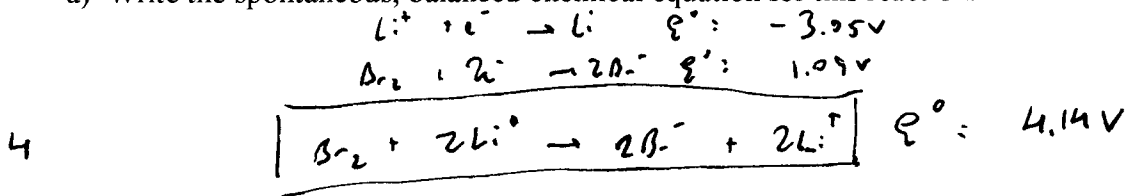


CHM 106  
Exam III

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



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



b) What is the standard cell potential  $E^\circ$  for this reaction?

3

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

c) Suppose that the concentration of  $[\text{Br}_2] = 6.00 \text{ M}$ ,  $[\text{Br}^-] = 0.10 \text{ M}$ , and  $[\text{Li}^+] = 0.10 \text{ M}$ . Should the potential of this cell be higher or lower than  $E^\circ$ ? Explain.

4

$E > E^\circ$  BECAUSE THE REACTION QUOTIENT ARE HIGHER AND PRODUCT CONCENT. ARE LOWER. BY LE CHATLIER'S PRINCIPLE, THIS SYSTEM WILL TEND ALIGHT.

d) What is the potential of the cell when  $[\text{Br}_2] = 6.00 \text{ M}$ ,  $[\text{Br}^-] = 0.10 \text{ M}$ , and  $[\text{Li}^+] = 0.10 \text{ M}$ ?

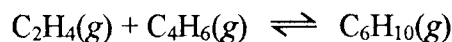
4

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad Q = \frac{[\text{Br}^-]^2 [\text{Li}^+]^2}{[\text{Br}_2]}$$

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

$$= \boxed{4.28\text{V}}$$

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



Substance	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol·K)
$\text{C}_2\text{H}_4(\text{g})$	52.4	219.6
$\text{C}_4\text{H}_6(\text{g})$	110.0	479.6
$\text{C}_6\text{H}_{10}(\text{g})$	-4.32	?

a) What is the value for  $\Delta H^\circ$  for this reaction?

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

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

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

$$\begin{aligned} \Delta G &= -RT \ln K \\ &= -8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \cdot 400 \text{ K} \cdot \ln 29.05 \\ &= \boxed{-11.2 \text{ kJ/mol}} \end{aligned}$$

c) Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature, use this value of  $\Delta G$  at 400 K to calculate  $\Delta S^\circ$  for this reaction.

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ -11.2 \frac{\text{kJ}}{\text{mol}} &= -166.7 \frac{\text{kJ}}{\text{mol}} - 400 \text{ K} \cdot \Delta S \\ \Delta S &= -0.389 \frac{\text{kJ}}{\text{mol}\cdot\text{K}} = \boxed{-389 \text{ J/mol}\cdot\text{K}} \end{aligned}$$

d) What is the standard entropy  $S^\circ$  for  $\text{C}_6\text{H}_{10}(\text{g})$ ?

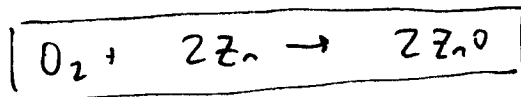
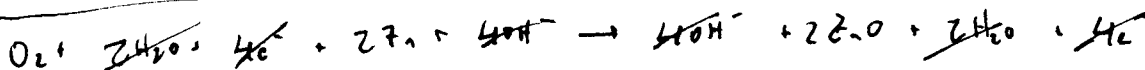
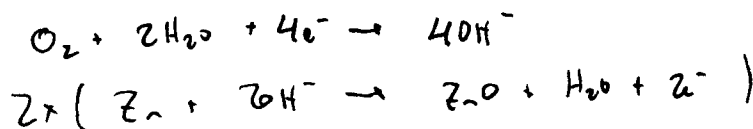
$$\Delta S = -389 = S^\circ - [219.6 + 479.6]$$

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

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

Half-reaction	$\mathcal{E}^{\circ}$
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \rightarrow 4 \text{OH}^-(\text{aq})$	0.40 V
$\text{ZnO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s}) + 2 \text{OH}^-(\text{aq})$	?

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



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

$$\mathcal{E}^{\circ} = 1.66 \text{ V} = 0.40 \text{ V} + \mathcal{E}^{\circ}_{\text{ZnO} \rightarrow \text{Zn}}$$

$$\mathcal{E}^{\circ}_{\text{ZnO} \rightarrow \text{Zn}} = 1.26 \text{ V}$$

$$\mathcal{E}^{\circ}_{\text{Zn} \rightarrow \text{ZnO}} = \boxed{-1.26 \text{ V}}$$

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



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

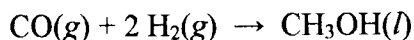
ZINC is the ANODE

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?

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

4. Methanol is synthesized from carbon monoxide and hydrogen:



Substance	$\Delta H_f^\circ$ (kJ/mol)
CO(g)	-110.5
H <sub>2</sub> (g)	0
CH <sub>3</sub> OH(l)	-239.1

a) What is the value for  $\Delta H^\circ$  for this reaction?

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

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

b) Is  $\Delta S^\circ$  positive or negative? Explain.

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

c) This reaction becomes spontaneous at  $T = 387 \text{ K}$ . What is the value of  $\Delta S^\circ$ ?

$$0 = \Delta H^\circ - T \Delta S^\circ = -128.6 \times 10^3 \frac{\text{J}}{\text{mol}} - 387 \text{ K} \cdot \Delta S^\circ$$

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

d) What is the value of  $\Delta G^\circ$  for this reaction?

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -128.6 \frac{\text{kJ}}{\text{mol}} - 298 \text{ K} \cdot (-0.332 \frac{\text{kJ}}{\text{mol}\cdot\text{K}})$$

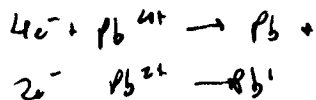
$$\Delta G^\circ = \boxed{-29.7 \text{ kJ/mol}}$$

e) Is this reaction spontaneous at  $25^\circ \text{C}$ ?

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<sub>4</sub>)<sub>2</sub> is half as much as the mass of Pb(s) produced when 1 Faraday is used to reduce PbCl<sub>2</sub>.

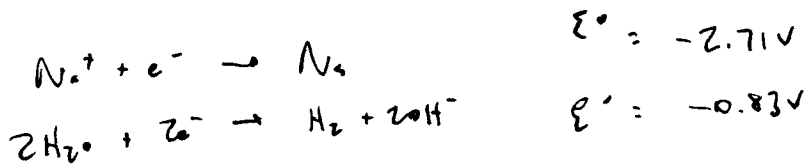


Pb<sup>4+</sup> (reduced) twice as many electrons as Pb<sup>2+</sup> so  
 reduce to Pb metal, so only half as much metal  
 is produced, per mol of e<sup>-</sup>.

b) Potassium permanganate (KMnO<sub>4</sub>) 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.

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



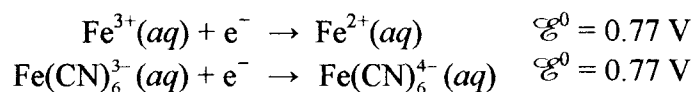
The reduction of water is more spontaneous than the  
 reduction of Na<sup>+</sup> (higher E<sup>o</sup>), so water will be  
 reduced before Na<sup>+</sup>.

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?

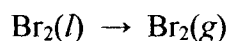
- (A)  $\Delta H < 0, \Delta S < 0$   
(B)  $\Delta H < 0, \Delta S > 0$   
(C)  $\Delta H > 0, \Delta S < 0$   
(D)  $\Delta H > 0, \Delta S > 0$   
(E) There are no conditions for which a reaction will always be spontaneous.

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



- (A)  $\text{Fe}^{2+}$  is more likely to be oxidized than  $\text{Fe}^{2+}$  complexed to  $\text{CN}^{-}$ .  
(B)  $\text{Fe}^{3+}$  is more likely to be reduced than  $\text{Fe}^{3+}$  complexed to  $\text{CN}^{-}$ .  
(C) Both A and B are true.  
(D) Complexation of Fe ions with  $\text{CN}^{-}$  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  $58.7^{\circ}\text{C}$ :



Which of the following statements are *false*?

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

- (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  $\Delta G$ .

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

- (A)  $\text{Ca}^{2+}$   $-2.76\text{V}$   
(B)  $\text{Ce}^{4+}$   $1.70\text{V}$   
(C)  $\text{Cu}^+$   $0.52\text{V}$   
(D)  $\text{F}^-$   ~~$-2.87\text{V}$~~   
(E)  $\text{Mg}$   $\text{---}$

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

- I. ✓ Choose a reagent with a more positive value of  $\mathcal{E}^0$  for the reduction half-reaction  
II. ✗ Choose a reagent with a more positive value of  $\mathcal{E}^0$  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

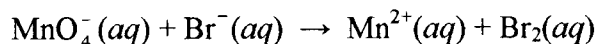
- (A) I and III  
(B) II and III  
(C) III and V  
(D) I, III, and V  
(E) II, III, and IV

12. For the reaction  $\text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \rightarrow \text{CH}_4(g) + 2 \text{O}_2(g)$ ,  $\Delta H^0 = 803 \text{ kJ/mol}$ . Which of the following will increase  $K$ ?

- (A) ✗ decrease the number of moles of  $\text{CH}_4(g)$   
(B) ✗ increase the volume of the system  
(C) ✓ increase the temperature of the system  
(D) ✗ all of the above  
(E) ✗ none of the above

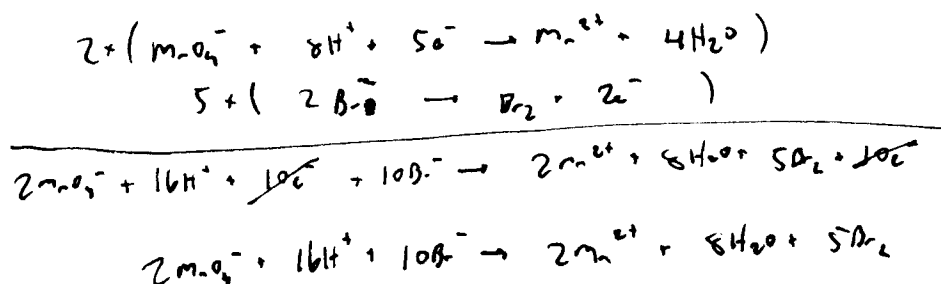
$$\ln K = \frac{-\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R}$$

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



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

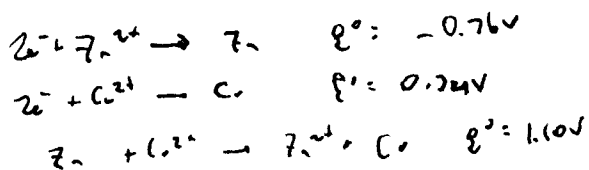
- (A) 1  
 (B) 2  
 (C) 5  
 (D) 10  
 (E) 20



14. Suppose the system  $\text{Zn}(s) \mid \text{Zn}^{2+}(aq) \parallel \text{Cu}^{2+}(aq) \mid \text{Cu}(s)$  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  $\mathcal{E}^0$  can be increased by increasing concentration of  $[\text{Zn}^{2+}]$ .  
 V. ✓ The cell potential  $\mathcal{E}$  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



15. Which of the following reactions has the largest positive value of  $\Delta S$  per mol of  $\text{Cl}_2$ ?

- (A)  $\text{Cl}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{Cl}_2\text{O}(g)$       1.5 → 1  
 (B)  $\text{Cl}_2(g) \rightarrow 2 \text{Cl}(g)$       1 → 2  
 (C)  $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$       2 → 2  
 (D)  $\text{Mg}(s) + \text{Cl}_2(g) \rightarrow \text{MgCl}_2(s)$       1 → 0  
 (E)  $2 \text{NH}_4\text{Cl}(s) \rightarrow \text{N}_2(g) + 4 \text{H}_2(g) + \text{Cl}_2(g)$       0 → 6