CH 223 Practice Problem Set #5

*This is a **practice problem set** and not the actual graded problem set that you will turn in for credit.*
Answers to each problem can be found at the end of this assignment.

Covering: **Chapter Sixteen, Chapter Seventeen** *and* **Chapter Guide Five**
Important Tables and/or Constants: **F = 96485 C/mol e$^-$, R = 8.3145 J mol^{-1} K^{-1}**, "**Redox Reactions**" *(Handout),* **Table of Redox Potentials** *at the end of problem set #5,* **Table of Thermodynamic values** *at the end of problem set #5 and here:* **http://mhchem.org/thermo**

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1. Classify each of the reactions according to their spontaneity. Are these reactions enthalpy and/or entropy driven?
   a. $Fe_2O_3(s) + 2\ Al(s) \rightarrow 2\ Fe(s) + Al_2O_3(s)$ $\Delta H° = -851.5$ kJ $\Delta S° = -375.2$ J/K
   b. $N_2(g) + 2\ O_2(g) \rightarrow 2\ NO_2(g)$ $\Delta H° = 66.2$ kJ; $\Delta S° = -121.6$ J/K
2. Heating some metal carbonates, among them calcium carbonate, leads to their decomposition.
   $$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$
   a. Calculate ΔH° and ΔS° for the reaction.
   b. Is the reaction spontaneous at 298 K?
   c. Is the reaction predicted to be spontaneous at higher temperatures?
3. Using values of $\Delta H°_f$ and $S°$, calculate $\Delta G°_{rxn}$ for the following reaction. Is the reaction product-favored? Is the reaction enthalpy or entropy driven?
   $$2\ Pb(s) + O_2(g) \rightarrow 2\ PbO(s, yellow)$$
4. Using values of $\Delta G°_f$, calculate $\Delta G°_{rxn}$ for each of the following reactions. Which are product-favored?
   a. $2\ K(s) + Cl_2(g) \rightarrow 2\ KCl(s)$
   b. $2\ CuO(s) \rightarrow 2\ Cu(s) + O_2(g)$
   c. $4\ NH_3(g) + 7\ O_2(g) \rightarrow 4\ NO_2(g) + 6\ H_2O(g)$
5. For the reaction: $BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$, $\Delta G°_{rxn} = +219.7$ kJ. Using this value and a table of thermodynamic data, calculate the value of $\Delta G°_f$ for $BaCO_3(s)$.
6. Estimate the temperature required to decompose HgS(s) into Hg(l) and S(g).
7. Calculate $\Delta G°$ and K_p at 25 °C for the reaction: $2\ HBr(g) + Cl_2(g) \rightarrow 2\ HCl(g) + Br_2(l)$ Is the reaction predicted to be product-favored under standard conditions? Comment on the sign of ΔG° and the magnitude of K_p.
8. Write balanced equations for the following half-reactions. Specify whether each is an oxidation or reduction.
   a. $Cr(s) \rightarrow Cr^{3+}(aq)$ (in acid)
   b. $AsH_3(g) \rightarrow As(s)$ (in acid)
   c. $VO_3^{-1}(aq) \rightarrow V^{2+}(aq)$ (in acid)
   d. $Ag(s) \rightarrow Ag_2O(s)$ (in base)

9. Balance the following redox equations. All occur in acid solution.
   a. $Ag(s) + NO_3^{-1}(aq) \rightarrow NO_2(g) + Ag^{+}(aq)$
   b. $MnO_4^{-1}(aq) + HSO_3^{-1}(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq)$
   c. $Zn(s) + NO_3^{-1}(aq) \rightarrow Zn^{2+}(aq) + N_2O(g)$
   d. $Cr(s) + NO_3^{-1}(aq) \rightarrow Cr^{3+}(aq) + NO(g)$
10. Balance the following redox equations. All occur in basic solution.
   a. $Al(s) + OH^{-1}(aq) \rightarrow Al(OH)_4^{-1}(aq) + H_2(g)$
   b. $CrO_4^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr(OH)_3(s) + SO_4^{2-}(aq)$
   c. $Zn(s) + Cu(OH)_2(s) \rightarrow [Zn(OH)_4]^{2-}(aq) + Cu(s)$
   d. $HS^{-1}(aq) + ClO_3^{-1}(aq) \rightarrow S(s) + Cl^{-1}(aq)$
11. A voltaic cell is constructed using the reaction of chromium metal and iron(II) ion.

$$2\ Cr(s) + 3\ Fe^{2+}(aq) \rightarrow 2\ Cr^{3+}(aq) + 3\ Fe(s)$$

   Complete the following sentences: Electrons in the external circuit flow from the ___ electrode to the ___ electrode. Negative ions move in the salt bridge from the ___ half-cell to the ___ half-cell. The half-reaction at the anode is ___ and that at the cathode is ___.
12. The half-cells $Fe(s)\ |\ Fe^{2+}(aq)\ ||\ O_2(g,\ 1\ atm)\ |\ H_2O(l,\ pH = 1.0)$ are linked to create a voltaic cell.
   a. Write equations for the oxidation and reduction half-reactions and for the overall (cell) reaction.
   b. Which half-reaction occurs in the anode compartment and which occurs in the cathode compartment?
   c. Complete the following sentences: Electrons in the external circuit flow from the ___ electrode to the ___ electrode. Negative ions move in the salt bridge from the ___ half-cell to the ___ half-cell.
13. Balance each of the following *unbalanced* equations, then calculate the standard redox potential, $E°$, and decide whether each is product-favored as written. All reactions occur in acid solution.
   a. $Sn^{2+}(aq) + Ag(s) \rightarrow Sn(s) + Ag^{+1}(aq)$
   b. $Al(s) + Sn^{4+}(aq) \rightarrow Sn^{2+}(aq) + Al^{3+}(aq)$
   c. $ClO_3^{-1}(aq) + Ce^{3+}(aq) \rightarrow Cl^{-1}(aq) + Ce^{4+}(aq)$ *Look these cell potentials up online*
   d. $Cu(s) + NO_3^{-1}(aq) \rightarrow Cu^{2+}(aq) + NO(g)$

14. Consider the following half-reactions:

Half-Reaction	***E*° (V)**
$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	+0.34
$Sn^{2+}(aq) + 2\ e^- \rightarrow Sn(s)$	-0.14
$Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)$	-0.44
$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$	-0.76
$Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$	-1.66

   a. Based on $E°$ values, which metal is the most easily oxidized?
   b. Which metals on this list are capable of reducing Fe^{2+}(aq) to Fe?
   c. Write a balanced chemical equation for the reaction of Fe^{2+}(aq) with Sn(s). Is this reaction product-favored or reactant-favored?
   d. Write a balanced chemical equation for the reaction of Zn^{2+}(aq) with Sn(s). Is this reaction product-favored or reactant-favored?

15. Calculate the voltage delivered by a voltaic cell using the following reaction if all dissolved species are 2.5×10^{-2} M. *Use the OpenStax text to find the cell potentials.*

$$Zn(s) + 2\ H_2O(l) + 2\ OH^{-1}(aq) \rightarrow [Zn(OH)_4]^{2-}(aq) + H_2(g)$$

16. Calculate $\Delta G°$ and the equilibrium constant for the following reactions.
   a. $2\ Fe^{3+}(aq) + 2\ I^{-1}(aq) \rightarrow 2\ Fe^{2+}(aq) + I_2(aq)$
   b. $I_2(aq) + 2\ Br^{-1}(aq) \rightarrow 2\ I^{-1}(aq) + Br_2(aq)$

17. A potential of +0.146 V is recorded (under standard conditions) for a voltaic cell constructed using the following half-reactions:

   Anode: $Ag(s) \rightarrow Ag^{+1}(aq) + e^-$

   Cathode: $Ag_2SO_4(s) + 2\ e^- \rightarrow 2\ Ag(s) + SO_4^{2-}(aq)$

   a. What is the standard reduction potential for the cathode reaction?
   b. Calculate the solubility product, K_{sp}, for Ag_2SO_4.

18. In the electrolysis of a solution containing Ni^{2+}(aq), metallic Ni(s) deposits on the cathode. Using a current of 0.150 A for 12.2 min, what mass of nickel will form?

19. Electrolysis of a solution of $CuSO_4$(aq) to give copper metal is carried out using a current of 0.66 A. How long should electrolysis continue to produce 0.50 g of copper?

20. Electrolysis of molten NaCl is done in cells operating at 7.0 V and 4.0×10^4 A. What mass of Na(s) and Cl_2(g) can be produced in one day in such a cell? What is the energy consumption in kilowatt-hours? (1 kWh = 3.6×10^6 J and 1 J = 1 C • V)

Answers to the Practice Problem Set: ***Please note*** *that all thermodynamic and electrochemical answers will vary slightly depending on the source of values used to solve the problems. The answers should be close, however.*

1. a. enthalpy driven, spontaneous at low temperatures b. non-spontaneous at all temperatures
2. a. ΔH^o = 191.59 kJ, ΔS^o = 141.9 J/K b. no c. yes
3. ΔH^o = -434.64 kJ, ΔS^o = -197.4 J/K, ΔG^o = –375.77 kJ; product favored, enthalpy driven
4. a. ΔG^o = –817.0 kJ; product favored b. ΔG^o = 259.4 kJ; reactant favored c. ΔG^o = –1101.3 kJ; product favored
5. $\Delta G_f^o[BaCO_3(s)]$ = –1134.4 kJ/mol
6. 2089 K or greater
7. ΔG^o = –83.74 kJ; $K_p = 4.8 \times 10^{14}$ Negative ΔG and large K_p indicate product-favored reaction
8. *Answers:*
   a. $Cr(s) \rightarrow Cr^{3+}(aq) + 3\ e^-$ oxidation
   b. $AsH_3(g) \rightarrow As(s) + 3\ H^+(aq) + 3\ e^-$ oxidation
   c. $VO_3^-(aq) + 6\ H^+(aq) + 3\ e^- \rightarrow V^{2+}(aq) + 3\ H_2O(\ell)$ reduction
   d. $2\ Ag(s) + 2\ OH^-(aq) \rightarrow Ag_2O(s) + H_2O(\ell) + 2\ e^-$ oxidation
9. *Answers:*
   a. $Ag(s) + NO_3^-(aq) + 2\ H^+(aq) \rightarrow Ag^+(aq) + NO_2(g) + H_2O(\ell)$
   b. $2\ MnO_4^-(aq) + H^+(aq) + 5\ HSO_3^-(aq) \rightarrow 2\ Mn^{2+}(aq) + 3\ H_2O(\ell) + 5\ SO_4^{2-}(aq)$
   c. $4\ Zn(s) + 2\ NO_3^-(aq) + 10\ H^+(aq) \rightarrow 5\ H_2O(\ell) + 4\ Zn^{2+}(aq) + N_2O(g)$
   d. $Cr(s) + NO_3^-(aq) + 4\ H^+(aq) \rightarrow Cr^{3+}(aq) + NO(g) + 2\ H_2O(\ell)$
10. *Answers:*
   a. $2\ Al(s) + 6\ H_2O(\ell) + 2\ OH^-(aq) \rightarrow 2\ Al(OH)_4^-(aq) + 3\ H_2(g)$
   b. $2\ CrO_4^-(aq) + 5\ H_2O(\ell) + 3\ SO_3^{2-}(aq) \rightarrow 2\ Cr(OH)_3(s) + 4\ OH^-(aq) + 3\ SO_4^{2-}(aq)$
   c. $Zn(s) + 2\ OH^-(aq) + Cu(OH)_2(s) \rightarrow Zn(OH)_4^{2-}(aq) + Cu(s)$
   d. $3\ HS^-(aq) + ClO_3^-(aq) \rightarrow 3\ S(s) + Cl^-(aq) + 3\ OH^-(aq)$
11. Electrons in the external circuit flow from the Cr electrode to the Fe electrode. Negative ions move in the salt bridge from the Fe/Fe^{2+} half-cell to the Cr/Cr^{3+} half-cell. The half-reaction at the anode is $Cr(s) \rightarrow Cr^{3+}(aq) + 3\ e^-$ and that at the cathode is $Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)$.
12. *Answers:*
   a. Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$
   Reduction: $O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(\ell)$
   Overall: $2\ Fe(s) + O_2(g) + 4\ H^+(aq) \rightarrow 2\ H_2O(\ell) + 2\ Fe^{2+}(aq)$
   b. Oxidation occurs in the anode compartment and reduction occurs in the cathode compartment.
   c. Electrons in the external circuit flow from the Fe electrode to the positive (site of O_2 reduction) electrode. Negative ions move in the salt bridge from the O_2/H_2O half-cell to the Fe/Fe^{2+} half-cell.

13. Answers:

a. $Sn^{2+}(aq) + 2\,Ag(s) \rightarrow Sn(s) + 2\,Ag^{+}(aq)$
$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (-0.14\text{ V}) - (+0.799\text{ V}) = -0.94\text{ V}$ not product-favored

b. $2\,Al(s) + 3\,Sn^{4+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,Sn^{2+}(aq)$
$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (+0.15\text{ V}) - (-1.66\text{ V}) = +1.81\text{ V}$ product-favored

c. $ClO_3^{-}(aq) + 6\,H^{+}(aq) + 6\,Ce^{3+}(aq) \rightarrow Cl^{-}(aq) + 3\,H_2O(\ell) + 6\,Ce^{4+}(aq)$
$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (+0.62\text{ V}) - (+1.61\text{ V}) = -0.99\text{ V}$ not product-favored

d. $3\,Cu(s) + 2\,NO_3^{-}(aq) + 8\,H^{+}(aq) \rightarrow 2\,NO(g) + 3\,Cu^{2+}(aq) + 4\,H_2O(\ell)$
$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (+0.96\text{ V}) - (+0.337\text{ V}) = +0.62\text{ V}$ product-favored

14. Answers:

a. Al(s)

b. Zn(s) and Al(s)

c. $Fe^{2+}(aq) + Sn(s) \rightarrow Fe(s) + Sn^{2+}(aq)$
$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (-0.44\text{ V}) - (-0.14\text{ V}) = -0.30\text{ V}$ reactant-favored

d. $Zn^{2+}(aq) + Sn(s) \rightarrow Zn(s) + Sn^{2+}(aq)$
$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = (-0.76\text{ V}) - (-0.14\text{ V}) = -0.62\text{ V}$ reactant-favored

15. 0.32 V

16. a. $\Delta G^{o} = -45.5$ kJ, $K = 9 \times 10^{7}$ b. $\Delta G^{o} = 110$ kJ, $K = 4 \times 10^{-19}$

17. a. 0.653 V b. $K_{sp} = 1 \times 10^{-5}$

18. 0.0334 g

19. 2300 s (38 min)

20. 8.2×10^{5} g Na, 1.3×10^{6} g Cl_2, 6700 kwh