CH 302 13 Answer Key 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.

Cu²⁺ + 2e⁻ \rightarrow Cu (reduction/cathode) 1 mol 2(6.02 x 10²³)e⁻ 1 mol 63.5 g 2(9.65 x 10⁴C) 63.5 g 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)?

 $7.50 \times 10^{3} \text{C} \times (1 \text{ mol e}^{-}/9.65 \times 10^{4} \text{C}) \times (22.4 \text{ L O}_{2}/4 \text{ mol e}^{-}) = 0.435 \text{ L O}_{2}$

2. What is the E° for the following electrochemical cell where Zn is the cathode?

$$Zn \mid Zn^{2+} (1.0 M) \parallel Fe^{2+} (1.0 M) \mid Fe$$

 $E^{\circ} (Zn) = -0.76$ $E^{\circ} (Fe) = -0.44$
 $E_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = -0.76 - (-0.44) = -0.32$

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: $Na^+ + 1e^- \rightarrow Na$ and $2Br^- \rightarrow Br_2 + 2e^-$ Oxidation occurs at the anode, so the $2Br^- \rightarrow Br_2 + 2e^-$ reaction is at the anode, and Reduction occurs at the cathode, so $Na^+ + 1e^- \rightarrow Na$ is at the cathode.

4. Calculate the potential, E, for the Fe^{3+}/Fe^{2+} electrode when the concentration of Fe^{2+} is exactly five times that of Fe^{3+} .

Fe³⁺ + e⁻
$$\rightarrow$$
 Fe²⁺ $E^{\circ} = +0.771 \text{ V}$
Q = [Red]^y/[[Ox]^x = [Fe²⁺]/[Fe³⁺] = 5[Fe³⁺]/[Fe³⁺] = 5
 $E = E^{\circ} - 0.0592/\text{n*logO} = +0.771 - 0.0592/\text{1*log5} = (0.771-0.041)\text{V} = 0.730 \text{ V}$

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.

$$Cu^{2^{+}} + 2e^{-} \rightarrow Cu$$
 $E^{\circ} = 0.337$
 $Cr^{3^{+}} + 3e^{-} \rightarrow Cr$ $E^{\circ} = -0.74$

 $\overline{\text{Cu}^{2^+}}$ ions spontaneously oxidize metallic Cr to $\overline{\text{Cr}^{3^+}}$ 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.

$$Sn^{4+} + 2e^{-} \rightarrow Sn^{2+}$$
 $E^{\circ} = +0.15$
 $NO_{3}^{-} + 4H^{+} + 3e^{-} \rightarrow NO + 2H_{2}O$ $E^{\circ} = +0.96$
 E°
 $2(NO_{3}^{-} + 4H^{+} + 3e^{-} \rightarrow NO + 2H_{2}O)$ $+0.96V$
 $3(Sn^{2+} \rightarrow Sn^{4+} + 2e^{-})$ $-0.15V$
 $2NO_{3}^{-} + 8H^{+} + 3Sn^{2+} \rightarrow 3Sn^{4+} + 4H_{2}O + 2NO$ $E^{\circ}_{cell} = +0.81V$

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, ΔG° , in J/mol at 25°C for the following reaction:

$$3 \operatorname{Sn}^{4+} + 2\operatorname{Cr} \to 3\operatorname{Sn}^{2+} + 2\operatorname{Cr}^{3+}$$

$$\operatorname{Sn}^{4+} + 2\operatorname{e}^{-} \to \operatorname{Sn}^{2+} \quad E^{\circ} = +0.15$$

$$\operatorname{E}^{\bullet}$$

$$3(\operatorname{Sn}^{4+} + 2\operatorname{e}^{-} \to \operatorname{Sn}^{2+}) \quad +0.15\operatorname{V}$$

$$2(\operatorname{Cr} \to \operatorname{Cr}^{3+} + 3\operatorname{e}^{-}) \quad -(-0.74\operatorname{V})$$

$$3\operatorname{Sn}^{4+} + 2\operatorname{Cr} \to 3\operatorname{Sn}^{2+} + 2\operatorname{Cr}^{3+} \quad E^{\circ}_{\operatorname{cell}} = 0.89\operatorname{V}$$

$$\Delta G^{\circ} = -nF E^{\circ}_{\operatorname{cell}} = -(6 \operatorname{mol e'/mol rxn})(9.65 \times 10^{4} \operatorname{J/V.mol e'})(+0.89\operatorname{V})$$

$$= -5.2 \times 10^{5} \operatorname{J/mol rxn}$$

8. Use the standard cell potential to calculate the value of the equilibrium constant, K, at 25°C for the following reaction.

$$2\text{Cu} + \text{PtCl}_{6}^{2^{-}} \rightarrow 2\text{Cu}^{+} + \text{PtCl}_{4}^{2^{-}} + \text{Cl}^{-}$$

$$\text{Cu}^{+} + \text{e}^{-} \rightarrow \text{Cu}; \ E^{\circ} = 0.521 \text{V and} \quad \text{PtCl}_{6}^{2^{-}} + 2\text{e}^{-} \rightarrow \text{PtCl}_{4}^{2^{-}} + 2\text{Cl}^{-}; \ E^{\circ} = +0.68 \text{V}$$

$$E^{\bullet}$$

$$2(\text{Cu} \rightarrow \text{Cu}^{+} + \text{e}^{-}) \qquad -(+0.521 \text{V})$$

$$\frac{\text{PtCl}_{6}^{2^{-}} + 2\text{e}^{-} \rightarrow \text{PtCl}_{4}^{2^{-}} + 2\text{Cl}^{-}}{\text{PtCl}_{6}^{2^{-}} + 2\text{Cu} \rightarrow \text{PtCl}_{4}^{2^{-}} + 2\text{Cl}^{-} + 2\text{Cu}^{+}} \quad E^{\circ}_{\text{cell}} = +0.16 \text{V}$$

$$\ln \text{K} = -n\text{F} \ E^{\circ}_{\text{cell}}/\text{RT} = (2)(9.65 \text{x} \ 10^{4} \text{ J/V.mol e})(0.16 \text{V})/(8.314 \text{J/mol.K})(298 \text{K}) = 12.5$$

$$\text{K} = e^{12.5} = 2.7 \text{ x} \ 10^{5}$$

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. $MnO_4-+8H^++5e^- \rightarrow Mn^{2+}+4H_2O$ $E^\circ=1.507$ V

$$Cl_2 + 2e^- \rightarrow 2Cl^- \qquad E^\circ = 1.360 \text{ V}$$

$$E^\bullet$$

$$2(\text{MnO}_{4^-} + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2^+} + 4\text{H}_2\text{O}) \qquad +1.507\text{V}$$

$$\underline{5(2\text{Cl}_{-} \rightarrow \text{Cl}_2 + 2e^-)} \qquad -1.360\text{V}$$

$$\underline{2\text{MnO}_{4^-} + 16\text{H}^+ + 10\text{Cl}_{-} \rightarrow 2\text{Mn}^{2^+} + 8\text{H}_2\text{O} + 5\text{Cl}_2 \qquad E^\circ_{\text{cell}} = 0.147\text{V}}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0592/\text{n*log} \{[\text{Mn}^{2^+}]^2(P_{\text{Cl}2})^5/[\text{MnO}_{4^-}]^2[\text{H}^+]^{16}[\text{Cl}^-]^{10}\}$$

$$= 0.147\text{V} - (0.0592/10) * \log [(0.100)^2(0.100)^5/(0.100)^2(0.100)^16(0.100)^10]$$

$$= 0.147\text{ V} - (0.0592/10) * \log (1.00 \times 10^21) = 0.017\text{V}$$