$

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

Li is OXIDIZED

1 S is REDUCED

c) Identify the oxidizing agent and the reducing agent in this reaction.

SO_2Cl_2 is OXIDIZING AGENT

1 Li is REDUCING AGENT

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

$$2 \cdot (Li \rightarrow Li^+ + e^-)$$

$$2e^- + SO_2Cl_2 \rightarrow 2Cl^- + SO_2$$

3 $$2Li + \cancel{2e^-} + SO_2Cl_2 \rightarrow 2Li^+ + \cancel{2e^-} + 2Cl^- + SO_2$$

$$2Li_{(s)} + SO_2Cl_2(l) \rightarrow 2Li^+ + 2Cl^- + SO_2(l)$$

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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?

$Li^+ + e^- \rightarrow Li \quad \mathscr{E}^\circ = -3.05\,V$

2 $SO_2Cl_2 + 2e^- \rightarrow 2Cl^- + SO_2 \quad \mathscr{E}^\circ = ?$

$3.9\,V = \mathscr{E}^\circ_{SO_2Cl_2} + 3.05\,V$

$\mathscr{E}^\circ_{SO_2Cl_2} = \boxed{0.85\,V}$

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?

$Li \mid Li^+ \parallel Cl^-, SO_2, SO_2Cl_2 \mid C$

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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?

$0.020\,\frac{C}{s} \cdot \frac{60\,s}{min} \cdot \frac{60\,min}{hr} \cdot 80\,hr \cdot \frac{1\,mol\,e^-}{96485\,C} \cdot \frac{1\,mol\,SO_2Cl_2}{2\,mol\,e^-} = 0.0298\,mol\,SO_2Cl_2$

$MW(SO_2Cl_2) = 134.97\,g/mol$

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$0.0298\,mol\,SO_2Cl_2 \cdot \frac{134.97\,g\,SO_2Cl_2}{mol\,SO_2Cl_2} = \boxed{4.02\,g\,SO_2Cl_2}$

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?

$$N_2O_3 \rightleftharpoons NO + NO_2$$

Init: 0.0400   0   0

Change: $-x$ $+x$ $+x$

EQ: $0.0400-x$ x x

$x = 0.0371M$

$$K = \frac{[NO][NO_2]}{[N_2O_3]} = \frac{0.0371^2}{0.0029}$$

$$\boxed{K = 0.4746}$$

$[NO] = [NO_2] = 0.0371M$ $[N_2O_3] = 0.0400 - 0.0371 = 0.0029M$

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b) What is the value of ΔG at 0 °C?

$$\Delta G = -RT \ln K = -8.314 \frac{J}{mol \cdot K} \cdot 273.15 K \cdot \ln 0.4746$$

$$= \boxed{1.69 \text{ kJ/mol}}$$

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

$$\Delta S^\circ = [210.7 + 240.0] - 308.5 = \boxed{142.2 \text{ J/mol} \cdot K}$$

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

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

$$1.69 \frac{kJ}{mol} = \Delta H^\circ - 273.15 K \cdot \left(142.2 \frac{J}{mol \cdot K} \cdot \frac{1 kJ}{1000 J}\right)$$

$$\Delta H^\circ = \boxed{40.53 \text{ kJ/mol}}$$

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

$$\Delta H^\circ = 40.53 = [90.3 + 33.1] - \Delta H_f^\circ$$

$$\Delta H_f^\circ = \boxed{+82.87 \text{ kJ/mol}}$$

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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.

	$\mathcal{E}°$
$Na^+ + e^- \rightarrow Na$	$-2.71\,V$
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$-0.83\,V$
$Cl_2 + 2e^- \rightarrow 2Cl^-$	$1.36\,V$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$1.23\,V$

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THE OXIDATION OF BOTH H_2O + Cl^- ARE CLOSE IN $\mathcal{E}°$ VALUES SO THEY BOTH OCCUR AT THE ANODE. HOWEVER, THE REDUCTION OF WATER IS MUCH MORE SPONTANEOUS THAN Na^+ SO ONLY H_2 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 $FeCl_3$.

$Fe^{2+} + 2e^- \rightarrow Fe$

$Fe^{3+} + 3e^- \rightarrow Fe$

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IRON (II) REQUIRES $\frac{2}{3}$ OF THE CHARGE THAT Fe (III) DOES, SO $\frac{3}{2} = 1.5\times$ AS MUCH IRON IS PRODUCED FROM THE REDUCTION OF IRON (II) AS IRON (III).

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.

CONDENSATION IS EXOTHERMIC SO ΔH IS NEGATIVE. THE REACTANT IS A GAS AND THE PRODUCT A LIQUID SO ΔS IS NEGATIVE. THEREFORE, CONDENSATION IS SPONTANEOUS ($\Delta G < 0$) FOR ALL TEMPERATURES LESS THAN THE BOILING POINT.

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d) The galvanic cell Zn | Zn^{2+} (1.0 M) ‖ Pb^{2+} (1.0 M) | Pb has the same potential as the galvanic cell | Zn^{2+} (0.010 M) ‖ Pb^{2+} (0.010 M) | Pb.

SINCE $\mathcal{E} = \mathcal{E}° - \frac{RT}{nF}\ln Q$, BOTH OF THESE CELLS HAVE THE SAME POTENTIAL BECAUSE THEIR NUMERICAL VALUES OF Q ARE EQUAL. $Q = \frac{[Zn^{2+}]}{[Pb^{2+}]} = 1.0$

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

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ANY REAL PROCESS LOSES ENERGY, SO ΔG REPRESENTS THE THEORETICAL MAXIMUM WORK A PROCESS CAN DO. THE REAL WORK MUST BE LESS THAN THIS VALUE.

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

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

			E°
(A)	Br_2	$2e^- + Br_2 \rightarrow 2Br^-$	1.09 V
(B)	Ce^{3+}	$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70 V
(C)	H_2	$2H^+ + 2e^- \rightarrow H_2$	0
(D)	Li^+	$Li^+ + e^- \rightarrow Li$	−3.05 V
(E)	Zn	$Zn^{2+} + e^- \rightarrow Zn$	−0.76 V

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

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

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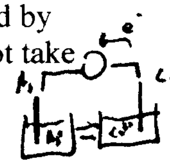
8. A strip of copper is placed in a 1.0 M solution of copper nitrate and a strip of silver is placed in a solution of 1.0 M silver nitrate. The two metal strips are connected to an electrical load by wires and the two solutions are connected by a salt bridge. Which of the following does not take place?

$2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$ E° 0.80 − 0.34 = 0.46 V



(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.

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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) −, −, +

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e^-

Anode → Cathode

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

$2\,Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$ $\mathcal{E}^\circ$: $1.66 + 0.34V = 2.00V$

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 $\mathcal{E}^0$ can be increased by increasing the concentration of $[Cu^{2+}]$.
IV. ✓ The cell potential $\mathcal{E}^0$ will be at a minimum when the system reaches equilibrium.
V. ✗ The reaction is spontaneous when aluminum is reduced and copper is oxidized.

	$\mathcal{E}^\circ$
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34V
$Al^{3+} + 3e^- \rightarrow Al$	−1.66V

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(A) **I, II, and IV**
(B) **II, III, and IV**
(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?

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(A) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
(B) $Cl_2(g) + \frac{1}{2} O_2(g) \rightarrow Cl_2O(g)$
(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:

$2\times(F_2 + 2e^- \rightarrow 2F^-)$
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
$4OH^- + 2F_2 + \cancel{2H_2O} \rightarrow 4F^- + O_2 + \cancel{4H^+} + \cancel{4OH^-}$
$4H_2O$
$2F_2 + 4OH^- \rightarrow 4F^- + O_2 + 2H_2O$

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(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?

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(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.

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

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, $\Delta G = -45.54$ kJ / mol, $\Delta H = -44.12$ kJ / mol, and $\Delta S = -4.76$ 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.

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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**

✓ 5

<u>Equations and Constants</u>

$$PV = nRT$$

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

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

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

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

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

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

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

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

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