3. (a) (i) Br^- is first order because when the $[Br^-]$ doubles, while $[BrO_3^-]$ and $[H^+]$ remain constant (as in Experiments 1 and 2), the rate of the reaction doubles. This shows $[Br^-]$ to the first power is directly proportional to rate of the reaction. So, the reaction is first order with respect to $[Br^-]$.

(ii) BrO_3^- is first order because when the $[BrO_3^-]$ increases by a factor of 1.5, while $[Br^-]$ and $[H^+]$ remain constant (as in Experiments 1 and 3), the rate of the reaction increases by a factor of 1.5. This shows $[BrO_3^-]$ to the first power is directly proportional to rate of the reaction. So, the reaction is first order with respect to $[BrO_3^-]$.

(iii) H^+ is second order because when the $[H^+]$ doubles the rate of the reaction quadruples. Experiments 3 and 4 best illustrate this relationship. In these two experiments $[Br^-]$ remains constant while $[BrO_3^-]$ and $[H^+]$ both double causing the rate of the reaction to increase by a factor of eight. Since it was shown above in 3 (a) (ii) that $[BrO_3^-]$ is first order, doubling $[BrO_3^-]$ will cause the rate to double; therefore, doubling the $[H^+]$ was responsible for the remaining increase in the rate of the reaction by a factor of four. This shows $[H^+]$ to the second power is directly proportional to rate of the reaction. So, the reaction is second order with respect to $[H^+]$.

(b) $\text{Rate} = k[Br^-][BrO_3^-][H^+]^2$

(c) Any of the four experiments can be chosen. For example, Experiment 1 shows the concentrations of each of reactants and the rate of the reaction. These values are substituted into the rate law in 3 (b) above and solve for the rate constant, k.

$\text{Rate} = k[Br^-][BrO_3^-][H^+]^2$

$$2.5 \times 10^{-4}\ \frac{\text{mole}}{\text{L}\cdot\text{s}} = k\left(0.00100\ \frac{\text{mole}}{\text{L}}\right)\left(0.00500\ \frac{\text{mole}}{\text{L}}\right)\left(0.100\ \frac{\text{mole}}{\text{L}}\right)^2$$

$$\boxed{k = 5000\ \frac{\text{L}^3}{\text{mol}^3\cdot\text{s}}}$$

(d) The first half reaction must be reversed and multiplied by $\frac{5}{2}$ so the coefficients will match those in the overall reaction producing the following table:

Half-reaction	E° (V)
$5Br^-(aq) \rightarrow \frac{5}{2} Br^2(l) + 5\ e^-$	-1.065
$BrO_3^-(aq) + 6\ H^+(aq) + 5\ e^- \rightarrow \frac{1}{2} Br_2(l) + 3\ H_2O(l)$	+1.52

So, the net cell potential would be -1.065 V + 1.52 V = $\boxed{0.46\ \text{V} = E^\circ}$

(e) The total number of electrons would be 5 moles (from the balanced half-reactions) times Avogadro's number of electrons in each mole.

$$(5\ \text{moles of electrons})\cdot\left(6.02 \times 10^{23}\ \text{electrons}/\text{mole}\right) = 3.01 \times 10^{24}\ \text{electrons}$$

$$\boxed{\text{total number of elecrons transferred} = 3.01 \times 10^{24}\ \text{electrons}}$$

2. (a) (i) $$?\text{ moles } \mathrm{Zn}^{2+}(aq) = 1.50\ \mathrm{gZn}(s)\left(\frac{1\text{ mole Zn}(s)}{65.39\text{ g Zn}(s)}\right)\left(\frac{1\text{ mole Zn}^{2+}(aq)}{1\text{ mole Zn}(s)}\right) = 0.0229\text{ moles } \mathrm{Zn}^{2+}(aq)$$

$$?\text{ moles } \mathrm{Zn}^{2+}(aq) = 250.\text{ mL } \mathrm{AgNO_3}\ (aq)\left(\frac{1\text{ L of AgNO}_3(aq)\text{ solution}}{1000\text{ mL of AgNO}_3(aq)\text{ solution}}\right)$$
$$\left(\frac{0.110\text{ moles AgNO}_3(aq)\text{ solution}}{1\text{ L of AgNO}_3(aq)\text{ solution}}\right)\left(\frac{1\text{ mole of Zn}^{2+}(s)}{2\text{ moles of Ag}^{+}(aq)}\right)$$
$$= 0.0138\text{ moles } \mathrm{Zn}^{2+}(aq)$$

Therefore, the $AgNO_3$ (*aq*) solution, or, more specifically, the $Ag^+(aq)$ solution is the limiting reagent because it produces less product and, therefore, it will be used up first.

(ii) $$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{Volume (L) of solution}} = \frac{0.0138\text{ moles Zn}^{2+}\text{ (aq)}}{0.250\text{ L of solution}} = \boxed{0.0552\text{ M Zn}^{2+}\text{ (aq)}}$$

(b) $2[\mathrm{Ag}^+ + e^- \rightarrow \mathrm{Ag}(s)]$ E° = 0.80 V

$\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+} + 2e^-$ E° = 0.76 V

$$\boxed{E^\circ = 1.56\text{ V}}$$

(c) $$\Delta G^\circ = -n\mathscr{F}E^\circ = -(2\text{ moles e}^-)\left(96{,}500\ \frac{\text{C}}{\text{mole of e}^-}\right)(0.46\text{ V})$$

$$\boxed{\Delta G^\circ = -8.9\times 10^4\text{ J}}$$

(d) $$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n}\log Q\ \ (25^\circ\text{C})\text{ where } Q = \frac{[\mathrm{Cu}^{2+}]}{[\mathrm{Ag}^+]^2} = \frac{(0.045\text{ M})}{(0.010\text{ M})^2} = 450$$

$$E_{\text{cell}} = 0.46\text{ V} - \frac{0.0592}{2}\log(450) = \boxed{0.38\text{ V}}$$

(e) The reaction in the cell under the conditions specified in part (d) is spontaneous because ΔG is negative. All spontaneous processes in nature tend toward a lower free energy.

7. (a) The zinc electrode would be the annode because it has the more negative reduction potential which means it is most likely to be oxidized.

Half Reaction: $Zn \rightleftharpoons Zn^{2+} + 2e^-$

(b) The overall net ionic reaction for the cell is as follows:

$$Zn(s) + Ni^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Ni(s)$$

$E^o_{cell} = E^o_{Ni} - E^o_{Zn}$ = -0.25 V - (-0.76 V)

$$\boxed{E^o_{cell} = 0.51 \text{ V}}$$

(c) Lowering the concentration of the reactant, Ni^{2+}, in the cell will will lower the value of E_{cell} since there will be less of a driving "force" to transfer the electrons. This can be calculated using the Nernst equation, $E_{cell} = E^o_{cell} - \frac{RT}{n\mathcal{F}} \ln Q \left(E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log Q \quad @ \ 25^\circ C \right)$, and $Q = \frac{[Zn^{2+}]}{[Ni^{2+}]}$. By lowering the concentration of the recatant, Ni^{2+}, Q will become larger so the log Q will become larger making E_{cell} smaller (there's a negative sign in front of the log term).

(d) The K_{eq} for the cell reaction will be greater than one because it produces a positive E_{cell} , therefore, a negative ΔG ($\Delta G^o = -n\mathfrak{F}E^o$) which indicates that the reaction is spontaneous. Therefore, this reaction will shift toward the products side (Zn^{2+}) and away from the reactants side (Ni^{2+}). This will produce a K_{eq} larger than one.

A second explanation: at equilibrium, $E_{cell} = 0$ and Q becomes K_{eq} so $E_{cell} = E^o_{cell} - \frac{RT}{n\mathcal{F}} \ln Q$ becomes $0 = E^o_{cell} - \frac{RT}{n\mathcal{F}} \ln K_{eq}$. Rearranging gives $E^o_{cell} = \frac{RT}{n\mathcal{F}} \ln K_{eq}$,and, finally, $\ln K_{eq} = \frac{E^o_{cell} n\mathcal{F}}{RT} \left(\text{or } \log K_{eq} = \frac{nE^o_{cell}}{0.0592} \quad @ \ 25^\circ C \right)$. Therefore, since E_{cell} is positive K_{eq} would have to be greater than one since the log of a number is only positive when that number is bigger than one.

2. (a) (i) $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$

(ii) $Zn(s) + Co^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Co(s)$

(iii) $E^o_{cell} = E^o_{Co} - E^o_{Zn} = -0.28 \text{ V} - (-0.76 \text{ V})$

$$\boxed{E^o_{cell} = 0.48 \text{ V}}$$

(b) (i) $\Delta G^o = -n\mathfrak{F}E^o$ $-(2 \text{ mol } e^-)(96{,}500 \text{C/mol } e^-)(0.55 \text{J/C})$

$$\boxed{\Delta G^o = -1.06 \times 10^5 \text{ J}}$$

(ii) $\Delta G^o = -RT \ln(K_{eq})$

$-1.06 \times 10^5 \text{ J} = -(8.31 \text{ J/K}\bullet\text{mol})(298 \text{ K})K_{eq}$

$$\boxed{K_{eq} = 42.8}$$

(iii) $E^o_{cell} = 1.23 \text{ V} - 0.55 \text{ V}$

$$\boxed{E^o_{cell} = 0.68 \text{ V}}$$

(c) $I = \dfrac{\Delta Q}{\Delta t}$

$$\Delta Q = I\Delta t = \left(100\frac{C}{s}\right)(1.00h)\left(\frac{60 \min}{1h}\right)\left(\frac{60s}{1 \min}\right) = 3.6 \times 10^5 \text{ C}$$

$$? \text{ moles } e^- = (3.6 \times 10^5 \text{ C})\left(\frac{1e^-}{1.6x10^{-19}C}\right)\left(\frac{1mole-e^-}{6.02x10^{23}\,e^-}\right) = 3.74 \text{ moles } e^-$$

$$? \text{ g Cu (s)} = 3.74 \text{ moles } e^-\left[\frac{1moleCu(s)}{2moles-e^-}\right]\left[\frac{63.55gCu(s)}{1moleCu(s)}\right]$$

$$\boxed{? \text{ g Cu (s)} = 119 \text{ g Cu (s)}}$$