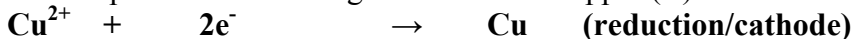**CH 302 Spring 2008**
Worksheet 10b: More Advanced Electrochemistry Problems

1. (a) Calculate the mass of copper metal produced at the cathode during the passage of 2.50 amps of current through a solution of copper (II) sulfate for 50.0 minutes.
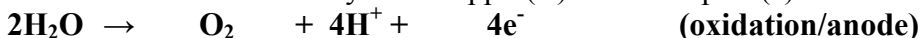
Cu^{2+} + 2e⁻ → Cu (reduction/cathode)
1 mol $2(6.02 \times 10^{23})$e⁻ 1 mol
63.5 g $2(9.65 \times 10^{4}C)$ 63.5g
50.0 min x (60s/1 min) x (2.50C/s) = 7.50 x 10³C
7.50 x 10³C x (1 mol e⁻/9.65 x 10⁴C) x (63.5 g Cu/2 mol e⁻) = 2.47 g Cu

(b) What volume of oxygen gas (measured at STP) is produced by the oxidation of water at the anode in the electrolysis of copper(II) sulfate in part (a)?
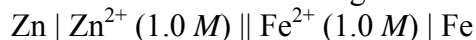
$2H_2O$ → O_2 + $4H^+$ + 4e⁻ (oxidation/anode)
           1 mol $4((6.02 \times 10^{23})$e⁻
           22.4 L $4(9.65 \times 10^{4}C)$
7.50 x 10³C x (1 mol e⁻/9.65 x 10⁴C) x (22.4 L O₂/4 mol e⁻) = 0.435 L O₂

2. What is the $E°$ for the following electrochemical cell where Zn is the cathode?
      $Zn \mid Zn^{2+}$ (1.0 M) $\| Fe^{2+}$ (1.0 M) $\mid$ Fe
      $E°$ (Zn) = -0.76 $E°$ (Fe) = -0.44
$E_{cell} = E°_{cathode} - E°_{anode}$ **= -0.76 – (-0.44) = -0.32**

3. For the electrolysis of molten sodium bromide, write the two half-reactions and show write which electrode at which each occurs (cathode or anode).
Two half-reactions: Na^+ + 1e⁻ → Na   **and**   **2Br⁻ → Br₂ + 2e⁻**
Oxidation occurs at the anode, so the 2Br⁻ → Br₂ + 2 e⁻ reaction is at the anode, and
Reduction occurs at the cathode, so Na^+ + 1e⁻ → Na is at the cathode.
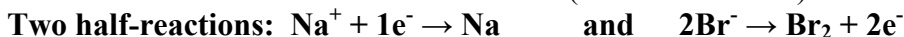
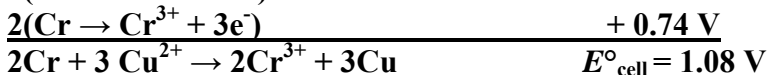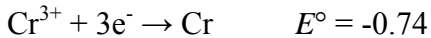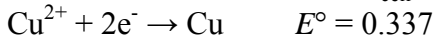**4.** Calulate the potential, E, for the Fe^{3+}/ Fe^{2+} electrode when the concentration of Fe^{2+} is exactly five times that of Fe^{3+}.
      Fe^{3+} + e⁻ → Fe^{2+} $E°$ = +0.771 V
Q = [Red]ʸ/[[Ox]ˣ = [Fe²⁺]/[Fe³⁺] = 5[Fe³⁺]/[Fe³⁺] = 5
E = E° - 0.0592/n*logQ = +0.771 – 0.0592/1*log5 = (0.771-0.041)V = 0.730 V

5. At standard conditions, will chromium (III) ions, Cr^{3+}, oxidize metallic copper to copper (II) ions, Cu^{2+}, or will Cu^{2+} ozidize metallic chromium to Cr^{3+} ions? Write the cell reaction and calculate $E°_{cell}$ for the spontaneous reaction.
Cu^{2+} + 2e⁻ → Cu $E°$ = 0.337
Cr^{3+} + 3e⁻ → Cr $E°$ = -0.74

                                        $E°$
3(Cu^{2+} + 2e⁻ → Cu)   **+0.337 V**
2(Cr → Cr^{3+} + 3e⁻)   **+ 0.74 V**
2Cr + 3 Cu^{2+} → $2Cr^{3+}$ + 3Cu   **$E°_{cell}$ = 1.08 V**
Cu^{2+} ions spontaneously oxidize metallic Cr to Cr^{3+} ions and are reduced to metallic Cu.

6. In an acidic solution at standard conditions, will tin(IV) ions, Sn^{4+}, oxidize gaseous nitrogen oxide, NO, to nitrate ions, NO_3^-, or will NO_3^- ozidize Sn^{2+} to Sn^{4+} ions? Write the cell reaction and calculate $E°_{cell}$ for the spontaneous reaction.
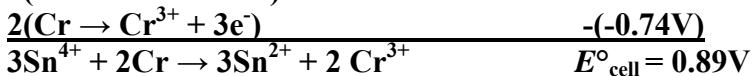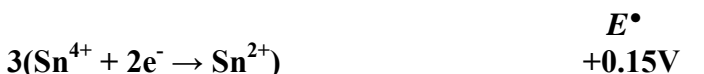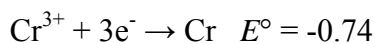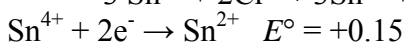
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ $\qquad\qquad\qquad$ $E° = +0.15$
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ $\qquad$ $E° = +0.96$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad E°$

$2(NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O)$ $\qquad\qquad$ **+0.96V**
$\underline{3(Sn^{2+} \rightarrow Sn^{4+} + 2e^-)}$ $\qquad\qquad\qquad\qquad\qquad$ **-0.15V**
$2NO_3^- + 8H^+ + 3Sn^{2+} \rightarrow 3Sn^{4+} + 4H_2O + 2NO$ $\qquad$ $E°_{cell} = $ **+0.81V**
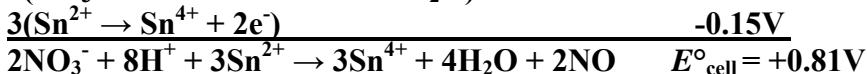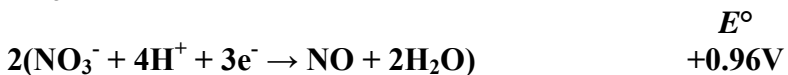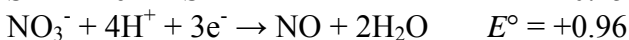
Nitrate ions spontaneously oxidize tin(II) ions to tin(IV) ions and are reduced to nitrogen oxide in acidic solution.

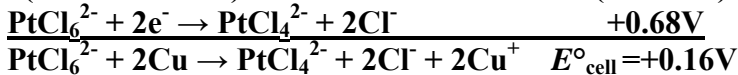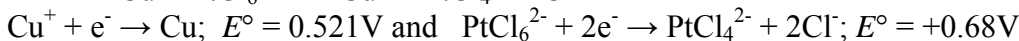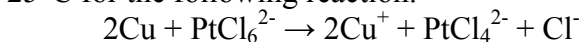**7.** Calculate the Gibbs free energy change, $\Delta G°$, in J/mol at 25°C for the following reaction:
$\qquad\qquad 3\ Sn^{4+} + 2Cr \rightarrow 3Sn^{2+} + 2Cr^{3+}$
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}\ \ E° = +0.15$ $\qquad\qquad\qquad$ $Cr^{3+} + 3e^- \rightarrow Cr\ \ E° = -0.74$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad E^{\bullet}$

$3(Sn^{4+} + 2e^- \rightarrow Sn^{2+})$ $\qquad\qquad\qquad\qquad$ **+0.15V**
$\underline{2(Cr \rightarrow Cr^{3+} + 3e^-)}$ $\qquad\qquad\qquad\qquad\qquad$ **-(-0.74V)**
$3Sn^{4+} + 2Cr \rightarrow 3Sn^{2+} + 2\ Cr^{3+}$ $\qquad\qquad$ $E°_{cell} = $ **0.89V**
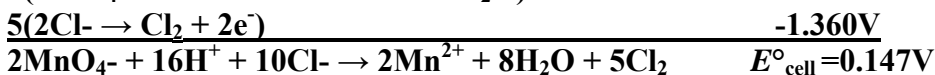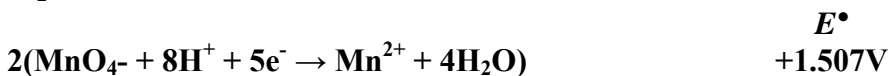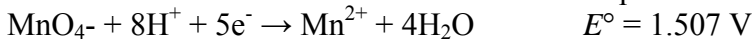$\Delta G° = -nF\ E°_{cell} = $ **-(6 mol e⁻/mol rxn)(9.65x 10^4 J/V.mol e⁻)(+0.89V)**
= -5.2 x 10^5 J/mol rxn

8. Use the standard cell potential to calculate the value of the equilibrium constant, K, at 25°C for the following reaction.
$\qquad\qquad 2Cu + PtCl_6^{2-} \rightarrow 2Cu^+ + PtCl_4^{2-} + Cl^-$
$Cu^+ + e^- \rightarrow Cu;\ \ E° = 0.521V$ and $\ \ PtCl_6^{2-} + 2e^- \rightarrow PtCl_4^{2-} + 2Cl^-;\ E° = +0.68V$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad E^{\bullet}$

$2(Cu \rightarrow Cu^+ + e^-)$ $\qquad\qquad\qquad\qquad\qquad$ **-(+0.521V)**
$\underline{PtCl_6^{2-} + 2e^- \rightarrow PtCl_4^{2-} + 2Cl^-}$ $\qquad\qquad\qquad$ **+0.68V**
$PtCl_6^{2-} + 2Cu \rightarrow PtCl_4^{2-} + 2Cl^- + 2Cu^+$ $\qquad$ $E°_{cell} = $**+0.16V**
$\ln K = -nF\ E°_{cell}/RT = $ **(2)(9.65x 10^4 J/V.mol e⁻)(0.16V)/(8.314J/mol.K)(298K) = 12.5**
$K = e^{12.5} = $ **2.7 x 10^5**

9. The following cell is maintained at 25°C. One half-cell consists of a chlorine/chloride, Cl_2/Cl^-, electrode with the partial pressure of $Cl_2 = 0.100$ atm and [Cl-] = 0.100 M. The other half-cell involves the MnO_4^-/Mn^{2+} couple in acidic solution with $[MnO_4^-] = 0.100$ M, $[Mn^{2+}] = 0.100$ M, and $[H^+] = 0.100$ M. Apply the Nernst equation to the overall cell reaction to determine the cell potential for this cell.

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $\qquad$ $E° = 1.507$ V
$Cl_2 + 2e^- \rightarrow 2Cl^-$ $\qquad\qquad\qquad\qquad\qquad$ $E° = 1.360$ V

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad E^{\bullet}$

$2(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)$ $\qquad\qquad$ **+1.507V**
$\underline{5(2Cl^- \rightarrow Cl_2 + 2e^-)}$ $\qquad\qquad\qquad\qquad\qquad$ **-1.360V**
$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$ $\qquad$ $E°_{cell} = $**0.147V**
$E_{cell} = E°_{cell} - 0.0592/n*\log\ \{[Mn^{2+}]^2(P_{Cl2})^5/[MnO_4^-]^2[H^+]^{16}[Cl^-]^{10}\}$
= 0.147V – (0.0592/10) * log [(0.100)^2(0.100)^5/(0.100)^2(0.100)^16(0.100)^10]
= 0.147 V - (0.0592/10) * log (1.00 x 10^21) = 0.017V