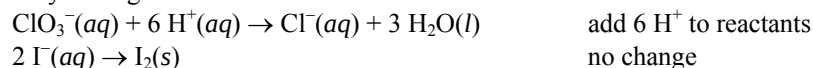


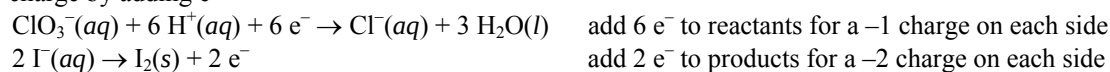
CHAPTER 21 ELECTROCHEMISTRY: CHEMICAL CHANGE AND ELECTRICAL WORK

- 21.1 Oxidation is the loss of electrons (resulting in a higher oxidation number), while reduction is the gain of electrons (resulting in a lower oxidation number). In an oxidation-reduction reaction, electrons transfer from the oxidized substance to the reduced substance. The oxidation number of the reactant being oxidized increases while the oxidation number of the reactant being reduced decreases.
- 21.2 **No**, one half-reaction cannot take place independently of the other because there is always a transfer of electrons from one substance to another. If one substance loses electrons (oxidation half-reaction), another substance must gain those electrons (reduction half-reaction).
- 21.3 Spontaneous reactions, $\Delta G_{\text{sys}} < 0$, take place in voltaic cells, which are also called galvanic cells. Nonspontaneous reactions take place in electrolytic cells and result in an increase in the free energy of the cell ($\Delta G_{\text{sys}} > 0$).
- 21.4 a) **True**
b) **True**
c) **True**
d) **False**, in a voltaic cell, the system does work on the surroundings.
e) **True**
f) **False**, the electrolyte in a cell provides a solution of mobile ions to maintain charge neutrality.
- 21.5 a) To decide which reactant is oxidized, look at oxidation numbers. **Cl⁻** is oxidized because its oxidation number increases from -1 in Cl⁻ to 0 in Cl₂.
b) **MnO₄⁻** is reduced because the oxidation number of Mn decreases from +7 in MnO₄⁻ to +2 in Mn²⁺.
c) The oxidizing agent is the substance that causes the oxidation by accepting electrons. The oxidizing agent is the substance reduced in the reaction, so **MnO₄⁻** is the oxidizing agent.
d) **Cl⁻** is the reducing agent because it loses the electrons that are gained in the reduction.
e) **From Cl⁻**, which is losing electrons, **to MnO₄⁻**, which is gaining electrons.
f) $8 \text{H}_2\text{SO}_4(aq) + 2 \text{KMnO}_4(aq) + 10 \text{KCl}(aq) \rightarrow 2 \text{MnSO}_4(aq) + 5 \text{Cl}_2(g) + 8 \text{H}_2\text{O}(l) + 6 \text{K}_2\text{SO}_4(aq)$
- 21.6 $2 \text{CrO}_2^-(aq) + 2 \text{H}_2\text{O}(l) + 6 \text{ClO}^-(aq) \rightarrow 2 \text{CrO}_4^{2-}(aq) + 3 \text{Cl}_2(g) + 4 \text{OH}^-(aq)$
a) The **CrO₂⁻** is the oxidized species because Cr increases in oxidation state from +3 to +6.
b) The **ClO⁻** is the reduced species because Cl decreases in oxidation state from +1 to 0.
c) The oxidizing agent is **ClO⁻**; the oxidizing agent is the substance reduced.
d) The reducing agent is **CrO₂⁻**; the reducing agent is the substance oxidized.
e) Electrons transfer from **CrO₂⁻ to ClO⁻**.
f) $2 \text{NaCrO}_2(aq) + 6 \text{NaClO}(aq) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{Na}_2\text{CrO}_4(aq) + 3 \text{Cl}_2(g) + 4 \text{NaOH}(aq)$
- 21.7 a) Divide into half-reactions:
 $\text{ClO}_3^-(aq) \rightarrow \text{Cl}^-(aq)$
 $\text{I}^-(aq) \rightarrow \text{I}_2(s)$
 Balance elements other than O and H
 $\text{ClO}_3^-(aq) \rightarrow \text{Cl}^-(aq)$ chlorine is balanced
 $2 \text{I}^-(aq) \rightarrow \text{I}_2(s)$ iodine now balanced
 Balance O by adding H₂O
 $\text{ClO}_3^-(aq) \rightarrow \text{Cl}^-(aq) + 3 \text{H}_2\text{O}(l)$ add 3 waters to add 3 O's to product
 $2 \text{I}^-(aq) \rightarrow \text{I}_2(s)$ no change

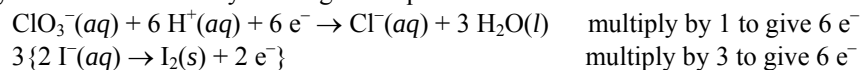
Balance H by adding H^+



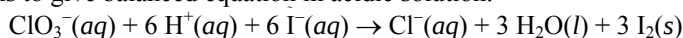
Balance charge by adding e^-



Multiply each half-reaction by an integer to equalize the number of electrons



Add half-reactions to give balanced equation in acidic solution.

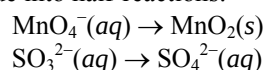


Check balancing:

Reactants:	1 Cl	Products:	1 Cl
	3 O		3 O
	6 H		6 H
	6 I		6 I
	-1 charge		-1 charge

Oxidizing agent is ClO_3^- and reducing agent is I^- .

b) Divide into half-reactions:



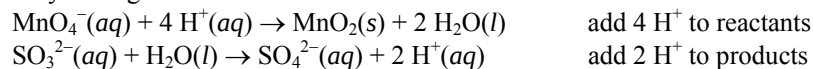
Balance elements other than O and H



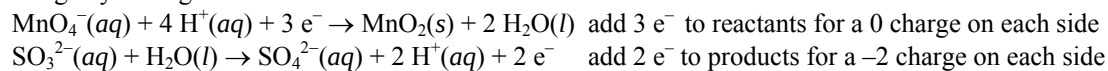
Balance O by adding H_2O



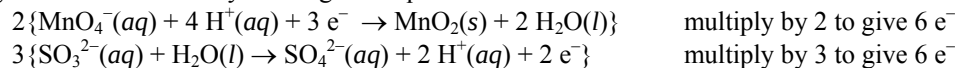
Balance H by adding H^+



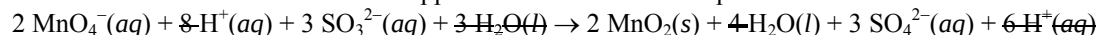
Balance charge by adding e^-



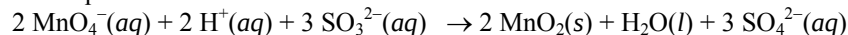
Multiply each half-reaction by an integer to equalize the number of electrons



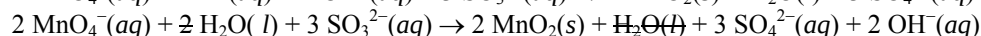
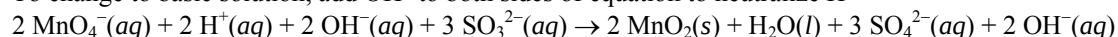
Add half-reactions and cancel substances that appear as both reactants and products



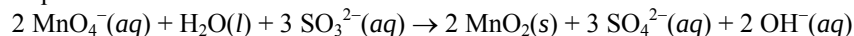
The balanced equation in acidic solution is:



To change to basic solution, add OH^- to both sides of equation to neutralize H^+



Balanced equation in basic solution:

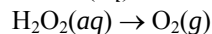
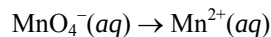


Check balancing:

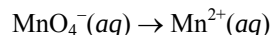
Reactants:	2 Mn	Products:	2 Mn
	18 O		18 O
	2 H		2 H
	3 S		3 S
	-8 charge		-8 charge

Oxidizing agent is MnO_4^- and reducing agent is SO_3^{2-} .

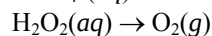
c) Divide into half-reactions:



Balance elements other than O and H

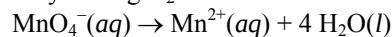


Mn is balanced

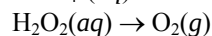


No other elements to balance

Balance O by adding H_2O

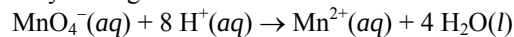


add 4 H_2O to products

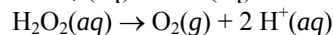


O is balanced

Balance H by adding H^+

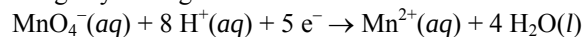


add 8 H^+ to reactants

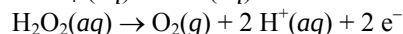


add 2 H^+ to products

Balance charge by adding e^-

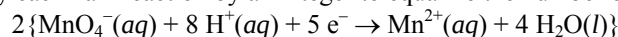


add 5 e^- to reactants for +2 on each side

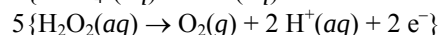


add 2 e^- to products for 0 charge on each side

Multiply each half-reaction by an integer to equalize the number of electrons

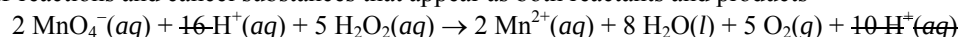


multiply by 2 to give 10 e^-

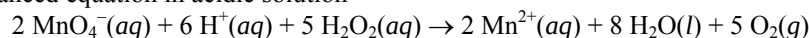


multiply by 5 to give 10 e^-

Add half-reactions and cancel substances that appear as both reactants and products



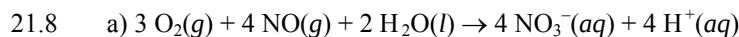
The balanced equation in acidic solution



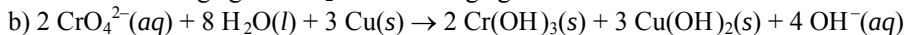
Check balancing:

Reactants:	2 Mn	Products:	2 Mn
	18 O		18 O
	16 H		16 H
	+4 charge		+4 charge

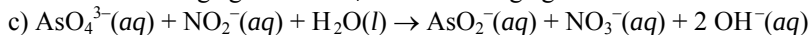
Oxidizing agent is MnO_4^- and reducing agent is H_2O_2 .



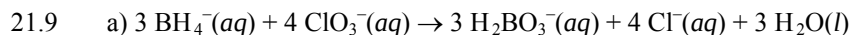
Oxidizing agent is O_2 and reducing agent: NO



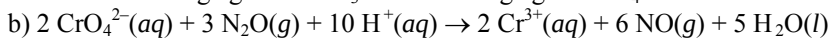
Oxidizing agent is CrO_4^{2-} and reducing agent: Cu



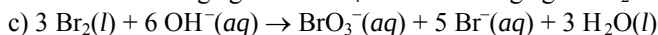
Oxidizing agent is AsO_4^{3-} and reducing agent: NO_2^-



Oxidizing agent is ClO_3^- and reducing agent: BH_4^-



Oxidizing agent is CrO_4^{2-} and reducing agent: N_2O

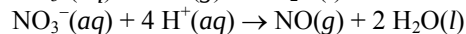


Oxidizing agent is Br_2 and reducing agent is Br_2

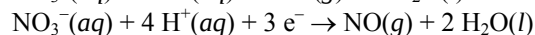
21.10 a) Balance the reduction half-reaction:



balance O

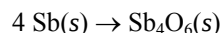


balance H

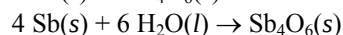


balance charge

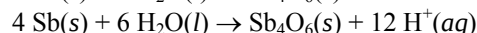
Balance oxidation half-reaction:



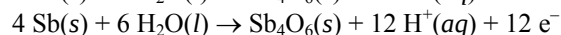
balance Sb



balance O

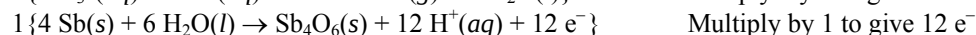
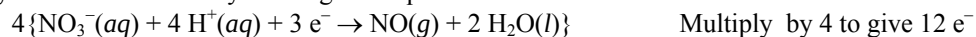


balance H

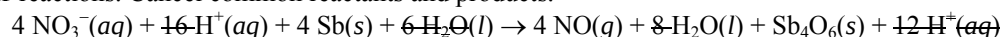


balance charge

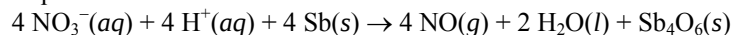
Multiply each half-reaction by an integer to equalize the number of electrons



Add half-reactions. Cancel common reactants and products.

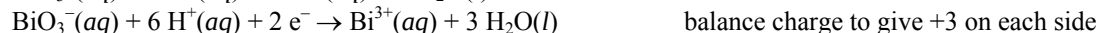
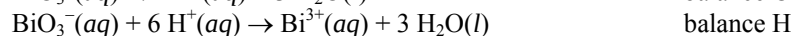


Balanced equation in acidic solution:

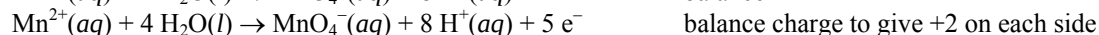
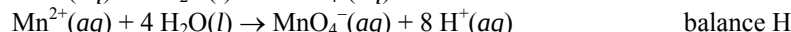
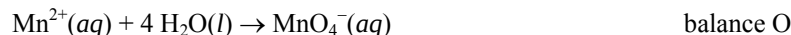


Oxidizing agent is NO_3^- and reducing agent is Sb.

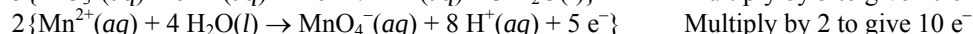
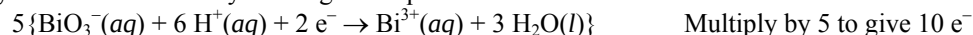
b) Balance reduction half-reaction:



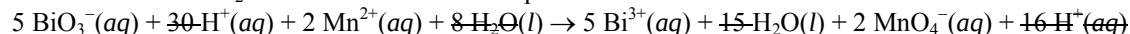
Balance oxidation half-reaction:



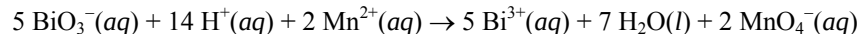
Multiply each half-reaction by an integer to equalize the number of electrons



Add half-reactions. Cancel H_2O and H^+ in reactants and products.

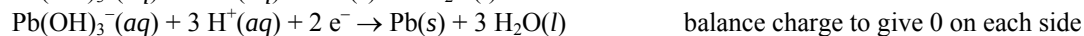
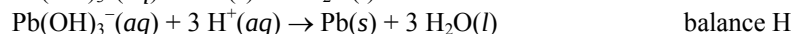


Balanced reaction in acidic solution:

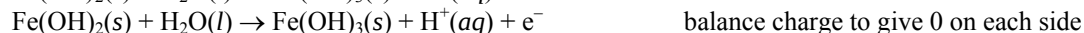
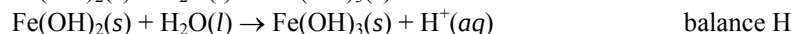
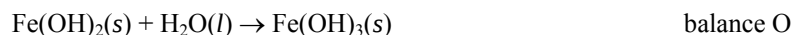


BiO_3^- is the oxidizing agent and Mn^{2+} is the reducing agent.

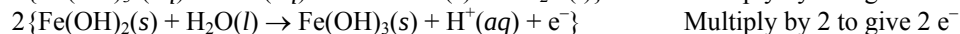
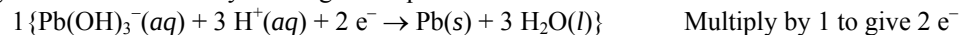
c) Balance the reduction half-reaction:



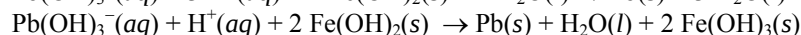
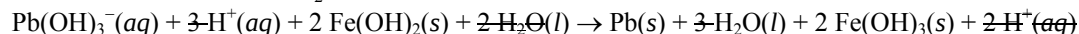
Balance the oxidation half-reaction



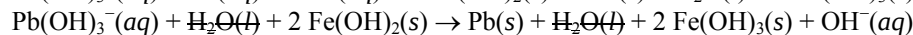
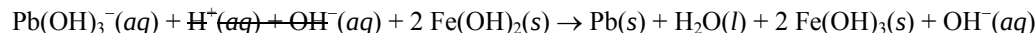
Multiply each half-reaction by an integer to equalize the number of electrons



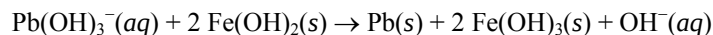
Add the two half-reactions. Cancel H_2O and H^+ .



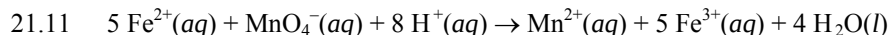
Add one OH^- to both sides to neutralize H^+ .



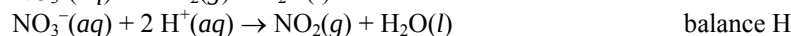
Balanced reaction in basic solution:



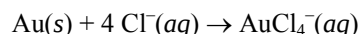
$\text{Pb}(\text{OH})_3^-$ is the oxidizing agent and $\text{Fe}(\text{OH})_2$ is the reducing agent.



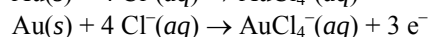
21.12 a) Balance reduction half-reaction:



Balance oxidation half-reaction:

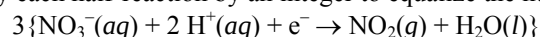


balance Cl

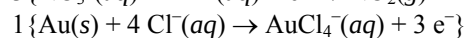


balance charge to -4 on each side

Multiply each half-reaction by an integer to equalize the number of electrons

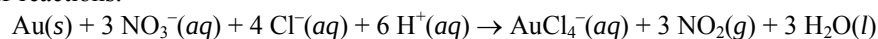


Multiply by 3 to give 3e^-



Multiply by 1 to give 3e^-

Add half-reactions.



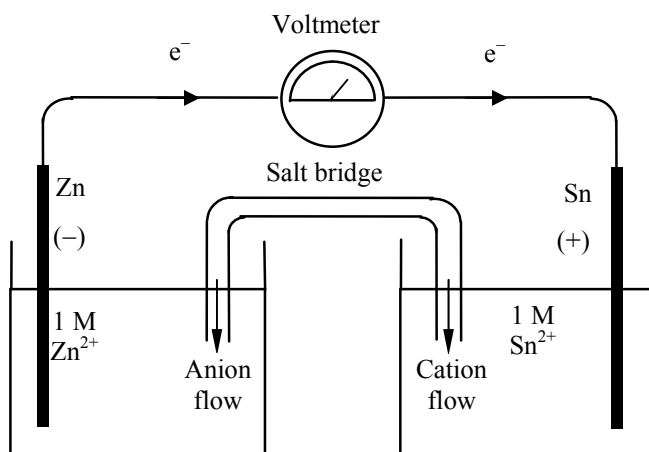
b) Oxidizing agent is NO_3^- and reducing agent is **Au**.

c) The HCl provides chloride ions that combine with the unstable gold ion to form the stable ion, AuCl_4^- .

- 21.13 a) **A** is the anode because by convention the anode is shown on the left.
 b) **E** is the cathode because by convention the cathode is shown on the right.
 c) **C** is the salt bridge providing electrical connection between the two solutions.
 d) **A** is the anode, so oxidation takes place there. Oxidation is the loss of electrons, meaning that electrons are leaving the anode.
 e) **E** is assigned a positive charge because it is the cathode.
 f) **E** gains mass because the reduction of the metal ion produced the solid metal.
- 21.14 Unless the oxidizing and reducing agents are physically separated, the redox reaction will not generate electrical energy. This electrical energy is produced by forcing the electrons to travel through an external circuit.
- 21.15 The purpose of the salt bridge is to maintain charge neutrality by allowing anions to flow into the anode compartment and cations to flow into the cathode compartment.
- 21.16 An active electrode is a reactant or product in the cell reaction, whereas an inactive electrode is neither a reactant nor a product. An inactive electrode is present only to conduct electricity when the half-cell reaction does not include a metal. Platinum and graphite are commonly used as inactive electrodes.
- 21.17 a) The metal **A** is being oxidized to form the metal cation. To form positive ions, an atom must always lose electrons, so this half-reaction is always an oxidation.
 b) The metal ion **B** is gaining electrons to form the metal **B**, so it is displaced.
 c) The anode is the electrode at which oxidation takes place, so metal **A** is used as the anode.
 d) Acid oxidizes metal **B** and metal **B** oxidizes metal **A**, so acid will oxidize metal **A** and **bubbles will form** when metal **A** is placed in acid. The same answer results if strength of reducing agents is considered. The fact that metal **A** is a better reducing agent than metal **B** indicates that if metal **B** reduces acid, then metal **A** will also reduce acid.
- 21.18 a) If the zinc electrode is negative, oxidation takes place at the zinc electrode:

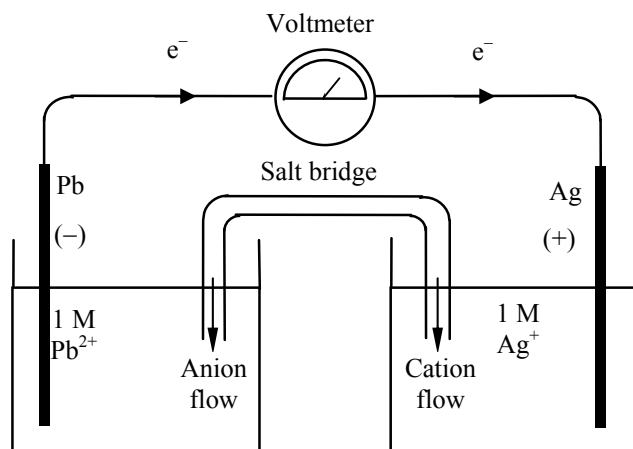
$$\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^-$$

 Reduction half-reaction: $\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn(s)}$
 Overall reaction: $\text{Zn(s)} + \text{Sn}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Sn(s)}$
 b)



- 21.19 a) (red half-rxn) $\text{Ag}^+(aq) + 1 e^- \rightarrow \text{Ag}(s)$
 (ox half-rxn) $\text{Pb}(s) \rightarrow \text{Pb}^{2+}(aq) + 2 e^-$
 (overall rxn) $2 \text{Ag}^+(aq) + \text{Pb}(s) \rightarrow 2 \text{Ag}(s) + \text{Pb}^{2+}(aq)$

b)



- 21.20 a) Electrons flow from the anode to the cathode, so **from the iron half-cell to the nickel half-cell**, left to right in the figure. By convention, the anode appears on the left and the cathode on the right.
 b) Oxidation occurs at the anode, which is the electrode in the **iron** half-cell.
 c) Electrons enter the reduction half-cell, the **nickel** half-cell in this example.
 d) Electrons are consumed in the reduction half-reaction. Reduction takes place at the cathode, **nickel** electrode.
 e) The anode is assigned a negative charge, so the **iron** electrode is negatively charged.
 f) Metal is oxidized in the oxidation half-cell, so the **iron** electrode will decrease in mass.
 g) The solution must contain nickel ions, so any nickel salt can be added. **1 M NiSO₄** is one choice.
 h) KNO₃ is commonly used in salt bridges, the ions being **K⁺ and NO₃⁻**. Other salts are also acceptable answers.
 i) **Neither**, because an inactive electrode could not replace either electrode since both the oxidation and the reduction half-reactions include the metal as either a reactant or a product.
 j) Anions will move towards the half-cell in which positive ions are being produced. The oxidation half-cell produces Fe²⁺, so salt bridge anions move **from right (nickel half-cell) to left (iron half-cell)**.
 k) Oxidation half-reaction: $\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2 e^-$
 Reduction half-reaction: $\text{Ni}^{2+}(aq) + 2 e^- \rightarrow \text{Ni}(s)$
 Overall cell reaction: $\text{Fe}(s) + \text{Ni}^{2+}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Ni}(s)$
- 21.21 a) The electrons flow **left to right**.
 b) Reduction occurs at the electrode on the **right**.
 c) Electrons leave the cell from the **left** side.
 d) The **zinc** electrode generates the electrons.
 e) The **cobalt** electrode has the positive charge.
 f) The **cobalt** electrode increases in mass.
 g) The anode electrolyte could be **1 M Zn(NO₃)₂**.
 h) One possible pair would be K⁺ and NO₃⁻.
 i) **Neither** electrode could be replaced because both electrodes are part of the cell reaction.
 j) The cations move from **left to right** to maintain charge neutrality.
 k) Reduction: $\text{Co}^{2+}(aq) + 2 e^- \rightarrow \text{Co}(s)$
 Oxidation: $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2 e^-$
 Overall: $\text{Zn}(s) + \text{Co}^{2+}(aq) \rightarrow \text{Co}(s) + \text{Zn}^{2+}(aq)$

- 21.22 In cell notation, the oxidation components of the anode compartment are written on the left of the salt bridge and the reduction components of the cathode compartment are written to the right of the salt bridge. A double vertical line separates the anode from the cathode and represents the salt bridge. A single vertical line separates species of different phases.
- Anode || Cathode
- a) Al is oxidized, so it is the anode and appears first in the cell notation:

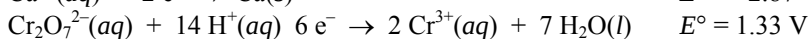
$$\text{Al(s)}|\text{Al}^{3+}(\text{aq})||\text{Cr}^{3+}(\text{aq})|\text{Cr(s)}$$
- b) Cu^{2+} is reduced, so Cu is the cathode and appears last in the cell notation. The oxidation of SO_2 does not include a metal, so an inactive electrode must be present. Hydrogen ion must be included in the oxidation half-cell.

$$\text{Pt}|\text{SO}_2(\text{g})|\text{SO}_4^{2-}(\text{aq}), \text{H}^+(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$$
- 21.23 a) $\text{Mn(s)} + \text{Cd}^{2+}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{Cd(s)}$
 b) $3 \text{Fe(s)} + 2 \text{NO}_3^-(\text{aq}) + 8 \text{H}^+(\text{aq}) \rightarrow 3 \text{Fe}^{2+}(\text{aq}) + 2 \text{NO(g)} + 4 \text{H}_2\text{O(l)}$
- 21.24 An isolated reduction or oxidation potential cannot be directly measured. However, by assigning a standard half-cell potential to a particular half-reaction, the standard potentials of other half-reactions can be determined relative to this reference value. The standard reference half-cell is a standard hydrogen electrode defined to have an E° value of 0.000 V.
- 21.25 A negative E°_{cell} indicates that the cell reaction is not spontaneous, $\Delta G^\circ > 0$. The reverse reaction is spontaneous with $E^\circ_{\text{cell}} > 0$.
- 21.26 Similar to other state functions, the sign of E° changes when a reaction is reversed. Unlike ΔG° , ΔH° and S° , E° is an intensive property, the ratio of energy to charge. When the coefficients in a reaction are multiplied by a factor, the values of ΔG° , ΔH° and S° are multiplied by the same factor. However, E° does not change because both the energy and charge are multiplied by the factor and their ratio remains unchanged.
- 21.27 a) Divide the balanced equation into reduction and oxidation half-reactions and add electrons. Add water and hydroxide ion to the half-reaction that includes oxygen.
- Oxidation: $\text{Se}^{2-}(\text{aq}) \rightarrow \text{Se(s)} + 2 \text{e}^-$
 Reduction: $2 \text{SO}_3^{2-}(\text{aq}) + 3 \text{H}_2\text{O(l)} + 4 \text{e}^- \rightarrow \text{S}_2\text{O}_3^{2-}(\text{aq}) + 6 \text{OH}^-(\text{aq})$
- b) $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$$E^\circ_{\text{anode}} = E^\circ_{\text{cathode}} - E^\circ_{\text{cell}} = -0.57 \text{ V} - 0.35 \text{ V} = \mathbf{-0.92 \text{ V}}$$
- 21.28 a) (red half-rxn) $\text{O}_3(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O(l)}$
 (ox half-rxn) $\text{Mn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O(l)} \rightarrow \text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^-$
- b) $E^\circ_{\text{cell}} = E^\circ_{\text{ozone}} - E^\circ_{\text{manganese}}$

$$\begin{aligned} E^\circ_{\text{manganese}} &= E^\circ_{\text{ozone}} - E^\circ_{\text{cell}} \\ &= 2.07 \text{ V} - 0.84 \text{ V} \\ &= \mathbf{1.23 \text{ V}} \end{aligned}$$
- 21.29 The greater (more positive) the reduction potential, the greater the strength as an oxidizing agent.
- a) From Appendix D:
- | | |
|--|----------------------------|
| $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$ | $E^\circ = 0.77 \text{ V}$ |
| $\text{Br}_2(\text{l}) + 2 \text{e}^- \rightarrow 2 \text{Br}^-(\text{aq})$ | $E^\circ = 1.07 \text{ V}$ |
| $\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu(s)}$ | $E^\circ = 0.34 \text{ V}$ |
- When placed in order of decreasing strength as oxidizing agents: $\text{Br}_2 > \text{Fe}^{3+} > \text{Cu}^{2+}$.

b) From Appendix D:

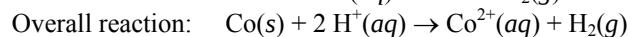
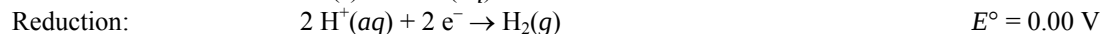
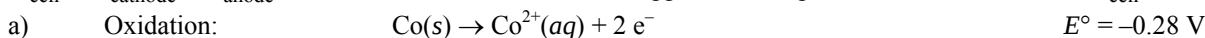


When placed in order of increasing strength as oxidizing agents: $\text{Ca}^{2+} < \text{Ag}^{+} < \text{Cr}_2\text{O}_7^{2-}$.

21.30 a) When placed in order of decreasing strength as reducing agents: $\text{SO}_2 > \text{MnO}_2 > \text{PbSO}_4$

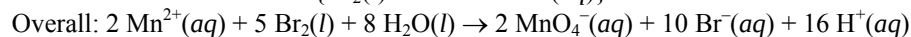
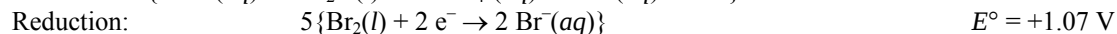
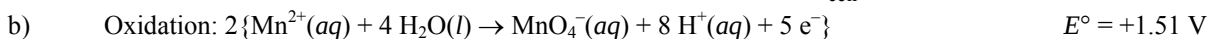
b) When placed in order of increasing strength as reducing agents: $\text{Hg} < \text{Sn} < \text{Fe}$

21.31 $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$ E° values are found in Appendix D. Spontaneous reactions have $E^{\circ}_{\text{cell}} > 0$.



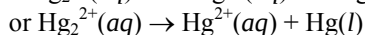
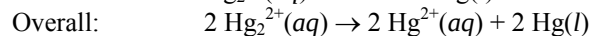
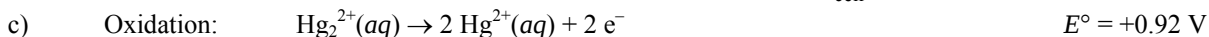
$$E^{\circ}_{\text{cell}} = 0.00 \text{ V} - (-0.28 \text{ V}) = \mathbf{0.28 \text{ V}}$$

Reaction is **spontaneous** under standard state conditions because E°_{cell} is positive.



$$E^{\circ}_{\text{cell}} = 1.07 \text{ V} - 1.51 \text{ V} = \mathbf{-0.44 \text{ V}}$$

Reaction is **not spontaneous** under standard state conditions with $E^{\circ}_{\text{cell}} < 0$.



$$E^{\circ}_{\text{cell}} = 0.85 \text{ V} - 0.92 \text{ V} = \mathbf{-0.07 \text{ V}}$$

Negative E°_{cell} indicates reaction is **not spontaneous** under standard state conditions.

21.32 a) $\text{Cl}_2(\text{g}) + 2 \text{Fe}^{2+}(\text{aq}) \rightarrow 2 \text{Cl}^{-}(\text{aq}) + 2 \text{Fe}^{3+}(\text{aq})$

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Cl}_2} - E^{\circ}_{\text{Fe}^{3+}} \\ &= 1.36 \text{ V} - (0.77 \text{ V}) \\ &= 0.59 \text{ V} \end{aligned}$$

The reaction is **spontaneous**.

b) $\text{Mn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 2 \text{Co}^{3+}(\text{aq}) \rightarrow \text{MnO}_2(\text{s}) + 4 \text{H}^{+}(\text{aq}) + 2 \text{Co}^{2+}(\text{aq})$

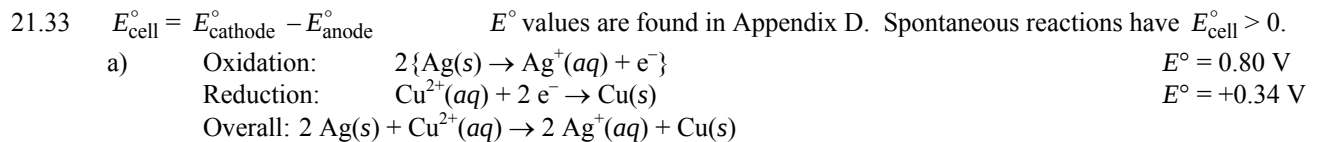
$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Co}^{3+}} - E^{\circ}_{\text{MnO}_2} \\ &= 1.82 \text{ V} - (1.23 \text{ V}) \\ &= 0.59 \text{ V} \end{aligned}$$

The reaction is **spontaneous**.

c) $3 \text{AgCl}(\text{s}) + \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow 3 \text{Ag}(\text{s}) + 3 \text{Cl}^{-}(\text{aq}) + \text{NO}_3^{-}(\text{aq}) + 4 \text{H}^{+}(\text{aq})$

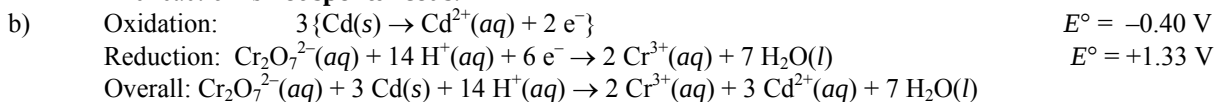
$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{AgCl}} - E^{\circ}_{\text{NO}_3^{-}} \\ &= 0.22 \text{ V} - (0.96 \text{ V}) \\ &= -0.74 \text{ V} \end{aligned}$$

The reaction is **nonspontaneous**.



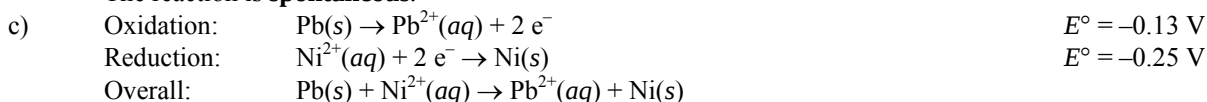
$$E^\circ_{\text{cell}} = +0.34 \text{ V} - 0.80 \text{ V} = \mathbf{-0.46 \text{ V}}$$

The reaction is **not spontaneous**.



$$E^\circ_{\text{cell}} = +1.33 \text{ V} - (-0.40 \text{ V}) = \mathbf{+1.73 \text{ V}}$$

The reaction is **spontaneous**.



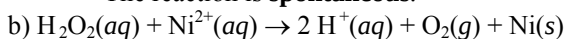
$$E^\circ_{\text{cell}} = -0.25 \text{ V} - (-0.13 \text{ V}) = \mathbf{-0.12 \text{ V}}$$

The reaction is **not spontaneous**.



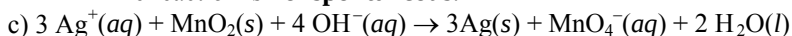
$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{PbO}_2} - E^\circ_{\text{Cu}^{2+}} \\ &= 1.70 \text{ V} - (0.15 \text{ V}) \\ &= 1.55 \text{ V} \end{aligned}$$

The reaction is **spontaneous**.



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{Ni}^{2+}} - E^\circ_{\text{O}_2} \\ &= -0.25 \text{ V} - (0.68 \text{ V}) \\ &= -0.93 \text{ V} \end{aligned}$$

The reaction is **nonspontaneous**.

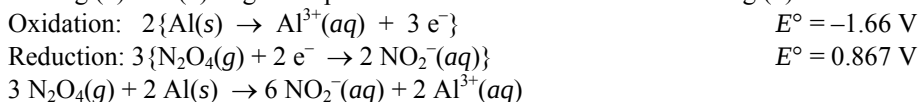


$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{Ag}^+} - E^\circ_{\text{MnO}_4^-} \\ &= 0.80 \text{ V} - (0.59 \text{ V}) \\ &= 0.21 \text{ V} \end{aligned}$$

The reaction is **spontaneous**.

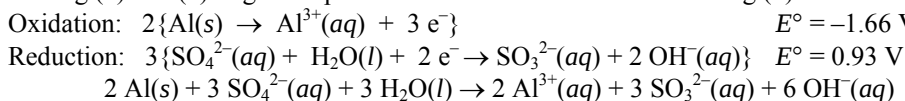
21.35 Spontaneous reactions have $E^\circ_{\text{cell}} > 0$. All three reactions are written as reductions. When two half-reactions are paired, one half-reaction must be reversed and written as an oxidation. Reverse the half-reaction that will result in a positive value of E°_{cell} .

Adding (1) and (2) to give a spontaneous reaction involves converting (1) to oxidation:



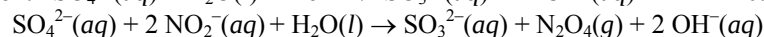
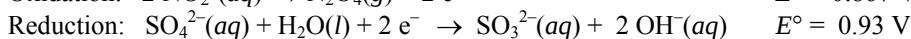
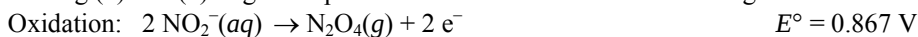
$$E^\circ_{\text{cell}} = 0.867 \text{ V} - (-1.66 \text{ V}) = \mathbf{2.53 \text{ V}}$$

Adding (1) and (3) to give a spontaneous reaction involves converting (1) to oxidation:

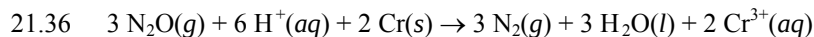


$$E^\circ_{\text{cell}} = 0.93 \text{ V} - (-1.66 \text{ V}) = \mathbf{2.59 \text{ V}}$$

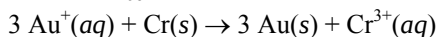
Adding (2) and (3) to give a spontaneous reaction involves converting 2 to oxidation:



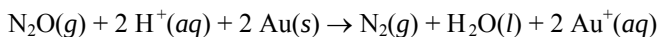
$$E_{\text{cell}}^\circ = 0.93 \text{ V} - 0.867 \text{ V} = \mathbf{0.06 \text{ V}}$$



$$E_{\text{cell}}^\circ = 1.77 \text{ V} - (-0.74 \text{ V}) = 2.51 \text{ V}$$



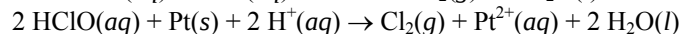
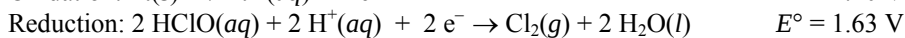
$$E_{\text{cell}}^\circ = 1.69 \text{ V} - (-0.74 \text{ V}) = 2.43 \text{ V}$$



$$E_{\text{cell}}^\circ = 1.77 \text{ V} - (1.69 \text{ V}) = 0.08 \text{ V}$$

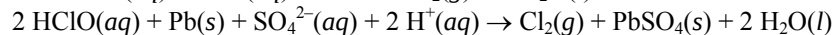
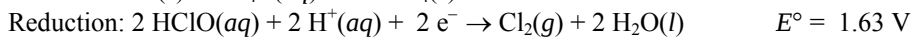
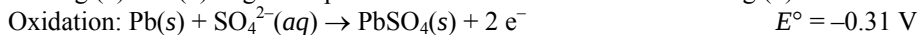
- 21.37 Spontaneous reactions have $E_{\text{cell}}^\circ > 0$. All three reactions are written as reductions. When two half-reactions are paired, one half-reaction must be reversed and written as an oxidation. Reverse the half-reaction that will result in a positive value of E_{cell}° .

Adding (1) and (2) to give a spontaneous reaction involves converting (2) to oxidation:



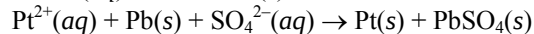
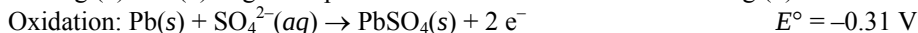
$$E_{\text{cell}}^\circ = 1.63 \text{ V} - 1.20 \text{ V} = \mathbf{0.43 \text{ V}}$$

Adding (1) and (3) to give a spontaneous reaction involves converting (3) to oxidation:

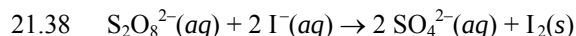


$$E_{\text{cell}}^\circ = 1.63 \text{ V} - (-0.31 \text{ V}) = \mathbf{1.94 \text{ V}}$$

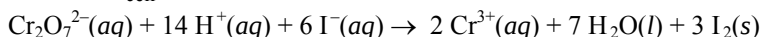
Adding (2) and (3) to give a spontaneous reaction involves converting (3) to oxidation:



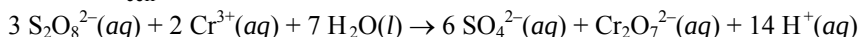
$$E_{\text{cell}}^\circ = 1.20 \text{ V} - (-0.31 \text{ V}) = \mathbf{1.51 \text{ V}}$$



$$E_{\text{cell}}^\circ = 2.01 \text{ V} - (0.53 \text{ V}) = 1.48 \text{ V}$$



$$E_{\text{cell}}^\circ = 1.33 \text{ V} - (0.53 \text{ V}) = 0.80 \text{ V}$$



$$E_{\text{cell}}^\circ = 2.01 \text{ V} - (1.33 \text{ V}) = 0.68 \text{ V}$$

- 21.39 Metal A + Metal B salt $\rightarrow$ solid colored product on metal A

Conclusion: Product is solid metal B. B is undergoing reduction and plating out on A. A is better reducing agent than B.

Metal B + acid $\rightarrow$ gas bubbles

Conclusion: Product is H_2 gas produced as result of reduction of H^+ . B is better reducing agent than acid.

Metal A + Metal C salt $\rightarrow$ no reaction

Conclusion: C is not undergoing reduction. C must be a better reducing agent than A.

Since C is a better reducing agent than A, which is a better reducing agent than B and B reduces acid, then **C would also reduce acid to form H_2 bubbles.**

The order of strength of reducing agents is: **C > A > B.**

21.40 a) **Copper** metal is coating the iron.

b) The oxidizing agent is Cu^{2+} and the reducing agent is **Fe**.

c) Yes, this reaction, being spontaneous, may be made into a voltaic cell.

d) $Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

$$\begin{aligned} e) E_{\text{cell}}^{\circ} &= E_{\text{Cu}^{2+}}^{\circ} - E_{\text{Fe}^{2+}}^{\circ} \\ &= 0.34 \text{ V} - (-0.44 \text{ V}) \\ &= 0.78 \text{ V} \end{aligned}$$

$$21.41 \quad E_{\text{cell}} = -\frac{0.0592 \text{ V}}{n} \log\left(\frac{Q}{K}\right) \text{ and } \Delta G = -nFE_{\text{cell}}$$

a) When $Q/K < 1$, the reaction is preceding to the right; $E_{\text{cell}} > 0$ and $\Delta G < 0$ and the reaction is spontaneous.

When $Q/K = 1$, the reaction is at equilibrium; $E_{\text{cell}} = 0$ and $\Delta G = 0$.

When $Q/K > 1$, the reaction is preceding to the left; $E_{\text{cell}} < 0$ and $\Delta G > 0$ and the reaction is not spontaneous.

b) Only when $Q/K < 1$ will the reaction proceed spontaneously and be able to do work.

21.42 At the negative (anode) electrode, oxidation occurs so the overall cell reaction is

$A(s) + B^+(aq) \rightarrow A^+(aq) + B(s)$ with $Q = [A^+]/[B^+]$.

a) The reaction proceeds to the right because with $E_{\text{cell}} > 0$ (voltaic cell), the spontaneous reaction occurs. As the cell operates, **$[A^+]$ increases and $[B^+]$ decreases.**

b) E_{cell} **decreases** because the cell reaction takes place to approach equilibrium, $E_{\text{cell}} = 0$.

c) E_{cell} and E_{cell}° are related by the Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^{\circ} - (RT/nF)\ln([A^+]/[B^+])$.

$E_{\text{cell}} = E_{\text{cell}}^{\circ}$ when $(RT/nF)\ln([A^+]/[B^+]) = 0$. This occurs when $\ln([A^+]/[B^+]) = 0$. Recall that $e^0 = 1$, so

$[A^+]$ must equal $[B^+]$ for E_{cell} to equal E_{cell}° .

d) **Yes**, it is possible for E_{cell} to be less than E_{cell}° when **$[A^+] > [B^+]$.**

$$21.43 \quad a) \text{ Examine the Nernst equation: } E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 RT}{nF} \log Q$$

$$E_{\text{cell}} = \frac{2.303 RT}{nF} \log K - \frac{2.303 RT}{nF} \log Q$$

$$E_{\text{cell}} = \frac{2.303 RT}{nF} \left(\log \frac{K}{Q} \right) = -\frac{2.303 RT}{nF} \left(\log \frac{Q}{K} \right)$$

If $Q/K < 1$, E_{cell} will decrease with a decrease in cell temperature. If $Q/K > 1$, E_{cell} will increase (become less negative) with a decrease in cell temperature.

$$b) E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 RT}{nF} \log \frac{[\text{Active ion at anode}]}{[\text{Active ion at cathode}]}$$

E_{cell} will decrease as the concentration of an active ion at the anode increases.

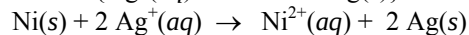
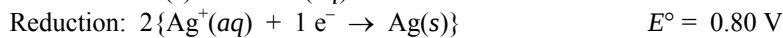
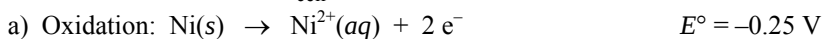
c) E_{cell} will increase as the concentration of an active ion at the cathode increases.

d) E_{cell} will increase as the pressure of a gaseous reactant in the cathode compartment increases.

21.44 In a concentration cell, the overall reaction takes place to decrease the concentration of the more concentrated electrolyte. The more concentrated electrolyte is reduced, so it is in the **cathode** compartment.

21.45 The equilibrium constant can be found by using $\ln K = \frac{nFE^\circ}{RT}$ or $\log K = \frac{nE^\circ}{0.0592}$. Use E° values from

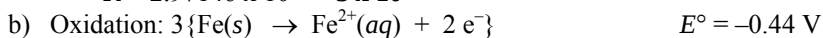
Appendix D to calculate E°_{cell} and then calculate K .



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80\text{ V} - (-0.25\text{ V}) = 1.05\text{ V}; 2\text{ electrons are transferred.}$$

$$\log K = \frac{nE^\circ}{0.0592} = \frac{2(1.05\text{ V})}{0.0592\text{ V}} = 35.47297 \text{ (unrounded)}$$

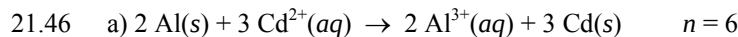
$$K = 2.97146 \times 10^{35} = \mathbf{3 \times 10^{35}}$$



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.74\text{ V} - (-0.44\text{ V}) = -0.30\text{ V}; 6\text{ electrons are transferred.}$$

$$\log K = \frac{nE^\circ}{0.0592} = \frac{6(-0.30\text{ V})}{0.0592\text{ V}} = -30.4054 \text{ (unrounded)}$$

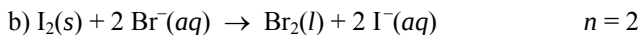
$$K = 3.9318 \times 10^{-31} = \mathbf{4 \times 10^{-31}}$$



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{Cd}^{2+}} - E^\circ_{\text{Al}^{3+}} \\ &= -0.40\text{ V} - (-1.66\text{ V}) \\ &= 1.26\text{ V} \end{aligned}$$

$$\log K = \frac{nE^\circ}{0.0592} = \frac{6(1.26\text{ V})}{0.0592\text{ V}} = 127.7027 \text{ (unrounded)}$$

$$K = 5.04316 \times 10^{127} = \mathbf{5 \times 10^{127}}$$



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{I}_2} - E^\circ_{\text{Br}_2} \\ &= 0.53\text{ V} - (1.07\text{ V}) \\ &= -0.54\text{ V} \end{aligned}$$

$$\log K = \frac{nE^\circ}{0.0592} = \frac{2(-0.54\text{ V})}{0.0592\text{ V}} = -18.24324 \text{ (unrounded)}$$

$$K = 5.7116 \times 10^{-19} = \mathbf{6 \times 10^{-19}}$$

21.47 Substitute J/C for V.

a) $\Delta G^\circ = -nFE^\circ = -(2\text{ mol e}^-)(96485\text{ C/mol e}^-)(1.05\text{ J/C}) = -2.026185 \times 10^5 = \mathbf{-2.03 \times 10^5\text{ J}}$

b) $\Delta G^\circ = -nFE^\circ = -(6\text{ mol e}^-)(96485\text{ C/mol e}^-)(-0.30\text{ J/C}) = 1.73673 \times 10^5 = \mathbf{1.73 \times 10^5\text{ J}}$

21.48 Substitute J/C for V.

a) $\Delta G^\circ = -nFE^\circ = -(6\text{ mol e}^-)(96485\text{ C/mol e}^-)(1.26\text{ J/C}) = -7.294266 \times 10^5 = \mathbf{-7.29 \times 10^5\text{ J}}$

b) $\Delta G^\circ = -nFE^\circ = -(2\text{ mol e}^-)(96485\text{ C/mol e}^-)(-0.54\text{ J/C}) = 1.042038 \times 10^5 = \mathbf{1.0 \times 10^5\text{ J}}$

21.49 Find ΔG° from the fact that $\Delta G^\circ = -RT \ln K$. Then use ΔG° value to find E°_{cell} from $\Delta G^\circ = -nFE^\circ$.

$$T = (273 + 25)\text{K} = 298\text{ K}$$

$$\Delta G^\circ = -RT \ln K = -(8.314\text{ J/mol}\cdot\text{K})(298\text{ K}) \ln (5.0 \times 10^4) = -2.68067797 \times 10^4 = \mathbf{-2.7 \times 10^4\text{ J}}$$

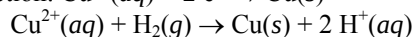
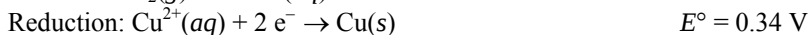
$$E^\circ = -\frac{\Delta G}{nF} = -\frac{-2.68067797 \times 10^4\text{ J}}{(1\text{ mol e}^-)(96485\text{ C/mol e}^-)} \left(\frac{1\text{ V}}{1\text{ J/C}} \right) = 0.27783365 = \mathbf{0.28\text{ V}}$$

21.50 Use $\log K = \frac{nE^\circ_{\text{cell}}}{0.0592}$ and $\Delta G^\circ = -RT \ln K$. $T = (273 + 25)\text{K} = 298 \text{ K}$

$$E^\circ_{\text{cell}} = (0.0592/n) \log K = (0.0592/2) \log 0.075 = -0.033298 = \mathbf{-0.033 \text{ V}}$$

$$\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K}) (298 \text{ K}) \ln (0.075) = 6.4175734 \times 10^3 = \mathbf{6.4 \times 10^3 \text{ J}}$$

21.51 Since this is a voltaic cell, a spontaneous reaction is occurring. For a spontaneous reaction between H_2/H^+ and Cu/Cu^{2+} , Cu^{2+} must be reduced and H_2 must be oxidized:



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= 0.34 \text{ V} - 0.00 \text{ V} \\ &= 0.34 \text{ V} \end{aligned}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log \frac{[\text{H}^+]^2}{[\text{Cu}^{2+}][\text{H}_2]}$$

For a standard hydrogen electrode $[\text{H}^+] = 1.0 \text{ M}$ and $[\text{H}_2] = 1.0 \text{ atm}$

$$0.22 \text{ V} = 0.34 \text{ V} - \frac{0.0592}{2} \log \frac{1.0}{[\text{Cu}^{2+}]1.0}$$

$$0.22 \text{ V} - 0.34 \text{ V} = -\frac{0.0592}{2} \log \frac{1.0}{[\text{Cu}^{2+}]1.0}$$

$$-0.12 \text{ V} = -\frac{0.0592}{2} \log \frac{1.0}{[\text{Cu}^{2+}]1.0}$$

$$4.054054 = \log \frac{1.0}{[\text{Cu}^{2+}]1.0} \quad \text{Raise each side to } 10^x.$$

$$1.132541 \times 10^4 = \frac{1}{[\text{Cu}^{2+}]}$$

$$[\text{Cu}^{2+}] = 8.8296999 \times 10^{-5} = \mathbf{8.8 \times 10^{-5} \text{ M}}$$

21.52 The cell reaction is: $\text{Pb}^{2+}(aq) + \text{Mn}(s) \rightarrow \text{Pb}(s) + \text{Mn}^{2+}(aq)$

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{Pb}^{2+}} - E^\circ_{\text{Mn}^{2+}} \\ &= -0.13 \text{ V} - (-1.18 \text{ V}) \\ &= 1.05 \text{ V} \end{aligned}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log \frac{[\text{Mn}^{2+}]}{[\text{Pb}^{2+}]}$$

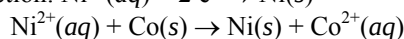
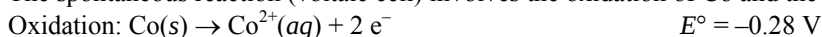
$$0.44 \text{ V} = 1.05 \text{ V} - \frac{0.0592}{2} \log \frac{[1.4]}{[\text{Pb}^{2+}]}$$

$$(0.44 \text{ V} - 1.05 \text{ V}) (-2 / 0.0592) = \log \frac{[1.4]}{[\text{Pb}^{2+}]} = 20.608108 \text{ (unrounded)}$$

$$\frac{[1.4]}{[\text{Pb}^{2+}]} = 4.056095$$

$$[\text{Pb}^{2+}] = 3.45160 \times 10^{-21} = \mathbf{3.5 \times 10^{-21} M}$$

21.53 The spontaneous reaction (voltaic cell) involves the oxidation of Co and the reduction of Ni^{2+} .



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = -0.25 \text{ V} - (-0.28 \text{ V}) = 0.03 \text{ V}$$

a) Use the Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log \frac{[\text{Co}^{2+}]}{[\text{Ni}^{2+}]}$ $n = 2 \text{e}^-$

$$E_{\text{cell}} = 0.03 \text{ V} - \frac{0.0592}{2} \log \frac{[0.20]}{[0.80]} = 0.047820975 \text{ V} = \mathbf{0.05 \text{ V}}$$

b) From part (a), notice that an increase in $[\text{Co}^{2+}]$ leads to a decrease in cell potential. Therefore, the concentration of cobalt ion must increase further to bring the potential down to 0.03 V. Thus, the new concentrations will be $[\text{Co}^{2+}] = 0.20 \text{ M} + x$ and $[\text{Ni}^{2+}] = 0.80 \text{ M} - x$ (There is a 1:1 mole ratio.)

$$0.03 \text{ V} = 0.03 \text{ V} - \frac{0.0592}{2} \log \frac{[0.20 + x]}{[0.80 - x]}$$

$$0 = -\frac{0.0592}{2} \log \frac{[0.20 + x]}{[0.80 - x]}$$

$$0 = \log \frac{[0.20 + x]}{[0.80 - x]} \quad \text{Raise each side to } 10^x.$$

$$1 = \frac{[0.20 + x]}{[0.80 - x]}$$

$$0.20 + x = 0.80 - x$$

$$x = 0.30 \text{ M}$$

$$[\text{Ni}^{2+}] = 0.80 - 0.30 = \mathbf{0.50 \text{ M}}$$

c) At equilibrium $E_{\text{cell}} = 0.00$, to decrease the cell potential to 0.00, $[\text{Co}^{2+}]$ increases and $[\text{Ni}^{2+}]$ decreases.

$$0.00 \text{ V} = 0.03 \text{ V} - \frac{0.0592}{2} \log \frac{[0.20 + x]}{[0.80 - x]}$$

$$-0.03 \text{ V} = -0.0296 \log \frac{[0.20 + x]}{[0.80 - x]}$$

$$1.0135135 = \log \frac{[0.20 + x]}{[0.80 - x]}$$

$$10.316052 = \frac{[0.20 + x]}{[0.80 - x]}$$

$$x = 0.7116332 \text{ (unrounded)}$$

$$[\text{Co}^{2+}] = 0.20 + 0.7116332 = 0.9116332 = \mathbf{0.91 \text{ M}}$$

$$[\text{Ni}^{2+}] = 0.80 - 0.7116332 = 0.08837 = \mathbf{0.09 \text{ M}}$$

- 21.54 The spontaneous reaction (voltaic cell) is $\text{Cd}^{2+}(\text{aq}) + \text{Mn}(\text{s}) \rightarrow \text{Cd}(\text{s}) + \text{Mn}^{2+}(\text{aq})$ with $E_{\text{cell}}^{\circ} = -0.40 \text{ V} - (-1.18 \text{ V}) = 0.78 \text{ V}$.

a) Use the Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Mn}^{2+}]}{[\text{Cd}^{2+}]}$ $n = 2 \text{ e}^{-}$

$$E_{\text{cell}} = 0.78 - \frac{0.0592}{2} \log \frac{[0.090]}{[0.060]}$$

$$= 0.774787698 \text{ V} = \mathbf{0.77 \text{ V}}$$

- b) For the $[\text{Cd}^{2+}]$ to decrease from 0.060 M to 0.050 M, a change of 0.010 M, the $[\text{Mn}^{2+}]$ must increase by the same amount, from 0.090 M to 0.100 M.

$$E_{\text{cell}} = 0.78 - \frac{0.0592}{2} \log \frac{[0.10]}{[0.050]}$$

$$= 0.771089512 \text{ V} = \mathbf{0.77 \text{ V}}$$

- c) Increase the manganese and decrease the cadmium by equal amounts. Total = 0.150 M

$$0.055 = 0.78 - \frac{0.0592}{2} \log \frac{[\text{Mn}^{2+}]}{[\text{Cd}^{2+}]}$$

$$([\text{Mn}^{2+}]/[\text{Cd}^{2+}]) = 3.1134596 \times 10^{24} \text{ (unrounded)}$$

$$[\text{Mn}^{2+}] + [\text{Cd}^{2+}] = 0.150 \text{ M}$$

$$[\text{Cd}^{2+}] = 4.81779 \times 10^{-26} \text{ M (unrounded)}$$

$$[\text{Mn}^{2+}] = 0.150 \text{ M} - [\text{Cd}^{2+}] = \mathbf{0.150 \text{ M}}$$

- d) At equilibrium $E_{\text{cell}} = 0.00$.

$$0.00 = 0.78 - \frac{0.0592}{2} \log \frac{[\text{Mn}^{2+}]}{[\text{Cd}^{2+}]}$$

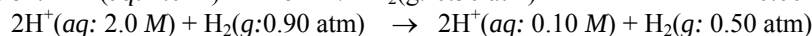
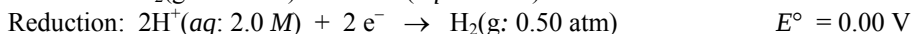
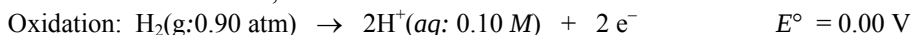
$$([\text{Mn}^{2+}]/[\text{Cd}^{2+}]) = 2.2456979 \times 10^{26} \text{ (unrounded)}$$

$$[\text{Mn}^{2+}] + [\text{Cd}^{2+}] = 0.150 \text{ M}$$

$$[\text{Cd}^{2+}] = 6.6794377 \times 10^{-28} = \mathbf{7 \times 10^{-28} \text{ M}}$$

$$[\text{Mn}^{2+}] = 0.150 \text{ M} - [\text{Cd}^{2+}] = \mathbf{0.150 \text{ M}}$$

- 21.55 The overall cell reaction proceeds to increase the 0.10 M H^{+} concentration and decrease the 2.0 M H^{+} concentration. Therefore, half-cell **A is the anode** because it has the lower concentration.



$$E_{\text{cell}}^{\circ} = 0.00 \text{ V} \quad n = 2 \text{ e}^{-}$$

$$Q \text{ for the cell equals } \frac{[\text{H}^{+}]_{\text{anode}}^2 P_{\text{H}(\text{cathode})}}{[\text{H}^{+}]_{\text{cathode}}^2 P_{\text{H}(\text{anode})}} = \frac{(0.10)^2 (0.50)}{(2.0)^2 (0.90)} = 0.001388889 \text{ (unrounded)}$$

$$E_{\text{cell}} = 0.00 \text{ V} - \frac{0.0592}{2} \log (0.001388889) = 0.084577 = \mathbf{0.085 \text{ V}}$$

- 21.56 $\text{Sn}^{2+}(0.87 \text{ M}) \rightarrow \text{Sn}^{2+}(0.13 \text{ M})$

Half-cell **B is the cathode**.

$$E_{\text{cell}} = 0.00 \text{ V} - (0.0592 \text{ V}) \log (0.13/0.87) = 0.024437 = \mathbf{0.024 \text{ V}}$$

- 21.57 Electrons flow from the anode, where oxidation occurs, to the cathode, where reduction occurs. The electrons always flow from the anode to the cathode, no matter what type of cell.

- 21.58 A D-sized battery is much larger than an AAA-sized battery, so the D-sized battery contains a greater amount of the cell components. The potential, however, is an intensive property and does not depend on the amount of the cell components. (Note that amount is different from concentration.) The total amount of charge a battery can produce does depend on the amount of cell components, so the D-sized battery produces more charge than the AAA-sized battery.
- 21.59 a) Alkaline batteries = $(6.0 \text{ V}) (1 \text{ alkaline battery}/1.5 \text{ V}) = \mathbf{4 \text{ alkaline batteries}}$.
 b) Voltage = $(6 \text{ Ag batteries}) (1.6 \text{ V/Ag battery}) = \mathbf{9.6 \text{ V}}$
 c) The usual 12 volt car battery consists of six 2 volt cells. If two cells are shorted only four cells remain.
 Voltage = $(4 \text{ cells}) (2 \text{ V/cell}) = \mathbf{8 \text{ V}}$
- 21.60 The Teflon spacers keep the two metals separated so the copper cannot conduct electrons that would promote the corrosion of the iron skeleton. Oxidation of the iron by oxygen causes rust to form and the metal to corrode.
- 21.61 Bridge supports rust more rapidly at the water line due to the presence of large concentrations of both O_2 and H_2O .
- 21.62 Sacrificial anodes are metals with E° less than that for iron, -0.44 V , so they are more easily oxidized than iron.
 a) $E^\circ(\text{aluminum}) = -1.66$. Yes, except aluminum resists corrosion because once a coating of its oxide covers it, no more aluminum corrodes. Therefore, it would not be a good choice.
 b) $E^\circ(\text{magnesium}) = -2.37 \text{ V}$. Yes, magnesium is appropriate to act as a sacrificial anode.
 c) $E^\circ(\text{sodium}) = -2.71 \text{ V}$. Yes, except sodium reacts with water, so it would not be a good choice.
 d) $E^\circ(\text{lead}) = -0.13 \text{ V}$. No, lead is not appropriate to act as a sacrificial anode because its value is too high.
 e) $E^\circ(\text{nickel}) = -0.25 \text{ V}$. No, nickel is inappropriate as a sacrificial anode because its value is too high.
 f) $E^\circ(\text{zinc}) = -0.76 \text{ V}$. Yes, zinc is appropriate to act as a sacrificial anode.
 g) $E^\circ(\text{chromium}) = -0.74 \text{ V}$. Yes, chromium is appropriate to act as a sacrificial anode.
- 21.63 a) Oxidation occurs at the **left** electrode (anode).
 b) Elemental M forms at the **right** electrode (cathode).
 c) Electrons are being released by ions at the **left** electrode.
 d) Electrons are entering the cell at the **right** electrode.
- 21.64 $3 \text{ Cd}^{2+}(\text{aq}) + 2 \text{ Cr}(\text{s}) \rightarrow 3 \text{ Cd}(\text{s}) + 2 \text{ Cr}^{3+}(\text{aq})$
 $E_{\text{cell}}^\circ = -0.40 \text{ V} - (-0.74 \text{ V}) = 0.34 \text{ V}$
 To reverse the reaction requires 0.34 V with the cell in its standard state. A 1.5 V supplies more than enough potential, so the cadmium metal oxidizes to Cd^{2+} and chromium plates out.
- 21.65 The $E_{\text{half-cell}}$ values are different than the $E_{\text{half-cell}}^\circ$ values because in pure water, the $[\text{H}^+]$ and $[\text{OH}^-]$ are $1.0 \times 10^{-7} \text{ M}$ rather than the standard-state value of 1 M .
- 21.66 The oxidation number of nitrogen in the nitrate ion, NO_3^- , is +5 and cannot be oxidized further since nitrogen has only five electrons in its outer level. In the nitrite ion, NO_2^- , on the other hand, the oxidation number of nitrogen is +3, so it can be oxidized to the +5 state.
- 21.67 Due to the phenomenon of overvoltage, the products predicted from a comparison of electrode potentials are not always the actual products. When gases (such as $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$) are produced at metal electrodes, there is an overvoltage of about 0.4 to 0.6 V more than the electrode potential indicates. Due to this, if H_2 or O_2 is the **expected** product, another species may be the true product.
- 21.68 Iron and nickel are more easily oxidized than copper, so they are separated from the copper in the roasting step and conversion to slag. In the electrolyrefining process, all three metals are oxidized into solution, but only Cu^{2+} ions are reduced at the cathode to form $\text{Cu}(\text{s})$.
- 21.69 Molten cryolite is a good solvent for Al_2O_3 .

- 21.70 a) At the anode, bromide ions are oxidized to form bromine (**Br₂**).
b) At the cathode, sodium ions are reduced to form sodium metal (**Na**).
- 21.71 a) At the negative electrode (cathode) barium ions are reduced to form barium metal (**Ba**).
b) At the positive electrode (anode), iodide ions are oxidized to form iodine (**I₂**).

21.72 Possible reductions:



Copper can be prepared by electrolysis of its aqueous salt since its reduction half-cell potential is more positive than the potential for the reduction of water. The reduction of copper is more spontaneous than the reduction of water. Since the reduction potentials of Ba^{2+} and Al^{3+} are more negative and therefore less spontaneous than the reduction of water, these ions cannot be reduced in the presence of water since the water is reduced instead.

Possible oxidations:



Bromine can be prepared by electrolysis of its aqueous salt because its reduction half-cell potential is more negative than the potential for the oxidation of water with overvoltage. The more negative reduction potential for Br^{-} indicates that its oxidation is more spontaneous than the oxidation of water.

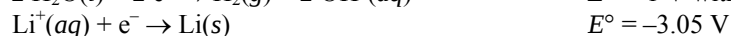
- 21.73 Strontium is too electropositive to form from the electrolysis of an aqueous solution. The elements that electrolysis will separate from an aqueous solution are **gold, tin, and chlorine**.

21.74 a) Possible oxidations:



Since the reduction potential of water is more negative than the reduction potential for F^{-} , the oxidation of water is more spontaneous than that of F^{-} . The oxidation of water produces oxygen gas (**O₂**), and hydronium ions (**H₃O⁺**) at the anode.

Possible reductions:



Since the reduction potential of water is more positive than that of Li^{+} , the reduction of water is more spontaneous than the reduction of Li^{+} . The reduction of water produces **H₂** gas and **OH⁻** at the cathode.

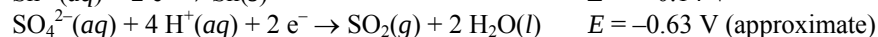
b) Possible oxidations:



The oxidation of water produces oxygen gas (**O₂**), and hydronium ions (**H₃O⁺**) at the anode.

The SO_4^{2-} ion cannot oxidize as S is already in its highest oxidation state in SO_4^{2-} .

Possible reductions:



The potential for sulfate reduction is estimated from the Nernst equation using standard state concentrations and pressures for all reactants and products except H^{+} , which in pure water is $1 \times 10^{-7} \text{ M}$.

$$E = 0.20 \text{ V} - (0.0592/2) \log [1/(1 \times 10^{-7})^4] = -0.6288 = -0.63 \text{ V}$$

The most easily reduced ion is Sn^{2+} with the most positive reduction potential, so **tin metal** forms at the cathode.

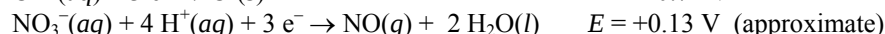
21.75 a) Possible oxidations:



The oxidation of water produces oxygen gas (O_2), and hydronium ions (H_3O^+) at the anode.

NO_3^- cannot oxidize since N is in its highest oxidation state in NO_3^- .

Possible reductions:



The potential for nitrate reduction is estimated from the Nernst equation using standard state concentrations and pressures for all reactants and products except H^+ , which in pure water is $1 \times 10^{-7} \text{ M}$.

$$E = 0.96 \text{ V} - (0.0592 / 2) \log [1 / (1 \times 10^{-7})^4] = 0.1312 = 0.13 \text{ V}$$

The most easily reduced ion is NO_3^- , with the most positive reduction potential so **NO gas** is formed at the cathode.

b) Possible oxidations:



The oxidation of chloride ions to produce **chlorine gas** occurs at the anode. Cl^- has a more negative reduction potential showing that it is more easily oxidized than water.

Possible reductions:



It is easier to reduce water than to reduce manganese ions, so **hydrogen gas and hydroxide ions** form at the cathode. The reduction potential of Mn^{2+} is more negative than that of water showing that its reduction is less spontaneous than that of water.

21.76 $\text{Mg}^{2+} + 2 \text{e}^- \rightarrow \text{Mg}$

$$\text{a) } (45.6 \text{ g Mg}) \left(\frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \right) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol Mg}} \right) = 3.75154257 = \mathbf{3.75 \text{ mol e}^-}$$

$$\text{b) } (3.75154257 \text{ mol e}^-) \left(\frac{96485 \text{ C}}{\text{mol e}^-} \right) = 3.619676 \times 10^5 = \mathbf{3.62 \times 10^5 \text{ coulombs}}$$

$$\text{c) } \left(\frac{3.619676 \times 10^5 \text{ C}}{3.50 \text{ h}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right) \left(\frac{\text{A}}{\text{C/s}} \right) = 28.727586 = \mathbf{28.7 \text{ A}}$$

21.77 $\text{Na}^+ + 1 \text{e}^- \rightarrow \text{Na}$

$$\text{a) } (215 \text{ g Na}) \left(\frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \right) \left(\frac{1 \text{ mol e}^-}{1 \text{ mol Na}} \right) = 9.351892127 = \mathbf{9.35 \text{ mol e}^-}$$

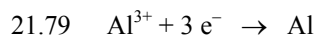
$$\text{b) } (9.351892127 \text{ mol e}^-) (96485 \text{ C / mol e}^-) = 9.0231731 \times 10^5 = \mathbf{9.02 \times 10^5 \text{ coulombs}}$$

$$\text{c) } \left(\frac{9.0231731 \times 10^5 \text{ C}}{9.50 \text{ h}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right) \left(\frac{\text{A}}{\text{C/s}} \right) = 26.383547 = \mathbf{26.4 \text{ A}}$$

21.78 $\text{Ra}^{2+} + 2 \text{e}^- \rightarrow \text{Ra}$

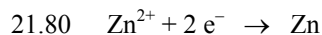
In the reduction of radium ions, Ra^{2+} , to radium metal, the transfer of two electrons occurs.

$$(235 \text{ C}) \left(\frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Ra}}{2 \text{ mol e}^-} \right) \left(\frac{226 \text{ g Ra}}{1 \text{ mol Ra}} \right) = 0.275224 = \mathbf{0.275 \text{ g Ra}}$$

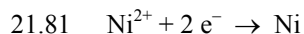


In the reduction of aluminum ions, Al^{3+} , to aluminum metal the transfer of three electrons occurs.

$$(305 \text{ C}) \left(\frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Al}}{3 \text{ mol e}^-} \right) \left(\frac{26.98 \text{ g Al}}{1 \text{ mol Al}} \right) = 0.028428944 = \mathbf{0.0284 \text{ g Al}}$$



$$\text{Time} = (65.5 \text{ g Zn}) \left(\frac{1 \text{ mol Zn}}{65.41 \text{ g Zn}} \right) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol Zn}} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{1}{21.0 \text{ A}} \right) \left(\frac{1 \text{ A}}{\text{C/s}} \right) = 9.20169 \times 10^3 = \mathbf{9.20 \times 10^3 \text{ seconds}}$$

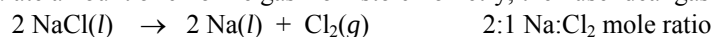


$$\text{Time} = (1.63 \text{ g Ni}) \left(\frac{1 \text{ mol Ni}}{58.69 \text{ g Ni}} \right) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol Ni}} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{1}{13.7 \text{ A}} \right) \left(\frac{1 \text{ A}}{\text{C/s}} \right) = 391.1944859 = \mathbf{391 \text{ seconds}}$$

21.82 a) The sodium sulfate makes the water conductive, so the current will flow through the water to complete the circuit, increasing the rate of electrolysis. Pure water, which contains very low (10^{-7} M) concentrations of H^+ and OH^- , conducts electricity very poorly.

b) The reduction of H_2O has a more positive half-potential (-1 V) than the reduction of Na^+ (-2.71 V); the more spontaneous reduction of water will occur instead of the less spontaneous reduction of sodium ion. The oxidation of H_2O is the only oxidation possible because SO_4^{2-} cannot be oxidized under these conditions. In other words, it is easier to reduce H_2O than Na^+ and easier to oxidize H_2O than SO_4^{2-} .

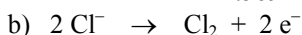
21.83 a) Calculate amount of chlorine gas from stoichiometry, then use ideal gas law to find volume of chlorine gas.



$$\text{Moles Cl}_2 = (30.0 \text{ kg Na}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \right) \left(\frac{1 \text{ mol Cl}_2}{2 \text{ mol Na}} \right) = 652.45759 \text{ mol Cl}_2 \text{ (unrounded)}$$

$$V = \frac{nRT}{P} = \frac{(652.45759 \text{ mol Cl}_2) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 580.) \text{ K})}{(1.0 \text{ atm})}$$

$$= 4.5692 \times 10^4 = \mathbf{4.6 \times 10^4 \text{ L}}$$



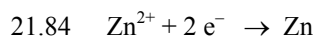
Two moles of electrons are passed through the cell for each mole of Cl_2 produced.

$$\text{Coulombs} = (652.45759 \text{ mol Cl}_2) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol Cl}_2} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^-} \right)$$

$$= 1.259047 \times 10^8 = \mathbf{1.26 \times 10^8 \text{ Coulombs}}$$

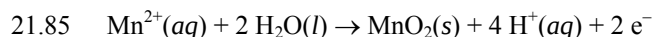
c) Current is charge per time with the amp unit equal to C/s.

$$(1.25904741 \text{ C}) \left(\frac{1 \text{ s}}{75 \text{ C}} \right) = 1.6787 \times 10^6 = \mathbf{1.68 \times 10^6 \text{ seconds}}$$



$$\text{Mass} = (0.855 \text{ A}) \left(\frac{\text{C/s}}{\text{A}} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) \left(\frac{24 \text{ h}}{1 \text{ day}} \right) (2.50 \text{ day}) \left(\frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Zn}}{2 \text{ mol e}^-} \right) \left(\frac{65.41 \text{ g Zn}}{1 \text{ mol Zn}} \right)$$

$$= 62.599998 = \mathbf{62.6 \text{ g Zn}}$$

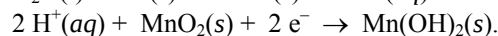
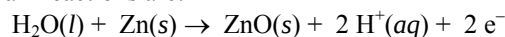


$$\text{Time} = (1.00 \text{ kg MnO}_2) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol MnO}_2}{86.94 \text{ g MnO}_2} \right) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol MnO}_2} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{1}{25.0 \text{ A}} \right) \left(\frac{\text{A}}{\text{C/s}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right)$$

$$= 24.66196 = \mathbf{24.7 \text{ hours}}$$

The MnO_2 product forms at the **anode**, since the half-reaction is an oxidation.

21.86 a) The half-reactions are:



2 moles of electrons flow per mole of reaction.

b) Mass of $\text{MnO}_2 = (4.50 \text{ g Zn}) \left(\frac{1 \text{ mol Zn}}{65.41 \text{ g Zn}} \right) \left(\frac{1 \text{ mol MnO}_2}{1 \text{ mol Zn}} \right) \left(\frac{86.94 \text{ g MnO}_2}{1 \text{ mol MnO}_2} \right) = 5.981196 = \mathbf{5.98 \text{ g MnO}_2}$

$$\text{Mass of H}_2\text{O} = (4.50 \text{ g Zn}) \left(\frac{1 \text{ mol Zn}}{65.41 \text{ g Zn}} \right) \left(\frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol Zn}} \right) \left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 1.23972 = \mathbf{1.24 \text{ g H}_2\text{O}}$$

c) Total mass of reactants = $4.50 \text{ g Zn} + 5.981196 \text{ g MnO}_2 + 1.23972 \text{ g H}_2\text{O} = 11.720916 = \mathbf{11.72 \text{ g}}$

d) Charge = $(4.50 \text{ g Zn}) \left(\frac{1 \text{ mol Zn}}{65.41 \text{ g Zn}} \right) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol Zn}} \right) \left(\frac{96485 \text{ coulombs}}{1 \text{ mol e}^-} \right) = 1.32757 \times 10^4 = \mathbf{1.33 \times 10^4 \text{ C}}$

e) An alkaline battery consists of more than just reactants. The case, electrolyte paste, cathode, absorbent, and unreacted reactants (less than 100% efficient) also contribute to the mass of an alkaline battery.

21.87 From the current 65.0% of the moles of product will be copper and 35.0% zinc. Assume a current of exactly 100 coulombs. The amount of current used to generate copper would be $(65.0\%/100\%) (100 \text{ C}) = 65.0 \text{ C}$, and the amount of current used to generate zinc would be $(35.0\%/100\%) (100 \text{ C}) = 35.0 \text{ C}$.

The half-reactions are: $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$ and $\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$.

$$\text{Mass copper} = (65.0 \text{ C}) \left(\frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} \right) \left(\frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} \right) = 0.021406177 \text{ g Cu (unrounded)}$$

$$\text{Mass zinc} = (35.0 \text{ C}) \left(\frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Zn}}{2 \text{ mol e}^-} \right) \left(\frac{65.41 \text{ g Zn}}{1 \text{ mol Zn}} \right) = 0.01186376 \text{ g Zn (unrounded)}$$

$$\text{Mass \% copper} = \left(\frac{0.021406177 \text{ g Cu}}{(0.021406177 + 0.01186376) \text{ g Sample}} \right) \times 100\% = 64.340900 = \mathbf{64.3\% \text{ Cu}}$$

21.88

	Voltaic Cell	Electrolytic Cell
--	--------------	-------------------

- | | | |
|----|----------------|----------------|
| a) | ΔG is negative | ΔG is positive |
| b) | Oxidation | Oxidation |
| c) | Reduction | Reduction |
| d) | (-) | (+) |
| e) | Anode | Anode |

21.89 The reaction is: $\text{Au}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Au}(\text{s})$

a) Find the volume of gold needed to plate the earring and then use density to find the mass and moles of gold needed. The volume of the gold is the volume of a cylinder.

$$V = \pi r^2 h$$

$$V = \pi \left(\frac{4.00 \text{ cm}}{2} \right)^2 (0.25 \text{ mm}) \left(\frac{10^{-3} \text{ m}}{1 \text{ mm}} \right) \left(\frac{1 \text{ cm}}{10^{-2} \text{ m}} \right) = 0.314159265 \text{ cm}^3$$

$$(0.314159265 \text{ cm}^3) \left(\frac{19.3 \text{ g Au}}{1 \text{ cm}^3} \right) \left(\frac{1 \text{ mol Au}}{197.0 \text{ g Au}} \right) = 0.03077803 \text{ mol Au (unrounded)}$$

$$\text{Time} = (0.03077803 \text{ mol Au}) \left(\frac{3 \text{ mol e}^-}{1 \text{ mol Au}} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{\text{A}}{\text{C/s}} \right) \left(\frac{1}{0.013 \text{ A}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right) \left(\frac{1 \text{ day}}{24 \text{ h}} \right)$$

$$= 7.931675 = \mathbf{8 \text{ days}}$$

b) The time required doubles once for the second earring of the pair and doubles again for the second side, thus it will take four times as long as one side of one earring.

$$\text{Time} = (4) (7.931675 \text{ days}) = 31.7267 = \mathbf{32 \text{ days}}$$

c) Start by multiplying the moles of gold from part (a) by four to get the moles for the earrings. Convert this moles to grams, then to troy ounces, and finally to dollars.

$$\text{Cost} = (4) (0.03077803 \text{ mol Au}) \left(\frac{197.0 \text{ g Au}}{1 \text{ mol Au}} \right) \left(\frac{1 \text{ Troy Ounce}}{31.10 \text{ g}} \right) \left(\frac{\$920}{\text{Troy Ounce}} \right) = 717.455 = \mathbf{\$717}$$

21.90 a) The half-reaction is: $2 \text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{e}^-$

Determine the moles of oxygen from the ideal gas equation. Use the half-reaction and the current to convert the moles of oxygen to time.

$$n = PV/RT = \left(\frac{(99.8 \text{ kPa})(10.0 \text{ L})}{\left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 28) \text{ K})} \right) \left(\frac{1 \text{ atm}}{1.01325 \times 10^5 \text{ Pa}} \right) \left(\frac{10^3 \text{ Pa}}{1 \text{ kPa}} \right)$$

$$= 0.398569696 \text{ mol O}_2 \text{ (unrounded)}$$

$$\text{Time} = (0.398569696 \text{ mol O}_2) \left(\frac{4 \text{ mol e}^-}{1 \text{ mol O}_2} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{\text{A}}{\text{C/s}} \right) \left(\frac{1}{1.3 \text{ A}} \right) \left(\frac{1 \text{ min}}{60 \text{ s}} \right)$$

$$= 1.97210 \times 10^3 = \mathbf{2.0 \times 10^3 \text{ min}}$$

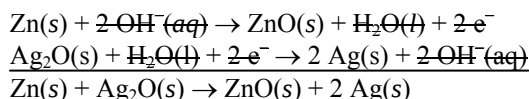
b) The balanced chemical equation is: $2 \text{H}_2\text{O}(l) \rightarrow 2 \text{H}_2(g) + \text{O}_2(g)$

The moles of oxygen determined previously and this chemical equation leads to the mass of hydrogen.

$$\text{Mass H}_2 = (0.398569696 \text{ mol O}_2) (2 \text{ mol H}_2/1 \text{ mol O}_2) (2.016 \text{ g H}_2/1 \text{ mol H}_2)$$

$$= 1.60703 = 1.61 \text{ g H}_2$$

21.91 The half-reactions and the cell reaction are:



The key is the moles of zinc. From the moles of zinc, the moles of electrons and the moles of Ag₂O may be found.

$$\text{Moles Zn} = (0.75 \text{ g Zn}) \left(\frac{80\%}{100\%} \right) \left(\frac{1 \text{ mol Zn}}{65.41 \text{ g Zn}} \right) = 0.00917291 \text{ mol Zn (unrounded)}$$

The 80% is assumed to have two significant figures.

$$\text{a) Time} = (0.00917291 \text{ mol Zn}) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol Zn}} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{\text{A}}{\text{C/s}} \right) \left(\frac{1 \mu\text{A}}{10^{-6} \text{ A}} \right) \left(\frac{1}{0.85 \mu\text{A}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right) \left(\frac{1 \text{ day}}{24 \text{ h}} \right)$$

$$= 2.410262 \times 10^4 = \mathbf{2.4 \times 10^4 \text{ days}}$$

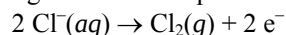
$$\text{b) Mass Ag} = (0.00917291 \text{ mol Zn}) \left(\frac{1 \text{ mol Ag}_2\text{O}}{1 \text{ mol Zn}} \right) \left(\frac{100\%}{95\%} \right) \left(\frac{2 \text{ mol Ag}}{1 \text{ mol Ag}_2\text{O}} \right) \left(\frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} \right)$$

$$= 2.0836989 = \mathbf{2.1 \text{ g Ag}}$$

$$\text{c) Cost} = (2.0836989 \text{ g Ag}) \left(\frac{95\%}{100\%} \right) \left(\frac{1 \text{ troy oz}}{31.10 \text{ g Ag}} \right) \left(\frac{\$13.00}{\text{troy oz}} \right) \left(\frac{1}{2.410262 \times 10^4 \text{ days}} \right)$$

$$= 3.433027 \times 10^{-5} = \mathbf{\$ 3.4 \times 10^{-5}/\text{day}}$$

- 21.92 This problem deals with the stoichiometry of electrolysis. The balanced oxidation half-reaction for the chlor-alkali process is given in the chapter:



Use the Faraday constant, F , ($1 F = 96485 \text{ C/mol e}^-$) and the fact that 1 mol of Cl_2 produces 2 mol e^- or $2 F$, to convert coulombs to moles of Cl_2 .

$$\begin{aligned} \text{Mass Cl}_2 &= (3 \times 10^4 \text{ A}) \left(\frac{\text{C/s}}{\text{A}} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) (8 \text{ h}) \left(\frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Cl}_2}{2 \text{ mol e}^-} \right) \left(\frac{70.90 \text{ g Cl}_2}{1 \text{ mol Cl}_2} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{2.205 \text{ lb}}{1 \text{ kg}} \right) \\ &= 699.9689 = \mathbf{7 \times 10^2 \text{ pounds Cl}_2} \end{aligned}$$

- 21.93 a) The half-reaction is: $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$

$$\text{Mass Cu} = (5.0 \text{ A}) \left(\frac{\text{C/s}}{\text{A}} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) (1.25 \text{ h}) \left(\frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} \right) \left(\frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} \right) = 7.40983 = \mathbf{7.4 \text{ g Cu}}$$

$$\text{b) Thickness} = (7.40983 \text{ g Cu}) (1 \text{ cm}^3/8.95 \text{ g Cu}) (1/50.0 \text{ cm}^2) = 0.016558 = \mathbf{0.017 \text{ cm}}$$

- 21.94 a) Aluminum half-reaction: $\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$, so $n = 3$. Remember that $1 \text{ A} = 1 \text{ C/s}$.

$$\begin{aligned} \text{Time} &= (1000 \text{ kg Al}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \right) \left(\frac{3 \text{ mol e}^-}{1 \text{ mol Al}} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{\text{A}}{\text{C/s}} \right) \left(\frac{1}{100,000 \text{ A}} \right) \\ &= 1.0728502 \times 10^5 \text{ s} = \mathbf{1.073 \times 10^5 \text{ s}} \end{aligned}$$

The molar mass of aluminum limits the significant figures.

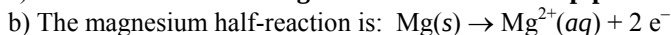
b) Multiply the time by the current and voltage, remembering that $1 \text{ A} = 1 \text{ C/s}$ (thus, $100,000 \text{ A}$ is $100,000 \text{ C/s}$) and $1 \text{ V} = 1 \text{ J/C}$ (thus, $5.0 \text{ V} = 5.0 \text{ J/C}$). Change units of J to $\text{kW}\cdot\text{h}$.

$$(1.0728502 \times 10^5 \text{ s}) \left(\frac{100,000 \text{ C}}{\text{s}} \right) \left(\frac{5.0 \text{ J}}{\text{C}} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) \left(\frac{1 \text{ kW}\cdot\text{h}}{3.6 \times 10^3 \text{ kJ}} \right) = 1.4900698 \times 10^4 = \mathbf{1.5 \times 10^4 \text{ kW}\cdot\text{h}}$$

c) From part (b), the $1.5 \times 10^4 \text{ kW}\cdot\text{h}$ calculated is per 1000 kg of aluminum. Use the ratio of $\text{kW}\cdot\text{h}$ to mass to find $\text{kW}\cdot\text{h/lb}$ and then use efficiency and cost per $\text{kW}\cdot\text{h}$ to find cost per pound.

$$\text{Cost} = \left(\frac{1.4900698 \times 10^4 \text{ kW}\cdot\text{h}}{1000 \text{ kg Al}} \right) \left(\frac{1 \text{ kg}}{2.205 \text{ lb}} \right) \left(\frac{0.90 \text{ cents}}{1 \text{ kW}\cdot\text{h}} \right) \left(\frac{100\%}{90\%} \right) = 6.757686 = \mathbf{6.8\text{¢/lb Al}}$$

- 21.95 a) Electrons flow **from magnesium bar to the iron pipe** since magnesium is more easily oxidized than iron.



Current is charge per time. The mass of magnesium can give the total charge. Convert the mass of magnesium to moles of magnesium and multiplying by 2 moles of electrons produced for each mole of magnesium and by Faradays constant to convert the moles of electrons to coulombs of charge. For units of amps time must be in seconds, so convert the 8.5 years to seconds.

$$\text{Current} = \frac{\text{Charge}}{\text{Time}}$$

$$\begin{aligned} &= \frac{(12 \text{ kg Mg}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \right) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol Mg}} \right) \left(\frac{96485 \text{ C}}{\text{mol e}^-} \right)}{(8.5 \text{ yr}) \left(\frac{365.25 \text{ days}}{1 \text{ yr}} \right) \left(\frac{24 \text{ h}}{1 \text{ day}} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right)} \left(\frac{\text{A}}{\text{C/s}} \right) = 0.35511 = \mathbf{0.36 \text{ A}} \end{aligned}$$

- 21.96 Statement: metal D + hot water $\rightarrow$ reaction Conclusion: D reduces water.

Statement: D + E salt $\rightarrow$ no reaction

Conclusion: D does not reduce E salt, so E reduces D salt. E is better reducing agent than D.

Statement: D + F salt $\rightarrow$ reaction

Conclusion: D reduces F salt. D is better reducing agent than F.

If E metal and F salt are mixed, the salt is reduced producing F metal because E has the greatest reducing strength of the three metals (E is stronger than D and D is stronger than F). The ranking of increasing reducing strength is **F < D < E**.

21.97 Substitute J/C for V.

a) Cell I: Oxidation number (O.N.) of H from 0 to +1, so 1 electron lost from each of 4 hydrogens for a total of 4 electrons. Oxygen O.N. goes from 0 to -2, indicating that 2 electrons are gained by each of the two oxygens for a total of 4 electrons. There is a transfer of **four electrons** in the reaction. The potential given in the problem allows the calculation of ΔG° :

$$\Delta G^\circ = -nFE^\circ = -(4 \text{ mol } e^-) (96485 \text{ C/mol } e^-) (1.23 \text{ J/C}) = -4.747062 \times 10^5 = \mathbf{-4.75 \times 10^5 \text{ J}}$$

Cell II: In $\text{Pb(s)} \rightarrow \text{PbSO}_4$ O.N. of Pb goes from 0 to +2 and in $\text{PbO}_2 \rightarrow \text{PbSO}_4$, O.N. goes from +4 to +2. There is a transfer of **two electrons** in the reaction.

$$\Delta G^\circ = -nFE^\circ = -(2 \text{ mol } e^-) (96485 \text{ C/mol } e^-) (2.04 \text{ J/C}) = -3.936588 \times 10^5 = \mathbf{-3.94 \times 10^5 \text{ J}}$$

Cell III: O.N. of each of two Na atoms changes from 0 to +1 and O.N. of Fe changes from +2 to 0. There is a transfer of **two electrons** in the reaction.

$$\Delta G^\circ = -nFE^\circ = -(2 \text{ mol } e^-) (96485 \text{ C/mol } e^-) (2.35 \text{ J/C}) = -4.534795 \times 10^5 = \mathbf{-4.53 \times 10^5 \text{ J}}$$

b) Cell I: Mass of reactants = $(2 \text{ mol } \text{H}_2) \left(\frac{2.016 \text{ g } \text{H}_2}{1 \text{ mol } \text{H}_2} \right) + (1 \text{ mol } \text{O}_2) \left(\frac{32.00 \text{ g } \text{O}_2}{1 \text{ mol } \text{O}_2} \right) = 36.032 \text{ g (unrounded)}$

$$\frac{w_{\max}}{\text{Mass of reactant}} = \left(\frac{-4.747062 \times 10^5 \text{ J}}{36.032 \text{ g}} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) = -13.17457 = \mathbf{-13.2 \text{ kJ/g}}$$

Cell II: Mass of reactants =

$$(1 \text{ mol Pb}) \left(\frac{207.2 \text{ g Pb}}{1 \text{ mol Pb}} \right) + (1 \text{ mol PbO}_2) \left(\frac{239.2 \text{ g PbO}_2}{1 \text{ mol PbO}_2} \right) + (2 \text{ mol H}_2\text{SO}_4) \left(\frac{98.09 \text{ g H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} \right) \\ = 642.58 \text{ g (unrounded)}$$

$$\frac{w_{\max}}{\text{Mass of reactant}} = \left(\frac{-3.936588 \times 10^5 \text{ J}}{642.58 \text{ g}} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) = -0.612622 = \mathbf{-0.613 \text{ kJ/g}}$$

$$\text{Cell III: Mass of reactants} = (2 \text{ mol Na}) \left(\frac{22.99 \text{ g Na}}{1 \text{ mol Na}} \right) + (1 \text{ mol FeCl}_2) \left(\frac{126.75 \text{ g FeCl}_2}{1 \text{ mol FeCl}_2} \right) \\ = 172.73 \text{ g (unrounded)}$$

$$\frac{w_{\max}}{\text{Mass of reactant}} = \left(\frac{-4.534795 \times 10^5 \text{ J}}{172.73 \text{ g}} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) = -2.625366 = \mathbf{-2.62 \text{ kJ/g}}$$

Cell I has the highest ratio (most energy released per gram) because the reactants have very low mass while Cell II has the lowest ratio because the reactants are very massive.

21.98 Examine each reaction to determine which reactant is the oxidizing agent by which reactant gains electrons in the reaction.

From reaction between $\text{U}^{3+} + \text{Cr}^{3+} \rightarrow \text{Cr}^{2+} + \text{U}^{4+}$, find that Cr^{3+} oxidizes U^{3+} .

From reaction between $\text{Fe} + \text{Sn}^{2+} \rightarrow \text{Sn} + \text{Fe}^{2+}$, find that Sn^{2+} oxidizes Fe.

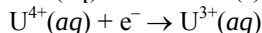
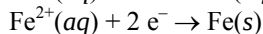
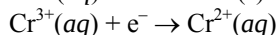
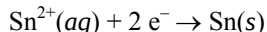
From the fact that there is no reaction that occurs between Fe and U^{4+} , find that Fe^{2+} oxidizes U^{3+} .

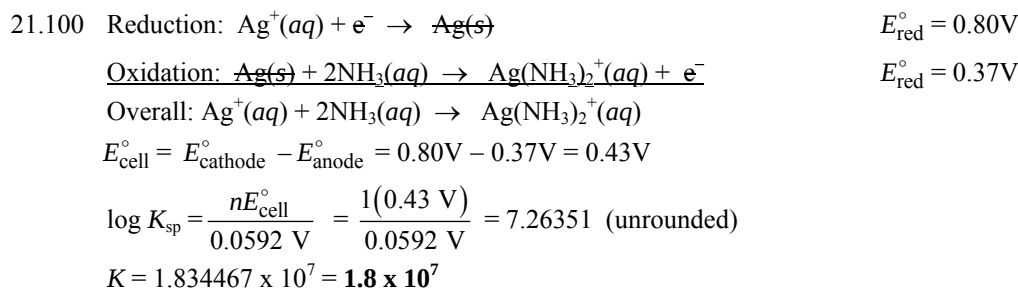
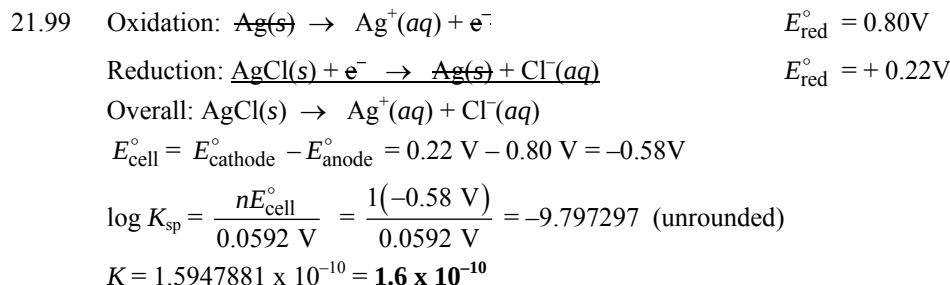
From reaction between $\text{Cr}^{3+} + \text{Fe} \rightarrow \text{Cr}^{2+} + \text{Fe}^{2+}$, find that Cr^{3+} oxidizes Fe.

From reaction between $\text{Cr}^{2+} + \text{Sn}^{2+} \rightarrow \text{Sn} + \text{Cr}^{3+}$, find that Sn^{2+} oxidizes Cr^{2+} .

Notice that nothing oxidizes Sn, so Sn^{2+} must be the strongest oxidizing agent. Both Cr^{3+} and Fe^{2+} oxidize U^{3+} , so U^{4+} must be the weakest oxidizing agent. Cr^{3+} oxidizes iron so Cr^{3+} is a stronger oxidizing agent than Fe^{2+} .

The half-reactions in order from strongest to weakest oxidizing agent:





- 21.101 Place the elements in order of increasing (more positive) E° .
 Reducing agent strength: **Li > Ba > Na > Al > Mn > Zn > Cr > Fe > Ni > Sn > Pb > Cu > Ag > Hg > Au**
 Metals with potentials lower than that of water (-0.83 V) can displace hydrogen from water by reducing the hydrogen in water. These can displace H_2 from water: **Li, Ba, Na, Al, and Mn**
 Metals with potentials lower than that of hydrogen (0.00 V) can displace hydrogen from acids by reducing the H^+ in acid. These can displace H_2 from acid: **Li, Ba, Na, Al, Mn, Zn, Cr, Fe, Ni, Sn, and Pb**
 Metals with potentials above that of hydrogen (0.00 V) cannot displace (reduce) hydrogen.
 These cannot displace H_2 : **Cu, Ag, Hg, and Au**

- 21.102 a) Use the stoichiometric relationships found in the balanced chemical equation to find mass of Al_2O_3 . Assume that 1 metric ton Al is an exact number.

$$2\text{Al}_2\text{O}_3 \text{ (in Na}_3\text{AlF}_6\text{)} + 3\text{C(gr)} \rightarrow 4\text{Al(l)} + 3\text{CO}_2\text{(g)}$$

$$\text{mass Al}_2\text{O}_3 = (1\text{ t Al}) \left(\frac{10^3\text{ kg}}{1\text{ t}} \right) \left(\frac{10^3\text{ g}}{1\text{ kg}} \right) \left(\frac{1\text{ mol Al}}{26.98\text{ g Al}} \right) \left(\frac{2\text{ mol Al}_2\text{O}_3}{4\text{ mol Al}} \right) \left(\frac{101.96\text{ g Al}_2\text{O}_3}{1\text{ mol Al}_2\text{O}_3} \right) \left(\frac{1\text{ kg}}{10^3\text{ g}} \right) \left(\frac{1\text{ t}}{10^3\text{ kg}} \right)$$

$$= 1.8895478 = \mathbf{1.890\text{ metric tons Al}_2\text{O}_3}$$

Therefore, **1.890 tons of Al_2O_3** are consumed in the production of 1 ton of pure Al.

- b) Use a ratio of 3 mol C: 4 mol Al to find mass of graphite consumed.

$$\text{mass C} = (1\text{ t Al}) \left(\frac{10^3\text{ kg}}{1\text{ t}} \right) \left(\frac{10^3\text{ g}}{1\text{ kg}} \right) \left(\frac{1\text{ mol Al}}{26.98\text{ g Al}} \right) \left(\frac{3\text{ mol C}}{4\text{ mol Al}} \right) \left(\frac{12.01\text{ g C}}{1\text{ mol C}} \right) \left(\frac{1\text{ kg}}{10^3\text{ g}} \right) \left(\frac{1\text{ t}}{10^3\text{ kg}} \right)$$

$$= 0.3338584 = \mathbf{0.3339\text{ tons C}}$$

Therefore, **0.3339 tons of C** are consumed in the production of 1 ton of pure Al, assuming 100% efficiency.

- c) The percent yield with respect to Al_2O_3 is **100%** because the actual plant requirement of 1.89 tons Al_2O_3 equals the theoretical amount calculated in part (a).

- d) The amount of graphite used in reality to produce 1 ton of Al is greater than the amount calculated in (b). In other words, a 100% efficient reaction takes only 0.3339 tons of graphite to produce a ton of Al, whereas real production requires more graphite and is less than 100% efficient. Calculate the efficiency using a simple ratio:

$$(0.45\text{ t}) (x) = (0.3338584\text{ t}) (100\%)$$

$$x = 74.19076 = \mathbf{74\%}$$

- e) For every 4 moles of Al produced, 3 moles of CO_2 are produced.

$$\text{moles C} = (1\text{ t Al}) \left(\frac{10^3\text{ kg}}{1\text{ t}} \right) \left(\frac{10^3\text{ g}}{1\text{ kg}} \right) \left(\frac{1\text{ mol Al}}{26.98\text{ g Al}} \right) \left(\frac{3\text{ mol CO}_2}{4\text{ mol Al}} \right) = 2.7798 \times 10^4\text{ mol CO}_2 \text{ (unrounded)}$$

The problem states that 1 atm is exact. Use the ideal gas law to calculate volume, given moles, temperature, and pressure.

$$V = nRT/P = \left(\frac{(2.7798 \times 10^4 \text{ mol CO}_2)(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(273 + 960.) \text{ K}}{1 \text{ atm}} \right) \left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}} \right)$$

$$= 2.812601 \times 10^3 = \mathbf{2.813 \times 10^3 \text{ m}^3}$$

- 21.103 a) The reference half-reaction is: $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s}) \quad E^\circ = 0.34 \text{ V}$
 Before the addition of the ammonia, $E_{\text{cell}} = 0$. The addition of ammonia lowers the concentration of copper ions through the formation of the complex $\text{Cu}(\text{NH}_3)_4^{2+}$. The original copper ion concentration is $[\text{Cu}^{2+}]_{\text{original}}$, and the copper ion concentration in the solution containing ammonia is $[\text{Cu}^{2+}]_{\text{ammonia}}$.
 The Nernst equation is used to determine the copper ion concentration in the cell containing ammonia.

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q$$

$$0.129 \text{ V} = 0.00 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[\text{Cu}^{2+}]_{\text{original}}}$$

$$0.129 \text{ V} = -\frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[0.0100]_{\text{original}}}$$

$$(0.129 \text{ V})(-2/0.0592) = \log \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[0.0100]_{\text{original}}}$$

$$-4.358108108 = \log \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[0.0100]_{\text{original}}}$$

$$4.3842154 \times 10^{-5} = \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[0.0100]_{\text{original}}}$$

$$[\text{Cu}^{2+}]_{\text{ammonia}} = 4.3842154 \times 10^{-7} \text{ M (unrounded)}$$

This is the concentration of the copper ion that is not in the complex. The concentration of the complex and of the uncomplexed ammonia must be determined before K_f may be calculated.

The original number of moles of copper and the original number of moles of ammonia are found from the original volumes and molarities:

$$\text{Original moles of copper} = \left(\frac{0.0100 \text{ mol Cu}(\text{NO}_3)_2}{\text{L}} \right) \left(\frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol Cu}(\text{NO}_3)_2} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (90.0 \text{ mL})$$

$$= 9.00 \times 10^{-4} \text{ mol Cu}^{2+}$$

$$\text{Original moles of ammonia} = \left(\frac{0.500 \text{ mol NH}_3}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (10.0 \text{ mL}) = 5.00 \times 10^{-3} \text{ mol NH}_3$$

Determine the moles of copper still remaining uncomplexed.

$$\text{Remaining moles of copper} = \left(\frac{4.3842154 \times 10^{-7} \text{ mol Cu}^{2+}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (100.0 \text{ mL})$$

$$= 4.3842154 \times 10^{-8} \text{ mol Cu}$$

The difference between the original moles of copper and the copper ion remaining in solution is the copper in the complex (= moles of complex). The molarity of the complex may now be found.

$$\text{Moles copper in complex} = (9.00 \times 10^{-4} - 4.3842154 \times 10^{-8}) \text{ mol Cu}^{2+}$$

$$= 8.995615 \times 10^{-4} \text{ mol Cu}^{2+} \text{ (unrounded)}$$

$$\text{Molarity of complex} = \left(\frac{8.9995615 \times 10^{-4} \text{ mol Cu}^{2+}}{100.0 \text{ mL}} \right) \left(\frac{1 \text{ mol Cu(NH}_3)_4^{2+}}{1 \text{ mol Cu}^{2+}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 8.9995615 \times 10^{-3} \text{ M Cu(NH}_3)_4^{2+} \text{ (unrounded)}$$

The concentration of the remaining ammonia is found as follows:

$$\text{Molarity of ammonia} = \left(\frac{(5.00 \times 10^{-3} \text{ mol NH}_3) - (8.9995615 \times 10^{-4} \text{ mol Cu}^{2+}) \left(\frac{4 \text{ mol NH}_3}{1 \text{ mol Cu}^{2+}} \right)}{100.0 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 0.014001753 \text{ M ammonia (unrounded)}$$

The K_f equilibrium is:

$$\text{Cu}^{2+}(\text{aq}) + 4 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu(NH}_3)_4^{2+}(\text{aq})$$

$$K_f = \frac{[\text{Cu(NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{[8.9995615 \times 10^{-3}]}{[4.3842154 \times 10^{-7}][0.014001753]^4} = 5.34072 \times 10^{11} = \mathbf{5.3 \times 10^{11}}$$

b) The K_f will be used to determine the new concentration of free copper ions.

Moles uncomplexed ammonia before the addition of new ammonia =

$$(0.014001753 \text{ mol NH}_3/\text{L}) (10^{-3} \text{ L/1 mL}) (100.0 \text{ mL}) = 0.001400175 \text{ mol NH}_3$$

Moles ammonia added = $5.00 \times 10^{-3} \text{ mol NH}_3$ (same as original moles of ammonia)

From the stoichiometry:

	$\text{Cu}^{2+}(\text{aq})$	+	$4 \text{NH}_3(\text{aq})$	$\rightarrow$	$\text{Cu(NH}_3)_4^{2+}(\text{aq})$
Initial moles:	$4.3842154 \times 10^{-8} \text{ mol}$		0.001400175 mol		$8.9995615 \times 10^{-4} \text{ mol}$
Added moles:			$5.00 \times 10^{-3} \text{ mol}$		
Cu^{2+} is limiting:	$-(4.3842154 \times 10^{-8} \text{ mol})$		$-4(4.3842154 \times 10^{-8} \text{ mol})$		$+(4.3842154 \times 10^{-8} \text{ mol})$
After the reaction:	0		0.006400 mol		$9.00000 \times 10^{-4} \text{ mol}$

Determine concentrations before equilibrium:

$$[\text{Cu}^{2+}] = 0$$

$$[\text{NH}_3] = (0.006400 \text{ mol NH}_3/110.0 \text{ mL}) (1 \text{ mL}/10^{-3} \text{ L}) = 0.0581818 \text{ M NH}_3$$

$$[\text{Cu(NH}_3)_4^{2+}] = (9.00000 \times 10^{-4} \text{ mol Cu(NH}_3)_4^{2+}/110.0 \text{ mL}) (1 \text{ mL}/10^{-3} \text{ L})$$

$$= 0.008181818 \text{ M Cu(NH}_3)_4^{2+}$$

Now allow the system to come to equilibrium:

	$\text{Cu}^{2+}(\text{aq})$	+	$4 \text{NH}_3(\text{aq})$	$\rightleftharpoons$	$\text{Cu(NH}_3)_4^{2+}(\text{aq})$
Initial molarity:	0		0.0581818		0.008181818
Change:	+x		+4x		-x
Equilibrium:	x		$0.0581818 + 4x$		$0.008181818 - x$

$$K_f = \frac{[\text{Cu(NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{[0.008181818 - x]}{[x][0.0581818 + 4x]^4} = 5.34072 \times 10^{11}$$

Assume $-x$ and $+4x$ are negligible when compared to their associated numbers:

$$K_f = \frac{[0.008181818]}{[x][0.0581818]^4} = 5.34072 \times 10^{11}$$

$$x = [\text{Cu}^{2+}] = 1.3369 \times 10^{-9} \text{ M Cu}^{2+}$$

Use the Nernst equation to determine the new cell potential:

$$E = 0.00 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[\text{Cu}^{2+}]_{\text{original}}}$$

$$E = -\frac{0.0592 \text{ V}}{2} \log \frac{[1.3369 \times 10^{-9}]}{[0.0100]}$$

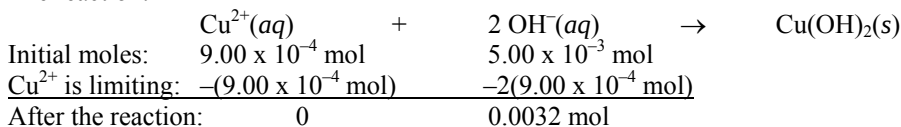
$$E = 0.203467 = \mathbf{0.20 \text{ V}}$$

c) The first step will be to do a stoichiometry calculation of the reaction between copper ions and hydroxide ions.

$$\text{Moles OH}^- = \left(\frac{0.500 \text{ mol NaOH}}{\text{L}} \right) \left(\frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (10.0 \text{ mL}) = 5.00 \times 10^{-3} \text{ mol OH}^-$$

The initial moles of copper ions were determined earlier: $9.00 \times 10^{-4} \text{ mol Cu}^{2+}$

The reaction:

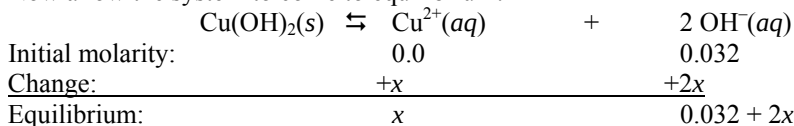


Determine concentrations before equilibrium:

$$[\text{Cu}^{2+}] = 0$$

$$[\text{NH}_3] = (0.0032 \text{ mol OH}^- / 100.0 \text{ mL}) (1 \text{ mL} / 10^{-3} \text{ L}) = 0.032 \text{ M OH}^-$$

Now allow the system to come to equilibrium:



$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^-]^2 = 2.2 \times 10^{-20}$$

$$K_{\text{sp}} = [x][0.032 + 2x]^2 = 2.2 \times 10^{-20}$$

Assume $2x$ is negligible compared to 0.032 M .

$$K_{\text{sp}} = [x][0.032]^2 = 2.2 \times 10^{-20}$$

$$x = [\text{Cu}^{2+}] = 2.1487375 \times 10^{-17} = 2.1 \times 10^{-17} \text{ M}$$

Use the Nernst equation to determine the new cell potential:

$$E = 0.00 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[\text{Cu}^{2+}]_{\text{original}}}$$

$$E = -\frac{0.0592 \text{ V}}{2} \log \frac{[2.1487375 \times 10^{-17}]}{[0.0100]}$$

$$E = 0.434169 = \mathbf{0.43 \text{ V}}$$

d) Use the Nernst equation to determine the copper ion concentration in the half-cell containing the hydroxide ion.

$$E = 0.00 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[\text{Cu}^{2+}]_{\text{original}}}$$

$$0.340 = -\frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[0.0100]}$$

$$(0.340 \text{ V}) (-2/0.0592) = \log \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[0.0100]}$$

$$-11.486486 = \log \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[0.0100]}$$

$$3.2622256 \times 10^{-12} = \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[0.0100]}$$

$$[\text{Cu}^{2+}]_{\text{hydroxide}} = 3.2622256 \times 10^{-14} \text{ M (unrounded)}$$

Now use the K_{sp} relationship:

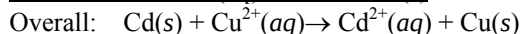
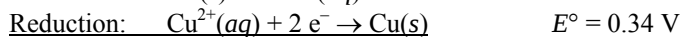
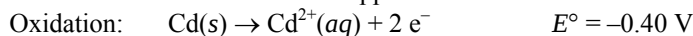
$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2 = 2.2 \times 10^{-20}$$

$$K_{sp} = [3.2622256 \times 10^{-14}][\text{OH}^-]^2 = 2.2 \times 10^{-20}$$

$$[\text{OH}^-]^2 = 6.743862 \times 10^{-7}$$

$$[\text{OH}^-] = 8.2121 \times 10^{-4} = 8.2 \times 10^{-4} \text{ M OH}^- = \mathbf{8.2 \times 10^{-4} \text{ M NaOH}}$$

21.104 a) The half-reactions found in the Appendix are:



$$\text{Calculate } E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

$$\text{Cu/Cd } E_{\text{cell}}^\circ = 0.34 \text{ V} - (-0.40 \text{ V}) = \mathbf{0.74 \text{ V}}$$

Note: Cd is a better reducing agent than Cu so Cu^{2+} reduces while Cd oxidizes.

$$\Delta G^\circ = -nFE^\circ$$

$$\Delta G^\circ = -(2 \text{ mol e}^-)(96485 \text{ C/mol e}^-)(0.74 \text{ J/C}) = -1.427978 \times 10^5 = \mathbf{-1.4 \times 10^5 \text{ J}}$$

$$\log K = \frac{nE_{\text{cell}}^\circ}{0.0592}$$

$$\log K = \frac{2(0.74)}{0.0592} = 25$$

$$K = \mathbf{1 \times 10^{25}}$$

b) The cell reaction is: $\text{Cu}^{2+}(\text{aq}) + \text{Cd(s)} \rightarrow \text{Cu(s)} + \text{Cd}^{2+}(\text{aq})$

Next, use the Nernst equation:

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q$$

$$E = 0.74 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cd}^{2+}]}{[\text{Cu}^{2+}]}$$

An increase in the cadmium concentration by 0.95 M requires an equal decrease in the copper concentration since the mole ratios are 1 : 1. Thus, when $[\text{Cd}^{2+}] = 1.95 \text{ M}$,

$$[\text{Cu}^{2+}] = (1.00 - 0.95) \text{ M} = 0.05 \text{ M.}$$

$$E = 0.74 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[1.95]}{[0.05]}$$

$$E = 0.69290 = \mathbf{0.69 \text{ V}}$$

c) At equilibrium, $E_{\text{cell}} = 0$, and $\Delta G = 0$

The Nernst equation is necessary to determine the $[\text{Cu}^{2+}]$.

Let the copper ion completely react to give $[\text{Cu}^{2+}] = 0.00 \text{ M}$ and $[\text{Cd}^{2+}] = 2.00 \text{ M}$. The system can now go to equilibrium giving $[\text{Cu}^{2+}] = +x \text{ M}$ and $[\text{Cd}^{2+}] = (2.00 - x) \text{ M}$.

$$0.00 \text{ V} = 0.74 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[2.00 - x]}{[x]}$$

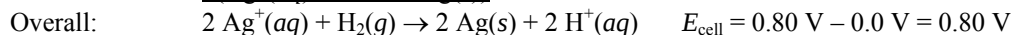
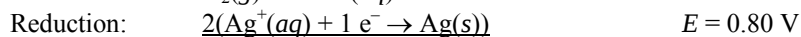
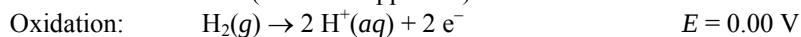
Assume x is negligible compared to 2.00.

$$(-0.74 \text{ V}) (-2/0.0592 \text{ V}) = \log \frac{[2.00]}{[x]}$$

$$25.0 = \log \frac{[2.00]}{[x]}$$

$$x = \mathbf{2.0 \times 10^{-25} \text{ M Cu}^{2+}}$$

21.105 The half-reactions are (from the Appendix):



The hydrogen ion concentration can now be found from the Nernst equation.

$$E = E^\circ - \frac{0.0592 \text{ V}}{2} \log Q$$

$$0.915 \text{ V} = 0.80 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 P_{\text{H}_2}}$$

$$0.915 \text{ V} - 0.80 \text{ V} = -\frac{0.0592 \text{ V}}{2} \log \frac{[\text{H}^+]^2}{[0.100]^2 (1.00)}$$

$$(0.915 \text{ V} - 0.80 \text{ V}) (-2/0.0592 \text{ V}) = \log \frac{[\text{H}^+]^2}{[0.100]^2 (1.00)}$$

$$-3.885135 = \log \frac{[\text{H}^+]^2}{[0.0100]}$$

$$1.30276 \times 10^{-4} = \frac{[\text{H}^+]^2}{[0.0100]}$$

$$[\text{H}^+] = 1.1413851 \times 10^{-3} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (1.1413851 \times 10^{-3}) = 2.94256779 = \mathbf{2.94}$$