START 9:30am

CHM 106
Exam III

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

$$Li \mid Li^+ \parallel Br^-, Br_2 \mid Pt$$

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

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

$Br_2 + 2e^- \rightarrow 2Br^- \quad \mathcal{E}^\circ = 1.09V$

$\boxed{Br_2 + 2Li^+ \rightarrow 2Br^- + 2Li^+} \quad \mathcal{E}^\circ = 4.14V$

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b) What is the standard cell potential $\mathcal{E}^0$ for this reaction?

$\mathcal{E}^\circ = 1.09 + -(-3.05) = \boxed{4.14V}$

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c) Suppose that the concentration of $[Br_2] = 6.00$ M, $[Br^-] = 0.10$ M, and $[Li^+] = 0.10$ M. Should the potential of this cell be higher or lower than E^0? Explain.

$\mathcal{E} > \mathcal{E}^\circ$ BECAUSE THE REACTANT CONCENTRATIONS ARE HIGHER AND PRODUCT CONC. ARE LOWER. BY LE CHÂTELIER'S PRINCIPLE, THIS SYSTEM WILL TEND RIGHT.

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d) What is the potential of the cell when $[Br_2] = 6.00$ M, $[Br^-] = 0.10$ M, and $[Li^+] = 0.10$ M?

$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF} \ln Q \qquad Q = \frac{[Br^-]^2[Li^+]}{[Br_2]} = \frac{0.1^2 \cdot 0.1^2}{6} = 1.67 \times 10^{-5}$

$\mathcal{E} = 4.14 - \frac{8.314 \cdot 298}{2 \cdot 96485} \ln 1.67 \times 10^{-5}$

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$= \boxed{4.28V}$

2. Ethylene reacts with butadiene to form cyclohexene in the gas phase:

$$C_2H_4(g) + C_4H_6(g) \rightleftharpoons C_6H_{10}(g)$$

Substance	ΔH_f^0 (kJ / mol)	S^0 (J / mol · K)
$C_2H_4(g)$	52.4	219.6
$C_4H_6(g)$	110.0	479.6
$C_6H_{10}(g)$	-4.32	?

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

$\Delta H^\circ = -4.32 - [52.4 + 110.0]$

$\Delta H^\circ = \boxed{-166.7 \text{ kJ/mol}}$

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b) At 400 K, the equilibrium constant for this reaction was measured to be K = 29.05. What is the value of ΔG at 400 K?

$\Delta G = -RT \ln K$

$= -8.314 \frac{J}{mol \cdot K} \cdot 400 K \cdot \ln 29.05$

$= \boxed{-11.2 \text{ kJ/mol}}$

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c) Assuming that ΔH^0 and ΔS^0 are independent of temperature, use this value of ΔG at 400 K to calculate ΔS^0 for this reaction.

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

$-11.2 \frac{kJ}{mol} = -166.7 \text{ kJ/mol} - 400 K \cdot \Delta S$

$\Delta S = -0.389 \text{ kJ/mol·K} = \boxed{-389 \text{ J/mol·K}}$

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d) What is the standard entropy S^0 for $C_6H_{10}(g)$?

$\Delta S = -389 = S^\circ - [219.6 + 479.6]$

$S^\circ = \boxed{310.2 \text{ J/mol·K}}$

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3. In the zinc-air battery, zinc metal reacts with oxygen and water under basic conditions to form solid zinc oxide.

Half-reaction	$\mathscr{E}^0$
$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$	0.40 V
$ZnO(s) + H_2O(l) + 2\ e^- \rightarrow Zn(s) + 2\ OH^-(aq)$	?

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

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$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$2 \times (Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-)$

$O_2 + 2H_2O + 4e^- + 2Zn + 4OH^- \rightarrow 4OH^- + 2ZnO + 2H_2O + 4e^-$

$$O_2 + 2Zn \rightarrow 2ZnO$$

b) The zinc-air battery has a standard cell potential of $\mathscr{E}^0 = 1.66$ V. What is the standard reduction potential of zinc oxide?

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$\mathscr{E}^\circ = 1.66\ V = 0.40\ V + \mathscr{E}^\circ_{Zn \rightarrow ZnO}$

$\mathscr{E}^\circ_{Zn \rightarrow ZnO} = 1.26\ V$ so $\mathscr{E}^\circ_{ZnO \rightarrow Zn} = \boxed{-1.26\ V}$

c) A typical zinc-air battery uses a carbon electrode upon which oxygen reacts. What is the line notation for this cell?

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$Zn, ZnO \mid OH^- \parallel OH^- \mid O_2 \mid C$

d) Identify which electrode is the anode and which electrode is the cathode.

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ZINC IS THE ANODE

CARBON IS THE CATHODE

e) One small zinc-air battery can provide 0.020 A of current for 10 hours before the battery is exhausted. What mass of zinc is present in the battery?

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$10\,h \cdot \frac{3600\,s}{1\,h} \cdot \frac{0.020\,C}{s} \cdot \frac{1\,mol\ e^-}{96485\,C} \cdot \frac{1\,mol\ Zn}{2\,mol\ e^-} \cdot \frac{65.409\,g\ Zn}{1\,mol\ Zn} = \boxed{0.24\,g\ Zn}$

4. Methanol is synthesized from carbon monoxide and hydrogen:

$$CO(g) + 2\,H_2(g) \rightarrow CH_3OH(l)$$

Substance	ΔH_f^0 (kJ / mol)
$CO(g)$	-110.5
$H_2(g)$	0
$CH_3OH(l)$	-239.1

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

$\Delta H^\circ = -239.1 - [-110.5 + 2(0)]$

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$\Delta H^\circ = \boxed{-128.6\ kJ/mol}$

b) Is ΔS^0 positive or negative? Explain.

$\Delta S^\circ < 0$ BECAUSE THERE ARE MORE GASEOUS REACTANTS THAN PRODUCTS AND GAS HAS HIGHER POSITIONAL ENTROPY.

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c) This reaction becomes spontaneous at T = 387 K. What is the value of ΔS^0?

$0 = \Delta H^\circ - T\Delta S^\circ = -128.6 \times 10^3\ J - 387K \cdot \Delta S^\circ$

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$\Delta S^\circ = \boxed{-332\ J/mol\cdot K}$

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

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -128.6\ kJ - 298K \cdot (-0.332\ kJ/K)$

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$\Delta G^\circ = \boxed{-29.7\ kJ/mol}$

e) Is this reaction spontaneous at 25 °C?

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YES. $\Delta G^\circ < 0$.

5. Explain the following phenomena.

a) The mass of Pb(*s*) produced when 1 Faraday (96,485 C) is used to reduce $Pb(SO_4)_2$ is half as much as the mass of Pb(*s*) produced when 1 Faraday is used to reduce $PbCl_2$.

$4e^- + Pb^{4+} \rightarrow Pb$

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

Pb^{4+} REQUIRES TWICE AS MANY ELECTRONS AS Pb^{2+} TO REDUCE TO Pb METAL, SO ONLY HALF AS MUCH METAL IS PRODUCED, PER MOL OF e^-.

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b) Potassium permanganate ($KMnO_4$) is a strong oxidizing agent, but permanganate never undergoes oxidation in its reactions.

OXIDIZING AGENTS CAUSE OTHER SPECIES TO BE OXIDIZED, SO THEY THEMSELVES UNDERGO REDUCTION.

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c) Metallic sodium cannot be produced by electrolysis in aqueous solution.

$Na^+ + e^- \rightarrow Na$ $\quad E^\circ = -2.71\,V$

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $\quad E^\circ = -0.83\,V$

THE REDUCTION OF WATER IS MORE SPONTANEOUS THAN THE REDUCTION OF Na^+ (HIGHER E°), SO WATER WILL BE REDUCED BEFORE Na^+.

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

6. Which one of the following conditions of enthalpy and entropy always result in a spontaneous reaction no matter what the temperature?

(A) $\Delta H < 0, \Delta S < 0$
(B) $\Delta H < 0, \Delta S > 0$
(C) $\Delta H > 0, \Delta S < 0$
(D) $\Delta H > 0, \Delta S > 0$
(E) There are no conditions for which a reaction will always be spontaneous.

7. Consider the following half-reactions and choose the correct statement.

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad \mathscr{E}^0 = 0.77\ V$$
$$Fe(CN)_6^{3-}(aq) + e^- \rightarrow Fe(CN)_6^{4-}(aq) \qquad \mathscr{E}^0 = 0.77\ V$$

(A) Fe^{2+} is more likely to be oxidized than Fe^{2+} complexed to CN^-.
(B) Fe^{3+} is more likely to be reduced than Fe^{3+} complexed to CN^-.
(C) Both A and B are true.
(D) Complexation of Fe ions with CN^- has no effect on their tendencies to become oxidized or reduced.
(E) None of the above are true.

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

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

Which of the following statements are *false*?

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

9. 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.

10. Which one of the following reagents is the strongest oxidizing agent?

(A) Ca^{2+} −2.76 V
(B) Ce^{4+} 1.70 V
(C) Cu^{+} 0.52 V
(D) F^{-} [illegible]
(E) Mg —

11. Which of the following can be utilized to increase the value of $\mathscr{E}$ 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 and III**
(B) **II and III**
(C) **III and V**
(D) **I, III, and V**
(E) **II, III, and IV**

12. For the reaction $CO_2(g) + 2\ H_2O(g) \rightarrow CH_4(g) + 2\ O_2(g)$, $\Delta H^0 = 803$ kJ / mol. Which of the following will increase K?

(A) ✗ decrease the number of moles of $CH_4(g)$
(B) ✗ increase the volume of the system
(C) ✓ increase the temperature of the system
(D) ✗ all of the above
(E) ✗ none of the above

$\ln K = \frac{-\Delta H^\circ}{R} \cdot \frac{1}{T} + \frac{\Delta S^\circ}{R}$

13. Permanganate reacts with bromide to form manganese (II) and bromine.

$$MnO_4^-(aq) + Br^-(aq) \rightarrow Mn^{2+}(aq) + Br_2(aq)$$

When this equation is balanced under acidic conditions, what is the coefficient of $Br^-(aq)$?

(A) 1
(B) 2
(C) 5
(D) 10
(E) 20

$2 + (MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)$

$5 + (2Br^- \rightarrow Br_2 + 2e^-)$

$2MnO_4^- + 16H^+ + 10e^- + 10Br^- \rightarrow 2Mn^{2+} + 8H_2O + 5Br_2 + 10e^-$

$2MnO_4^- + 16H^+ + 10Br^- \rightarrow 2Mn^{2+} + 8H_2O + 5Br_2$

14. Suppose the system $Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$ is to be utilized as a galvanic cell. Which of the following statements are *true*?

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

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

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

$Cu^{2+} + 2e^- \rightarrow Cu \quad E^\circ = 0.34V$

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \quad E^\circ = 1.10V$

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

(A) $Cl_2(g) + \frac{1}{2} O_2(g) \rightarrow Cl_2O(g)$ 1.5 → 1
(B) $Cl_2(g) \rightarrow 2\,Cl(g)$ 1 → 2
(C) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ 2 → 2
(D) $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$ 1 → 0
(E) $2\,NH_4Cl(s) \rightarrow N_2(g) + 4\,H_2(g) + Cl_2(g)$ 0 → 6