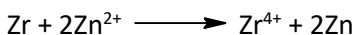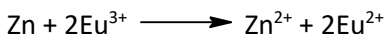SURREY SUPPLEMENT: ELECTROCHEMISTRY
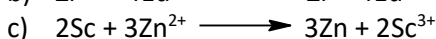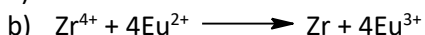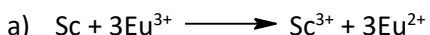
1) A voltaic cell with Mn/Mn^{2+} and Cd/Cd^{2+} half-cells has the following starting concentrations: $[Mn^{2+}] = 0.010$ M and $[Cd^{2+}] = 0.100$ M.

   a) What is the initial ε_{cell}? **[0.81 V]**
   b) What is ε_{cell} when the $[Mn^{2+}]$ has reached 0.055 M ? **[0.78 V]**
   c) What are the concentrations of the ions at equillibrium? **[[Mn²⁺] = 0.110 M and [Cd²⁺] = 4.8 x 10⁻²⁸ M]**

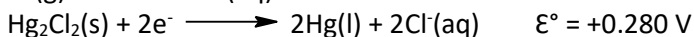2) The following reactions occur at 25°C with all soluble substance present in 1 M concentrations:

   $$Zn + 2Eu^{3+} \longrightarrow Zn^{2+} + 2Eu^{2+}$$
   $$Zr + 2Zn^{2+} \longrightarrow Zr^{4+} + 2Zn$$
   $$4Sc + 3Zr^{4+} \longrightarrow 4Sc^{3+} + 3Zr$$

   From this information alone, predict whether the following reactions will occur under similar conditions:

   a) $Sc + 3Eu^{3+} \longrightarrow Sc^{3+} + 3Eu^{2+}$
   b) $Zr^{4+} + 4Eu^{2+} \longrightarrow Zr + 4Eu^{3+}$
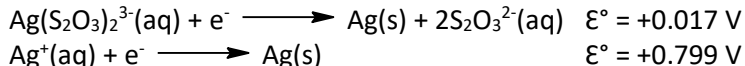   c) $2Sc + 3Zn^{2+} \longrightarrow 3Zn + 2Sc^{3+}$

   YOUR ANSWERS MUST BE RATIONALIZED BY INDICATING A RELATIVE SCALE OF EMF FOR THE FOUR ELEMENTS IN QUESTION. **[Yes, No, Yes]**

3) Explain why copper is oxidized by nitric acid and not by hydrochloric acid.
   [See next page for answer.]

4) The corrosion of iron involves oxidation of the metal and the subsequent formation of the oxide. Which metal, zinc or nickel, will provide the better protection against corrosion if coated in a thin layer on the iron? **[See next page for answer.]**

5) A solution contains the following metal ions: $[Au^{3+}] = 1.0 \times 10^{-6}$ M, $[Fe^{3+}] = 0.50$ M, and $[Ni^{2+}] = 1.0 \times 10^{-3}$ M. Which metal will plate out first if this solution is electrolyzed? *(HINT: Use the Nernst equation to calculate $\varepsilon_{half\text{-}cell}$ for each half-reaction.)* **[See next page for answer.]**

6) A voltaic cell employs the following two half-reactions:

   $$H_2(g) \longrightarrow 2H^+(aq) + 2e^- \qquad\qquad \varepsilon° = 0.00 \text{ V}$$
 $$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq) \qquad \varepsilon° = +0.280 \text{ V}$$

   Write the overall cell reaction and calculate ε_{cell} if the pH = 4.00 and all other substances are at standard conditions. **[See next page for answer.]**

7) Given the following standard reduction potentials at 25 C

$Ag(S_2O_3)_2^{3-}(aq) + e^- \longrightarrow Ag(s) + 2S_2O_3^{2-}(aq)$ $\mathcal{E}° = +0.017$ V
$Ag^+(aq) + e^- \longrightarrow Ag(s)$ $\mathcal{E}° = +0.799$ V

a) Calculate the value of the equilibrium constant at 25°C for the reaction:

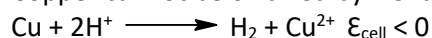$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$
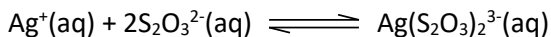
b) Write the conventional cell notation for the cell you have sketched.
[See below for answers.]

Answer to Q. 3:
Copper cannot be oxidized by HCl because for the reaction:
$Cu + 2H^+ \longrightarrow H_2 + Cu^{2+}$ $\mathcal{E}_{cell} < 0$
However for either of the reactions:
$Cu + HNO_3 \longrightarrow Cu^{2+} + NO_2$ $\mathcal{E}_{cell} > 0$
$Cu + HNO_3 \longrightarrow Cu^{2+} + NO$ $\mathcal{E}_{cell} > 0$
so copper will react with HNO_3.
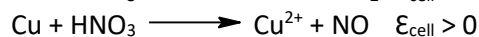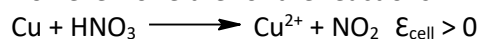
Answer to Q. 4:
Zinc would be better than nickel because it has a more positive value for its oxidation potential than does iron, and thus would be oxidized more readily than iron. However if iron were coated with nickel, the iron would be oxidized before the nickel and thus would not protect the iron.
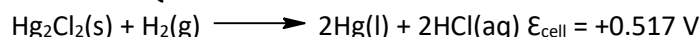
Answer to Q. 5:
For $[Au^{3+}] = 1.0 \times 10^{-6}$ M, $\mathcal{E}_{half-cell} = +1.380$ V
For $[Fe^{3+}] = 0.50$ M, $\mathcal{E}_{half-cell} = -0.0419$ V
For $[Ni^{2+}] = 1.0 \times 10^{-3}$ M, $\mathcal{E}_{half-cell} = -0.3387$ V
Since $\mathcal{E}_{half-cell}$ for the Au^{3+}/Au half-reaction is the most positive it will be the first metal to plate out of the solution.

Answer to Q. 6:
$Hg_2Cl_2(s) + H_2(g) \longrightarrow 2Hg(l) + 2HCl(aq)$ $\mathcal{E}_{cell} = +0.517$ V
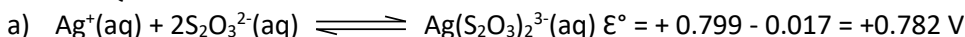
Answers to Q. 7:
   a) $Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$ $\mathcal{E}° = + 0.799 - 0.017 = +0.782$ V
At equilibrium $\mathcal{E} = 0$ and therefore the Nernst equation becomes

$0 = 0.782 - \dfrac{0.059159}{1} \log K_{eq}$ and $K_{eq} = 1.65 \times 10^{13}$

   b) (Assuming standard conditions since we're given no other information:)
$Ag(s)|Ag(S_2O_3)_2^{3-}(aq, 1 M), S_2O_3^{2-}(aq, 1 M) || Ag^+(aq, 1 M)|Ag(s)$