## CH 302 Spring 2006

Worksheet 12b: Electrochemistry

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.
$\mathbf{C u}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathbf{C u} \quad$ (reduction/cathode)
$1 \mathrm{~mol} \quad 2\left(6.02 \times 10^{23}\right) \mathrm{e}^{-} 1 \mathrm{~mol}$
$63.5 \mathrm{~g} \quad 2\left(9.65 \times 10^{4} \mathrm{C}\right) \quad 63.5 \mathrm{~g}$
$50.0 \mathrm{~min} \times(60 \mathrm{~s} / 1 \mathrm{~min}) \times(2.50 \mathrm{C} / \mathrm{s})=7.50 \times 10^{3} \mathrm{C}$
$7.50 \times 10^{3} \mathrm{C} \times\left(1 \mathrm{~mol} \mathrm{e} / 9.65 \times 10^{4} \mathrm{C}\right) \times(63.5 \mathrm{~g} \mathrm{Cu} / 2 \mathrm{~mol} \mathrm{e})=2.47 \mathrm{~g} \mathrm{Cu}$
(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)?
```
2H2O}->\quad\mp@subsup{\textrm{O}}{2}{\prime
    1 mol 4((6.02 x 100 23)e
    22.4 L 4(9.65 x 104C)
\(7.50 \times 10^{3} \mathrm{C} \times\left(1 \mathbf{~ m o l ~ e}-/ 9.65 \times 10^{4} \mathrm{C}\right) \times\left(22.4 \mathrm{~L} \mathrm{O}_{2} / 4 \mathrm{~mol} \mathrm{e}\right)=0.435 \mathrm{~L} \mathrm{O}_{\mathbf{2}}\)
```

2. What is the $E^{\circ}$ for the following electrochemical cell where Zn is the cathode?

$$
\begin{gathered}
\mathrm{Zn}\left|\mathrm{Zn}^{2+}(1.0 \mathrm{M}) \| \mathrm{Fe}^{2+}(1.0 \mathrm{M})\right| \mathrm{Fe} \\
E^{\circ}(\mathrm{Zn})=-0.76 \quad E^{\circ}(\mathrm{Fe})=-0.44 \\
\boldsymbol{E}_{\text {cell }}=\boldsymbol{E}_{\text {cathode }}^{\circ}-\boldsymbol{E}_{\text {anode }}^{\circ}=\mathbf{- 0 . 7 6}-\mathbf{( - 0 . 4 4 )}=\mathbf{- 0 . 3 2}
\end{gathered}
$$

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: $\mathrm{Na}^{+}+1 \mathrm{e}^{-} \rightarrow \mathrm{Na}$ and $2 \mathrm{Br}^{-} \rightarrow \mathrm{Br}_{2}+2 \mathrm{e}^{-}$
Oxidation occurs at the anode, so the $2 \mathrm{Br}^{-} \rightarrow \mathrm{Br}_{2}+2 \mathrm{e}^{-}$reaction is at the anode, and Reduction occurs at the cathode, so $\mathrm{Na}^{+}+1 \mathrm{e}^{-} \rightarrow \mathrm{Na}$ is at the cathode.
4. Calulate the potential, $E$, for the $\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}$ electrode when the concentration of $\mathrm{Fe}^{2+}$ is exactly five times that of $\mathrm{Fe}^{3+}$.

$$
\begin{gathered}
\mathrm{Fe}^{3+}+\mathrm{e}^{-} \rightarrow \mathrm{Fe}^{2+} \quad E^{\circ}=+0.771 \mathrm{~V} \\
\mathbf{Q}=\left[\mathrm{Red}^{\mathrm{y}} /\left[[\mathrm{Ox}]^{\mathrm{x}}=\left[\mathrm{Fe}^{2+}\right] /\left[\mathrm{Fe}^{\mathbf{3 +}}\right]=\mathbf{5}\left[\mathrm{Fe}^{3+}\right] /\left[\mathrm{Fe}^{\mathbf{3 +}}\right]=\mathbf{5}\right.\right. \\
\boldsymbol{E}=\boldsymbol{E}^{\circ} \mathbf{- 0 . 0 5 9 2} / \mathbf{n}^{*} \operatorname{logQ}=+\mathbf{0 . 7 7 1}-\mathbf{0 . 0 5 9 2} / \mathbf{1} * \log 5=(\mathbf{0 . 7 7 1 - 0 . 0 4 1}) \mathrm{V}=\mathbf{0 . 7 3 0} \mathrm{V}
\end{gathered}
$$

5. At standard conditions, will chromium (III) ions, $\mathrm{Cr}^{3+}$, oxidize metallic copper to copper (II) ions, $\mathrm{Cu}^{2+}$, or will $\mathrm{Cu}^{2+}$ ozidize metallic chromium to $\mathrm{Cr}^{3+}$ ions? Write the cell reaction and calculate $E^{\circ}$ cell for the spontaneous reaction.

$$
\begin{array}{lc}
\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu} & E^{\circ}=0.337 \\
\mathrm{Cr}^{3+}+3 \mathrm{e}^{-} \rightarrow \mathbf{C r} & E^{\circ}=-0.74 \\
& \\
\left.\mathbf{3 ( C u} \mathbf{C u}^{\mathbf{2 +}}+\mathbf{2} \mathbf{e}^{-} \rightarrow \mathbf{C u}\right) & \boldsymbol{E}^{\circ} \\
\mathbf{2 ( \mathbf { C r } \rightarrow \mathbf { C r } ^ { \mathbf { 3 + } } + \mathbf { 3 e } )} & +\mathbf{0 . 3 3 7} \mathbf{V} \\
\mathbf{2 \mathbf { C r } + \mathbf { 3 } \mathbf { C u } ^ { 2 + } \rightarrow \mathbf { 2 C r }}{ }^{3+}+\mathbf{3 C u} & +\mathbf{0 . 7 4} \mathbf{V} \\
\mathbf{2 +} & \mathbf{E}^{\circ}{ }_{\text {cell }}=\mathbf{1 . 0 8} \mathbf{~ V}
\end{array}
$$

$\mathrm{Cu}^{2+}$ ions spontaneously oxidize metallic Cr to $\mathrm{Cr}^{3+}$ ions and are reduced to metallic Cu .
6. In an acidic solution at standard conditions, will tin(IV) ions, $\mathrm{Sn}^{4+}$, oxidize gaseous nitrogen oxide, NO , to nitrate ions, $\mathrm{NO}_{3}{ }^{-}$, or will $\mathrm{NO}_{3}{ }^{-}$ozidize $\mathrm{Sn}^{2+}$ to $\mathrm{Sn}^{4+}$ ions? Write the cell reaction and calculate $E^{\circ}$ cell for the spontaneous reaction.
$\mathrm{Sn}^{4+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Sn}^{2+} \quad E^{\circ}=+0.15$
$\mathrm{NO}_{3}{ }^{-}+4 \mathrm{H}^{+}+3 \mathrm{e}^{-} \rightarrow \mathrm{NO}+2 \mathrm{H}_{2} \mathrm{O} \quad E^{\circ}=+0.96$
$2\left(\mathrm{NO}_{3}{ }^{-}+4 \mathrm{H}^{+}+3 \mathrm{e}^{-} \rightarrow \mathrm{NO}+\mathbf{2 H} \mathrm{H}_{2} \mathrm{O}\right) \quad+0.96 \mathrm{~V}$
$3\left(\mathbf{S n}^{2+} \rightarrow \mathbf{S n}^{4+}+2 \mathrm{e}^{-}\right) \quad-0.15 \mathrm{~V}$
$2 \mathrm{NO}_{3}{ }^{-}+\mathbf{8 H} \mathrm{H}^{+}+\mathbf{3 \mathrm { Sn } ^ { 2 + } \rightarrow 3 \mathrm { Sn } ^ { 4 + } + 4 \mathrm { H } _ { 2 } \mathrm { O } + 2 \mathrm { NO } \quad E ^ { \circ } { } _ { \text { cell } } = + 0 . 8 1 \mathrm { V }}$
Nitrate ions spontaneously oxidize $\operatorname{tin}($ II) ions to $\operatorname{tin}(I V)$ ions and are reduced to nitrogen oxide in acidic solution.
7. Calculate the Gibbs free energy change, $\Delta \mathrm{G}^{\circ}$, in $\mathrm{J} / \mathrm{mol}$ at $25^{\circ} \mathrm{C}$ for the following reaction:

$$
\begin{aligned}
& 3 \mathrm{Sn}^{4+}+2 \mathrm{Cr} \rightarrow 3 \mathrm{Sn}^{2+}+2 \mathrm{Cr}^{3+} \\
& \mathrm{Sn}^{4+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Sn}^{2+} \quad E^{\circ}=+0.15 \quad \mathrm{Cr}^{3+}+3 \mathrm{e}^{-} \rightarrow \mathrm{Cr} \quad E^{\circ}=-0.74 \\
& \boldsymbol{E}^{\circ} \\
& \text { 3( } \left.\mathrm{Sn}^{4+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Sn}^{2+}\right) \quad+0.15 \mathrm{~V} \\
& \underline{2\left(\mathrm{Cr} \rightarrow \mathrm{Cr}^{3+}+3 \mathrm{e}^{-}\right)} \quad-(-0.74 \mathrm{~V}) \\
& 3 \mathrm{Sn}^{4+}+2 \mathrm{Cr} \rightarrow 3 \mathrm{Sn}^{2+}+2 \mathrm{Cr}^{3+} \quad E_{\text {cell }}^{\circ}=0.89 \mathrm{~V} \\
& \Delta G^{\circ}=-n F E^{\circ}{ }_{\text {cell }}=-\left(6 \mathrm{~mol} \mathrm{e}^{-} / \mathrm{mol} \mathrm{rxn}\right)\left(9.65 \times 10^{4} \mathrm{~J} / \mathrm{V} . \mathrm{mol} \mathrm{e} \mathrm{e}^{-}\right)(+0.89 \mathrm{~V}) \\
& =-5.2 \times 10^{5} \mathrm{~J} / \mathrm{mol} \mathrm{rxn} \\
& \text { 8. Use the standard cell potential to calculate the value of the equilibrium constant, } K \text {, at } \\
& 25^{\circ} \mathrm{C} \text { for the following reaction. } \\
& 2 \mathrm{Cu}+\mathrm{PtCl}_{6}{ }^{2-} \rightarrow 2 \mathrm{Cu}^{+}+\mathrm{PtCl}_{4}{ }^{2-}+\mathrm{Cl}^{-} \\
& \mathrm{Cu}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Cu} ; E^{\circ}=0.521 \mathrm{~V} \text { and } \mathrm{PtCl}_{6}{ }^{2-}+2 \mathrm{e}^{-} \rightarrow \mathrm{PtCl}_{4}{ }^{2-}+2 \mathrm{Cl}^{-} ; E^{\circ}=+0.68 \mathrm{~V} \\
& E^{\circ} \\
& 2\left(\mathrm{Cu} \rightarrow \mathrm{Cu}^{+}+\mathrm{e}^{-}\right) \\
& -(+0.521 \mathrm{~V}) \\
& \mathrm{PtCl}_{6}{ }^{2-}+2 \mathrm{e}^{-} \rightarrow \mathrm{PtCl}_{4}{ }^{2-}+2 \mathrm{Cl}^{-} \quad+0.68 \mathrm{~V} \\
& \mathrm{PtCl}_{6}{ }^{2-}+2 \mathrm{Cu} \rightarrow \mathrm{PtCl}_{4}{ }^{2-}+2 \mathrm{Cl}^{-}+2 \mathrm{Cu}^{+} \quad E^{\circ} \text { cell }=+0.16 \mathrm{~V} \\
& \operatorname{lnK}=-n F E^{\circ}{ }_{\text {cell }} / \mathrm{RT}=(2)\left(9.65 \mathrm{x} 10^{4} \mathrm{~J} / \mathrm{V} . \mathrm{mol} \mathrm{e}\right)(0.16 \mathrm{~V}) /(8.314 \mathrm{~J} / \mathrm{mol} . \mathrm{K})(298 \mathrm{~K})=12.5 \\
& K=e^{12.5}=2.7 \times 10^{5}
\end{aligned}
$$

9. The following cell is maintained at $25^{\circ} \mathrm{C}$. One half-cell consists of a
chlorine/chloride, $\mathrm{Cl}_{2} / \mathrm{Cl}^{-}$, electrode with the partial pressure of $\mathrm{Cl}_{2}=0.100 \mathrm{~atm}$ and [Cl-] $=0.100 \mathrm{M}$. The other half-cell involves the $\mathrm{MnO}_{4}{ }^{-} / \mathrm{Mn}^{2+}$ couple in acidic solution with $\left[\mathrm{MnO}_{4-}^{-}\right]=0.100 \mathrm{M},\left[\mathrm{Mn}^{2+}\right]=0.100 \mathrm{M}$, and $\left[\mathrm{H}^{+}\right]=0.100 \mathrm{M}$. Apply the Nernst equation to the overall cell reaction to determine the cell potential for this cell.
$\mathrm{MnO}_{4^{-}}+8 \mathrm{H}^{+}+5 \mathrm{e}^{-} \rightarrow \mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}$
$E^{\circ}=1.507 \mathrm{~V}$
$\mathrm{Cl}_{2}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Cl}^{-}$
$E^{\circ}=1.360 \mathrm{~V}$
$2\left(\mathrm{MnO}_{4}{ }^{-}+\mathbf{8} \mathrm{H}^{+}+5 \mathrm{e}^{-} \rightarrow \mathrm{Mn}^{2+}+\mathbf{4 \mathrm { H } _ { 2 } \mathrm { O } )} \quad \stackrel{E^{\circ}}{+\mathbf{1 . 5 0 7} \mathrm{V}}\right.$
$\mathbf{5 ( 2 \mathrm { Cl } - \rightarrow \mathrm { Cl } _ { 2 } + 2 \mathrm { e } ^ { - } ) \quad - 1 . 3 6 0 \mathrm { V }}$
$2 \mathrm{MnO}_{4}{ }^{-}+\mathbf{1 6 H}+\mathbf{1 0 C l}-\mathbf{2} \mathrm{Mn}^{2+}+\mathbf{8} \mathrm{H}_{2} \mathrm{O}+5 \mathrm{Cl}_{2} \quad E^{\circ}$ cell $=0.147 \mathrm{~V}$
$E_{\text {cell }}=E^{\circ}{ }_{\text {cell }}-0.0592 / \mathrm{n} * \log \left\{\left[\mathrm{Mn}^{2+}\right]^{2}\left(\mathrm{P}_{\mathrm{Cl2}}\right)^{5} /\left[\mathrm{MnO}_{4}-\right]^{2}\left[\mathrm{H}^{+}\right]^{16}\left[\mathrm{Cl}^{-}\right]^{10}\right\}$
$=0.147 \mathrm{~V}-(0.0592 / 10) * \log \left[(0.100)^{\wedge} 2(0.100)^{\wedge} 5 /(0.100)^{\wedge} 2(0.100)^{\wedge} 16(0.100)^{\wedge} 10\right]$
$=0.147 \mathrm{~V}-(0.0592 / 10) * \log (1.00 \times 10 \wedge 21)=0.017 \mathrm{~V}$
